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Bivariate distribution of chain length and composition in multicomponent polymerization

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The theory of Markovian processes is used to investigate the bivariate distribution of chain length and composition in free-radical polymerization consisting of N types of monomer. By following the matrix calculation procedure, it is straightforward to determine the full composition distribution of polymers with a given chain length numerically, with the help of computer softwares capable of conducting symbolic calculations. For long polymer chains, the instantaneous composition distribution is approximated by a Gaussian distribution and the variance is inversely proportional to the chain length. These features are the same as those for copolymers ($N = 2$), which is conveniently represented by the Stockmayer bivariate distribution. Simpler numerical methods to determine the variance of the composition distribution are proposed. The Gaussian approximation of the composition distribution is a practical method to theoretically calculate the bivariate distribution formed in multicomponent polymerizations. © 1998 Published by Elsevier Science Ltd. All rights reserved.

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INTRODUCTION

In statistical copolymerization, the chain length of a copolymer is finite, and the chemical compositions as well as the chain lengths of individual chains cannot be identical. Therefore, even within the polymer chains produced in a very small time interval (instantaneously), there exists a bivariate distribution of composition and chain length. Simha and Branson[1] proposed a very extensive and complete treatment of the statistics of copolymerization by application of the terminal model for copolymerization. However, their results were in complex formulations and difficult to apply to practical problems. Stockmayer[2] proposed a simple expression by replacing summations with integrals and factorials with expressions based on Stirling's approximation. The Stockmayer bivariate distribution is useful not only for the practical purposes but to clarify the important characteristics of the chains formed through a Markovian process. The Stockmayer bivariate distribution, $\mathrm{W}(r,y)$ consists of the product of weight-based chain length distribution $\mathrm{W}(r)$ and composition distribution $\mathrm{Comp}(y|r)$ that is given by the conditional probability distribution given the chain length r.

$$\mathrm{W}(r,y) = \mathrm{W}(r)\mathrm{Comp}(y|r) \tag{1}$$

where $y = F_1 - F_{1,\infty}$, F_1 is the instantaneous mole fraction of monomer 1 bound to an individual chain, and $F_{1,\infty}$ is that for infinitely long chains that is equal to the composition given by the copolymer composition equation[3]. The copolymer composition distribution in Stockmayer's equation is given by the following Gaussian distribution:

$$\mathrm{Comp}(y|r) = \frac{1}{\sigma\sqrt{2\pi}}\exp\left(-\frac{y^2}{2\sigma^2}\right) \tag{2}$$

$$\sigma^2 = F_{1,\infty}F_{2,\infty}K/r \tag{3}$$

$$K = \sqrt{1 + 4F_{1,\infty}F_{2,\infty}(r_1 r_2 - 1)} \tag{4}$$

where r_1 and r_2 are the reactivity ratios.

Free-radical polymerizations that involve more than two types of monomer are widely used commercially. To optimize the industrial multicomponent polymerization processes, a bivariate distribution as simple as Stockmayer's equation, if available, is in great demand. It was shown[4,5] that the pseudo-kinetic rate constant method in which a multicomponent polymerization reduces to that for homopolymerization provides an excellent approximation for the chain length distribution, $\mathrm{W}(r)$, including the cases with penultimate effects. In the present report, therefore, we focus our attention to the chemical composition distribution term, $\mathrm{Comp}(y|r)$.

Engelmann and Schmidt-Naake[6] proposed a Gaussian distribution for the composition distribution with $N > 2$ on the basis of the inference that the Stockmayer's parameter K can be formally related to the index of sequential inhomogeneity of Tosi and Catinella[7]. According to the expression by Engelmann and Schmidt-Naake, however, the individual rate constants are required to obtain the variance, which is obviously wrong from the point of view of the Markovian statistics whose exact matrix expressions are shown later. On the other hand, Xu[8] extended Simha and Branson's equation[1] to terpolymerizations ($N = 3$) quite recently. In addition to the disadvantage that his equation is limited to the three-component systems, his equation is complex and difficult to use practically.

The process of multicomponent polymerization is a typical example of a Markovian process. Detailed mathematical procedure to formulate multicomponent polymerization (any number of N) in a matrix form was elucidated by Price[9]. Price's formula is quite general and can be used for any order of Markovian processes (i.e. higher order effects such as penultimate and penpenultimate effects can be accounted for). Price's matrix formula can be used to obtain the chain length distribution directly by calculating the rth power of the transition matrix. Concerning the composition distribution, however, Price showed the variance solely for $N = 2$. He showed neither full distribution profiles nor the variance for $N > 2$. To obtain the full composition distribution profiles, partial differentiation of a generating function that involves rth power of a matrix is required. Although the generating function method is suitable to obtain analytical solutions for simpler systems (such as to obtain the analytical solution of the variance of composition distribution for $N = 2$, as was shown by Price[9]), such a method has been considered unfit for numerical calculations using computers. However, with the advent of software capable of making symbolic calculations, it has become possible to conduct such types of calculations even with a personal computer. In the present report, we show the exact calculation results of the instantaneous composition distribution for multicomponent polymer chains, and then we show that the distribution is approximated well with a Gaussian distribution whose average and variance can be estimated in a straightforward manner.

MARKOVIAN APPROACH TO MULTICOMPONENT POLYMERIZATION

We consider a free-radical polymerization consisting of N types of monomer, $M_1, M_2, \cdots, M_i, \cdots, M_N$. Because it was already shown that the present theory can be extended to higher order Markovian statistics without changing general matrix formalism[9], we illustrate the method only for the terminal model. We define the transition probability, P_{ij}, which is the probability that a growing polymer chain with M_i end adds monomer M_j. The explicit expression for P_{ij} is given by:

$$P_{ij} = \frac{\dfrac{f_j}{r_{ij}}}{\sum_{m=1}^{N} \dfrac{f_m}{r_{im}}} \tag{5}$$

where f_j is the mole fraction of M_j in the monomer mixture, and r_{ij} is the reactivity ratio defined by k_{ii}/k_{ij}. Note that $r_{ii} = 1$, and that the usual expression of the reactivity ratios for binary systems, r_1 and r_2 are represented by r_{12} and r_{21}, respectively, in the present notation.

Average composition of long polymer chains

The average composition of polymer chains with infinite length can be given only by the transition probability defined by equation (5). By using the transition matrix, $\mathbf{P} = (P_{ij})$, the row vector for the steady state composition, $\mathbf{V}$ is given by:

$$\mathbf{VP} = \lambda \mathbf{V} \tag{6}$$

where λ is the eigenvalue of $\mathbf{P}$.

Therefore, what we seek is an eigenvector for the transpose of $\mathbf{P}$. By defining a square matrix, $\mathbf{A} = (a_{ij}) = \mathbf{P} - \mathbf{I}$, where $\mathbf{I}$ is the unit matrix, the solution for the elements of $\mathbf{V}$ is given by[9]:

$$v_i = c\tilde{a}_{ii} \tag{7}$$

where c is a constant, and $\tilde{a}_{ii}$ is the cofactor of a_{ii}.

The mean copolymer composition (copolymer composition at $r \to \infty$) is, therefore, given by:

$$F_{i,\infty} = \frac{\tilde{a}_{ii}}{\sum_{j=1}^{N} \tilde{a}_{jj}} \tag{8}$$

For example, the mean copolymer composition of a binary system is given by the following well-known equation:

$$F_{1,\infty} = \frac{P_{21}}{P_{12} + P_{21}} \tag{9}$$

Chemical composition distribution of polymer chains

For polymer chains with infinite length, the variance of the composition distribution is zero; however, there exists a nonzero variance for finite chains. The method shown here is essentially equivalent to that proposed by Price[9]. Suppose the mole fraction that the initial growing chain end is M_i is given by e_i, i.e. the type of the starting monomer unit of polymer chains formed at a given instant is determined by the probability, e_i. Then, we define the following vector and matrix:

$$\mathbf{E}_s = (se_1, e_2, \cdots, e_N) \tag{10}$$

$$\mathbf{P}_s = \begin{pmatrix} sP_{11} & P_{12} & \cdots & P_{1N} \\ sP_{21} & P_{22} & \cdots & P_{2N} \\ \vdots & \vdots & \vdots & \vdots \\ sP_{N1} & P_{N2} & \cdots & P_{NN} \end{pmatrix} \tag{11}$$

In addition, we use a column vector, $\mathbf{1}$ whose elements are all unity.

We define the generating function for the composition distribution of the living polymer chain with chain length r as follows:

$$g(s, r) = \mathbf{E}_s \mathbf{P}_s^{r-1} \mathbf{1} \tag{12}$$

Note that as long as the probability of chain stoppage is small enough, i.e. the number-average chain length is large enough, the composition of the dead polymer chains is essentially the same as that for living chains.

For example, $g(s,2)$ for a binary system ($N = 2$) is given by:

$$g(s, 2) = s^2 e_1 P_{11} + se_2 P_{21} + se_1 P_{12} + e_2 P_{22} \tag{13}$$

As illustrated by equation (13), the number of M_1 units in the polymer chain is given by the power of s in the generating function $g(s,r)$, irrespective of the values of N and r.

Therefore, the probability that the polymer chain with chain length r consists of m units of M_1 (i.e. $F_1 = m/r$) is given by:

$$\mathrm{Comp}(F_1|r) = \frac{\left.\dfrac{\partial^m g(s, r)}{\partial s^m}\right|_{s=0}}{m!} \tag{14}$$

In principle, we can obtain the composition distribution from equation (14). Although conventional numerical calculators are not suitable to conduct the above partial differentiation, this can be done with the help of symbolic calculator in a straightforward manner. We used the software, *Mathematica*® for this purpose.

The average number of M_1 units $\bar{m}_r$ and the average chemical composition of polymers with chain length r, $F_{1,r}$ ($= \frac{\bar{m}_r}{r}$) is given by:

$$\bar{m}_r = \left.\frac{\partial g(s, r)}{\partial s}\right|_{s=1} \tag{15}$$

$$F_{1,r} = \frac{\left.\dfrac{\partial g(s,r)}{\partial s}\right|_{s=1}}{r} \tag{16}$$

The variance of the composition distribution in terms of the number of M_1 units, V_m is given by:

$$V_m = \left.\frac{\partial^2 g(s,r)}{\partial s^2}\right|_{s=1} + \left.\frac{\partial g(s,r)}{\partial s}\right|_{s=1} - \left\{ \left.\frac{\partial g(s,r)}{\partial s}\right|_{s=1} \right\}^2 \tag{17}$$

The variance in terms of the composition F_1, σ^2 is given by:

$$\sigma^2 = \frac{V_m}{r^2} \tag{18}$$

Variance for a binary system

For a binary system ($N = 2$), it is straightforward to obtain the analytical solution for the σ^2 value[9]. For long chains, the effects of chain ends become relatively unimportant. In order to remove the end effects, we use:

$$e_1 = F_{1,\infty} = \frac{P_{21}}{P_{12} + P_{21}} \tag{19}$$

In this case, one obtains:

$$\bar{m}_r = \frac{rP_{21}}{P_{12} + P_{21}} \tag{20}$$

$$V_m = \frac{P_{12}P_{21}}{(P_{12}+P_{21})^4}\{2(r+1)(P_{12}+P_{21}) - r(P_{12}+P_{21})^2 + 2(1 - P_{12} - P_{21})^{r+1} - 2\} \tag{21}$$

Therefore, in terms of the fractions, one obtains:

$$F_{1,r} = F_{1,\infty} \tag{22}$$

$$\sigma^2 = \frac{F_{1,\infty}F_{2,\infty}}{r}\left[\frac{2}{P_{12}+P_{21}} - 1 + \frac{2}{r(P_{12}+P_{21})} \times \left\{(1 - P_{12} - P_{21})^r - 1\right\}\right] \tag{23}$$

For large chain lengths, equation (23) is approximated by:

$$\sigma^2 \approx \frac{F_{1,\infty}F_{2,\infty}}{r}\left(\frac{2}{P_{12}+P_{21}} - 1\right) \quad (\text{for } r \gg 1) \tag{24}$$

It is straightforward to show that the variance given by equation (24) is the same as that for Stockmayer's composition distribution (equation (3)), and that the K-value in Stockmayer's equation is given by:

$$K = \frac{P_{11} + P_{22}}{P_{12} + P_{21}} \tag{25}$$

In principle, the present method could be used to obtain the variance of the composition distribution analytically for the cases with $N > 2$, although up to the present we have not succeeded in deriving a general expression of σ^2. Instead of obtaining analytical solutions, we calculated the variance numerically using equations (17) and (18), by application of the symbolic calculation software.

Table 1 Calculation conditions investigated in this work

Two-component system
(1: styrene, 2: methyl methacrylate)
Monomer composition: $f_1 = 0.2, f_2 = 0.8$
Reactivity ratios: $r_1 = 0.52$, $r_2 = 0.46$
Three-component system
(1: styrene, 2: methyl methacrylate, 3: acrylonitrile)
$f_1 = f_2 = 0.35, f_3 = 0.3$
$r_{12} = 0.52$, $r_{13} = 0.4$, $r_{21} = 0.46$, $r_{23} = 1.2$, $r_{31} = 0.04$, $r_{32} = 0.15$
Four-component system
(1: styrene, 2: methyl methacrylate, 3: acrylonitrile, 4: vinyliden chloride)
$f_1 = f_2 = f_3 = f_4 = 0.25$
$r_{12} = 0.52$, $r_{13} = 0.4$, $r_{14} = 2.0$, $r_{21} = 0.46$, $r_{23} = 1.2$, $r_{24} = 2.53$, $r_{31} = 0.04$, $r_{32} = 0.15$, $r_{34} = 1.2$, $r_{41} = 0.14$, $r_{42} = 0.2$, $r_{43} = 0.49$

From equation (23), it might be expected that the variance, σ^2 for $N > 2$ at a given reaction condition has a functional form:

$$r\sigma^2 = \xi_\infty + \frac{Z}{r} \tag{26}$$

where ξ_∞ is a constant that is equal to $\lim_{r\to\infty}(r\sigma^2)$, and Z is essentially a constant, at least for large r-values. The validity of equation (26) is examined later in this report.

RESULTS AND DISCUSSION

To make illustrative calculations, we chose four types of monomer in free-radical polymerization, styrene (St), methyl methacrylate (MMA), acrylonitrile (AN) and vinyliden chloride (VC). The monomer composition and reactivity ratios we have used are summarized in *Table 1*, i.e. St/MMA for $N = 2$, St/MMA/AN for $N = 3$, and St/MMA/AN/VC for $N = 4$.

Fundamental characteristics of chemical composition distribution of polymer chains for a binary system

The end group effects cannot be neglected for smaller chains. In the two-component system shown in *Table 1*, $F_{1,\infty} = 0.2846$. If the mole fraction of the initial unit e_1 is different from $F_{1,\infty}$, it is expected that the average composition $F_{1,r}$ is different from $F_{1,\infty}$ for smaller r-values. In addition, the distribution profile is expected to deviate from a Gaussian distribution.

Figure 1 shows the calculated copolymer composition distribution for the cases with $e_1 = 0.5$ and $e_1 = F_{1,\infty}$. For copolymer chains with $r = 10$, the differences of e_1-values are significant. With $e_1 = 0.5$ (×), clear deviation from the Stockmayer equation (equation (2)) is observed, and even the Gaussian distribution, whose average and variance are the same as those for the distribution given by ×-symbols, does not fully coincide, which shows that the distribution is not Gaussian. With $e_1 = F_{1,\infty}$, the Gaussian fit is slightly better than the Stockmayer equation, but both curves could be a reasonable approximation. It is shown that for smaller chains: (1) the end effect is significant on both average and variance of the copolymer composition distribution; and (2) the distribution is not Gaussian in a strict sense.

At $r = 50$ in the present example, the end effects become negligible. In the present report, because we are mainly interested in long chains, we show the calculation results only with $e_1 = F_{1,\infty}$, otherwise noted.

Stockmayer's composition distribution clearly shows that the variance of the composition distribution is inversely proportional to the chain length, i.e. the distribution becomes narrower as chain length increases. Another important factor influencing the breadth of the distribution is the randomness of copolymerization.

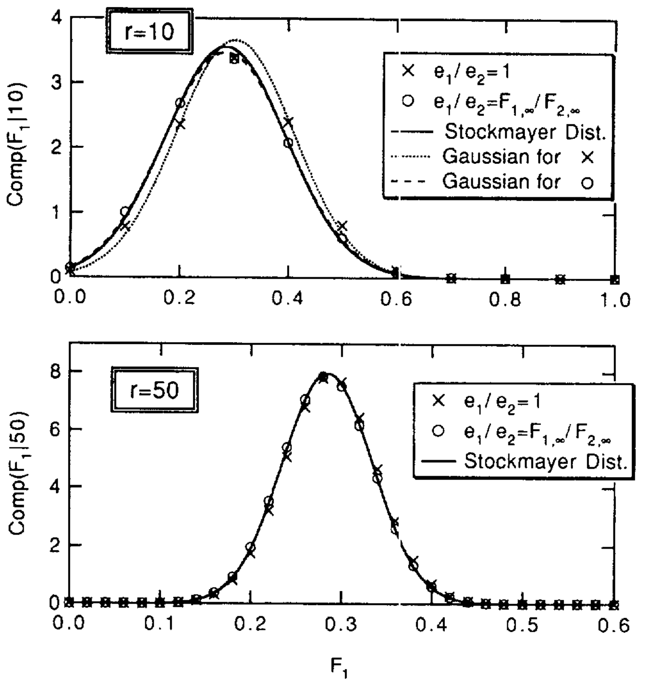

Figure 1 Calculated copolymer composition distribution for the two-component system (St/MMA) at chain length $r = 10$ and 50. The symbols are the exact distribution calculated from equation (14), and the solid curves show the Stockmayer copolymer composition distribution, equation (2). The dotted curves are the Gaussian distributions whose average and variance are obtained from equations (16) and (18), respectively

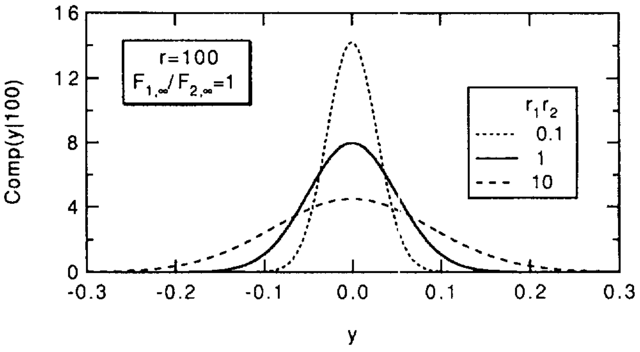

Figure 2 Effect of randomness on the copolymer composition distribution calculated from the Stockmayer equation. In the figure, $y = F_1 - F_{1,\infty}$

Figure 2 shows the effects of the product of the reactivity ratios on the composition distribution, calculated from Stockmayer's composition distribution, equation (2). As the alternating tendency increases (r_1r_2 becomes smaller), the K-value in Stockmayer's equation becomes smaller and the distribution narrower. When the copolymerization is random, i.e. $r_1r_2 = 1$, the K-value is unity and the composition distribution becomes a binomial distribution (in terms of the number of M_1 units, m).

Three-component system

Figure 3 shows the effect of the chain length on the variance of composition distribution for St/MMA/AN. The variance was calculated from equations (17) and (18). It is shown that $r\sigma^2$ approaches a constant value fairly rapidly, and σ^2 is inversely proportional to chain length for larger chains.

Next, we examined the validity of equation (26). *Figure 4* shows the relationship between $r\sigma^2$ and $1/r$. The solid line is the regression line to $B + C/r$. It is shown that the functional form given by equation (26) is an excellent approximation.

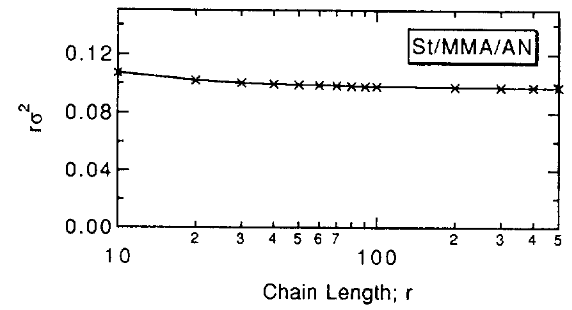

Figure 3 Calculated variance of the instantaneous composition distribution for the three-component system (St/MMA/AN)

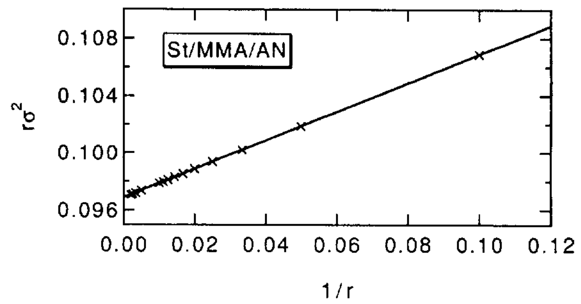

Figure 4 Relationship between $r\sigma^2$ and $1/r$ for the three-component system

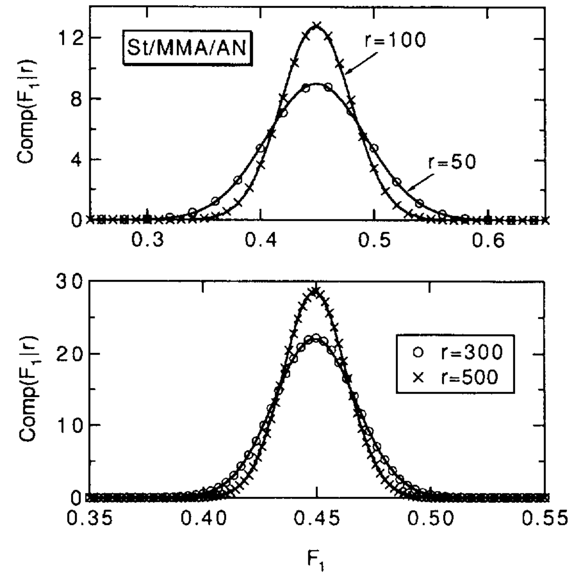

Figure 5 Calculated instantaneous composition distribution of polymer chains for the three-component system. The symbols are the exact distribution, while the solid curves are the Gaussian approximation

From the results shown in *Figures 3 and 4*, we propose two methods to estimate the variance of the composition distribution.

(1) As shown in *Figure 4*, it is straightforward to obtain the ξ_∞-value ($\xi_\infty = \lim_{r\to\infty}(r\sigma^2)$) based on a few σ^2-values for rather smaller r-values. The ξ_∞-value so obtained could be used as a representative value to estimate the variance for a given chain length based on the fact that

$r\sigma^2$ is approximately constant for long chains, as utilized in Stockmayer's composition distribution.

(2) Because $r\sigma^2$ does not change much for long chains, say $r > 100$, we may be able to use $r\sigma^2$ obtained from $r = 100$ as a representative value. Often, the chain length range of major interest is limited; therefore, it may be better to use some representative chain length, r within such practical limitation, than to use ξ_∞.

Figure 5 shows the chemical composition distribution of polymer chains. The symbols are the exact distribution obtained from equation (14), while the solid curves are the Gaussian distribution. The average of the Gaussian distribution is $F_{1,\infty}$ and the variance obtained from $r = 100$ was used as a representative value of $r\sigma^2$. As shown in the figures, the composition distribution is Gaussian, and the σ^2-value estimated from $r = 100$ is a reasonable approximation.

Four-component system

Figure 6 shows the effect of chain length on the variance of composition distribution for the four-component system, St/MMA/AN/VC. Again, $r\sigma^2$ approaches a constant value fairly rapidly, and σ^2 is inversely proportional to chain length for larger chains.

Figure 7 shows the relationship between $r\sigma^2$ and $1/r$. The functional form given by equation (26) is an excellent approximation also for $N = 4$. To estimate the variance for a specific chain length, the same strategy proposed for the three-component system can be used also for $N = 4$, and it would be reasonable to expect such methods are valid for any value of N.

Figure 8 shows the chemical composition distribution of polymer chains. The symbols are the exact distribution obtained from equation (14), while the solid curves are the Gaussian distribution. The average of the Gaussian distribution is $F_{1,\infty}$ and the variance obtained from $r = 100$ was used as a representative value of σ^2. Again, such a type of Gaussian approximation gives an excellent fit for the distribution.

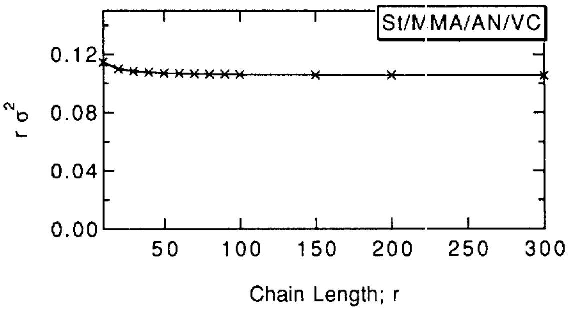

Figure 6 Calculated variance of the instantaneous composition distribution for the four-component system (St/MMA/AN/VC)

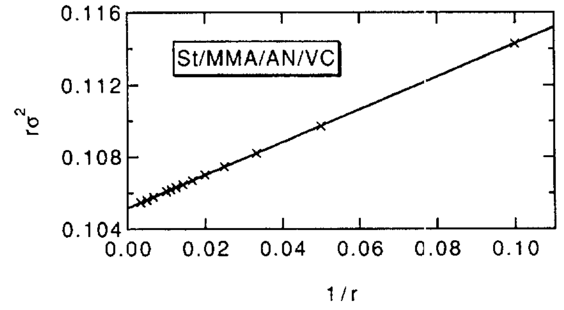

Figure 7 Relationship between $r\sigma^2$ and $1/r$ for the four-component system

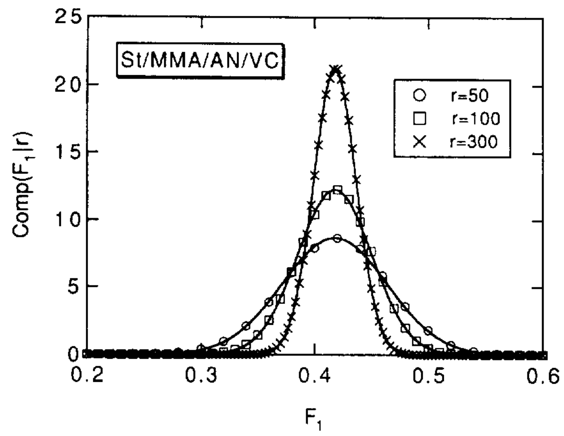

Figure 8 Calculated instantaneous composition distribution of polymer chains for the four-component system. The symbols are the exact distribution, while the solid curves are the Gaussian approximation

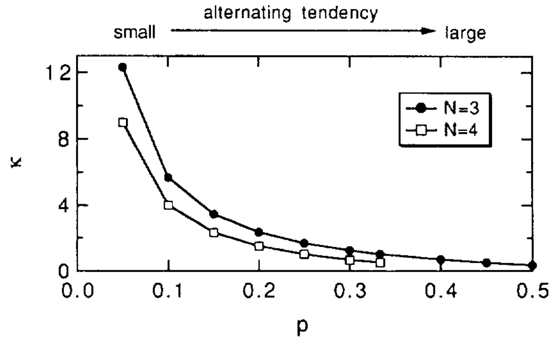

Figure 9 Effect of the alternating tendency on the κ-factor

In summary, the composition distribution is Gaussian for any multicomponent polymerization as long as the chain length is large enough, and the variance is inversely proportional to chain length for large chains. The variance can be estimated effectively either from a certain large r-value or from a few σ^2 values for smaller chain lengths.

Inference on the functional form of ξ_∞

The ξ_∞-value ($\xi_\infty = \lim_{r\to\infty}(r\sigma^2)$) would be expressed as a function of the transition probabilities, P_{ij}. As shown in Stockmayer's copolymer composition distribution, ξ_∞ for a binary system is given by:

$$\xi_\infty = F_{1,\infty}(1 - F_{1,\infty})K \quad (\text{for } N = 2) \qquad (27)$$

The K-factor, $K = P_{11} + P_{22})/(P_{12} + P_{21})$, represents the randomness of copolymerization. The value of K is unity if the copolymerization is random. As the alternating tendency increases, the K-value becomes smaller, while it becomes larger as the tendency to form block copolymers increases.

Similarly, it may be reasonable to expect that ξ_∞ for $N > 2$ is given by:

$$\xi_\infty = F_{1,\infty}(1 - F_{1,\infty})\kappa \qquad (28)$$

where the physical meaning of κ would be the same as K for $N = 2$.

We calculated ξ_∞-values under a special condition with $P_{ij} = p$ for $i \neq j$, i.e. $P_{12} = P_{13} = P_{21} = P_{23} = P_{31} = P_{32} = p$

for $N = 3$. A larger p-value means that the alternating tendency is large.

Figure 9 shows the change of κ as a function of p for $N = 3$ and 4. We obtained $\kappa = 1$ at $p = 1/3$ for $N = 3$, and at $p = 1/4$ for $N = 4$, where the polymerization is 'random'. The κ-factor becomes smaller as the alternating tendency increases, similarly with the K-value for the Stockmayer distribution. The κ-factor could be expressed analytically as a function of the transition probabilities P_{ij}; however, we have not succeeded in deriving general solutions for $N > 2$.

CONCLUSIONS

The theory of Markovian processes can be used to obtain the instantaneous bivariate distribution of chain length and composition in multicomponent polymerization directly, with the help of computer softwares capable of conducting symbolic calculations. It was found that the instantaneous composition distribution is approximated by a Gaussian distribution and the variance is inversely proportional to the chain length, irrespective of the number of components, N. We have proposed simpler methods to estimate the variance of the composition distribution. The Gaussian approximation for the composition distribution would be a practical method to theoretically calculate the full bivariate distributions formed in real multicomponent polymerization systems.

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