An investigation of the kinetics of copolymerization of methyl methacrylate/ *p*-methyl styrene to high conversion: Modelling diff"sion-controlled termination and propagation by free-volume theory

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An experimental investigation of the kinetics of the free radical copolymerization of methyl methacrylate (MMA) and *p*-methylstyrene (PMS) initiated with azobisisobutyronitrile (AIBN) was conducted at temperatures of 60°C and 80°C. Three levels of initiator concentration and initial monomer composition were studied. Conversions were measured gravimetrically and by gas chromatography (g.c.) and the weight average molecular weight ($\bar{M}_w$) by low-angle laser light scattering photometry (LALLSP). A kinetic model using free volume theory seems adequately to account for diffusion-controlled termination and propagation. The model also accounts for segmental-diffusion control of termination at low conversions and termination by reaction diffusion at high conversions. Model predictions are in reasonable agreement with published data on homopolymerization of MMA (ref. 1) as well as with data on copolymerization of these monomers reported herein. This model should find use in the design, simulation, optimization and control of polymer reactor systems for the production of MMA/PMS copolymers.

(Keywords: methyl methacrylate; *p*-methyl styrene; copolymerization kinetics; chemical initiation; free-volume theory)

INTRODUCTION

The objective of the present study was to obtain kinetic data for MMA/PMS copolymerization and to develop a computer model for this chemically initiated copolymerization at low temperatures.

The present model is based on the model of Marten and Hamielec[2], which describes the kinetics of homopolymerization of MMA and accounts for diffusion-controlled termination and propagation reactions using free volume theory. Their model has been modified for copolymerization and to include segmental-diffusion control at low conversions[3] and termination by reaction diffusion at high conversions[4].

THEORY

Diffusion-controlled termination and propagation

During the initial stages of polymerization, a reduction in the rate of polymerization due to an increase in the termination rate constant k_t has been reported by North and Reed[5] and by Ludwico and Rosen[6]. At low conversion, the rate of termination of the macroradical coils can be governed by segmental diffusion of the coil ends. The increasing polymer concentration lowers the thermodynamic quality of the solvent, shrinking the macroradical coils and thereby increasing the segment concentration gradient across them[5].

A model to describe this initial increase in k_t was developed by North and Reed[5] and by Mahabadi and O'Driscoll[3]. The termination rate constant at low conversions is given by:

$$\frac{k_t}{k_{t0}} \simeq \frac{k_{tseg}}{k_{t0}} = 1 + \delta c \quad (1)$$

where k_{t0} is the termination rate constant at zero polymer concentration; k_{tseg} is the segmental diffusion-controlled termination rate constant; c is the polymer concentration; δ is a parameter dependent on macroradical molecular weight and solvent quality.

As the reaction proceeds and the polymer concentration increases, there is a transition from segmental to translational diffusion control (referred to hereafter as diffusion control). At this point, the termination rate constant k_t is approximately equal to the translational diffusion-controlled rate constant k_T. This transition corresponds to the onset of the gel effect[7] and is associated with a critical conversion X_{CRIT1}.

For polymerizations below T_{gp}, the glass transition temperature of the polymer being synthesized, the reaction mixture becomes a glass at monomer conversions less than 100% and during this transition to a glassy state, the propagation rate constant and polymerization rate fall to effectively zero in the normal time scale[2].

A semi-empirical model based on the free volume theory proposed by Marten and Hamielec[2,8] accounts for both the onset of the gel effect and the limiting conversion due to the glassy state transition. This model involves the determination of a critical conversion X_{CRIT1} which

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signifies the onset of the gel effect, a relationship relating k_t as a function of free volume and polymer molecular weight and a similar relationship for the propagation rate constant. The derivations of these relationships may be found elsewhere[2].

During a bulk polymerization, the free volume is assumed to decrease according to[9]:

$$V_F = (0.025 + a_p(T - T_{gp}))\frac{V_p}{V_t} + (0.025 + a_m(T - T_{gm}))\frac{V_m}{V_t} \quad (2)$$

where subscripts *m*, *p* represent monomer and polymer, and:

- T is the polymerization temperature;
- V is the volume;
- V_t is the total volume;
- T_g is the glass transition temperature;
- a is $a_l - a_g$;
- a_l is the thermal expansion coefficient for the liquid state;
- a_g is the thermal expansion coefficient for the glassy state.

At X_{CRIT1}, the corresponding free volume and weight average molecular weight of the polymer are denoted as V_{Fcr1} and $\bar{M}_{wcr1}$ respectively and the following relationship holds[2]:

$$K_3 = \bar{M}^m_{wcr1} \exp(A/V_{Fcr1}) \quad (3)$$

where K_3 is a temperature dependent parameter; m is a constant equal to 0.5; A is an adjustable parameter. Since equation (3) applies at low conversions, the accumulated and instantaneous M_w of the polymer are effectively the same and directly related to M_w for the macroradicals.

The diffusion controlled k_T is given by[2]:

$$k_T = k_t^*\left(\frac{\bar{M}_{wcr1}}{\bar{M}_w}\right)^n \exp\left(-A\left(\frac{1}{V_F} - \frac{1}{V_{Fcr1}}\right)\right) \quad (4)$$

where n is a constant equal to 1.75 and k_t^* is the value of k_t when equation (3) is satisfied.

As the polymer concentration increases, the translational mobility of the chains becomes highly restricted and eventually the trapped macroradical chains move via monomer addition by propagation. This 'reaction diffusion'[4] may be significant at very high conversions. A second term, k_{trd}, is added to the previous equation for k_T to give the overall k_t.

$$k_{trd} = \frac{8\pi N_A}{1000} \cdot \delta \cdot D \quad (5)$$

where

$$\delta = \left(\frac{6V_m}{\pi N_A}\right)^{1/3}$$

$$D = \frac{n_s l_0^2}{6} k_p[M]$$

and

- N_A is Avogadro's number;
- D is the reaction diffusion coefficient;
- δ is the reaction radius;
- V_m is the molar volume;
- n_s is the number of monomer units in one polymer chain segment;
- l_0 is the length of monomer unit;
- [M] is the total monomer concentration.

In the homopolymerization of MMA, the fraction of radicals terminating by disproportionation is given by an expression after Stickler, Panke and Hamielec[10] and is of the form:

$$\lambda = \frac{k_{td}}{k_t} = \exp(a - b/T) \quad (6)$$

where $k_t = k_{tc} + k_{td}$; k_{td}, k_{tc} are termination rate constants for disproportionation and combination; a, b are constants; T is temperature.

A second critical conversion, X_{CRIT2}, during the polymerization is defined as the point at which the propagation reactions become diffusion-controlled. The free volume at this conversion is designated as V_{Fcr2} and the diffusion-controlled k_p is given by[2]:

$$\frac{k_p}{k_{p0}} = \exp\left(-B\left(\frac{1}{V_F} - \frac{1}{V_{Fcr2}}\right)\right) \quad (7)$$

where

- k_p is the propagation rate constant;
- k_{p0} is the chemically-controlled propagation rate constant;
- B is a constant equal to unity.

Model development

The reactions considered in the model include:

Initiation.

$$I \xrightarrow{k_d} 2R\cdot_c$$

$$R\cdot_c + M_1 \xrightarrow{k_1} R\cdot_{1,1}$$

$$R\cdot_c + M_2 \xrightarrow{k_2} R\cdot_{1,2}$$

where I represents an initiator molecule, $R\cdot_c$ is a primary radical and M_1 and M_2 represent the monomer molecules MMA and PMS, respectively. $R\cdot_{s,i}$ is a radical with s monomer units and monomer i as the terminal unit. The rate of initiation R_I for isothermal polymerization is given by:

$$R_I = 2fk_d[I]_0 \exp(-k_d t)/(1 - \varepsilon x) \quad (8)$$

where

- f is the initiator efficiency;
- $[I]_0$ is the initial initiator concentration;
- t is time;

x is the fractional conversion $=(N_0-N)/N_0$;
N_0 is the total moles of monomers 1 and 2 at $t=0$;
N is the total moles of monomers 1 and 2 at $t=t$;
ε equals $\left(\frac{1}{G_1\rho_1+G_2\rho_2}\right)\times\left[\frac{\rho_p(G_1\rho_2+G_2\rho_1)-\rho_1\rho_2}{\rho_p}\right]$;
ρ_p is the density of polymer;
ρ_i is the density of monomer i;
G_i is the weight fraction of monomer i in the monomer phase.

Propagation.

$$R\cdot_{r,1}+M_1\xrightarrow{k_{11}}R\cdot_{r+1,1}$$

$$R\cdot_{r,1}+M_2\xrightarrow{k_{12}}R\cdot_{r+1,2}$$

$$R\cdot_{r,2}+M_1\xrightarrow{k_{21}}R\cdot_{r+1,1}$$

$$R\cdot_{r,2}+M_2\xrightarrow{k_{22}}R\cdot_{r+1,2}$$

Chain transfer to monomer.

$$R_{r,1}+M_1\xrightarrow{k_{f11}}R\cdot_{1,1}+P_r$$

$$R\cdot_{r,1}+M_2\xrightarrow{k_{f12}}R\cdot_{1,2}+P_r$$

$$R\cdot_{r,2}+M_1\xrightarrow{k_{f21}}R\cdot_{1,1}+P_r$$

$$R\cdot_{r,2}+M_2\xrightarrow{k_{f22}}R\cdot_{1,2}+P_r$$

P_r is a dead polymer chain containing r monomer units. Chain transfer to PMS via abstraction of methyl hydrogens is expected to be much greater than chain transfer to MMA.

Termination.

Diffusion-controlled termination

$$R\cdot_{r,1}+R\cdot_{s,1}\xrightarrow{k_t}\lambda(P_r+P_s)$$

$$R\cdot_{r,1}+R\cdot_{s,1}\xrightarrow{k_t}(1-\lambda)P_{r+s}$$

$$R\cdot_{r,1}+R\cdot_{s,2}\xrightarrow{k_t}\lambda'(P_r+P_s)$$

$$R\cdot_{r,1}+R\cdot_{s,1}\xrightarrow{k_t}(1-\lambda')P_{r+s}$$

$$R\cdot_{r,2}+R\cdot_{s,2}\xrightarrow{k_t}P_{r+s}$$

where λ' is the fraction of cross-termination occurring by disproportionation. For PMS, termination by disproportionation is considered negligible[17].

Rate of polymerization

The rate of copolymerization is given by:

$$\frac{dx}{dt}=\frac{k_p}{k_t^{1/2}}(R_I)^{1/2}(1-x) \tag{9}$$

Equation (9) may be rewritten as

$$\frac{dx}{dt}=\phi(x)(1-x) \tag{10}$$

where

$$\left(\frac{dx}{dt}\right)_{t=0}=\phi_0$$

$$\phi_0=\frac{k_{p0}R_{I0}^{1/2}}{k_{t0}^{1/2}}$$

When composition drift is not significant and propagation is chemically controlled (i.e. $k_p=k_{p0}=$constant) the ratio of ϕ_0 to $\phi(x)$ reduces to

$$\frac{\phi_0}{\phi(x)}=\left(\frac{k_t}{k_{t0}}\right)^{1/2} \quad \text{if } R_I\simeq R_{I0}$$

where R_{I0} is the initial rate of initiation.

$\phi(x)$ gives the change in k_t with conversion and is a measure of diffusion-controlled termination.

The onset of diffusion control for the individual propagation rate constants depends on the reactivity of the reactions. This model neglects this and assumes that all propagation reactions become diffusion controlled at the same V_{Fcr2} according to equation (7) and thus that the reactivity ratios do not change. The Meyer–Lowry equation[11], in conjunction with an iterative search routine, is used to find the f_1 value (mole fraction of monomer 1) corresponding to the conversion at that time.

In summary, this model divides the polymerization into three intervals and accounts for segmental diffusion control of termination, translational diffusion control of termination and translational diffusion control of propagation.

Interval 1.
$(X\leqslant X_{CRIT1})$

$$k_t=k_{tseg}=k_{t0}(1+\delta c)$$

$$k_p=k_{p0}$$

Interval 2.
$(X>X_{CRIT1})$

$$k_t=k_T+k_{trd}$$

$$k_p=k_{po}$$

Interval 3.
$(X>X_{CRIT2})$

$$k_t=k_T+k_{trd}$$

$$k_p=k_{po}\exp\left(-B\left(\frac{1}{V_F}-\frac{1}{V_{Fcr2}}\right)\right)$$

where

$$k_{po}=k_{11}k_{22}(r_1f_1^2+2f_1f_2+r_2f_2^2)/(k_{22}f_1r_1+k_{11}f_2r_2)$$

Molecular weight development

The instantaneous number and weight-average molecular weights for linear copolymer chains are given by:

$$M_n = M_0 \frac{2}{(2\tau + \beta)} \quad (11)$$

$$M_w = M_0 \frac{2\tau + 3\beta}{(\tau + \beta)^2} \quad (12)$$

where

$$\beta = \frac{k_{tc} R_p}{k_p^2 [M]^2} = \frac{k_{tc} R_I^{1/2}}{k_p [M] k_t^{1/2}}$$

$$\tau = \frac{k_{td} R_p}{k_p^2 [M]^2} + C_m$$

$$C_m = \frac{k_{fm}}{k_p}$$

$$[M] = [M_1] + [M_2]$$

where

$$k_{fm} = \frac{(k_{21} k_{f11} f_1^2 + f_1 f_2 (k_{21} k_{f12} + k_{12} k_{f21}) + k_{12} k_{f22} f_2^2)}{(k_{21} f_1 + k_{12} f_2)}$$

and M_0 is the effective molecular weight of the repeat unit

$$M_0 = (MW1 \times F_1) + (MW2(1 - F_1)) \quad (13)$$

$MW1$ and $MW2$ are the molecular weights of monomers 1 and 2 and F_1 is the instantaneous mole fraction of monomer 1 bound in the copolymer.

The cumulative molecular weight averages are given by

$$\bar{M}_n = w \Big/ \int_0^w \frac{dw}{M_n} \quad (14)$$

$$\bar{M}_w = \frac{1}{w} \int_0^w M_w dw \quad (15)$$

where w is total monomer conversion on a weight basis.

EXPERIMENTAL

The monomers MMA and PMS were supplied by Fisher Scientific Ltd. and Mobil Chemical Co., respectively. The inhibitors (hydroquinone in MMA and t-butylcatechol in PMS) were removed by washing the monomers with 10% KOH solution, rinsing repeatedly with distilled water and drying over sodium sulphate. The monomers were then distilled under vacuum. AIBN initiator (Kodak Chemical Co.) was recrystallized twice from methanol.

Three initial monomer compositions ($f_{10} = 0.21$, 0.54, 0.83) and three initiator concentrations ($[I]_0 = 0.0057$, 0.0157, 0.0252 mol l^{-1}) were studied. The solutions, placed in glass ampoules, were degassed by repeated freezing and thawing in liquid nitrogen under vacuum. The polymerizations were done in bulk and isothermally at 60°C and 80°C.

Residual monomer compositions and conversions were measured by g.c. Gravimetry was used to obtain an independent measure of conversion for most samples. Weight-average molecular weights of homogeneous copolymers were measured by LALLSP (KMX-6). The refractive index increment (dn/dc) for the copolymer was measured with a laser differential refractometer (KMX-16). All measurements were done at room temperature with ethyl acetate as solvent.

RESULTS AND DISCUSSION

Model parameter estimation

The Meyer–Lowry equation[11] expressing total conversion as a function of residual and initial monomer compositions was used to calculate the reactivity ratios r_1 and r_2. The simplified error in variable method[12] was used and the non-linear estimation routine was fed with the best starting values available for this system ($r_1 = 0.405$, $r_2 = 0.44$)[13]. A set of random experiments was conducted scanning the entire range of comonomer composition at 60°C. The converged estimates of the reactivity ratios provided an azeotropic composition. Polymerizations at this azeotropic composition at 60°C and 80°C revealed no composition drift within experimental error.

The theoretical relationship for δ in equation (1) developed by Mahabadi and O'Driscoll[3] contains parameters unavailable in the literature for the copolymer system MMA/PMS. Therefore, the δ previously calculated for MMA bulk polymerization[3] was chosen as a starting value for estimation purposes. It was found that, for the MMA/PMS system, δ is nearly constant and insensitive to the levels of temperature, initiator and copolymer composition. The value for δ was 0.031 g^{-1}.

The overall termination rate constant, k_t, was estimated as follows:

$$k_t = k_{td} + k_{tc}$$

Assuming that λ' is 0.5, equations (16) and (17) were derived as shown in the Appendix

$$\frac{k_{td}}{k_t} = \lambda \phi_1^2 + \phi_1 \phi_2 \quad (16)$$

$$\frac{k_{tc}}{k_t} = \phi_1^2 (1 - \lambda) + \phi_1 \phi_2 + \phi_2^2 \quad (17)$$

where

$$\phi_1 = k_{21} f_1 / (k_{21} f_1 + k_{12} f_2)$$

$$\phi_2 = k_{12} f_2 / (k_{21} f_1 + k_{12} f_2)$$

ϕ_0 was estimated from the initial slope of conversion–time data. k_{p0} was calculated from the values of f_{10} and k_{ij} ($i,j = 1,2$). k_{t0} was obtained from ϕ_0, k_{p0} and R_{I0}. Values of k_{t0} are listed in *Table 1*. These values show a dependence on composition, a very small temperature dependence and negligible dependence on initiator level, and for high MMA levels approach closely the value recently reported by Meyerhoff *et al.*[18] ($k_{t0} = 1.2 \times 10^9$ l mol^{-1} min^{-1}).

The initial value of C_m defined as C_{m0} was obtained from equation (12) using values of M_w measured by LALLSP at low conversions. The C_m was set equal to C_{m0} up to $X = X_{CRIT2}$ since the individual rate constants k_{f12} and k_{f21} were not available. This approximation is reasonable because of the small value of C_{m0}.

The kinetic model based on free volume theory contains six adjustable parameters A, B, m, n, K_3, V_{Fcr2}. The values for three of these were set equal to those suggested by Marten and Hamielec[2]:

$$B = 1.0, m = 0.5, n = 1.75$$

The remaining three were estimated from the data. Fitting only the azeotrope runs from low to moderate conversion, a simultaneous search for K_3 and A indicated A as a constant of 1.24 for all conditions. It was later found that this constant value satisfied the remaining runs as well. With A fixed, a search for V_{Fcr2} for all conversion–time data was conducted. Both K_3 and V_{Fcr2} were independent of initiator concentration with V_{Fcr2} exhibiting a very weak dependence on temperature and K_3 a very strong dependence on temperature. Values of these parameters are given in *Table 1*.

Parameters found for copolymer characterization

The refractive index increment for various copolymer compositions is given in *Table 2*.

Kinetic model parameters

For AIBN:

$k_d = 6.32 \times 10^{16} \exp(-15\,460/T)\,\mathrm{min}^{-1}$ (ref. 2)

$f = 1.0$

$C_{m0} = 6.0 \times 10^{-6}$ ($T = 60°C$)

$= 20.9 \times 10^{-6}$ ($T = 80°C$)

Table 1 Experimental conditions and kinetic parameters estimated for bulk copolymerization of MMA/PMS

T (°C)	$[I]_0$ (mol l^{-1})	f_{10}	k_{t0} (10^{-9}) (l mol^{-1} min^{-1})	V_{Fcr2}	K_3 (10^{-4})
60	0.0157	0.21	2.1	0.08	1.7
60	0.0252	0.21	2.1	0.09	1.8
60	0.0157	0.83	1.1	0.09	1.9
60	0.0157	0.54	2.1	0.08	2.2
60	0.0057	0.21	2.3	0.09	1.9
60	0.0057	0.54	2.3	0.08	2.3
80	0.0157	0.21	2.1	0.11	1.1
80	0.0157	0.83	1.2	0.10	1.1
80	0.0252	0.21	2.6	0.11	0.9
80	0.0057	0.23	2.6	0.11	1.2
80	0.0157	0.54	2.4	0.09	1.1
80	0.0057	0.54	2.4	0.09	1.2

Table 2 Refractive index increment for various copolymer compositions at 25°C in ethyl acetate with $\lambda = 632.8$ nm

Weight fraction of MMA in copolymer	dn/dc (c in g cm^{-3})
0.138	0.198
0.159	0.190
0.518	0.165
0.541	0.159
0.661	0.132
0.773	0.142

$k_{11} = 9.72 \times 10^8 \exp(-3500/T)\,\mathrm{l\,mol^{-1}\,min^{-1}}$ (ref. 2)

$k_{22} = 6.31 \times 10^8 \exp(-3560/T)\,\mathrm{l\,mol^{-1}\,min^{-1}}$ (ref. 14)

$r_1 = 0.498 \pm 0.020$

$r_2 = 0.419 \pm 0.030$

All temperatures in Kelvin.

Parameters used for equation (6) are taken from Stickler, Panke and Hamielec[10]:

$$a = 3.55 \qquad b = 1460$$

The free volume was calculated using the following equation and parameters:

$$V_F = (0.025 + a_p(T - T_{gp}))\frac{V_p}{V_t} + (0.025 + a_{m1}(T - T_{gm1}))\frac{V_{m1}}{V_t} + (0.025 + a_{m2}(T - T_{gm2}))\frac{V_{m2}}{V_t}$$

$a_p = 0.48 \times 10^{-3}\,\mathrm{K}^{-1}$ (ref. 2)

$T_{gp} = 114°C$ (refs. 2 and 15)

$a_m = a_{m1} = a_{m2} = 2.2 \times 10^{-3}\,\mathrm{K}^{-1}$

$T_{gm1} = -114°C$

$T_{gm2} = -123°C$ (ref. 14)

$\rho_1 = 0.973 - 0.001\,164 \times T(°C)\,\mathrm{g\,cm^{-3}}$ (ref. 2)

$\rho_2 = 0.9261 - 0.000\,918 \times T(°C)\,\mathrm{g\,cm^{-3}}$ (ref. 14)

$\rho_p = 1.11\,\mathrm{g\,cm^{-3}}$ (average of two homopolymer densities) (refs. 2 and 15)

Limiting conversions for two sets of data were used to estimate values of a_m and T_{gm1}. These were then used throughout without further adjustment.

Parameters for equation (5) were obtained from Stickler[4] for MMA homopolymerization as the appropriate values for the copolymer are not available.

$$n_s = 10, \; l_0 = 25$$

Comparison of predicted and measured conversion–time curves

The fits of the experimentally measured data with model predictions are shown in *Figures 1*, *2*, *3* and *4* for copolymerization of MMA/PMS. The model reasonably predicts data at various temperatures, initiator concentrations and initial comonomer compositions.

In *Figure 5* the data of Balke[1] for the bulk homopolymerization of MMA at various temperatures is plotted with the model predictions. At high temperatures, the model appears adequate. However at the lowest temperature, the model is only fair in its prediction of the data.

Composition drift

Figures 6 and *7* show the change in residual monomer composition with conversion for temperatures of 60°C and 80°C. Agreement is within experimental error with

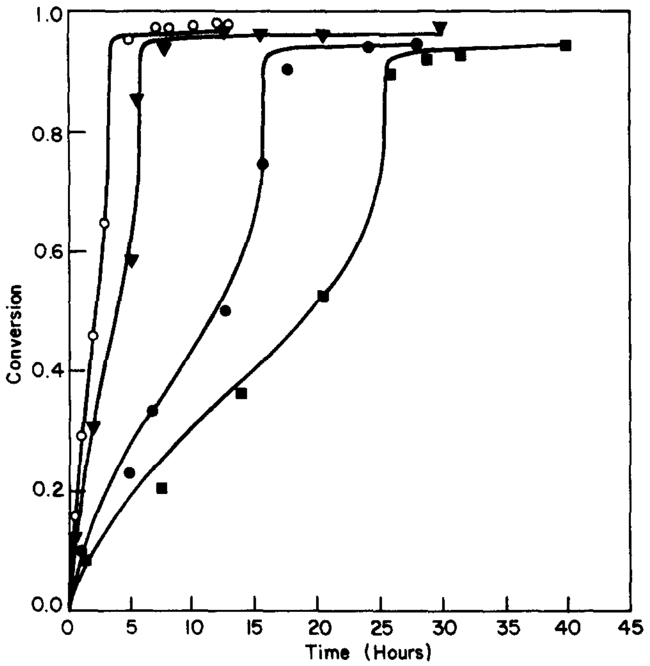

Figure 1 Measured (○, $T=80°C$, $[I]_0=0.0157\ mol\ l^{-1}$; ▼, $T=80°C$, $[I]_0=0.0057\ mol\ l^{-1}$; ●, $T=60°C$, $[I]_0=0.0157\ mol\ l^{-1}$; ■, $T=60°C$; $[I]_0=0.0057\ mol\ l^{-1}$) and predicted conversion vs. time at $f_{10}=0.54$

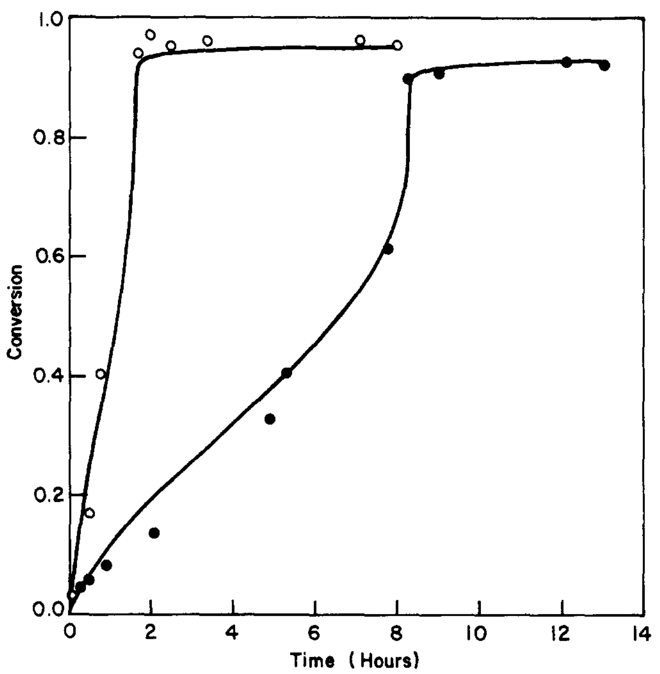

Figure 2 Measured (○, $T=80°C$; ●, $T=60°C$) and predicted conversion vs. time at $[I]_0=0.0157\ mol\ l^{-1}, f_{10}=0.83$

good fits at both low and high conversions. These data fits indicate that the assumption used to impose diffusional limitation on the individual propagation constants is consistent with observations. The application of the integrated copolymer composition equation in this model implies that the reactivity ratios are independent of conversion. However, under diffusion-controlled propagation, the rate constants of the individual propagation reactions are determined by the diffusion of the monomer and one would therefore expect that those rate constants dependent on the diffusion of the same monomer, i.e., k_{ij}, k_{jj}, $i \neq j$, would be approximately equal under these conditions. This implies that the reactivity ratios do change with conversion such that $r_1 r_2 = 1$ as $x \to 1$. To test the sensitivity of the data to this hypothesis, the differential form of the Meyer–Lowry equation was solved with r_1 and r_2 changing with conversion. It was shown that the data at very high conversions were not sufficiently accurate to either prove or disprove this hypothesis.

Molecular weight/conversion curves

Figures 8 and *9* show measured M_w by LALLSP plotted *versus* conversion for the azeotrope data at temperatures of 60°C and 80°C. Each plot represents a different initiator concentration. The model predictions agree with

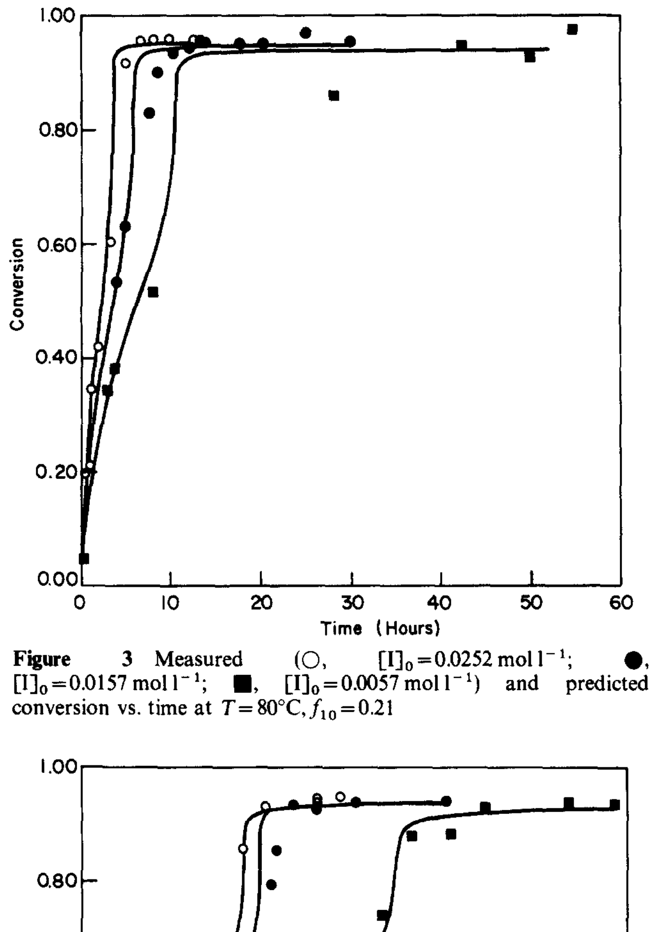

Figure 3 Measured (○, $[I]_0=0.0252\ mol\ l^{-1}$; ●, $[I]_0=0.0157\ mol\ l^{-1}$; ■, $[I]_0=0.0057\ mol\ l^{-1}$) and predicted conversion vs. time at $T=80°C, f_{10}=0.21$

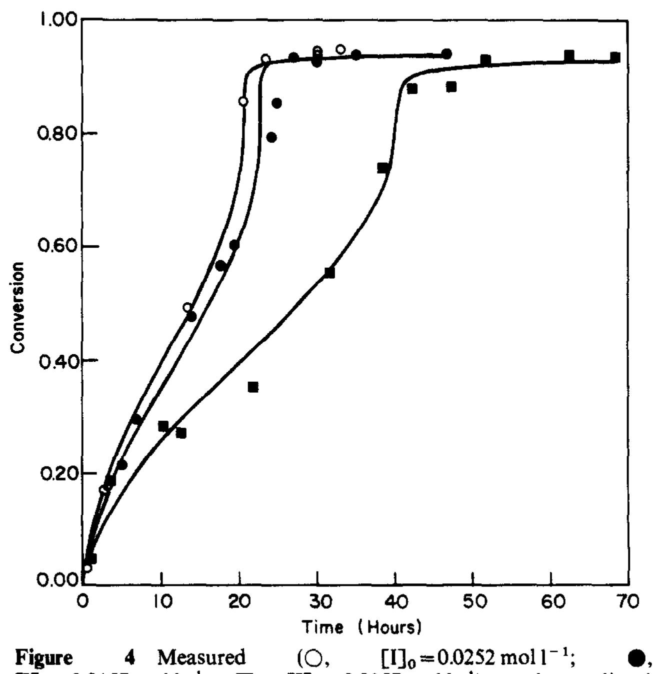

Figure 4 Measured (○, $[I]_0=0.0252\ mol\ l^{-1}$; ●, $[I]_0=0.0157\ mol\ l^{-1}$; ■, $[I]_0=0.0057\ mol\ l^{-1}$) and predicted conversion vs. time at $T=60°C, f_{10}=0.21$

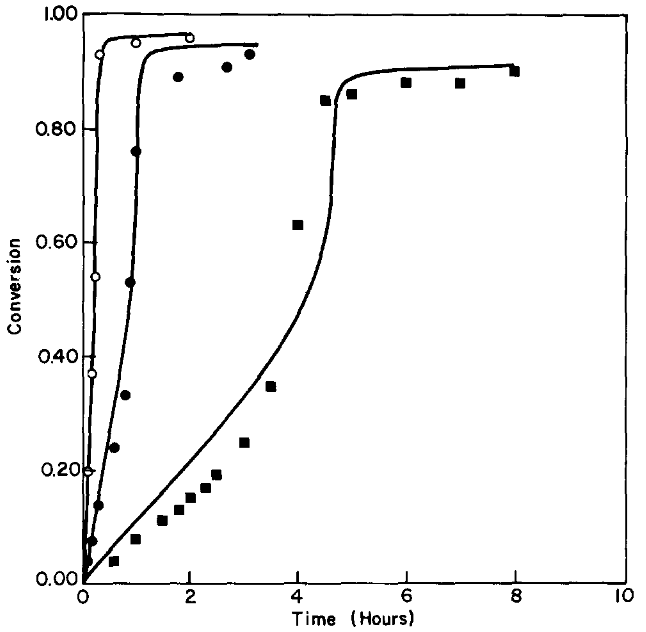

Figure 5 Measured (■, $T=50°C$; ●, $T=70°C$; ○, $T=90°C$) and predicted conversion vs. time at $[I]_0=0.0252$ mol l^{-1}, $f_{10}=1.0$

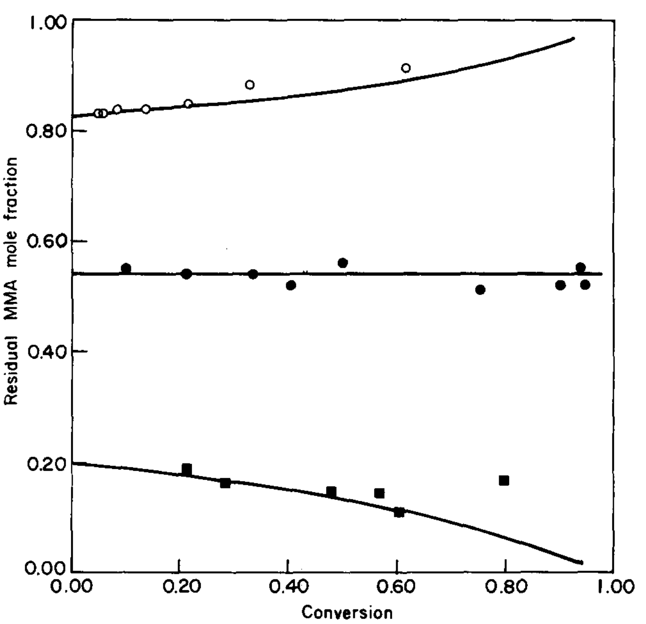

Figure 6 Measured (○, $f_{10}=0.83$; ●, $f_{10}=0.54$; ■, $f_{10}=0.21$) and predicted residual MMA mole fraction vs. conversion at $T=60°C$, $[I]_0=0.0157$ mol l^{-1}

measured data within experimental error except at intermediate conversions, where experimental values increase more rapidly with conversion.

Figures 10, 11 and *12* are plots of M_n and M_w measured by size exclusion chromatography (s.e.c.) for homopolymerization of MMA. All data were taken from Balke and Hamielec[1]. Also shown are M_n and M_w predicted by the kinetic model. There is good agreement with M_n, but with M_w agreement is only fair at moderate to high conversions. Soh and Sundberg[16] have included chain length dependence of k_t in their model and obtained good fits to both M_n and M_w suggesting that a chain-length dependent termination constant may be appropriate.

SUMMARY

An experimental study of the kinetics of the free radical copolymerization of MMA/PMS was conducted. A kinetic model using free volume theory and which accounts for segmental-diffusion controlled termination at low conversions and reaction diffusion at high conversions seems reasonably to predict kinetic data (x, M_n, M_w vs. time) on copolymerization of MMA/PMS as well as published data on the homopolymerization of MMA[1] and should find use in the design, optimization and control of polymer reactor systems for the production of MMA/PMS copolymers.

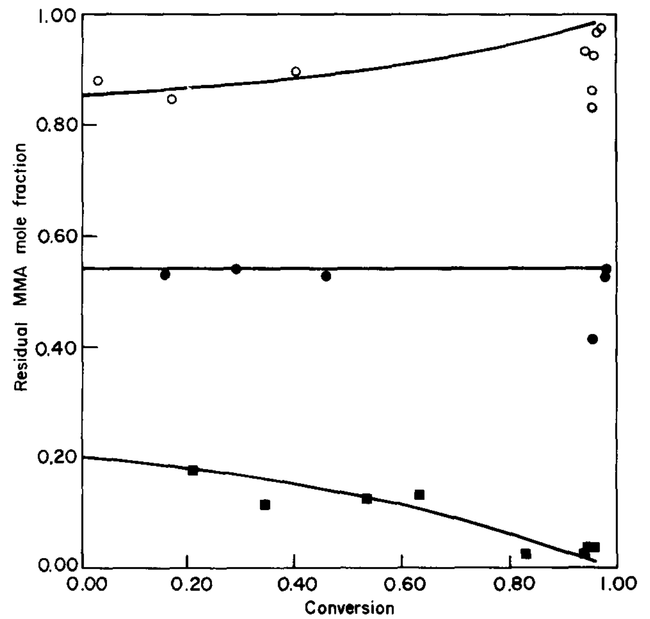

Figure 7 Measured (○, $f_{10}=0.83$; ●, $f_{10}=0.54$; ■, $f_{10}=0.21$) and predicted residual MMA mole fraction vs. conversion at $T=80°C$, $[I]_0=0.0157$ mol l^{-1}

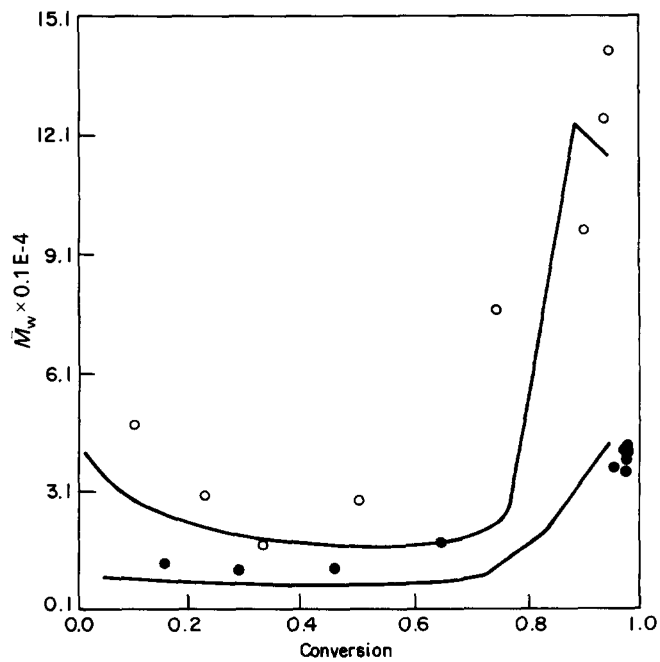

Figure 8 Measured (○, $T=60°C$; ●, $T=80°C$) and predicted weight average molecular weights vs. conversion at $[I]_0=0.0157$ mol l^{-1}, $f_{10}=0.54$

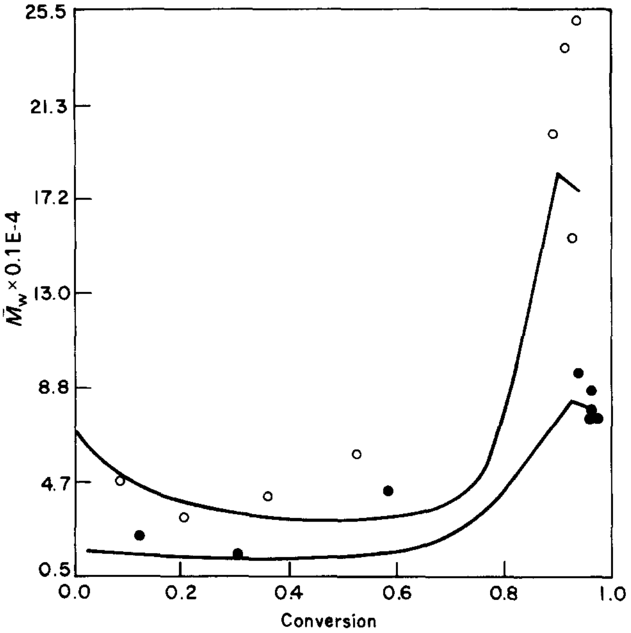

Figure 9 Measured (○, $T=60°C$; ●, $T=80°C$) and predicted weight average molecular weights vs. conversion at $[I]_0=0.0057$ mol l^{-1}, $f_{10}=0.54$

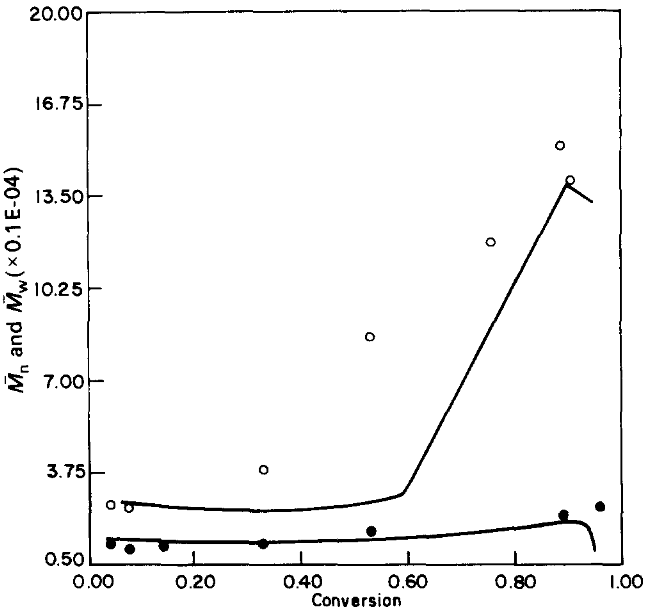

Figure 11 Measured (○, $\bar{M}_w$; ●, $\bar{M}_n$) and predicted number and weight average molecular weights vs. conversion at $[I]_0=0.0252$ mol l^{-1}, $T=70°C, f_{10}=1.0$

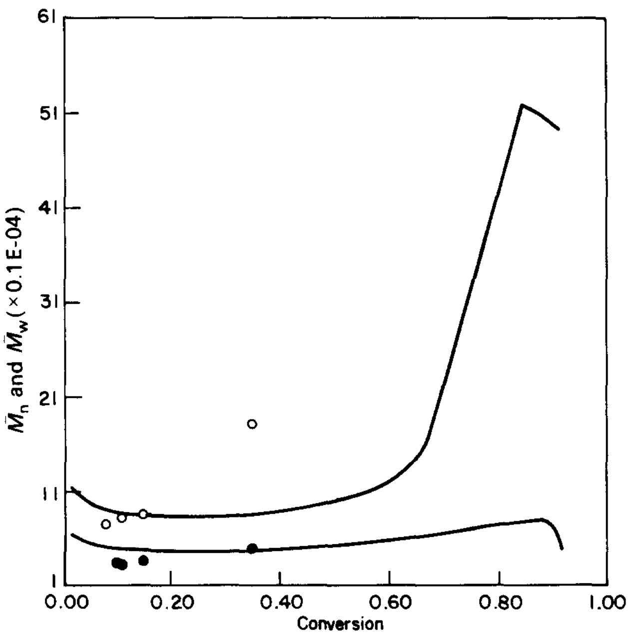

Figure 10 Measured (○, $\bar{M}_w$; ●, $\bar{M}_n$) and predicted number and weight average molecular weights vs. conversion at $[I]_0=0.0252$ mol l^{-1}, $T=50°C, f_{10}=1.0$

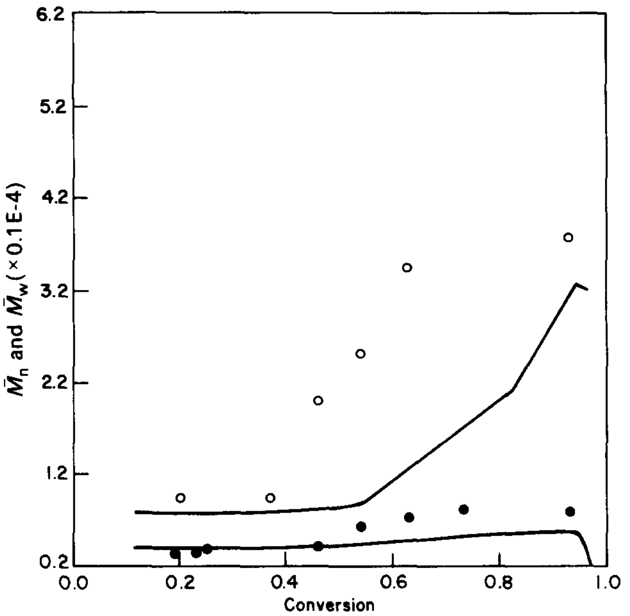

Figure 12 Measured (○, $\bar{M}_w$; ●, $\bar{M}_n$) and predicted number and weight average molecular weights vs. conversion at $[I]_0=0.0252$ mol l^{-1}, $T=90°C, f_{10}=1.0$

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APPENDIX

Based on the kinetic scheme outlined in the model development section, the rate expression for dead polymer is given by

$$\frac{1}{V}\frac{dN_r}{dt}=k_{fm}[M][R_r^{\cdot}]+\Big(\lambda[R^{\cdot}_{r,1}]\sum_{s=1}^{\infty}[R^{\cdot}_{s,1}]+\frac{(1-\lambda)}{2}\sum_{s=1}^{r-1}[R^{\cdot}_{s,1}][R^{\cdot}_{r-s,1}]+(1-\lambda')\sum_{s=1}^{r-1}[R^{\cdot}_{s,1}][R^{\cdot}_{r-s,2}]+\lambda'[R^{\cdot}_{r,1}]\sum_{s=1}^{\infty}[R^{\cdot}_{s,2}]+\lambda'[R^{\cdot}_{r,2}]\sum_{s=1}^{\infty}[R^{\cdot}_{s,1}]+\frac{1}{2}\sum_{s=1}^{r-1}[R_{s,2}][R_{r-s,2}]\Big)k_t \quad (20)$$

where N_r is the number of g moles of dead polymer in volume V and

$$[R_r^{\cdot}]=[R^{\cdot}_{r,1}]+[R^{\cdot}_{r,2}]$$

Assuming $\lambda'=1/2$ and taking

$$\phi_1=k_{21}f_1/(k_{21}f_1+k_{12}f_2)=[R^{\cdot}_1]/[R^{\cdot}]$$

$$\phi_2=k_{12}f_2/(k_{21}f_1+k_{12}f_2)=[R^{\cdot}_2]/[R^{\cdot}]$$

$$[R^{\cdot}]=[R^{\cdot}_1]+[R^{\cdot}_2]$$

$$[R^{\cdot}_i]=\sum_{r=1}^{\infty}[R^{\cdot}_{r,i}] \qquad i=1,2$$

we obtain

$$\frac{1}{V}\frac{dN_r}{dt}=k_{fm}[M][R_r^{\cdot}]+\Big(\lambda\phi_1^2[R_r^{\cdot}][R^{\cdot}]+\frac{(1-\lambda)}{2}\phi_1^2\sum_{s=1}^{r-1}[R_s^{\cdot}][R^{\cdot}_{r-s}]+\frac{1}{2}\phi_1\phi_2\sum_{s=1}^{r-1}[R_s^{\cdot}][R^{\cdot}_{r-s}]+\frac{1}{2}\phi_1\phi_2[R^{\cdot}][R_r^{\cdot}]+\frac{1}{2}\phi_1\phi_2[R_r^{\cdot}][R^{\cdot}]+\frac{1}{2}\phi_2^2\sum_{s=1}^{r-1}[R_s^{\cdot}][R^{\cdot}_{r-s}]\Big)k_t \quad (21)$$

Now,

$$[R_r^{\cdot}]=\phi^{\cdot r}\frac{R_p}{k_p[M]}(\tau'+\beta') \quad (22)$$

where τ' and β' represent the effective values for copolymerization. In addition, the rate of polymerization R_p is expressed as

$$R_p=k_p[M][R^{\cdot}] \quad (23)$$

The substitution of equation (22) into equation (21), following algebraic manipulation, results in

$$\frac{1}{V}\frac{dN_r}{dt}=\phi^{\cdot r}R_p(\tau'+\beta')\Big(\frac{\tau'+\beta'}{2}\times\frac{[R^{\cdot}]r}{k_p[M]}k_t\{(1-\lambda)\phi_1^2+\phi_2^2+\phi_1\phi_2\}+C_m+\frac{[R^{\cdot}]}{k_p[M]}\times k_t\{\lambda\phi_1^2+\phi_1\phi_2\}\Big) \quad (24)$$

Simplification of equation (24) provides an expression analagous to that for homopolymerization

$$\frac{1}{V}\frac{dN_r}{dt}=\phi^{\cdot r}R_p(\tau'+\beta')\left[\frac{(\tau'+\beta')}{2}\times r\beta'+\tau'\right] \quad (25)$$

where

$$\tau'=\frac{R_p}{k_p^2[M]^2}[\{\lambda\phi_1^2+\phi_1\phi_2\}k_t]+C_m$$

$$\beta'=\frac{R_p}{k_p^2[M]^2}[\{(1-\lambda)\phi_1^2+\phi_2^2+\phi_1\phi_2\}k_t]$$

and

$$k_{tc}=(\phi_1^2(1-\lambda)+\phi_1\phi_2+\phi_2^2)k_t$$

$$k_{td}=(\lambda\phi_1^2+\phi_1\phi_2)k_t$$