bath (Model 1280-3, ±0.01°) for a specified time. After removal from the bath, the polymer was precipitated in a rapidly swirling large excess of 30-60° petroleum ether. The polymer solution was diluted with more solvent when necessary so fine particles of polymer precipitated rather than large chunks. This process was repeated three times to ensure that all monomers and other contaminants had been washed from the polymer. After the last precipitation, the polymer was filtered and dried in a vacuum drying oven at 60° for 24 hr and weighed.

Infrared and Nmr Spectra. Infrared spectra were obtained on a Perkin-Elmer Model 237 spectrometer in KBr pellets. Nmr spectra were obtained on a Varian Model HA-100 spectrometer.

Gel Permeation Chromatography. A Waters Associates Model 200 gel permeation chromatograph was used to determine the $\bar{M}_n$, $\bar{M}_w$, and overall molecular weight distributions of the polymers. The polymers were chromatographed in tetrahydrofuran, and the chromatograms were analyzed in the standard fashion advocated by Cazes[20] using points every half-count.[21] The chromatograms were not first corrected for gaussian instrumental spreading as advocated by Tung[22] because this correction is not important in polymers with broad molecular weight distributions, and it only becomes important with increasingly narrow polymer fractions.[22]

As an absolute standard, the values of $\bar{M}_n$ were first determined by vapor pressure osmometry. This value of $\bar{M}_n$ was then used to assign the value of $\bar{M}_n$ at the position in the chromatogram which was the number-average chain length ($\bar{A}_n$). In this way a Q factor was determined, equal to $\bar{M}_n/\bar{A}_n$. Once Q had been obtained on several samples of the polymer, a Q value for that polymer was established as the average of those obtained, and this value was used in calculations of $\bar{M}_w$ and the overall molecular weight distribution. Homopolymers of BAC exhibited a Q of 94.

Viscosity Measurements. Viscosity measurements were made with a Cannon–Ubbelohde semimicro dilution viscometer (50L631) at 30 ± 0.01° and were run in *N*,*N*-dimethylformamide.

Initial concentrations of polymer were 0.2–0.5 g in 5 ml of solvent, with 5-ml dilutions being made directly into the viscometer Five minutes was sufficient for the contents to reach equilibrium; *i.e.*, subsequent timings differed no more than 0.3 sec. The intrinsic viscosity of the polymer was found by plotting

$$\lim_{C\to 0} \eta\ \mathrm{sp}/C\ vs.\ C$$

(C = concentration of polymer solution in grams per 100 ml of solvent). Table I summarizes the molecular weight and intrinsic viscosity data.

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The Role of Monomer Charge-Transfer Complexes in Free Radical Copolymerization. I. Derivation of Terminal Complex Model Equations[1a]

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ABSTRACT: Copolymerization of monomers through charge-transfer complexes has been investigated qualitatively in the literature. This paper presents a quantitative theory relating deviations of copolymer composition from those predicted by the simple terminal model to the concentration and reactivity of the charge-transfer complexes. Succeeding papers will treat literature examples and show that this approach is an alternate to the penultimate and antepenultimate effect approach.

Compositional deviations from those predicted by terminal polymerization mechanisms[2] have been explained by many authors using penultimate or even antepenultimate models.[3-7] Although these models may rationalize composition quite well, when tested more severely by monomer sequence analysis[8] they frequently predict quite poorly.

A second rationalization of deviations from the simple terminal model was proposed in 1946 for copolymers of maleic anhydride with various monomers.[9] This was the charge-transfer model; electropositive and electronegative monomers can form charge-transfer complexes with each other. When this complex is attacked, both monomers in the complex add as a unit.[10,11] Copolymer compositions tend to be constant.

The model was considered seriously for all copolymerizations but gradually lost favor. Initial attempts to derive copolymer compositions suffered because concepts at that time were not sufficiently advanced. While the concept seemed applicable to some copolymerizations, *e.g.*, maleic anhydride copolymers[9] and styrene–SO_2 copolymers,[10-13] efforts to apply the concept as a mechanism in more conventional polymerizations showed that it was not useful. The

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

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classic experiment, change in copolymer composition (or reactivity ratios) with dilution of monomers, was tested for styrene–methyl methacrylate.[14] There was no change in composition with dilution.

However, maleic anhydride–styrene copolymerizations do show changes in calculated reactivity ratio with changes of solvent or dilution.[15] Recently several investigators have demonstrated drastic composition changes with concentration in terpolymerizations[16–18] for many systems involving maleic anhydride, fumaronitrile, etc.

Strong charge-transfer complexes tend to produce polymers of constant composition and have been recognized for 25 years. However, there should be an intermediate region of weaker charge-transfer complexes where the concentration of complex is so low that normal copolymerization can compete. Here, composition would not be constant as feed composition changes. It is the purpose of the present paper to quantify such a model. This involves only terminal chain end effects but also includes the effect of monomer–monomer charge-transfer complexes. Free radical copolymerization is a complex process which may occur by a variety of mechanisms. When seeking to determine which polymerization route a particular pair of monomers follows, the proposed model should be included as a possibility.

It was shown by Walling[19] that reversible copolymerization produces deviations from the simple copolymer equation, and he proposed that as a possible alternative to charge-transfer complex copolymerization in the case of styrene–SO_2 and ethylene–CO. This is certainly another route that monomers can follow and must be considered for bulky or unusually stable monomers such as SO_2 or CO. However, for molecules of high and opposite polarities, the copolymer composition does not depend on substituent size nor on temperature to a great degree, and charge-transfer complex copolymerization is a reasonable model. Even for styrene–SO_2 copolymerization, at −20°, one gets a constant composition of 1.34 styrene-1.0 SO_2,[13] independent of monomer ratio. This can be explained by complex copolymerization but not by depropagation copolymerization.

Discussion

The classical terminal copolymerization model involves four equations.[2] Here radicals of monomers A and B, A· and B·, at the end of a chain may react with either monomer as indicated by terminal model equations (1–4).

$$\sim\mathrm{A}\cdot + \mathrm{A} \longrightarrow \sim\mathrm{AA}\cdot \tag{1}$$

$$\sim\mathrm{A}\cdot + \mathrm{B} \longrightarrow \sim\mathrm{AB}\cdot \tag{2}$$

$$\sim\mathrm{B}\cdot + \mathrm{A} \longrightarrow \sim\mathrm{BA}\cdot \tag{3}$$

$$\sim\mathrm{B}\cdot + \mathrm{B} \longrightarrow \sim\mathrm{BB}\cdot \tag{4}$$

The penultimate scheme, while still considering two monomers and two radicals, assumes second-order Markov effects.[3,4] Here there may be four different radical configurations at the end of the polymer chain. These may react with either monomer as indicated by penultimate model equations (5–12). In this model, full second-order influence is assigned to chain end groupings.

$$\sim\mathrm{AA}\cdot + \mathrm{A} \longrightarrow \sim\mathrm{AAA}\cdot \tag{5}$$

$$\sim\mathrm{AA}\cdot + \mathrm{B} \longrightarrow \sim\mathrm{AAB}\cdot \tag{6}$$

$$\sim\mathrm{BA}\cdot + \mathrm{A} \longrightarrow \sim\mathrm{BAA}\cdot \tag{7}$$

$$\sim\mathrm{BA}\cdot + \mathrm{B} \longrightarrow \sim\mathrm{BAB}\cdot \tag{8}$$

$$\sim\mathrm{AB}\cdot + \mathrm{A} \longrightarrow \sim\mathrm{ABA}\cdot \tag{9}$$

$$\sim\mathrm{AB}\cdot + \mathrm{B} \longrightarrow \sim\mathrm{ABB}\cdot \tag{10}$$

$$\sim\mathrm{BB}\cdot + \mathrm{A} \longrightarrow \sim\mathrm{BBA}\cdot \tag{11}$$

$$\sim\mathrm{BB}\cdot + \mathrm{B} \longrightarrow \sim\mathrm{BBB}\cdot \tag{12}$$

If one considers the possibility of charge-transfer complex formation, another scheme presents itself. Other workers have explored this route qualitatively.[9–14,16–19] Assuming that monomers A and B form a reversible AB complex, simple dissociative rules can be used. Thus, this equilibrium appears as

$$\mathrm{A} + \mathrm{B} \rightleftharpoons [\mathrm{AB}] \equiv [\mathrm{C}] \tag{13}$$

$$K = \frac{[\mathrm{AB}]}{([\mathrm{A_0}] - [\mathrm{AB}])([\mathrm{B_0}] - [\mathrm{AB}])} \tag{14}$$

where $[A_0]$ and $[B_0]$ are the concentrations of each monomer if there is no complex formation while [A] and [B] are the true monomer concentrations. Yamashita[16] and others[17,18] have explored the possibility of the AB complex polymerizing as a unit to generate alternating copolymers.

We propose a generalized scheme in this paper, which includes the possibilities of either monomer or either side of the AB complex reacting with chains ending in A· or B· radicals. When a complex is attacked both monomer units add into the polymer chain. For illustration, if the A side of the complex is attacked, it adds into the chain as ∼AB·. Once the complex adds, the radical formed must be that of one of the monomers. If it is attacked on the A side, the result is ∼B·. Attack on the B side of the complex must produce ∼A·.

An interesting question is why the complex should be postulated to be more reactive than either of the two monomers separately. This can be rationalized on the basis of polarizability of the complex *vs.* polarizability of the individual monomers. The charge-transfer complex has a larger π electron system (two monomers), making the system as a whole highly polarizable. As such, it can interact more readily with an approaching radical of the correct polarity than an individual monomer can. The activation energy is therefore reduced. The preexponential factor may also increase in such a case as successful attack may be achieved over a wider solid angle.

The eight equations required to describe this scheme are shown in terminal complex model equations (15–22). In

$$\sim\mathrm{A}\cdot + \mathrm{A} \xrightarrow{k_{11}} \sim\mathrm{AA}\cdot \tag{15}$$

$$\sim\mathrm{A}\cdot + \mathrm{B} \xrightarrow{k_{12}} \sim\mathrm{AB}\cdot \tag{16}$$

$$\sim\mathrm{B}\cdot + \mathrm{A} \xrightarrow{k_{21}} \sim\mathrm{BA}\cdot \tag{17}$$

$$\sim\mathrm{B}\cdot + \mathrm{B} \xrightarrow{k_{22}} \sim\mathrm{BB}\cdot \tag{18}$$

$$\sim\mathrm{A}\cdot + [\mathrm{AB}] \xrightarrow{k_{1\mathrm{C}1}} \sim\mathrm{AAB}\cdot \tag{19}$$

$$\sim\mathrm{A}\cdot + [\mathrm{BA}] \xrightarrow{k_{1\mathrm{C}2}} \sim\mathrm{ABA}\cdot \tag{20}$$

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$$\sim\!\mathrm{B}\cdot + [\mathrm{AB}] \xrightarrow{k_{2\mathrm{C}1}} \sim\!\mathrm{BAB}\cdot \qquad (21)$$

$$\sim\!\mathrm{B}\cdot + [\mathrm{BA}] \xrightarrow{k_{2\mathrm{C}2}} \sim\!\mathrm{BBA}\cdot \qquad (22)$$

this notation, k_{11} is the rate constant for addition of radical $\sim\!\mathrm{A}\cdot$ to monomer A, etc., while $k_{1\mathrm{C}1}$ is the rate constant for attack of radical $\sim\!\mathrm{A}\cdot$ on the A side of the complex, etc. Note that eq 15–18 are identical with eq 1–4. Equations 19 and 21 show radical attack on the A side of the AB complex and eq 20 and 22 show attack on the B side.

Using conditional probability nomenclature[20] and assigning y to the molar ratio of A to B in the polymer and x to the ratio of $\mathrm{A_0}$ to $\mathrm{B_0}$ in the monomer state, a relatively straightforward derivation is possible.

$$F(\mathrm{AB}) = F(\mathrm{BA}) \qquad (23)$$

$$F(\mathrm{AB}) = F(\mathrm{A})P(\mathrm{B/A}) = F(\mathrm{B})P(\mathrm{A/B}) = F(\mathrm{BA}) \qquad (24)$$

$$\therefore \quad y = \frac{F(\mathrm{A})}{F(\mathrm{B})} = \frac{P(\mathrm{A/B})}{P(\mathrm{B/A})} \qquad (25)$$

This states that the molar ratio of monomers in the polymer equals the ratio of the probability that a B unit adds A to the probability that an A unit adds B.

Introducing the reaction steps, eq 15–22, and factoring out [A·] and [B·], respectively, we obtain

$$P(\mathrm{B/A}) = \frac{k_{12}[\mathrm{B}] + (k_{1\mathrm{C}1} + k_{1\mathrm{C}2})[\mathrm{C}] + k_{2\mathrm{C}1}[\mathrm{C}]\dfrac{[\mathrm{B}\cdot]}{[\mathrm{A}\cdot]}}{k_{11}[\mathrm{A}] + k_{12}[\mathrm{B}] + [2k_{1\mathrm{C}1} + k_{1\mathrm{C}2}][\mathrm{C}] + k_{2\mathrm{C}1}[\mathrm{C}]\dfrac{[\mathrm{B}\cdot]}{[\mathrm{A}\cdot]}} \qquad (26)$$

$$P(\mathrm{A/B}) = \frac{k_{21}[\mathrm{A}] + (k_{2\mathrm{C}2} + k_{2\mathrm{C}1})[\mathrm{C}] + k_{1\mathrm{C}2}[\mathrm{C}]\dfrac{[\mathrm{A}\cdot]}{[\mathrm{B}\cdot]}}{k_{22}[\mathrm{B}] + k_{21}[\mathrm{A}] + [2k_{2\mathrm{C}2} + k_{2\mathrm{C}1}][\mathrm{C}] + k_{1\mathrm{C}2}[\mathrm{C}]\dfrac{[\mathrm{A}\cdot]}{[\mathrm{B}\cdot]}} \qquad (27)$$

where [C] is the molar concentration of complex, C1 refers to attack at the A side of the complex, and C2 refers to attack at the B side. Note that in eq 26 a term must be included where a chain ending in radical B· attacks complex, since addition of this radical to the A side of the complex generates one AB link. Likewise in eq 27, radical A· terms must be considered. Also, addition of $\sim\!\mathrm{A}\cdot$ to the A side of the complex produces one AA sequence and one AB sequence in the polymer chain.

In order to simplify these equations the radical ratios in the last term of each must be eliminated. Utilizing the steady-state approximation of equal radical turnovers, four turnover equations must be considered.

$$[\mathrm{A}\cdot] + [\mathrm{B}] \xrightarrow{k_{12}} [\mathrm{AB}\cdot]$$

$$[\mathrm{A}\cdot] + [\mathrm{C}] \xrightarrow{k_{1\mathrm{C}1}} [\mathrm{AAB}\cdot]$$

$$[\mathrm{B}\cdot] + [\mathrm{A}] \xrightarrow{k_{21}} [\mathrm{BA}\cdot]$$

$$[\mathrm{B}\cdot] + [\mathrm{C}] \xrightarrow{k_{2\mathrm{C}2}} [\mathrm{BBA}\cdot]$$

Now, equating turnovers

$$[\mathrm{A}\cdot] \longrightarrow [\mathrm{B}\cdot] = [\mathrm{B}\cdot] \longrightarrow [\mathrm{A}\cdot \qquad (28)$$

$$k_{12}[\mathrm{A}\cdot][\mathrm{B}] + k_{1\mathrm{C}1}[\mathrm{A}\cdot][\mathrm{C}] = k_{21}[\mathrm{B}\cdot][\mathrm{A}] + k_{2\mathrm{C}2}[\mathrm{B}\cdot][\mathrm{C}] \qquad (29)$$

$$\frac{[\mathrm{A}\cdot]}{[\mathrm{B}\cdot]} = \frac{k_{21}[\mathrm{A}] + k_{2\mathrm{C}2}[\mathrm{C}]}{k_{12}[\mathrm{B}] + k_{1\mathrm{C}1}[\mathrm{C}]} \qquad (30)$$

If we substitute (30) into (26) and (27), multiply (26) and (27) by $(1/k_{12}[\mathrm{B}])/(1/k_{12}[\mathrm{B}])$ and $(1/k_{21}[\mathrm{A}])/(1/k_{21}[\mathrm{A}])$ where appropriate, and substitute into (25), we obtain the completely general terminal complex equation (31). As usual $r_{12} = k_{11}/k_{12}$, $r_{1\mathrm{C}1} = k_{11}/k_{1\mathrm{C}1}$, $r_{1\mathrm{C}2} = k_{11}/k_{1\mathrm{C}2}$, $r_{21} = k_{22}/k_{21}$, $r_{2\mathrm{C}1} = k_{22}/k_{2\mathrm{C}1}$, and $r_{2\mathrm{C}2} = k_{22}/k_{2\mathrm{C}2}$, where the respective reactions involving the rate constants are shown in eq 15–22. We will

$$y = \frac{\dfrac{1 + \left(\dfrac{r_{21}}{r_{2\mathrm{C}2}} + \dfrac{r_{21}}{r_{2\mathrm{C}1}}\right)\dfrac{[\mathrm{C}]}{[\mathrm{A}]} + \dfrac{r_{12}}{r_{1\mathrm{C}2}}\dfrac{[\mathrm{C}]}{[\mathrm{B}]}\,\dfrac{1 + \dfrac{r_{21}}{r_{2\mathrm{C}2}}\dfrac{[\mathrm{C}]}{[\mathrm{A}]}}{1 + \dfrac{r_{12}}{r_{1\mathrm{C}1}}\dfrac{[\mathrm{C}]}{[\mathrm{B}]}}}{r_{21}\dfrac{[\mathrm{B}]}{[\mathrm{A}]} + 1 + \left(\dfrac{2r_{21}}{r_{2\mathrm{C}2}} + \dfrac{r_{21}}{r_{2\mathrm{C}1}}\right)\dfrac{[\mathrm{C}]}{[\mathrm{A}]} + \dfrac{r_{12}}{r_{1\mathrm{C}2}}\dfrac{[\mathrm{C}]}{[\mathrm{B}]}\,\dfrac{1 + \dfrac{r_{21}}{r_{2\mathrm{C}2}}\dfrac{[\mathrm{C}]}{[\mathrm{A}]}}{1 + \dfrac{r_{12}}{r_{1\mathrm{C}1}}\dfrac{[\mathrm{C}]}{[\mathrm{B}]}}}}{\dfrac{1 + \left(\dfrac{r_{12}}{r_{1\mathrm{C}1}} + \dfrac{r_{12}}{r_{1\mathrm{C}2}}\right)\dfrac{[\mathrm{C}]}{[\mathrm{B}]} + \dfrac{r_{21}}{r_{2\mathrm{C}1}}\dfrac{[\mathrm{C}]}{[\mathrm{A}]}\,\dfrac{1 + \dfrac{r_{12}}{r_{1\mathrm{C}1}}\dfrac{[\mathrm{C}]}{[\mathrm{B}]}}{1 + \dfrac{r_{21}}{r_{2\mathrm{C}2}}\dfrac{[\mathrm{C}]}{[\mathrm{A}]}}}{r_{12}\dfrac{[\mathrm{A}]}{[\mathrm{B}]} + 1 + \left(\dfrac{2r_{12}}{r_{1\mathrm{C}1}} + \dfrac{r_{12}}{r_{1\mathrm{C}2}}\right)\dfrac{[\mathrm{C}]}{[\mathrm{B}]} + \dfrac{r_{21}}{r_{2\mathrm{C}1}}\dfrac{[\mathrm{C}]}{[\mathrm{A}]}\,\dfrac{1 + \dfrac{r_{12}}{r_{1\mathrm{C}1}}\dfrac{[\mathrm{C}]}{[\mathrm{B}]}}{1 + \dfrac{r_{21}}{r_{2\mathrm{C}2}}\dfrac{[\mathrm{C}]}{[\mathrm{A}]}}}} \qquad (31)$$

in addition define $k_{1\mathrm{C}} = k_{1\mathrm{C}1} + k_{1\mathrm{C}2}$, $k_{2\mathrm{C}} = k_{2\mathrm{C}1} + k_{2\mathrm{C}2}$, $r_{1\mathrm{C}} = k_{11}/(k_{1\mathrm{C}1} + k_{1\mathrm{C}2}) = k_{11}/k_{1\mathrm{C}}$, $r_{2\mathrm{C}} = k_{22}/(k_{2\mathrm{C}1} + k_{2\mathrm{C}2}) = k_{22}/k_{2\mathrm{C}}$. These will be used later. Depending upon the assumptions which one is willing to make, eq 31 can be cast into several very useful forms. Returning to eq 14, if one assumes weak complex formation, where $K \leq 0.03$, then the concentration of complex must be much lower than that of either uncomplexed monomer: $[\mathrm{A}] \gg [\mathrm{C}]$ and $[\mathrm{B}] \gg [\mathrm{C}]$ and $[\mathrm{A_0}] \cong [\mathrm{A}]$ and $[\mathrm{B_0}] \cong [\mathrm{B}]$

$$\therefore\ K \cong \frac{[\mathrm{C}]}{[\mathrm{A}][\mathrm{B}]} \qquad (32)$$

which can be written

$$[\mathrm{C}] \cong K[\mathrm{A}][\mathrm{B}] \qquad (33)$$

$$y = \frac{\dfrac{1 + (r_{21}/r_{2\mathrm{C}2} + r_{21}/r_{2\mathrm{C}1})K[\mathrm{B}] + \dfrac{Kr_{12}}{r_{1\mathrm{C}2}}[\mathrm{A}]\dfrac{1 + Kr_{21}[\mathrm{B}]/r_{2\mathrm{C}2}}{1 + Kr_{12}[\mathrm{A}]/r_{1\mathrm{C}1}}}{r_{21}[\mathrm{B}]/[\mathrm{A}] + 1 + (2r_{21}/r_{2\mathrm{C}2} + r_{21}/r_{2\mathrm{C}1})K[\mathrm{B}] + \dfrac{Kr_{12}}{r_{1\mathrm{C}2}}[\mathrm{A}]\dfrac{1 + Kr_{21}[\mathrm{B}]/r_{2\mathrm{C}2}}{1 + Kr_{12}[\mathrm{A}]/r_{1\mathrm{C}1}}}}{\dfrac{1 + (r_{12}/r_{1\mathrm{C}1} + r_{12}/r_{1\mathrm{C}2})K[\mathrm{A}] + \dfrac{Kr_{21}}{r_{2\mathrm{C}1}}[\mathrm{B}]\dfrac{1 + Kr_{12}[\mathrm{A}]/r_{1\mathrm{C}1}}{1 + Kr_{21}[\mathrm{B}]/r_{2\mathrm{C}2}}}{r_{12}[\mathrm{A}]/[\mathrm{B}] + 1 + (2r_{12}/r_{1\mathrm{C}1} + r_{12}/r_{1\mathrm{C}2})K[\mathrm{A}] + \dfrac{Kr_{21}}{r_{2\mathrm{C}1}}[\mathrm{B}]\dfrac{1 + Kr_{12}[\mathrm{A}]/r_{1\mathrm{C}1}}{1 + Kr_{21}[\mathrm{B}]/r_{2\mathrm{C}2}}}} \qquad (34)$$

If we substitute (33) into (31), we obtain eq 34.

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(20) K. Ito and Y. Yamashita, *J. Polym. Sci., Part A*, 3, 2165 (1965).

It can be seen that each complex reactivity ratio is associated with K. This weak complex form of the equation can now be specialized still further for application to specific systems. An example is the special case where radical B· does not add to monomer B or to the B side of the complex. In this case $P(\mathrm{A/B}) = 1.0$ and the numerator of eq 34 can be rearranged to the form

$$(y - 1)\left[1 + \frac{Kr_{21}[\mathrm{B}]}{r_{2\mathrm{C}1}}(1 + Kr_{12}[\mathrm{A}]/r_{1\mathrm{C}1}) + Kr_{12}[\mathrm{A}](1/r_{1\mathrm{C}1} + 1/r_{1\mathrm{C}2})\right] = r_{12}[\mathrm{A}]/[\mathrm{B}] + Kr_{12}[\mathrm{A}]/r_{1\mathrm{C}1} \quad (35)$$

Note that for high dilution, eq 34 reduces to the classical Alfrey–Merz–Goldfinger equation[3]

$$y = \frac{1 + r_{12}[\mathrm{A}]/[\mathrm{B}]}{1 + r_{21}[\mathrm{B}]/[\mathrm{A}]} \quad (36)$$

and eq 35 reduces to the form

$$y = 1 + r_{12}[\mathrm{A}]/[\mathrm{B}] \quad (37)$$

This is expected in light of the fact that, at high dilution, complex formation becomes negligible. Therefore, the model reverts to the classical terminal case.

If we define $k_{1\mathrm{C}} = k_{1\mathrm{C}1} + k_{1\mathrm{C}2}$, then

$$r_{1\mathrm{C}} = \left(\frac{1}{r_{1\mathrm{C}1}} + \frac{1}{r_{1\mathrm{C}2}}\right)^{-1}$$

Equation 35 may then be rearranged to take the form

$$y - 1 = \frac{r_{1\mathrm{C}}}{r_{1\mathrm{C}1}} + \frac{r_{1\mathrm{C}}}{K[\mathrm{B}]}\left[1 - \frac{(y - 1)[\mathrm{B}]}{r_{12}[\mathrm{A}]}(1 + \theta)\right] \quad (38)$$

where

$$\theta = \frac{Kr_{21}[\mathrm{B}]}{r_{2\mathrm{C}1}}(1 + Kr_{12}[\mathrm{A}]/r_{1\mathrm{C}1}) \quad (39)$$

One can run linear regression analyses on eq 38 if one has sufficient and accurate data. However, in analyses of experimental data from the literature, it was found that for the cases considered, within experimental error θ could be neglected. This means that $Kr_{21}[\mathrm{B}] \ll r_{2\mathrm{C}1}\,(\equiv k_{2\mathrm{C}1}[\mathrm{C}] \ll k_{21}[\mathrm{A}])$. It is reasonable to argue that for weak complexes where [C] is small, this is true. Equation 38 then simplifies to

$$y - 1 = r_{1\mathrm{C}}/r_{1\mathrm{C}1} + \frac{r_{1\mathrm{C}}}{K[\mathrm{B}]}\left[1 - \frac{(y - 1)}{r_{12}}\frac{[\mathrm{B}]}{[\mathrm{A}]}\right] \quad (40)$$

If r_{12} is known (generally from high dilution data), this equation can be utilized directly to yield $r_{1\mathrm{C}}/K$ from the slope, and $r_{1\mathrm{C}}/r_{1\mathrm{C}1}$ from the intercept of a

$$(y - 1)\ vs.\ \frac{1}{[\mathrm{B}]}\left(1 - \frac{(y - 1)}{r_{12}}\frac{[\mathrm{B}]}{[\mathrm{A}]}\right)$$

plot.

If r_{12} is not known, then successive approximation methods may be used which simplify eq 40 still further but leave it valid for some portion of the copolymerization curve. As an example, if $k_{1\mathrm{C}1}$ is postulated very small compared to $k_{1\mathrm{C}2}$ (50:50 copolymer at high [B]), then eq 40 reduces to (41).

$$1/[\mathrm{B}] = (y - 1)/[\mathrm{A}]r_{12} - K/r_{1\mathrm{C}2} \quad (41)$$

Alternatively, one may postulate a value for $r_{1\mathrm{C}}/r_{1\mathrm{C}1}$, which must be between 0 and 1, and rearrange eq 40 to (42). A

$$(y - 1 - r_{1\mathrm{C}}/r_{1\mathrm{C}1})[\mathrm{B}] = r_{1\mathrm{C}}/K - (r_{1\mathrm{C}}/Kr_{12})(y - 1)[\mathrm{B}]/[\mathrm{A}] \quad (42)$$

plot of $(y - 1 - r_{1\mathrm{C}}/r_{1\mathrm{C}1})[\mathrm{B}]$ *vs.* $(y - 1)/x$ then has a slope of $-r_{1\mathrm{C}}/Kr_{12}$ and an intercept of $r_{1\mathrm{C}}/K$. We have found this approach to be very fruitful in analyzing the data.

If the data are accurate enough and over a very wide range, three-parameter least-squares reduction can be used to find the reactivity ratios.

Several general points should be noted. The theory predicts that dilution in a solvent should raise reactivity ratios calculated from a terminal model; this is known to happen.[15–17] Also, shifting from an inert to a complexing solvent should strongly reduce the equilibrium constant between monomers, and therefore also raise calculated reactivity ratios. This has been observed.[15] (In some cases, people working with such copolymerizations changed concentrations and solvents arbitrarily, as they believed that it should not affect the results.) When changing monomer concentrations, the dielectric constant of the medium could vary tremendously, *e.g.*, styrene–acrylonitrile; this should also affect the equilibrium constant.

While we have considered the charge-transfer complex as having an equilibrium concentration in this paper, this may not be a completely correct approach. In standard equilibrium measurements, when solvents are changed, the extinction coefficient of the complex, ϵ, can increase as K decreases so that $K\epsilon$ remains approximately constant. This is due to contact charge transfer: some molecules are so oriented with respect to one another that one gets photoinduced electron transfer during random collision.[21,22] In a copolymerization, such contact pairs may also copolymerize as a unit if they have, by chance, the correct orientations and therefore are highly polarizable. Since each monomer will usually be in contact with several molecules of comonomer, this is not impossible. However, validation or refutation of this amendment must await good experimental data.

In subsequent papers the theory in its simplified forms will be applied to literature data to illustrate its power and to rationalize data previously explained by a penultimate effect; in many cases this theory fits the data better.

(21) R. S. Mulliken, *Recl. Trav. Chim. Pays-Bas*, **68**, 147 (1949).
(22) L. E. Orgel and R. S. Mulliken, *J. Amer. Chem. Soc.*, **79**, 4839 (1957).