Table III

Comparison of Triad Probabilities from the Various Theories with Experimental

y^a	$P_3(AAA)$				$P_3(BAA) + P_3(AAB)$				$P_3(BAB)$			
	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.

(2) M. Litt and J. Seiner, *Macromolecules*, **4**, 314 (1971).

(3) (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).

(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).

$$y - 1 = \frac{r_{12}[\mathrm{A}]/[\mathrm{B}] + (Kr_{12}/r_{1\mathrm{C}1})[\mathrm{A}]}{1 + (Kr_{12}/r_{1\mathrm{C}})[\mathrm{A}] + \theta} \qquad (1)$$

This is a slight rearrangement of eq 35 in the previous paper.[2] As usual, $r_{12} = k_{11}/k_{12}$, $r_{1\mathrm{C}1} = k_{11}/k_{1\mathrm{C}1}$, and $r_{1\mathrm{C}} = k_{11}/(k_{1\mathrm{C}1} + k_{1\mathrm{C}2})$ and

$$\theta = Kr_{21}/r_{2\mathrm{C}1}[\mathrm{B}][1 + Kr_{12}/r_{1\mathrm{C}1}[\mathrm{A}]] \qquad (2)$$

Empirically, we have found that θ is negligible and can be ignored for these cases. This must mean that $k_{2\mathrm{C}1}K \ll k_{21}$. However, until experimental work is done to show this point, it will remain an important but untested simplification. The equation applicable to these cases is therefore

$$y - 1 = \frac{r_{12}[\mathrm{A}]/[\mathrm{B}] + (Kr_{12}/r_{1\mathrm{C}1})[\mathrm{A}]}{1 + (Kr_{12}/r_{1\mathrm{C}})[\mathrm{A}]} \qquad (3)$$

TABLE I

VINYL ACETATE–4FK. COMPARISON OF EXPERIMENTAL AND CALCULATED m_2 FOR DIFFERENT COPOLYMERIZATION THEORIES

Feed data		m_2		
[A]/[B]	[A], mol/l.	Penultimate[a]	Exptl[a]	Complex[b]
19.75	10.1	0.083	0.088 ± 0.010	0.088
9.81	9.47	0.144	0.142 ± 0.011	0.143
4.02	8.06	0.220	0.221 ± 0.008	0.225
3.00	7.42	0.244	0.248 ± 0.007	0.250
3.08	7.50	0.242	0.252 ± 0.011	0.248
0.844	4.15	0.332	0.325 ± 0.012	0.334
0.252	1.69	0.377	0.387 ± 0.018	0.383
0.086	0.645	0.427	0.424 ± 0.012	0.425

[a] Taken from ref 5. The calculations use the equation $y = 1 + 5.6[\mathrm{A}]/[\mathrm{B}][(1 + 0.41[\mathrm{A}]/[\mathrm{B}])/(1 + 5.6[\mathrm{A}]/[\mathrm{B}])]$ based on the penultimate effect, $m_2 = 1/(y + 1)$. [b] Based on data of ref 5, using eq 3 of this paper, where $r_{12} = 5.4$, $r_{1\mathrm{C}}/K = 5.1$, $r_{1\mathrm{C}1}/K = 25.6$, $r_{1\mathrm{C}}/r_{1\mathrm{C}1} = 0.20$.

TABLE II

VINYL ACETATE–6FK. COMPARISON OF EXPERIMENTAL AND CALCULATED m_2 FOR DIFFERENT COPOLYMERIZATION THEORIES

Feed data		m_2		
[A]/[B]	[A], mol/l.	Penultimate[a]	Exptl[a]	Complex[b]
22.4	10.15	0.176	0.166 ± 0.012	0.183
9.71	9.46	0.242	0.179 ± 0.013	0.251
6.15	8.83	0.272	0.304 ± 0.030	0.281
4.24	8.19	0.291	0.307 ± 0.012	0.301
0.993	4.59	0.344	0.339 ± 0.013	0.349
0.312	2.04	0.387	0.383 ± 0.017	0.380

[a] Taken from ref 5. The calculations use the equation $y = 1 + 4.1[\mathrm{A}]/[\mathrm{B}][(1 + 0.12[\mathrm{A}]/[\mathrm{B}])/(1 + 4.1[\mathrm{A}]/[\mathrm{B}])]$, based on the penultimate effect. [b] Based on data from ref 5, using eq 3 of this paper, where $r_{12} = 1.14$, $r_{1\mathrm{C}}/K = 1.4$, $r_{1\mathrm{C}1}/K = 1.63$, $r_{1\mathrm{C}}/r_{1\mathrm{C}1} = 0.8$.

TABLE III

REACTIVITY RATIOS FOR FLUORO KETONES *vs.* VINYL ACETATE

Fluoro ketone		r_{12}	$r_{1\mathrm{C}}/r_{1\mathrm{C}1}$	$r_{\mathrm{C}1}/K$
sym-Dichlorotetrafluoroacetone (4FK)		5.4	0.20	5.1
Hexafluoroacetone (6FK)	a	0.74	1.0	1.4
	b	∞	0.5	1.4

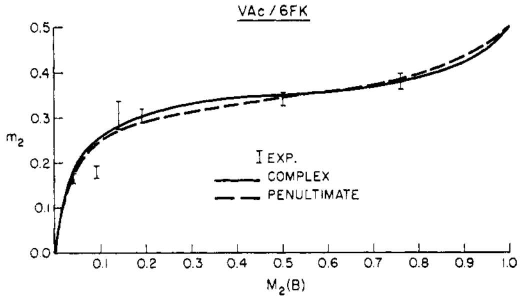

Figure 1. Copolymerization of vinyl acetate (VAc) with hexafluoroacetone (6FK). Comparison of theoretical curves for penultimate and complex copolymerization with experimental data.

Equation 3 can be recast easily into a form suitable for solving for the constants.

$$y - 1 = r_{1\mathrm{C}}/r_{1\mathrm{C}1} + r_{1\mathrm{C}}/K[\mathrm{B}] - (r_{1\mathrm{C}}/Kr_{12})(y - 1)[\mathrm{A}] \qquad (4)$$

In the following discussion, the parameters of eq 4 for two pairs of comonomers have been determined by least squares. For the other two, the data were too few and scattered and graphical methods were used.

Vinyl Acetate–Fluorochloroacetones[5]

In this paper, Litt and Bauer postulate a strong penultimate effect and get almost perfect agreement with the data in one case, dichlorotetrafluoroacetone (4FK), and reasonable agreement in the other, hexafluoroacetone (6FK). The data and predictions from both theories are presented in Tables I–III. (The density of 4FK is *ca.* 1.5 while that of 6FK is *ca.* 1.3; [A] has been calculated from summing up the volumes of the two monomers and calculating the molarity.) Table I presents the 4FK results while Table II gives the 6FK results. As usual, m_2 is the mole fraction of monomer 2 (4FK or 6FK) in the copolymer and y is the molar ratio of the two monomers in the copolymer. The data will be discussed after the tables are presented.

For comparison, the range of parameters which fit the experimental data for the two cases is given in Table III. The comparison for 6FK of the two theories is shown graphically in Figure 1. The agreement for 4FK from both theories is so close, a graph cannot show the difference. The penultimate effect values given in the paper for the 4FK–vinyl acetate curves are not the best possible fit, as only two of the eight calculated points are higher than the experimental points. Therefore, the fit is almost perfect for both theories. In the 6FK–vinyl acetate case, the predictions are measurably different and the terminal complex model gives slightly better results. As can be seen from Table III, r_{12} cannot be extracted from the data; it can vary between 0.74 and ∞, affecting the goodness of fit only marginally. The attack of vinyl acetate radical on complex is determined exactly from the equations, showing that this reaction is, in general, the important one in the copolymerization. An independent measure of r_{12} can be obtained by polymerizing in a solvent and thus lowering monomer concentrations and perhaps K also. These effects increase the importance of r_{12}; extrapolation of the results to infinite dilution will then give an exact value for r_{12}. Two conclusions can be drawn from this set of data: (1) the terminal complex model of copolymerization gives a slightly better fit for the data than the penultimate model and (2) as expected, the complex of vinyl acetate with hexafluoroacetone is more reactive than that with *sym*-dichlorotetrafluoroacetone. This may be due to a larger K, or a

TABLE IV
VINYL ACETATE–TCCP (M_2). COMPARISON OF EXPERIMENTAL AND CALCULATED m_2 FOR DIFFERENT COPOLYMERIZATION THEORIES

Feed data		m_2			
[A]/[B]	[A], mol/l.	Penultimate[a]	Exptl[a]	Complex I[b]	Complex II[c]
18.6	10.3	0.061	0.06	0.059	0.060
8.09	9.49	0.113	0.11	0.115	0.113
3.17	7.84	0.189	0.18	0.188	0.191
2.03	6.78	0.224	0.23	0.226	0.218
1.38	5.75	0.250	0.26	0.256	0.256
0.887	4.55	0.274	0.28	0.286	0.283
0.515	3.20	0.297	0.32	0.316	0.308
0.235	1.73	0.316	0.35	0.354	0.338
0.109	0.88	0.324	0.35	0.382	0.356

[a] Data taken from ref 6. Calculation for penultimate effect for m_2 taken from the same reference, $y = 2 + 0.72x$, $m_2 = 1/(y + 1)$. [b] Calculated from the data of ref 6, using eq 3, where $r_{12} = 12.3$, $r_{1C}/K = 8.93$, $r_{1C}/r_{1C1} = 0$. [c] Calculated from the data of ref 6, using eq 3, where $r_{12} = 33.2$, $r_{1C}/K = 8.3$, $r_{1C}/r_{1C1} = 0$.

TABLE V
STYRENE–TCCP (M_2). COMPARISON OF EXPERIMENTAL AND CALCULATED m_2 FOR DIFFERENT COPOLYMERIZATION THEORIES

Feed data		m_2			
[A]/[B]	[A], mol/l.	Penultimate[a]	Exptl[a]	Complex I[b]	Complex II[c]
6.69	11.9	0.024	0.033	0.032	0.033
2.45	8.80	0.059	0.060	0.065	0.065
1.70	7.45	0.079	0.079	0.080	0.080
1.13	5.95	0.106	0.104	0.099	0.098
0.724	4.46	0.140	0.135	0.122	0.121
0.429	3.00	0.184	0.153	0.153	0.152
0.190	1.50	0.245	0.263	0.216	0.216
0.090	0.75	0.285	0.289	0.288	0.287

[a] Data taken from ref 6. Calculated values for m_2 with penultimate effect taken from the same reference, $y = 2 + 5.7x$. [b] Calculated from the data of ref 6, using eq 3, where $r_{12} = 20$, $r_{1C}/K = 66$, $r_{1C1} = 0$. [c] Calculated from the data of ref 6, using eq 3, where $r_{12} = 17.3$, $r_{1C}/K = 65$, $r_{1C}/r_{1C1} = 1.0$.

TABLE VI
REACTIVITY RATIOS FOR TCCP (m_2) *vs.* VINYL ACETATE AND STYRENE

Comonomer	r_{12}	r_{1C}/r_{1C1}	r_{1C}/K
Vinyl acetate	12–33	0	8.9–8.3
Styrene a	19 ± 1	0	67 ± 3
b	17 ± 1	1.0	63 ± 3

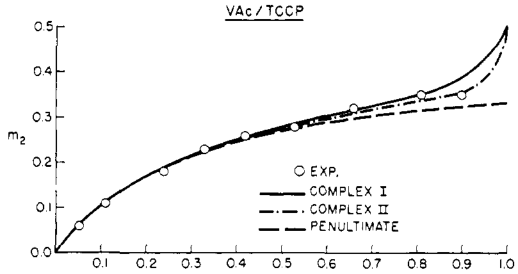

Figure 2. Copolymerization of vinyl acetate (VAc) with tetrachlorocyclopropene (TCCP). Comparison of theoretical curves for penultimate and complex copolymerization with experimental data. See Table IV for parameter values for complex I and complex II curves.

larger k_{1C} because of the lower steric hindrance of the hexafluoroacetone.

An interesting point is that the equations fit only if it is postulated that a vinyl acetate radical attacks the vinyl acetate side of the complex 20% of the time in the case of 4FK and 50% or more of the time in the 6FK case. This goes against the naïve intuition that a negative radical should attack only the positive end of the complex and *vice versa*. It may be that vinyl acetate radical is near enough to neutrality that it is relatively unaffected by polarity and attacks the least hindered end.

A referee has drawn attention to the possibility that similar copolymer composition curves may also arise from a copolymerization where one of the monomers can depropagate.[7] While this may be applicable in some cases, it probably does not apply here. At low ratios of [B] to [A], 6FK copolymerizes about twice as rapidly as 4FK. At high ratios, the copolymer composition ratios are almost identical. Thus the larger, more hindered fluoro ketone is incorporated relatively better at high concentrations than it was at low concentrations. One would not expect this if depropagation were important. In addition, in our laboratories, the azeotropic monomer feed composition, $y = x = 3.00$, was constant from 60 to 0°. This is possible in a charge-transfer complex copolymerization, but not in a reversible copolymerization, due to the high activation energy for depolymerization.

Tetrachlorocyclopropene (TCCP) Copolymerizations

Hecht and Ojha copolymerized this monomer with vinyl acetate and styrene.[6] The data and predictions for the two theories are given in Tables IV and V. As Hecht gives no error range, we can go only by the nearness of fit. The data for Table IV are shown graphically in Figure 2, using an arbitrary error of ±0.01 in mole fraction for monomer and polymer. The data for Table V are shown graphically, Figure 3, using an arbitrary error of ±0.01 in the mole fractions of M_2 and m_2. It is difficult to decide in this case which of the theoretical curves for penultimate or complex copolymerization fit the data better. They both miss some points, and while being very different shapes, agree about as well.

We can now compare the variation in parameters which allows fits to the experimental data. This is given in Table VI.

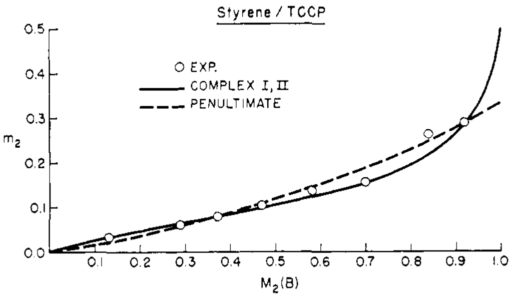

Figure 3. Copolymerization of styrene with tetrachlorocyclopropene (TCCP). Comparison of theoretical curves for penultimate and complex copolymerization with experimental data. See Table V for parameter values for complex I, II curve.

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(7) C. Walling, *J. Polym. Sci.*, **16**, 315 (1955).

Examination of the data and Figures 2 and 3 shows that, with vinyl acetate, the terminal complex model gives a better fit than that with the parameters chosen by Hecht.[6] However, he set r' ($=k_{221}/k_{212}$) = 0. A judicious choice of r' could give a better fit. As can be seen, one cannot choose easily between the models in the styrene case, within the possible experimental errors. Here, one cannot even choose between the possibilities of whether a radical attacks the A or B side of a complex. This is due to the high reactivity ratios. However, polymerization in a solvent should fix r_{12} and decide the question. Probably, the B side is attacked as this produces a stable styryl radical at the polymer end.

Another difficult point is interpretation of the data at high TCCP ratios. This is suspect, as the molecular weights are quite low (about 2000). Thus, end effects could lower or raise the mole ratios depending on the assumed termination steps. This can be seen, for example, in the complex I curve in Figure 2. Here the curve is within ±0.01 mol fraction of the experimental points, except for the last point.

Finally, we can compare the reactivity ratios in Table IV. One might expect that r_{12} for vinyl acetate should be closer to 12 than to 33 since r_{12} for styrene is about 19. The lack of sensitivity indicates that most of the incorporation of TCCP with vinyl acetate occurs through the complex. On the other hand, r_{1C}/K for styrene is about 65 compared to about 8.5 for vinyl acetate. Therefore, complex copolymerization of TCCP with styrene is relatively unimportant except at high mole fractions of A.

It is possible too that in this case a true steric penultimate effect or reversible copolymerization may be occurring.[7] This could be settled by copolymerization at lower temperatures. Since in the VAc–TCCP copolymer, an m_2 of 0.35 was found, lowering the polymerization temperature should raise this rapidly toward 0.5. If complexes are operating, the change should be slight and related to changes in the equilibrium constant with temperature.

In summary, copolymerization of vinyl acetate with fluorochloroacetones and vinyl acetate and styrene with TCCP both can be rationalized by a terminal complex copolymerization model as well as or better than by a penultimate model. It is truly remarkable how well two different equations can fit the same data. As usual, changing from a less to a more reactive comonomer (4FK to 6FK with vinyl acetate, styrene to vinyl acetate with TCCP) lowers the reactivity ratios and the copolymer curves show greater alternation. Neither paper gives sufficient data to allow a choice between models. One needs solution polymerization at various dilutions to decide.

Quinone Copolymerization. II. Reactions of 1,4,5,8-Tetrachloroanthraquinone, 2,3-Dichloro-1,4-naphthoquinone, and 2,3,5,6-Tetramethyl-*p*-benzoquinone with Vinyl Monomers under Free Radical Initiation

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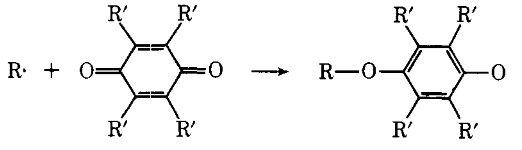
ABSTRACT: The copolymerization reactions of certain vinyl monomers with 1,4,5,8-tetrachloroanthraquinone, 2,3-dichloro-1,4-naphthoquinone, and 2,3,5,6-tetramethyl-*p*-benzoquinone were studied. No general correlations were observed between the quinone redox potentials and their copolymerizability with vinyl monomers. The 1,4,5,8-anthraquinone copolymerized readily with a variety of monomers to afford high molecular weight products. The mechanism proposed for these reactions involves a 1,4-butadiene-type addition of the vinyl monomer to the fused ring(s) of the anthraquinone. In contrast to the anthraquinone reactions, neither the naphthoquinone nor the tetramethylbenzoquinone showed a general tendency to copolymerize with the vinyl monomers. However, interesting polymeric products were obtained from some of the reaction mixtures of these latter quinones.

Quinones have long been associated with polymer chemistry as retarders or inhibitors to free radical vinyl polymerization. Consensus has been that quinones retard by addition to radicals, forming relatively stable semiquinones (I) which do not add to vinyl monomer (eq 1). Some recent publications on the inhibition of vinyl polymerization by quinones, however, have demonstrated that semiquinones (I) once formed do not always assume a passive role. Indeed, some of these species were active enough to add to certain vinyl monomers and, to a very limited extent, regenerate polymer chains.[2] Although the quinone/monomer ratios in the regenerated chains were minute, the quinones were incorporated within the chains and not present solely as end groups.



(1)

More recently, Tudos[3] studied the inhibition to vinyl polymerization by certain quinones and observed the occasional incorporation of quinone into the polymer products. As an explanation for the incorporation phenomenon, Tudos

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[1] To whom inquiries should be addressed.

[2] (a) J. C. Bevington, *et al.*, *Trans. Faraday Soc.*, **51**, 946 (1955); (b) *J. Chem. Soc.*, 2822 (1955); (c) J. C. Bevington and H. W. Melville, *Usp. Khim.*, **25**, 1336 (1956); (d) F. L. Funt and F. D. Williams, *J. Polym. Sci.*, **46**, 139 (1960); (e) *ibid.*, **57**, 711 (1962).

[3] F. Tudos, *Acta Chim. Acad. Sci. Hung.*, **44**, 403 (1965).