

# Bulk copolymerization of styrene and acrylonitrile: Experimental kinetics and mathematical modelling

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The kinetics of styrene-acrylonitrile bulk copolymerization have been experimentally investigated over a wide range of conditions. The effects of temperature, and initiator and of comonomer concentrations on rate of polymerization and on copolymer properties including chain microstructure and molecular weight averages are reported. A mathematical model which uses the free volume theory to account for diffusion controlled termination and propagation reactions is developed. The model is capable of predicting the conversion, composition and sequence length development up to limiting conversions.

(Keywords: styrene-acrylonitrile; copolymerization; gel-effect; free volume theory; kinetics)

## INTRODUCTION

Despite a number of experimental investigations on the copolymerization of styrene-acrylonitrile<sup>1-3</sup> there is limited information available on its kinetics. Most research has focussed on the evaluation of reactivity ratios and initial rates of polymerization using low conversion data, although some evaluations of termination rate constants and solvent effects have been reported<sup>4,5</sup>. There have been no comprehensive studies on the kinetic modelling of styrene-acrylonitrile (SAN) throughout the entire course of polymerization and over a range of temperatures, initiator concentrations and comonomer compositions. In this paper we present the results of such an extensive experimental study on the bulk copolymerization of SAN<sup>6</sup>. We will also develop a comprehensive kinetic model capable of predicting the development of conversion, copolymer composition, and number average sequence length with time. The development and implementation of the analytical techniques required for the characterization of the SAN copolymers are described elsewhere<sup>6,8,9</sup>.

## EXPERIMENTAL

### Reagents

The initiator: 2,2' azobisisobutyronitrile (AIBN) was recrystallized twice from absolute methanol. The monomers styrene and acrylonitrile industrial grade were distilled under vacuum and stored at  $-5^{\circ}\text{C}$  until used. Tetrahydrofuran (THF) industrial grade was distilled under vacuum from cuprous chloride and stored under nitrogen. All other solvents used in the course of various analyses were used directly without further purification.

### Polymerization procedure

Polymerizations were carried out in standard 25.4 cm long glass ampoules of two different diameters: 10 mm

outer diameter and 13 mm outer diameter for the two conversion ranges, low conversions  $<30\%$  and high conversions  $>30\%$ , respectively. These two surface-to-volume ratios are sufficiently large to ensure isothermal polymerization ( $\pm 0.2^{\circ}\text{C}$ ), and to provide sufficient polymer samples for characterization.

### Design of experiments

For the selection (design) of experimental conditions, several approaches are possible, depending on the objectives of the design. In this particular case, given the scarcity of published experimental data, it was decided to run a factorial design on the variables that are known to affect primarily the molecular weight and production rate (i.e. temperature and initiator concentration) and to use a range of compositions at each of these factorial points. The experimental conditions are summarized in Table 1.

## ANALYTICAL METHODS

### Conversion and average composition

Conversions were determined gravimetrically and by gas chromatography (g.c.). The copolymer compositions were determined by several methods; analysing the copolymer by infra-red spectroscopy (i.r.) and proton nuclear magnetic resonance ( $^1\text{H}$  n.m.r.), and by a mass balance on the residual monomer composition as measured with gas chromatography. I.r. spectra were obtained on a Beckman IR-5 from films cast from 10% W/V THF or  $\text{CH}_2\text{Cl}_2$  solutions and from 0.05  $\text{g cm}^{-3}$  solutions in  $\text{CHCl}_3$ . Absorptions at the  $\text{-C}\equiv\text{N}$  stretching band at approximately  $2222\text{ cm}^{-1}$  ( $4.5\text{ }\mu\text{m}$ ) and at the band at approximately  $1610\text{ cm}^{-1}$  ( $6.3\text{ }\mu\text{m}$ ) were used to measure the copolymer composition.

### Molecular weight and sequence length

The development of techniques for molecular weight and sequence length characterization is detailed elsewhere<sup>6,8,9</sup>. A brief outline is presented here. Weight average molecular weights were obtained by viscometry

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**Table 1** Experimental conditions

	$T_1 = 40^\circ\text{C}$	$T_2 = 60^\circ\text{C}$
	$[I]_1 = 0.01 \text{ M}$ $[I]_2 = 0.05 \text{ M}$	$[I]_1 = 0.01 \text{ M}$ $[I]_2 = 0.05 \text{ M}$
Mol fraction of styrene in feed	0.1 0.2 0.3 0.4	0.5 0.6 0.7 0.8 0.9
Experimental range	Conversion < 0.2	0 < Conversion < 1

using the Mark-Houwink parameters reported by Lange and Baumann<sup>9,10</sup> and determined in our laboratories<sup>6,7</sup>. Viscosity measurements were carried out using Cannon Ubbelohde viscometers (capillary diameters of 0.26 and 0.305 mm). The solvents used were DMF at  $20^\circ\text{C}$  and THF at  $25^\circ\text{C}$ . The intrinsic viscosities were estimated from Huggin's equation.

Molecular weight distributions for selected samples were determined by size exclusion chromatography (s.e.c.), based on the universal calibration procedure. Measurements were done at room temperature with THF as the mobile phase. The column combination used was a set of five 1.22 m Stryagel columns ( $10^6$ ,  $10^5$ ,  $10^4$ ,  $10^3$ ,  $500 \text{ \AA}$ ) from Waters Scientific. A u.v. detector and a differential refractometer were used to determine copolymer composition as a function of molecular size. Axial dispersion corrections and molecular weight calculations are described in refs. 6 and 8.

Sequence lengths were obtained using a high resolution Fourier transform proton n.m.r.<sup>6</sup> The assignment of the resonance bands was verified using  $^{13}\text{C}$  n.m.r. and by comparison with those assignments reported by Shaefer<sup>11</sup> and Pichot and Pahn<sup>5</sup>.

## RESULTS

### Reproducibility

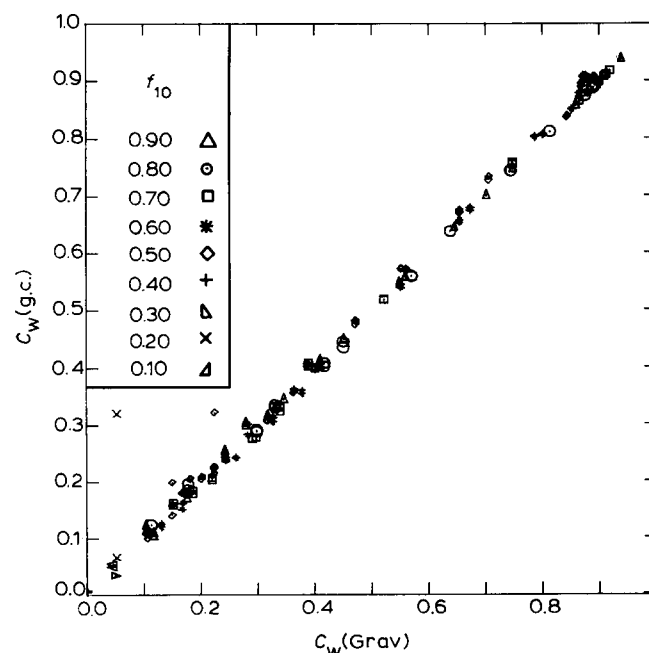
The reproducibility and consistency of the experimental results were verified by replication and by the determination of the same polymer property using a variety of techniques<sup>6</sup>. Reproducibility of the conversion histories accounts for two kinds of errors: measurement errors and sampling errors. The uncertainties related to the preparation of reactants were minimized by preparing sufficiently large quantities so that weighing errors were negligible. The initial monomer compositions were verified by g.c. prior to filling of the ampoules. Figure 1 shows the agreement between conversions obtained gravimetrically and by g.c. The reproducibility of conversion measurement was, in general, better than 2%, although errors of about 2% were possible during extreme gel effect conditions (i.e. high polymerization rates).

The reproducibility of composition data (mole%) was verified routinely as part of the conversion replication measurements. The standard deviation for residual monomer fraction analysis on the same sample was, in general, smaller than 1%. The i.r. and n.m.r. replications indicate errors of up to 5% depending on the concentration of acrylonitrile and the purity of the polymer samples. The error associated with the intrinsic viscosity measurements is of the order of  $\pm 0.5\%$  which translates into  $\pm 3.0\%$  for the weight average molecular weights, assuming that the Mark-Houwink parameters are correct.

The reproducibility of size exclusion chromatograms was tested in the usual way by measuring the standard deviation of the normalized heights for replicate injections<sup>12</sup>. Reproducibility was observed to be excellent at the central portions of the chromatograms and to deteriorate towards the tails, particularly the low molecular weight tail. The reproducibility of the molecular weight averages depends, of course, on the significance of the tails in the calculations of the respective moments. For the samples investigated, the reproducibility of the number and weight average molecular weight was between 5 and 10% for the same sample.

### Conversion and composition histories

The bulk copolymerization of styrene-acrylonitrile is a homogeneous process throughout most of the conversion range for styrene-rich copolymers ( $f_{10} \geq 0.5$ ) and for low conversion acrylonitrile-rich copolymers ( $0.5 \geq f_{10} \geq 0.10$ ). The polymerization is initiated readily by light, by azo and peroxy compounds, or, in general, by any source of free radicals. Therefore, care must be taken to avoid prolonged exposure to light, particularly once the ampoules have been degassed. Once initiated, the polymerization proceeds rapidly through what is believed to be mainly a cross-propagation reaction. As the viscosity of the mixture increases, regions of hard and soft polymer in the ampoules become evident. These regions are clearly distinguishable towards the end of the reaction. If the fraction of acrylonitrile is increased ( $f_{10} < 0.5$ ), then the hard transparent regions turn into a white solid very much like polyacrylonitrile indicating, therefore, that these regions are due to the heterogeneity of at least the composition distribution and also due to the poor distribution of monomer in the reacting mixture arising from the lack of mixing within the ampoules. The copolymers and the data obtained from the ampoule experiments are probably more representative of a suspension polymerization than of a well-mixed bulk polymerization process. The dissolution of the reacting mixture in DMF and the subsequent precipitation in me-



**Figure 1** Comparison of conversion histories obtained gravimetrically and by gas chromatography for several feed compositions

thanol homogenized the polymer samples. It was often observed, however, that the different regions in the ampoule appeared to have different solubility characteristics. An analysis of the polymer obtained in different regions of the ampoule was not carried out. A more detailed investigation of this heterogeneity might provide information on the effect of a homogeneous or a segregated environment on the copolymer properties.

The conversion and composition results for each of the runs of the experimental design (Table 1), obtained by g.c. and gravimetric measurements, are shown in Figures 2–5. (The actual data is reported in ref. 6. It is available either on an IBM compatible diskette or on a 9-track magnetic tape by writing to the first author.) The conversion histories follow the sigmoidal shape typical of bulk vinyl polymerizations with the reaction rate increasing from low to high acrylonitrile content in the monomer feed. The extent of the gel effect varies as a function of the temperature and the styrene and initiator concentrations. The limiting conversion appears to be a function of the initial monomer composition as well as a function of the polymerization temperature. The experimental error, unfortunately, does not allow a good estimation of the limiting conversion. The curves shown in the Figure are predictions given by the mathematical model of the polymerization process developed in the following sections of this paper. The initial polymerization rate (see Figure 6) does show a non-linear behaviour with respect to the initial

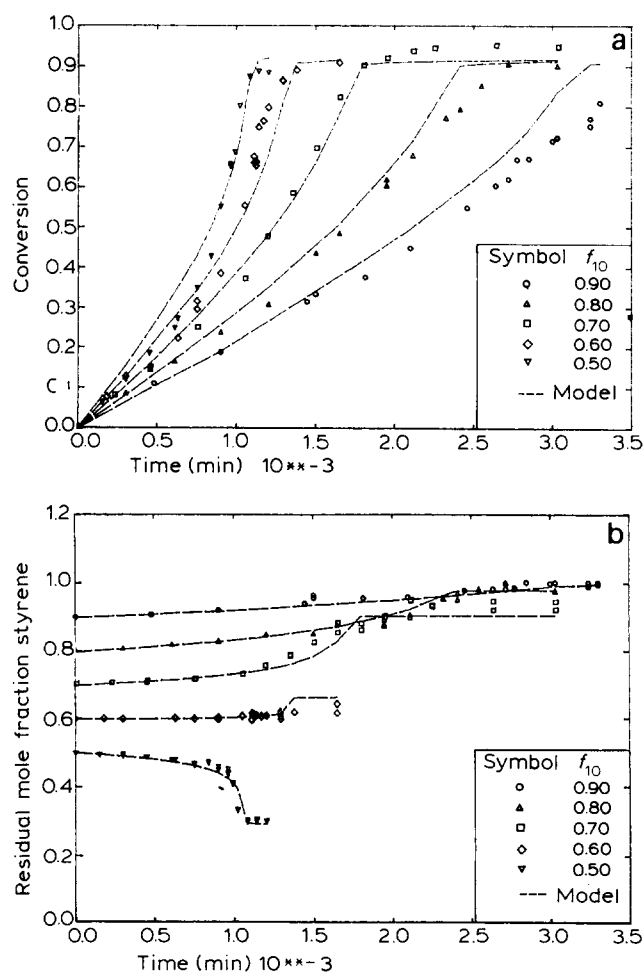


Figure 2 Conversion and composition histories for SAN copolymerizations at 40°C and  $[I]_0 = 0.05$  M AIBN

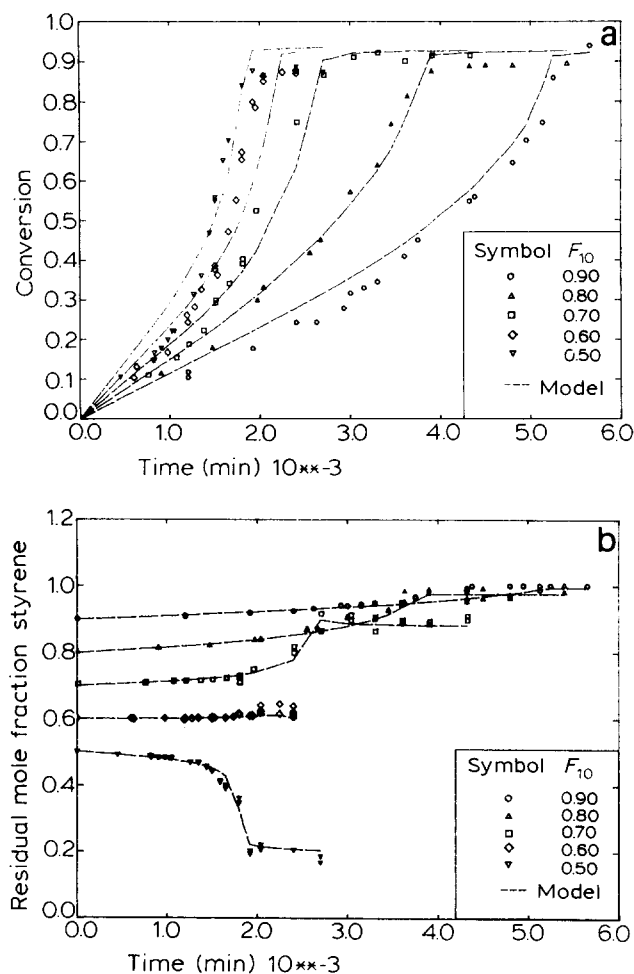


Figure 3 Conversion and composition histories for SAN copolymerizations at 40°C and  $[I]_0 = 0.01$  M AIBN

monomer composition. The data obtained is consistent with previous experimental data of Blanks and Shah<sup>13</sup>. Clearly, the initiation step in styrene–acrylonitrile copolymerization with AIBN appears to be more complex than initially anticipated. The initial polymerization rate rises rapidly with increasing acrylonitrile content up to approximately 30% to 40% styrene in the feed, after which it declines rapidly.

The composition histories do not show any of the features observed by Dionisio and O'Driscoll<sup>14</sup> for styrene–methylmethacrylate copolymers. The scatter observed in the data can be attributed, in most cases, to errors either in the feed or in the estimation of the copolymer composition.

#### Molecular weight

Figures 7 and 8 show the dependence of the molecular weight averages on temperature, initial concentration and initial monomer composition. The molecular weight development is analogous to that of polystyrene at similar polymerization conditions. The weight average molecular weight increases rapidly with conversion and acrylonitrile content. The number average molecular weight, on the other hand, is relatively independent of monomer composition and increases at a slower rate, thereby increasing the breadth of the molecular weight distribution. The zero conversion polydispersity also increases as a function of the initial monomer composition from a value of approximately 1.67 at  $f_{10} = 0.9$  to approximately 1.83 at

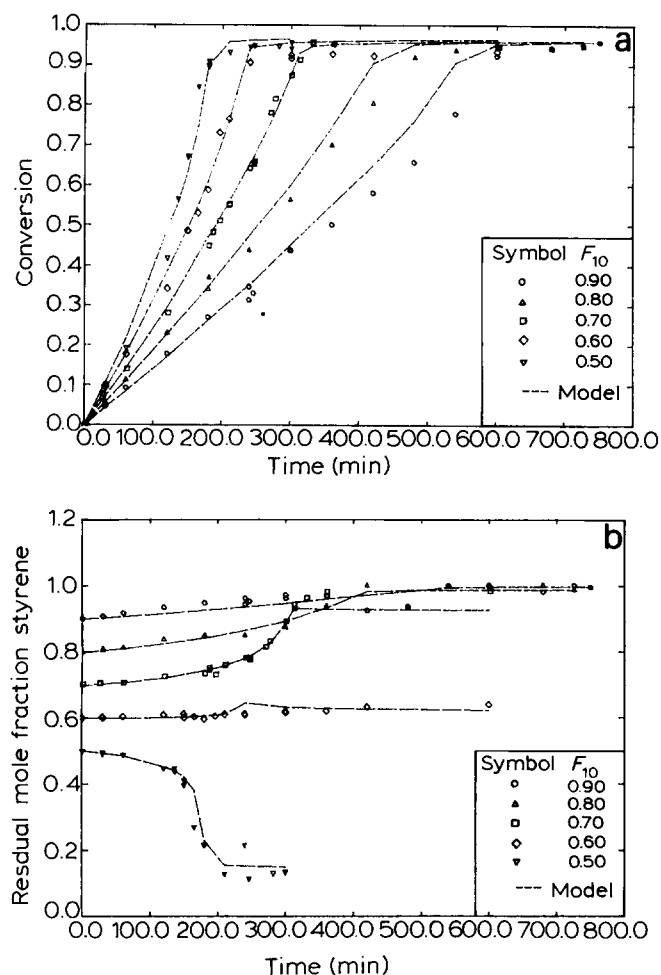


Figure 4 Conversion and composition histories for SAN copolymerizations at 60°C and  $[I]_0 = 0.05$  M AIBN

$f_{10} = 0.5$ . This is an intermediate behaviour between the polydispersity observed for bulk styrene ( $M_w/M_n \approx 1.5$ ) and acrylonitrile ( $M_w/M_n \approx 2.1$ ) polymerizations. Since the molecular weight controlling mechanisms (in the temperature range 40–80°C) are termination by combination for styrene<sup>15</sup> and transfer to monomer for acrylonitrile<sup>6</sup> bulk polymerization, this behaviour is expected. The rapid increase in the weight average molecular weight can be related to the significant increase in the gel effect in the presence of acrylonitrile<sup>16</sup>.

The molecular weight distribution for the copolymers cannot be readily estimated<sup>5,8</sup>. The molecular weight, copolymer composition, and sequence length distribution form a three-dimensional joint distribution for which, to date, there are no analytical techniques available to measure it. Only some averages, calculated as functions of the molecular size, can be obtained from the g.p.c. measurements. Therefore, variations in the number average molecular weight ( $M_n$ ), the average copolymer composition, and the average styrene sequence length as functions of the molecular size (retention volume) and the corresponding normalized mass concentration detector response (weight fraction) have been reported in refs. 6 and 8.

The autoacceleration behaviour of the reaction rate apparent in Figures 2–5 is a consequence of diffusion controlled termination reactions and is dependent upon the molecular weight and composition of the macro-

radicals and accumulated copolymer. Figures 9 and 10 compare the copolymerization histories at two different initiator concentrations at the same initial compositions and the same polymerization temperatures. Although the curves tend to superimpose at low conversions indicating that classical chemical kinetics hold in this region, they do not superimpose at higher conversions. The smaller the initiator concentration, the larger the molecular weight of the macroradicals and the accumulated copolymer and the stronger the gel effect and, therefore, the larger the deviation from classical kinetics.

## ESTIMATION OF REACTIVITY RATIOS

As a first step in the modelling of SAN bulk copolymerization, the integral form of the selectivity equation was used to estimate the reactivity ratios using the 'error in variables' method as approximated by Sutton and MacGregor<sup>17</sup> (see Appendix 1).

The reactivity ratios were estimated in three conversion regions:  $0 < c_w < 0.30$ ;  $0.30 \leq c_w < 0.60$  and  $0.60 \leq c_w$  at each temperature and initiator concentration. Figures 11 and 12 show the 95% confidence regions for the reactivity ratios as functions of conversion and initiator concentration for the two temperature levels investigated (60°C and 40°C). The confidence regions for the parameters overlap significantly, indicating that, based on these data, the reactivity ratios do not appear to be

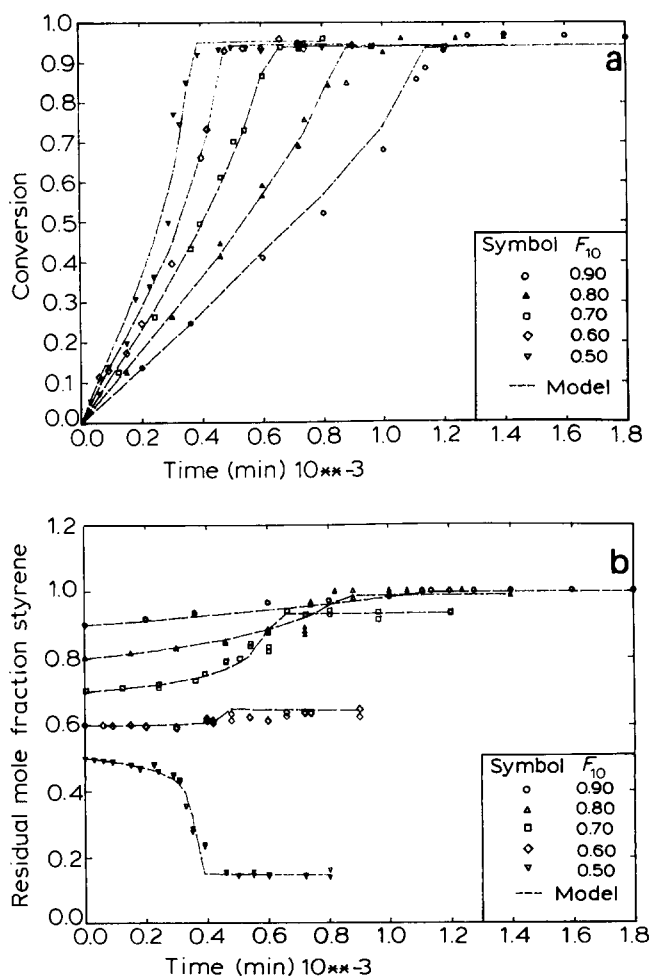


Figure 5 Conversion and composition histories for SAN copolymerizations at 60°C and  $[I]_0 = 0.01$  M AIBN

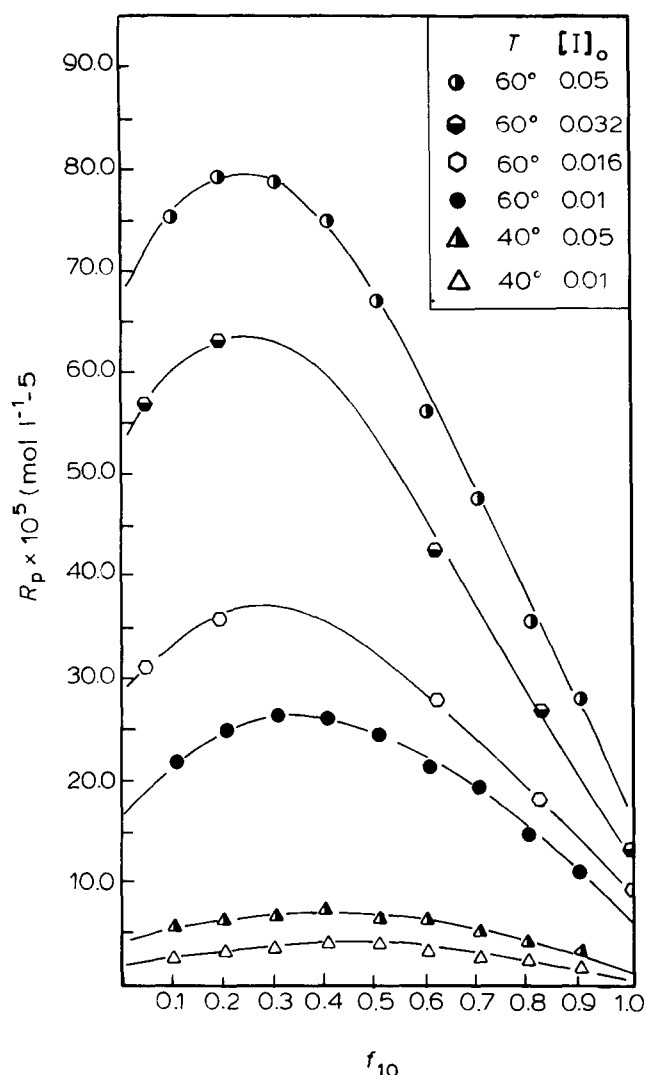


Figure 6 Initial polymerization rates of styrene acrylonitrile bulk polymerization as function of the monomer feed composition

significantly dependent upon conversion or temperature. A broader temperature range would be required in order to be able to identify any functional dependence of the reactivity ratios on the polymerization temperature. Note that the confidence regions stretch considerably along the  $r_2$  axis (acrylonitrile). This can be attributed to the insensitivity of the parameter  $r_2$  in the composition region investigated. The statistical designs suggested by Behnken<sup>18</sup> and Tidwell and Mortimer<sup>19</sup> indicate that very low styrene compositions are required ( $f_{10} \approx 0.03$ ) in order to obtain good estimates of  $r_2$ . However, since rich acrylonitrile copolymers were beyond the scope of this investigation, an improvement in the estimates of  $r_2$  was not pursued. The confidence regions obtained for the parameters  $r_1$  and  $r_2$  are, nevertheless, sufficient to allow the conclusions that the integral form of the copolymerization equation adequately represents SAN copolymerizations at low conversions for all initial compositions and over the entire conversion histories for  $0.5 \leq f_{10} < 1$ .

#### DIFFUSION CONTROLLED POLYMERIZATIONS

As shown in Figures 2–5, the free radical copolymerization of SAN exhibits an autoacceleration in the reaction rate and a limiting conversion of less than 1.0. The

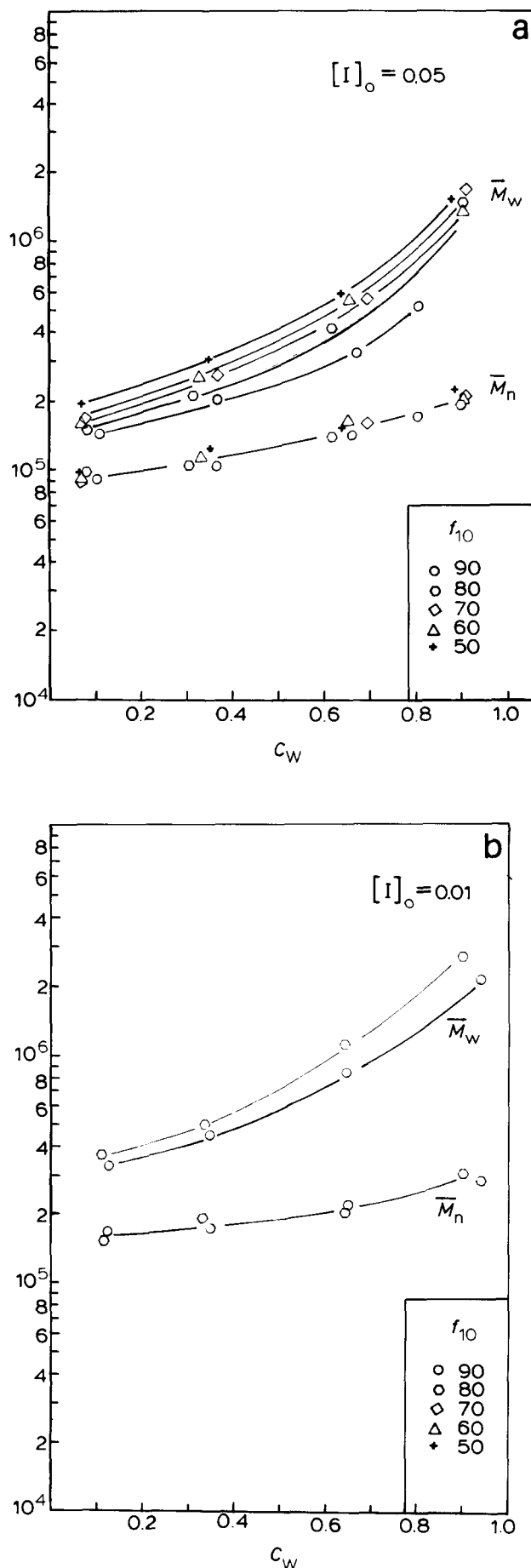


Figure 7 Molecular weight averages as a function of styrene mole fraction in the feed ( $f_{10}$ ) and gravimetric conversion ( $c_w$ ) for SAN copolymers (40°C)

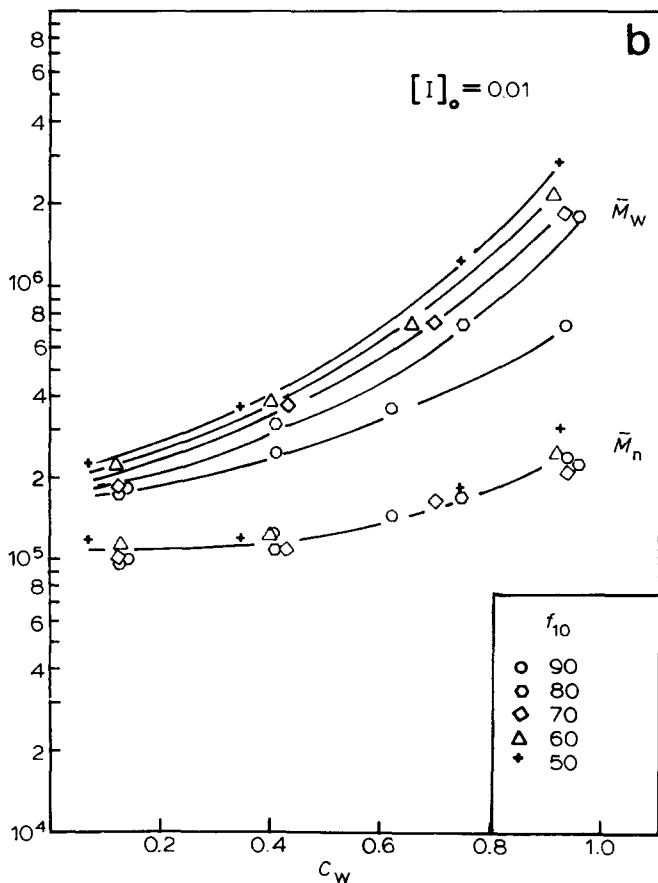
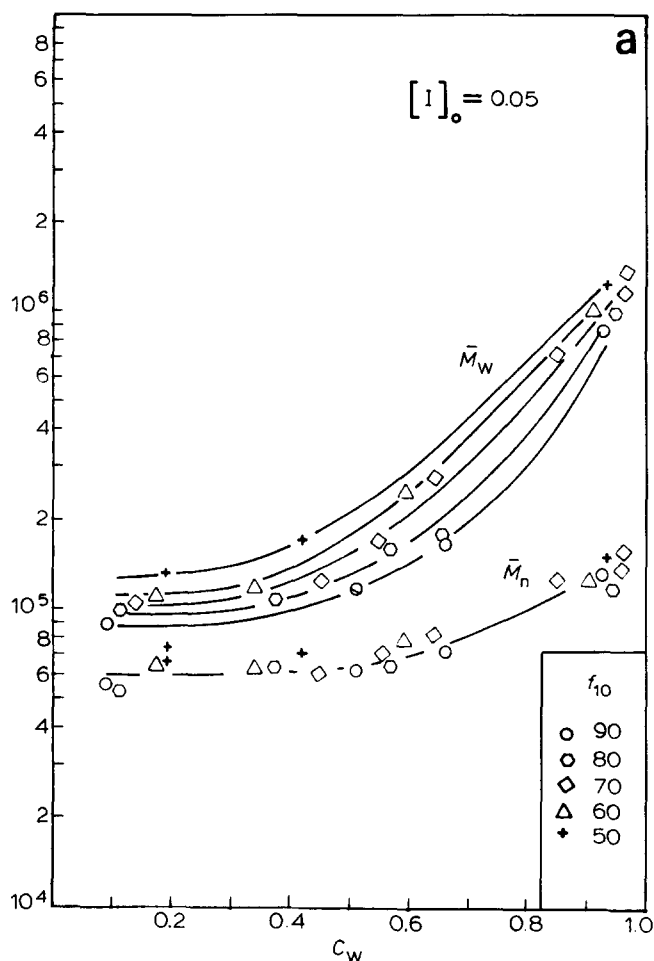


Figure 8 Molecular weight averages as a function of styrene mole fraction in the feed ( $f_{10}$ ) and gravimetric conversion ( $c_w$ ) for SAN copolymers (60°C)

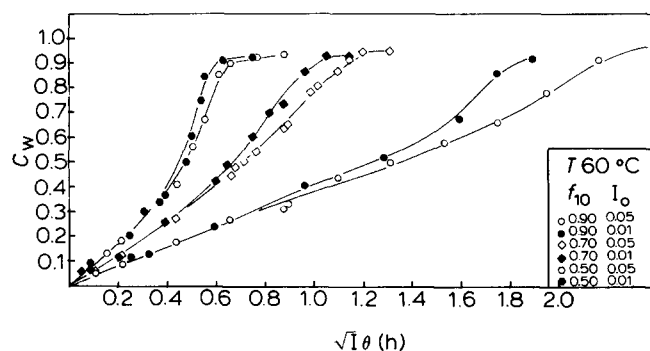


Figure 9 Conversion histories of SAN copolymers (60°C) plotted against the product of the square root of the molar initiator concentration  $[I]_0$  and polymerization time  $\theta$  (h)

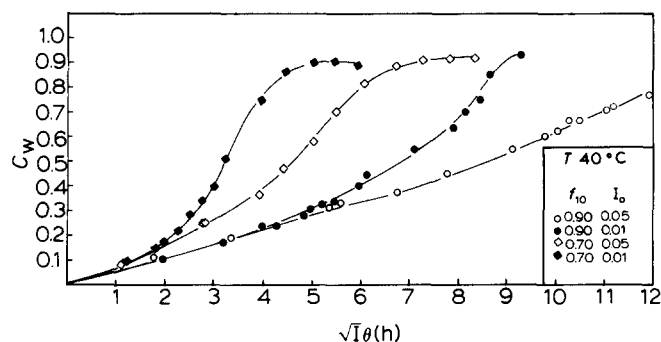


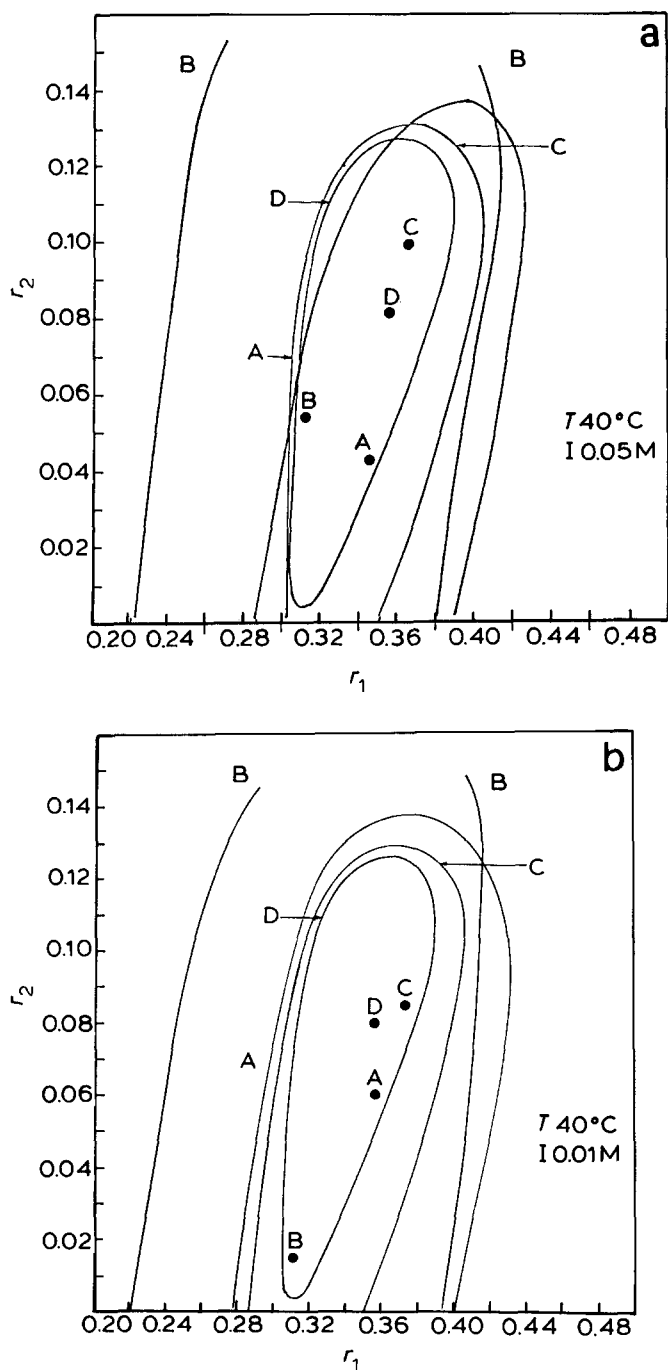
Figure 10 Conversion of SAN copolymer (40°C) plotted against the product of the square root of the molar initiator concentration  $[I]_0$  and polymerization time  $\theta$  (h)

autoacceleration in the rate is usually referred to as the 'gel' or 'Trommsdorff' effect, and is associated with the onset of chain entanglements and diffusion controlled termination at higher conversions. Several recent papers<sup>20-22</sup> have reviewed the influence of the gel effect on homopolymerization rates and on the resulting polymer properties. A limiting conversion less than 1.0 indicates that the rate of polymerization falls to zero prior to depletion of all the monomer. This effect is observed when polymerizations are done at temperatures below the glass transition temperature of the polymer ( $T_{gp}$ ), and is associated with diffusion controlled propagation reactions.

#### Diffusion controlled termination reactions

Termination reactions involving high molecular weight macroradicals can become diffusion controlled at relatively low conversion levels. Attempts at modelling the apparent decrease in the termination rate constant have included strictly empirical models<sup>23,24</sup>, semi-empirical models which include a chain-length dependence<sup>25,26</sup>, semi-theoretical models based on the free volume theory<sup>27-29</sup> and more fundamental models based on the reptation theory<sup>21,22</sup>. In this paper, we use an extension of the free volume homopolymerization model of Marten and Hamielec<sup>27,28</sup> to model the diffusion controlled reactions in SAN copolymerization.

Although one might expect that three termination rate constants ( $k_{11}$ ,  $k_{12}$ ,  $k_{22}$ ) would be required in modelling copolymerizations, a single termination rate constant ( $k_t$ ) is usually adequate after the onset of diffusion control, since then the termination rate is dependent upon the diffusion rate of the growing macroradicals in the reaction



**Figure 11** 95% confidence regions for the reactivity ratios obtained using data in different conversion regions: (a)  $0 < c_w < 30$ ; (b)  $30 < c_w < 60$ ; (c)  $60 < c_w < 100$ ; (d)  $0 < c_w < 100$  ( $60^\circ\text{C}$ )

mixture. This diffusion rate should be independent of the ultimate monomer unit on the radical chain.

Using Bueche's<sup>30</sup> work on relating diffusion coefficients of macromolecules to the free volume fraction in the solution, Marten and Hamielec<sup>27,28</sup> showed that in the diffusion controlled region, the termination rate constant could be modelled as

$$k_t = k_{t0} \left( \frac{\bar{M}_{wCr}}{\bar{M}_w} \right)^n \exp \left\{ -A \left( \frac{1}{V_F} - \frac{1}{V_{FCr}} \right) \right\} \quad (1)$$

where:

$V_{FCr}$  = critical free volume fraction of the solution at the onset of diffusion control;

$\bar{M}_{wCr}$  = cumulative weight average molecular weight of the copolymer at  $V_{FCr}$ ;

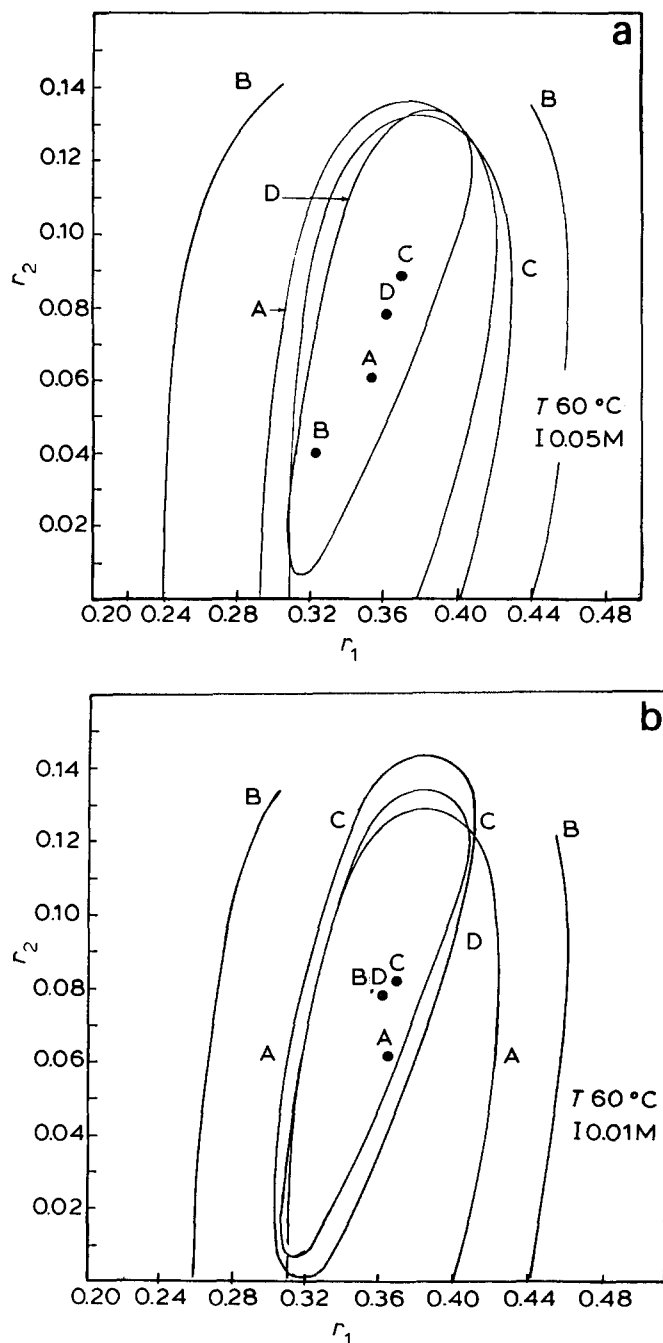
$\bar{M}_w$  = cumulative weight average molecular weight at free volume  $V_F (> V_{FCr})$  corresponding to conversions above the onset of diffusion control

$A$  = a parameter which determines the rate at which  $k_t$  falls off with decreasing free volume.

and the free volume fraction of the mixture is given as the weighted sum

$$V_F = (0.025 + \alpha_p(T - T_{gp}))\phi_p + (0.025 + \alpha_1(T - T_{g1}))\phi_1 + (0.025 + \alpha_2(T - T_{g2}))\phi_2 \quad (2)$$

Here,  $\alpha_1$  is the difference in the thermal expansion coefficient above and below the glass transition tempera-



**Figure 12** 95% confidence regions for the reactivity ratios obtained using data in different conversion regions: (a)  $0 < c_w < 30$ ; (b)  $30 < c_w < 60$ ; (c)  $60 < c_w < 100$ ; (d)  $0 < c_w < 100$  ( $40^\circ\text{C}$ )

ture  $T_g$  (subscripts p, 1 and 2 stand for polymer, monomer 1 and monomer 2), and  $\phi_i$  is the volume fraction of the particular component in the solution.

The exponent  $n$  determines the extent of the dependence of  $k_t$  on the molecular weight of the polymer. Theory predicts a wide range of possible values for this exponent<sup>21,22</sup>.

#### Diffusion controlled propagation reactions

When polymerizing below the glass transition temperature of the polymer being formed, the reaction mixture eventually undergoes a transition to the glassy state at some high conversion (the limiting conversion). On approaching this conversion, even the propagation reactions involving the small monomer molecules will become diffusion controlled. In this diffusion controlled region, the four propagation rate constants can be modelled using the free volume theory by

$$k_{ij} = k_{ij0} \exp \left\{ -B \left( \frac{1}{V_F} - \frac{1}{V_{FCr ij}} \right) \right\} \quad (3)$$

where the  $k_{ij0}$ s are the chemically controlled propagation rate constants,  $B$  is a parameter which determines the rate at which the  $k_{ij}$  fall off with decreasing free volume, and the  $V_{FCr ij}$ s are the critical free volume fractions at the onset of diffusion controlled propagation for the  $i$ th radical type and the  $j$ th monomer type (1 or 2).

It is assumed that the onset of diffusion control will occur earlier for the propagation reaction which is chemically more reactive, when considering the same monomer. In the copolymerization of styrene and acrylonitrile, the propagation reaction involving an acrylonitrile radical and a styrene monomer molecule is the fastest, followed by the reaction between an acrylonitrile radical and an acrylonitrile monomer molecule. Let the critical free volume fractions for these two reactions be denoted by  $V_{Cr21}$  and  $V_{Cr22}$  (1 = styrene; 2 = acrylonitrile). Under diffusion controlled propagation one would expect that

$$k_{22} = k_{12} \quad (\text{acrylonitrile diffusing}) \quad (4)$$

and

$$k_{11} = k_{21} \quad (\text{styrene diffusing}) \quad (5)$$

since the propagation rates should then depend only upon the diffusion coefficients of the monomers (1 or 2) and no longer upon the radical type. (This implies that the product of the reactivity ratios  $r_1 r_2$  should tend towards unity as one approaches limiting conversions. However, this will occur rapidly near the very end of the reaction ( $0.85 < c_w < 0.95$ ), and although it may strongly influence the instantaneous copolymer composition at the end, it will have a much less noticeable effect on the cumulative copolymer composition. This might explain why the reactivity ratios estimated from the higher conversion data ( $0.60 \leq c_w$ ) in section 5 did not reveal any significant change from those estimated from the lower conversion data.) The critical free volumes  $V_{FCr12}$  and  $V_{FCr11}$  can then be obtained in terms of  $V_{FCr21}$  and  $V_{FCr22}$  by substituting the free volume expression in equation (3) for the appropriate  $k_{ij}$  in equations (4) and (5) to yield

$$V_{FCr12} = B / [ (B/V_{FCr22}) + \ln(k_{220}/k_{120}) ] \quad (6)$$

and a similar expression for  $V_{FCr11}$ .

#### REACTOR MODEL

In this section, we will develop the equations necessary to model the dynamic behaviour of SAN copolymerization in batch, semi-batch or continuously stirred tank reactor systems.

#### Rate expressions

Expressions for the rates of polymerization of monomers 1 and 2 can be derived based on the following assumptions:

- (i) only ultimate group effects are important,
- (ii) the steady-state hypothesis for radical species is valid,
- (iii) all monomer consumed in reactions other than propagation is negligible,
- (iv) for long chains, the number of times a monomer 1 unit follows a monomer 2 unit is equal to the number of times a monomer 2 unit follows a monomer 1 unit (long chain approximation).

Using these commonly employed assumptions, the following rate expressions can be obtained for each monomer.

$$R_1 = \left( \frac{R_i}{k_t} \right)^{1/2} \left( \frac{k_{11} k_{22} (r_1 [M_1]^2 + [M_1][M_2])}{k_{11} r_2 [M_2] + k_{22} r_1 [M_1]} \right) \quad (7)$$

$$R_2 = \left( \frac{R_i}{k_t} \right)^{1/2} \left( \frac{k_{11} k_{22} ([M_1][M_2] + r_2 [M_2]^2)}{k_{11} r_2 [M_2] + k_{22} r_1 [M_1]} \right) \quad (8)$$

where

$[M_i]$  is the molar concentration of monomer  $i$  (1 = styrene; 2 = acrylonitrile)

$r_1 = k_{11}/k_{12}$  and  $r_2 = k_{22}/k_{21}$  are the reactivity ratios

$R_i$  = rate of initiation =  $2f k_d [I]$

$[I]$  = initiator concentration

$R_p = R_1 + R_2$  is the total polymerization rate

$k_d$  = dissociation constant for the initiator

$f$  = initiator efficiency

The propagation and termination rate parameters ( $k_{ij}$  and  $k_t$ ) in these expressions will change with time when diffusion control is present. The free volume models (equations (1) and (3)) in the previous section are used to predict this behaviour. These rate expressions in turn appear in the material balances to follow.

#### Material balances

For bulk polymerization, material balances are necessary for the monomers, initiator and polymer in the reactor. These are given below in general form.

Monomer balances:

$$\frac{dN_1}{dt} = F_{1,in} - \frac{N_1}{V} \cdot v_{out} - R_1 \cdot V \quad (10)$$

$$\frac{dN_2}{dt} = F_{2,in} - \frac{N_2}{V} \cdot v_{out} - R_2 \cdot V \quad (11)$$



$N_1, N_2$  = moles of monomers  $M_1$  and  $M_2$  in the reactor  
 $F_{1,in}, F_{2,in}$  = molar flow of monomers into the reactor  
 (mol s<sup>-1</sup>)  
 $V$  = reacting volume in the reactor (l)  
 $v_{out}$  = volumetric flow out of the reactor (l s<sup>-1</sup>)  
 $R_1, R_2$  = net rate of disappearance of monomer by  
 reaction (mol s<sup>-1</sup> l<sup>-1</sup>)

### Reaction volume

Since there is usually a change in density as the monomers are converted to polymers, the reaction volume ( $V$ ) of a batch reactor will shrink, and in a continuous flow reactor, the volumetric outflow ( $v_{out}$ ) will not equal the volumetric inflow. These changes in reaction volume can be accounted for by the equation

$$\begin{aligned} \frac{dV}{dt} &= v_{in} - \text{shrinkage} - v_{out} \\ &= (F_{1,in} \cdot MW_1 / \rho_1 + F_{2,in} \cdot MW_2 / \rho_2) \\ &\quad - \left[ R_1 \cdot MW_1 \left( \frac{1}{\rho_1} - \frac{1}{\rho_p} \right) + R_2 \cdot MW_2 \left( \frac{1}{\rho_2} - \frac{1}{\rho_p} \right) \right] V - v_{out} \end{aligned} \quad (12)$$

where  $MW_1, MW_2$  are the molecular weights of the monomers and  $\rho_1, \rho_2, \rho_p$  are the densities of the monomers and polymer.

In a batch or semi-batch reactor  $v_{out} = 0$ , and equation (3) provides an expression for the changing reaction volume. In a CSTR (continuous-flow stirred tank reactor), the reaction volume is constant ( $dV/dt = 0$ ) and equation (3) provides an expression for  $v_{out}$ .

### Polymer balances

In a batch reactor where there is no inflow or outflow of polymer from the reactor, the total amount of polymer formed and its composition can be obtained from the monomer material balances directly by considering the net change in moles of monomers 1 and 2. However, in a semi-batch or continuous flow reactor with inflow and outflow of polymer and monomer, additional balances are needed for the moles of monomers 1 and 2 in the reactor that are bound as polymer, i.e.

$$\frac{dP_1}{dt} = F_{p1,in} - \frac{P_1}{V} \cdot v_{out} + R_1 \cdot V \quad (13)$$

$$\frac{dP_2}{dt} = F_{p2,in} - \frac{P_2}{V} \cdot v_{out} + R_2 \cdot V \quad (14)$$

where  $P_1, P_2$  are the moles of monomers 1 and 2 bound as polymer and  $F_{p1,in}, F_{p2,in}$  are the molar inflows of monomers 1 and 2 that are bound as polymer.

### Initiator balance

In order to calculate the rates of polymerization and the molecular weight development, a balance is also needed for the initiator.

$$\frac{dN_1}{dt} = F_{1,in} - \frac{N_1}{V} \cdot v_{out} - R_1 \cdot V \quad (15)$$

### Calculated quantities

From these balances, a number of variables of interest can be calculated directly. For example, the total molar conversion of monomers to polymer can be calculated by

$$X = \frac{P_1 + P_2}{N_1 + N_2 + P_1 + P_2} \quad (16)$$

and the accumulated copolymer composition as mole fraction of monomer 1 can be calculated by

$$F_1 = \frac{P_1}{P_1 + P_2} \quad (17)$$

The differential mass balance equations presented in this section are valid for the general case of an unsteady-state CSTR. For a CSTR operating a steady-state, the accumulation derivative terms can be set equal to zero to give a set of algebraic equations. For a semi-batch reactor, the outflow terms should be eliminated, and for a strictly batch reactor, all inflow and outflow terms should be eliminated. However, it is usually advantageous to consider complete equations since one has the flexibility of handling all these reactor situations with a single model.

### Copolymer sequence length modelling

Sequence length distribution of a copolymer can be a very important property of a copolymer, particularly when the properties of the individual homopolymers are very different (e.g. SAN). In batch reactors where considerable composition drift can occur throughout the batch, the instantaneous number average sequence length can change dramatically, especially towards the end of the batch. This drift will show up less markedly in the cumulative number average sequence lengths.

Assuming that penultimate effects are not important, a probabilistic approach can be used to derive expressions for the sequence length distribution. Following Ray and Laurence<sup>31</sup>, the fraction of all styrene sequences which have length  $n$  at any instant is given by

$$S_n = \frac{\alpha^{n-1}}{(1+\alpha)^n} \quad (18)$$

where  $\alpha = r_1 f_1 / (1 - f_1)$ . Similarly for the acrylonitrile sequences

$$A_n = \frac{\beta^{n-1}}{(1+\beta)^n} \quad (19)$$

where  $\beta = r_2 f_2 / (1 - f_2)$ . The instantaneous number average sequence lengths are readily obtained as

$$\bar{n}_1 = \sum_{n=1}^{\infty} n S_n = 1 + \alpha \quad (20)$$

$$\bar{n}_2 = \sum_{n=1}^{\infty} n A_n = 1 + \beta \quad (21)$$

The number average sequence lengths in the cumulative copolymers is obtained by appropriately weighting these values by the amount of polymer formed over all con-

version intervals, i.e.

$$\bar{N}_1 = \int_0^x S_n F_1 dx \quad (22)$$

$$\bar{N}_2 = \int_0^x A_n (1 - F_1) dx \quad (23)$$

## COMPARISON WITH EXPERIMENTAL RESULTS

In the Results section, the experimental results of the styrene-acrylonitrile bulk polymerizations carried out in ampoules were reported. The general model presented in the last section can be applied to a batch reactor by eliminating the inflow and outflow terms in the material balance equations. The model consists of the set of four simultaneous differential equations (10)–(12) and (15) for the material balances with the rate expressions given in (7)–(9), and the cumulative number average sequence length equations (22) and (23).

### Conversion and composition predictions

There are a large number of parameters in the model, some of which can be reasonably taken as known from the literature. These literature values are given in Table 2. Basically, estimates for all the physical property data ( $T_g$ 's and  $\alpha$ 's) and the propagation rate constants at zero conversion ( $k_{ij0}$ 's) were available. Other parameters had to be estimated from the data. These included the chemically controlled termination rate parameter  $k_{t0}$  (60°C), its activation energy  $E$ , and the exponential diffusion parameter  $A$ . The overall termination rate constant at zero conversion was assumed to follow an Arrhenius dependence upon temperature as

$$k_{t0} = k_{t0}(60^\circ\text{C}) \cdot \exp\left\{-\frac{E}{R}\left(\frac{1}{T} - \frac{1}{333.2}\right)\right\} \quad (24)$$

The critical free volume for the termination reaction ( $V_{FCr}$ ) was taken to be that at zero conversion, since diffusion controlled termination appeared to be present right from the start. Furthermore,  $k_{t0}$  was taken to be independent of feed composition since, because of the very different values of the reactivity ratios, most of the macroradicals would be styrene terminated at all the feed compositions

studied. The unknown diffusion controlled propagation parameters were the exponential diffusion parameter  $B$ , and the critical free volumes  $V_{FCr,21}$  and  $V_{FCr,22}$ . The other critical free volumes,  $V_{FCr,12}$  and  $V_{FCr,11}$  were dependent upon these according to equation (6). The molecular weight exponent parameter ( $n$ ) was taken to be equal to 1.75 after Marten and Hamielec<sup>27</sup> since it was found to be highly correlated with the other unknown parameters of the model and could not be estimated independently.

The six unknown parameters were estimated by minimizing a weighted nonlinear least squares criterion involving the molar conversions and the residual styrene monomer mole fractions, i.e.

$$\text{Min} \left[ \sum_{i=1}^n (c_{wi} - \hat{c}_{wi})^2 + w \sum_{i=1}^n (f_{1,i} - \hat{f}_{1,i})^2 \right] \quad (25)$$

where  $c_w$  and  $\hat{c}_w$  are the weight conversion and its estimated value, and  $f_1$  and  $\hat{f}_1$  are the residual styrene monomer mole fraction and its estimate.  $w$  is a weighting parameter reflecting the relative precisions of the measured conversion and mole fractions ( $w = \sigma_c^2 / \sigma_{f_1}^2$ ). Statistically more rigorous estimation procedures would have been to use either the multiresponse estimation procedure of minimizing the determinant of the sum of squares and cross-products of the observations<sup>32</sup> or a multifunctional error in variables method<sup>33</sup>. But, given the uncertainties in the assumed literature values, the criterion in equation (25) was considered adequate for our purposes. A total of over 600 observations were used in the estimation. The parameter estimates are listed in Table 3, and the resulting fits of the model are shown as the curves in Figures 2–5. Noticeable discrepancies are in the fit of the high initial styrene data ( $f_{10} = 0.90$ ) where the fit is consistently too high at longer times. This might be explained by our use of a constant AIBN initiator efficiency. There is evidence that the initiator efficiency ( $f$ ) may vary with viscosity and with copolymer composition<sup>34</sup>. The estimated activation energy for the termination reaction also appears to be too large 6335 cal mol<sup>-1</sup> when compared with more accepted values for styrene (< 1000 cal mol<sup>-1</sup>). This together with the low value of  $\hat{A}$ , is probably a consequence of our assumption that the termination reaction is diffusion controlled right from the start (i.e.  $V_{FCr} = V_f$  at  $c_w = 0$ ). However, on the whole, this simple free volume theory model was felt to explain the data extremely well over the entire range of temperatures (40°C–60°C) and AIBN initiator concentrations (0.1 M–0.5 M). Separate fittings of the model to data at the different temperatures and at the different initiator levels revealed that the parameter estimates changed little with these conditions. This fact tends to confirm that the model is more than simply an empirical fit to some data, and should be capable of predicting the diffusion controlled polymerization of

**Table 2** Literature parameters used in the model for diffusion controlled copolymerization of styrene/acrylonitrile

Parameter	Literature value	Reference
$T_{gM1}$	−88.2°C	27
$T_{gM2}$	−82.8°C	27
$T_{gp}$	105.0°C	6
$\alpha_{M1}$	$1.00 \times 10^{-3}$	22
$\alpha_{M2}$	$1.25 \times 10^{-3}$	
$\alpha_p$	$25 \times 10^{-3}$	37
$k_{11,0}$	$1.051 \times 10^7 \exp(-3557/T) \text{ l mol}^{-1} \text{ s}^{-1}$	
$k_{22,0}$	$1.047 \times 10^8 \exp(-3663/T) \text{ l mol}^{-1} \text{ s}^{-1}$	2
$r_1$	0.36	6
$r_2$	0.078	6
$k_d$	$1.58 \times 10^{15} \exp(-30800/RT) \text{ l mol}^{-1} \text{ s}^{-1}$	38

**Table 3** Parameter estimates from the data of this paper

Parameter	Estimate
$k_{t0}$ (at 60°C)	$6.78 \times 10^9$
$E_t$	6335 cal/mol
$A$	0.307
$B$	1.7
$V_{FCr,21}$	0.031
$V_{FCr,22}$	0.030

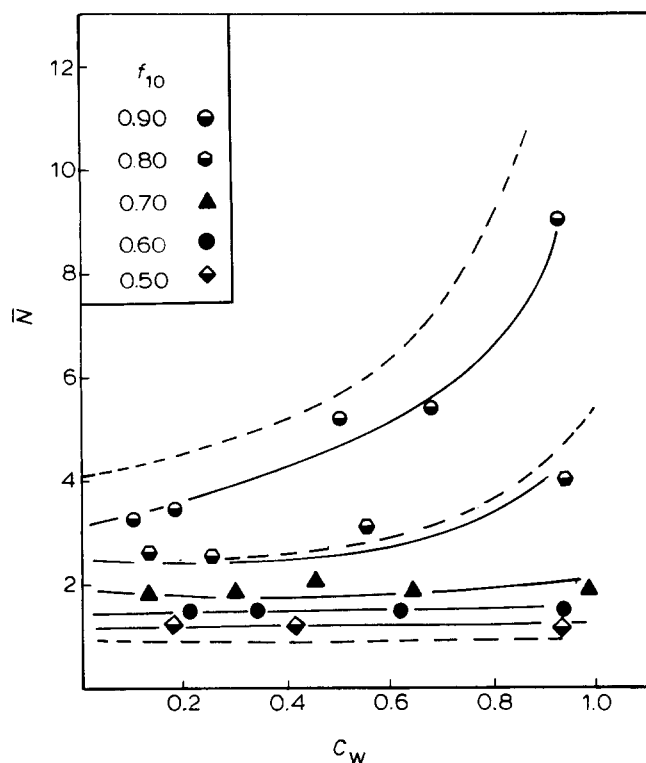


Figure 13 Comparison between n.m.r. and calculated average sequence lengths for several feed compositions. Dashed line represents the model predictions

styrene-acrylonitrile at other conditions, such as polymerizations with temperature-time programming and polymerization in another reactor type.

#### Sequence length

The cumulative number average sequence length of styrene units obtained by  $^1\text{H}$ -n.m.r. are compared against the model predictions given by equation (22) for one set of experimental conditions ( $t = 60^\circ\text{C}$ ) and  $[\text{I}]_0 = 0.05 \text{ M}$ ) in Figure 13. The dashed lines (----) represent the model predictions, while the solid lines are interpolations put through the data points to aid in visual inspection. Sequence length behaviour at the other conditions are similar<sup>6</sup>, and in all cases, the model predictions appeared to be adequate.

#### SUMMARY

The results of an extensive experimental investigation on the bulk copolymerization of styrene and acrylonitrile have been reported, and a model capable of predicting the conversion, composition and sequence length history up to limiting conversions has been developed. An extension of this model to enable prediction of the entire joint molecular weight, copolymer composition, and sequence length distributions is in progress.

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#### APPENDIX 1

##### STATISTICAL ESTIMATION OF THE REACTIVITY RATIOS

Under the assumptions of model adequacy, independent experiments and normality of the residuals, maximization of the likelihood function  $L(\theta|y)$  is approximately equivalent to

$$\min \sum_{i=1}^n \frac{\varepsilon_i^2}{\text{Var}(\varepsilon_i)} \quad (\text{A1})$$

where  $\theta$  are unknown parameters,  $y$  represents the vector of observations and  $\varepsilon_i$  and  $\text{Var}(\varepsilon_i)$  are the residuals and their corresponding variances.

In this study the residuals  $\varepsilon_i$  were defined in terms of the weight conversion as

$$\varepsilon_i = c_{w_i} - \hat{c}_{w_i} \quad (\text{A2})$$

where

$$\hat{c}_w = 1 - \left( \frac{N}{N_0} \right) \left( \frac{M_s f_1 + M_A (1 - f_1)}{M_s f_{10} + M_A (1 - f_{10})} \right) \quad (\text{A3})$$

$$\left( \frac{N}{N_0} \right) = \left( \frac{f_1}{f_{10}} \right)^\alpha \left( \frac{1 - f_1}{1 - f_{10}} \right)^\beta \left( \frac{f_{10} - \delta}{f_1 - \delta} \right)^\gamma \quad (\text{A4})$$

$$\alpha = \frac{r_2}{1 - r_2} \quad \beta = \frac{r_1}{1 - r_1}$$

$$\gamma = \frac{1 - r_1 r_2}{(1 - r_1)(1 - r_2)} \quad \delta = \frac{1 - r_2}{2 - r_1 - r_2}$$

The residuals  $\varepsilon_i$  are functions of three measured variables: the weight conversion  $c_w$ , the initial feed composition,  $f_{10}$ , and the composition of styrene in the reacting mixture  $f_1$ . Under these conditions, the variance of the residuals can be approximated by:

$$\text{Var}(\varepsilon_i) \doteq \left( \frac{\partial \varepsilon_i}{\partial c_w} \right)^2 \sigma_{c_w}^2 + \left( \frac{\partial \varepsilon_i}{\partial f_{10}} \right)^2 \sigma_{f_{10}}^2 + \left( \frac{\partial \varepsilon_i}{\partial f_1} \right)^2 \sigma_{f_1}^2 \quad (\text{A5})$$

where the partial derivatives are evaluated at the measured values of the  $i$ th experiment and are given by:

$$\left( \frac{\partial \varepsilon_i}{\partial c_w} \right) = 1 \quad (\text{A6})$$

$$\left( \frac{\partial \varepsilon_i}{\partial f_{10}} \right) = \left( \frac{M_r}{M_0} \right) \left( \frac{N}{N_0} \right) \left( -\frac{\alpha}{f_{10}} + \frac{\beta}{1 - f_{10}} + \frac{\gamma}{f_{10} - \delta} - \frac{M_s - M_A}{M_0} \right) \quad (\text{A7})$$

$$\left( \frac{\partial \varepsilon_i}{\partial f_1} \right) = \left( \frac{M_r}{M_0} \right) \left( \frac{N}{N_0} \right) \left( -\frac{\alpha}{f_1} + \frac{\beta}{1 - f_1} + \frac{\gamma}{f_1 - \delta} - \frac{M_s - M_A}{M_r} \right) \quad (\text{A8})$$

where

$$\begin{aligned} M_r &= M_s f_1 + M_A (1 - f_1) \\ M_0 &= M_s f_{10} + M_A (1 - f_{10}) \\ M_s &= 104.14 \text{ (molecular weight of styrene monomer)} \\ M_A &= 53.06 \text{ (molecular weight of acrylonitrile)} \end{aligned}$$

The variances of  $c_w$  and  $f_{10}$  are fairly constant ( $\sigma_{c_w}^2 = 4 \times 10^{-3}$ ,  $\sigma_{f_{10}}^2 = 0.26 \times 10^{-3}$ ) and independent of the conversion and composition levels. The variance of the  $f_1$ , on the other hand, showed a dependence on the styrene concentration, which in turn, varies with conversion and feed composition. Investigation of this variation as a function of the raw g.c. measurements (ratios of areas of the monomers to area of the internal standard) indicated that the variance of the ratio  $R_s$  (area of styrene/area internal standard) is a function of the styrene concentration (Figure A1). This variance was approximated by:

$$\sigma_{R_s}^2 = [0.279 - 0.0191 R_s + 0.0067 R_s^2]^2 \quad (\text{A9})$$

The ratio  $R_A$  (area of acrylonitrile/area internal standard), on the other hand, is practically constant (i.e.  $\sigma_{R_A}^2 = 0.672 \times 10^{-4}$  with 95% confidence limits of  $0.398 \times 10^{-4}$  and  $1.373 \times 10^{-4}$ ).

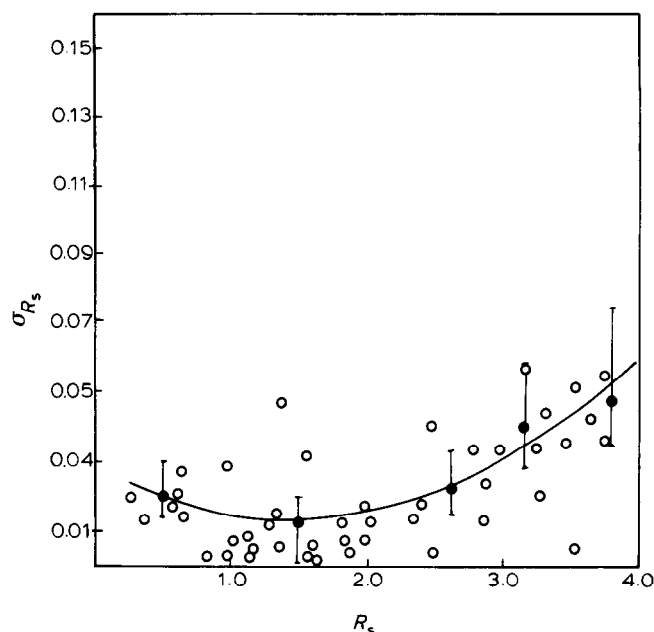


Figure A1 Standard deviation of the area ratio in g.c. analysis of the residual monomer

Transformation of equation (A5) to include the variance of  $R_A$  and  $R_s$  yields

$$\begin{aligned} \text{Var}(\varepsilon_i) &= \left( \frac{\partial \varepsilon_i}{\partial c_w} \right)^2 \sigma_{c_w}^2 + \left( \frac{\partial \varepsilon_i}{\partial f_{10}} \right)^2 \sigma_{f_{10}}^2 + \left( \frac{\partial \varepsilon_i \partial f_1}{\partial f_1 \partial R_s} \right)^2 \sigma_{R_s}^2 \\ &\quad + \left( \frac{\partial \varepsilon_i \partial f_1}{\partial f_1 \partial R_A} \right)^2 \sigma_{R_A}^2 \end{aligned} \quad (\text{A10})$$

where

$$\frac{\partial f_1}{\partial R_s} = \left[ \frac{k_1 \cdot k_2 R_A / M_s \cdot M_A}{\frac{k_1}{M_s} R_s + \frac{k_2}{M_A} R_A} \right]^2 \quad (\text{A11})$$

$$\frac{\partial f_1}{\partial R_A} = \left[ \frac{k_1 \cdot k_2 R_s / M_s \cdot M_A}{\frac{k_1}{M_s} R_s + \frac{k_2}{M_A} R_A} \right]^2 \quad (\text{A12})$$

$k_1$  and  $k_2$  are the g.c. calibration constants for styrene and acrylonitrile.

Equations (A6), (A7), (A8), (A11) and (A12) were used with equations (A1) and (A10) for the estimation of the reactivity ratios as functions of conversion for low and intermediate conversions. At high conversions, where the residual monomer composition could not be adequately measured, the residuals were defined in terms of the styrene weight fraction as

$$\varepsilon = f_{1w} - \hat{f}_{1w} \quad (\text{A13})$$

where  $f_{1w}$  was obtained from conversion and copolymer composition measurements:

$$f_{1w} = \frac{f_{10w} - c_w P_{1w}}{(1 - c_w)} \quad (\text{A14})$$

The variance of  $\varepsilon_i$  was approximated as:

$$\text{Var}(\varepsilon_i) \doteq \left( \frac{\partial \varepsilon_i}{\partial f_{10w}} \right)^2 \sigma_{f_{10w}}^2 + \left( \frac{\partial \varepsilon_i}{\partial c_w} \right)^2 \sigma_{c_w}^2 + \left( \frac{\partial \varepsilon_i}{\partial P_{1w}} \right)^2 \sigma_{P_{1w}}^2 \quad (\text{A15})$$

$$\left( \frac{\partial \varepsilon_i}{\partial c_w} \right) = \frac{P_{1w}}{(1-c_w)^2} + 1 \quad (\text{A17})$$

$$\left( \frac{\partial \varepsilon_i}{\partial P_{1w}} \right) = \frac{-c_w}{(1-c_w)} \quad (\text{A18})$$

where

$$\begin{aligned} \left( \frac{\partial \varepsilon_i}{\partial f_{10w}} \right) &= \frac{M_A M_S}{(1-c_w)(f_{10} M_S + (1-f_{10}) M_A)^2} \\ &+ (1-c_w) \left( -\frac{\alpha}{f_{10}} + \frac{\beta}{1-f_{10}} + \frac{\gamma}{f_{10}-\delta} - \frac{M_S - M_A}{M_0} \right) \end{aligned} \quad (\text{A16})$$