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## High Permittivity Siloxanes as Promising Materials for Dielectric Elastomer Transducers: From Synthesis to Application

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par

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## Abstract

The speed of change in the modern world is impressive. Within the last 50 years, many devices and technologies have significantly transformed their appearance, intrinsic characteristics and improved their performance. Computers have changed from the size of several cubic meters to thin laptops. Photo and video camera, recorder, computer, and phone are not anymore five devices but have converged to one small smart device that anyone can put in the pocket. Autonomous vehicles can drive and park themselves. The progress did not disregard such industrial fields as medicine, robotics, energy harvesting, and others looking for new materials and technologies with breakthrough potential.

Dielectric Elastomers (DEs) are versatile and smart materials that operate in three modes as actuators, generators, or sensors. Actuators change their form in response to an applied electric field. They could be used as artificial muscles in biomedical applications. As generators, DEs can convert mechanical energy into electricity. Finally, they can also be capacitive sensors.

Among all DEs, polysiloxanes possess all requirements for constructing robust and reliable devices, including artificial muscles that can outperform the characteristics of natural muscles in terms of stress and strain. However, the performance of polysiloxane-based devices is restricted by their low dielectric permittivity value ( $\epsilon$ '~2.8). A higher dielectric permittivity would increase sensor sensitivity, the energy generated, or reduce the actuator operation voltage, which is typically in the kV range.

Chemical modification of polymers with polar groups allows for an increase in dielectric permittivity but may also increase the glass transition temperature, which would ideally remain significantly below room temperature. However, a systematic investigation on how different polar groups and degree of functionalization alters the dielectric and thermal properties is missing.

This thesis presents a systematic approach to polysiloxanes modified with different types and contents of polar groups and explores the potential of such polar silicones as dielectric materials in transducers.

To this end, we set out from polysiloxanes with different vinyl group content. These groups were then transformed into various polar groups by an efficient one-step thiol-ene addition post-polymerization modification. The resulting collection of novel materials was ideally suited for the first step towards elucidating structure-property relationships, which are essential for finding the optimum material. It has allowed us to select the most promising polar polysiloxanes for a defined application.

Next, a strategy was developed to cross-link the most promising polar polysiloxane to thinfilm elastomers with useful mechanical and electromechanical properties.

An incomplete functionalization of the vinyl groups on polymethylvinylsiloxanes with less than stoichiometric amount of thiols allowed us to obtain polymers with around 2.5% unreacted

vinyl side groups. They were subsequently cross-linked into thin films with tuneable properties via the fast and reliable thiol-ene addition.

Finally, single membrane DE actuators were constructed, and their electromechanical performance was tested. The best materials showed around 7.5% actuation strain at only 300 V, while a visible actuation at 200 V was also detected. Actuators that can be operated for more than 50'000 cycles were obtained with some DEs.

**Keywords**: dielectric elastomers, dielectric elastomer transducers, polysiloxanes, silicones, polar siloxanes, high permittivity elastomers, thiol-ene reaction, modified siloxanes, dielectric elastomer actuators.

## Zusammenfassung

Die Geschwindigkeit des Wandels in der modernen Zeit ist äusserst beeindruckend. In den letzten 50 Jahren wurden Form, Eigenschaften und Leistung vieler Geräte und Technologien entscheidend weiterentwickelt. So hat sich die Form von Computern von riesigen Objekten zu Laptops verwandelt. Fotoapparat und Videorekorder, Computer und Telefon sind heutzutage nicht mehr verschiedene Geräte, sondern in einem einzigen Smartphone vereint, das in eine Hosentasche passt. Auf der Suche nach neuen Materialien und Technologien mit Durchbruchspotential hat es in vielen wissenschaftlichen Bereichen wie Medizin, Robotik oder Energiespeicherung enorme Fortschritte gegeben.

Dielektrische Elastomere (DEs) finden seit ihrer Entdeckung Verwendung in vielen wissenschaftlichen Disziplinen. DEs sind vielseitige, intelligente Materialien, die in drei unterschiedlichen Funktionen verwendet werden können: als Aktoren, Generatoren, und Sensoren. Als Aktoren können sie unter Einfluss eines elektrischen Feldes ihre Form verändern und so beispielsweise als künstliche Muskeln verwendet werden. Als Generatoren können sie mechanische in elektrische Energie umwandeln, als Sensoren mechanische in elektrische Signale verwandeln.

Polysiloxane erfüllen alle Anforderungen um aus ihnen robuste und zuverlässige Sensoren, Generatoren und Aktoren herzustellen, besitzen allerdings eine niedrige Dielektrizitätskonstante. Eine höhere Dielektrizitätskonstante würde sowohl die sensorische Empfindlichkeit, als auch die erzeugte Energie eines Generators erhöhen. Des Weiteren könnte dadurch die notwendige Betriebsspannung für Aktoren reduziert werden, die zur Zeit im Bereich einiger Kilovolt liegt.

Chemische Modifikation von Polymeren mit polaren funktionellen Gruppen erlaubt die Erhöhung der Dielektrizitätskonstante, allerdings unter Erhöhung der Glasübergangstemperatur, die idealerweise deutlich unterhalb der Raumtemperatur bleiben sollte. Bislang fehlt eine systematische Studie über den Einfluss von unterschiedlichen polaren Gruppen und dem Grad der Funktionalisierung auf die dielektrischen und thermischen Eigenschaften von Polysiloxan-basierten DEs.

In der vorliegenden Doktorarbeit haben wir daher in einem ersten Schritt Poly(dimethyl-comethylvinyl)siloxane mit unterschiedlichem Vinylgruppen-Gehalt synthetisiert. Diese Polysiloxane wurden über eine einstufige Thiol-En Reaktion mit unterschiedlichen polaren Gruppen funktionalisiert. Die daraus resultierenden polaren Polysiloxane eignen sich für eine grundlegende Untersuchung des Zusammenhangs von chemischer Struktur und Materialeigenschaften. Zur weiteren Optimierung konnten die Materialein mit den besten Eigenschaften ausgewählt werden.

Der nächste Schritt bestand in der Wahl einer geeigneten Methode für die Vernetzung der polaren Siloxane, um letztendlich dünne Elastomer-Filme mit guten elektromechanischen Eigenschaften herzustellen. Durch unterstöchiometrische Zugabe der Thiole konnten wir Polysiloxane mit etwa 2.5% unreagierten Vinyl-Gruppen herstellen. Sie wurden anschliessend mittels schneller und effektiver Thiol-En Reaktion zu dünnen Filmen vernetzt.

Schliesslich wurden DE Aktoren konstruiert, die aus einer einzelnen Polysiloxanmembran bestehen. Bei Untersuchung der elektromechanischen Eigenschaften wies das beste Material eine Dehnung von 7.5% unter einer Betriebsspannung von 300 V auf, wobei eine sichtbare Dehnung bereits bei 200 V zu beobachten war. Die hergestellten Aktoren konnten bis zu 50'000 Betriebszyklen überstehen.

**Stichwörter**: Dielektrische Elastomere, dielektrische elastomerische Umwandler, Polysiloxane, polare Siloxane, Elastomere mit hoher Permittivität, Thiol-En Reaktion, modifizierte Siloxane, dielektrische elastomerische Aktoren.

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# **List of Abbreviations**

EAP	Electroactive polymer					
CNT	Carbon nanotube					
IPMC	ionic polymer-metal composite					
V	voltage					
PVDF	poly(vinylidene difluoride)					
P(VDF-TrFE)	poly(vinylidene fluoride – trifluoroethylen)					
LCE	liquid crystal elastomer					
DE	dielectric elastomer					
ν	Poisson ratio					
S	strain					
Vo	initial volume					
$V_s$	volume at strain <i>s</i>					
DEA	dielectric elastomer actuator					
DET	dielectric elastomer transducer					
Q	electrostrictive coefficient					
ε <sub>0</sub>	permittivity of free space					
ε <sub>r</sub>	relative permittivity					
Ε	electric field					
Sel	elastic compliance					
d	thickness					
Y	Young's modulus					
DES	dielectric elastomer sensor					
С	capacitance					
A	active area					
DEG	dielectric elastomer generator					
$W_x$	electrical energy at moment x					
$D_0$	electric flux density					
Р	electric polarization					
Es	static relative permittivity					
χ	electric susceptibility					
μe	dipole moment					

R	atom radius
εr	relative dielectric permittivity
$\mathcal{E}_r$	dielectric loss
ω	angular frequency
E∞	high-frequency permittivity
BDIS	Broadband Dielectric Impedance Spectroscopy
$\sigma'$	real part of conductivity
$\sigma''$	imaginary parts of conductivity
E <sub>br</sub>	breakdown electric field
EMI	electromechanical instability
$T_g$	glass transition temperature
L	length
Н	Helmholtz free energy
dU	change in the internal energy
Т	temperature
dS	entropy change
Ν	number of polymer chains in the network
k <sub>B</sub>	Boltzmann constant
λ	relative length change
W	work
f	external forces
т	network density
G	shear modulus
ρ	density
R	gas constant
Mc	number-average molecular weight between the cross-links
$\sigma$	stress
t	time
η	viscosity
Ε'	storage modulus
<i>E''</i>	loss modulus
DEMES	dielectric elastomer minimum energy structure
DOF	degree-of-freedom
PDMS	polydimethylsiloxane

PANi	polyaniline
PU	polyurethane
ROP	ring-opening polymerization
DMPA	dimethoxy-2-phenylacetophenone
IPN	interpenetrating network
ТМАН	tetramethylammonium hydroxide
THF	tetrahydrofuran
NMR	nuclear magnetic resonance
DSC	differential scanning calorimetry
PV	polymethylvinylsiloxane
EB	end-blocker
D <sub>4</sub>	octamethylcyclotetrasiloxane
V <sub>4</sub>	tetramethyl-1,3,5,7-tetravinyl cyclotetrasiloxane
GPC	gel permeation chromatography
TGA	thermogravimetric analysis
PVA	polyvinyl alcohol
DMA	dynamic mechanical analysis

#### **CHAPTER ONE**

## 1. Introduction

#### 1.1. Electroactive Polymers

Electroactive polymers (EAPs) are soft materials capable of changing their shape and size in response to an applied electric field. EAPs are commonly called artificial muscles if they are biocompatible, and their force and energy densities are similar to those of skeletal muscles. They can emulate the operation of biological muscles in high fracture toughness and are generally inexpensive, soft, and lightweight. Depending on the mechanism responsible for actuation, they can be divided into two following groups: ionic EAPs and electronic EAPs.

#### 1.1.1. Ionic Electroactive Polymers

The working principle of ionic EAPs is based on the transfer or diffusion of ions or molecules under an applied external electric field. Such devices usually are considered "wet" because they require an electrolyte as a medium for ions. The most popular ionic EAPs are ionic polymer-metal composites (IPMCs), carbon nanotubes (CNTs), ionic polymer gels, and conductive polymers.

**IPMCs** are ideal candidates for soft bending actuators and sensors. They consist of two flexible metallic (Au, Pt, Ag) or carbon-based electrodes separated by an ion-exchange polymeric membrane swollen in a solvent, typically water. The driving force of IPMC is the migration of ions. When a low electric field is applied, cations surrounded by solvent molecules move to the anode, causing a change in concentration, therefore bending the polymeric film towards the anode side (Figure 1.1 a). The most popular membrane materials are Nafion that contains perfluorosulfonate groups, Flemion with perfluoro carboxylate groups, and other sulfonated aromatic ionic polymers.<sup>[1]</sup> Such membranes are usually only cation permeable. Cations can migrate through special hydrophilic channels produced by ionic segments of polymer chains.<sup>[2]</sup> Small, highly mobile cations like Li<sup>+</sup> facilitate fast ion migration, therefore increasing the bending response.<sup>[3]</sup> The driving potential of IPMCs usually stays around a few volts, and for water-based systems, it must not exceed 1.23 V, the potential at which water electrolysis occurs.<sup>[4]</sup> Because ions cannot follow a fast change in the direction of the electric field, IPMCs have to be operated at low frequency, usually below 10 Hz.<sup>[3]</sup> It was shown that this type of ionic polymers could find application in many fields where

bending-like actuation is required: valves, micropumps, catheters, micro-robotics, sensors, and biomedical devices. Such systems are biocompatible, flexible, noiseless, exhibit large deformation, and show actuation stress as high as 30 MPa.<sup>[2,5-7]</sup> However, their low actuation strain (~3%) and actuation nature, which requires wet electrolytes, can hinder their use in many types of applications.<sup>[2]</sup>



Figure 1.1 a) IPMC, b) CNT, c) ionic polymer gels, d) conductive polymers (adapted with permission from <sup>[5,8]</sup>).

Thanks to the possibility of electrical activation of **CNTs**, they also found use in the field of EAPs.<sup>[4]</sup> Application of a voltage between a counter-electrode and CNTs dispersed in the electrolyte induces migration of ions to the surface of the CNTs. The electric double layer formed on the surface is compensated by an opposite electronic charge inside the tubes (Figure 1.1b). Due to the formation of a high concentration of charges within the CNTs, repulsion among the carbon atoms induces a small elongation of carbon-carbon bonds that, in turn, results in macroscopic changes of the network consisting of entangled CNTs.<sup>[8]</sup> Among single-walled and multi-walled CNTs, the former are preferred due to their higher surface area that can be accessed by solvent and ions. Therefore, in single-walled CNTs, the resulting actuation strain is higher.<sup>[9]</sup> The approximate strain of typical CNTs actuators is below 2% while driving voltage stays around 1 V. They also exhibit a fast response (in the millisecond range), enormous work densities (~200 MJ/m<sup>3</sup>), and high actuation stress (~26 MPa).<sup>[2,8]</sup> However, besides low actuation strain, CNT-based actuators also suffer from high cost, low scalability, and poor electromechanical coupling.

**lonic polymer gels** is another class of ionic EAPs. They consist of a cross-linked polymer gel, such as polyacrylic acid, polyacrylonitrile, or poly(methyl methacrylate), immersed in an electrolyte solution.<sup>[5]</sup> These gels can change their size and shape in response to an applied external stimulus, such as an

electrical or chemical pH change. However, using a chemically driven pH change results in difficulties, such as undesirable salt formation that causes deformation of gels and blocks the polymer-electrolyte interface. Therefore, electrically stimulated systems are more desirable.<sup>[8]</sup> In a weak electric field, the electrolysis of water occurs and increases the basicity of the electrolyte around the cathode, while the region around the anode becomes more acidic. Because of this phenomenon, and due to the migration of ions and water in the electrolyte and within the gel, an actuator made of an ionic polymer gel exhibits bending behavior (Figure 1.1c). Diffusion of ions is also a reason for the slow response time of actuators made of ionic polymer gels. Other drawbacks of such systems are their poor mechanical properties and the need for encapsulation.<sup>[2,5,8]</sup>

Actuators consisting of **conductive polymers** typically exhibit a sandwich-like structure, where an electrolyte is placed between two electrodes consisting of conductive polymers such as polyaniline, polypyrrole, or polythiophene.<sup>[5]</sup> The actuation is based on the reversible ion exchange during oxidation and reduction of polymers (Figure 1.1d). Thus, ions and solvent molecules can migrate from the electrolyte towards the electrodes and back, causing swelling when ions enter the polymer material, and contraction when they are removed. A secondary process, which also causes deformation, involves conformation changes of the polymer backbone.<sup>[8]</sup> Generally, the driving voltage of such actuators is around 1–2 V, while actuation strain up to 40%<sup>[2,4]</sup> and force densities above 100 MPa can be achieved.<sup>[9]</sup> Such actuators have a low cost<sup>[5]</sup> and sometimes can be operated at frequencies up to 40 Hz.<sup>[3]</sup> The main drawbacks of conductive polymers are poor electromechanical coupling (<1%), low efficiency (~1%)<sup>[4]</sup>, and short lifetime.<sup>[3]</sup> Additionally, such actuators have to be encapsulated due to the presence of an electrolyte.<sup>[4]</sup>

Generally, ionic actuators are flexible, lightweight, and can be operated at low voltage showing large bending actuation. To date, various promising applications of IEAPs have been reported, such as bionic robots,<sup>[5]</sup> sensors, micropumps, tactile displays, etc.<sup>[10]</sup> However, their slow response, low efficiency, low force, and necessity to keep them in a wet state can significantly limit their employment in many devices.<sup>[3,8]</sup>

#### 1.1.2. Electronic Electroactive Polymers

Contrary to ionic EAPs, electronic EAPs, or so-called field-induced polymers, do not contain any electrolyte, and their working principle is based on Coulomb forces. Since the electric field between applied electrodes drives such polymers, and there is no need for the migration of ions like in ionic polymers, the actuation speed of electronic EAPs is much faster, usually in the microseconds range. They can be operated in air, have a high energy density, are efficient, and are considered temperature and humidity insensitive. However, they require high electric fields to be activated, which sometimes can be close to the breakdown voltage of the material. Among all electronic EAPs, the most commonly used are

ferroelectric polymers, electrostrictive graft elastomers, liquid crystal elastomers (LCEs), and dielectric elastomers (DEs).

Ferroelectric polymers are materials with non-centrosymmetric structures, which have permanent electric polarization due to aligned polar dipoles. To remove the polarization in such materials, they must either be heated to above the Curie temperature, when polarization is disrupted, or subjected to a reverse electric field. The best known representatives of ferroelectric polymers are poly(vinylidene difluoride) (PVDF) and the copolymer poly(vinylidene fluoride - trifluoroethylen) (P(VDF-TrFE)), in which the electronegative fluorine atoms produce local dipoles. Applying an electric field causes the alignment of domains consisting of local dipoles, leading to a polymer contraction in the direction of an electric field.<sup>[8,11]</sup> Actuators made of PVDF-based copolymers can generate up to 10% actuation strain, they exhibit a high efficiency of electromechanical conversion,<sup>[2]</sup> and have a large modulus (1-10 Pa), all of which results in high mechanical energy density.<sup>[8]</sup> The main limitation of these materials for practical applications lies in the high temperature at which the transition between ferroelectric and paraelectric phases occurs and in large hysteresis.<sup>[12]</sup> Due to the latter, a high electric field in the opposite direction is needed to reverse the polarization. Therefore, a significant amount of energy is dissipated.<sup>[11]</sup> These issues were overcome by Huang et al.<sup>[12]</sup> via modification of PVDF copolymers by introducing defects. So-called relaxor ferroelectric polymers were obtained either by high-energy electron irradiation or by introducing a small amount of a disruptive monomer (e.g., chlorofluoroethylene or hexafluoropropylen).<sup>[2]</sup> Such modifications allowed to reduce the transition temperature close to room temperature, broaden the transition temperature range, and, more importantly, diminish or eliminate the hysteresis.<sup>[12]</sup> The main drawbacks of such actuators are significant hysteresis due to the high dissipation of energy, the need for a high electric field (~150 V/ $\mu$ m), and fatigue of electrodes because of a large strain.<sup>[8]</sup>

**Electrostrictive graft elastomers** consist of two polymers: the first one has a flexible backbone, while the second one is grafted to the first and capable of producing crystalline domains. Such domains may act as physical cross-linking points and as polarizable moieties in an electric field responsible for the deformation of the material.<sup>[3]</sup> Electrostrictive graft elastomers are considered to be stiff materials, with a typical modulus of 550 MPa. Therefore, actuators exhibiting high mechanical energy density and large force can be constructed. An actuation strain of 5% was reported for such polymers. They can show fast operation and are easily processable.<sup>[8,11]</sup> However, similar to other electronic EAPs, electric fields around 150 V/ $\mu$ m are required to induce actuation.<sup>[11]</sup>

In **LCEs**, the properties of elastic polymer networks and crystal molecules (mesogens) are combined. While the former ensure sufficient motion freedom due to the flexibility of the backbone, the latter can be reoriented under a thermal or electrical stimulus, producing stress and strain. Thermal activation can be induced electrically, optically, and magnetically, and actuation strain as high as 45% can be achieved.<sup>[11]</sup> However, due to the heat diffusion, the actuation speed is very slow and requires 10 s for relaxation. On the other hand, electrical activation is very fast, with typical response times of 10 ms, and can achieve strains of up to 5%. Actuation speed strongly depends on the size of the mesogens, cross-linking density of the polymer, and its backbone structure.<sup>[9]</sup> In comparison to ferroelectric polymers, the driving electric

field in LCEs is much lower, in the range of 1.5-25 V/ $\mu$ m. Because LCEs have low stiffness and tensile strength, they exhibit low work density and low resonant frequency, while employment of stiffer materials results in the reduction of actuation strain to 2%.<sup>[2]</sup>

Among all available electroactive polymers, **dielectric elastomers** have properties that are closest to those of natural muscles. Like muscles, they are soft materials, which can change their shape and length under an applied stimulus and induce large force. Meijer *et al.*<sup>[13]</sup> investigated the properties of three different elastomers and compared them with biological muscles. It was shown that dielectric elastomers have similar characteristics to natural muscles. They can even outperform natural muscles in terms of strain, stress, work density, speed, and power. A good comparison of their properties can be seen in Table 1.1.<sup>[14]</sup> Like muscles, DEs can also exhibit self-sensing properties. Additionally, energy harvesting devices can be constructed from them.

The main shortcoming of DEs and all electronic EAP is the need for high electric fields to drive them. In the following chapters, the working principle of DEs will be discussed as well as approaches for reducing their driving voltage.

-	Strain	Strace	Work	Density	Strain	Cycle life	Modulus	Voltage	
	Strain	50,635	WOIK	Density	Stram	cycle life	woodulus	voltage	
	[%]	[MPa]	density	[kg/m³]	rate		[MPa]	[V]	
			[kJ/m³]		[%/s]				
Natural Muscle	20-40	0.1-0.35	8-40	1037	>50	>10 <sup>9</sup>	10-60	<1	
Dielectric Elastomers	10 to >100	0.1-9	10-150	1000	>450	10 <sup>6</sup> at 50% strain	0.1-3	>1000	

Table 1.1.1 Comparison of properties of natural muscles and dielectric elastomers (adapted with permission from <sup>[14]</sup>).

### 1.2. Dielectric Elastomer Transducers

#### 1.2.1. Working Principle

As shown in the 1990s by the pioneers of this technology, Pelrine *et al.*,<sup>[15]</sup> dielectric elastomer transducers (DETs) can be considered as stretchable parallel plate capacitors in which a dielectric elastomeric membrane is placed between two compliant electrodes. When the capacitor is charged, electrostatic forces are generated between two electrodes, squeezing the polymer. However, under applied stress, elastomers do not exhibit a volume change. From the equation (Eq. 1.) derived by Rinde<sup>[16]</sup>:

$$v = \frac{1}{2} \left[ 1 - \frac{1}{V_0} \left( \frac{dV_s}{ds} \right) \right]$$
 Eq. 1

where v is the Poisson ratio, s is the strain,  $V_0$  is the initial volume, and V is the volume at the strain s, it can be determined that elastomers have a Poisson ratio very close to 0.5. Therefore, elastomers are considered to be incompressible materials with a constant volume, and they expand in the lateral area upon compressive stress. In an applied electric field (in z-direction), the material contracts in the z-direction (thickness) and expands in x and y directions (area). Such operation is called actuation. This principle is used for the fabrication of dielectric elastomer actuators (DEAs) (Figure 1.2a). Nowadays, it is considered that two main phenomena are responsible for the deformation of an elastomer in an applied electric field. The first one is called electrostriction. This phenomenon originates in the change in dielectric properties caused by the field-induced polarization of dipoles.<sup>[17]</sup> The second mechanism responsible for the actuation is the "Maxwell stress". It arises after the generation of opposite charges on both electrodes. Thus, like charges on each electrode are repelled from each other, while opposite charges from the two opposite electrodes attract one another.<sup>[18]</sup> Both above-mentioned phenomena cause a quadratic dependence in mechanical deformation of the elastomer on the electric field and can be expressed in the following way:

$$S_{elstr} = -Q\varepsilon_0^2(\varepsilon_r - 1)^2 E^2$$
 Eq. 2

$$S_{Maxw} = -s_{el}\varepsilon_0\varepsilon_r E^2$$
 Eq. 3

where  $S_{elstr}$  and  $S_{Maxw}$  are thickness strains generated by electrostriction and Maxwell pressure, respectively, Q is the the electrostrictive coefficient,  $\varepsilon_0$  is the the permittivity of free space (8.854\*10<sup>-12</sup> F/m),  $\varepsilon_r$  is the the relative permittivity of elastomer, E is the the applied electric field, and  $s_{el}$  is the elastic compliance.<sup>[2,11]</sup>

Since it is difficult to separate electrostriction and Maxwell stress, and there is no need for doing so because both exhibit the same compression effect on the elastomer, a formula derived by Pelrine *et al.*<sup>[15]</sup> is often used to calculate the pressure acting on the membrane:

$$p = \varepsilon_0 \varepsilon_r E^2 = \varepsilon_0 \varepsilon_r (\frac{V}{d})$$
 Eq. 4

where *V* is the applied voltage, and *d* is the thickness of the elastomer. However, it is difficult to compare various materials without considering their intrinsic properties, such as their modulus of elasticity. Therefore, the same authors took into account the boundary conditions and theory of linear elasticity and predicted the actuation strain in z-direction (thickness change) as follows:

$$s_z = -\varepsilon_0 \varepsilon_r \frac{V^2}{Yd^2}$$
 Eq. 5

where *Y* is Young's modulus. It has to be mentioned that Equation 5 is valid only for small strains (<10%). From equations 4 and 5 it can be seen, that actuation pressure and strain are proportional to the relative dielectric constant of the utilized elastomer. They are also proportional to the applied voltage. On the other hand, actuation strain is reversely proportional to the elastic modulus of the polymer and its

thickness. It should also be mentioned that equation 5 assumes the dielectric constant and modulus of elasticity of the material to be independent of electric field and strain. Other parameters, which can also influence the actuation, are not considered either.<sup>[19]</sup>

This description of electric energy converted into mechanical work is valid for DETs operating in the actuation mode. However, DETs can also be operated as sensors and generators. The simplest representation of dielectric elastomer sensors (DESs) is shown in Figure 1.2b. Similar to actuator devices, sensors consist of an active dielectric layer placed between two electrodes. The initial capacitance of the sensor can be calculated by equation 6:

$$C = \varepsilon_0 \varepsilon_r \frac{A}{d}$$
 Eq. 6

where *A* is the active area. When a compressive or tensile stress is applied, the initial capacitance changes due to the possible changes in thickness and area of the sensor. The sensitivity of sensors is proportional to the capacitance difference between the relaxed and deformed states.<sup>[20]</sup> So far, various capacitive sensors have been developed using DET technology. *Artificial Muscle Inc.* developed the EPAM<sup>™</sup> (Electroactive Polymer Artificial Muscle<sup>™</sup>) capacitor, which can be used as a sensor or actuator. They also presented an actuator that exhibits self-sensing properties. The EPAM material can be employed to fabricate soft robotics, pressure sensors, and capacitive sensor electronics.<sup>[21]</sup> Böse *et al.* presented wearable operation gloves<sup>[22]</sup> and sensor mats.<sup>[23]</sup> Huang *et al.* proposed a wrist motion tracker to analyze wrist skin deformation and muscle contraction.<sup>[24]</sup> Kwon *et al.* developed a flexible sensor that was embedded in wearable devices with the possibility of measuring wrist pulse.<sup>[25]</sup> The promise of DE-based sensors for applications such as game controllers, strain gauges, switches, textiles, rehabilitation, and many others have also been reported.<sup>[6]</sup>

In generator mode, DETs can convert mechanical energy into electrical energy. As shown above, the DEA and DES working principles include two states: a relaxed state (when neither voltage nor stress is applied) and an activated state (when a voltage is applied to an actuator and stress is applied to a sensor). By contrast, in dielectric elastomer generators (DEGs) the working cycle comprises four stages (Figure 1.2c). The simplest generator consists of a DE film with two electrodes on both sides. In the first step, external forces stretch the DEG leading to the change in thickness and area of electrodes. Therefore, the capacitance is increased. Then, during the second step, the charges from an external voltage supply are applied to the DE. The external forces are removed in the third step, and the DE relaxes back until electrostatic forces compensate the elastic force. In this state, the thickness of the film is increased, while the active area is reduced. Since the number of charges is conserved, electrical energy is increased due to the spatial separation of unlike charges and squeezing of the like charges. Finally, during the fourth step, the DEG is discharged and electrical energy is harvested.<sup>[26]</sup> The working principle of DEGs can be expressed by the following formulas proposed by Pelrine *et al.*<sup>[26]</sup>:

$$W_x = 0.5C_x V^2$$
 Eq. 7

where  $W_x$  is the electrical energy at the moment x,  $C_x$  is the capacitance at the moment x that can be expressed with equation 6, and V is the applied voltage; and

$$W_g = 0.5Ad\varepsilon_0\varepsilon_r(E_c^2 - E_s^2)$$
 Eq. 8

where  $W_g$  is the energy gain per cycle, and  $E_c$  as well as  $E_s$  are the electric fields in contracted and stretched states, respectively. From equation 8, it can be stated that the maximum amount of energy collected in one operation cycle depends on the electrical breakdown of the material and the maximum strain that the material can withstand.<sup>[27]</sup> It was demonstrated that DEGs could generate up to 0.4 J/g, which is three times higher than the value obtained from generators based on piezoelectric ceramics and ten times higher than electromagnetic generators. According to theoretical calculations, even an energy density output above 1.5 J/g should be feasible.<sup>[26]</sup>

Already at the early stage of DEGs, a generator prototype inserted into a shoe heel was introduced and prospects of using such technology in engine-driving generators, remote sensors, and wave energy harvesting have been described.<sup>[26]</sup> Ten years later, two prototypes of wave energy harvesting devices were successfully developed and tested.<sup>[28]</sup> Many other wave generators were reviewed by Zanini.<sup>[29]</sup> Another type of generator, which uses running water instead of waves, was designed as a watermill and produced 35 mJ per rotation.<sup>[28]</sup> The same authors report that one of their rolled energy harvesting transducers, similar to the one that was used for wave energy harvesting, was able to withstand over 5 million cycles. Guijuan and Kesheng utilized DEG to harvest wind energy, showing that with DEGs, five times higher energy density is produced than with piezoelectric polymers.<sup>[30]</sup>



Figure 1.2 Schematic representation of the working principle of a) DEA, b) DES, c) DEG.

## 1.2.2. Parameters Responsible for the Performance of Dielectric Elastomer Transducers

#### 1.2.2.1. Polarization and Dielectric Permittivity

Generally, materials can be divided into conductors and insulators. Conductor materials can sustain particles that move in an applied electric field, such as electrons in metals. In insulators, such free-charge carriers are absent. Therefore no current flow can be observed in such materials. Dielectrics are considered to be a class of insulating materials that can be polarized in an electric field. In fact, dielectrics are not completely insulators, but their conductivity is in the range of 10<sup>-18</sup> to 10<sup>-6</sup> S/cm, and it arises due to the presence of imperfections and impurities in the material.<sup>[31,32]</sup>



Figure 1.3 Parallel-plate capacitor with a) vacuum, b) dielectric material in the absence of an electric field, and c) dielectric material between the plates.

For a deeper understanding of the intrinsic processes in dielectric materials and certain dielectric polymers, a parallel plate capacitor should be considered. In the presence of an external electric field V, a capacitor having electrodes with an area A and vacuum distance between two electrodes d will experience a build-up of charges  $\pm \sigma$  on both electrodes with concentrations  $\pm A\sigma$  (Figure 1.3a). While the electric field between the electrodes can be written as E = V/d, the electric flux density (or electric displacement)  $D_0$  originating from the charge density and capacitance  $C_0$  can be expressed as:

$$D_0 = \varepsilon_0 E$$
 Eq. 9

$$C_0 = \frac{A\sigma}{V} = \frac{A\varepsilon_0}{d}$$
 Eq. 10

When a dielectric material is placed between the electrodes (instead of vacuum), it will be polarized, giving rise to a charge density on both plates to  $\pm(\sigma+p)$  (Figure 1.3b, c). Therefore, capacitance and electric flux density will increase:

$$C = \frac{A(\sigma + p)}{V}$$
 Eq. 11

$$D = \varepsilon_0 E + P$$
 Eq. 12

where *P* is the electric polarization that appears due to the response of dipoles in the dielectric material that can align to an applied electric field. Because it is known that the relative permittivity is a main characteristic parameter of dielectric materials, in a static electric field, it can be expressed as:

$$\varepsilon_S = \frac{c}{c_0} = \frac{\sigma + p}{\sigma} = \frac{P + E\varepsilon_0}{E\varepsilon_0} = \frac{P}{E\varepsilon_0} + 1 = \chi + 1$$
 Eq. 13

where  $\chi$  is the electric susceptibility, which indicates how polarizable is the dielectric material in an electric field.<sup>[32]</sup>



Figure 1.4 Polarization mechanisms that can occur in materials at different frequencies.

In general, four types of polarization can be distinguished in the dielectric material (Figure 1.4) that occur at different frequencies.<sup>[19]</sup> The first one is electronic polarization, which is a consequence of the displacement of the electron cloud of any material in an electric field. Because electrons are low in mass, this process occurs at high frequencies, from 10<sup>12</sup> to 10<sup>15</sup> Hz.<sup>[33]</sup> The dipole moment caused by such polarization depends on the applied electric field and can be calculated using the following equation:

$$\mu_e = (4\pi\varepsilon_0 r^3)E$$
 Eq. 14

where r is the radius of the atom in which the charge is uniformly distributed. Equation 13 also states that, with increasing the atom size, the effect of electronic polarization also increases.

lonic polarization, also known as atomic polarization, occurs at lower frequencies (from 10<sup>10</sup> to 10<sup>12</sup> Hz). It originates in the displacement of atoms or ions when an electric field is applied. This effect is more pronounced in inorganic ionic materials. Usually, it is much lower than electronic polarization and can be calculated from the permittivity values obtained at different frequencies by subtracting electronic contributions.<sup>[33,34]</sup>

Orientation polarization generally appears in materials consisting of atoms with different electronegativity. Thus, the materials have permanent dipoles, which can align in the direction of the electric field. This polarization can be observed at frequencies around 10<sup>4</sup> to 10<sup>6</sup> Hz, and is a temperature-dependent process. At higher temperatures, the thermal motion of molecules is more pronounced, thereby counteracting the orientation polarization.<sup>[33]</sup>

The three polarization mechanisms discussed above are material-dependent, whereas an additional interfacial polarization mechanism arises because of the diffusion of charges within the material. They can accumulate on the interface between the electrode and dielectric material or the interface in heterogeneous systems such as polymer composites and give an increase in conductivity and permittivity. Such polarization happens at frequencies below 1 kHz because, at high frequencies, the impurities that cause this phenomenon do not have sufficient time to respond.<sup>[19,34]</sup>



Frequency [Hz]

Figure 1.5 Dependence of dielectric constant on frequency.

The effect of each mechanism of polarization on the dielectric constant of the material is summarized in Figure 1.5. The permittivity presented in equation 13 is calculated for a constant electric field. However, in an alternating electric field, both a delay in the polarization of dielectric material and a partial dissipation of energy are observed. Therefore, it is more common to present permittivity as a complex, frequency-dependent function:

$$\varepsilon^*(\omega) = \varepsilon'_r - i\varepsilon''_r$$
 Eq. 15

where  $\varepsilon_{r'}$  is the real part (relative dielectric permittivity),  $\varepsilon_{r''}$  is the imaginary part (dielectric loss),  $i = (-1)^{0.5}$ , and  $\omega = 2\pi f$  is the angular frequency of the electric field. The real part of dielectric permittivity represents the energy stored in the capacitor, while the imaginary part indicates dissipated energy.

#### 1.2.2.2. Dielectric Loss and Relaxation

Contrary to an ideal dielectric material, in which the current leads the voltage by 90°, in real dielectrics due to the polarization, the angle between current phasor and voltage phasor will be (90°- $\delta$ ), where  $\delta$  is the loss angle. Often, instead of the loss angle, the dissipation factor (or loss factor) is presented as *tan*  $\delta$ , which can be expressed as:

$$\tan \delta = \varepsilon_r'' / \varepsilon_r'$$
 Eq. 16

Both  $tan \delta$  and  $\varepsilon_r$ " are frequency dependent. The behavior of dielectric loss and the real part of permittivity versus frequency is shown in Figure 1.6, which is derived from the Debye relaxation model.<sup>[35,36]</sup>



Frequency [Hz]

Figure 1.6 Real and imaginary part of dielectric permittivity as a function of frequency (adapted from <sup>[35]</sup>).

Dielectric loss originates in the inability of dipoles to follow the oscillating electric field, and it depends on the relaxation time of a certain dipole. It indicates the time within which the dipole can completely orient in an electric field. At low frequencies,  $\varepsilon_r$ ' is high because of conductivity, and  $\varepsilon_r$ '' remains low. With increasing frequency, eventually reaching the value corresponding to relaxation time,  $\varepsilon_r$ ' diminishes. Close to relaxation time,  $\varepsilon_r$ '' starts to grow due to the impossibility for dipoles to follow the electric field, and therefore they convert electric energy into heat. After going through a maximum at the frequency corresponding to the relaxation time  $\omega = 1/\tau_r$  the dielectric loss decreases again. The basic Debye model represents the relation between dielectric properties and relaxation time. However, it is valid only for small spherical dipoles, which have only one relaxation time and do not exhibit any dipole-dipole interactions. Moreover, it considers the loss peak as symmetric and ideal, while in reality, it is asymmetric and exhibiting broadening from both sides. According to the literature, several empirical model functions such as Cole-Cole, Cole-Davidson, and Williams-Watt were derived from the Debye model to better describe the peak broadening.<sup>[33,35]</sup> The combination of the first two functions was presented in more general formula derived by Havriliak and Negami<sup>[33]</sup>:

$$\varepsilon^*(\omega) = \varepsilon_{\infty} + \frac{\varepsilon_s - \varepsilon_{\infty}}{(1 + (i\omega\tau)^a)^b}$$
 Eq. 17

where  $\varepsilon_{\infty}$  is the high-frequency permittivity,  $\varepsilon_s$  is the static permittivity, *a* and *b* have values between 0 and 1. The last two describe symmetric and asymmetric broadening and are called shape parameters. Equation 17 correlates the dielectric properties of materials with the relaxation time. Parameters  $\tau$ , *a* and *b* are temperature dependent. They can be calculated by applying the least-squares fit of Havriliak-Negami function to the dielectric loss spectrum plotted versus frequency, which can be obtained with Broadband Dielectric Impedance Spectroscopy (BDIS). If several relaxation processes are observed in the sample, additional Havriliak-Negami elements are added. The main relaxation process that can happen in dielectric elastomers is the  $\alpha$ -relaxation, which is associated with the segmental motion of the polymer backbone and usually occurs at the glass transition temperature. Other processes are called secondary relaxations. Generally, they are related to localized motions such as rotation or libration of the side groups.<sup>[35]</sup>

#### 1.2.2.3. Conductivity and Dielectric Strength

The desirable conductivity of dielectric materials for application in DETs should be below 10<sup>-15</sup> S/cm.<sup>[37]</sup> However, in some elastomers, an increase in conductivity of several orders of magnitude can be observed due to the presence of ionic impurities.<sup>[37,38]</sup> Similar to complex permittivity, the complex conductivity can be derived as:

$$\sigma^*(\omega) = \sigma'(\omega) + i\sigma''(\omega) = i\varepsilon_0 \omega \varepsilon^*$$
 Eq. 18

where  $\sigma'$  and  $\sigma''$  are, respectively, the real and the imaginary parts of conductivity. This formula shows the dependence of conductivity on dielectric loss and frequency. Normally, conductivity increases with frequency; however, there is a critical frequency value below which conductivity is frequencyindependent, because of the diffusion of charge carriers through the material and the formation of a conductive pathway.<sup>[39]</sup>

It is known that the conductivity of dielectric materials can also increase with the increase in an applied electric field due to the stronger migration of charges and the occurrence of a leakage current.<sup>[40]</sup> The

highest electrical field that a dielectric material can sustain is called the breakdown strength and can be defined as:

$$E_{br} = \frac{V}{d}$$
 Eq. 19

where  $E_{br}$  is the breakdown electric field, and it is a materials-specific parameter. The mechanism of an electrical breakdown is guite complex and includes intrinsic and extrinsic factors. Chemical degradation of the material on a molecular level can be referred to as the intrinsic reason for the breakdown. It happens when electrons obtain a sufficient ionization energy, speed up by an electric field, and create an electron avalanche.<sup>[41]</sup> It was shown that other intrinsic parameters, such as the elastic modulus, also affect the breakdown strength, which increases when a material with a higher modulus is employed.<sup>[42]</sup> Factors such as area, shape and nature of electrodes, frequency, temperature, humidity, structure imperfections like voids and cavities, impurities, prestretch of the material and electromechanical instabilities (EMI) (as will be discussed in Chapter 1.2.2.5) are extrinsic parameters.<sup>[38,43,44]</sup> Namely, materials defects and impurities can result in a lower dielectric strength ( $E_{br}$  = 3 V/µm for air, while  $E_{br}$  = 30 V/µm for conventional polysiloxanes) and therefore can cause a breakdown due to internal discharge.<sup>[45]</sup> This explains why membranes with higher prestrain and smaller electrode area have better dielectric strength - in thinner films and smaller area, the probability of observing a defect is diminished.<sup>[44]</sup> It was also reported that dielectric strength is higher for samples with rigid electrodes compared to compliant electrodes because the latter can be susceptible to electromechanical instability breakdown.<sup>[44]</sup> High dielectric loss is responsible for dielectric breakdown through heating of the material. At higher temperatures, the conductivity of the material also increases, leading to an additional rise in leakage current. Finally, degradation of the dielectric material occurs due to thermal breakdown.<sup>[46]</sup> In principle, any mechanism of breakdown leads to thermal runaway, which causes irreversible degradation of elastomer by its melting or vaporization.<sup>[40]</sup> One possible way to improve the dielectric strength of the material is to apply a series of high electric fields for a short time. That can remove charge carriers such as ionic impurities from the dielectric.<sup>[47]</sup> Estimation of dielectric breakdown can be done using equation derived by Stark and Garton,<sup>[48]</sup> which takes into account EMI and assumes elastomer to be completely homogeneous and elastic at low strain:

$$E_{br\,0} = 0.6 \left(\frac{Y}{\varepsilon_0 \varepsilon_r}\right)^{0.5}$$
 Eq. 20

Typical dielectric strength values of DE are in the range from 10 to 100 V/ $\mu$ m.<sup>[49]</sup> Generally, materials with high dielectric strength are more desirable for applications as DETs, because devices with higher performance can be constructed and their premature failure can be avoided.
#### 1.2.2.4. Mechanical Parameters

The distinguishing characteristic of elastomers among other solid materials (other polymers, metals, and ceramics) is their possibility to undergo repeated reversible relaxation after being subjected to large strains. A number of properties and applications of polymers depend on their mechanical behavior, which can be characterized by stress-strain tests. Figure 1.7 represents a comparison of the elastomer stress-strain curve with other polymers. Typical elastomers can be subjected to large strains of up to 500% or even 1000%, while exhibiting comparably low stress values;<sup>[50]</sup> more importantly, they show complete recoverability over millions of cycles. These physical properties impose requirements on the chemical structures of elastomers.<sup>[51]</sup>



Figure 1.7 Stress-strain curves of a typical rigid plastic (a), fiber (b), flexible plastic (c), and elastomer (d) (adapted with permission from <sup>[50]</sup>).

First of all, such materials must be based on high molecular weight polymers that offer a large number of spatial arrangements called "conformations" (Figure 1.8). Upon stretching, neither chemical bonds in elastomers nor bond angles exhibit any deformation. Elongation of the polymer molecules is achieved only due to the rotation of repeating units around single bonds.<sup>[52]</sup>



Figure 1.8 A polymeric chain consisting of 30 repeating units: a) random-coil conformation, b) extended linear conformation.

Secondly, polymers have to be operated above their glass transition temperature  $(T_g)$ .<sup>[53]</sup> This is the transition temperature below which a polymer shows glassy-like behavior, while above this temperature, it is a flexible, extensible elastomer. Below the  $T_g$ , when all polymer chains are frozen and cannot move freely, the polymer exhibits brittle behavior (Figure 1.7), with a high stiffness but a low strain-to-failure. Contrary, above  $T_g$ , polymer chains can freely change their conformation and therefore show high strain-at-break and much smaller stiffness.

Another essential requirement that allows a material to show elastomeric behavior is the cross-linking of the polymer chains into a three-dimensional network, which prohibits viscous behavior and yielding. Three types of cross-linking can be used to obtain elastomers. "Chemical cross-linking" is introduced by the chemical reaction of polymer chains. For the first time, it was done in 1839 by Charles Goodyear, who performed cross-linking of natural rubber by vulcanization using sulfur as a cross-linker.<sup>[54]</sup> Alternatively, "physical cross-linking" can be achieved by either chain entanglement or crystalline domains (Figure 1.9). Because the latter reinforce the elastomer, and polymers with such cross-links in the context of DEs result in LCE EAPs, this type of cross-linking is usually not employed in DEs. At the same time, chain entanglements cannot be avoided and are always present in cross-linked networks, especially when high molecular weight polymers are used. Usually, such entanglements also increase the stiffness of polymers.<sup>[51]</sup>



Figure 1.9 Three types of cross-links in elastomers: chemical, physical entanglements, crystalline domains.

The degree of cross-linking of elastomers significantly affects the mechanical properties of a material.<sup>[55]</sup> Figure 1.10 presents the impact of the degree of vulcanization (cross-linking) on the indicated properties. Therefore, the performance of DETs can be adjusted by choosing an elastomer with a certain degree of cross-linking density. The most relevant mechanical properties for DETs are tensile strain, modulus of elasticity, and viscoelastic properties, as will be discussed in more detail in what follows.





#### 1.2.2.4.1. Tensile Strain

Tensile strain at break is the measure of the maximum strain that a material can withstand under tension. When external forces stretch the material with an original length  $L_{0}$ , the material will be deformed to a new state with the length L. The tensile strain is thus defined as:

tensile strain 
$$=$$
  $\frac{L-L_0}{L_0} = \frac{\Delta L}{L_0}$  Eq. 21

Equation 21 shows the measure of the deformation of an object under applied stress. Usually, high molecular weight polymers result in elastomers with larger strain at break.<sup>[52]</sup> For application in DEAs, the strain values at break are not so important, while DESs and DEGs are more dependent on this parameter.<sup>[56]</sup> When stretch sensors are constructed, large tensile deformations may be applied to them, while in the case of generators, a higher amplitude is required to collect more electrical energy.

#### 1.2.2.4.2. Tensile Stress and Elastic Modulus

The elastic behavior of elastomers is described by parameters such as the elastic modulus (or Young's modulus), which is typically much lower compared to other materials. Thermodynamically, the elasticity of elastomers is fundamentally different from the elastic behavior of other solids. If a strip of metal is subjected to heating, it would expand because of an increase in distance between metal atoms. The opposite effect will be observed for an elastomer.<sup>[51]</sup> Under stretching, polymer chains change their conformation from a random coil, where a large number of conformations is available, to a more extended state with a more limited number of possible conformations.<sup>[52]</sup> Therefore, the entropy of the elastomer will decrease and the polymer chains will tend to return to the initial state, which is the origin

of the elastic behavior. Upon heating, the entropy contribution increases, rendering the random coil state to be more preferred, which causes a contraction.

The change in internal energy due to the deformation can be calculated using Helmholtz free energy:

$$dH = dU - TdS$$
 Eq. 22

where dU is the change in the internal energy of elastomer, T is the absolute temperature, dS is the entropy change. According to Mark,<sup>[57]</sup> the change of entropy in a polymer network that is deformed under load in all three dimensions can be defined as:

$$\Delta S = -0.5Nk_B(\lambda_x^2 + \lambda_y^2 + \lambda_z^2 - 3)$$
 Eq. 23

where *N* is the number of polymer chains in the network,  $k_B$  is the Boltzmann constant, and  $\lambda$  is the relative length change in a certain direction (x, y, or z). Assuming that the main contribution to the Helmholtz energy arises from entropy, it can be expressed as:

$$\Delta H = -T\Delta S = -0.5Nk_BT(\lambda_x^2 + \lambda_y^2 + \lambda_z^2 - 3)$$
 Eq. 24

As already mentioned before, an elastomer is considered incompressible material, which keeps a constant volume upon deformation. Therefore:

$$\lambda_X \lambda_y \lambda_z = 1$$
  

$$\lambda_x = \lambda, \lambda_y = \lambda_z = \lambda^{-0.5}$$
  

$$\Delta H = 0.5Nk_B T (\lambda^2 + 2\lambda^{-1} - 3)$$
  
Eq. 25

The Helmholtz free energy can also be considered as a work  $W = f \Delta L$  required by external forces f to achieve deformation  $\Delta L$ . By applying a force to a cross-sectional area, the mechanical stress can be defined as an engineering stress, which is normalized to the initial cross-sectional area:

$$\sigma = nk_B T V^{-1} (\lambda - \lambda^{-2}) = mk_B T (\lambda - \lambda^{-2})$$
Eq. 26

where  $nV^{1}$  is the network density *m*. More commonly, the relation of stress to the deformation is presented as a shear modulus *G*.

$$G = mk_B T = \rho RTM_c^{-1}$$
 Eq. 27

where  $\rho$  is the density of the polymer, *R* is the gas constant, and *M*<sub>c</sub> is the number-average molecular weight between the cross-links. It is known that in isotropic materials, the Young modulus is related to the shear modulus as:

$$Y = 2(1+v)G Eq. 28$$

where v is the Poisson ratio of elastomer (v = 0.5). Therefore, the Young's modulus can also be rewritten as:

$$Y = 3G = 3mk_BT Eq. 29$$

Thus, equation 29 and equation 27 show a correlation of elastic modulus with temperature and crosslinking density. Modulus increases at high temperatures and with large cross-linking density, while longer polymeric chains between the cross-linking points can diminish it.

The relation between stress and strain for materials in the elastic regime can be described using Hook's law, where the deformation of a material is proportional to applied stress. Therefore, elastic modulus can be derived:

$$\sigma = Ys$$
 Eq. 30

$$Y = \sigma s^{-1}$$
 Eq. 31

where *s* is the obtained strain,  $\sigma$  is the applied stress. Equation 30 can also be derived from the equation 26 when very small changes in length ( $\lambda = 1 + e$ , *e* is close to 1) are considered:

$$\sigma_s = eG = eY/3$$
 Eq. 32

where *e*/3 is a material constant.

However, equations 32, 30, and 26 are valid only for ideal elastomers that can rapidly equilibrate and obey Hook's law in the whole strain range.<sup>[52]</sup> In reality, a highly non-linear behavior is observed at large strains, as it is depicted in Figure 1.11.<sup>[58]</sup> Therefore, a more general theory has to be developed, taking into account other parameters.<sup>[56]</sup> Figure 1.11 presents three distinct regions. At very small strains (region **a**), a high Young's modulus is observed, showing the 'hardness' of the material. That is due to the entanglements that are formed between polymer chains. At some point, a transition of this 'hard' region **a** into a 'softer' region **b**, which looks like a plateau, occurs. In this region, the polymer chains are considered to be disentangled and require less energy for unfolding. A drastic stiffening characterizes region **c**. It is the point when many polymeric chains have reached their elastic limit, and more energy is needed for the subsequent stretching, which causes a rupture of the material.<sup>[58]</sup>

Another reason for the non-linear behavior is the presence of structural defects within the network, which can cause viscoelastic behavior<sup>[59]</sup> and/or hardening of the material.<sup>[57]</sup> The presence of dangling or uncross-linked chains gives rise to the former phenomena due to the slower relaxation of the elastomer,<sup>[59]</sup> while physical cross-links increase the modulus.<sup>[57]</sup>

Not only mechanical properties but also  $T_{g}$ , dielectric loss, and dielectric constant depend on the crosslinking density, even though some researchers state that the latter is not affected too much.<sup>[47]</sup>



Figure 1.11 The stress-strain curve of an elastomer.

It was shown that cross-linking density is an important parameter affecting the tensile strength and elastic modulus, while the non-linear behavior of elastomers can sometimes hinder the prediction of the mechanical properties. To fabricate a reliable DE device, the material has to be sufficiently cross-linked to give good elastic properties and a long lifetime. However, while for DEGs and DESs, the elastic modulus does not contribute to their performance, in the case of DEAs the lateral actuation strain is reversely proportional to the elastic modulus. Therefore, better performance can be obtained when the material has a lower modulus. Besides reducing cross-linking density, a decrease in Young's modulus can also be achieved by using low molecular weight plasticizers, increasing the molecular weight of polymer chains between cross-linking points, or a bimodal network of polymers with a large difference in molecular weight. However, it should be mentioned, that during reduction of the cross-linking density, care must be taken not to deteriorate other important properties of the material. Stress at break of elastomers, output force of actuators, longtime stability, and response time can also decrease due to the appearance of more pronounced viscoelastic properties.<sup>[34]</sup>

#### 1.2.2.4.3. Viscoelasticity

All elastomers are considered to be viscoelastic materials, exhibiting both elastic behavior like solids and viscous behavior similar to fluids.<sup>[60]</sup> The predomination of viscous properties can be significantly reduced with an increasing degree of cross-linking. Highly cross-linked elastomers almost do not show any viscoelastic behavior, while the presence of structural defects such as dangling chains or uncross-linked chains and plasticizers can lead to a higher viscoelastic loss and creep.<sup>[34]</sup> In elastic materials, energy is usually preserved in the elastic recovery of polymer chains, whereas the viscoelastic nature facilitates the conversion of energy through molecular motions into heat.

For a better understanding of viscoelastic behavior, mechanical analogs can be considered. For this purpose, the elastic behavior of elastomer can be represented by a mechanical spring, while the hydraulic dashpot defines the viscous component. These two components can be connected either in series,

representing the Maxwell model, or in parallel, representing the Kelvin-Voigt model (Figure 1.12). In the first case, the total strain equals the sum of the strain of both elements.<sup>[61]</sup> The stress on both elements is identical, and it equals the applied stress. In the case when a constant load to the system is applied, the strain response can be described by the following equation:

$$s(t) = \eta^{-1}\sigma_0 t + \sigma_0 Y^{-1}$$
 Eq. 33



Figure 1.12 Graphical representation of Maxwell model (left) and Kelvin-Voigt model (right) (adapted from <sup>[61]</sup>).

Figure 1.13a can graphically represent the result of equation 33. It is shown that a spring can instantaneously respond to the applied stress, while subsequent creep appears due to the viscous behavior of dashpot. When the stress is released, the spring relaxes instantaneously, whereas the viscous component remains irretrievably deformed.

Another test can be done by subjecting the same system to a constant strain (Figure 1.13b). The stress can be expressed as:

$$\sigma_s = \sigma_0 \exp(\eta Y^{-1})t \qquad \qquad \text{Eq. 34}$$

where the stress shows exponential decay with the relaxation time constant ( $\tau = \eta Y^{-1}$ ).

The Maxwell model is good for estimation of primary elastic deformation and exponential relaxation; however, it fails in the prediction of time-dependent recovery and creep (in Figure 1.13a a Newtonian flow is observed instead of creep, which is not true).<sup>[61,62]</sup>

The Kelvin-Voigt model is a more general model for the representation of creep. It considers a parallel arrangement of spring and dashpot. Therefore, instead of an immediate spring extension under applied stress as detected in the previous model, deformation will be time-dependent with an exponential increase until it reaches the maximum value of strain (Figure 1.13c). When the stress is removed, the opposite process of recovering the initial length occurs. However, this model cannot describe an immediate response, any irreversible deformations, and time-dependent relaxation.<sup>[61]</sup> For a more general model, which can describe both phenomena such as creep and relaxation in a more precise way or even





Figure 1.13 a) Creep and b) relaxation predicted by Maxwell model; c) creep and recovery response according to Kelvin-Voigt model (adapted from <sup>[62]</sup>).

Viscoelastic properties are very important for predicting the mechanical parameters and working performance of different materials and devices. Therefore, there is a need for reliable methods, which can be used for this purpose. Most such techniques include a stepwise increase of stress or strain and the measurement of the resulting response in strain or stress over time.<sup>[63]</sup> One of the easiest methods to measure viscoelasticity is by doing cyclic uniaxial stress-strain measurements. During such tests, elastomers can show hysteresis (Figure 1.14), where one stress-strain curve is obtained during the loading, while the material follows another curve during the unloading. Usually, such curves do not overlap, and the larger the hysteresis, the more viscoelastic the material is. The area between both curves is attributed to the energy that was dissipated as heat.

Another common technique for materials characterization is dynamic mechanical analysis (DMA).<sup>[56]</sup> In this method, a sinusoidal stress is measured in response to an applied sinusoidal strain. The measured stress usually has the same frequency as the input strain, but may be out of phase and also has a different amplitude in viscoelastic materials. The phase lag indicated as the angle  $\delta$  usually stays in the range from 0° (for a purely elastic material) to 90° (for an ideal viscous material).<sup>[63]</sup> Because the resulting stress is considered to consist of two components, where one is in phase with the strain and another one is out of phase,<sup>[62]</sup> the stress-strain relationship can be presented as a complex modulus:

$$E^* = E'(\omega) + iE''(\omega) \qquad \qquad \text{Eq. 35}$$

where E' defines the energy stored in the sample and is called as storage modulus, and E'' is the loss modulus indicating how much energy was dissipated. Often, viscoelastic properties are characterized through the ratio between E'' and E', which is called a loss tangent:

$$tan \,\delta = E''/E'$$
 Eq. 36

Materials with  $tan \delta$  below 1 are considered to be mainly elastic, while a  $tan \delta$  above 1 indicates that a material is mainly viscous.<sup>[64]</sup> Generally, DEs have  $tan \delta$  values below 0.1.<sup>[56]</sup>



Figure 1.14 An example of a hysteresis curve.

While certain applications can benefit from the material exhibiting viscoelastic properties at a specific frequency,<sup>[64]</sup> for application in DETs, materials with more elastic behavior are preferred.<sup>[34]</sup> That can be explained by taking as an example a DEG consisting of a viscoelastic material. Due to the longer relaxation time, which sometimes can be above the value of the operation cycle of DEG (around 1 s), such an elastomer cannot be stretched to the expected value in the DEG. This will cause a smaller difference in capacitance and lead to a smaller output energy and lower efficiency.<sup>[65]</sup>

#### 1.2.2.5. Failure Modes

It is common for all electrical and mechanical devices to have different kinds of failures. The same is true for DETs. Usually, four different failure modes are observed in DEAs: mechanical rupture, wrinkling or buckling, breakdown, and electromechanical instability (EMI).<sup>[66]</sup> The first failure depends on the extent of stretching. It was proposed that the reason behind this effect is the rupturing of the material due to the extension of polymer chains beyond the maximum possible level.<sup>[67]</sup> Buckling and wrinkling appear when, during the application of an electric field, the mechanical stress acting on the membrane switches from being tensile to compressive. This can cause an out-of-plane deformation such as buckling and subsequent wrinkling. During such failure, a DEA will not be destroyed like during the mechanical

rupturing or electrical breakdown.<sup>[65]</sup> Electrical breakdown and EMI are considered two failure modes that keep actuators from achieving large deformations by voltage.<sup>[68]</sup> The former failure mode is considered to be the more predominant one<sup>[69]</sup> and was already discussed in the previous chapters. EMI failure is caused by the viscoelastic properties of elastomers and can lead to either mechanical failure due to rupture or electrical failure because of breakdown.<sup>[34,67]</sup> It takes place when, due to a high electric field, compression of elastomer occurs. Therefore polymer layer between the electrodes becomes thinner, and the same voltage causes an even higher electric field acting on the membrane. It could happen that the originated Maxwell stress will be greater than the mechanical resistance of the material, which will result in the occurrence of an EMI, that is, a drastic reduction in thickness and appearance of a complex 3D wrinkling pattern (Figure 1.15a).<sup>[67]</sup>



Figure 1.15 a) Material before (left) and after (right) pull-in instability (reprinted with permission from <sup>[43]</sup>). b) Actuator capable of achieving more than 1600% of strain. Before EMI (left), after EMI (right) (reprinted with permission from <sup>[70]</sup>).

Zhao and Wang<sup>[43]</sup> proposed two methods for suppressing EMI. One option would be to use a soft elastomer that exhibits strain-hardening at the strain range before EMI occurs. Such materials were obtained using nanostructured polymers, triblock copolymers, and interpenetrating polymer networks, and actuation above 300% strain was achieved.<sup>[43]</sup> Suo developed a theory that an EMI can also be avoided by using a polymeric network that has folded polymer chains or polymers that have side chains.<sup>[68]</sup> Another option to avoid EMI is to prestretch the polymer before the device fabrication.<sup>[43]</sup> Thus, the material is mechanically transferred to the strain-hardening region.

However, it should also be mentioned that, sometimes, an EMI can be purposefully used with good results. Achieving an actuation strain above 1600% (Figure 1.15b) with an inflated diaphragm configuration by harnessing an EMI was reported by Li *et al.*<sup>[70]</sup>

# 1.3. Design of Dielectric Elastomer Transducers

# 1.3.1. Configurations of Dielectric Elastomer Transducers

As it was mentioned earlier, the basic configuration of a DEA consists of a single membrane with two compliant electrodes on both sides. In an applied electric field, such a DEA can show an expansion in area

and simultaneous thickness contraction. Such a design can be a good starting point for the comparison of different materials, because many additional parameters, which have to be considered in more complicated devices, can be avoided. However, there are not many practical applications of such a single membrane actuator due to the multilateral actuation and low actuation force. Therefore, new configurations have been constructed and adapted for various applications. All actuators can be divided into two types: linear thickness contraction and area expansion devices.<sup>[71]</sup>

The basic design of an actuator with only a single elastomer layer can be presented in several configurations: framed, diaphragm, strip-in plane, cone, bowtie, dielectric elastomer minimum energy structure (DEMES), and others. Many of them will be described below in this chapter.



Figure 1.16 An example of different configurations of DEAs (reprinted with permission from <sup>[72]</sup>).

A framed configuration consists of a dielectric film that is stretched within a rigid frame. The frame keeps a membrane in a pre-stretched state to avoid buckling, holds film under tension, and generates unidirectional or bidirectional movement.<sup>[73,74]</sup> One example of such an actuator is presented in Figure 1.16. To generate in-plane linear actuation, Pelrine *et al.* mounted an addition output shaft to the pre-stretched film.<sup>[15]</sup> Thus, a push-pull motion of a central part can be achieved.

Kornbluh *et al.*<sup>[75]</sup> proposed a very simple optical switch consisting of a single framed actuator (Figure 1.17a). In the absence of an electric field, the membrane is relaxed. Actuation of the film strains the black electrode material, which becomes less dense and, therefore, turns from opaque to transparent. Another example of an electrically tuned transparency of a polymeric membrane was reported by Chen *et al.*<sup>[76]</sup> In that case, a transparent electrode material was used. Authors were able to develop two different actuation modes, showing that film can be either transparent in a relaxed state and opaque in an actuated state or vice versa. A more complex actuator structure for optical applications was developed by Carpi *et al.*<sup>[77]</sup> A tunable lens was constructed, which consists of a fluid elastomeric lens embedded in the middle between

the two layers of dielectric membranes. An electrode in an annular form was applied on both sides of the films. Application of different voltage allows tuning the focal length of the lens due to its deformation.



Figure 1.17 a) An example of optical switch; b) motor based on two bowtie actuators (adapted with permission from <sup>[72]</sup>).

In a bowtie shape configuration, uniaxial linear actuation is obtained by coupling a bidirectional movement (Figure 1.16).<sup>[75]</sup> It is achieved using a compliant frame, which can move in one direction during the membrane expansion. Such configuration allows constructing a 20 mm long bowtie bender actuator that can exhibit up to 15° of bending and can be utilized to fabricate modular robotic arms.<sup>[78]</sup> Recently, it was also shown that the combination of two bowtie actuators opens the opportunity to construct a motor, which produced up to 600 rpm (Figure 1.17b).<sup>[73]</sup> Plante and Dubowsky<sup>[79]</sup> developed a diamond actuator where the elastomer is sandwiched between compliant frames having a diamond shape. Around 100% of linear strain was achieved by them.



Figure 1.18 Strip-in-plane actuator made by Hau et al.<sup>[80]</sup> (reprinted with permission from <sup>[80]</sup>).

Another configuration, called strip-in-plane, was proposed by Hau *et al.*<sup>[80]</sup> Instead of using a frame on all sides as it was done in the previous configurations, the authors clamped the membrane only from two sides (Figure 1.18), one of which was stationary, while a negative-rate bias was applied to the other. An actuation strain of 45% with 0.38 N force output was detected upon applying an electric field. Because

the use of rigid frames is not consistent with the principles of soft robotics, Kofod *et al.*<sup>[81]</sup> have designed a dielectric elastomer minimum-energy structure (DEMES) by laminating a pre-strained elastomeric membrane to a flexible polymeric foil. The elastomer can release the stored elastic energy by contraction, therefore the flexible foil together with the elastomer is bent. During the actuation of such a device, internal tension decreases and the structure becomes flat. The same authors utilized this approach to fabricate a tulip-shaped gripper: when a voltage is applied, it opens, while when the voltage is removed, it can grasp an object giving possibilities to lift it (Figure 1.19a).<sup>[82]</sup> Later, the DEMES concept was extended by Araromi et al.<sup>[83,84]</sup> They developed a deployable gripper using multisegment DEMES actuators (Figure 1.19b). At a weight of 0.65 g, the device was able to achieve a tip angle change of 60°, a 2.2 mN maximum gripping force, and survived 860'000 cycles. Similar bending behavior can be obtained with unimorph and bimorph actuators. To determine a direction of bending, either two electrodes with different stiffnesses are employed,<sup>[85]</sup> or the elastomer has to be laminated to a flexible substrate. So far, many applications of unimorph actuators were presented. Ahmed *et al.*<sup>[86]</sup> fabricated a multilayer actuator that has an origami structure and is capable of complete folding and unfolding. In another work, a similar multilayer structure showed a fast actuation up to 30 Hz, which can be applied to different segments of a single actuator.<sup>[87]</sup> Shintake et al.<sup>[88]</sup> developed a soft gripper based on unimorph structure. The gripper with a weight of 1 g was able to pick up a raw egg with a weight of 60 g (Figure 1.19c). Contrary to unimorph configurations, bimorph structures allow for a controlled bending in both directions. Implementation of such structures into devices allowed Shintake et al.<sup>[89]</sup> and Berlinger et al.<sup>[90]</sup> to construct miniature underwater robots.

In extender configuration, a linear extension of one side is achieved, while the other side of the actuator is fixed. Bolzmacher *et al.*<sup>[91]</sup> utilized such a configuration for the fabrication of a wearable, flexible actuator. Instead of using rigid frames for pre-stretching, the authors reinforced the actuator with nylon fibers, which can hold elastomers in a prestrained state and bias the actuator to move in one direction. An example of a practical application of an extender actuator consisting of several layers can be found in the work of Carpi *et al.*<sup>[92]</sup> Namely, an active orthosis for hand rehabilitation was developed using a dielectric elastomer.

A diaphragm configuration can be a good choice when a large out-of-plane deformation is needed. Due to the pressure gradient during such a high displacement, actuators with diaphragm configurations can be suitable for pump fabrication. Thus, a dual-membrane pump capable of pumping a large volume of liquid was made by Li *et al.*<sup>[93]</sup> Christianson *et al.*<sup>[94]</sup> presented a pump made of silicone and driven by a fluid electrode dielectric elastomer actuator. They showed that the surrounding conductive fluid could act as compliant electrodes and simplify the pump's structure. A DEA micropump that can be operated at 3 Hz giving a flow rate of 42  $\mu$ L/s was constructed by Ghazali *et al.*<sup>[95]</sup> while Kornbluh *et al.*<sup>[75]</sup> demonstrated a single-membrane pump made of an acrylic elastomer with a flow rate of 35 mL/min. The main advantage of DEA pumps is that they consist of a cheap material, exhibit silent operation without vibration, and can be manufactured in small sizes. Another interesting application of diaphragm actuators is loudspeakers, which can be fabricated in a flat form,<sup>[96]</sup> or as a hemisphere capable of operation up to

16 Hz.<sup>[97]</sup> Actuators of such configuration have also found applications in many other devices such as valves, smart skin, Braille displays<sup>[75]</sup> and robotics.<sup>[98,99]</sup>



Figure 1.19 a) DEMES actuator that can lift an object, b) gripper based on DEMES actuators (© 2015 IEEE), c) soft gripper based on unimorph actuators (adapted from <sup>[82, 84, 88]</sup>).

So far, the described configurations contain mainly one, two, or sometimes several layers of the dielectric film. However, to obtain a device with a higher output force and stroke, the combination of many layers has to be used. One of the configurations, which allows the fabrication of a multilayer structure, is a rolled actuator. It comprises a stack of two dielectric films and two electrodes wrapped around a core, whereas core-free structures can also exist.<sup>[100]</sup> Like natural muscles, rolled actuators have a cylindrical structure and can generate linear expansion in axial direction under actuation<sup>[73]</sup> and withstand more than 10 million cycles with only little degradation.<sup>[75]</sup> More than 20 years ago, rolled actuators with small dimensions (length <20 mm, diameter <5 mm) that could produce up to 10% strain were developed.<sup>[15]</sup> Later, a 15 g actuator which showed 25% strain and generated forces above 5 N was reported.<sup>[75]</sup> In this work, authors also described a six-legged robot in which two rolled actuators drove each leg and a small inchworm robot consisting of a single roll. Zhang et al.<sup>[100]</sup> developed a low-weight portable force feedback device. A maximum force of 7.2 N and actuation of the active zone as high as 31% were detected for that device. A combination of more than 250 rolled actuators was used by Kovacs et al.<sup>[101]</sup> for the construction of an arm-wrestling robot for a competition at the SPIE conference in 2005. Pei et al. [102] constructed a one-degree-of-freedom (1-DOF) actuator exhibiting 25% strain and up to 15 N force using a compressed spring as a core. Further development and a special alignment of the electrodes allowed them to design 2-DOF and 3-DOF actuators, which can actuate linearly and show a bending behavior. The largest actuation strain obtained for a rolled actuator was detected by Huang *et al.*<sup>[103]</sup> using nylon fibers to reinforce the dielectric layer. Around 35.8% of strain was detected for an actuator fabricated of an elastomer at 40% prestrain. However, the driving voltage of this actuator was extremely high, around 21 kV.

The working principle of all the above-mentioned actuators is based on the areal expansion of the DE. However, for certain applications, a contraction activation is required, when the device's thickness is reduced during the actuation. That can be achieved by using a stack actuator consisting of many alternating layers of dielectrics and electrodes. Up to now, three types of multilayer actuators working in contraction mode can be distinguished: helical structures, folded structures, and stacked structures. The first type was proposed by Carpi *et al.*<sup>[104]</sup> and had a very simple configuration (Figure 1.20a). It consists of two helices cut from dielectric elastomer tubes. After two compliant electrodes are deposited on one helix, as shown in Figure 1.20a (middle), another helix is inserted into the first one. The actuator showed -5% of contraction strain at 14 V/µm. While the fabrication of such actuators is straightforward and fast, the main disadvantage of this approach is the thickness of the obtained helix, which is 0.8 mm. Because the helical structure is achieved by blade cutting a tube, it will not be easy to fabricate structures thinner than 100 µm. Using a single elastomer stripe, Carpi *et al.* developed a folded actuator (Figure 1.20b) which can be prepared in a very fast and simple manner.<sup>[105]</sup> First, the film has to be coated with an electrode, and then it is simply folded into a multilayer stack. An actuation strain of -16% at 12 V/µm was detected for that actuator.

A stack configuration with a number of similar segments consisting of a dielectric film with spattered electrodes that were stacked on top of one another was, for the first time, presented by Kovacs and Düring<sup>[106]</sup> in 2009. Using a modified acrylic elastomer that can be used without prestretching, the authors fabricated several actuators consisting of 210-400 layers of elastomers with 16 mm active diameter. The total length of the devices varied from 14 to 25 mm.<sup>[107]</sup> For one actuator with free ends, they obtained a contraction strain of up to 46% at 4.1 kV, while another actuator lifted 4.5 kg showing 5% contraction.<sup>[106]</sup> In the work of Nguyen *et al.*,<sup>[108]</sup> a walking robot with four legs made of 2-DOF stack actuators was proposed. Each stacked actuator had a length of about 23 mm and contained 58 layers of elastomer. At a mass of 9.68 g, it contracted by 3.6% with a 900 g load upon actuation. Recently, a new application of dielectric stack actuators was proposed by Solano-Arana *et al.*<sup>[109]</sup> They used a combination of modules (30 layers of dielectrics per module) to fabricate a micromixer. The device had a pumping chamber that comprised four modules in series and a mixing chamber with four consecutive modules. The detected flow rate at the mixer outlet was 21.5  $\mu$ L/min when a voltage of 1500 V at 10 Hz was applied.

While a range of configurations of dielectric elastomer actuators has been discussed in this chapter, it is worth mentioning that other configurations like zipper, balloon, cone-shaped, hinge, etc., also exist, and with the development of DEA technology, researchers will come up with even more designs. Even though many types of devices can be fabricated from any of these structures, it is clear that stack actuators have advantages to obtain devices with performance similar to the natural muscles. Stack actuators are

lightweight and soft, can exhibit large forces and strain, and in some cases can survive more than 3 billion actuation cycles.<sup>[71,110]</sup>



Figure 1.20 a) Helical actuator (adapted with permission from <sup>[104]</sup>). b) Folded actuator (copied with permission from <sup>[105]</sup>).

# 1.3.2. Electrodes

Coulomb interactions, generated due to the creation of surface charges on the dielectric elastomers when the electrodes are connected to the voltage source, are the main driving force of DEAs. In principle, the deformation can be obtained even without electrodes as recently shown by Keplinger *et al.*<sup>[111]</sup> The charges on the film were sprayed by a corona discharge, thereby bringing the elastomer into actuation. Because the elastomer is a non-conductive material, the charges are immobile, therefore global and local pull-in instabilities are avoided.<sup>[49]</sup> While such an approach helps to avoid many electrode-related problems, the main limitation comes with removing charges. In the presence of electrodes, the discharging can be done much faster. In addition, electrodes can be patterned in different designs with defined shapes, therefore only a certain location of the device can be actuated.<sup>[112]</sup> Because of this reason, the application of the electrode-free technique seems to be a good choice for scientific characterization of different materials, whereas, for fabrication of different devices and their practical applications, the presence of electrodes is essential.

A number of electrode materials have been tested in the field of DETs. Besides having a high conductivity, a good electrode should also be compliant and capable of large deformations. Compliance of the electrode means that it should not constrain the elastomer when the latter is extended in the area due to electrostriction.<sup>[15]</sup> Since it has already been known that elastomers can achieve actuation strain above 100%, electrodes that can also follow such high actuation and remain conductive are needed.<sup>[113]</sup> Additionally, electrodes should be thin, with a low elastic modulus and good adhesion to the elastomer, and they should be able to withstand millions of operating cycles.<sup>[112,114]</sup>

Generally, metals are very conductive and can be easily applied, consequently, they are considered a good electrode material for electronics. However, because the modulus of metals is in the range of GPa, they cannot be considered compliant materials. Even a very thin layer (8 nm) of metallic gold results in a

significant increase in the modulus of 30.6 µm PDMS film by 440%.[115] The maximum extensibility of metal electrodes is in the range of 2-3%. At higher strains, they crack, and conductivity drops. Nevertheless, some researchers are still conducting experiments trying to develop metal-based electrodes that can withstand high deformations. Thus, Benslimane et al.<sup>[116]</sup> deposited metallic silver on a corrugated silicone membrane. Due to such a design, the electrode was stiff in the lateral direction (perpendicular to the waves), while in the corrugated direction it maintained conductivity to up to 33% strain. Still, the modulus of elastomer was increased by a factor of two. A slightly different approach was realized by Lacour *et al.*<sup>[117]</sup> who achieved a wavy structure by depositing gold on a prestretched substrate. Electrodes remained conductive up to 22% strain. Using gold electrodes, a higher strain (up to 80%) was achieved by Pelrine et al.<sup>[118]</sup> Gold electrodes in zig-zag patterns with 5 µm width were applied to an elastomer using photolithography. However, in that case, the membrane can be stretched only in one direction. Because zig-zag stripes do not cover the whole area of the elastomer, additional electrode material, even with much higher resistance, is still needed between the zig-zags. It was also reported that thin films of gold (around 50 nm) sputtered onto an elastomeric membrane can be uniaxially stretched to 20% for more than 250'000 cycles and remain conductive.<sup>[119]</sup> That is achieved due to the formation of interconnected islands of gold after the metallic film is cracked. In the work of Rosset et al.<sup>[120]</sup> stretchable metallic electrodes were obtained by implantation of metal ions. During this procedure, mobile nanoclusters that stayed conductive to up to 175% of strain were created on the surface of the elastomer. Compared with palladium and titanium, gold showed superior properties and sustained more than 100'000 cycles at 30% strain. Still, an around 50-100% increase in elastic modulus of elastomer was observed, and special equipment is required for the implementation of such a method. Recent studies have shown a potential application of liquid metals as electrodes for DEAs. Finkenauer and Majidi<sup>[121]</sup> used liquid Gallium-Indium alloy for constriction a bending actuator. However, the authors also reported on fabrication problems, and no data for the elastic modulus and reliability were presented. In the work of Delille et al.,<sup>[122]</sup> an investigation of metal-polymer composites for application as electrode material was conducted. Embedding of a platinum salt into a polymeric matrix and successive reduction of the salt into metal allowed them to fabricate an electrode that remained conductive up to 40% strains.

Contrary to metal electrodes, carbon-based electrodes are considered more compliant and were used in DETs from the early stage of technology.<sup>[112]</sup> Carbon black, which is applied either as a powder or as grease, is the most widely used electrode for DETs,<sup>[114]</sup> while materials like graphite, graphene, or CNTs have been frequently utilized, as well. The main advantage of carbon or graphite powders as electrode materials is that they do not significantly increase the modulus of the elastomer to which they are applied.<sup>[112]</sup> To deposit such electrodes, a simple brush painting or dispersion of powder in a volatile solvent and subsequent screen-printing can be employed. The drawbacks of such electrodes are their disordered nature and the impossibility of obtaining a uniform layer.<sup>[118]</sup> While single-layer or double-layer actuators might not cause any problems, the fabrication of a stack actuator requires very smooth electrodes to obtain a reliable device.<sup>[118]</sup> Additionally, the powder can detach from the membrane within the actuation cycles, so that the conductivity in some areas may decrease. Due to that reason, powders are mostly used together with sticky elastomers, such as acrylic VHB from the company 3M, which can

provide a stronger binding.<sup>[112]</sup> Nevertheless, a stack actuator was fabricated by Lotz et al. by spraying graphite powder onto PDMS.<sup>[123]</sup> Low adhesion of powders to silicones should not be considered as an essential drawback for stack actuators, because in that case, every layer of the electrode is covered by the next layer of the elastomer. A better way to employ carbon electrodes is to use them in the form of grease when, for example, a carbon black powder is mixed with oil. This material has better adhesion, can be easily applied in a well-defined shape, and like carbon powder, it does not constrain the elastomer.<sup>[124]</sup> Carbon grease was used in many works, e.g., for the fabrication of a rectangular actuator,<sup>[125]</sup> a membrane actuator with different electrode patterns,<sup>[126]</sup> a rolled bending actuator,<sup>[124]</sup> a positioning system based on membrane actuator<sup>[127]</sup> and a planar oscillator.<sup>[128]</sup> However, as it was stated in the latter work, commercial carbon grease is not always compatible with silicones that are commonly used for actuators. Grease contains oils that can cause the elastomeric membrane to swell, or they can dry. Because it is uncured, grease can be damaged when touched, or show creep when the device is tilted. Therefore, it is difficult to consider grease as a long-term electrode. A comparison of carbon grease with other electrode materials like graphite powder, graphite spray, or thickened electrolyte solution was conducted by Carpi et al.<sup>[129]</sup> The researchers showed that a thickened electrolyte solution has a better performance at electric fields below 25 V/µm. At higher fields, using graphite spray is more desirable. Moreover, the work of Yuan et al.<sup>[130]</sup> indicated that in comparison to SWCNT-oil electrodes, actuators made with carbon grease electrodes exhibited a 25 times shorter lifetime when operated at 150% area strain. The reason behind this difference in lifetimes lies in the self-healing properties of CNT-based electrodes. When CNTs decompose around the short circuit, they isolate the remaining electrode from the breakdown area, allowing the actuator to work again. Several other authors have also shown a similar behavior of CNTbased electrodes. Yuan et al.<sup>[131]</sup> presented an actuator made of VHB and SWCNTs, which can reach 200% actuation strain and exhibit self-healing properties. Duduta et al.<sup>[132]</sup> observed self-clearing in their stack actuator. Stoyanov et al.<sup>[133]</sup> presented results, where an actuator with SWCNTs electrodes that survived self-clearing more than 30 times was able to withstand 85'000 actuation cycles giving almost 20% strain (Figure 1.21). Not only self-healing, but also transparent properties of SWCNTs electrodes were described in the work of Shian *et al.*,<sup>[134]</sup> where almost 91% of optical transparency was detected at 190% strain. A comparison of three self-clearing electrodes was perfomed by Yuan et al.[135] They investigated selfclearing mechanisms and time of SWCNTs, PANi and P3DOT electrodes. It was shown that upon applying a similar voltage (3 kV) SWCNTs can self-clean in 3 s after the breakdown, P3DOT required 3-4 s, while for PANi it took 10 s. Another electrode material which can show self-healing properties was developed by Michel et al.<sup>[114]</sup> It was made of a cured composite material, which consists of 20 wt% graphite nanoplatelets dispersed in silicone. The electrode was shown to be compliant, stretchable and had a very low sheet resistance. Using cross-linked electrode material is a good approach to avoid the disordered nature of particles and grease and their segregation from the membrane. A cross-linked electrode consisting of a mixture of silicone and carbon black was utilized by Carpi et al.<sup>[105]</sup> for the fabrication of their folded stack actuator. Bozlar et al.<sup>[136]</sup> compared actuators made with cured electrodes (carbon black mixed with silicone) and fully compliant electrodes (carbon grease). They state that gualitatively similar performance was achieved with both electrodes, giving almost 70% strain under actuation. More recently,

an automatic industrial procedure for printing small-scale rubber-based electrodes was developed by Rosset and Shea.<sup>[137]</sup> It was realized by pad printing of a carbon black mixture with a cross-linkable silicone on a DE membrane with subsequent curing at 80 °C for 30 min. The obtained electrodes were compliant and therefore were utilized for fabrication of different devices such as a tunable lens, a motor, or a rolling robot. Up to now some of them survived more than 400 million actuation cycles.



Figure 1.21 Actuator with self-clearing electrodes cycled for more than 20'000 cycles (copied with permission from <sup>[133]</sup>).



Figure 1.22 Transparent electrode with tunable transparency (copied from <sup>[76]</sup>).

In principle, many other electrode materials are suitable for application in DEAs. Some of them are specially made to serve certain criteria, for example, being stretchable and transparent, such as a PEDOT-PSS-based electrode prepared by Chen *et al.*<sup>[76]</sup> for application in lenses or smart windows (Figure 1.22). Silver nanowires, hydrogels, and ionic conductors are also good candidates for applications where transparency and self-healing are needed.<sup>[74,112]</sup> For a better and more detailed understanding of electrodes materials, their properties, and applications, readers are referred to a seminal review published by Rosset and Shea.<sup>[112]</sup>

In the work presented in this thesis, carbon black powder has been used as a material of choice for singlelayer dielectric elastomer actuators. This helped to avoid any undesirable constraints on the new dielectric elastomers investigated here, and, therefore, better characterization data for a comparison of the different materials can be obtained.

## 1.3.3. Elastomers

The employed elastomer is the most important component of every DET. All properties of elastomers directly affect the performance and durability of DETs. Therefore, a suitable polymer has to be carefully chosen for a particular application. The first elastomer subjected to the application of electric charges was natural rubber, by Roentgen in 1880. Much later, in the early 1990s, Pelrine and others discovered that all insulating elastomers exhibited an electromechanical response when charged. Silicone elastomers were the most popular during that time, until Pelrine discovered the prospect of acrylic elastomers in 1999. Acrylics immediately achieved strains above 100%, making them interesting candidates for DEs.<sup>[138]</sup> The first application of urethanes dates back to 1994 when Zhenyi *et al.*<sup>[139]</sup> studied electrostrictive polymers of semi-crystalline polyurethane. Nowadays, silicones and acrylic elastomers are the most widely used materials for DETs,<sup>[140]</sup> because the former are very efficient, have a fast response time, and long lifetime, while acrylics are commercially available, can be stretched up to 36 times, and exhibit an adhesive nature that facilitates their handling.<sup>[66,140]</sup>

Besides the four indicated elastomers, there are some works that have utilized other elastomeric polymers as DEs. Yang *et al.*<sup>[141]</sup> synthesized polyester elastomer with varied cross-linking density and dielectric constant ranging from 5 to 8. Their best actuator exhibited 11.9% of lateral actuation strain at 15.6 V/µm. Another material, chloroprene, was investigated by Waché *et al.*<sup>[142]</sup> It was shown that this polymer has a permittivity value of 10, keeping the conductivity below  $10^{-11}$  S/cm, and  $T_g$  of -30 °C. However, the actuation of this material was quite low, around 2 % at an electric field below 20 V/µm.

In the next chapter, more details will be given about recent developments in DETs using polysiloxanes, acrylics, polyurethanes elastomers, and those that have a structure similar to natural rubber.

# 1.4. Elastomers Used for Dielectric Elastomer Transducers

## 1.4.1. Polyurethanes

Polyurethanes (PUs) are synthesized by a step-growth polyaddition reaction between a dialcohol and diisocyanate. In many polymerization reactions, mixtures of diols and diamines are employed, therefore, the formed polymer may contain both urea and urethane repeat units. Because polyurethanes are often used to fabricate foamed products, water can also be added to the reaction mixture. It can react with isocyanates producing carbon dioxide as a blowing agent and a urea linkage.<sup>[50]</sup> The properties of PUs are very versatile and can be tuned by variations in chemical structure of their (aliphatic saturated,

unsaturated, or aromatic) repeat units, and the degree of cross-linking, which can be achieved either using multifunctional reactive units, through unsaturated double bond in the repeat unit, or physically via crystalline domains.<sup>[34,143]</sup>

Two first papers describing the application of PU elastomers in DETs were published in 1997. Ueda *et al.*<sup>[144]</sup> obtained a PU elastomer by reacting a polyester glycol with paraphenylenediisocyanate and diand trifunctional diols as chain extenders. A monomorphic bending actuator was constructed from a 200 µm thick film, which showed 50 mm bending displacement at 1000 V. The best PU with polyestertype segments had a relative permittivity of 6.5 and was able to generate stress of 15 kPa. In another paper, the elastic response, dielectric constant, and electrostrictive coefficient of a commercial PU were investigated at different temperatures.<sup>[145]</sup> One year later, Pelrine *et al.*<sup>[15]</sup> investigated the performance of PUs and other elastomers. In comparison to silicone, PU-based elastomers had almost 24 times higher Young's modulus, 17 MPa versus 0.7 MPa, and the actuation strain of PU was only 11%, while for silicone it was 32%. Nevertheless, the PU elastomer showed a much higher operation energy density and pressure, 0.1 J cm<sup>-3</sup> and 1.9 MPa, when for the silicone elastomer, these parameters were 0.034 J cm<sup>-3</sup> and 0.21 MPa, respectively. This was attributed to the higher permittivity of the PU elastomer, which was around 7. Later, the coupling efficiency of the same materials was also compared, which is a constant characterizing the ratio between the energy converted into mechanical work and the applied energy. For the PU elastomer, this coefficient was around 21%.<sup>[118]</sup>

Due to the limiting actuation strain of PU elastomers in DEA mode, especially in comparison to silicones and acrylics, the researchers have changed their focus area towards the preparation of PU-based composites.<sup>[2]</sup> Galantini et al.<sup>[146]</sup> prepared a porous PU film and subjected it to the Corona discharge. The material exhibited electret-like properties in which a dielectric constant of 11 was observed. In another work of Galantini et al.<sup>[147]</sup> a series of composites consisting of chemically functionalized CNTs and a commercial PU matrix was prepared. They showed that, depending on the nature and amount of CNTs, a dielectric constant can be increased from 7.6 at 50 Hz for the neat PU to up to 200 at 50 Hz for material containing 1 wt% of CNTs. However, a very strong increase in dielectric loss from 17.6 to 1088, and a small actuation response of 1.1% at almost 6 V/µm was reported in this work. A huge increase in relative permittivity in a PU elastomer was reported by Cameron et al.<sup>[148]</sup> For the sample with 33 wt% of graphite in the PU matrix, a relative permittivity of 4469 was calculated. The actuation stress was increased by a factor of 587. But a five times increase in modulus, a dramatic enlargement of dielectric loss and current leakage, and a reduction of actuation strain were also observed for this sample. In the work of Yin et al.,<sup>[149]</sup> barium titanate particles as high permittivity fillers and dibutyl phthalate as a plasticizer were chosen to prepare a PU elastomer composite having a relative permittivity of 7.4 in the neat state. The obtained materials were used in the fabrication of energy harvesting devices. For one of their best samples, relative permittivity increased to 9.4, while Young's modulus decreased by 43%. Four times higher energy harvesting density was obtained with the composite in comparison to the pure PU elastomer. The results of many other research works describing PU-based composites are discussed in the book of Carpi.<sup>[143]</sup>

The main advantages of PUs are the easy processibility due to their thermoplastic nature and their inherently high relative permittivity due to urethane groups.<sup>[150]</sup> At the same time, they also have much higher ionic conductivity and lower dielectric strength. Their glass transition temperature is significantly higher compared to silicones,<sup>[64]</sup> and due to their chemical structure, they are more sensitive to humidity.<sup>[150]</sup> However, in many publications, the chemical composition of the employed PUs is not indicated, which can complicate deriving a correlation of their properties with structures.<sup>[38]</sup>

# 1.4.2. Polybutadiene and Polyisoprene Polymers

Natural rubber, which is a polyisoprene, has a flexible backbone and a low glass transition temperature,  $T_{a_i}$  of -73 °C. Another widely used unsaturated polyolefin is polybutadiene, which has an even lower  $T_{a_i}$ of below -90 °C.<sup>[50]</sup> Both materials are inexpensive elastomers that are produced on a large scale worldwide. Their Young's modulus is in the range of 0.85–1.7 MPa<sup>[15]</sup> and they can exhibit a tensile strain at break above 400%.<sup>[60]</sup> They were already tested in actuators in 1998, and both showed 11-12% of actuation strain, whereas, in terms of energy density and pressure, polybutadiene exhibited almost two times better performance, closer to the values typically observed for silicones.<sup>[15]</sup> Both polymers have a dielectric constant of 2.5 at 1 kHz and a very low dielectric loss.<sup>[60]</sup> Tröls *et al.*<sup>[44]</sup> compared natural rubber with acrylic polymer for application in DEGs. They suggested that natural rubber has more advantages for such application: its relative permittivity value is strain-independent, and it has a higher breakdown strength. Kaltseis et al.<sup>[151]</sup> compared three commercial products: the acrylic polymer VHB 4910, a natural rubber containing 23% of filler (ZruElast A1040), and physiotherapy rubber (Oppo Band 8003). Both rubbers had a larger Young's modulus and smaller hysteresis loss compared to the acrylic polymer. The generator fabricated of natural rubber demonstrated an energy density as high as 369 mJ/g and a power density of 200 mW/g. To decrease the modulus of polyisoprene, Naito et al.<sup>[152]</sup> cross-linked the polymer with ionic groups attached to the polymer chain. The obtained elastomer showed a field-dependent modulus, which was 0.39 MPa in the absence of an electric field, while it increased by a factor of 1.4 at  $3 V/\mu m$ . The dielectric constant of the obtained elastomer was around 3. Instead of using neat polymers, many researchers investigated copolymers of polybutadienes with other materials, which can have higher permittivity values. Thus, several studies were published by Jung et al., [153,154] who investigated polyacrylonitrile butadiene rubber (NBR). The dielectric constant of their material was 14, while the modulus increased to up to 4 MPa. An actuation strain of 20% at 50 V/µm was detected for this material, which is slightly lower than values observed in silicone and acrylic elastomers. However, the elastic energy density of the new material was more than two times higher. Nguyen et al.[155] attempted to improve the properties of the same NBR using a barium titanate filler in parallel with plasticizers. The relative permittivity of material with the highest filler load (40 wt%) increased to up to 20 at 1 kHz, compared to 10 for the pure matrix. At the same time, the modulus also increased from 0.14 MPa to 0.45 MPa. Electromechanical tests of this material showed an actuation strain of 3.5% at almost 15 V/ $\mu$ m, which is around 0.2% smaller compared to neat NBR. Another material with a smaller load of barium titanate showed a 0.2% higher actuation strain. One of the largest actuation strains was obtained by Lei et al. who

employed an isoprene copolymer.<sup>[156]</sup> More specifically, they prepared a copolymer of polyisoprene and poly(di-n-butyl itaconate). Thus, permittivity and  $T_g$  increased to 5.5 and –38 °C, respectively. An actuation strain as high as 22% at 34 V/µm was observed.

Polybutadiene and polyisoprene are commercial materials that have found applications in many industries. However, only a few publications relate these materials to the application in DETs, especially compared to acrylics and silicone elastomers. Additionally, similar to PUs, many researchers do not present any structural information of the utilized materials, which can lead to difficulties in comparing different results and materials.

## 1.4.3. Acrylics

One of the reasons for the success of acrylic elastomers in DETs is their commercial availability. For more than 20 years, they have existed as the VHB<sup>™</sup> brand supplied by the company 3M in the form of tape with thicknesses ranging from 50 µm to 1 mm. That is why most of the DETs so far were constructed using this type of elastomer. Additionally, VHB films show outstanding performance suitable for DETs: a large strain at break (above 800%),<sup>[56]</sup> high energy density (3.4 MJ/m<sup>3</sup>) and actuation pressure (8.2 MPa), low Young's modulus (0.1-3 MPa), moderate relative permittivity (around 4.5-4.8) and, of course, a large actuation strain.<sup>[157]</sup> Already in 2000, Pelrine et al.<sup>[113]</sup> were able to report 160% relative area strain and 7.2 MPa compressive stress in a circular shape and up to 215% strain and 2.4 MPa stress in the linear configuration for actuators made of VHB. It has to be mentioned that this was the first publication where prestraining of the DEs was applied before fabrication of the actuators. It was shown that this procedure significantly improved the performance of both silicone and acrylic elastomers. For the circular and linear actuators, biaxial prestrain (300% in both directions) and uniaxial prestrain (540% and 75% in two directions) were applied, respectively. For comparison, a circular actuator with 15% biaxial prestrain was also constructed, and it showed only 40% of relative actuation strain. Later, the effect of prestretching was investigated by Kofod<sup>[158]</sup> in more detail. Generally, prestretching improves breakdown strength, efficiency, and actuation strain by altering the geometrical dimension of the actuator, and it is crucial for acrylic elastomers.<sup>[66]</sup> Later, La and Lau<sup>[159]</sup> made an attempt to increase both breakdown strength and actuation strain not only by prestretching, but also by encapsulation of the electrode-VHB-electrode structure in a silicone gel. They reported an increase of the breakdown strength from 315 V/µm for the non-encapsulated samples to 523 V/µm for the encapsulated devices. Moreover, the actuation strain increased from 189% to 228%. This result was attributed to the weaker oxygen concentration near the electrode, which delays the electro-thermal breakdown. One of the highest reported actuation strains of 380% for acrylic VHB elastomer was achieved by Pelrine et al.<sup>[160]</sup> More recently, a linear actuation of 500% strain with the same material was achieved by Goh et al.[161] using prestretching to a certain level and application of longitudinal preload.

Not only the commercial VHB acrylic elastomer but also custom-made acrylic polymers were utilized in DETs. Yin *et al.*<sup>[162]</sup> designed a new polyacrylate polymer and cross-linked it to an elastomeric film using

a difunctional agent. A material with low modulus (0.073 MPa), large strain at break (2400%), and increased dielectric constant value (5.75) was achieved. The authors achieved an actuation strain of 118% at 70 V/ $\mu$ m, combined with a rapid response. A motor constructed from this material reached 15 times higher rotation speed compared to the VHB material. Zhao *et al.*<sup>[163]</sup> presented a self-made acrylic elastomer that can be used without prestretching and shows actuation at a lower voltage than VHB. The modulus of their elastomers was in the range of 0.11 to 0.41 MPa, coupled with dielectric constants of 5.67 to 5.92. The softest material, which also had the lowest relative permittivity, showed 52% of actuation strain at 21.57 V/ $\mu$ m. Acrylic elastomers were also employed for the fabrication of more complex structures. Thus, Duduta *et al.*<sup>[132]</sup> used UV-curable acrylic elastomers for spin coating of single elastomeric membranes, which were later subjected to the application of electrodes and either stacked into a multilayer structure or rolled. The obtained devices demonstrated energy densities as high as 19.8 J/kg in a contraction mode with 24% of actuation strain. The applied electric field was between 100 V/ $\mu$ m and 150 V/ $\mu$ m, and some devices persisted more than 100'000 cycles.

Except for actuation performance, many other investigations were carried out using acrylic elastomers. Chen *et al.*<sup>[164]</sup> studied how the breakdown strength changes under different measurement conditions. Sahu *et al.*<sup>[165]</sup> explored the mechanical behavior of acrylics by stretching them up to 1642%.

However, acrylic elastomers also have some drawbacks. Their main weaknesses are their viscoelastic nature and large viscous loss, which prevent the application of acrylic elastomers at high frequencies. Nice comparisons between silicone and acrylic elastomers were carried out by Michel *et al.*<sup>[166]</sup> and Molberg *et al.*<sup>[167]</sup> The first work showed that, under the same conditions, an actuation strain of 8.5% can be achieved by a silicone elastomer in 3 s, and the same time is required for the relaxation. By contrast, acrylic polymers reached the same strain only after 150 s, and the value of strain had not even stabilized. The second work showed that VHB had a more significant hysteresis than silicone and a styrene-isoprene block copolymer thermoplastic elastomer after being prestretched for 2 h. Moreover, the authors compared the dependence of actuation strain on frequency. It was presented that, while for a PDMS elastomer a frequency change from 1 mHz to 1 Hz gives a strain reduction of 33%, for VHB and the thermoplastic elastomer, this reduction was more than 98%. Also, acrylics have high glass transition temperatures and show a strongly temperature-dependent Young's modulus. VHB is very soft above 50 °C and becomes more than ten times stiffer at -25 °C, while silicones have a more constant modulus within this temperature range.<sup>[168]</sup> High charge leakage is also observed for acrylic elastomers.<sup>[65]</sup>

## 1.4.4. Polysiloxanes

Nowadays, many commercial silicones are available on the market, such as *Sylgard 186*, *NuSil CF19-2186*, *HS3*, or *Elastosil*<sup>®</sup>.<sup>[56]</sup> All contain polydimethylsiloxane (PDMS) as the main polymer and are considered the most popular materials for DETs.<sup>[169]</sup> Before discovering the impressive actuation strains of acrylic elastomers, silicones exhibited the highest values of up to 32% of actuation strain. The elastic modulus and actuation pressure of silicones were 0.7 MPa and 0.21 MPa, respectively.<sup>[15]</sup> After realizing that

prestretching of elastomers positively affects the actuation strain, Pelrine *et al.*<sup>[113]</sup> detected 93% of actuation strain for a circular actuator made of a biaxially prestretched film, and 117% of strain for a uniaxially prestretched linear actuator. Both were achieved with a silicone elastomer that can withstand more than 300% of elongation and was already utilized in the fabrication of a loudspeaker capable of operation at up to 20 kHz.<sup>[170]</sup> During the electromechanical tests, the silicone elastomer was able to show a full strain response at frequencies of up to 170 Hz.<sup>[113]</sup> The same authors also developed DEGs based on a silicone elastomer introduced into a shoe heel, which can harvest energy from human motion.<sup>[26]</sup> Since 2000, the reported 117% actuation strain is still considered the highest for silicone elastomers. The work of many researchers is dedicated either to the development of new designs of different devices or to a change in mechanical properties that can affect actuation performance. As an example, Tugui *et al.*<sup>[171]</sup> used different cross-linking strategies and investigated their influence on the modulus, strain at break, and other mechanical parameters. The best material had a dielectric strength above 100 V/µm and resulted in 15% of lateral actuation strain at 20 V/µm.

Lately, many different configurations and devices have been fabricated using silicone elastomers. Phung *et al.*<sup>[172]</sup> presented a bidirectional tactile display based on a silicone DEA integrated with an electrostrictive actuator. The device can produce up to 185 mN force with 680  $\mu$ m displacement and cause different haptic feelings to the operator. Zhao *et al.*<sup>[173]</sup> constructed a rolled actuator, which is suitable for an application in tactile displays. Operating frequencies of up to 200 Hz were tested, and the device showed a lifetime of more than 50'000 cycles. Many robots such as a worm-like crawling robot, <sup>[174]</sup> insect-like walking robots, flapping, and swimming robots were constructed using different silicone elastomers.<sup>[71]</sup> An impressive example of a robot was developed by Ji *et al.*<sup>[175]</sup> They constructed an insect-like robot with a weight of 190 mg, which was able to carry a load of 950 mg. In the meantime, the unloaded insect was able to move as fast as 30 mm/s and was driven by a voltage below 450 V. One study in which a very low actuation voltage was observed for a silicone DEA was published by Poulin *et al.*<sup>[176]</sup> They reported the successful fabrication of a 3  $\mu$ m thick silicone membrane that achieved 7.5% of lateral actuation strain at 245 V. For achieving devices with higher output forces, silicone elastomers were also utilized in the fabrication of stack actuators with more than 100 layers.<sup>[177]</sup> Up to 20% actuation strain for this stack was achieved.

Generally, silicones outperform acrylic elastomers in response time, efficiency, reliability, and operating temperature range.<sup>[66]</sup> Silicones are more elastic materials than acrylics, with mechanical loss tangents typically below 0.05 at 80 Hz, whereas for VHB film, this parameter is around 0.18 at 20 Hz.<sup>[160]</sup> Therefore, silicones can operate at much higher frequencies. Additionally, a higher value (90%) of maximum efficiency was detected for silicones compared to acrylics (60–80%), operation temperature range is broader (from –100 °C to 240 °C),<sup>[157,160]</sup> prestretching is not as important as for acrylics,<sup>[66]</sup> and actuators that can survive more than 400 million cycles are known to date. Moreover, humidity does not affect the performance of silicone DEAs as much as devices based on acrylics.<sup>[157]</sup> A more detailed comparison can be found in a comprehensive investigation by Albuquerque and Shea,<sup>[178]</sup> where the influence of

temperature, humidity, and prestretching level on dielectric strength of silicones and VHB was investigated.

Despite the outstanding properties of silicone elastomers, they also have one drawback that significantly limits the actuation performance of the DEAs, which is their low dielectric constant, of typically around 2.8. However, several approaches exist for increasing this parameter and many studies have been conducted, as will be discussed in more detail in Chapter 1.6.

# 1.5. Chemistry of Polysiloxanes

Polysiloxanes, also referred to as silicones, are polymers consisting of an alternating silicone-oxygen backbone and two residues (H, alkyl, aryl, or other) linked to the silicon atom (Scheme 1.1).

Scheme 1.1 General chemical structure of polysiloxanes.

While the first organosilicon compounds were discovered in the 1860s, the first linear and cyclic polydimethylsiloxanes were synthesized in 1901 by F.S. Kipping. During the synthesis of R<sub>2</sub>SiCl<sub>2</sub>, the product was hydrolyzed. However, the researchers expected to obtain a silicon analog to ketone, and named the product of hydrolysis as 'silicone'. Only later they have realized that the actual product consists of a compound with Si-O-Si bonds. The beginning of the industrial synthesis and application of silicones dates back to the 1930s. Since then, the interest in this class of polymers has grown significantly.<sup>[179,180]</sup> In 2013, silicone manufacturing became an \$11 billion industry when 2.1 million tonnes of silicone-containing products were sold.<sup>[181]</sup> According to Grand View Research, in 2020, the silicone market was about \$14.4 billion and is supposed to give around 4.3% of annual growth until 2028.<sup>[182]</sup>

Nowadays, silicones and silicone-containing products are widely used in most cosmetics products, the medical industry (heart valves, tubes, contact lenses, prosthetic parts), automotive industry (cables, adhesives, gaskets, sealants, electrical insulator), construction (sealants, adhesives, coatings) and many other industries (electronics, energy, oil and gas, textile, etc.).<sup>[181]</sup> The reason for this strong industrial interest in silicones is due to their outstanding properties. They are chemically stable and unreactive, biocompatible, hydrophobic, have a low moisture uptake, and exhibit good insulation characteristics. Many properties of silicones exist because of unusual structural features of bond length and bond angle between silicone and oxygen atoms. Namely, the bond length Si–X between Si and other atoms is much longer than in the case of C–X (Table 1.2), the low electronegativity of the silicon atom renders the Si–O bond strongly polarized, and therefore highly electrostatic in nature,<sup>[183]</sup> the Si–O–Si angle in silicones can vary between 140° and 180°,<sup>[184,185]</sup> which is much larger than typical C–O–C angle (111.5°).<sup>[186]</sup> Therefore,

the rotation barrier in siloxanes along the Si–O axis is very low. Additionally, the Si–O bond is thermally more stable, with a bond dissociation energy of 110 kcal/mol, while for C–O and C–C bonds these values are 85.5 kcal/mol and 82.6 kcal/mol, respectively.<sup>[187]</sup> All these criteria are responsible for rendering the polymer chain very flexible and the glass transition temperature very low (–130 °C). Additionally, they give silicones a low viscosity,<sup>[188]</sup> a more hydrophobic nature,<sup>[189]</sup> and low surface energy.<sup>[190]</sup>

Element (X)	Bond length (Å)		lonic character (%)	
	Si–X	-X	Si–X	C–X
Si	2.34	1.88	-	12
С	1.88	1.54	12	-
Н	1.47	1.07	2	4
0	1.63	1.42	50	22

Table 1.2 Parameters of chemical bond of Si-X and C-X (adapted from <sup>[183]</sup>).

The most widely used polysiloxane is polydimethylsiloxane (PDMS), which comprises two methyl groups at the silicon atom.<sup>[191]</sup> Meanwhile, there are many silicones in which other functional groups replace one methyl group. For instance, phenyl groups help to reduce the crystallization temperature and increase the heat resistance; trifluoropropyl groups improve solvent resistance and further decrease the surface energy; aminoalkyl groups enhance physical adsorption properties.<sup>[183,191]</sup> Substitution of a methyl group with hydrogen or vinyl groups opens up the possibilities for cross-linking and chemical modification of the silicones.

Synthetic ways towards polysiloxanes, their cross-linking reactions, and postpolymerization modification of polymer chains will be explained in the following chapters.

### 1.5.1. Monomers

Polydimethylsiloxane (PDMS) is considered the most common and widely used silicone among many various polysiloxanes with different functional groups.<sup>[192]</sup> Based on PDMS as the example, different synthetic routes to polysiloxanes will be described in this chapter.

Because there is no natural source of organosilicon compounds, all monomers have to be prepared synthetically. The first step in synthesizing organosilicons starts with reducing silica (SiO<sub>2</sub>), which is a major component of sand, to elemental silicon through a carbothermic reaction. The reaction happens at very high temperatures, above 1400 °C, during which carbon reduces silica through an intermediate SiC into metallic silicon (Si).<sup>[193]</sup>

Usually, organosilicons can be produced in three different ways. During the first process, silicon can be chlorinated by the reaction with chlorine, giving tetrachlorosilane, which can be subsequently alkylated by the reaction with an organometallic compound (Scheme 1.2). The pioneers of this synthesis were Friedel and Crafts, who obtained tetraethylsilane in 1863 after the reaction of tetrachlorosilane and diethylzinc.<sup>[184,194]</sup> With the development of Grignard reagents, Kipping in 1904 was able to obtain almost exclusively ethyltrichlorosilane by reaction of tetrachlorosilane with ethylmagnesium bromide.<sup>[195]</sup> Due to numerous disadvantages of using Grignard syntheses, such as volatile and flammable solvents, side reactions, and difficulties in isolating the main product, it is not suitable for industrial manufacturing of organosilanes.<sup>[194,196]</sup> However, today, it is still used for the fabrication of special silanes on the laboratory scale.<sup>[197]</sup>

Si +  $X_2$   $\longrightarrow$  Si $X_4$ Si $X_4$  +  $ZnR_2$   $\longrightarrow$  Si $R_4$  +  $ZnX_2$ RMgX  $\longrightarrow$  Si $R_aX_{4-a}$  + Mg $X_2$ 

Scheme 1.2 Halogenation of silicone and subsequent reaction with organometallic reagents.

Another possible route for the synthesis of organosilanes is to transform metallic silicon into silyl hydrides by reaction with hydrochloric acid. Subsequently, the obtained products can participate in hydrosilylation reactions with multiple bonds (Scheme 1.3).<sup>[184,191]</sup>

Si + HCl  $\longrightarrow$  HSiCl<sub>3</sub> + H<sub>2</sub>SiCl<sub>2</sub> + SiCl<sub>4</sub> HSiCl<sub>3</sub> + C<sub>8</sub>H<sub>16</sub>  $\longrightarrow$  Cl<sub>3</sub>Si-C<sub>8</sub>H<sub>17</sub>

Scheme 1.3 Synthesis of silyl hydrides and their hydrosilylation reaction with unsaturated compounds.

The third process is the most commonly employed for the commercial production of organosilanes. It is the so-called "direct synthesis", which was independently discovered by Müller and Rochow in the 1940s and based on the reaction of metallic silicon with alkyl or aryl halides in the presence of a copper catalyst (Scheme 1.4). Usually, methyl chloride is utilized as a reagent in industry, giving dimethyldichlorosilane as the final product in almost 99,9% yield after distillation from side products. A high purity is essential for the subsequent synthesis of silicone polymers, because even small traces of methyltrichlorosilanes and tetrachlorosilanes may cause undesired cross-linking reaction.<sup>[195,196,198]</sup> In principle, the variation of the metal catalyst used in this reaction can shift its selectivity towards methyltrichlorosilane (when a tin catalyst is employed), methyldichlorosilane (lead catalyst), or trimethylchlorosilane (calcium catalyst).<sup>[194]</sup> While the direct reaction is successfully employed for the production of chlorosilanes bearing methyl and phenyl substituents, application of long alkyl chain halides, vinyl and allyl chlorides is hindered by a very

low yield and side products, separation of which can be difficult.<sup>[196]</sup> Organosilanes containing groups different from methyl and phenyl can be prepared via hydrosilation reaction using methyldichlorosilane as the starting material and a platinum catalyst. In this way n-alkylmethyldichlorosilanes, 3,3,3-trifluoropropylpropylmethyldichlorosilane and vinylmethyldichlorosilane were successfully synthesized.<sup>[191]</sup>

Si + MeCl  $\longrightarrow$  Me<sub>2</sub>SiCl<sub>2</sub> + MeSiCl<sub>3</sub> + Me<sub>3</sub>SiCl + other products

Scheme 1.4 General scheme of the 'Direct synthesis' of silicones.

Dichlorosilanes are monomers for the synthesis of polysiloxanes because they can be hydrolyzed and immediately participate in a condensation reaction, producing linear and cyclic oligomers (Scheme 1.5).<sup>[199]</sup> Depending on the reaction conditions, the process can be shifted to linear or cyclic products. Alternatively, they can also be inter-converted into one another.<sup>[184]</sup> While the addition of a small amount of potassium hydroxide helps to shift the reaction towards the cyclic product,<sup>[197]</sup> Le Roux *et al.* also reported the effect of the solvent on the ratio of cyclic siloxanes with six- (D<sub>3</sub>), eight- (D<sub>4</sub>) and tenmebered (D<sub>5</sub>) rings.<sup>[200]</sup> According to the literature, usually, only low molecular weight oligomers can be obtained by way of such a condensation reaction due to an almost 35 times decrease in reaction rate of the dimer in comparison to the monomer dimethylsilanediol.<sup>[184]</sup> It is also challenging to control the molecular weight distribution of polymers during the polycondensation reactions. Therefore, this reaction is usually used for the synthesis of cyclic siloxanes, which have a great industrial importance as monomers for the synthesis of high molecular weight polysiloxanes via ring-opening polymerization (ROP).

$$R_2SiCl_2 + 2H_2O \longrightarrow R_2Si(OH)_2 + 2HCI$$
  
 $nR_2Si(OH)_2 \longrightarrow H[OSiR_2]_mOH + [OSiR_2]_p + (n-1)H_2C$ 

Scheme 1.5 Hydrolysis of dichlorosilanes and subsequent condensation into cyclic and linear siloxanes.

# 1.5.2. Ring-Opening Polymerization of Cyclic Siloxanes

Control over the ROP of siloxanes can be achieved thermodynamically when equilibrium conditions between cyclic and linear species are reached, and kinetically, when polymerization is quenched earlier before the equilibrium is achieved. The first process does not depend on the initiator (anionic or cationic) and monomer ring size, and it is considered as an entropy-driven process. The change in enthalpy is close to zero, because the starting cyclic monomers (except the cyclic trimer, which can be neglected), as well as the produced polymers, are unstrained molecules, and there is no change in the number of chemical bonds during polymerization. Meanwhile, linear polymer chains result in an increase in conformational freedom, which increases entropy. Generally, during the thermodynamically controlled ROP, the reaction does not have to be quenched and it proceeds until equilibrium between the cycles and linear chains is established. The distribution between cyclic and linear species was predicted by Jacobson and Stockmayer (Figure 1.23).<sup>[201]</sup> They assumed that the conformation of PDMS chains could be described by a Gaussian distribution, and the equilibrium concentration of cycles should decrease with increasing ring size. However, it was later found that this theory was invalid for small cycles, which were formed in much higher concentrations than predicted.



Figure 1.23 Typical molecular distribution for an equilibrium between polymeric chains and rings (reprinted with permission from <sup>[201]</sup>; Copyright 1983, American Chemical Society).

The main limitation of the thermodynamically controlled system is that polymer yield significantly drops when the size of the monomer and its polarity increase (Table 1.3). Thus, equilibration of polydiphenylsiloxane does not result in any polymer formation. It is also known that dilution of the polymerization mixture promotes cyclization (Ziegler-Ruggli principle), reducing the polymer yield. That is why thermodynamically controlled bulk polymerizations are usually performed to synthesize polysiloxanes with small substituents, like polydimethylsiloxanes, polymethylethylsiloxane, and polymethylvinylsiloxanes.<sup>[199]</sup>

Table 1.3 Dependence of the yield of linear polysiloxane on substituent in undiluted equilibrate conditions (adapted from <sup>[199]</sup>).

R-	R'-	Approximate yield, %
Me	Me	82
Me	Et	74
Me	$CF_3CH_2CH_2$	17

Ph	Me	70
Ph	Ph	0

Contrary to the thermodynamically controlled polymerization, the kinetically controlled polymerization is enthalpy-driven, which is favored by the release of ring strain. Strained cyclic monomers, such as hexamethylcyclotrisiloxane are more reactive. That makes the propagation reaction much faster than the back-biting or chain-transfer reactions. Therefore the reaction has to be quenched at the moment when the maximum conversion is reached, but before the equilibrium is attained. In such a way, a high yield of a high molecular weight polymer, a narrow molecular weight distribution, and a small amount of cyclic side products can be achieved.

#### 1.5.2.1. Anionic Ring-Opening Polymerization

Depending on the nature of the initiator used to polymerize siloxanes, the reactions can be divided into anionic ROP and cationic ROP. Anionic ROP is frequently applied in industry for the synthesis of siloxanes. Normally, strong organic, inorganic, or metalorganic bases act as initiators. Reacting with cyclic monomers, they produce an active silanolate anion (Scheme 1.6a), which becomes a propagating center of the polymer chain. The propagation reaction is reversible and the rate-determining step (Scheme 1.6b). It is known that the propagation chain reactivity is strongly affected by the size of the counter ion and different association phenomena. Thus, reactivity increases in the following order: Li<Na<K<Rb<Cs, tetraorganoammonium, tetraorganophosphonium. Due to the strong ion aggregation of the living chain ends into complexes and the ion-ion association between the silanolate anions with the Li<sup>+</sup> or Na<sup>+</sup> counter ions, the reactivity of a propagation center with the latter counter ions becomes very low. With an increasing the size of the counter cation, ion-ion interactions weaken. Therefore cesium, because of its large size, produces looser aggregates, while tetraorganoammonium and tetraorganophosphonium ions do not aggregate at all.<sup>[202]</sup> It is also worth mentioning that the addition of uncharged nucleophiles such as THF, DMSO, DMF can significantly enhance the polymerization rate, even when Li<sup>+</sup> is used as the counter ion because of the solvation of the cation liberates the reactive anion.<sup>[203]</sup> Thus, PDMS with a dispersity as low as 1.2 was obtained using a THF-Li<sup>+</sup> system at room temperature, while without THF, the reaction has to be carried out at 200 °C.<sup>[199]</sup>

The size of the cyclosiloxane used in the reaction also affects the polymerization rate. Cyclotrisiloxane  $D_3$  is highly reactive due to its ring strain. The reactivity of cyclotetrasiloxane is 34–80 times lower than cyclotrisiloxane, depending on the initiator and whether the reaction is performed in bulk or a non-polar inert solvent. When increasing the ring size further, the reactivity increases again, reaching a value twice as high as the one of  $D_3$  for  $D_7$  (a cyclic dimethylsiloxane with a 14 membered ring).

Backbiting is a process where the active chain end attacks the same polymer chain (Scheme 1.6c). During this process, cyclic monomers of various ring sizes can be produced. Another side reaction is chain transfer (Scheme 1.6d), when the active chain end of one chain attacks another chain, leading to chain

randomization, which causes a broadening of the molecular weight distribution and hence an increase in dispersity.

Generally, polymerization proceeds without termination if the reaction mixture does not contain any acidic contaminations and, therefore, it has to be quenched. Deterioration of siloxanes' thermal properties can be observed when not every living chain end is neutralized. In case when unreactive end groups are needed, quenching can be performed by chlorotrimethylsilane. To obtain a star-branched polymer, multifunctional agents like tetrachlorosilane or trichloromethylsilane are applied. Triorganochlorosilanes bearing functional reactive groups open possibilities for subsequent cross-linking reactions. Simple treatment with water or alcohol usually introduces silanol end-groups. These end-groups are very useful because they can undergo condensation reactions, which can be used either in cross-linking or in polymer functionalization reactions. Siloxanes with silanol end-groups can also be synthesized using thermolabile initiators. Polysiloxanolates produced with alkylammonium hydroxides having hydrogen in the  $\beta$ -position can be easily deactivated and removed by heating the reaction mixture above 130 °C.<sup>[199]</sup> Control over polysiloxane end groups and molecular weight can also be achieved using chain-blocking agents such as hexamethyldisiloxanes, divinyltetramethyldisiloxanes, and other organic disiloxanes.<sup>[204]</sup>



Scheme 1.6 Anionic ROP: a) initiation, b) propagation c) backbiting and d) chain transfer.

### 1.5.2.2. Cationic Ring-Opening Polymerization

Lewis acids and strong Brønsted acids are known to be initiators for the cationic ROP of cyclic siloxanes and were used for the synthesis of some of the very first commercial high molecular weight polymers.<sup>[203]</sup> Due to the formation of a large number of cyclic oligomers at the beginning of the reaction, cationic ROP cannot be employed for the kinetically controlled polymerization. However, it is a good choice for the synthesis of linear polysiloxanes at a high rate even at room temperature, especially when polymers with substituents that are unstable under basic conditions are to be prepared, e.g., Si-CH<sub>2</sub>-COOH, Si-H, Si-Cl, Si-CH<sub>2</sub>-Cl.<sup>[205]</sup> Cationic ROP is quite sensitive to different impurities. Ethers can decrease the reaction rate, while weak acids can accelerate it. Traces of water can either inhibit the reaction or promote it. An interesting kinetic behavior in the polymerization of D<sub>3</sub> was observed after the addition of traces of water. Thus, without water, the activation energy is very small, and the reaction is only 30-50 times faster than in the case of D<sub>4</sub>. The addition of water enhances activation energy and renders the polymerization reaction 100–1000 times faster. It was also shown that a silyl ester produced during the initiation step cannot open the monomer ring in water-free conditions. For D<sub>4</sub>, a small addition of water gives only a three-fold increase in reaction rate at room temperature, while a higher amount of water significantly diminishes the polymerization rate.<sup>[199]</sup>

Similar to the anionic ROP, the D<sub>3</sub> monomer is much more reactive in the cationic ROP than D<sub>4</sub>, whereas bulky and electronegative substituents in the monomer decrease the rate of the reaction.<sup>[199]</sup> Side reactions such as backbiting and chain randomization usually happen when monomer D<sub>4</sub> is used, but are minor in the case of D<sub>3</sub>. The polymerization of D<sub>4</sub> occurs slowly due to the competition between polymerization and depolymerization reactions. Polymers with a high molecular weight can be obtained only after an induction period, during which end group condensation of silanol groups with themself or silyl esters occur. For the D<sub>3</sub> monomer, a significant amount of cyclic species is generated together with linear polymers at the beginning of the reaction, with a big fraction of D<sub>3x</sub> cycles. The concentration of cycles increases linearly with monomer conversion and can reach up to 50 wt%. The polymer fraction shows the same linear increase. The reason for such a high formation of cycles D<sub>3x</sub> was explained by the cyclization end-closure mechanism.<sup>[184]</sup>

Although the mechanism of cationic ROP is complex and still unclear, many researchers suggest that the following two processes happen simultaneously: acidolysis-condensation and addition polymerization. According to Patnode *et al.*, who proposed the first mechanism, during initiation an acid splits a siloxane bond in a monomer (Scheme 1.7a) and then the polymer is formed via the condensation reaction through the end groups (Scheme 1.7b).<sup>[199,206]</sup> In the addition polymerization pathway, it is stated that, after initiation, the monomer is directly added to the active propagation center, which is either a silylenium ion or tertiary silyloxonium ion (Scheme 1.7c).<sup>[199]</sup>



Scheme 1.7 Cationic ROP: a) initiation, b) acidolysis-condensation propagation, c) propagation according to addition process.

## 1.5.3. Cross-linking of Polysiloxanes

Polysiloxanes are viscous fluids over a wide range of temperatures. To obtain useful materials (rubbers, resins, or coatings), they have to be cross-linked into elastomers. The latter occupy a share of approximately 50% of the commercial applications of silicones. Generally, there are four most popular methods for cross-linking silicones: hydrosilylation, condensation, hydridosilane-silanol, and radical reactions.<sup>[199,207,208]</sup>



Scheme 1.8 Cross-linking via hydrosilylation reaction.

The hydrosilylation reaction is based on the formation of a new Si–C bond by adding the hydrosilane to the siloxane containing unsaturated carbon-carbon bonds in the presence of a platinum catalyst (Scheme 1.8). In practice, this reaction is most frequently used to cross-link vinyl groups on polysiloxanes.<sup>[143]</sup> The benefit of hydrosilylation reactions is that they are very efficient and do not result in any low molecular weight by-products, which can cause the formation of voids in elastomers. The latter may have a strong influence on the breakdown properties of the elastomer. Platinum-catalyzed hydrosilylation reactions demonstrate good regioselectivity and exhibit very good functional group tolerance: halogens, esters,

acetals are compatible with this reaction.<sup>[199]</sup> However, sulfur-containing materials can poison the platinum catalyst and impede the cross-linking reaction.<sup>[56]</sup>

Another common pathway is condensation, also known as room temperature vulcanization.<sup>[66]</sup> It relies on the reaction between a silanol-terminated polysiloxane and a tri- or tetrafunctional silane, for which alkoxy silanes (tetraethoxysilane, tetramethoxysilane, trimethoxy propylsilane) or acyloxy silanes (triacetoxy(methyl)silane) are commonly employed (Scheme1.9). This process is very slow; therefore, the addition of a catalyst is vital for this reaction. Typical catalysts for these reactions are tin or titaniumbased organic complexes. It is also known that the reaction is catalyzed by atmospheric moisture. Firstly, the catalyst is partially hydrolyzed by moisture producing a metal hydroxide group, which reacts with the alkoxy or acyloxy silanes. Then, a condensation reaction occurs with the release of alcohol. The main advantage of this reaction is that it allows obtaining so-called 'pure' silicones, where all cross-links and polymer backbones consist of Si-O bonds. It is worth mentioning that condensation reactions are usually slower than hydrosilylations, and the curing rate is more sensitive to the humidity level.<sup>[143,199]</sup> Another problem is the high toxicity of the utilized metals, especially tin. Therefore, it has to be used in small amounts and can prohibit the application of the obtained silicones in some industries.<sup>[56]</sup>



Scheme 1.9 An example of condensation reaction.

The hydridosilane-silanol cross-linking reaction can be classified as both, a condensation and a hydrosilylation reaction. It happens even at room temperature and can be catalyzed either by tin or platinum-based complexes. The reaction can be represented according to Scheme 1.10. However, this cross-linking has not found much attention in industrial settings because the reaction rate is difficult to control at room temperature and because of the evolution of hydrogen.<sup>[199]</sup>



Scheme 1.10 Hydridosilane-silanol cross-linking reaction.

Different from the above-mentioned strategies, radical reactions do not require any metals, and their initiation can be well controlled by applying an external stimulus. Two types of radical reactions can be distinguished. High-temperature vulcanization is the commercial name of a reaction that is based on creating the radical due to the thermal decomposition of peroxides, such as tertbutyl peroxide or benzoyl peroxide. In the subsequent step, these radicals abstract hydrogens from the carbons bonded next to the silicon (methyl group, vinyl group). The resulting carbon radicals can be connected together, producing the cross-link (Scheme 1.11).<sup>[208]</sup> However, during this reaction, the cross-links are introduced randomly along the chain. This results in poor control over the cross-linking network and impaired mechanical properties. Moreover, the residues of peroxides deteriorate the thermal stability of the material.<sup>[56]</sup>



Scheme 1.11 Methyl-to-methyl cross-linking initiated by t-butyl peroxide.

A more controlled cross-linking can be achieved via a thiol-ene addition reaction between a thiol and carbon double bond, such as vinyl groups, which can be introduced to polysiloxanes either as terminal or side groups. This reaction has numerous advantages, including mild reaction conditions, high reaction rates, or regioselectivity, and it is not sensitive to oxygen compared to the peroxide-activated reaction.<sup>[209]</sup> A thiol-ene addition reaction is commonly activated either by a thermal initiator, such as azobis(isobutyronitril), or by a photoinitiator like dimethoxy-2-phenylacetophenone (DMPA) or benzophenone. Generally, the mechanism of the reaction can be represented according to Scheme 1.12. During the first step, the reaction starts with the thermal dissociation or photocleavage of the initiator. The initiator radical subsequently abstracts the hydrogen atom from the thiol. The resulting thiyl radical is extremely reactive and can react with a carbon-carbon double bond, thus producing an intermediate carbon-centered radical that participates in the chain transfer with a second thiol molecule, giving the addition product with anti-Markovnikov orientation. A new thiyl radical is generated in the process and continues the sequence that is described above. Termination usually occurs by radical-radical coupling.<sup>[209,210]</sup>


Scheme 1.12 Mechanism of thiol-ene addition reaction.

The efficiency of the thiol-ene reaction has allowed researchers to use it for both cross-linking and functionalization of polysiloxanes. Particularly, Xue *et al.*<sup>[211]</sup> demonstrated an efficient approach to the preparation of polysiloxanes with various functional groups using thiol-ene reactions. Wickard *et al.*<sup>[212]</sup> reported a two-step modification of hydrogen-terminated silicon surfaces involving either initial grafting of poly(1,2-butadiene) followed by thiol-ene functionalization or partial thiol-ene modification of parent poly(1,2-butadiene) in solution followed by subsequent surface grafting. Rissing and Son<sup>[213]</sup> have exploited radical thiol-ene chemistry in the preparation of branched organosilanes as well as in the synthesis of carbosilane-thioether dendrimers. Cole and Bowman<sup>[214]</sup> showed the excellent potential of this reaction as the setting mechanism in dental impression materials. Gan *et al.*<sup>[215]</sup> have prepared new photo-curable silicone resins based on thiol-ene photopolymerization and demonstrated the possibility of encapsulating LED chips into the polymer matrix. Müller *et al.*<sup>[216]</sup> published an article relating specifically to the photoinduced thiol-ene cross-linking of modified silicones. Finally, functionalization of a high molecular weight hydroxyl-terminated polymethylvinylsiloxane with 3-mercaptopropionitrile following by cross-linking with 2,2-(ethylenedioxy)diethanethiol was conducted by Dünki *et al.*<sup>[217]</sup>

## 1.6. Towards High Permittivity Polysiloxanes

DETs are novel and encouraging devices that have already found various applications. However, one of the factors limiting broader usage is the high driving voltage needed to bring DEAs into actuation. As was mentioned in the previous chapter, the dielectric constant of elastomers is one of the intrinsic properties that influence the value of the required voltage. Silicones have one of the lowest dielectric constants (~2.8) among all elastomers. Therefore, actuators made of silicones generally require a high electric field. Usually, researchers distinguish two approaches that can enhance the dielectric constant of silicones and other elastomers. The first one is based on mixing the silicone matrix with high permittivity fillers. In another approach, chemical functionalization of the polymer backbone is conducted, during

which polarizable dipoles are bound to the polymer and make it more polarizable in an electric field. Both strategies will be discussed below, while more detailed reviews are also available in the literature.<sup>[38,66]</sup>

#### 1.6.1. Polysiloxane Based Composites

The addition of high dielectric constant or conductive organic, inorganic, metallic, ceramic, or polymeric particles is considered the most common approach towards high permittivity silicones.<sup>[2,150]</sup> Normally, such fillers are dispersed with a SpeedMixer, roll-milling, or tip sonicator in a mixture of PDMS with a cross-linker and a solvent. Then, a catalyst is added to the solution, followed by degassing and subsequent film preparation.<sup>[143]</sup> The minimum dielectric constant of the obtained composite can be estimated using the following equation<sup>[66]</sup>:

$$\varepsilon_c = \frac{\varepsilon_1 \varepsilon_2}{\theta_1 \varepsilon_1 + \theta_2 \varepsilon_2}$$
 Eq. 37

where  $\varepsilon_c$  is the dielectric constant of the obtained composite, and  $\varepsilon_1$ ,  $\varepsilon_2$ ,  $\theta_1$ ,  $\theta_2$  are the dielectric constants and the volume fractions of components 1 and 2, respectively.

Titanium dioxide is probably the best known and most studied high dielectric constant filler used to prepare silicone composites. For the first time, [56] it was employed by Szabo et al. [218] together with other fillers such as barium titanate and lead magnesium niobate-lead titanate. The authors observed an increase in modulus and dielectric constant with the increase in filler content. The actuation strain was tested only for composites containing barium titanate, and it was concluded that the composites showed a smaller actuation strain than pure silicone. Later, titanium dioxide was utilized by Carpi and De Rossi, <sup>[219]</sup> who used the crystalline rutile form with a dielectric constant of 114 and dispersed it in a commercial PDMS. At a load of 30 wt% of titania, the measured dielectric constant increased to 8, agreeing with the values predicted by different models. At an electric field of 10 V/µm, the authors detected 11% of transverse strain, which was almost eight times higher than the value obtained for the neat silicone at the same electric field. The same 11% strain for neat silicone was obtained only at 15.5 V/ $\mu$ m. Mechanical properties of the composite were also improved: the modulus decreased while the strain at break increased. Later, Stoyanov et al.<sup>[220]</sup> investigated a mixture of PDMS with different amounts of titanium dioxide nanoparticles functionalized with short PDMS chains. Around 30% of actuation strain was detected for a composite with 5% titania, while samples without fillers showed 25% strain. A 10% load of particles resulted in a slightly higher actuation strain than neat PDMS. At higher loads, such as 15% and 20%, a lower actuation strain was detected. In the meantime, all reinforced samples showed improved values of force output and work density. Both parameters were enhanced with increasing filler content. Even higher contents of up to 35 wt% of titania as a filler in a low viscosity silicone rubber, was investigated by Yu and Skov.<sup>[221]</sup> A material with this concentration had a dielectric constant around 4.9 at 1 Hz, and exhibited an increase in breakdown strength up to 160 V/µm, a tensile strength up to 5.3 MPa, and an actuation strain of 10% at 50 V/ $\mu$ m. At higher load of filler, the authors observed aggregation and deterioration of some properties. Contrary to the above mentioned work of Szabo *et al.*,<sup>[218]</sup> Zhang *et al.*,<sup>[222]</sup> achieved a larger actuation strain with a silicone loaded with 3%, 5%, and 10% of barium titanate compared to the neat polymer. Due to the huge dielectric constant of barium titanate (>3000), only 3% load of the fillers resulted in a dielectric permittivity of the obtained composites as high as 90. At a 10% load, that value increased to 300. The latter sample showed 28% actuation strain at 9 V/ $\mu$ m, which is more than 20 times higher than silicone. However, the modulus of composites also increased while the breakdown strength decreased. Recently, an actuation strain as high as 18% was obtained by Kumar *et al.*,<sup>[223]</sup> for a silicone composite with 15 wt% of barium titanate. That was achieved after curing the composite in the presence of an electric field, which, according to their work, also resulted in better mechanical and dielectric properties.

Materials with even larger dielectric constant values are also known to be tested for enhancing permittivity of silicones: calcium copper titanate ( $\varepsilon_r > 10'000$ ),<sup>[224]</sup> magnesium niobate-lead titanate ( $\varepsilon_r > 18'000$ ),<sup>[225]</sup> and copper-phthalocyanine oligomer (CPO) ( $\varepsilon_r > 10'000$ ).<sup>[168]</sup> In particular, using the latter filler in concentrations below 10%, a very small increase in dielectric constant (up to 5) was observed. At a 40% load, the dielectric constant increased to 11.8. The sample containing 20 wt% of fillers showed an almost two times increase in actuation strain at 27 V/µm compared to neat PDMS.<sup>[226]</sup> Since Opris *et al.*<sup>[227]</sup> demonstrated that the dielectric constant of CPO is not an intrinsic property, but rather due to the absorbed water, the use of this filler has sharply decreased. Other materials such as clays or conductive fillers like CNTs, silver, graphene, graphite, poly(3-hexylthiophene), and polyaniline (PANI) were also frequently embedded into silicone matrix.<sup>[66]</sup> Because conductive fillers cause an increase in permittivity through the increase in conductivity, they can be encapsulated into a non-conductive shell.<sup>[169]</sup> As an example, Molberg *et al.*<sup>[228]</sup> encapsulated PANI into PVDF. Dispersing 25 wt% of these particles in a PDMS matrix led to a composite with a dielectric constant around 4, which showed 12% of actuation strain at 30 V/µm, while VHB film exhibited only 3% strain at the same electric field.<sup>[229]</sup>

Although the described fillers can be easily dispersed in a silicone matrix, can increase the dielectric constant, and sometimes improve other parameters, they often result in changing other properties in undesirable ways, such as increasing Young's modulus and dielectric loss while decreasing dielectric strength.<sup>[143]</sup> Additionally, fillers increase the lower limit of the film thickness, which is usually not below 75 µm.<sup>[56]</sup> Finally, composites are more susceptible to the Mullins effect (Figure 1.24) than neat silicone elastomers.<sup>[66]</sup> This effect is also called stress-softening and is explained in the literature using different approaches: bond rupture, molecular slipping, filler rupture, and disentanglement.<sup>[230]</sup> As an example, a silicone with 35 wt% titania exhibited an almost two-fold reduction in Young's modulus after being stretched for two months, while a silicone without fillers does not show such a trend.<sup>[66]</sup>



Figure 1.24 Stress-softening of styrene-butadiene rubber filled with carbon black (adapted with permission from [230]).

#### 1.6.2. Functionalized Polysiloxanes

An alternative approach towards polymers with increased dielectric permittivity is the chemical functionalization of polysiloxanes with polar side groups that have a high dipole moment. This can help avoid many challenges that researchers face when creating composites and polymer blends. However, there is a general trend that the  $T_g$  also increases with an increasing amount of polar groups grafted to the polymer chain.<sup>[38]</sup> This happens due to a decrease in the chain mobility of the functionalized polymers.<sup>[64]</sup> Two strategies exist for compensation of this decrease in  $T_g$ . The first one uses plasticizers, which are low molecular weight species, such as silicone oils. They can decrease not only the  $T_g$  value but also Young's modulus of the elastomers.<sup>[56]</sup> However, the main drawback of plasticizers is their propensity to leak out of the polymer matrix and, therefore, alter the mechanical properties and the lifetime of the material in a negative way.<sup>[34]</sup> An alternative strategy towards polar polymers with low  $T_g$  is based on a polymer with very low  $T_g$  as a starting material. That is why polysiloxanes are considered to be the best option for this approach, given that they are the polymers with the some of the lowest  $T_g$ , of, e.g., –123 °C for PDMS.<sup>[38,231]</sup>

The first polar silicone used for DETs was a fluorosilicone Dow Corning 730. The material has a dielectric constant of 6.9 at 1 kHz and a Young's modulus of 0.5 MPa. It gives 28% actuation strain at 80 V/µm, while PDMS showed 32% strain at a significantly higher electric field of 235 V/µm. However, a considerable creep was observed for fluorosilicone, which could be the reason for the more than three times lower energy density and pressure as compared to PDMS.<sup>[15,118]</sup> Since then, many polar groups and different approaches to functionalize the polysiloxane chains have been explored. A comprehensive review was recently published by Opris,<sup>[38]</sup> where several pathways towards high dielectric permittivity siloxanes and current advances were described. Namely, the author distinguished five common synthetic strategies (Figure 1.25).



Figure 1.25 Synthetic strategies towards polar siloxanes: a) nonpolar polymer with reactive end groups and polar cross-linker; b) nonpolar and polar polymers with reactive end groups a nonpolar cross-linker; c) nonpolar polymer with reactive side groups that can be simultaneously functionalized and cross-linked into elastomer; d) polymer with polar side groups that can be cross-linked through reactive side groups; e) polar polymer with reactive end groups that can be used for cross-linking (adapted with permission from <sup>[38]</sup>).

The first pathway (Figure 1.25a), when polysiloxanes are cross-linked with a multifunctional cross-linker bearing a polar group, is probably the most straightforward. An example of such a strategy is presented in the work of Madsen et al.<sup>[232]</sup> They modified an azide-functional silicone cross-linker by grafting 1ethynyl-4-nitrobenzene or alkyne-functional nitroazobenzene. Two tetrafunctional polar cross-linkers were subsequently employed for cross-linking of hydride-terminated PDMS. However, a very small increase in dielectric constant was observed: from 2.8 to 3.3 when 1.35 wt% of the first cross-linker was used, and to 3.2 when the same amount of the second cross-linker was used. Using a similar cross-linking approach, Madsen et al.<sup>[233]</sup> also tested six other bulky polar groups. However, a very small increase in permittivity was observed. Bele et al.<sup>[234]</sup> tried to employ less bulky polar trialkoxysilanes, bearing methyl, phenyl, 3-aminopropyl, 3-chloropropyl, and 3-cyanopropyl groups. The highest values of permittivity obtained in this work were detected for cross-linker with 3-cyanopropyl group (~3.7) and 3-aminopropyl group (~3.3). The authors also observed that by increasing the molecular weight of the polymer, the permittivity decreases due to the dilution of the polar cross-linker. A slightly higher permittivity of 3.9, was obtained by another author using 3-cyanopropyltriethoxysilane as a cross-linker.<sup>[235]</sup> The reason for such a low increase in permittivity, even when large amounts of cross-linkers are used, is the formation of silsesquioxane structures. The latter can entrap the polar groups and prevent their polarization in an electric field.<sup>[38]</sup> From these examples, it can be seen that in spite of the straightforward synthetic approach, this strategy of using cross-linkers bearing polar groups does not result in a significant increase of permittivity, which remains below the values typically observed for acrylic elastomers (~4.5).

The second synthetic approach (Figure 1.25b) implements the preparation of the polar network via mixing at least two components and cross-linking them into an interpenetrating network (IPN).<sup>[38]</sup> The first component usually is a high molecular weight polymer (PDMS), which is responsible for the mechanical properties of the final network. Another component has a lower molecular weight, but it possesses polar

groups that give rise to permittivity in the final network. One of the first works that implemented this strategy was published by Böse et al.<sup>[236]</sup> They mixed a commercial two-component PDMS, in which one component has vinyl groups and another one has silane groups, with a vinyl-terminated poly(trifluoropropyldimethyl)-siloxane. The final IPN with a 45% content of the fluorinated polymer had a permittivity of 5.5 at 1 kHz and showed a decrease in the breakdown strength and Young's modulus. Actuators made of this IPN exhibited a five times higher actuation strain at a lower electric field (10 V/ $\mu$ m) than PDMS. In another work, Risse et al.<sup>[237]</sup> synthesized polar polymers themselves. Specifically, they simultaneously functionalized a trimethylsiloxy-terminated polymethylhydrosiloxane with 3-propionitrile groups as a polar component and propyltrimethylsilane as a component for increasing compatibility with PDMS. The reaction was performed with a substoichiometric amount of the reagent. Therefore, some unreacted hydrosilane groups were still present in the polymer. This polar component was mixed with PDMS in different concentrations. The authors also showed that, with increasing content of polar polymer up to 38.9%, the Young's modulus decreased from 1 MPa to 0.3 MPa, while the breakdown strength decreased from 80 V/µm to 25 V/µm. An IPN comprising 38.9 wt% of the polar component exhibited a permittivity of 5. Their best sample showed 7% actuation strain at 20 V/µm. Similar work was accomplished by Racles et al.<sup>[238]</sup> Instead of propyltrimethylsilane, they used the butyl group to increase miscibility with non-polar PDMS. They determined the permittivity of the polar component containing 89% of 3-cyanopropyl component and 11% of hydrosilyl groups to be 15.9 at 10 kHz. To obtain an IPN, the authors first mixed the polar component with tetraethoxysilane, and then with hydroxy-terminated high molecular weight PDMS. While the best material with the highest load (28.6 wt%) of the polar component had a permittivity of 4.9 at 10 kHz, it did not perform well during electromechanical tests. Nevertheless, another IPN with 27 wt% of the polar component had a permittivity around 4.5 and showed 8% strain at 56 V/ $\mu$ m, which is almost eight times higher than for PDMS.

In the work of Zhang et al.<sup>[239]</sup> the polar component was not grafted to the polymer before introduction to the IPN, but rather participated in the cross-linking reaction as a separate reagent. Thus, azobenzene bearing a nitro moiety on one side and two hydroxyl groups on the other side was mixed with hydroxyterminated PDMS and tetraethylorthosilicate cross-linker (Figure 1.26). At 10.2 wt% load of the dipole, a dielectric constant of 4.82 at 1 kHz was achieved, and Young's modulus increased from 268 kPa for neat PDMS to 367 MPa. This sample also showed the highest actuation of 12% strain at a low electric field of 55 V/µm, while for PDMS the strain value was almost three times smaller. Not only dipoles, but also ions can be grafted onto polymer chains to increase permittivity.<sup>[240]</sup> An ionic network was obtained by mixing aminofunctional PDMS with carboxylic acid functional PDMS. Then, this network was mixed with PDMS and silica. For the obtained IPNs the authors detected a permittivity in the range of 2.8 to 5 at 1 MHz, while at 0.1 Hz, values from 6.7 to as high as 2100 were observed. The latter one is probably due to interfacial polarization. A surprisingly high breakdown strength was detected for IPNs, which was more than two times higher compared to PDMS. The Young's modulus in many samples did not show significant changes. However, no data regarding actuation performance was reported in this work. Another example of IPN based on an ionic compound was presented by Kang et al.,<sup>[241]</sup> who grafted an imidazole-based ionic liquid to chloropropylsiloxane. Subsequently, various concentrations of this polar

silicone were dispersed in a silanol-terminated PDMS and silica, and cross-linked into an elastomeric network. One of the best materials was a homogeneous IPN, and showed almost no difference in strain at break and slightly reduced Young's modulus, compared to PDMS. The permittivity at 1 MHz increased to 3.9, and at 0.1 Hz it increased to 22.3. While the breakdown strength decreased more than 3 times, the authors reported figures for actuators made of this IPN 8 times larger than for PDMS. However, neither actuator performance nor long-term stability of this material were presented. Though the last two works reported high permittivity values at very low frequencies, no material using IPN with permittivity above 6 at 1–10 kHz was prepared so far. Whereas at lower frequencies, interfacial polarization gives rise to high permittivities, orientational polarization usually takes place at the 1–10 kHz range, so that different materials can be clearly compared. Moreover, preparation of IPN is often accompanied by problems such as phase separation; therefore, large amount of solvents and quick cross-linking reactions are needed.<sup>[38]</sup>



Figure 1.26 Synthesis of elastomer consisting of PDMS network with grafted azobenzene (reprinted with permission from <sup>[239]</sup>).

Another synthetic method (Figure 1.25c) is based on the in-situ grafting of polar groups to the siloxane and simultaneous cross-linking reaction. This approach was first used by Kussmaul et al., [242] who synthesized a push-pull dipole such as N-allyl-N-methyl-p-nitroaniline and mixed it with a vinylterminated PDMS and methylhydrosiloxane as a cross-linker. They showed that with an increasing amount of dipoles of up to 13.4%, the permittivity increased to 5.98 at 1 kHz, while the breakdown strength decreased from 129 V/µm to 39 V/µm. However, the actuation of the best material was very small, 1.4% strain at 24 V/µm. Later, the same authors applied this strategy to two commercial formulations: Sylgard 184 from Dow Corning and Elastosil RT 625 from Wacker Silicones. Because the latter has a lower Young's modulus, a composite made of this material had a better performance compared to a composite made of Sylgard 184. At a 10.7 wt% load of the polar component, 2.5% of actuation strain at 10 V/µm was detected.<sup>[243]</sup> A much higher increase in permittivity was achieved by Dünki et al.<sup>[244]</sup> by grafting 3-mercaptopropionitrile and butanethiol to poly(vinyl siloxane) in combination with a simultaneous cross-linking reaction with 2,2-(ethylenedioxy)diethanethiol. They showed that, with an increasing concentration of 3-mercaptopropionitrile, the dielectric permittivity also increased, reaching the value as high as 17.4 at 1 kHz for a material with almost 100% of polar side groups and 4.8 wt% of silica particles. A Young's modulus of 155 kPa and a breakdown strength of 15.6 V/µm were detected for this material. It also exhibited a large strain at break of 300%, and 14.1% of actuation strain at only 10 V/ $\mu$ m, while the maximum actuation strain detected for this sample was 21% at about 12 V/ $\mu$ m.

The  $T_g$  of the sample with the highest concentration of dipoles was around -45 °C. While such an approach looks promising, it is challenging to prepare very thin films with it. The authors conducted the reaction between two glass plates, where the thickness was adjusted using 100  $\mu$ m spacers. It might be difficult to reduce the thickness below this value, therefore the driving voltage is still in the kV range. Also the breakdown and conductivity have to be considered, which can be negatively affected because of the presence of ions inside products obtained during the thiol-ene addition reaction. Mixing all the reagents also requires a large amount of solvent, which can additionally cause some defects and upscaling problems.

A better but still not optimal solution would be to graft the dipole to the polymeric chain, purify the obtained polymer, *i.e.*, from unreacted compounds or side products, and further cross-link the obtained polar polymer into an elastomeric network (Figure 1.25d). An attempt to realize such an approach was performed by Racles *et al.*<sup>[245]</sup> Starting from poly(methylhydro)siloxane, they grafted different amounts of allyl cyanide and *n*-hexene as the polar and non-polar components, respectively, via a hydrosilylation reaction. Even though an excess of the alkene was taken, there were still some unreacted hydrosilyl groups left after the reaction. Thus, in the case when only a polar component was used, the conversion was 89%, and a polymer with a permittivity of 15.9 at 10 kHz was obtained. The authors did not attempt to cross-link the obtained polymers. However, they observed cross-linking of the polymer during storage. That was due to the possible hydrolysis of unreacted hydrosilyl groups into hydroxyl groups, and subsequent condensation reaction. Another example with a more controlled synthetic pathway will be presented in this thesis later (Chapters 3–5).

The most elegant way to synthesize polar siloxane elastomer would be the one presented in Figure 1.25e. It is based on the preparation of a polar silicone and subsequent cross-linking through the reactive end groups. Only with such an approach does the material exhibit the best performance in terms of mechanical properties. This is because the distance between the cross-linking points is well controlled, the network is more homogeneous, and the highest possible number of polar side groups can be introduced. Additionally, the polar polymer can be synthesized, purified, and analyzed before the cross-linking reaction, and sometimes this can allow for solvent-free processing into thin films.

Three possible routes towards polar siloxanes with defined end-groups are described in the literature.<sup>[53]</sup> The first is the polymerization of a cyclic monomer bearing polar groups. However, according to Table 1.3, the yield of such a reaction is usually very small. That was also proved by Dünki *et al.*,<sup>[235]</sup> who tried to polymerize two monomers with nitrile groups. One monomer was prepared using a thiol-ene addition reaction of 2-cyanoethanthiol to 2,4,6,8-tetramethyl-2,4,6,8-tetravinylcyclotetrasiloxane (V<sub>4</sub>), while the second monomer was obtained through a hydrosilylation reaction between allyl cyanide and 2,4,6,8-tetramethylcyclosiloxane (D<sub>4</sub>H). In the case of functionalized V<sub>4</sub>, only 3% of the polymer. Hydroxyl end groups were introduced through the decomposition of the initiator, while vinyl end groups were introduced through the decomposition of the initiator, while vinyl end groups were introduced.

The second route is based on the condensation polymerization reaction of chlorosilanes bearing a polar group. At the end of the reaction, functional end-groups can be introduced with an end-blocker.<sup>[38]</sup> Such reaction was realized by the company Wacker and reported in their patent, where a permittivity of 6.8 at 100 kHz for an elastomer prepared from a siloxane with 59.4% of chloromethyl side groups was detected.<sup>[246]</sup> Elastomers with azide, nitrobenzene, or propoxysulfolane side groups, which were synthesized in the same way, are also known in the literature.<sup>[38]</sup> A permittivity of 11 at 1 kHz was detected for a polymer with 60% of propoxysulfolane groups. However, the hydrosilylation reaction does not allow for the formation of a high molecular weight polymer. Also, the molecular weight distribution after this reaction is broad, compared to silicones made by ROP.

The best synthetic strategy would be the postpolymerization modification of silicones with polar groups with subsequent cross-linking into an elastomer. For example, Racles et al.<sup>[247]</sup> synthesized a copolymer of PDMS with 8% vinyl functions and a copolymer of PDMS with 8% of hydrosilyl side groups via cationic ROP. Furthermore, the vinyl groups were reacted with 3-chloro-1-propanethiol or 3-mercaptopropionic acid through a thiol-ene addition reaction under irradiation with UV light. The hydrosilyl groups were converted by reaction with allyl cyanide, allyl glycidyl ether, allyl benzaldehyde, or disperse red 1. In comparison to hydrosilylation reaction, where conversion varied from 84% to 97%, depending on the reagent, post-functionalization with thiol-ene addition reaction was very efficient with 100% conversion. Due to the low concentration of polar groups, the highest permittivity value was 5.4 at 10 kHz for a polymer with disperse red 1 side groups. However, the dielectric loss and conductivity were also the highest for this polymer. Moreover, the authors attempted to react glycidyl ether side groups with 4amino pyridine. Thus, an even higher permittivity of 7.4 was achieved, while a more than 20 times increase in dielectric loss and conductivity was also observed. Because the authors used polymers that had unreactive trimethylsilyl end groups, it was not possible to obtain a cross-linked elastomer. A much higher degree of postpolymerization functionalization was achieved by Perju *et al.*<sup>[248]</sup> They grafted thioacetic acid to a polyvinylsiloxane via a thiol-ene addition reaction, achieving 100% functionalization of the vinyl side groups. Cross-linking of the polymer through the hydroxyl end groups allowed for the formation of an elastomer with a permittivity of 4.7. Their materials had a high strain at break of 250%, a relatively low Young's modulus below 210 kPa, and they showed an actuation strain as high as 14.5% at 30 V/ $\mu$ m. Reducing the membrane's thickness allowed them to achieve 5.6% of actuation strain at 650 V. Similar work was published by Caspari et al., [249] who obtained 100% functionalization of a polyvinylsiloxane using seven different alkylthiols, from ethanethiol to 1-dodecanthiol. A permittivity of 5.4 was detected for the siloxane functionalized with ethanethiol and cross-linked through the hydroxyl end groups with methylhydrosiloxane-dimethylsiloxane. The material showed a low modulus, a high strain at break, and 12% of actuation strain at 15 V/µm. The authors also cross-linked the polar polysiloxane with a polar trifunctional cross-linker and obtained permittivity as high as 7. However, this material also had a much higher conductivity and almost 33% of the extractable uncross-linked low molecular weight species. Whereas another material with a permittivity of 5.4 and only 13.4% of extractables showed a stable actuation over 50'000 cycles giving 10% strain at 27 V/ $\mu$ m. So far, one of the highest permittivities at 10 kHz was reported by Dünki et al.<sup>[250]</sup> In particular, by grafting 2-(methylsulfonyl)-ethanethiol or 3mercaptosulfolane via a thiol-ene addition reaction to polyvinylsiloxane, they were able to achieve almost 100% conversion, and polymers with a permittivities of 22.7 and 7.4, respectively. However, the author presented results only for liquid polymers, and did not cross-link them into elastomers.

Other polar siloxanes prepared by postpolymerization modification have also been described in the literature.<sup>[38]</sup> However, it was sometimes reported to be challenging to cross-link them. For example, platinum catalysts commonly used for hydrosilylation reactions can be poisoned by polar groups or sulfur.<sup>[34]</sup> The same can also happen with tin catalysts.<sup>[56]</sup> Also, care must be taken using other reactive end groups that are not affected during the postpolymerization modification. Thus, the introduction of vinyl end groups into polyvinylsiloxane is not possible, because they can be reacted in the thiol-ene addition reaction together with the side groups. Reactive hydrosilyl side groups are also not compatible with vinyl end groups, because of the possible hydrosilylation reaction. Therefore, it might not be easy finding a good synthetic strategy during which post-polymerization modification doesn't affect the functional end-groups.

## 1.7. Scope and Goals of the Thesis

Since their discovery, dielectric elastomer transducers (DETs) have found widespread applications, and a number of devices have been fabricated from them. While any elastomer can serve as a dielectric in DETs, polydimethylsiloxane-based elastomers are the most investigated. They are cheap, biocompatible, and have good mechanical properties, tunable modulus, and a low  $T_{g}$ . However, they suffer from a low dielectric permittivity value, which impacts the operation voltage of DETs. Literature shows that highly polarizable fillers enhance the dielectric permittivity of polysiloxanes, but a high volume fraction needs to be used. At high loadings, the price for an increased permittivity is a deterioration of mechanical properties and an increase in dielectric loss. Additionally, the composites are not homogenous, and thus, the dielectric breakdown is reduced. Increasing the permittivity of siloxanes through chemical functionalization with polar groups is preferable over composites since this allows obtaining materials that are homogenous at a molecular level. Such materials could have a high breakdown strength and more controllable mechanical properties and may allow the construction of transducers with improved performance.

Many synthetic strategies have been employed to chemically modify the polysiloxane backbone with polar groups to increase permittivity. However, different starting materials, types and contents of polar groups and synthetic chemistry have been used. This complicates the interpretation of the results and makes it impossible to correlate the structure of the synthesized polymers to different properties, mainly due to the many factors that changed simultaneously. Sometimes, the cross-linking procedure and the electromechanical investigations of the reported elastomers are missing. Additionally, only a few cases of polysiloxanes with permittivity values above 8 have been reported, while most are modified with the nitrile groups.

This work aims to understand the structure-property relationships of polar siloxanes. It should result in a rational design of materials for DET, with the final aim of achieving novel dielectric elastomers and actuators operated at unprecedentedly low voltages.

We aim to elucidate how the chemical modification of polysiloxane modified with different types and contents of polar groups impacts the dielectric properties and the  $T_g$ . Different polar groups will be attached to polysiloxanes by efficient chemistry, and the thermal and dielectric properties will be investigated. This will eventually allow us to select the most appropriate molecular structure that functions best as a dielectric in DET applications.

After selecting the most promising polar groups, a synthetic strategy for polar polysiloxanes that can be processed into thin films will be developed. The films will be cross-linked under ambient conditions to elastomers using a click reaction. This will allow elucidating how the dielectric and mechanical properties of the synthesized elastomers affect the electromechanical properties. It may also allow us to achieve devices operated at unprecedentedly low voltages and that can withstand high dielectric breakdown fields.

The synthesis of the best elastomers should be upscaled, stack actuators should be constructed, and their performance should be evaluated.

At the end of the thesis, an outstanding dielectric elastomer and a milestone in the rational design of DET materials should be achieved.

In Chapter 2, 13 different polar thiols were grafted in different concentrations to polyvinylsiloxanes under identical conditions using exactly the same starting materials. The impact of polar groups attached to the polysiloxane backbone on the dielectric properties of the material (permittivity, conductivity, dielectric losses) and  $T_g$  value is investigated.

In Chapter 3, a novel approach for synthesizing polar nitrile-containing siloxanes and their processing into thin films is developed. Siloxane bearing around 95% nitrile side groups and 2.3% of vinyl side groups is presented. It is shown that the functionality of the cross-linker used significantly affects the actuation performance and the breakdown strength.

In Chapter 4 and Chapter 5, novel polar siloxane with dimethylacrylamide and sulfonyl side groups are presented. The impact of the amount and nature of cross-linker on the mechanical properties is investigated. The effect of the polar groups on  $T_g$ , dielectric properties, and actuation performance is investigated. The potential of the polysiloxanes modified with these polar groups as a dielectric in sensors with increased sensitivity is also explored.

### **CHAPTER TWO**

## 2. Siloxanes Modified With Different Types and Contents of Polar Groups: Synthesis, Structure, Thermal, and Dielectric Properties

This chapter is based on the paper

Polysiloxanes modified with different types and contents of polar groups: synthesis, structure, thermal, and dielectric properties

by

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Author Contributions:

Y. Sheima performed the synthesis and characterization of compounds and contributed to the manuscript.

## 2.1. Abstract

Polymers with high dielectric permittivity are promising for the construction of next generation transducers and energy storage devices with improved energy density. Here, we report the synthesis, the glass transition temperature ( $T_9$ ), and the dielectric properties of polysiloxanes with different polarity. For this, we set out from poly(dimethyl-co-methyvinyl)siloxanes with different vinyl group content. The vinyl groups were then transformed into polar groups of various nature by an efficient one-step thiol-ene addition post-polymerization modification. We used the resulting collection of materials to establish structure-property relationships, side group design, thermal, and dielectric properties. Our results show that the  $T_g$  increases with the polar group content and the strength of the polar group. A similar trend is observed for the dielectric permittivity as long as the  $T_g$  of the polymer is well below 0 °C. Smaller polar groups tend to show a smaller increase in  $T_g$ , and an increased linker length helps to decreases  $T_g$ , which is generally favourable for high permittivity. Our findings guided us to design polysiloxanes with a permittivity as high as 27.7 and a  $T_g$  of -18.2 °C. To the best of our knowledge, this is the highest dielectric permittivity of a polymer with a  $T_g$  well below room temperature.

## 2.2. Introduction

High dielectric permittivity ( $\epsilon$ ') polymers are key to many innovative technologies including transducers,<sup>[251–253]</sup> energy harvesting<sup>[27,254]</sup> and energy storage devices,<sup>[255]</sup> soft robots,<sup>[72,175,256–258]</sup> as well as in stretchable and printable electronics.<sup>[259]</sup> Polydimethylsiloxane (PDMS) elastomers are the most extensively used dielectrics in transducers and stretchable electronics.<sup>[260]</sup> This is mainly due to their excellent dielectric and mechanical properties and their commercial availability. Although PDMS elastomers have found many applications as dielec-trics, their low dielectric permittivity of about  $\epsilon$ ' = 3 is a major drawback.<sup>[19]</sup> Polysiloxane elastomers with significantly increased dielectric permittivity would be very attractive to broaden the application potential of these elastomers in electrical devices, such as actuators, sensors, and generators.<sup>[26,72,251,261]</sup> High dielectric permittivity polymers are also searched for as electrolytes, which are needed in solid-state Li-ion batteries, ionic actuators, and electrochromic devices.<sup>[255]</sup> Despite the wide range of applications and the impact high dielectric permittivity polymers may have on various fields, so far, little attention has been given to their synthesis.<sup>[19]</sup>

The dielectric permittivity of a material is a measure of its polarizability. Electronic, ionic, dipolar, and interfacial polarization are the four different kinds of polarizations which occur in a material.<sup>[262]</sup> Chemical modification with polar groups allows to increase the dielectric permittivity of polymers via the dipolar polarization, supposed the dipoles are mobile and are amenable to polarization.<sup>[263]</sup> Dielectric permittivity increases with the strength of the individual dipole moment and the dipole density. However, chemical modification of polymers with polar groups has a downside. When increasing the density of such groups, the  $T_g$  of the modified polymers inevitably increases and often even exceeds room temperature, so that

the materials' extensi-bility in elastic deformation is reduced.<sup>[264]</sup> This has been convincingly illustrated for a variety of polymers.<sup>[265]</sup> To circumvent this problem, we have proposed to use highly flexible polysiloxanes, whose  $T_g$  is so low that a large number of functional groups can be attached before the backbone' flexibility is affected.

As of now, a number of polar groups have been grafted to polysiloxane by us and other laboratories.<sup>[66,237,242,250,266–271]</sup> Occasionally, attractive permittivities have been reported, but a comparison of values from different laboratories is hampered by the fact that different molar masses, different dipole densities and end groups, as well as different synthetic procedures were used. The current paper tries to overcome this situation by a highly systematic approach. We report a library of more than 60 different polysiloxane materials using a total of 13 different polar functional groups. All starting polymers have similar degrees of polymerization, and, in all cases, the functional group density has been systematically varied. Furthermore, all chains carry the same trimethylsilyl end groups to avoid end group contributions to permittivity. For all polymers, we measured  $T_{g}$ , dielectric permittivity, dielectric loss, and conductivity at 20 °C at different frequencies (0.01–1 MHz). This collection of data has resulted in the discovery of several materials candidates with promising properties and, moreover, is a useful basis for further developing structure-property relationships.

## 2.3. Experimental Section

#### 2.3.1. Materials

Unless otherwise stated, all chemicals were reagent grade and used without purification. 1,3,5,7-Tetramethyl-1,3,5,7-tetravinyl cyclotetrasiloxane ( $V_4$ ), hexamethyldisiloxane 98% (**EB** – end-blocker), octamethylcyclotetrasiloxane ( $D_4$ ) 97%, diethyl methylphosphonate, dithiothreitol were purchased from ABCR. 2,2-Dimethoxy-2-phenylacetophenone (DMPA), calcium hydrate, tetramethylammonium hydroxide 25wt% in water (TMAH), anhydrous benzene, methanol, tetrahydrofuran (THF), thioacetic acid, 2-mercaptoethanol, ethyl thioglycolate, 3-mercaptopropionic acid, sulfur, 2.5 M n-butyllithium solution in hexane (nBuLi), hydrochloric acid, chloroform, triethylamine, magnesium sulfate, vinyl carbonate, ethanedithiol, 1-vinyl-2-pyrrolidinone, pyrrolidine, N,N-dimethylacrylamide, sodium hydroxide, 3-chloro-1-propanethiol, 3-sulfolane, chlorotrimethylsilane, thionyl chloride, triethylamine, acetic acid, hydrogen peroxide, LiAlH<sub>4</sub>, 3-chloropropionitrile, thiourea, sodium hydroxide, sulfuric acid were purchased from Sigma Aldrich. Diethyl thiomethylphosphonate (12),<sup>[273]</sup> 2-(Methylsulfonyl)-ethanethiol (6),<sup>[273]</sup> nitroethanethiol (10),<sup>[274,275]</sup> 3-mercaptosulfolane (12),<sup>[273]</sup> 2-cyanoethanethiol (13)<sup>[276]</sup> were prepared according to the literature.<sup>[244]</sup>

## 2.3.2. Methods

A Hönle UVA HAND 250 GS UV lamp was used. <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded at 298 K on a BrukerAvance 400NMR spectrometer using a 5 mm broadband inverse probe at 400.13 and 100.61 MHz, respectively. Chemical shifts ( $\delta$ ) in ppm are calibrated to residual solvent peaks (CDCl<sub>3</sub>:  $\delta$  = 7.26 and 77.16 ppm, DMSO-d<sub>6</sub>:  $\delta$  = 2.50 and 39.52 ppm). Gel permeation chromatograms were recorded using an Agilent 1100 Series HPLC (columns: serial coupled PSS SDV 5 m, 100Å and PSS SDV 5 m, 1000 Å, detector: DAD, 235 nm and 360 nm; refractive index), where THF was the mobile phase. Differential scanning calorimetry (DSC) investigations were undertaken on a Perkin Elmer Pyris Diamond instrument under a nitrogen flow (50 ml min<sup>-1</sup>) in aluminum crucibles, which were shut with pierced lids and contained about 10 mg sample mass. Two heating and one cooling steps with a heating and cooling rate of 20 °C min<sup>-1</sup> were conducted per measurement under a nitrogen flow (50 ml min<sup>-1</sup>). The second cooling step was considered for the evaluation of the *T*<sub>g</sub>.

Dielectric permittivity measurements were performed in the frequency range from  $10^{-2}$  Hz to  $10^{6}$  Hz using a Novocontrol Alpha-A frequency analyzer. The V<sub>RMS</sub> (root mean square voltage) of the probing AC electric signal applied to the samples was 1 V. Stainless steel electrodes were used. The samples were squeezed between two electrodes. The thickness of 100 µm was adjusted with two silica glass spacers. All samples were kept in the vacuum oven at 60 °C for 12 hours before the measurement.

Synthesis of polymethylvinylsiloxane (**PV**) and poly(dimethylsiloxane-co-methylvinylsiloxane) (**PM<sub>x</sub>V<sub>y</sub>**)

Polymers were synthesized by anionic ring-opening polymerization of  $V_4$  and  $D_4$  using TMAH as an initiator. Before the synthesis  $V_4$ ,  $D_4$ , and **EB** were dried over CaH<sub>2</sub>, distilled and kept in an inert atmosphere. For the polymerization, a 250 ml Schlenk flask equipped with magnetic stirrer and a septum was used. It was dried at 500 – 600 °C with a heating gun under high vacuum (10<sup>-2</sup> mbar) for 5 min. Then TMAH was added in the flask and dried by azeotropic distillation with benzene followed by the corresponding addition of  $D_4$ ,  $V_4$ , and **EB** (Table 2.1). The reaction mixture was stirred at RT for 1 hour, followed by an additional stirring at 80 °C for 18 h. Then, the reaction mixture was heated at 140 °C for 4 h. The unreacted cycles were distilled at 140 °C and 10<sup>-2</sup> mbar for 6 h.

**PM**<sub>8</sub>**V**<sub>2</sub>: <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz),  $\delta$ : 6.07-5.86 (m, 2H, =C<u>H</u><sub>2</sub>); 5.85-5.74 (m, 1H, Si-C<u>H</u>=); 0.2-0.12 (m, 3H, -CH-Si-C<u>H</u><sub>3</sub>), 0.11-0 (m, 6H, C<u>H</u><sub>3</sub>-Si-C<u>H</u><sub>3</sub>); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz), 137.2; 132.9; 1.9; 1.2; -0.5;  $M_n = 10'400 \text{ g/mol}, M_w = 18'000 \text{ g/mol}, PDI = 1.8$  (Figure 2.5).

**PM<sub>6</sub>V<sub>4</sub>**: <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz),  $\delta$ : 6.08-5.85 (m, 2H, =C<u>H</u><sub>2</sub>); 5.84-5.73 (m, 1H, Si-C<u>H</u>=); 0.19-0.11 (m, 3H, -CH-Si-C<u>H</u><sub>3</sub>), 0.11-0.01 (m, 6H, C<u>H</u><sub>3</sub>-Si-C<u>H</u><sub>3</sub>); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz), 137.2; 133; 1.9; 1.2; -0.5;  $M_n = 15'300 \text{ g/mol}, M_w = 26'600 \text{ g/mol}, PDI = 1.74$  (Figure 2.5).

**PM<sub>4</sub>V<sub>6</sub>:** <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz),  $\delta$ : 6.08-5.85 (m, 2H, =C<u>H</u><sub>2</sub>); 5.85-5.73 (m, 1H, Si-C<u>H</u>=); 0.14 (s, 3H, -CH-Si-C<u>H</u><sub>3</sub>), 0.11-0.02 (m, 6H, C<u>H</u><sub>3</sub>-Si-C<u>H</u><sub>3</sub>); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz), 137; 133.1; 1.9; 1.2; -0.4;  $M_n = 12'500 \text{ g/mol}, M_w = 23'200 \text{ g/mol}, PDI = 1.86$  (Figure 2.5).

**PM<sub>2</sub>V<sub>8</sub>**: <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz),  $\delta$ : 6.07-5.85 (m, 2H, =C<u>H</u><sub>2</sub>); 5.85-5.7 (m, 1H, Si-C<u>H</u>=); 0.2-0.11 (m, 3H, - CH-Si-C<u>H</u><sub>3</sub>), 0.11-0.02 (m, 6H, C<u>H</u><sub>3</sub>-Si-C<u>H</u><sub>3</sub>), 0.09 (s, -Si-(CH<sub>3</sub>)<sub>3</sub>); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz), 136.9; 133.2; 1.9; 1.2; -0.4;  $M_n$  = 12'300 g/mol,  $M_w$  = 27'200 g/mol, *PDI* = 2.21 (Figure 2.5).

**PV**: <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz),  $\delta$ : 6.05-5.85 (m, 2H, =C<u>H</u><sub>2</sub>); 5.85-5.73 (m, 1H, Si-C<u>H</u>=); 0.19-0.11 (m, 3H, -CH-Si-C<u>H</u><sub>3</sub>), 0.09 (s, -Si-(CH<sub>3</sub>)<sub>3</sub>); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz), 136.9; 133.2; 1.9; 1.2; -0.4;  $M_n$  = 12'500 g/mol,  $M_w$  = 36'400 g/mol, *PDI* = 2.918 (Figure 2.5).

Table 2.1. Amount of reagents used for the synthesis of starting polymers **PV** and **PM<sub>x</sub>V<sub>y</sub>** end-blocked with trimethylsilyl groups and their  $M_n$ ,  $M_w$ , *PDI* values as determined by GPC.

Sample name	M:V ratio	Mole vinyl groups <sup>a</sup>	<b>D</b> ₄ [ml]	<b>V₄</b> [ml]	<b>EB</b> [ml]	TMAH <sup>b</sup> [ml]	<i>M</i> n [kDa]	<i>M</i> w [kDa]	PDI	Yield [%]
$PM_8V_2$	8:2	19%	82	22.8	3.5	0.3	10.4	18.8	1.8	87
$PM_6V_4$	6:4	39%	61.5	45.7	3.5	0.3	15.3	26.6	1.7	85
$PM_4V_6$	4:6	58%	39.2	68.3	3.5	0.3	12.5	23.2	1.9	82
$PM_2V_8$	2:8	78%	20.5	91.3	3.5	0.3	12.3	27.2	2.2	87
PV	0:1	100%	0	114.2	3.5	0.3	12.5	36.4	2.9	89

<sup>a</sup>Calculated by using <sup>1</sup>H NMR end group analysis. <sup>b</sup>A solution of 25 wt% in H<sub>2</sub>O was used.

#### Synthesis of diethyl thiomethylphosphonate (4)

The synthesis of **4** was performed according to the literature.<sup>[272]</sup> Diethylmethylphosphonate (24.25 g, 1 eq) was dissolved in dry THF (180 ml) in a Schlenk flask. The solution was cooled to -78 °C when a 2.5 M solution of nBuLi in hexane (65.2 ml, 1.02 eq) was added dropwise under an inert atmosphere. After stirring for 30 min at -78 °C, elementary sulfur (5.21 g, 1.02 eg) was added. The reaction mixture was slowly heated to -20 °C and diluted with water (150 ml). THF was evaporated at reduced pressure and the aqueous phase was extracted with chloroform (2×100 ml). The aqueous layer was cooled to 0 °C and acidified with 1 N hydrochloric acid to pH = 1. Then it was extracted with chloroform (4×100 ml). Combined organic phases were washed with brine, dried over MgSO<sub>4</sub>, and the solvent was removed under reduced pressure. According to the literature, diethyl thiomethylphosphonate can be either purified by distillation <sup>[277]</sup> or used as it is without purification <sup>[278]</sup>. However, the <sup>1</sup>H and <sup>31</sup>P NMR (Figures 2.6 and 2.7) showed the presence of impurities and thus purification was needed. Our attempts to purify this compound by distillation at 10<sup>-2</sup> mbar and temperatures up to 140 °C, were not successful. <sup>1</sup>H NMR analysis of the mixture showed that the mercapto groups oxidized to disulfide. To reduce the disulfide to 4, dithiothreitol (DTT) was used.<sup>[279]</sup> Thus, to 1 eq of disulfide in THF, 2 eq of DTT were added under an inert atmosphere. Then several drops of triethylamine were added to adjust the pH to 7-8. This mixture was stirred for 1 h at RT. Thereafter water was added and the pH was adjusted to 4 using 1N HCl. The two phases were separated. The aqueous phase was extracted with chloroform (3×100 ml). The combined organic phases were washed with brine, dried over MgSO<sub>4</sub> and concentrated under reduced pressure. The product was purified by column chromatography over silica gel using EA/Heptane (1:1) and few drops of acetic acid. The product was stored under argon in the fridge. Yield: 66 %. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz), δ: 4.22-4.08 (m, 4H), 2.72-2.6 (dd, 2H), 1.86-1.78 (dt, 1H), 1.32 (t, 6H); <sup>13</sup>C NMR (CDCI<sub>3</sub>, 100 MHz), δ: 63.1; 18.5; 17; 16.5; <sup>31</sup>P NMR (CDCI<sub>3</sub>, 161 MHz), δ: 24.6 (Figures 2.6-2.9).

Synthesis of 2-(methylsulfonyl)-ethanethiol (6)

The synthesis of **6** was performed according to the literature.<sup>[273]</sup>

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz), δ: 3.31-3.23 (m, 2H), 2.96-2.89 (m, 5H), 1.8 (t, 1H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz), δ: 58.0; 41.5; 17.1 (Figures 2.10, 2.11).

Synthesis of 4-((2-mercaptoethyl)thio)-1,3-dioxolan-2-one (7)

Vinyl carbonate (1 g, 11.62 mmol), ethanedithiol (5.47 g, 58.1 mmol) and DMPA (140 mg) were mixed in THF (40 ml). The reaction mixture was degassed three times by freeze-pump-thaw-cycles. After cooling the reaction mixture to about 0 °C it was irradiated for 10 min by UV light. The solvent was evaporated under reduced pressure. The product was purified by column chromatography over silica gel using EA/Heptane (1:4) as eluent, giving 86% yield. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz),  $\delta$ : 5.87 (dd, 1H), 4.73 (dd, 1H), 4.18 (dd, 1H), 3.07 – 2.98 (m, 2H), 2.92 – 2.76 (m, 2H), 1.70 (t, 1H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz),  $\delta$ : 154.0; 82.4; 69.1; 36.1; 25.2 (Figures 2.12-2.14).

Synthesis of S-(2-oxopyrrolidin-1-yl)ethyl thioacetate

To a solution of 1-vinyl-2-pyrrolidinone (3 g, 0.027 mol) in THF (30 ml) thioacetic acid (2.46 g, 0.032 mol) and DMPA (30 mg) were added. The reaction mixture was degassed three times by freeze-pump-thaw-cycles and irradiated with UV-light for 10 min. THF and excess of thioacetic acid were distilled under reduced pressure. The white crystals obtained were sufficiently pure and were used without purification in subsequent reaction. Yield: 98%. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz),  $\delta$ : 3.47-3.40 (m, 4H), 3.06-3 (t, 2H), 2.4-2.32 (t, 2H), 2.32 (s, 3H), 2.0 (m, 2H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz),  $\delta$ : 195.6; 175.5; 47.7; 42.2; 30.9; 30.7; 26.8; 18.1. (Figures 2.15 – 2.16).

#### Synthesis of 1-(2-mercaptoethyl)-2-pyrrolidinone (8)

S-(2-Oxopyrrolidin-1-yl)ethyl thioacetate (5 g, 0.027 mol) was dissolved in dry chloroform (20 ml). Then pyrrolidine (2.1 g, 0.0297 mol) was added dropwise under an inert atmosphere at 0 °C. The mixture was stirred for 5 h at 0 °C. The solvent was removed under reduced pressure and product was purified by column chromatography (silica gel, EtOAc), giving the desired thiol with 85% yield. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz),  $\delta$ : 3.50-3.40 (m, 4H), 2.73-2.63 (q, 2H), 2.43-2.35 (t, 2H), 2.1-1.98 (m, 2H), 1.37 (t, 1H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz),  $\delta$ : 175.4; 47.7; 45.8; 30.9; 22.4; 18.1 (Figures 2.17 – 2.18).

Synthesis of N,N-dimethyl-3-mercaptopropanamide (9)[280]

To N,N-dimethylacrylamide (17.82 g, 0.18 mol) cooled to 0 °C, thioacetic acid (13.7 g, 0.18 mol) was added dropwise under inert atmosphere. The mixture was stirred for 4 h at RT. Then MeOH (90 ml) was added and the mixture was cooled to 0 °C. Aqueous NaOH (3 M, 90 ml) was added to the reaction mixture and stirred for 2 h at RT. The obtained mixture was neutralized with concentrated HCl. Methanol was removed under reduced pressure. The aqueous layer was extracted with  $CH_2CI_2$  (3×100 ml). The organic phases were combined, washed with brine, dried over MgSO<sub>4</sub> and concentrated. The product was purified by distillation at 10<sup>-2</sup> mbar and 66 °C, giving yellowish liquid. Yield: 83%. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz),  $\delta$ : 2.97

# (s, 3H), 2.92 (s, 3H), 2.81-2.74 (m, 2H), 2.62 (t, 2H), 1.74 (t, 1H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz), δ: 170.8; 37.3; 37.1; 35.4; 20.1 (Figures 2.19, 2.20).

#### Synthesis of nitroethanethiol (10)

*Method a*: The synthesis of **10** was performed according to the literature.<sup>[274]</sup> Firstly  $\beta$ -nitroethylacetate was synthesized starting from of nitroethanol (1 eq) and glacial acetic acid (1.3 eq) in benzene in the presence of catalytic amount of concentrated sulfuric acid. The mixture was refluxed for 16 hours and the water was removed using a Dear-Stark head. The obtained mixture was concentrated with rotary and distilled under vacuum, yielding 95% of colorless  $\beta$ -nitroethylacetate.

Trisodium thiophosphate was synthesized by reaction of thiophosphoryl chloride (1 eq) with sodium hydroxide (6 eq) in water at 80 °C. After keeping the reaction mixture in the fridge at 0 °C overnight, white crystals were isolated, filtered, dissolved in water and reprecipitated again with ethanol. White crystals were filtered, washed with ethanol, and dehydrated by stirring in absolute methanol for 2 hours. The final white product was dried for 1 hour at 105 °C under vacuum.

For the synthesis of nitroethanthiol, to a solution of sodium thiophosphate (1 eq) and benzyltriethylammonium chloride (0.008 eq) in water, 1 eq of  $\beta$ -nitroethylacetate was added dropwise, keeping the temperature of the reaction mixture below 20 °C. Then, the mixture was stirred for 16 hours at RT. The product was acidified with concentrated HCl and stirred for additional 1 hour. The final mixture was extracted with ethyl acetate, washed with saturated solution of sodium chloride, dried over MgSO<sub>4</sub>, concentrated with rotary evaporation and distilled at 40 °C and high vacuum. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz),  $\delta$ : 4.56 (t, 2H), 3.08 (dt, 2H), 1.70 (t, 1H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz),  $\delta$ : 58.8; 21.2 (Figures 2.21, 2.22).

#### Method b:

#### Synthesis of nitroethylene

The synthesis of nitroethylene was done according to the literature.<sup>[275] 1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz),  $\delta$ : 7.09 (dd, 1H), 6.58 (dd, 1H), 5.88 (d, 1H) ((Figure 2.23).

#### Synthesis of nitroethyl thioacetate

Thioacetic acid (5.2 g, 1 eq) was added dropwise to a cooled to 0 °C solution of nitroethylene (5 g, 1 eq) in dry diethylether (130 ml). Then trimethylamine (0.34 g, 0.05 eq) was added and the mixture was stirred for 2 h. The obtained mixture was washed with 1M hydrochloric acid (70 ml) and water. The organic phase was separated and dried over MgSO<sub>4</sub>. The solvent was removed under reduced pressure, and the product was purified by column chromatography over silica gel using EA/Heptane (1:10) as eluent. Yield: 45%. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz),  $\delta$ : 4.53 (t, 2H), 3.41 (t, 2H), 2.36 (s, 3H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz),  $\delta$ : 194.6; 73.9; 30.6; 25.5 (Figure 2.24- 2.25).

#### Synthesis of nitroethanethiol (10)

To a degassed solution of nitroethyl thioalcetate (3.8 g, 1 eq) in MeOH (50 ml) 3 M HCl (51 ml) was added under Ar. The mixture was stirred for 12 h at 60 °C. Then MeOH was removed under reduced vacuum and residue was extracted with DCM (3×70 ml). The combined organic phases were washed with brine, dried over MgSO<sub>4</sub> and concentrated. The product was distilled at 10<sup>-2</sup> mbar and 40 °C. Yield: 67%. <sup>1</sup>H NMR

(CDCl<sub>3</sub>, 400 MHz), δ: 4.56 (t, 2H), 3.08 (dt, 2H), 1.69 (t, 1H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz), δ: 58.8, 21.2 (Figure 2.26-2.27).

#### Synthesis of 3-mercaptosulfolane (12)

The synthesis of **12** was done according to the literature.<sup>[273]</sup> <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz),  $\delta$ : 3.66-3.54 (m, 1H), 3.53-3.45 (m, 1H), 3.38-3.28 (m, 1H), 3.16-3.05 (m, 1H), 3.01-2.93 (m, 1H), 2.71-2.56 (m, 1H), 2.22-2.09 (m, 1H), 2.03 (d, 1H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz),  $\delta$ : 60.0; 52.3; 33.9; 33.7 (Figures 2.28, 2.29).

#### Synthesis of 2-cyanoethanethiol (13)

The synthesis of **13** was done according to the literature.<sup>[276]</sup> <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz), δ: 2.80-2.72 (m, 2H), 2.70-2.62 (m, 2H), 1.78 (t, 1 H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz), δ: 117.9; 22.9; 20.6 (Figures 2.30-2.31).

#### General procedure for grafting polar groups to PV and $PM_xV_y$

To a solution of **PV** or **PM<sub>x</sub>V<sub>y</sub>** (1.5 g) in THF (35 ml), thiol (1.5 eq to vinyl groups) and 0.01 eq of DMPA were added. The mixture was degassed three times by freeze-pump-thaw-cycles. Then it was irradiated for 5 min by UV light. The reaction mixture was concentrated and the product was precipitated either in MeOH (for less polar polysiloxane) or cyclohexane (for polar polysiloxanes). The precipitate was separated from the solvent and dissolved again in THF and precipitated in a non-solvent. Such procedure was repeated several times until a satisfying purity was achieved. All polymers were dried at  $10^{-2}$  mbar and 60 °C for 24 h.

For simplicity, we present NMR data for **PV-z** only, where z indicates the thiol used for modification. The chemical shifts for different **PM<sub>x</sub>V<sub>y</sub>-z** are similar to **PV-z**, only the intensity of the signals is different. All spectra are included in the SI (Figures 2.32-2.60).

**PV-1**: <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz), δ: 2.95-2.86 (m, 2H), 2.298 (s, 3H), 1.0-0.84 (m, 2H), 0.23-0.13 (m, 3H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz), δ: 195.8; 30.7; 24.3; 18.3; 1.2, -0.2.

**PV-2**: <sup>1</sup>H NMR (DMSO-d<sub>6</sub>, 400 MHz), δ: 4.74 (t, 1H), 3.57-3.49 (m, 2H), 2.62-2.52 (m, 4H), 0.85 (t, 2H), 0.135 (s, 3H); <sup>13</sup>C NMR (DMSO-d<sub>6</sub>, 100 MHz), δ: 60.8; 33.8; 25.8; 18.0; -0.34.

**PV-3**: <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz), δ: 4.18-4.10 (m, 2H), 3.20 (s, 2H), 2.67 (t, 2H), 1.24 (t, 3H), 0.89 (t, 2H), 0.13 (s, 3H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz), δ: 170.3; 61.2; 33.5; 27.1; 17.7; 14.3; -0.1.

**PV-4**: <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz), δ: 4.13 (quint, 4H), 2.81-2.67 (m, 4H), 1.31 (t, 6H), 0.88 (t, 2H), 0.13 (s, 3H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz), δ: 62.6; 28.2; 26.2; 24.7; 17.8; 16.6; 0.02. <sup>31</sup>P NMR (CDCl<sub>3</sub>, 161 MHz), δ: 24.4.

**PV-5**: <sup>1</sup>H NMR (DMSO-d<sub>6</sub>, 400 MHz), δ: 12.2 (s, 1H), 2.67 (t, 2H), 2.55 (t, 2H), 2.47 (t, 2H), 0.88 (t, 2H), 0.17 (s, 3H); <sup>13</sup>C NMR (DMSO-d<sub>6</sub>, 100 MHz), δ: 172.9; 34.3; 26.2; 25.5; 17.7; -0.3.

**PV-6**: <sup>1</sup>H NMR (DMSO-d<sub>6</sub>, 400 MHz), δ: 3.38-3.32 (m, 2H), 3.01 (s, 3H), 2.91-2.81 (m, 2H), 2.63 (t, 2H), 0.85 (t, 2H), 0.13 (s, 3H); <sup>13</sup>C NMR (DMSO-d<sub>6</sub>, 100 MHz), δ: 53.6; 40.4; 25.6; 23.4; 17.5; -0.2.

**PV-7**: <sup>1</sup>H NMR (DMSO-d<sub>6</sub>, 400 MHz), δ: 6.23-6.1 (m, 1H), 4.87-4.78 (m, 1H), 4.32-4.22 (m, 1H), 3.04-2.90 (m, 2H), 2.86-2.73 (m, 2H), 2.65-2.57 (m, 2H), 2.87 (t, 2H), 0.15 (s, 3H); <sup>13</sup>C NMR (DMSO-d6, 100 MHz), δ: 153.8; 82.3; 68.9; 31.5; 31.0; 25.6; 17.8; -0.3.

**PV-8**: <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz), δ: 3.50-3.40 (m, 4H), 2.68 (t, 2H), 2.60 (t, 2H), 2.35 (t, 2H), 2.03 (quint, 2H), 0.89 (t, 2H), 0.16 (s, 3H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz), δ: 175.0; 47.6; 42.1; 31.0; 29.7; 26.4; 18.4; 18.1; 0.1.

**PV-9**: <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz), δ: 3.07-2.82 (m, 6H), 2.76 (t, 2H), 2.62-2.51 (m, 4H), 0.85 (t, 2H), 0.10 (s, 3H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz), δ: 171.3; 37.3; 35.4; 33.6; 27.4; 26.7; 18.7; 0.1.

**PV-10**: <sup>1</sup>H NMR (DMSO-d6, 400 MHz), δ: 4.72 (t, 2H), 3.06 (t, 2H), 2.60 (t, 2H), 0.86 (t, 2H), 0.14 (s, 3H); <sup>13</sup>C NMR (DMSO-d6, 100 MHz), δ: 74.8; 27.6; 25.7; 17.6; -0.4

**PV-11**: <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz), δ: 3.66 (t, 2H), 2.68 (t, 2H), 2.57 (t, 2H), 2.03 (quint, 2H), 0.91 (t, 2H), 0.16 (s, 3H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz), δ: 43.8; 32.3; 29.0; 26.6; 18.4; 0.1.

**PV-12**: <sup>1</sup>H NMR (DMSO-d<sub>6</sub>, 400 MHz), δ: 3.67-3.5 (m, 2H), 3.31-3.25 (m, 1H), 3.19-3.07 (m, 1H), 2.98-2.87 (m, 1H), 2.65 (t, 2H), 2.51-2.434 (m, 1H), 2.06-1.94 (m, 1H), 0.88 (t, 2H), 0.17 (s, 3H); <sup>13</sup>C NMR (DMSO-d<sub>6</sub>, 100 MHz), δ: 56.7; 51.2; 38.5; 29.3; 25.0; 17.6; -0.2.

**PV-13**: <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz), δ: 2.82(t, 2H), 2.74-2.62 (m, 4H), 0.92 (t, 2H), 0.18 (s, 3H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz), δ: 118.8; 27.6; 26.8; 19.2; 18.2; 0.1.

#### 2.3.3. Results and Discussions

#### 2.3.3.1. Synthesis of Polar Polysiloxanes

Polymethylvinylsiloxane homopolymers (**PV**) and poly(dimethyl-*co*-methylvinyl)siloxanes copolymers (**PM**<sub>x</sub>**V**<sub>y</sub>) with ratios x:y = 2:8, 4:6, 6:4, and 8:2 were used in this study (Scheme 2.1a). These polymers were prepared by anionic ring-opening polymerization of the corresponding **D**<sub>4</sub> and **V**<sub>4</sub> monomers in presence of hexamethyldisiloxane as an end-capping agent. The synthesis was performed on a 100 g scale, which allowed us to use the exact same batch of polymers for the subsequent functionalization with different thiols (Scheme 2.1b).<sup>[199]</sup> We prepared polymers of intermediate molecular weight of 10–15 kDa as determined by GPC (Figure 2.5). In this range, we expect the *T*<sub>g</sub> and the dielectric properties to be independent of molar mass. Additionally, the low viscosity of the functionalized polymers should facilitate sample preparation for dielectric measurements. End group analysis by <sup>1</sup>H NMR spectroscopy cannot be employed for *M*<sub>n</sub> determination of **PM**<sub>x</sub>**V**<sub>y</sub> because the signal of the trimethylsilyl end groups overlaps with the one of the dimethylsilyl groups from the copolymers (Figure 2.32). Only for **PV**, the signal of the end groups was well separated (Figure 2.33) at a chemical shift of ~ 0.09 ppm and allowed us to calculate an *M*<sub>n</sub> = 11 kDa, which is in agreement with the GPC results. A clear indication that the trimethylsilyl end groups are present also in the copolymers is the small peak observed at ~1.9 ppm in all <sup>13</sup>C NMR spectra (Figure 2.34).



Scheme 2.1 Structures of the starting polysiloxanes **PV** and **PMxVy** (a) and of the polar thiols selected for their functionalization (b).

Scheme 2.1b shows the different polar thiols selected for our investigations. While thiols **1**,<sup>[248]</sup> **5**,<sup>[281–283]</sup> **6**,<sup>[273]</sup> **11**,<sup>[281]</sup> **12**,<sup>[273]</sup> and **13**<sup>[244]</sup> had previously been used before for the functionalization of polysiloxanes, thiols **2**, **3**, **4**, **7**, **8**, **9**, and **10** have never been used before for such purpose. The thiols **1**, **2**, **3**, **5**, **11**, and **13** are commercially available. Thiol **7** is a new compound and was prepared starting from vinyl carbonate and an excess of ethanedithiol via a UV induced thiol-ene reaction (Scheme 2.2a, Figures 2.12–2.13). All other thiols were synthesized using either published or modified synthetic protocols (Scheme 2.2).<sup>[284]</sup> Thiols **6**, **8**, **9**, **10**, and **12** were prepared using either a thiol-ene or Michael addition reaction of thioacetic acid to vinyl compounds that carry a polar group (Scheme 2.2b). The formed thioesters were deprotected to the respective thiols either in acidic or basic conditions. Thiol **8** has been prepared before starting from 1-(2-chloroethyl)-2-pyrrolidinone and hydrogen disulfide. This synthesis was however difficult to reproduce. The thiol-ene addition of thioacetic acid to 1-vinyl-2-pyrrolidinone, followed by the cleavage of thioacetate with pyrrolidine allowed us to synthesize **8** in 85% yield.<sup>[285]</sup> Thiol **13** was synthesized starting from thiourea and 3-chloropropionitrile (Scheme 2.2c).<sup>[267]</sup>

Diethyl thiomethylphosphonate (**4**) was synthesized in one step starting from diethylmethylphosphonate, nBuLi, and elementary sulfur (Scheme 2.2d). According to literature, thiol **4** can be either purified by distillation<sup>[277]</sup> or used as it is without purification.<sup>[278]</sup> <sup>1</sup>H and <sup>31</sup>P NMR spectra (Figures 2.5-2.9) showed the presence of impurities and thus purification was performed. Attempts to distill **4** resulted in the oxidation of the thiol to disulfide, as shown by the <sup>1</sup>H NMR analysis where the characteristic signal of the thiol at 1.87–1.80 ppm disappeared (Figure 2.6). Additionally, the <sup>31</sup>P NMR spectrum did not show a signal at 24.65 ppm characteristic for compound **4**. Reduction of the disulfide to **4** using dithiothreitol (DTT)<sup>[279]</sup> furnished **4** of reasonable purity after column chromatography.

The synthesis of thiol **10** was challenging and difficult to achieve on a large scale.<sup>[274,275]</sup> Two strategies were followed, both starting from nitroethanol. First, an esterification reaction between nitroethanol and acetic acid was conducted, followed by the treatment of the obtained ester with thiophosphonate ester, which furnished  $\beta$ -nitroethanethiol in low yield. The second attempt used the dehydration of nitroethanol

in presence of phthalic anhydride at elevated temperature, where nitroethylene was distilled off and reacted with thioacetic acid under Michael conditions, followed by deprotection of the formed thioester in acidic conditions. The last method is however recommended, because it is faster.



Scheme 2.2 Grafting of ethanedithiol to vinyl carbonate under high dilution conditions to give thiol **7** (a). Thiol-ene (top) and Michael-type addition (bottom) of thioacetic acid followed by acid or base deprotection to give thiols **6**, **8**, **9**, **10** and **12** (b). Synthesis of 2-cyanoethanethiol **13** (c). Synthesis of diethyl thiomethylphosphonate **4** (d). Synthesis of 2-nitroethanethiol **10** (e).



Scheme 2.3 Thiol-ene addition of polar thiols 1-13 to polysiloxanes PMxVy and PV.

The thiol-ene chemistry used to graft the polar thiols to the vinyl groups of the starting polymers is known to proceed fast and with high conversion, gives little side products, and it can even be conducted in ambient conditions.<sup>[209]</sup> Thiol addition to vinyl groups occurs predominantly with anti-Markovnikov regioselectivity, although negligible amounts of Markovnikov regioisomers can be identified in some of our reactions.<sup>[209]</sup>

The thiols **1–13** were grafted to the four copolymers  $PM_xV_y$  and the homopolymer PV to give 63 polymers  $PM_xV_y$ -z and PV-z of different polarities, where z represents the polar thiol used for functionalization.<sup>+</sup> For this functionalization, identical batches of the starting polymers were used. The success of functionalization was determined by <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy, which showed the disappearance of the vinyl signals and the appearance of new signals characteristic for the polar groups (Figure 2.32–2.60). Figure 2.1 shows the <sup>1</sup>H NMR spectra for the modified polymers **PV-z** with signal assignment. These spectra are representative for all polymers prepared and reflect the high level of structural perfection and purity achieved.

The molecular weights and the molecular weight distributions of all polymers were determined by GPC (Figures 2.61), except for  $PM_xV_y$ -5 and PV-5 which interacted with the GPC column and  $PM_xV_y$ -10 and PV-10, which turned insoluble after drying. For the polymers modified with the thiols 2, 6, and 12, the apparent molecular weight decreased with increasing amount of polar side groups despite the factual increase in molecular weight due to the functionalization, which we attribute to a progressive underestimation of molecular weight with decreasing solubility.<sup>[273]</sup> A similar trend was observed for the polymers modified with thiols 4, 8, and 9.

#### 2.3.3.2. Thermal Transitions

The effect of the polar groups on the glass transition temperature,  $T_{q}$ , of the respective polymers was investigated by differential scanning calorimetry (DSC) in the temperature range of -100 °C to +50 °C. The obtained  $T_g$  and  $\Delta C_p$  values of the transitions are summarized in Table 2.2. All polymers showed a single  $T_{q}$ , which is characteristic for random copolymers and amorphous homopolymers. With an increasing concentration of polar side groups, a concomitant increase in  $T_{q}$  is observed, as expected. A typical example is shown in Figure 2.2a for the series of  $PM_xV_y$ -8 and PV-8. Their  $T_g$  increased with increasing polarity from -78.9 °C for PM<sub>8</sub>V<sub>2</sub>-8 to -40.7 °C for PV-8. Figures 2.2b-n show the T<sub>g</sub> as a function of polar group content for different polymers. For a given polar group, an initial steep increase in  $T_g$  is observed for the polymers at a low degree of functionalization with polar groups, followed by a slower increase and flattening of the curve at a higher degree of functionalization. This indicates that, for the polymers with a low content of polar groups, the dipoles are more effective in linking adjacent chains by dipolar interaction likely with the oxygen in the polysiloxane backbone, thus negatively affecting chain mobility and increasing  $T_{q}$ . A similar behaviour has been reported before for *co*-polysiloxanes composed of dimethylsiloxane and carboxypropylmethylsiloxane [(2-hydroxyethoxycarbonyl) or propyl]methylsiloxan units, where hydrogen bonds between the carboxylic or hydroxyl groups and the oxygen atoms in dimethylsiloxy units occur.<sup>[286]</sup> At higher polar group content, dipole-dipole interactions start to play a role, but their impact on  $T_g$  seems to be less pronounced. As will be discussed below, they have a stronger impact on the mobility of the dipoles in an electric field and thus on the dielectric permittivity. Importantly, all polymers show  $T_g$  values significantly below room temperature (Figures 2.62–2.74). This is attractive since a low  $T_g$  implies that cross-linking will result in highly extensible elastic materials. The polymers modified with group **12** are, to some extent, an exception as their  $T_g$  increased to about 0 °C at high dipole density. This is likely due to the high dipole strength of **12** combined with the steric demand of the sulfolane group. Additionally, the short linker between the polysiloxane chain and this polar group may further reduce the mobility of the polysiloxane chains.

#### 2.3.3.3. Dielectric Properties

Broadband dielectric spectroscopy was used to investigate the dielectric properties of the obtained polymers at 20 °C and in a frequency range between 0.01–1 MHz. Dielectric permittivity  $\varepsilon'$  and dielectric loss  $\varepsilon''$ , as well as the real part of the complex conductivity  $\sigma'$  and  $tan \delta$  for all polymers are presented in Figures 2.75–2.87. An overview of  $T_g$  values, dielectric permittivity at 10 kHz and conductivity at 0.01 Hz is presented in Table 2.2. Figure 2.2b–n shows how the chemical modification with different amounts and types of polar groups influences both  $T_g$  and dielectric permittivity  $\varepsilon'$  at 10 kHz. Most polymers show an almost linear increase in dielectric permittivity with polar group content. The increase in permittivity is commonly more pronounced for polymers with a lower degree of functionalization and slightly less pronounced for higher degree of functionalization, respectively.

However, polymers modified with thiopropionic acid **5** and with cyclic sulfolane thiol **12** show a different behavior. Their dielectric permittivity saturates or even drops at higher degree of functionalization. The reason behind the reduced increase in dielectric permittivity with increasing content of carboxylic acid can be attributed to the known tendency of carboxylic groups to form hydrogen bonds by dimerization.<sup>[286–288]</sup> The dimerization results in an antiparallel orientation of the dipoles and thus dipole cancellation.

Polymers **PM<sub>x</sub>V<sub>y</sub>-12** show a linear increase in dielectric permittivity with increasing dipole content at low polar group concentration. This increase is in line with the low  $T_g$  of the respective polymers. After this initial increase in permittivity, a drop in permittivity is observed when the dipole content of **12** surpasses 50 mol%. This is due to the fact that the  $T_g$  of these polymers reach values near 0 °C, which starts to impede the mobility of the sulfolane groups in an electric field even at room temperature.

Figure 2.3 shows three examples of how dielectric properties are influenced by the types and contents of polar groups as a function of frequency (see Figures 2.75–2.87 for the complete data set). All polymers show a steep increase in permittivity at frequencies below about 10 Hz. This is due to electrode polarization, which occurs when ions move within the sample to electrode interfaces where they accumulate. The presence of ionic conductivity in all polymers is observed on the dielectric loss spectra,

which show at low frequencies the straight line with the slope of –1. For all samples, conductivity stays in the range of insulators. However, three different behaviors can be observed at higher frequencies, as illustrated in the three panels of Figure 2.3 using  $PM_xV_y$ -1 and PV-1 (left),  $PM_xV_y$ -7 and PV-7 (center), as well as  $PM_xV_y$ -12 and PV-12 (right) as representative examples.

**PM<sub>x</sub>V<sub>y</sub>-1** and **PV-1** show an increase in permittivity with the dipole content at all frequencies above 10 Hz. The dipoles of these polymers can thus be easily polarized at room temperature within the entire frequency range investigated. Dipole relaxation occurs above  $10^6$  Hz. A similar behaviour is found for polymers modified with thiols **1-4**, **8-11**, and **13**. The  $T_g$  of all these polymers is significantly below 0 °C.

 $PM_xV_y$ -7 and PV-7 show the expected increase in permittivity with increasing grafting density; however, the dipoles relax at frequencies above 10<sup>5</sup> Hz. This is reflected by a drop in the dielectric permittivity at higher frequencies for polymers with high polar group contents. A similar behavior is observed for polymers modified with thiols **5** and **6**.

Finally,  $PM_xV_y$ -12 and PV-12 show a strong frequencydependence of permittivity with dipole content. Apparently, the combination of the strong dipole moment of the sulfolane group, its high steric demand, and the use of a short linker to the polysiloxane chain increases the  $T_g$  and reduces the flexibility of the polymer backbone. This is further reflected by the dielectric measurements. An increase in the dielectric permittivity with the dipole content can be observed at low frequencies for all polymers. However, there is a strong dispersity in the relaxation frequency of dipoles for different concentrations. Thus, despite the strong polarity of 12 and high dipole density of PV-12, the dielectric permittivity at high frequency of PV-12 is smaller than expected.



Figure 2.1 <sup>1</sup>H NMR spectra of a series of functionalized polymers **PV-z** and signal assignment. The peaks marked with (\*) are due to the Markovnikov product.

Sample	Polar thiol	Tg	$\Delta C_{p}$	$\mathcal{E}^{'}$	σ'	Mn	Mw	PDI
		[°C]	[J (g*°C)⁻1]		[S cm⁻¹]	[kDa]	[kDa]	
PM <sub>8</sub> V <sub>2</sub> -1	0	< -100	-	3.4	1.77×10 <sup>-13</sup>	14.1	28.8	2.05
$PM_6V_4-1$	Ĭ	-85.6	0.364	4.0	2.43×10 <sup>-13</sup>	20.6	43.1	2.09
PM <sub>4</sub> V <sub>6</sub> -1	HS	-73.6	0.389	4.3	3.80×10 <sup>-13</sup>	20.5	49.6	2.41
PM <sub>2</sub> V <sub>8</sub> -1		-64.2	0.382	4.7	5.50×10 <sup>-12</sup>	17.9	57.5	3.2
PV-1		-57.6	0.389	4.9	1.11×10-11	17.9	59.7	3.34
PM <sub>8</sub> V <sub>2</sub> -2		-91.6	0.491	5.0	2.11×10 <sup>-10</sup>	18.8	33	1.75
PM <sub>6</sub> V <sub>4</sub> -2	HS	-73.5	0.431	7.0	6.70×10-10	16.1	34.4	2.14
PM <sub>4</sub> V <sub>6</sub> -2	110	-62.5	0.437	9.0	3.72×10 <sup>-9</sup>	11.4	27.7	2.43
PM <sub>2</sub> V <sub>8</sub> -2		-58.7	0.441	10.6	3.80×10-3	7.3	16.4	2.24
PV-2		-55.6	0.439	12.0	1.40×10 <sup>-3</sup>	3.8	8.3	2.17
$PIVI_8V_2-3$		< -100	-	4.2	9.80×10 <sup>-12</sup>	17.8	20.5	1.0
	HS	-04.0	0.433	5.0	5.60×10 <sup>-1</sup>	51.5	20.1 45.6	1.00
PIVI4V6-5 DM-V-2	Ö	-76.9	0.463	5.0 6.2	2.50×10 <sup>-11</sup>	23.2	45.0 57.7	1.90
P1V12V8-5		-72.5	0.504	6.8	1.55×10 1.65×10 <sup>-11</sup>	22.4	68	2.50
PM-V-J	0	-09.0	0.303	5.4	$\frac{1.03 \times 10}{6.03 \times 10^{-10}}$	20.3	28.1	1 78
PM8V2-4		-70.3	0.405	J. <del>4</del> 7	$1.03 \times 10^{-9}$	24.2	48.2	1.70
PM₄V <sub>6</sub> -4	HS	-62.2	0.458	82	$1.50 \times 10^{-9}$	15.5	30	1.93
PM <sub>2</sub> V <sub>8</sub> -4	0	-58.4	0.449	9.2	$1.24 \times 10^{-9}$	10.2	17.3	1.7
PV-4		-55.3	0.437	10.3	5.83×10 <sup>-9</sup>	6.4	11.3	1.78
PM <sub>8</sub> V <sub>2</sub> -5		-79.1	0.331	4.2	4.18×10 <sup>-12</sup>	-	-	-
PM <sub>6</sub> V₄-5	HS、 🔨 ,OH	-53	0.420	5.3	1.72×10 <sup>-11</sup>	-	-	-
PM <sub>4</sub> V <sub>6</sub> -5	$\sim$ $\parallel$ $\sim$	-41.8	0.431	5.9	2.73×10 <sup>-11</sup>	-	-	-
PM <sub>2</sub> V <sub>8</sub> -5	0	-37.9	0.496	6.5	3.51×10 <sup>-11</sup>	-	-	-
PV-5		-34.6	0.515	6.5	4.65×10 <sup>-11</sup>	-	-	-
PM <sub>8</sub> V <sub>2</sub> -6		-66.9	0.262	8.4	6.90×10 <sup>-10</sup>	19.6	32.9	1.67
PM <sub>6</sub> V <sub>4</sub> -6	0, <i>"</i> 0	-45.1	0.416	13.8	1.03×10 <sup>-9</sup>	17.6	37.7	2.14
PM <sub>4</sub> V <sub>6</sub> -6	HS	-33.1	0.455	17.6	8.24×10 <sup>-10</sup>	12.9	27.4	2.12
PM <sub>2</sub> V <sub>8</sub> -6		-25.3	0.460	19.7	3.70×10 <sup>-10</sup>	8.74	14	1.6
PV-6		-18.3	0.456	21.7	2.12×10 <sup>-9</sup>	3.8	4.9	1.3
PM <sub>8</sub> V <sub>2</sub> -7		-61.1	0.303	9.7	2.67×10 <sup>-10</sup>	17.1	45.8	2.68
PM <sub>6</sub> V <sub>4</sub> -7	HS S S	-37.8	0.469	16.3	1./8×10 <sup>-9</sup>	8.4	11.6	1.38
$PIM_4V_6-7$		-27	0.458	21.1	$2.77 \times 10^{-10}$	8.5	21.4	2.51
	-0	-22.6	0.421	25 27 7	7.57×10 <sup>10</sup>	8.2 11.6	17.6	2.15
		- 10.2	0.460	21.1	$2.10 \times 10^{-9}$	10.0	21.1	2.30
	$\left  \right\rangle$	-70.9	0.251	0.U 12.7	2.10×10 <sup>-9</sup>	10.9	30.9 22.2	1.95
PIVI6V4-0	HS	-02.5	0.400	16.2	5.24×10° 2.22×10-9	10	22.2 20	2.22
P1V14V6-0 DMaVa-8	O NO	-32.3	0.479	18.9	$2.32 \times 10^{-9}$	4.9	0.9	1.05
PV-8		-40.7	0.511	20.7	$1.05 \times 10^{-9}$	0.66	0.73	1.09
PM <sub>8</sub> V <sub>2</sub> -9	0	-81.2	0.282	8.0	2.54×10 <sup>-9</sup>	18.7	30.2	1.62
PM6V4-9	, ľ,	-62	0.438	12.3	5.65×10 <sup>-9</sup>	16.3	41.1	2.51
PM <sub>4</sub> V <sub>6</sub> -9	HS´ `` `Ņ´	-53.4	0.471	15.1	4.94×10 <sup>-9</sup>	12	31.4	2.61
PM <sub>2</sub> V <sub>8</sub> -9	Ι	-46.1	0.490	18	5.20×10 <sup>-09</sup>	10.7	21.4	1.99
PV-9		-45.5	0.489	21.5	8.23×10 <sup>-09</sup>	9.7	17.9	1.84
PM <sub>8</sub> V <sub>2</sub> -10		-92.8	0.437	7.1	1.15×10 <sup>-10</sup>	-	-	-
PM <sub>6</sub> V <sub>4</sub> -10	ПЪ <sup></sup>	-73.3	0.456	10.9	2.14×10 <sup>-9</sup>	-	-	-
PV-10		-48.6	0.406	20.2	2.34×10 <sup>-8</sup>	-	-	-
PM <sub>8</sub> V <sub>2</sub> -11		< -100	-	4.6	7.30×10 <sup>-12</sup>	13.3	26.1	1.97
PM <sub>6</sub> V <sub>4</sub> -11		-91.6	0.220	5.8	7.51×10 <sup>-11</sup>	17	41.8	2.46
$PIM_4V_6-11$	HS	-85.2	0.356	6.8	3.50×10 <sup>-10</sup>	13.6	35.1	2.58
$P_{1}V_{12}V_{8}-11$		-82.1	0.37	1.5	5.22×10-10	15.2	45.3	2.97
PV-11 DM-1/ 12		-öU.4	0.3/3	0.U	3.30×10 '°	10.2	25.0 25.7	5.44
PIVI8V2-12	1 0	ا .50- ەد	0.445	0.U 10 1	1.04×10 <sup>10</sup>	14.4 17.0	20.1 20.7	1./ð 1.00
F 1V16 V 4- 1 Z DM .V/a= 1 2	S O	-20 -10 2	0.571	12.1 12	0.00×10 1 20×10-11	10.0	52.1 11 Q	1.92 1.47
PM <sub>2</sub> V <sub>2</sub> -12		-10.5	0.314	97	$1.30 \times 10^{-11}$	2 26	14.0 1 21	1.47
PV-12		-24	0.304	9.4 9.1	$1.17 \times 10^{-11}$	-	54	-
PM.V12		 91 २	0 352	71	2 32 × 10 <sup>-10</sup>	17 २	30.1	1 74
PM <sub>4</sub> V <sub>4</sub> -13		-72 7	0.479	10.9	$4.03 \times 10^{-10}$	30.1	57.1	1.9
PM₄V₄-13	.CN	-62.2	0.513	14.2	5.50×10 <sup>-10</sup>	17.3	35.1	2.02
PM <sub>2</sub> V <sub>8</sub> -13	HS	-56.4	0.531	16.7	5.16×10 <sup>-10</sup>	14.2	37.9	2.67
PV-13		-50.8	0.497	18.8	2.82×10 <sup>-10</sup>	15.3	42.7	2.8

Table 2.2. Polymers prepared in this study:  $T_g$  and  $C_p$  data from DSC second heating scans,  $\varepsilon'$  values at 10 kHz and 20 °C, and conductivities at 10<sup>-2</sup> Hz and 20 °C as well as the molar mass characteristics obtained from GPC.



Figure 2.2 DSC curves of **PMxVy-8** and **PV-8** (a), and dielectric permittivity at 10 kHz and  $T_g$  of polysiloxanes with different mol% of polar groups (b-n).



Figure 2.3 Dielectric properties as a function of frequency for **PMxVy-1** and **PV-1** (left), **PMxVy-7** and **PV-7** (center), and **PMxVy-12** and **PV-12** (right) at different frequencies.

#### 2.3.3.4. Interrelation of Thermal Transitions, Dielectric Properties, and Conductivity

The comprehensive data obtained from the various substituted polysiloxanes permits us to perform a comparative analysis the interrelation of thermal transitions, dielectric properties, and conductivities (Figure 2.4).

As can be seen from the plots of dielectric permittivity at 10 kHz as function of  $T_g$  shown in Figure 2.4a, some polymers show a strong increase in  $T_g$  and a low increase in the permittivity, some show a moderate increase in both  $T_g$  and dielectric permittivity, while again others show a low increase in  $T_g$  and a strong increase in permittivity. The latter behavior is preferred, because of the larger operating temperature window.

For instance, polymers modified with thiols **1** and **5** show a small increase in dielectric permittivity and a strong increase in  $T_g$ . The low dielectric permittivity of polymers modified with **1** is due to the small dipole moment of **1**. Their large increase in  $T_g$  is due to the short linker in **1** and hydrogen-bonds in **5**.

Thiol **12** allows formation of polymers with a moderate increase in dielectric permittivity at low grafting density. However, the  $T_g$  eventually increases steeply at high grafting density. Therefore, the dipoles in **PV-12** cannot be polarized at high frequency and room temperature, so that its dielectric permittivity is only 9.1 (r.t., 10 kHz).

Polymers modified with thiols **2**, **3**, **4**, and **11** display both a moderate increase in the dielectric permittivity and in  $T_g$ .

Polymers modified with **6**, **7**, **8**, **9**, **10**, and **13** show a promising behavior because their dielectric permittivity can reach values aroud 20, while their  $T_g$  is significantly below room temperature. Because of their low  $T_g$  and high dielectric permittivity, these polymers are attractive for low-temperature applications.

It can be noted that **PV-6** has about the same permittivity as **PV-8**, **PV-9**, **PV-10**, and **PV-13** but its  $T_g$  is significantly higher as compared to the latter polymers. Since the respective polar groups are connected to the polysiloxane chain by  $-(CH_2)_2-S-(CH_2)_2-$  linker, the only difference which may explain this behaviour is the polar group itself. **6** is highly polar and will form strong dipole-dipole interactions increasing the  $T_g$ .

Interestingly, **PV-7** has the highest dielectric permittivity of  $\varepsilon' = 27.7$ , while its  $T_g$  of -18 °C is still attractively low for room temperature applications. Despite increased permittivity of **PV-7**, its  $T_g$  is about the same as **PV-6**, which has a dielectric permittivity of  $\varepsilon' = 21.7$ . The low  $T_g$  can probably be attributed to the longer  $-(CH_2)_2-S-(CH_2)_2-S$  linker in the case of thiol **7** as compared to the shorter  $-(CH_2)_2-S-$  linker in **6**. A similar behaviour was recently reported for some nitrile modified acrylates.<sup>[289]</sup>

The impact the volume of the polar groups has on the  $T_g$  and dielectric permittivity can be observed when comparing the dielectric properties of polymers modified with **6** and **12**. **PM<sub>8</sub>V<sub>2</sub>-6** and **PM<sub>8</sub>V<sub>2</sub>-12** have a low content of polar groups and thus the dipole-dipole interactions remain weak at this dipole concentration. Their  $T_g$  and dielectric permittivity is about the same, which may indicate that the two groups have a similar dipole moment (See Table 2.1). Because the cyclic sulfolane group **12** is bulkier as compared to **6**, the  $T_g$  of **PM<sub>x</sub>V<sub>y</sub>-12** increases more strongly with the dipole content and reaches 0 °C for the fully functionalized polymer. By contrast, **PV-6** still has a reasonably low  $T_g$  and high permittivity.

It has been recognized that high dielectric permittivity polymers are useful as electrolytes.<sup>[255]</sup> Because of their increased polarity, such polymers can dissolve lithium salts and thus may be useful as solid electrolytes in Li-ion batteries. Indeed, polysiloxanes modified with nitrile<sup>[290]</sup> and with carbonate groups<sup>[291]</sup> were shown to be promising electrolytes in such devices but a systematic investigation on how dielectric permittivity affects ionic conductivity has been missing to date.



Figure 2.4 Dielectric permittivity at 10 kHz and 20 °C as a function of  $T_g$  (a) and of conductivity (b) for **PM<sub>x</sub>V<sub>y</sub>**z and **PV-z**.

Figure 2.4b shows how the dielectric permittivity  $\varepsilon'$  of the synthesized polymers is influencing the ionic conductivity  $\sigma'$ .

It can be observed that a high dielectric permittivity is often accompanied by a high conductivity, which is undesirable for dielectric applications, but useful for applications where the polymer should serves as an electrolyte. It is important to note that the type of polar group appears to have a stronger impact on the conductivity than the degree of functionalization with a given functionality. For example, the conductivity of polymers modified with **13** increases from  $\varepsilon' = 2.32 \cdot 10^{-10}$  S/cm for **PM**<sub>8</sub>**V**<sub>2</sub>-**13** to  $5.50 \cdot 10^{-10}$  S/cm for **PM**<sub>4</sub>**V**<sub>6</sub>-**13**, and then drops again to  $2.82 \cdot 10^{-10}$  S/cm for **PV-13**. The lowest conductivities are observed for **PM**<sub>x</sub>**V**<sub>y</sub>-**1** and **PV-1**, while **PV-10** exhibits the highest conductivity of  $\sigma' = 2.34 \cdot 10^{-8}$  S/cm is observed for.

**PV-1** shows a maximum value of  $\varepsilon' = 4.9$ , a  $T_g = -57.6$  °C, and a conductivity of  $\sigma' = 1.11 \cdot 10^{-11}$  S/cm. This polymer can be easily prepared on a large scale. Its low conductivity and moderate permittivity render it highly attractive for applications in capacitors and energy harvesting.

The ionic conductivities of all polymers modified with **5** remains below  $10^{-10}$  S/cm. The reason may, again, be the dimerization of the carboxylic acid groups by strong hydrogen bonding. By contrast, polymers modified with the hydroxy-functional thiol **2** show ionic conductivities as high as  $3.80 \cdot 10^{-9}$  S/cm.

**PV-7** shows the highest value of the permittivity of  $\varepsilon' = 27.7$ , a  $T_g = -18.2$  °C, and a conductivity of  $2.10 \cdot 10^{-9}$  S/cm. Due to its relatively low  $T_g$  and excellent dielectric permittivity, this polymer is a promising candidate for both application as a dielectric and as an electrolyte.

Polymers modified with thiols **8**, **9**, and **10** exhibit the overall highest conductivities, with the conductivities of **PM<sub>x</sub>V<sub>y</sub>-10** and **PV-10** being strongly affected by the dipole content. In contrast to the latter polymers, the polymers modified with **8** and **9** can be easily prepared on a large scale, have a high dielectric permittivity, and a low  $T_g$ . Since a low  $T_g$  is of high importance for the synthesis of solid electrolytes because it increases the mobility of the polymer chains and hence the ionic transport in a materials, polymer **PV-9** seems particularly attractive from that point of view. It has the second-highest dielectric permittivity of all polymers investigated in this work ( $\varepsilon' = 21.5$ ), a low  $T_g = -45.5$  °C, and a comparably high conductivity of  $\sigma' = 8.23 \cdot 10^{-9}$  S/cm.

## 2.4. Conclusion

We have synthesized different polar thiols and used them in a thiol-ene post-polymerization modification of polysiloxanes with different molar fractions of methylvinylsiloxy units. This has allowed us to synthesize a library of polysiloxanes with well tailored polarities. The materials were investigated by differential scanning calorimetry and broadband impedance spectroscopy. The type, strength, and volume of the polar groups as well as the length of the linker between the polar group and the polysiloxane backbone play a crucial role for both glass transition temperatures  $T_g$  and dielectric permittivities  $\varepsilon'$ . Generally, an increase in both  $T_g$  and  $\varepsilon'$  with the dipole density and dipole strength can be observed, with an increasing volume of the polar group reducing the threshold frequency for dipole relaxation. By increasing the length of the linker, it is possible to achieve polymers with high dielectric permittivity and low

 $T_{g}$ . This manifests itself in the example of **PV-7** that exhibits the highest permittivity  $\varepsilon' = 27.7$  of the entire library of polymers reported here. Furthermore, its low  $T_{g} = -18.2$  °C and ionic conductivity  $\sigma' = 2.10 \cdot 10^{-9}$  S/cm render it a promising candidate for new dielectric materials in actuators, generators, and sensors. The straightforward synthesis of thiols **6**, **8**, **9**, **13** and the respective polymers, all of which can reach dielectric permittivities above 20, will facilitate exploring their potential as dielectric materials and as electrolytes in Li-ion batteries.

## 2.5. Supporting information



Figure 2.5 GPC elugrams of starting polysiloxanes **PV** and **PM<sub>x</sub>V<sub>y</sub>**.



Figure 2.6 <sup>31</sup>P NMR spectra of the starting compound (bottom) and of thiol **4** before (middle) and after distillation (top).



Figure 2.7 <sup>1</sup>H NMR spectra of the starting compound (bottom), thiol **4** (middle), and disulfide (top).



Figure 2.8 <sup>1</sup>H NMR spectrum of thiol **4** in CDCl<sub>3</sub>.



Figure 2.9 <sup>13</sup>C NMR spectrum (top) and <sup>31</sup>P NMR spectrum (bottom) of thiol **4** in CDCl<sub>3</sub>.



Figure 2.10 <sup>1</sup>H NMR spectrum of compound **6** in CDCI<sub>3</sub>.


Figure 2.11 <sup>13</sup>C NMR spectrum of compound **6** in CDCl<sub>3</sub>.



Figure 2.12 MS data obtained for thiol 7.



Figure 2.13 <sup>1</sup>H NMR spectrum of compound **7** in CDCl<sub>3</sub>.



Figure 2.14 <sup>13</sup>C NMR spectrum of compound **7** in CDCl<sub>3</sub>.



Figure 2.15 <sup>1</sup>H NMR spectrum of S-(2-oxopyrrolidin-1-yl)ethyl thioacetate in CDCl<sub>3</sub>



Figure 2.16<sup>13</sup>C NMR spectrum of compound S-(2-oxopyrrolidin-1-yl)ethyl thioacetate in CDCl<sub>3</sub>.



Figure 2.17 <sup>1</sup>H NMR spectrum of compound **8** in CDCl<sub>3</sub>.

.



Figure 2.18 <sup>13</sup>C NMR spectrum of compound **8** in CDCl<sub>3</sub>.



Figure 2.19 <sup>1</sup>H NMR spectrum of compound **9** in CDCl<sub>3</sub>.



Figure 2.20 <sup>13</sup>C NMR spectrum of compound **9** in CDCl<sub>3</sub>.



Figure 2.21 <sup>1</sup>H NMR spectrum of thiol **10** in CDCl<sub>3</sub> prepared by *Method a*.



Figure 2.22 <sup>13</sup>C NMR spectrum of thiol **10** in CDCl<sub>3</sub> prepared by *Method a*.



Figure 2.23 <sup>1</sup>H NMR spectrum of nitroethylene in CDCl<sub>3</sub>.



Figure 2.24 <sup>1</sup>H NMR spectrum of nitroethyl tioacetate in CDCI<sub>3</sub>.



Figure 2.25 <sup>13</sup>C NMR spectrum of nitroethyl tioacetate in CDCl<sub>3</sub>.



Figure 2.26 <sup>1</sup>H NMR spectrum of thiol **10** in CDCl<sub>3</sub> prepared by *Method b*.



Figure 2.27 <sup>13</sup>C NMR spectrum of thiol **10** in CDCl<sub>3</sub> prepared by *Method b*.



Figure 2.28 <sup>1</sup>H NMR spectrum of thiol **12** in CDCl<sub>3</sub>.



Figure 2.29 <sup>13</sup>C NMR spectrum of thiol **12** in CDCl<sub>3</sub>.



Figure 2.30 <sup>1</sup>H NMR spectrum of thiol **13** in CDCl<sub>3</sub>.



Figure 2.31 <sup>13</sup>C NMR spectrum of thiol **13** in CDCl<sub>3</sub>.



Figure 2.32 <sup>1</sup>H NMR spectra of  $PM_xV_y$  and PV in CDCl<sub>3</sub>.



Figure 2.33 <sup>1</sup>H NMR spectrum of  $\mathbf{PV}$  in  $\mathbf{CDCl}_3$ .



Figure 2.34  $^{\rm 13}{\rm C}$  NMR spectra of  $PM_xV_y$  in CDCl3.



Figure 2.35 <sup>1</sup>H NMR spectra of **PM<sub>x</sub>V<sub>y</sub>-1** and **PV-1**.



Figure 2.36 <sup>13</sup>C NMR spectra of  $PM_xV_y$ -1 and PV-1.



Figure 2.37 <sup>1</sup>H NMR spectra of **PM<sub>x</sub>V<sub>y</sub>-2** and **PV-2**.





Figure 2.39 <sup>1</sup>H NMR spectra of **PM<sub>x</sub>V<sub>y</sub>-3** and **PV-3**.



Figure 2.40 <sup>13</sup>C NMR spectra of **PM<sub>x</sub>V<sub>y</sub>-3** and **PV-3**.



Figure 2.41 <sup>1</sup>H NMR spectra of **PM<sub>x</sub>V<sub>y</sub>-4** and **PV-4**.





Figure 2.43 <sup>1</sup>H NMR spectra of **PM<sub>x</sub>V<sub>y</sub>-5** and **PV-5**.



Figure 2.44 <sup>13</sup>C NMR spectra of **PM<sub>x</sub>V<sub>y</sub>-5** and **PV-5**.



Figure 2.45 <sup>1</sup>H NMR spectra of **PM<sub>x</sub>V<sub>y</sub>-6** and **PV-6**.



Figure 2.46 <sup>13</sup>C NMR spectra of **PM<sub>x</sub>V<sub>y</sub>-6** and **PV-6**.



Figure 2.47 <sup>1</sup>H NMR spectra of **PM<sub>x</sub>V<sub>y</sub>-7** and **PV-7**.



Figure 2.48  $^{13}$ C NMR spectra of **PM<sub>x</sub>V<sub>y</sub>-7** and **PV-7**.



Figure 2.49 <sup>1</sup>H NMR spectra of **PM<sub>x</sub>V<sub>y</sub>-8** and **PV-8**.



Figure 2.50 <sup>13</sup>C NMR spectra of **PM<sub>x</sub>V<sub>y</sub>-8** and **PV-8**.



Figure 2.51 <sup>1</sup>H NMR spectra of **PM<sub>x</sub>V<sub>y</sub>-9** and **PV-9**.



Figure 2.52 <sup>13</sup>C NMR spectra of **PM<sub>x</sub>V<sub>y</sub>-9** and **PV-9**.



Figure 2.53 <sup>1</sup>H NMR spectra of **PM<sub>x</sub>V<sub>y</sub>-10** and **PV-10**.



Figure 2.54 <sup>13</sup>C NMR spectra of **PM<sub>8</sub>V<sub>2</sub>-10** and **PV-10**.



Figure 2.55 <sup>1</sup>H NMR spectra of **PM<sub>x</sub>V<sub>y</sub>-11** and **PV-11**.



Figure 2.56 <sup>13</sup>C NMR spectra of **PM<sub>x</sub>V<sub>y</sub>-11** and **PV-11**.



Figure 2.57 <sup>1</sup>H NMR spectra of **PM<sub>x</sub>V<sub>y</sub>-12** and **PV-12**.



Figure 2.58 <sup>13</sup>C NMR spectra of  $PM_xV_y$ -12 and PV-12.


Figure 2.59 <sup>1</sup>H NMR spectra of **PM<sub>x</sub>V<sub>y</sub>-13** and **PV-13**.



Figure 2.60 <sup>13</sup>C NMR spectra of **PM<sub>x</sub>V<sub>y</sub>-13** and **PV-13**.



Figure 2.61 GPC elugrams of  $PM_8V_2$ -z,  $PM_6V_4$ -z,  $PM_4V_6$ -z,  $PM_2V_8$ -z, and PV-z in THF. The GPC elugrams of polymers modified with thiol **7** are rather broad and polydisperse. The reason behind this may be side reactions of carbonate groups, which occurred before the GPC measurements were recoded. We observed a change in their viscosity with time, which may indicate that they are unstable under normal conditions.<sup>[292]</sup> Additionally, some polymers show a bimodal distribution, which is likely due to side reaction between different polymer chains.



Figure 2.62 DSC curves of **PV-1** and **PM<sub>x</sub>V<sub>y</sub>-1**.



Figure 2.63 DSC curves of **PV-2** and **PM<sub>x</sub>V<sub>y</sub>-2**.



Figure 2.64 DSC curves of **PV-3** and **PM<sub>x</sub>V<sub>y</sub>-3**.



Figure 2.65 DSC curves of **PV-4** and **PM<sub>x</sub>V<sub>y</sub>-4**.



Figure 2.66 DSC curves of **PV-5** and **PM<sub>x</sub>V<sub>y</sub>-5**.



Figure 2.67 DSC of curves **PV-6** and **PM<sub>x</sub>V<sub>y</sub>-6**.



Figure 2.68 DSC curves of **PV-7** and **PM<sub>x</sub>V<sub>y</sub>-7**.



Figure 2.69 DSC curves of **PV-8** and **PM<sub>x</sub>V<sub>y</sub>-8**.



Figure 2.70 DSC curves of **PV-9** and **PM<sub>x</sub>V<sub>y</sub>-9**.



Figure 2.71 DSC curves of **PV-10** and **PM<sub>x</sub>V<sub>y</sub>-10**.



Figure 2.72 DSC curves of **PV-11** and **PM<sub>x</sub>V<sub>y</sub>-11**.



Figure 2.73 DSC curves of **PV-12** and **PM<sub>x</sub>V<sub>y</sub>-12**.



Figure 2.74 DSC curves of PV-13 and  $PM_{x}V_{y}\text{-}13.$ 



Figure 2.75 Dielectric properties of PV-1 and  $PM_xV_y-1$  at different frequencies.



Figure 2.76 Dielectric properties of PV-2 and  $PM_xV_y-2$  at different frequencies.



Figure 2.77 Dielectric properties of **PV-3** and **PM<sub>x</sub>V<sub>y</sub>-3** at different frequencies.



Figure 2.78 Dielectric properties of PV-4 and  $PM_xV_y\text{-}4$  at different frequencies.



Figure 2.79 Dielectric properties of **PV-5** and  $PM_xV_y$ -5 at different frequencies.



Figure 2.80 Dielectric properties of **PV-6** and **PM<sub>x</sub>V<sub>y</sub>-6** at different frequencies.



Figure 2.81 Dielectric properties of **PV-7** and **PM**<sub>x</sub> $V_y$ -7 at different frequencies.



Figure 2.82 Dielectric properties of **PV-8** and  $PM_xV_y$ -8 at different frequencies.



Figure 2.83 Dielectric properties of **PV-9** and **PM<sub>x</sub>V<sub>y</sub>-9** at different frequencies..



Figure 2.84 Dielectric properties of **PV-10** and **PM<sub>x</sub>V<sub>y</sub>-10** at different frequencies.



Figure 2.85 Dielectric properties of **PV-11** and **PM<sub>x</sub>V<sub>y</sub>-11** at different frequencies.



Figure 2.86 Dielectric properties of **PV-12** and **PM<sub>x</sub>V<sub>y</sub>-12** at different frequencies.



Figure 2.87 Dielectric properties of **PV-13** and  $PM_xV_y$ -13 at different frequencies.

#### **CHAPTER THREE**

# 3. Artificial Muscles: Dielectric Elastomers Responsive to Low Voltages

This chapter is based on the paper Artificial Muscles: Dielectric Elastomers Responsive to Low Voltages by Yauhen Sheima<sup>a,b</sup>, Philip Caspari<sup>a,b</sup>, Dorina M. Opris<sup>a</sup>\*

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Author Contributions:

Y. Sheima performed the synthesis and characterization of compounds, fabricated and tested devices and contributed to the manuscript.

#### 3.1. Abstract

The lack of soft high-dielectric permittivity elastomers responsive to a low voltage has been a long-standing obstacle for the industrialization of dielectric elastomer actuators (DEA) technology. Here, elastomers that do not only possess high dielectric permittivity of 18 and good elastic and insulating properties, but are also processable in very thin films by conventional techniques are reported. Additionally, the elastic modulus can be easily tuned by the type of cross-linker used. A soft elastomer with a storage modulus of E' = 350 kPa, a  $tan \delta = 0.007$  at 0.05 Hz, and a lateral actuation strain of 13% at 13 V/µm is prepared. A stable lateral actuation over 50'000 cycles at 10 Hz is demonstrated. A stiffer elastomer with a storage modulus E' = 790 kPa, a  $tan \delta = 0.0018$  at 0.05 Hz, a large out of plane actuation at 41 V/µm, and breakdown fields of almost 100 V/µm is also developed. Such breakdown fields in actuators operable at a voltage as low as 200 V are also demonstrated. Because the materials used are cheap and easily available, and the chemical reactions leading to them allow upscaling, they have the potential to advance the DEA technology.

### 3.2. Introduction

Soft and elastic capacitors, also known as dielectric elastomer actuators (DEA), reversibly change their shape under an electric stimulus.<sup>[113]</sup> Their rather simple construction and operation and the fact that they mimic natural muscles gave them the name of artificial muscles.<sup>[2]</sup> A large variety of prototypes were constructed, which one day will find applications in automobiles, robotics, electronics, aerospace, medical products and medicine.<sup>[69]</sup> While a large variety of insulating elastomers can be used as dielectric,<sup>[37,53,293]</sup> one issue associated with the DEA technology is the high driving voltage required for actuation, which is in the kV range.<sup>[294]</sup>

Attempts to reduce the driving voltage include decreasing film thickness, reducing the elastic modulus, and increasing the dielectric permittivity of the dielectric elastomer used. Thickness reduction is attractive since both actuation strain as well as actuation pressure increase inversely proportional to the squared thickness.<sup>[15]</sup> Previous work showed that actuators constructed from a 3  $\mu$ m thin silicone elastomer film ( $\varepsilon' \sim 3$ ) gave 7.5% lateral actuation at 245 V.<sup>[176]</sup> A further reduction of the thickness of the silicone elastomer to 1.4  $\mu$ m allowed access to actuators driven at 100 V.<sup>[295]</sup> Although these results are promising, the implementation of such thin films in DEA large-scale production is challenging, since a thickness reduction of the dielectric films below 20  $\mu$ m is associated with increased fabrication costs.<sup>[296]</sup> Additionally, the mechanical properties of electrodes have a strong impact on actuation especially when ultra-thin films are used.<sup>[176]</sup> Low voltage actuators can be in principle achieved with soft elastomers. They can be prepared either by reducing the cross-linking density,<sup>[229]</sup> using plasticizers,<sup>[297]</sup> synthesizing bimodal heterogeneous networks,<sup>[298]</sup> or

incorporating bottlebrush segments into the polymer network.<sup>[299]</sup> However, the dielectric breakdown of such soft elastomers is a hurdle still to be overcome.<sup>[300,301]</sup> Moreover, because these elastomers have a low permittivity, their actuation pressure is also rather low.<sup>[113]</sup> Though challenging, the last approach is nevertheless the most promising, since it does not only allow reducing the driving voltage, but also increasing the actuation pressure.

Materials solutions to high dielectric permittivity elastomers include blending the elastomer with highly polarizable fillers or chemical modification with polar groups. Both approaches are however limited either by an increased stiffness or a reduced breakdown field, or both.<sup>[37,53]</sup> Additionally, thin film formation turns challenging, especially for blends. Chemical modification of polymers with polar groups is associated by a large increase in the glass transition temperature.<sup>[53]</sup> It is therefore not surprising that only few polymers furnish low  $T_g$  materials after chemical modification with polar groups. A polymer class that meets this requirement is polysiloxane. Their modification by the polar nitrile groups allowed formation of elastomers with  $\varepsilon'$  of about 18, which is amongst the highest dielectric permittivity value reported for polysiloxanes.<sup>[217,244,250,302]</sup> Furthermore, they actuate at rather low electric fields of 10 V/µm. While all this looks attractive, it turned out to be challenging to process the material into sufficiently thin films under technologically relevant conditions. Because it was not possible to reduce the thickness of the films below 100 µm, the required actuation voltage was still above 1000 V.<sup>[266]</sup>

Up to date, there are no actuators reported that use high permittivity elastomers which can be processed into very thin films. Such actuators are expected to be operated at attractively low voltages, while still generating a reasonable actuation pressure.<sup>[176]</sup> The desired elastomer combines properties such as good elasticity, low elastic modulus, low viscoelastic losses, high dielectric permittivity, high breakdown field, low leakage current density, and last but not least – processability in very thin films. This is the point where the current work sets in. We have developed a new synthetic pathway to nitrile modified polysiloxane elastomers with high dielectric permittivity, which can be processed into very thin films. Furthermore, the elastic modulus can be easily tuned by the amount and type of cross-linker used. This led to intriguing materials that actuate at unprecedentedly low voltages and low electric fields. Additionally, materials with large actuation and unprecedentedly high dielectric breakdown were developed.

### 3.3. Results and Discussions

In contrast to previous reports on nitrile-functionalized silicones prepared by an in situ process in which the functionalization with nitrile groups and the cross-linking into thin films occurred simultaneously, here we split the synthesis into two steps (Figure 3.1a).<sup>[217,244]</sup> First, the polysiloxane was functionalized with polar groups and then purified *via* a dissolutionprecipitation step. In an independent second step, this material was processed into films of desired thickness and then cross-linked. More concretely, a polymethylvinylsiloxane of high molar mass ( $M_n = 84'800$  Da,  $M_w = 192'000$  Da, and a *PDI* = 2.3) was modified with 3mercaptopropionitrile at a stoichiometry to leave some vinyl groups unreacted (0.95 eq. 3mercaptopropionitrile to vinyl). The resulting polymer **P1** was obtained several times on the 5 g scale, followed by a 40 g preparation. Repeated precipitation of a THF solution of **P1** into methanol afforded pure material, which was conveniently stored as 40 wt% solution in THF. For relevant NMR spectra see Figure 3.4. NMR spectroscopy gave a vinyl content of **P1** of 2.35% (Figure 3.5), which is somewhat lower than the expected 5%. The reason for this was not investigated, but is likely due to a side reaction between the vinyl groups during thiol addition. The GPC elugram of **P1** is slightly broader as compared to the starting polymer (Figure 3.6), which may indicate this side reaction occurs intermolecular despite the fact that the reagents were diluted.



Figure 3.1 a) Synthesis of polysiloxane **P1** containing polar nitrile and unreacted vinyl groups starting from polymethylvinylsiloxane *via* thiol-ene reaction and its cross-linking to elastomers *via* a thiol-ene reaction in presence of DMPA UV-light initiator. b) Chemical structures of the thiols used as cross-linkers: 2,2'- (ethylenedioxy)diethanethiol (**CL**<sub>2</sub>) and pentaerythritol tetrakis(3-mercaptopropionate) (**CL**<sub>4</sub>). c) Photographs of a "thick" film which ruptured after cross-linking (left), which curled after it was detached from the substrate (middle), and of a smooth film, which neither ruptured nor curled (right). d) The idealized structure of the chemical network formed.

In the second step, thin films were prepared using dilute THF solutions of **P1**, multifunctional thiol cross-linker and photoinitiator. This way, the viscosity was kept low such that simple doctor blading afforded the desired homogeneous films, which were cross-linked by exposure to UV light. Two different cross-linkers (Figure 3.1b) 2,2'-(ethylenedioxy)diethanethiol (CL<sub>2</sub>) and pentaerythritol tetrakis(3-mercaptopropionate) (CL<sub>4</sub>) were tested. As it will be explained later, thicker films (~100  $\mu$ m) for the dielectric and mechanical characterizations and thin films (20  $\mu$ m to 55  $\mu$ m) for electromechanical tests were prepared. The amounts of reagents used for each material denoted as **E-CL<sub>2</sub>**, **E-CL<sub>4</sub>**, and **E-3.5CL<sub>4</sub>** are presented in Table 3.1.

We initially processed the material into thick films using a Teflon substrate. As mentioned above, a solution of **P1** in THF had to be used, to adjust **P1** viscosity such that the processing into thin films is possible. However, thicker films (> 80  $\mu$ m) ruptured when not immediately detached from substrate, and upon detaching, they underwent spontaneous extreme bending (Figure 3.1c). Reducing film thickness to 30  $\mu$ m hindered rupturing on the substrate, but the films turned too fragile to be peeled off the substrate without tearing. Therefore, the film formation process was optimized. Self-rupturing of thick films may be due to the internal stress generated during UV-curing because of solvent evaporation.<sup>[303]</sup> To overcome the above mentioned problem, the films were allowed to stand for 1 h at room temperature prior to cross-linking. This time was sufficient to evaporate most solvent. After UV irradiation, smooth films which neither ruptured nor curled formed.

Figure 3.2a shows the stress-strain curves of different materials, which represent the average of three different samples. The strain at break represents the lowest value obtained from the three measurements. Elastomer **E-CL**<sub>2</sub> showed an average strain at break of 82%,  $Y_{10\%} = 462$  kPa, and a tensile strength of 287 kPa, material **E-CL**<sub>4</sub> showed an average strain at break of 42%,  $Y_{10\%} = 785$  kPa, and a tensile strength of 290 kPa, and **E-3.5CL**<sub>4</sub> showed an average strain at break of 38%,  $Y_{10\%} = 862$  kPa, and a tensile strength of 304 kPa. The mechanical properties of polysiloxane elastomers can be improved by using silica filler.<sup>[244]</sup> This is also the case for our polar elastomer (Figure 3.7), when the addition of only 2.5 wt% of hexamethyldisilazane treated silica particles to **E-CL**<sub>2</sub> increased the average strain at break to 109%. However, processing composites in very thin films is challenging, since the film thickness may reach the length scale of filler and filler agglomerates and may reduce the dielectric breakdown. Therefore, the addition of filler was avoided in this work.

Cyclic uniaxial tensile tests at different strain levels (5 cycles for each strain) were conducted (Figure 3.2b,c). The strain on **E-CL**<sub>2</sub> was successively increased from 25%, to 40% and to 50% strain, while for the more fragile sample **E-CL**<sub>4</sub> the strains used were slightly lower, of 10%, 20% and 25%. Both materials recovered immediately the initial length after the stress was released. The curves showed no hysteresis between loading and unloading, an indication of the excellent elastic properties of these materials. These results are also supported by DMA and electromechanical cyclic tests. Frequency dependence of the storage moduli (E'), and loss (E'') of **E-CL**<sub>2</sub>, **E-CL**<sub>4</sub>, and **E-3.5CL**<sub>4</sub> (Figure 3.2d) are compared to Elastosil® Film 2030 250, a well know polysiloxane-based commercial elastomer used as a reference. At 0.05 Hz material **E-CL**<sub>2</sub> has a E' = 350 kPa and a *tan*  $\delta$  = 0.007, **E-CL**<sub>4</sub> has a E' = 665 kPa and a *tan*  $\delta$  = 0.0027,

E-3.5CL4 has a E' = 790 kPa and a  $tan \delta$  = 0.0018, and the reference material Elastosil has an E' = 1.2 MPa and a  $tan \delta$  = 0.017, respectively. For all materials, the elastic moduli did not change much over the investigated frequency ranges. The mechanical losses of all materials are very low. For Elastosil and **E-CL**<sub>4</sub> only a slight increase in the losses over the investigated frequency range was observed. All other materials show a slight increase in  $tan \delta$  with the frequency, but the losses at the investigated frequency range were below 0.13. Dynamic mechanical analysis conducted at temperatures between +50 °C to -80 °C and temperature ramping of -5 °C shows that these elastomers are glassy below -50 °C. At this temperature, all samples ruptured during the DMA measurements (Figure 3.2e). The transition between the glassy and rubbery phase is reflected by the strong increase in the elastic modulus at temperatures below -20 °C. Above -20 °C the storage modulus remains rather constant, which is very attractive for actuators. Differential scanning calorimetry (DSC) revealed a glass transition at about -46 °C (Figure 3.8). No further transitions were observed in the DSC curves, whose slope remains constant up to 50 °C.

The dielectric properties were investigated at room temperature and different frequencies (Figure 3.2f) as well as at temperatures ranging from -80 °C to 100 °C (Figure 3.9). Below  $T_{q}$ , the nitrile groups are frozen and thus they cannot be oriented in an electric field. Therefore,  $\varepsilon'$  is rather low below  $T_q$  ( $\epsilon' = 4.7$ ). Above  $T_q$ , the polymer chains are mobile and the polar groups are able to orient and thus contribute to the permittivity value by orientation polarization. Consequently, the permittivity of the prepared elastomers increased to  $\varepsilon' \sim 18$  at 10<sup>4</sup> Hz (Figure 3.2f). Above  $T_{q}$ , not only the dipoles are able to orient in an electric field, but also the ion impurities with which the materials are unavoidable contaminated. The presence of ion impurities is reflected by the steep increase in permittivity at low frequencies, which is often referred to as electrode polarization.<sup>[33]</sup> For the synthesis of the three materials the same batch of polymer P1 was used, therefore only slight differences in the permittivity values were observed, which are likely related to error measurements. Two relaxation peaks are present in all materials. One appears at rather low frequencies between 1 and 10 Hz and is due to ion impurities present in materials, while the other appears above 10<sup>6</sup> Hz and is due to the relaxation of the polar nitrile groups.<sup>[302]</sup> The conductivity of all materials was rather low, below  $3.2 \times 10^{-9}$  S cm<sup>-1</sup> which is also attractive for actuators.

Electromechanical tests conducted on circular actuators showed that actuation with these materials was possible at rather low electric fields, but the driving voltage above 1000 V was still rather high. An actuator constructed from a 109  $\mu$ m thick film of **E-CL**<sub>4</sub> was actuated at an electric field of 10 V/ $\mu$ m, thus 1090 V, and at different frequencies of 0.25 Hz, 0.5 Hz, 1 Hz, 2 Hz, 5 Hz, and 10 Hz, respectively, and showed a stable actuation, which supports excellent elasticity (Figure 3.10). At frequencies between 0.25 Hz to 2 Hz the actuation strain remained almost unchanged of 3.5% at 10 V/ $\mu$ m. However, when increasing the frequency to 5 Hz, the actuation decreased to about 2.5% strain at the same electric field. Although the actuator was tested also at 10 Hz for 100 cycles, the actuation measurement is not precise, because of the limitation of the camera used. Long term measurements of over 10'000 cycles clearly support that the prepared materials are rather robust (Figure 3.11).



Figure 3.2 a) Stress-strain curves of materials **E-CL<sub>2</sub>**, **E-CL<sub>4</sub>** and **E-3.5CL<sub>4</sub>** at a strain rate of 50 mm/min. b) Cyclic uniaxial tensile tests of **E-CL<sub>4</sub>** at 10%, 20%, and 25% strain. c) Cyclic uniaxial tensile tests of **E-CL<sub>2</sub>** at 25%, 40%, and 50% strain. d) Dynamic mechanical analysis of **E-CL<sub>2</sub>**, **E-CL<sub>4</sub>**, **E-3.5CL<sub>4</sub>** and Elastosil at 2% strain and a frequency range between 0.05 to 3 Hz. e) Dynamic mechanical analysis at different temperatures and 1 Hz for **E-CL<sub>2</sub>**. f) Dielectric properties (permittivity, dielectric loss, conductivity, and loss factor) as a function of frequency for **E-CL<sub>2</sub>**, **E-CL<sub>4</sub>**, **E-3.5CL<sub>4</sub>**.

To demonstrate that actuators operable at lower voltages can be constructed with our materials, very thin films had to be prepared and manipulated. A special process was developed that allowed us manipulating thin films (Figure 3.3a). To avoid mechanical peeling the films off the substrate, sacrificial polyvinyl alcohol (PVA) layer was used. Sacrificial layer was previously used for the formation of thin polymer films and has recently been introduced to actuator technology.<sup>[304]</sup> After depositing a thin PVA layer on a glass substrate, a film of our material was formed on top and cross-linked by UV irradiation. Thereafter, the two layers were detached from the glass substrate. Part of the film was cut and fixed between two plastic frames and immersed in a water bath to dissolve the PVA. Using this procedure, any mechanical stress on the film was avoided and films with a thickness around 20  $\mu$ m could be investigated. No further attempts were conducted to reduce the thickness of the films even further, but this should in principle be possible.

Next, circular actuators with electrodes diameter of 8 mm made of carbon black powder were constructed. Figure 3.3b shows the lateral actuation strain as function of nominal electric field

for the three new materials developed as well as for Elastosil silicone film, a well-known material to the DEAs community. It should be mentioned that due to the lack of prestrain in actuators, the lateral actuation stain was precisely measured only up to a certain electric field. Above this electric field, expansion in the lateral direction is hindered and wrinkles and out of plane actuation were noted. The onset for this process is indicated in Figure 3b on the actuation curves by the arrows. The best actuators constructed from E-CL<sub>2</sub>, E-CL<sub>4</sub>, and E-3.5CL<sub>4</sub> showed a lateral actuation of 13% at 13 V/µm, of 14% at 18 V/µm, and of 11.5% at 26 V/µm, respectively. Thus high actuations at rather low electric fields were demonstrated with these actuators. Contrary, Elastosil ( $\epsilon' \sim 3$ ), shows only a very small actuation below 1% at comparable electric fields. The nominal dielectric breakdown, calculated using the breakdown voltage divided by the initial thickness for these actuators was 15.2 V/µm, 29 V/µm, and 50 V/µm for E-CL<sub>2</sub>, E-CL<sub>4</sub>, and E-3.5CL<sub>4</sub>, respectively, whereas the dielectric breakdown of Elastosil was 58 V/µm. It should be said that not all actuators performed equally well, although all showed actuation at very low voltages (Figure 3.12). We identified three reasons that may explain this deviation: film defects, presence of residual PVA on the films surface, and measurement error. At least five actuators were evaluated for each material. Actuators' average  $E_b$  was 19 V/µm for E-CL<sub>2</sub>, 25.5 V/µm E-CL<sub>4</sub>, and 73.6 V/µm E-3.5CL<sub>4</sub> for thin films, and decreased to 16 V/µm for E-CL<sub>2</sub>, 22.7 V/µm E-CL<sub>4</sub>, and 26.7 V/µm E-3.5CL<sub>4</sub> for thick films. These values are higher as compared to the previously reported one of 15.6 V µm<sup>-1</sup> for a material with similar chemical composition.<sup>[22,23]</sup> The reason behind this increase is seen in the higher purity of the prepolymer used, in the increased elastic modulus of the new materials, and in the improved processability in thin films. The much higher  $E_b$  of **E-3.5CL<sub>4</sub>** as compared to **E-CL<sub>2</sub>** and **E-CL<sub>4</sub>** is explained by the lower elastic modulus of the latter. For **E-3.5CL**<sub>4</sub> the *E*<sub>b</sub> of thick and thin actuators differ significantly, e.g., the  $E_b$  increased from 26.7 V/µm for thick films to an average of 73.6 V/µm for thin one. Some devices withstood electric fields up to 100 V/ $\mu$ m, where large out of plane actuation occurred (Figure 3.3c). Large actuations have been reported before, but because the elastomers used had a low dielectric permittivity, actuation occurred at significantly higher voltages.<sup>[1,30-37]</sup> The high  $E_b$  observed in this material may be explained by the lower probability of defects present in thin films. Whether or not the polarization saturation plays a role in overcoming the snap-through instability by altering the voltage-stretch curve,



Figure 3.3 a) Illustration of the process used for preparation and manipulation of very thin films. b) Lateral actuation strain as a function of electric field for circular actuators constructed from thin films of **E-CL**<sub>2</sub>, **E-CL**<sub>4</sub>, **E-3.5CL**<sub>4</sub>, and Elastosil and insert a photograph of the transparent silicone film of **E-CL**<sub>2</sub> with a thickness of about 20  $\mu$ m from which a circular actuator was constructed. c) An actuator constructed from a 38  $\mu$ m thick **E-3.5CL**<sub>4</sub> films that withstood electric fields as high as 100 V/ $\mu$ m. d) Lateral actuation strain at different voltages for an actuator constructed from **E-CL**<sub>2</sub> (35  $\mu$ m) and from **E-3.5CL**<sub>4</sub> (24  $\mu$ m). Out of plane deformation was observed for **E-3.5CL**<sub>4</sub> at voltages above 500 V. e) Photographs of actuators constructed from **E-CL**<sub>2</sub> in the relaxed state and in actuated state at 300 V (E = 8.6 V/ $\mu$ m). f) Photographs of actuators constructed from **E-3.5CL**<sub>4</sub> in the relaxed state and in actuated state at 1000 V (E = 41 V/ $\mu$ m) with large out of plane deformation. g) Cyclic tests conducted on an actuator constructed from **E-CL**<sub>2</sub> (35  $\mu$ m) at 300 V and 1 Hz. i) An actuator constructed from **E-CL**<sub>2</sub> (43  $\mu$ m) actuated at 600 V, where three dielectric breakdown events indicated by the arrows, followed by self-reparation events can be seen. j) Stable lateral actuation of **E-CL**<sub>4</sub> (55  $\mu$ m) at 10 V/ $\mu$ m for 600 s.

as suggested by Suo's et al. in theoretical studies, needs more investigations.<sup>[305]</sup> Furthermore, the leakage current density of all materials was as low as 0.5  $\mu$ A/cm<sup>2</sup> and increased slightly when approaching the dielectric breakdown.

To demonstrate that actuation at very low voltages is possible, Figure 3.3d shows the lateral actuation at increasing voltages for **E-CL**<sub>2</sub> and **E-3.5CL**<sub>4</sub>. Both actuators respond to voltages as low as 300 V and the actuation strain increases with increasing voltage. Figures 3.3e,f show photographs of two actuators while being actuated: **E-CL**<sub>2</sub> (35  $\mu$ m) at 300 V and **E-3.5CL**<sub>4</sub> (24  $\mu$ m) at 1000 V. In the latter, a huge out of plane deformation can be seen. It is important to note that despite the rather low strain at break measured for **E-3.5CL**<sub>4</sub> in the tensile test, none of the actuators suffered mechanical failure despite their huge actuation (Figure 3.3f). Why the elastic network is mechanically more resistant under electrical stress needs further investigations.

Figure 3.3g,h shows the long term actuation of a device constructed from **E-CL**<sub>2</sub> exhibiting 4% and 7% actuation at 200 V and 300 V, respectively, for 100 cycles at 1 Hz (see **Video S7**). Another actuator constructed from **E-CL**<sub>2</sub> showed 9.7% actuation strain at 400 V (**Figure 3.13**). The actuator constructed from **E-CL**<sub>2</sub> had a thickness of 35  $\mu$ m and actuated at 200 V, a value which is extremely low in dielectric elastomer actuators. While, low voltage dielectric elastomer actuators were demonstrated before with a 1.4  $\mu$ m thick regular silicone film, which actuated at 100 V,<sup>[13]</sup> our materials actuated at similar voltages, although more than ten times thicker films were used. The thrilling aspect of our materials is, that further reduction of film thickness should enable to reduce the driving voltage even further, possibly into a range where application in human bodies comes into reach.

Additionally, our devices were able to self-repair after a breakdown, which is quite advantageous as this increases actuator's reliability and lifetime. Figure 3.3i shows an actuator operated at 600 V for 50 cycles at 0.25 Hz. Three dielectric breakdown events followed by self-reparation events can be seen. After self-reparation, only a very small decrease in actuation performance was noted. Self-reparation of actuators has been reported before and it was either due to electrode material which degraded at the breakdown site or due to flowing of plasticizer into defects.<sup>[114]</sup> In this case, the self-reparation of the actuators is due to combustion of the conductive path. During electrical breakdown, the small spark produced burns part of the electrode and thus insulates the conductive path. An actuator subjected to 600 V for 600 s demonstrated the material to have low creep and very fast strain recovery (Figure 3.3j).

### 3.4. Conclusion

In conclusion, we have developed new dielectric elastomer materials based on nitrile modified silicone for which the mechanical properties can be easily tuned by the type and content of cross-linker used. The elastomers have a dielectric permittivity of 18 and a low leakage current density of  $0.5 \,\mu\text{A/cm}^2$ , which slightly increases only when approaching the dielectric breakdown. We describe how to create and manipulate films with a thickness of down to

20  $\mu$ m, which makes our elastomers unmatched in terms of high permittivity in thin elastomeric films. We constructed actuators operable at unprecedentedly low voltages of 200 V and reproducibly observed the films to efficiently self-repair after a breakdown. Self-repair is key to long actuator lifetimes and high reliability. The stiffer actuators withstand electric fields up to 100 V/ $\mu$ m. This is rather high for soft elastomers with a dielectric permittivity value of 18 and suggests their applicability to actuators that can generate high electrostatic forces. With this unprecedented property combination our materials are not only attractive for simple actuators, but also promise to be applicable for stacked actuators. Such devices are composed of many thin actuator layers stacked on top of each other and will be constructed next to exploit the full potential of our materials. In parallel we will additionally reduce the film thickness even further to reduce the driving voltage into a range (approx. 40 V) required to in vivo applications.

### 3.5. Experimental Section

#### Materials

Unless otherwise stated, all chemicals were reagent grade and used without purification. 1,3,5,7-tetramethyl-1,3,5,7-tetravinyl cyclotetrasiloxane (V<sub>4</sub>) was purchased from ABCR. 2,2-Dimethoxy-2-phenylacetophenone (DMPA), 2,2'-(ethylenedioxy)diethanethiol, benzene, toluene, 3-chloropropionitril, tetramethylammonium hydroxide 25% in MeOH (TMAH), and thiourea were purchased from Aldrich. Methanol and tetrahydrofuran were purchased from VWR. An as received solution of PVA in isopropanol/2-butanol from Suter Kunststoffe AG was used as sacrificial layer. Elastosil films with a thickness of 200  $\mu$ m were purchased from Wacker. Polymethylvinylsiloxane (M<sub>n</sub> = 87'800 Da, M<sub>w</sub> = 200'000 Da, PDI = 2.3) and 3-mercaptoproprionitrile were prepared according to the literature.<sup>[22]</sup>

#### Characterization

<sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded at 298 K on a Bruker Avance 400 NMR spectrometer using a 5 mm broadband inverse probe at 400.13 and 100.61 MHz, respectively. Chemical shifts ( $\delta$ ) in ppm are calibrated to residual solvent peaks (CDCl<sub>3</sub>:  $\delta$  = 7.26 and 77.16 ppm). Size exclusion chromatograms were taken with an Agilent 1100 Series HPLC (Columns: serial coupled PSS SDV 5  $\mu$ m, 100 Å and PSS SDV 5  $\mu$ m, 1000 Å, Detector: DAD, 235 nm and 360 nm; refractive index), with THF as mobile phase. PDMS standards were used for the calibration and toluene as internal standard.

As UV source a lamp from Peschl Ultraviole SwiftCure HL-250 ( $\sim$ 35 mW cm<sup>-2</sup>) placed at 20 cm distance from the film was used.

Differential scanning calorimetry (DSC) investigations were undertaken on a Perkin Elmer Pyris Diamond DSC instrument. Two heating and one cooling steps with a heating and cooling rate of 20 °C min<sup>-1</sup> in the temperature range of -90 °C to 50 °C were conducted per measurement under a nitrogen flow (50 ml min<sup>-1</sup>). The second heating step was considered for the evaluation of the  $T_g$ . About 10 mg sample was weighted in aluminum crucibles shut with pierced lids. The tensile tests and the cyclic uniaxial tensile stress tests were performed on a Zwick Z010 tensile test machine with a crosshead speed of 50 mm/min (278 %/min). Tensile test specimens with a gauge width of 2 mm and a gauge length of 18 mm were prepared by die cutting. The strain was determined over the traverse moving sensor. The curves were averaged from 3 different samples *per* material. The tensile modulus was determined from the slope of the stress-strain curves using a linear fit to the data points within 10% strain.

Dynamic mechanical analysis was carried out on a RSA 3 DMA from TA Instruments. Stripes of 10 mm × 20 mm were measured under a dynamic load of 2.5 g, at 2% strain in the frequency range of  $0.05^{-3}$  Hz at 25 °C and 65% humidity. Dynamic mechanical analysis at temperatures between -50 °C to 50 °C was conducted on a RSA 3 DMA from TA Instruments. Stripes of 10 mm × 20 mm were measured at a frequency of 1 Hz under a dynamic load of 2 g at 2% strain. The measurements were started at 50 °C and the samples were tested from 50 °C down to - 50 °C in 5 °C interval.

Permittivity measurements were done in the frequency range of 0.1 Hz to 1 MHz using a Novocontrol Alpha-A Frequency Analyzer. The  $V_{RMS}$  (root mean square voltage) of the probing AC electric signal applied to the samples was 1 V. The samples were squeezed between two electrodes (diameter of 20 mm).

Circular electrodes (8 mm diameter) of carbon black powder were applied to each side of the film. A FUG HCL-35-12500 high voltage source served as power supply for actuator tests. The voltage was increased by 100 V steps every 2 s up to breakdown. The actuation strain was measured optically as the extension of the diameter of the electrode area *via* a digital camera, using an edge detection tool of a LabView program to detect the boundary between the black electrode area and the transparent silicone film.

#### Synthesis of poly(3-ethylsulfanyl propionitrile methyl-co-methylvinyl)siloxane (P1)

To a solution of polymethylvinylsiloxane (20 g, 0.232 mol, 1 eq) in distilled THF (600 ml), DMPA (564 mg, 0.009 eq) and 2-cyanoethylthiol (19.2 g, 0.220 mol, 0.95 eq) were added. The reaction mixture was degassed three times using the freeze-pump-thaw technique and irradiated for 20 min with a UV light. Then, it was concentrated at a rotary evaporator to about one third of the initial volume and the functionalized polymer was precipitated in methanol. This purification procedure was repeated four times by dissolution/precipitation in THF/methanol. The polymer was only slightly dried in order to avoid unwanted polymer cross-linking. It was then dissolved in THF, and the solvent was distilled off once more in order to remove more of the residual methanol. This process was repeated few times and then the final concentration of the polymer solution in THF was adjusted to 40 wt%. A yellowish transparent solution was obtained.

#### Formation of thin films

A solution of PVA in isopropanol and butanol was cast on a glass plate and dried. On top of the PVA layer, a solution of 40 wt% **P1** in THF, the cross-linker (see Table 3.1), and DMPA was cast in thin films by doctor blade technique. The films were let to stand at room temperature for 60 min and were then cross-linked by irradiating with UV light. The PVA layer on which the silicone film was cross-linked was easily removed from the glass substrate. The necessary film

shape for actuator construction was cut, fixed between two circular plastic frames and put into water for 6 h at 50 °C. During this time, the PVA sacrificial layer was dissolved. All samples after cross-linking were dried under reduced pressure at 60 °C for 24 h. Using this procedure, very thin actuators were prepared and their actuation performance could be tested. Some of the characteristics of the prepared materials are summarized in Table 3.2.

Sample	CL [µl] <sup>a)</sup>	mmol CL	THF [g] <sup>a)</sup>	DMPA [mg] <sup>a)</sup>
E-CL <sub>2</sub>	CL <sub>2</sub> [5]	0.0307	1.5	5
E-CL <sub>4</sub>	CL <sub>4</sub> [5.7]	0.015	1.5	5
E-3.5CL <sub>4</sub>	CL <sub>4</sub> [20]	0.0525	1.5	5

Table 3.1. The amount of reagents used for the synthesis of thin films.

<sup>a)</sup> Amount of reagents used	per 1 g of dry <b>P1</b> .

Table 3.2. The mechanical and dielectric characteristics of the three different materials developed.

Material	S <sup>a</sup>	Y <sub>10%</sub>	Max. stress	E' <sup>b</sup> @	tan $\delta^{b}$	$E_b$ thin <sup>c</sup>	$E_b$ thick <sup>c</sup>	Sz <sup>d</sup>
	[%]	[kPa]	[kPa]	[kPa]		[V/µm]	[V/µm]	[%]
E-CL <sub>2</sub>	82	462	287	350	0.007	19	16	13@13 V/μm
E-CL <sub>4</sub>	42	785	290	665	0.0027	25.5	22.7	14@18 V/μm
E-3.5CL₄	38	862	304	790	0.0018	73.6	26.7	11.5@26 V/μm

<sup>a</sup>Average strain at break, <sup>b</sup>measured at 0.05 Hz, <sup>c</sup>electrical breakdown of thin (<55  $\mu$ m) and thick films measured (100  $\mu$ m to 130  $\mu$ m) during the actuator tests, <sup>d</sup>lateral actuation strain at a certain electric field of the best actuators.

## 3.6. Supporting Information



Figure 3.4 <sup>1</sup>H NMR spectra of the 3-mercaptopropionitril (A), of the starting polymer (B), and of 40 wt% **P1** solution in THF (C).



Figure 3.5 <sup>1</sup>H NMR of a 40wt% solution of **P1** in THF, with the integrals of protons of vinyl and of methylsilyl groups.



Figure 3.6 GPC data of starting polyvinylmethylsiloxane (left) and of P1 (right).



Figure 3.7 Stress-strain curves **E-CL**<sub>2</sub>, **E-CL**<sub>4</sub>, and **E-3.5CL**<sub>4</sub> as well as of a material **E-CL**<sub>2-silica</sub> that contains 2.5 wt.% silica. For each material at least three samples were measured. The red curves in the graphs represent the average. On these curves, however the minimum and not the average strain at break is given.



Figure 3.8 DSC of  $\mathbf{E}$ - $\mathbf{CL}_2$  (top) and  $\mathbf{E}$ - $\mathbf{CL}_4$  (bottom).



Figure 3.9 Dielectric permittivity ( $\varepsilon$ ), dielectric loss ( $\varepsilon$ '), conductivity ( $\sigma$ ), and tan  $\delta$  of **E-CL**<sub>2</sub> at different temperatures and frequencies.



Figure 3.10 An actuator constructed from a 109  $\mu$ m thick **E-CL**<sub>4</sub> film subjected to an electric field of 10 V/ $\mu$ m and different frequencies of 0.25 Hz (20 cycles), 0.5 Hz (100 cycles), 1 Hz (100 cycles), 2Hz (100 cycles), 5 Hz (100 cycles), and 10 Hz (100 cycles), respectively, showed a very stable actuation.



Figure 3.11 Long term measurements of over 10'000 cycles at 2.5 Hz for **E-CL<sub>4</sub>** (109  $\mu$ m) and 50'000 cycles at 10 Hz for **E-3.5CL<sub>4</sub>** (40  $\mu$ m) clearly support that the prepared materials are rather robust.



Figure 3.12 A device constructed from **E-CL**<sub>2</sub> that gave slightly less actuation.



Figure 3.13 An actuator constructed from  $\textbf{E-CL}_{2}$  (42  $\mu m)$  actuated at 400 V for 30 cycles.

Video S1. 50'000 cyclic actuations at 1500 V constructed from **E-3.5CL**<sub>4</sub> (36 μm).

Video S2. A 23  $\mu m$  thin actuator operated at 150 V.

Video S3. Large out of plane deformation for a 30  $\mu$ m thin film actuated at increasingly high voltages, up to 3000 V.

Video S4. Large actuation of material  $\textbf{E-3.5CL}_4$  (19  $\mu$ m) at 2000 V. The leakage current is also shown.

Video S5. An actuator constructed from  $\textbf{E-CL}_{2}$  (23  $\mu m)$  actuated at low voltages.

Video S6. Actuation at increasing voltages for  $\textbf{E-3.5CL}_4$ . (24 µm) up to 1000 V.

Video S7. Long term actuation of a device constructed from  $\mathbf{E}$ - $\mathbf{CL}_2$  at 200 V, 300 V, 400 V, and 700 V for the 100 cycles at 1 Hz.

The videos can be found online: <u>https://onlinelibrary.wiley.com/doi/10.1002/marc.201900205</u>
#### **CHAPTER FOUR**

## 4. Dielectric Elastomer Actuators Made of Novel Elastomers Based on Polysiloxanes Carrying Amido Side Groups

by

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Y. Sheima performed the synthesis and characterization of compounds, fabricated and tested devices and contributed to the manuscript.

#### 4.1. Abstract

Dielectric elastomers are key materials in stretchable capacitive transducers. They have found a wide application ranging from actuators, sensors, energy harvesters, and personalized medicine to stretchable electronics and Li-ion batteries. However, after years of research, it is still a great challenge to achieve dielectric elastomers with increased dielectric permittivity and fast recovery of initial shape when subjected to mechanical and electrical stress. Here we show that chemical modification of a polymethylvinylsiloxane with a N,N-dimethyl-3mercaptopropanamide via thiol-ene reaction allows access to dielectric elastomers with uniquely attractive properties. They have a dielectric permittivity of 21, a strain at break that can reach 150%, and low viscoelastic losses, with a tan  $\delta$  significantly below 0.05 at low frequency. Actuators constructed with them respond to a low electric field of 6.2 V/µm and low voltage, give reversible and reliable actuation of 4% for more than 30'000 actuation cycles at 5 Hz, while one of them has survived 450'000 cycles at 10 Hz and 3.6 V/ $\mu$ m. The best actuator showed 10% strain at 7.5 V/µm. Additionally, capacitive sensors show a more than six-fold increase in sensitivity compared to regular polydimethylsiloxane elastomer. The elastomers slowly depolymerize in a normal environment, making it attractive for one-use disposable devices. Furthermore, the hydrolyzed material restores its properties when heated to elevated temperatures and thus may allow recyclability.

### 4.2. Introduction

Recently, we synthesized a library of polysiloxanes modified with different types and contents of polar groups and investigated their glass transition temperatures and dielectric properties in parallel plate capacitors on highly viscous liquids.<sup>[306]</sup> We have shown that appropriate chemical modification of polyvinylsiloxanes with polar thiols afford polymers with increased dielectric permittivity and glass transition temperatures ( $T_g$ ) significantly below room temperature. This comprehensive study eventually allowed us to select several polar groups that may give rise to promising elastic materials for application in dielectric elastomer transducers (DETs).

Encouraged by the higher dielectric permittivity of the polysiloxane modified with *N*,*N*-dimethyl-3-mercaptopropanamide than the one modified by 2-cyanoethanethiol recently reported by our lab,<sup>[307]</sup> which showed very promising electromechanical properties in cross-linked films, here we wish to explore the potential of polysiloxane modified with *N*,*N*-dimethyl-3-mercaptopropanamide as dielectric elastomers in transducers. This polymer shows a dielectric permittivity as high as 21.5 and a glass transition temperature ( $T_g$ ) of -45.5 °C.<sup>[306]</sup> Additionally, the starting materials can be easily synthesized on a multigram scale. The synthesized polymer seems stable in time, does not change colour, and does not cross-link spontaneously.

This work aims to synthesize polysiloxane modified with *N,N*-dimethyl-3mercaptopropanamide, which carry suitable groups that can be subsequently used for crosslinking into thin films. For this, a fast and easy synthetic pathway for cross-linking via thiol-ene reaction with multifunctional thiols is used. The mechanical properties are optimized to achieve materials with good elasticity. The dielectric and electromechanical properties are investigated and compared to the literature.

The polymer is prepared by anionic ring-opening polymerization of 1,3,5,7-tetramethyl-1,3,5,7-tetravinyl cyclotetrasiloxane (V<sub>4</sub>) monomer, while the thiol is obtained from N,N-dimethylacrylamide, and thioacetic acid, followed by the deprotection of the thioester in basic conditions.

## 4.3. Experimental Section

#### Materials

Unless otherwise stated, all chemicals were reagent grade and used without purification. 1,3,5,7-Tetramethyl-1,3,5,7-tetravinyl cyclotetrasiloxane (V<sub>4</sub>) was purchased from ABCR. 2,2-Dimethoxy-2-phenylacetophenone (DMPA), 2,2'-(ethylenedioxy)diethanethiol, benzene, toluene, sodium hydroxide, *N*,*N*-Dimethylacrylamide, tetramethylammonium hydroxide 25% in MeOH (TMAH), hydrochloric acid, and thioacetic acid were purchased from Aldrich. Methanol and tetrahydrofuran were purchased from VWR. As a sacrificial layer, we used a solution of PVA in isopropanol/2-butanol from Suter Kunststoffe AG. Elastosil films with a thickness of 200 µm were purchased from Wacker. Polymethylvinylsiloxane (PV) (M<sub>n</sub> = 105'480 Da, M<sub>w</sub> = 375'000 Da, PDI = 3.55) and *N*,*N*-dimethyl-3-mercaptopropanamide were prepared according to the literature.<sup>[217,306]</sup>

#### Characterization

<sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded at 298 K on a Bruker Avance 400 NMR spectrometer using a 5 mm broadband inverse probe at 400.13 and 100.61 MHz, respectively. Chemical shifts ( $\delta$ ) in ppm are calibrated to residual solvent peaks (CDCl<sub>3</sub>:  $\delta$  = 7.26 and 77.16 ppm). Sizeexclusion chromatograms were taken with an Agilent 1100 Series HPLC (Columns: serial coupled PSS SDV 5 µm, 100 Å and PSS SDV 5 µm, 1000 Å; detector: DAD, 235 nm and 360 nm; refractive index), with THF as mobile phase. PDMS standards were used for the calibration and toluene as internal an standard. As UV source a Hönle UVA HAND 250 GS UV lamp was used. DSC investigations were undertaken on a Perkin Elmer Pyris Diamond DSC instrument. Two heating and one cooling steps with a heating and cooling rate of 20 °C min<sup>-1</sup> in the temperature range of –90 to 50 °C were conducted per measurement under a nitrogen flow (50 mL min<sup>-1</sup>). The second heating step was considered for the evaluation of the *T*<sub>g</sub>. About 10 mg sample was weighted in aluminum crucibles shut with pierced lids. The tensile tests and the cyclic uniaxial tensile stress tests were performed on a Zwick Z010 tensile test machine with a crosshead speed of 50 mm min<sup>-1</sup>. Tensile test specimens with a gauge width of 2 mm and a gauge length of 18 mm were prepared by die-cutting. The strain was determined over the traverse moving sensor. The curves were averaged from three different samples per material. The tensile modulus was determined from the slope of the stress-strain curves using a linear fit to the data points within 10% strain. Dynamic mechanical analysis was carried out on a RSA 3 DMA from TA Instruments. Stripes of 10 mm × 25 mm were measured under a dynamic load of 2 g, at 2% strain in the frequency range of 0.05-10 Hz at 25 °C and 65% humidity. Permittivity measurements were done in the frequency range of 0.1 Hz to 1 MHz using a Novocontrol Alpha-A Frequency Analyzer. The VRMS (root mean square voltage) of the probing AC electric signal applied to the samples was 1 V. The samples were squeezed between two electrodes (diameter of 20 mm). The actuation strain was measured optically as the extension of the diameter of the electrode area via a digital camera, using an edge detection tool of a LabView program to detect the boundary between the black electrode area and the transparent silicone film. Circular electrodes (8 mm diameter) of carbon black powder were applied to each side of the film. A FUG HCL-35-12500 high voltage source served as a power supply for actuator tests. For the thick actuators (above 80 µm), 5% of prestrain was applied. Thinner actuators prepared using sacrificial PVA layer were not prestrained. The sensors were tested using commercial traction sliding machine Zaber A-LSQ300A-E01 for stretching, while for capacitance measurement Keithley DMM6500 was utilized. As electrode material for sensors, commercially available Elastosil<sup>®</sup> LR 3162 a/b from Wacker was used. It was prepared by blade casting the mixture of two components and its subsequent cross-link at 100 °C for 2 h and drying at 60 °C in the vacuum oven.

For fabrication of the sensor, one layer of elastomer (PDMS or **EX**) was covered with crosslinked electrodes Elastosil<sup>®</sup>. The active sensing area had the following dimensions:  $25 \times 10 \times 0.2$  mm. To insulate the sensor, VHB<sup>™</sup> 4910 film from 3M was used. Each sensor was cycled 10 times at 10%, 20%, 40%, 50%, 60%, 70%, and 80% strain. From each measurement, the average capacitance in strained form was taken. From this value, the average capacitance in unstrained form was subtracted, and the graph  $\Delta C$  versus applied strain was obtained.

# General synthesis of polysiloxane containing N,N-dimethyl-3-mercaptopropanamide and 3.3% of vinyl groups (**P1**)

PV (10 g, 0.116 mol repeat units, 1 eq.), *N*,*N*-dimethyl-3-mercaptopropanamide (14.7 g, 0.11 mol, 0.95 eq.) and DMPA (0.297 g, 1.16 mmol, 0.01 eq.) were dissolved in 250 ml of THF. The reaction mixture was degassed three times using the freeze-pump-thaw technique and irradiated for 20 min with UV light. The solution was concentrated with a rotary evaporator, and the polymer was purified three times by dissolving it in THF and precipitating in cyclohexane. The obtained polymer was dissolved in THF, filtered through a glass filter, and the solvent was evaporated. Finally, the concentration of polymer was adjusted to 70 wt% in THF.

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz),  $\delta$ : 6.03-5.9 (m, 2H), 5.87-5.73 (m, 1H) 3.00 (s, 6H), 2.83 (t, 2H), 2.7–2.54 (m, 4H), 0.85 (t, 2H), 0.15 (s, 3H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz),  $\delta$ : 171.3; 136.9; 133.2; 37.3; 35.4; 33.6; 27.4; 26.7; 18.7; 0.1.

#### Formation of polar elastomers (**EX**)

Polymer **P1** (1.43 g of 70 wt% **P1** in THF) was mixed with a certain amount of cross-linker (for amounts, see Table 4.1) and DMPA (4.5 mg). The obtained mixture was centrifuged for 2 min

at 6000 rpm to remove the bubbles. Thick films (>80  $\mu$ m) were cast directly on Teflon substrate, while thin films were cast on a glass coated with a sacrificial PVA layer. Thick films were kept in air for 30 min and then cross-linked by irradiation with UV light for 5 min, and dried 12 hours in the vacuum oven at 60 °C. Thin films were cross-linked directly after casting, and after dissolving the PVA layer, they were dried in the vacuum oven at 60 °C. Before all tests, materials were stored in the vacuum oven at 60 °C.

#### 4.4. Results and Discussions

The two-step synthetic process to cross-linked polar elastomer is presented in Scheme 4.1. First, **PV** ( $M_n = 105'480 \text{ g/mol}$ ,  $M_w = 375'000 \text{ g/mol}$ , PDI = 3.55, Figure 4.4a) was functionalized with less than an equimolar amount of polar thiols to vinyl group using UV-induced thiol-ene reaction. The vinyl groups left unreacted in this step (approx. 3.3 % by NMR integration) will be used subsequently for cross-linking. The <sup>1</sup>H NMR spectrum of functionalized polymer **P1** is presented in Figure 4.4a. The molecular weight of **P1** and its weight distribution were investigated with GPC (Figure 4.4b). The GPC elugram of **P1** has a much lower molecular weight compared to the starting polysiloxane. That could be due to the smaller hydrodynamic volume of **P1**.

For cross-linking **P1** into elastomeric thin films, a thiol-ene reaction was used, whereby two different thiols, 2,2'-(ethylenedioxy)diethanethiol (**CL2**) and pentaerythritol tetrakis (3-mercaptopropionate) (**CL4**), were used. To optimize the properties of the elastomers, the amount of cross-linker was tuned to give 11 elastomers denoted as **EX**. The amount of reagents used for each elastomeric material and some characteristic properties are summarized in Table 4.1.



Scheme 4.1 Synthesis of dimethylamide modified polysiloxane **P1** containing polar side groups and its crosslinking into elastomeric films **EX**.

The synthesized elastomers were subjected to tensile testing. Stress-strain curves of materials E1-E11 are presented in Figure 4.5, while their Young's modulus (Y) at 10% strain and average strain at break (sav) are indicated in Table 4.1. For materials **E1-E9**, cross-linked with an increasing amount of **CL2**, the elastic modulus Y initially increased from 111 kPa for **E1** to 454 kPa for E4, while a further increase in CL2 used resulted in softer materials (E5 to E9). Thus material **E9**, cross-linked with the larger amount of **CL2**, showed a Y = 112 kPa and was as soft as E1. In contrast to Y, the strain at break showed an opposite trend. Material E1 exhibited 81% tensile strain, which decreased when a larger amount of cross-linker was used. The smallest value for the tensile strain of 31% was measured for material E4, which had the highest Y. The tensile strain increased again from E4 to E9 and reached a value of 153% for material E9. Among all films, only material E1 looked very viscoelastic and difficult to handle. Many samples ruptured even before any measurement could be done with it. Materials E10 and E11 were prepared using CL4 cross-linker. The amount of mercapto groups in CL4 for preparation of materials E10 and E11 was the same as the amount of mercapto groups in CL2 used for E3 and E9, respectively. Obtained material E10 showed Y of 632 kPa, which is an almost 50% higher than material E3 with a Y = 428 kPa. Similar to the difference between Y of E3 and E9, material **E11** synthetized with a larger amount of cross-linker also showed a smaller Y = 363kPa than E10. While CL4 increased the modulus of the materials E10 and E11 compared to E1-E9, a large reduction in the strain at break was observed for E10-E11. For E10 the tensile strain was 28%, and for **E11** was 36%. The increase in strain at break and the decrease in Y might be due to the ratio between the mercapto and vinyl groups. For E3 the ratio of mercapto to vinyl groups was almost 1, while for E4 to E9, this was higher than 1. Therefore, the excess of thiol groups either creates disulfide bridges, which increase the distance between cross-linking points or acts as a plasticizer. Therefore, the materials become softer. The average stress-strain curves of each sample are presented in Figure 4.6.

For subsequent investigations, four materials are selected: **E9** has a large strain at break and low Y, **E3** has the largest *Y*, and **E10** and **E11** were cross-linked by **CL4**.

The selected samples were subjected to cyclic uniaxial tensile tests (Figure 4.1b). Each sample was initially strained five times from 0% to 20% strain and then relaxed back to 0% strain. After that, the strain was increased with an increment of 20% until the material broke. A minimal mechanical hysteresis for all materials was observed, which indicates their good elastic properties.

The tensile tests suggest that material **E9** might be the best candidate for the application in DEA due to the low Young's modulus, high strain at break, low mechanical hysteresis. Therefore, **E9** was further used in electromechanical tests. Several measured actuators showed a drift in the baseline of the actuation strain (Figure 4.8a, b). Such behavior is typical for elastomers with viscoelastic losses. Similar behavior was reported by Opris *et al.* for a VHB film.<sup>[229]</sup> An actuator photo after being subjected to 1000 actuation cycles shows some irreversible deformation, which can be observed at the edge between the active and passive parts in the actuator (Figure 4.9).

Sample	CL2ª	CL4ª	–SH in	Y	S	E′ @ 0.05	<i>tan</i> δ @
Name	[µl]	[µl]	CLX	[kPa]	[%]	Hz	0.05 Hz
			[mmol]	[Ki ŭ]	[,0]	[kPa]	
E1	20		0.049	111	81		
E2	40		0.098	294	45		
E3	55		0.135	428	39	304	0.005
E4	70		0.172	454	32		
E5	85		0.209	322	37		
E6	100		0.246	317	37-80		
E7	120		0.295	204	60		
E8	150		0.369	164	80		
E9	200		0.492	112	153	167	0.007
E10		64	0.135	632	28	532	0.002
E11		232	0.492	363	35	267	0.006

Table 4.1: Recipes	of the films	made of sile	oxane with	dimethylacr	ylamide side	groups.
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<sup>a</sup>A 20 vol% solution of CLX in THF was used, <sup>b</sup>volume of CLX solution in THF (µl) added to ES (1 g).

For a better investigation of the elastic properties, dynamic mechanical analysis (DMA) of E3, E9, E10, and E11 was performed (Figure 4.1c) and the results are compared with a commercial polydimethylsiloxane elastomer – Elastosil Film 2030 250. All samples have a very low *tan*  $\delta$ , below 0.01 at 0.05 Hz, which is even below the value of Elastosil. However, at higher frequencies, the *tan*  $\delta$  of E3, E10, and E11 slowly increases to 0.02 at 1-2 Hz, while *tan*  $\delta$  of E9 shows a sharp increase to 0.1 at 1 Hz. Films made using cross-linker CL4 (E10, E11) have lower *tan*  $\delta$  than E3 and E9 over the entire range of frequencies and could be due to the higher cross-linking density of these materials. The storage modulus for all materials was almost constant within the whole range of frequency with only a minor increase at 8-10 Hz. The value of the storage modulus at low frequency is in agreement with *Y* (Table 4.1). Because materials E3 and E10 had a lower *tan*  $\delta$  over the entire frequency range, both were chosen for the subsequent electromechanical tests in actuators.

DSC measurements showed that all samples'  $T_g$  is well below the room temperature. It is - 41 °C for materials **E3** and **E9** and -37 °C for materials **E10** and **E11**. The slight increase in the  $T_g$  for the latter materials is due to the higher cross-linking density since a tetrafunctional cross-linker was used (Figure 4.10).

The dielectric properties of materials **E3** and **E10** were investigated at different temperatures (from -100 °C to +100 °C) (Figure 4.11). Below  $T_g$ , all materials show a rather low dielectric permittivity of about 4.5 because the dipoles are frozen and cannot orient in an electric field. Above  $T_g$ , the dipoles become mobile and can be polarized, which is reflected by an increase in permittivity to values that can reach up to 21 at 10 kHz and 20 °C (Figure 4.1d). The conductivity of both materials is rather low, between  $5 \times 10^{-9}$  and  $1.2 \times 10^{-9}$  S cm<sup>-1</sup>, and thus within the range of dielectrics.



Figure 4.1 Average stress-strain curves (a); five cyclic uniaxial tensile tests from 0% to 20% strain (b); DMA (c); dielectric properties (permittivity ( $\epsilon$ '), dielectric loss ( $\epsilon$ ''), conductivity ( $\sigma$ ') and *tan*  $\delta$ ) as a function of frequency (d) of elastomers **E3**, **E9**, **E10**, and **E11**.

For electromechanical tests, several actuators were prepared from materials **E3** and **E10**. They showed more stable and reversible actuation compared to **E9**. In Figure 4.2 frequency-dependent actuation of material **E3** (actuator 1, 122  $\mu$ m) at different electric fields can be observed. At a lower electric field, the frequency dependence is more pronounced. At 0.25 Hz and 500 V actuator shows 2.7% of lateral actuation strain, while at 10 Hz, the actuation becomes almost two times smaller, around 1.3%. When the voltage is increased to 1000 V, the lateral actuation strain increases to 6% at 0.25 Hz, and it decreases to 5% by increasing the frequency to 10 Hz. Photos of actuators made from **E3** and **E9**, show no visible degradation after more than 1000 actuation cycles for the former and some degradation for the latter, respectively (Figure 4.9).

A second 120  $\mu$ m thick actuator made of **E3** gave 5% strain at 0.25 Hz and 750 V, which corresponds to 6.25 V/ $\mu$ m (Figure 4.12). It also survived 30'000 cycles at 5 Hz, showing 4% lateral actuation strain at 750 V. When the voltage was increased in a step of 100 V from 0 V to the breakdown, the actuator showed a maximum lateral actuation of 8.3% and a breakdown of 10.4 V/ $\mu$ m.

The third actuator has a 138  $\mu$ m thickness and survived more than 450'000 actuation cycles at low electric fields (2.9-3.6 V/ $\mu$ m). It showed around 1-2% lateral actuation strain at an electric field in the range of 2.9-3.6 V/ $\mu$ m (Figure 4.13). However, during the last 150'000 cycles, the actuation strain was significantly reduced. The breakdown of this actuator was reached at 6.5 V/ $\mu$ m.



Figure 4.2 Actuation of actuator 1 (122  $\mu$ m) made of material **E3** at different frequencies: a) at 500 V; b) at 1000 V.

One of the best actuators made of material **E3** had a thickness of 66  $\mu$ m and gave almost 10% lateral actuation at 2 Hz and 500 V (Figure 4.3), which corresponds to 7.6 V/ $\mu$ m. When the material was tested for 20'000 cycles at 500 V and 5 Hz, a decrease in lateral actuation from almost 10% to 6.5% was observed. This decrease may be due to some degradation in the dielectric or electrode material and has been observed before in other dielectric materials.<sup>[56]</sup>



Figure 4.3 A 66  $\mu$ m thick actuator made of material **E3**. Photos of the actuator in the relaxed (a, bottom) and actuated (a, top) at 500 V (7.6 V/ $\mu$ m) states; lateral actuation strain at 500 V and 2 Hz for 50 cycles (b), and lateral actuation strain at 500 V and 5 Hz for 20'000 cycles (c). A decrease in actuation in time is observed.

Material **E10** showed inferior actuation compared to **E3** (SI Figures 4.14 and 4.15). The reason behind this could be the increased value of elastic modulus (Y = 632 kPa) for **E10**. A 120  $\mu$ m thick actuator showed 4% strain at 750 V (6.25 V/ $\mu$ m). It survived 50'000 cycles at 2.5 Hz and 750 V, but the actuation strain decreased from 3.5% at the beginning to 1.8% at the end.

Subsequent application of the same voltage at 0.25 Hz resulted in only 1.8% actuation strain (Figure 4.14).

Another actuator constructed from a 120  $\mu$ m thick film of **E10** showed only 2% at 750 V and 0.25 Hz (Figure 4.15). It was also subjected to 100'000 cycles at 5 Hz, showing 2% of actuation. This actuator achieved 4.5% strain at 0.25 Hz only when the voltage was increased to 1500 V. A smaller actuation strain of actuators made of **E9** could be due to the higher Young's modulus of **E9** compared with **E3**.

The average breakdown strength of materials **E3** and **E10** were tested by placing films between two metallic electrodes with a 1 mm<sup>2</sup> active area. The voltage was gradually increased until the breakdown. Ten samples of each elastomer were tested. Materials **E3** and **E10** showed a breakdown of 18 V/ $\mu$ m and 26.6 V/ $\mu$ m, respectively. The reason behind the higher dielectric breakdown for **E10** is the higher elastic modulus.

So far, we have shown that the polysiloxane functionalized with dimethylacrylamide side groups has a high permittivity and a low  $T_q$  value. Its mechanical properties can be easily tuned by the amount of a cross-linker used. The films show good elastic properties, and actuators made from them can produce high lateral actuation strain and can survive many actuation cycles at lower voltages as compared to conventional polydimethylsiloxanes. However, it also has some drawbacks. Elastomers made of this polymer have low strain at break, and they depolymerize during storing for several months in the air. However, the materials are stable when stored in dried conditions (vacuum oven or GloveBox). Figure 4.16 shows photos of three samples stored in air (top) and GloveBox (bottom). Samples E3 and E6, when stored in air, depolymerized, while those stored in the GloveBox did not. Materials E3, E6, and E11 did not depolymerize to the same extent when stored in air. For instance, it can be seen that material E11 depolymerizes less than E3 and E6. While the latter have changed their appearance from cross-linked films to liquid droplets, sample E11 kept its shape, but the film was more viscoelastic. The slower depolymerization of E11 is attributed to the higher degree of crosslinking in this sample and, therefore, a somewhat decreased mobility of the chain ends. <sup>1</sup>H NMR of the starting polymer P1 before cross-linking and of materials ES3 after depolymerization shows that there is no degradation of the polymer sde group (Figure 4.20). GPC measurements conducted on the starting polymer P1 taken after the synthesis and one year later, show that depolymerization of the polymer when it is stored in THF does not occur (Figures 4.21). This may be due to the fact that the polymer was stored in a closed atmosphere and therefore protected from humidity. Due to the increased polarity of **EX**, they absorb water from the environment and which, together with the amide groups, facilitate the cleavage of the polymer backbone.

To investigate the possibility of re-cross-linking, the depolymerized material **E3** was heated to 120 °C and solidified within 20 minutes. Rheological measurements conducted on a depolymerized sample and a heat-treated one support this statement (Figure 4.17). The depolymerized sample shows a typical liquid behavior at RT, with a storage modulus G' below the loss modulus over the entire frequency range (Figure 4.17a, red curve). The time-dependent rheological measurement at 120 °C and 1 rad/s shows that after 280 s, the G' crossover G'' and

indicates that the material solidified (Figure 4.17b). After keeping the material for 60 min at 120 °C, another frequency-dependent measurement at RT was conducted (Figure 4.17a, blue curve) and showed that G' is significantly higher than G", and thus a solid-like behavior.

Depolymerization of dielectric materials in devices may be disadvantageous, however, it can be avoided by encapsulating into a waterproof membrane. It also offers the opportunity to recycle the materials after being used or degrade after being disposed of.

High dielectric permittivity elastomers are not only attractive as dielectrics in actuators but also in stretchable capacitance sensors. Such sensors may find applications in personalized medicine, where degradable high dielectric permittivity elastomer may be a plus. Therefore, we further explored the potential of the developed materials in sensors. Material E9 was selected because of its high strain at break, low Young's modulus, a low tan  $\delta$ . To better assess its potential, the results obtained from a capacitive sensor made from E9 are compared with those of a regular PDMS, one of the current most explored dielectrics in capacitive sensors. The slope of the change in capacitance versus applied strain is a measure of sensitivity. It increased from 0.29 pF for PDMS to 1.84 pF for E9 (Figure 4.18). An enhancement of more than six times in sensitivity is observed for our sensor. Cyclic tests at 40% strain function of capacitance for E9 are presented in Figure 4.19. The sensor showed a reversible change in capacitance from 290 pF at 0% strain to 380 pF at 40% strain over 100 stretching cycles, respectively. When subjected to 80% strain, a slightly bigger change in capacitance can be detected. When the sensor is stored for two days in air, a large change in capacitance is observed. An almost two times increase in the initial capacitance from 290 pF to 590 pF is observed, while the difference in capacitance of the unstretched and 40% stretched sensor is three times higher. Thus  $\Delta C$  at 40% strain increased from 90 pF for the dried sensor to 290 pF for the sensor kept in air. This is an additional indication that the material is susceptible to water uptake from the environment.

## 4.5. Conclusion

Novel elastomers with increased dielectric permittivity of 21 based on polysiloxane bearing 95% polar *N*,*N*-dimethyl-3-thiopropanamide side groups were synthesized via thiol-ene reaction starting from polymethylvinylsiloxane and less than stoichiometric amount of *N*,*N*-dimethyl-3-mercaptopropanamide to vinyl groups. The unreacted vinyl groups are subsequently used for cross-linking with multifunctional thiols. Elastomers with Young's modulus in the range from 111 kPa to 632 kPa, and strain at break from 28% to 153% were synthesized. Obtained elastomers exhibit low glass transition temperatures (-37 °C and -41 °C). DMA measurements show that the materials have viscous losses below the value of a commercial polydimethylsiloxane elastomer at low frequencies. Some actuators withstood 450'000 actuation cycles at electric fields below 3.6 V/µm and gave an actuation strain in the range of 1.2-1.8%. The best actuator showed almost 10% strain at only 7.6 V/µm (500 V), which reflects the potential of our material for low voltage applications. Capacitive sensors exhibited a sixfold increase in sensitivity for the polar elastomer compared to conventional silicone

rubber. Depolymerization of these materials under a normal environment opens the possibility of using them in transient electronics as well as for recycling.

## 4.6. Supporting Information



Figure 4.4 a) <sup>1</sup>H NMR spectra of siloxanes functionalized with N,N-dimethyl-3-mercaptopropanamide side groups (70 wt% in THF); b) GPC elugrams of starting polysiloxanes **PV** and **P1**.



Figure 4.5 Stress-strain curves of elastomers **E1-E11**. The red curve on each graph is the average of several measurements.



Figure 4.6 Average stress-strain curves of elastomers **E1-E11**.



Figure 4.7 Cyclic uniaxial tensile tests of materials **E3**, **E6**, **E8**, **E9**, **E10**, **E11** at different strains. For each measurement 5 loading-unloading cycles were done. For material **E9** at 120% strain sample survived only 3 cycles.



Figure 4.8 Actuation performance of actuators made of **E9**. a) 35  $\mu$ m thick actuator shows creeping behavior at 100 V, giving from 0.5% to 1.8% of strain within 120 s. During the cyclic tests at 0.25 Hz and 0.5 Hz at 200 V and 300 V, correspondingly, also creeing behavior and drift of the base line was observed, indicating viscoelatic nature of the material. b) Another 35  $\mu$ m thick actuator that shows drift of the baselined during five cyclic tests, when voltage from 200 V to 600 V was applied at 0.25 Hz or 0.5 Hz during 100 cycles.



Figure 4.9 Actuator made of material **E9** (left) and actuator made of material **E3** (right) after approximately 1000 cycles of actuation.



Figure 4.10 DSC of E3, E9, E10, and E11, conducted from -100 °C to +50 °C.



Figure 4.11 Dielectric permittivity ( $\epsilon'$ ), dielectric loss ( $\epsilon''$ ), conductivity ( $\sigma'$ ), and *tan*  $\delta$  of **E3**, **E9**, **E10**, **E11** at different temperatures (from -100 °C to +100 °C) and frequencies (from 10<sup>-2</sup> to 10<sup>6</sup> Hz).



Figure 4.12 Actuation tests of the actuator (120  $\mu$ m) made of material **E3**. Cyclic tests (top), showing 5% strain at 0.25 Hz and 750 V during 100 cycles. It also withstood 10'000 and 20'000 cycles at 5 Hz and 750 V giving almost 4% strain. Step voltage increase test (bottom) during which the voltage was stepwise increased with a step of 100 V up to the breakdown.



Figure 4.13 Actuator (138  $\mu$ m) made of **E3** which survived more than 450'000 cycles at 10 Hz and low voltages (first 100'000 cycles were operated at 400 V, then the voltage was increased to 500 V).



Figure 4.14 Actuator (120  $\mu$ m) made of material **E10** and actuated at 750 V. First 100 cycles it shows 4% strain at 0.25 Hz. During the following measurements at 2.5 Hz, the actuation strain decreased from 3.5% to 1.8%

strain withing 50'000 cycles. During the subsequent measurement at 0.25 Hz it doesn't restore the strain value that was achieved during the first measurement. Strain around 2% was detected in the beginning of the measurement, and it was decreased to 1.8% within 100 cycles.



Figure 4.15 Actuator (120  $\mu$ m) made of material **E10**. It shows 2% strain during 100 cycles at 750 V and 0.25 Hz. Increasing frequency to 5 Hz and voltage to 1000 V results in the same 2% actuation strain, which was recorded during 100'000 cycles. Subsequent measurement at 1500 V and 0.25 Hz gave 4.2% of a stable actuation strain within 100 cycles.



Figure 4.16 Photo of samples **E3**, **E6**, and **E11** on polyethylene film which were kept in the air (top) and in a GloveBox (bottom).



Figure 4.17 a) Rheological measurements of depolymerized sample **E3** before and after cross-linking at elevated temperature. b) Time-dependent rheological measurement at 120 °C and 1 rad/s every 30 s.



Figure 4.18 Change in capacitance with strain for **E9** and PDMS.



Figure 4.19 Cyclic tests of sensors at 40% strain (top) and 80% strain (bottom). Left: freshly prepared sensor from **E9** taken from vacuum oven. Right: after storing the sensor for 2 days in air.



Figure 4.20 <sup>1</sup>H NMR of polymer E3 before cross-linking (bottom) and after depolymerization (top).



Figure 4.21 GPC-elugramms of P1 one year apart.

#### **CHAPTER FIVE**

## 5. High Permittivity Polysiloxanes Containing Sulfonyl Groups and Their Frequency and Temperature Dependent Actuation

by

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Y. Sheima performed the synthesis and characterization of compounds, fabricated and tested devices and contributed to the manuscript.

## 5.1. Abstract

Dielectric elastomer transducers is a young technology that has already been widely applied in many industries: from millimeter size soft robotics to large ocean wave generators. High dielectric permittivity elastomers are searched for this technology. When properly designed, these materials can not only be used for converting electrical into mechanical energy and viceversa but also to convert thermal into electrical energy and backward. Decisive whether a polymer can be used for one or the other application is the glass transition temperature. This should be significantly below room temperature for the first, while it should be around room temperature for the last. Here we synthesized polar polysiloxane elastomers modified with sulfonyl side groups. They have a dielectric permittivity as high as 18.4 at 10 kHz and 20 °C and rather low conductivity of 5×10<sup>-10</sup> S cm<sup>-1</sup>. Variation of cross-linker nature allows adjusting mechanical properties of the elastomer. One material exhibited a glass transition temperature of -13.6 °C, which although significantly below room temperature, impacts material's response in actuators. Some actuators show a large lateral actuation strain of 14% at 24 V/µm. However, significant differences were observed in the response of the materials not only at different frequencies and temperatures, but also in films with different thicknesses. The unusual but reproducible response may be connected to the close to room temperature glass transition temperature of this material and thus the somewhat hindered mobility of polar groups. Polar polymers operating near transition temperatures may show pyroelectric and electrocaloric effects, which may be responsible for the observed anomaly. However, further investigations are needed to clarify the observed behavior and the process responsible for it.

#### 5.2. Introduction

Artificial muscles, transducers, stretchable capacitive sensors, and generators at first glance are just different technologies that have nothing in common. Nevertheless, one thing merges these four indicated technologies – they all can be constructed from dielectric elastomers (DEs).<sup>[308,309]</sup> DEs are versatile and unique materials that can change their shape in response to an applied voltage. They contract and elongate and thus mimic the behavior of natural muscles. They can be used in soft robotics,<sup>[71]</sup> which in 2020 attained an estimated market value of 1 billion.<sup>[310]</sup> The potential of these devices goes beyond actuators, sensors, or generators, as they could be used in solid-state refrigeration, as recently demonstrated with poly(vinylidene fluoride-*co*-trifluoroethylene).<sup>[311]</sup>

For a better understanding of devices made of DEs, a stretchable capacitor has to be imagined. It consists of one layer of a DE film, both sides of which are covered with electrodes. After applying a voltage to the electrodes, the generated Maxwell pressure compresses the material in the z-direction. However, elastomers are considered to be incompressible, therefore they expand in both x and y directions.<sup>[113]</sup> The dipoles in amorphous polar elastomers orient in an electric field and relax back to their random orientation after removing the voltage. This change

in entropy causes a temperature change in the material and can, in principle, be used for solidstate refrigeration.

In sensor mode, when external stress like pressure or mechanical stress is applied to the stretchable capacitor, its area and thickness are changed. These changes affect the capacitance value, which can be used for sensing.<sup>[21]</sup>

Finally, after being deformed by external force in the generator mode, the film is electrically charged. Then, during the relaxation, generators convert mechanical energy into electrical, when the voltage of the capacitor is increased.<sup>[312]</sup>

It is known that the performance of actuators, sensors, and generators made of DEs is directly proportional to the dielectric permittivity value. Therefore, DEs with higher permittivity values are preferred. Such materials significantly reduce the driving voltage of dielectric elastomer actuators (DEAs), achieve higher sensitivity of sensors, and collect more energy by generators. While silicones have many advantages over polyurethanes and acrylics polymers, one limitation negatively affects their performance – very low permittivity ( $\varepsilon$ ) value of 2.8. Among the two known approaches towards polysiloxanes with increased permittivity values, the chemical modification of polymers is preferred over the fabrication of composites.<sup>[53,66]</sup> The first allows synthesizing materials homogenous at the molecular level, which have a long lifetime and high dielectric breakdown and show no stress softening. Up to now, a number of various polar groups with different concentrations have been tested for the functionalization of polysiloxanes.<sup>[53]</sup> However, some materials show high permittivity only at a very low frequency, due to electrode polarization and increased conductivity, while others do not give an attractive increase in permittivity. For some polymers, the properties were measured in a non-crosslinked state. Cross-linking is crucial for achieving elastic materials. However, it is often a great challenge to cross-link films with defined thickness and upscale the process.

Recently, we have developed a simple two-step process towards high permittivity elastomers.<sup>[307]</sup> Less than a stoichiometric amount of polar thiol to vinyl was grafted to polyvinylsiloxane, leaving around 2.3% of unreacted vinyl side groups. That allowed us to purify the polar polysiloxane and investigate its structure. The synthesized polymer was processed into thin films, which were cross-linked on demand by a thiol-ene addition reaction induced by UV light. Elastomers with a permittivity as high as 18 were obtained. Variation of cross-linking density allowed to fabricate elastomers with high breakdown strength and a huge out-of-plane actuation.

Motivated by the high dielectric permittivity of the liquid polysiloxane functionalized with 2-(methylsulfonyl)-ethanethiol,<sup>[250]</sup> here we wish to explore the possibility of achieving crosslinked elastomers and investigate their potential in applications. For this, a highly efficient thiolene addition reaction on a polar siloxane bearing around 95% polar sulfonyl side group and a few vinyl groups was successfully used for cross-linking. This was achieved using two different kinds of multifunctional thiols. The glass transition temperature, the dielectric, mechanical and electromechanical properties were investigated.

## 5.3. Experimental Section

#### Materials

Unless otherwise stated, all chemicals were reagent grade and used without purification. 1,3,5,7-Tetramethyl-1,3,5,7-tetravinyl cyclotetrasiloxane (V<sub>4</sub>) was purchased from ABCR. 2,2-Dimethoxy-2-phenylacetophenone (DMPA), 2,2'-(ethylenedioxy)diethanethiol, benzene, toluene, sodium hydroxide, tetramethylammonium hydroxide 25% in MeOH (TMAH), hydrochloric acid, and thioacetic acid were purchased from Aldrich. Methanol, dimethylsulfoxide (DMSO), acetonitrile (ACN) and tetrahydrofuran (THF) were purchased from VWR. As a sacrificial layer, a solution of PVA in isopropanol/2-butanol from Suter Kunststoffe AG was used. Elastosil films with a thickness of 200  $\mu$ m were purchased from Wacker. Polymethylvinylsiloxane (PV) (M<sub>n</sub> = 105'480 Da, M<sub>w</sub> = 375'000 Da, PDI = 3.55) and 2-(methylsulfonyl)-ethanethiol were prepared according to the literature.

#### Characterization

<sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded at 298 K on a Bruker Avance 400 NMR spectrometer using a 5 mm broadband inverse probe at 400.13 and 100.61 MHz, respectively. Chemical shifts ( $\delta$ ) in ppm are calibrated to residual solvent peaks (CDCl<sub>3</sub>:  $\delta$  = 7.26 and 77.16 ppm). Sizeexclusion chromatograms were taken with an Agilent 1100 Series HPLC (Columns: serial coupled PSS SDV 5 µm, 100 Å, and PSS SDV 5 µm, 1000 Å; detector: DAD, 235 nm and 360 nm; refractive index), with THF as mobile phase. PDMS standards were used for the calibration and toluene as an internal standard. As UV source a Hönle UVA HAND 250 GS UV lamp was used. DSC investigations were undertaken on a Perkin Elmer Pyris Diamond DSC instrument. Two heating and one cooling steps with a heating and cooling rate of 20 °C min<sup>-1</sup> in the temperature range of -90 to 50 °C were conducted per measurement under a nitrogen flow (50 mL min<sup>-1</sup>). The second heating step was considered for the evaluation of the T<sub>q</sub>. About 10 mg sample was weighted in aluminum crucibles shut with pierced lids. The tensile tests and the cyclic uniaxial tensile stress tests were performed on a Zwick Z010 tensile test machine with a crosshead speed of 50 mm min<sup>-1</sup>. Tensile test specimens with a gauge width of 2 mm and a gauge length of 18 mm were prepared by die-cutting. The strain was determined over the traverse moving sensor. The curves were averaged from three different samples per material. The tensile modulus was determined from the slope of the stress-strain curves using a linear fit to the data points within 10% strain. Dynamic mechanical analysis was carried out on a RSA 3 DMA from TA Instruments. Stripes of 10 mm × 25 mm were measured under a dynamic load of 2 g, at 2% strain in the frequency range of 0.05–10 Hz at 25 °C and 65% humidity. Permittivity measurements were done in the frequency range of 0.1 Hz to 1 MHz using a Novocontrol Alpha-A Frequency Analyzer. The VRMS (root mean square voltage) of the probing AC electric signal applied to the samples was 1 V. The samples were squeezed between two electrodes (diameter of 20 mm). The actuation strain was measured optically as the extension of the diameter of the electrode area via a digital camera, using an edge detection tool of a LabView program to detect the boundary between the black electrode area and the transparent silicone film. Circular electrodes (8 mm diameter) of carbon black powder were applied to each side of the film. A FUG HCL-35-12500 high voltage source served as a power supply for actuator tests. For the thick actuators (above 80  $\mu$ m) 5% of prestrain was applied. Thinner actuators prepared using sacrificial PVA layer were not prestrained. The sensors were tested using commercial traction sliding machine Zaber A-LSQ300A-E01 for stretching, while for capacitance measurement Keithley DMM6500 was utilized. As electrode material, commercially available Elastosil<sup>®</sup> LR 3162 a/b from Wacker was used. It was prepared by blade casting the mixture of two components and its subsequent cross-link at 100 °C for 2 h and drying at 60 °C in the vacuum oven.

# General synthesis of polysiloxane containing 95% 2-(methylsulfonyl)-ethanethiol and 3.3% of vinyl groups (**ES**)

PV (10 g, 0.116 mol repeat units, 1 eq.), 2-(methylsulfonyl)-ethanethiol (15.43 g, 0.11 mol, 0.95 eq.) and DMPA (0.297 g, 1.16 mmol, 0.01 eq.) were dissolved in the mixture of ACN:THF (1:1.5, 250 ml). The reaction mixture was degassed three times using the freeze-pump-thaw technique and irradiated for 20 min with UV light. The solution was concentrated with a rotary evaporator, and the polymer was purified three times by dissolving it in ACN and precipitating in methanol. Some solvent was removed at rotary evaporator and ACN was added and the concentration of polymer was adjusted to 60 wt%.

#### Formation of polar elastomers (**ESX**)

Polymer **ES** (1.67 g) was mixed with a certain amount of cross-linker (for amounts, see Table 5.1) and DMPA (4.5 mg). The obtained mixture was centrifuged for 2 min at 6000 rpm to remove the bubbles. Thick films (>80  $\mu$ m) were cast directly on Teflon substrate, while thin films were cast on a glass coated with a sacrificial PVA layer. Thick films were kept in air for 30 min and then cross-linked by irradiation with UV light for 5 min, and dried 12 hours in the vacuum oven at 60 °C.

### 5.4. Results and discussions

Encouraged by the high dielectric permittivity of 22.7 at 10 kHz measured for an uncross-linked polysiloxane modified at every repeat unit with a 2-(methylsulfonyl)-ethanethiether, here we wish to explore the possibility of cross-linking such polymers to elastomers with useful mechanical, dielectric, and electromechanical properties and to explore their potential in different applications.

The synthesis starts from a polymethylvinylsiloxane (PV) ( $M_n = 105'480$  Da,  $M_w = 375'000$  Da, PDI = 3.55), which was reacted with 2-(methylsulfonyl)-ethanethiol (**1**) via thiol-ene reaction (Scheme 5.1). Our previous attempts to synthesize a polysiloxane fully functionalized with polar thiol **1** showed that the functionalized polymer is not completely soluble in THF. Therefore, the thiol-ene addition of thiol **1** to PV was conducted using a mixture of THF and DMSO, which allowed dissolving both the starting PV and the modified polymer. Incomplete functionalization of PV using less than stoichiometric amount of thiol was successful, giving

polymer **ES**, which has around 3.3% unreacted vinyl groups (Scheme 1). Our attempts to remove the high boiling DMSO at reduced pressure and elevated temperature were unsuccessful. Insoluble particles formed and the polymer solution turned dark. This may indicate that the vinyl groups of **ES** may be involved in an unwanted cross-linking reaction.



Scheme 5.1 Synthesis of polysiloxanes **ESX** containing polar side groups and their cross-linking into elastomeric films.

Therefore, the solvent used for the synthesis was replaced by ACN. This allowed us to achieve **ES** as a transparent yellowish solution after purification. <sup>1</sup>H NMR spectrum of **ES** shows typical signals of the polar thioether groups and small signals at about 6 ppm for the vinyl groups (Figure 5.2). The obtained polymer is highly viscous, and to turn it elastic, cross-links have to be introduced. For this, again, a thiol-ene reaction was used since it is fast and insensitive to atmospheric conditions. For cross-linking, different amounts of 2,2'-(ethylenedioxy)diethanethiol (CL2) and pentaerythritol tetrakis (3-mercaptopropionate) (CL4) cross-linkers were used. The formed elastic materials are denoted as ESX. For the amounts of reagents used, see Table 1. The obtained materials were subjected to the tensile tests and DMA. Figure 5.1a shows the average stress-strain curves for six different materials ES1-ES6. The stress-strain curve is the average of three different samples (Figure 5.3). Materials ES1 to ES3 prepared using an increasing amount of CL2 show a decrease in the strain at break from 135.8% to 52.5% and an increased Young's modulus from 270 kPa to 628 kPa for ES1 to **ES3**, respectively. DMA measurements (Figure 5.1c) show that the storage modulus E' increases from 235 kPa for **ES1** to 518 kPa for **ES3**, while the mechanical loss factor tan  $\delta$  decreases from 0.166 for material ES1 to 0.04 for ES3. However, when a larger amount of CL2 was used, as was the case for **ES4**, a decrease in Young's and storage modulus and an increase in the tensile strain to 114.3% was observed, but *tan*  $\delta$  has increased 0.1.

When **CL2** was replaced with **CL4**, a drastic increase in Young's modulus was observed. Materials **ES5** and **ES6** were prepared with **CL4**, for which the number of reactive mercapto groups in **CL4** was equal to the number of mercapto groups in **CL2** as in **ES2** and **ES3**, respectively. Young's modulus of **ES5** and **ES6** increased to 863 kPa and 1100 kPa, whereas **ES2** and **ES3** showed Young's modulus of 551 kPa and 628 kPa, respectively. This indicates a higher cross-linking density in materials **ES5** and **ES6**. A similar increase was observed for the storage modulus, while the *tan*  $\delta$  decreased to 0.058 for **ES5** and 0.026 for **ES6**. For the latter, it became close to the value of Elastosil, a commercial polydimethylsiloxane elastomer (*tan*  $\delta$  = 0.018). However, **CL4** negatively affected the tensile strength, which was reduced to 55.8% for **ES5** and 38.8% for **ES6**. Also, it should be mentioned that contrary to Elastosil, which mechanical parameters are stable within the whole frequency range, the loss factor, E' and E'' of materials **ES1** to **ES6** showed a substantial rise with increasing the frequency. That indicates the frequency-dependent nature of the materials with more pronounced viscoelastic behavior at higher frequencies. For our subsequent investigations, two materials with the lowest loss factor and better elastic properties were chosen: **ES3** and **ES6**.

strain at bre	eak (s <sub>av</sub> ), storage mo	odulus (E'), and <i>tan</i> δ	<b>.</b>			
Name	CL2ª [μΙ]	CL4ª [μΙ]	۲ <sub>10%</sub> [kPa]	S <sub>av</sub> [%]	E' @ 0.05 Hz [kPa]	<i>tan</i> δ @ 0.05 Hz
ES1	25 <sup>b</sup>		270	135.8	235	0.166
ES2	50 <sup>b</sup>		551	91.3	382	0.082

628

318

863

1100

52.5

114.3

55.8

38.8

518

238

697

1005

0.04

0.1

0.058

0.026

Table 5.1: Amount of reagents used for the synthesis of **ESX** and their Young's modulus ( $Y_{10\%}$ ), average strain at break ( $s_{av}$ ), storage modulus (E'), and *tan*  $\delta$ .

100<sup>b</sup>

200<sup>b</sup>

ES3

ES4

ES5

ES6

<sup>a</sup>A 20 vol% solution of CL1 and CL2 in THF was used, <sup>b</sup>volume of CL1 and CL2 solution in THF ( $\mu$ l) added to **ES** (1 g).

58<sup>b</sup>

117<sup>b</sup>



Figure 5.1 (a) Average stress-strain curves of elastomers **ES1-ES6**. (b) DSC of samples **ES3** and **ES6**. (c) DMA of materials **ES1-ES6** in comparison with Elastosil Film. (d) Dielectric properties (permittivity ( $\epsilon$ '), dielectric loss ( $\epsilon$ ''), conductivity ( $\sigma$ '), and *tan*  $\delta$ ) as a function of frequency for the two most promising materials **ES3** and **ES6**.

The glass transition temperature of samples **ES3** and **ES6** was evaluated using DSC (Figure 5.1b). As expected, due to the high polarity of sulfonyl groups, the  $T_g$  of the modified polymer is approaching 0 °C. Materials **ES3** and **ES6** have a  $T_g$  of -13.6 °C and -12.2 °C, respectively. These values are slightly higher than the reported  $T_g$  of the uncross-linked **ES**.<sup>[250,306]</sup> This

increase for cross-linked **ESX** is expected since the flexibility of polymer chains decreases upon cross-linking.

The thermal stability of the chosen samples was investigated by TGA analysis. Figures 5.17 and 5.18 show that both materials are stable up to 300 °C, while at 410 °C, about 48.5% of elastomer's weight is lost.

Dielectric properties of materials **ES3** and **ES6** were investigated at different frequencies in a wide temperature range from -100 to +100 °C (Figure 5.4). Due to the high  $T_g$ , the permittivity of both materials stays around 5 at 10 kHz up to -20 °C, because the dipoles are frozen. Above  $T_g$ , the mobility of the polymer chains increases significantly, and the dipoles can orient in an electric field and therefore contribute to the permittivity. Both samples showed increased permittivity at 20 °C up to 18.4 at 10 kHz (Figure 5.1d). At low frequencies, a steep increase of permittivity is observed, which is attributed to electrode polarization due to the accumulation of ions at the electrode-sample interface. The conductivity of samples is relatively low,  $5 \times 10^{-10}$  S cm<sup>-1</sup>, which is attractive for application in DEAs.

Electromechanical tests of materials ES3 and ES6 were conducted using both thick and thin dielectric films. A thick film actuator (101 µm) made of ES3 showed 1% lateral actuation strain at only 200 V and 0.25 Hz (Figure 5.5), which corresponds to an electric field of about 2 V/ $\mu$ m. Another actuator (98 µm) showed 2% strain at 300 V (3 V/µm) (Figure 5.6a). However, three actuators made of this material did not show a better actuation at a higher voltage. A typical behavior at a higher voltage can be observed in Figure 5.6, while many other tests are not presented, because they don't show good actuation. When 500 V was applied at 0.25 Hz to the 98 µm thick actuator, the actuation strain diminished after several cycles and the actuator was not able to relax back to its initial strain. Similar behavior was detected with the 101 µm thick actuator at 300 V (Figure 5.5). Another typical behavior was observed in several actuators when a 100 V step every 2 s was applied up to 1000 V (Figure 5.5 and 5.6). The actuators showed 0.75% actuation at 300 V, however, when the voltage was increased further to 1000 V, the lateral actuation strain did not increase, but rather stayed at the same value. In both cases, no increase in the leakage current was observed, which indicates that the actuators did not suffer a dielectric breakdown. Additionally, after the voltage is removed, the actuator does not relax back immediately, but within 5 s. The leakage current during all measurements was constant in the range of 4  $\mu$ A.

Thick actuators made of **ES6** showed a slightly better performance than **ES3**. A 100  $\mu$ m thick actuator displayed almost 2% actuation strain at 500 V (5 V/ $\mu$ m) and 0.5 Hz (Figure 5.7a). This actuator also showed a stable actuation over 1000 cycles at 500 V and 0.5 Hz. When the voltage was increased to 600 V, the actuation strain increased to almost 3% at 0.25 Hz but decreased to 2.3% at 0.5 Hz (Figure 5.7b). At 1 Hz, the actuation strain showed even higher lessening to around 1.8%, while at 5 Hz, only 1% strain was detected and the actuator didn't have sufficient time to relax back to its initial state. When the voltage was increased to 1000 V, an actuation of 4% was detected at the beginning. However, within 100 cycles, a significant decrease in actuation strain together with drifting of the baseline was observed (Figure 5.7c), similar to the behavior of material **ES3**. Also here, no increase in the leakage current was measured. A similar

tendency at the same voltage was observed for another actuator constructed from material **ES6** (Figure 5.8). A 99  $\mu$ m thick actuator exhibited 2.5% strain at 600 V at 0.25 Hz. With increasing the voltage to 800 V, the actuation strain also increased to 3.5%. However, at 1000 V, deterioration of the actuation strain was observed, as it is shown in Figure 5.8b. Interestingly, there is no increase in the leakage current. The leakage current was below 5  $\mu$ A for both actuators, indicating that no breakdown happened in the material. Further application of a lower voltage (600 V) even at 0.125 Hz to the same actuator showed the same trend: low actuation strain during the five cycles with subsequent deterioration of actuation. The third actuator with a thickness of 101 µm showed even worse performance (Figure 5.9). While at 300 V, an actuation of around 1.8% was detected, a further increase in voltage to 500 V resulted in deterioration of the actuation strain after 50 cycles. In Figure 5.9, it can be observed that after the second measurement, it was still possible to do additional measurements. However, even at a lower frequency of 0.16 Hz, the actuator didn't have enough time to relax (Figure 5.9). When a 100 V step was applied up to 1400 V (13.86 V/ $\mu$ m), the actuator showed almost 1.5% actuation at 500 V, followed by a gradual decrease to 0.8% when the voltage increased to 1400 V. When the actuator was subjected to 1500 V for 20 s voltage, the actuator was not able to keep a constant actuation. Initially, the actuation strain was almost 3%, while within 20 s, it gradually decreased to 1% (Figure 5.9b). During the measurements, the leakage current was always below 5 µA. Similar to ES3, from two measurements in Figure 5.9b it can be concluded that the actuator needed at least 5 s to relax back after the voltage was removed.

Contrary to thick films, thin-film actuators exhibited much better performance with a larger actuation strain. Thus, an actuator made of material **ES3** with a thickness of 35  $\mu$ m showed a 9.5% stable actuation strain within 100 cycles at 350 V and 0.25 Hz. Also, thin actuators made from **ES3** showed a strong frequency dependence response (Figure 5.10a). The actuation at 350% decreased from 9.5% to 7.5%, to 4.5% and 2% when the frequency increased from 0.25 Hz to 0.5 Hz, to 1 Hz, and 5 Hz, respectively. The largest actuation strain of 12% at 11.4 V/ $\mu$ m was detected at a frequency of 0.25 Hz and 400 V (Figure 5.10b). At 0.5 Hz and 400 V, the actuator showed a stable actuation of 9% within 1000 cycles (Figure 5.10c). However, when the voltage was increased to 500 V, after a few cycles where actuation was observed, the actuation deteriorated (Figure 5.10d). Neither breakdown nor increase in current leakage, which stayed below 5  $\mu$ A, were observed. Subsequent application of 400 V to the same actuator did not produce any actuation. However, when the voltage was decreased to 300 V, a small actuation of around 3% was measured (Figure 5.10e).

Another actuator with a thickness of 33  $\mu$ m showed an even larger actuation strain and withstood higher voltages (Figure 5.11). In the beginning, it exhibited 9% strain at 600 V and 0.25 Hz and showed a similar decreasing of actuation strain trend with increasing the frequency. However, after measuring 100 cycles at 1 Hz and 5 Hz, and again 1000 cycles at 1 Hz, measurement at 600 V and 0.25 Hz resulted in a decrease of actuation to 7.5% strain. Nevertheless, the subsequent increase in voltage led to actuation strain up to 14% at 800 V and 0.25 Hz. Applying higher frequency twice smaller actuation strain was observed at the same voltage: 7% at 5 Hz.

However, not all thin-film actuators made of material **ES3** showed good performance. An actuator with a thickness of 35  $\mu$ m had 3% actuation strain at only 200 V (5.7 V/ $\mu$ m) (Figure 5.12) and didn't show larger actuation at a higher voltage. Contrary, during the step voltage increase test, it showed around 1.1% actuation, which started at 200 V, and then actuation was gradually increased to only 2.2% at 40 V/ $\mu$ m. Similar behavior was also detected for another 32  $\mu$ m thick actuator. During the first step voltage increase test, the maximum applied voltage was 1400 V. At 500 V (15.6 V/ $\mu$ m), the actuator showed a drastic increase in actuation up to 3% strain, and then no further increase was observed. The final voltage applied was 2800 V within the second measurement, corresponding to 87.5 V/ $\mu$ m. Again, a drastic increase in strain up to 3% appeared at 500 V, and almost no subsequent increase in actuation was detected until 2800 V. But the actuation strain rather first drop to around 2% when the voltage reached the value of 1500 V, and then it increased to 3.25% strain at 2800 V. As it can be seen from Figure 5.12, the leakage current during this measurement was below 5  $\mu$ A.

Thin-film actuators made from material **ES6** showed worse performance than material **ES3**. A very small actuation strain of 1.5% was observed for actuators made of this material at 200-400 V. The higher Young's modulus may explain the lower actuation for **ES6**. The actuators show only 1.5-2% strain at higher voltages and stay near this value until the measurement is completely stopped (Figure 5.13).

A possible reason for the bad actuation of many actuators could be their operation at a temperature not far from  $T_{q}$ . Because materials **ES3** and **ES6** in actuation tests were operated at a temperature 30 °C above the  $T_{q_i}$  we decided to test how the actuation is influenced by temperature. Figure 5.14 represents results of a thin-film actuator (36 µm) tested at temperatures from 5 °C to 40 °C and 400 V. First, the actuator was tested at RT at 0.25 Hz (Figure 5.14a), giving 5.3% strain and complete relaxation to 0% strain after voltage removal. At 1 Hz the actuator was also able to achieve 5.3% strain, but because it was not able to follow such frequency completely, relaxation to 0.7% strain was observed during the actuation. Then the surrounding temperature was slowly increased to 40 °C. When the temperature reached 30 °C, a measurement at 0.25 Hz was started. The actuator showed 7.6% strain during 50 working cycles. However, when the temperature reached 40 °C, only 6% strain was observed during the actuation at 0.25 Hz. Surprisingly, during the second measurement at a higher frequency (1 Hz), a higher actuation strain of 6.9% was obtained, while the relaxation to 0.5% strain was observed. The actuator was also able to show around 4.8% strain at 5 Hz, increasing the baseline to 0.85% strain. After this measurement, the heating was turned off and the actuator was cooled to RT. Around 6% strain was detected at RT and 0.25 Hz and 400 V, which was rather similar to the initial actuation (Figure 5.14b). After that, the actuator was tested at lower temperatures. Under 400 V at 0.25 Hz and 10 °C the actuator gave 5.2% actuation, while the baseline has increased to 1.22%, which shows that the actuator cannot relax back to the initial shape. The same measurement was repeated and gave about the same result: actuation of 5.9% strain and a baseline of 1.7%. When the temperature decreased to 5 °C, an almost similar result was obtained at 0.25 Hz. Increasing the frequency to 1 Hz resulted in a reduction

of actuation to 4.5% strain and in an increase of the baseline to 2.2%. Finally, at 5 Hz the actuation has a pattern as is presented in Figure 5.14b.

The possible reason for a reduced actuation strain at lower temperatures could be a significant increase of Young's modulus. Therefore, a DMA test at different temperatures for material **ES3** was performed (Figure 5.16). The obtained results show more than three times increase in Young's modulus at 10 °C compared to 40 °C. On the other hand, the inability of material to follow the electric field and relax back to 0% strain during the measurement is most probably attributed to the operation of the material above the frequency at which relaxation of dipoles occurs. Thus, according to the *tan*  $\delta$  *versus* frequency graph in Figure 5.19, at 10 °C and around 0.25 Hz, material **ES3** has the highest *tan*  $\delta$ , which means that at this frequency, the dipoles are not completely oriented and cannot completely follow an applied electric field.

The leakage current and the breakdown strength of materials **ES3** and **ES6** were also tested in a separate measurement by placing the material between two metallic electrodes with 1 mm<sup>2</sup> size. The voltage was gradually increased until the breakdown. At least ten samples with thickness in the range of 100-130  $\mu$ m for each material were tested. Both materials showed a constant leakage current of 2-3  $\mu$ A until the voltage was close to the breakdown voltage. Then, sometimes the current increased to 4-8  $\mu$ A for a voltage that was 100-200 V lower than the breakdown, while in other cases, the breakdown just happened abruptly. The average breakdown strength of **ES3** is 26.4 V/ $\mu$ m and for **ES6** it is 30.4 V/ $\mu$ m.

Another possible application of the obtained polymers could be stretchable sensors. However, this requires elastomers with higher tensile strength. Material **ES2** serves best such an application because it has better tensile strength than material **ES3** and **ES6**. For the preparation of sensors, one layer of material **ES2** was covered from both sides with cross-linked electrodes Elastosil<sup>®</sup>. The active sensing area (where electrodes overlap each other) had the following dimensions:  $25 \times 10 \times 0.2$  mm. VHB<sup>M</sup> 4910 film from 3M was used to insulate the sensor and to increase its mechanical stability.

Each sensor was cycled 10 times at 10%, 20%, 40%, 50%, 60%, 70%, and 80% strain. From each measurement, the average capacitance at a defined strain was taken. The average capacitance in unstrained form was subtracted from the capacitance value of the strained sensor to give  $\Delta C$ . Figure 5.15a shows the  $\Delta C$  *versus* applied strain. The slopes of sensors made of **ES2** and PDMS were 1.83 pF and 0.29 pF, respectively. An enhancement of more than six times in sensitivity is observed for material **ES2**. Figure 5.15b presents the result of measurement at which the sensor was stretched 10 times to 80% strain and shows a constant maximum value. Additionally, the sensor was subjected to 100 cycles at 50% strain (Figure 5.15c). It showed a stable change in capacitance within the whole measurement from around 215 pF in relaxed form to 290 pF in the strained form.
# 5.5. Conclusion

We have shown that polysiloxane bearing methyl sulfone side groups can be successfully crosslinked into thin-film elastomers using a thiol-ene addition reaction. An elastomer with permittivity as high as 18.4 at 10 kHz and 20 °C was obtained, while the conductivity value was in the range of  $5 \times 10^{-10}$  S cm<sup>-1</sup>. The best actuator showed actuation of 14% at 24.2 V/µm and 0.25 Hz, while at 18.2 V/µm and 1 Hz it had a stable actuation of 8%. Due to the high glass transition temperature (around -12 °C), the material exhibited a strong frequency-dependent actuation, giving almost two times reduction in actuation strain when the frequency is increased from 0.25 Hz to 5 Hz. During the actuation tests at different temperatures, it was found, that at temperature 40 °C almost the same actuation strain at 5 Hz can be achieved as at 5 °C and 0.25 Hz while reducing the frequency results in a higher strain. Additionally, the material was tested in application as a capacitance sensor. It showed six times higher sensitivity compared to conventional silicone rubber, and stable capacitance detection within 100 cycles of stretching to 50% strain. However, as of now, we cannot explain the behavior of thick actuators at increased frequency. More investigations are needed to clarify whether or not the electrochaloric effect plays a role here.

# 5.6. Supporting Information



Figure 5.2 <sup>1</sup>H NMR spectrum of polysiloxane functionalized with 2-(methylsulfonyl)-ethanethiol side groups (60 wt% in acetonitrile).



Figure 5.3 Stress-strain curves of elastomers **ES1-ES6**. The red curve in each graph is the average of several measurements.



Figure 5.4 Dielectric permittivity ( $\epsilon'$ ), dielectric loss ( $\epsilon''$ ), conductivity ( $\sigma'$ ), and *tan*  $\delta$  of **ES3** (left) and **ES6** (right) at different temperatures and frequencies.



Figure 5.5 Actuator made of material **ES3** with thickness 101  $\mu$ m. Four of more than ten measurement are presented, which describe the typical behavior of this actuator. First, the measurements were done at 200 V. When voltage was increased to 300 V, deterioration of actuation happened. Subsequent application of 800 V didn't result in a higher actuation strain.



Figure 5.6 Actuators made of material **ES3** with a thickness of a) 98  $\mu$ m and b) 108  $\mu$ m. The first actuator (a) was cycled at 0.25 Hz and 300 V for 100 cycles, showing around 2% strain. During the second test at large voltage, deterioration of actuation happened. The actuation strain decreased from 2% to 0.75%, and the actuator was not able to follow the applied voltage at 0.25 Hz. In the third measurement, the voltage was increased every 2 s in a step of 100 V up to 1000 V. Another actuator (b) showed only 0.5% strain at around 200 V, and then the strain was constant until 1000 V.



Figure 5.7 Actuation of a 100  $\mu$ m thick actuator made of material **ES6**: a) 1000 cycles at 0.5 Hz and 500 V; b) 100 cycles at 600 V and different frequencies; c) degradation of the actuation strain at 1000 V and 0.25 Hz within 100 cycles.



Figure 5.8 Actuation of a 99  $\mu$ m thick actuator made of material **ES6**: a) stable actuation over 100 cycles at 600 V and 800 V and 0.25 Hz; b) degradation of actuation during the 100 cycles test at 1000 V and 0.25 Hz, and subsequent bad actuation at 600 V and 0.125 Hz.



Figure 5.9 Actuation of a 101  $\mu$ m thick actuator made of material **ES6**: a) a 1.8% strain is detected at 300 V and 0.25 Hz. Increasing the voltage to 500 V resulted in deterioration of actuation. Subsequent application of 500 V at lower frequency (0.16 Hz) resulted in 1.8% actuation, but it can be seen that the actuator doesn't have enough time to relax back to the initial state; b) step voltage increase measurement up to 1500 V and a constant application of 1500 V withing 20 s.



Figure 5.10 Actuation of a 35  $\mu$ m thick actuator made of material **ES3**: a) cyclic actuation test at 350 V and different frequencies: 0.25 Hz, 0.5 Hz, 1 Hz and 5 Hz; b) 12% actuation strain during 100 cycles at 400 V and 0.25 Hz; c) 9% actuation strain within 1000 cycles at 400 V and 0.5 Hz; d) deterioration of actuation after increasing the voltage to 500 V; e) actuation at lower voltage shows that the actuator shows different behavior.



Figure 5.11 Actuation of a 33  $\mu$ m thick actuator made of material **ES3**: a) actuation at 600 V and different frequencies; b) actuation at 800 V and different frequencies; c) photo of the actuator in relaxed and actuated (800 V, 0.25 Hz, 20c) states.



Figure 5.12 Two actuators made of thin films of **ES3**, which did not perform well: a) with thickness 35  $\mu$ m; b) with thickness 32  $\mu$ m.



Figure 5.13 Bad performance of actuators made of **ES6**: a) 34  $\mu m$  film; b) 33  $\mu m$  film.



Figure 5.14 A 36  $\mu$ m thick actuator made from **ES3** which was tested at 400 V a) in the temperature range from RT to 30 °C and 40 °C; b) in the temperature range from RT to 10 °C and 5 °C.



Figure 5.15 a) Change in capacitance with strain for **ES2** and PDMS. b) 10 cycles at 80% strain. c) Stability test of a sensor made of material **ES2**: 100 cycles at 50% strain.



Figure 5.16 Temperature-dependent DMA of **ES3** at 1 Hz.



Figure 5.17 TGA curve of ES3



Figure 5.18 TGA curve of ES6



Figure 5.19 Dielectric permittivity ( $\varepsilon'$ ), dielectric loss ( $\varepsilon''$ ), conductivity ( $\sigma'$ ), and *tan*  $\delta$  of **ES3** at 0-40 °C.

## **CHAPTER SIX**

# 6. Conclusions

To date, many research works have been published on improving the dielectric properties of siloxanes. The chemical functionalization of polymers with polar groups is considered to be among the best approaches due to the possibility of obtaining homogeneous materials with both optimized dielectric and mechanical properties. However, due to the large number of polar groups available, the possible variation of their concentration, different starting materials, and chemistries employed for functionalization, it is difficult to compare the properties of different polymers across different studies and to select the most suitable polar group for a given DET application.

This thesis aimed to systematically investigate the extent to which chemical modification using different dipolar functional groups and the variation of their concentrations affects the dielectric properties and glass transition temperature of polysiloxanes. The aim was to synthesize and characterize such polymers under the same conditions and thus to achieve reliable data that may allow for structure-property relation evaluations. The most promising polar polymers were cross-linked into elastomers, and actuators responsive at unprecedented low voltages were fabricated.

In Chapter 2, a systematic study of the effect of 13 polar groups on the corresponding properties of siloxane was conducted. First, appropriate starting reagents and chemical reactions were carefully chosen, and five end-blocked polysiloxanes with a molar mass of about 12 kDa and a vinyl group content from 20% to 100% were synthesized. For the subsequent functionalization of the polysiloxanes with polar groups, the highly efficient thiol-ene addition reaction was employed, resulting in a library of 63 polymers with systematically varied amounts of different dipolar groups. We found that, with increasing the dipole strength of the polar groups, an increase in dielectric permittivity usually increase almost linearly with an increasing amount of polar groups. However, polar groups attached via a flexible spacer between the dipole and the polymer backbone afforded polymers with a lower  $T_g$  and high permittivities. The polysiloxane functionalized with 4-((2-mercaptoethyl)thio)-1,3-dioxolan-2-one exhibited the highest permittivity of 27.7 at 10 kHz, the ionic conductivity of 2.10×10<sup>-9</sup> S/cm, and a  $T_g$  of -18 °C. However, not only the permittivity and the  $T_g$ , but also the conductivity and chemical

stability of polymers have to be taken into account when selecting a polymer for future use. Based on these considerations, only the polar polymers functionalized with 3mercaptopropionitrile, *N*,*N*-dimethyl-3-mercaptopropanamide, and 2-(methylsulfonyl)ethanethiol were considered promising for dielectric applications.

Many polar siloxanes cannot be cross-linked by conventional methods developed for PDMS. Therefore, a new cross-linking strategy was developed for polar siloxanes as part of Chapter 3. Using a sub-stoichiometric amount of thiol to vinyl groups during functionalization, we prepared polar polysiloxane containing some unreacted vinyl groups used in a subsequent cross-linking by a thiol-ene reaction with multifunctional thiols as cross-linkers. This strategy allowed us to tune the elastomers' mechanical, electrical, and electromechanical properties. Among other examples, an elastomer with nitrile side groups exhibited a  $T_g$  of -46 °C, a permittivity of 18 at 10 kHz, a breakdown strength of 19 V/µm, and a Young's modulus of 462 kPa. Actuators made of this material exhibited self-healing properties and achieved 7.5% actuation strain at only 300 V (8.7 V/µm), while a visible actuation at 200 V was also detected.

In Chapters 4 and 5, the same synthetic procedure was then applied for grafting N,N-dimethyl-3-mercaptopropanamide and 2-(methylsulfonyl)-ethanethiol to polyvinylsiloxane and subsequent cross-linking into thin films. The polar siloxane modified with amide groups when cross-linked gave elastomers with a  $T_g$  of -41 °C and a permittivity of 21 at 10 kHz. It was observed that, with an increasing amount of cross-linker, the Young's modulus initially increases but passes through a maximum and then decreases again. The opposite trend was observed for strain at break. A possible explanation is that, when the amount of mercapto groups in the cross-linker is below or similar to that of vinyl groups, the modulus increases and strain at break decreases due to the formation of a network with a larger cross-linking density. Similar trends were also observed for materials functionalized with the methyl sulfone side group. However, elastomers functionalized with methyl sulfone side groups exhibited a one order of magnitude higher viscous loss than those modified with amide groups. This could result from the higher  $T_q$  (-12 °C) of the former materials. Elastomers with both polar groups were also subjected to electromechanical tests. Amido-functionalized elastomer showed around 1.5% actuation strain over 450 000 cycles at low electric fields (2.9-3.6 V/µm) and 10 Hz. The best material exhibited 10% strain at 0.25 Hz and 500 V (7.6 V/ $\mu$ m). The breakdown strength of this material during the actuation tests was 10.4 V/µm. For elastomer fabricated from sulfone-based siloxane, maximum actuation of 14% strain was achieved at 800 V  $(24.2 \text{ V}/\mu\text{m})$  and 0.25 Hz. The breakdown strength of this polymer during the actuation test was as high as 87.5 V/µm. Finally, the two types of polar elastomers were also used in stretchable capacitive sensors, apart from actuators. It was shown that both types of material exhibited six times higher sensitivities compared to PDMS and can exhibit a stable operation within 100 cycles.

Polysiloxanes functionalized with nitrile groups were considered the most suitable for application in DETs, and were utilized to fabricate a prototype of a stack actuator. After optimization of the employed molecular weight for better processing, three techniques for fabricating stack actuators were tested (Figure 6.1): slot-die coating, manual stacking of

preformed dielectric films, and doctor blading of several layers. The electrodes were applied by spray coating through a mask. Only the slot-die coating technique allowed for the fabrication of a stack actuator without any visible defects. In other approaches, many defects can be observed due to dust. A stack actuator consisting of 5 dielectric layers with a thickness of 1250  $\mu$ m actuated at 800 V showed a maximum actuation of 24  $\mu$ m in thickness change at 1000 V, which corresponds to almost 2% strain.



Figure 6.1 Small stack actuators prepared by a) slot-die coating (1250 µm, 5 layers, all active); b) manual stacking (8 layers, all active); c) doctor blading (3 layers, 2 active). Blue circles indicate the visible defects.



Figure 6.2 Actuation measurement of stack depicted in Figure 6.1a at 1000 V.

Based on the results of this thesis project, it can be concluded that the goals set at the beginning of this thesis were successfully implemented. Among the 13 polar siloxanes evaluated under similar conditions, three can be considered to be highly promising materials for applications in DETs, based on a combination of the stability of the functionalized polymers, high permittivities, low conductivities, and glass transitions significantly below the room temperature. Among these polar polysiloxanes, those containing nitrile side groups exhibit the lowest  $T_g$  and conductivities, while still having high permittivities. These materials also show a more stable actuation within wider frequencies and very low actuation voltages, giving the largest actuation strain. The polar group exhibits high stabilities, and the polymer could be stored at ambient conditions for a long time. Preliminary results showed that the materials can be processed by different techniques into thin films as well as into a stack actuator consisting of several single layers stacked on top of each other. The resulting stacks can be actuated at voltages below 1000 V, showing perspectives of synthesized polar siloxanes for application in DETs.

## **CHAPTER SEVEN**

## 7. Outlook

The field of dielectric elastomer transducers is rather diverse and there are several unsolved issues and unanswered questions. One of them is related to the deeper analysis of the dielectric properties and factors responsible for increasing the dielectric permittivity in polar polymers. So far, dielectric characterizations are typically conducted at room temperature. However, analyzing the dielectric properties over a broader temperature range will help identify the nature of the underlying relaxation processes in polymers at different frequencies and temperatures and how they contribute to permittivity, conductivity, and dielectric loss in the materials.

Other issues are related to the obtained elastomers and their glass transition temperatures. For instance, actuators made of polysiloxane elastomers modified with methyl sulfone groups did not show reliable actuation, even though their conductivity in the range of  $5 \times 10^{-10}$  S cm<sup>-1</sup> is sufficiently low. These materials showed a strongly frequency-dependent actuation at room temperature. Additionally, some actuators showed a deterioration of actuation strain when an electric field above a certain value was applied for extended periods of time. One explanation for these behaviors can be the  $T_g$  of the elastomer that is close to room temperature. Therefore, after the material is exposed to an electric field, more and more dipoles are oriented, and a permanent polarization is probably induced in the material. This hypothesis can be confirmed by conducting more actuation tests at different temperatures with films of different thicknesses. Another hypothesis is the electrocaloric effect, which is more pronounced for polar polymers operated in the vicinity of  $T_g$ . This can be proven by measuring the temperature of the active area during actuation with an infrared camera.

The elastomers modified with amide groups showed good actuation achieving large strain. They were able to operate at high frequencies with little deterioration of actuation. Since these materials slowly hydrolyze in ambient conditions, applications in transient electronics and personalized medicine, e.g., electronic skin, can be envisioned.

The very large actuation and the high dielectric breakdown field measured for the elastomers modified with nitrile groups makes these materials extremely attractive for artificial muscles and soft robotic applications, as they can, in principle, deliver both large deformations and forces. Therefore, future work should be focused on improving their processability so that stack actuators can be made by a layer-by-layer technique, such as slot-die coating. For this purpose, the molecular weight of the polar siloxanes can be reduced in order to obtain a polymer that

can be processed in solvent-free conditions. The cross-linking of such polymer can be conducted through the introduced reactive end groups, and simultaneous chain propagation using a difunctional molecule will potentially result in materials with improved mechanical properties.

The functioning of stack actuators, however, depends not only on the dielectric materials used but also on the quality, homogeneity, and surface roughness of the electrodes. Therefore, future studies should also be conducted to find suitable electrodes for stack actuator manufacturing, that are compatible with the employed dielectric materials.

Regarding DET applications, the present work has shown a high potential of polar siloxanes in actuators and sensors. However, due to the high worldwide electricity consumption and the industry's transition to green energy, polar siloxanes can also be considered a promising material for applications in DEGs. To the best of our knowledge, there is no polar siloxane employed in generators so far. We expect that similar to sensors and actuators, the performance of generators made of such siloxanes still has significant room for improvement, rendering the continued investigation of structure-property relationships in dielectric polymer materials indispensable.

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### **Publications**

- 2021 M. Iacob, A. Verma, T. Buchner, **Y. Sheima**, R. Katzschmann, D. Opris. Slot-die coating of an on-the-shelf polymer with increased dielectric permittivity for stack actuators. *ACS Applied Polymer Materials*. Submitted.
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