Reaction Probability Model for Four-Component Copolymerization†

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ABSTRACT: The theoretical expressions corresponding to the composition of four-component copolymerization are derived as a function of first-order Markovian probabilities. These expressions enable the sequence distributions of a tetrapolymer to be readily calculated. An approach is also suggested for the generalization to the case of multicomponent copolymerization.

Introduction

The use of reaction probability models is widespread in the studies of copolymerization.[1-4] Most copolymers conform to Bernoullian, first-order Markovian, and second-order Markovian statistical models. The first-order Markovian model (i.e., terminal mechanism of copolymerization) is especially used in most experimental studies. For a binary copolymer involving comonomers A and B, the copolymer composition is given by[1-4]

$$F_a = kP_{ba} \tag{1a}$$

$$F_b = kP_{ab} \tag{1b}$$

where P_{ba} is the reaction probability of monomer A adding to a propagating chain terminating in unit B and $k = (P_{ab} + P_{ba})^{-1}$ in this case. F_a and F_b are the molar fractions of A and B in the copolymer. For a terpolymer, the corresponding expressions are[1]

$$F_a = k(P_{ba}P_{ca} + P_{ba}P_{cb} + P_{bc}P_{ca}) \tag{2a}$$

$$F_b = k(P_{cb}P_{ab} + P_{cb}P_{ac} + P_{ca}P_{ab}) \tag{2b}$$

$$F_c = k(P_{ac}P_{bc} + P_{ac}P_{ba} + P_{ab}P_{bc}) \tag{2c}$$

These molar composition expressions, $\{F_i\}$, are important because they are the starting points for the derivation of reaction probability expressions for comonomer sequences.[2,4,5] From the reaction probability expressions, we can then use NMR or other spectroscopic data to test for the validity of different statistical models.[3-7]

Although the $\{F_i\}$ expressions for binary and ternary copolymerizations are well-known, such expressions have not been reported for four-component copolymers (tetrapolymers). In a classic work, Walling and Briggs[8] developed the multicomponent copolymerization theory. Their expressions were given in determinant forms, and a computer program was written using the equations to calculate the composition from a list of reactivity ratios. In our efforts to use NMR spectroscopy to study four-component copolymers, we found it more convenient to have explicit expressions in reaction probabilities. It is the purpose of this work to derive such expressions.

Results and Discussion

I. Theoretical Considerations. In the first-order Markovian model, there are 16 possible propagating steps for the four-component copolymerization.

$$-M_1^* + M_1 \xrightarrow{k_{11}} -M_1M_1^*$$

$$-M_1^* + M_2 \xrightarrow{k_{12}} -M_1M_2^*$$

$$-M_1^* + M_3 \xrightarrow{k_{13}} -M_1M_3^*$$

$$-M_1^* + M_4 \xrightarrow{k_{14}} -M_1M_4^* \tag{3}$$

where the asterisk denotes the radical, anion, cation, or catalytic site, depending on the propagating mechanism, and k_{ij} is the rate constant for the addition of monomer j adding to a propagating chain terminating in a unit i. Twelve more equations can be written for $-M_2^*$, $-M_3^*$, and $-M_4^*$. The reaction probability is defined as

$$P_{ij} = \frac{k_{ij}(M_j)}{\sum_{j'=1}^{4} k_{ij'}(M_{j'})} \tag{4}$$

For example

$$P_{14} = \frac{k_{14}(M_4)}{k_{11}(M_1) + k_{12}(M_2) + k_{13}(M_3) + k_{14}(M_4)} = \frac{(M_4)/r_{14}}{(M_1) + (M_2)/r_{12} + (M_3)/r_{13} + (M_4)/r_{14}} \tag{5}$$

In eq 5, use has been made of the definition of reactivity ratio, $r_{ij} = k_{ii}/k_{ij}$. The term (M_i) refers to the molar concentration of comonomer M_i; for brevity, it will be abbreviated M_i hereinafter. We follow the standard approach[4,8] to set up the material balance equations.

$$dF_1/dt = (k_{21}F_2M_1 + k_{31}F_3M_1 + k_{41}F_4M_1) - k_{12}F_1M_2 - k_{13}F_1M_3 - k_{14}F_1M_4 \tag{6a}$$

$$dF_2/dt = (k_{12}F_1M_2 + k_{32}F_3M_2 + k_{42}F_4M_2) - k_{21}F_2M_1 - k_{23}F_2M_3 - k_{24}F_2M_4 \tag{6b}$$

$$dF_3/dt = (k_{13}F_1M_3 + k_{23}F_2M_3 + k_{43}F_4M_3) - k_{31}F_3M_1 - k_{32}F_3M_2 - k_{34}F_3M_4 \tag{6c}$$

$$dF_4/dt = (k_{24}F_2M_4 + k_{34}F_3M_4 + k_{14}F_1M_4) - k_{41}F_4M_1 - k_{42}F_4M_2 - k_{43}F_4M_3 \tag{6d}$$

We make the usual steady-state assumption and set all time derivatives to zero. The results are four equations

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Table I
Reactivity Ratios and Reaction Probabilities in the Tetrapolymerization Example

M_i	M_j	r_{ij}	r_{ji}	P_{ij}	P_{ji}
styrene	methyl methacrylate	0.50 ± 0.02	0.50 ± 0.02	0.3396	0.4734
styrene	vinylidene chloride	2.0 ± 0.1	0.14 ± 0.05	0.0797	0.4754
methyl methacrylate	vinylidene chloride	2.53 ± 0.1	0.24 ± 0.05	0.0887	0.2803
methyl methacrylate	acrylonitrile	1.20 ± 0.14	0.15 ± 0.07	0.1987	0.1994
acrylonitrile	vinylidene chloride	0.91 ± 0.1	0.37 ± 0.1	0.0308	0.1812
styrene	acrylonitrile	0.41 ± 0.08	0.04 ± 0.04	0.4128	0.7399

Table II
Comparison of Feed Concentration and Polymer Composition in the Tetrapolymer Example

		mol % in the copolymer		
monomer	monomer feed	found (ref 4)	calcd (ref 4)	calcd (this work)
styrene	25.21	40.7	41.3	41.3
methyl methacrylate	25.48	25.5	27.4	27.4
acrylonitrile	25.40	25.8	24.5	24.4
vinylidene chloride	23.91	8.0	6.9	6.9

and four unknowns (F_1, F_2, F_3, and F_4).

$$F_1(k_{12}M_2 + k_{13}M_3 + k_{14}M_4) - F_2(k_{21}M_1) - F_3(k_{31}M_1) - F_4(k_{41}M_1) = 0 \quad (7a)$$

$$F_1(k_{12}M_2) - F_2(k_{21}M_1 + k_{23}M_3 + k_{24}M_4) + F_3(k_{32}M_2) + F_4(k_{42}M_2) = 0 \quad (7b)$$

$$F_1(k_{13}M_3) + F_2(k_{23}M_3) - F_3(k_{31}M_1 + k_{32}M_2 + k_{34}M_4) + F_4(k_{43}M_3) = 0 \quad (7c)$$

$$F_1(k_{14}M_4) + F_2(k_{24}M_4) + F_3(k_{34}M_4) - F_4(k_{41}M_1 + k_{42}M_2 + k_{43}M_3) = 0 \quad (7d)$$

In view of the complexity of subsequent expressions, the following substitutions are made.

$$\begin{aligned} a &= k_{12}M_2 + k_{13}M_3 + k_{14}M_4 & J &= k_{13}M_3 \\ b &= k_{21}M_1 & K &= k_{23}M_3 \\ c &= k_{31}M_1 & L &= k_{31}M_1 + k_{32}M_2 + k_{34}M_4 \\ d &= k_{41}M_1 & m &= k_{43}M_3 \\ e &= k_{12}M_2 & n &= k_{14}M_4 \\ g &= k_{21}M_1 + k_{23}M_3 + k_{24}M_4 & o &= k_{24}M_4 \\ h &= k_{32}M_2 & p &= k_{34}M_4 \\ I &= k_{42}M_2 & q &= k_{41}M_1 + k_{42}M_2 + k_{43}M_3 \end{aligned} \quad (8)$$

The four equations can now be recast as follows:

$$aF_1 - bF_2 - cF_3 - dF_4 = 0 \quad (9a)$$

$$eF_1 - gF_2 + hF_3 + IF_4 = 0 \quad (9b)$$

$$JF_1 + KF_2 - LF_3 + mF_4 = 0 \quad (9c)$$

$$nF_1 + oF_2 + pF_3 - qF_4 = 0 \quad (9d)$$

In addition, there is another dependent equation that can be used in place of any one of the equations 9a–d.

$$F_1 + F_2 + F_3 + F_4 = 1 \quad (10)$$

Putting eq 9a–d and 10 in matrix form, we get

$$\left[\begin{array}{cccc|c} a & -b & -c & -d & 0 \\ e & -g & h & I & 0 \\ J & K & -L & m & 0 \\ 1 & 1 & 1 & 1 & 1 \end{array}\right] \quad (11)$$

Reduction of the matrix in eq 11 to the row echelon form followed by back-substitution will result in the solutions:

Table III
Calculated Diad and Triad Intensities[a] for the Tetrapolymer Example

AA	6.93						
AB	26.97	BB	6.55				
AC	35.13	BC	10.32	CC	0.73		
AD	6.57	BD	4.36	CD	2.00	DD	0.44
AAA	1.16						
AAB	4.53	BAB	4.40				
AAC	5.90	BAC	11.49	CAC	7.47		
AAD	1.10	BAD	2.15	CAD	2.80	DAD	0.26
ABA	6.63						
ABB	6.45	BBB	1.57				
ABC	5.09	BBC	2.47	CBC	0.97		
ABD	2.16	BBD	1.04	CBD	0.82	DBD	0.17
ACA	12.60						
ACB	7.42	BCB	1.08				
ACC	1.05	BCC	0.31	CCC	0.02		
ACD	1.45	BCD	0.42	CCD	0.06	DCD	0.04
ADA	1.56						
ADB	2.07	BDB	0.68				
ADC	0.95	BDC	0.65	CDC	0.14		
ADD	0.41	BDD	0.28	CDD	0.13	DDD	0.03

[a] The following designations have been used: A = styrene, B = methyl methacrylate, C = acrylonitrile, and D = vinylidene chloride.

$$\left[\begin{array}{cccc|c} 1 & -b/a & -c/a & -d/a & 0 \\ 1 & -g/e & h/e & I/e & 0 \\ 1 & K/J & -L/J & m/J & 0 \\ 1 & 1 & 1 & 1 & 1 \end{array}\right] \quad (12)$$

$$\rightarrow \left[\begin{array}{cccc|c} 1 & -b/a & -c/a & -d/a & 0 \\ 0 & -(g/e-b/a) & (h/e+c/a) & (I/e+d/a) & 0 \\ 0 & (K/J+b/a) & -(L/J-c/a) & (m/J+d/a) & 0 \\ 0 & (1+b/a) & (1+c/a) & (1+d/a) & 1 \end{array}\right] \quad (13)$$

After carrying out the remaining algebraic manipulations, back-substitution, and factoring of common terms, we obtain the following expressions:

$$F_4 \propto La^2g - Jacg - aLbe + bceJ - a^2hK - ahbJ - aceK - bceJ \quad (14a)$$

$$F_3 \propto a^2mg + Jadg - emab - Jebd + Ia^2K + IbJa + eadK + Jebd \quad (14b)$$

$$F_2 \propto mha^2 + dahJ + mcae + Jedc + LIa^2 - JcIa + dLea - Jecd \quad (14c)$$

$$F_1 \propto abhm + abIL + acgm + acKI + adgL - adhK \quad (14d)$$

If we use the definition of the reaction probability P_{ij}

$$P_{ij} = \frac{k_{ij}M_j}{\sum_{j'=1}^{4} k_{ij'}M_{j'}}$$

and substituting for variables a–m as defined in eq 8, we

obtain the final expressions:

$$F_1 \propto P_{21}P_{31}P_{41} + P_{21}P_{31}P_{42} + P_{21}P_{31}P_{43} + P_{21}P_{32}P_{41} + P_{21}P_{32}P_{42} + P_{21}P_{32}P_{43} + P_{21}P_{34}P_{41} + P_{21}P_{34}P_{42} + P_{23}P_{31}P_{41} + P_{23}P_{31}P_{42} + P_{23}P_{31}P_{43} + P_{23}P_{34}P_{41} + P_{24}P_{31}P_{41} + P_{24}P_{31}P_{43} + P_{24}P_{32}P_{41} + P_{24}P_{34}P_{41} \quad (15a)$$

$$F_2 \propto P_{12}P_{32}P_{42} + P_{12}P_{32}P_{41} + P_{12}P_{32}P_{43} + P_{12}P_{31}P_{42} + P_{12}P_{31}P_{41} + P_{12}P_{31}P_{43} + P_{12}P_{34}P_{42} + P_{12}P_{34}P_{41} + P_{13}P_{32}P_{42} + P_{13}P_{32}P_{41} + P_{13}P_{32}P_{43} + P_{13}P_{34}P_{42} + P_{14}P_{32}P_{42} + P_{14}P_{32}P_{43} + P_{14}P_{31}P_{42} + P_{14}P_{34}P_{42} \quad (15b)$$

$$F_3 \propto P_{23}P_{13}P_{43} + P_{23}P_{13}P_{42} + P_{23}P_{13}P_{41} + P_{23}P_{12}P_{43} + P_{23}P_{12}P_{42} + P_{23}P_{12}P_{41} + P_{23}P_{14}P_{43} + P_{23}P_{14}P_{42} + P_{21}P_{13}P_{43} + P_{21}P_{13}P_{42} + P_{21}P_{13}P_{41} + P_{21}P_{14}P_{43} + P_{24}P_{13}P_{43} + P_{24}P_{13}P_{41} + P_{24}P_{12}P_{43} + P_{24}P_{14}P_{43} \quad (15c)$$

$$F_4 \propto P_{24}P_{34}P_{14} + P_{24}P_{34}P_{12} + P_{24}P_{34}P_{13} + P_{24}P_{32}P_{14} + P_{24}P_{32}P_{12} + P_{24}P_{32}P_{13} + P_{24}P_{31}P_{14} + P_{24}P_{31}P_{12} + P_{23}P_{34}P_{14} + P_{23}P_{34}P_{12} + P_{23}P_{34}P_{13} + P_{23}P_{31}P_{14} + P_{21}P_{34}P_{14} + P_{21}P_{34}P_{13} + P_{21}P_{32}P_{14} + P_{21}P_{31}P_{14} \quad (15d)$$

II. Test of the Derived Expressions. The expressions given in eqs 15a–d have been tested with actual data. The classic example[4,8] is the tetrapolymer system styrene–methyl methacrylate–acrylonitrile–vinyl chloride. The reactivity ratios and the monomer feed are given in Tables I and II. From the feed concentrations and reactivity ratios, the reaction probabilities are calculated (Table I). These 12 reaction probabilities (P_{ij}) are then the parameters that enable us to calculate molar composition and n-ad sequence intensities.

As a test of these results, the molar composition (F_i) can be calculated from eqs 15a–d. The result is given in Table II. For comparison, the observed molar composition is also given, together with the molar composition obtained via the Walling–Briggs approach.[4,8] The close agreement in the three sets of values indicates the correctness of the expressions in eqs 15a–d.

The diad sequence intensities can be readily calculated as well. The expressions for the first four diads are as follows:

$$(AA) = kF_aP_{aa} \quad (16a)$$

$$(AB) = kF_aP_{ab} + kF_bP_{ba} \quad (16b)$$

$$(AC) = kF_aP_{ac} + kF_cP_{ca} \quad (16c)$$

$$(AD) = kF_aP_{ad} + kF_dP_{da} \quad (16d)$$

where k is a normalization constant. The expressions for (AB), (AC), and (AD) contain two terms corresponding to the two directions of propagation. These terms are equivalent because the first-order Markov mechanism is reversible.[9] Similar expressions can be written for the other 12 diads.

The triad sequence intensities can be calculated in like fashion. The expressions for the first four triads are given here:

$$(AAA) = kF_aP_{aa}P_{aa} \quad (17a)$$

$$(AAB) = kF_aP_{aa}P_{ab} + kF_bP_{ba}P_{aa} \quad (17b)$$

$$(AAC) = kF_aP_{aa}P_{ac} + kF_cP_{ca}P_{aa} \quad (17c)$$

$$(AAD) = kF_aP_{aa}P_{ad} + kF_dP_{da}P_{aa} \quad (17d)$$

A total of 40 triads are possible. The complete diad and triad intensities for the styrene–methyl methacrylate–acrylonitrile–vinylidene chloride tetrapolymer are given in Table III. The calculation of higher n-ad sequence intensities can be carried out in a similar fashion.

III. Computer Program. In view of the complexity of eqs 15a–d, a computer program was written to simplify computation. It was written in BASIC and called TETRAP. The program accepts as input either the 12 reaction probabilities or the six reactivity ratios plus the four feed concentrations. The program then proceeds to give the composition and the diad and triad sequence distributions. A listing of the program is available as Supplementary Material.

IV. Multicomponent Copolymerization. The functional form of F_1–F_4 (eqs 15a–d) can be generalized into a single equation by use of the Boolean function NOT. The use of this function lends itself readily to computer applications since many computer languages (such as TK!Solver) use this function. The syntax is NOT(larg), where larg is a logical argument. As in most computer languages, a true logical argument gives a functional value of 1, and a false argument gives a functional value of 0. The characteristics of the Boolean function NOT can be summarized thus:

larg	input to Boolean function	result of Boolean function
true	1	0
false	0	1

The use of the NOT function allows the tetrapolymer model to be written in the following general way:

$$F_n \propto \sum_{i=1}^{4} P_{ai} \sum_{j=1}^{4} P_{bj} \sum_{k=1}^{4} P_{ck} \cdot [\text{NOT } (i=a)] \cdot [\text{NOT } (j=b)] \cdot [\text{NOT } (k=c)] \cdot [\text{NOT } (i \cdot j = b \cdot a)] \cdot [\text{NOT } (i \cdot k = c \cdot a)] \cdot [\text{NOT } (j \cdot k = c \cdot b)] \cdot [\text{NOT } (i \cdot j \cdot k = b \cdot c \cdot a)] \quad (18)$$

where a, b, and c take on the following values:

For $n = 1$: $a = 2, b = 3, c = 4$

For $n = 2$: $a = 1, b = 3, c = 4$

For $n = 3$: $a = 2, b = 1, c = 4$

For $n = 4$: $a = 2, b = 3, c = 1$

Heuristically, each F_n expression should contain all possible contributions of probability terms such that each component i (where $i \neq n$) will have a pathway to form n. For example, in the case of F_1, each probability term must have a combination of probabilities so that the subscripts 2, 3, and 4 have a pathway to form 1. Thus, the terms $P_{21}P_{31}P_{41}$ and $P_{21}P_{34}P_{41}$ are both allowed, but $P_{21}P_{34}P_{43}$ is not because components P_{34} and P_{43} form a loop in which there is no way to form 1. Similarly, there should be no P_{ii} terms because they loop with themselves.

Note that in two-component copolymerization each F_i consists of only one term with one probability (eq 1). In three-component copolymerization each F_i consists of sums of pairs of probabilities (eq 2). In four-component copolymerization the F_i expression is made up of terms each consisting of three probabilities (e.g., $P_{21}P_{31}P_{41}$). By induction, in an N-component copolymerization, each term in the F_i expression should consist of $N - 1$ probabilities.

With the insight obtained from the four-component copolymerization, one can write the general expression for the fraction F_n in an N-component copolymerization.

Again in the Boolean NOT function form, the general expression is

$$F_n \propto \sum_{i=1}^{N} P_{ai} \sum_{j=1}^{N} P_{bj} \cdots \sum_{k=1}^{N} P_{zk} \cdot [\text{NOT } (i{=}a)] \cdot [\text{NOT } (j{=}b)] \cdot \ldots [\text{NOT } (k{=}z)] \cdot [\text{NOT } (i{\cdot}j{=}b{\cdot}a)] \cdot [\text{NOT } (i{\cdot}k{=}c{\cdot}a)] \cdot \text{etc. (all 2-term combinations)} \cdot [\text{NOT } (i{\cdot}j{\cdot}k{=}b{\cdot}c{\cdot}a)] \cdot \text{etc. (all 3-term combinations)} \cdot \text{etc. (up to all } (N-1)\text{-term combinations)} \quad (19)$$

where a, b, c, ..., z take on the following values:

For $n = 1$: $a = 2, b = 3, c = 4, \ldots, z = N$

For $n = 2$: $a = 1, b = 3, c = 4, \ldots, z = N$

For $n = N$: $a = 2, b = 3, c = 4, \ldots, z = 1$

The application of eq 19 can be shown for the terpolymer case. Each term only has $(N - 1) = 2$ probabilities. The general terpolymer form is shown below:

$$F_n \propto \sum_{i=1}^{3} P_{ai} \sum_{j=1}^{3} P_{bj} \cdot [\text{NOT } (i{=}a)] \cdot [\text{NOT } (j{=}b)] \cdot [\text{NOT } (i{\cdot}j{=}a{\cdot}b)] \quad (20)$$

For F_1, $a = 2$ and $b = 3$:

$$F_1 \propto P_{21}(P_{31} + P_{32}) + P_{23}(P_{31}) = P_{21}P_{31} + P_{21}P_{32} + P_{23}P_{31}$$

For F_2, $a = 1$ and $b = 3$:

$$F_2 \propto P_{12}(P_{31} + P_{32}) + P_{13}(P_{32}) = P_{12}P_{31} + P_{12}P_{32} + P_{13}P_{32}$$

For F_3, $a = 2$ and $b = 1$:

$$F_3 \propto P_{21}(P_{13}) + P_{23}(P_{12} + P_{13}) = P_{21}P_{13} + P_{23}P_{12} + P_{23}P_{13}$$

These are the same expressions as in eq 2.

To further illustrate the use of eq 19 we shall apply it to a five-component copolymer.

1. Pairwise combinations: ij, ik, il, jk, jl, kl
2. Three-member combinations: ijk, ijl, ikl, jkl
3. Four-member combinations: $ijkl$

Equation 19 now takes on the following form:

$$F_n \propto \sum_{i=1}^{5} P_{ai} \sum_{j=1}^{5} P_{bj} \sum_{k=1}^{5} P_{ck} \sum_{i=1}^{5} P_{dl} \cdot [\text{NOT } (i{=}a)] \cdot [\text{NOT } (j{=}b)] \cdot [\text{NOT } (k{=}c)] \cdot [\text{NOT } (l{=}d)] \cdot [\text{NOT } (i{\cdot}j{=}a{\cdot}b)] \cdot [\text{NOT } (i{\cdot}k{=}a{\cdot}c)] \cdot [\text{NOT } (j{\cdot}k{=}b{\cdot}c)] \cdot [\text{NOT } (i{\cdot}l{=}a{\cdot}d)] \cdot [\text{NOT } (j{\cdot}l{=}b{\cdot}d)] \cdot [\text{NOT } (k{\cdot}l{=}c{\cdot}d)] \cdot [\text{NOT } (i{\cdot}j{\cdot}k{=}a{\cdot}b{\cdot}c)] \cdot [\text{NOT } (i{\cdot}j{\cdot}l{=}a{\cdot}b{\cdot}d)] \cdot [\text{NOT } (i{\cdot}k{\cdot}l{=}a{\cdot}c{\cdot}d)] \cdot [\text{NOT } (j{\cdot}k{\cdot}l{=}b{\cdot}c{\cdot}d)] \cdot [\text{NOT } (i{\cdot}j{\cdot}k{\cdot}l{=}a{\cdot}b{\cdot}c{\cdot}d)] \quad (21)$$

This compact expression can be written out in five equations, where

For $n = 1$: $a = 2, b = 3, c = 4, d = 5$

For $n = 2$: $a = 1, b = 3, c = 4, d = 5$

For $n = 3$: $a = 2, b = 1, c = 4, d = 5$

For $n = 4$: $a = 2, b = 3, c = 1, d = 5$

For $n = 5$: $a = 2, b = 3, c = 4, d = 1$

These equations can be further written out term for term when combined with the definition of the Boolean NOT. Owing to the large number of terms involved, these are not explicitly given.

Supplementary Material Available: Listing of computer program TETRAP (3 pages). Ordering information is given on any current masthead page.

References and Notes

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Registry No. Styrene, 100-42-5; methyl methacrylate, 80-62-6; acrylonitrile, 107-13-1; vinyl chloride, 75-01-4.