# Copolymerization of $\alpha$ -Methylstyrene with Methyl Methacrylate. III. Emulsion Process: Experimental Data on Kinetics, Particle Size, Composition, Molecular Weight, and Glass Transition Temperature

## F. MARTINET, J. GUILLOT

Laboratoire de Chimie et Procédés de Polymérisation–LCPP/CNRS–CPE, Bât 308 F, 43 Boulevard du 11 Novembre 1918, 69616 Villeurbanne Cedex, France

Received 10 February 1998; accepted 1 June 1998

ABSTRACT:  $\alpha$ -methylstyrene–methyl methacrylate emulsion copolymerizations have been investigated at various temperatures (60, 70, 85°C) on the whole composition range. The kinetic behavior has been studied, such as conversion, particle size, and the average number of radicals per particle ( $\tilde{n}$ ), as well as the following characteristics of the copolymers: composition, microstructure, molecular weights (MWD), and glass transition temperature ( $T_g$ ). One of the main results is the possibility to synthesize stable copolymers with high  $T_g$  (i.e., 132–140°C). © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 72: 1627–1643, 1999

**Key words:**  $\alpha$ -methylstyrene; methyl methacrylate; emulsion copolymerization; kinetics; copolymer properties

# **INTRODUCTION**

The main objective in this work was to increase the glass transition temperature  $T_g$  of copolymers of  $\alpha$ -methylstyrene ( $\alpha$ MSt) with methyl methacrylate (MMA) and to investigate the role of the various experimental conditions in an emulsion batch process. In previous articles dealing with solution<sup>1</sup> and bulk<sup>2</sup> copolymerization processes, it has been shown that it is not possible to generate copolymers with sufficiently high molecular weights to increase  $T_g$  above that of pure MMA, that is, 105°C. On the contrary, too low of molecular weights lead to  $T_g$ s lower than  $T_{g,MMA}$ . However, bulk copolymerization have allowed to precise the reactivity ratios  $r_{ij}$  and the copolymer microstructure, which confirmed that the depropagation limited drastically the length of  $\alpha$ MSt sequences and that an azeotropic composition did exist, which is slightly shifted towards MMA-rich monomer feeds when the temperature was increased. In the same way, the  $\alpha$ MSt copolymer content was higher at a high temperature and  $\alpha$ MSt mol % in the monomer feed.

The modeling developed gave a satisfactory agreement with solution and bulk experimental data on kinetics, composition, microstructure, molecular weight distribution (MWD), and limited  $T_g$ s. It is believed that the main parameters involved in these quantitative models could also be used in emulsion copolymerization since, indeed, in emulsion, the actual main locus of polymerization, above all, with low hydrophily monomers, is the bulky polymer particle swollen by monomers, with two other main differences being monomer partitioning

Correspondence to: J. Guillot.

Contract grant sponsor: EC BRITE-Euram Project INTELPOL CT; contract grant number: 93-0553.

Journal of Applied Polymer Science, Vol. 72, 1627–1643 (1999) © 1999 John Wiley & Sons, Inc. CCC 0021-8995/99/121627-17

(for MMA, as a matter of fact) and the colloidal nature of the emulsion process.

It is noteworthy, however, that some of the model parameters had unusual values: low propagation rate constants for  $\alpha$ MSt, namely,  $k_{p\alpha MSt}$  equals 47 L mol<sup>-1</sup> s<sup>-1</sup> along with a depropagation equilibrium constant, K<sub>11</sub>, increasing with temperature from 7, at 60°C, up to 13, at 85°C, with a very high termination rate constant, that is,  $k_{t11} = 5$  and/or 10 10<sup>9</sup> L mol<sup>-1</sup> s<sup>-1</sup> (close to 10 times the values for usual monomers), as well as a higher transfer rate constant of  $\alpha$ MSt radicals on monomers.

One of the more interesting features of bulk copolymerization was the low radical concentration, which was of the order of magnitude of  $5.10^{-9}$  mol  $L^{-1}$ , computed as well from the following classical equation:  $[R^{\bullet}] = \sqrt{\frac{2fk_d[\text{Init}]}{k_t}}$ , as from the basic experimental data,  $[R^{\bullet}] = \frac{R_p}{k_p[M_{\text{tot}}]}$ , where *f* is the initiator efficiency,  $k_d$  is the rate of initiator decomposition, [Init] is its concentration,  $k_p$  and  $k_t$  are the rate constants for the propagation and the termination, respectively,  $[M_{tot}]$  is the total monomer concentration, and  $R_p$  the rate of polymerization in mol  $L^{-1} s^{-1}$ ). This a rather low value of radical concentration, in addition to the lower values of  $k_p$  due to the depropagation effect induced by  $\alpha MSt$  (see Martinet and Guillot<sup>2</sup>) was an explanation of the very low rate of polymerization  $R_p$  obtained in solution and bulk processes.

So, it was expected that the huge compartimentalization of the emulsion process would confine the active centers within particles and, this way, increase the apparent radical concentration by increasing the average lifetime of a radical in each polymer particle. Another direct expected consequence would be much higher molecular weights. Indeed, in solution or bulk processes,  $R_p$  and the kinetic length  $\nu$  are connected by the following relation  $R_p \nu = \frac{k_p^2 [M_{tot}]^2}{k_t}$ , while, in emulsion, they are disconnected, owing to the colloidal nature of the process and, hence, it is possible to increase simultaneously both  $R_p$  and  $\nu$ , that is, the molecular weights.

Few works have been published on emulsion copolymerization of  $\alpha$ -methylstyrene. Golubeva et al.<sup>3</sup> investigated the copolymerization with styrene (St), MMA, and 2,5-dichlorostyrene and found that the rates of polymerization were larger

than in solution or bulk processes. Some properties were also studied by this author, such as viscosity and the mechanical module. The latter were found to drastically decrease with the amount of  $\alpha$ MSt in the copolymers, while the thermal stability was increased, with the effect being more pronounced with MMA than with styrene. Rudin and Samanta<sup>4–6</sup> have also studied the effect of the temperature, of the  $\alpha$ MSt content in monomer feed, and of the emulsifier on conversion, copolymer composition, and molecular weights.

# EXPERIMENTAL PART

The reactor was a double-wall glass vessel of 1 L, equipped with a condenser and a stirrer of the Rushton turbine type. The reactor temperature was controlled by a thermostated bath within  $\pm 0.1^{\circ}$ C. Samples were withdrawn through a bottom valve. Monomers (from Jansen Chimica, 99% pure grade) were distilled under vacuum and kept under nitrogen at  $-40^{\circ}$ C. Deionized water was deoxygenated by bubbling nitrogen before the reaction. Emulsifier sodium dodecylsulfate (SDS) and initiator potassium persulfate (KPS) were pure grade and were used as received (from Acrôs S.A.).

Conversion was determined by gravimetry. Copolymer composition was investigated by gas chromatography (Hewlett Packard 5890 II-column DBWAX 15 m) and <sup>1</sup>H nuclear magnetic resonance (<sup>1</sup>H-NMR). (Bruker 250 MHz). Particle size was measured by light scattering (Brookhaven BI 8000). Molecular weights were investigated by gel permeation chromatography (GPC) on a WA-TERS apparatus, equipped with a PSS gel mixed B column of 1.2 m. Styrene mass standards were used for calibration. Glass transition behavior was studied by differential thermal analysis (SETARAM DSC 101), at a heating rate 10°C  $\min^{-1}$ , on 40–60-mg samples. The glass transition temperature  $T_g$  was defined as the intercept of base line at low temperature with the tangent at an inflection point.

For these series of emulsion copolymerization, the solids content was always maintained at 10% weight, with 0.8 g of KPS and 2.7 g of SDS, for 100 g of monomers (total). Table I gives the references of experiments carried out at 60, 70, and 85°C.

Mol Content of $\alpha$ MSt in the	Temperature			
Monomer Feed (mol %)	60°C	70°C	85°C	
0	Em0-60	Em0-70		
10	Em10-60	Em10-70	Em10-85	
25	Em25-60	Em25-70	Em25-85	
35	Em35-60	Em35-70	Em35-85	
50	Em50-60	Em50-70	Em50-85	
75	Em75-60	Em75-70	Em75-85	

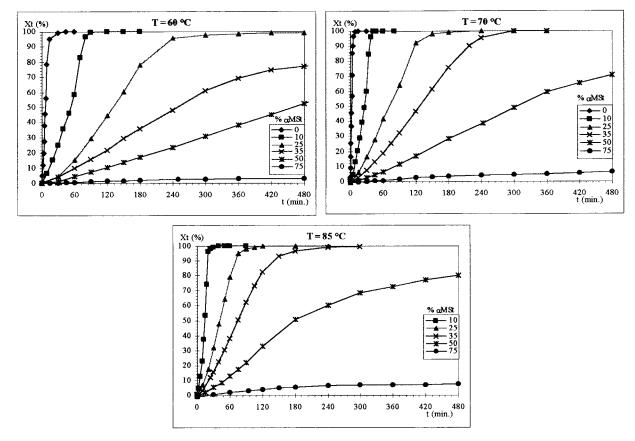
Table I References for the Copolymerizations  $\alpha$ MSt-MMA, Carried Out in Emulsion at 60, 70, and 85°C

# **RESULTS AND DISCUSSION**

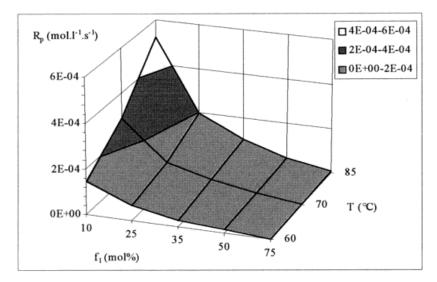
## Conversion

Overall conversion was determined by gravimetry on small emulsion samples withdrawn at regular time intervals. Figure 1 reports the experimental data at various temperatures and  $\alpha$ MSt contents.

Obviously, whatever the temperature may be, the conversion is decreased with increasing  $\alpha$ MSt contents. A similar behavior was observed in solution<sup>1</sup> and bulk<sup>2</sup> copolymerization of  $\alpha$ MSt, as well as with acrylonitrile,<sup>7</sup> styrene,<sup>8,9</sup> or MMA.<sup>2,3,7</sup> However, by comparison with solution and bulk processes, emulsion allowed us to reach 100% conversion within reasonable polymerization times and with longer times, when temperature is lower. It should be, nevertheless, noticed that at  $\alpha$ MSt content above 50%, a limit conversion is practically observed; and the lower the level, the higher the  $\alpha$ MSt contents. This drastic difference observed at any temperature between 35  $\alpha$ MSt% content, at which monomer depletion was reached in few hours, and 50%  $\alpha$ MSt, at which it was not anymore possible to reach 100% conversion in a realistic time, should be assigned to the azeotropic composition behavior induced by



**Figure 1** Experimental conversion  $(X_t \%)$  for emulsion copolymerizations  $\alpha$ MSt-MMA, at 60, 70, and 85°C versus time (t) and the molar content of  $\alpha$ MSt in the monomer feed (mol %; figures in blocks).



**Figure 2** Experimental rates of polymerization for the emulsion copolymerizations  $\alpha$ MSt–MMA ( $R_p$ ) versus mole content of  $\alpha$ MSt ( $f_1$ , mol %) and temperature (T, °C).

the reactivity ratios. Indeed, below  $30-35 \alpha MSt\%$ in the monomer feed,  $\alpha MSt$  was consumed the faster, and MMA was accumulated, with a quite rapid end of polymerization, while above this, azeotropic composition, on the contrary,  $\alpha MSt$ was accumulated with increasing conversion, which derides  $k_p$  very much.<sup>1,2</sup> Furthermore, above 75%  $\alpha MSt$ , the conversion is of the order of 5–10%, that is, within the nucleation stage.

The temperature has also a huge effect. All the rates of polymerization  $R_p$  increased with the temperature, despite the fact the copolymerizations have been carried out above the ceiling temperature of  $\alpha$ MSt (i.e., 61°C). If homopolymerization is impossible, copolymerization appeared always feasible, as the kinetic curves showed. For the same  $\alpha$ MSt content, the rate of polymerization always increased with temperature, as it was observed in the copolymerization of  $\alpha$ MSt with styrene.<sup>9</sup>

The homopolymerization of MMA is very fast in our conditions. At 70°C, it is less than 15 min to consume all the monomers, and a quite large exotherm has been observed. It was not even possible to polymerize MMA at 85°C for the reaction medium was not any more controllable nor was the withdrawing of samples.

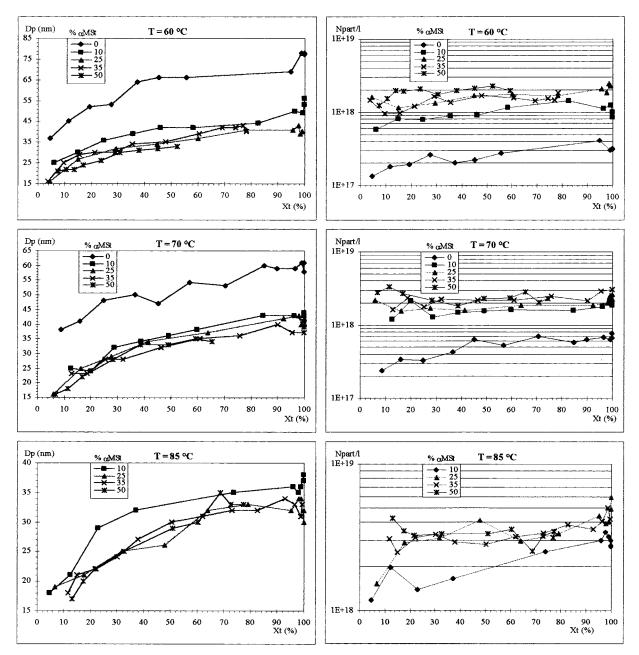
Figure 2 expresses, in a graphic mode, the rate of change of  $R_p$  versus temperature and  $\alpha$ MSt contents above 10%. There is a drastic decrease of  $R_p$  when the  $\alpha$ MSt content increased in the monomer feed. The  $\alpha$ MSt content should be kept below

25% for  $R_p$  to be above  $2.10^{-4}$  mol L<sup>-1</sup> s<sup>-1</sup>  $R_p$  for pure MMA has been measured as  $10^{-3}$  mol L<sup>-1</sup> s<sup>-1</sup> at 60°C and  $3.10^{-3}$  mol L<sup>-1</sup> s<sup>-1</sup> at 70°C and, so, were not reported on the three-dimensional (3-D) graph. 10%  $\alpha$ MSt in the feed decreased the rate of polymerization 10-fold.

# Particles Size and Number

In the operation conditions, the particle sizes were always small, as often observed with MMA copolymers (see, e.g., Nomura and Fujita<sup>10</sup>) for MMA-styrene emulsion copolymerization. As a consequence, the number of particles per volume unit  $N_p$  was quite large. However, on the contrary to what was observed with MMA-styrene, the particle size  $D_p$  was decreasing with an increasing  $\alpha$ MSt content; hence, the tendency for  $N_p$  was to increase with the  $\alpha$ MSt amount. Figure 3 shows the experimental data at 60°C, 70°C and 85°C.

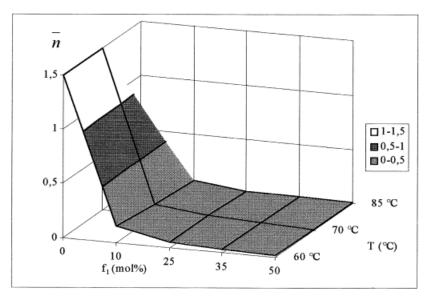
A similar trend was observed in  $\alpha$ MSt-St emulsion copolymerization,<sup>9</sup> with larger  $D_p$ , nevertheless. The introduction of  $\alpha$ -methylstyrene in the monomer feed had a drastic effect on the particle size lowering. 10%  $\alpha$ MSt decreased by half the  $D_p$ . Further increases of  $\alpha$ MSt had a more limited consequence, and  $D_p$  is kept within the range of 20–40 nm, with a tendency towards lower sizes at higher temperatures.  $N_p$  was of the order of magnitude  $3.10^{17}$  L<sup>-1</sup> for MMA and  $10^{19}$  L<sup>-1</sup> for copolymerization with  $\alpha$ MSt. Castellanos Ortega<sup>9</sup>



**Figure 3** Particle size  $(D_p)$  and particle number  $(N_{\text{part L}})$  per litre of emulsion for the copolymerizations carried out at 60°C, versus conversion (gravimetry,  $X_t \%$ ) and  $\alpha$ MSt content (mol %) in the monomer feed.

showed than in a copolymerization of  $\alpha$ MSt with styrene, the numbers of particles  $N_p$  were closer for homo- and copolymerization, with the same tendency to increase with  $\alpha$ MSt content, that is, also in contrast with the MMA–styrene system. With MMA, the decrease of  $D_p$  with  $\alpha$ MSt content corresponds to an increase of  $N_p$  with  $\alpha$ MSt and temperature. As a matter of fact, the average  $N_p$  varied from  $10^{18}$  L<sup>-1</sup>, at 60°C, up to 4.10<sup>18</sup> L<sup>-1</sup>, at 85°C.

It seems clear that  $\alpha$ MSt leads to generate much lower size particles when copolymerized with S or MMA. Above 75%  $\alpha$ MSt, it was even very hard to measure with a good reproducibility the  $D_p$ , for these sizes were at the limit of the light scattering apparatus. It is noteworthy that,



**Figure 4** Average number of radical per particle  $\tilde{n}$  for emulsion copolymerizations at various temperatures (°C) versus the temperature and the  $\alpha$ MSt content in the monomer feed ( $f_1$ , mol %).

as a general trend,  $N_{\boldsymbol{p}}$  was to be kept constant during all the polymerization with  $\alpha$ MSt, while a significant increase with conversion was observed with pure MMA. It seemed that nucleation took place in very short time, owing to a high rate of oligoradical generation in the water, induced by the hydrophilicity and high  $k_{p22}$  for MMA, on one hand, and a favorable hydrophilic-lipophilic balance (HLB) of these oligoradicals, which can be easily surface-active due to the pronounced hydrophobic nature of  $\alpha$ MSt units, on the other hand, which improved fast nucleation of very tiny particles. Owing to large interfacial forces, the swelling of these small particles is limited; the glass transition temperature of these poorly swollen particles could then be high enough, in connection with the high  $T_{g\alpha MSt} \cong 180^{\circ}$ C, to prevent from easy flocculation. As their total surface area is very soon quite large, the oligoradicals generated in the water phase have a large surface to be captured and a lower probability to renucleate a new crop of particles. The large number of particles explained the rather high rates of polymerization observed, at least up to 30-35% aMSt. Indeed, in emulsion,  $R_p$  is directly proportional to  $N_p$ , as follows:

$$R_{p} = \mathbf{K}_{p} \cdot [M]_{p} \cdot (\tilde{n}/\mathcal{N}_{a}) \cdot N_{p} \tag{1}$$

where  $K_p$  is the global(pseudokinetic) propagation rate constant L mol<sup>-1</sup> L<sup>-1</sup>,  $[M]_p$  is the total monomer concentration in the particle,  $\tilde{n}$  is the average number of radical per particle, and  $\mathcal{N}_a$  is Avogadro's number.

#### Average Number of Radicals per Particle *ñ*

The average number of radicals per particle  $\tilde{n}$  is the other basic parameter in the emulsion process since it represents the number of active centers per polymerization locus and  $(\tilde{n}/N_a)$ .  $N_p$  is, to some extent, the apparent global active center concentration for the whole volume unit of emulsion ( $\equiv [R^{\circ}]$ ; see Fig. 4).

This crucial kinetic parameter  $\tilde{n}$  can be computed from more or less rigorous theories (see, e.g., Nomura et al.<sup>10</sup> and O'Toole<sup>11</sup>) or else can be derived from experimental data with eq. (1).

$$\tilde{n} = \frac{R_p \cdot \mathcal{N}_a}{\mathrm{K}_p \cdot [M]_p \cdot N_p} \tag{2}$$

 $R_p$  and  $N_p$  are easily obtainable experimental data.  $[M]_p$  can be either determined from experience, swelling + centrifugation + CG analysis,<sup>12</sup> or estimated from thermodynamics.<sup>13,14</sup> In our conditions,  $[M]_p$  at saturation varied from 2.5–3 mol L<sup>-1</sup>.

The global propagation rate constant  $K_p$  is a complex function, but nevertheless, computable. Indeed, in the classical copolymerization of N monomers,

Temperature	Identification Emulsion	$\begin{array}{c} \alpha MSt \ Fraction \\ (mol \ \%) \end{array}$	$\overline{\mathrm{K}_{\!p}}  \operatornamewithlimits{\mathrm{L}}_{\mathbf{S}^{-1}} \mathrm{mol}^{-1}$	$\bar{n}$
60°C	Em 0-60	0	500	2,809
60°C	Em10-60	10	290	0,155
60°C	Em25-60	25	191	0,050
$60^{\circ}\mathrm{C}$	Em35-60	35	153	0,037
60°C	Em50-60	50	115	0,020
$70^{\circ}C$	Em 0-70	0	652	2,031
$70^{\circ}C$	Em10-70	10	442	0,105
$70^{\circ}C$	Em25-70	25	317	0,047
$70^{\circ}C$	Em35-70	35	258	0,028
$70^{\circ}C$	Em50-70	50	191	0,015
$85^{\circ}C$	Em10-85	10	786	0,073
$85^{\circ}C$	Em25-85	25	617	0,022
$85^{\circ}C$	Em35-85	35	531	0,015
85°C	Em50-85	50	407	0,008

Table II Global Propagation Rate Constant  $(K_p)$  and Average Radical Number per Particle  $(\tilde{n})$  for the Emulsion Copolymerizations Carried out at 60, 70, and 85°C

$$\mathbf{K}_{p} = \sum_{1}^{N} \sum_{1}^{N} \mathbf{k}pij \cdot \Phi i \cdot fj$$

where  $\Phi i$  is the molar fraction of radical of type *i*, derived from the steady-state assumption, and *fj* is the mole fraction of monomer *j*.

When depropagation does occur, as in  $\alpha$ MSt copolymerizations,  $K_p$  is modified and expressed as follows<sup>1,2</sup>:

$$\mathbf{K}_{p} = \sum_{1}^{N} \sum_{1}^{N} \mathbf{k}pij \cdot \Phi i \cdot fj - \frac{\mathbf{K}_{11}}{[\mathbf{M}_{tot}]} \sum_{m=2}^{\infty} \Phi_{1,m} \qquad (3)$$

Where  $K_{11}$  is the equilibrium constant for depropagation,<sup>15</sup>  $[M_{tot}]$  is the total monomer concentration, and *m* is the length of the  $\alpha$ MSt sequences in the terminal  $\alpha$ MSt growing radical. Note that in this series of articles,  $\alpha$ MSt is always referred as to monomer 1 and MMA is referred to as monomer 2.

 $\rm K_{11}$  varies with temperature<sup>8,15,16</sup> as  $[M_{tot}]$  does with conversion. As a consequence,  $\rm K_p$ , in such copolymerizing systems, decreases with increasing temperature and  $\alpha \rm MSt$  content and also with decreasing monomer concentration. In Table II,  $\rm K_p$  has been computed from the kinetic parameters used in the previous articles<sup>1,2</sup>; in particular  $\rm k_{p11}$  was assumed equal to 47 L mol<sup>-1</sup> s<sup>-1</sup> (at

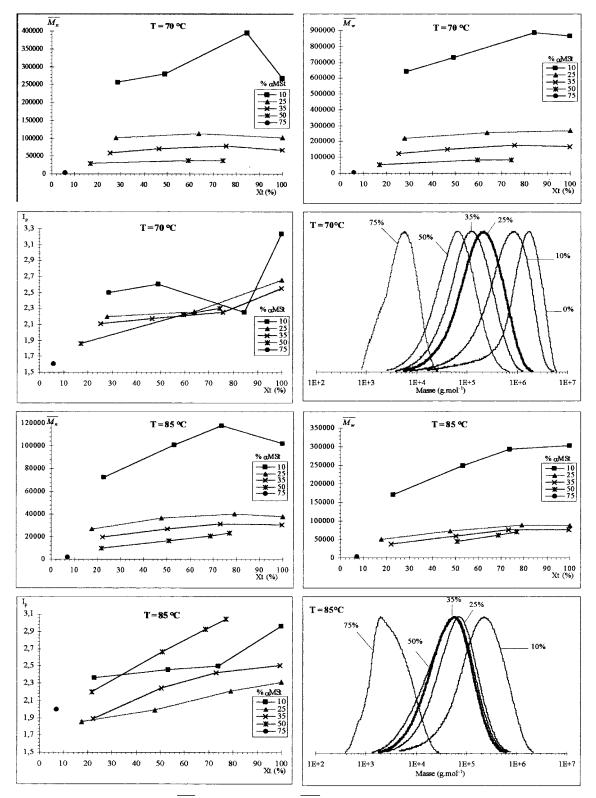
60°C);  $E_{ap1} = 13$  kcal mol<sup>-1</sup>;  $K_{11} = 7.1$ , 9.1, and 14.0 mol L<sup>-1</sup> at 60, 70, and 85°C, respectively, for  $\alpha$ MSt;  $k_{p22} = 500$  L mol<sup>-1</sup> s<sup>-1</sup> (at 60°C);  $E_{ap2} = 6$  kcal mol<sup>-1</sup>, for MMA.

A drastic change of  $\tilde{n}$  was observed as soon as  $\alpha$ MSt was added in the monomer feed. With pure MMA,  $\tilde{n}$  is larger than the ideal value  $\tilde{n} = 0.5$ , certainly in connection with a huge gel effect. The lower the values of  $\tilde{n}$ , the higher the  $\alpha$ MSt content, at a given temperature, and the higher the temperature, at a given  $\alpha$ MSt content. This behavior, different from what was observed in the copolymerization  $\alpha$ MSt-St,<sup>9</sup> where  $\tilde{n}$  was kept close to  $\tilde{n} \approx 0.5$ .

However, a similar trend has been observed in the copolymerization of MMA–St (Nomura), where low  $\tilde{n}$  values have been derived and explained as a consequence of radical desorption mechanism.

# **Molecular Weight Distribution**

Figure 5 shows the experimental data at 60°C and 85°C for the number- and weight-average molecular weights,  $\overline{M_n}$  and  $\overline{M_w}$ , as well as the polydispersity,  $I_p = \overline{M_w}/\overline{M_n}$ . Molecular weights were very sensitive to the amount of  $\alpha$ MSt. For instance, at 60°C, the average number of monomer units was decreased from 5500, at 10%  $\alpha$ MSt, down to 80, at 75%  $\alpha$ MSt. On the other hand, as shown in Table III, the decrease in molar mass



**Figure 5** Number  $(\overline{M_n})$ , weight-average  $(\overline{M_w})$  molecular weights, and polydispersity index  $(I_p)$  for emulsion copolymers synthesized at 70 and 80°C versus conversion (gravimetry,  $X_t \%$ ) and mol %  $\alpha$ MSt in the monomer feed (figures in blocks). Bottomright: molecular weight distribution at various  $\alpha$ MSt mol % in the monomer feed.

Measurement	Em 0-70	Em 10-70	
$\overline{M_n}$	1,089,220	268,080	
$\overline{M_w}$	1,904,960	865,920	
$I_p$	1.75	3.23	

was well marked between the MMA homopolymer and copolymers with only 10%  $\alpha$ MSt.

Indeed, at 60°C, 10%  $\alpha$ MSt decreased by half the molecular weights and by four times, at 70°C. A general tendency was for the number-average molecular weights to diminish at high conversion, while, on the contrary, for the weight-average to increase. That should be connected with the generation of lower molecular weight chains, at high conversion, and was corroborated by the increase of polydispersity index  $I_p$  at the end of polymerization. The higher rate of increase of  $I_p$  with conversion for copolymers with 50%  $\alpha$ MSt should be connected with azeotropy and the generation of lower and lower masses with conversion in this feed composition range. Surprisingly, there was a clear skewing towards the low molecular weights for MMA homopolymerization, which could be attributed to a small amount of macromolecules generated and terminated in the water phase, or, else, due to transfer reactions.

The temperature also had an important and decreasing effect on the molecular weights. As an illustration, Figure 6 shows the behavior of copolymers with 25%  $\alpha$ MSt versus temperature. The number-average molecular weight  $M_n$  was decreased six times, when temperature was increased from 60 to 85°C. All molecular weight distribution was shifted towards lower  $I_p$  Em 25–85 = 2.3. As a general trend, quite low molecular weight chains were produced at high  $\alpha$ MSt contents (>35% wt  $\alpha$ MSt) and higher temperatures. Nevertheless, in emulsion, molecular weights were much higher than in bulk or solution. For instance, at 25%,  $\alpha MSt$  $\overline{M_n}$ (bulk) = 6,000 g mol<sup>-1</sup>,  $\overline{M_n}$ (Em) = 200,000 g  $mol^{-1}$ ; at 50%,  $\alpha MSt M_n(bulk) = 3.500 \text{ g mol}^{-1}, M_n$  $(Em) = 8.500 \text{ g mol}^{-1}.$ 

## **Copolymer Composition and Microstructure**

The chemical composition of copolymers was determined by <sup>1</sup>H-NMR. It is expressed as the mole percent of  $\alpha$ MSt,  $F_1$ , in Figure 7.

The initial copolymers seemed to be richer in MMA than expected from the reactivity ratios determined in bulk:  $r_1 = 0.5 \pm 0.03$  and  $r_2 = 0.49 \pm 0.02$ , particularly, at the higher  $\%\alpha$ MSt. In the same way, the copolymer composition, at intermediate conversions, were slightly richer in  $\alpha$ MSt than in solution or bulk processes.

These differences should be related to monomer partitioning in emulsion, above all that of MMA, the more hydrophilic monomer, the amount of which, in the water phase, was not anymore negligible at the solids content used, that is,  $\approx 10\%$ . At low conversion, the copolymers generated in water were richer in MMA, and their contribution to  $F_1$  was larger at the beginning since the particle phase was yet at a low level, which is not the case anymore above 10-20%conversion. A similar behavior was observed, for example, in the emulsion copolymerization of MMA-butyl acrylate<sup>17</sup> or MMA-St.<sup>16</sup>

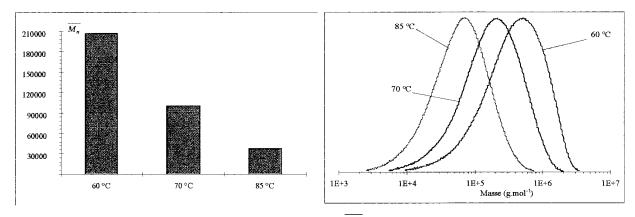
The copolymer composition data clearly put in evidence an azeotropic behavior, also in emulsion, with an azeotropic monomer feed close to 30-35% mol  $\alpha$ MSt. Indeed, below this composition, the chemical composition drift is downward; while above 35%  $\alpha$ MSt, the drift was, on the contrary, upward.

The copolymer composition of emulsion copolymers was more sensitive to experimental operative conditions than in bulk, owing mainly to the monomer partitioning and water phase polymerization.

A tentative investigation of the sequence distribution was also done by <sup>13</sup>C nuclear magnetic resonance (<sup>13</sup>C-NMR) on the copolymers synthesized at 70°C. Indeed, the main practical objective was to increase the glass transition temperature of the copolymers by introducing long  $\alpha$ MSt sequences since  $T_{g\alpha MSt} \approx 180$ °C. But, unfortunately, depropagation plays the opposite role and tends to drastically limit the length of  $\alpha$ MSt sequences.

Two carbons seemed more favorable for investigating the copolymer microstructure, namely, the  $C_{\infty}$  of PMMA (45 ppm) and  $C_{\infty}$  of P $\alpha$ MSt (44 ppm). The former is with a low configuration effect, and the latter is without any configuration effect, but both are close to one another. Assignments based on the spectrum of copolymer Em 10-70 (rich in MMA) lead to the following triad resonances: 45.8–46.5 ppm, M<sub>1</sub> M<sub>2</sub> M<sub>1</sub> triad; 45.0–45.8 ppm, M<sub>2</sub> M<sub>2</sub> M<sub>1</sub> triad; 44.5–45.0 ppm, M<sub>2</sub> M<sub>2</sub> M<sub>2</sub> triad.

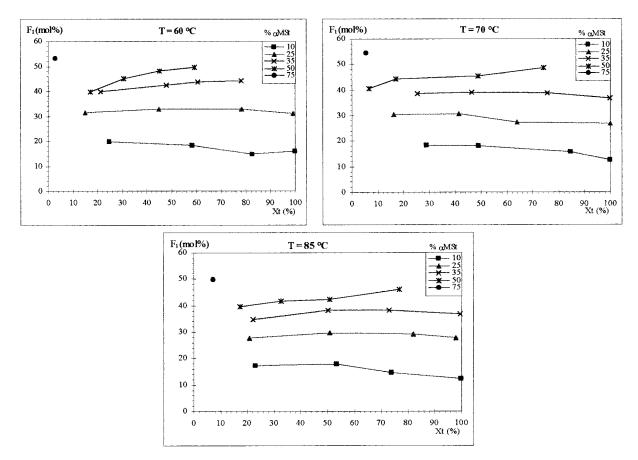
However, with the copolymers richer in  $\alpha$ MSt, the compositional effect did not seem large enough, and it was preferable to base the investigation on the  $C_{\alpha}$  of  $\alpha$ MSt (41-44 ppm)



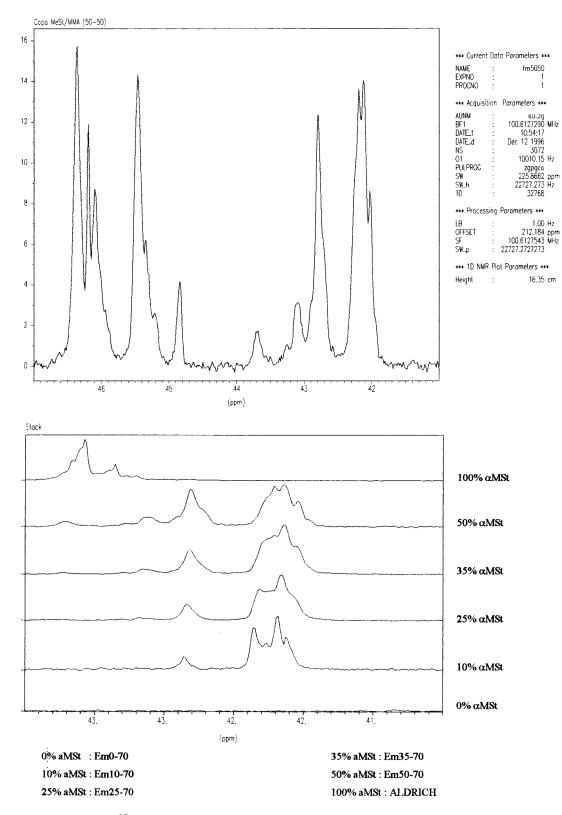
**Figure 6** Number-average molecular weight  $(M_n)$  and molecular weight distribution for emulsion copolymerizations with 25 mol %  $\alpha$ MSt, at 60, 70, and 85°C.

with the following assignments (Fig. 8): 43.5–44 ppm,  $M_1 M_1 M_1$  triad; 42.5–43.5 ppm,  $M_2 M_1 M_1$  triad; 41.5–42.5 ppm,  $M_2 M_1 M_2$  triad.

These <sup>13</sup>C-NMR sequences were compared to the computed one, based on conditional probabilities for various linkage (see Martinet and Guillot<sup>2</sup>). The influence of  $\alpha$ MSt was quite large on the



**Figure 7** Molar content of  $\alpha$ MSt in the emulsion copolymers  $(F_1)$  versus conversion  $(X_t \%)$  and  $\alpha$ MSt content of monomer feed (mol %, figures in blocks), polymerized at 60, 70, and 85°C.



**Figure 8** <sup>13</sup>C-NMR spectroscopy of emulsion copolymers of various compositions ( $\alpha$ MSt mol %), synthesized at 70°C. Upper diagram: detailed spectrum for copolymer Em 50-70. Lower diagram: spectra for the various copolymers, prepared in emulsion at 70°C, and various monomer feed compositions.

Emulsion Copolymer	$M_{1}M_{1}M_{1}$	$M_1M_1M_2$		$M_2M_1M_2$		
	Aire 1	$F_{11}$	Aire 2	$F_{11}$	Aire 3	<i>F</i> <sub>212</sub>
Em 10-70	2.0	0.1	9.3	4.5	88.8	95.5
Em 25-70	1.5	0.3	13.4	10.4	85.1	89.3
Em 35-70	1.3	0.6	25.0	14.8	73.7	84.5
Em 50-70	4.1	1.5	39.3	21.8	56.6	76.7

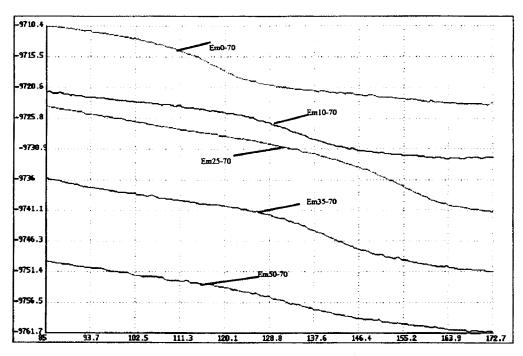
Table IV Experimental (Aire %) and Computed (F %) Data According to the Model of Triads Assignment for the Emulsion Copolymers Synthesized at 70°C

 $^{13}\text{C-NMR}$  spectra. The  $M_1\,M_1\,M_1$  always was kept at low level and was even difficult to measure at a high MMA content. Most triads are of the  $M_2\,M_1$   $M_2$  type, that is, with isolated  $\alpha \text{MSt}$  units. Table IV reports  $^{13}\text{C-NMR}$  of copolymers prepared at 70°C.

However, the simple assignment scheme used in this approach overestimated the  $M_2 M_1 M_2$ triads and underestimated the  $M_1 M_1 M_2$ . Nevertheless, this study confirmed that the probability to have  $\alpha$ MSt sequences with more than three  $\alpha$ MSt units was very low and justify the assumption made in our kinetic scheme (see Martinet and Guillot<sup>1</sup>) of the actual absence of  $\alpha$ MSt sequences longer than five  $\alpha$ MSt units. There was a strong tendency to alternation in these  $\alpha$ MSt–MMA copolymers.

## Glass Transition Temperature $T_g$

The glass transition temperatures  $T_g$  have been determined by differential thermal analysis (DTA) at the same heating rate of 10°C min<sup>-1</sup>. An important point to be raised when dealing with  $T_g$ s is the exact definition of the value, above all when the thermogramme (DSC or DTA) is complex. In this work, the following two parameters have been measured: namely, the glass transition temperature  $T_g$ , defined as the intercept of the base line at low temperature with the tangent at



**Figure 9** Differential thermal analysis (DTA;  $10^{\circ}$ C min<sup>-1</sup> heating rate) diagrams of copolymers synthesized at 70°C, with various  $\alpha$ MSt contents.

$\alpha$ MSt Content in Monomer Feed			
(mol %)	60°C	70°C	$85^{\circ}C$
0	105	105	
10	117.5	118.9	115.8
25	127.9	132.3	117.4
35	115.9	126.5	103.6
50	111.1	122.5	98.9
75	40	66.9	60.3

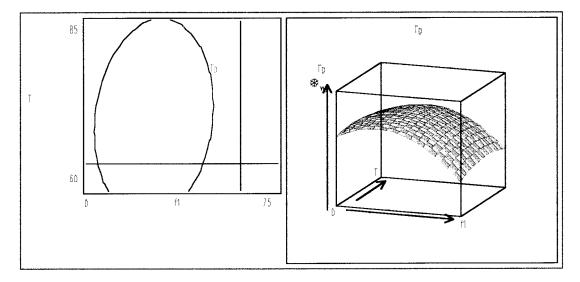
Table V Glass Transition Temperatures (°C) of Emulsion Copolymers Synthesized at 60, 70, and 85°C Versus  $\alpha$ MSt Content in the Monomer Feeds (mol %)

the inflection point; and the width  $\Delta T_g$  between base lines at higher and lower temperatures. Indeed, from Figure 9, the tendency was clearly to a broader and broader transition temperature range  $\Delta T_g$  at increasing  $\alpha \rm MSt$  content, along with a skewing of the derivative towards the lower temperatures when  $\alpha \rm MSt$  content was higher, which should be connected with the presence of a low-molecular-weight fraction in the mixture of macromolecules that the final polymer was.  $\Delta T_g$  varied from  $\Delta T_g \cong 15\,^{\circ}\rm C$  for pure PMMA up to  $\Delta T_g = 45-50\,^{\circ}\rm C$  for 50%  $\alpha \rm MSt$  copolymers, whatever the temperature may be. However, the effect of polymerization temperature and the amount of  $\alpha \rm MSt$  both played a complex role on  $T_g$ s, as reported in Table V.

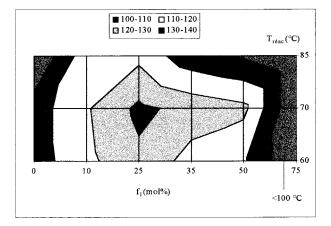
At a given temperature, copolymer  $T_g$ s passed through a maximum value at an increasing  $\alpha$ MSt amount with an optimal value in the composition range of 25–30% mol  $\alpha$ MSt. In the same way, at a given  $\alpha$ MSt content, copolymer  $T_{g}$ s had an optimal value at temperature close to 70°C. There was obviously an optimum in the operation conditions to increase  $T_{g}$  in the range 75°C and 25 mol %  $\alpha$ MSt, where the measured value is 136°C for our series of copolymers. Of course,  $T_g$  would be higher by  $\cong 15^{\circ}$ C if measured at the inflection point, that is,  $\approx 150^{\circ}$ C. Furthermore, it is worth noting that at this  $\alpha$ MSt composition range, the chemical shift is low because it is close to the azeotropic composition and, in addition, on the better side, that is, with the tendency to accumulate MMA at increasing conversion, which allowed a quite easy total monomer depletion and quite large molecular weights, even at high temperature.

Figures 10 and 11 are tentative 3-D illustrations of the variation of  $\alpha$ MSt–MMA copolymer  $T_g$ s versus  $\alpha$ MSt content and temperature. The isotemperature curves have been reported on figures as function of the monomer feed composition and reaction temperature. The  $T_g$ s higher than 130°C are located within a very limited domain as well with  $\alpha$ MSt% as with temperature.

A statistical treatment of our data have been tried to estimate the relative weights of temperature (T) and feed composition  $(f_1)$  on the control



**Figure 10** 3-D representation for the glass transition temperature  $(T_g)$  of emulsion copolymers versus temperature (T; °C) and  $\alpha$ MSt content in monomer feed  $(f_1, mol \%)$ . The left diagram is a cross section of the 3-D  $T_g$ 's surface at 92.3°C.



**Figure 11** Isothermal curves of  $T_{\mathcal{S}}$  s versus polymerization temperature ( $T_{\text{reac}}$ ) and  $\alpha \text{MSt}$  content in the monomer feed ( $f_1$ ; mol %).

of  $T_g$ s. Reduced variables (*CX*) have been defined for parameter *X*, as follows:

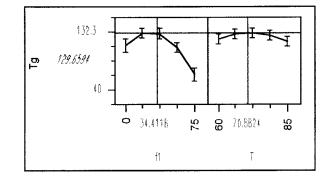
$$CX = 2 \cdot (X - \bar{X}) / (X_{\text{max}} - X_{\text{min}})$$
(4)

where  $\overline{X}$  is the average value of X on the domain limited by the  $X_{\text{max}}$  and  $X_{\text{min}}$  values. If the statistical model is of the polynomial type,

$$T_{g} = A_{1}Cf_{1} + A_{2}Cf_{1} * Cf_{1} + A_{3}CT + A_{4}CT * CT + A_{5}CT * Cf_{1}$$
(5)

The software program determines the parameters  $A_1-A_5$  and the confidence, through a PARETO's diagram (Fig. 12). The two parameters with the higher statistical weights on  $T_g$ s are  $Cf_1 * Cf_1$  (50%) and  $Cf_1$  (20%); this is not surprising from Figure 13, which showed indeed that  $T_g$  is more sensitive to the  $\alpha$ MSt content than to the temperature.

The model lead to the optimum value of  $f_1$  and T for increasing  $T_g$ . The maximum was calculated at 34.4 mol %  $\alpha$ MSt and  $T = 70.9^{\circ}$ C, for an



**Figure 13** Determination of the optimal conditions to maximize the glass transition temperature of the  $\alpha$ MSt-MMA emulsion copolymers. Polymerization temperature (*T*) and  $\alpha$ MSt content in monomer feed ( $f_1$ ; mol %) are the two independent variables under consideration.

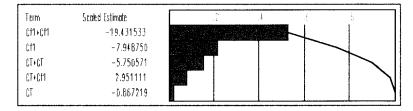
optimal computed  $T_g = 129.7$  (Fig. 14). However, the higher experimental  $T_g$  was found at 132°C for experiment Em 25-70, which was repeated and reproducible with  $T_g = 132$ °C  $\pm$  1°C.

The statistical model did not provide further explanation, except that, perhaps, it should be completed.

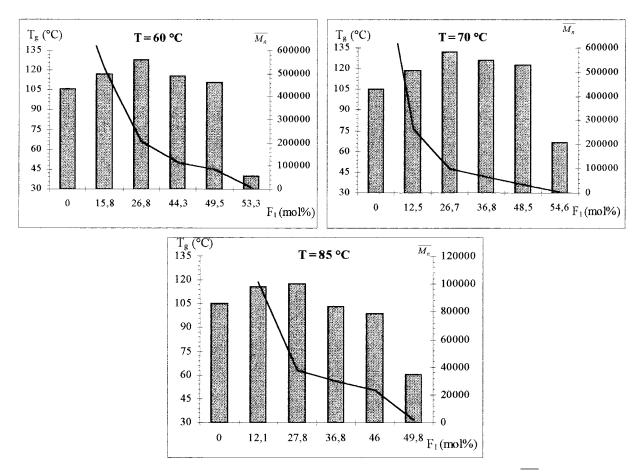
On the other hand, from a more deterministic point of view, the similar variations of  $T_g$ s observed at any temperature should be connected with the molecular weight distribution of the copolymers, as done in Figure 14. It is, indeed, well known than polymer  $T_g$ s are sensitive to  $M_n$ , as stated, for example, by the Fox–Flory equation,<sup>18</sup> as follows:

$$T_g = T_{g^{\infty}} - \frac{\mathrm{K}_{\mathrm{Flory}}}{\overline{M}_n} \tag{3}$$

The glass transition behavior is obviously the result of the competition of the following two opposite tendencies induced by the basic characteristics of  $\alpha$ -methylstyrene: (1) the increase of  $T_g$ s by



**Figure 12** PARETO's diagram of the statistical treatment of the glass transition temperature for the emulsion copolymers, according to eq. (5).



**Figure 14** Glass transition temperatures  $(T_g)$  and weight molecular weight  $(M_n)$  for emulsion copolymers synthesized at 60, 70, and 85°C versus copolymer  $\alpha$ MSt contents  $(F_1; \text{mol } \%)$ .

incorporation of longer  $\alpha$ MSt sequences in the copolymer chain, related to the high  $T_g$  of pure  $\alpha$ MSt ( $T_{g\alpha$ MSt} \cong 180°C); (2) the decreasing effect on  $T_g$ s of low-molecular-weight chains induced by the propagation, along with a the depropagation mechanism enhanced by high temperature and  $\alpha$ MSt content, as discussed in previous articles, the effect of much higher mobility of the chainend sequences.

# CONCLUSIONS

Owing to the huge compartimentalization of the polymerizing medium induced by the emulsion process, it was possible to reach our main objective of increasing the glass transition temperature of  $\alpha$ MSt-MMA copolymers. This was not possible in bulk or solution at all, as the consequence

of enhanced contribution of the depropagation in this latter process, in addition with a very high value of the  $\alpha$ MSt termination rate constant:  $k_{t\alpha MSt} \approx 5.10^9 \text{ L mol}^{-1} \text{ s}^{-1}$ . In emulsion, as a consequence of the huge number of particles (several 10<sup>18</sup> per L), the active centers (radicals) are somewhat entrapped for a few seconds within a particle, which leads to the increase of both the rate of polymerization and molecular weights. For instance, in bulk, at 70°C, the order of magnitude of the concentration of radicals is  $[R^{\circ}] \approx 5.10^{-9}$ mol  $L^{-1}$ , while in emulsion, the apparent concentration of active centers  $(\tilde{n}/Na) N \approx 2 \text{ to } 5 \text{ } 10^{-7}$ mol  $L^{-1}$ , that is, 50–100 times higher. As said in the introduction, the compartimentalization of emulsion allows to disconnect  $R_p$  and  $\nu$  (kinetic length) and then allows  $R_p$  and  $\nu$  to both increase simultaneously. The rather large radical desorption mechanism, induced by the MMA monomer,

for which lower  $\tilde{n}$  does not decrease the rate of polymerization or the molar masses too much.

From a process standpoint, the existence of an azeotropic composition, induced by the reactivity ratios,  $r_{ii}$ , is a key parameter. Indeed, at monomer feed composition containing less than  $\sim 30\%$  $\alpha$ MSt (mol),  $\alpha$ MSt is consumed faster, which allows for the incorporation of more  $\alpha$ MSt units and leads to accumulation of MMA by the end of reaction, that is, without significant lowering of  $R_n$ . This is not anymore the case beyond the azeotropic composition, where it is more and more difficult to incorporate  $\alpha$ MSt and, in addition, at a lower and lower rate of polymerization. The molecular weights are sensitive to the same parameters, but they are also much influenced by the depropagation mechanism, above all, by the end of the reaction when monomer concentration is at a low level, which enhances the effect of depropagation [eq. (2)].

As a consequence of the generation of too low molecular weight polymers at a high temperature (*T*) and  $\alpha$ MSt content ( $f_1$ ), it was not possible to increase the glass transition temperature  $T_{\sigma}$ above 132–135°C at least in the batch process. The main reason for the existence of optimal values for T and  $f_1$  is the competition between the following two opposite trends induced by  $\alpha$ -methylstyrene: the increase of  $T_g \mathbf{s}$  by incorporation of longer sequences of  $\alpha$ MSt, and the decreasing effect of low molecular weights on  $T_g$ s. This way, a key to reach higher  $T_{gs}$  would be to avoid the generation of too low molecular weights by improved copolymerization and polymerization processes.

The modeling developed for solution<sup>1</sup> and bulk<sup>2</sup> copolymerization of aMSt/MMA has been extended also to the emulsion process in good agreement with the experimental data presented in this article and will be presented in the next article of the series.<sup>19</sup> It allowed for the connection of many features of such a copolymerization with one another.

A last point, connected with the colloidal features of emulsion, is the clear tendency to lower the particle size when increasing  $f_1$  and T as well in the copolymerization of  $\alpha$ MSt with MMA as with styrene. An opposite behavior with that observed in the emulsion copolymerization of MMA with styrene,<sup>10</sup> which leads to tiny nonporous spherical and hard particles with a huge specific area of the order of  $100-200 \text{ m}^2 \text{ g}^{-1}$ .

The work was financially supported by the EC BRITE-Euram Project INTELPOL CT 93-0553.

## NOMENCLATURE

- particle size (nm)
- $\begin{array}{c} D_p \\ E_{\rm api} \end{array}$ activation energy of the propagation rate constant for monomer *i* (kcal mol<sup>-1</sup>)
- f efficiency of the initiator
- $f_i$ molar fraction of the monomer i in the monomer phase
- $F_{i}$ molar fraction of the monomer i in the polymer
- polymolecularity index
- $\begin{matrix} I_p \\ \mathbf{k}_d \end{matrix}$ dissociation rate constant of the initiator  $(s^{-1})$
- propagation rate constant of the reaction k<sub>pij</sub> monomer i + monomer j (L mol<sup>-1</sup> s<sup>-1</sup>)
- K<sub>11</sub> depropagation rate constant of  $\alpha$ -methylstyrene  $(s^{-1})$
- Fox Flory equation constant (K  $g^{-1}$ K<sub>Flory</sub>  $mol^{-1}$ )
- global polymerization rate constant (L  $\mathbf{K}_p$  $\text{mol}^{-1} \text{s}^{-1}$
- termination rate constant of the reaction k<sub>tii</sub> monomer i + monomer j (L mol<sup>-1</sup> s<sup>-1</sup>)
- global termination rate constant (L mol<sup>-1</sup> k<sub>t</sub>  $s^{-1}$ )
- total concentration of monomers (mol  $L^{-1}$ )  $[M_{tot}]$
- $[M]_{p}$ total concentration of monomers in the particle (mol  $L^{-1}$ )
- $\overline{M_n}$ number-average molecular weight  $(\mathbf{g}$  $mol^{-1}$ )
- $\overline{M_{m}}$ weight-average molecular weight  $(\mathbf{g}$  $mol^{-1}$ )
  - average number of radicals per particle
  - Avogrado's number 6.023 10<sup>23</sup> mol<sup>-1</sup>
- $\begin{array}{c} \mathcal{N}_{a} \\ \mathcal{N}_{p} \\ r_{1} \\ r_{2} \\ [R^{\circ}] \end{array}$ particle number  $(L^{-1})$

ñ

- reactivity ratio aMSt to MMA
- reactivity ratio MMA to  $\alpha$ MSt
- total radical concentration (mol  $L^{-1}$ )
- $R_i^{\bullet}$ radical ended by a monomer i unit (mol  $L^{-1}$ )
  - polymerization rate (mol  $L^{-1} s^{-1}$ )
  - time of polymerization (min)
- $R_p t T T_g X_t \Phi_i$ reaction temperature (°C)
  - glass transition temperature (°C)
  - conversion of the monomer (%)
  - mole fraction of radical ended by a monomer *i* unit
- $\Phi_{1,m}$ fraction of radical ended with  $m \alpha$ -methylstyrene units ν
  - kinetic length

# REFERENCES

- 1. Martinet, F.; Guillot, J. J Appl Polym Sci 1997, 65, 2297.
- 2. Martinet, F.; Guillot, J. J Appl Polym Sci to appear.
- Golubeva, A. V.; Usmanova, N. F.; Vandheidt, A. A. J Polym Sci 1961, 52, 63.
- Rudin, A.; Samanta, M. C. J Appl Polym Sci 1979, 24, 1665.
- Rudin, A.; Samanta, M. C. J Appl Polym Sci 1979, 24, 1899.
- Rudin, A.; Samanta, M. C.; Van Der Hoff, B. M. E. J Appl Polym Sci, Polym Chem Ed 1979, 17, 493.
- 7. Wittmer, P. Makromol Chem 1967, 103, 188.
- 8. Fischer, J. P. Makromol Chem 1972, 155, 211.
- Castellanos Ortega, J. R. Thesis, University of Nancy-France, 1996.

- Nomura, M.; Fujita, K. Makromol Chem Suppl 1985, 10/11, 25.
- 11. O'Toole, J. T. J Appl Polym Sci 1965, 9, 1291.
- Guillot, J.; Rios, L. Makromol Chem 1982, 183, 1979.
- Krigbaum, W. R.; Charpentier, D. K. J Polym Sci 1954, 14, 241.
- 14. Guillot, J. Acta Polym 1981, 32(10), 593.
- 15. McCormick, H. W. J Polym Sci 1957, 25, 488.
- Ramirez-Marquez, W.; Guillot, J. Makromol Chem 1988, 189, 379.
- 17. Emelie, B.; Pichot, C.; Guillot, J. Makromol Chem 1991, 192, 1629.
- 18. Fox, T. G.; Flory, P. J. J Appl Phys 1950, 21, 581.
- Castellanos, R.; Martinet, F.; Pla, F.; Guillot, J. Proceedings of the ECCE-1 Meeting, Florence, Italy, 1997, p. 209.