The Role of Monomer Charge-Transfer Complexes in Free Radical Copolymerization. III. Methyl Acrylate–Diphenylethylene Copolymers. Comparison with Penultimate Hypothesis[1a]

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ABSTRACT: The data of Ito and Yamashita[9] on copolymerization of methyl acrylate with 1,1-diphenylethylene have been reinvestigated using the charge-transfer complex copolymerization approach. The original data using both terminal and penultimate models did not fit too well in composition or triad probabilities, P_3(B*A*B), P_3(B*A*A), and P_3(A*A*A). The present approach fits the data better than the two models used by the authors. However, there are not enough data given to resolve ambiguities in the values of the reactivity ratios under the present theory.

Deviations of polymer composition from that predicted by the terminal model of copolymerization[2] have usually been ascribed to penultimate effects.[3-6] A different model was presented in an earlier paper based on addition of the terminal radical to monomer or to a charge-transfer complex of the two monomers.[7] In such a case, both monomers add as a unit.

We have applied it to several cases where one monomer does not homopolymerize, but where only copolymer composition was determined.[8] In this paper the theory will be used to analyze the data of Ito and Yamashita,[9] who determined sequence distributions as well as copolymer composition from nmr measurements in a case where monomer 2 cannot homopolymerize, methyl acrylate and diphenylethylene.

Discussion

As one monomer does not add to itself and the equilibrium constant of complexing is probably small, the equation developed in the previous papers[7,8] is appropriate.

$$y = 1 + \frac{r_{12}[A]/[B] + \dfrac{r_{12}K}{r_{1C1}}[A]}{1 + \dfrac{r_{12}K}{r_{1C}}[A]} \qquad (1)$$

Here y is the molar ratio of monomer 1 to monomer 2 in the polymer. [A] is the concentration (moles per liter) of monomer 1, and [B] the concentration of monomer 2. As usual, r_{12} is the reactivity ratio[2] of $\sim$A· toward monomers 1 and 2; $r_{21} = 0$ since radical $\sim$B· cannot add to B. r_{1C} is the reactivity ratio for addition of $\sim$A· to either side of the complex *vs.* addition to A. r_{1C1} is the reactivity ratio for addition of $\sim$A· to the A side of the complex.

Equation 1 can be rearranged to a form amenable for graphical analysis.

$$[B]\left(y - 1 - \frac{r_{1C}}{r_{1C1}}\right) = \frac{r_{1C}}{K} - \frac{r_{1C}}{Kr_{12}}\frac{(y-1)[B]}{[A]} \qquad (2)$$

Here, by assuming different values of r_{1C}/r_{1C1} between 0 and 1, one can plot the left side of eq 2 *vs.* $(y - 1)[B]/[A]$. If a straight line with a negative slope is obtained, the parameters can be determined. As will be shown, several values of r_{1C}/r_{1C1} may satisfy these conditions. In such a case, r_{12} must be determined independently to get unequivocal parameters. However, this does not affect the fit of the data.

When we apply eq 2 to the data of Ito and Yamashita,[9] given in Table I, we find the results shown in Figure 1. The enclosed areas for the points on Figure 1 encompass the variations in y of Table I. The various parameter values for different r_{1C}/r_{1C1} are given in Table II.

It can be seen that we cannot decide which end of the complex is attacked or the importance of r_{12} *vs.* r_{1C}/K, as all three values of r_{1C}/r_{1C1} give straight line plots for the data. The closeness of fit is better for the case $r_{1C}/r_{1C1} = 0$, and these values will therefore be used for the rest of the discussion. Copolymerization over a wider range or dilution experiments in an inert solvent or both would be necessary to determine the exact parameters. (It can be seen in Figure 1 that $(y - 1)[B]$ is almost constant. If it were exactly constant, then $(y - 1)[B] = r_{1C}/K \approx 0.83$, and the data are fitted with one parameter, implying that incorporation of monomer B into the polymer can be exclusively through complex polymerization. However, if one postulates that attack on the complex would leave the most stable radical, the attack should be on side A, $r_{1C}/r_{1C1} = 1.0$, since the diphenylethylene radical is more stable than methyl acrylate.)

Copolymer Compositions

The predictions for y from the present theory can now be compared with those of Ito and Yamashita using the penultimate and terminal copolymerization theories. The following equation is used.

$$y - 1 = \frac{[A]/[B]}{1.18[A] + 0.036} \qquad (3)$$

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(1) (a) This paper was given at the Candian High Polymer Conference, Aug 1969; (b) Case Western Reserve University; (c) PPG Industries; (d) this work was performed while J. Seiner was on leave as an Industrial Research Associate at CWRU.

(2) (a) F. R. Mayo and F. M. Lewis, *J. Amer. Chem. Soc.*, **66**, 1594 (1944); (b) T. Alfrey, Jr., and G. Goldfinger, *J. Chem. Phys.*, **12**, 205 (1944).

(3) E. T. Mertz, T. Alfrey, Jr., and G. Goldfinger, *J. Polym. Sci.*, **1**, 75 (1946).

(4) G. E. Ham, *ibid.*, **54**, 1 (1961).

(5) W. G. Barb, *ibid.*, **11**, 117 (1953).

(6) M. Litt and F W. Bauer, *ibid.*, *Part C*, **No. 16**, 1551 (1967).

(7) J. Seiner and M. Litt, *Macromolecules*, **4**, 308 (1971).

(8) M. Litt and J. Seiner, *ibid.*, **4**, 316 (1971), and subsequent papers.

(9) K. Ito and Y. Yamashita, *J. Polym. Sci.*, *Part A-1*, **4**, 631 (1966).

TABLE I
DATA OF ITO AND YAMASHITA[d]

[A],[a] mol/l.	[B],[a] mol/l.	y[b]	y[c]
6.03	2.59	1.28	1.36
8.32	1.42	1.55	1.61
9.11	1.01	1.83	1.79
9.97	0.73	2.16	2.17
10.25	0.43	2.90	3.23
10.75	0.176	5.85	5.40

[a] Calculated from [A]/[B] given in ref 9 from the known densities and molar volumes of the monomers. [b] From the relative areas of the phenyl proton nmr resonance. [c] From the triad fractions of the methyl proton resonances according to eq 7, ref 9, $y = 1/[\mathrm{F(AAB)} + \mathrm{F(BAB)}]$. See ref 9 for data. [d] See ref 9.

TABLE II
PARAMETERS OF TERMINAL COMPLEX MODEL FROM GRAPHICAL SOLUTIONS OF EQUATION 2

r_{1C}/r_{1C1}	r_{1C}/K	r_{12}
0.0	0.85	28
0.5	2.5	0.109
1.0	3.9	0.088

This is a variation of eq 1 obtained by dividing the numerator and denominator of the fraction by r_{12}, using the parameters from Table II, $r_{1C}/r_{1C1} = 0$. Other values of the parameters give almost as good results. Values of y calculated from the terminal and penultimate models[9] and y calculated from eq 3 are compared with the experimentally determined values in Figure 2. As can be seen, the complex model is clearly a better fit to the data than either of the other two models. It seems to fit the compositions obtained from the phenyl proton resonance much better than that obtained from triad fractions. The latter is much more sensitive to small errors; indeed, resolution of the triad data was estimated to be no better than ±5–10%,[9] thus making compositions derived from it suspect.

Triad Probabilities

The triad fractions are easily derived for the case where one monomer does not add to itself. This was done by Ito and Yamashita.[9] It can be done slightly differently and the results are then easily seen and applied

$$F_3(\mathrm{B}A\mathrm{B}) = F(\mathrm{B})P_3(\mathrm{B}A\mathrm{B}) =$$

$$F(\mathrm{B})P(\mathrm{A/B})P(\mathrm{B/A}) = F(\mathrm{B})P(\mathrm{B/A}) \quad (4)$$

When B does not add to itself, $y = 1/P(\mathrm{B/A})$,[7] and we can write

$$F_3(\mathrm{B}A\mathrm{B}) = \frac{1}{y+1}\,\frac{1}{y} \quad (5)$$

The foregoing says that the fraction of BAB units in a chain equals the fraction of B units times the probability that B adds A times the probability that A adds B. In this case, B cannot add to itself; therefore $P(\mathrm{A/B}) = 1$, and $P(\mathrm{B/A}) = 1/y$.[7]

Similarly, one can derive the other triad fractions

$$F_3(\mathrm{A}A\mathrm{B}) = F_3(\mathrm{B}A\mathrm{A}) \quad (6)$$

$$F_3(\mathrm{B}A\mathrm{A}) = F(\mathrm{B})P(\mathrm{A/A}) = \frac{1}{y+1}\left(1 - \frac{1}{y}\right) =$$

$$\frac{y-1}{y(y+1)} \quad (7)$$

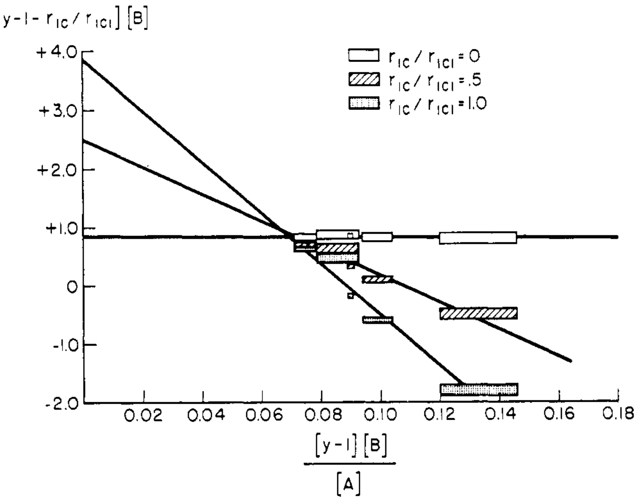

Figure 1. Determination of parameters of eq 2, for copolymerization of methyl acrylate and diphenylethylene: r_{1C}/r_{1C1} as defined in figure.

$$F_3(\mathrm{A}A\mathrm{B}) = F(\mathrm{A})P(\mathrm{A/A})P(\mathrm{B/A}) =$$

$$\frac{y}{y+1}\cdot\frac{y-1}{y}\,\frac{1}{y} = \frac{y-1}{y(y+1)} \quad (8)$$

and

$$F_3(\mathrm{A}A\mathrm{A}) = F(\mathrm{A})[P(\mathrm{A/A})]^2 =$$

$$\frac{y}{y+1}\cdot\left(\frac{y-1}{y}\right)^2 = \frac{(y-1)^2}{y(y+1)} \quad (9)$$

These can be normalized to probabilities by dividing by the sum of the fractions

$$F_3(\mathrm{A}A\mathrm{A}) + F_3(\mathrm{A}A\mathrm{B}) + F_3(\mathrm{B}A\mathrm{A}) + F_3(\mathrm{B}A\mathrm{B}) = \frac{y}{y+1} \quad (10)$$

$$P_3(\mathrm{A}A\mathrm{A}):P_3(\mathrm{A}A\mathrm{B}) + P_3(\mathrm{B}A\mathrm{A}):P_3(\mathrm{B}A\mathrm{B}) =$$

$$(y-1)^2/y^2 : 2(y-1)/y^2 : 1/y^2 \quad (11)$$

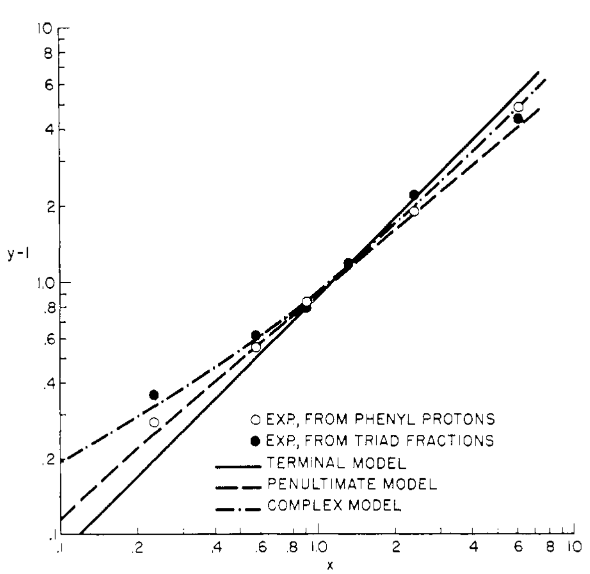

Figure 2. Comparison of experimental data with theoretical curves for terminal, penultimate, and complex models: x = mole ratio M_1/M_2 in monomer feed and y = mole ratio m_1/m_2 in copolymer.

TABLE III
COMPARISON OF TRIAD PROBABILITIES FROM THE VARIOUS THEORIES WITH EXPERIMENTAL

	$P_3(AAA)$				$P_3(BAA) + P_3(AAB)$				$P_3(BAB)$			
y^a	Exptl^b	C^c	T^d	P^e	Exptl^b	C^c	T^d	P^e	Exptl^b	C^c	T^d	P^e
1.28	0.09	0.06	0.03	0.03	0.35	0.37	0.29	0.35	0.56	0.57	0.68	0.62
1.55	0.16	0.14	0.13	0.10	0.44	0.47	0.45	0.52	0.40	0.39	0.42	0.38
1.83	0.20	0.21	0.21	0.17	0.48	0.49	0.57	0.57	0.32	0.30	0.30	0.26
2.16	0.28	0.28	0.30	0.25	0.52	0.50	0.50	0.57	0.20	0.22	0.20	0.18
2.90	0.48	0.44	0.47	0.40	0.42	0.45	0.43	0.51	0.10	0.11	0.10	0.09
5.85	0.70	0.69	0.72	0.65	0.23	0.28	0.26	0.33	0.07	0.03	0.02	0.02

[a] Taken from ref 9, phenyl proton resonance. [b] Mole fraction determined from triad fractions.[9] [c] Complex-copolymerization predictions using y from eq 3. [d] Terminal copolymerization predictions.[9] [e] Penultimate copolymerization predictions.[9]

The approach also provides an internal check on the triad values. They should agree with those calculated from the experimental values of y. In Ito and Yamashita's case, the agreement is very poor, again showing the large uncertainty in the triad determinations. It must be emphasized that the above relationships hold only when one monomer cannot add to itself.

The complex copolymerization theory can now be tested against the other possible theories by calculating triad possibilities for all theories and comparing them against the experimentally determined ones. This is given in Table III. It is apparent that while the penultimate equations give a reasonable fit to copolymer composition data, their predictions give the poorest fit to triad data. The terminal model is better and fits over most of the range, except at low values of y. The complex model gives the best fit to the triad distributions over the whole range and fits much better at low y than any of the other models.

In summary, in this paper we have examined a case where two monomers copolymerize well, and one of them cannot add to itself. We found that the complex copolymerization model fitted the composition data better than the two used in the original paper, the terminal and penultimate models. When sequence distributions were examined, the same was found to be true. The complex model was closer to the experimental values than the other two models. In no case was it more than 0.05 mol fraction away, which was within the limits of error given in the paper. However, ambiguities arose in determining constants which can only be settled by further experiments. In addition, some useful relationships between y and triad fractions were defined, though these are implicit in earlier work.

The Role of Monomer Charge-Transfer Complexes in Free Radical Copolymerization. IV. Comparison with the Penultimate Hypothesis for Several Simple Systems[1a]

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ABSTRACT: The terminal complex model of copolymerization has been applied to four systems where one comonomer does not homopolymerize and which had been interpreted in terms of a penultimate effect. These are vinyl acetate–*sym*-dichlorotetrafluoroacetone, vinyl acetate–hexafluoroacetone, vinyl acetate–tetrachlorocyclopropene, and styrene–tetrachlorocyclopropene. It is shown that the present model fits the data as well as or better than the ones used in the other papers.

In the previous paper[2] the basic equations for copolymerization in the presence of charge-transfer complexes of the monomers were derived. The hypothesis can therefore be tested by applying it to systems which deviate from the Mayo–Alfrey equations.[3] Usually these deviations have been explained by recourse to the hypothesis of a penultimate effect.[4] Since the initial applications of a theory should be the simplest, we will work in this paper with systems where one of the monomers absolutely cannot add to itself and the equilibrium constant for complex formation is probably small (K <0.03). Two papers were chosen which cover four systems, vinyl acetate with dichlorotetrafluoro- and hexafluoroacetone[5] and vinyl acetate and styrene with tetrachlorocyclopropene.[6]

Discussion

The basic equation that is used when monomer B does not add to itself and the equilibrium constant for complex formation, K, is <0.03 is

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[1] (a) This paper presented at the Canadian High Polymer Conference Aug 1969; (b) Case Western Reserve University; (c) PPG Industries; (d) this work was performed while J. Seiner was on leave as an Industrial Research Associate at CWRU.

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[4] W. G. Barb, *J. Polym. Sci.*, **11**, 117 (1953); G. E. Ham, *ibid.*, **54**, 1 (1961); E. T. Mertz, T. Alfrey, and G. Goldfinger, *ibid.*, **1**, 75 (1946).

[5] M. Litt and F. W. Bauer, *ibid., Part C*, **No. 16**, 1551 (1967).

[6] J. K. Hecht and N. D. Ojha, *Macromolecules*, **2**, 94 (1969).