Polymerization of the new double-charged monomer bis-1,3(*N,N,N*-trimethylammonium dicyanamide)-2-propylmethacrylate and ionic conductivity of the novel polyelectrolytes

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The achievement of high ionic conductivity in single-ion conducting polymer electrolytes is one of the important aims for various electrochemical devices including modern lithium batteries. One way to enhance the ionic conductivity in polyelectrolyte systems is to increase the quantity of charge carriers in each monomer unit. Highly charged poly(bis-1,3(*N,N,N*-trimethylammonium)-2-propylmethacrylate) with one of the most conducting anions, namely dicyanamide, was prepared via free radical bulk polymerization or using ionic liquids as reaction medium. The cationic polymers of the double-charged monomer have molar masses up to $\overline{M}_w = 1{,}830{,}000$ g/mol and the ionic conductivity equal to 5.51×10^{-5} S/cm at 25°C. The film forming ability, crystallinity, thermal stability, and glass transition temperatures of the new polymeric ionic liquids obtained from detailed studies are presented. Copyright © 2009 John Wiley & Sons, Ltd.

Keywords: ionic liquids; ionic conductivity; polymer electrolytes; conducting polymers

INTRODUCTION

The development of non-volatile and non-flammable ion conductive materials is important for improving the safety and durability of the currently used batteries and for satisfying the increasing demand for modern electronic devices. While the use of aqueous electrolytes is restricted to a narrow temperature range, the application of organic solvents is becoming prohibited due to their volatile and harmful nature. Therefore, among other candidates, the room temperature ionic liquids (RTILs or ILs) have been extensively studied during the last ten years due to their unique properties such as negligible vapor pressure, non-flammability, high ionic conductivity, and good thermal and electrochemical stability.[1–7] For the most recent critical review describing electrochemical properties of Ils, see Reference [8]. Nevertheless, due to the potential leakage of ILs, the role of highly convenient materials for applications in electronic devices is predicted either for the gel-type polymer electrolytes (see for example Reference [9]) or even for all solid-state polymer electrolytes (SPEs,[10]) incorporating ILs as a structural unit.[11–14] Thus, one of the advanced strategies consists of the polymerization of ILs containing polymerizable groups and the preparation of "polyionic liquids" (PILs), which constitute a new class of polymer materials with exceptional and unique properties inherent for molten salts themselves.

Specific functions of PILs such as transport of target ions, specific polar environment, and mechanical strength were found to be strongly dependent on both the ionic liquid like monomer structure and the nature of the polymer main chain.[14–32] The polymerization of various ionic liquids like monomers (ILMs) was described in numerous papers and patents. However, all the studies on charged synthetic monomers were limited to those that yield polyelectrolytes with a maximum of one charge per 0.25 nm monomer unit length. Thus, the original idea, consisting

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of the increase in the charge carriers in each monomer unit that would allow for increase in the ionic conductivity of the resulting polymer, was realized for the first time in the presented work.

As it is known,[33–36] the dicyanamide, tricyanomethanide, and thiocyanate ionic liquids were found to be the most conductive electrolytes among the available representatives of the ILs family. The electrochemical windows of various imidazolium and pyrrolidinium corresponding ionic salts investigated by cyclic voltammetry were determined to be in the range of 2.4–3.5 V, while their ionic conductivity approached approx. 2×10^{-2} S/cm at $20°C$. Simultaneously, it was demonstrated[25,26,31] that during the polymerization of different monomers based on the 1-vinyl-3-ethylimidazolium cation, the reaction rate, monomer conversion, and polymer molar mass were found to depend on the nature of the anion used. In particular, the highest polymer molecular weight and the highest conductivity were achieved upon the polymerization of 1-vinyl-3-ethylimidazolium dicyanamide.[31]

Therefore, in our continuous efforts[30–32,37,38] to develop various SPE, we would like to describe the other approach consisting of the polymerization of bis-1,3(N,N,N-trimethylammonium dicyanamide)-2-propylmethacrylate, composed of a double-charged cation and one of the most conductive anions.

EXPERIMENTAL

Materials

Phosphorus pentoxide (>98%, Fluka), CaH_2 (98%, Aldrich), bis-1,3(N,N,N-trimethylammonium)-2-propylmethacrylate dichloride (**M1**) (TAMINCO N.V., Gent Belgium), silver nitrate (99%, Fluka), and sodium dicyanamide (98%, Acros) were used as received. Alkyl bromides (Acros Organics) as well as N-methylimidazole (98%, Aldrich) were distilled under inert atmosphere from CaH_2. Reagent-grade methylene chloride, DMF and ethanol were dried by vacuum distillation over P_2O_5 and magnesium pellets plus iodide, respectively. 2,2′-Azobisisobutyronitrile (AIBN) (Aldrich, 98%) was recrystallized from methanol. Tetradecyltrihexylphosphonium chloride ionic liquid was received from Cytec (Cytec Canada Inc.) and used without any purification.

Monomer synthesis

Bis-1,3(N,N,N-trimethylammonium)-2-propylmethacrylate dichloride (M1)

The obtained dichloride monomer[39] was fully characterized prior to further use. M.p. = $219–221°C$ (with decomposition); Anal. Calcd. for ($2[C_{13}H_{28}N_2O_2Cl_2$ (315.28)] $\times 1[H_2O]$): C, 48.15%; H, 9.01%; N, 8.64%. Found: C, 48.16%; H, 9.27%; N, 8.63%. ^{1}H NMR (400 MHz, D_2O): $\delta = 1.82$ (s, 3 H, $CH_2=C(-\underline{CH_3})-CO$), 3.11 (s, 18 H, $-N(\underline{CH_3})_3$,), 3.64–3.68 (dd, 2H, CH–$\underline{CH_2}$–N(CH_3)_3, $J_{H,H} = 2.4$ Hz), 3.88–3.93 (m, 2H, CH–$\underline{CH_2}$–N(CH_3)_3, $J_{H,H} = 7.2$ Hz), 5.79 (s, 1H, $-C(CH_3)=\underline{CH_2}$), 5.86–5.88 (m, 1H, $-O-\underline{CH}-(CH_2)_2-$, $J_{H,H} = 2.4$ Hz), 6.19 (s, 1H, $-C(CH_3)=\underline{CH_2}$); ^{13}C NMR (400 MHz, D_2O): $\delta = 17.1$ ($CH_2=C(-\underline{CH_3})-CO$), 54.3 ($-N(\underline{CH_3})_3$), 63.6 ($-O-\underline{CH}-(CH_2)_2-$), 66.8 (CH–$\underline{CH_2}$–N(CH_3)_3), 130.5 ($-\underline{C}(CH_3)=CH_2$), 134.4 ($CH_2=\underline{C}(-CH_3)-CO$), 166.9 ($-\underline{C}(CH_3)=CH_2$); IR (KBr pellet): 3466 (s), 3426 (s), 3251 (m), 3011 (m), 2951 (w), 1707 (vs, ν_{CO}), 1634 (m), 1479 (s), 1330 (s), 1301 (m), 1156 (vs), 1139 (vs), 1052 (m), 1015 (w), 978 (s), 950 (s), 918 (s), 903 (w), 876 (w), 824 (w), 718 (w), 653 (w) 614 (w) cm^{-1}.

Bis-1,3(N,N,N-trimethylammonium dicyanamide)-2-propylmethacrylate (M2)

This ionic monomer was prepared as described previously[33,34] for the synthesis of dicyanamide ionic liquids. An excess of freshly prepared silver dicyanamide (6.98 g, 0.040 mol), obtained from aqueous solution of sodium dicyanamide and silver nitrate, was added to an aqueous solution of **M1** (5.76 g, 0.018 mol) and gently heated up to $35°C$ under stirring for 2 hr. The solid precipitate (silver chloride and the excess of silver dicyanamide) was filtered off and the water was removed by rotary evaporation at $30°C$. The resulting colorless viscous oil was dried in vacuo (9–14 mm Hg) at $25–30°C$ for 0.5–1 hr using a flask filled with P_2O_5 introduced into the vacuum line. The yield was quantitative. Anal. Calcd. for ($1[C_{17}H_{28}N_8O_2$ (376.46)] $\times 2.5[H_2O]$): C, 48.44%; H, 7.89%; N, 26.58%. Found: C, 48.17%; H, 7.94%; N, 26.11%; Water content according to Karl Fisher titration: 10.2 wt%. ^{1}H NMR (400 MHz, DMF-d7): $\delta = 2.14$ (s, 3 H, $CH_2=C(-\underline{CH_3})-CO$), 3.65 (s, 18 H, $-N(\underline{CH_3})_3$,), 4.29–4.33 (dd, 2H, CH–$\underline{CH_2}$–N(CH_3)_3, $J_{H,H} = 3.6$ Hz), 4.39–4.45 (m, 2H, CH–$\underline{CH_2}$–N(CH_3)_3, $J_{H,H} = 6.0$ Hz), 6.08 (s, 1H, $-C(CH_3)=\underline{CH_2}$), 6.26–6.29 (m, 1H, $-O-\underline{CH}-(CH_2)_2-$, $J_{H,H} = 2.8$ Hz), 6.45 (s, 1H, $-C(CH_3)=\underline{CH_2}$); ^{13}C NMR (400 MHz, DMF-d7): $\delta = 17.6$ ($CH_2=C(-\underline{CH_3})-CO$), 53.9 ($-N(\underline{CH_3})_3$), 64.4 ($-O-\underline{CH}-(CH_2)_2-$), 67.2 (CH–$\underline{CH_2}$–N(CH_3)_3), 128.3 ($-\underline{C}(CH_3)=CH_2$), 135.7 ($CH_2=\underline{C}(-CH_3)-CO$), 165.6 ($-\underline{C}(CH_3)=CH_2$); IR (KBr pellet): 3485 (s), 3441 (s), 3136 (w), 3027 (m), 2986 (w), 2817 (w), 2255 (vs, $\nu_{C\equiv N}$), 2230 (vs, $\nu_{C\equiv N}$), 2193 (vs, $\nu_{C\equiv N}$), 2141 (vs, $\nu_{C\equiv N}$), 1701 (vs, $\nu_{C=O}$), 1634 (m), 1483 (s), 1327 (vs), 1298 (vs), 1158 (vs), 1139 (vs), 1047 (m), 976 (m), 947 (s), 914 (m), 876 (w), 824 (w), 718 (w), 526 (m) cm^{-1}.

1-Vinyl-3-ethylimidazolium dicyanamide (M3)

The monomer was synthesized under very mild conditions as previously reported.[31]
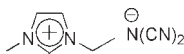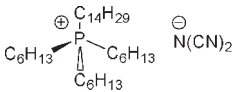
Ionic liquids

ILs, namely, 1-methyl-3-ethylimidazolium dicyanamide ([1-Me-3-Etim]N(CN)₂) and tetradecyltrihexylphosphonium dicyanamide were synthesized according to References [33,34,40] and characterized by elemental and Karl Fisher analysis, NMR, and IR spectroscopy prior to use. The purity of ILs estimated by these methods was higher than 98%.

Polymerization procedures

Poly(bis-1,3(N,N,N-trimethylammonium)-2-propylmethacrylate dicyanamide) synthesis (poly-M2)

Representatively, the synthesis of **poly-7** (Table 1) is described here. AIBN (0.0016 g, 0.5 wt%) was dissolved in the 0.350 g of [1-Me-3-Etim]N(CN)₂ ionic liquid at room temperature in a 5 ml round-bottom pear-shaped flask. Then **M2** (0.350 g, 0.83 mmol) was added under stirring. The formation of a clear solution was observed. The flask was slowly connected to the vacuum line with inserted trap filled with P_2O_5 and was placed in the heated oil bath. The polymerization was carried out under vacuum (c.a. <1 mm Hg) at $60°C$ for 6 hr. The polymer solutions were slightly diluted with DMF and precipitated in an excess of methanol. After the separation of the polymer, it was thoroughly washed with methanol, filtered, and dried under high vacuum at $70–80°C$ until the weight was constant. The yield was 0.20 g (65%). The inherent viscosity was determined as 4.29 dl/g in DMF and 0.71 dl/g in 1 M aq. NaCl corresponding to $\overline{M}_w = 1\,830\,000$ g/mol (1 M aq. NaCl).

Table 1. Synthesis of poly(bis-1,3(N,N,N-trimethylammonium dicyanamide)-2-propylmethacrylate)

No.	Solvent	AIBN (wt%)	Time (hr)	T (°C)	Monomer concentration [M] (mol/L)	Yield (%)	η_{inh} (dl/g)[a]	Crystallinity (%)[b]
Poly-1	—	—	6	25	—	11.5	—[c]	>98
Poly-2	—	—	6	60	—	10	—[c]	>98
Poly-3	—	—	6	80	—	15	—[c]	>98
Poly-4	—	0.5	6	60	—	27	3.98	13
Poly-5	$-N\overset{\oplus}{N}\diagdown N(CN)_2^{\ominus}$	—	6	60	2.1	14.5	0.10	—[d]
Poly-6		0.3	6	60	2.1	58	4.15	21
Poly-7		0.5	6	60	2.1	65	4.29[e]	20
Poly-8		0.5	8	60	2.1	69	3.74	19
Poly-9		0.5	10	60	2.1	69	3.99	19
Poly-10		0.5	6	60	1.4	61.5	3.15	11
Poly-11		0.5	6	60	1.0	54	2.63	11
Poly-12		0.7	6	60	2.1	74	3.84	10
Poly-13[f]		0.5	6	60	2.1	59	3.15[g]	Amorphous
Poly-14	$C_6H_{13}\overset{\oplus}{\underset{C_6H_{13}}{\overset{C_{14}H_{29}}{P}}}C_6H_{13}\quad N(CN)_2^{\ominus}$	0.5	6	60	2.1	21	1.10	Amorphous
Poly-15	DMF	0.5	6	60	2.1	14	0.27	—[d]

[a] For the solution of 0.05 g of polymer in 10.0 ml of DMF at 25.0°C.

[b] Determined for polymer powder by X-ray diffraction measurements.

[c] Polymer is insoluble in common organic solvents.

[d] Not determined.

[e] $\overline{M}_w = 1,830,000$ g/mol determined by static light scattering procedure in 1 M aq. NaCl, η_{inh} (1 M aq. NaCl) = 0.71 dl/g.

[f] Copolymer with 1-vinyl-3-ethylimidazolium dicyanamide in 50:50 wt ratio.

[g] $\overline{M}_w = 990,000$ g/mol determined by static light scattering procedure in 1 M aq. NaCl, η_{inh} (1 M aq. NaCl) = 0.60 dl/g.

Further characteristics of **poly-7**: $T_g \geq 175$°C; onset loss temperature is 175°C. IR (KBr pellet): 3027 (m), 2962 (w), 2922 (w), 2239 (vs, $\nu_{C\equiv N}$), 2197 (s, $\nu_{C\equiv N}$), 2133 (vs, $\nu_{C\equiv N}$), 1733 (s, $\nu_{C=O}$), 1481 (s), 1384 (m), 1361 (m), 1321 (s), 1245 (w), 1134 (m), 1087 (w), 979 (w), 952 (m), 931 (m), 921 (m), 524 (m) cm^{-1}.

Poly(vinyl-3-ethylimidazolium dicyanamide) synthesis (**poly-M3**)

The polymerization reaction was carried out as described previously.[31,38] $\eta_{inh} = 5.00$ dl/g in DMF; $\overline{M}_z = 1\,130\,000$ g/mol by sedimentation analysis in an analytical ultracentrifuge in DMF; $T_g = +19$°C; onset loss temperature is 210°C. IR (KBr pellet): 3500 (m), 3422 (m), 3137 (m), 3090 (m), 2241 (vs, $\nu_{C\equiv N}$), 2197 (s, $\nu_{C\equiv N}$), 2141 (vs, $\nu_{C\equiv N}$), 1642 (w), 1571 (m), 1552 (s), 1450 (w), 1387 (w), 1317 (s), 1165 (s), 905 (w), 849 (w), 758 (w), 651 (m), 625 (w), 416 (vs) cm^{-1}.

Copolymer synthesis (**poly-M2/M3**)

The copolymer **poly-13** was synthesized according to the procedure described for **poly-7**. M2 (0.350 g, 0.83 mmol) and M3 (0.313 g, 1.65 mmol) were placed into the solution of AIBN (0.0031 g, 0.5 wt%) in 0.662 g of [1-Me-3-Etim]N(CN)$_2$ ionic liquid and stirred at room temperature until the formation of a clear solution. Then the flask was evacuated and heated up to 60°C for 6 hr. The obtained polymer solution was diluted with DMF and precipitated into the methanol excess. **Poly-13** was filtered off and dried in vacuum at 70–80°C. Yield was 0.37 g (59%); $\eta_{inh} = 3.15$ dl/g in DMF and 0.60 dl/g in 1 M aq. NaCl; $\overline{M}_w = 990\,000$ g/mol (1 M aq. NaCl); $T_g = +22$, $+150$°C; onset loss temperature is 190°C. IR (KBr pellet): 3141 (m), 3089 (m), 3030 (s), 2963 (m), 2933 (m), 2859 (w), 2252 (vs, $\nu_{C\equiv N}$), 2200 (s, $\nu_{C\equiv N}$), 2148 (vs, $\nu_{C\equiv N}$), 1734 (s, $\nu_{C=O}$), 1634 (s), 1568 (m), 1553 (m), 1483 (s), 1383 (vs), 1320 (s), 1246 (m), 1206 (m), 1161 (s), 1128 (s), 1036 (w), 984 (w), 954 (m), 921 (m), 762 (w), 655 (m), 526 (s) cm^{-1}.

Film preparation

Poly(bis-1,3(N,N,N-trimethylammonium dicyanamide)-2-propyl-methacrylate) and poly(vinyl-3-ethylimi-dazolium dicyanamide) films were cast from their 5% polymer solutions in DMF on a golden electrode surface and Teflon® support, respectively. The solvent was slowly evaporated by heating to 80°C. The **poly-M3** film was released from Teflon® surface, while the **poly-M2** coating was left on the electrode surface, whereupon the film and the coating were dried in vacuum at 70°C for 12 hr.

Blending of the **poly-M2** with **poly-M3** was completed within 1 hr by vigorous stirring in DMF (at different weight ratios). Films

consisting of the polymer blends were cast from 5% polymer solutions on clean Teflon® supports, followed by slow solvent evaporation at 80–90°C. The final drying of the self-standing films was carried out *in vacuo* at 70°C for 12 hr.

Measurements

A NICOLET MAGNA-750 was used to record IR spectra. NMR data were obtained at 400.13 MHz for proton and 100.61 MHz for carbon working frequency in the indicated solvent at 25°C on a Bruker AMX-400 spectrometer and are listed in ppm downfield from tetramethylsilane. Inherent viscosities (η_{inh}) were measured using Ostwald capillary viscometer (0.05 g of polymer in 10.0 ml of solvent at 25.0°C). Reduced viscosities ($\eta_{sp}/c = (\eta_{rel} - 1)/c$ with $\eta_{rel} = t/t_o$ the ratio of the flow times of the polymer solution and the solvent) were estimated in a Ubbelohde type capillary viscometer at 25.0°C. The weight average molar mass ($\overline{M}_w$) was estimated by static light scattering in 1 M aq. NaCl. The measurements were made at 25 ± 0.1°C with a Fica-50 photogoniodiffusometer (France) in a vertically polarized light at $\lambda = 546$ nm in the angular range from 30 to 150°. Prior to measurements, the polymer solutions were filtered through Millipore 0.45 μm filters. The refractive index increments *dn/dc* for **poly-7** and **poly-13** were measured separately at 25°C in a vertically polarized light at $\lambda = 546$ nm and were found to be 0.183 and 0.195, respectively.

The glass transition temperature (T_g) of the polymers was determined thermo-mechanically using a UIP-70M (Russia) thermomechanical analyzer at a heating rate of 2.5°C/min. Dynamic thermogravimetric analysis (TGA) was performed in air using a Q-1500 MOM derivatograph (Hungary) at a heating rate of 5°C/min. DSC data were recorded by heating under nitrogen atmosphere at 5°C/min on a NETZSCH DSC 204F1 differential scanning calorimeter equipped with auto-cool and calibrated using special samples from NETZSCH company.

X-ray diffraction measurements of polymer powders were carried out with a Bruker D8 Advance diffractometer equipped with Goebel mirror and scintillator detector at room temperature with the step size of 0.02 Å and 5 sec for each step. The parallel geometry in the reflection mode was used for recording diffraction patterns. The profiles of diffraction peaks were approximated analytically using Gaussian, Lorentzian, and Pearson7 curves. All calculations were carried out with Origin7 software.

X-ray diffraction crystallography experiments were carried out with Bruker APEX II CCD area detector, using graphite monochromated Mo-Kα radiation ($= 0.71073$ Å, ω-scans) at 100 K. Reflection intensities were integrated using SAINT software[41] and the absorption correction was applied semi-empirically using the SADABS program.[42] The structures were solved by direct method and refined by the full-matrix least-squares against F^2 in the anisotropic approximation for no-hydrogen atoms. Hydrogen atoms were located from the Fourier density synthesis and refined in the isotropic approximation. Crystal data and structure refinement parameters for **M1** and **M2** are given in Table 2. All calculations were performed using the SHELXTL software.[43] The crystallographic data have been deposited with the Cambridge Crystallographic Data Center with CCDC 721260 number for **M1** and CCDC 721261 for **M2**. Copies of this information may be obtained free of charge from: The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

Dielectric spectroscopy studies were run on a Novocontrol Broadband Dielectric Spectrometer equipped with an Alpha

Table 2. Crystallographic data and parameters of refinement for **M1** and **M2**

	M1	M2
Formula	$(C_{13}H_{28}N_2O_2)^{2+}$ 2 (Cl)$^-$ (3H$_2$O)	$(C_{17}H_{28}N_2O_2)^{2+}$ 2 (C$_2$N$_3$)$^-$
M	369.32	376.47
T (K)	100	100
Space group	Pnma	$P-1$
Z	4	2
a (Å)	12.8986(10)	9.2461(14)
b (Å)	12.4515(9)	9.604(2)
c (Å)	12.0876(9)	12.450(3)
α (°)	90.00	82.333(5)
β (°)	90.00	72.916(4)
γ (°)	90.00	71.436(5)
V (Å^3)	1941.4(3)	1000.8(4)
ρ (g cm^{-3})	1.264	1.249
μ (MoKα) (cm^{-1})	3.56	0.87
F(000)	800	404
2θ max	58	56
Number of measured refl.	10,660	9378
Number of independent refl. (R(int))	2693	4837
Number of observed refl. with $I > 2\sigma$	1890	3745
Parameters	189	253
R1 calculated against F	0.0350	0.0497
WR2	0.0981	0.1317
GOF	1.023	1.041
ρ_{min}/ρ_{max} (e Å^{-3}) (d_{min}/d_{max})	0.395/−0.278	0.459/−0.380

analyzer and a Quatro temperature controller. The films or polymer coatings on gold-coated copper plate were sandwiched between the gold-coated brass electrodes. The experiments were carried out isothermally, increasing the temperature from 20 to 50°C in 10°C steps in the 10^{-1}–10^7 Hz frequency range.
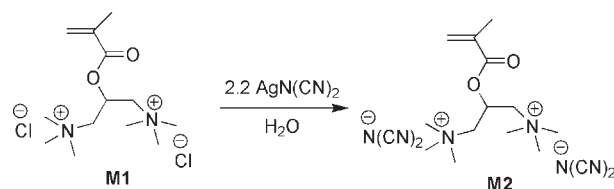
RESULTS AND DISCUSSION

Monomer synthesis

It is well known that the ionic conductivity of ionic liquid like monomers (ILMs) decreases remarkably after their polymerization due to the reduction of ion mobility in the polymer chains. Therefore, the original idea of the presented work consisted of the increase in the number of ionic carriers in each monomer unit without the increase in the monomer's unit length, having two charges per 0.25 nm of polymer backbone. Due to the good solubility of bis-1,3(N,N,N-trimethylammonium)-2-propylmethacrylate dichloride in water, the ion exchange reaction was carried out in an aqueous media with the silver salt in analogy to the synthesis of dicyanamide ILs[31,32] (Scheme 1).

Bulk polymerization

However, the isolation of the desired **M2** became complicated due to its spontaneous polymerization in aqueous solution under vacuum even at 30°C. Thus, it was not possible to obtain pure monomer **M2** and to carry out its bulk polymerization. Similar spontaneous solution polymerization of ionic vinyl monomers (vinylpyridinium salts in particular[44,45]) and of some ionic methacrylates[46] has been observed previously. Upon detailed investigation it was observed that the polymerization started spontaneously at a monomer concentration higher than 90 wt%

Scheme 1. Synthesis of bis-1,3(N,N,N-trimethylammonium dicyanamide)-2-propylmethacrylate.

(23.9 mol/L). Interestingly, similar monomer solutions with [**M2**] <90 wt% can be easily stored even at room temperature until the removing of oxygen. The **M2** spontaneous polymerization yielded polymers insoluble in common organic solvents (Table 1, **poly-1–3**). To check for any crystalline domains, X-ray diffraction experiments were carried out. Studying the polymer powders generally revealed the presence of three reflections (d = 15.1, 8.8 and 4.2 Å^{-1}, Fig. 1) that were attributed to the crystalline regions in the samples. Thus the calculated crystallinity of the polymers from bulk polymerization was found to be nearly 98%. Such high crystallinity partly explains the observed poor solubility. Higher polymerization temperature only slightly raised the polymer yield (Table 1, **poly-1–3**). Addition of the radical initiator AIBN (Table 1, **poly-4**) allowed for the synthesis of a polymer with high inherent viscosity, but still with low yield (27%). Nevertheless, the crystallinity of the polymer was reduced from 98 to 13% (Table 1, **poly-1–3** and **4**). Moreover, the polymer became soluble in water and some amide type organic solvents (DMF, DMA, NMP, etc.).

Polymerization in ionic liquids and other solvents

As it was shown previously[31,38,47–55] ionic liquids can accelerate free radical polymerizations, particularly the chain propagation rate, and simultaneously increase the conversion of several monomers. Therefore, in order to synthesize polymers with higher molar mass and in higher yield, the 1-methyl-3-ethylimidazolium dicyanamide ionic solvent ([1-Me-3-Etim]N(CN)$_2$) was taken. Although [1-Me-3-Etim]N(CN)$_2$ does not appear to be the optimal ionic solvent for free radical polymerization process,[31,47,51] the choice of the dicyanamide anion was justified by the presence of the latter in **M2**. Otherwise, according to the *Le Chatelier* principle, counterion exchange between the monomer and polymer on the one hand and the reaction medium on the other hand would take place[30] favoring a polymer mainly based on the most abundant anion. Moreover, the anion exchange is favored for anions with higher mobility. The non-volatility of the reaction media allowed for performing the polymerization of **M2** under vacuum and remove the residual water. The polymerization without a radical initiator (Table 1, **poly-5**) produced only a low molar mass polymer and 15% yield. However, upon the addition of different amounts of AIBN it was possible to increase both the inherent viscosity of the polymers and their yields (Table 1, **poly-6**, **7** and
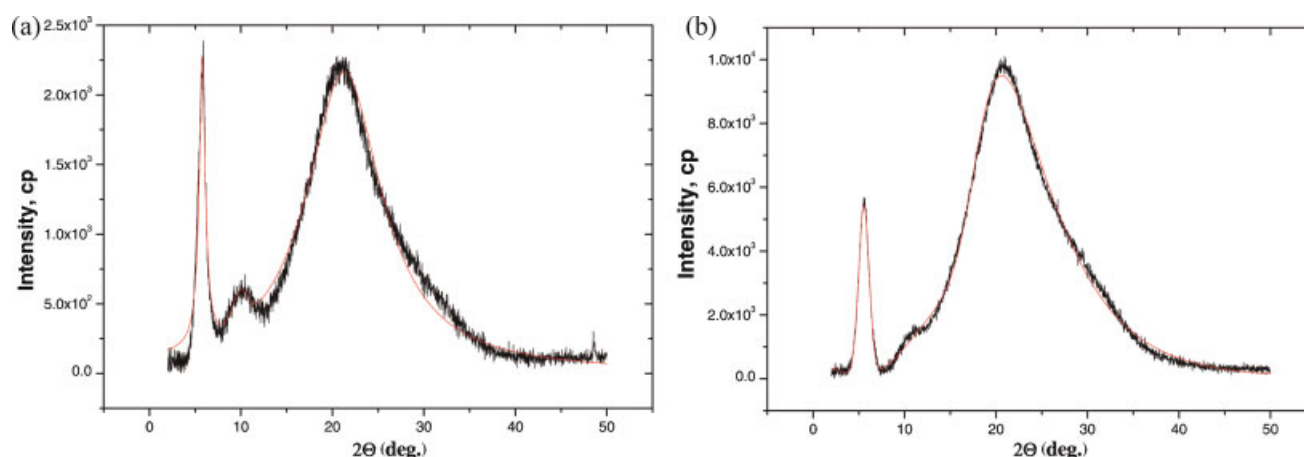
Figure 1. X-ray diffraction of **poly-7** powder (a) and **poly-7** film (b). This figure is available in color online at www.interscience.wiley.com/journal/pat

12). Thus, the increase in the added AIBN amount from 0.3 to 0.7 wt% resulted in up to 74% conversion and reduced the crystallinity to 10% (Table 1, **poly-12**). It was further observed that the reaction time practically does not affect either the molar mass or the yield (Table 1, **poly-7**–**9**). Higher **M2** concentration led to both higher yield and η_{inh} (Table 1, **poly-7, 10** and **11**). It is worth mentioning that, independently of the reaction media (water or imidazolium IL), the precipitation of polymer was observed during the polymerization process.

Taking into account that the nature of the IL strongly influences all steps of the polymerization process, ionic solvent based on the phosphonium cation, which proved itself one of the best for radical polymerization, was tested.[31,47,56] The polymerization of **M2** in tetradecyltrihexylphosphonium dicyanamide surprisingly resulted in the amorphous **poly-14** with an inherent viscosity approximately four times lower than a **M2**-polymer synthesized in imidazolium IL under the same conditions (Table 1, **poly-7** and **14**). This result can be explained by fast precipitation of the polymer as a result of the lower solubility in this medium preventing long polymer chain growth.

Due to the good solubility of the **M2** based polymers in DMF, the latter was also used as reaction medium (Table 1, **poly-15**). In spite of the fact that the polymerization in DMF occurred in the solution during the whole time of the reaction, the **poly-15** had a significantly lower molar mass. Radical transfer in the organic solvent and the presence of the residual water in the medium could be the reasons for such result.

Solution properties of the polymers

It was interesting to investigate the behavior of the **M2** polymers in solution as well as to estimate their molar mass. Initially, the reduced viscosity of **poly-7** was studied in DMF, water, and 1 M aq. NaCl (Fig. 2). The reduced viscosity in water increased exponentially with the decrease in polymer concentration (Fig. 2, curve 1), which is typical for polyelectrolytes. The addition of the low molar mass electrolyte (NaCl) reduces the Debye length. Consequently, the repulsion along the chain is reduced, the polymer chains become more flexible, and the hydrodynamic dimensions decrease, resulting in lower viscosity. Under such conditions, the polyelectrolyte molecules behave similar as neutral chains allowing for the determination of the intrinsic
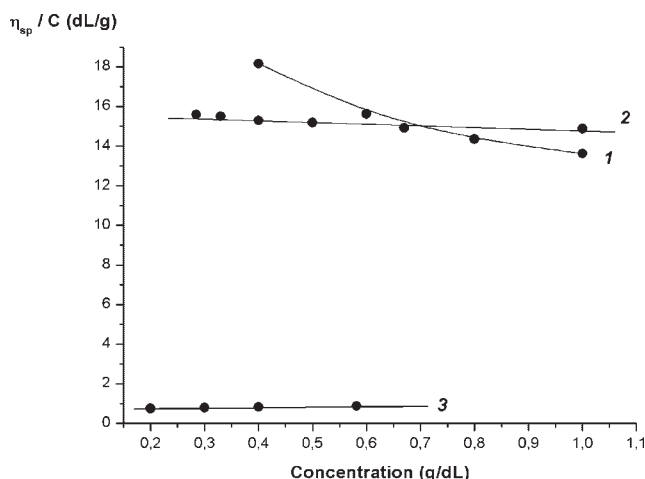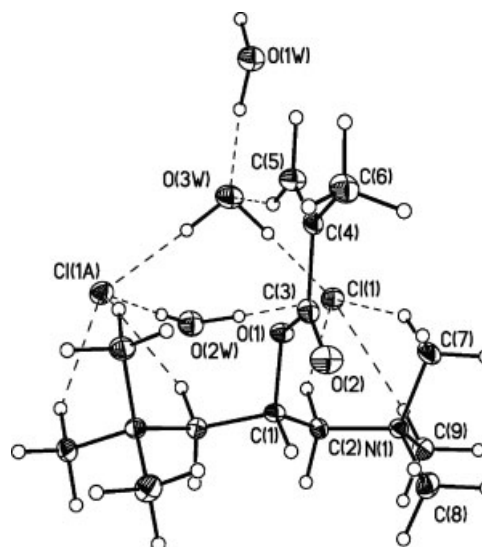
viscosity $[\eta] = 0.73$ dl/g by linear extrapolation (Fig. 2, curve 3). The classical polyelectrolyte behavior was not observed for **poly-7** in the less polar DMF (Fig. 2, curve 2). Almost linear concentration dependence of the reduced viscosity was observed while determining the intrinsic viscosity as $[\eta] = 15.8$ dl/g. Nevertheless, the intrinsic viscosity value in DMF reveals a much more extended coil conformation than in NaCl aqueous solution.

The attempt to dissolve **poly-7** in DMF containing LiCl as low molar mass electrolyte was also performed. However, the addition of LiCl to the polymer solution in DMF resulted in immediate **poly-7** precipitation, while all the attempts to dissolve **poly-7** in DMF already containing various amounts of LiCl were unsuccessful.

Further, the molar mass of **poly-7** was determined by static light scattering in 1 M aq. NaCl. A weight average molar mass $\overline{M}_w$ of 1,830,000 g/mol was obtained for **poly-7**. This value exceeds the previously determined number average molar mass of **poly-M1** by a factor of 9.[37] Such difference is in accordance with the properties observed for vinylethylimidazolium monomers.[31,38] As it was revealed earlier, polymers based on vinylethylimidazolium dicyanamide possess higher molar masses than their analogs with bis(trifluoromethylsulfonyl)imide, bromide, or trifluoromethanesulfonate anions. The reason for this anomalous dependence is not obvious a priori. Therefore, the specific interactions between the cation and anion have been studied.

X-ray diffraction analysis

The peculiarities of the dication geometry as well as cation...anion interaction in a crystal of **M1** and **M2** were analyzed by X-ray diffraction analysis (Table 2). The general view of **M1** and **M2** are shown in Figs 3 and 4, respectively. The dichloride monomer **M1** crystallized as a solvate with three water molecules. The geometry found for the dications in salts of **M1** and **M2** is slightly different. In the crystal of **M1**, the dication occupies the special position—mirror plane passing through the ester moiety, while in the crystal of **M2** the same dication is located in general position. The main difference between the dications in **M1** and **M2** is reflected in the conformation of the $(CH_3)_3NCH_2CHCH_2N(CH_3)_3$

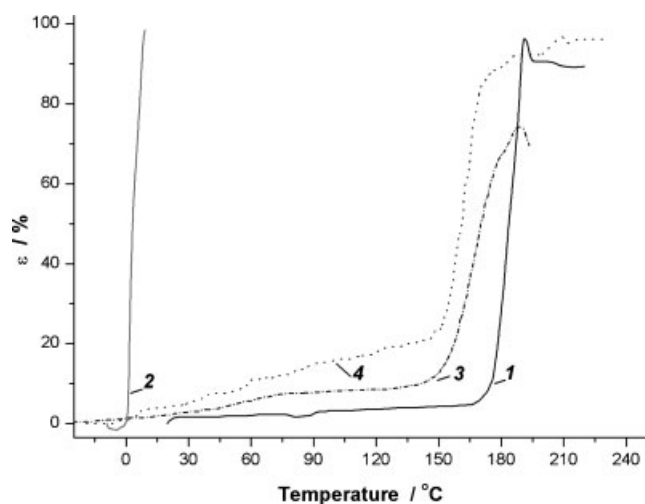**Figure 2.** Reduced viscosity plots for **poly-7** measured in water (*1*), DMF (*2*), and 1 M aq. NaCl (*3*).

Figure 3. The cation-anion pair in the crystal of **M1** (representation of atoms is performed by thermal ellipsoids ($p = 50\%$)).

Figure 4. The cation-anion pair in the crystal of **M2** (representation of atoms is performed by thermal ellipsoids ($p = 50\%$)).

Figure 5. TGA curves of **poly-7** (*1*), poly(vinyl-3-ethylimidazolium dicyanamide) (*2*), copolymer **poly-13** (*3*), and mechanical blend of **poly-7**/poly(vinyl-3-ethylimidazolium dicyanamide) 50:50 ratio (*4*) in air.

fragment, which is characterized by *all-trans* conformation in **M1**. In **M2**, one of the NCCC torsion angles is equal to 96.9°. The said variation leads to significant shortening of the distance between two $N(CH_3)_3$ cationic centers, which equals to 5.154(2) and 4.820(2) Å in **M1** and **M2**. Analysis of crystal packing revealed that the main type of cation...anion interactions in both crystals is a weak C–H...anion one, i.e. C–H...Cl in **M1** and C–H...N in **M2**. At the same time, the $N(CN)_2$ anion in **M2** also participates in $\pi...\pi$ interaction. As it can be seen in Fig. 4, the dicyanamide anion is involved in the interaction with the $CH_2=C(CH_3)$–C=O fragment with almost parallel arrangement of NCN and $CH_2=C(CH_3)$–C=O parts, and the C(10)...C(4) and N(3)...C(3) distances become equal to 3.343(2) and 3.116(2)Å, correspondingly. Thus, the superior stabilization of the formed **M2•** radical is suggested due to the described additional interaction, which results in the higher molar mass of the obtained polymer.

Thermal analysis of the obtained polymers

TGA analysis of **poly-7** (Fig. 5, curve 1) revealed that its thermal stability is in the range detected for ionic polymers containing the dicyanamide anion[31,38] and does not exceed 200°C. Thus, **poly-7** has an onset temperature of 165°C and a 5 wt% mass loss at 175°C (Table 3, entry 1). Comparing TGA curves for **poly-7** and

Table 3. Ionic conductivity of self-standing films and coatings

No.	Film composition (wt%)		T_{onset} (°C)[a]	T_g (°C)	Conductivity plateau value (σ_{dc}) (S/cm) at 25°C
	(methacrylate bis-dicyanamide monomer)	(vinyl-3-methylimidazolium $N(CN)_2$)			
	Polymers				
1	100	—	175	~175[b]	5.51×10^{-5}
2	—	100	210	19	1.31×10^{-5}
3	70	30	190	22, 150	3.59×10^{-5}
	Polymer blends				
4	60	40	—	—	1.08×10^{-5}
5	50	50	200	150	9.61×10^{-6}
6	40	60	—	—	5.76×10^{-6}
7	30	70	—	—	4.83×10^{-6}

[a] Onset loss temperature according to TGA.
[b] T_g of polymer either coincides with the decomposition onset or exceeds it.

Figure 6. TMA of polymers **poly-7** (*1*), poly(vinyl-3-ethylimidazolium dicyanamide) (*2*), copolymer **poly-13** (*3*), and mechanical blend of **poly-7**/poly(vinyl-3-ethylimidazolium dicyanamide) 50:50 ratio (*4*) in air.

poly(vinyl-3-ethylimidazolium dicyanamide) (Fig. 5, curves 1 and 2) it is clearly visible that the latter is more thermally stable. This is in a good agreement with the difference found for imidazolium and ammonium ILs with the given anion.[57] Interestingly, the DSC analysis did not detect any glass transition temperature for **poly-7**, while the more sensitive thermomechanical method (Fig. 6, curve 1) revealed that the T_g of **poly-7** either coincides with the temperature of decomposition at the beginning or exceeds it.

Films and coatings

The attempt to cast a film from **poly-7** resulted in polymer coating directly on the golden electrode. Unfortunately, all **poly-7** films prepared from DMF solutions were opaque and brittle. Probably, this fact can be explained by the degree of crystallinity in **poly-7**. In order to check this point, the X-ray diffraction experiments were carried out on the films as well (Fig. 1). In contrast to polymer powders, the intensity of the first reflection is considerably decreased compared to the third one. The latter reflection is significantly wider such that the second diffraction peak is almost shaded. The difference in the diffraction patterns from both the polymer powder and the polymer film can be interpreted as an increase in the crystallites disorder due to the formation of the polymer film. Nevertheless, the samples have nearly the same crystallinity ($\sim$20%), which shows the retention of the ratio between the crystalline and amorphous regions after the film preparation. Therefore, in order to obtain self-standing polymer films, two different approaches of the investigation were selected.

The first one consisted in the preparation of various blends with amorphous poly(vinyl-3-ethylimidazolium dicyanamide) ($M_z = $ 1,130,000 g/mol[31]). The latter was selected due to its ability to form elastic, strong films, bearing the same anion and because of its good conductivity.[30,31] As a result, four self-standing, tight films were obtained by varying the weight ratios from 60:40 to 30:70 (Table 3, entries 4–7). Their onset loss temperatures practically coincided with that determined for poly(vinyl-3-ethylimidazolium dicyanamide) and were around

200°C (Fig. 5, curves 2 and 4). The thermomechanical study of a 50:50 blend revealed only one quite high T_g value of 150°C.

The second approach uses a copolymer based on **M2** and **M3**, which was synthesized under optimal conditions developed for the **M2** homopolymerization (see *vide supra*). Due to the expected different reactivities of the two monomers, the copolymerization of **M1** and **M2** yielded copolymers with a composition (70:30) differing from the initial monomer feed composition (50:50) as was determined by ^{1}H NMR (Table 3, entry 3). The molar mass of the **poly-13** was studied by light scattering and was found to be 990,000 g/mol in 1 M aq. NaCl. Interestingly, the onset loss temperature for **poly-13** was found to be in between the corresponding values for **poly-7** and the mechanical blend with a 50:50 ratio (Fig. 5, curves 1, 4 and 3). Upon the thermomechanical investigation of **poly-13** it was demonstrated that it has two glass transition temperatures, namely at 22°C and at 150°C. The presence of two T_g could mean that the synthesized **poly-13** represented rather a block than random copolymer.

Finally, the ionic conductivity (σ) of the polymers was investigated. Figure 7 presents typical conductivity spectra of the studied films and the **poly-7** coating. As visible in Fig. 7, the conductivity increased with the rise in the applied frequency (f). Usually conducting materials are characterized by the σ_{dc} (direct current conductivity) value, which corresponds to the plateau region on $\sigma(f)$ curves. In the observed case (Fig. 7) such plateau region is not clearly visible. However, with additional information from the frequency dependence of the loss tangent (Fig. 8), which has a maximum, and from the imaginary part of conductivity, it was possible to conclude that this region lies in the range of 10^5–10^7 Hz. The plateau region is partly masked by the electrode polarization effects that arise at low frequencies and result in the reduction of σ values with frequency decrease. The demonstrated behavior is typical for the systems with high ionic conductivities.[31,58] It is known, that very often the Cole–Cole plots are used for the determination of the ionic conductivity value. However, both methods: the mentioned one and the one presented here are based on the same impedance measuring technique. It was proved previously[59] that the conductivity values obtained simultaneously by these methods are absolutely equal.
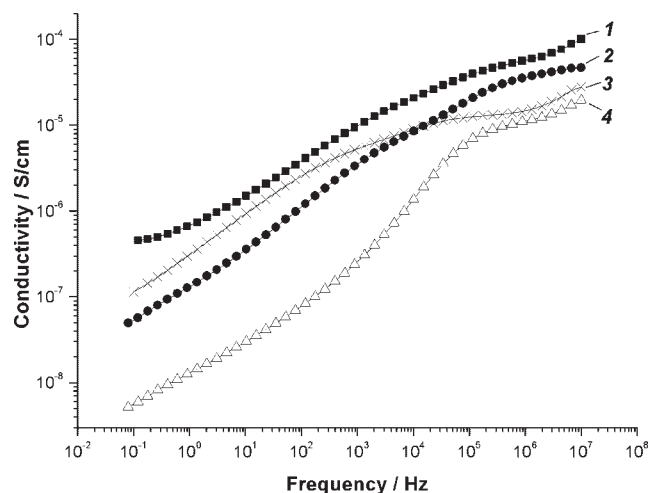

Figure 7. Frequency dependence of the conductivity at 25°C for **poly-7** (*1*), copolymer **poly-13** (*2*), poly(vinyl-3-ethylimidazolium dicyanamide) (*3*), and for mechanical blend of **poly-7**/poly(vinyl-3-ethylimidazolium dicyanamide) in 50:50 ratio (*4*).
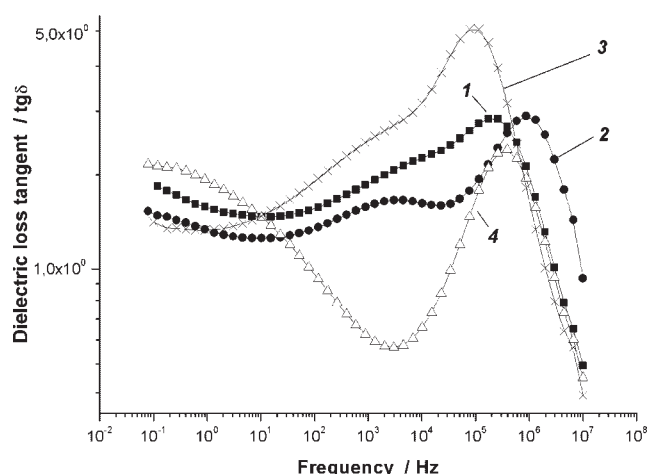
Figure 8. Frequency dependence of the dielectric loss tangent at 25°C for **poly-7** (*1*), copolymer **poly-13** (*2*), poly(vinyl-3-ethylimidazolium dicyanamide) (*3*), and for mechanical blend of **poly-7**/poly(vinyl-3-ethylimidazolium dicyanamide) in 50:50 ratio (*4*).

The conductivity study of the **poly-7** coating revealed rather high $\sigma_{dc} = 5.5 \times 10^{-5}$ S/cm at 25°C (Table 3, entry 1). It was previously stated,[15,18–20,22,30,31,60,61] that the lower is the T_g of the polymer, the higher is in general its conductivity. Thus, the best conductivity is achieved when the polymer glass transition temperature lies below 10°C. However, some exceptional systems are also known.[62] Taking into account the high T_g (~175°C) of **poly-7**, the observed ionic conductivity seems to be very interesting and can be explained only by the presence of a large quantity of ionic carriers, which overcomes some limitations of the glassy polymer state. Blending the polymers resulted in a decrease of the σ_{dc} in comparison with the conductivity of **poly-7** and poly(vinyl-3-ethylimidazolium dicyanamide) (Table 3, entries 1–3). Probably, this is partly caused by some incompatibility in the polymers and partly by a more chaotic distribution of the polymer chains on the films surface. The increase in the **poly-7** content in the blend composition accompanied by an increase in the amount of free ions resulted in a one order of magnitude rise in ionic conductivity (Table 3, entries 4–7). In contrast to polymer blends, the copolymer film showed ionic conductivity equal to 3.6×10^{-5} S/cm at 25°C, which is in between the σ_{dc} values of **poly-7** and poly(vinyl-3-ethylimidazolium dicyanamide).

CONCLUSIONS

A novel monomer bearing two ammonium cations and two dicyanamide anions per one acrylic molecule, namely bis-1,3(*N,N,N*-trimethylammonium dicyanamide)-2-propylmethacrylate, was synthesized and used for the preparation of polyelectrolytes via free radical polymerization. It was found that this monomer is subjected to spontaneous polymerization in aqueous solutions at concentrations higher than 90 wt%, yielding highly crystalline insoluble polymers. The dicyanamide ionic liquids used as reaction medium allowed the synthesis of high molecular weight polyelectrolytes having $\overline{M}_w$ up to 1 830 000 g/mol and reduced (~20%) the crystallinity. Inspite of the high glass transition temperature of approx. 175°C, the polymers exhibited ionic conductivity of 5.51×10^{-5} S/cm at 25°C that can be explained

only by the presence of high quantity of charge carriers. However, such polymers were able to form only tight coatings, but brittle films. The problem of the preparation of self-standing films without a significant loss in conductivity was successfully solved by the copolymerization of the new monomer with 1-vinyl-3-ethylimidazolium dicyanamide.

Summarizing the current results, it can be concluded that the suggested approach consisting of the increase in the number of ionic carriers in each monomer unit allows for the synthesis of polyelectrolytes having moderate ionic conductivity even when the T_g of the polymer exceeds the room temperature.

SYMBOLS AND ABBREVIATIONS

AIBN	2,2′-azo-bis-iso-butyronitrile
IL	ionic liquid
ILM	ionic liquid like monomer
M1	bis-1,3(*N,N,N*-trimethylammonium)-2-propylmethacrylate dichloride
M2	bis-1,3(*N,N,N*-trimethylammonium dicyanamide)-2-propylmethacrylate
PIL	polyionic liquid
SPE	solid-state polymer electrolyte
[1-Me-3-Etim]N(CN)$_2$	1-methyl-3-ethylimidazolium dicyanamide

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