Macromolecules 1982, 15, 960–966

usually denotes the main-chain carbon next to the branch carbon as α.[9]

(9) Randall, J. C. *J. Polym. Sci., Polym. Phys. Ed.* **1973**, *11*, 275–287.

(10) Cais, R. E.; Spencer, C. P. *Eur. Polym. J.* **1982**, *18*, 189–198.

(11) Beckwith, A. L. J.; Blair, I.; Phillipou, G. *J. Am. Chem. Soc.* **1974**, *96*, 1613–1614.

(12) Starnes, W. H., Jr., private communication.

(13) Strunk, R. J.; DiGiacomo, P. M.; Aso, K.; Kuivila, H. G. *J. Am. Chem. Soc.* **1970**, *92*, 2849–2856.

(14) Starnes, W. H., Jr.; Schilling, F. C.; Plitz, I. M.; Cais, R. E.; Bovey, F. A. *Polym. Bull.* **1981**, *4*, 555–562.

(15) Bovey, F. A.; Schilling, F. C.; Starnes, W. H., Jr. *Polym. Prepr., Am. Chem. Soc., Div. Polym. Chem.* **1979**, *20* (2), 160–163.

Analysis of the Mechanism of Copolymerization of Styrene and Acrylonitrile

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

Department of Chemistry, University of Queensland, Brisbane, Australia 4067.

Received November 2, 1981

ABSTRACT: The copolymerization of styrene and acrylonitrile in bulk at 60 °C has been investigated by measurement of the copolymer/comonomer composition relationship and of the monomer sequence distributions using ^{13}C NMR. Alternative models for the mechanism of the copolymerization have been evaluated in the most general forms, with allowance for nonzero conversions, by deriving reactivity ratios from composition data and then comparing predicted and experimental sequence distributions. The system shows significant deviations from the terminal model. Compositions cannot differentiate between penultimate and complex participation models, both of which give significant improvement over the terminal model. The measured sequence distributions are quite close to the predictions of the penultimate model but substantially different from those of the complex participation model, showing clearly that the penultimate model is the most appropriate of the models considered. We have obtained $r_{SS} = 0.22_9$, $r_{AA} = 0.03_9$, $r_{AS} = 0.63_4$, and $r_{SA} = 0.09_1$. No significant improvement was observed with the antepenultimate model.

Introduction

There have been numerous studies of the copolymerization of styrene (S) and acrylonitrile (A). The terminal model for copolymerization has frequently been assumed to apply and values for the two reactivity ratios have been derived. Sandner and Loth[1] have recently summarized the reported values. However, some workers have interpreted their copolymer/comonomer composition relationships as deviating from the terminal model and considered the applicability of more sophisticated mechanisms. Thus, Ham[2] in 1954 interpreted apparent deviations from the terminal model on the basis of penultimate effects. Guyot and Guillot (1967–1968)[3,4] reported the necessity to introduce both penultimate and antepenultimate effects to describe their data for the copolymerization in dimethylformamide and toluene solutions. More recently, Sandner and Loth (1976)[1] investigated the bulk copolymerization and claimed that penultimate and antepenultimate effects were not the actual causes of deviation from the terminal model. Sandner et al. also reported[5] an equilibrium constant, K_x ($\approx$0.5), for the formation of a 1:1 comonomer complex at 60 °C (concentrations in mole fractions) and suggested that complex participation was involved in the copolymerization. Kucher et al.[6] have presented a kinetic treatment for the copolymerization from which they deduce that the experimental rates of polymerization can be fitted by participation of a comonomer complex, which is 8 and 13 times more reactive in propagation than styrene and acrylonitrile, respectively.

Since Seiner and Litt[7] published the first mathematical analysis of the complex participation model for copolymerization in 1971, it has been possible to evaluate quantitatively whether this model is appropriate to a particular copolymerization. Most studies have used limitations on the model for calculating the reactivity ratios in order to avoid the complicated expression for copolymer composition developed by Seiner and Litt. However, Pittman and Rounsefell[8] demonstrated that the reactivity ratios and the equilibrium constant for complex formation could be obtained by computer techniques using the unrestricted form of Seiner and Litt's equation.

Recently, we reported an alternative to Seiner and Litt's method of analysis of the complex participation model.[9] Moreover, we have demonstrated how the monomer sequence distribution in the copolymer as well as the copolymer composition can be related to the equilibrium constant, six different reactivity ratios, and the comonomer feed composition.

Most investigations for the mechanism of copolymerization involve an analysis of the composition of the initial copolymers formed, but it is often difficult to distinguish between the various models for copolymerization on the basis of their fit to the composition data alone. The distribution of monomer sequences in the copolymer contains more information about the polymerization system than the copolymer composition (although the sequence distributions cannot be determined at present with the same accuracy). This information, together with copolymer composition for copolymers prepared over the range of comonomer composition, should discriminate between the terminal, penultimate, and complex participation models. Recent developments in the characterization of polymer microstructure mean that sequence distributions can be obtained for a variety of copolymers.

In a recent analysis of the acrylonitrile–styrene copolymerization system, we demonstrated[10] that, by using sequence distribution information, it would be possible to distinguish between the penultimate and complex participation models, both of which could explain the polymer composition data.

The sequence distributions of acrylonitrile–styrene copolymers were analyzed by ^{13}C NMR spectroscopy by Schaefer (1971)[11] and Stejskal and Schaefer (1974),[12] who determined triad fractions and number-average sequence lengths. Subsequently, Sandner and co-workers[13] analyzed the spectra for dyad fractions as well as styrene- and acrylonitrile-centered triad fractions. Recently, Pichot and

0024-9297/82/2215-0960$01.25/0

Table I

Comonomer (X_S) and Copolymer (Y_S) Compositions Expressed As Mole Fraction of Styrene with Conversions and Experimental Triad Fractions for the Copolymerization of Acrylonitrile (A) and Styrene (S) at 60 °C in Bulk

				triad fractions[d]					
				S centered			A centered		
		Y_S							
X_S	conv,[a] %	b	c	SSS	SSA + ASS	ASA	AAA	AAS + SAA	SAS
0.021	0.2	0.234							
0.053	0.4	0.333							
0.104	1.2	0.406	0.400	0.00	0.15	0.85	0.11	0.55	0.34
0.221	1.8	0.476	0.485	0.00	0.27	0.73	0.00	0.37	0.63
0.314	3.0	0.510	0.509	0.02	0.34	0.64	0.01	0.29	0.69
0.416	2.2	0.542	0.548	0.06	0.42	0.52	0.00	0.22	0.78
0.530	2.3	0.582	0.597	0.07	0.41	0.42	0.00	0.17	0.83
0.631	0.8	0.627	0.610	0.12	0.56	0.32	0.00	0.12	0.88
0.696	1.2	0.649	0.638	0.16	0.59	0.25	0.00	0.08	0.92
0.802	0.7	0.705	0.693	0.30	0.55	0.15	0.00	0.06	0.94
0.889	0.5	0.772	0.760	0.44	0.50	0.06	0.00	0.00	1.00
0.939	0.3	0.829	0.827	0.61	0.37	0.02	0.00	0.00	1.00

[a] Weight percent of total monomer feed. [b] From % N elemental analysis; estimated error in Y_S ±1.6%. [c] From number-average sequence lengths: $\bar{n}_S/(\bar{n}_S + \bar{n}_A)$, calculated from triad fractions. [d] From ^{13}C NMR; estimated absolute error in triad fraction ±0.03.

Pham[14] confirmed the triad assignments of Sandner et al. and attempted to assign all the carbon resonances. They also calculated reactivity ratios for the terminal model from their sequence distribution information. Arita et al.[15] have also calculated the triad fractions from the ^{13}C NMR and compared these with the predictions of the terminal model.

The aim of the present work has been to analyze the bulk copolymerization of acrylonitrile and styrene by using experimentally determined polymer compositions and sequence distributions together with computational techniques described previously.[10] On the basis of this analysis it should be possible to evaluate the applicability of the three models in describing this copolymerization.

Experimental Section

Materials. Acrylonitrile and styrene were distilled at reduced pressure under nitrogen at 60 °C. 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. The required amounts of monomers and initiator 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 3%. For these low conversions, the copolymer formed remained soluble in the reaction mixture in all cases. The polymers were recovered by addition of the solution to a tenfold excess of methanol and purified twice by reprecipitation from chloroform solution into methanol. Dimethyl sulfoxide was used as a solvent for polymers of high acrylonitrile content. The purified polymers were dried in vacuo at 60 °C for 16 h.

Characterization. The compositions of the copolymers were determined (i) by duplicate percent nitrogen analysis by the micro-Kjeldahl technique and (ii) from the relative intensities of the aromatic (S units) and methylene and methine (A + S) resonances in the ^{1}H NMR spectra. These spectra were obtained on a JEOL PS100 NMR spectrometer at 50 °C, with $CDCl_3$ or Me_2SO-d_6 as solvent.

The pulse-FT ^{13}C NMR spectra were recorded on a JEOL FX100 spectrometer (25.2 MHz) at 50 °C in 10-mm-o.d. sample tubes. Solutions up to 25 w/v % in Me_2SO-d_6 or $CDCl_3$ were used. Spectra were run with either (i) a 1-s pulse cycle time and 60° pulse angle or (ii) a 90° pulse angle and 10-s pulse cycle. No difference was observed in the relative intensities of the triad peaks. (Relaxation time measurements showed that 10 s is longer than $5T_1$ for the slowest relaxing carbon atom.)

Results and Discussion

The experimentally determined copolymer compositions are given in Table I together with the comonomer feed compositions and the conversions. The ^{1}H NMR results showed good agreement with the compositions determined from % N elemental analysis. The % C and % H analyses proved unsatisfactory for determination of polymer composition because of very poor reproducibility. The compositions are in agreement with those reported by Sandner et al.[1] for the bulk polymerization at 60 °C and by Fordyce and Chapin[16] and Smith[17] for the polymerization at 75 °C.

The ^{13}C NMR spectrum of the copolymer has previously been reported to exhibit triad sequence distribution information.[11-14] Both the quaternary aromatic carbon resonance of the styrene residue (139–144 ppm relative to Me_4Si) and the nitrile carbon resonance of the acrylonitrile residue (117–120 ppm) are suitable for sequence analysis (Figure 1). The assignments of the resonances within both groups can be deduced directly from the dependence of the component resonances on polymer composition, as is clearly shown in Figure 1; they are in agreement with those reported previously.

The resolution of the major resonances in each group is satisfactory for spectrometer integration of the relative intensities and these results were confirmed by cutting and weighing of the peaks. The triad fractions are given in Table I. The fine structure on the major peaks could be the result of either tacticity or pentad effects. There is insufficient evidence to separate these effects, which should both result in chemical shift differences about an order of magnitude less than shifts resulting from triad effects. Pichot and Pham[14] have attempted to assign the fine structure on the basis of tacticity.

For the terminal, penultimate, and complex participation models it is possible to calculate the number-fraction sequence length distribution and the number-average sequence length of each comonomer from these ^{13}C NMR resonances. From the ratio of the average sequence lengths of the two monomers, the polymer composition can be calculated and the results of this calculation are also given in Table I. The agreement with the compositions calculated from elemental analysis is quite good, confirming the assignments of the triad resonances and the accuracy of the integrations.

Testing of Alternative Models

In a critical review of methods of determining reactivity ratios for the terminal model, Tidwell and Mortimer[18] pointed out the defects of the different linear methods and suggested the use of a nonlinear least-squares procedure. The importance of the nonlinear analysis was reiterated

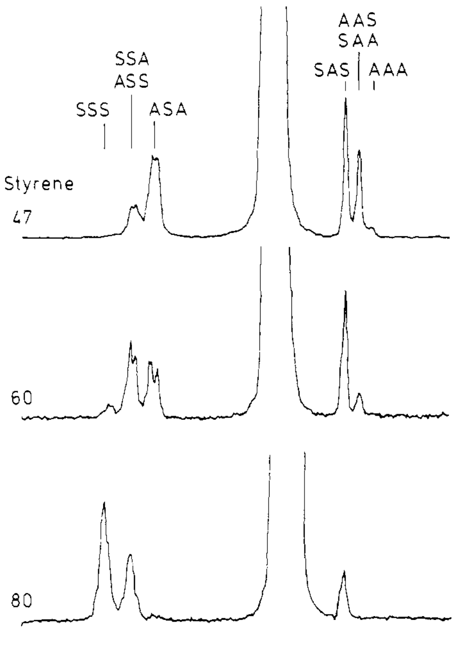

Figure 1. ^{13}C NMR spectra of the aromatic and nitrile carbon region of styrene (S) and acrylonitrile (A) copolymers showing the variations of peak intensities with copolymer composition. Triad assignments are shown at the top of the figure.

by McFarlane et al.[19] in a hypothetical study which compared six common linear methods of analyzing copolymer composition data with the nonlinear technique. Computational procedures have also been described[20] that use an integrated form of the terminal model equation and take into account errors in both copolymer and comonomer feed composition.

The nonlinear search method we have used for obtaining "best estimates" of the reactivity ratios of the complex participation model has been described earlier.[9] An iterative procedure within the computer program allows us to take account of the effect of conversion on the polymer composition. The error involved in the values of the monomer feed composition is considered small enough that it is only necessary to consider the error in the polymer compositions when determining reactivity ratios. The sensitivity of the estimated reactivity ratios to errors in polymer composition and percent conversion have been investigated for our computational procedure.[21] This nonlinear least-squares procedure was also used to obtain reactivity ratios for the terminal and penultimate models.

Terminal and Penultimate Models. The best fits of these two models to the experimental polymer compositions are shown in Figure 2. Only a small difference separates these two curves, though the penultimate model is in better agreement with the experimental points across the entire composition range, with no discernible structure to the deviations of the experimental points about the fitted line.

The corresponding reactivity ratios based on the definitions given in Table II are given in Table III.

The penultimate model composition equation

$$\frac{m_S}{m_A} = \frac{1 + r_{AS}(X_S/X_A)(r_{SS}X_S + X_A)/(r_{AS}X_S + X_A)}{1 + r_{SA}(X_A/X_S)(r_{AA}X_A + X_S)/(r_{SA}X_A + X_S)}$$

where m_S/m_A is the mole ratio of the monomer units in the polymer and X_S and X_A are the mole fractions of the monomers in the feed, has not previously been applied to the acrylonitrile–styrene system in its most general form.

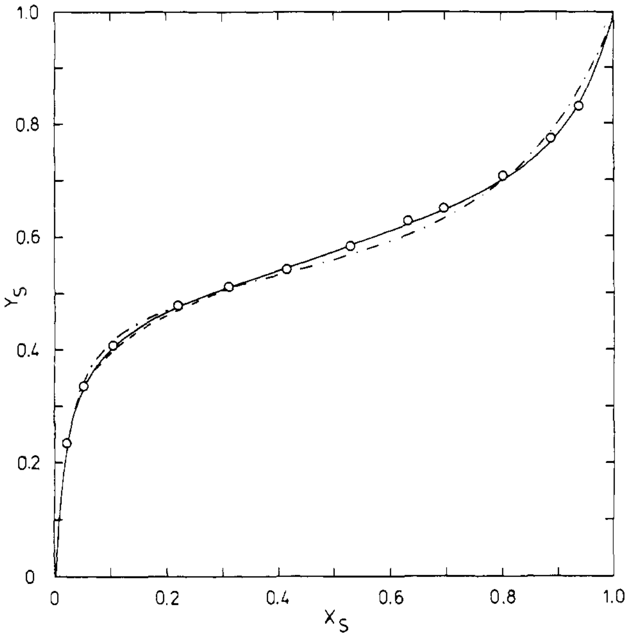

Figure 2. Copolymer composition curve for the copolymerization of acrylonitrile and styrene in bulk at 60 °C. (Y_S = mole fraction styrene in copolymer; X_S = mole fraction styrene in monomer): (○) experimental data; (—) penultimate model and complex model with no restriction (case 1); (– – –) complex model with K_x fixed at 0.52 (case 2); (–·–) terminal model.

Table II
Kinetic Equations and Reactivity Ratio Definitions for the Three Polymerization Models

Terminal Model

$\sim S\cdot + S \longrightarrow \sim S\cdot$	k_{SS}
$\sim S\cdot + A \longrightarrow \sim A\cdot$	k_{SA}
$\sim A\cdot + S \longrightarrow \sim S\cdot$	k_{AS}
$\sim A\cdot + A \longrightarrow \sim A\cdot$	k_{AA}

$r_S = k_{SS}/k_{SA}$ $\quad$ $r_A = k_{AA}/k_{AS}$

Complex Model

4 propagation steps of the terminal model above, plus

$\sim S\cdot + \overline{AS} \longrightarrow \sim S\cdot$	$k_{S\overline{AS}}$
$\sim S\cdot + \overline{SA} \longrightarrow \sim A\cdot$	$k_{S\overline{SA}}$
$\sim A\cdot + \overline{AS} \longrightarrow \sim S\cdot$	$k_{A\overline{AS}}$
$\sim A\cdot + \overline{SA} \longrightarrow \sim A\cdot$	$k_{A\overline{SA}}$

$$S + A \overset{K_x}{\rightleftharpoons} \overline{SA}$$

$r_S = k_{SS}/k_{SA}$ $\quad$ $r_A = k_{AA}/k_{AS}$
$p_S = k_{S\overline{SA}}/k_{S\overline{AS}}$ $\quad$ $p_A = k_{A\overline{AS}}/k_{A\overline{SA}}$
$s_S = k_{S\overline{AS}}/k_{SA}$ $\quad$ $s_A = k_{A\overline{SA}}/k_{AS}$

Penultimate Model

$\sim SS\cdot + S \longrightarrow \sim SS\cdot$	k_{SSS}
$\sim SS\cdot + A \longrightarrow \sim SA\cdot$	k_{SSA}
$\sim AS\cdot + S \longrightarrow \sim SS\cdot$	k_{ASS}
$\sim AS\cdot + A \longrightarrow \sim SA\cdot$	k_{ASA}
$\sim SA\cdot + A \longrightarrow \sim AA\cdot$	k_{SAA}
$\sim SA\cdot + S \longrightarrow \sim AS\cdot$	k_{SAS}
$\sim AA\cdot + A \longrightarrow \sim AA\cdot$	k_{AAA}
$\sim AA\cdot + S \longrightarrow \sim AS\cdot$	k_{AAS}

$r_{SS} = k_{SSS}/k_{SSA}$ $\quad$ $r_{AA} = k_{AAA}/k_{AAS}$
$r_{AS} = k_{ASS}/k_{ASA}$ $\quad$ $r_{SA} = k_{SAA}/k_{SAS}$

With r_{AA} and r_{SA} close to zero, the denominator in the above equation reduces to unity at high styrene fractions in the monomer mixture. The resulting two-variable equation has been solved linearly to yield penultimate reactivity ratios for styrene: r_{SS} = 0.30 and r_{AS} = 0.45 in bulk[2] and r_{SS} = 0.30 and r_{AS} = 0.55 in toluene solution.[3]

Table III
Reactivity Ratios[a] Derived Using the Terminal or Penultimate Models for the Bulk Copolymerization of Acrylonitrile (A) and Styrene (S) at 60 °C

parameter	value	error range[b]
	Terminal Model	
r_A	0.053	0.04-0.07
r_S	0.331	0.27-0.42
S_y[c]	1×10^{-2}	
	Penultimate Model	
r_{AA}	0.039	0.035-0.045
r_{SA}	0.091	0.079-0.110
r_{AS}	0.634	0.57-0.73
r_{SS}	0.229	0.21-0.26
S_y[c]	5×10^{-3}	

[a] For definitions of reactivity ratios, see Table II. [b] Error range calculated as described in ref 9. [c] Standard error, determined according to the equation $S_y = [\Sigma(y_e - y_c)^2/(n - p)]^{1/2}$, where y_e is the experimental mole fraction in the polymer, y_c is the calculated mole fraction in the polymer, n is the number of experimental points, and p is the number of variable parameters in model.

Penultimate reactivity ratios for acrylonitrile have also been determined by substituting the two reactivity ratios for styrene already calculated into the general equation. The reactivity ratios calculated by Guyot and Guillot,[4] $r_{AA} = 0.33$ and $r_{SA} = 0.08$, in dimethylformamide solution using this approach are quite different from those reported above. The initial polymer compositions reported by Guyot and Guillot differ substantially, however, from those found in bulk polymerizations here and by other workers.

By using the general form of the penultimate model equation in a nonlinear fit, we have obtained much better agreement with the experimental polymer compositions than the previous workers and have found significant penultimate effects for both types of chain end radicals. A value of $S_y = 5 \times 10^{-3}$ was estimated for the standard error in the mole fraction composition of the copolymers, using the definition of S_y given in Table III. This value compares well with the internal experimental error in the polymer compositions of 4×10^{-3} estimated from repeated measurements. The standard error from the best fit of the terminal model is $S_y = 1 \times 10^{-2}$.

Sandner and Loth[1] ruled out the penultimate model because of poor agreement with the experimental data for monomer feeds containing more than 75% in styrene. This rejection does not seem justified since the authors did not calculate reactivity ratios based on their own data but only tested the reactivity ratios for styrene reported by Ham[2] for the experimental data of Fordyce and Chapin.[16]

F Test. When fitting linearized equations for the compositions based on the terminal model (e.g., Fineman–Ross[22] or Kelen–Tüdös[23] equations), workers have generally used deviations from linearity as evidence for penultimate effects. It has been shown, however, that curvature in these plots may be caused by random analytical error, because of the error structure of the transformed variables, and that it may not be justified to use a higher order model.[24] Objective tests such as the statistical **F** test[25] provide a better assessment of the accuracy of copolymerization models but have rarely been used.

The test is based on the ratio **F** of the residual sums of the squares (SS) of two models A and B, where model B is a special case of model A, according to the formula

$$\mathbf{F} = \frac{(SS_B - SS_A)/(p_A - p_B)}{SS_A/(n - p_A)}$$

where p_A and p_B are the number of parameters for each model and n is the number of experimental observations. The ratio **F** is compared with critical values of $\mathbf{F}(\alpha)$ for selected probability levels α which are available in tables.[25]

Table IV
Reactivity Ratios[a] and Equilibrium Constant Derived Using the Complex Participation Model for the Bulk Copolymerization of Acrylonitrile (A) and Styrene (S) at 60 °C

parameter	case 1[b]	error range[d]	case 2[c]	error range[d]
r_A	0.0221	0.020-0.024	0.0508	0.046-0.056
r_S	1.20	1.1-1.3	0.505	0.46-0.55
p_A	5.80	5.3-6.3	7.92	6.5-9.5
p_S	19.7	18.7-20.8	30.1	25-35
s_A	0.0718	0.067-0.077	0.170	0.14-0.20
s_S	0.290	0.27-0.31	0.140	0.12-0.16
K_x[e]	9.98	8.8-11.5	0.52	
S_y[f]	4×10^{-3}		6×10^{-3}	

[a] For definition of reactivity ratios, see Table II. [b] All parameters allowed to assume "best values". [c] K_x fixed at 0.52. Six reactivity ratios allowed to assume "best values". [d] Error range calculated as described in ref 9. [e] K_x defined in terms of mole fractions. [f] Standard error definition given in Table III.

Application of this test in a comparison of the fits obtained to the experimental compositions in Table I using the penultimate and terminal models shows that the penultimate model provides a significant improvement in the fit with a level of probability $\alpha = 99.5\%$. The terminal model is therefore rejected as inadequate in comparison with the penultimate model.

Many copolymerization systems of nitrile monomers with styrene exhibit deviations from simple terminal model behavior. This has generally been explained on the basis of repulsive electrostatic forces between the highly polar nitrile groups affecting the addition of a nitrile monomer to a polymer chain containing a nitrile unit near the growing end.[26] This is consistent with the reactivity ratios reported here.

Complex Model. The complex participation model can be fitted to the experimental copolymer/comonomer composition relationship by allowing the six reactivity ratios together with the equilibrium constant to assume those values that best fit the data. A completely general analysis of this kind leads to the estimates given in Table IV (case 1). The resulting polymer composition curve is shown in Figure 2. The position of the curve is indistinguishable from that calculated as the best fit of the penultimate model to the experimental data. In determining the equilibrium constant for complex formation between acrylonitrile and styrene using UV spectroscopy, Sandner et al.[5] found substantial deviations from the linear Benesi–Hildebrand or Scott relationships. Thus, the certainty of their reported value of $K_x = 0.52$ at 60 °C may not be very high. However, the value of $K_x = 10$ predicted by the best fit of our composition data using the complex participation model is much larger (and larger than expected on the basis of K values measured in similar systems).

The composition data were also fitted by allowing only the six reactivity ratios to vary and keeping the equilibrium constant fixed at 0.52. The resulting parameters of the best fit are given in Table IV as case 2. The calculated copolymer composition curve is almost indistinguishable from that for the penultimate model or complex model (case 1) (Figure 2). By application of the **F** test in comparison with the terminal model, the complex participation model is shown to provide a significant improvement in the fit to the experimental compositions, with a level of probability $\alpha = 99.5\%$ for both case 1 and case 2. Thus, on the basis of polymer composition data alone it is not possible to discriminate between the penultimate and complex participation models.

An examination of the reactivity ratios in Table IV derived for either case 1 or case 2 of the complex participation model shows that, for addition to an acrylonitrile radical on the chain end, styrene addition is favored over acrylonitrile addition for the free monomer ($r_A < 1$), whereas the complex prefers to add from the acrylonitrile direction ($p_A > 1$). This may be explained on the basis that it is more favorable to have a styryl radical as the resultant radical. For addition to a styrene radical on the chain end the situation is different. The rates of acrylonitrile and styrene addition are comparable for the free monomers ($r_S \approx 1$), whereas addition of the complex from the styrene end to form an acrylonitrile radical is the most favored step ($p_S > 1$). This could be taken as indicating that the complex model is physically unrealistic.

From a kinetic analysis of the acrylonitrile–styrene system, Kucher et al.[6] concluded that participation of a comonomer complex was consistent with their experimental rates of copolymerization. The complex was estimated to be 8 and 13 times more reactive than styrene and acrylonitrile, respectively. These results are questionable, however, because of the simplifying assumptions used in the calculations. For example, $k_{\overline{\mathrm{SSA}}}$ and $k_{\overline{\mathrm{AAS}}}$ were assumed to be neglibible and the values of r_S and r_A for the complex participation equation were calculated from a terminal model analysis, which had been shown not to be in agreement with the experimental data. The analysis of Sandner and Loth[1] from copolymer composition data is also inconclusive about the participation of comonomer complexes because the simplifications used in the calculations are not justified.

Sequence Distributions. The reactivity ratios for the various models that give the best fits to the composition data can be used to predict the sequence distributions in the copolymer.[9,27] For a wide range of comonomer feed compositions the penultimate and complex participation models give quite different predictions for the distribution. This is true for both the styrene-centered and acrylonitrile-centered sequences. For the three models considered here (terminal, penultimate, and complex), the number-fraction sequence length distributions of the two monomers can be calculated from the areas under the ^{13}C NMR resonance peaks for the appropriate triads. The relationships are of the same mathematical form for each of these models:

$$N_{\mathrm{ASA}} = \frac{2A_{(\mathrm{ASA})}}{2A_{(\mathrm{ASA})} + A_{(\mathrm{ASS+SSA})}}$$

$$N_{\mathrm{ASSA}} = \frac{A^2_{(\mathrm{ASS+SSA})}}{(2A_{(\mathrm{ASA})} + A_{(\mathrm{ASS+SSA})})(2A_{(\mathrm{SSS})} + A_{(\mathrm{ASS+SSA})})}$$

and

$$N_{\mathrm{AS}_n\mathrm{A}} = N_{\mathrm{ASSA}}P^{n-2} \qquad n > 2$$

where

$$P = \frac{2A_{(\mathrm{SSS})}}{2A_{(\mathrm{SSS})} + A_{(\mathrm{ASS+SSA})}}$$

where $N_{\mathrm{AS}_n\mathrm{A}}$ is the number fraction of styrene sequences of length n when $n > 2$ and $A_{(\mathrm{ASA})}$, $A_{(\mathrm{ASS+SSA})}$, and $A_{(\mathrm{SSS})}$ are the peak areas for the triads ASA, ASS + SSA, and SSS, respectively. Analogous equations apply for the comonomer, acrylonitrile.

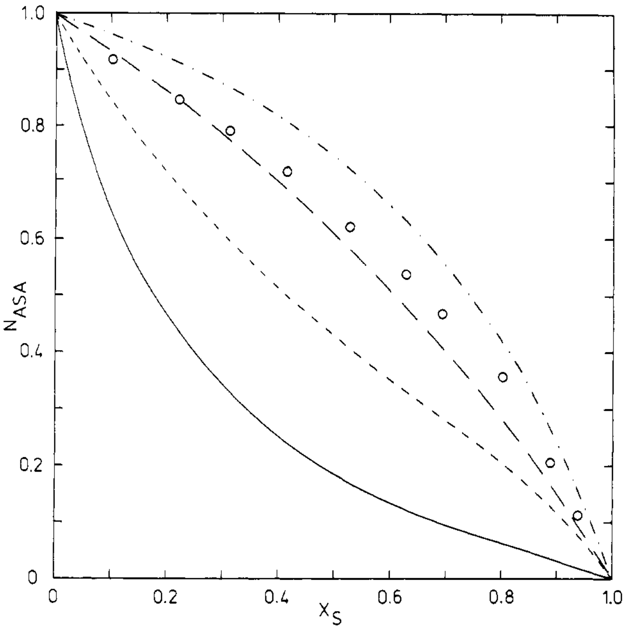

Figure 3. Number fraction of single styrene sequences in copolymers of acrylonitrile and styrene: (○) experimental points; (—) complex model with no restriction (case 1); (- - -) complex model with K_x fixed at 0.52 (case 2); (— —) penultimate model; (-·-) terminal model.

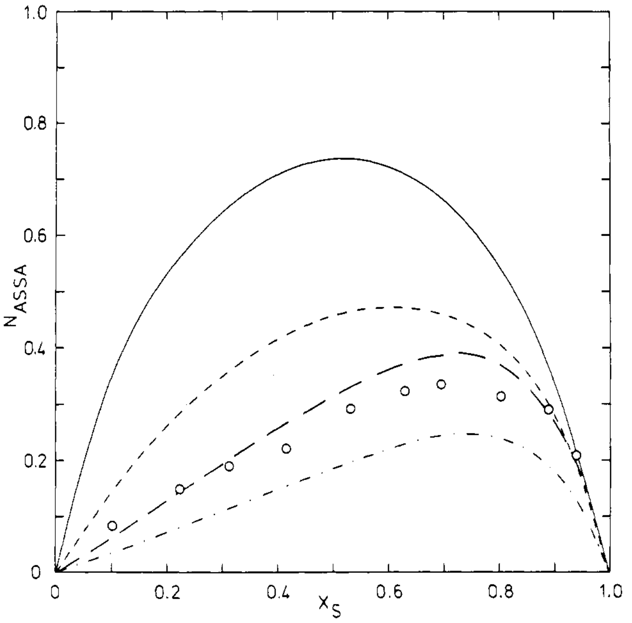

Figure 4. Number fraction of styrene sequences of length two in copolymers of acrylonitrile and styrene: symbols as for Figure 3.

The complete number-fraction sequence length distribution contains all the information about the average distribution of a particular monomer unit in the chain. This information is condensed into only three triad fractions. For this reason we believe it is worthwhile to consider the distribution of each sequence length when differentiating between these three copolymerization models. The distributions for sequences of one- and two-unit length for both monomers have been calculated and are shown in Figures 3–6, where they are compared with the predictions from the different models.

The copolymerization of styrene and acrylonitrile is particularly suitable for utilization of monomer sequence

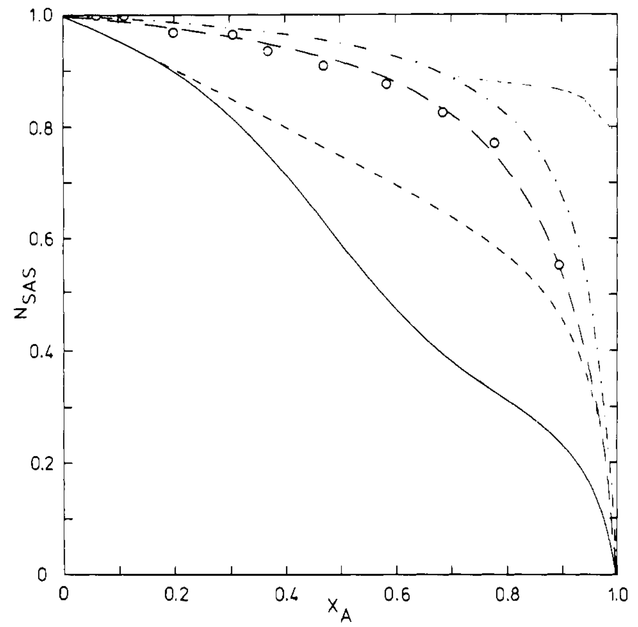

Figure 5. Number fraction of single acrylonitrile sequences in copolymers of acrylonitrile and styrene: symbols as for Figure 3.

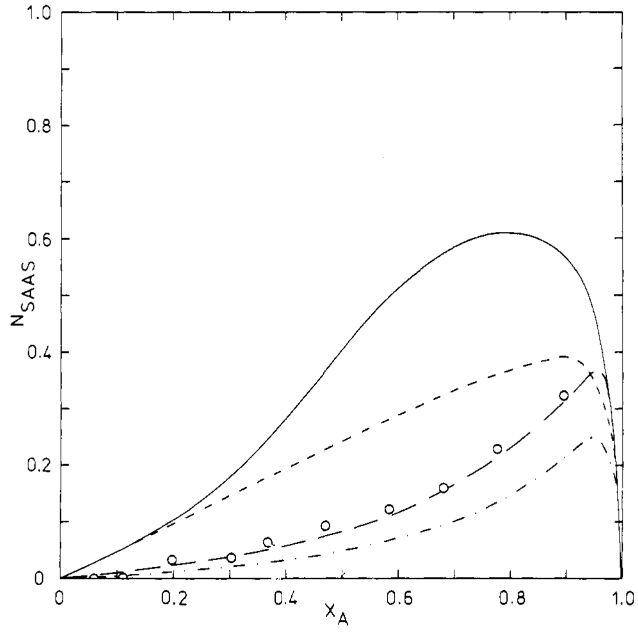

Figure 6. Number fraction of acrylonitrile sequences of length two in copolymers of acrylonitrile and styrene: symbols as for Figure 3.

distributions to distinguish between alternative polymerization mechanisms. The copolymer/comonomer composition relationships calculated by the different models are very similar, but the corresponding predictions for the monomer sequence distributions differ greatly. The experimental determinations of the number fractions of ASA and ASSA sequences shown in Figures 3 and 4 cannot be reconciled with the complex participation model (or the terminal model) but give a good fit to the penultimate model. Even better agreement with the penultimate model, but not any of the other models, is shown for the SAS and SAAS sequences in Figures 5 and 6. Similar agreement with predictions based on the penultimate model is demonstrated for the distribution of longer sequences of both acrylonitrile and styrene. A comparison of the triad fractions calculated from the ^{13}C NMR peak areas with those predicted by the three models also shows good agreement with the penultimate model, as expected.

The triad fractions calculated by Arita et al.[15] from the ^{13}C NMR agree with those shown in Table I within experimental error. These workers claim that the distributions coincide sufficiently with the predictions of the terminal model, but the correspondence is no better than that shown for the terminal model in Figures 3–6. Moreover, we have demonstrated that the penultimate model provides much better agreement with the experimental sequence distributions.

Thus, we have obtained four reactivity ratios based on the penultimate model that provide good agreement with both copolymer compositions and monomer sequence distributions for the copolymerization of acrylonitrile and styrene in bulk at 60 °C. We have demonstrated that, although the complex participation model will give a set of reactivity ratios that provide an adequate fit to the copolymer compositions, they do not provide a satisfactory fit to the sequence distributions for this system. Although weak molecular complexes are formed in the comonomer mixture,[5] they do not appear to participate significantly in the copolymerization.

Other Factors

There are various other procedures that have been reported as tests for complex participation in copolymerization systems. In particular, the absence of a change in polymer composition with significant change in overall monomer concentration has been used to demonstrate that complexes are not involved in propagation.[28] Dilution should decrease the relative concentrations of the comonomer complex and enhance the participation of free monomer in the copolymerization. It would be difficult to interpret similar dilution experiments in the copolymerization of styrene and acrylonitrile because there are few solvents in which the system remains homogeneous even at low conversion. Experiments in solution may also be complicated by the formation of monomer–solvent complexes.[29] The marked effect of the nature of the solvent on the composition of these copolymers has been reported.[30] Guyot and co-workers[31] have discussed the possibility of acrylonitrile–dimethylformamide association by dipole–dipole interaction or mixing effects between styrene and acrylonitrile involving preferential adsorption onto the polymer as an explanation for the peculiarities in dimethylformamide and toluene solution polymerizations.

This study has been concerned with choosing between the terminal, penultimate, and complex participation models for the copolymerization of styrene and acrylonitrile. Although the penultimate model provides good agreement with all the experimental data, it is possible that another mechanism of copolymerization provides a better explanation of this system. For bulk polymerizations of these two monomers of different polarity the nature of the medium will change across the total comonomer composition range. However, we have found no evidence in the comparison between predicted and experimental data to lead us to believe this effect is significant.

For polymerizations in toluene solution, Guyot and Guillot[3] found it necessary to incorporate antepenultimate effects for addition to the $\sim SS\cdot$ radical in order to explain the experimental data at the extreme styrene end of the monomer composition range. The authors used a simplified form of the antepenultimate model composition equation in order to analyze their data in a linear form. We have investigated the completely general antepenultimate model over the entire monomer composition range for our bulk copolymerizations and found that it gives no significant improvement over the penultimate model in fitting the experimental composition data. If the polymer compositions would be determined with greater accuracy, then the antepenultimate model might be found to provide a better fit.

The small, systematic deviations from the predictions of the penultimate model for the ASA and ASSA sequences shown in Figures 3 and 4 may arise from the quantitative analysis of the ^{13}C NMR spectra. Alternatively, they may indicate a small contribution from comonomer complexes. A decrease in the temperature of the comonomer mixture will favor complex formation. Evidence for a variation in the participation of comonomer complexes with copolymerization temperature based on various measurements of polymer microstructure has been reported for a number of systems.[32] We are presently investigating the copolymerization of styrene and acrylonitrile at lower temperatures, where complex participation should be enhanced.

Acknowledgment. We thank the Australian Research Grants Committee and the Australian Institute of Nuclear Science and Engineering for supporting our research. We are indebted to the National NMR Centre for some of the ^{13}C NMR spectra.

References and Notes

(1) Sandner, B.; Loth, E. *Faserforsch. Textiltech.* **1976**, *27*, 571.
(2) Ham, G. E. *J. Polym. Sci.* **1954**, *14*, 87.
(3) Guyot, A.; Guillot, J. *J. Macromol. Sci., Chem.* **1967**, *A1*, 793.
(4) Guyot, A.; Guillot, J. *J. Macromol. Sci., Chem.* **1968**, *A2*, 889.
(5) Sandner, B.; Kraemer, S.; An, B. T. *Acta Polym.* **1979**, *30*, 265.
(6) Kucher, R. V.; Zaitsev, Yu. S.; Bondarenko, A. V.; Zaitseva, V. V. *Theor. Exp. Chem. (Engl. Transl.)* **1979**, *14*, 631.
(7) Seiner, J. A.; Litt, M. *Macromolecules* **1971**, *4*, 308.
(8) Pittman, C. U.; Rounsefell, T. D. *Macromolecules* **1975**, *8*, 46.
(9) Cais, R. E.; Farmer, R. G.; Hill, D. J. T.; O'Donnell, J. H. *Macromolecules* **1979**, *12*, 835.
(10) Farmer, R. G.; Hill, D. J. T.; O'Donnell, J. H. *J. Macromol. Sci., Chem.* **1980**, *A14*, 51.
(11) Schaefer, J. *Macromolecules* **1971**, *4*, 107.
(12) Stejskal, E. O.; Schaefer, J. *Macromolecules* **1974**, *7*, 14.
(13) Sandner, B.; Keller, F.; Roth, H. *Faserforsch. Textiltech.* **1975**, *26*, 278.
(14) Pichot, C.; Pham, Q. T. *Makromol. Chem.* **1979**, *180*, 2359.
(15) Arita, K.; Ohtomo, T.; Tsurumi, Y. *J. Polym. Sci., Polym. Lett. Ed.* **1981**, *19*, 211.
(16) Fordyce, R. G.; Chapin, E. C. *J. Am. Chem. Soc.* **1947**, *69*, 581.
(17) Smith, W. V. *J. Am. Chem. Soc.* **1948**, *70*, 2177.
(18) Tidwell, P. W.; Mortimer, G. A. *J. Macromol. Sci., Rev. Macromol. Chem.* **1970**, *C4*, 281.
(19) McFarlane, R. C.; Reilly, P. M.; O'Driscoll, K. F. *J. Polym. Sci., Polym. Chem. Ed.* **1980**, *18*, 251.
(20) Van der Meer, R.; Linssen, H. N.; German, A. L. *J. Polym. Sci., Polym. Chem. Ed.* **1978**, *16*, 2915.
(21) Farmer, R. G.; Hill, D. J. T.; O'Donnell, J. H.; O'Sullivan, P. W., submitted for publication.
(22) Fineman, M.; Ross, S. D. *J. Polym. Sci.* **1950**, *5*, 259.
(23) Kelen, T.; Tüdös, F. *J. Macromol. Sci., Chem.* **1975**, *A9*, 1.
(24) McFarlane, R. C.; Reilly, P. M.; O'Driscoll, K. F. *J. Polym. Sci., Polym. Lett. Ed.* **1980**, *18*, 81.
(25) Wilson, E. B. "An Introduction to Scientific Research"; McGraw-Hill: New York, 1952; p 204.
(26) Young, L. J. In "Copolymerization"; Ham, G. E., Ed.; Interscience: New York, 1964; p 441.
(27) Ham, G. E. In "Copolymerization"; Ham, G. E., Ed.; Interscience: New York, 1964; pp 1–65.
(28) Dodgson, K.; Ebdon, J. R. *Eur. Polym. J.* **1977**, *13*, 791.
(29) Hill, D. J. T.; O'Donnell, J. H.; O'Sullivan, P. W. *Prog. Polym. Sci.*, in press.
(30) Sandner, B.; Loth, E. *Faserforsch. Textiltech.* **1976**, *27*, 633.
(31) Pichot, C.; Zaganiaris, E.; Guyot, A. *J. Polym. Sci., Polym. Symp.* **1975**, *No. 52*, 55.
(32) Seymour, R. B.; Garner, D. P. *Polym. News* **1978**, *4*, 209.

Binding of the Fluorescent Probes 2-*p*-Toluidinonaphthalene-6-sulfonate and 8-Anilinonaphthalene-1-sulfonate to Poly(vinylbenzo-18-crown-6) and Poly(vinylbenzoglyme)

Keiichi Kimura and Johannes Smid*

Polymer Research Institute, Chemistry Department, College of Environmental Science and Forestry, State University of New York, Syracuse, New York 13210.
Received December 29, 1981

ABSTRACT: The fluorescent probes 2-*p*-toluidinonaphthalene-6-sulfonate (TNS) and 8-anilinonaphthalene-1-sulfonate (ANS) were used in the binding of solutes to poly(vinylbenzo-18-crown-6) (P18C6) and to poly(vinylbenzoglyme) (PVBG, a polystyrene with two $O(CH_2CH_2O)_2CH_3$ substituents per phenyl group) in aqueous media. The binding of these two fluorophores to the polysoap-type macromolecules causes a strong enhancement in their fluorescence intensity. From data obtained at either constant polymer or constant dye concentration, the first and intrinsic binding constants and the enthalpies and entropies of binding of TNS and ANS to P18C6 and PVBG were calculated. Addition of crown ether complexable cations converts the neutral polycrown ether into a polycation, resulting in an increase in the binding of the two anionic fluorophores. This increase is a measure of the binding capacity of the cations to P18C6 except for cations such as Tl^+ and Pb^{2+}, which bind to P18C6 but can quench the fluorescence of bound dye. Addition of dioxane or alcohol causes chain expansion of the tightly coiled macromolecules, and the penetrating water molecules quench the fluorescence of the bound dye.

Introduction

Recently reported preliminary data on the fluorescence of aqueous solutions of 2-*p*-toluidinonaphthalene-6-sulfonate (TNS) and of 8-anilinonaphthalene-1-sulfonate (ANS) in the presence of poly(vinylbenzo-18-crown-6) (P18C6) demonstrated the strong affinity of these fluorescent probes to this polymer.[1] The neutral macromolecule P18C6, its structure depicted in Chart I, acts in water as a polysoap and interacts with a variety of neutral and ionic solutes.[2,3] Addition of crown ether complexable

0024-9297/82/2215-0966$01.25/0