## Study of the Role of Charge-Transfer Complexes in Some Bulk-Phase Free-Radical Polymerizations

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# Study of the Role of Charge-Transfer Complexes in Some Bulk-Phase Free-Radical Polymerizations

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## ABSTRACT

Literature copolymer composition data on the bulk polymerizations of maleic anhydride-styrene, acrylonitrile-styrene, and fumaronitrile-styrene have been considered in terms of the complex participation model. An assessment has been made in each case as to whether sequence information would be able to distinguish between the complex and penultimate polymerization models.

## INTRODUCTION

In 1944 Lewis and Mayo [1] introduced the first kinetic analysis of free-radical polymerization, the so-called terminal mechanism. Although this polymerization model has had considerable success in predicting the composition of the initial polymers which are formed in many polymerizations, a number of systems were encountered which could not be explained by the simple model. This led Alfrey and co-workers [2] in 1946 to suggest that penultimate groups in the propagating polymer chain also played a role in the polymerization process, and they outlined what came to be known

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as the penultimate model. In the same year, Bartlett and Nozaki [3] brought forward another suggestion. They proposed that, in some cases at least, the deviations from the terminal model may be associated with the participation of a comonomer complex in the polymerization process. These complexes were known to exist in mixtures of styrene and maleic anhydride and of styrene and fumaronitrile, for example.

The mathematical analysis of the penultimate model was relatively simple and a copolymer composition equation expressing the polymer composition as a function of the monomer feed composition and the various reactivity ratios was readily deduced. However, the analysis of the complex model was considerably more involved and Bartlett and Nozaki did not deduce an expression for the copolymer composition. As a result, penultimate effects came to be used almost exclusively to account for any deviations from the simple terminal model. It was not until Seiner and Litt [4] introduced their mathematical analysis of the complex model in 1971 that great interest was again generated in this model. Since then a number of studies have been reported in which the complex model has been considered in a quantitative way [5] [6].

Seiner and Litt's work [4] yielded a fairly complicated expression for the polymer composition, and they were only able to calculate reactivity ratios under certain special conditions - namely where one monomer does not homopolymerize and where the equilibrium constant for complex formation is small. Later, Pittman and Rounsefell [7] reconsidered Seiner and Litt's equations, and demonstrated how the reactivity ratios and the equilibrium constant for complex formation may be obtained by computer techniques without recourse to these special conditions.

Recently we have reported [8] an alternative to Litt and Seiner's method of analysis of the complex model, and we have demonstrated how the sequence distribution in the copolymer, the triad fractions, and the polymer composition can be obtained from a knowledge of the equilibrium constant, the various reactivity ratios, and the monomer feed composition.

Two of the copolymer systems which were among the first recognized to deviate from the simple terminal model were the maleic anhydride-styrene and the fumaronitrile-styrene systems. Over the past quarter of a century these two systems have been studied in both the bulk phase and in solution by a number of workers. However, no clear indication as to whether these polymerizations follow a penultimate or complex model has yet been forthcoming. Herein we report the results we have obtained from a reconsideration of the bulk polymerization data reported in two of these studies: that on maleic acid-styrene at 60°C by Dodgson and Eldon [5] and that on fumaronitrile-styrene at 79°C by Fordyce and Ham [9]. These data have been treated according to the methods we have developed.

We have also considered the bulk polymerization of styrene and acrylonitrile in terms of the complex model. This copolymerization

has also received considerable attention and has been previously interpreted according to the penultimate model by Ham [11]. However, in a recent study, Guyot and Guillot [12] report the necessity to introduce a consideration of pen-penultimate effects to describe their copolymerization data in toluene. Although, we know of no reports of any charge transfer complex formation by these two monomers, such complexes have been reported to be formed between both fumaronitrile [13, 14] and tricyanoethylene [15], two closely related nitriles, and styrene. It would thus not be surprising if a weak complex could be formed between acrylonitrile and styrene. In our study here we have used the bulk copolymerization data of Fordyce and Chapin [16] and Smith [17] at 75°C.

In each of the cases reported here the copolymer composition data have been used to obtain estimates of the reactivity ratios and the equilibrium constant for complex formation. These parameters have then been used to predict the sequence distribution in the copolymer. This has been done with a view to examining whether the experimental determination of the sequence distribution would be likely to resolve the question as to which model best describes these polymerizations.

## THEORY

The complex participation model can be described on a kinetic-probabilistic basis. The eight kinetic equations required to represent the polymerization process are shown in Eqs. (1)-(8):

$$\sim 0 + 0 \xrightarrow{k_{00}} \sim 0 \tag{1}$$

$$\sim 0 + 1 \xrightarrow{k_{01}} \sim 1 \tag{2}$$

$$\sim 0 + \overline{10} \xrightarrow{k_{0\overline{10}}} \sim 0 \tag{3}$$

$$\sim 0 + \overline{01} \xrightarrow{k_{0\overline{01}}} \sim 1 \tag{4}$$

$$\sim 1 + 0 \xrightarrow{k_{10}} \sim 0 \tag{5}$$

$$\sim 1 + 1 \xrightarrow{k_{11}} \sim 1 \tag{6}$$

$$\sim 1 + \overline{10} \xrightarrow{k_{1\overline{10}}} \sim 0 \tag{7}$$

$$\sim 1 + \overline{01} \xrightarrow{k_{1\overline{01}}} \sim 1 \tag{8}$$

where the symbols $\overline{10}$ and $\overline{01}$ are used to represent the complex, which

is formed according to Eq. (9) and which may add from either side in the polymerization process. In this form then, the model is completely general.

$$1 + 0 \underset{\longleftarrow}{\overset{K}{\longrightarrow}} \overline{10} \ (= \overline{01}) \tag{9}$$

The polymerization reactivity ratios can be defined in the following way:

$r_0 = k_{00}/k_{01}$

$p_0 = k_{0\overline{01}}/k_{0\overline{10}}$

$s_0 = k_{0\overline{10}}/k_{01}$

$r_1 = k_{11}/k_{10}$

$p_1 = k_{1\overline{10}}/k_{1\overline{01}}$

$$s_1 = k_{1\overline{01}}/k_{10} \tag{10}$$

and the transition probabilities for the state space of events given by Eqs. (1) to (8) can be represented by the symbols $P_{00}$, $P_{01}$, $P_{010}$, $P_{0\overline{01}}$, $P_{10}$, $P_{11}$, $P_{1\overline{10}}$ and $P_{\overline{101}}$, respectively.

We have demonstrated elsewhere [8] that the probability $p_1(1^n)$ of selecting a sequence of 1 units of any particular length n can be expressed in terms of these transition probabilities and the probability, $p_0$, of selecting from the chain an 0 unit which entered the chain as either a single 0 or as a $\overline{10}$ (where here the specification of the direction of addition of the complex is important). The general relationships are:

$$p_1(1^1) = p_0 \frac{((1 - P_{11})(P_{10} + P_{\overline{101}})(P_{01} + P_{0\overline{01}}) + P_{0\overline{10}}(P_{1\overline{10}} + P_{10}))}{(P_{1\overline{10}} + P_{10})} \tag{11}$$

and for all $n > 1$

$$p_1(1^n) = p_0 P_{11}{}^{(n-2)} \frac{(1 - P_{11})(P_{01} + P_{0\overline{01}})(P_{10} \cdot P_{11} + P_{\overline{101}} \cdot P_{11} + P_{1\overline{10}})}{(P_{1\overline{10}} + P_{10})} \tag{12}$$

The number fraction of sequences of 1 units of any length n can then be calculated from the relationship:

$$N_1(1^n) = p_1(1^n)/\sum_{m=1}^{\infty} p_1(1^m) \tag{13}$$

The expression for the copolymer composition can be deduced by counting the number of 1 and 0 units in each of the sequences of 1's and 0's. The mole ratio of 1 units to 0 units is given by the expression:

$$\frac{m_1}{m_0} = \frac{(1 - P_{00})(P_{10} + P_{1\overline{10}}) + (1 - P_{10})(P_{01} + P_{0\overline{01}})}{(1 - P_{01})(P_{01} + P_{1\overline{10}}) + (1 - P_{11})(P_{01} + P_{0\overline{01}})} \tag{14}$$

The polymer composition and the number fraction of sequences are functions of the transition probabilities only, which are in turn functions of only the reactivity ratios, the equilibrium constant for complex formation, and the instantaneous composition of the monomer mixture. Therefore, if a sufficient number of different initial copolymers are formed from a wide range of reactant monomer compositions, and if these are analyzed for copolymer composition, then in principle it is possible to calculate "best values" for the various reactivity ratios and the equilibrium constant for complex formation. The sequence distributions can then be calculated and if these can be experimentally determined, then a critical test may be provided for the applicability of the model. The methods used for performing these calculations have been outlined in our earlier paper [8]. They involve no simplifying assumptions and are completely general.

## RESULTS AND DISCUSSION

### Maleic Anhydride-Styrene

The bulk polymerization data reported by Dodgson and Ebdon [5] are undoubtedly the most comprehensive and accurate data available for this system. These workers examined their results in terms of both the penultimate and complex models, though in the latter case they used the simplified treatment of Seiner and Litt [4]. This is somewhat of an oversimplification in this case, because separate experimental measurements of the equilibrium constant for complex formation show that it does not satisfy the condition of being very small [7], one of the requirements of the simplified treatment. We have thus re-examined their polymer composition data, firstly by allowing all the reactivity ratios and the equilibrium constant to assume those values which best fit the data (case 1), and secondly by making the simplifying assumption that maleic anhydride forms only

TABLE 1. Reactivity Ratios and Equilibrium Constant for the Bulk Polymerization of Maleic Anhydride ($M_0$) and Styrene ($M_1$) at $60°C$[a]

| Parameter | Case 1[b] | Case 2[c] |
|---|---|---|
| $r_0$ | $8 \times 10^{-3}$ | 0 |
| $r_1$ | 0.54 | 0.16 |
| $p_0$ | $4 \times 10^{-5}$ | 0 |
| $p_1$ | 1.24 | 1.3 |
| $s_0$ | $< 10^{-5}$ | $< 10^{-7}$ |
| $s_1$ | 19.6 | 3.55 |
| $K$[d] | 0.19 | 3.2 |
| $S_{Y_1}$[e] | $8 \times 10^{-3}$ | $9 \times 10^{-3}$ |

[a]Experimental data taken from Dodgson and Ebdon [5].

[b]All parameters allowed to assume "best" values.

[c]Only single maleic anhydride sequences allowed (i. e., $r_0$ and $p_0$ to set equal to zero).

[d]$K$ defined with concentration units of mole/dm$^3$.

[e]Determined according to the equation: $S_{Y_1} = \sqrt{(Y_1 - Y_c)^2/n - p}$,

where $Y_1$ = experimental mole fraction in polymer, $Y_c$ = calculated mole fraction in polymer, n = number of experimental points, p = number of parameters in equation.

single unit sequences in the polymer (i. e., $r_0 = p_0 = 0$) (case 2). The results of these calculations are given in Table 1, and the nature of the fit to the experimental data is demonstrated in Fig. 1.

Both cases 1 and 2 provide very good agreement with the experimental data, with the standard errors in the polymer mole fractions being $8 \times 10^{-3}$ and $9 \times 10^{-3}$, respectively. Dodgson and Ebdon do not quote the accuracy of their composition data, but one would expect it to be about this magnitude. The two curves for the complex model lie extremely close to one another, except at low styrene feed concentrations, where they deviate because in case 2 only single maleic anhydride units can be formed in the polymer. The curves obtained by Dodgson and Ebdon for their penultimate and terminal models are also shown in Fig. 1 for comparison. In the case of their penultimate model they made the same simplifying assumption we have made in case 2 above, namely, that maleic anhydride forms only single unit sequences. Obviously, the complex model provides a much better fit to these experimental data than does the penultimate model.

In both cases 1 and 2 the equilibrium constant for complex formation was made a variable parameter and allowed to assume its "best"
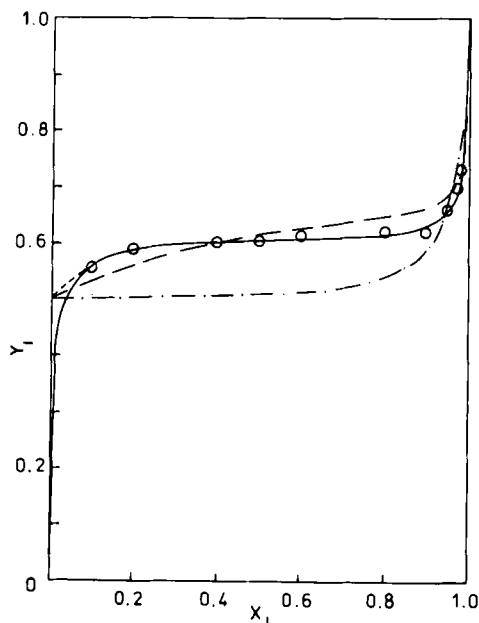
FIG. 1. Copolymer composition curves for the system maleic anhydride-styrene ($Y_1$ = mole fraction styrene in the polymer; $X_1$ = mole fraction styrene in the monomer): ( $\circ$ ) experimental data [5]; (—) complex model with no restriction on maleic anhydride sequence; (- -) complex model with only single maleic anhydride sequences; (– –) penultimate model of Dodgson and Ebdon [5]; (– · –) terminal model of Dodgson and Ebdon [5].

value. The equilibrium constant for formation of this complex has been determined in nonpolar solvents by both Ebdon and Dodgson [5] and Tsuchida and co-workers [19] at 60°C, where values of 0.25 and 0.28, respectively, have been obtained in cyclohexane and n-hexane. The value of the equilibrium constant obtained from case 1 above (0.20) agrees reasonably well with these figures, but that obtained in case 2 (3.2) differs by an order of magnitude. This could be taken as an indication that case 1 better represents the polymerization process, and maleic anhydride exhibits a small tendency to form some sequences of length greater than one unit. In fact, it has been reported [5] that maleic anhydride can be homopolymerized under special conditions.

The sequence distribution of styrene units in the polymer has been calculated from the parameters given in Table 1. The variations in the number fractions of single and double styrene sequences with
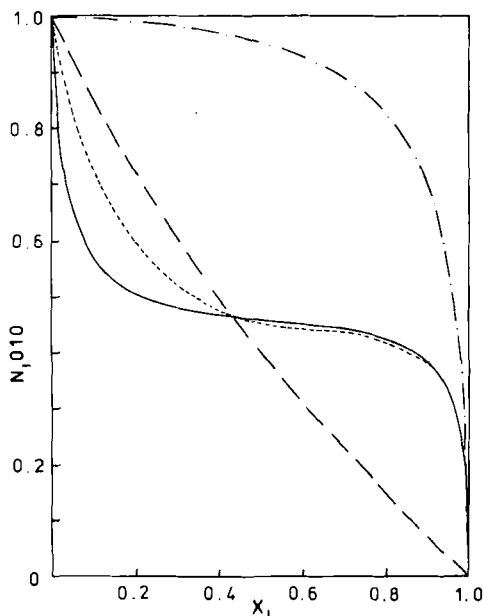
FIG. 2. Number fraction of single styrene sequences in the maleic anhydride-styrene copolymer: (—) complex model with no restriction on maleic anhydride sequences; (- -) complex model with only single maleic anhydride sequences; (– –) penultimate model of Dodgson and Ebdon [5]; (– · –) terminal model of Dodgson and Ebdon [5].

monomer composition are shown in Figs. 2 and 3, respectively. We have calculated the sequence distributions from the reactivity ratios obtained by Dodgson and Ebdon for the terminal and penultimate models, and these are also shown in Figs. 2 and 3 for comparison. The results clearly indicate that sequence information could distinguish between these four models. The great difference in the sequence distributions produced by the penultimate and the complex models should be easily detected by nuclear magnetic resonance studies of a series of polymers produced over an appropriate range of monomer feed compositions. Nuclear magnetic resonance studies should also be able to distinguish between cases 1 and 2 of the complex model. Not only should differences be observable from the styrene sequences, but at high maleic anhydride compositions, sequences of two maleic anhydride residues should also be observable for case 1 (see Table 2). Work is in progress in our laboratory along these lines.

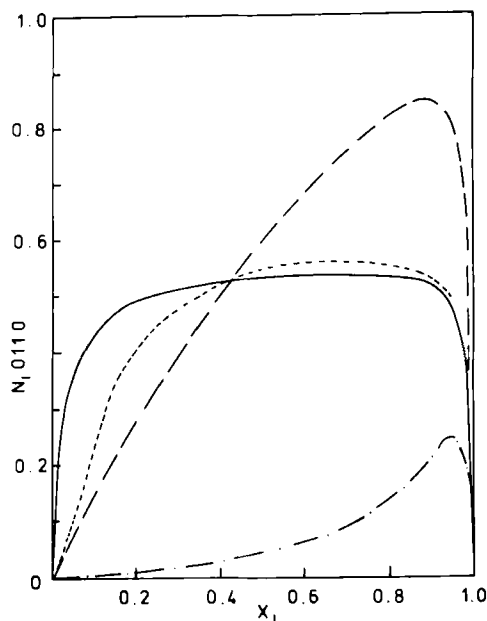    In order to show the relative importance of each of the polymerization

FIG. 3. Number fraction of double styrene sequences in the maleic anhydride-styrene copolymer: (—) complex model with no restriction on maleic anhydride sequences; (- -) complex model with only single maleic anhydride sequences; (– –) penultimate model of Dodgson and Ebdon [5]; (– · –) terminal model of Dodgson and Ebdon [5].

steps [Eqs. (1-8)] in the formation of the various sequences in a particular copolymer, the different possible combinations of successive addition of the monomers and complex have been examined. These sequence profiles can be calculated from the transition probabilities, and they will thus vary with the composition of the feed. In Table 3 the sequence profiles for single and double styrene sequences are given for an overall monomer feed mole fraction $(X_1)_m$ of 0.5 for styrene. At this comonomer composition the complex concentration will be a maximum. Under these conditions, i. e., $(X_1)_m$, $K$, $r_0$, we see that almost all the maleic anhydride would add via the complex, but styrene would add via both monomer and complex. (At this comonomer composition the polymer would be made up almost entirely of single and double styrene sequences and single units of maleic anhydride.) We can further observe from Table 3 that many sequences are completed by addition of complex with the formation of a maleic anhydride radical. This has been a point which has

TABLE 2.  Number Fractions of Maleic Anhydride Sequences in the Copolymers Calculated by Using the Parameters for Case 1 in Table 1[a]

| $X_1$[b] | No101 | No1001 | No10001 |
|---|---|---|---|
| 0.4 | 0.99 | 0.01 | - |
| 0.2 | 0.96 | 0.04 | - |
| 0.1 | 0.89 | 0.09 | 0.02 |

[a]Maleic anhydride given symbol 0.
[b]Overall mole fraction of styrene in the monomer feed.


TABLE 3.  Proportions of the Different Modes of Addition to Form Sequences 010 and 0110 in the Bulk Polymerization of Styrene and Maleic Anhydride Calculated for the Complex Model Case 1 with the Parameters given in Table 1 for $(X_1)_m = 0.5$[a]

| 010[b] | | 0110[b] | |
|---|---|---|---|
| Type | Fraction | Type | Fraction |
| 010 | 0.04 | 0110 | <0.01 |
| 0$\overline{10}$ | <0.01 | 01 $\overline{10}$ | 0.56 |
| 010$\overline{1}$ | 0.52 | 011 $\overline{01}$ | 0.01 |
| $\overline{0}$10 | 0.03 | $\overline{01}$ 10 | <0.01 |
| $\overline{010}$1 | 0.40 | $\overline{01}$ 1 $\overline{01}$ | 0.01 |
| | | $\overline{01}$ $\overline{10}$ | 0.42 |

[a]At this mole fraction almost 100% of the styrene sequences are 010 and 0110.
[b]Styrene given the symbol 1.


caused many authors to dismiss the complex participation model (e. g., Dodgson and Ebdon [5]).  These authors suggest there should be a preference for formation of the styryl radical because of its greater resonance stabilization.  However, the UV spectrum of the complex indicates there has been some rearrangement of the electronic energy levels when the complex is formed, which may well enhance addition of complex without regard to direction.  Further, Tsuchida and co-workers [18] have reported that chain transfer to N,N-dimethyl-aniline can occur easily in this polymerization, which they cite as

TABLE 4.  Reactivity Ratios and Equilibrium Constants for the Bulk Polymerization of Acrylonitrile and Styrene at 75°C and Fumaronitrile and Styrene at 79°C[a]

| Parameter[b] | Acrylonitrile-styrene | Fumaronitrile-styrene[c] |
|---|---|---|
| $r_0$ | 0.039 | 0 |
| $r_1$ | 0.71 | 0.47 |
| $p_0$ | 5.8 | 0 |
| $p_1$ | 5.4 | 9.2 |
| $s_0$ | 0.13 | 2.0 |
| $s_1$ | 0.61 | 1.3 |
| K | 0.13 | 0.09 |
| $S_{Y_1}$ [d] | $9 \times 10^{-3}$ | $4 \times 10^{-3}$ |

[a]Experimental data for acrylonitrile-styrene from Fordyce and Chapin [16] and Smith [17]; experimental data for fumaronitrile-styrene from Fordyce and Ham [9].
[b]Styrene given symbol 1.
[c]Only single fumaronitrile sequence allowed.
[d]See Table 1 for definition.

supporting the case for formation of maleic anhydride radicals in the chain propagation steps.

In summary, we have shown that the complex model can account for the copolymer composition data and we have observed some evidence that maleic anhydride sequences may be formed at high maleic anhydride concentrations.  We have shown that a study of the distribution of styrene sequences may be able to resolve whether or not the complex does play a dominant role in this polymerization.

## Acrylonitrile-Styrene

In 1954 Ham [11] examined the data for the acrylonitrile-styrene system reported by Fordyce and Chapin [16].  He commented that the terminal model did not completely account for the copolymer composition data, and he interpreted the results according to the penultimate model, which he rationalized in terms of electrostatic effects associated with the nitrile groups.

We have considered the data of Fordyce and Chapin [16] and of Smith [17] for this polymerization at 75°C in terms of the complex model.  The results of this analysis are shown in Table 4, and the
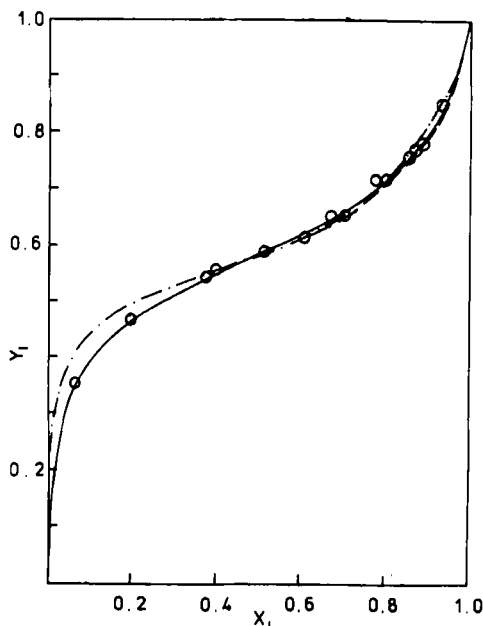
FIG. 4. Copolymer composition curves for the system acrylonitrile-styrene ($Y_1$ = mole fraction styrene in the polymer $X_1$ = mole fraction styrene in the monomer): ( o ) experimental data [ 16, 17];
(—) complex model; (– –) penultimate model of Ham [ 11]; (– • –) terminal model of Ham [ 11].

good fit to the experimental data is demonstrated in Fig. 4, where the results of Ham's calculations for the terminal and penultimate models [ 11] are shown for comparison. In this case no experimental values for any equilibrium constant are available, but the value we calculated of 0.13 is of the order of magnitude one would expect on the basis of the value reported for the equilibrium constant for the formation of the styrene-fumaronitrile donor-acceptor complex [ 14] (0.5 at 75°C).

The sequence profiles given in Table 5 at a monomer mole fraction 0.5 show clearly that the predominant propagation steps would be additions of uncomplexed monomer units. The sequence distributions have also been calculated, and the variation in the number fractions of single and double styrene sequences with monomer composition have been shown in Figs. 5 and 6. Clearly, again in this case, experimental determination of sequence distributions should be capable of distinguishing between the penultimate and complex models. This should be possible using NMR techniques, though we do not know of any such study on this copolymer system.

TABLE 5. Proportions of the Different Modes of Addition to Form Sequences 010 and 0110 in the Bulk Polymerization of Styrene and Acrylonitrile Calculated for the Complex Model with the Parameters shown in Table 4 for $(X_1)_m = 0.5$[a]

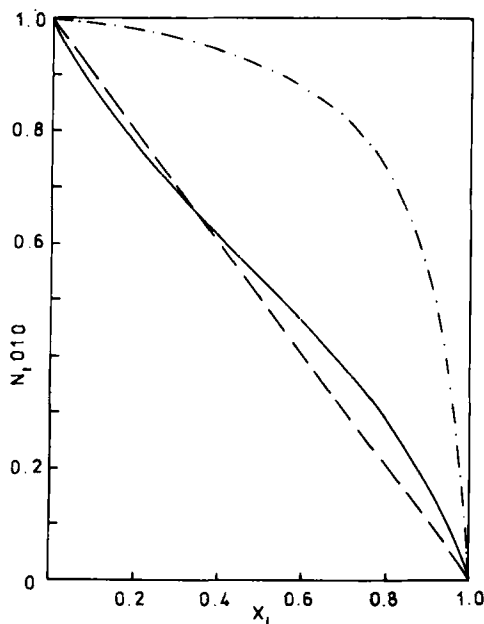| 010 | | 0110 | |
|---|---|---|---|
| Type | Fraction | Type | Fraction |
| 010 | 0.47 | 0110 | 0.58 |
| $0\overline{10}$ | 0.10 | $01\overline{10}$ | 0.02 |
| $010\overline{1}$ | 0.14 | $011\overline{01}$ | 0.04 |
| $\overline{01}0$ | 0.22 | $\overline{01}10$ | 0.01 |
| $\overline{010}\overline{1}$ | 0.07 | $\overline{011}\overline{01}$ | 0.27 |
| | | $\overline{0110}$ | 0.08 |

[a]Styrene given the symbol 1.



FIG. 5. Number fraction of single styrene sequences in the acrylonitrile-styrene copolymer: (—) complex model; (– –) penultimate model of Ham [11]; (– • –) terminal model of Ham [11].
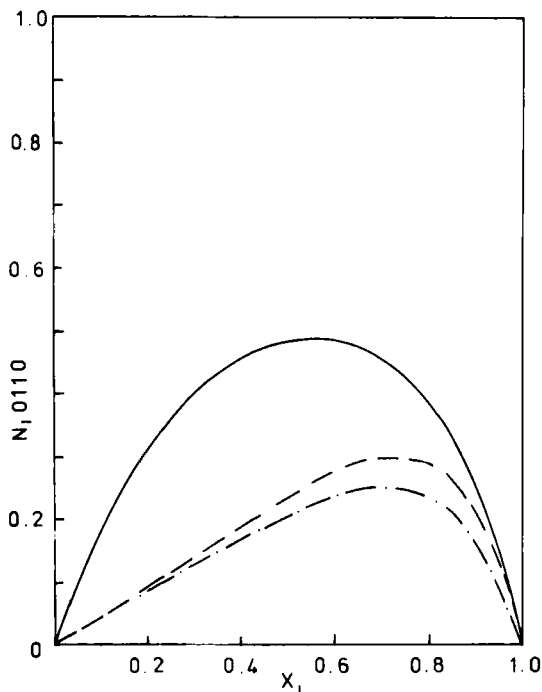
FIG. 6. Number fraction of double styrene sequences in the acrylonitrile-styrene copolymer: (—) complex model; (− −) penultimate model of Ham [11]; (− · −) terminal model of Ham [11].

## Fumaronitrile-Styrene

The most comprehensive study of the bulk polymerization of fumaronitrile and styrene was that reported by Fordyce and Ham [9]. This system is experimentally difficult to study because of the insolubility of fumaronitrile in styrene at low temperatures. In their study Fordyce and Ham only covered the composition range up to approximately 50% fumaronitrile. This precluded a completely general analysis of the system by our procedures because well defined values for the reactivity ratios for production of fumaronitrile sequences could not be obtained. We therefore introduced the assumption that only single units of fumaronitrile would be produced in the polymer. This is a reasonable assumption because fumaronitrile is not known to homopolymerize.

The results obtained from our analysis are given in Table 4. The estimated value of the equilibrium constant is of the order of
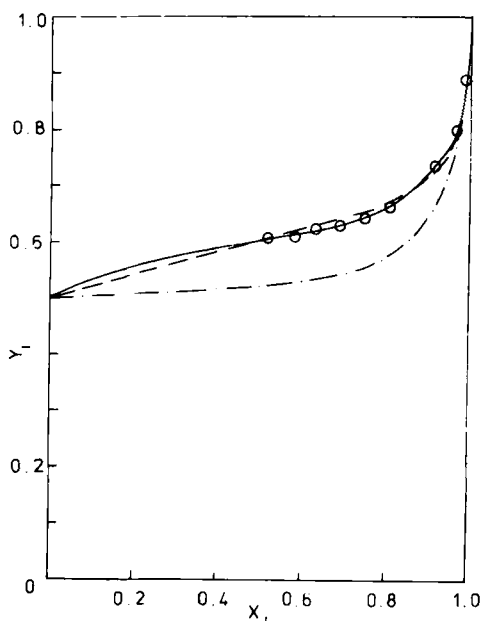
FIG. 7. Copolymer composition curves for the system fumaro-
nitrile-styrene ($Y_1$ = mole fraction styrene in the polymer; $X_1$ =
mole fraction styrene in the monomer): ( o ) experimental data [9];
(—) complex model; (– –) penultimate model of Barb [10]; (– · –)
terminal model of Fordyce and Ham [9].

magnitude one would expect on the basis of the estimates of the equi-
librium constant measured in polar solvents [14] ( $\approx$ 0.5).

Once again a very good fit to the experimental data was obtained
as shown in Fig. 7, where the results of Ham and Fordyce's analysis
[9] of this system in terms of the terminal model and Barb's [10]
analysis in terms of the penultimate model are also shown.

The sequence profiles are given in Table 6 for formation of single
and double styrene sequences at an overall monomer feed mole
fraction of 0.5 for styrene. Here, as was observed in the maleic
anhydride-styrene case, the complex plays a predominant role for
incorporation of fumaronitrile in the polymer. However, in the
fumaronitrile-styrene polymerization there are very few styryl end
radicals produced when the complex adds in the chain propagation
step. This could be rationalized by an enhanced reactivity of the
vinyl group in styrene arising from the three-dimensional aromaticity
of the complex, where the double bond of the fumaronitrile will be
located above the center of the benzene ring [19].

TABLE 6. Proportions of the Different Modes of Addition to Form Sequences 010 and 0110 in the Bulk Polymerization of Styrene and Fumaronitrile Calculated for the Complex Model with the Parameters given in Table 4 for $(X_1)_m = 0.5$[a]

| 010 | | 0110 | |
|---|---|---|---|
| Type | Fraction | Type | Fraction |
| 010 | 0.15 | 0110 | 0.02 |
| $0\overline{10}$ | 0.63 | $01\overline{10}$ | 0.89 |
| $01\overline{01}$ | 0.07 | $011\overline{01}$ | 0.01 |
| $\overline{010}$ | 0.14 | $\overline{0110}$ | <0.01 |
| $\overline{0101}$ | 0.01 | $\overline{01101}$ | <0.01 |
| | | $\overline{0110}$ | 0.08 |

[a]Styrene given the symbol 1.
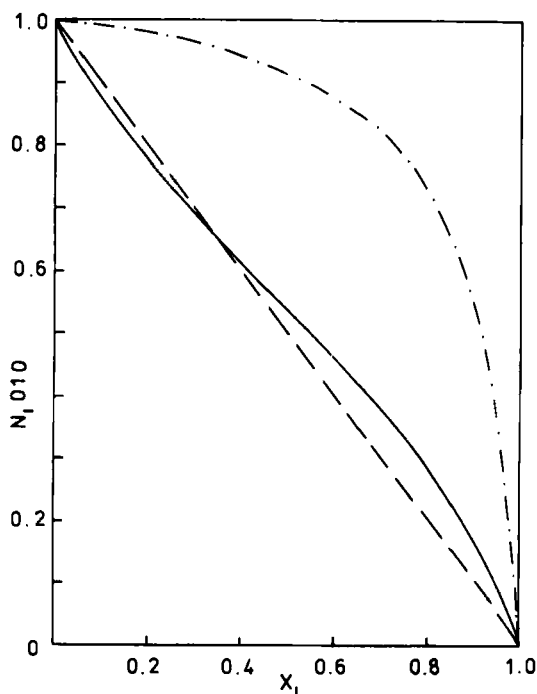


FIG. 8. Number fraction of single styrene sequences in the fumaronitrile-styrene copolymer: (—) complex model; (− −) penultimate model of Barb [10]; (− · −) terminal model of Fordyce and Ham [9].
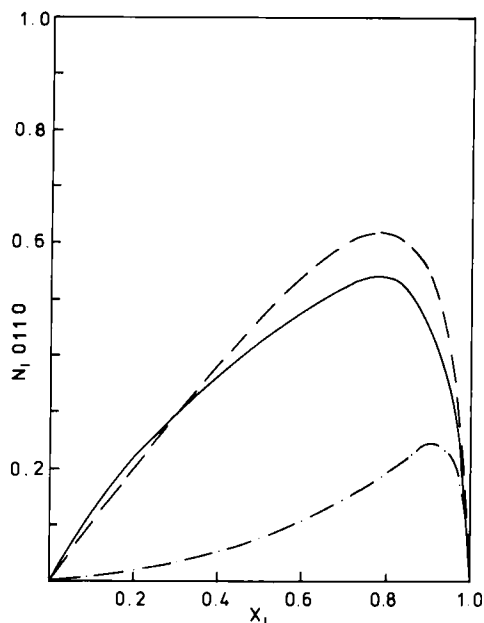
FIG. 9. Number fraction of double styrene sequences in the fumaronitrile-styrene copolymer: (—) complex model; (– –) penultimate model of Barb [10]; (– · –) terminal model of Fordyce and Ham [9].

In Figs. 8 and 9 we compare the variation in the number fractions of single and double styrene sequences with monomer composition. These variations have also been calculated for the terminal and penultimate reactivity ratios obtained by Ham and Fordyce and by Barb, respectively. The curves show that in this particular case it would be more difficult to distinguish between the complex and penultimate models on the basis of sequence distributions. This demonstrates that while studies of sequence distribution can sometimes clearly distinguish between the penultimate and complex models, this will not always be the case.

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