Macromolecules

The Role of Monomer Charge-Transfer Complexes in Free Radical Copolymerization. II. Styrene–β-Cyanoacrolein Copolymers. Comparison with Penultimate Hypothesis

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ABSTRACT: The copolymerization of β-cyanoacrolein and styrene has been recalculated using the charge-transfer complex copolymerization theory developed recently. The authors used a penultimate copolymerization approach; this fitted the data poorly. The present theory fits very well and implies that, in this case, most of the copolymerization goes through complex.

Deviations of polymer compositions from those predicted by the Alfrey–Mayo equation[1,2] have usually been explained by penultimate effects.[3–5] Another possible hypothesis to explain the deviations was proposed over 20 years ago[6] and has been expanded qualitatively in the last 10 years by several investigators.[7,8] This is the hypothesis of the formation of charge-transfer complexes by monomers of opposite polarity; these are much more reactive than the monomers are individually. The complex, though present in low concentration, copolymerizes rapidly in amounts that affect the copolymer composition. If its polymerization is more rapid than that of the monomers separately, the polymer can have 50/50 or some other constant composition over a wide monomer feed range.

This idea has been quantified and a theory developed to describe exactly charge-transfer complex copolymerization as a factor in normal copolymerization,[9] from cases where the complex is weak, to where it is strong and dominates the polymerization. This theory has been applied to several cases where one monomer does not homopolymerize (see succeeding articles in this series); the penultimate approach was originally used in those cases and could also fit the data, though not quite as well as the complex approach.

In this paper the case of β-cyanoacrolein copolymerizing with styrene[10] is considered. Here the penultimate hypothesis also was used to explain the data, but the fit is very poor. The curves are highly reminiscent of those for fumaronitrile–styrene,[11] which will be considered in a later paper.

Discussion

The polymerization procedure used was as follows. Appropriate weights of the monomers were mixed with an equal volume of tetrahydrofuran, AIBN was added, and the mixture was sealed under vacuum and heated at 60°. The polymers were precipitated into methanol several times and dried to constant weight under vacuum at 50°. (This is a dangerous procedure. If one wants to remove *all* solvent, the final stage should be freeze drying and then heating the spongy mass at, or slightly above, T_g under high vacuum to constant weight.[12])

The moles of monomers used have been transformed into moles per liter for use in this paper from the known densities and concentrations in the THF solutions. The recalculated data are given in Table I.

It is obvious from inspection of the m_2 column that the error is at least ±0.02 mole fraction. However, the extra significant figures are included as it is easier to calculate. The error will be included at the end. The equation that was developed which fits the above case, equilibrium constant fairly small, and one monomer not adding to itself,[9] is

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

r_{12} is defined as usual, the reactivity ratio for radical $\sim\mathrm{A}\cdot$ against monomers A and B. r_{1C} is the reactivity ratio for radical $\sim\mathrm{A}\cdot$ against monomer 1 and the complex. r_{1C1} is the reactivity ratio for attack of $\sim\mathrm{A}\cdot$ on the A side of the complex, [AB], *vs.* attack on A. Equation 1 can be rearranged to a form where the variables can be handled, as shown below.

$$(y - 1 - r_{1C}/r_{1C1})[\mathrm{B}] = r_{1C}/K - (r_{1C}/Kr_{12})(y - 1)/x \qquad (2)$$

Here if a value is postulated for r_{1C}/r_{1C1}, a plot of the left side of eq 2 *vs.* $(y - 1)/x$ yields a straight line whose intercept is r_{1C}/K and whose slope is r_{1C}/Kr_{12}. The plot is shown in Figure 1 for several values of r_{1C}/r_{1C1}. It can be seen that the fit in the region of $r_{1C}/r_{1C1} = 0.4$–0.5 is much better than when $r_{1C}/r_{1C1} = 1.0$. There is tremendous experiment scatter; if circles were drawn to show the error assuming ±0.02 in m_1 and m_2, the points near $y - 1 = 0$ would be circles about ten times larger than those shown. The parameter values are given in Table II.

The parameters found at $r_{1C}/r_{1C1} = 0.4$–0.5 give calculated values for y whose differences cannot be seen on a graph. At $r_{1C}/r_{1C1} = 1$, the curve fits the data appreciably less well. The experimental values for m_2 *vs.* M_2 (B) are plotted against (1) the theoretical curve using the penultimate theory parameters obtained by the authors,[12] $r_1 = 0.09$ and $r_1' = 0.27$, and (2) the theoretical curve using the parameters from Table I with $r_{1C}/r_{1C1} = 0.4$. The equation is

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(10) H. Sumimoto and K. Azuma, *Polym. Lett.*, **4**, 883 (1966).

(11) R. G. Fordyce and G. E. Ham, *J. Amer. Chem. Soc.*, **73**, 1186 1951).

(12) M. Litt and F. W. Bauer, *J. Polym. Sci., Part C*, **No. 16**, 1551 (1967).

$$y = 1.0 + \frac{1.0x + 0.88[A]}{1.0 + 2.2[A]} \tag{3}$$

The data and theoretical curves are shown in Figure 2.

The curve using penultimate theory is the best that can be fitted. Any attempt to fit the right-hand portion of the curve makes the fit worse on the left. It would be necessary to invoke antepenultimate effects to get a fit, and thus say that groups eight atoms away from the radical affect its reactivity. On the other hand, the charge-transfer complex theory fits very well over the whole curve, though one cannot define r_{12} better than 0.75 ± 0.25. r_{1C}/K is about 0.45–0.48; the fact that it varies so little shows that addition of complex is the major growth step in the polymerization.

For this polymerization, the data cannot fit at all if $r_{1C}/r_{1C1} < 0.38$. Hence, at least 38%, and probably 40–50% of the time, radical $\sim$A· adds to the A end of the complex, [AB]. This explains the plateau a tabout $M_2 = 0.4$. If all copolymerization is through the complex,t he polymer would have the composition $[BA]_{0.6}[ABA]_{0.4} = A_{0.58}B_{0.42}$.

In summary, when β-cyanoacrolein is used as a comonomer with styrene, the resulting copolymer composition cannot be rationalized on the basis of penultimate model theory. It does, however, fit the charge-transfer complex copolymerization theory very well. However, as usual when literature data are used, r_{12} cannot be found exactly. One must do experiments at high dilution to define r_{12}. Also, the data fit only if one assumes that radical $\sim$A· at the end of the polymer chain attacks the A side of the complex, [AB], at least 38% of the time. This is susceptible to proof by nmr analysis of sequence distributions and head or tail placements along the chain.

TABLE I
COPOLYMERIZATION OF STYRENE (M_1) WITH β-CYANOACROLEIN (M_2).[a] REVISED DATA

M_1 in polymerization feed[b]	x = [A]/[B]	[A], mol/l.	[B], mol/l.	m_2	y[c]
0.05	0.013	0.302	5.75	0.46	1.175
0.10	0.111	0.591	5.32	0.41	1.44
0.20	0.250	1.14	4.56	0.41	1.44
0.30	0.429	1.65	3.84	0.42	1.38
0.40	0.667	2.11	3.17	0.41	1.44
0.50	1.00	2.55	2.55	0.40	1.50
0.60	1.50	2.95	1.97	0.43	1.33
0.70	2.333	3.33	1.425	0.40	1.50
0.80	4.00	3.69	0.922	0.36	1.78
0.90	9.00	4.00	0.444	0.305	2.28
0.95	19.00	4.18	0.220	0.235	3.25

[a] See ref 12. [b] Mole fraction. [c] = d(A)/d(B) = m_1/m_2.

TABLE II
PARAMETERS OF TERMINAL COMPLEX MODEL IN COPOLYMERIZATION OF STYRENE (M_1) AND β-CYANOACROLEIN

r_{1C}/r_{1C1}	$r_{1C}K$	r_{12}
<0.38[a]		
0.4	0.45	1.0
0.5	0.48	0.50
1.0[b]	0.87	0.16

[a] No values possible below $r_{1C}/r_{1C1} \approx 0.38$; r_{12} then is negative. [b] Not a good fit.

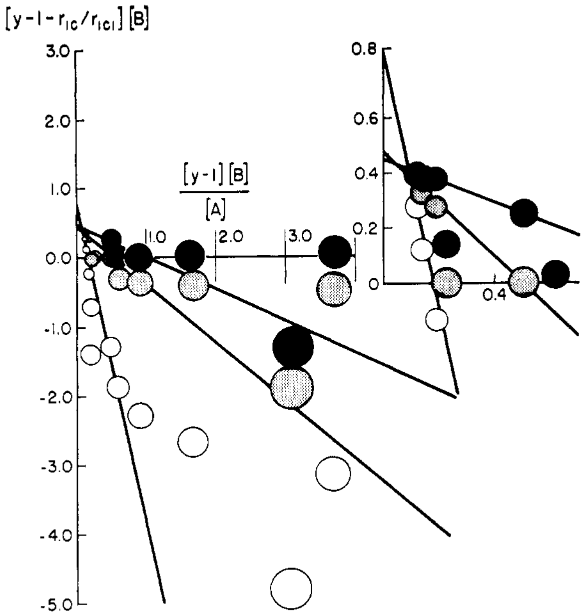

Figure 1. Determination of parameters of eq 2 for copolymerization of styrene (M_1) with β-cyanoacrolein (M_2): ●, $r_{1C}/r_{1C1} = 0.4$; ◍, $r_{1C}/r_{1C1} = 0.5$; ○, $r_{1C}/r_{1C1} = 1.0$. Points near $[y - 1]$ [B]/[A] = 0 omitted on main graph. This region is shown in expanded form in inset on right.

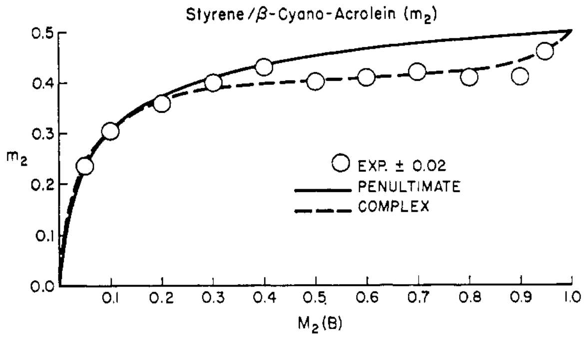

Figure 2. Comparison of experimental data with theoretical curves for penultimate and complex copolymerization models. See text for parameter values.