Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

Special Forms of Copolymer Composition Equations

Chong Wha Pyun[a]
[a] Department of Chemistry, Lowell Technological Institute, Lowell, Massachusetts

To cite this Article Pyun, Chong Wha(1971) 'Special Forms of Copolymer Composition Equations', Journal of Macromolecular Science, Part A, 5: 4, 769 — 775
To link to this Article: DOI: 10.1080/00222337108061057
URL: http://dx.doi.org/10.1080/00222337108061057

J. MACROMOL. SCI.–CHEM., A5(4), pp. 769-775, July, 1971

Special Forms of Copolymer Composition Equations

CHONG WHA PYUN

Department of Chemistry
Lowell Technological Institute
Lowell, Massachusetts 01854

SUMMARY

A theoretical explanation is presented for the experimentally observed binary copolymer composition equations in the form of $y = Kx^a$, where y is the ratio of the numbers of two monomers being incorporated in the polymer, x is the number or concentration ratio of the two monomers in the feed, and K and "a" are constants characteristic of the copolymerization system. The value of "a," found experimentally, ranges from 0 to near 4. It is shown that the composition equation of this form with a = 0, 1, 2, 3, and 4 can be obtained under various limiting conditions from the conventional copolymer composition equations which take into account the terminal and penultimate effects. This simplification is often accompanied with reduction in the order of Markovian comonomer sequence distribution statistics associated with the original standard composition equations. It is also pointed out that the conventional composition equations can account for $y = Kx^a$ with noninteger "a" for limited experimental ranges of x.

Composition equations for binary copolymers of A and B relate the ratio of the number of A and B being incorporated into the polymer $y \equiv d(A)/d(B)$ with that existing in the monomer feed mixture $x \equiv (A)/(B)$. Here, (X) stands for the concentration of the monomer species X (= A,B) in the feed solution. It has recently been pointed out [1] that for many binary copolymers, experimental composition data may be approximated by

$$y = Kx^a \tag{1}$$

where K and "a" are constants characteristic of the copolymerization system. The value of "a" experimentally observed ranges [1] from 0 to 3.5 (with x substantially independent of time).

The conventional "terminal effect" copolymer composition equation [2, 3] gives y in terms of x as well as two reactivity ratios $r_A \equiv k_{AA}/k_{AB}$ and $r_B \equiv k_{BB}/k_{BA}$, where k_{XY} is the rate constant for the addition of monomer Y to the growing polymer chains whose last comonomer unit is an X:

$$y = [(1 + r_A x)/(r_B + x)]x \tag{2}$$

As expected, the comonomer sequence distribution in the resulting copolymer is first-order Markovian in general. The "terminal effect" equation (Eq. 2) simplifies to Eq. (1) with a = 0, 1, and 2 under various well-defined conditions

$$y = 1;\ 1/r_A >> x >> r_B \tag{3}$$

$$y = r_A x;\ x >> 1/r_A,\ r_B \tag{4}$$

$$y = x/r_B;\ x << 1/r_A,\ r_B \tag{5}$$

$$y = r_A x = x/r_B;\ k_{AA} = \kappa k_{BA},\ k_{AB} = \kappa k_{BB} \tag{6}$$

$$y = (r_A/r_B)x^2;\ 1/r_A << x << r_B \tag{7}$$

The first (Eq. 3) describes regularly alternating A and B comonomers with the minimum possible value (1/2) of the persistence ratio [4] ρ. The next three (Eqs. 4-6) give Bernoullian comonomer sequence distributions (ρ = 1). Note that Eq. (6) applies whether $\kappa = 1$ (no terminal effects [5]) or $\kappa \neq 1$ (special terminal effects [6]). The last (Eq. 7) indicates [7] formation of very long "blocks" of A and of B in the copolymer ($\rho \to \infty$). The "terminal effect" equation can also account [7] for Eq. (1) with noninteger values of "a" ($0 < a < 2$) for limited ranges of x experimentally investigated. It cannot [1], however, explain Eq. (1) for $a > 2$.

The purpose of this communication is to point out the possibility that the standard "penultimate effect" copolymer composition equation [8, 9] can account for the copolymerization behavior expressed by Eq. (1) for $0 \leqslant a \leqslant 4$.

The "penultimate effect" equation [8, 9] reads

$$y = \frac{R_1 x + 1}{R_2 + x} x \tag{8}$$

with

$$R_1 = \frac{r_1 x + 1}{r_1' x + 1} r_1', \quad R_2 = \frac{r_2 + x}{r_2' + x} r_2' \tag{9}$$

where

$$r_1 = \frac{k_{AAA}}{k_{AAB}}, \; r_1' = \frac{k_{BAA}}{k_{BAB}}, \; r_2 = \frac{k_{BBB}}{k_{BBA}}, \; r_2' = \frac{k_{ABB}}{k_{ABA}} \tag{10}$$

Here, k_{XYZ} (X,Y,Z = A,B) is the rate constant for the addition of monomer Z to the growing polymer chains whose penultimate and terminal monomer units are X and Y, respectively. The comonomer sequence distribution associated with Eq. (8) is in general second-order Markovian with the ρ and Ω factors [4, 10, 11] given by

$$\frac{1}{\rho} = P_{AB} + P_{BA} = \frac{r_1' x + 1}{r_1' x + 1 + r_1' x(r_1 x + 1)} + \frac{x(r_2' + x)}{x(r_2' + x) + r_2'(r_2 + x)} \tag{11}$$

$$\Omega_A = \frac{P_{AAA}}{P_{AA}} = \frac{r_1}{r_1'} \frac{r_1' x + 1 + r_1' x(r_1 x + 1)}{(r_1 x + 1)^2} \tag{12}$$

$$\Omega_B = \frac{P_{BBB}}{P_{BB}} = \frac{r_2}{r_2'} \frac{x(r_2' + x) + r_2'(r_2 + x)}{(r_2 + x)^2} \tag{13}$$

where P_{AAB}, for example, is the conditional probability of finding a B comonomer given that its two immediate predecessors are both A.

We have $r_1 = r_1'$ if $k_{AAA} = \kappa_1 k_{BAA}$ and $k_{AAB} = \kappa_1 k_{BAB}$ whether

Table 1. Special Forms of Eq. (8) with Values of ρ, Ω_A, and Ω_B

	I	IV	III	II, V	i	ii
A	$r_1 r_1' x^4/r_2 r_2'$	$r_1 r_1' x^3/r_2$	$r_1 r_1' x^2/2$ **	$r_1 r_1' x^2$ **	$r_1 r_1' x^3/r_B$	$r_1 r_1' x^2$ **
	$\infty; 1; 1$	$\infty; 1; 1$	$2; 1; 0$	$1; 1; \infty, \frac{r_2}{r_2'}$	$\infty; 1; 1$	$1; 1; 1$
D	$r_1 x^3/r_2 r_2'$	$r_1 x^2/r_2$	$r_1 x/2$ **	$r_1 x$ **	$r_1 x^2/r_B$	$r_1 x$ **
	$\infty; 1; 1$	$\infty; 1; 1$	$2; 1; 0$	$1; 1; \infty, \frac{r_2}{r_2'}$	$\infty; 1; 1$	$1; 1; 1$
C	$2x^2/r_2 r_2'$ *	$2x/r_2$ *	1	2	$2x/r_B$ *	2
	$2; 0; 1$	$2; 0; 1$	$1; 0; 0$	$\frac{2}{3}; 0; \infty, \frac{r_2}{r_2'}$	$2; 0; 1$	$\frac{2}{3}; 0; 1$
B, E	$x^2/r_2 r_2'$ *	x/r_2 *	1/2	1	x/r_B *	1
	$1; \infty, \frac{r_1}{r_1'}; 1$	$1; \infty, \frac{r_1}{r_1'}; 1$	$\frac{2}{3}; \infty, \frac{r_1}{r_1'}; 0$	$\frac{1}{2}; \infty, \frac{r_1}{r_1'}; \infty, \frac{r_2}{r_2'}$	$1; \infty, \frac{r_1}{r_1'}; 1$	$\frac{1}{2}; \infty, \frac{r_1}{r_1'}; 1$
a	$r_A x^3/r_2 r_2'$	$r_A x^2/r$	$r_A x/2$ **	$r_A x$ **	$r_A x^2/r_B$	$r_A x$ **
	$\infty; 1; 1$	$\infty; 1; 1$	$2; 1; 0$	$1; 1; \infty, \frac{r_2}{r_2'}$	$\infty; 1; 1$	$1; 1; 1$

b	x^2/r_2r_2' *	x/r_2 *	1/2	1	x/r_B *	1
	1; 1; 1	1; 1; 1	$\frac{2}{3}$; 1; 0	$\frac{1}{2}$; 1; ∞, $\frac{r_2}{r_2'}$	1; 1; 1	$\frac{1}{2}$; 1; 1

Key to symbols:

* $y \ll 1$; ** $y \gg 1$

A $r_1 x \gg 1 \gg r_1' x, r_1 r_1' x^2 \gg 1$ ($P_{AAA} = 1; P_{AB} = 0$)

B $r_1 x \gg 1 \gg r_1' x, r_1 r_1' x^2 \ll 1$ (1; 1)

C $r_1 x \ll 1 \ll r_1' x$ (0; 1/2)

D $r_1 x, r_1' x \gg 1$ (1; 0)

E $r_1 x, r_1' x \ll 1$ (0; 1)

a $r_1 = r_1' \equiv r_A; r_A x \gg 1$ (0; 1)

b $r_1 = r_1' \equiv r_A; r_A x \ll 1$ (1; 0)

I $r_2 \gg x \gg r_2', r_2 r_2' \gg x^2$ ($P_{BBB} = 1; P_{BA} = 0$)

II $r_2 \gg x \gg r_2', r_2 r_2' \ll x^2$ (1; 1)

III $r_2 \ll x \ll r_2'$ (0, 1/2)

IV $r_2, r_2' \gg x$ (1; 0)

V $r_2, r_2' \ll x$ (0; 1)

i $r_2 = r_2' \equiv r_B; r_B \gg x$ (1; 0)

ii $r_2 = r_2' \equiv r_B; r_B \ll x$ (0; 1)

$\kappa_1 = 1$ or not. Under the circumstances, Eq. (8) reduces to

$$y = \frac{r_A x + 1}{R_2 + x} x \tag{14}$$

where r_A is used for r_1 ($= r_1'$). Similarly, if we have $r_2 = r_2'$ ($\equiv r_B$) resulting from $k_{BBB} = \kappa_2 k_{ABB}$ and $k_{BBA} = \kappa_2 k_{ABA}$ whether $\kappa_2 = 1$ or not, Eq. (8) simplifies to

$$y = \frac{R_1 x + 1}{r_B + x} x \tag{15}$$

If we have both $r_1 = r_1'$ and $r_2 = r_2'$, then Eq. (8) takes the form of the "terminal effect" equation [2, 3], which is, however, slightly more general than the original equation in the sense that it includes the cases where $\kappa_1 \neq 1$ and/or $\kappa_2 \neq 1$ in addition to the case where $\kappa_1 = \kappa_2 = 1$.

A summary of special forms derived under various conditions from Eq. (8), either directly or via Eqs. (14) and (15), is given in Table 1. The first line of each entry gives the right-hand side f(x) of the composition equation y = f(x) under the combination(s) of specified conditions, and the second line lists the values of ρ, Ω_A, and Ω_B.

Condition A, for example, is realized if $1/r_1 x \ll r_1' x \ll 1$ and Condition I holds if $x/r_2 \ll r_2'/x \ll 1$. Under the combination of these two conditions, Eq. (8) reduces to Eq. (1) with a = 4 and the resulting comonomer sequence distribution is first-order Markovian with very long blocks of A and of B prevailing. Under the combination of Conditions C and III, we have regularly alternating AA and BB pairs. If Conditions C and II (or V) hold, we have another regular pattern . . .AABAABAAB. . . .

As pointed out [7] previously, it is also quite conceivable that the experimental data fitting Eq. (1) with noninteger values of "a" for limited ranges of x can also fit Eq. (8) or one of its variants. If we accept this interpretation, then the experimental data approximated by Eq. (1) with $a > 2$ may be taken as an indication of the presence of penultimate effects (or possibly the effects of farther removed units) in the copolymerization. This does not, of course, preclude other possible interpretations. For example, O'Driscoll has previously derived [12] Eq. (1) with a = 2 for a mixture of two homopolymers (which could be mistaken for a copolymer) produced by a special initiation mechanism. For such polymeric blends generated by two independent homopropagations, Szwarc [13] mentions derivation of Eq. (1) with a = 1 and a = 3 with special termination mechanisms.

REFERENCES

[1] T. Higashimura, T. Masuda, and K. F. O'Driscoll, *J. Polym. Sci., Part B*, **6**, 841 (1968).
[2] F. R. Mayo and F. M. Lewis, *J. Amer. Chem. Soc.*, **66**, 1594 (1944).
[3] T. Alfrey and G. Goldfinger, *J. Chem. Phys.*, **12**, 205 (1944).
[4] B. D. Coleman and T. G Fox, *J. Polym. Sci., Part A*, **1**, 3183 (1963).
[5] F. T. Wall, *J. Amer. Chem. Soc.*, **63**, 1862 (1941).
[6] K. F. O'Driscoll and I. Kuntz, *J. Polym. Sci.*, **61**, 19 (1962).
[7] C. W. Pyun, *J. Polym. Sci., Part A-2*, **9**, 383 (1971).
[8] E. Merz, T. Alfrey, and G. Goldfinger, *J. Polym. Sci.*, **1**, 75 (1946).
[9] G. E. Ham, *J. Polym. Sci.*, **45**, 169 (1960).
[10] B. D. Coleman, T. G Fox, and M. Reinmöller, *J. Polym. Sci., Part B*, **4**, 1029 (1966).
[11] C. W. Pyun, *J. Polym. Sci., Part A-2*, **8**, 1111 (1970).
[12] K. F. O'Driscoll, *J. Polym. Sci.*, **57**, 721 (1962).
[13] M. Szwarc, *Carbanions, Living Polymers, and Electron Transfer*, Wiley (Interscience), New York, 1968, pp. 522-523.

Accepted by editor January 5, 1971
Received for publication January 13, 1971