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Analysis of the Mechanism of Copolymerization of Styrene and Maleic Anhydride

David J. T. Hill,* James H. O'Donnell, and Paul W. O'Sullivan

Department of Chemistry, University of Queensland, Brisbane, Australia 4067.
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ABSTRACT: The mechanism of copolymerization of styrene and maleic anhydride in bulk at 60 °C has been investigated by measurements of copolymer compositions using ^{13}C NMR and of monomer sequence distributions using DEPT pulse programs to distinguish CH_2 subspectra, which have been attributed to styrene-centered triads. The strong tendency to alternation observed by most previous workers was confirmed. Nonlinear, least-squares analysis of the compositions of copolymers prepared over a wide comonomer composition range showed that the penultimate model gave a better fit to the data than the terminal model with a confidence level >95%. There was only a penultimate effect for styrene-terminated chain radicals. A similar analysis of the composition data of Bamford and Barb for comonomer mixtures with high styrene contents gave reactivity ratios in good agreement with the values derived from our composition data. The complex-participation and complex-dissociation models could also be fitted to the composition data but there was a strong correlation between different reactivity ratios, indicating extensive minima on the hypersurface. The monomer sequence distributions were in good agreement with the predictions of both the penultimate and complex-participation models and could not distinguish between them.

Introduction

The copolymerization of styrene (S) and maleic anhydride (MAn) has been studied extensively over many years. Alfrey and Lavin[1] and subsequent workers[2–5] have used the terminal model to analyze copolymer compositions. However, Barb[6] considered that the terminal model was inadequate and proposed a penultimate effect for styrene-ended radicals to explain the composition data from copolymerizations in acetone and methyl propyl ketone. The penultimate model was also used by Enomoto et al.[7] to explain the copolymerization at high pressure.

Donor–acceptor complexes are known to form between S and MAn and equilibrium constants ranging from 0.34 $dm^3\ mol^{-1}$ at 22 °C to 0.25 $dm^3\ mol^{-1}$ at 60 °C have been reported from UV and ^{1}H NMR measurements.[8–10]

A maximum in the initial rate of copolymerization at a mole fraction, X_S, of styrene in the comonomer feed of *ca.* 0.5 has been suggested as evidence of copolymerization via the comonomer complex.[4,8,11–13] Addition of one monomer following dissociation of the complex during the propagation step has also been suggested.[14]

The position of the initial rate maximum as a function of feed composition can be analyzed for the separate contributions of free monomers and the comonomer complex in propagation.[15] However, Raetzsch et al.[12,16] have shown that variation in the position of the rate maximum can be explained by the terminal model without involvement of complex if termination is taken into account, namely cross-termination and the two homoterminations. Their analyses of the S–MAn copolymerization in acetone and 1,2-dichloroethane are in agreement with reactivity ratios derived from composition analyses using the terminal model and rate constants for homopolymerizations.

The participation of comonomer complexes has been proposed for terpolymerizations involving added donors or acceptors,[14,17,18] although the terpolymer equation derived from the terminal model has also been found adequate to describe some of these systems.[14]

Dodgson and Ebdon[10,19] studied the copolymerization in bulk and in a variety of solvents and also terpolymerizations with methyl methacrylate. They found that the composition data were fitted markedly better by the penultimate and complex-participation models than by the terminal model. They concluded from the effects of (i) dilution on the polymerization in methyl ethyl ketone and (ii) added electron acceptor on both the copolymer composition and initial polymerization rate, that their study did not provide evidence consistent with the complex-participation model which could not be accounted for by the penultimate model. Thus, they suggested that a S–MAn complex was not involved in propagation.

Both monomers form donor–acceptor complexes with the solvents used in their study and the effect of this complexation on monomer reactivity may be important. The dilution studies did show a small dilution effect, less than predicted by the complex model, but not zero as predicted by the penultimate model. The dilution effect may be due to involvement of monomer–solvent complexes or other solvent effects, so that an unequivocal assignment of a model on the basis of this effect is not possible.

We have previously[20] reexamined the composition data of Dodgson and Ebdon for the bulk copolymerization using a nonlinear least-squares (NLLS) analysis and shown that both the complex[21] and penultimate models could adequately describe the data. However, the sequence distributions predicted from the reactivity ratios derived for these models, and for the terminal model, were quite different and their experimental determination should enable the correct model to be distinguished.

We have also developed composition and sequence distribution equations for the complex-dissociation model in its general form.[22] In this model, the comonomer complex competes with free monomers in propagation but dissociates during addition so that only one monomer is

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incorporated into the polymer. This model also provided a good fit to the composition data of Dodgson and Ebdon for the bulk copolymerization. The resultant reactivity ratios gave predicted sequence distributions which differ from those of the penultimate and complex-participation models.

The monomer sequence distributions in styrene–maleic anhydride copolymers have been investigated by ^{13}C NMR by Buchak and Ramey[23] and Roth et al.,[5] using the quaternary aromatic resonances to determine the fractions of styrene-centered triads. However, the considerable uncertainty in the assignments of these resonances due to overlap and comparable tacticity and sequence chemical shifts causes the results to be unreliable.

We have recently shown that styrene-centered sequence distributions can be calculated from three resonances observed in the ^{13}C NMR CH_2 subspectra generated by using the DEPT spectral editing pulse sequence.[24]

This paper presents a detailed analysis of experimental data for the bulk copolymerization of styrene and maleic anhydride at 60 °C. NLLS procedures are applied to the experimentally determined copolymer compositions to calculate the "best values" for the reactivity ratios and to estimate the joint uncertainty in these values for the terminal, penultimate, complex-participation, and complex-dissociation models. Statistical tests of significance are applied. Sequence distributions determined by ^{13}C NMR are compared with predictions based on the reactivity ratios of each of the models and are used independently to estimate reactivity ratios and test the validity of the various models.

Experimental Section

Materials. Styrene was distilled at reduced pressure under nitrogen at 60 °C. Maleic anhydride was sublimed at 50 °C and 2.5 kPa and used immediately. The initiator, benzoyl peroxide, was recrystallized twice from chloroform by addition of methanol. Polymerizations were performed in the absence of solvent in Pyrex glass ampules. A small amount (less than 5 mg per 50 g monomers) of inhibitor, hydroquinone, was also added to prevent polymerization prior to the monomer mixture becoming homogeneous at the reaction temperature. The required amounts of monomers, initiator, and inhibitor were accurately weighed into the ampules, thoroughly freeze–thaw degassed, and sealed under vacuum. The polymerizations were carried out at 60 °C to conversions less than 5 wt %. For polymerizations with monomer feeds in the range 50–97.5% styrene, the polymer precipitated on formation; at lower styrene content, the reaction mixture remained homogeneous. (These observations are consistent with those observed by Bamford and Barb,[2] who reported that polymer precipitated in their concentration region 90–98.5% styrene but was soluble above 98.5% styrene.) The polymers were recovered by addition of the polymerization mixture to a 10-fold excess of methanol or chloroform and purified twice by reprecipitation from acetone solution into methanol or chloroform. The purified polymers were dried in vacuo at 50 °C for 16 h.

Characterization. The pulse-FT ^{13}C NMR spectra were recorded on either a Bruker CXP300 spectrometer (75.46 MHz ^{13}C) or a JEOL FX100 spectrometer (25.2 MHz ^{13}C) at ambient temperature in 10 mm o.d. sample tubes. Solutions were approximately 10% w/v in acetone-d_6. Relaxation time (T_1) measurements were determined by using an inversion–recovery sequence, and nuclear Overhauser enhancement factors (NOEF) were determined by comparison of a fully decoupled spectrum with that obtained by using gated decoupling to remove NOE. In all measurements, pulse recycle times were sufficiently long to allow full recovery of all copolymer carbons.

The compositions of the copolymers were determined from the relative areas of the carbonyl and the total aromatic carbon resonances from the ^{13}C NMR spectrum with recycle time $>5T_1$ of the slowest relaxing carbon and gated decoupling to remove NOE. Compositions were also determined by using (i) % C and % H elemental analysis, (ii) nonaqueous microtitrations in acetone using sodium methoxide as titrant, and (iii) from the relative intensities of the aromatic (S units) and the methylene and methine (MAn + S) resonances in the ^{1}H NMR spectra. These spectra were obtained on a JEOL PS100 NMR spectrometer at ambient temperature, with acetone-d_6 as solvent.

The DEPT technique to generate the CH, CH_2, and CH_3 ^{13}C NMR subspectra has been described previously, together with the procedure used to calculate the styrene-centered sequence distributions from the CH_2 subspectrum.[24]

Table I
Comonomer (X_S) and Copolymer (Y_S) Compositions Expressed as Mole Fraction of Styrene with Conversions and Resonance Areas for the Methylene Subspectrum from ^{13}C NMR Spectra for the Copolymerization of Styrene (S) and Maleic Anhydride (M) in Bulk at 60 °C

		Y_S		CH_2 resonance areas,[d,e] ppm		
X_S	conv[a]	b	c	42–47	37–42	33–37
0.102	1.1	0.500				
0.203	1.4	0.508				
0.599	2.8	0.504				
0.653	1.6	0.517	0.515	0.00	0.12	0.88
0.697	2.4	0.510				
0.698	2.6	0.520	0.522	0.00	0.16	0.84
0.744	1.3	0.522	0.520	0.01	0.14	0.85
0.753	4.2	0.525				
0.813	2.2	0.533				
0.859	1.4	0.538				
0.897	1.4	0.546				
0.898	1.3	0.548	0.558	0.03	0.35	0.62
0.950	0.4	0.600				
0.950	0.4	0.601	0.608	0.12	0.47	0.41
0.975	0.3	0.654	0.650	0.17	0.59	0.24

[a] Wt % of total monomer feed. [b] From the relative areas of the carbonyl and total aromatic signals in the ^{13}C NMR spectra. [c] From triad fractions according to eq 1. [d] Expressed as fraction of total CH_2 area; estimated error ±0.05. [e] Assigned to triad fractions in the following way: F_{SSS} 42–47 ppm, $F_{MSS+SSM}$ 37–42 ppm, and F_{MSM} 33–37 ppm.

Results and Discussion

NMR Analysis. The experimental copolymer compositions determined from ^{13}C NMR spectra together with comonomer feed compositions and conversions are given in Table I. ^{13}C NMR spectroscopy has advantages over other techniques, such as elemental analysis, nonaqueous titration and ^{1}H NMR spectroscopy, because it is not sensitive to (i) the presence of water, which is difficult to exclude from the polymer,[18] or (ii) partial esterification, which occurs readily during precipitation in methanol.[24]

Roth et al.[5] used the relative areas of the carbonyl and quaternary aromatic resonances in the ^{13}C NMR spectra to calculate the compositions of copolymers produced in acetone or benzene. The maleic anhydride contents derived from NMR were lower than the values obtained by chemical analysis, which may have been due to residual water. However, they did not consider the effects of the different relaxation times (T_1) and NOEF. On the basis of our measurements of T_1 and NOEF, shown in Table II, we have found that their NMR measurements would give low MAn contents.

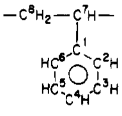
The NOEF values are all substantially lower than the maximum value of 3.0, which is frequently assumed to apply to polymers. The relaxation times of the carbonyl and quaternary aromatic carbons are nearly an order of magnitude greater than for the other carbon atoms.

Three resonances are exhibited in the CH_2 subspectrum of the ^{13}C NMR of S–MAn copolymers. The resolution of these resonances is adequate for determination of the relative intensities by computer integration and are given in Table I. Buchak and Ramey[23] and Roth et al.[5] have calculated triad fractions from the quaternary aromatic

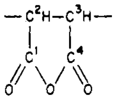
Table II
Relaxation Times (T_1) and Overhauser Enhancement Factors (NOEF) for ^{13}C NMR Resonances of Styrene–Maleic Anhydride Copolymers[a,b]

carbon[c]	chem shift, ppm	T_1, s 75 MHz	T_1, s 25 MHz	NOEF, 25 MHz
M1,4	173	1.6	1.4	1.8
S1	137–145	1.3	0.75	1.65
S2-6	129	0.19		1.8
M2,3	52	0.26	0.13	1.7
S7 M2,3	43	0.19	0.07	1.95
S8	35	0.10		

[a] Measured for 10% w/v solution in acetone-d_6 at ambient temperature. [b] Estimated error in T_1 and NOEF = ±10%. [c] The carbon atoms corresponding to the following structures:



styrene (S)



maleic anhydride (M)

resonances, but estimation of areas from the overlapping resonances leads to large uncertainties. Roth et al. also found it necessary to assume an asymmetric line shape for the resonance assigned to MSM sequences in order to obtain triad fractions consistent with their composition measurements. There is no clear division into triad groups in the quaternary aromatic region and calculations based on the assignments of Buchak and Ramey cannot be made with any certainty.

The three resonances in the CH_2 subspectra could arise either through triad sequences or through cis–trans diads. We have previously presented arguments[24] which support the assignment of the resonances to triad sequences. If these assignments are correct, then the compositions of these copolymers can be calculated from the relative areas of the triad resonances according to the formula

$$\frac{F_S}{F_M} = 1 + \frac{2A_{SSS} + A_{SSM+MSS}}{2A_{MSM} + A_{SSM+MSS}} \tag{1}$$

where F_S/F_M is the mole ratio of residues in the copolymer and A_{SSS}, $A_{MSS+SSM}$, and A_{MSM} are the relative areas of the resonances assigned to the respective triad fractions (see Table I). This equation assumes that the MAn is present only as single-unit sequences. The low homopolymerizability of MAn and the fact that measurements were only made on copolymers produced from monomer feeds containing ≥60% styrene justifies this assumption.

The copolymer compositions calculated from the triad fractions are in good agreement with the compositions determined from the relative areas of the carbonyl and total aromatic resonances (Table I). This agreement is good evidence that the copolymer compositions derived from the NMR spectra and the assignments of the triad resonances in the CH_2 subspectra are correct. There is no direct evidence for SMMS sequences, but they may be present in minor amounts in copolymers prepared from comonomer mixtures containing high proportions of maleic anhydride.

The compositions of this work are in agreement with those obtained for the bulk copolymerization by Bamford and Barb,[2] who analyzed the copolymers by nonaqueous titration of the MAn. However, the results of this work differ from those of Dodgson and Ebdon[10] for bulk copolymerization. They determined the MAn content by ^{14}C labeling and obtained lower values than in this work. Dodgson and Ebdon also reported lower MAn contents than previous values in the literature for polymerizations in several solvents.[6,9] It was found in the present work that, for copolymerizations without added inhibitor, polymer is formed before the maleic anhydride is fully dissolved. The polymer isolated after polymerization to the usual conversion had a higher styrene content than in the presence of inhibitor.

Testing of Alternative Models. Tidwell and Mortimer[25,26] and Behnken[27] have pointed out the deficiencies of different linear methods for determining reactivity ratios for the terminal model of copolymerization and advocated the use of nonlinear least-squares procedures (NLLS) to analyze polymer/copolymer composition data. The importance of nonlinear analysis was reiterated by McFarlane et al.[28] and Leicht and Fuhrmann,[29] who compared common linear methods with the NLLS procedure for analyzing copolymer composition data.

It is important to express the copolymer compositions in a form which maintains the basic assumption of the least-squares analysis, i.e., that the errors are normally distributed with constant variance.[27,30] It is also necessary to consider the extent of conversion and the error associated with the measurement of conversion.[25–27,30]

In the present work, the conversions were maintained sufficiently small compared to the amount of the minor component, so that, even if the conversions were underestimated by a factor of 2, the change in the computed polymer compositions would be less than the experimental error in the measurement of the comonomer composition. The error in the comonomer feed composition in the present work was negligible compared to that in the copolymer composition. Therefore, it is only necessary to consider the error in the copolymer compositions when determining the reactivity ratios.

The nonlinear search method used to obtain "best estimates" of the reactivity ratios is based on that described previously for the complex-participation model.[21] An iterative procedure within the computer program accounts for the extent of conversion and the equations for the copolymer composition have been expressed in a form which is consistent with the basic assumption of the least-squares procedure. We have investigated the sensitivity of the estimated reactivity ratios to errors in polymer compositions and found that the program will converge rapidly to the global minimum containing the "best values" of the reactivity ratios from a variety of different initial estimates of the reactivity ratios.

However, the definitions of the reactivity ratios for the complex-participation model of Cais et al.[21] $r_1 = k_{11}/k_{10}$, $p_1 = k_{1\bar{1}\bar{0}}/k_{1\bar{0}\bar{1}}$, and $s_1 = k_{1\bar{0}\bar{1}}/k_{10}$, have proved to be unsuitable in some cases for analyses involving the seven parameters of the general model because of the correlation in the uncertainties of p and s, especially when either of these parameters is close to zero. It should be noted that the parameter, p, is present in the composition equation only as the product ps. New definitions of reactivity ratios r, q, and s, which are the same as those defined previously by us for the complex-dissociation model[22] and by Natansohn et al.[31] for their complex-participation model have reduced this difficulty considerably. The propagation reactions, individual rate constants, and reactivity ratios for the four copolymerization models considered in this paper are shown in Table III. The NLLS procedure was used to obtain "best estimates" of the reactivity ratios for all of the models and of the equilibrium contant, K, for the complex models.

Terminal and Penultimate Models. The calculated copolymer/comonomer composition relationships for the terminal and penultimate models are compared with the

Table III
Kinetic Equations and Reactivity Ratio Definitions for the Four Polymerization Models

Terminal Model

$\sim S + S \rightarrow \sim S$	k_{SS}
$\sim S + M \rightarrow \sim M$	k_{SM}
$\sim M + S \rightarrow \sim S$	k_{MS}
$\sim M + M \rightarrow \sim M$	k_{MM}

$r_S = k_{SS}/k_{SM}$ $\quad$ $r_M = k_{MM}/k_{MS}$

Penultimate Model

$\sim SS + S \rightarrow \sim SS$	k_{SSS}	$\sim MM + M \rightarrow \sim MM$	k_{MMM}
$\sim SS + M \rightarrow \sim SM$	k_{SSM}	$\sim MM + S \rightarrow \sim MS$	k_{MMS}
$\sim MS + S \rightarrow \sim SS$	k_{MSS}	$\sim SM + M \rightarrow \sim MM$	k_{SMM}
$\sim MS + M \rightarrow \sim SM$	k_{MSM}	$\sim SM + S \rightarrow \sim MS$	k_{SMS}

$r_{SS} = k_{SSS}/k_{SSM}$ $\quad$ $r_{MS} = k_{MSS}/k_{MSM}$
$r_{SM} = k_{SMM}/k_{SMS}$ $\quad$ $r_{MM} = k_{MMM}/k_{MMS}$

Complex-Participation Model Four Propagation Steps of Terminal Model Above, Plus

$\sim S + \overline{MS} \rightarrow \sim S$	$k_{S\overline{MS}}$
$\sim S + \overline{SM} \rightarrow \sim M$	$k_{S\overline{SM}}$
$\sim M + \overline{MS} \rightarrow \sim S$	$k_{M\overline{MS}}$
$\sim M + SM \rightarrow \sim M$	$k_{M\overline{SM}}$

$r_S = k_{SS}/k_{MM}$ $\quad$ $q_S = k_{S\overline{SM}}/k_{SM}$ $\quad$ $s_S = k_{S\overline{MS}}/k_{SM}$
$r_M = k_{MM}/k_{MS}$ $\quad$ $q_M = k_{M\overline{MS}}/k_{MS}$ $\quad$ $s_M = k_{M\overline{SM}}/k_{MS}$

Complex-Dissociation Model Four Propagation Steps of Terminal Model Above, Plus

$\sim S + \overline{MS} \rightarrow \sim M + S$	$k'_{S\overline{MS}}$
$\sim S + \overline{SM} \rightarrow \sim + M$	$k'_{S\overline{SM}}$
$\sim M + \overline{MS} \rightarrow \sim M + S$	$k'_{M\overline{MS}}$
$\sim M + \overline{SM} \rightarrow \sim S + M$	$k'_{M\overline{SM}}$

$r_S = k_{SS}/k_{SM}$ $\quad$ $q_S' = k'_{S\overline{SM}}/k_{SM}$ $\quad$ $s_S' = k'_{S\overline{MS}}/k_{SM}$
$r_M = k_{MM}/k_{MS}$ $\quad$ $q_M' = k'_{M\overline{MS}}/k_{MS}$ $\quad$ $s_S' = k'_{M\overline{SM}}/k_{MS}$

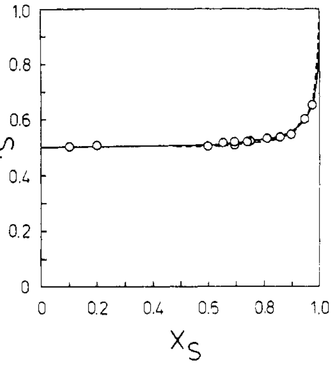


Figure 1. Copolymer composition curve for styrene–maleic anhydride copolymerization in bulk at 60 °C (Y_S = mole fraction styrene in copolymer and X_S = mole fraction styrene in monomer): (O) experimental data; (—) penultimate, complex-participation, and complex-dissociation models; (- - -) terminal model.

experimental compositions in Figure 1. Only small differences separate both the calculated curves and the experimental points, although the penultimate model shows slightly better agreement over the complete composition range. The "best estimates" of the reactivity ratios for each model are given in Table IV, together with the calculated standard error, s_y, in the measurements of polymer compositions obtained from the fit of the model to the data. The values of s_y compare well with a separate estimate of 0.005 for the error associated with determining the experimental compositions.

Table IV
Reactivity Ratios Derived by Using the Terminal or Penultimate Models for the Bulk Copolymerization of Styrene (S) and Maleic Anhydride (M) at 60 °C

parameter	value *a*	 *b*
	Terminal Model	
r_S	0.025	0.022
r_M	0.000	0.000
s_Y	0.0058	0.011
	Penultimate Model	
r_{SS}	0.0177	0.0186
r_{MS}	0.0288	0.0263
r_M	0.000	0.000
s_Y	0.0050	0.010

[a] From the experimental data of this work. [b] From the data reported by Bamford and Barb.[2]

All the reactivity ratios have been allowed to relax during the NLLS treatment of the data for both models. The best estimate of r_M for the terminal model is zero, indicating that MAn is present only as single-unit sequences. The best estimates of r_{MM} and r_{SM} for the penultimate model are both zero, indicating that there is no penultimate effect for MAn-ended radicals. Thus, the penultimate model can be reduced to the special case of three reactivity ratios, r_{SS}, r_{MS}, and r_M.

The statistical *F*-test[32] shows that the three-parameter, penultimate model provides a significant improvement over the terminal model to a level of confidence α >95%.

Best estimates of the reactivity ratios are determined simultaneously by the NLLS procedure and they are not statistically independent. Therefore, it is necessary to specify joint confidence regions within which the correct set of parameter values (reactivity ratios) are believed to exist with a given certainty or confidence level. We have used a computational procedure which enables construction of confidence regions which encompass all parameter sets, Θ, which satisfy the inequality of eq 2 in the region of the best values of the parameters, $\hat{\Theta}$:

$$\mathrm{SS}(\Theta) - \mathrm{SS}(\hat{\Theta}) \le \frac{p}{n-p}\mathrm{SS}(\hat{\Theta})\mathbf{F}_{\alpha(p,-p)} \qquad (2)$$

SS(Θ) and $\mathrm{SS}(\hat{\Theta})$ are the sums of the squares of the differences between the calculated and experimental polymer compositions for various parameter sets, *p* is the number of parameters, *n* is the number of experimental points, and $\mathbf{F}_{\alpha(p,n-p)}$ is the value of the **F** statistic at significance level α, for *p* and $n - p$ degrees of freedom.

The resultant joint confidence regions will be bounded by *p*-dimensional surfaces. For $p > 2$ the surface can be represented by two-dimensional cross sections for various values of the remaining parameters. The 95% confidence surface for the three parameters, r_M, r_{MS}, and r_{SS} is represented in Figure 2 by two-dimensional cross sections of this surface plotted as r_M vs. r_{SS} (Figure 2a) and r_{MS} vs. r_{SS} (Figure 2b) for various values of the third reactivity ratio. The maximum range of r_M is ±0.008 at the best r_{SS} and r_{MS}. The special case where $r_{MS} = r_{SS}$ lies just within the 95% joint confidence region on the hypersurface, suggesting that the terminal model should not be excluded. However, while eq 2 gives the correct shape of the confidence contours, the level of confidence of each controur is not exact.[33] Therefore, the applicability of the terminal model should be examined more closely.

We have also applied the NLLS procedure to the composition data of Bamford and Barb[2] which was obtained for polymerization in bulk with comonomer feed compositions containing much higher styrene contents than in

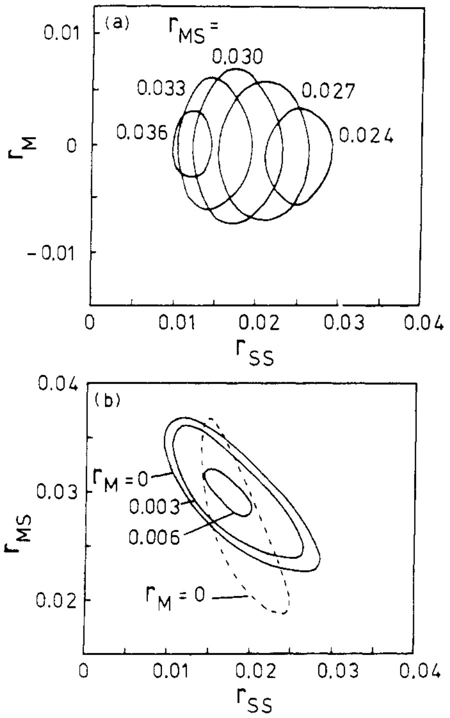


Figure 2. 95% joint confidence surface for the three parameters of the simplified penultimate model applied to the styrene–maleic anhydride copolymerization. Cross sections in the plane of (a) $r_M - r_{SS}$ and (b) $r_{MS} - r_{SS}$ for various values of the third parameter: (—) data of this work; (- - -) data of Bamford and Barb.[2]

this work. The best estimates of the reactivity ratios for both the terminal and penultimate models are in good agreement with the values derived from our experimental data (see Table IV). The estimates of s_y indicate a greater uncertainty in their measurements of copolymer composition.

Application of the F-test on the fits to their data shows an improvement for the penultimate model over the terminal model to a confidence level α >90%. The 95% joint confidence region for the reactivity ratios of the penultimate model is shown in Figure 2b. There is considerable uncertainty in the value of r_M from their data (approximately ±1), which results because of their experiments were conducted with very high proportions of styrene in the comonomer feed.

The region of overlap of the 95% confidence surfaces from the data of this work and that of Bamford and Barb includes the best estimates of the reactivity ratios from both sets of data and can be regarded as the appropriate 95% confidence region for these parameters. The point on the hypersurface where $r_{MS} = r_{SS}$ is not included within this region of overlap, and thus, on the basis of the combined data, the terminal model can be excluded.

The penultimate reactivity ratios for styrene-ended radicals indicate an increased preference for addition of S compared to MAn when a MAn residue occupies the penultimate position in the chain. This would be expected as a result of repulsive interactions between the carbonyl groups of the incoming MAn monomer and the MAn unit in the chain. This penultimate effect is not large and the very different polarity of the two monomers, which causes the tendency to alternation, is the dominating influence in the copolymerization.

The reactivity ratios in Table IV are in reasonable agreement with those calculated by trial and error by Barb[6] (r_{SS} = 0.017, r_{MS} = 0.063) for polymerizations in acetone and methyl propyl ketone. It might therefore be deduced that these solvents do not significantly influence the copolymerization. The reactivity ratios reported by Dodgson and Ebdon[10] for the copolymerization in bulk (r_{SS} = 0.01; r_{MS} = 1.5) are quite different and this reflects the very different copolymer compositions obtained by them.

Table V
Selected Examples of Parameter Sets Derived by Using the Complex-Participation Model for the Bulk Copolymerization of Styrene (S) and Maleic Anhydride (M) at 60 °C[a]

parameter	values			
r_S	0.01	0.1	1	10
q_S	0.060	0.15	20	50
s_S	1.5	0.0063	42	590
r_M	0	0	0	0
q_M	0	0	0	0
s_M	0.14	5.6	49	32
K[b]	0.26	0.26	0.26	0.26
s_Y[c]	0.0055	0.0055	0.0053	0.0054

[a] Parameter sets with $r_M = q_M = 0$ and K = 0.26 dm^3 mol^{-1} were chosen. [b] Units of K are dm^3 mol^{-1}. [c] Calculated assuming only four adjustable parameters.

Complex-Participation Model. The best fit of the complex-participation model to the composition is indistinguishable from that of the penultimate model (Figure 1). However, there is a wide range of reactivity ratio sets which give equally good agreement with the compositions. An indication of this range is given in Table V where selected parameter sets with $r_M = q_M = 0$ and K = 0.26 dm^3 mol^{-1} are shown. Thus, the variation of r_S, for example, over 3 orders of magnitude can give an equally good fit of the model to the data.

Investigations of the hypersurface, defined for NLLS analysis as the sum of the squares of the differences between the calculated and experimental conditions, show that all of these parameter sets are part of the same extensive minimum. For fixed values of six of the parameters, the uncertainty in the remaining parameter may be large, but in general the extent of the hypersurface minimum is the result of the joint uncertainty of two, or several, parameters.

The correlation of the uncertainty in the various parameters may be understood if the competing influences within the complex model are considered. The S–MAn composition data can be explained almost equally well by simple addition of free monomers or by predominant incorporation of the comonomer complex. A change in the magnitude of the reactivity ratio r_S, for example, can be balanced by a change in reactivity ratios describing the addition of complex so that the calculated copolymer composition is unaffected.

The extent of the minimum in the hypersurface containing the parameter sets which provide a good description of the composition data can be seen by plotting two-dimensional cross sections of the 95% confidence surface. Examples are given in Figures 3–5 to show the strong correlations between several of the parameters. Only a small range of values in the vicinity of zero is possible for the parameters r_M and q_M. This uncertainty is independent of the values of the other parameters except s_M, increasing markedly as s_M increases. Changing the value of K in the range 0.1–0.5 dm^3 mol^{-1} changes the allowed values of the other parameters without affecting the strong correlations which are characteristic of the confidence surface.

The estimate of s_y from the fit to the data is close to that estimated experimentally, indicating that the fit is the best that could be expected for this data. Although the model was fitted by allowing all seven parameters to assume their

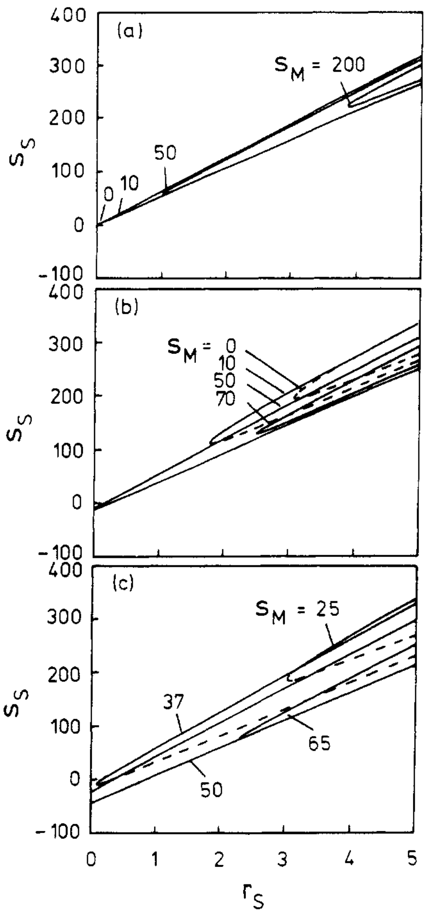


Figure 3. 95% joint confidence surface for the parameters of the complex-participation model applied to the styrene–maleic anhydride copolymerization. Cross sections in the plane of s_S – r_S for the following values of the remaining parameters: (a) q_S = 0; (b) q_S = 10; (c) q_S = 50. In all cases r_M = 0, q_M = 0, and K = 0.26 dm^3 mol^{-1}.

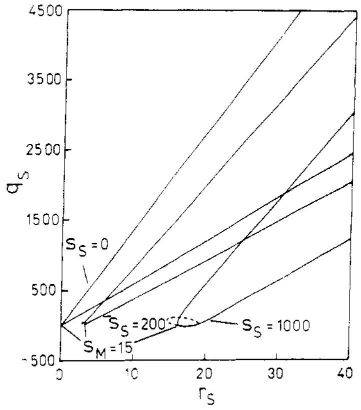


Figure 4. 95% joint confidence surface for the parameters of the complex-participation model applied to the styrene–maleic anhydride copolymerization. Cross sections in the plane of q_S – r_S for the following values of the remaining parameters: (—) s_M = 50; (- - -) s_M = 15. In all cases r_M = 0, q_M = 0, and K = 0.26 dm^3 mol^{-1}.

best values, the model can be restricted to one of four parameters without worsening the goodness of fit. Parameter sets containing the values r_M = q_M = 0, which might be expected from the low homopolymerizability of MAn, and K = 0.26 dm^3 mol^{-1}, which is in agreement with spectroscopic measurements,[8-10] are part of the hypersurface minimum. Even with this assumption of only four adjustable parameters, application of the statistical *F*-test shows that the complex model does not provide a significant improvement over the terminal model. Thus, the terminal model cannot be rejected in this comparison.

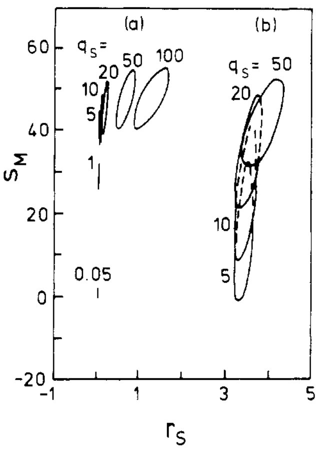


Figure 5. 95% joint confidence surface for the parameters of the complex-participation model applied to the styrene–maleic anhydride copolymerization. Cross sections in the plane of s_M – r_S for the following values of the remaining parameters: (a) s_S = 0; (b) s_S = 200. In all cases r_M = 0, q_M = 0, and K = 0.26 dm^3 mol^{-1}.

Application of the NLLS routine to the data of Bamford and Barb[2] gave similar results to those observed for our experimental data, including the strong correlations between the uncertainties of several of the parameters. The curve shapes for cross sections of the 95% confidence surface were similar and, as for the penultimate model, overlapped in some regions with those obtained from the data of this work.

Although the 95% confidence surface for the fit of the complex-participation model to the composition data of other systems, such as styrene–acrylonitrile, may be extensive, no strong correlations between the parameters have been observed.[34] The correlations in the case of the S–MAn system may be the result of the strongly alternating tendency of this copolymerization or the larger uncertainty in the polymer composition measurements. The similar behavior observed when fitting the data of Bamford and Barb shows that the choice of feed compositions has no noticeable effect.

Complex-Dissociation Model. The best fit of this model to the composition data is indistinguishable from that of the penultimate or complex-participation models. As for the complex-participation model, the minimum in the hypersurface is quite extensive due to a strong correlation between r_S and s_S'. The value of q_S' increases with increases in r_S and s_S'.

If r_M = q_M' = 0 and K = 0.26 dm^3 mol^{-1}, the complex-dissociation model is reduced to three adjustable parameters. The value of s_M' has no effect on the calculated composition or sequence distribution in this circumstance, since it is the ratio of rate constants of two reactions which have the same result—incorporation of a single S unit—and it is the only possible propagation step for a MAn-ended radical.

Even with the assumption of only three adjustable parameters, application of the *F*-test shows that a significant improvement of the complex-dissociation model over the terminal model cannot be distinguished. A selection of parameter sets within the hypersurface minimum is given in Table VI. A change in the value of K in the range 0.1–0.5 dm^3 mol^{-1} affects the position, but not the overall shape, of the joint confidence region of the parameters. The uncertainty in r_M and q_M' is relatively independent of all other parameters except s_M' and can be expressed for convenience as an appropriate error range: r_M = 0 ±

Table VI
Selected Examples of Parameter Sets Derived by Using the Complex-Dissociation Model for the Bulk Copolymerization of Styrene (S) and Maleic Anhydride (M) at 60 °C[a]

parameter	values				
r_S	0.0072	0.01	0.1	1	10
q_S'	0.031	0.035	0.15	1.1	10
s_S'	0	0.18	5.8	61	610
r_M	0	0	0	0	0
q_M'	0	0	0	0	0
s_M'	1	1	1	1	1
K^b	0.26	0.26	0.26	0.26	0.26
$s_Y{}^c$	0.0052	0.0052	0.0053	0.0054	0.0054

[a] Parameter sets with $r_M = q_M' = 0$ and $K = 0.26$ dm^3 mol^{-1} were chosen; the magnitude of s_M' does not affect the calculated copolymer composition under these conditions. [b] Units of K are dm^3 mol^{-1}. [c] Calculated assuming only three adjustable parameters.

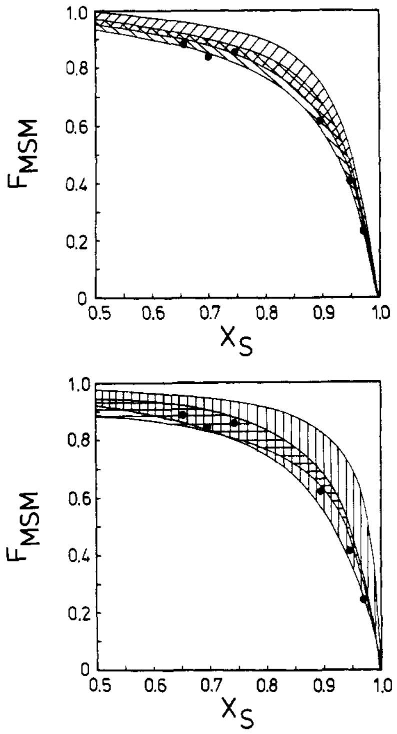


Figure 6. Triad fraction F_{MSM} vs. monomer feed for the copolymerization of styrene (S) and maleic anhydride (M). (X_S = mole fraction styrene in monomer feed). Shaded areas represent predictions from parameter sets within 95% confidence region of the best fit of the model to the composition data: right oblique lines, penultimate model; left oblique lines, complex-participation model; horizontal lines, complex-dissociation model; vertical lines, terminal model; (●) experimental points.

0.017 and $q_M' = 0 \pm 0.09$ at $s_M' = 1$; $r_M = 0 \pm 0.9$ and $q_M' = 0 \pm 1.7$ at $s_M' = 100$.

NLLS analysis of the data of Bamford and Barb gave similar results with regions of overlap between the 95% confidence surfaces for the two data sets. Application of the F-test showed that the complex-dissociation model provides a significant improvement over the terminal model (α >90%) for the data of Bamford and Barb, if the values of r_M, q_M', and K are assumed to be known independently.

Sequence Distributions. The measurement and assignment of the ^{13}C NMR methylene resonances of the styrene residues in these copolymers have been discussed previously.[24] These resonances appear to exhibit either diad or triad sequence effects, although the assignment to diad sequences is not consistent with the available evidence. Assignment to triad sequences, on the other hand, provides good agreement with the composition data obtained by independent measurements.

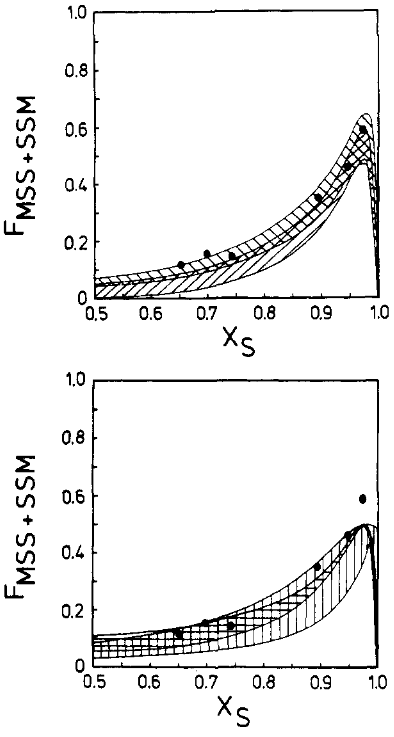


Figure 7. Triad fraction $F_{MSS+SSM}$ vs. monomer feed for the copolymerization of styrene (S) and maleic anhydride (M). Legend as for Figure 6.

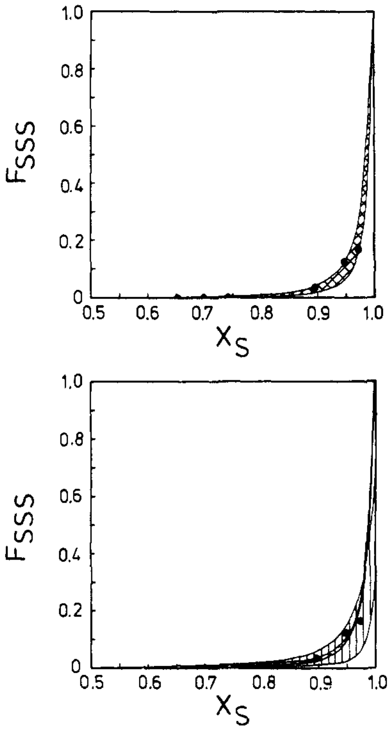


Figure 8. Triad fraction F_{SSS} vs. monomer feed for the copolymerization of styrene (S) and maleic anhydride (M). Legend as for Figure 6.

Sequence distributions predicted by the reactivity ratios of the four models considered here are shown for comparison in Figures 6–8. The range of sequence values for each model includes the predictions from representative parameter sets within the 95% confidence region of the best fit of each model to the composition data. A change in K in the range 0.1–0.5 dm^3 mol^{-1} for either complex

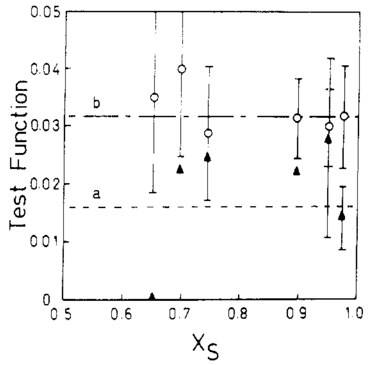


Figure 9. Functions of the styrene-centered triad fractions based on eq 3 and used to test the validity of the copolymerization model for the styrene–maleic anhydride copolymerization (X_S = mole fraction styrene in monomer feed): (▲) function *a*; (○) function *b*; (- - -) weighted mean of *a*; (-—-) weighted mean of *b*. Error bars used to calculate relative weights as shown. Points without error bars have negligible weight.

model does not affect the range of predicted sequence values. For the complex models there are many possible parameter sets which are consistent with the composition data, covering a wide range in the values of the individual parameters. However, the total range of sequence distributions predicted by these sets is quite narrow.

The triad fraction predictions are similar for each of the models and close to the experimental values based on the assignment of the ^{13}C NMR methylene resonances to triad fractions. The penultimate model provides slightly better agreement with the experimental values than the complex-participation model. The predictions of $F_{\mathrm{MSS+SSM}}$ for the complex-dissociation model can be distinguished from those of the other models in the region of $X_S = 0.9$.

It is unlikely that one could discriminate between the models considered here on the basis of the predicted triad fractions. It is even less likely that the models could be distinguished by predicted values of the diad fractions, F_{SS} and F_{MS}, since these variables contain less information than triad fractions.

If the calculation of triad fractions from the ^{13}C NMR methylene resonances is assumed to be correct, then these values can be used to test the adequacy of the different copolymerization models directly. Consider the two quantities *a* and *b*:

$$a = \frac{[\mathrm{M}]}{[\mathrm{S}]}\,\frac{2F_{\mathrm{SSS}}}{F_{\mathrm{MSS+SSM}}} \qquad b = \frac{[\mathrm{M}]}{[\mathrm{S}]}\,\frac{F_{\mathrm{MSS+SSM}}}{2F_{\mathrm{MSM}}} \qquad (3)$$

If $a = b$ = constant for all compositions, then the terminal model applies and $a = b = r_S$. If *a* and *b* are constant for all compositions, but $a \neq b$, then the penultimate model applies and $a = r_{\mathrm{SS}}$ and $b = r_{\mathrm{MS}}$. For the complex-dissociation model to apply, $a = b$, but the value may vary with composition. The complex-participation model requires that $a \neq b$ and *a* and *b* may vary with composition.

There is considerable scatter in the values of *a* and *b* across the monomer composition range as shown in Figure 9. However, in all cases *a* is less than *b*, which indicates that the terminal and complex-dissociation models cannot explain the data. The values of *a* and the values of *b* are constant within the experimental error for each of the sample points so the data may be explained by the penultimate or the complex-participation model.

The reactivity ratios for the penultimate model can be calculated from the weighted means of *a* and *b*: $r_{\mathrm{SS}} = 0.0161 \pm 0.01$ and $r_{\mathrm{MS}} = 0.0316 \pm 0.006$. Application of the *t*-test[35] shows that these values are significantly different to a level of confidence, $\alpha > 95\%$. Thus, the terminal model is rejected in comparison with the penultimate model. These reactivity ratios are in very good agreement with those predicted by the best fit of the penultimate model to the composition (see Figure 2).

Interpretations of copolymerization mechanisms based on these simple relationships can be misleading because of the large uncertainties in the experimental triad fractions. Moreover, because a ratio of triad fractions is involved, the uncertainties in *a* and *b* are dependent on the magnitudes of the triad fractions and may vary greatly across the composition range.

If assignment of the ^{13}C NMR methylene resonances to SS, *trans*-MS, *cis*-MS diads,[24] rather than triad sequences, is correct, then the relative contents of cis/trans M–S linkages in the copolymers may provide evidence for a particular copolymerization mechanism. In their study of copolymers of *N*-phenylmaleimide (NPM) and chloroethyl vinyl ether (CEVE), Olson and Butler[36] demonstrated that the fraction of NPM units having cis configuration in the copolymer correlated with the fraction of NPM monomer complexed to CEVE in the monomer feed.

Calculations based on diad assignments for the ^{13}C NMR methylene resonances in the present work show that there would be a decrease in the fraction of MAn having a cis configuration in the copolymer with decreasing MAn content of the monomer feed. However, the dependence of the cis content on the fraction of MAn monomer complexed to styrene in the feed would not be linear.

Conclusions

The experimental compositions and sequence distributions indicate a strong tendency to alternation in the copolymerization, in agreement with the composition data reported by some previous workers. The parameters estimated by fitting the composition data of this work and those estimated from the data of Bamford and Barb are in good agreement for all models. The uncertainty in the estimated parameters could be reduced by considering the overlap between the confidence surfaces for the two sets of data.

Reactivity ratios which gave good agreement with both the composition and triad fraction data were calculated for the penultimate and complex-participation models. The complex-dissociation model provided a good fit to the composition data, but this model, together with the terminal model, can be rejected since they are inconsistent with the triad fractions, assuming the ^{13}C NMR methylene resonances can be assigned to these triads.

Although the measurement of compositions or sequence distributions with better precision may lessen the uncertainty in the fitted parameters, it is unlikely that the penultimate and complex-participation models could be distinguished by considering only these facets of the S–MAn copolymerization. Other data are required, e.g., from rate measurements or from the effect of added donors or acceptors. However, the strong complexing effects of solvents, the larger number of unknown parameters in rate equations, and the difficulties of interpreting the effects of added donors or acceptors make conclusions based on these techniques unreliable at present.

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trometer is operated by the Brisbane NMR Centre.

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$$\frac{\mathrm{SS}(\hat{\theta})_{\mathrm{B}} - \mathrm{SS}(\hat{\theta})_{\mathrm{A}}}{p_{\mathrm{A}} - p_{\mathrm{B}}} \Bigg/ \frac{\mathrm{SS}(\hat{\theta})_{\mathrm{A}}}{n - p_{\mathrm{A}}} \geq \mathbf{F}_{\alpha(p_{\mathrm{A}}-p_{\mathrm{B}},\, n-p_{\mathrm{A}})}$$

where model B is a special case of model A. Model A provides a significant improvement over model B if the inequality is true.
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Free-Radical Copolymerization. 3. Determination of Rate Constants of Propagation and Termination for the Styrene/Methyl Methacrylate System. A Critical Test of Terminal-Model Kinetics[1]

Takeshi Fukuda,* Yung-Dae Ma, and Hiroshi Inagaki

Institute for Chemical Research, Kyoto University, Uji, Kyoto 611, Japan.
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ABSTRACT: The validity of terminal-model kinetics of free-radical copolymerization was critically tested against a complete set of experiments carefully carried out on the bulk copolymerization of styrene and methyl methacrylate at 40 °C. The experiments involved determining the copolymer composition, the initiation rate, the polymerization rate, the volume contraction factor, and the radical lifetime, and thus the rate constants of propagation and termination were individually evaluated as a function of monomer composition. In the rotating-sector experiments, a new system was introduced which automatically measures the migration rate of the dilatometer meniscus with high precision. The following results were obtained: The copolymer composition conforms to the terminal model (Mayo–Lewis equation) within experimental error, whereas the propagation rate constant is entirely different from what the model predicts. As far as numerical values are concerned, the experimental data are well represented by the penultimate model. As to the termination step, the previous results indicating large, composition-dependent values of the Walling cross-termination factor ϕ are erroneous, since the validity of the terminal model is assumed in those analyses. The observed values of the termination rate constant are well represented by the chemical model with $\phi = 1$ as well as by the North diffusion model.

Introduction

The composition curves of most free-radical copolymerizations are, at least to good approximations, represented by the terminal-model equation, commonly termed the Mayo–Lewis equation.[2] This is equivalent to saying that the ratios of the propagation rate constants (reactivity ratios) are effectively constant, independent of feed-monomer composition. It seems that this is one of the main reasons why no serious doubt has ever been thrown on the essential validity of terminal-model kinetics.

Recently, we[3] noted that the composition curve for a *p*-chlorostyrene–methyl acrylate system exhibits significant deviations from the terminal-model curve, which could be interpreted, at least numerically, by the penultimate model.[4] Hill et al.,[5] who studied the composition and the sequential distributions of a styrene–acrylonitrile system,

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