

# A New Copolymerization Equation

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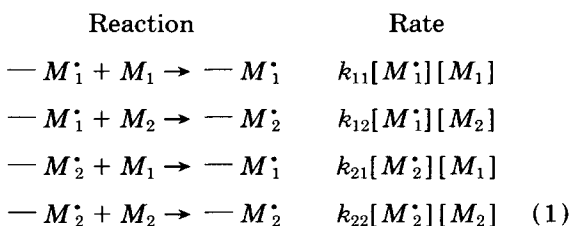
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## SYNOPSIS

A new copolymerization equation is suggested for the calculation of copolymer composition. The new equation is independent of reactivity ratios, so we can obtain the copolymer composition from experimental data when the reactivity ratios are unknown. The new equation has been verified by experimental data (styrene/methyl methacrylate, methyl methacrylate/vinyl chloride, and styrene/acrylonitrile systems). The results of the comparisons suggest that the new equation is satisfactory. © 1995 John Wiley & Sons, Inc.

## INTRODUCTION

According to Meyer,<sup>1</sup> the reaction of copolymerization was first described in 1914 by Klatte,<sup>2</sup> who carried out the copolymerization of a mixture of vinyl esters. In 1936, Dostal<sup>3</sup> suggested four reactions of chain growth in copolymerization under some conditions:



where  $M_1$  and  $M_2$  represent the two monomers and  $M_1^{\cdot}$  and  $M_2^{\cdot}$  are chains ending in  $M_1$  and  $M_2$  units, respectively. In 1941, the necessity of expressing copolymer compositions in terms of easily measurable parameters was realized by Wall.<sup>4</sup> In 1944, besides the work of Simha and Bronson,<sup>5</sup> three independent developments of what is now generally termed the "copolymerization equation" were published by Alfrey and Goldfinger,<sup>6</sup> Mayo and Lewis,<sup>7</sup> and Wall.<sup>8</sup> In every case, three assumptions are necessary: first, that one was dealing with a chain reaction involving long chains so that consumption of monomer could be discussed solely in terms of chain propagation

reaction; second, that these chains had very short lives compared to the duration of the overall reaction, so that steady-state expression might be set up for the concentrations of active centers; and, finally, that the propagation reactions could be adequately described by eqs. (1). Under these assumptions, many kinds of copolymerizations equations were obtained:

- (1) The rate of disappearance of the two monomer in a copolymerization:

$$-d[M_1]/dt = k_{11}[M_1^{\cdot}][M_1] + k_{21}[M_2^{\cdot}][M_1] \quad (2a)$$

$$-d[M_2]/dt = k_{12}[M_1^{\cdot}][M_2] + k_{22}[M_2^{\cdot}][M_2] \quad (2b)$$

- (2) Mayo-Lewis differential equation<sup>7</sup> (also see refs. 9 and 10):

$$\frac{d[M_1]}{d[M_2]} = \frac{[M_1](r_1[M_1] + [M_2])}{[M_2]([M_1] + r_2[M_2])} \quad (3a)$$

or

$$F_1 = \frac{d[M_1]}{d[M_1] + d[M_2]} = \frac{r_1 f_1^2 + f_1 f_2}{f_1^2 + 2f_1 f_2 + r_2 f_2^2} \quad (3b)$$

where  $f_1$  and  $f_2$  are mol fractions of monomer  $M_1$  and  $M_2$  in the feed, respectively, and  $r_1$

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and  $r_2$ , defined as usual, represent monomer reactivity ratios.

(3) Mayo-Lewis integral equation<sup>7</sup>:

$$\log \frac{[M_2]}{[M_2]_0} = \frac{r_2}{1-r_2} \log \frac{[M_2]_0[M_1]}{[M_1]_0[M_2]} - \frac{1-r_1r_2}{(1-r_1)(1-r_2)} \log \frac{(r_1-1)[M_1]/[M_2]_0 - r_2 + 1}{(r_1-1)[M_1]_0/[M_2]_0 - r_2 + 1} \quad (4)$$

where  $[M_1]$ ,  $[M_2]$ ,  $[M_1]_0$ , and  $[M_2]_0$  are defined as usual.

(4) Walling-Briggs equation<sup>11</sup>:

$$\frac{\log [M_1]/[M_1]_0}{\log [M_2]/[M_2]_0} = \frac{r_1[M_1]_0 + [M_2]_0}{[M_1] + r_2[M_2]} \quad (5)$$

(5) Skeist equation<sup>12</sup>:

$$\log M/M_0 = \int_{(f_1)_0}^{f_1} df_1/F_1 - f_1 \quad (6)$$

where  $M$  is the total concentration of the monomer and the subscript 0 represents the initial values.

(6) Meger equation<sup>13-15</sup>:

$$c = 1 - M/M_0 = 1 - \left[ \frac{f_1}{(f_1)_0} \right]^\alpha \left[ \frac{f_2}{(f_2)_0} \right]^\beta \left[ \frac{(f_1)_0 - \delta}{f_1 - \delta} \right]^\gamma \quad (7)$$

where  $\alpha$ ,  $\beta$ ,  $\gamma$ , and  $\delta$  are dependent of monomer reactivity ratios.

Up to now, no one has raised any objections to all the above equations and no other new copolymerization can be found. This article focuses attention on suggesting a new copolymerization equation that is simpler than the above-discussed equations. One of the prominent advantages of the new equations is that the composition of copolymer is independent of monomer reactivity ratios.

## MATHEMATICAL DERIVATION

It is quite evident that eqs. (2a) and (2b) may be integrated to yield following equations, respectively:

$$\ln [M_1]/[M_1]_0 = (k_{11}[M_1^*] + k_{21}[M_2^*])t \quad (8a)$$

$$\ln [M_2]/[M_2]_0 = (k_{22}[M_2^*] + k_{12}[M_1^*])t \quad (8b)$$

where  $t$  is the time of polymerization. Dividing (8a) by (8b) gives

$$\frac{\ln [M_1]/[M_1]_0}{\ln [M_2]/[M_2]_0} = \frac{k_{11}[M_1^*] + k_{21}[M_2^*]}{k_{12}[M_1^*] + k_{22}[M_2^*]} \quad (9)$$

and the relationship between  $[M_1^*]$  and  $[M_2^*]$  is given by the steady-state expression.

$$k_{21}[M_2^*][M_1] = k_{12}[M_1^*][M_2] \quad (10)$$

Substituting  $[M_2^*]$  in eq. (9) by its equivalent from eq. (10) and multiplying the numerator and denominator of the right-hand member of eq. (9) by  $[M_1]/k_{12}$  gives

$$\frac{\ln [M_1]/[M_1]_0}{\ln [M_2]/[M_2]_0} = \frac{k_{11}/k_{12}[M_1] + [M_2]}{[M_1] + k_{22}/k_{21}[M_2]} \quad (11)$$

As usual, we define  $r_1$  as  $k_{11}/k_{12}$  and  $r_2$  as  $k_{22}/k_{21}$ ; eq. (11) then becomes

$$\frac{\ln [M_1]/[M_1]_0}{\ln [M_2]/[M_2]_0} = \frac{r_1[M_1] + [M_2]}{[M_1] + r_2[M_2]} \quad (12)$$

Equation (12) may be rewritten as eq. (13) by substituting the instantaneous monomer concentration ( $[M_1]$  and  $[M_2]$ ) with their molar fraction ( $f_1$  and  $f_2$ ) and the overall conversion

$$\frac{\ln(1-c)f_1 - \ln(f_1)_0}{\ln(1-c)f_2 - \ln(f_2)_0} = \frac{r_1f_1 + f_2}{f_1 + r_2f_2} \quad (13)$$

It is obvious that the right-hand term of eq. (13) is equal to  $F_1f_2/F_2f_1$  or  $F_1f_2/(1-F_1)f_1$ , which can be obtained from eq. (3). Substituting the right-hand term of eq. (13) by  $F_1f_2/F_2f_1$ , the following equation can be obtained:

$$F_1 = \frac{f_1 \ln(1-c)f_1/(f_1)_0}{f_1 \ln(1-c)f_1/(f_1)_0 + f_2 \ln(1-c)f_2/(f_2)_0} \quad (14)$$

Equation (14) is a new copolymerization equation that is independent of monomer reactivity ratios.

## RESULTS AND DISCUSSION

In copolymerization, the copolymer composition, especially the instantaneous composition, is one of the ultimate aims of our work, so the relation between the instantaneous composition and feed or the conversion of the monomer is particularly im-

Table I Composition Data of the Systems for St/MMA, St/An, and MMA/Vc<sup>a</sup>

System	No.	$f_1$	$(f_1)_0$	$c$	$F_1$	$F_1^*$
St/MMA	1	0.18355	0.1966	27.8	0.233	0.233
	2	0.37579	0.3994	62.6	0.400	0.400
	3	0.63338	0.5994	60.5	0.595	0.598
	4	0.85974	0.7996	61.5	0.804	0.805
MMA/Vc	1	0.654	0.800	62.8	0.837	0.836
	2	0.395	0.500	34.2	0.656	0.652
	3	0.0755	0.200	42.7	0.224	0.233
St/AN	1	0.824	0.800	20.6	0.740	0.730
	2	0.478	0.500	21.3	0.568	0.570
	3	0.056	0.200	48.0	0.380	0.200

$F_1$ : obtained by eq. (3);  $F_1^*$ : obtained by Eq. (14). The experimental data of the table are taken from Refs. 20 and 21.

<sup>a</sup> St: styrene; MMA: methyl methacrylate; An: acrylonitrile; Vc: vinyl chloride.

portant, because the properties of the copolymer vary with the instantaneous composition of copolymer. As we know, all the existing copolymerization composition equations relate to monomer reactivity ratios. At present, all the values of the reactivity ratios are estimated<sup>18-19</sup> and various authors give different or contradictory data of the same copolymerization system. One of the reasons for the differences may arise from the conditions of copolymerization, i.e., these parameters refer to some specific environment and changing of the environment of copolymerization exerts an enormous effect on the values of the parameters. Furthermore, these parameters are unknown for a new copolymerization system, so that eq. (14) is very ideal because it is independent of monomer reactivity ratios.

Equation (14) relates the instantaneous copolymer composition being formed at any instant,  $F_1$ , with a polymerizing mixtures of two monomers at mol fraction  $f_1$  by means of the conversion of the monomer, so that the instantaneous copolymer composition can be easily obtained from eq. (14) without knowing the monomer reactivity ratios. Table I shows that the results of eq. (14) are the same as those of the Mayo-Lewis eq. (3).

## CONCLUSIONS

Generally, the relation between  $F_1$  and  $f_1$  is decided by the parameters  $r_1$  and  $r_2$ , but eq. (14) is independent of  $r_1$  and  $r_2$ , i.e., the value of  $F_1$  can be obtained from eq. (14) without any restrictions of experimental conditions by means of  $f_1$  and  $c$ . In addition, eq. (14) can be also used to verify the values of  $r_1$  and  $r_2$  when the result of eq. (14) is the same as that of eq. (3) for the same system and experimental data; it shows that the values of  $r_1$  and  $r_2$  are correct. Table I shows that, e.g., the values of  $r_1$  and  $r_2$  reported by Refs. 20 and 21 are very good because

the results of eq. (14) are agreement with the results of eq. (3).

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