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CHARACTERIZATION OF SEGREGATION IN A TUBULAR POLYMERIZATION REACTOR BY A NEW CHEMICAL METHOD

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ABSTRACT

Micromixing in a tubular polymerization reactor is characterized by the molecular mass of polystyrene obtained in the presence of a chain transfer agent. Monomer and the transfer agent are fed separately into the reactor. For constant overall inlet concentrations, the mean molecular mass produced is strongly dependent on mixing intensity.

Experiments were carried out in a pilot plant loop tubular reactor of different configurations and monomer conversions up to 80 %. The degree of segregation as a function of energy dissipation and the characteristic reaction time can be described by an empirical correlation. It could be shown that the design of the mixer can change considerably the micromixing efficiency.

KEYWORDS

Micromixing, polymerization, molecular mass distribution, tubular reactor, static mixer, segregation, mixing.

INTRODUCTION

Due to their simplicity, tubular reactors for homogeneous polymerization are of special industrial interest. One of the most important features of polymerization reactions is the large increase of viscosity with monomer conversion. Reaction kinetics as well as heat, mass and momentum transfer, mixing time and residence time distribution are significantly affected by the change of viscosity. To overcome the mentioned problems a new tubular reactor equipped with motionless mixers was developed (Nguyen *et al.*, 1985). The mixers improve considerably the heat transfer in the viscous medium and avoid the broad residence time distribution, normally observed for laminar flow. For the motionless mixer SMX (Sulzer, 1985) with an internal tube diameter of d_t = 40 mm, Flaschel et al. (1985) determined a Péclet number of Pe = $(u \cdot d_t / D_{ax})$ = 3.2 in the range of 10^{-4} < Re < 10^2. This corresponds to approximately 40 ideal mixers per meter. For the mixer type SMXL, having a more open structure, Juvet (1989) found a slightly broader residence time distribution corresponding to 25-30 ideal mixers per meter. The results prove an effective macroscopic radial mixing, but do not yield any information on the micromixing quality.

For complex reactions such as copolymerization, the quality of micromixing will strongly influence the product quality in terms of mean molecular mass and its distribution, the composition of copolymers and the sequence of monomer units (Ranz, 1986 ; Fields and Ottino, 1987). Preliminary studies (Meyer *et al.*, 1989) using an aqueous system of low viscosity ($\mu \leq 2 \cdot 10^{-3}$ Pa•s) have shown that the micromixing time in a static mixer is about 10 times smaller compared to mixing times in an empty tube under laminar conditions.

In the present contribution, a suitable test system for the characterization of micromixing in highly viscous liquids will be presented and used to compare the efficiency of different motionless mixers.

MEASUREMENT PRINCIPLES

The influence of micromixing on chemical processes may be characterized by two time-constants:
- the characteristic mixing time t_m depending on the flow conditions and mechanism of mixing involved
- the characteristic reaction time t_r depending on the initial reaction rate and reactant concentration.

Whereas for low viscous aqueous systems several model reactions were proposed to characterize the segregation behaviour (Barthole *et al.*, 1982 ; David *et al.*, 1984), only a few experimental studies on the determination of segregation in high-viscous polymerization reactions are known (Sahm, 1978).

In the present study the use of a chain transfer agent in the free-radical polymerization is proposed to characterize the degree of segregation in highly viscous homogeneous systems. The model reaction is based on the thermal bulk polymerization of styrene in the presence of a high active chain transfer agent (Meyer, 1989).

According to Mayo and Gregg (1948), the mean degree of polymerization is modified in the following way by the transfer agent:

$$\frac{1}{P_{N,S}} = \frac{1}{P_N} + K_{tr} \cdot \frac{C_S}{C_M} \tag{1}$$

P_N and $P_{N,S}$ are the degrees of polymerization without and in the presence of the transfer agent respectively. For a continuous well mixed reactor, eq. 1 leads to

$$\frac{1}{P_{N,S}} = \frac{1}{P_N} + K_{tr} \cdot \frac{F_{So}}{F_{Mo}} \cdot \frac{1}{[1 - X_M (1 - K_{tr})]} \tag{2}$$

with F_{Mo}, F_{So} the molar feed of monomer and transfer agent respectively. The chain transfer constant K_{tr} for the used tetrachloro-methane (CCl$_4$) is dependant on the reaction temperature (Mayo et al., 1948, Breitenbach et al., 1965; Földes-Berezsnich et al.; 1981) :

$$K_{tr} = 5.58 \exp(-2155/T) \tag{3}$$

The kinetics of the styrene polymerization can be described satisfactorily by a model proposed by Hui and Hamielec (1972).

$$R_P = A \, C_M^{5/2} ; \quad A = A_0 \exp(A_1 X_M + A_2 X_M^2 + A_3 X_M^3) \tag{4}$$

$$A_0 = 3.928 \cdot 10^5 \exp(-10040/T) \qquad A_1 = 2.57 - 5.05 \cdot 10^{-3} \cdot T$$
$$A_2 = 9.56 - 1.76 \cdot 10^{-2} \cdot T \qquad A_3 = -3.03 + 7.85 \cdot 10^{-3} \cdot T$$

The characteristic time constant of the polymerization process is defined as:

$$t_r = C_{Mo}/R_{Po} = A^{-1} C_{Mo}^{-3/2}, \text{ with } X_M = 0 \tag{5}$$

As for simple chemical reactions, the main parameter controlling the influence of segregation is given by the ratio t_r/t_m. If t_r/t_m is large, the fluid may be considered as well micromixed: the obtained polymer will have the molecular mass according to eq. 1 or 2. Conversely, when t_r/t_m is small, microscopic concentration gradients will appear and the fluid will be segregated. At the limit, for a completely segregated fluid, the separately introduced transfer agent will not influence the polymerization process and the mean molecular mass will not be changed.

EXPERIMENTAL

The pilot plant polymerization reactor is shown schematically in Fig. 1. It consists of a recycle tubular reactor, in series with a tubular reactor and is constructed entirely of stainless steel 316. The tubular part of the plant has a diameter of d_t = 20 mm and a total length of 1500 mm. Segregation studies were effected only in the loop reactor.

At inlet A 90% of the total monomer feed was introduced, 10% were added at position B. This secondary feed contains the chain transfer agent. The overall inlet concentration of the transfer agent was kept constant at 0.2% volume. Experiments were realized for different reaction temperatures, space times, reactor configurations and mixer types (Table 1). Within each experimental run, the recycle ratio (φ) and hence the energy dissipation was varied in a broad domain from approximately 20 to 120. The different experimental conditions are summarized in Table 2. The indicated conversion and dynamic viscosity is obtained for polymerization without chain transfer agent at a reference recycle ratio of φ = 40.

Whereas the effect of the chain transfer agent on the conversion can be neglected, the mean molecular mass is drastically reduced, which influences the viscosity of the reaction mixture.

Table 1:   Experimental configurations

Configuration	Tubes		
	1	2	3
SMXL 1	SMX d = 20 mm	SMXL d = 20 mm	SMXL d = 20 mm
	L = 500 mm	L = 500 mm	L = 500 mm
SMXL 2	SMXL d = 20 mm	SMXL d = 20 mm	SMXL d = 20 mm
	L = 500 mm	L = 500 mm	L = 1000 mm
	+ SMX d = 20 mm		
	L = 500 mm		
SMXL 3	SMX d = 20 mm	SMXL d = 20 mm	SMXL d = 10 mm
	L = 500 mm	L = 500 mm	L = 500 mm
SMX	SMX d = 20 mm	SMXL d = 20 mm	SMX d = 20 mm
	L = 500 mm	L = 500 mm	L = 500 mm

Table 2:   Experimental conditions

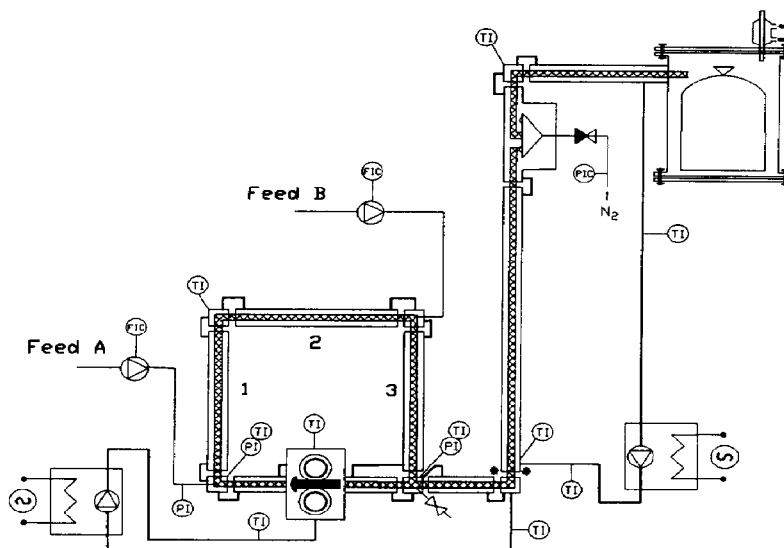| Run	Configuration	T_w °C	Q_0 ml/min	τ min	X -	μ Pa·s
SMXL 1A	SMXL 1	180	8	69	0.71	7.3
SMXL 1B	SMXL 1	160	4	137	0.64	16.8
SMXL 1C	SMXL 1	180	4	137	0.81	9.8
SMXL 2D	SMXL 2	160	6	137	0.64	17.3
SMXL 2E	SMXL 2	180	6	137	0.79	10.1
SMXL 3F	SMXL 3	160	3.2	137	0.63	18.1
SMXL 3G	SMXL 3	180	3.2	137	0.81	12.5
SMX A	SMX	160	4	137	0.62	16.9
SMX B	SMX	180	4	137	0.79	11.7

Fig. 1:   Experimental set-up

EXPERIMENTAL RESULTS

The polymerization loop reactor behave as an ideal continuous flow tank reactor for recycle ratios higher than 20. This was verified by measuring the residence time distribution, using a inert die as a tracer. Under the chosen experimental conditions, a complete macromixing can be assumed (Meyer, 1989). The influence of recycle ratio in the loop reactor on the mean molecular mass obtained is shown in Fig. 2.
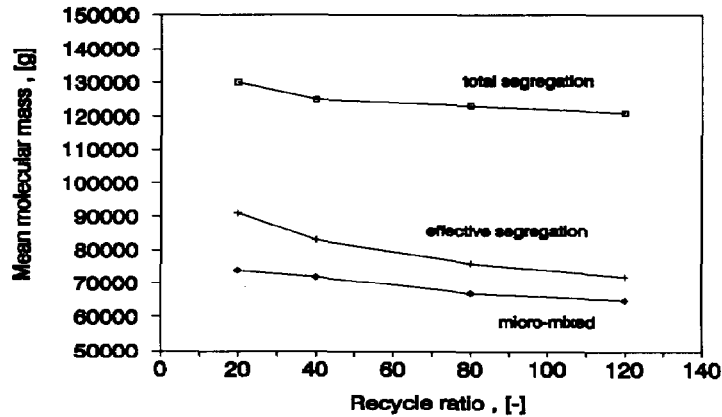

Fig. 2:   Mean molecular mass vs. recycle ratio (SMXL 1C)

To characterize the segregation in the reactor a linear scale between complete segregation and micromixing was assumed. The two limits can be determined experimentally. By premixing the monomer with the transfer agent, the polymer product corresponds to an ideal micromixed reactor (MM). The complete segregation (ST) is realized by injecting the pure monomer. The effective segregation (ES) is determined by injecting monomer and transfer agent separately as explained above. Based on the mean molecular masses obtained, a segregation index X_s is defined as follows:

$$X_s = \frac{\overline{M_w}\,(ES) - \overline{M_w}\,(MM)}{\overline{M_w}\,(ST) - \overline{M_w}\,(MM)} \tag{6}$$

where $\overline{M_w}$ is the mean molecular mass determined by Gel-Permeation-Chromatography.

Increasing recycle ratio, hence increasing energy dissipation in the reactor, leads to better micromixing. Figure 3 shows the determined segregation index for the motionless mixer types SMX and SMXL and two different characteristic reaction times of 27 and 10 min. The presented examples prove the strong influence of energy dissipation, reaction rate and mixer design on the micromixing quality.
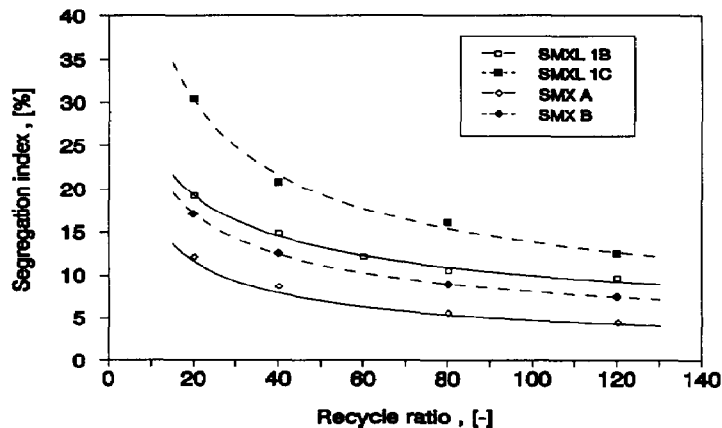

Fig. 3:   Segregation index vs. recycle ratio

DISCUSSION

The degree of segregation in a reactor depends on the ratio of the characteristic time constants for reaction and micromixing :

$$X_s = f\,(t_m\,/\,t_r) \tag{7}$$

The segregation index tends to higher values with increasing mixing time and decreasing reaction time (higher reaction rate). A very simple way to represent partial segregation in fluids is to consider it as a mixture of macrofluid (completely segregated fluid fraction X_s) and a microfluid (ideally micromixed fraction $1 - X_s$). An empirical relationship between the ratio of microfluid to macrofluid fraction (α) and the time constants was proposed by Villermaux and David (1983) and Villermaux (1986) :

$$\alpha = \frac{1 - X_s}{X_s} = a\,(t_r\,/\,t_m)^b \qquad \text{a, b constants} \tag{8}$$

Under conditions of laminar flow, the following relationship between micromixing time, specific energy dissipation (ε) and kinematic viscosity (v) of the fluid was found (Bourne, 1984; Geisler et al., 1988) :

$$t_m \sim \left(\frac{v}{\varepsilon}\right)^{1/2} ; \qquad \varepsilon = P/m \tag{9}$$

The energy dissipated in the reactor can be calculated by equation (10)

$$P = Q \cdot \Delta p ; \qquad \Delta p = \frac{4}{\pi}\, Ne\, Re_d \cdot \mu \cdot L/d^4{}_t \cdot Q \tag{10}$$

$$Ne\, Re_d \quad = \quad 250 \text{ (static mixer SMXL) (Sulzer, 1985)}$$

$$Ne\, Re_d \quad = \quad 1200 \text{ (static mixer SMX)}$$

The volumetric flow rate in the tubes is depending on the feed and the recycle ratio. The energy dissipation can be expressed as:

$$P = K\,(\varphi + 1)^2 \qquad \text{where K is a constant of proportionality} \tag{11}$$

In Fig. 4, the micromixedness ratio (α) is plotted versus $(\varepsilon/v)^{1/2}$ corresponding to the inverse mixing time.

In the logarithmic plot two straight lines are obtained for the experiments at 160° and 180° C. The configuration of the loop reactor has no influence on the segregation index. Only the energy dissipation and the viscosity are important for the micromixing behavior. It is interesting to remark, that at the reaction temperature of 160° C the segregation index is roughly 30 % smaller compared to runs at 180° C. The difference can be explained by the increase of the reaction rate with temperature.

Plotting α against the ratio of reaction time and mixing time all experimental results for one mixer type can be represented by a unique relationship resulting from equations 8 and 9 :

$$\alpha = a' \left[t_r\,(\varepsilon/v)^{1/2}\right]^b \tag{12}$$

In a logarithmic scale a straight line is obtained from which the model parameters a' and b can be determined.

In Fig. 5 all experimental results are summarized. It is important to note that for the two motionless mixer types SMX and SMXL, two parallel lines result indicating that the parameter b is identical for both mixers and parameter a' characterizes the mixer type.

$$\text{SMXL} \quad : \quad a'_L \quad = \quad 1.72 \cdot 10^{-3} \qquad\qquad b \quad = \quad 0.62$$

$$\tag{13}$$

$$\text{SMX} \quad : \quad a'_X \quad = \quad 2.82 \cdot 10^{-3} \qquad\qquad b \quad = \quad 0.62$$
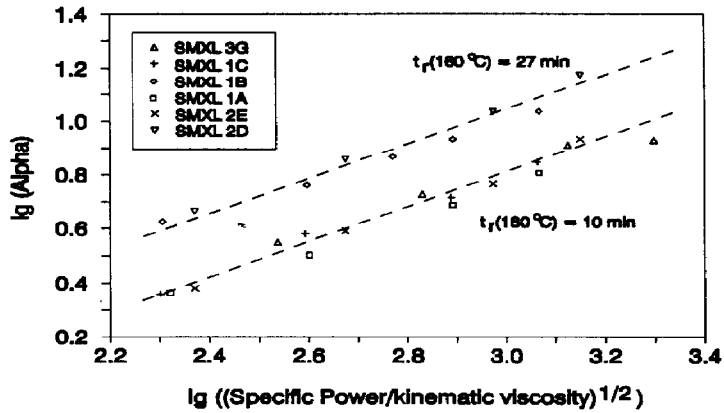
Fig. 4:   Logarithmic representation of α vs. $(\varepsilon / \nu)^{1/2}$
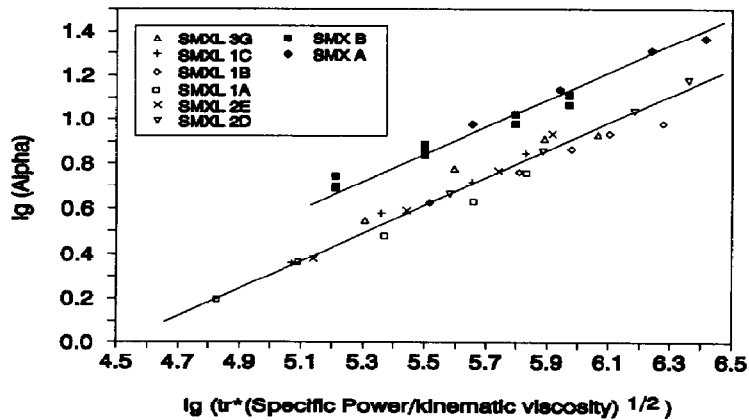

Fig. 5:   Logarithmic representation of α vs. $[t_r (\varepsilon / \nu)^{1/2}]$

Replacing a' in eq. 12 by the individual values and dividing the resulting equations one obtains with equation 8 :

$$\frac{\alpha_X}{\alpha_L} = \frac{a'_X}{a'_L} = \left(\frac{t_{m,L}}{t_{m,X}} \right)^b \tag{14}$$

Combining eqs. 13 and 14 leads to

$$\frac{t_{m,L}}{t_{m,X}} \approx 2 \tag{15}$$

This means that the mixing time in a SMXL motionless mixer is about two times longer than in the mixing element SMX for the same reaction time and energy dissipation. Under identical conditions the segregation in a SMXL mixer is always higher compared to the SMX element. For the experiment described, the ratio of the indexes seems to be independent from reaction conditions :

$$\frac{X_{s,L}}{X_{s,X}} \approx 1.5 \tag{16}$$

CONCLUSION

Besides the macroscopic behaviour of chemical reactors, micromixing is an important parameter influencing the product distribution in complex chemical systems as in co-polymerizations. Therefore, a knowledge of micromixing quality is essential for reactor design.

With the proposed chemical method, the micromixing behaviour in high viscous polymer solutions can be studied. For the used tubular loop reactor a relationship between segregation, power input and viscosity is presented, which can be used for scale-up purposes. A further important factor is the design of the mixing element. It is shown that the mixing efficiency of mixers can be quite different which leads to various micromixing times for identical energy dissipation.

NOMENCLATURE

Latin symbols

C	concentration, mol/m^3
D	dispersion coefficient, m^2/s
d	diameter, m
d_t	tube diameter, m
d_h	hydraulic diameter of mixer
K_{tr}	chain transfer constant, -
L	length, m
m	mass, kg
M_w	molecular mass, g
P_N	chain length, -
P	power, kg•m^2/s^3
Q	flow rate, m^3/s
u	superficial velocity, m/s
T	temperature, K
t	time, s
X	conversion, -
X_s	segregation index, -

Greek symbols

α	ratio of micro- and macrofluid volumes
Δp	pressure drop, bar
ε	specific power dissipation, W/kg
ε_v	void fraction, -
μ	dynamic viscosity, Pa•s
ξ	friction factor
ρ	density, kg/m^3
τ	space time, s
φ	recycle ratio, -

Index

L	SMXL-mixer
X	SMX-mixer

$$Ne = \xi \frac{d_t}{2 \cdot \varepsilon_v \cdot d_n} \quad \text{Newton-number}$$

$$Re_d = \frac{u \cdot d_t \cdot \rho}{\mu} \quad \text{Reynolds-number}$$

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