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A Modified Copolymerization Equation for Three-Component Systems

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Synopsis

A modified copolymerization equation substantiated by experimental evidence has been proposed for tricomponent systems.

To eliminate the complexities and assumptions made in the integration of the rate equation put forward by Alfrey and Goldfinger[1] and Walling and Briggs[2] for tri- and multicomponent copolymerization systems an attempt has been made in this paper to modify their equations.

It is known that in the copolymerization of three monomers, M_1, M_2, and M_3, the chain propagation reactions are

$$M_1^* + M_1 \xrightarrow{K_{11}} M_1^* + M_1$$

$$M_1^* + M_2 \xrightarrow{K_{12}} M_2^* + M_1$$

$$M_1^* + M_3 \xrightarrow{K_{13}} M_3^* + M_1$$

$$M_2^* + M_1 \xrightarrow{K_{21}} M_1^* + M_2$$

$$M_2^* + M_2 \xrightarrow{K_{22}} M_2^* + M_2$$

$$M_2^* + M_3 \xrightarrow{K_{23}} M_3^* + M_2$$

$$M_3^* + M_1 \xrightarrow{K_{31}} M_1^* + M_3$$

$$M_3^* + M_2 \xrightarrow{K_{32}} M_2^* + M_3$$

$$M_3^* + M_3 \xrightarrow{K_{33}} M_3^* + M_3$$

where M_1^*, M_2^* and M_3^* are different growing chain ends. Therefore, the rates of disappearance of the monomers, M_1, M_2, and M_3, would be as follows:

$$-dM_1/dt = K_{11}M_1^*M_1 + K_{21}M_2^*M_1 + K_{31}M_3^*M_1 = M_1(K_{11}M_1^* + K_{21}M_2^* + K_{31}M_3^*) \quad (1)$$

$$-dM_2/dt = K_{12}M_1^*M_2 + K_{22}M_2^*M_2 + K_{32}M_3^*M_2 = M_2(K_{12}M_1^* + K_{22}M_2^* + K_{32}M_3^*) \quad (2)$$

$$-dM_3/dt = K_{13}M_1^*M_3 + K_{23}M_2^*M_3 + K_{33}M_3^*M_3 = M_3(K_{13}M_1^* + K_{23}M_2^* + K_{33}M_3^*) \quad (3)$$

Applying the conventional steady-state assumption to each radical, we have the following.

For M_1^*:

$$K_{12}M_1^*M_2 + K_{13}M_1^*M_3 = K_{21}M_2^*M_1 + K_{31}M_3^*M_1 \tag{4}$$

or

$$K_{21}M_2^* + K_{31}M_3^* = (M_1^*/M_1)(K_{12}M_2 + K_{13}M_3) \tag{4a}$$

For M_2^*:

$$K_{21}M_2^*M_1 + K_{23}M_2^*M_3 = K_{12}M_2M_1^* + K_{32}M_3^*M_2 \tag{5}$$

or

$$K_{12}M_1^* + K_{32}M_3^* = (M_2^*/M_2)(K_{21}M_1 + K_{23}M_3) \tag{5a}$$

For M_3^*:

$$K_{31}M_3^*M_1 + K_{32}M_3^*M_2 = K_{13}M_1^*M_3 + K_{23}M_2^*M_3 \tag{6}$$

or

$$K_{13}M_1^* + K_{23}M_2^* = (M_3^*/M_3)(K_{31}M_1 + K_{32}M_2) \tag{6a}$$

Equations (4), (5), and (6) are replicas of the equations of Walling and Briggs.[2] From eqs. (1), (2), (3), (4), (5a), and (6a) we have the following.

$$\begin{aligned} -dM_1/dt &= M_1[K_{11}M_1^* + (M_1^*/M_1)(K_{12}M_2 + K_{13}M_3)] \\ &= M_1^*(K_{11}M_1 + K_{12}M_2 + K_{13}M_3) \end{aligned} \tag{7}$$

$$\begin{aligned} -dM_2/dt &= M_2[K_{22}M_2^* + (M_2^*/M_2)(K_{21}M_1 + K_{23}M_3)] \\ &= M_2^*(K_{21}M_1 + K_{22}M_2 + K_{23}M_3) \end{aligned} \tag{8}$$

$$\begin{aligned} -dM_3/dt &= M_3[(M_3^*/M_3)(K_{31}M_1 + K_{32}M_2) + K_{33}M_3^*] \\ &= M_3^*[K_{31}M_1 + K_{32}M_2 + K_{33}M_3] \end{aligned} \tag{9}$$

From eqs. (4), (5), and (6) we have the following.

$$M_1^*(K_{12}M_2 + K_{13}M_3) - K_{21}M_2^*M_1 - K_{31}M_3^*M_1 = 0 \tag{10}$$

$$-K_{12}M_1^*M_2 + M_2^*(K_{21}M_1 + K_{23}M_3) - K_{32}M_3^*M_2 = 0 \tag{11}$$

$$-K_{13}M_1^*M_3 - K_{23}M_2^*M_3 + M_3^*(K_{31}M_1 + K_{32}M_2) = 0 \tag{12}$$

We know that

$$\begin{aligned} a_1X + b_1Y + c_1Z &= 0 \\ a_2X + b_2Y + c_2Z &= 0 \\ a_3X + b_3Y + c_3Z &= 0 \end{aligned}$$

$$\begin{aligned} X/Y &= (b_1c_3 - b_3c_1 - b_1c_2 + b_2c_1)/(a_1c_2 - a_2c_1 - a_1c_3 + a_3c_1) \\ X/Z &= (b_3c_1 - b_1c_3 - b_2c_1 + b_1c_2)/(a_1b_2 - a_2b_1 - a_1b_3 + a_3b_1) \\ Y/Z &= (a_3c_1 - a_1c_3 - a_2c_1 + a_1c_2)/(a_2b_1 - a_1b_2 - a_3b_1 + a_1b_3) \end{aligned}$$

Let X, Y, and Z be equal to M_1^*, M_2^*, and M_3^*, respectively. Then,

$$\begin{aligned} a_1 &= (K_{12}M_2 + K_{13}M_3), \quad b_1 = -K_{21}M_1, \quad \text{and } c_1 = -K_{31}M_1 \\ a_2 &= -K_{12}M_2, \quad b_2 = (K_{21}M_1 + K_{23}M_3), \quad \text{and } c_2 = -K_{32}M_2 \\ a_3 &= -K_{13}M_3, \quad b_3 = -K_{23}M_3, \quad \text{and } c_3 = (K_{31}M_1 + K_{32}M_2) \end{aligned}$$

Therefore,

$$M_1^*/M_2^* = M_1(K_{21}K_{31}M_1 + K_{21}K_{32}M_2 + K_{23}K_{31}M_3)/M_2(K_{12}K_{31}M_1 + K_{12}K_{32}M_2 + K_{13}K_{32}M_3) \quad (13)$$

$$M_1^*/M_3^* = M_1(K_{21}K_{31}M_1 + K_{21}K_{32}M_2 + K_{23}K_{31}M_3)/M_3(K_{13}K_{21}M_1 + K_{12}K_{23}M_2 + K_{13}K_{23}M_3) \quad (14)$$

$$M_2^*/M_3^* = M_2(K_{12}K_{31}M_1 + K_{12}K_{32}M_2 + K_{13}K_{32}M_3)/M_3(K_{13}K_{21}M_1 + K_{12}K_{23}M_2 + K_{13}K_{23}M_3) \quad (15)$$

Again,

$$\begin{aligned} a_1X + b_1Y + c_1Z &= 0 \\ a_2X + b_2Y + c_2Z &= 0 \\ a_3X + b_3Y + c_3Z &= 0 \end{aligned}$$

$$a_1(b_2c_3 - b_3c_2) + b_1(c_2a_3 - c_3a_2) + c_1(a_2b_3 - a_3b_2) = 0$$

But

$$a_1 \neq 0, \quad b_1 \neq 0, \quad \text{and } c_1 \neq 0$$

Therefore,

$$\begin{aligned} b_2c_3 - b_3c_2 &= 0 \quad \text{or} \quad b_2/b_3 = c_2/c_3 \\ c_2a_3 - c_3a_2 &= 0 \quad \text{or} \quad c_2/c_3 = a_2/a_3 \\ a_2b_3 - a_3b_2 &= 0 \quad \text{or} \quad a_2/a_3 = b_2/b_3 \end{aligned}$$

$$\therefore\ a_2/a_3 = b_2/b_3 = c_2/c_3$$

$$\therefore\ -K_{12}M_2/-K_{13}M_3 = (K_{21}M_1 + K_{23}M_3)/-K_{23}M_3 = -K_{32}M_2/(K_{31}M_1 + K_{32}M_2) \quad (16)$$

From eq. (16) we have

$$\text{(i)} \quad K_{12}K_{23}M_2 = -K_{13}K_{21}M_1 - K_{13}K_{23}M_3$$

or

$$K_{13}K_{21}M_1 + K_{12}K_{23}M_2 + K_{13}K_{23}M_3 = 0 \quad (17)$$

$$\text{(ii)} \quad K_{21}K_{31}M_1^2 + K_{23}K_{31}M_1M_3 + K_{21}K_{32}M_1M_2 = 0$$

or

$$M_1(K_{21}K_{31}M_1 + K_{21}K_{32}M_2 + K_{23}K_{31}M_3) = 0$$

But $M_1 \neq 0$ (N.B.: M_1 is equal to zero only on completion of the reaction). Therefore

$$K_{21}K_{31}M_1 + K_{21}K_{32}M_2 + K_{23}K_{31}M_3 = 0 \quad (18)$$

and

$$\text{(iii)}\quad -K_{12}K_{31}M_1M_2 - K_{12}K_{32}M_2^2 = K_{13}K_{32}M_2M_3$$

or

$$K_{12}K_{31}M_1 + K_{12}K_{32}M_2 + K_{13}K_{32}M_3 = 0 \tag{19}$$

From eqs. (17), (18), and (19);

$$K_{12}K_{31}M_1 + K_{12}K_{32}M_2 + K_{13}K_{32}M_3 = K_{13}K_{21}M_1 + K_{12}K_{23}M_2 + K_{13}K_{23}M_3 = K_{21}K_{31}M_1 + K_{21}K_{32}M_2 + K_{23}K_{31}M_3 \tag{20}$$

From eqs. (13), (14), (15), and (20) the following equations are deduced:

$$M_1^*/M_2^* = M_1/M_2, \quad M_1^*/M_3^* = M_1/M_3 \quad \text{and} \quad M_2^*/M_3^* = M_2/M_3$$

$$\therefore M_2^* = (M_2/M_1)/M_1^* \tag{21}$$

$$\text{and} \quad M_3^* = (M_3/M_1)/M_1^* \tag{22}$$

From eqs. (7), (8), (9), (21), and (22) the following equations are deduced:

$$-dM_1/dt = M_1^*(K_{11}M_1 + K_{12}M_2 + K_{13}M_3)$$
$$-dM_2/dt = (M_2/M_1)(K_{21}M_1 + K_{22}M_2 + K_{23}M_3)M_1^*$$
$$-dM_3/dt = (M_3/M_1)(K_{31}M_1 + K_{32}M_2 + K_{33}M_3)M_1^*$$

Therefore

$$-dM_1/(K_{11}M_1 + K_{12}M_2 + K_{13}M_3) = M_1^*dt$$
$$-(dM_2 \cdot M_1)/M_2(K_{21}M_1 + K_{22}M_2 + K_{23}M_3) = M_1^*dt$$
$$-(dM_3 \cdot M_1)/M_3(K_{31}M_1 + K_{32}M_2 + K_{33}M_3) = M_1^*dt$$

Therefore

$$dM_1/(K_{11}M_1 + K_{12}M_2 + K_{13}M_3) = (dM_2 \cdot M_1)/M_2(K_{21}M_1 + K_{22}M_2 + K_{23}M_3) = (dM_3 \cdot M_1)/M_3(K_{31}M_1 + K_{32}M_2 + K_{33}M_3)$$

or

$$dM_1/M_1(K_{11}M_1 + K_{12}M_2 + K_{13}M_3) = dM_2/M_2(K_{21}M_1 + K_{22}M_2 + K_{23}M_3) = dM_3/M_3(K_{31}M_1 + K_{32}M_2 + K_{33}M_3) \tag{23}$$

From eqs. (17), (18), and (19) we have

$$K_{12}M_2 + K_{13}M_3 = -(K_{13}K_{21}/K_{23})M_1 \tag{24}$$

$$K_{21}M_1 + K_{23}M_3 = -(K_{21}K_{32}/K_{31})M_2 \tag{25}$$

$$K_{31}M_1 + K_{32}M_2 = -(K_{13}K_{32}/K_{12})M_3 \tag{26}$$

From eqs. (23), (24), (25), and (26) we have

$$dM_1/M_1[K_{11}M_1 - (K_{13}K_{21}/K_{23})M_1] = dM_2/M_2[K_{22}M_2 - (K_{21}K_{32}/K_{31})M_2] = dM_3/M_3[K_{33}M_3 - (K_{13}K_{32}/K_{12})M_3]$$

or

$$[K_{23}/(K_{11}K_{23} - K_{13}K_{21})](dM_1/M_1^2) = [K_{31}/(K_{22}K_{31} - K_{21}K_{32})](dM_2/M_2^2) = [K_{12}/(K_{12}K_{33} - K_{13}K_{32})](dM_3/M_3^2)$$

On integration we have

$$[K_{23}/(K_{11}K_{23} - K_{13}K_{21})][1/(M_1) - 1/(M_1)_0] = [K_{31}/(K_{22}K_{31} - K_{21}K_{32})][(1/(M_2) - 1/(M_2)_0] = [K_{12}/(K_{12}K_{33} - K_{13}K_{32})][1/(M_3) - 1/(M_3)_0] \quad (27)$$

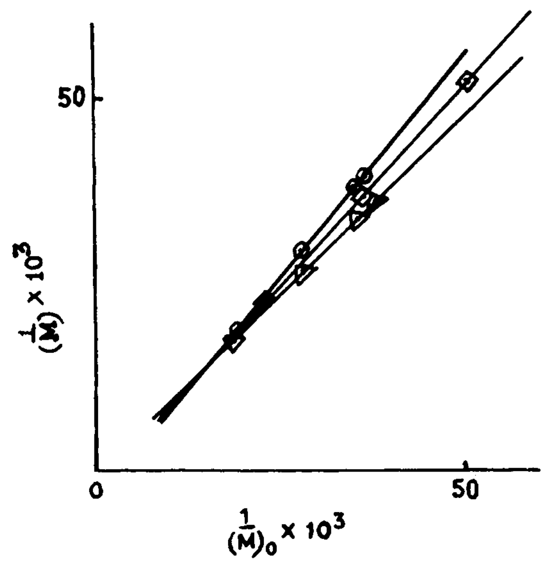

Fig. 1. Plots of $1/(M)_0$ versus $1/(M)$ for copolymerization of three-component system consisting of styrene ⊙, methyl methacrylate ◬, and acrylonitrile ⊡.

where $(M_1)_0$, $(M_2)_0$, and $(M_3)_0$ are the initial concentrations of the monomers and (M_1), (M_2), and (M_3) are their respective concentrations after time t. In this equation one part is equivalent to another part.

Let us suppose that

$$[K_{23}/(K_{11}K_{23} - K_{13}K_{21})][1/(M_1) - 1/(M_1)_0] = [K_{31}/(K_{22}K_{31} - K_{21}K_{32})][1/(M_2) - 1/(M_2)_0] = [K_{12}/(K_{12}K_{33} - K_{13}K_{32})][1/(M_3) - 1/(M_3)_0] = A$$

$$K_{23}/(K_{11}K_{23} - K_{13}K_{21}) = X$$

$$K_{31}/(K_{22}K_{31} - K_{21}K_{32}) = Y$$

$$K_{12}/(K_{12}K_{33} - K_{13}K_{32}) = Z$$

Then

$$[1/(M_1) - 1/(M_1)_0] = A/X \quad \text{or} \quad 1/(M_1) = A/X + 1/(M_1)_0 \quad (28)$$

$$[1/(M_2) - 1/(M_2)_0] = A/Y \quad \text{or} \quad 1/(M_2) = A/Y + 1/(M_2)_0 \quad (29)$$

$$[1/(M_3) - 1/(M_3)_0] = A/Z \quad \text{or} \quad 1/(M_3) = A/Z + 1/(M_3)_0 \quad (30)$$

In these equations A, X, Y, and Z are constants. Therefore, the respective plots of $1/(M_1)$, $1/(M_2)$, and $1/(M_3)$ versus $1/(M_1)_0$, $1/(M_2)_0$, and $1/(M_3)_0$ would be linear. To test the validity of these equations, values of (M_1), (M_2), and (M_3) and $(M_1)_0$, $(M_2)_0$, and $(M_3)_0$ in terms of mole per cent were computed from the data of experiments 4, 5, 6, and 7 of Walling and Briggs.[2] Plots of the data are shown in Figure 1. Linear plots support the plausibility of these equations. Further, it may be added that the equations would be equally applicable in cases in which composition and time of reaction are variant or one of them is variable and other constant.

References

1. T. Alfrey and G. Goldfinger, *J. Chem. Phys.*, **12**, 322 (1944).
2. C. Walling and E. R. Briggs, *J. Am. Chem. Soc.*, **67**, 1774 (1945).

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