An investigation of the kinetics of copolymerization of *p*-methylstyrene/acrylonitrile to high conversion: Modelling diffusion-controlled termination and propagation by free-volume theory

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An experimental investigation of the kinetics of the bulk free-radical copolymerization of *p*-methylstyrene (PMS) and acrylonitrile (AN) initiated with azobisisobutyronitrile was conducted at temperatures of 40, 60 and 80°C. Two levels of initiator concentration and three initial monomer compositions were studied. Conversions were measured gravimetrically and by gas chromatography. Weight average molecular weights were measured by low-angle laser light scattering photometry and size exclusion chromatography, and number average weights by size exclusion chromatography. A kinetic model incorporating free-volume theory seems to account reasonably for diffusion-controlled termination and propagation. The model also accounts for segmental-diffusion control of termination rate at low conversion and termination by reaction diffusion at high conversion. Model predictions are in reasonable agreement with experimental data on copolymerization of these monomers. This model should find use in the design, simulation, optimization and control of polymer reactor systems for the production of PMS/AN copolymers.

(Keywords: copolymerization; free volume theory; kinetics; methyl styrene; acrylonitrile)

INTRODUCTION

The objective of the present study was to obtain kinetic data for *p*-methylstyrene/acrylonitrile (PMS/AN) copolymerization and to model this chemically initiated copolymerization at low temperatures.

The present model structure is analogous to that used by Jones *et al.*[1] for the copolymerization of PMS and methyl methacrylate (MMA). This model is a generalization of the homopolymerization model of Marten and Hamielec[2] which accounts for diffusion-controlled termination and propagation reactions using free-volume theory and describes the homopolymerization kinetics of methyl methacrylate reasonably well. In the present work the Marten–Hamielec model was modified for copolymerization and includes the influence of polymer concentration on termination rate at low conversion (segmental-diffusion control)[3] and termination by reaction diffusion at high conversion[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 in 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 is governed by the 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 segmental concentration gradient across them[4].

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

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

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 and 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 (hereafter referred to 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 familar gel effect[7] and is associated with a critical conversion $X_{crit\,1}$.

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

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A semiempirical model based on free-volume theory proposed by Marten and Hamielec[2,8] accounts for both diffusion-controlled termination and propagation. This model involves the determination of the critical conversion $X_{\mathrm{crit}\,1}$, 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 derivation of these relationships may be found elsewhere[2].

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

$$V_F = [0.025 + \alpha_p(T - T_{gp})]\frac{V_p}{V_t} + [0.025 + \alpha_m(T - T_{gm})]\frac{V_m}{V_t} \tag{2}$$

where subscripts m and 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, α is equal to $\alpha_l - \alpha_g$, α_l is the thermal expansion coefficient for the liquid state, and α_g is the thermal expansion coefficient for the glassy state. For copolymerization, another group of terms are added to equation (2) to account for the free-volume fraction generated by the second monomer.

At $X_{\mathrm{crit}1}$, the corresponding free volume and weight average molecular weight of the polymer are denoted as $V_{\mathrm{Frc}1}$ and $\bar{M}_{\mathrm{wcr}1}$ respectively and the following relationship is applicable (see ref. 2 for derivation):

$$K_3 = \bar{M}_{\mathrm{wcr}1}^{m}\exp(A/V_{\mathrm{Fcr}1}) \tag{3}$$

where K_3 is a temperature-dependent parameter, m is a constant, and A is an adjustable parameter. It should be noted that K_3 is constant for isothermal polymerization. The right side of equation (3) accounts for the fact that, when high molecular weight polymer (i.e. high molecular weight macroradicals) is being produced, translational-diffusion-controlled termination occurs at a lower polymer concentration (lower conversion, higher V_F). At some critical polymer concentration, which depends on the size of the macroradicals and presumably also on the molecular weight distribution (*MWD*) of the accumulated polymer, polymer–polymer interaction is sufficient to cause a significant lowering of the diffusion coefficients of the macroradicals and of the conversion for onset of translational-diffusion-controlled termination. 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 termination constant k_T is given by [2]:

$$k_T = k_t^*\left(\frac{\bar{M}_{\mathrm{wcr}1}}{\bar{M}_w}\right)^n \exp\left[-A\left(\frac{1}{V_F} - \frac{1}{V_{\mathrm{Fcr}1}}\right)\right] \tag{4}$$

where n is a constant and k_t^* is the value of k_t when equation (3) is satisfied, i.e. at $X_{\mathrm{crit}1}$. The usefulness of equation (3) to define the conversion where the termination reaction becomes translation-diffusion-controlled depends on how well the conversion vs. time curve is fitted when autoacceleration is significant, given the values of A and $V_{\mathrm{Fcr}1}$ in equation (4).

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] can be significant at very high conversions. At such conversions where the macroradicals are trapped in the matrix (the centre of mass has zero velocity and the self-diffusion coefficient is zero), the radical centre moves by propagation. Reaction diffusion would be important to take into account in calculating higher molecular weight averages. It appears to have an insignificant effect on the total radical concentration and the mean termination constant which is used to calculate the rate of polymerization and $\bar{M}_n$. In fact the reaction-diffusion term does not play a significant role in the present model because only an average k_T with no chain length dependence of macroradicals is used. To account for reaction diffusion a second term, k_{trd}, is added to the previous equation for k_T to give the overall k_t:

$$k_{\mathrm{trd}} = \frac{8\pi N_A \bar{\delta} D}{1000} \tag{5}$$

where

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

$$D = \frac{n_s l_0^2}{6} k_p[\mathrm{M}] \tag{7}$$

and N_A is Avogadro's number, D is the self-diffusion coefficient, $\bar{\delta}$ is the reaction radius, V_m is the molar volume of the monomer, n_s is the number of monomer units in one polymer chain segment, l_0 is the length of monomer unit and $[\mathrm{M}]$ is the total monomer concentration.

A second critical conversion, $X_{\mathrm{crit}2}$, 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 $V_{\mathrm{Fcr}2}$ and the diffusion-controlled k_p is given by[2]:

$$\frac{k_p}{k_{p0}} = \exp\left[-B\left(\frac{1}{V_F} - \frac{1}{V_{\mathrm{Fcr}2}}\right)\right] \tag{8}$$

where k_p is the propagation rate constant, k_{p0} is the chemically controlled propagation rate constant and B is an adjustable parameter.

Model development

The reactions considered in the model include the following.

Initiation

$$\mathrm{I} \xrightarrow{k_d} 2\mathrm{R}_c^{\bullet}$$

$$\mathrm{R}_c^{\bullet} + \mathrm{M}_1 \xrightarrow{k_1} \mathrm{R}_{1,1}^{\bullet}$$

$$\mathrm{R}_c^{\bullet} + \mathrm{M}_2 \xrightarrow{k_2} \mathrm{R}^{\bullet}{}_{1,2}$$

where I represents an initiator molecule, $\mathrm{R}_c^{\bullet}$ is the primary radical and M_1 and M_2 represent the monomer molecules PMS and AN respectively. $\mathrm{R}_{s,i}^{\bullet}$ is a radical with s monomer units and monomer i as the terminal unit. The rate of initiation R_I is given by:

$$R_I = 2fk_d[\mathrm{I}] \tag{9}$$

where f is the initiator efficiency, k_d is the rate constant for initiator decomposition and [I] is the initiator concentration.

Propagation

$$\mathrm{R}^{\bullet}_{r,1} + \mathrm{M}_1 \xrightarrow{k_{11}} \mathrm{R}^{\bullet}_{r+1,1}$$

$$\mathrm{R}^{\bullet}_{r,1} + \mathrm{M}_2 \xrightarrow{k_{12}} \mathrm{R}^{\bullet}_{r+1,2}$$

$$\mathrm{R}^{\bullet}_{r,2} + \mathrm{M}_1 \xrightarrow{k_{21}} \mathrm{R}^{\bullet}_{r+1,1}$$

$$\mathrm{R}^{\bullet}_{r,2} + \mathrm{M}_2 \xrightarrow{k_{22}} \mathrm{R}^{\bullet}_{r+1,2}$$

Chain transfer to monomer

$$\mathrm{R}^{\bullet}_{r,1} + \mathrm{M}_1 \xrightarrow{k_{f11}} \mathrm{R}^{\bullet}_{1,1} + \mathrm{P}_r$$

$$\mathrm{R}^{\bullet}_{r,1} + \mathrm{M}_2 \xrightarrow{k_{f12}} \mathrm{R}^{\bullet}_{1,2} + \mathrm{P}_r$$

$$\mathrm{R}^{\bullet}_{r,2} + \mathrm{M}_1 \xrightarrow{k_{f21}} \mathrm{R}^{\bullet}_{1,1} + \mathrm{P}_r$$

$$\mathrm{R}^{\bullet}_{r,2} + \mathrm{M}_2 \xrightarrow{k_{f22}} \mathrm{R}^{\bullet}_{1,2} + \mathrm{P}_r$$

where P_r is a dead polymer chain containing r monomer units.

Termination

$$\mathrm{R}^{\bullet}_{r,j} + \mathrm{R}^{\bullet}_{s,i} \xrightarrow{k_t} \mathrm{P}_{r+s}$$

where $i,j = 1,2$. Under diffusion-controlled termination, it is sufficient to use a single termination rate constant (i.e. end groups need not be considered). Termination by disproportionation is considered negligible in comparison to termination by combination for both PMS[10] and AN[11].

Rate of polymerization

The rate of isothermal copolymerization is given by:

$$\frac{\mathrm{d}x}{\mathrm{d}t} = \frac{k_{p0}}{k_t^{1/2}}(R_I)^{1/2}(1-x) \tag{10}$$

where $x = (N_0 - N)/N_0$ is the fractional conversion, N_0 is total moles of monomers 1 and 2 at $t = 0$, N is total moles of monomers 1 and 2 at $t = t$ and

$$k_{p0} = k_{11}k_{22}(r_1 f_1^2 + 2f_1 f_2 + r_2 f_2^2)/(k_{22} f_1 r_1 + k_{11} r_2 f_2) \tag{11}$$

where r_i is reactivity ratio $(= k_{ii}/k_{ij},\ i \neq j)$ and f_i is residual monomer i mole fraction.

Equation (10) may be rewritten as:

$$\mathrm{d}x/\mathrm{d}t = \Phi(x)(1-x) \tag{12}$$

where

$$(\mathrm{d}x/\mathrm{d}t)_{t=0} = \Phi(0) \tag{13}$$

$$\Phi(0) = k_{p0} R_{I0}^{1/2}/k_{t0}^{1/2} \tag{14}$$

When composition drift is not significant and propagation is chemically controlled, k_{p0} depends on temperature only. The ratio of $\Phi(0)$ to $\Phi(x)$ then reduces to:

$$\Phi(0)/\Phi(x) = (k_t/k_{t0}) \qquad \text{if } R_I \simeq R_{I0} \tag{15}$$

where R_{I0} is initial rate of initiation. The ratio $\Phi(0)/\Phi(x)$ gives the change in k_t with conversion and is a measure of diffusion-controlled termination. (This ratio may have to be corrected for change in initiation rate at high conversions.) With k_{p0} and R_{I0} as known quantities and $\Phi(0)$ estimated from the initial slope of conversion–time data, a value of k_{t0} may be extracted for each set of conditions.

The onset of diffusion control for the individual propagation rate constants depends on chemical reactivity and monomer diffusion coefficients. The present model neglects this and assumes that these rate constants can be lumped into a single pseudo rate constant k_{p0} which becomes diffusion-controlled at V_{Fcr2} according to equation (8). An iterative search routine is used to find X_{crit2}. This routine gives the minimum sum of squares of differences between measured and model-calculated conversions at different polymerization times, i.e. the minimum sum of squares of errors.

In summary, the present 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. $X \leqslant X_{crit1}$, $V_F \geqslant V_{Fcr1}$:

$$\begin{aligned} k_t &= k_{tseg} = k_{t0}(1 + \delta c) \\ k_p &= k_{p0} \end{aligned} \tag{16a}$$

Interval 2. $X > X_{crit1}$, $V_F < V_{Fcr1}$:

$$\begin{aligned} k_t &= k_T + k_{trd} \\ k_p &= k_{p0} \end{aligned} \tag{16b}$$

Interval 3. $X > X_{crit2}$, $V_F < V_{Fcr2}$:

$$\begin{aligned} k_t &= k_T + k_{trd} \\ k_p &= k_{p0}\exp\left[-B\left(\frac{1}{V_F} - \frac{1}{V_{Fcr2}}\right)\right] \end{aligned} \tag{16c}$$

Molecular weight development

The instantaneous number and weight average molecular weights for linear copolymer chains are expressed as:

$$\bar{M}_n = M_0 \frac{2}{(2\tau + \beta)} \tag{17}$$

and

$$\bar{M}_w = M_0 \frac{2\tau + 3\beta}{(\tau+\beta)^2} \tag{18}$$

where

$$\beta = \frac{k_t R_p}{k_p^2 [M]^2} = \frac{k_t^{1/2} R_I^{1/2}}{k_p [M]} \tag{19}$$

$$\tau = C_m \tag{20}$$

$$C_m = k_{fm}/k_p \tag{21}$$

$$[M] = [M_1] + [M_2] \tag{22}$$

R_p is rate of monomer consumption in mol l^{-1} s^{-1}, M_0 is effective molecular weight of the repeat unit

$$M_0 = MW_1(F_1) + MW_2(1 - F_1) \tag{23}$$

MW_1 is molecular weight of monomer 1, MW_2 is molecular weight of monomer 2, and F_1 is instantaneous mole fraction of monomer 1 bound in the copolymer.

The cumulative molecular weight averages are given by:

$$\bar{M}_n = x_w \Bigg/ \int_0^{x_w} \frac{dx_w}{M_n} \tag{24}$$

$$\bar{M}_w = \frac{1}{x_w} \int_0^{x_w} M_w dx_w \tag{25}$$

where x_w is total monomer conversion on a weight basis.

EXPERIMENTAL

The chemically initiated copolymerization of PMS and AN was done in bulk in sealed glass ampoules. Polymerizations were carried out isothermally at 40, 60 and 80°C, respectively. Three initial monomer compositions ($f_{10} = 0.56$, 0.8, 0.9; monomer 1 is PMS) and two initiator concentrations ($[I]_0 = 0.01$ and 0.05 mol l^{-1}) were studied. The monomers were supplied by Mobil Chemical Co. (PMS) and Aldrich (AN). The inhibitors (hydroquinone in AN and t-butylcatechol in PMS) were removed by washing the monomers with 10% KOH solution, rinsing repeatedly with deionized water and drying over sodium sulphate. The monomers were then distilled under vacuum. The initiator azobisisobutyronitrile (AIBN) (Kodak Chemical Co.), was recrystallized twice from methanol. Oxygen was removed from the solutions by vacuum degassing using the freeze–thaw technique.

Residual monomer compositions and conversions were measured by gas chromatography (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 low-angle laser light scattering photometry (l.a.l.l.s.p., Chromatix KMX-6 detector). The refractive index increment (dn/dc) for the copolymer was measured with a laser differential refractometer (Chromatix KMX-16). All measurements were done at room temperature with tetrahydrofuran (THF) as solvent. The number and weight average molecular weights were also measured by size exclusion chromatography (s.e.c.) (Du Pont Bimodal) using THF as the mobile phase at 25°C. The molecular weight calibration curve for the copolymer was found using the universal calibration curve based on polystyrene and two broad *MWD* homogeneous copolymer standards with known $\bar{M}_w$ found by using l.a.l.l.s.p. off-line[12].

RESULTS AND DISCUSSION

Model parameter estimation

The Meyer–Lowry equation[13], expressing total conversion as a function of residual and initial monomer compositions, was used to estimate the reactivity ratios r_1 and r_2. The simplified error in variables method[14] was used, and the nonlinear estimation routine was supplied with the best starting values available for this system ($r_1 = 0.33$, $r_2 = 0.05$)[15]. A set of random experiments were conducted scanning the range of comonomer compositions from $f_{10} = 0.56$ to 0.90 at 60 and 80°C. The converged estimates of the reactivity ratios provided an azeotropic composition ($f_1 = 0.56$). Polymerizations at this azeotropic composition at 60 and 80°C revealed no composition drift within experimental error. The converged estimates of reactivity ratios found were: $r_1 = 0.26 \pm 0.02$ and $r_2 = 0.066 \pm 0.029$.

Using the following rate constants obtained from the liberature[17]:

$$k_{d(AIBN)} = 9.48 \times 10^6 \exp(-15\,500/T)\ \text{min}^{-1} \qquad f = 1.0$$

$$k_{11} = 6.306 \times 10^8 \exp(-3557/T)\ \text{l mol}^{-1}\ \text{min}^{-1}$$

$$k_{22} = 6.282 \times 10^9 \exp(-3663/T)\ \text{l mol}^{-1}\ \text{min}^{-1}$$

the following additional model parameters were estimated from the data:

Values of k_{t0} were estimated from initial rate data (dx/dt at $t = 0$). Values of k_{t0} are listed in *Table 1*. These values appear to be a function of temperature and monomer mole fraction.

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 PMS/AN. Therefore, the δ previously calculated for PMS bulk homopolymerization[10] was chosen as a starting value for estimation purposes. The value of δ from the PMS/AN system was estimated using conversion–time data at low conversion before the onset of translation-diffusion-controlled termination, and was found to be constant at 2.5×10^{-3} l g^{-1} for all conditions.

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

$$B = 1.0 \qquad m = 0.5 \qquad n = 1.75$$

The remaining three parameters were estimated from the rate data using the following expression and parameters to calculate free-volume fraction:

$$V_F = [0.025 + \alpha_p(T - T_{gp})]\frac{V_p}{V_t} + [0.025 + \alpha_{m1}(T - T_{gm1})]\frac{V_{m1}}{V_t} + [0.025 + \alpha_{m2}(T - T_{gm2})]\frac{V_{m2}}{V_t} \tag{26}$$

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

T (°C)	$[I]_0$ (mol l^{-1})	f_{10}	$k_{t0} \times 10^{-9}$ (l mol^{-1} min^{-1})	$K_3 \times 10^{-5}$	V_{Fcr1}	X_{crit1}	X_{crit2}	$\bar{M}_{wcr1} \times 10^{-5}$
40	0.01	0.9	5.2	4.1	0.132	0.187	0.699	4.33
40	0.05	0.9	5.2	4.4	0.122	0.265	0.695	1.75
40	0.01	0.8	5.0	3.0	0.142	0.114	0.695	5.84
40	0.05	0.8	5.0	2.8	0.135	0.171	0.700	2.76
60	0.01	0.9	6.0	2.1	0.136	0.288	0.758	1.64
60	0.05	0.9	6.0	2.0	0.128	0.345	0.753	0.703
60	0.01	0.8	5.8	1.6	0.147	0.220	0.753	2.46
60	0.05	0.8	5.8	1.8	0.133	0.316	0.758	0.911
60	0.01	0.56	8.2	1.3	0.160	0.167	0.776	4.11
60	0.05	0.56	8.2	1.4	0.145	0.274	0.775	1.632
80	0.01	0.9	7.0	0.93	0.147	0.325	0.806	0.823
80	0.05	0.9	7.2	0.96	0.134	0.404	0.807	0.288
80	0.01	0.8	7.0	0.80	0.154	0.293	0.809	1.028
80	0.05	0.8	7.0	0.82	0.142	0.367	0.808	0.430
80	0.01	0.56	8.6	0.86	0.160	0.297	0.824	1.806
80	0.05	0.56	8.6	0.87	0.147	0.373	0.826	0.720

$\alpha_p = 2.5 \times 10^{-4}$ K^{-1}, $T_{gp} = 378.2$ K, $\alpha_{m1} = 1.0 \times 10^{-3}$ K^{-1}, $T_{gm1} = 185.0$ K, $\alpha_{m2} = 1.25 \times 10^{-3}$ K^{-1}, $T_{gm2} = 190.38$ K^{-1}, $\rho_p = 1.12$ g ml^{-1}, $\rho_1 = 0.892 - 0.000918\ (T - 298.15)$ g ml^{-1}, $\rho_2 = 0.806 - 0.001052\ (T - 293.15)$ g ml^{-1}. These parameters were obtained from the work of Lord[16] for styrene/acrylonitrile polymerization.

Fitting at first the azeotrope conversion–time curves from low to moderate conversion, a simultaneous search for K_3 and A indicated A as being constant with a value of 0.85 for all conditions. It was later found that this constant value satisfied the remaining non-azeotropic runs as well. K_3 was found to be independent of initiator concentration, slightly dependent on copolymer composition, but exhibited a very strong dependence on temperature. With A and K_3 fixed, a search for X_{crit2} for all conversion–time data was conducted. From X_{crit2} values V_{Fcr2} was found to be approximately 0.06 for all conditions. (This is equivalent to total monomer conversions of about 0.70 to 0.825.) Parameter values for each run are given in *Table 1*. These data are discussed below.

An initial value of C_m defined as C_{m0} was obtained from equation (18), using a value of M_w measured by l.a.l.l.s.p. at low conversions. It was found that the molecular weight data were best fit by setting C_{m0} equal to zero. This was somewhat surprising since transfer to monomer is assumed to control *MWD* in the homopolymerization of AN[11], and it was expected that chain transfer to PMS via abstraction of methyl hydrogens would be important.

Comparison of predicted and measured conversion–time curves

The fits of the experimentally measured data with model predictions are shown in *Figures 1–6* for copolymerization of PMS/AN. The model fits the data reasonably at the various temperatures, initiator concentrations and initial comonomer compositions. The main discrepancies in the model fits are for the non-azeotrope data where the conversion predictions are consistently higher than experimental values at high conversions (> 70%). In these conditions chains of widely varying composition are being produced. Such chains may not be thermodynamically compatible and microphase separation may occur. This effect could substantially modify the diffusion behaviour of both macroradicals and monomers. The model does not address such complexities and thus in a sense it is remarkable that the predictions are reasonable and should be useful for reactor calculations.

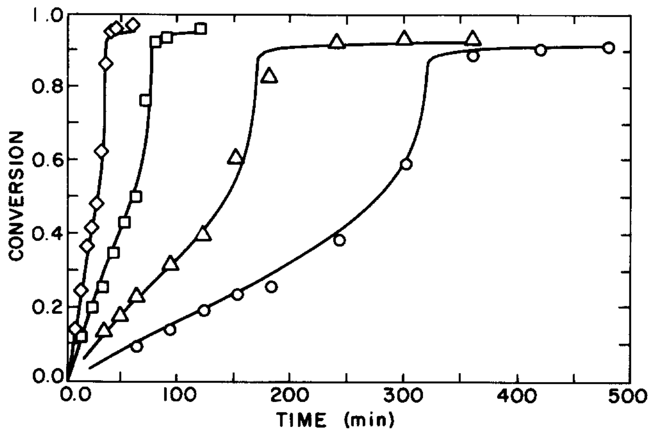

Figure 1 Measured (data points) and predicted (full curves) conversion vs. time at $f_{10} = 0.56$ (azeotrope composition): ◇, $T = 80$°C, $[I]_0 = 0.05$ M; □, $T = 80$°C, $[I]_0 = 0.01$ M; △, $T = 60$°C, $[I]_0 = 0.05$ M; ○, $T = 60$°C, $[I]_0 = 0.01$ M

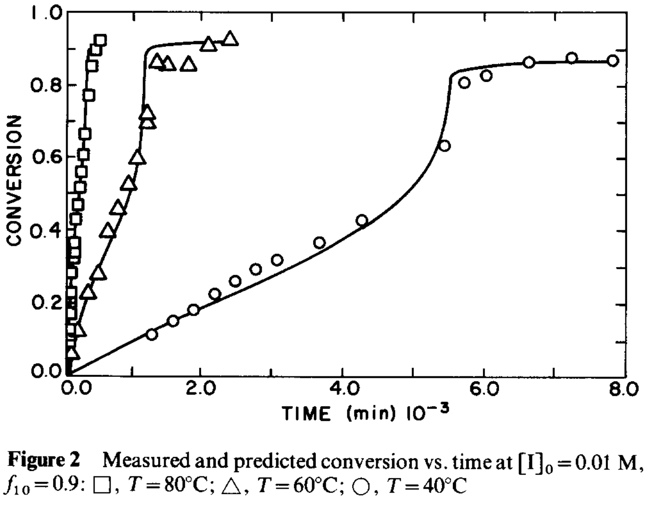

Figure 2 Measured and predicted conversion vs. time at $[I]_0 = 0.01$ M, $f_{10} = 0.9$: □, $T = 80$°C; △, $T = 60$°C; ○, $T = 40$°C

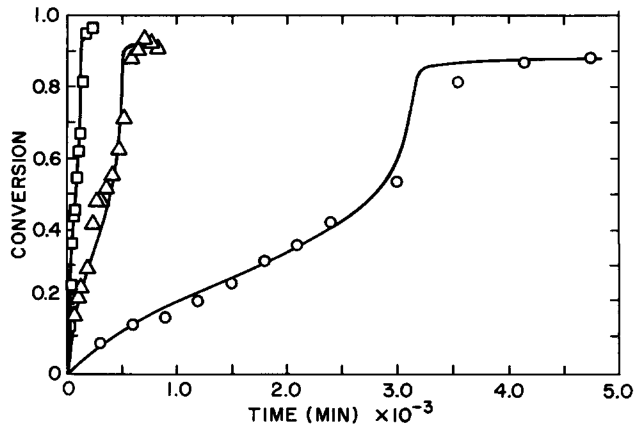

Figure 3 Measured and predicted conversion vs. time at $[I]_0 = 0.05$ M, $f_{10} = 0.9$: □, $T = 80$°C; △, $T = 60$°C; ○, $T = 40$°C

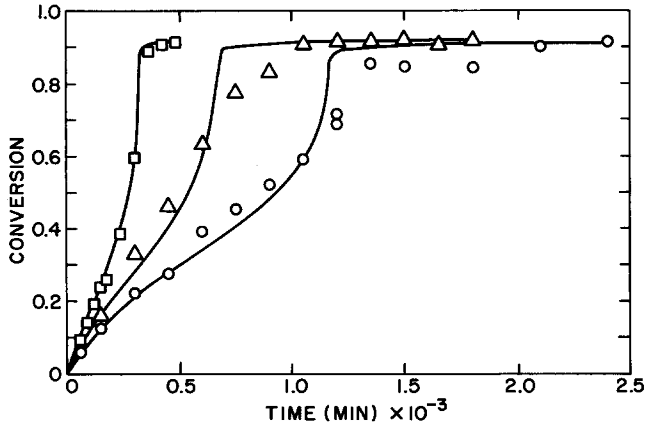

Figure 4 Measured and predicted conversion vs. time at $T = 60$°C, $[I]_0 = 0.01$ M: ○, $f_{10} = 0.9$; △, $f_{10} = 0.8$; □, $f_{10} = 0.56$

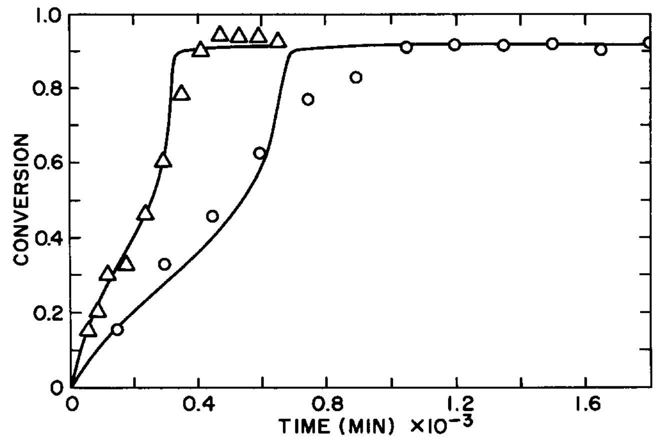

Figure 5 Measured and predicted conversion vs. time at $T = 60$°C, $f_{10} = 0.8$: △, $[I]_0 = 0.05$ M; ○, $[I]_0 = 0.01$ M

As can be seen from *Table 1* the change of $X_{\text{crit}1}$ and $\bar{M}_{\text{wcr}1}$ are as expected in every case, with translational-diffusion-controlled termination occurring at lower polymer concentrations when higher molecular weight polymer is produced. Also $X_{\text{crit}2}$ increases as the temperature increases and this is also as expected.

Composition drift

Figures 7, 8 and *9* show the measured and predicted change in residual monomer composition with conversion for temperatures of 40, 60 and 80°C, and initial initiator concentration of 0.01 M. Agreement is quite good, particularly at high conversions. These good fits suggest that the assumption that individual propagation constants have the same critical V_F for diffusion control is acceptable for modelling this system. This gives constant r_1 and r_2.

Molecular weight–conversion curves

Figures 10, 11, 12 and *13* show $\bar{M}_w$ measured by l.a.l.l.s.p. and s.e.c., $\bar{M}_n$ measured by s.e.c., and predicted values of $\bar{M}_w$ and $\bar{M}_n$ plotted *versus* conversion for the

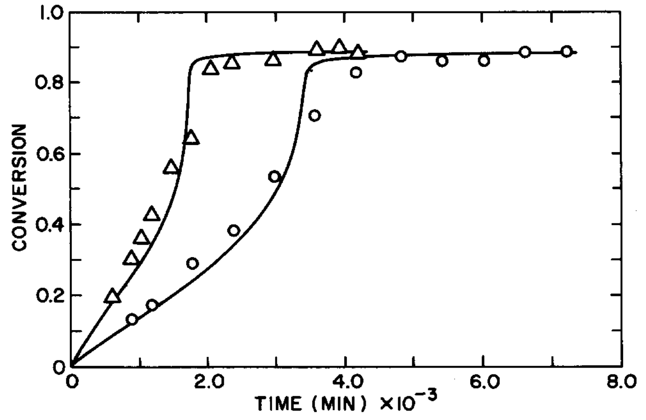

Figure 6 Measured and predicted conversion vs. time at $T = 40$°C, $f_{10} = 0.8$: △, $[I]_0 = 0.05$ M; ○, $[I]_0 = 0.01$ M

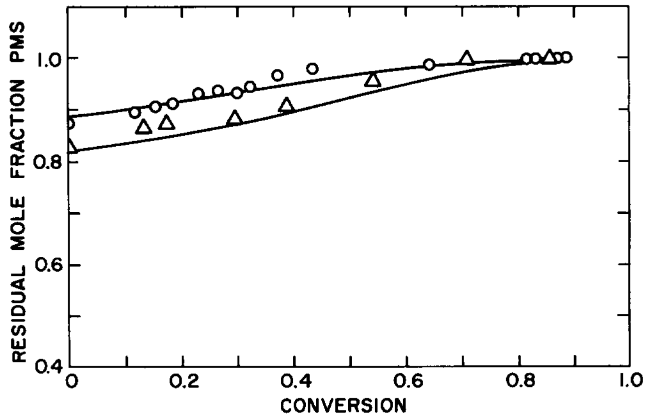

Figure 7 Measured and predicted residual PMS mole fraction vs. conversion at $T = 40$°C, $[I]_0 = 0.01$ M: ○, $f_{10} = 0.9$; △, $f_{10} = 0.8$

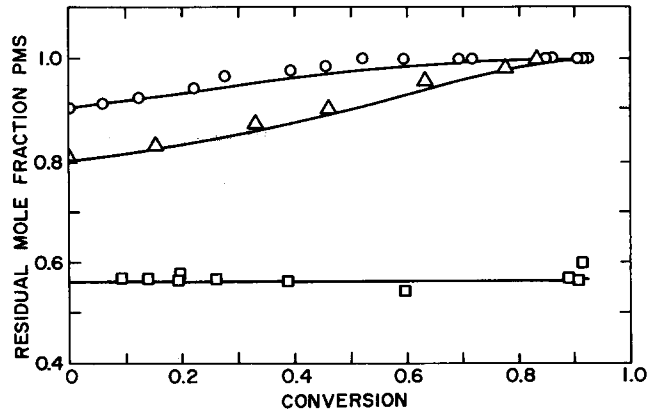

Figure 8 Measured and predicted residual PMS mole fraction vs. conversion at $T = 60$°C, $[I]_0 = 0.01$ M: ○, $f_{10} = 0.9$; △, $f_{10} = 0.8$; □, $f_{10} = 0.56$

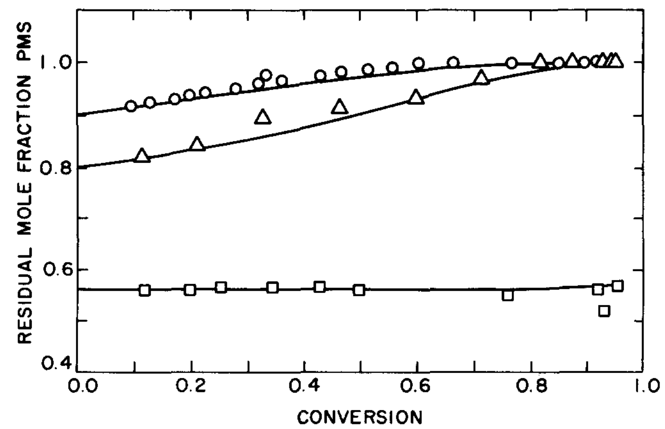

Figure 9 Measured and predicted residual PMS mole fraction vs. conversion at $T=80°C$, $[I]_0=0.01$ M: ○, $f_{10}=0.9$; △, $f_{10}=0.8$; □, $f_{10}=0.56$

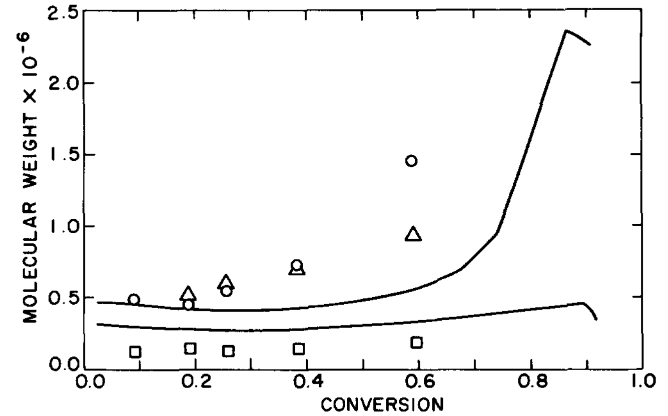

Figure 10 Measured and predicted number and weight average molecular weights at $T=60°C$, $[I]_0=0.01$ M, $f_{10}=0.56$: ○, M_w from l.a.l.l.s.p.; △, M_w from s.e.c.; □, M_n from s.e.c.

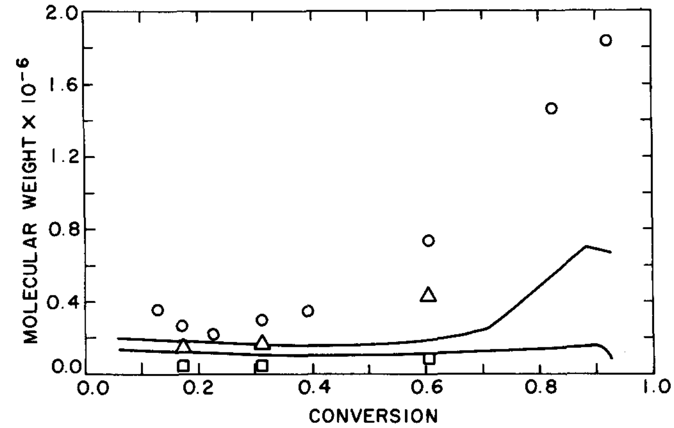

Figure 11 Measured and predicted number and weight average molecular weights at $T=60°C$, $[I]_0=0.05$ M, $f_{10}=0.56$: ○, M_w from l.a.l.l.s.p.; △, M_w from s.e.c.; □, M_n from s.e.c.

azeotrope data at temperatures of 60 and 80°C, and initiator concentrations of 0.01 and 0.05 M. The model predictions agree with measured data within experimental error at low conversions (0–50%), but underestimate $\bar{M}_w$ at higher conversions. If chain length dependence of k_t were included in the model, predictions of $\bar{M}_w$ would be better at high conversions. This approach, used by Soh and Sundberg[17], seems to predict M_w and higher molecular weight averages quite well.

Predicted termination rate constant versus *conversion*

Figure *14* is a plot of the model's prediction for k_t *versus* conversion and shows a slight initial increase followed by a dramatic decrease shortly after the onset of the gel effect and the eventual fall to approximately zero during the glassy state transition. The contribution of termination by 'reaction diffusion' is felt at conversions very near the limiting conversion.

Dependence of K_3 *on temperature and copolymer composition*

As can be seen from *Table 1* and *Figure 15* there is an Arrhenius dependence of K_3 on temperature and a significant dependence of K_3 on polymer composition.

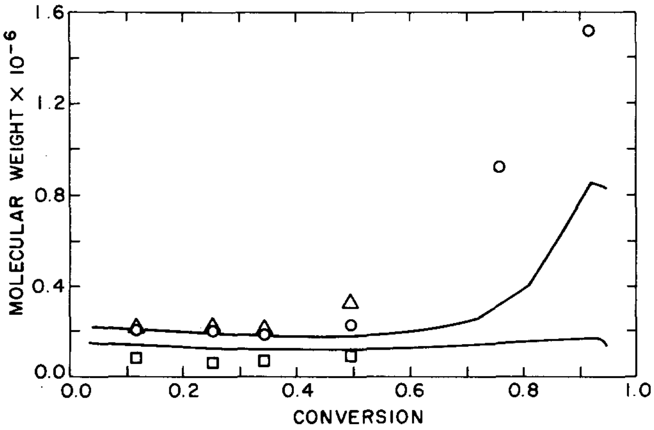

Figure 12 Measured and predicted number and weight average molecular weights at $T=80°C$, $[I]_0=0.01$ M, $f_{10}=0.56$: ○, M_w from l.a.l.l.s.p.; △, M_w from s.e.c.; □, M_n from s.e.c.

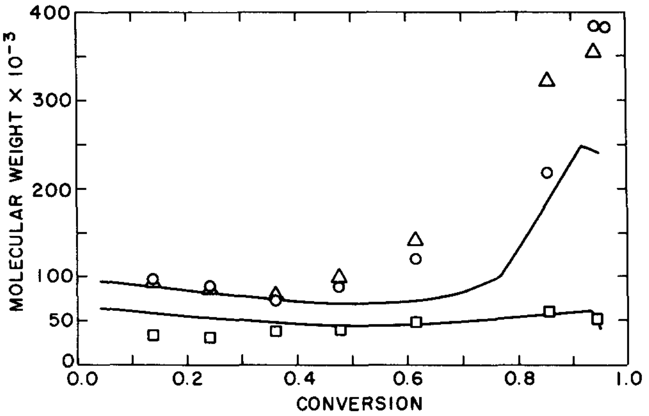

Figure 13 Measured and predicted number and weight average molecular weights at $T=80°C$, $[I]_0=0.05$ M, $f_{10}=0.56$: ○, M_w from l.a.l.l.s.p.; △, M_w from s.e.c.; □, M_n from s.e.c.

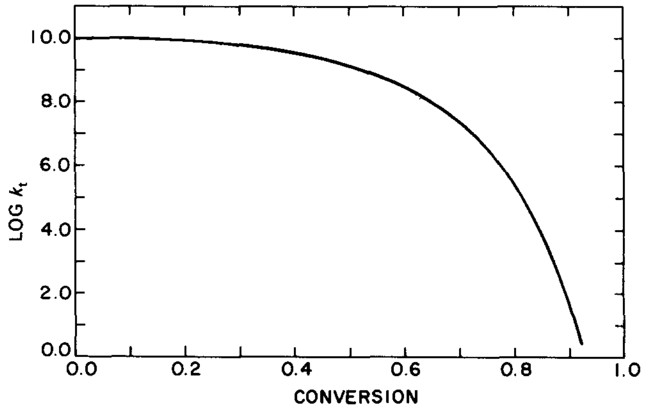

Figure 14 Predicted termination rate constant vs. conversion at $[I]_0=0.01$ M, $T=60°C$, $f_{10}=0.56$

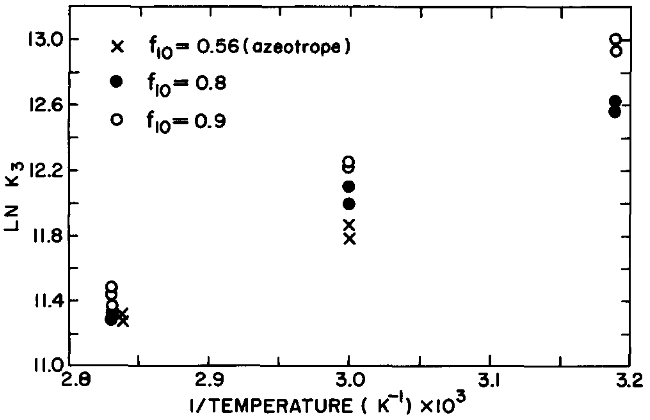

Figure 15 Arrhenius temperature dependence and copolymer composition dependence of K_3: ×, f_{10} = 0.56 (azeotrope); ●, f_{10} = 0.80; ○, f_{10} = 0.90

Both of these results are expected. The polymer coil size depends on composition, molecular weight and goodness of solvent and the effect of polymer–polymer interactions would be reduced at higher temperatures.

SUMMARY

An experimental study of the kinetics of the free-radical copolymerization of PMS/AN was made. A kinetic model which uses free-volume theory to model diffusion-controlled termination and propagation and accounts for the effect of polymer concentration on segmental diffusion at low conversions and reaction diffusion at high conversions seems to predict kinetic data ($x, f_1, \bar{M}_n, \bar{M}_w$ vs. time) reasonably for copolymerization of PMS/AN. Although $\bar{M}_w$ predictions underestimate the measured values, this model should find use in the design, optimization and control of polymer reactors for the production of PMS/AN copolymers.

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