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An Analysis of the Complex Participation Model for Free-Radical Copolymerization

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ABSTRACT: The probability theory has been used to derive equations for the complex participation model for free-radical copolymerization, showing how the composition, the triad fractions, and the number fractions of sequences in a copolymer are related to the reactivity ratios, the equilibrium constant, and the monomer composition. We show how a patterned search method can be used to yield "best" estimates of the reactivity ratios and the equilibrium constant, using the experimentally determined copolymer composition, triad fractions, or number fractions of sequences provided sufficient data are available. Experimental data for the 1,1-diphenylethylene–methyl acrylate system available in the literature have been used to demonstrate this method of analysis.

Deviations in the composition of a copolymer from the predictions made on the basis of the simple terminal model for polymerization can be accounted for by amending this model in one of a number of ways. The deviations may be ascribed to effects associated with the penultimate and/or other preceding residues in the chain or to the formation of a comonomer complex which competes with monomer in the polymerization process. This latter modification was the subject of a series of papers by Litt and Seiner,[3-6] wherein they presented a quantitative theory relating the composition of a copolymer to the concentrations of the reacting monomers, the various reactivity ratios, and the equilibrium constant for formation of the complex. Herein we present an alternative to their treatment of the complex participation model. We have derived, for the first time, equations expressing the number fractions of sequences in terms of the transition probabilities and indicate how expressions for the triad fractions and the copolymer composition can be obtained.

For systems which can be represented by the complex participation model, we show how "best estimates" of the reactivity ratios and the equilibrium constant can be calculated either from the experimentally determined copolymer composition, or the triad fractions, or the number fractions of sequences using these relationships, provided that information is available for a sufficient number of initial polymers prepared from monomer mixtures which cover the complete composition range.

To demonstrate these methods, the data available in the literature[7] for the 1,1-diphenylethylene–methyl acrylate system have been used.

Theory

The complex participation model can be described on a kinetic–probabilistic basis. The eight kinetic equations required to represent the polymerization process are:

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

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

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

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

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

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

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

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

where the symbols $\overline{10}$ and $\overline{01}$ are used to represent the complex, which may add from either side in the polymerization process. In this form then, the model is completely general. Polymerization reactivity ratios can be defined in the following way:[8]

$$\begin{gathered} r_0 = k_{00}/k_{01},\ r_1 = k_{11}/k_{10} \\ p_0 = k_{0\overline{01}}/k_{0\overline{10}},\ p_1 = k_{1\overline{10}}/k_{1\overline{01}} \\ s_0 = k_{0\overline{10}}/k_{01},\ s_1 = k_{1\overline{01}}/k_{10} \end{gathered} \tag{9}$$

and the transition probabilities for the state space of events given by the 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 this basis

$$P_{00} + P_{01} + P_{0\overline{10}} + P_{0\overline{01}} = 1 \tag{10}$$

$$P_{11} + P_{10} + P_{1\overline{10}} + P_{1\overline{01}} = 1 \tag{11}$$

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

$$P_{0x} = \frac{\text{rate of addition of substrate } x \text{ to } \sim 0}{\sum_{x}(\text{rate of addition of substrate } x \text{ to } \sim 0)} \tag{12}$$

$$P_{1x} = \frac{\text{rate of addition of substrate } x \text{ to } \sim 1}{\sum_{x}(\text{rate of addition of substrate } x \text{ to } \sim 1)} \tag{13}$$

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

It follows that 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:

$$\begin{aligned} P_{00} &= r_0[0]/\textstyle\sum 0 & P_{01} &= [1]/\textstyle\sum 0 \\ P_{0\overline{10}} &= s_0[\overline{01}]/\textstyle\sum 0 & P_{0\overline{01}} &= s_0 p_0[\overline{01}]/\textstyle\sum 0 \\ P_{10} &= [0]/\textstyle\sum 1 & P_{11} &= r_1[1]/\textstyle\sum 1 \\ P_{1\overline{10}} &= s_1 p_1[\overline{01}]/\textstyle\sum 1 & P_{1\overline{01}} &= s_1[\overline{01}]/\textstyle\sum 1 \end{aligned} \tag{14}$$

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

$$\textstyle\sum 0 = r_0[0] + [1] + s_0[\overline{01}][1 + p_0] \tag{15}$$

$$\textstyle\sum 1 = [0] + r_1[1] + s_1[\overline{01}][1 + p_1] \tag{16}$$

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.

Given these transition probabilities (eq 14), it is possible to calculate the sequence distribution of 1 units, say, 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 can arise in five ways, viz., 010, $01\overline{01}$, $0\overline{10}$, $\overline{01}0$, and $\overline{01}\,\overline{01}$. Likewise, a sequence of two 1 units can arise in six ways, viz., 0110, $011\overline{01}$, $01\overline{10}$, $\overline{01}10$, $\overline{01}\,1\overline{01}$, and $\overline{01}\,\overline{10}$. Sequences of length greater than two residues arise because of the addition of an appropriate number of single 1 units in the middle of any one of the six possibilities outlined above for a sequence of two 1 units. The number fraction of sequences can now be calculated.

Suppose that in the copolymer the probability of selecting an 0 unit which entered the chain as either a single 0 or as a $\overline{10}$ (here the specification of the direction of addition of the complex is important) is p_0 and the probability of selecting a 1 unit which entered the chain as a 1 or an $\overline{01}$ (again direction of addition is as specified) is p_1. Then, since the only way an 0 can enter the chain other than as an 0 or a $\overline{10}$ is by adding an $\overline{01}$ to either a terminal 1 or 0 unit on the growing chain, the probability of selecting an 0 unit which entered the chain as $\overline{01}$ ($p_{\overline{01}}$) must be given by the expression:

$$p_{\overline{01}} = p_0 \cdot P_{0\overline{01}} + p_1 \cdot P_{1\overline{01}} \tag{17}$$

Then, 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:

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

and thus that:

$$p_{\overline{01}} = p_0 \left[P_{0\overline{01}} + P_{1\overline{01}} \left(\frac{P_{0\overline{01}} + P_{01}}{P_{1\overline{10}} + P_{10}} \right) \right] \tag{19}$$

It is then a simple 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. These probabilities are given by the following simplified general relationships: (A) for sequences of a single 1 unit (which must have been formed in one of the five ways described earlier)

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

(B) for sequences of n 1 units where $n > 1$ (which must have been formed in one of the six ways described earlier)

$$p_1(1^n) = p_0 {P_{11}}^{(n-2)} \frac{(1 - P_{11})(P_{01} + P_{0\overline{01}})(P_{10} \cdot P_{11} + P_{1\overline{01}} \cdot P_{11} + P_{1\overline{10}})}{(P_{1\overline{10}} + P_{10})} \tag{21}$$

where $p_1(1^n)$ is the probability of selecting from the copolymer chain a sequence of 1 units of length n.

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

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

Obviously the probability p_0 can be eliminated from the top and bottom line in eq 22, so that the number fraction of sequences is dependent only on the transition probabilities.

It is also then a straightforward matter to deduce an expression for the copolymer composition. This can be done 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 $X(1)$ is given by the expression:

$$X(1) = \frac{(1 - P_{00})(P_{10} + P_{1\overline{10}}) + (1 - P_{10})(P_{01} + P_{0\overline{01}})}{(1 - P_{01})(P_{10} + P_{1\overline{10}}) + (1 - P_{11})(P_{01} + P_{0\overline{01}})} \tag{23}$$

The triad fractions for 1 units can be calculated by accounting for all possible triad sequences in the polymer. These are given by:

$$F_{(010)} = \frac{p_1(1^1)(1 - P_{11})^2}{p_1(1^1)(1 - P_{11})^2 + p_1(1^2)(2 - P_{11})} \tag{24}$$

$$F_{(011+110)} = \frac{2p_1(1^2)(1 - P_{11})}{p_1(1^1)(1 - P_{11})^2 + p_1(1^2)(2 - P_{11})} \tag{25}$$

$$F_{(111)} = \frac{p_1(1^2) \cdot P_{11}}{p_1(1^1)(1 - P_{11})^2 + p_1(1^2)(2 - P_{11})} \tag{26}$$

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 22–26 indicates that the polymer composition, the number fraction 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.

Results

One of the most convenient methods of obtaining the "best values" of the reactivity ratios and the equilibrium constant from the available experimental information is the 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 it's hypersurface. The values of the reactivity ratios and equilibrium constant which correspond to this minimum then can be considered to best fit the experimental data. Our computer was programmed to perform these computations, using the direct search method developed by Chandler.[10]

Chandler's programs provide for estimation of the standard errors in each of the adjustable parameters. However, care must be exercised when these standard errors are used as indicators of the reliability of the determined parameters. For example, when the number of data points, and hence the number of degrees of freedom, is small, any statistically based error estimate may be highly unreliable. The application of any constraints on the variables may also render the calculated standard errors meaningless.[10] However, the topography of the hypersurface in the region of the minimum can be examined in order to gauge how well each parameter has been defined by the data fit.

In order to demonstrate the application of this technique it has been applied to the experimental data reported by Ito and Yamashita[7] for the methyl acrylate–1,1-diphenylethylene (MA-DPE) system. Ito and Yamashita considered their data in terms of the terminal and penultimate models. Their data suffer from the disadvantage that the number of data points is limited, but the choice of this particular set of data for further consideration here was influenced by the fact that Litt and Seiner[5] considered Ito and Yamashita's data, using a complex participation model. To simplify the calculations, they severely constrained the model, and thus their method enabled them to calculate an absolute value of only one reactivity ratio, that of r_1 ($=k_{11}/k_{10}$) for which they obtained a value of 28. This value is much higher than one might anticipate from a knowledge of other copolymer systems, on which basis a value less than unity would be expected. So even though Litt and Seiner were able to represent the experimental data using this constrained model, their value of r_1 cast doubt as to whether the copolymerization could be explained by participation of a complex. A more general analysis would show whether or not the high value of r_1 resulted from some of the constraints they applied.

Ito and Yamashita reported polymer compositions and triad fractions for six different copolymers determined by NMR techniques. Their composition data are reported in Table I. Herein we have chosen to use their polymer compositions based on the phenyl proton resonance as the experimental information to be used in the analysis (since these are likely to be more accurate than those calculated from the methoxy proton resonances) and to use a "goodness-of-fit" parameter defined as the sum of the squares of the differences between the experimentally determined compositions and the corresponding calculated values. In addition, since 1,1-diphenylethylene is known to show no propensity to homopolymerize, the reactivity ratios of those steps which would yield a sequence of two or more DPE residues were set equal to zero.

Table I
Experimental and Calculated Polymer Compositions for the Methyl Acrylate-1,1-Diphenylethylene System

mol ratio[a] of MA in monomer feed	mol ratio of MA in polymer[a]		calcd mol ratio in polymer[b]
	phenyl resonance	methoxy resonances	
2.33	1.28	1.35	1.27
5.86	1.55	1.61	1.57
9.04	1.83	1.79	1.82
13.3	2.16	2.17	2.14
24.1	2.90	3.23	2.96
61.3	5.85	5.40	5.78

[a] Experimental data from Ito and Yamashita.[7] [b] Data obtained from the analysis presented here for the complex model using the polymer compositions obtained on the basis of the phenyl proton resonance.

Table II
The Reactivity Ratios[a] and Equilibrium Constant[b] Obtained from an Analysis of the MA-DPE Polymer Composition Data from Ito and Yamashita Using the Treatment Presented for the Complex Participation Model

parameter	"best value"	range[c]
r_0[d]	0	
p_0[d]	0	
s_0	0.13	0–3
r_1	9.7×10^{-2}	$(9.5\text{–}10.0) \times 10^{-2}$
p_1	0.83	0.6–1.1
s_1	2.1	1.9–2.4
K	1.0×10^{-2}	$(0.8\text{–}1.2) \times 10^{-2}$

[a] The symbol 1 refers to methyl acrylate and the symbol 0 refers to 1,1-diphenylethylene. [b] The units of concentration used were mol dm^{-3}. [c] Defined by setting an upper limit on τ equal to twice the value of τ at the global minimum. [d] Set equal to zero.

The calculated "best-fit" values for the reactivity ratios and the equilibrium constant are shown in Table II. The standard errors associated with these parameters have not been reported here because insufficient experimental data are available for these to provide meaningful estimates of their reliability. However, it is possible to map the hypersurface in the vicinity of the minimum value of the "goodness-of-fit" parameter τ and thereby to assign to each parameter a plausible range of values consistent with an adequate representation of the experimental data, as defined by some upper limit placed on the value of τ. The range of values given in Table I has been assigned by putting a limit on τ of twice the value of τ at the minimum. This limit is consistent with an external estimate of the standard error in the polymer composition 1.4 times greater than that provided by the "best-fit" parameters. These ranges show that the minimum on the hypersurface is well defined and sharp in the direction of all parameters except s_0, where the minimum, though clearly defined, is relatively shallow.

The calculated polymer compositions based upon the "best values" of the parameters are given in Table I along with the experimental data. Ito and Yamashita reported the triad fractions calculated from the methoxy proton resonances (they cannot be obtained from the phenyl proton resonance which appeared as a single peak in the spectrum). In Table III the calculated triad fractions are compared with these experimental values and also with calculated triad fractions reported by Ito and Yamashita

Table III
Experimental and Calculated Triad Fractions for the Terminal, Penultimate, and Complex Models of the MA-DPE Copolymer System

mol ratio of MA^a in	$F_{(111)}$				$F_{(110+011)}$				F_{010}			
polymer	exptl^b	T^c	P^c	C^d	exptl^b	T^c	P^c	C^d	exptl^b	T^c	P^c	C^d
1.28	0.09	0.03	0.03	0.05	0.35	0.29	0.35	0.34	0.56	0.68	0.62	0.62
1.55	0.16	0.13	0.10	0.13	0.44	0.45	0.52	0.46	0.40	0.42	0.38	0.41
1.83	0.20	0.21	0.17	0.20	0.48	0.57	0.57	0.50	0.32	0.30	0.26	0.30
2.16	0.28	0.30	0.25	0.29	0.52	0.50	0.57	0.50	0.20	0.20	0.18	0.22
2.90	0.48	0.47	0.40	0.44	0.42	0.43	0.51	0.45	0.10	0.10	0.09	0.11
5.85	0.70	0.72	0.65	0.69	0.23	0.26	0.33	0.28	0.07	0.02	0.02	0.03

[a] Taken from Ito and Yamashita.[7] [b] Taken from Ito and Yamashita[7] based upon methoxy proton resonances. [c] Taken from the calculation of Ito and Yamashita.[7] [d] Calculated from the data in Table II by the method presented here.

Table IV
The Number Fraction of Sequences for Ito and Yamashita's MA-DPE Copolymers[7] Calculated Using the Reactivity Ratios and Equilibrium Constant Given in Table II

polymer comp mol ratio of MA^a	1.28	1.55	1.83	2.16	2.90	5.85
$N_1 010$	0.77	0.61	0.52	0.43	0.31	0.15
$N_1 0110$	0.19	0.27	0.29	0.28	0.25	0.15
$N_1 01^m0/N_1 0110$ for $m > 2$	$0.16^{(m-2)}$	$0.31^{(m-2)}$	$0.41^{(m-2)}$	$0.51^{(m-2)}$	$0.65^{(m-2)}$	$0.82^{(m-2)}$

[a] Experimental polymer compositions as reported by Ito and Yamashita.

based upon their use of the terminal and penultimate models for the polymerization process. In Table IV the number fractions of sequences is given for a single methyl acrylate residue and for a sequence of two methyl acrylate residues. A general relationship for the calculation of the number fractions for sequences of greater length is also given.

Discussion

Ito and Yamashita[7] analyzed their data in terms of both the terminal and the penultimate models. They concluded that the penultimate model gave a better fit to the composition data than did the terminal model, but the terminal model gave the best fit to the triad fraction data. As mentioned previously, Litt and Seiner[5] have applied the complex participation model to Ito and Yamashita's experimental results. They concluded that this model provided a better fit to the data than either of the other two models for both the copolymer compositions and the triad fractions, though their method of analysis contained some simplifying assumptions. Their analysis did not yield absolute values for all the reactivity ratios or for the equilibrium constant, but they were able to report that the polymer compositions could be best represented if the various reaction rate constants (eq 1-8) obeyed the relationships given in Table V.

In contrast to Litt and Seiner's method of data analysis, the method reported herein is completely general and does not require any simplifying assumptions. However, because of the small number of data points available for this system, we have applied two physically reasonable constraints on the method of analysis, that r_0 and p_0 equal zero (since 1,1-diphenylethylene does not homopolymerize). In this particular application then, our method is not completely general in the mathematical sense, but the constraints we have applied to the system are not as severe as those used by Litt and Seiner. The results obtained from this analysis are compared with those of Litt and Seiner in Table V.

Table V
Comparison of the Results Obtained by Litt and Seiner[5] with Those Obtained Herein for the Complex Participation Model for the MA-DPE Copolymer System

function^a	Litt and Seiner[5]	present work
k_{00}/k_{01}	0	0
$k_{00}/k_{0\overline{10}}$	0	0
$k_{1\overline{10}}/(k_{1\overline{10}} + k_{1\overline{01}})$	0	0.45
$k_{11}/[K(k_{1\overline{10}} + k_{1\overline{01}})]$	0.85	2.5
$Kk_{0\overline{10}}/k_{01}$	0	1.3×10^{-3}
k_{11}/k_{10}	28	0.097

[a] The symbol 1 refers to methyl acrylate and the symbol 0 refers to 1,1-diphenylethylene.

The most striking difference between the two sets of results in Table V is that for the reactivity ratio k_{11}/k_{10} (r_1), the rate constant for addition of a methyl acrylate monomer to a methyl acrylate residue on the chain terminus relative to that for addition of a diphenylethylene monomer to this residue. Based upon the present analysis, we found the rate constant for addition of the methyl acrylate monomer to be about ten times smaller than that for addition of the diphenylethylene monomer, the reverse of the finding reported by Litt and Seiner[5] that methyl acrylate was 28 times more reactive than diphenylethylene. By contrast, our value of r_1 (0.097) is only slightly greater than that obtained by Ito and Yamashita (0.092 ± 0.01) based upon the simple terminal model. Our observations are supported by the known rate constants for addition of styrene and methylacrylate monomers to a methyl acrylate radical. Here the rate for methyl acrylate addition is reported to be seven times smaller than that for styrene addition (2.09×10^3 and 1.4×10^4 dm^3 mol^{-1} at 60 °C, respectively[11]). It would be expected that the rate constant for addition of diphenylethylene would be greater than that for styrene because of the greater resonance stabilization of the diphenylethylene chain radical.

For a methyl acrylate residue on the terminus of the growing chain, the rate constants for addition of the complex (which shows almost equal propensity to add from either side $k_{1\overline{10}}/k_{1\overline{01}} = 0.83$) are slightly greater than that for addition of the diphenylethylene monomer and slightly more than an order of magnitude greater than that for addition of methyl acrylate monomer. This is not altogether surprising since it is well known that the components of such low-energy interacting systems may display fundamental properties different from those of the parent molecules. For example, the electron densities about some of the atoms of the complex could be changed markedly, such that the complex may be considered to be in an "activated" state. It is quite likely that the reactivity of one member of the complex could be more enhanced than that of the other member.

If the end residue on the growing chain is diphenylethylene, the "best-fit" value for s_0 predicts that the rate constant for addition of methyl acrylate monomer is greater than that for addition of the complex. But, s_0 is not as clearly defined as the other parameters, and this prediction could be reversed, since it is plausible that s_0 could be slightly greater than unity. However, the "best-fit" prediction is not unrealistic since, for example, it is known[11] that the rate constant for addition of methyl acrylate to a styrene radical is about 1.4 times larger than that for addition of styrene to this radical. This observation has been explained[11] in terms of the polarity of the two monomers and the two chain radicals and the relatively low reactivity of a resonance stabilized chain radical. The polarity of the complex would be expected to differ from that of methyl acrylate monomer, which could account for its lower rate constant. The relatively smaller rate constant for addition of the complex could also be afforded, at least in part, by a consideration of the bulk of both the complex and of the diphenylethylene residue on the chain terminus.

The calculated "best values" of the reactivity ratios and the equilibrium constant provide a good fit to the composition data (see Table I). The standard deviation in the copolymer composition (expressed as a mole ratio) as determined from the curve fit was 0.09 (i.e., 5% on average), which compares favorably with the value of 0.32 based upon the fit of the penultimate model as determined by Ito and Yamashita. The internal check provided by the triad fractions is also very good, though the accuracy of the experimental data is only in the range 5-10%. A comparison of the triad fractions calculated for the three models—terminal, penultimate, and complex—shows that the complex model fits the data much better than do the other two. However, before any detailed comparison of the suitability of these models could be made, it would be necessary to obtain accurate composition and triad fraction data for a large number of copolymers representative of the whole range of reactant monomer compositions.

In summary, we have presented a method by which the "best values" of the reactivity ratios and the equilibrium constant can be calculated for systems which can be represented by the complex participation model for free-radical polymerization. We have shown how the triad fractions and the sequence distribution can be calculated from these parameters. We have also demonstrated how this method is applied by calculating the parameters and the triad fractions for the 1,1-diphenylethylene–methyl acrylate copolymer system. We have shown that, even though the number of available data on this system is limited, the magnitudes of the "best-fit" parameters are physically realistic when compared with out knowledge of other copolymer systems, and the fit to the experimental data is acceptable. Thus the complex participation model cannot be ruled out as a possible mechanism for this copolymerization. Unfortunately, no unequivocal choice between the complex participation and other mechanisms could be made, because of the lack of a sufficient number of experimental data points. Thus the assignment of a mechanism must await further studies of the system in which copolymer compositions, triad fractions, or sequence distributions are obtained for a greater number of copolymers representative of the whole monomer composition range.

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(7) K. Ito and Y. Yamashita, *J. Polym. Sci., Part A-1*, 4, 631–637 (1966).
(8) These definitions of the reactivity ratios have some advantages over those used by Seiner and Litt,[3] since if one monomer does not show any propensity to homopolymerize, the reactivity ratios for the monomer always remain defined. This is not so with Seiner and Litt's definitions.
(9) Here only the 1 units will be considered, but the treatment for 0 units is exactly the same but with 0's exchanged for 1's and vice versa.
(10) J. P. Chandler, Quantum Chemistry Program Exchange, 1976, no. 11, p 307.
(11) F. W. Billmeyer, "Textbook of Polymer Science", Wiley, New York, 1971, pp 342–347.