Copolymerization with Depropagation: Experiments and Prediction of Kinetics and Properties of α-Methylstyrene/Methyl Methacrylate Copolymers. I. Solution Copolymerization

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ABSTRACT: α-Methylstyrene (α-MSt) and methyl methacrylate were copolymerized at 60°C in toluene by radical polymerization induced by azobisisobutyronitrile. The kinetics were followed by gravimetry and correlated with the molecular weights, microstructure, and glass transition temperature. A model was developed taking into account the equilibrium of the α-MSt homopolymerization that could not be neglected at 60°C and higher temperatures. The model is in good agreement with all the experimental data. © 1997 John Wiley & Sons, Inc. J Appl Polym Sci **65**: 2297–2313, 1997

Key words: α-methylstyrene; methyl methacrylate; equilibrium of propagation; ceiling temperature; kinetics; molecular weights; copolymer composition; glass transition temperature; software calculations

INTRODUCTION

The use of α-methylstyrene (α-MSt) instead of styrene (St) for acrylonitrile/butadiene/styrene (ABS) graft copolymers produces molding plastics of higher heat resistance.[1] Indeed, the incorporation of α-MSt instead of St is expected to increase the glass transition temperature (T_g) of the grafted polymer, owing to its much higher T_g: Polystyrene, $T_g = 100$°C; Poly(α-MSt), $T_g = 177$°C. However, α-MSt is also known to depropagate at typical polymerization temperatures (above 40°C), thus limiting the overall conversion and polymer chain length. The presence of the methyl group in the α position makes the vinyl group less reactive than the vinyl group in St monomer.[2] This reduced reactivity may be due to steric hindrance or to the presence of the three allylic hydrogens that can contribute to degradative chain-transfer reactions.

Lowry[3] explained the apparent decrease in activity of α-MSt in copolymerization by assuming that, when three or more α-MSt units are added consecutively, the chain end tends to depropagate at a rate equal to or faster than the rate of addition of further monomer units. The ceiling temperature (T_c) of α-MSt[4] is equal to 61°C. Above this temperature, it is impossible to convert monomer into high polymer.

The influence of the α-MSt content in the monomer mixture on the kinetics, the microstructure (sequence distribution), the glass transition temperature, and the molecular weights of the polymers is examined in this work.

The free radical bulk copolymerization of α-MSt was studied in the past. Bulk copolymerization of α-MSt with St, methyl methacrylate (MMA), or acrylonitrile at 70–200°C using peroxide initiators gives copolymers of low molecular weights.[5] At ordinary temperature and pressure conditions, Erbaugh and Calfee[6] required 20 days at 102°C to obtain a low molecular weight copoly-

mer with a 15–85 mol % monomers mixture. They were able to prepare a higher molecular weight copolymer of the same monomer composition at lower initiator concentration in only 5 h, but under a 35,000 psi pressure. Wittmer[7] studied the bulk copolymerization of α-MSt with MMA or acrylonitrile over the whole composition range at nine different temperatures. He determined the composition of the copolymer and deduced from a theoretical treatment the reactivity ratios for these two systems at different temperatures.

However, in the presence of ionic catalysts (SnCl$_4$, BF$_3$, metallic sodium, and others) α-MSt is easily polymerized[8-11] at low temperatures.

Golubeva et al.[3] studied the suspension copolymerization of α-MSt with St, MMA, and acrylonitrile using a polyvinyl alcohol suspending agent and a peroxide initiator. The copolymerization rate and the molecular weights were very low. Higher rates and degrees of copolymerization were obtained in emulsion systems. Golubeva et al.[12] found that the copolymerization of α-MSt with St, MMA, and 2,5-dichlorostyrene by a free-radical mechanism was faster than in suspension or mass polymerization. They made a screening of these systems over the entire concentration range of α-MSt, using potassium persulfate (KPS) as initiator, and determined the extent of conversion, the composition of the formed copolymers, and their intrinsic viscosities. They also studied their physicomechanical and dielectric properties. With increasing α-MSt content, the mechanical strength of the copolymers decreases considerably in all cases, while the thermal stability is raised; these phenomena are more important with MMA than with St. The results of Golubeva et al.[12] are presented in Figure 1.

Neither global work (including kinetics, molecular weight distribution, microstructure, and glass transition temperature) nor global modeling has been published so far. This is the first publication dealing with the solution copolymerization of α-MSt with MMA.

EXPERIMENTAL

The copolymerizations of α-MSt/MMA were carried out in toluene. Monomers and solvent (from Jansen Chimica) were distilled under a vacuum, purged by nitrogen, and kept at $-40°C$ under nitrogen. The initiator, azobisisobutyronitrile (AIBN, 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, $\approx$ 300 rpm). The temperature in the reactor was controlled by a thermostated bath and a thermocouple (resolution $\pm$ 0.01°C, recording each 6 s). The weight composition of the reactor is defined as follows:

$$\frac{\alpha\text{-MSt} + \text{MMA}}{\text{toluene}} = 1 \quad \text{and} \quad \frac{\text{AIBN}}{\text{monomers}} = 0.005$$

Five experiments were carried out in solution 60°C. The operating conditions are described in Table I. The polymerization rate was followed by gravimetric analysis. The polymers were charac-
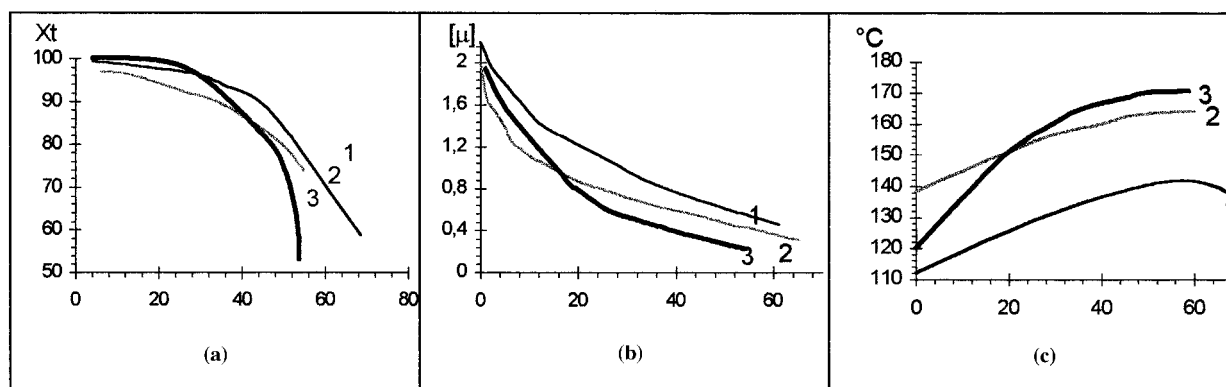

Figure 1   Curves of conversion (X_t), intrinsic viscosity ($[\mu]$), and thermal stability (°C) versus fraction of α-methylstyrene (α-MSt) in copolymer (mol %); adapted from Golubeva et al.[12] (1) α-MSt + styrene (St); (2) α-MSt + 2,5-dichloro St; (3) α-MSt + methyl methacrylate. Abscissa: α-MSt in copolymer (mol %). (a) Effect of α-MSt content on X_t in polymerization. (b) Effect of α-MSt content on $[\mu]$. (c) Effect of α-MSt on the thermal stability (Vicat thermal stability) (°C).

terized by gel permeation chromatography (GPC) differential thermal analysis (DTA), differential scanning calorimetry (DSC), and nuclear magnetic resonance (^{1}H-NMR).

Kinetic Curves

The conversion versus time for the different α-MSt contents (0, 10, 25, 50, 75 wt % α-MSt) is plotted in Figure 2. In Figure 3 the conversion versus fraction of α-MSt (mol %) in the monomer mixture is plotted at $t = 4$ h (five experiments) and $t = 28$ h (only the copolymers S2 → S5) after the beginning of the reaction.

It appears that the decrease in the polymerization rates is drastic. Even for only 10% α-MSt in the monomer mixture, it is divided by at least 10. Then, when the α-MSt amount in the monomer mixture increases the conversions decrease, but much less so: after 4 h of reaction, if the S2 experiment (10% α-MSt) is compared with the S5 experiment (75% α-MSt) the conversion is only divided by 6, $X_t (S2) = 6*X_t (S5)$. In table II the polymerization rates (R_p) of the five experiments are plotted versus the α-MSt content in the monomer mixture (mol %). It shows a strong decrease of R_p when the α-MSt content increases.

Molecular Weights

The molecular weights were determined on the raw materials to keep all the small molecules that could be lost by a purification, such as dissolution in tetrahydrofuran and precipitation in methanol or ether. The calibration of the column was made by polystyrene standards with weights between 580 and 1,020,000. In Table III the number, weight, and Z average molecular weights are given versus the fraction of α-MSt in the monomer mixture (mol %). The weight average molecular weights (M_w) are also plotted versus the fraction of α-MSt (mol %).

Molecular weights decrease very rapidly as a function of the α-MSt content in the monomer mixture. For 10% α-MSt, the M_w is only 10% of the M_w of the poly(MMA). These low values of

M_w were generally very hard to estimate by GPC measurements. A great difference appears between the characteristics of the homopolymerization of MMA and its copolymers with α-MSt. Figure 4 shows the experimental molecular weight distributions for the five experiments; the normalized intensity of the peak is plotted versus the macromolecule weight.

A small family of macromolecules of only four or five monomer units appears for the copolymers of α-MSt and MMA. It can be noted that, in the solution copolymers of α-MSt and MMA, M_w remains lower than 40,000, which means that there are no more than ~ 400 monomer units in the polymer.

Composition of Copolymers

The copolymers were also characterized by ^{1}H-NMR. The copolymers composition (expressed in mol % of α-MSt) and the α-MSt content in the monomer mixture (mol %) are gathered in Table IV. The copolymers composition are determined as follows:

α-MSt
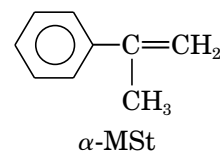
Five hydrogens of the phenyl group ⟶ δ 6.6–7.8 ppm; intensity I_1.

MMA
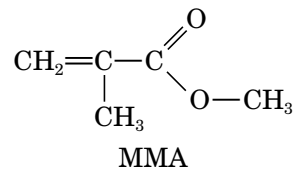
Three hydrogens of the O—CH$_3$ group ⟶ δ 2.6–3.8 ppm; intensity I_2.

The α-MSt content of the copolymer expressed in mol % is

Table I   Operating Conditions for Solution Experiments (g)

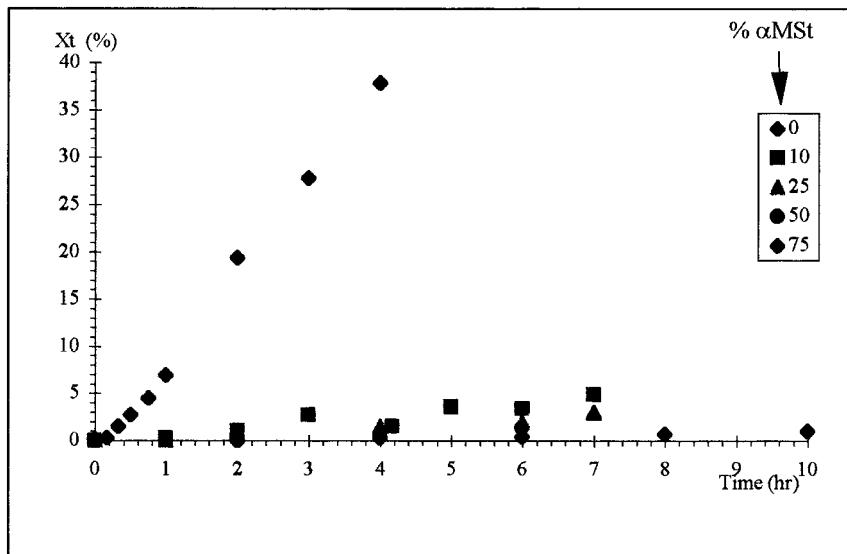|	S1 0/100	S2 10/90	S3 25/75	S4 50/50	S5 75/25
α-MSt	0	25.94	49.53	100.42	151.68
MMA	200.49	181.6	150.44	100.55	52.7
Toluene	202.23	199.32	210.78	206.27	197.8
AIBN	1.0144	0.8758	1.0444	1.0068	1.0253

Figure 2 Conversion versus time of the five solution copolymerizations at 60°C.

$$comp(mol\ \%) = 100\ \frac{\dfrac{I_1}{5}}{\dfrac{I_1}{5} + \dfrac{I_2}{3}}$$

Figure 5 plots the α-MSt compositions of the polymers (experimental results and modeling) versus the α-MSt content in the monomer mixture.

The experimental compositions are compared with the results of the model. The theoretical bases of the model are explained in more details later in this article. The experimental curve crossed the dashed line in Figure 5 for 40.8 mol % of α-MSt in the monomer mixture or 44.9 wt %. This monomer composition is the azeotropic composition of the system. This means that no composition drift is observed for a polymerization with this monomer mixture composition of α-MSt.

The azeotropic composition found by the model is the same (40.7 mol % or 44.7 wt %). The model is in good agreement with the experimental data for the composition of α-MSt in the monomer mixture lower than 60%. We can notice that for 75% α-MSt in the monomer mixture, for example, the molecular weights are very low ($M_w = 2258$), which means that there are only 20 monomer units in the polymer chain. So the influence of the molecular weights on the propagation rate constant of the homopolymerization of α-MSt (k_{p11}) can be conceivable or a penultimate effect for high contents of α-MSt in the monomer mixture can be involved in these noticeable differences between experience and simulation. Furthermore, this very low molecular weight lowers the NMR accuracy and small amounts of solvent (toluene) in the raw material may increase the experimental
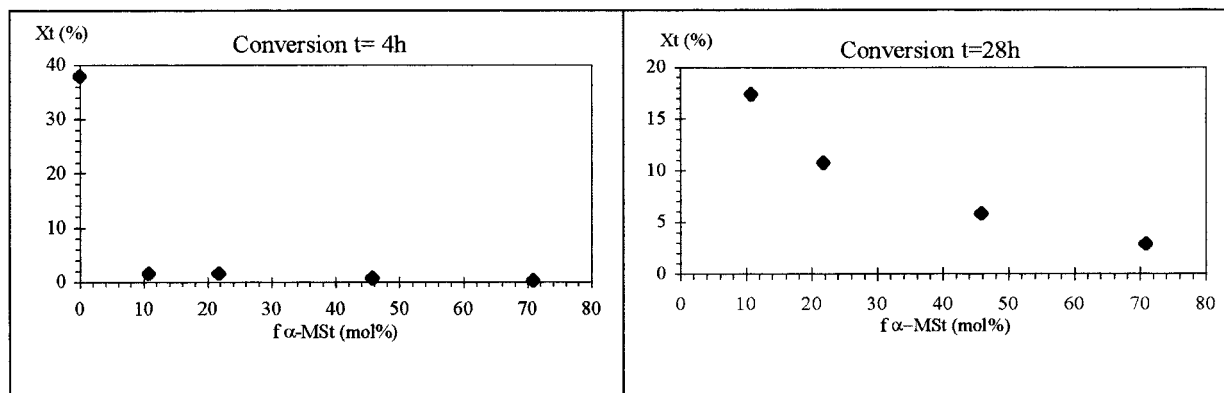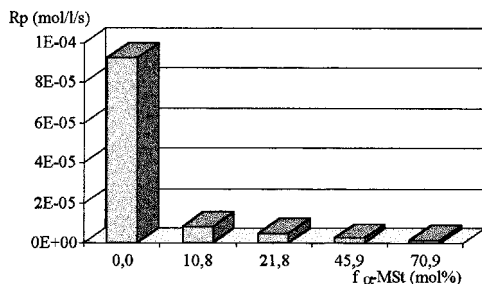

Figure 3 Conversion versus fraction of α-MSt in monomer mixture.

Table II   Rates of Polymerization

fα-MSt (mol %)	R_p (mol L^{-1} s^{-1})
0	9.23E-05
10.8	8.16E-06
21.81	4.56E-06
45.94	2.41E-06
70.9	1.25E-06

value of the copolymer composition by increasing the phenyl peak value in the NMR spectra. But copolymers of α-MSt and MMA obtained by a solution process are not interesting due to the very low molecular weights observed, so we did not try to improve the model for high α-MSt contents.

Glass Transition Temperature

It is well known that glass transition temperature depends on the molecular weights. Cowie[13] gives some general features between T_g and molecular weight relations for α-MSt polymers, including an asymptotic value of T_g for 600 monomeric units for poly(α-MSt). We tried to measure the glass transition temperature on the raw materials, but molecular weights were so low that it was difficult to perform reliable and reproducible measurements. The results of the glass transition measurements are summarized and compared with the calculation of Johnston[14] and the calculation of the software in Table V. The Johnston's equation is described as follows:

$$\frac{1}{T_g} = \frac{W_1 \cdot P_{11}}{T_{g_1}} + \frac{W_1 \cdot P_{12} + W_2 \cdot P_{21}}{T_{g_{12}}} + \frac{W_2 \cdot P_{22}}{T_{g_2}} \quad (1)$$

where P_{ij} is the probability of addition of an M_j monomer unit on a radical R_i^* (ended by an M_i monomer unit) and W_i is the weight fraction of monomer M_i in the polymer Johnston[14] made some experimental studies on the α-MSt/acrylonitrile copolymers and found $T_{g_{12}} = 122°C$. He tried to compare this experimental result with the T_g calculated with the Fox[15] equation, eq. (2). To

obtain an identical result, he stated that the glass transition temperature of an α-MSt unit in a dyad is 130°C when the glass transition temperature of poly(α-MSt) is 177°C.

$$\frac{1}{T_g} = \frac{W_1}{T_{g_1}} + \frac{W_2}{T_{g_2}} \quad (2)$$

This value of 130°C for the glass transition of the α-MSt unit involved in a dyad with a comonomer is used to estimate the $T_{g_{12}}$ of our system by analogy of the calculation of Johnston[14] for the α-MSt/acrylonitrile system. Because an α-MSt/MMA dyad is 54 wt % α-MSt and 46 wt % MMA, the $T_{g_{12}}$ is calculated from eq. (2) and is found to be equal to 118°C (Table VI). The glass transition temperatures of homopolymers and the alternate copolymer used in the software and in Johnston's[14] calculations are presented in Table VI. Table V gives the different results of the experimental measurements and the simulated data. These experimental values were determined on the DTA DSC 101-SETARAM (France) apparatus with a high weight of raw product in the cell (≈ 70 mg). No glass transition in the S4 and S5 experiments (high contents of α-MSt) was reasonably determined.

In the DTA apparatus the temperature difference between the two cells is measured; in the DSC apparatus the difference in heat flow between a sample and an inert reference is measured as a function of time and temperature. The sample and the reference are subjected to a con-

Table III   Average Molecular Weights Versus Fraction of α-MSt in Monomer Mixture

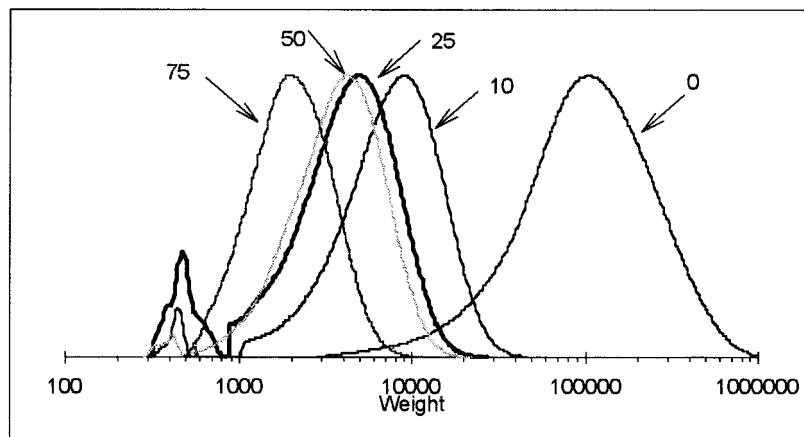| fα-MSt (mol %)	M_n	M_w	M_w/M_n	M_z
0	64,294	143,345	2.23	249,384
10.8	7099	14,899	2.1	20,224
12.81	5606	9090	1.62	11,917
45.84	2837	4361	1.54	5820
70.9	1598	2258	1.41	2989
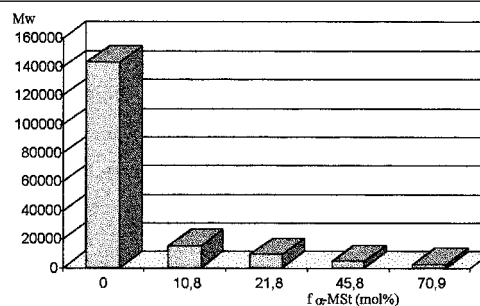
Figure 4   Molecular weight distribution for different weight ratios of α-MSt.

trolled environment of time, temperature, atmosphere, and pressure. The temperature regime seen in the sample and reference is linear for heating and cooling rates ($10°C$ min^{-1}). The reference pan is an empty pan with the same nature as the sample pan. The apparatus is calibrated with metallic standards: Hg, Ga, In, Sn, Pb, Zn (Fig. 6).

In Figure 7 the experimental DTA diagrams (Setaram) are presented. These diagrams allow the estimation of the glass transition temperature of the S2 (10% of α-MSt) and S3 (25% of α-MSt), which were respectively equal to 76 and 61°C. Furthermore, the glass transition is spread over a large range of temperatures (≈ 50–$60°C$). Note that the weight of polymer in the cell was high.

Some measurements on the TA Instruments DSC apparatus with a lower weight of polymer in the cell (10 mg) were carried out. More complex glass transitions can be noted:

1. S2 experiment (10% of α-MSt): three glass transition temperatures 70, 115, and 130°C with a very slight amplitude.
2. S3 experiment (25% of α-MSt): three glass

transition temperatures 50, 115, and 130°C with a very slight amplitude.

Three families of macromolecules can be tentatively defined and connected with these more complex diagrams: a small one with molecular weight (MW) between 1000 and 4000, a middle one with MW between 4000 and 10,000, and a large one with MW larger than 10,000. This complex phenomenon could be explained by assuming that each family of macromolecules has a specific glass transition temperature lowered by the well-known effect of the molecular weight. But the difference between the two apparatuses is so high that the results must be taken cautiously. However, it seems that the low molecular weights have a definite effect on the glass transition.

Software Development

A program was developed to calculate the conversion, molecular weights, microstructure, and glass transition temperature. The confrontation of all these values provides a better understand-

Table IV   Composition of (α-MSt/MMA) Copolymers by ^{1}H-NMR

Reference	Time (h)	X_t (%)	Copolymer Composition (mol % α-MSt)	Monomer (mol % α-MSt)
S2	22	17.72	20.35	10.80
S3	6	1.95	28.12	21.81
S4	20.25	4.53	43.96	45.84
S5	10	1	58.04	70.92
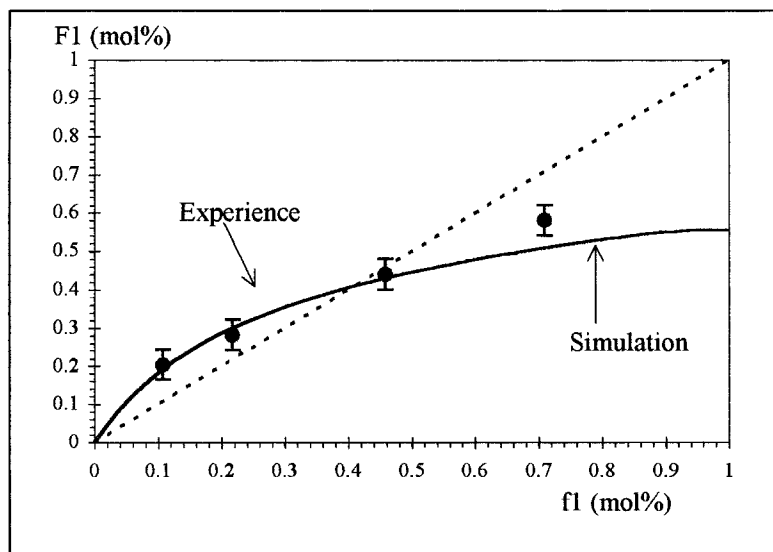
Figure 5 Composition of copolymer in α-MSt (F1) versus fraction of α-MSt in the monomer mixture. ($\bullet$) Experimental results with error bars; (—) composition of the copolymer in α-MSt calculated with the software (described further); (---) diagonal (F1 = f1).

ing of the system and the propagation–depropagation mechanism.

Kinetic Scheme

The monomers are designated as follows: M_1, α-MSt and M_2, MMA. Dainton and Ivin[16,17] indicated that the ceiling temperature, observed in the formation of such polymers, is due to a reverse propagation reaction, called the depolymerization reaction. The rate of reaction depends upon the difference between the propagation rate and the depropagation rate. The ceiling temperature (T_c) is the temperature above which the rate of depropagation is greater than the rate of propagation and, therefore, above which the homopolymerization of α-MSt will not proceed. This ceiling temperature is a thermodynamic phenomenon[13] and, in general, is not changed by the mechanism of initiation or of polymerization.

Table V Comparison Between Experience and Simulated T_g (°C)

	Experience	Johnston[14]	Simulation
S1 0/100	105	105	105
S2 10/90	76	112.9	78
S3 25/75	61	115.6	61
S4 50/50	?	121.6	39
S5 75/25	?	128.5	0

$$T_c = \frac{\Delta H^0_{ss}}{\Delta S^0_{ss} + R \ln[M_{eq}]} \qquad (3)$$

ΔH^0_{ss} is the enthalpy of polymerization and ΔS^0_{ss} is the entropy of polymerization in an appropriate standard state. This equation shows that for a given monomer concentration, there is a temperature above which the depropagation reaction is predominant. The concentration of the monomer at equilibrium $[M_{eq}]$ is identical to the equilibrium constant K for the propagation–depropagation reaction.

$$K = \frac{k_{depropagation}}{k_{propagation}} \qquad (4)$$

with k being the polymerization rate constant for the propagation or the depropagation reaction. In Table VII[18–23] the enthalpy and entropy of polymerization of α-MSt are given, according to six different authors. These results are compared

Table VI Parameters for Glass Transition Temperature Calculation (°C)

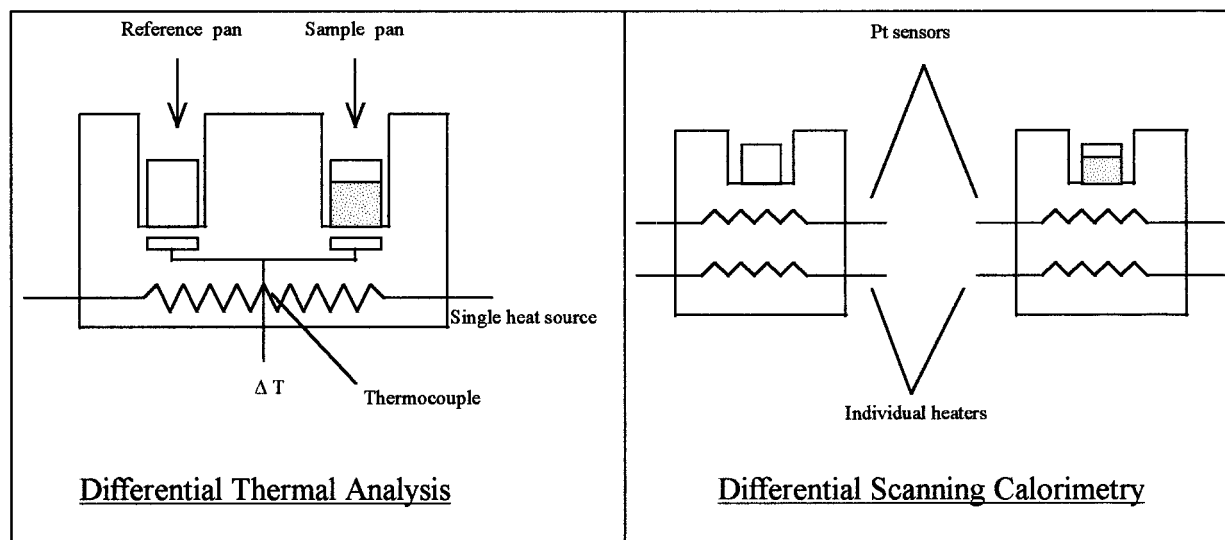|	α-MSt	MMA
α-MSt	177	118
MMA	118	105

Figure 6 Scheme of the DTA and DSC apparatus.

with the values of St and MMA (Table VIII).[24] It can be noticed that the enthalpy of polymerization of α-MSt is relatively low compared with other monomers. K was calculated by McCormick[4] in 1957 (Table IX).

At 80°C $K_{\alpha\text{-MSt}} = 12.9$ mol L^{-1} and $K_{\text{MMA}} = 0.049$ mol L^{-1}.[7] The ceiling temperature of MMA is 155.5 or 135°C.[25,26] So, at 60°C the depropagation

of MMA units is negligible, and we did not take this into account it in the software.

Lowry[3] described three models for the effect of depropagation on copolymer composition. In his second model (case II), he assumed the following conditions:

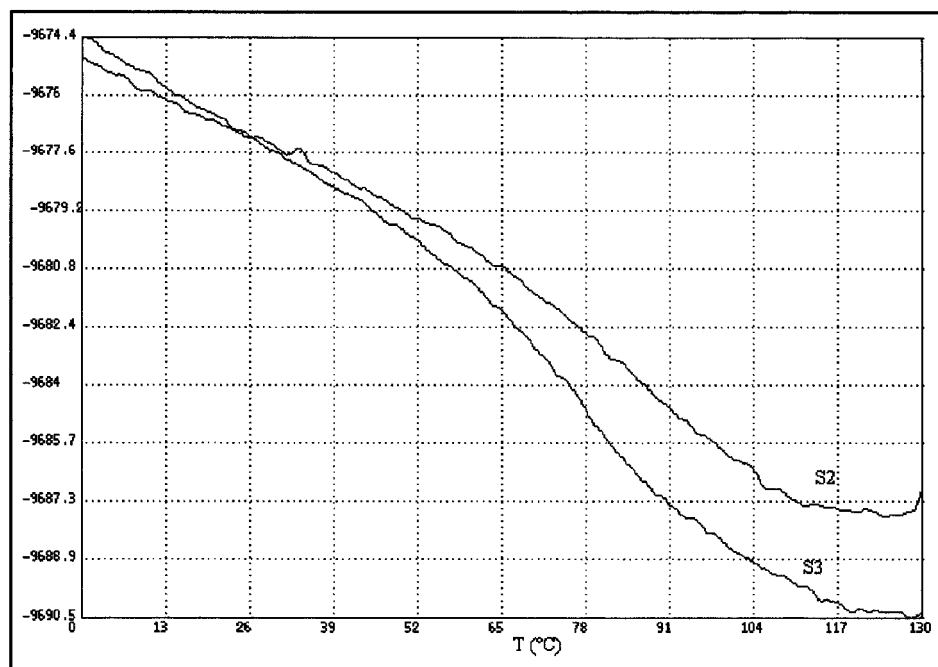1. M_2 has a negligible tendency to depolymer-

Figure 7 DTA experimental diagrams for S2 (10% α-MSt) and S3 (25% α-MSt).

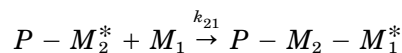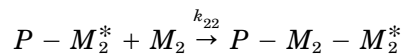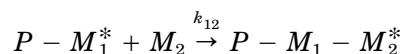**Table VII   Enthalpy and Entropy of Polymerization of α-MSt**
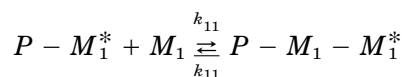
Reference	ΔH^0_{SS} (kcal mol^{-1})	ΔS^0_{SS} (cal mol^{-1} K^{-1})	Measurement Method
McCormick[4]	6.96	24.8	Anionic copolymerization
Worsfold and Bywater[18,19]	8.02	28.75	Anionic copolymerization
Hopff and Lussi[20]	8.5	30.6	Anionic copolymerization
Roberts and Jessup[21]	8.42	—	Calorimetry
Cottam and Cowie[22]	9.31	—	
Cunningham[23]	11.39	39	Thermodynamic (Van't Hoff)

ize, regardless of the nature of the penultimate chain unit.

2. M_1 has a negligible tendency to depolymerize only if it is attached to an M_2 unit or to a single M_1 unit.
3. M_1 has an appreciable tendency to depolymerize whenever it is attached to a sequence of two or more M_1 units.
4. The rate of addition of a particular monomer to any given growing chain, or the rate of removal of a particular monomer unit from any given growing chain, is independent of the composition of the remainder of the chain within the above specified limits.

Thus, from this theory, the maximum number of consecutive α-MSt units in the chain would be two. Ham[27−29] emphasized the kinetic nature of the growing chain and the impossibility of particular reactions. His model needs more parameters than Lowry's[3] one (case II needs the two reactivity ratios and the equilibrium constant of α-MSt, no penultimate effect). O'Driscoll and colleagues[30−35] also worked on the depropagation problem. The experimental applicability of Lowry's[3] model was studied by O'Driscoll and Gaspacho[30] and Ivin and Spensley.[36,37] They concluded that case II was an adequate description of the copolymer composition data for a variety of systems undergoing free radical or ionic polymer-

ization where one monomer was able to depropagate. The kinetic scheme of Fischer[38] and Wittmer[12,39,40] was chosen for its simplicity and was included in the model.

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

$$P - M_1^* + M_2 \overset{k_{12}}{\rightarrow} P - M_1 - M_2^*$$

$$P - M_2^* + M_2 \overset{k_{22}}{\rightarrow} P - M_2 - M_2^*$$

$$P - M_2^* + M_1 \overset{k_{21}}{\rightarrow} P - M_2 - M_1^*$$

This scheme assumes that only the homopolymerization of α-MSt is reversible and there is no re-

Table IX   Equilibrium Constant of α-MSt Homopolymerization

T (°C)	K (mol/L)	T (°C)	K (mol/L)
0	0.7	80	12.9
10	1.1	90	16.9
20	1.7	100	22.9
30	2.53	110	27.9
40	3.65	120	35
50	5.1	130	43
60	7.1	140	54
70	9.1	150	67

Adapted from McCormick.[4]
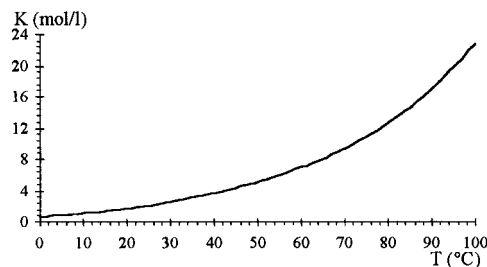
Table VIII   Enthalpy and Entropy of Polymerization of St and MMA

	ΔH^0_{SS} (kcal mol^{-1})	ΔS^0_{SS} (cal mol^{-1} K^{-1})
St[24]	17	26.64
MMA[24]	13.5	22.88

striction on the length of the depropagating α-MSt units.

By defining the reactivity ratios r and the equilibrium constant K,

$$r_1 = \frac{k_{11}}{k_{12}}; \quad r_2 = \frac{k_{22}}{k_{21}}$$

$$K = \frac{\overline{k}_{11}}{k_{11}}$$

Wittmer[7] determined the polymer composition of experiments performed without solvent and deduced the calculated copolymer compositions and the reactivity ratios from this kinetic scheme. He assumed that, with MMA as comonomer, the equilibrium constant of the α-MSt homopolymerization is independent of the length of the monomer sequence. This means that no penultimate effect is taken into account.

Simulation Generalized to N Monomers Where Only First (M₁) Depropagates

It is of interest to model an N monomers system (one of which being α-MSt) in order to simulate copolymers, terpolymers, and higher and to adjust the physical and chemical properties of the polymer for a given application. The probability of occurrence of a long α-MSt sequence decreases with the chain length m. The population balance of growing macromolecules ending with a sequence of m α-MSt monomer units can be computed. In addition, the quasi-steady-state assumption requires that

$$\sum_{m=1}^{\infty} [R^*_{1,m}] + \sum_{i=2}^{N} [R^*_i] = [R^*_{\text{tot}}] \quad (5)$$

and

$$\frac{d[R^*_{\text{tot}}]}{dt} = 0 \quad (6)$$

where $[R^*_{\text{tot}}]$ is the total concentration of radicals in the system calculated by eq. (7),

$$2fk_d[I] = \overline{K}_t[R^*_{\text{tot}}]^2 \quad (7)$$

$$\frac{d[R^*_{1,1}]}{dt} = \overline{k}_{11}[R^*_{1,2}] + [M_1] \sum_{i=2}^{N} k_{i1}[R^*_i]$$

$$- [R^*_{1,1}] \sum_{i=1}^{N} k_{i1}[M_i] = 0 \quad (8)$$

$$\frac{d[R^*_{1,m}]}{dt} = k_{11}[M_1][R^*_{1,m-1}] - \overline{k}_{11}[R^*_{1,m}]$$

$$- [R^*_{1,m}] \sum_{i=1}^{N} k_{1i}[M_i] + \overline{k}_{11}[R^*_{1,m+1}] = 0 \quad (9)$$

and for $j \geq 2$,

$$\frac{d[R^*_j]}{dt} = k_{1j}[M_j] \sum_{m=1}^{\infty} [R^*_{1,m}] - [R^*_j] \sum_{i=1,i \neq j}^{N} k_{ji}[M_i]$$

$$+ M_j \sum_{i=2,i \neq j}^{N} k_{ij}[R^*_i] = 0 \quad (10)$$

In the determination of the concentration of each radical, the termination reactions are not taken into account. This is an hypothesis to simplify the calculations; but although this assumption of long chains may be invalid here due to the very low molecular weights observed, the software gives good results in terms of conversions and molecular weights as will be seen later. This system of linear equations can be rewritten as

$$\|k_{ij}, K, r_{ij}\| * \begin{bmatrix} [R^*_{1,1}] \\ [R^*_{1,2}] \\ . \\ [R^*_2] \\ . \\ [R^*_N] \end{bmatrix} = \begin{bmatrix} 0 \\ 0 \\ . \\ . \\ . \\ 1 \end{bmatrix} [R^*_{\text{tot}}] \quad (11)$$

where $\|k_{ij}, K, r_{ij}\|$ is a square matrix.

So the concentration of each growing radical at each time and the polymerization rate for any monomer can be computed from eq. (11).

$$-\frac{d[M_1]}{dt} = k_{11}[M_1] \sum_{m=1}^{\infty} [R^*_{1,m}]$$

$$- \overline{k}_{11} \sum_{m=2}^{\infty} [R^*_{1,m}] + [M_1] \sum_{i=2}^{N} k_{i1}[R^*_i] \quad (12)$$

and for $j \geq 2$,

$$-\frac{d[M_j]}{dt}$$

$$= k_{1j}[M_j] \sum_{m=1}^{\infty} [R^*_{1,m}] + [M_j] \sum_{i=2}^{N} k_{ij}[R^*_i] \quad (13)$$

By defining Φ_i as the mole fraction of radical i and $\Phi_1 = \sum_{m=1}^{\infty} \Phi_{1,m}$, then

$$[R^*_{1,m}] = \Phi_{1,m}[R^*_{\text{tot}}] \qquad (14)$$

and

$$[R^*_i] = \Phi_i[R^*_{\text{tot}}] \qquad (15)$$

and $\overline{K_t} = \sum_i \sum_j \Phi_i \Phi_j k_{tij}$ where k_{tij} is the termination rate constant for the termination reaction of a radical R^*_i and a radical R^*_j. k_{t12} is calculated by eq. (16).

$$k_{t12} = \phi\sqrt{k_{t11}k_{t22}} \qquad (16)$$

where ϕ is an adjusting parameter that can be necessary in some copolymerization systems where the termination mechanism is not well understood. For all the experiments in our case, $\phi = 1$. The global rate constant of termination $\overline{K_t}$ does not take into account problems of the diffusion of radicals, the predominance of small or large radical termination, or dependence on the kinetic length. Furthermore, these relations are

Table X   Global Polymerization Rate Constant Versus Fraction of α-MSt in Monomer Mixture at 60°C

m_1 (g)	$f1$ (mol %)	K_p (L mol^{-1} s^{-1})
0	0.00	500
10	0.09	294
20	0.17	214
30	0.27	168
40	0.36	135
50	0.46	109
60	0.56	87
70	0.66	66
75	0.72	56
80	0.77	46
90	0.88	25
100	1.00	0
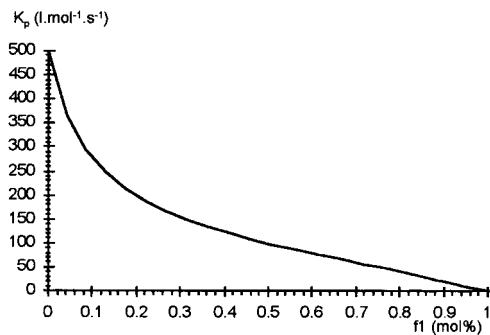
Table XI   Global Termination Rate Constant ($\overline{K_t}$) Versus Fraction of α-MSt in Monomer Mixture (f_1) at 60°C

m_1 (g)	f_1 (mol %)	k_t (L mol^{-1} s^{-1})
0	0.00	6.0E+07
10	0.09	2.8E+09
20	0.17	5.1E+09
30	0.27	6.5E+09
40	0.36	7.5E+09
50	0.46	8.2E+09
60	0.56	8.7E+09
70	0.66	9.2E+09
80	0.77	9.5E+09
90	0.88	9.8E+09
100	1.00	1.0E+10
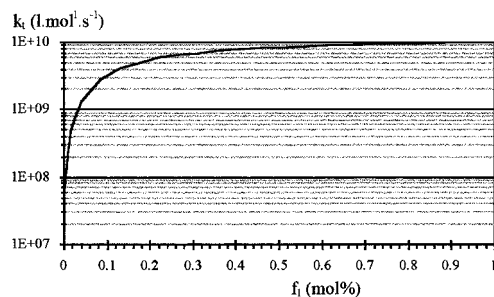
not well understood and would require a lot of new hypothetical coefficients.

Hence, a new overall global propagation rate constant, $\overline{K_p}$, can be defined with

$$-\frac{d[M_{\text{tot}}]}{dt} = -\sum_{i=1}^{N} \frac{d[M_i]}{dt}$$

$$= \left(\sum_{i=1}^{N} \sum_{j=1}^{N} k_{ij}\Phi_i f_j - \frac{\overline{k_{11}}}{M_{\text{tot}}} \sum_{m=2}^{\infty} \Phi_{1,m} \right)[M_{\text{tot}}][R^*_{\text{tot}}]$$

$$= \overline{K_p}[M_{\text{tot}}][R^*_{\text{tot}}] \qquad (17)$$

where f_j is the mole fraction of monomer j. Note that $\overline{K_p}$ is sensitive to k_{ij}, $\overline{k_{11}}$, and monomer concentration. As a consequence, the rate of polymerization, kinetic length, and sequence distribution will be changed with the monomer feed composition, the concentrations, and the temperature.

By definition

$$\sigma = \frac{\sum_{i=2}^{\infty} R^*_{1,i}}{\sum_{i=1}^{\infty} R^*_{1,i}} \qquad (18)$$

Table XII   Constants Used for Calculations

	MMol (g mol^{-1})	dens M	dens P	k_p (L mol^{-1} s^{-1})	$E_{a,p}$ (kcal mol^{-1})	k_t (L mol^{-1} s^{-1})	$E_{a,t}$ (kcal mol^{-1})
α-MSt	118	0.8751	1.15	47[a]	13	1.10[b,c]	2
MMA	100	0.8998	1.19	500[d]	6.05[d]	6.10[d,e]	1.55[d]

Transfer Rate Constants to Solvent	α-MSt	MMA
k_{trS} (L mol^{-1} s^{-1})	0.001	0.1

Transfer Rate Constants to Monomers		
k_{trM} (L mol^{-1} s^{-1})	α-MSt	MMA
α-MSt	0.01	0.005
MMA	0.005	0.0065

Initiator	MMol (g mol^{-1})	k_d (s^{-1})[d]	$E_{a,d}$ (kcal mol^{-1})[d]	Efficiency
AIBN	164	$9 \cdot 10^{-6}$	31	0.62

[a] Fischer.[38]
[b] Hersberger et al.[10]
[c] O'Driscoll and Dickson.[31]
[d] Brandrup and Immergut.[24]
[e] Wittmer.[7]

The overall global propagation rate can be calculated as follows in the case of a copolymerization:

$$\overline{K_p} = \frac{\left[r_1 \dfrac{[M_1]}{[M_2]} \left(1 - \dfrac{K\sigma}{[M_1]} \right) + 1 \right] f_1 + \left[\dfrac{[M_1]}{[M_2]} + r_2 \right] f_2}{\dfrac{r_1}{k_{11}} \dfrac{[M_1]}{[M_2]} + \dfrac{r_2}{k_{22}}} \quad (19)$$

If $K = 0$ (no depropagation reaction involved), one can find the well known equation of the polymerization rate constant for two monomers. In Table X the global polymerization rate calculated by eq. (19) is presented versus the fraction of α-MSt in the monomer mixture (mol %).

Table XIII   Parameters Used for Gel Effect

	α-MSt	MMA	Toluene
α_m (°C^{-1})	1×10^{-3}	1×10^{-3}	1×10^{-3}
T_{gm} (°C)	-80.2	-106	-140
α_p (°C^{-1})	2×10^{-3}	2.6×10^{-3}	
T_{gp} (°C)	175	114	

O'Driscoll and Dickson[31] postulated that rapid termination of copolymerization occurs because of the presence in the system of low molecular weight free radicals of poly(α-MSt) with a chain length of three or less. From the calculation of $\overline{K_t}$ for some α-MSt/St experiments, they found that $k_{t\alpha\text{-MSt}}$ was 10^3 greater than $k_{t\text{St}}$; so with $k_{t\text{St}}$ (60°C) $= 10^7$ L mol^{-1} s^{-1}, $k_{t\alpha\text{-MSt}}$ (60°C) $= 10^{10}$ L mol^{-1} s^{-1}. This number is about as large as termination rate constants can be when one is dealing with a diffusion-controlled reaction between two small molecules in solution.[41] In Table 11 the global termination rate ($\overline{K_t}$) calculated by the software is presented versus the fraction of α-MSt in the monomer mixture (f_1).

Moreover, two values for the propagation rate constant of the homopolymerization of α-MSt are found in the literature: the first is given by Kang et al.,[34] assuming that the ratio of rate constants of methylacrylate to MMA at 60°C is equal to that of St to α-MSt: $k_{p\alpha\text{-MSt}}$ (60°C) $= 26$ L mol^{-1} s^{-1}. The second one is given by Fischer[38] who found $k_{p\alpha\text{-MSt}}$ (60°C) $= 47$ L mol^{-1} s^{-1} through measurements on the St/α-MSt copolymerization.

In the program, the constants presented in Table XII were used. The reactivity ratios and the equilibrium constant of α-MSt homopolymeriza-

Table XIV Results of Simulation

	Time (h)	X_t (%)		M_w		% α-MSt in Copolym.		T_g (°C)	
		Exp.	Simul.	Exp.	Simul.	Exp.	Simul.	Exp.	Simul.
S1 0/100	2.9	26.48	26.95	143,345	143,698	0	0	105	105
S2 10/90	7	4.7	4.28	14,899	14,160	20.35	19.06	76	78
S3 25/75	22	7.5	7.81	9090	8000	28.12	30.01	61	61
S4 50/50	28	4.72	4.94	4361	4440	43.96	43.94	?	39
S5 75/25	28	2.89	2.48	2258	2260	58.04	53.36	?	0

X_t, conversion; M_w, average weight molecular weight; composition of the polymer in α-MSt by ^{1}H-NMR and glass transition temperature by DTA.

tion are $r_1 = 0.4$, $r_2 = 0.39$, $K = 7.1$ mol L^{-1}. For the simulation of the MMA homopolymerization and MMA-rich copolymers, the free volume theory of Marten and Hamielec[42] was used to take into account the gel effect observed during the reaction.

$$\frac{k_t}{k_{t0}} = \left(\frac{M_w^{\text{crit}}}{M_w} \right)^{1.75}$$

$$\times \exp\left\{ -\text{Abuecht}\left(\frac{1}{V_f} - \frac{1}{V_f^{\text{crit}}} \right) \right\} \quad (20)$$

$$\frac{k_p}{k_{p0}} = \exp\left\{ -\left(\frac{1}{V_f} - \frac{1}{V_f^{\text{crit}}} \right) \right\} \quad (21)$$

$$V_f = \sum_{i=1}^{n} [0.025 + \alpha_i (T - T_{gi})] \Phi_i \quad (22)$$

k_{t0} is the MMA termination rate constant without any gel effect.

The gel effect was considered for the simulation of the MMA homopolymerization (S1) with the following parameters (Table XIII): Abuecht $= 0.35$, $V_f^{\text{crit}} = 0.202$, $M_w^{\text{crit}} = 910$, $k_{t,c}$ is the termination rate constant per combination and $k_{t,d}$ is the termination rate constant per disproportionation. $k_{t,c} + k_{t,d} = k_t$ and $k_{t,d} = \lambda k_t$, so $k_{t,c} = (1 - \lambda)k_t$.

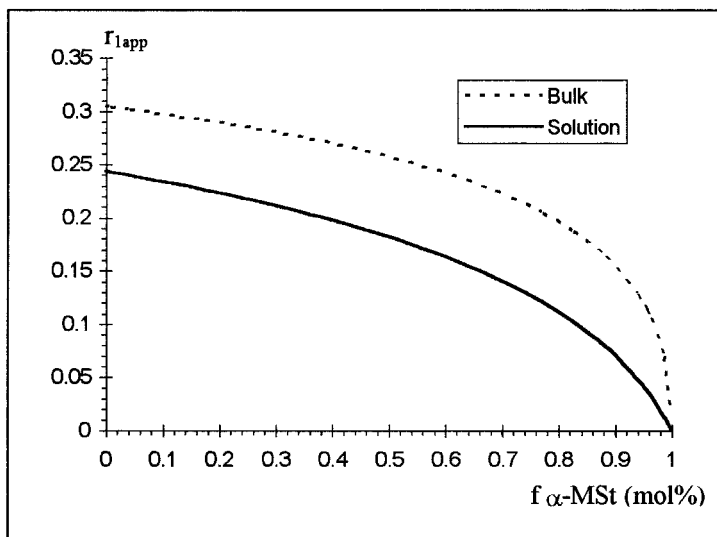For all experiments λ was assumed to be equal to unity, so every termination reaction is realized by dismutation.

Figure 8 Apparent reactivity ratio defined by eq. (23) versus molar fraction of α-MSt. (—) Calculation for a solution process at 60°C; (---) calculation for a bulk process at 60°C.
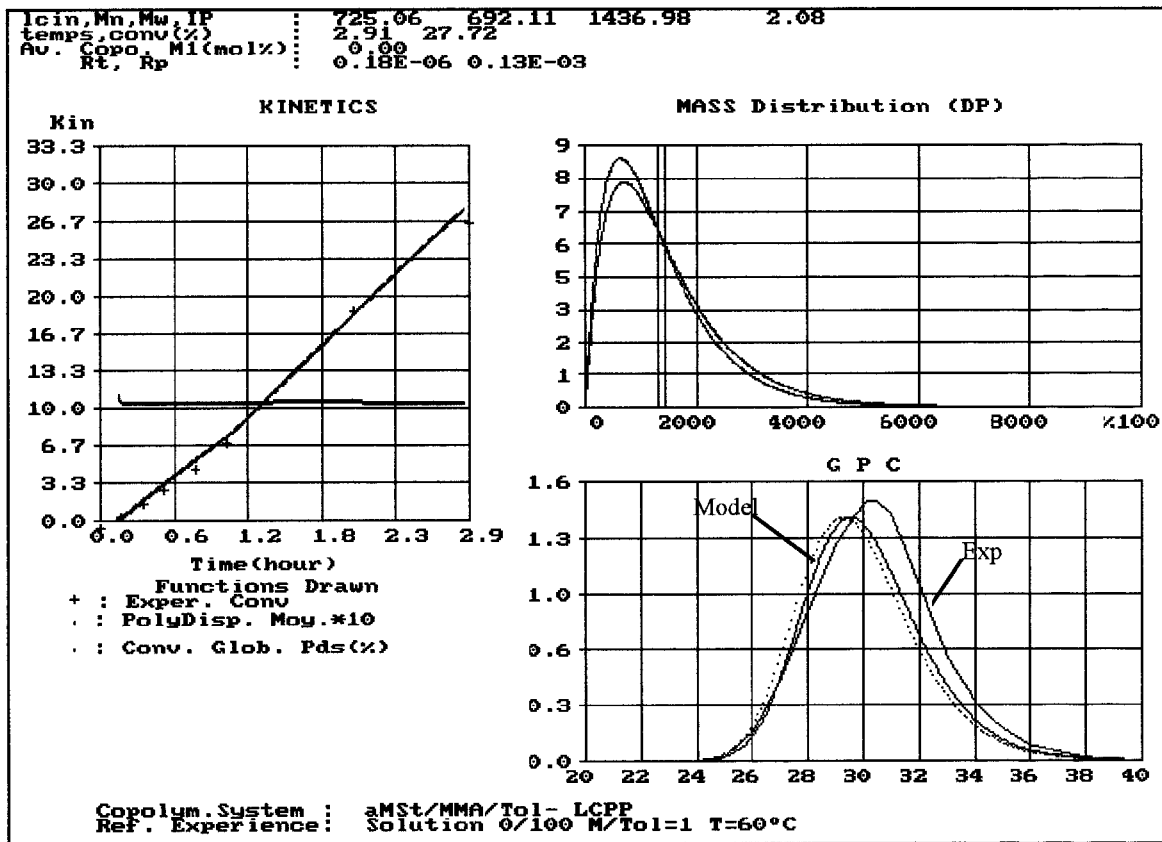
Figure 9   Results of the simulation of the S1 (0/100) experiment.

$$R_a^* + R_b^* \xrightarrow{k_{\text{tab}}} P_a + P_b$$

The results of the simulation are given in Table XIV; a good agreement is generally observed between experimental and simulated data. It is noteworthy to say that there are no adjusting parameters for the four copolymerizations. In the case of the MMA homopolymerization, the only adjusting parameter is M_w^{crit}. The deviation observed on the copolymer composition for the S5 experiment (75% of α-MSt) could also be assigned to the effect of the depropagation at high α-MSt content as shown in eqs. (12)–(15), which also predict that it is impossible to have only one set of reactivity ratios for the whole composition range. From eq. (19) an apparent reactivity ratio can be deducted, r_{1app}, and it can be defined by eq. (23).

$$r_{\text{1app}} = r_1\left(1 - \frac{K\sigma}{[M_1]}\right) \qquad (23)$$

This apparent reactivity ratio depends on K, σ, and the α-MSt monomer concentration. The in-

fluence of the amount of α-MSt can be observed in Figure 8 as well as the influence of the process on the reactivity ratio. With the chosen experimental conditions, the reactivity ratio is divided by 2 if the S1 and S5 experiments are compared (respectively, 10 and 75% of α-MSt in the monomer mixture).

The apparent reactivity ratio evolves from 0.25 to almost 0 in the composition range, which explains the form of the simulated curve for the copolymer composition (Fig. 5). With the bulk process, the decrease of r_{1app} is less drastic: r_{1app} is divided by 2 only when the α-MSt fraction in the monomer mixture is 0.9 compared with 0% of α-MSt. Figures 9 and 10 illustrate two examples of simulations (S1 and S4 experiments, 0 and 50% of α-MSt) and show that the simulation is very close to experimental data. A subroutine of this software gives the microstructure and the glass transition temperature. The GPC diagram is given for the GPC apparatus with the calibration curve of the column used.

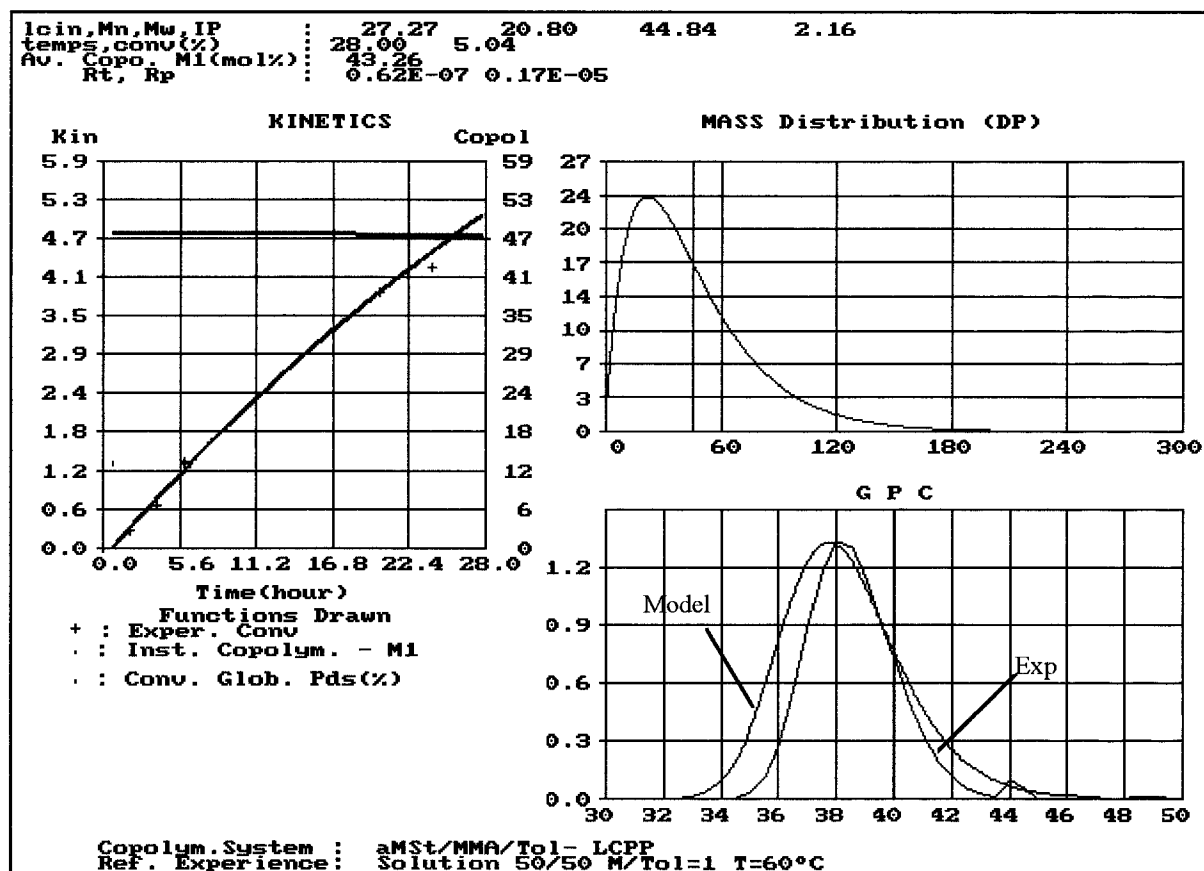$$\ln M = A_0 + A_1 V_{\text{el}} \qquad (24)$$

Figure 10 Results of the simulation of the S4 (50/50) experiment.

$$\bar{v} = \frac{R_p}{\sum R_t} \qquad (25)$$

With R_p and R_t being the polymerisation (p) and termination (t) rate constants, respectively. Indeed, for each instantaneous kinetic length $\bar{v}$, defined by eq. (25), the software computes the instantaneous molecular weight distribution (deduced from the characteristics and calibration with polystyrene standards of the column) as well as the cumulative molecular weight distribution. For each chain it also determines from the calibration curve [eq. (24)] the theoretical elution volume (V_{el}) and makes the summations required by the overlapping. This simulated curve can be directly compared with the experimental GPC diagram. It can be seen in Figure 10 that the simulated GPC distribution is broader than the experimental one. The calibration of the column is a linear one [eq. (24)], which is not pertinent for very small molecular weights. So the real experimental diagram is broader than the observed one ($M_w/M_n = 1.54$, which is too low). Furthermore,

in the software a summation method must be applied to the calculation of these very low molecular weight distributions. The simulation and experiments are in better agreement for the homopolymerization of the MMA (Fig. 9). The kinetic experimental points were obtained by gravimetry.

CONCLUSION

This kinetic study shows that this simplified model with the assumption of long chains is pertinent for the parameters investigated. There is no adjusting parameter and no hypothesis is made for the mechanism of termination (small or large terminations are not considered predominant, nor are problems of diffusion of radicals). However, the model seems less reliable for high fractions of α-MSt in the polymer (more than 60%). In all the copolymerizations small polymerization rates and small molecular weights are obtained. The polymerization rate and the weight average molecular weight are divided by 10 when only 10% α-MSt is

introduced in the monomer mixture. Because of the low molecular weights, the glass transition temperatures are very hard to estimate and must be carefully interpreted. In a further work, these copolymerizations will be carried without solvent but keeping the same initiator (AIBN). The same investigations will be done on the kinetics, the molecular weights, the microstructure, and the glass transition temperature. Another article will deal with emulsion polymerization at various temperatures.

NOMENCLATURE

dens M	monomer density
dens P	polymer density
E_a	activation energy (kcal mol^{-1})
f_i	molar fraction of monomer i
I	initiator (AIBN)
K	equilibrium constant of the α-MSt homopolymerization (mol L^{-1})
k_d	initiator dissociation rate constant (s^{-1})
k_{ij}	propagation rate constant of the reaction monomer i + monomer j (L mol^{-1} s^{-1})
$\overline{k_{11}}$	depropagation rate constant of α-MSt (s^{-1})
$\overline{K_p}$	global polymerization rate constant (L mol^{-1} s^{-1})
$\overline{K_t}$	global termination rate constant (L mol^{-1} s^{-1})
k_{tij}	termination rate constant of the reaction monomer i + monomer j (L mol^{-1} s^{-1})
$[M_i]$	concentration of monomer i (mol L^{-1})
$[M_{tot}]$	total concentration of monomers (mol L^{-1})
MMol	molecular weight (g mol^{-1})
M_n	number average molecular weight
M_w	weight average molecular weight
M_z	Z average molecular weight
MW	molecular weight (g mol^{-1})
r	reactivity ratio
R_i^*	radical ended by a monomer i unit (mol L^{-1})
$R_{1,m}^*$	radical ended with m α-MSt units (mol L^{-1})
R_p	polymerization rate (mol L^{-1} s^{-1})
R_t	termination rate (mol L^{-1} s^{-1})
t	time of polymerization (h)
T_g	glass transition temperature (°C)
T_c	ceiling temperature (°C)
V_{el}	elution volume for the GPC apparatus (mL)
V_f	free volume fraction
α	volume expansion coefficient of monomer (α_m) or polymer (α_p) (°C^{-1})
ΔH_{ss}^0	enthalpy of polymerization (kcal mol^{-1})
ΔS_{ss}^0	entropy of polymerization (kcal mol^{-1} K^{-1})
$\overline{v}$	kinetic length
Φ_i	mole fraction of radical ended by a monomer i unit
$\Phi_{1,m}$	fraction of radical ended with m α-MSt units
λ	ratio of the termination rate constants per disproportionation and global

APPARATUS

GPC	PSS mixed gel B 1.20-m columns; Waters 410 refractometer; LC spectrophotometer, UV 254 nm; eluent flow rate, 1.2 mL/min; polystyrene calibration 580, 1450, 3770, 9770, 20,800, 34,300, 70,000, 133,000, 350,000, 771,000, 1,020,000; injection loop, 20 μL
NMR	Bruker 250 MHz; solvent CDCl$_3$, without TMS
DTA	Setaram DSC 101; calibration by Hg, Ga, In, Sn, Pb, Zn metallic standards
DSC	DSC 2920 modulated DSC, TA instruments; calibration by Hg, Ga, In, Sn, Pb, Zn metallic standards

REFERENCES

1. W. C. Calvert, U.S. Pat. 2,908,661 (1957) (to Borg Warner).
2. *High Polymers,* Vol. XVIII, Interscience, New York, p. 476.
3. G. G. Lowry, *J. Polym. Sci.,* **42,** 463 (1960).
4. H. W. McCormick, *J. Polym. Sci.,* **25,** 111 (1957).
5. A. V. Golubeva, N. F. Usmanova, and K. A. Sivograkova, *Soviet Plast.,* [English transl.], **12,** 6 (1960).
6. L. E. Erbaugh and J. D. Calfee, U.S. Pat. 2,921,932 (1960) (to Monsanto Chemical Co.).
7. P. Wittmer, *Adv. Chem. Ser.,* **99,** 140 (1971).
8. G. D. Jones, R. E. Friedrich, T. E. Werkema, and R. L. Zimmerman, *Ind. Eng. Chem.,* **48,** 2123 (1956).
9. D. J. Worsfold and S. Bywater, *J. Am. Chem. Soc.,* **79,** 4917 (1956).

10. A. B. Hersberger, J. G. Reid, and R. G. Heilingman, *Ind. Eng. Chem.,* **37,** 1073 (1945).
11. I. V. Andreeva and M. M. Koton, *Izvest. Akad. Nauk SSSR,* **3,** 552 (1959).
12. A. V. Golubeva, N. F. Usmanova, and A. A. Vansheidt, *J. Polym. Sci.,* **52,** 63 (1961).
13. J. M. G. Cowie, *Eur. Polym. J.,* **11,** 297 (1974).
14. N. W. Johnston, *Macromolecules,* **6,** 453 (1973).
15. T. G. Fox, *Bull. Am. Phys. Soc.,* **1,** 123 (1956).
16. F. S. Dainton and K. J. Ivin, *Nature,* **162,** 705 (1948).
17. F. S. Dainton and K. J. Ivin, *Q. Rev. (Lond.),* **12,** 61 (1958).
18. D. J. Worsfold and S. Bywater, *J. Polym. Sci.,* **26,** 299 (1957).
19. D. J. Worsfold and S. Bywater, *Can. J. Chem.,* **36,** 1141 (1958).
20. H. Hoppf and H. Lüssi, *Makromol. Chem.,* **62,** 31 (1963).
21. D. E. Roberts and R. S. Jessup, *J. Res. Natl. Bur. Std.,* **46,** 11 (1951).
22. B. J. Cottam, J. M. G. Cowie, and S. Bywater, *Makromol. Chem.,* **86,** 116 (1965).
23. R. E. Cunningham, *Polymer,* **19,** 729 (1978).
24. *Polymer Handbook,* 3d ed., Brandrup and Immergut, Eds., Wiley–Interscience, New York.
25. S. Bywater, *Trans. Faraday Soc.,* **51,** 1267 (1955).
26. T. Otsu, B. Yamada, T. Mari, and M. Inoue, *J. Polym. Sci., Polym. Lett. Ed.,* **14,** 283 (1976).
27. G. E. Ham, *J. Polym. Sci.,* **45,** 169 (1960).
28. G. E. Ham, *J. Polym. Sci.,* **45,** 177 (1960).
29. G. E. Ham, *J. Polym. Sci.,* **45,** 183 (1960).
30. K. F. O'Driscoll and F. P. Gaspacho, *J. Macromol. Sci. Chem.,* **A1,** 643 (1967).
31. K. F. O'Driscoll and J. R. Dickson, *J. Macromol. Sci. Chem. Part A2,* **3,** 449 (1968).
32. M. Izu and K. F. O'Driscoll, *J. Polym. Sci. Part A1,* **8,** 1675 (1970).
33. M. Izu and K. F. O'Driscoll, *J. Polym. Sci. Part A1,* **8,** 1687 (1970).
34. B. K. Kang, K. F. O'Driscoll, and J. A. Howel, *J. Polym. Sci. A1,* **10,** 2349 (1972).
35. B. K. Kang and K. F. O'Driscoll, *Macromolecules,* **7,** 886 (1974).
36. K. J. Ivin and R. H. Spensley, *J. Macromol. Sci.,* **A1,** 653 (1967).
37. K. J. Ivin, *Pure Appl. Chem.,* **4,** 271 (1962).
38. J. P. Fischer, *Makromol. Chem.,* **155,** 211 (1972).
39. P. Wittmer, *Makromol. Chem.,* **103,** 188 (1967).
40. P. Wittmer, *Makromol. Chem.,* **177,** 991 (1976).
41. S. Benson, *Foundations of Chemical Kinetics,* McGraw–Hill, New York, 1960, p. 503.
42. F. L. Marten and A. E. Hamielec, *ACS Symp. Ser.,* **104,** 43 (1979).