Copolymerization with Depropagation: Prediction of Kinetics and Properties of α -Methylstyrene–Methyl Methacrylate Copolymers. II. Bulk Copolymerization

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ABSTRACT: In order to calculate some kinetic parameters, such as the reactivity ratios, of the system α -methylstyrene–methyl methacrylate, the bulk copolymerization of these two monomers with azobis isobutironitrile (AIBN) as a radical initiator was studied. Experiments were performed at the various temperatures of 50, 60, and 80°C with 0.5 mol % of initiator (AIBN). The kinetics, molecular weights, microstructure, and glass transition temperature (T_g) of the copolymers were followed. A software, previously developed (part I), taking into account the equilibrium of the homopolymerization of α -methylstyrene, was used to simulate the experimental data. The model was in good agreement with all the experimental data. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 72: 1611–1625, 1999

Key words: α -methylstyrene, methyl methacrylate; depropagation; bulk kinetics; molecular weights; microstructure; glass transition; modelling

INTRODUCTION

In a first article,¹ solution copolymerization of α -methylstyrene (α MSt) and methyl methacrylate (MMA) in toluene has been investigated at 60°C. The kinetics, molecular weights, copolymer compositions, and the glass transition temperature (T_g) were quantitatively related. A general modeling for the copolymerization of N monomers was also developed. This model takes into account the depropagation reaction of the α -methylstyrene monomer that could not be neglected at 60°C. Molecular weights and glass transition temperatures were found to be very low, and the model was in good agreement with those experimental results. This article deals with the bulk

copolymerization of α MSt–MMA with AIBN as a radical initiator at various temperatures. Various monomers compositions were investigated (10, 25, 50, 75, and 90 mol % of α MSt) at 50, 60, and 80°C. The kinetics, molecular weights, copolymer composition, and glass transition temperature were followed.

EXPERIMENTAL

Monomers and solvent (both from Jansen Chimica) were distilled under vacuum, purged by nitrogen, and kept at -40°C under nitrogen. The initiator, azobis isobutironitrile (Jansen Chimica, 98%) was used without any further purification. The reactor used for these experiments was a 1-L glass, jacketed vessel equipped with a condenser and a stirrer (radial glass blade, ≈ 300 rpm). The temperature in the reactor was controlled by a thermostated bath and a thermocouple (resolu-

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$f_1 \pmod{\%}$	50°C	60°C	80°C
10	M10-50	M10-60	M10-80
25	M25-50	M25-60	M25-80
50	M50-50	M50-60	M50-80
75	M75-50	M75-60	M75-80
90	M90-50	M90-60	M90-80

Table ISynopsis of the ExperimentsPerformed

tion \pm 0.01°C, recording each 6 s). All the experiments were performed with 0.5 mol % of AIBN. Table I gives the synopsis and the identification of the experiments performed. The first number after the M is the fraction of α MSt in the monomer mixture, while the last number is the reaction temperature. As an example, for the experiment M50-60, the monomer mixture is composed of 50 mol % of α MSt and 50 mol % of MMA, and the reaction temperature was 60°C.

RESULTS

Conversions

The conversion of the monomers was followed by gravimetry. The conversions versus time of the nine copolymerizations performed are given in Figure 1. These conversions are always very low and remain generally below 1% in 8 h of reaction at 50°C. For the experiment M90-50, containing 90 mol % of α MSt in the monomer mixture, due to the very low conversions observed, the determination of molecular weights nor the estimation of the copolymer composition were done. With a reaction temperature of 60°C, the conversions remain below 4% in 8 h. The global conversion of the monomer mixture decreases when the fraction of α MSt in the monomer mixture increases. At 80°C, there is a high difference between M10-80 and M25-80. For experiment M10-80, a high gel effect was observed during the reaction, which increases the polymerization rate of this reaction with regard to the others. Only the copolymerizations of α MSt–MMA performed at 80°C allow conversions higher than 30% in 8 h of reaction. The experimental conversion versus time curves allow the calculation of the polymerization rates. These polymerization rates are gathered in Table II and illustrated in Figure 2.

Only the copolymerizations performed at 80°C have important polymerization rates with regard to the polymerizations at 50 and 60°C. The polymerization rate of M25-80 is 30 times higher than the polymerization rate of M25-50. Even if the depropagation reaction of α MSt units becomes higher with the increase of the temperature, the global polymerization rate of the copolymerization of α MSt with MMA increases with the temperature.

Molecular Weights

The molecular weights were estimated by gel permeation chromatography (GPC) for all copolymerizations. Table III gives the average molecular weights of the polymers synthesized at 50, 60, and 80°C. Molecular weights measured on α MSt– MMA copolymers are always very low; they decreased with the increase of the α MSt content in the monomer mixture but also with the increase of the reaction temperature. Figure 3 illustrates the decrease of the weight-average molecular weights with the content of α MSt and the reaction temperature.

It can be noted that the polymolecularity indices are often lower than 1.5, which is impossible in radical polymerization with a high transfer to the monomer. It is possible that the GPC columns used had a bad separation for very low-molecularweight polymers. Also, a linear standard curve was used instead of a third-degree polynomial curve. This linear calibration overestimate the low molecular weights. The polynomial curve was then tried, the polymolecularity indices increased and became higher than 1.5, but the average number molecular weight was then lower than 100 g mol⁻¹ in some cases, which is no more possible. An other explanation for these very low polymolecularity indices is the uncommon hydrodynamic structure of the polymer in solution in THF. These α MSt–MMA copolymers have high glass transition temperatures, which means that their structure is rigid and their hydrodynamic morphology is perhaps more a small stick than a sphere. So, the general Mark-Houwink laws are probably not applicable any more and give these bad results.

Copolymer Composition and Microstructure

The compositions of the polymers were determined by ¹H nuclear magnetic resonance (¹H-



Figure 1 Conversion (X_t) versus time (t) for α MSt–MMA bulk copolymerizations performed at 50, 60, and 80°C.

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$f_1 \pmod{\%}$	50°C	60°C	80°C
10 25 50 75	1E-05 3E-06 2.2E-06 1.4E-06	1.8E-05 1.3E-05 8E-06 5.1E-06	3.9E-04 8.7E-05 4.9E-05 2.2E-05

Table II Polymerization Rates $R_p \pmod{L^{-1} s^{-1}}$ Versus the Molar Fraction of α MSt (f_l) in the Monomer Mixture and the Reaction Temperature (T)

NMR). The samples had always a conversion lower than 5% so as to limit the composition drift. These experimental copolymer compositions allowed for estimation of the reactivity ratios of the α MSt-MMA monomer system. The values of the reactivity ratios are compared to those of Wittmer² and to the Alfrey and Price Q-e scheme.³

The reactivity ratios could be estimated by the Fineman–Ross,⁴ or the Kelen-Tüdös⁵ methods but also by the software. Meanwhile, there are also some other methods to estimate the reactivity ratios, like the methods of Tidwell and Mortimer,⁶ Kuo and Chen,⁷ Bauduin and Meghabar,⁸ or Alfrey et al.⁹ The approximate methods, the curves adjustment methods, the line intersection method, the linearisations methods, and the non-linear regression methods could be differentiated.

Figure 4 shows the experimental and calculated copolymer compositions (molar fraction of



Figure 2 Polymerization rates $R_p \pmod{L^{-1} s^{-1}}$ versus molar fraction of $\alpha MSt f_1 \pmod{\%}$ in the monomer mixture and reaction temperature (T).

aMSt in the copolymer F_1) versus the fraction of aMSt in the monomer mixture (f_1) , for the three reaction temperatures. The composition curve estimated by the software is also plotted. One can see the good agreement found between the experiment and the model. The relative error on the determination of the experimental copolymer composition is about 4%. The azeotropic composition at each reaction temperature could be also determined, as follows: 41.3 mol % of aMSt at 50°C; 39.3 mol % of aMSt at 60°C; 37.7 mol % of aMSt at 80°C.

Table IV gives the reactivity ratios calculated with the experimental copolymer compositions by

Т	Experiment	$f_1 \pmod{\%}$	$\overline{M_n}$	$\overline{M_w}$	$\overline{M_z}$	I_p
50°C	M10-50	10	8800	12,600	23,200	1.54
50°C	M25-50	25	7100	8500	10,100	1.21
$50^{\circ}C$	M50-50	50	4100	4800	5500	1.16
$50^{\circ}\mathrm{C}$	M75-50	75	2500	2800	3300	1.14
$50^{\circ}\mathrm{C}$	M90-50	90	?	?	?	?
60°C	M10-60	10	5900	12,700	20,200	2.14
60°C	M25-60	25	6000	7400	9000	1.24
60°C	M50-60	50	3400	3800	4300	1.14
60°C	M75-50	75	1700	2100	2600	1.24
60°C	M90-60	90	1600	1800	1300	1.11
80°C	M10-80	10	6400	11,500	28,100	1.8
80°C	M25-80	25	3400	5400	7500	1.59
80°C	M50-80	50	2100	3000	4000	1.44
80°C	M75-80	75	1300	1800	2400	1.39
80°C	M90-80	90	700	900	1100	1.24

Table III Average Molecular Weights Versus Molar Fraction of $\alpha MSt(f_I)$ in the Monomer Mixture for the Experiments Performed at 50, 60, and 80°C



Figure 3 Average weight molecular weights of α MSt-MMA bulk copolymers versus the molar fraction of α MSt in the monomer mixture (f_1) and the reaction temperature (T).

the different linearizations methods and by the software. The reactivity ratios are close to 0.4 and 0.5 for the three reaction temperatures. The Alfrey and Price scheme Q-e gives $r_1 = 0.47$ and r_2 = 0.5, which is in agreement with the values calculated by the software. It can be also noticed that the fraction of α MSt incorporated in the copolymer decreased with the temperature; for an α MSt fraction in the monomer mixture of 75 mol %, the copolymer composition (mol % of α MSt) was 62.8 mol % at 50°C and 54.4 mol % at 80°C. This temperature influence appeared from 30 mol % of α MSt in the monomer mixture and increased with the fraction of α MSt. Let M_1 be the α -methylstyrene and M_2 be the methyl methacrylate. A specific kinetic scheme is taken into consideration in the software, including a reversible propagation step only for the homopolymerization of α MSt, in the limited temperature range investigated $(50-80^{\circ}C)$. This specific scheme is the same that the model of Lowry¹⁰ or Wittmer,² who explained the presence of a ceiling temperature in the synthesis of such polymers by a reversible propagation step.

$$P - M_1^{\bullet} + M_1 \underset{k_{11}}{\rightleftharpoons} P - M_1 M_1^{\bullet}$$

$$P - M_1^{\bullet} + M_2 \underset{k_{12}}{\longrightarrow} P - M_1 - M_2^{\bullet}$$



Figure 4 Composition of copolymer in α MSt (F_1) versus fraction of α MSt in the monomer mixture (f_1) : (\bullet) experimental results with error bars; (—) composition of the copolymer in α MSt calculated with the software; (\cdots) diagonal $(F_1 = f_1)$.

Model

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	$T = 50^{\circ}\mathrm{C}$		$T = 60^{\circ}\mathrm{C}$		$T = 80^{\circ}\mathrm{C}$	
	r_1	r_2	r_1	r_2	r_1	
Fineman–Ross	0.31	0.46	0.25	0.51	0.002	
Kelen–Tüdös	0.32	0.47	0.25	0.51	0.12	
Wittmer	0.51	0.55	0.6	0.55	0.81	

0.47

Table IV Reactivity Ratios at 50, 60, and 80°C

$$P-M_2^{ullet}+M_2 \xrightarrow{\mathrm{k}_{22}} P-M_2-M_2^{ullet}$$

0.47

$$P - M_2^{\bullet} + M_1 \xrightarrow{k_{21}} P - M_2 - M_1^{\bullet}$$

By defining the reactivity ratios r_{1} and the equilibrium constant K,

$$r_1 = \frac{\mathbf{k}_{11}}{\mathbf{k}_{12}}; \ r_2 = \frac{\mathbf{k}_{22}}{\mathbf{k}_{21}} \text{ and } \mathbf{K} = \frac{\mathbf{k}_{11}}{\mathbf{k}_{11}}$$

K has been calculated by McCormick¹¹ at various temperatures. It is well known that the many distributions that characterize random copolymers can be computed from adequate conditional probabilities, for example, monomer sequence distribution. The conditional probability can be defined as the ratio of the rate of addition of a monomer M_i on the radical R_j^{\bullet} and the sum of all the rates of possible reactions of this radical R_j^{\bullet} , whatever the number of comonomers may be.

$$P_{ij} = \frac{\mathbf{k}_{ij}[M_i][R_j^{\bullet}]}{\sum_{i} \mathbf{k}_{ij}[M_i][R_j^{\bullet}]}$$
(1)

For instance, in the case of a binary copolymerization, for the specific kinetic scheme described above, the following relationships can be written:

$$\sigma = \frac{\sum_{i=2}^{\infty} [R_{1,i}^{\bullet}]}{\sum_{i=1}^{\infty} [R_{1,i}^{\bullet}]}$$
(2)

 σ is the ratio between the sum of the concentrations of αMSt radicals having more than two

 αMSt units at the end and the sum of all the concentrations of αMSt radicals. Then,

0.51

$$P_{12} = \frac{f_2}{f_2 + r_1 f_1 \left(1 - \frac{K\sigma}{[M_1]}\right)}$$
(3)

0.49

 r_2

0.43

0.47

0.65

0.47

and

0.53

$$P_{21} = \frac{f_1}{f_1 + r_2 f_2} \tag{4}$$

Furthermore, $P_{11} + P_{12} = 1$ and $P_{21} + P_{22} = 1$. One can see in eq. (3) that the conditional probability P_{12} will depend on the temperature (term K) and also on the real monomer concentration in the system (concentration of α MSt); particularly, the microstructure and the glass transition temperature of the copolymer formed are dependent of the process used. Let (M_i) be the content of monomer i in the copolymer then we have $(M_1)P_{12} = (M_2)P_{21}$, so

$$\frac{(M_1)}{(M_2)} = \frac{P_{21}}{P_{12}} = \frac{1 + r_1 \frac{[M_1]}{[M_2]} \left(1 - \frac{K\sigma}{[M_1]}\right)}{1 + r_2 \frac{[M_2]}{[M_1]}}$$
(5)

The well-known Mayo–Lewis equation is recognized, corrected by the term $\left(1 - \frac{K\sigma}{[M_1]}\right)$, which characterizes the depropagation step. An apparent α MSt–MMA reactivity ratio $r_{1\text{app}}$ can be defined by $r_{1\text{app}} = r_1 \left(1 - \frac{K\sigma}{[M_1]}\right)$. In fact, we cannot define only one set of reactivity rations for the α MSt–MMA system, but also an apparent reactivity ratio, which depends on the temperature and the real monomer composition.



Figure 5 Apparent α MSt-MMA reactivity ratio r_{1app} versus the molar fraction of α MSt in the monomer mixture (f_1) at 50, 60, and 80°C.

The evolutions of $r_{1\text{app}}$ with the α MSt fraction in the monomer composition and the reaction temperature are presented in Figure 5. This reactivity ratio is decreased when the fraction of α MSt in the monomer mixture and the reaction temperature are increased. This explains the decrease of the incorporated α MSt fraction in the copolymer when the reaction temperature is increased.

It is also of interest to estimate the microstructure of α MSt–MMA copolymers through the ¹H-NMR spectra. There are many studies on the microstructure of styrene–methyl methacrylate copolymers, but none on the α -methylstyrene– methyl methacrylate copolymers. The methoxy ¹H-NMR signals of the 2.5 to 3.8 ppm region for statistical α MSt–MMA copolymers have been reassigned in terms of MMA-centered dyads and triads. The simplest model, including the less adjusting parameters must be chosen. The spectra were made on a 250 and a 400 MHz spectrometer. No finer structure could be defined on the 400 MHz spectrometer for these copolymers.

The new peak assignment model includes MMA-centered dyad or triad and the coisotactic-



Figure 6 Bulk α MSt–MMA copolymer spectra recorded in CDCl₃ at 298 K on a 250-MHz spectrometer.



Figure 7 Methoxy region of α MSt–MMA bulk copolymers synthesized at 60°C. The spectra were recorded in CDCl₃ at 298 K on a 250-MHz spectrometer. The three peak regions of the OCH₃ are plotted.

ity parameter σ' . This coisotacticity parameter σ' characterizes the preference of a monomer to add on the polymer chain with an iso or syndiotactic configuration (Koenig¹²). The OCH₃ region of the spectra can be cut into the following three groups: peak I, 3.25 to 3.8 ppm; peak II, 2.85 to 3.25 ppm; peak III, 2.5 to 2.85 ppm.

The spectra of the α MSt–MMA copolymer could be seen in Figure 6. In Figure 7, the meth-

oxy region of the α MSt–MMA bulk copolymers synthesized at 60°C is represented. The following equations apply to MMA-centered triads: $(M_2M_2M_2)$ with a MMA-centered monomer fraction; F_{222} ; $(M_2M_2M_1) = (M_1M_2M_2)$ with a MMAcentered monomer fraction, F_{221} ; $(M_1M_2M_1)$ with a MMA-centered monomer fraction, F_{121} .

The new peak assignment model includes MMA-centered dyad or triad and the coisotactic-

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Experiment	f_1^a	F_1	F_{222}	F_{221}	F_{121}
M10-60	0.099	0.181	0.6626	0.3028	0.0346
M25-60	0.249	0.300	0.3496	0.4833	0.1670
M50-60	0.504	0.455	0.1031	0.4360	0.4609
M75-60	0.750	0.588	0.0191	0.2380	0.7430
M90-60	0.896	0.759	0.0028	0.0998	0.8974

Table V MMA-Centered Monomer Fractions for Bulk Copolymers at 60°C^a

 ${}^{a}f_{1}$ and F_{1} are the molar fractions of α MSt in the monomer mixture and in the copolymer, respectively. Reactivity ratios are as follows: $r_{1} = 0.53$; $r_{2} = 0.51$.

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Experiment	F_1	Area 1	Calc 1	Area 2	Calc 2	Area 3	Calc 3	Δ (%)	
M10-60	0.1827	91.08	66.26	8.75	30.28	0.17	3.46	381.34	
M25-60	0.2995	78.96	34.96	18.43	48.33	2.61	16.70	32.18	
M50-60	0.4546	68.16	10.31	27.57	43.60	4.27	46.09	97.08	
M75-60	0.5884	58.51	1.91	34.10	23.80	7.40	74.30	82.84	
M90-60	0.7592	59.01	0.28	36.27	9.98	4.72	89.74	326.41	

Table VI Comparison of Experimental (Area) and Calculated (Calc) Fractions with the First Assignment of the Methoxy Region of 2.5 to 3.8 ppm

αMSt-MMA bulk copolymerizations performed at 60°C.

ity parameter σ' . This coisotacticity parameter σ' characterizes the preference of a monomer to add on the polymer chain with an iso or syndiotactic configuration.¹² The OCH₃ region of the spectra can be cut into the following three groups: peak I, 3.25 to 3.8 ppm; peak II, 2.85 to 3.25 ppm; peak III, 2.5 to 2.85 ppm.

The spectra of an α MSt–MMA copolymer can be seen in Figure 6. In Figure 7, the methoxy region of the α MSt-MMA bulk copolymers synthesized at 60°C is represented. The following equations apply to MMA-centered triads: $(M_2M_2M_2)$ with a MMA-centered monomer fraction, F_{222} ; $(M_2M_2M_1) = (M_1M_2M_2)$ with a MMA-centered monomer fraction; F_{221} ; $(M_1M_2M_1)$ with a MMAcentered monomer fraction, F_{121} .

The following fractions could be expressed in terms of conditional probabilities: $(M_2M_2M_2)$ = $(M_2)P_{22}^2$, so $F_{222} = P_{22}^2 = (1 - P_{21})^2$; $(M_2M_2M_1)$ = $(M_2)P_{22}P_{21}$, so $F_{221} = 2P_{22}P_{21} = 2(1 - P_{21})P_{21}$; $(M_1M_2M_1) = (M_1M_2)P_{21} = (M_2M_1)P_{21} = (M_2)P_{21}^2$, so $F_{121} = P_{21}^2$.

Two assignments have been tried for the three peaks regions I, II, and III. The first assignment is as follows: peak I, $M_2M_2M_2 \rightarrow \text{calc } 1 = F_{222}$; peak II, $M_2M_2M_1 \rightarrow \text{calc } 2 = F_{221}$; peak III, $M_1M_2M_1 \rightarrow \text{calc } 3 = F_{121}$. This first assignment is

simpler. It does not take into account the coisotacticity parameter σ' , but only the MMA monomer centered triads fractions.

The second assignment is as follows: peak I, $M_2M_2M_2 + (1 - \sigma')M_2M_2M_1 + (1 - \sigma')^2M_1M_2M_1$ \rightarrow calc $1 = F_{222} + (1 - \sigma')F_{221} + (1 - \sigma')^2F_{121}$; peak II, $2\sigma'(1 - \sigma')M_1M_2M_1 + \sigma'M_2M_2M_1 \rightarrow$ calc $2 = \sigma'F_{221} + 2\sigma'(1 - \sigma')F_{121}$; peak III, $\sigma'^2M_1M_2M_1 \rightarrow$ calc $3 = \sigma'^2F_{121}$.

This assignment is similar to those of Ito and Yamashita¹³ and Bovey.¹⁴ The calculated area (calc) could be compared to the experimental area of each peak (area).

Table V gives the predicted MMA-monomercentered fractions for bulk copolymers synthesized at 60°C. Table VI compares the experimental and calculated fractions areas for each peak with the first assignment for the α MSt–MMA copolymers made at 60°C. One can see a huge deviation between experiments and calculations.

Table VII compares the experimental and calculated fractions areas for each peak with the second assignment for the α MSt–MMA copolymers made at 60°C. This second assignment gives better results in terms of agreement between experiment and calculation. A coisotacticity param-

Table VIIComparison of Experimental (Area) and Calculated (Calc) Fractionswith the Second Assignment of the Methoxy Region of 2.5 to 3.8 ppm

Experiment	F_1	Area 1	Calc 1	Area 2	Calc 2	Area 3	Calc 3	Δ (%)
M10-60	0.181	91.08	90.92	8.75	8.87	0.17	0.22	0.07
M25-60	0.300	78.96	80.61	18.43	18.35	2.61	1.04	0.36
M50-60	0.455	68.16	68.94	27.57	28.18	4.27	2.88	0.11
M75-60	0.588	58.51	61.55	34.10	33.81	7.40	4.64	0.14
M90-60	0.759	59.01	58.24	36.27	36.15	4.72	5.61	0.04

Coisotacticity parameter $\sigma' = 0.25$. α MSt–MMA bulk copolymerizations were performed at 60°C.



Figure 8 Experimental and calculated peak fractions for the second assignment versus the molar fraction of α MSt in the copolymer (F_1): (—) peak I; (–––) peak II; (···) peak III. α MSt–MMA bulk copolymers at 60°C.

eter of 0.25 have been optimized for this set of experiments.

These results are represented in Figure 8 versus the molar fraction of α MSt in the copolymer (F_1) . Tables VIII and IX show the experimental and calculated fraction areas of each peak for the α MSt-MMA bulk copolymerizations performed at 50 and 80°C, respectively.

The calculations are made with the second assignment, and a coisotacticity parameter $\sigma' = 0.25$. Figures 9 and 10 represent the results of Tables VIII and IX; the fraction area of each peak is plotted versus the molar fraction of α MSt in the copolymer (F_1). The coisotacticity parameter σ' was found to be equal to 0.25 for the three reaction temperatures, which shows a high tendency for the syndiotacticity. This parameter is lower than that found with the styrene-methyl methacrylate monomer system,¹⁵ as follows: $\sigma' = 0.44$. To conclude this part, a simple model based on triads and on the coisotacticity parameter was built to predict the microstructure of α MSt-MMA bulk copolymers through the ¹H-NMR spectra.

Glass Transition Temperature

The glass transition temperatures were estimated on raw products so as to keep all the low-molecular-weight polymers. It was very hard to give a reliable value to the T_g of such copolymers in some cases. The T_g are given in the Table X for the experiments performed at 50, 60, and 80°C.

All T_g remain very low and always lower than the T_g of the polymethyl methacrylate (105°C). Even if the T_g of the two homopolymers are high, the T_g of the bulk α MSt–MMA copolymers is low due to the low molecular weight of the copolymer formed. The influence of the molecular weights on the determination of the T_g couldn't be neglected, and the software was improved to take into account such an influence. There is no really quantitative known relations between the glass transition temperature of a copolymer and its molecular weights distribution. To describe the T_g of a copolymer, the Fox¹⁶ [eq. (6)] or the Johnston¹⁷ [eq. (7)] relations could be used.

The Fox model takes into account the weight fractions of each monomer W_1 and W_2 in the copolymer and the T_g of the homopolymers T_{g1} and T_{g2} in K, as follows:

$$\frac{1}{T_g} = \frac{W_1}{T_{g1}} + \frac{W_2}{T_{g2}} \tag{6}$$

The Johnston model takes into account the dyads distributions $(P_{11}, P_{12}, P_{21}, P_{22})$, and this equation predicts more correctly the glass transition temperature of copolymers than the Fox one. This equation includes the weight fractions of the monomers in the copolymer W_1 and W_2 and the T_g of the homopolymers T_{g1} (α MSt) and T_{g2} (MMA) but also the T_g of an alternated copolymer defined by (M_1M_2) = 1, so (M_1M_1) = (M_2M_2) = 0.

$$\frac{1}{T_g} = \frac{W_1 \cdot P_{11}}{T_{g11}} + \frac{W_1 \cdot P_{12} + W_2 \cdot P_{21}}{T_{g12}} + \frac{W_2 \cdot P_{22}}{T_{g22}} \quad (7)$$

Table VIIIComparison of Experimental (Area) and Calculated (Calc) Fractionswith the Second Assignment of the Methoxy Region of 2.5 to 3.8 ppm

Experiment	F_{1}	Area 1	Calc 1	Area 2	Calc 2	Area 3	Calc 3	Δ (%)
M10-50	0.171	88.37	90.42	9.85	9.34	1.77	0.24	0.75
M25-50	0.318	79.13	80.09	18.65	18.81	2.23	1.10	0.25
M50-50	0.475	69.86	68.65	27.22	28.41	2.91	2.94	0.00
M75-50	0.628	63.36	61.58	33.36	33.78	3.29	4.63	0.17

Coisotacticity parameter $\sigma' = 0.25$. α MSt–MMA bulk copolymerizations performed at 50°C.

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Experiment	F_1	Area 1	Calc 1	Area 2	Calc 2	Area 3	Calc 3	Δ (%)
M10-80	0.175	89.56	90.52	8.49	9.25	1.94	0.24	0.78
M25-80	0.282	83.37	80.51	15.54	18.43	1.09	1.06	0.04
M50-80	0.446	68.58	68.99	27.58	28.14	3.85	2.87	0.06
M75-80	0.544	58.84	61.51	32.77	33.84	8.38	4.65	0.20
M90-80	0.612	60.02	58.25	35.20	36.14	6.15	5.61	0.01

Table IX Comparison of Experimental (Area) and Calculated (Calc) Fractions with the Second Assignment of the Methoxy Region of 2.5 to 3.8 ppm

Coisotacticity parameter $\sigma' = 0.25$. α MSt–MMA bulk copolymerizations performed at 80°C.

The models of Barton¹⁸ or Couchman,¹⁹ which also consider the dyad distribution, could also be mentioned. To take into account the influence of the molecular weights, Fox and Flory²⁰ found the empirical equation,⁸ as follows:

$$T_g = T_{g^{\infty}} - \frac{\mathrm{K}_{\mathrm{Flory}}}{\overline{M}_n} \tag{8}$$

where $T_{g^{\infty}}$ is the glass transition temperature of a high-molecular-weight polymer.

In the software, the Johnston equation [eq. (7)] was modified to take into account the influence of the chain ends. A mass $M_{\rm term}$ (g mol⁻¹) equivalent to the molecular weight of the end chain and a new T_g 's $T_{g\rm term}$ (K) assigned to the glass transition temperature of this terminal dyad were introduced. So the equation of Johnston was modified as follows:

$$\frac{1}{T_g} = \frac{W_1 P_{11}}{T_{g1}} + \frac{W_1 P_{12} + W_2 P_{21}}{T_{g12}} + \frac{W_2 P_{22}}{T_{g2}} + 2 * \frac{W_{\text{term}} P_{\text{term}}}{T_{g\text{term}}} \quad (9)$$



Figure 9 Experimental and calculated peak fractions for the second assignment versus the molar fraction of α MSt in the copolymer (F_1): (—) peak I; (–––) peak II; (····) peak III. α MSt–MMA bulk copolymers at 50°C.

where P_{term} is the conditional probability of occurrence of the terminal dyads, which are directly connected with the molar mass of any individual macromolecule, computed in the work at any time, and W_{term} is the weight fraction of chain ends in a polymer chain of mass M. $T_{g1} = 450$ K; $T_{g2} = 378$ K.

The difficulty is to adjust the two new variables M_{term} and $T_{g\text{term}}$. Good results were obtained using the solution process with $M_{\text{term}} = 200 \text{ g mol}^{-1}$ and $T_{g\text{term}} = 190 \text{ K}$.

Software for Prediction of Polymer Quality

The software have been extensively described in the first part of this work.¹ Some modeling studies were undertaken to model the bulk copolymerization of α MSt–MMA (rates of polymerization, molecular weights, glass transition temperature, and copolymer composition) with this software. The constants used in the program are gathered in Table XI. In this table, the very high value of the termination rate constant can be noticed, but



Figure 10 Experimental and calculated peak fractions for the second assignment versus the molar fraction of α MSt in the copolymer (F_1): (—) peak I; (–––) peak II; (····) peak III. α MSt–MMA bulk copolymers at 80°C.

Table X Glass Transition Temperature of Bulk α -MSt-MMA Copolymers (°C) Versus the Molar Fraction of α MSt in the Monomer Mixture (f_I) and the Reaction Temperature

$f_1 \pmod{\%}$	$50^{\circ}\mathrm{C}$	60°C	80°C
10	40.8	58.9	70
25	59	61.5	69.2/85.2
50	59.4	33	62.7
75	?	15.3/32.6	34.4
90	?	4.5	20.9

Table XII Transfer to Monomer Rate Constant k_{trM} (L mol⁻¹ s⁻¹) Used in the Modeling at the Three Reaction Temperatures

Temperature	ktrM11	k_{trM12}	$\mathbf{k}_{tr\mathbf{M}22}$
50°C 60°C 80°C	$0.11\\0.11\\3$	$0.06 \\ 0.06 \\ 0.95$	$0.045 \\ 0.045 \\ 0.3$

But for copolymerizations, there are few values. Moad and Solomon²³ give for the methyl methacrylate, $\lambda = 0.44$, and for the α -methylstyrene, λ = 0.07. For the copolymerization styrene–methyl methacrylate, they give $\lambda = 0.36$. In the software, $\lambda = 0.3$ is used.

 $\begin{array}{ll} \lambda = 0.3 \text{ is used.} \\ & \lambda = 0.3 \text{ is used.} \\ & \text{Furthermore, to find the experimental data,} \\ & \text{Furthermore, to find the experimental data,} \\ & \text{Furthermore, to find the experimental data,} \\ & \text{an adjusting parameter was used to increase} \\ & \text{the weight of the cross termination reaction} \\ & R_p \\ \hline \hline [M_{\text{tot}}]\overline{\text{K}_p} \end{array} \qquad \begin{array}{l} & \text{(k}_{t12}) \text{ compared with the two homopolymeriza-} \\ & \text{tion termination processes (k}_{t11} \text{ and } \text{k}_{t22})\text{: k}_{t12} \\ & = \Phi_t \sqrt{\text{k}_{t11}\text{k}_{t22}} \end{array}$

The values of the transfer to monomer rate constants used in the modeling are gathered in Table XII. These values were deduced from GPC measurements on α MSt–MMA copolymers made by the emulsion process, with high molecular weights (part III). The Gilbert method²⁴ was used to estimate these transfer rate constants. In addition, for the simulation of the experiments at 80°C, the free volume theory of Marten and Hamielec²⁵ was used to take into account the gel effect observed during the reaction.

$$\frac{\mathbf{k}_{t}}{\mathbf{k}_{t0}} = \left(\frac{M_{w}^{\text{crit}}}{M_{w}}\right)^{1.75} \exp\left\{-\text{Abuecht}\left(\frac{1}{\mathbf{V}_{\text{f}}} - \frac{1}{\mathbf{V}_{\text{f}}^{\text{crit}}}\right)\right\} \quad (10)$$

$$\frac{\mathbf{k}_p}{\mathbf{k}_{p0}} = \exp\left\{-\left(\frac{1}{V_f} - \frac{1}{V_f^{\text{crit}}}\right)\right\}$$
(11)

$$V_f = \sum_{i=1}^{n} [0.025 + \alpha_i (T - T_{gi})] \frac{V_i}{V_t}$$
(12)

this value is reasonable from experimental data. In experiment M25-60, the rate of polymerization is $R_p = 1.32.10^{-5} \text{ mol } \text{L}^{-1} \text{ s}^{-1}$; the global propagation rate constant is $\overline{\text{K}_p} = 191 \text{ L mol}^{-1} \text{ s}^{-1}$, and the total monomer concentration $[M_{\text{tot}}] = 8.54 \text{ mol } \text{L}^{-1}$; $R_p = \overline{\text{K}_p}[\text{M}_{\text{tot}}][R^{\bullet}]$ so $[R^{\bullet}] = \frac{R_p}{[M_{\text{tot}}]\overline{\text{K}_p}} = 8.1.10^{-9} \text{ mol } \text{L}^{-1}$.

In solution and bulk polymerizations, the radical concentration can also be computed from initiation and termination steps with the steadystate assumption, as follows: $[R^{\bullet}] = \sqrt{\frac{2/k_{\rm d}[I]}{\overline{K}_{\rm t}}}$ with f = 0.62; $k_{\rm d} = 9.10 - 6 \text{ s}^{-1}$; $[I] = 0.045 \text{ mol } \text{L}^{-1}$. A value of $\overline{K}_{\rm t} = 9.10^9 \text{ L mol}^{-1} \text{ s}^{-1}$ leads to $[R^{\bullet}]$ $= 7.5.10^{-9} \text{ mol } \text{L}^{-1}$.

The experimental and the calculated value of $[R^{\bullet}]$ are close to each other, so the high value of k_{t11} taken in the software was reasonable. However, to estimate the global termination constant, it is necessary to know the process of termination, as follows: termination by combination or disproportionation. If $k_{t,c}$ is the termination rate constant by combination and $k_{t,d}$ is the termination rate constant by disproportionation, then $k_{t,c}$ + $k_{t,d} = k_t$ and $k_{t,d} = \lambda k_t$. This coefficient λ , which characterizes the termination process, is not well known. It is estimated for some model molecules like styrene or methyl methacrylate.

Table XIConstants Used for the Calculations ($T = 60^{\circ}$ C)

Component	mmol (g mol ⁻¹)	d_p	$\stackrel{k_p}{(L \text{ mol}^{-1} \text{ s}^{-1})}$	$\begin{array}{c} E_{a,p} \\ (\mathrm{kcal} \ \mathrm{mol}^{-1}) \end{array}$	$\overset{k_t}{(L \text{ mol}^{-1} \text{ s}^{-1})}$	$\begin{array}{c} E_{a,t} \\ (\text{kcal mol}^{-1}) \end{array}$	$\overset{k_{d}}{(s^{-1})}$
$lpha { m MSt} { m MMA} { m AIBN}$	118 100 164	1.15 1.19	$47 \ {}^{21}_{500} \ {}^{22}_{}$	$\begin{array}{c} 13 \ ^{21} \\ 6.05 \ ^{22} \\ 31 \ ^{22} \end{array}$	$\begin{array}{c} 4.10 \ ^9 \\ 6.10 \ ^{7,22} \end{array}$	$2 \\ 1.55$ 22	9.10^{-6} ²²

Table XIII Parameters Us	ed for th	e Gel I	Effect
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Parameter	$lpha \mathbf{MSt}$	MMA
$ \begin{array}{c} \alpha_m (^{\circ} \mathbb{C}^{-1}) \\ T_{gm} (^{\circ} \mathbb{C}) \end{array} $	$1.10^{-3} \\ -80.2$	$1.10^{-3} \\ -106$
$\alpha_p^{\circ} (^{\circ}\mathrm{C}^{-1})$	2.10^{-3}	$2.6.10^{-3}$
T_{gp} (°C)	177	105

For the copolymerizations at 80°C, the following parameters were used: Abuecht = 0.35 and V_f^{crit} = 0.202.

The values of the volume expansion coefficients are gathered in Table XIII.

The values of the reactivity ratios and the equilibrium constant of the homopolymerization of α MSt (K) and of the factor Φ_t for the three reaction temperatures are given in Table XIV.

Table XV gives the values of the factor Φ_t and of the critical molecular weights $(M_w^{\rm crt0})$ used in the modeling for the α MSt–MMA copolymerizations performed at 80°C.

To estimate the values of the glass transition temperature of these copolymers, the following parameters were used in the software: $T_{gterm} = 190 \text{ K}; M_{term} = 200 \text{ g mol}^{-1} \text{ at } 50 \text{ and } 60^{\circ}\text{C}, \text{ and} M_{term} = 230 \text{ g mol}^{-1} \text{ at } 80^{\circ}\text{C}.$

So to compare experiments and modeling, both results are gathered in Table XVI in terms of conversions, molecular weights, copolymer compositions, and glass transition temperatures. The agreement between the experiment and modeling is good. This modeling, which includes a depropagation reaction for the homopolymerization of the α MSt, is a good way to understand the mechanisms of the bulk α MSt-MMA copolymerization. It is also useful to quantify the relationships between the kinetics, microstructure, and properties, such as molecular weight distribution and the glass transition temperature.

Table XIVReactivity Ratios andthe Equilibrium Constant of theHomopolymerization of αMSt

r_1	r_2	$K \;(mol \; L^{-1})$	Φ_t
0.47 0.51	0.47 0.48	5.1 7.1	50 40
	r_1 0.47 0.51 0.49	$\begin{array}{ccc} r_1 & r_2 \\ \hline 0.47 & 0.47 \\ 0.51 & 0.48 \\ 0.49 & 0.47 \end{array}$	$\begin{array}{c cccc} r_1 & r_2 & {\rm K}({\rm mol}\;{\rm L}^{-1}) \\ \hline 0.47 & 0.47 & 5.1 \\ 0.51 & 0.48 & 7.1 \\ 0.49 & 0.47 & 12.9 \end{array}$

Table XV	Values of Φ_t and of the Critical
Molecular	Weight (M_w^{crt0}) Used in the Modeling
of aMSt-M	MA Bulk Copolymerizations
Performed	at 80°C Versus the Molar Fraction
of aMSt in	the Monomer Mixture (f_1)

$f_1 \pmod{\%}$	Φ_t	$M_w^{ m crt0}$
10	2	120
25	20	45
50	40	No
75	60	No
90	70	No

CONCLUSION

In all α MSt–MMA bulk copolymerizations, at the three reaction temperatures, small polymerization rates and small molecular weights were obtained. Because of the low molecular weights, the glass transition temperatures were very hard to estimate and must be carefully interpreted. It was shown with this kinetic study that the model was pertinent for the parameters investigated. A model was built up to estimate the microstructure of α MSt–MMA bulk copolymers through ¹H-NMR measurements. This model, including three groups of peaks for the methoxy region of the spectra and a triad scheme, allowed for the determination of a coisotacticity parameter $\sigma' = 0.25$ for the three reaction temperatures. In a further work, these copolymerizations will be carried using the emulsion process. The same investigations will be done on the kinetics, the molecular weights, the microstructure, and the glass transition temperature.

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NOMENCLATURE

Symbols

 \overline{E}_a

 f_i

 I_p K

 \mathbf{k}_d

- d_p density of polymer
 - activation energy (kcal mol^{-1})
 - molar fraction of monomer *i*
 - polymolecularity index
 - equilibrium constant of the homopolymerization of $\alpha MSt \pmod{L^{-1}}$
 - dissociation rate constant of the initiator (s^{-1})

					Temperatu	re (°C)				
$\frac{\text{Conversion (\%)}}{f_1 \text{ (mol \%)}}$	50°C				60°C			80°C		
	<i>t</i> (h)	Exp	Simul	<i>t</i> (h) Exp	Simul	<i>t</i> (h) Exp	Simul	
10	23.4	7.9	4.1	1	0.7	0.7	1.5	23.9	22.2	
25	8	0.8	1.0	8	3.8	3.7	4	16.1	16.2	
50	8	0.6	0.7	8	2.5	2.4	4	9.1	7.8	
75	8	0.4	0.4	8	1.5	1.5	6	5.4	5.4	
90	41.2	1.7	1.7	19	2.2	2.0	8	2.3	3.1	
Average Number	Temperature (°C)									
Weights \overline{M}_n	50°C				60°C		80°C			
$f_1 \pmod{\%}$	<i>t</i> (h)	Exp	Simul	t (h)	Exp	Simul	<i>t</i> (h) Exp	Simul	
10	23.4	8800	6300	1	5900	5000	1.5	6400	10000	
25	8	7100	4300	8	6000	3700	4	3400	4200	
50	8	4100	3200	8	3400	2600	4	2100	2000	
75	8	2500	2100	8	1700	1500	6	1300	1200	
90	41.2	?	1400	19	1600	1000	8	700	700	
Average Weight	Temperature (°C)									
$\frac{\text{Molecular}}{\text{Weights }\overline{M}_w}$	50°C			60°C			80°C			
$f_1 \pmod{\%}$	<i>t</i> (h)	Exp	Simul	<i>t</i> (h)) Exp	Simul	t (l	n) Exp	Simul	
10	23.4	12600	11400	1	12700	9400	1.5	5 11500	18500	
25	8	8500	8300	8	7400	6900	4	5400	9000	
50	8	4800	6100	8	3800	4900	4	3000	3900	
75	8	2800	4000	8	2100	2900	6	1800	2500	
90	41.2	?	2700	19	1800	2000	8	900	1600	
Molar Fraction					Temperatu	re (°C)				
of α MSt in the Copolymer (F_1)		50°C			60°C			80°C		
$f_1 \; (\mathrm{mol} \; \%)$	<i>t</i> (h)	Exp	Simul	<i>t</i> (h)	Exp	Simul	<i>t</i> (h) Exp	Simul	
10	23.4	17.1	16.8	1	18.1	15.4	1.5	17.5	15.7	
25	8	31.8	31.8	8	30	30.4	4	28.2	30.3	
50	8	47.5	47.3	8	45.5	46.6	4	44.6	45.0	
75	8	62.8	60.4	8	58.8	60.0	6	54.4	55.5	
90	41.2	?	74.4	19	75.9	72.5	8	61.2	63.2	
Glass Transition		Temperature (°C)								
(°C)		$50^{\circ}\mathrm{C}$		60°C				80°C		
$f_1 \pmod{\%}$	<i>t</i> (h)	Exp	Simul	<i>t</i> (h)	Exp	Simul	<i>t</i> (h)	Exp	Simul	
10	23.4	40.8	73.9	1	58.9	60	1.5	70	82	
25	8	59	69.7	8	61.5	57.5	4	69.2/85.2	49/78/98.5	
50	8	59.4	57.5	8	33	43.7	4	62.7	0/41.2	
75	8	?	24	8	15.3/32.6	0	6	34.4	-18.6/22.1	
90	41.2	?	-4	19	4.5	-32	8	20.9	-8.3	

Table XVI Experimental and Modeling Results of the α MSt-MMA Bulk Copolymerizations Performed at 50, 60, and 80°C: Conversions (X_t) , Molecular Weights $(\overline{M_n}, \overline{M_w}, \text{Copolymer}$ Compositions (F_I) , and Glass Transition Temperature (T_g) are Gathered Versus the Molar Fraction of α MSt in the Monomer Mixture (f_I)

k _{ii}	propa	gation ra	te cons	stant	of t	he re	acti	on
-5	mo	nomer i +	- mono	mer j	(L	mol	$^{-1} s^{-1}$	$^{-1})$
1	1	. •				C	11	1

К ₁₁	depropagation	rate	constant	01	α -methyl-
	styrene (s^{-1}))			

Fox–Flory equation constant (K g^{-1} mol⁻¹) K_{Florv}

- $\overline{\mathrm{K}_p}$ global polymerization rate constant (L $\text{mol}^{-1} \text{ s}^{-1}$
- k_{p0} polymerization rate constant without gel effect (L mol⁻¹ s⁻¹)
- termination rate constant of the reaction k_{tij} monomer i + monomer j (L mol⁻¹ s⁻¹)
- $\overline{\mathbf{K}}_{t}$ global termination rate constant (L mol⁻¹ s^{-1})
- kt0 termination rate constant without gel effect (L mol⁻¹ s⁻¹)
- $[M_i]$ concentration of monomer $i \pmod{L^{-1}}$
- total concentration of monomers (mol $[M_{\rm tot}]$ L^{-1})
- molecular weight of the component (g mmol mol^{-1})
- $\overline{M_n}$ number-average molecular weight (g mol^{-1})
- $\overline{M_w}$ weight-average molecular weight (g mol^{-1})
- $\overline{M_{z}}$ Z-average molecular weight (g mol⁻¹)
- P_{ij} conditional probability of addition of a monomer M_i to a radical R_i
- r_1 reactivity ratio aMSt-MMA
- reactivity ratio MMA $-\alpha$ MSt r_2
- $\bar{R_i}$ radical ended by a monomer *i* unit (mol L^{-1})
- R_p polymerization rate (mol $L^{-1} s^{-1}$)
- t time of polymerization (min.)
- Treaction temperature
- glass transition temperature (°C)
- $T_g V_i$ volume of component i for the gel effect calculation
- free volume fraction
- $V_f V_t$ total reaction volume
- volume expansion coefficient of monomer α (α_m) or polymer (α_p) (°C⁻¹)
- Φ_i mole fraction of radical ended by a monomer *i* unit
- adjusting parameter for the cross-termi- Φ_t nation reaction $R_1^{\cdot} + R_2^{\cdot}$
- fraction of radical ended with $m \alpha$ -meth- $\Phi_{1,m}$ ylstyrene units
- ratio of constants of termination per disλ proportionation and global

Apparatus

PSS mixed gel B, 1.20 m columns; Refrac-GPC tometer Waters 410; LC spectrophotometer, UV 254 nm; Eluent flow rate, 1.2 mL min^{-1} ; Polystyrene calibration: 580, 1450, 3770, 9770, 20,800, 34,300, 70,000, 133,000, 350,000; 771,000, and 1,020,000; Injection loop, 20 μ l

- NMR Bruker 250 MHz; Solvent CDCl₃, without TMS.
- DTA Setaram DSC 101; calibration by metallic standards: Hg, Ga, In, Sn, Pb, and Zn.
- DSC DSC 2920 modulated DSC; TA Instruments Calibration by metallic standards: Hg, Ga, In, Sn, Pb, and Zn.

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