Representation of Chain-Growth Copolymerization in Terms of Active Centers

Michael H. Theil[a]

[a] Department of Textile, Chemistry School of Textiles North Carolina State University, Raleigh, North Carolina

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MICHAEL H. THEIL

Department of Textile Chemistry
School of Textiles
North Carolina State University
Raleigh, North Carolina 27650

ABSTRACT

The nearest-neighbor, chain-growth copolymerization equation is expressed in terms of active center concentrations and active center reactivity ratios, $R_i = k_{ii}/k_{ji}$. Alternate but equivalent derivations of the conventional version and the new version of the copolymerization equation are presented and discussed. Some active center reactivity ratios are calculated from data previously reported, and contrasting trends between these and monomer reactivity ratios are found. The Alfrey-Price scheme for predicting monomer reactivity ratios is adapted to the prediction of active center reactivity ratios.

INTRODUCTION AND THEORY

The copolymerization equation [1-3] predicts the instantaneous composition of a binary copolymer formed from a given monomer feed composition in a specific chain-growth copolymerization system. In its derivation it is assumed that the propagation step is far more important than the initiation or the termination step, i.e., the chain is limitless. As the equation was initially conceived [1-3], only the interactions between the terminal units at the polymeric active centers and the mono-

mers determine the copolymer. Analogous equations have since been derived for more complex copolymerization systems; those in which units remote from the active center influence the reaction [4], those in which depropagation is important [5-7], multicomponent systems [4, 7], and systems in which the reactants form complexes [7]. These copolymerization equations have been rendered experimentally tractable by formulating them in terms of the concentrations of monomers rather than in terms of transient active center concentrations. While this practice needs no justification, additional insights into the copolymerization process can be obtained if the copolymerization equation is reformulated in terms of active center concentrations. The present work applies this approach to the early nearest neighbor model of chain-growth copolymerization. Hence, the model considered consists of four distinguishable propagation reactions involving monomers A and B and macromolecular active center chain ends designated A* and B*. These reactions may be expressed by equations of the form

$$i^* + j \rightarrow j^* \tag{1}$$

which in turn are characterized by rate constants of the form k_{ij}. Thus, k_{ij} is the rate constant for the reaction in which active center i^* adds to monomer j; both i and j can be either A or B. Two rate equations may then be written that give the rates at which the monomers disappear. When one equation is divided by the other, the relative rates at which these monomers are being consumed are given by

$$\frac{d[A]}{d[B]} = \frac{k_{AA}[A^*][A] + k_{BA}[B^*][A]}{k_{BB}[B^*][B] + k_{AB}[A^*][B]} \tag{2}$$

Here the brackets denote concentrations of the species involved. In the conventional treatment [1-4, 7] the steady-state assumption that the rate of formation of an active center is equal to its rate of consumption

$$k_{AB}[A^*][B] - k_{BA}[B^*][A] = 0 \tag{3}$$

is solved for either [A*] or [B*], and the concentration of active centers in Eq. (2) can thereby be eliminated. The resulting copolymerization equation

$$\frac{d[A]}{d[B]} = \frac{[A]}{[B]} \left(\frac{r_A[A] + [B]}{[A] + r_B[B]} \right) \tag{4}$$

in which $r_A = k_{AA}/k_{AB}$ and $r_B = k_{BB}/k_{BA}$ can also be derived by statistical procedures [4, 7-9]. The monomer reactivity ratios r_A and r_B are used because their constituent rate constants cannot be separately determined from a simple copolymerization experiment.

One may recast the copolymerization equation in terms of active center concentrations rather than monomer concentrations by solving Eq. (3) for one of the monomer concentrations and substituting that result in Eq. (2). The copolymerization equation then becomes

$$\frac{d[A]}{d[B]} = \frac{[A^*]}{[B^*]}\left(\frac{R_A[A^*] + [B^*]}{[A^*] + R_B[B^*]}\right) \tag{5}$$

in which $R_A = k_{AA}/k_{BA}$ and $R_B = k_{BB}/k_{AB}$. R_A and R_B are, respectively, the ratios of propagation rate constants of the two active centers with monomer A and with monomer B. Therefore, one should call R_A and R_B the active center reactivity ratios.

The resonance stabilizations of active centers are greater than those of the corresponding monomers. The differences between monomers and active centers are such that the most reactive monomers are those for which corresponding active centers are the most highly resonance stabilized [7, 10]. Thus the active centers are ultimately decisive in establishing the relative reactivities of the monomers. It is, therefore, useful to characterize the copolymerization with respect to relative active center reactivity as well as directly evaluating the relative monomer reactivities. Determination of R_A and R_B by direct experiment is, of course, difficult since it involves finding the relative concentrations of the active centers, species which are present in extremely low concentrations. In the case of free radical polymerization, electron paramagnetic resonance spectroscopy may provide such capability.

Other modes of derivation of a copolymer composition equation using the steady-state assumption are possible, but the equations thus produced are essentially equivalent to those already reported. The relative rate of disappearance of active centers in a binary chain-growth copolymerization is

$$\frac{d[A^*]}{d[B^*]} = \frac{k_{AA}[A^*][A] + k_{AB}[A^*][B]}{k_{BB}[B^*][B] + k_{BA}[B^*][A]} \tag{6}$$

When Eq. (3) is solved for an active center concentration as before, and the appropriate substitution is made in Eq. (6), then

$$\frac{d[A^*]}{d[B^*]} = \frac{[A]}{[B]}\left(\frac{r_A[A] + [B]}{[A] + r_B[B]}\right) \tag{7}$$

is the result. When Eq. (3) is solved for a monomer concentration and that solution is applied to Eq. (6), then

$$\frac{d[A^*]}{d[B^*]} = \frac{[A^*]}{[B^*]}\left(\frac{R_A[A^*] + [B^*]}{[A^*] + R_B[B^*]}\right) \tag{8}$$

The right-hand sides of Eqs. (7) and (8) are, respectively, identical to those of Eqs. (4) and (5). Thus $d[A]/d[B] = d[A^*]/d[B^*]$ which is axiomatic for this system: the relative rates of the formation of the two different active centers is equal to the relative rates of the disappearance of the two different monomers. Alternate derivations of these copolymerization equations are possible using statistical methods previously developed [4-7, 9].

By the definition of the various reactivity ratios given, the product $R_A R_B$ is equal to $r_A r_B$ for a given copolymerization system. Thus $R_A R_B$ serves as a parameter to characterize the randomness of a copolymerization system, just as does $r_A r_B$.

Can the copolymerization equation in the form of Eq. (5) directly give the azeotropic composition as does Eq. (4) when $d[A]$ is set equal to $[A]$ and $d[B]$ is set equal to $[B]$? It cannot because, in general, the ratio $[A^*]:[B^*]$ is not equal to $[A]:[B]$ and is, therefore, not equal to $d[A]/d[B]$ at the azeotropic composition.

CALCULATION OF ACTIVE CENTER REACTIVITY RATIOS

While the determination of active center reactivity ratios by direct measurements of active center concentrations in a copolymerizing system is more difficult than the determination of monomer reactivity ratios, R_A and R_B values can be estimated from monomer reactivity ratios and homopropagation rate constants. By definition $R_A = (k_{AA}/k_{BB})r_B$ and $R_B = (k_{BB}/k_{AA})r_A$. Values of homopropagation rate constants and reactivity ratios for the free-radical chain-growth homo- and copolymerization of five monomers at 60°C were obtained from data tabulated by others [7, 11, 12] and are given in Table 1. The R_A

TABLE 1. Propagation Rate Constants, Monomer Reactivity Ratios, and Active Center Reactivity Ratios for Radical Chain-Growth Polymerizations[a]

Mon A[b]	Mon B[b]	$k_{AA} \times 10^{-3}$	$k_{BB} \times 10^{-3}$	r_A	r_B	R_A	R_B
AN	MA	1.96	2.09	1.26	0.67	$6.2_8 \times 10^{-1}$	1.34×10^0
AN	MMA	1.96	0.515	0.15	1.20	$4.5_7 \times 10^0$	$3.9_4 \times 10^{-2}$
AN	STY	1.96	0.165	0.04	0.40	$4._8 \times 10^0$	$3._4 \times 10^{-3}$
AN	VA	1.96	2.30	5.4	0.050	4.3×10^{-2}	6.3×10^0
MA	MMA	2.09	0.515	0.25	3.22	$1.3_1 \times 10^1$	$6.1_6 \times 10^{-2}$
MA	STY	2.09	0.165	0.20	0.75	9.5×10^0	1.6×10^{-2}
MA	VA	2.09	2.30	9	0.1	9×10^{-2}	1×10^1
MMA	STY	0.515	0.165	0.46	0.52	1.6×10^0	1.5×10^{-1}
MMA	VA	0.515	2.30	20	0.015	3.4×10^{-3}	8.9×10^1
STY	VA	0.165	2.30	55	0.01	7×10^{-4}	8×10^2

[a]All values are based on data collected at 60°C.
[b]AN = acrylonitrile, MA = methylacrylate, MMA = methyl methacrylate, STY = styrene, VA = vinyl acetate.

and R_B values calculated from these rate constants and reactivity ratios are displayed in the last two columns of Table 1. Two trends are noteworthy. Let the reactivity ratios be ordered within each pair so that $r_i > r_j$; then $R_j > R_i$. Furthermore, $R_j/R_i > r_i/r_j$. These relationships reflect the circumstances that radicals corresponding to monomers made stable by resonance will be even more stabilized themselves [7, 10]. Therefore, resonance-stabilized monomers tend to be reactive because of the stability of their product radicals, but the radicals become less reactive as their extents of resonance stabilization increase. Since these effects are primarily due to properties of the radicals, they are magnified when expressed in terms of active center reactivity ratios rather than monomer reactivity ratios.

Alfrey and Price developed a method, now called the Q-e scheme, for predicting monomer reactivity ratios in untried pairs of monomers [13, 14]. It is possible to construct an analogue to the Q-e scheme, based directly on the original Alfrey-Price treatment, that may be used to predict active center reactivity ratios. Alfrey and Price proposed that a propagation rate constant in a copolymerization may be represented by $k_{ij} = P_i Q_j \exp\{-e_i e_j\}$ in which j may equal i. Here P_i is characteristic of the reactivity of radical i, and Q_j is characteristic of monomer j; e_i and e_j were said to represent the charges on the end group of radical i and the double bond of monomer j, respectively. In practice, however, the same value has been assigned to e regardless of whether it is meant to represent the charge on an active center or a monomer. The monomer reactivity ratios are calculated from the ratios k_{ii}/k_{ij} in terms of Q and e values; the P values are the same in the numerator and the denominator of the ratio and cancel out. By using the same expression for k_{ij} the active center reactivity ratios can be expressed as k_{jj}/k_{ij} in which i and j may equal A or B, but here $i \neq j$. In this case Q cancels out of the expression and $R_j = (k_{jj}/k_{ij}) = (P_j/P_i) \exp\{-e_j(e_j - e_i)\}$. The P and e values for a set of active centers may be established in much the same way as are Q and e values. As was done for the Q-e scheme, base values for P and e must be chosen as references. In order to be able to compare P and e values with existing Q and e values, the reference species is made the styryl radical and it is assigned a P value of 1.000 and an e value of -0.800. The P and e values for the species of Table 1 were calculated according to the equations $e_i = e_j \pm (\ln R_i R_j)^{1/2}$ and $P_i = (P_j/R_j) \exp\{-e_j(e_j - e_i)\}$ and are listed in Table 2. The P and e values of Lines 2-5 were calculated using the reactivity ratio data with reference to styrene. The more rigorous mapping method of Alfrey, Bohrer, and Mark [14] was not used; it is the intent here, with the limited data available, only to test the potential for the application of the Alfrey-Price treat-

TABLE 2. P and e Values for Indicated Active Centers Compared with Corresponding Q and e Values

Line	Species	Ref. species/line	P	e	Q^a	e^a
1	STY	Base values	1.000	-0.800	1.000	-0.800
2	AN	STY/1	58.33	1.233	0.600	1.200
3	MA	STY/1	21.03	0.577	0.420	0.600
4	MMA	STY/1	2.611	0.397	0.740	0.400
5	VA	STY/1	751.3	-0.027	0.026	-0.220
6	AN	MMA/4	111.4	1.706		
7	AN	VA/5	114.9	1.117		
8	MA	MMA/4	51.00	0.863		
9	MMA	MA/3	1.230	0.112		
10	MMA	AN/2	2.541	-0.076		
11	VA	AN/2	334.1	0.089		
12	VA	MMA/4	502.6	-0.700		

[a]From Ref. 12. These are average values and may be compared with Lines 6-12 as well.

ment to active centers. In a check of consistency, the P and e values listed in Lines 6-12 were calculated using the indicated reference values for active center reactivity ratios (Table 1) and P and e values from Table 2, Lines 2-5. The P and e values thus calculated may be compared among themselves and with the Q and e values listed in Lines 2-5 of Table 2. The e values calculated here are close to the average e values for the corresponding monomers in a Q-e tabulation [12]. The P values tabulated are very different from the corresponding Q values. Where the Q values are relatively small the P values are relatively large and vice versa. The range of the P values is about two and one-half orders of magnitude, and all are greater or equal to one in this set of values. Styryl, the most resonance stabilized radical, has the appropriately lowest P value. The corresponding Q values range over slightly less than two orders or magnitude and are consistently less than or equal to one. R_A and R_B values calculated from these P and e values show fair agreement with those given in Table 1. For example, for the methyl methacrylate (monomer A)-vinyl acetate (monomer B) system R_A and R_B from P-e values are

2.9×10^{-3} and 2.8×10^{2}; for the acrylonitrile (monomer A)-vinyl acetate (monomer B) system R_A is 1.6×10^{-2} and R_B is 1.2×10^{1}.

The existence of explicable trends among the calculated values of R_A and R_B when compared with corresponding r_A and r_B values, the at least semiquantitative ability of an extension of the Q-e scheme to predict reactivity ratios, and the logical ordering of calculated P values suggest that viewing copolymerizations in terms of active centers is a valid and useful concept.

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