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Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597274>

Derivation of Copolymer Composition Equation Through Kinetic Theory in Binary Copolymerization Systems with Antepenultimate Effect

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To cite this Article Liu, Chang Xin , Zhang, Shu Xiang , Wang, Hui Zhong and Kong, Xiang Zheng(1991) 'Derivation of Copolymer Composition Equation Through Kinetic Theory in Binary Copolymerization Systems with Antepenultimate Effect', Journal of Macromolecular Science, Part A, 28: 10, 1063 — 1077

To link to this Article: DOI: 10.1080/00222339108054084

URL: <http://dx.doi.org/10.1080/00222339108054084>

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DERIVATION OF COPOLYMER COMPOSITION EQUATION THROUGH KINETIC THEORY IN BINARY COPOLYMERIZATION SYSTEMS WITH ANTEPENULTIMATE EFFECT

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ABSTRACT

A new treatment to characterize copolymer composition in binary copolymerization systems was developed by using a steady-state assumption for free radicals. It gives a copolymer composition equation solely through classical kinetic theory with the antepenultimate effect taken into account. This equation and its derivation procedure are compared with those previously published.

INTRODUCTION

Early quantitative treatments of copolymer composition and copolymerization rates in free radical polymerization were all based on the assumption that the reactivity of a growing polymeric free radical is only determined by its terminal monomer unit [1-7]. Among the earliest result was the well-known Mayo-Lewis copolymer composition equation [1]. This equation has been extensively studied, and diverse methods have been established to estimate monomer reactivity ratios, copolymer composition, and/or sequence distribution in various copolymerization systems. In many cases these studies showed good agreement with experimental results obtained from reliable accurate analyses such as ^{13}C NMR, GC [8-11], etc.

However, several cases of free radical copolymerization reportedly failed to obey the Mayo-Lewis equation [12-16], particularly with monomers of high polarity. The earliest observations of this deviation from the Mayo-Lewis equation probably stemmed from Ham and Barb. In Ham's studies on styrene/fumaronitrile [13] copolymer and acrylonitrile copolymers [15], and Barb's studies on styrene/sulfur dioxide [17] and styrene/maleic anhydride [14], they claimed that the last second monomer unit (the one immediately preceding the radical possessing monomer unit) in a growing polymeric free radical has a significant effect upon the addition of one or both of the comonomers to the active polymeric chain. There are by now many data showing the effects of monomer units other than the terminal one on the reactivity of growing chains adding monomers [18-23]. Besides monomers of high polarity mentioned above, examples also include vinylidene cyanide, 1,2-disubstituted olefins, as well as unconjugated monomers such as vinyl acetate and vinyl chloride [21]. All of this work showed the obvious need for equations which weigh the contributory effects of monomer units more remote than terminal unit or and even the penultimate unit. In fact, several authors have sought theoretical models to describe copolymer composition and sequence distribution for such systems since the early 1960s. The various approaches which have been made can be summarized as follows.

a). The Markov process theory. With the assistance of an astochastic matrix, Price [24] was probably the first to give complete and quantitative copolymer composition equations for cases where terminal, penultimate, and antepenultimate effects coexist.

b). The statistical stationary process theory [25]. This method has

been employed by several authors (Pyun [26], Ito et al. [27]). Based on the conditional probability of a monomer adding to a given polymeric free radical, they were able to derive copolymer composition and sequence distribution equations up to the antepenultimate effect. Ham [16, 28, 29] also gave simplified equations with certain assumptions; some of his equations are simple and useful [29]. However, as pointed out by several authors [24, 30, 31], some others are not exact.

c). Classical kinetic theory. Based on the steady-state assumption for free radicals, this theory was first used by Mayo and Lewis in obtaining a copolymer composition equation with only the terminal effect taken into account. On the same basis, Merz et al. [32] extended the Mayo-Lewis equation to copolymerization systems with the penultimate effect.

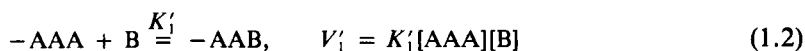
To date, there has not been any reported work on a copolymer composition equation derived through kinetics and including the antepenultimate effect. Moreover, as pointed out in previous reports [30], methods a) and b) are excessively complicated and a sequence reversibility principle was used every time in addition to the steady-state assumption.

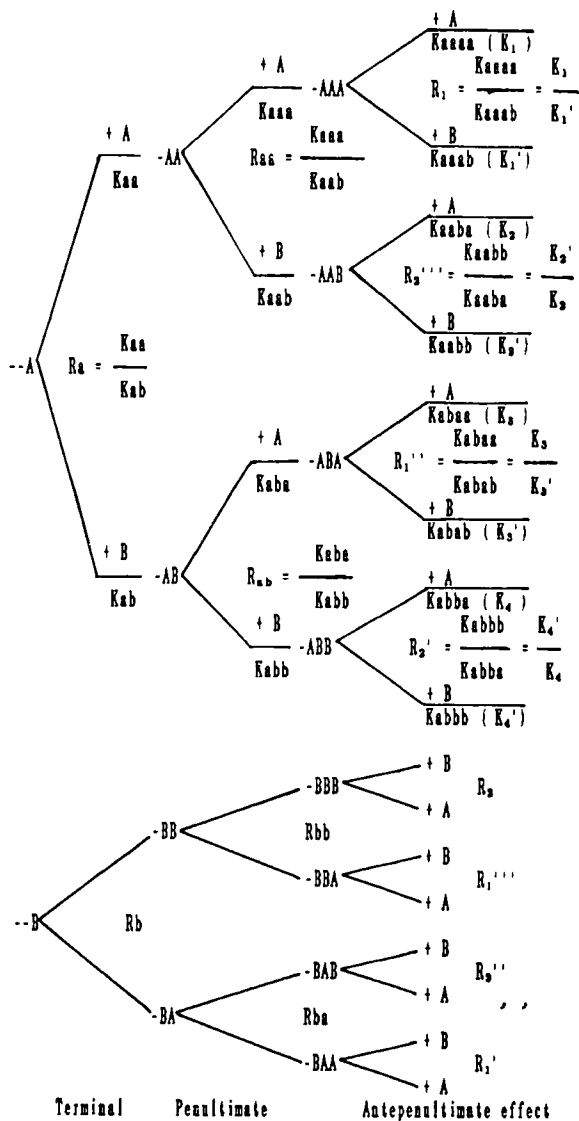
In contrast with this, it is our belief that the classical kinetic theory is much simpler, more direct, and more explicit. It needs only the steady-state assumption, and the same results as from a) and b) have been obtained. This paper presents the procedure for deriving a copolymer composition equation with the antepenultimate effect considered via the classic kinetic theory.

DEMONSTRATION AND RESULTS

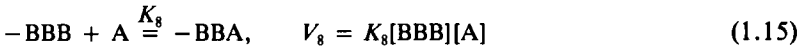
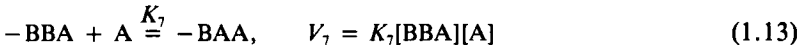
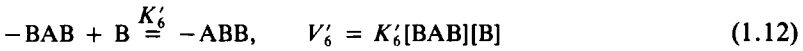
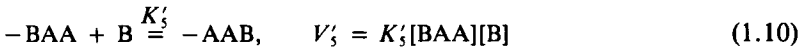
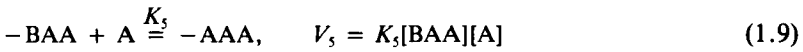
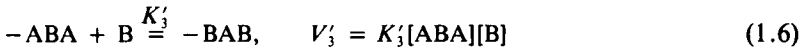
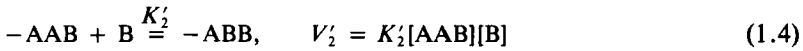
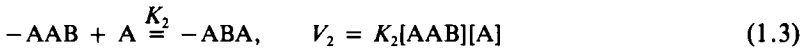
In the Mayo-Lewis equation, it was sufficient to take four chain propagation reactions into account (two reactivity ratios); if the penultimate effect is considered, there are eight chain propagations (four reactivity ratios) to be taken into account; and there are 16 propagation reactions (eight reactivity ratios) if the antepenultimate effect is considered to be as in Scheme 1.

The propagation reactions and polymerization rate equations corresponding to the schema can be written as follows:





SCHEME 1.



Reactivity ratio definitions are given by the following equations:

$$R_1 = K_1/K'_1 = V_1/(V'_1X) \text{ or } V_1/V'_1 = R_1X \quad (2.1)$$

$$R'_1 = K_5/K'_5 = V_5/(V'_5X) \text{ or } V_5/V'_5 = R'_1X \quad (2.2)$$

$$R_1'' = K_3/K_3' = V_3/(V_3'X) \text{ or } V_3/V_3' = R_1''X \quad (2.3)$$

$$R_1''' = K_7/K_7' = V_7/(V_7'X) \text{ or } V_7/V_7' = R_1'''X \quad (2.4)$$

$$R_2 = K_8'/K_8 = (V_8'X)/V_8 \text{ or } V_8'/V_8 = R_2/X \quad (2.5)$$

$$R_2' = K_4'/K_4 = (V_4'X)/V_4 \text{ or } V_4'/V_4 = R_2'/X \quad (2.6)$$

$$R_2'' = K_6'/K_6 = (V_6'X)/V_6 \text{ or } V_6'/V_6 = R_2''/X \quad (2.7)$$

$$R_2''' = K_2'/K_2 = (V_2'X)/V_2 \text{ or } V_2'/V_2 = R_2'''/X \quad (2.8)$$

In the above equations, $X = [A]/[B]$.

Assumption of steady state for free radicals gives:

For -AAA:

$$V_1 = V_5 \text{ or } K_1'[\text{AAA}][B] = K_5[\text{BAA}][A] \quad (3.1)$$

For -AAB:

$$V_2 + V_2' = V_1 + V_5 = V_5 + V_5' \text{ or} \\ (K_2[A] + K_2'[B])[\text{AAB}] = (K_5[A] + K_5'[B])[\text{BAA}] \quad (3.2)$$

For -ABA:

$$V_3 + V_3' = V_2 + V_6 \text{ or} \\ (K_3[A] + K_3'[B])[\text{ABA}] = K_2[A][\text{AAB}] + K_6[A][\text{BAB}] \quad (3.3)$$

For -ABB:

$$V_4 + V_4' = V_2 + V_6' \text{ or} \\ (K_4[A] + K_4'[B])[\text{ABB}] = K_2'[B][\text{AAB}] + K_6'[B][\text{BAB}] \quad (3.4)$$

For -BAA:

$$V_5 + V_5' = V_3 + V_7 \text{ or} \\ (K_5[A] + K_5'[B])[\text{BAA}] = K_3[A][\text{ABA}] + K_7[A][\text{BBA}] \quad (3.5)$$

For -BAB:

$$V_6 + V_6' = V_3 + V_7' \text{ or} \\ (K_6[A] + K_6'[B])[\text{BAB}] = K_3[B][\text{ABA}] + K_7[B][\text{BBA}] \quad (3.6)$$

For -BBA:

$$V_7 + V_7' = V_4 + V_8 = V_4 + V_4' \text{ or} \\ (K_7[A] + K_7'[B])[\text{BBA}] = (K_4[A] + K_4'[B])[\text{ABB}] \quad (3.7)$$

For -BBB:

$$V_4 = V_8 \text{ or } K_4'[B][\text{ABB}] = K_8[A][\text{BBB}] \quad (3.8)$$

[M] and [MMM] (M = A or B) in the above equations represent the concentrations of monomer M and the polymeric free radicals, respectively. If dA and dB are defined as monomer A and B polymerized in a given time interval, the composition of copolymer formed (monomer mole ratio) can be expressed as

$$\frac{dA}{dB} = \frac{V_1 + V_2 + V_3 + V_4 + V_5 + V_6 + V_7 + V_8}{V'_1 + V'_2 + V'_3 + V'_4 + V'_5 + V'_6 + V'_7 + V'_8} \quad (4)$$

From Eqs. (3.2), (3.3), (3.6), and (3.7), Eq. (4) becomes

$$\frac{dA}{dB} = \frac{V_1 + V_3 + V_5 + V_7 + V_3 + V'_3 + V_7 + V'_7}{V'_2 + V'_4 + V'_6 + V'_8 + V_2 + V'_2 + V_6 + V'_6} \quad (5)$$

Simultaneous addition of both sides of Eq. (3.5) with Eq. (3.6) immediately gives

$$V_5 + V'_5 + V_6 + V'_6 = V_3 + V'_3 + V_7 + V'_7 \quad (6.1)$$

Since we have from Eq. (3.2)

$$V_5 + V'_5 = V_2 + V'_2$$

therefore

$$V_2 + V'_2 + V_6 + V'_6 = V_3 + V'_3 + V_7 + V'_7$$

or

$$(V_2 + V'_2 + V_6 + V'_6)/(V_3 + V'_3 + V_7 + V'_7) = 1 \quad (6.2)$$

Multiplying Eq. (5) by Eq. (6.2), we get:

$$\frac{dA}{dB} = \frac{1 + (V_1 + V_3 + V_5 + V_7)/(V_3 + V'_3 + V_7 + V'_7)}{1 + (V'_2 + V'_4 + V'_6 + V'_8)/(V_2 + V'_2 + V_6 + V'_6)} \quad (7)$$

Simultaneously multiplying the numerator and the denominator of the term $(V_1 + V_3 + V_5 + V_7)/(V_3 + V'_3 + V_7 + V'_7)$ in Eq. (7) by $1/(V_3 + V_7)$ and similarly for term $(V'_2 + V'_4 + V'_6 + V'_8)/(V_2 + V'_2 + V_6 + V'_6)$ by $1/(V'_2 + V'_6)$, Eq. (7) becomes

$$\frac{dA}{dB} = \frac{1 + \frac{1 + (V_1 + V_5)/(V_3 + V_7)}{1 + (V'_3 + V'_7)/(V_3 + V_7)}}{1 + \frac{1 + (V'_4 + V'_8)/(V'_2 + V'_6)}{1 + (V_2 + V_6)/(V'_2 + V'_6)}} \quad (8)$$

Equation (8) contains four parts: $(V_1 + V_5)/(V_3 + V_7)$, $(V'_3 + V'_7)/(V_3 + V_7)$, $(V'_4 + V'_8)/(V'_2 + V'_6)$, and $(V_2 + V_6)/(V'_2 + V'_6)$, which need to be further treated in order to be presented by monomer concentration ratio (X) and reactivity ratios.

From Eq. (3.5) we have

$$\begin{aligned} (V_1 + V_5)/(V_3 + V_7) &= (V_1 + V_5)/(V_5 + V'_5) \\ &= (V_1/V'_5 + 1)/(1 + V'_5/V_5) \end{aligned}$$

since $V_5 = V'_1$ (Eq. 3.1), hence

$$(V_1 + V_5)/(V_3 + V_7) = (V_1/V'_1 + 1)/(V'_5/V_5 + 1) \quad (9)$$

This equation, combined with Eqs. (2.1) and (2.2), enables us to get

$$\frac{V_1 + V_5}{V_3 + V_7} = \frac{1 + R_1 X}{1 + 1/(R'_1 X)} = R'_1 X \frac{1 + R_1 X}{1 + R'_1 X} \quad (10)$$

Similarly, from Eq. (3.4), one has

$$(V'_4 + V'_8)/(V'_2 + V'_6) = (1 + V'_8/V'_4)/(1 + V_4/V'_4)$$

By using Eq. (3.8) ($V_8 = V'_4$) first and then Eqs. (2.5) and (2.6), one can readily get

$$\frac{V'_4 + V'_8}{V'_2 + V'_6} = \frac{1 + R_2/X}{1 + X/R'_2} = \frac{R'_2}{X} \frac{R_2 + X}{R'_2 + X} \quad (11)$$

To solve $(V'_3 + V'_7)/(V_3 + V_7)$ and $(V_2 + V_6)/(V'_2 + V'_6)$, the extended polymerization rate equations in Eqs. (3.1) to (3.8) were used.

Equations (3.2) and (3.7) can be rearranged into the form of Eqs. (12) and (13):

$$[\text{AAB}] = \frac{K_3[\text{A}] + K'_3[\text{B}]}{K_2[\text{A}] + K'_2[\text{B}]} [\text{BAA}] \quad (12)$$

$$[\text{BBA}] = \frac{K_4[\text{A}] + K'_4[\text{B}]}{K_7[\text{A}] + K'_7[\text{B}]} [\text{ABB}] \quad (13)$$

Substituting [AAB] in Eq. (3.3) by Eq. (12):

$$(K_3[A] + K'_3[B])[ABA] = K_2[A] \frac{K_3[A] + K'_3[B]}{K_2[A] + K'_2[B]} [BAA] + K_6[A][BAB] \quad (14.1)$$

or

$$[ABA] = \frac{K_2[A]}{K_3[A] + K'_3[B]} \frac{K_3[A] + K'_3[B]}{K_2[A] + K'_2[B]} [BAA] + \frac{K_6[A]}{K_3[A] + K'_3[B]} [BAB] \quad (14.2)$$

Substituting [AAB] in Eq. (3.4) by Eq. (12):

$$(K_4[A] + K'_4[B])[ABB] = K'_2[B] \frac{K_3[A] + K'_3[B]}{K_2[A] + K'_2[B]} [BAA] + K'_6[B][BAB] \quad (15.1)$$

or

$$[ABB] = \frac{K_3[A] + K'_3[B]}{K_4[A] + K'_4[B]} \frac{K'_2[B]}{K_2[A] + K'_2[B]} [BAA] + \frac{K'_6[B]}{K_4[A] + K'_4[B]} [BAB] \quad (15.2)$$

Substituting [BBA] in Eq. (3.5) by Eq. (13) gives

$$(K_5[A] + K'_5[B])[BAA] = K_3[A][ABA] + K_7[A] \frac{K_4[A] + K'_4[B]}{K_7[A] + K'_7[B]} [ABB] \quad (16)$$

Substituting [BBA] in Eq. (3.6) by Eq. (13) gives

$$(K_6[A] + K'_6[B])[BAB] = K'_3[B][ABA] + K'_7[B] \frac{K_4[A] + K'_4[B]}{K_7[A] + K'_7[B]} [ABB] \quad (17.1)$$

or

$$[BAB] = \frac{K'_3[B][ABA]}{K_6[A] + K'_6[B]} + \frac{K_4[A] + K'_4[B]}{K_6[A] + K'_6[B]} \frac{K'_7[B]}{K_7[A] + K'_7[B]} [ABB] \quad (17.2)$$

Substituting Eqs. (14.2) and (15.2) for [ABA] and [ABB], respectively, in Eq. (16):

$$\begin{aligned} (K_5[A] + K'_5[B])[BAA] &= K_2[A] \frac{K_3[A][BAA]}{K_3[A] + K'_3[B]} \frac{K_5[A] + K'_5[B]}{K_2[A] + K'_2[B]} \\ &+ \frac{K_3[A]K_6[A]}{K_3[A] + K'_3[B]} [BAB] + \frac{K_3[A] + K'_3[B]}{K_2[A] + K'_2[B]} \frac{K_7[A]K'_2[B]}{K_7[A] + K'_7[B]} [BAA] \\ &+ \frac{K_7[A]K'_6[B][BAB]}{K_7[A] + K'_7[B]} \end{aligned}$$

or

$$\begin{aligned} (K_5[A] + K'_5[B])[BAA] &\left(1 - \frac{K_2[A]}{K_2[A] + K'_2[B]} \frac{K_3[A]}{K_3[A] + K'_3[B]} \right. \\ &\left. - \frac{K'_2[B]}{K_2[A] + K'_2[B]} \frac{K_7[A]}{K_7[A] + K'_7[B]} \right) = [BAB] \left(\frac{K_3[A]K_6[A]}{K_3[A] + K'_3[B]} \right. \\ &\left. + \frac{K_7[A]K'_6[B]}{K_7[A] + K'_7[B]} \right) \end{aligned}$$

or

$$\begin{aligned} &1 - \frac{K_2[A]}{K_2[A] + K'_2[B]} \frac{K_3[A]}{K_3[A] + K'_3[B]} - \frac{K'_2[B]}{K_2[A] + K'_2[B]} \frac{K_7[A]}{K_7[A] + K'_7[B]} \\ &\frac{\left(\frac{K_3[A]}{K_3[A] + K'_3[B]} K_6[A] + \frac{K_7[A]}{K_7[A] + K'_7[B]} K'_6[B] \right) [BAB]}{[BAA](K_5[A] + K'_5[B])} \end{aligned} \quad (18.1)$$

Multiplying both sides of Eq. (18.1) by $V_6 = (K_6[A] + K'_6[B])[BAB]$:

$$\begin{aligned} &1 - \frac{K_2[A]}{K_2[A] + K'_2[B]} \frac{K_3[A]}{K_3[A] + K'_3[B]} - \frac{K'_2[B]}{K_2[A] + K'_2[B]} \frac{K_7[A]}{K_7[A] + K'_7[B]} \\ &\frac{K_3[A]}{K_3[A] + K'_3[B]} \frac{K_6[A]}{K_6[A] + K'_6[B]} + \frac{K_7[A]}{K_7[A] + K'_7[B]} \frac{K'_6[B]}{K_6[A] + K'_6[B]} \\ &= \frac{(K_6[A] + K'_6[B])[BAB]}{(K_5[A] + K'_5[B])[BAA]} = \frac{V_6 + V'_6}{V_5 + V'_5} \end{aligned} \quad (18.2)$$

Note that $(V_6 + V'_6)/(V_5 + V'_5) = (V'_3 + V'_7)/(V_3 + V_7)$ if Eqs. (3.5) and (3.6) are divided by one another. Thus, Eq. (18.2) can be written as

$$\frac{V'_3 + V'_7}{V_3 + V_7} = \frac{1 - \frac{X}{X + K'_2/K_2} \frac{X}{X + K'_3/K_3} - \frac{K'_2/K_2}{X + K'_2/K_2} \frac{X}{X + K'_7/K_7}}{\frac{X}{X + K'_3/K_3} \frac{X}{X + K'_6/K_6} + \frac{X}{X + K'_7/K_7} \frac{K'_6/K_6}{X + K'_6/K_6}} \quad (18.3)$$

From Eqs. (2.1) to (2.8), the following equation can be obtained:

$$\begin{aligned} \frac{V'_3 + V'_7}{V_3 + V_7} &= \frac{1 - \frac{X}{X + R''_2} \frac{X}{X + 1/R''_1} \frac{R''_2}{X + R''_2} \frac{X}{X + 1/R''_1}}{\frac{X}{X + 1/R''_1} \frac{X}{X + R''_2} + \frac{X}{X + 1/R''_1} \frac{R''_2}{X + R''_2}} \\ &= \frac{\frac{1}{R''_1 X} \left(1 + \frac{R''_2}{X} \frac{1 + R''_1 X}{1 + R''_1 X} \right)}{\frac{R''_2}{X} \frac{X + R''_2}{X + R''_2} \left(\frac{X}{R''_2} + \frac{R''_1}{R''_1} \frac{1 + XR''_1}{1 + XR''_1} \right)} \end{aligned} \quad (18.4)$$

Similarly, as we have done to obtain Eqs. (18), by simultaneously substituting Eqs. (16) and (17.2) into Eq. (15.1) to replace $(K_5[A] + K'_5[B])[BAA]$ and $[BAB]$, respectively, the following equation can be easily derived:

$$\begin{aligned} (K_4[A] + K'_4[B])[ABB] &= \frac{K'_2[B]K_3[A][ABA]}{K_2[A] + K'_2[B]} \\ &+ \frac{K'_2[B]K_7[A]}{K_2[A] + K'_2[B]} \frac{K_4[A] + K'_4[B]}{K_7[A] + K'_7[B]} [ABB] + \frac{K'_3[B]K'_6[B]}{K_6[A] + K'_6[B]} [ABA] \\ &+ \frac{K'_6[B]K'_7[B]}{K_6[A] + K'_6[B]} \frac{K_4[A] + K'_4[B]}{K_7[A] + K'_7[B]} [ABB] \end{aligned}$$

or

$$1 - \frac{K'_6[B]}{K_6[A] + K'_6[B]} \frac{K'_7[B]}{K_7[A] + K'_7[B]} - \frac{K'_2[B]}{K_2[A] + K'_2[B]} \frac{K_7[A]}{K_7[A] + K'_7[B]}$$

$$\frac{\left(\frac{K'_6[B]}{K_6[A] + K'_6[B]} K'_3[B] + \frac{K'_2[B]}{K_2[A] + K'_2[B]} K_3[A] \right) [ABA]}{[ABA](K_4[A] + K'_4[B])} \quad (19.1)$$

Multiplying the two sides of Eq. (19.1) by $(K_3[A] + K'_3[B])[ABA]$:

$$1 - \frac{K'_6[B]}{K_6[A] + K'_6[B]} \frac{K'_7[B]}{K_7[A] + K'_7[B]} - \frac{K'_2[B]}{K_2[A] + K'_2[B]} \frac{K_7[A]}{K_7[A] + K'_7[B]}$$

$$\frac{K'_6[B]}{K_6[A] + K'_6[B]} \frac{K'_3[B]}{K_3[A] + K'_3[B]} + \frac{K'_2[B]}{K_2[A] + K'_2[B]} \frac{K_3[A]}{K_3[A] + K'_3[B]}$$

$$= \frac{(K_3[A] + K'_3[B])[ABA]}{(K_4[A] + K'_4[B])[ABB]} = \frac{V_3 + V'_3}{V_4 + V'_4} \quad (19.2)$$

From Eqs. (3.3) and (3.4), $(V_3 + V'_3)/(V_4 + V'_4) = (V_2 + V_6)/(V'_2 + V'_6)$, and therefore

$$\frac{V_2 + V_6}{V'_2 + V'_6} = \frac{V_3 + V'_3}{V_4 + V'_4}$$

$$= \frac{1 - \frac{1}{XK_6/K'_6 + 1} \frac{1}{XK_7/K'_7 + 1} - \frac{1}{XK_2/K'_2 + 1} \frac{XK_7/K'_7}{XK_7/K'_7 + 1}}{\frac{1}{XK_6/K'_6 + 1} \frac{1}{XK_3/K'_3 + 1} + \frac{1}{XK_2/K'_2 + 1} \frac{XK_3/K'_3}{XK_3/K'_3 + 1}} \quad (19.3)$$

From Eqs. (2.1) to (2.8), Eq. (19.4) follows:

$$\frac{V_2 + V_6}{V'_2 + V'_6} = \frac{1 - \frac{1}{X/R''_2 + 1} \frac{1}{XR''_1 + 1} - \frac{1}{X/R''_2 + 1} \frac{R''_1 X}{R''_1 X + 1}}{\frac{1}{X/R''_2 + 1} \frac{1}{XR''_1 + 1} + \frac{1}{X/R''_2 + 1} \frac{XR''_1}{XR''_1 + 1}}$$

$$= \frac{\frac{1}{XR''_1} \frac{1 + XR''_1}{1 + XR''_1} \left(XR''_1 + \frac{X + R''_2}{X + R''_2} \right)}{\frac{1}{X} \left(R''_2 + \frac{R''_2}{XR''_1} \frac{X + R''_2}{X + R''_2} \right)} \quad (19.4)$$

Substituting Eqs. (10), (11), (18.4), and (19.4) into Eq. (8), we get

$$\frac{dA}{dB} = \frac{1 + \frac{1 + R_1'X \left(\frac{1 + R_1X}{1 + R_1'X} \right)}{1 + \frac{1}{R_1''X} \left(1 + \frac{R_2''}{X} \frac{1 + R_1''X}{1 + R_1''X} \right)}}{1 + \frac{\frac{R_2''}{X} \frac{R_2'' + X}{R_2'' + X} \left(\frac{X}{R_2''} + \frac{R_1''}{R_1''} \frac{1 + R_1''X}{1 + R_1''X} \right)}{1 + \frac{R_2''}{X} \left(\frac{R_2 + X}{R_2'' + X} \right)}} \cdot \frac{1 + \frac{1}{R_1''X} \frac{1 + R_1''X}{1 + R_1''X} \left(R_1''X + \frac{R_2'' + X}{R_2'' + X} \right)}{1 + \frac{1}{X} \left(R_2'' + \frac{R_2''}{R_1''X} \frac{R_2'' + X}{R_2'' + X} \right)} \tag{20}$$

Equation (20) is the same as that obtained by Price [24] by using the Markov process theory, and when compared with that of Ito [27], an error was found. The r_B'' (in Eq. 21 in Ref. 27, corresponding to R_2'' in this paper) in $(r_B''/x)(1 + r_A''x)/(1 + r_A''x)$ should be replaced by r_B''' . This can also be checked by substituting Ito's Relation (16) into Eq. (20) in his paper, which gives r_B''' instead of the aforementioned r_B'' .

CONCLUSION

Based solely on the steady-state assumption for free radicals in binary copolymerization systems with an antepenultimate effect, a copolymer composition equation is derived through classical kinetic theory. This equation is in the same form as that previously obtained from the Markov process or the statistical stationary process, but without the need for any other principles or assumptions than the steady-state assumption for free radicals. An error in the earlier reported equation was found when it was compared with the newly obtained equation.

ACKNOWLEDGEMENTS

The authors are grateful to Dr. G. E. Ham (Briarcliff Manor, New York) and Dr. A. Guyot (L.M.O., C.N.R.S., Vernaison, France) for their helpful advice.

REFERENCES

- [1] F. R. Mayo and F. M. Lewis, *J. Am. Chem. Soc.*, **66**, 1594 (1944).
- [2] N. Fineman and S. D. Ross, *J. Polym. Sci.*, **5**, 259 (1950).
- [3] R. M. Joshi and S. L. Kapur, *Ibid.*, **14**, 508 (1954).
- [4] P. W. Tidwell and G. A. Mortimer, *Ibid.*, **A3**, 369 (1965).
- [5] T. Kelen and F. Tüdös, *J. Macromol. Sci. – Chem.*, **A9**, 1 (1975).
- [6] V. Jaacks, *Makromol. Chem.*, **161**, 161 (1972).
- [7] R. M. Joshi and S. G. Joshi, *J. Macromol. Sci. – Chem.*, **A5**, 1329 (1971).
- [8] C. Pichot, M. F. Llauro, and Q. T. Pham, *J. Polym. Sci., Polym. Chem. Ed.*, **19**, 2619 (1981).
- [9] X. Z. Kong, C. Pichot, and J. Guillot, *Eur. Polym. J.*, **24**, 485 (1988).
- [10] S. P. Rao, S. Ponratnam, and S. L. Kapur, *J. Polym. Sci., Polym. Lett. Ed.*, **14**, 513 (1976).
- [11] M. F. Llauro, C. Pichot, J. Guillot, L. R. Guerrero, M. A. Cruz, and C. Guzman, *Polymer*, **27**, 889 (1986).
- [12] P. M. Tidwell and G. A. Mortimer, *J. Macromol. Sci. – Rev. Macromol. Chem.*, **C4**, 281 (1970).
- [13] R. G. Fordyce and G. E. Ham, *J. Am. Chem. Soc.*, **73**, 1186 (1951).
- [14] W. G. Barb, *J. Polym. Sci.*, **11**, 117 (1953).
- [15] G. E. Ham, *Ibid.*, **14**, 87 (1954).
- [16] G. E. Ham, *Ibid.*, **45**, 169, 177 (1960).
- [17] W. G. Barb, *Ibid.*, **10**, 49 (1953).
- [18] M. Szwarc, *J. Am. Chem. Soc.*, **85**, 533 (1963).
- [19] F. A. Bovey and G. V. D. Tiers, *J. Polym. Sci.*, **44**, 173 (1960).
- [20] R. L. Miller and L. E. Nielson, *Ibid.*, **56**, 375 (1962).
- [21] C. Pichot, J. Guillot, and A. Guyot, *J. Macromol. Sci. – Chem.*, **A5**, 753 (1971).
- [22] J. Guillot, J. Vialle, and A. Guyot, *Ibid.*, **A5**, 735 (1971).
- [23] K. F. O'Driscoll and F. P. Gasparra, *J. Macromol. Chem.*, **1**, 643 (1967).
- [24] F. Price, *J. Chem. Phys.*, **36**, 209 (1962).
- [25] B. D. Coleman and T. G. Fox, *J. Polym. Sci.*, **A1**, 3185 (1963).
- [26] C. W. Pyun, *J. Polym. Sci., Part A-1*, **8**, 1111 (1970).
- [27] K. Ito and Y. Yamashita, *J. Polym. Sci.*, **A3**, 2165 (1965).
- [28] G. E. Ham, *J. Macromol. Sci. – Chem.*, **A5**, 453 (1971).
- [29] G. E. Ham, *Copolymerization*, Wiley-Interscience, New York, 1964, Chap. 1.

- [30] J. Guillot, in *Proceeding of the 2nd European Symposium on Polymer Spectroscopy, Rome, 1973*, pp. 189–205.
- [31] Tang Aoqing, in *Statistical Theory in Macromolecular Reactions*, China Science (Chinese ed.), Beijing, 1985, pp. 300–302.
- [32] E. Merz, T. Alfrey, and G. Goldfinger, *J. Polym. Sci.*, *1*, 75 (1946).

Received February 22, 1991

Revision received April 28, 1991