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Analysis of the Complex-Dissociation Model for Free-Radical Copolymerization

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ABSTRACT: Probability theory has been used to derive equations for the complex-dissociation model for free-radical copolymerization showing how the composition, the triad fractions, and the number fractions of sequences in the copolymer are related to the comonomer composition through the reactivity ratios and the equilibrium constant for complex formation. It is shown how these equations can be used to estimate "best" values of the reactivity ratios and the equilibrium constant using experimentally determined copolymer compositions. This model has been applied to the data of Dodgson and Ebdon for the styrene–maleic anhydride copolymerization in bulk at 60 °C. The complex-dissociation model, the penultimate model, and the complex-participation model fit the copolymer/comonomer composition data equally well. However, the predicted styrene sequence distributions of the three models are quite different, and experimental determinations, for example, by ^{13}C NMR, would enable discrimination between the models.

Introduction

Over the past decade considerable interest has been generated in the study of polymerization mechanisms, particularly for systems that have been shown to deviate from the terminal model. Higher order models, such as the penultimate and complex-participation models, have been proposed in order to explain these deviations. Both of these models have been treated mathematically: for example, the work of Alfrey and co-workers[1] and Ham[2] on the penultimate model and of Seiner and Litt[3] and Pittman and Rounsefell[4] on the complex model. We recently reported[5] a probabilistic treatment of the general complex-participation model and described how "best estimates" of the reactivity ratios and the equilibrium constant can be obtained for this model from copolymer/comonomer composition information. We also showed how these copolymerization parameters can be used to predict the number fractions of sequences in the copolymers.

According to the complex-participation model, complexed monomer competes with free monomer in the propagation steps and, when addition of complex takes place, both members of the complex become incorporated in the polymer chain. However, in 1971 Tsuchida and Tomono[6] suggested that, under some circumstances, the complex may be disrupted during the addition step, with only one of the two monomers entering the growing chain. They suggested that this was the case in copolymerization of styrene and maleic anhydride when the complex formed between these two monomers added to a maleic anhydride chain-end radical. They suggested that repulsive forces between the maleic anhydride chain radical and maleic anhydride in the complex was a possible cause for the disruption of the complex during propagation.

These ideas were extended by Karad and Schneider[7] in 1978 when they described what we will call the complex-dissociation model. In this model complex competes with the free monomer in the copolymerization, but the complex is always disrupted in the addition process, and only one monomer component of the complex enters the chain. In their application of this model to the fumaronitrile–styrene copolymerization, Karad and Schneider did not provide a mathematical analysis of the model in its general form but employed a constrained form of the model in which one monomer does not homopropagate through either the free monomer or the complex. This constraint simplified the mathematical analysis of the model but, of course, restricts its application to systems that are known to satisfy this requirement.

For the restricted form of the complex-dissociation model, the mathematical expression for the composition of the polymer is identical in form with that derived by Seiner and Litt[3] for the complex-participation model when this model is constrained so that one monomer does not

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homopropagate and the magnitude of the equilibrium constant for complex formation is small (less than ≈ 0.03). Thus, as Karad and Schneider pointed out, under these circumstances it would not be possible to distinguish between the complex-dissociation and complex-participation models on the basis of copolymer/comonomer compositions. However, the predicted sequence distribution of monomer units in the copolymers (predicted from the reactivity ratios) may be different for the different models and a discrimination between the models could then be made on this basis.[8]

The complex-dissociation model may provide an important route for the involvement of donor–acceptor complexes in some copolymerizations, especially in cases where the bonding in the complex is weak or where particularly strong interactions occur between the members of the complex and the end radicals of the propagating chains. However, a general interpretation of the complex-dissociation model can also account for those copolymerizations in which the complex does not dissociate, but where the second member remains complexed to the chain-end radical. Thus, the complex-dissociation model may be considered as a general model for copolymerizations in which, for one reason or another, the second member of the complex does not become incorporated in the chain. In these polymerizations the role of the complex would be either to enhance or depress the reactivity toward chain-end radicals of complexed monomer relative to free monomer.

In this paper we present the first analysis of the complex-dissociation model in its general form, without restrictions on the magnitude of the equilibrium constant or on any of the possible propagation steps involving free or complexed monomer. We have deduced the functional relationship between the copolymer composition and the equilibrium constant for complex formation, the reactivity ratios, and the composition of the feed mixture. We have also derived for the first time equations that enable the monomer sequence distributions in the polymer to be calculated from the polymerization parameters. These sequence distributions offer the possibility of greater discrimination between the complex-dissociation and other models, as we have shown[5] previously to be the case for discrimination between the terminal, penultimate, and complex-participation models.

Theory

The complex-dissociation model can be described on a kinetic probabilistic basis. The eight kinetic equations required to describe the propagation reactions are

$$\sim 0\cdot + 0 \xrightarrow{k_{00}} \sim 0\cdot \qquad (1)$$

$$\sim 0\cdot + 1 \xrightarrow{k_{01}} \sim 1\cdot \qquad (2)$$

$$\sim 0\cdot + \overline{10} \xrightarrow{k_{0\overline{10}}} \sim 1\cdot + 0 \qquad (3)$$

$$\sim 0\cdot + \overline{01} \xrightarrow{k_{0\overline{01}}} \sim 0\cdot + 1 \qquad (4)$$

$$\sim 1\cdot + 0 \xrightarrow{k_{10}} \sim 0\cdot \qquad (5)$$

$$\sim 1\cdot + 1 \xrightarrow{k_{11}} \sim 1\cdot \qquad (6)$$

$$\sim 1\cdot + \overline{10} \xrightarrow{k_{1\overline{10}}} \sim 1\cdot + 0 \qquad (7)$$

$$\sim 1\cdot + \overline{01} \xrightarrow{k_{1\overline{01}}} \sim 0\cdot + 1 \qquad (8)$$

where the symbols $\overline{10}$ and $\overline{01}$ are used to represent the complex. In this form then, the model is completely general. We have defined the polymerization reactivity ratios as follows:

$$r_0' = \frac{k_{00}}{k_{01}}, \quad q_0' = \frac{k_{0\overline{01}}}{k_{01}}, \quad s_0' = \frac{k_{0\overline{10}}}{k_{01}}$$

$$r_1' = \frac{k_{11}}{k_{10}}, \quad q_1' = \frac{k_{1\overline{10}}}{k_{10}}, \quad s_1' = \frac{k_{1\overline{01}}}{k_{10}} \qquad (9)$$

The transition probabilities for the state space of events given by eq 1–8 can be represented by the symbols P_{00}, P_{01}, $P_{0\overline{10}}$, $P_{0\overline{01}}$, P_{10}, P_{11}, $P_{1\overline{10}}$, and $P_{1\overline{01}}$, respectively, defined on the basis

$$P_{00} + P_{01} + P_{0\overline{10}} + P_{0\overline{01}} = 1 \qquad (10)$$

and

$$P_{11} + P_{10} + P_{1\overline{10}} + P_{1\overline{01}} = 1 \qquad (11)$$

It therefore follows that the individual transition probabilities can be represented by one or other of the general equations

$$P_{0x} = \frac{\text{rate of addition of substrate } x \text{ to } \sim 0\cdot}{\sum_x (\text{rate of addition of substrate } x \text{ to } \sim 0\cdot)} \qquad (12)$$

$$P_{1x} = \frac{\text{rate of addition of substrate } x \text{ to } \sim 1\cdot}{\sum_x (\text{rate of addition of substrate } x \text{ to } \sim 1\cdot)} \qquad (13)$$

where $x = 1, 0, \overline{01}$, or $\overline{10}$.

The transition probabilities can be expressed in terms of the reactivity ratios, the instantaneous concentrations of the reacting monomers, and the instantaneous concentration of the complex. These expressions are

$$P_{00} = r_0'[0]/\Sigma 0 \qquad P_{01} = [1]/\Sigma 0$$

$$P_{0\overline{10}} = s_0'[\overline{01}]/\Sigma 0 \qquad P_{0\overline{01}} = q_0'[\overline{01}]/\Sigma 0$$

$$P_{10} = [0]/\Sigma 1 \qquad P_{11} = r_1'[1]/\Sigma 1$$

$$P_{1\overline{10}} = q_1'[\overline{01}]/\Sigma 1 \qquad P_{1\overline{01}} = s_1'[\overline{01}]/\Sigma 1 \qquad (14)$$

where [0], [1], and $[\overline{01}]$ are the concentrations of the monomers 0 and 1 and of the complex $\overline{01}$ in units of mol dm^{-3} and $\Sigma 0$ and $\Sigma 1$ are given by the expressions

$$\Sigma 0 = r_0'[0] + [1] + s_0'[\overline{01}] + q_0'[\overline{01}] \qquad (15)$$

$$\Sigma 1 = [0] + r_1'[1] + s_1'[\overline{01}] + q_1'[\overline{01}] \qquad (16)$$

Assuming that the complex is formed according to the equilibrium

$$0 + 1 \overset{K}{\rightleftharpoons} \overline{01}\ (=\overline{10})$$

it is possible to express the equilibrium concentrations of the monomers and the complex in terms of the equilibrium constant and the total concentration of the monomers present in the reaction mixture.

Suppose that in the copolymer the probability of selecting a 0 unit is p_0 and the probability of selecting a 1 unit is p_1. Then, since the only way a 0 can enter the chain is by adding a 0 or a $\overline{01}$ and the only way a 1 can enter the chain is by adding a 1 or a $\overline{10}$, and making use of the steady-state assumption that the number of transfers of the terminal species 0 to 1 must equal the number of transfers 1 to 0, it can be shown that

$$p_0 P_{01} + p_0 P_{0\overline{10}} = p_1 P_{10} + p_1 P_{1\overline{01}} \qquad (17)$$

The instantaneous composition of the copolymer can now be calculated from the transition-state probabilities.

The mole ratio of 1 units to 0 units in the polymer, m_1/m_0, is given by

$$\frac{m_1}{m_0} = \frac{p_1}{p_0} = \frac{P_{01} + P_{0\overline{10}}}{P_{10} + P_{1\overline{01}}} \tag{18}$$

$$= \frac{([1] + s_0'[\overline{01}])(r_1'[1] + [0] + s_1'[\overline{01}] + q_1'[\overline{01}])}{([0] + s_1'[\overline{01}])(r_0'[0] + [1] + s_0'[\overline{01}] + q_0'[\overline{01}])} \tag{19}$$

From the transition probabilities, it is also possible to calculate the sequence distribution of 1 or 0 units in the initial copolymer.[9] To do this it is first necessary to delineate the various ways in which each sequence can arise. For example, a sequence of a single 1 unit, 010, can arise in four ways, namely, 0,1,0, 0,1,$\overline{01}$, 0,$\overline{10}$,0, and 0,$\overline{10}$,$\overline{01}$. Likewise, a sequence of two 1 units, 0110, can arise in eight ways, viz., 0,1,1,0, 0,1,1,$\overline{01}$, 0,1,$\overline{10}$,0, 0,1,$\overline{10}$,$\overline{01}$, 0,$\overline{10}$,1,0, 0,$\overline{10}$,1,$\overline{01}$, 0,$\overline{10}$,$\overline{10}$,0, and 0,$\overline{10}$,$\overline{10}$,$\overline{01}$. Sequences of length greater than two residues arise because of the incorporation of an appropriate number of single 1 units in the middle of any one of the eight possibilities outlined above for a sequence of two 1 units. This can occur by addition of either a 1 or a $\overline{10}$ to the 1 radical on the end of the chain.

It is a straightforward matter to calculate the probability of selecting from the copolymer chain a sequence of 1 units of any particular length. This can be expressed in terms of the probability p_0:

$$p_1(1^n) = p_0(P_{10} + P_{1\overline{01}})(P_{01} + P_{0\overline{10}})(P_{11} + P_{1\overline{10}})^{n-1} \tag{20}$$

where $p_1(1^n)$ is the probability of selecting from the copolymer chain a sequence of 1 units of length n. The corresponding probability of selecting a sequence of 0 units of length n, $p_0(0^n)$, is given by

$$p_0(0^n) = p_0(P_{01} + P_{0\overline{10}})^2(P_{00} + P_{0\overline{01}})^{n-1} \tag{21}$$

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

$$N_1(1^n) = p_1(1^n)/\sum_{m=1}^{\infty} p_1(1^m) \tag{22}$$

The probability p_0 can be eliminated from the numerator and denominator in eq 22, so that the number fraction of sequences is dependent only on the transition probabilities.

$$N_1(1^n) = (P_{01} + P_{0\overline{10}})(P_{00} + P_{0\overline{01}})^{n-1} \tag{23}$$

The triad fractions for 1 units (or 0 units) can be calculated by accounting for all possible triad sequences in the polymer. For the 1 units these are given by

$$F_{010} = (P_{10} + P_{101})^2 \tag{24}$$

$$F_{011+110} = 2(P_{11} + P_{110})(P_{10} + P_{101}) \tag{25}$$

$$F_{111} = (P_{11} + P_{110})^2 \tag{26}$$

where F_{010}, $F_{011+110}$, and F_{111} are the triad fractions for the triads 010, (011 + 110), and 111, respectively.

An examination of eq 18–26 indicates that the polymer composition, the number fractions of sequences, and the triad fractions are all functions of only the transition probabilities, 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 either copolymer composition, triad fractions, or number fractions of sequences, then, in principle, it is possible to calculate "best values" for the various reactivity ratios and the equilibrium constant for complex formation from the appropriate equations given above.

Table I
Reactivity Ratios[a] and Equilibrium Constant[b] Obtained from an Analysis of the Maleic Anhydride-Styrene Polymer Compositions Using the Treatment Presented for the Complex-Dissociation Model

parameter	best value	range[c]
r_0'	0.028	0.008-0.05
q_0'	5×10^{-6}	0-0.08
s_0'	2.9	1.6-10
r_1'	0.31	0.27-0.35
q_1'	9.2	8.6-9.8
s_1'	16.5	15.7-17.4
K	2.2	0.6->100

[a] The symbol 0 refers to the maleic anhydride and the symbol 1 refers to styrene. [b] The units of concentration are mol dm^{-3}. [c] Calculated according to ref 5.

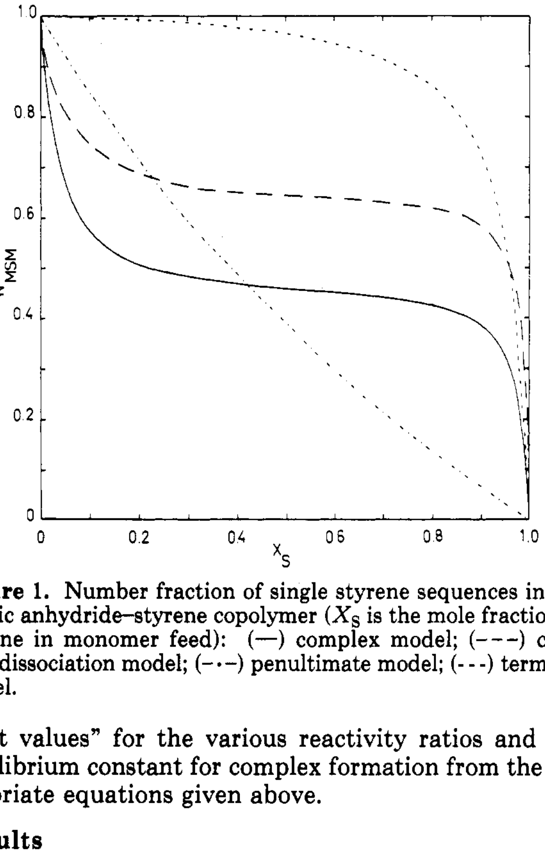

Figure 1. Number fraction of single styrene sequences in the maleic anhydride–styrene copolymer (X_S is the mole fraction of styrene in monomer feed): (—) complex model; (– – –) complex-dissociation model; (-•-) penultimate model; (- - -) terminal model.

Results

One convenient method of obtaining the "best values" of the reactivity ratios and the equilibrium constant from experimental copolymer compositions is by application of a direct search method. Here, it is necessary to define some "goodness-of-fit" parameter (τ) and then to successively change the values of the reactivity ratios and equilibrium constant in a patterned manner so as to locate the minimum value of τ on this hypersurface. An appropriate definition of τ is one in which τ is set equal to the sum of the squares of the differences between the experimentally determined copolymer compositions and the corresponding calculated values. The values of the reactivity ratios and equilibrium constant that correspond to this minimum then can be considered to "best fit" the experimental data. Our computer was programed to perform these computations using the direct search method developed by Chandler.[10] We have used this method previously to perform analogous calculations for our treatment[5] of the complex-participation model.

To demonstrate the application of this technique we have applied the model in its most generalized form (that is, with no constraints imposed on the reactivity ratios or

Table II

Experimental[a] and Calculated Polymer Compositions for the Complex-Dissociation, Complex-Participation, and Penultimate Models for Copolymerization of Maleic Anhydride with Styrene

mole fraction of styrene in feed (X_1)	mole fraction of styrene in polymer (Y_1)	calcd styrene mole fractions		
		complex dissociation	complex participation	penultimate
0.1	0.558	0.559	0.558	0.534
0.2	0.590	0.587	0.589	0.562
0.4	0.603	0.604	0.604	0.603
0.5	0.604	0.608	0.607	0.619
0.6	0.615	0.610	0.610	0.632
0.8	0.624	0.618	0.618	0.654
0.9	0.621	0.632	0.632	0.666
0.95	0.661	0.657	0.657	0.678
0.975	0.700	0.698	0.698	0.697
0.984	0.733	0.734	0.734	0.720
S_{Y_1} [b]		9×10^{-3}	8×10^{-3}	3×10^{-2}

[a] Experimental data taken from Dodgson and Ebdon. [b] Defined according to the equation $S_{Y_1} = [\Sigma(Y_1 - Y_c)^2/(n-p)]^{1/2}$, where Y_1 is the polymer composition, Y_c is the calculated polymer composition, n is the number of experimental points, and p is the number of parameters in the equation for the model.

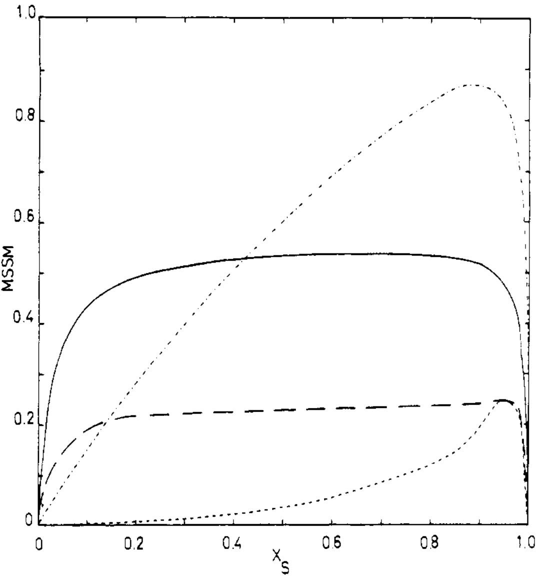

Figure 2. Number fraction of double styrene sequences in the maleic anhydride–styrene copolymer: legend as for Figure 1.

the equilibrium constant) to the data of Dodgson and Ebdon for the copolymerization of styrene and maleic anhydride in bulk at 60 °C. The "best values" of the reactivity ratios and the equilibrium constant obtained from the data fit are given in Table I, and the experimental and calculated copolymer compositions are given in Table II. In Figures 1 and 2 the predicted number fractions of sequences for the styrene units in the copolymers are shown as a function of the monomer feed composition.

Discussion

The copolymerization of styrene with maleic anhydride has been the subject of many investigations. Barb[11] and Enomoto et al.[12] observed a deviation from terminal model behavior and interpreted this in terms of a penultimate unit effect. Tsuchida and Tomomo[6] suggested a mechanism that allowed for only alternating styrene and maleic anhydride units in the chain, in order to explain the observed variation in the rate of copolymerization of the monomers in various solvents. They suggested that free maleic anhydride and the comonomer complex compete for addition to styryl chain-end radicals but that only the complex adds to maleic anhydride chain-end radicals and, in doing so, is disrupted by repulsive forces between the chain radical and the maleic anhydride of the complex so that only the styrene unit enters the chain. This interpretation of the mechanism of the copolymerization is questionable, however, because it neglects the effect of solvent–monomer complexes, which are known to form in these systems, and because later studies[13,14] indicate that the copolymers formed between styrene and maleic anhydride are not strictly alternating—a requirement of Tsuchida and Tomomo's mechanism.

Dodgson and Ebdon[13] have reported an extensive study of the styrene–maleic anhydride copolymerization in bulk and in solution in dimethyl sulfoxide, chloroform, or methyl ethyl ketone at 60 °C. They showed that both styrene and maleic anhydride form complexes with these solvents. Simplified forms of the terminal, penultimate, and complex-participation models, in which maleic anhydride cannot homopropagate, were used to analyze the composition data. The authors showed that both the penultimate and complex-participation models in these constrained forms could represent the composition data adequately, but, on the basis of the magnitude of the predicted reactivity ratios, the lack of a significant dilution effect in methyl ethyl ketone and the results of a later study[15] of the terpolymerizations with methyl methacrylate as the third monomer, they concluded that the copolymerization was best described by the penultimate model.

Subsequently, we[16] reexamined Dodgson and Ebdon's bulk polymerization data in terms of the penultimate and complex-participation models in which no constraints were applied to restrict the sequences of maleic anhydride. The reactivity ratios and the equilibrium constant for donor–acceptor complex formation were calculated by fitting the polymer compositions to the complex model. The predicted value of the equilibrium constant was in close agreement with that measured experimentally by Dodgson and Ebdon. On this basis we concluded that the complex-participation model could not be eliminated as a possible description of Dodgson and Ebdon's data for polymerization in bulk. We also showed that it would be possible to distinguish between the penultimate and complex-participation models on the basis of the monomer sequence distribution in the copolymers. However, no experimental confirmation has yet been reported.

Roth, Arnold, and Raetzsch[14] recently reported a ^{13}C NMR study of the copolymers formed by polymerization of styrene and maleic anhydride in solution in benzene or acetone—solvents that also complex strongly with maleic anhydride or styrene. They measured the copolymer compositions using the ^{13}C NMR resonances of the carbonyl carbons of maleic anhydride and the aromatic quaternary carbons of styrene. They supported their values using an independent method involving chemical analysis for maleic anhydride. The styrene contents of their copolymers were found to be considerably lower than those of the copolymers produced at corresponding comonomer compositions by Dodgson and Ebdon, who used ^{14}C-labeled maleic anhydride and scintillation counting to determine the copolymer compositions. Roth et al. used the terminal model as a basis for an analysis of their experimental results.

Thus the question of which model best describes the copolymerization behavior of styrene with maleic anhydride is still undecided. The terminal, penultimate, and complex-participation models have been examined by several workers but, by contrast with these models, no attention has been given to the possibility that the comonomer complex may be involved through a complex-dissociation mechanism. We have therefore considered this possibility for one particular set of polymerization data.

As described above, there is disagreement in the literature between copolymer compositions for styrene and maleic anhydride produced in bulk or in different solvents. To avoid considering the effect of solvent–monomer complexes, we have chosen not to use data for polymerizations in solvents that complex with styrene or maleic anhydride. Dodgson and Ebdon[13] report the only study of the bulk copolymerization of these monomers that provides composition data at a sufficient number of different points across the comonomer composition range to allow an analysis. However, it should be emphasized that in choosing Dodgson and Ebdon's data to demonstrate our techniques we do not thereby endorse this set of copolymerization data as being the most reliable. Rather, our objective is to show that the complex-dissociation model should be considered along with the other higher order models when the question of polymerization mechanism is being considered, particularly if complexes are formed between the comonomers.

As shown by the results in Table II, we have found that the complex-dissociation model applied without simplifying restrictions provides a close fit to Dodgson and Ebdon's composition data for the bulk copolymerization. The calculated standard error in the copolymer compositions (expressed as mole ratio) is about 10^{-2}. Statistical tests for discrimination between models show this value is significantly better than that obtained for the terminal model and that it compares favorably with the values obtained for the penultimate and complex-participation models.[16]

An examination of the parameters given in Table I shows that while the reactivity ratios for the styryl end radical could be determined fairly precisely, the maleic anhydride reactivity ratios and the equilibrium constant were not so well-defined. That this is so is not surprising because it is well-known that maleic anhydride does not homopolymerize easily, so that the "best values" of r_0' and q_0' were both found to be small ($\approx 10^{-2}$ and $\approx 10^{-6}$, respectively) and relatively large perturbations on these small values have little effect on the copolymer composition. For the styrene reactivity ratios, however, small variations caused a marked worsening of the fit. The fact that maleic anhydride has a low tendency to homopropagate whereas the incorporation of styrene varies considerably over the monomer feed range may provide the explanation for this difference.

The "best values" of the styrene reactivity ratios given in Table I predict that the reactivity toward a styryl end radical of complexed maleic anhydride is approximately 15 times greater than the free monomer and that of styrene in the complex is approximately 30 times greater than that of free styrene. The "best value" of the equilibrium constant obtained from the curve fit was 2, but the uncertainty associated with this value is such that a value an order of magnitude less, corresponding to the reported equilibrium constant of 0.25,[13] would still provide an adequate fit to the data.

The predicted sequence distributions for styrene units in the copolymers are shown in Figures 1 and 2, where those values predicted on the basis of the terminal, penultimate, and complex-participation models are shown for comparison. Here, we can see that the sequence distributions for both single- and double-unit styrene sequences are quite different for the four models, particularly at certain monomer feed concentrations. The styrene sequence distributions are functions of the styrene reactivity ratios and are unaffected by any variation in the maleic anhydride reactivity ratios within their uncertainty. It should be possible, therefore, to distinguish between the three models on the basis of these sequence distributions.

There have been no reports in the literature of the sequence distributions of styrene (or maleic anhydride) units in maleic anhydride–styrene copolymers obtained by bulk polymerization, although it might be anticipated that such information could be obtained from ^{13}C NMR studies. Recently, two reports of the ^{13}C NMR spectra of styrene–maleic anhydride copolymers have been published. Buchak and Ramey[17] found that the spectrum in the region of the quaternary aromatic carbon resonance of three copolymers varied with the polymer composition. The relative positions of the four triad peaks was assigned by using this information but the resolution of the peaks was so poor that the extent of overlap due to broadening of the peaks by tacticity effects could not be determined. Roth, Arnold, and Raetzsch[14] examined a series of copolymers produced in benzene and acetone across a wider range of polymer compositions and arrived at triad assignments similar to those of Buchak and Ramey. In order to determine the relative areas of the poorly resolved triad peaks they found it necessary to assume an asymmetric line shape to account for tacticity effects. Thus, the determination of accurate sequence distributions for styrene–maleic anhydride copolymers by ^{13}C NMR presents a considerable obstacle. Nevertheless an examination of Figures 1 and 2 shows that the sequence distribution curves predicted for the various models are well separated at a monomer feed mole fraction around 0.8, so that a considerable uncertainty in the sequence distributions could be tolerated in this region. In addition, the predictions for the complex-participation and complex-dissociation models both indicate there should be little change in the copolymer sequence distributions (and hence in the quaternary carbon resonances of the ^{13}C NMR) over a fairly wide range of comonomer compositions, whereas the predictions for the penultimate model indicate a much more distinct change.

Registry No. Styrene, 100-42-5; maleic anhydride, 108-31-6.

References and Notes

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Synthesis and Homopolymerization Kinetics of α-Methylene-δ-valerolactone, an Exo-Methylene Cyclic Monomer with a Nonplanar Ring System Spanning the Radical Center

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ABSTRACT: α-Methylene-δ-valerolactone (α-MVL) has been synthesized and homopolymerized by bulk and solution methods. The poly(α-MVL) is soluble in DMF and Me_2SO at room temperature. Thermogravimetric analysis of poly(α-MVL) showed a 10% weight loss at 280 °C in air. The α-MVL has a low ceiling temperature, $T_c = 83$ °C at the standard state of 1 mol/L of monomer. Kinetics of α-MVL homopolymerization have been investigated in DMF solutions using azobis(isobutyronitrile) (AIBN) as an initiator. Depolymerization was competitive with polymerization. The rate of polymerization (R_p) followed the expression $R_p = k[\mathrm{AIBN}]^{0.44}\cdot([\mathrm{M}] - [\mathrm{M}]_e)^{1.1}$, considering the depolymerization step. The overall activation energy was calculated to be 79.5 kJ/mol. The heat of polymerization (ΔH_p) and entropy of polymerization (ΔS°_p), obtained from a linear relationship between ln $[M]_e$ vs. $1/T$, were −38.8 kJ/mol and 108.8 J/(K·mol), respectively. The low ΔH is most likely a reflection of the low ceiling temperature of the polymerization. A low T_c is expected based on steric constraints in this nonplanar lactone ring monomer.

Introduction

A large number of polymerization studies of alkyl methacrylates and related compounds have been reported.[1-5] However, very little attention has been paid to the polymerization of their cyclic analogues, except for the synthesis of poly(α-methylene-γ-butyrolactone) (α-MBL).[6] As part of our research program on the study of structure–reactivity relationships of vinyl monomers in their radical polymerizations and copolymerizations, our group has recently begun an investigation of the polymerization behavior of exo-methylene cyclic monomers. In an earlier paper, we reported kinetic studies of the radical polymerization of α-MBL.[7] This investigation revealed that α-MBL polymerization follows the normal vinyl free-radical polymerization mechanism. The Q and e values for α-MBL were larger than those of methyl methacrylate (MMA). The planarity of α-MBL results in a favorable approach between the growing radical and the monomer, and planarity favors delocalization into the carbonyl group.

The next target is to verify the radical polymerizability of α-methylene-δ-valerolactone (α-MVL), an analogue of α-MBL, which has a nonplanar lactone ring spanning the α positions. The present paper describes the synthesis of poly(α-MVL), properties of the polymer obtained, and kinetic studies of the radical polymerization of α-MVL. In addition, homo- and copolymers of α-MVL are currently being studied for potential lithographic resist applications.

Experimental Section

Materials. Azobis(isobutyronitrile) (AIBN) was recrystallized from methanol. *N,N*-Dimethylformamide (DMF) was purified as follows. Reagent grade DMF (750 mL) was mixed with 90 mL of benzene and 40 mL of water and distilled at atmospheric pressure. Then it was distilled at reduced pressure under nitrogen. Other reagents were used as received.

Monomer. Preparation of α-Methylene-δ-valerolactone (α-MVL). This monomer was prepared according to the procedure of Ksander et al.[8] First, α-ethoxalyl-δ-valerolactone was prepared in 88% yield from diethyl oxalate and δ-valerolactone in the presence of sodium ethoxide in ethanol. This compound was used in the next step without purification. IR (NaCl) ν(C═O) 1740, 1640 cm^{-1}; NMR (in $CDCl_3$) δ = 1.25 (m, 3 H), 1.90 (m, 2 H), 2.75 (t, 2 H), 3.40 (q, 2 H), 4.25 (m, 2 H), 13.15 (s, 1 H). To a 1-L three-necked flask equipped with a mechanical stirrer, condenser, and dropping funnel were added sodium hydride (2.9 g, 0.12 mol) and 300 mL of THF. To this mixture was added

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