procedure indicates that it is an excellent method for determining k_p values.

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Kinetic Treatment of Sequence Distributions Occurring in Vinyl Polymerization According to Bernoulli and First- and Second-Order Markoff Processes

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ABSTRACT: Sets of kinetic differential equations corresponding to Bernoulli and to first- and second-order Markoff processes employed in the description of vinyl polymerizations are set up and solved, with appropriate initial conditions, in order to obtain expressions for the probabilities of finding various diads, triads, and tetrads in the product sequence structures. Since a non-steady-state stage exists, during which the configurational sequence structures of products change with polymerization parameters, for both first- and second-order Markoff processes, a simple experimental method for distinguishing first- and second-order Markoff processes from Bernoulli processes emerges: A plot of the sequence structures versus any polymerization parameter (such as monomer conversion) is characteristic of a Bernoulli process if it gives a horizontal straight line over the entire reaction process. Otherwise, it should likely be classified as a Markoff process. Experimental results for the polymerization of methyl methacrylate are utilized to illustrate this expectation.

1. Introduction

Sequence distribution and chain configuration in polymers are both of practical importance and theoretical interest. Much work on this problem has been carried out[1-6] since the pioneering paper by Bovey and Tiers[7] on the application of NMR to the study of the configurational sequence in poly(methyl methacrylate). Configuration sequences in polyolefins, however, depend upon their history of generation, with the consequence being that statistical theory can be applied to sequence distributions of vinyl polymers without consideration of the kinetics of the polymerization process only under stationary conditions. A kinetics study of the sequence distribution of vinyl polymers, based upon stationarity, has been carried out by Figni.[8] The same problem has been treated by one of the authors[9] in terms of kinetics without stationarity. Because the method was so complicated, only first-order Markoff processes could be included at that time. Using the simpler non-steady-state kinetics method developed later,[10] we have obtained exact solutions for the same problem from the Bernoulli process to the second-order Markoff process. As these results show that there are non-steady-state stages of Markoff processes of polymerization of vinyl monomer even in the case of instantaneous initiation, and that no such stages occur for Bernoulli processes, a simple method can be proposed for judging the polymerization mechanism.

2. Bernoulli Processes

If the configuration of any placement in vinyl polymers is independent of its previous placement, the polymerization generating these polymer chains is a Bernoulli process. Let m^* and m' represent the "living" and "dead" meso diad, and r^* and r' denote the "living" and "dead" racemic diad, with I and N^* indicating initiator and active monomer adjacent to initiator. The polymerization of vinyl polymers initiated instantaneously can be expressed by Figure 1, where only the living diads formed in the reaction

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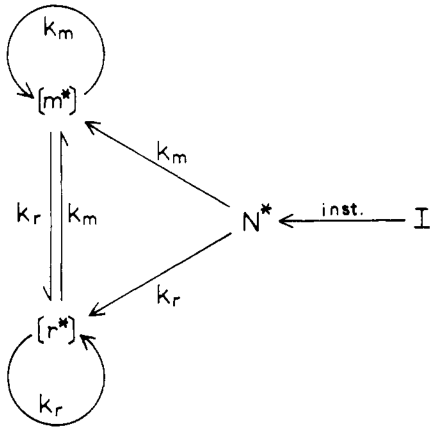


Figure 1. Bernoulli polymerization process of vinyl monomers.

are shown, and the dead diads formed and the monomer (M) taking part in the reaction are omitted. Square brackets represent the relative concentration without normalization. According to Figure 1, the kinetic differential equations for the Bernoulli process are

$$dN^*/dt = -(k_m + k_r)N^*M \tag{2.1}$$

$$d[m^*]/dt = k_mN^*M - k_r[m^*]M + k_m[r^*]M \tag{2.2}$$

$$d[r^*]/dt = k_rN^*M - k_m[r^*]M + k_r[m^*]M \tag{2.3}$$

$$d[m']/dt = (k_m + k_r)[m^*]M \tag{2.4}$$

$$d[r']/dt = (k_m + k_r)[r^*]M \tag{2.5}$$

$$-dM/dt = (k_m + k_r)N^*M + (k_m + k_r)[m^*]M + (k_m + k_r)[r^*]M = (k_m + k_r)I_0M \tag{2.6}$$

with initial conditions

$$N^*|_{t=0} = I_0, \quad [m^*]|_{t=0} = [r^*]|_{t=0} = [m']|_{t=0} = [r']|_{t=0} = 0, \quad M|_{t=0} = M_0 - I_0$$

In addition, the reaction system must fulfil the constraint conditions

$$I_0 = N^* + [m^*] + [r^*], \quad M_0 - M - I_0 = [m] + [r] \tag{2.7}$$

where $[m] = [m^*] + [m']$ and $[r] = [r^*] + [r']$, respectively. If we set $K = k_m/(k_m + k_r)$ and make the transformation

$$X = \int_0^t (k_m + k_r)M\, dt \tag{2.8}$$

eq 2.1–6 can be expressed as a set of linear differential equations (not given here explicitly). By combining eq 2.2 and 2.4, we obtain

$$\frac{d[m]}{dX} = \frac{d([m^*] + [m'])}{dX} = K(N^* + [m^*] + [r^*]) = KI_0 \tag{2.9}$$

where eq 2.7 has been employed. It follows from this result that

$$[m] = KI_0X \tag{2.10}$$

A similar expression for $[r]$ is obtained by replacing K by $1 - K$. Such a derivation is called hereinafter the reciprocal method. The probability of finding a meso placement at any moment in the polymerization is given by

$$p_m = \frac{[m]}{[m] + [r]} = K = \frac{k_m}{k_m + k_r} \tag{2.11}$$

while the equivalent expression for a racemic diad is

$$p_r = 1 - p_m = 1 - K = \frac{k_r}{k_m + k_r} \tag{2.12}$$

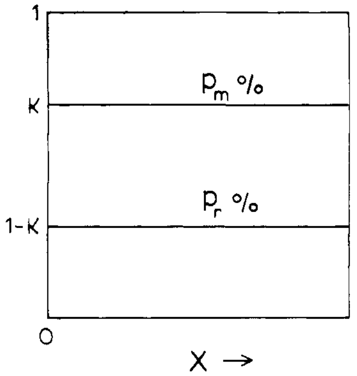


Figure 2. Relation between tacticity and X for a Bernoulli process: $K = 0.7$.

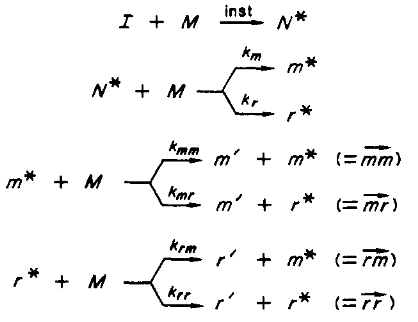
The sequence structure of vinyl polymers of a rapidly initiated Bernoulli process is thus found to be independent of the reaction parameter X. This relation is shown in Figure 2. The other n-ads, such as triads or tetrads, can be calculated directly from diads according to the relations given in Table I of ref 6. From eq 2.6 and 2.7, we obtain

$$X = \frac{M_0}{I_0}Y - 1 \tag{2.13}$$

where Y represents monomer conversion. This result allows a change of the unit along the abscissa from Y to X, so that experimental data can be compared with Figure 2.

3. First-Order Markoff Processes

When the ultimate configuration formed in polymerization is influenced by the configuration of the penultimate placement of active chains, the polymerization is defined as a first-order Markoff process. As in ref 10, we first obtain expressions for active diads, from which other structural parameters, such a m', r', mm, mr, and rr, can be derived. The reaction equations for forming different sequences in vinyl polymers can be expressed in the form



$$I + M \xrightarrow{\text{inst}} N^* \tag{3.1}$$

$$N^* + M \begin{cases} \xrightarrow{k_m} m^* \\ \xrightarrow{k_r} r^* \end{cases} \tag{3.2}$$

$$m^* + M \begin{cases} \xrightarrow{k_{mm}} m' + m^* \quad (=\overrightarrow{mm}) \\ \xrightarrow{k_{mr}} m' + r^* \quad (=\overrightarrow{mr}) \end{cases} \tag{3.3}$$

$$r^* + M \begin{cases} \xrightarrow{k_{rm}} r' + m^* \quad (=\overrightarrow{rm}) \\ \xrightarrow{k_{rr}} r' + r^* \quad (=\overrightarrow{rr}) \end{cases} \tag{3.4}$$

where the triads in parentheses are formed from the addition of the preceding dead diad and the next living diad; they are vectors. The kinetic differential equations adapted to this reaction scheme are then

$$dN^*/dt = -(k_m + k_r)N^*M \tag{3.5}$$

$$d[m^*]/dt = k_mN^*M - k_{mr}[m^*]M + k_{rm}[r^*]M \tag{3.6}$$

$$d[r^*]/dt = k_rN^*M - k_{rm}[r^*]M + k_{mr}[m^*]M \tag{3.7}$$

$$d[m']/dt = (k_{mm} + k_{mr})[m^*]M \tag{3.8}$$

$$d[r']/dt = (k_{rm} + k_{rr})[r^*]M \tag{3.9}$$

for the diads, and

$$d[\overrightarrow{mm}]/dt = k_{mm}[m^*]M \tag{3.10}$$

$$\mathrm{d}[\overrightarrow{mr}]/\mathrm{d}t = k_{mr}[m^*]M \qquad (3.11)$$

$$\mathrm{d}[\overrightarrow{rm}]/\mathrm{d}t = k_{rm}[r^*]M \qquad (3.12)$$

$$\mathrm{d}[\overrightarrow{rr}]/\mathrm{d}t = k_{rr}[r^*]M \qquad (3.13)$$

for the triads, with initial conditions

$$N^*|_{t=0} = I_0 \qquad M|_{t=0} = M_0 - I_0$$

$$[m^*]|_{t=0} = [r^*]|_{t=0} = [m']|_{t=0} = [r']|_{t=0} = [\overrightarrow{mm}]|_{t=0} = 0$$

$$[\overrightarrow{mr}]|_{t=0} = [\overrightarrow{rm}]|_{t=0} = [\overrightarrow{rr}]|_{t=0} = 0$$

These equations are all subject to the constraint condition (2.7). For convenience, we shall set $\alpha = k_{mm}/(k_m + k_r) = k_{mm}/k_p$, $\beta = k_{rr}/k_p$, $\mu = k_{mr}/k_p$, and $\nu = k_{rm}/k_p$. Once again utilizing transformation (2.8), we can change eq 3.5–13 into a set of linear differential equations (also omitted here).

The solution of eq 3.5 is

$$N^* = I_0 e^{-X} \qquad (3.14)$$

while the simultaneous equations (3.6) and (3.7) give rise to

$$[m^*] = I_0\left\{\frac{\nu}{\mu+\nu}[1 - e^{-(\mu+\nu)X}] + \frac{K-\nu}{\mu+\nu-1}[e^{-X} - e^{-(\mu+\nu)X}]\right\} \qquad (3.15)$$

When K, μ, and ν have been replaced by $(1 - K)$, ν, and μ, respectively, the expression for $[r^*]$ is immediately obtained. By substituting the expression for $[m^*]$ (or $[r^*]$) into eq 3.8–13, expressions for $[m']$, $[r']$, $[\overrightarrow{\mathrm{mm}}]$, $[\overrightarrow{\mathrm{mr}}]$, and $[\overrightarrow{\mathrm{rr}}]$ can be obtained. For example

$$[\overrightarrow{mr}] = I_0\mu\left\{\frac{K-\nu}{\mu+\nu-1}[1 - e^{-X}] - \frac{K-\nu}{(\mu+\nu)(\mu+\nu-1)}[1 - e^{-(\mu+\nu)X}] - \frac{\nu}{(\mu+\nu)^2}[1 - e^{-(\mu+\nu)X}] + \frac{\nu}{\mu+\nu}X\right\} \qquad (3.16)$$

However, since the measurable triads are independent of the direction of these triads, the concentrations are

$$[mm] = [\overrightarrow{mm}] \qquad [rm] = [mr] = [\overrightarrow{mr}] + [\overrightarrow{rm}] \qquad [rr] = [\overrightarrow{rr}] \qquad (3.17)$$

Percentages (probabilities) can be obtained by normalization. The respective probabilities of finding diads m and r and triads mm, mr, and rr are hence

$$p_m = \frac{[m]}{[m] + [r]} = \frac{[m]}{[m^*] + [m'] + [r^*] + [r']}$$

$$p_r = 1 - p_m \qquad (3.18)$$

$$p_{mm} = \frac{[mm]}{[mm] + [mr] + [rr]} = \frac{[mm]}{\sum \text{triads}}$$

$$p_{mr} = \frac{[mr]}{\sum \text{triads}} \qquad p_{rr} = 1 - p_{mm} - p_{mr} \qquad (3.19)$$

The variation of diads and triads with X is shown respectively in Figures 3 and 4. In contrast to sequence structures in Bernoulli processes, the sequence structures of vinyl polymers for first-order Markoff processes are functions of the reaction parameter X. By replacing the scalar triads in the numerator of eq 3.19 by vector expressions, we obtain

$$p_{\overrightarrow{mm}} = p_{mm} \qquad p_{\overrightarrow{mr}} = [\overrightarrow{mr}]/\sum \text{triads}$$
$$p_{\overrightarrow{mm}} + p_{\overrightarrow{mr}} + p_{\overrightarrow{rm}} + p_{\overrightarrow{rr}} = 1 \qquad (3.19\text{a})$$

According to L'Hôpital's rule, eq 3.18 and 3.19 lead to

$$\lim_{X\to 0} p_m = K = \frac{k_m}{k_m + k_r} \qquad (3.20)$$

$$\lim_{X\to\infty} p_m = \frac{(\alpha+\mu)\nu}{(\alpha+\mu)\nu + (\beta+\nu)\mu} = \frac{k_{rm}(k_{mm} + k_{mr})}{k_{rm}(k_{mm} + k_{mr}) + k_{mr}(k_{rr} + k_{rm})} \qquad (3.21)$$

$$\lim_{X\to 0} p_{\overrightarrow{mm}} = \frac{\alpha K}{(\alpha+\mu)K + (\beta+\nu)(1-K)} = \frac{k_m k_{mm}}{k_m(k_{mm} + k_{mr}) + k_r(k_{rr} + k_{rm})} \qquad (3.22)$$

$$\lim_{X\to 0} p_{\overrightarrow{mr}} = \frac{\mu K}{(\alpha+\mu)K + (\beta+\nu)(1-K)} \qquad (3.23)$$

$$\lim_{X\to\infty} p_{\overrightarrow{mm}} = \frac{\alpha\nu}{\alpha\nu + 2\mu\nu + \beta\mu} = \frac{k_{mm}k_{rm}}{k_{mm}k_{rm} + 2k_{mr}k_{rm} + k_{rr}k_{mr}} \qquad (3.24)$$

$$\lim_{X\to\infty} p_{\overrightarrow{mr}} = \frac{\mu\nu}{\alpha\nu + 2\mu\nu + \beta\mu} \qquad (3.25)$$

By using the reciprocal method (in addition to the rules mentioned above, replacing α by β or β by α in this case), two types of limiting expression for p_r, $p_{\overrightarrow{rm}}$, and $p_{\overrightarrow{rr}}$ can readily be obtained. Under steady-state conditions, we find

$$\lim_{X\to\infty} p_{m/m} = \lim_{X\to\infty} p_{\overrightarrow{mm}}/\lim_{X\to\infty} p_m = \frac{\alpha}{\alpha+\mu} = \frac{k_{mm}}{k_{mm} + k_{mr}} \qquad (3.26)$$

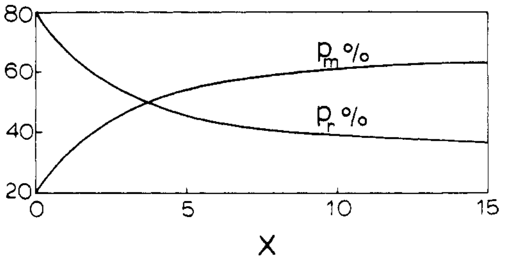


Figure 3. Variation of diads with X for first-order Markoff process: $K = 0.2$; $\alpha = 0.6$; $\beta = 0.3$; $\mu = 0.22$; $\nu = 0.4$.

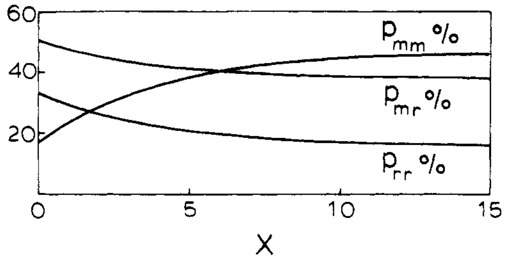


Figure 4. Variation of triads with X for first-order Markoff process: Values of K, α, β, μ, and ν are the same as those used in Figure 3.

$$\lim_{X\to\infty} p_{m/r} = \lim_{X\to\infty} p_{\overline{mr}}/\lim_{X\to\infty} p_m = \frac{\mu}{\alpha + \mu} = \frac{k_{mr}}{k_{mm} + k_{mr}} \quad (3.27)$$

Expressions for $\lim_{X\to\infty} p_{r/m}$ and $\lim_{X\to\infty} p_{r/r}$ can be obtained by using the reciprocal method. The conditional probability is then found to depend upon the ratio of the rate constant of the favorable reaction to the sum of those of the competitive propagations (3.3) and (3.4). In this case, kinetics and statistics attain the same goal by different routes. All the probabilities obtained here under steady-state conditions are in accord with those in ref 6. However, kinetics tells us more than statistics in that there is a non-steady stage when the structural parameters do not obey statistical rules.

As defined in eq 2.8, X is a dimensionless parameter which is the product of the integrated amount of monomer consumed in the polymerization and the reaction constants. In a reaction system, $X \to \infty$ represents in practice a system in which the reaction time is very long, corresponding to the production of long polymer chains in living anionic polymerization. It is clear that $X \to \infty$ is a sufficient condition for the steady state but not always a necessary one. Alternatively, $X \to 0$, which is a sufficient condition for a non-steady state, represents the start of polymerization. For the convenience of checking experimental data, we can use the result

$$Y = \frac{M_0 - M}{M_0} = \frac{I}{M_0}\left\{1 + (1 - e^{-X})\left[1 + \frac{(\alpha + \mu)(K - \nu) + (\beta + \nu)(1 - K - \mu)}{\mu + \nu - 1}\right] - [1 - e^{-(\mu+\nu)X}]\frac{(K\mu + k\nu - \nu)(\alpha + \mu - \beta - \nu)}{(\mu + \nu - 1)(\mu + \nu)^2} + \frac{\alpha\nu + 2\mu\nu + \beta\mu}{\mu + \nu}X\right\} \quad (3.28)$$

which can easily be obtained by substitution of the expressions for $[m]$ and $[r]$ into eq 2.7. Obviously, X depends upon monomer conversion, the molar ratio of the initial concentration of monomer to initiator, and the parameters α, β, μ, and ν. We shall not present the relation for equivalent second-order Markoff processes because of its complexity, but X has a similar interpretation for that process. Once X has been determined from the polymerization conditions, so too are the configurational sequences and hence we can control the sequence structures of vinyl polymers by regulating reaction conditions.

4. Second-Order Markoff Processes

If the configuration of the last placement formed in propagation depends both upon that of the penultimate and ultimate placements of active chains, the polymerization is a second-order Markoff process. Certain polymerizations belong to this category.[2,16] The mathematical derivation for such second-order Markoff processes is more complicated than that for Bernoulli processes and first-order Markoff processes. By employing Laplace transformations, a set of differential equations for four living triads can be converted into a set of algebraic equations that can be solved readily. The roots of the differential equations are then obtained by inverse Laplace transformation. This route allows the problem to be solved smoothly, though tiresomely. If we adopt the notation utilized above, the second-order Markoff process can be illustrated by Figure 5, where only the living diads and triads formed in the polymerization are illustrated, while the dead diads and triads formed, as well as the monomer participating in the reaction, are omitted. Thus, according to Figure 5, we have

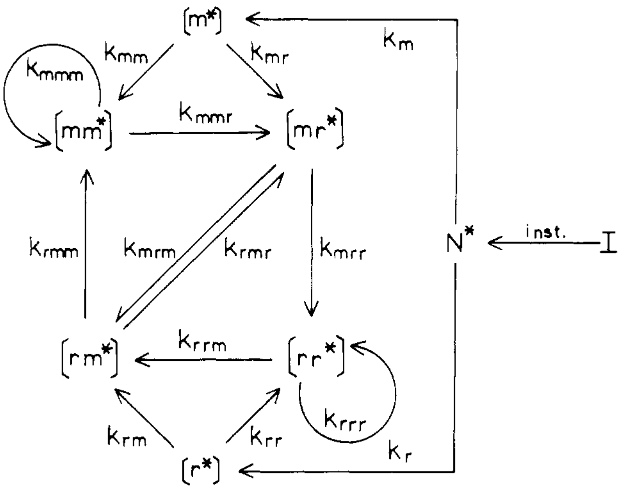


Figure 5. Polymerization scheme for vinyl monomers according to a second-order Markoff process.

$$dN^*/dt = -(k_m + k_r)N^*M \quad (4.1)$$

$$d[m^*]/dt = k_m N^*M - (k_{mm} + k_{mr})[m^*]M \quad (4.2)$$

$$d[r^*]/dt = k_r N^*M - (k_{rr} + k_{rm})[r^*]M \quad (4.3)$$

$$d[mm^*]/dt = k_{mm}[m^*]M - k_{mmr}[mm^*]M + k_{rmm}[rm^*]M \quad (4.4)$$

$$d[mr^*]/dt = k_{mr}[m^*]M - (k_{mrr} + k_{mrm})[mr^*]M + k_{mmr}[mm^*]M + k_{rmr}[rm^*]M \quad (4.5)$$

$$d[rm^*]/dt = k_{rm}[r^*]M - (k_{rmm} + k_{rmr})[rm^*]M + k_{rrm}[rr^*]M + k_{mrm}[mr^*]M \quad (4.6)$$

$$d[rr^*]/dt = k_{rr}[r^*]M - k_{rrm}[rr^*]M + k_{mrr}[mr^*]M \quad (4.7)$$

$$d[mm']/dt = (k_{mmm} + k_{mmr})[mm^*]M \quad (4.8)$$

$$d[mr']/dt = (k_{mrr} + k_{mrm})[mr^*]M \quad (4.9)$$

$$d[rm']/dt = (k_{rmm} + k_{rmr})[rm^*]M \quad (4.10)$$

$$d[rr']/dt = (k_{rrm} + k_{rrr})[rr^*]M \quad (4.11)$$

In fact, Figure 5 can also represent the reaction forming tetrads. The arrows linking triads denote the propagation; i.e., a living triad adds a monomer to form a new living triad and turns itself in to a dead triad. Obviously these two triads, joined by a chemical bond, form a tetrad. They are regarded as vectors here since they are living tetrads of which the order is not exchangeable. Put into equations, we obtain

$$d[m\vec{m}m]/dt = k_{mmm}[mm^*]M \quad (4.12)$$

$$d[m\vec{m}r]/dt = k_{mmr}[mm^*]M \quad (4.13)$$

$$d[m\vec{r}m]/dt = k_{mrm}[mr^*]M \quad (4.14)$$

$$d[m\vec{r}r]/dt = k_{mrr}[mr^*]M \quad (4.15)$$

$$d[r\vec{m}r]/dt = k_{rmr}[rm^*]M \quad (4.16)$$

$$d[r\vec{m}m]/dt = k_{rmm}[rm^*]M \quad (4.17)$$

$$d[r\vec{r}m]/dt = k_{rrm}[rr^*]M \quad (4.18)$$

$$d[r\vec{r}r]/dt = k_{rrr}[rr^*]M \quad (4.19)$$

The initial conditions for eq 4.1–19 are

$$N^*|_{t=0} = I_0 \qquad M|_{t=0} = M_0 - I_0$$

$$[m^*]|_{t=0} = [r^*]|_{t=0} = [mm^*]|_{t=0} = [mr^*]|_{t=0} = [rm^*]|_{t=0} = [rr^*]|_{t=0} = 0$$

$$[mm']|_{t=0} = [mr']|_{t=0} = [rm']|_{t=0} = [rr']|_{t=0} = 0$$

The constraint conditions become

$$I_0 = N^* + [m^*] + [r^*] + [mm^*] + [mr^*] + [rm^*] + [rr^*]$$

$$M_0 - M - I_0 = [m^*] + [r^*] + [mm] + [mr] + [rr] \tag{4.20}$$

where

$$[mm] = [mm^*] + [mm']$$

$$[rm] = [mr] = [mr^*] + [mr'] + [rm^*] + [rm'] \tag{4.21}$$

$$[rr] = [rr^*] + [rr']$$

$$[mmm] = [m\vec{m}m]$$

$$[mmr] = [rmm] = [m\vec{m}r] + [r\vec{m}m]$$

$$[mrm] = [m\vec{r}m] \tag{4.22}$$

$$[mrr] = [rrm] = [m\vec{r}r] + [r\vec{r}m]$$

$$[rmr] = [r\vec{m}r] \qquad [rrr] = [r\vec{r}r]$$

For convenience, let $k_{mmm}/(k_m + k_r) = k_{mmm}/k_p = a$, $k_{rrr}/k_p = b$, $k_{mmr}/k_p = c$, $k_{rmm}/k_p = d$, $k_{mrr}/k_p = e$, $k_{mrm}/k_p = f$, $k_{rmr}/k_p = g$, and $k_{rrm}/k_p = h$; K, α, β, μ, and ν are defined as in the previous section. We shall employ transformation (2.8) so that eq 4.1–19 can be converted into a set of linear differential equations (again omitted here).

The solutions of eq 4.2 and 4.3 are

$$[m^*] = \frac{KI_0}{1 - \alpha - \mu}[e^{-(\alpha+\mu)X} - e^{-X}] \tag{4.23}$$

$$[r^*] = \frac{(1 - K)I_0}{1 - \beta - \nu}[e^{-(\beta+\nu)X} - e^{-X}] \tag{4.24}$$

In accordance with the definition of the Laplace transformation, we define

$$MM = \int_0^\infty e^{-sX}[mm^*]\ \mathrm{d}X \tag{4.25a}$$

$$s(MM) = \int_0^\infty e^{-sX}\frac{\mathrm{d}[mm^*]}{\mathrm{d}X}\ \mathrm{d}X \tag{4.25b}$$

Similarly, let MR, RM, and RR represent the Laplace transformations for $[mr^*]$, $[rm^*]$, and $[rr^*]$, respectively. Then, by substituting eq 4.23 and 4.24 into eq 4.4–7, this set of simultaneous differential equations can be changed into the set

$$s(MM) + c(MM) - d(RM) = \frac{KI_0\alpha}{(1 - \alpha - \mu)(s + \alpha + \mu)} - \frac{KI_0\alpha}{(1 - \alpha - \mu)(s + 1)} \tag{4.26}$$

$$s(MR) + (e + f)(MR) - c(MM) - g(RM) = \frac{KI_0\mu}{(1 - \alpha - \mu)(s + \alpha + \mu)} - \frac{KI_0\mu}{(1 - \alpha - \mu)(s + 1)} \tag{4.27}$$

$$s(RM) + (d + g)(RM) - h(RR) - f(MR) = \frac{(1 - K)I_0\nu}{(1 - \beta - \nu)(s + \beta + \nu)} - \frac{(1 - K)I_0\nu}{(1 - \beta - \nu)(s + 1)} \tag{4.28}$$

$$s(RR) + h(RR) - e(MR) = \frac{(1 - K)I_0\nu}{(1 - \beta - \nu)(s + \beta + \nu)} - \frac{(1 - K)I_0\beta}{(1 - \beta - \nu)(s + 1)} \tag{4.29}$$

of simultaneous equations, whose solutions are

$$MM = \frac{I_0}{D}\{k\alpha s^4 + n_{13}s^3 + n_{12}s^2 + n_{11}s + n_{10}\} \tag{4.30}$$

$$MR = \frac{I_0}{D}\{kus^4 + n_{23}s^3 - n_{22}s^2 - n_{21}s + n_{20}\} \tag{4.31}$$

$$RM = \frac{I_0}{D}\{(1 - K)\nu s^4 + n_{33}s^3 - n_{32}s^2 - n_{31}s + n_{30}\} \tag{4.32}$$

$$RR = \frac{I_0}{D}\{(1 - K)\beta s^4 + n_{43}s^3 + n_{42}s^2 + n_{41}s + n_{40}\} \tag{4.33}$$

The quantities n_{1j}, n_{2j}, and D are given by

$$n_{13} = \nu d(1 - K) + K\alpha\{(\beta + \nu) + k_1\}$$

$$n_{12} = (1 - K)d[\nu(\alpha + \mu + f + e) + h(\nu + \beta)] + K[d(f\mu + h\alpha) + k_1\alpha(\beta + \nu) + k_{11}\alpha]$$

$$n_{11} = (\alpha + u)[de\nu(1 - K) + dh(\nu + \beta) + df\nu + Kk_{111}] + (\beta + \nu)[(k_{11}\alpha - dh\mu)K + (1 - K)k_{111}] + kdf(\beta\mu - \alpha\nu)$$

$$n_{10} = k_{111}(\alpha + \mu)(\beta + \nu)$$

$$n_{23} = \nu g(1 - K) + K[\mu(\nu + \beta + h + d + g) + c(\alpha + \mu)]$$

$$n_{22} = (1 - K)\{h(c\nu - g\beta) - \nu[k_{22} + g(\alpha + \mu)]\} + K[h(g\alpha - ud) - (\beta + \nu)(c\alpha + uk_2) - k_{22}(\alpha + \mu)]$$

$$n_{21} = (\alpha + \mu)[h(1 - K)(c\nu - g\beta) - k_{22}(\nu + K\beta) - Kk_{222}] + (\beta + \nu)[kh(g\alpha - du) - (1 - K)k_{222}]$$

$$n_{20} = k_{222}(\alpha + \mu)(\beta + \nu)$$

and

$$D = s(s + 1)(s + \alpha + \mu)(s + \beta + \nu)(s^3 + c_1s^2 + c_2s + c_3)$$

where

$$k_1 = d + e + f + g + h$$

$$k_{11} = de + df + eg + eh + fh + gh$$

$$k_{111} = dh(e + f)$$

$$k_2 = c + d + g + h$$

$$k_{22} = cd + cg + ch + gh$$

$$k_{222} = ch(d + g)$$

$$c_1 = c + d + e + f + g + h$$

$$c_2 = (c + h)(d + e + f + g) + ch + de + df + eg$$

$$c_3 = c(d + g)(e + h) + h(c + d)(e + f)$$

Expressions for n_{3i} and n_{4i} (i = 0, ..., 3) can be obtained by the reciprocal method. For convenience, we define the reciprocal rule for the second-order Markoff process in Table I. Numerous complementary expressions can be obtained by changing symmetry pairs.

Expressions for $[mm^*]$, $[mr^*]$, $[rm^*]$, and $[rr^*]$ must be obtained by the inverse Laplace transformation. According to the Riemann-Mellin integral

$$[mm^*] = \frac{1}{2\pi i}\int_{\gamma-i\infty}^{\gamma+i\infty}(MM)e^{sX}\ \mathrm{d}X = \sum_j \mathrm{Res}\ \{(MM)e^{sX}\}_{s=s_j} \tag{4.34}$$

where γ is any real number greater than zero and "Res" denotes residue. The solutions for $[mr^*]$, $[rm^*]$, and $[rr^*]$ have similar forms. The order of the pole s_j depends on the solution of the polynomial $(s^3 + c_1s^2 + c_2s + c_3)$. Since the probability of triply repeated roots for this polynomial is zero and the probability of doubly repeated roots is rare,

Table I
Reciprocal Rule

triad	corresponding element	symmetry pairs
MM (mm*)	n_{1i} k_1 k_{11} k_{111}	(1,4) (2,3) (K,1–K)
MR (mr*)	n_{2i} k_2 k_{22} k_{222}	(α,β) (μ,ν) (a,b)
RM (rm*)	n_{3i} k_3 k_{33} k_{333}	(c,h) (d,e) (g,f)
RR (rr*)	n_{4i} k_4 k_{44} k_{444}	(m,r) (M,R)

we consider only the practical case in which the denominator has seven distinct roots. We can therefore write

$$[mm^*] = \sum_j \left(\frac{k\alpha s^4 + n_{13}s^3 + n_{12}s^2 + n_{11}s + n_{10}}{7s^6 + 6d_5s^5 + 5d_4s^4 + 4d_3s^3 + 3d_2s^2 + 2d_1s + d_0} e^{sX} \right)_{s_j} \tag{4.35}$$

where

$$d_5 = c_1 + 1 + \alpha + \mu + \beta + \nu$$

$$d_4 = c_1(1 + \alpha + \mu + \beta + \nu) + c_2 - [1 - (1 + \alpha + \mu)(1 + \beta + \nu)]$$

$$d_3 = (\beta + \nu)(\alpha + \mu) - c_1[1 - (1 + \alpha + \mu)(1 + \beta + \nu)] + c_2(1 + \alpha + \mu + \beta + \nu) + c_3$$

$$d_2 = c_3(1 + \alpha + \mu + \beta + \nu) - c_2[1 - (1 + \alpha + \mu)(1 + \beta + \nu)] + c_1(\alpha + \mu)(\beta + \nu)$$

$$d_1 = c_2(\alpha + \mu)(\beta + \nu) - c_3[1 - (1 + \alpha + \mu)(1 + \beta + \nu)]$$

$$d_0 = c_3(\alpha + \mu)(\beta + \nu)$$

The quantity s_j ($j = 1, ..., 7$) is a root of the denominator D in eq 4.30–33 and hence is the first-order pole of $[(MM)e^{st}]$ in eq 4.34. Expressions for [mr*], [rm*], and [rr*] can be obtained by the reciprocal method. Now the expressions for dead triads and vector tetrads can be obtained readily by integration of eq 4.8–19.

From the experimental viewpoint, it is the sequence structure and not the sequence direction that can be identified by NMR. The necessary relationships are eq 4.21 and 4.22. Since the spectral data are the percentages of the configurational sequences, the probability of finding a specific triad or tetrad can be obtained by normalization as

$$P_{mm} = \frac{[mm]}{[mm] + [mr] + [rr]} \tag{4.36a}$$

$$P_{mm} \equiv [mm]/\sum\text{triads} \tag{4.36b}$$

$$P_{mr} = [mr]/\sum\text{triads} \tag{4.37}$$

$$P_{rr} = 1 - P_{mm} - P_{mr} \tag{4.38}$$

$$P_{mmm} = \frac{[mmm]}{[mmm] + [mmr] + [mrm] + [mrr] + [rmr] + [rrr]} \tag{4.39a}$$

$$P_{mmm} \equiv [mmm]/\sum\text{tetrads} \tag{4.39b}$$

$$P_{m\vec{m}m} = [m\vec{m}m]/\sum\text{tetrads} \tag{4.39c}$$

$$P_{mmr} = [mmr]/\sum\text{tetrads} \tag{4.40a}$$

$$P_{m\vec{m}r} = [m\vec{m}r]/\sum\text{tetrads} \tag{4.40b}$$

$$P_{mmm} + P_{mmr} + P_{mrm} + P_{mrr} + P_{rmr} + P_{rrr} = 1 \tag{4.41a}$$

$$P_{m\vec{m}m} + P_{m\vec{m}r} + P_{r\vec{m}m} + P_{m\vec{r}m} + P_{m\vec{r}r} + P_{r\vec{r}m} + P_{r\vec{m}r} + P_{r\vec{r}r} = 1 \tag{4.41b}$$

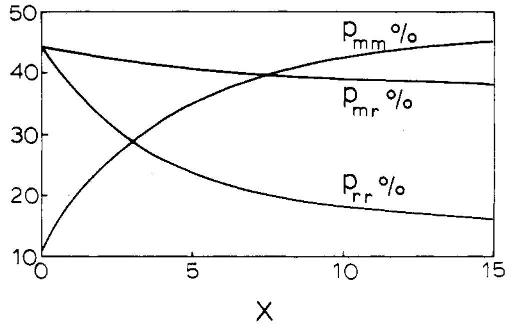


Figure 6. Relation between triads and X for second-order Markoff process: $K = 0.2$; $\alpha = 0.5$; $\beta = 0.45$; $\mu = 0.22$; $\nu = 0.4$; $a = 0.6$; $b = 0.3$; $c = 0.2$; $d = 0.55$; $e = 0.35$; $f = 0.55$; $g = 0.25$; $h = 0.4$.

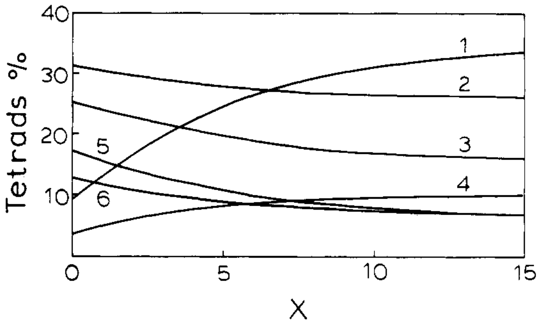


Figure 7. Relation between tetrads and X for second-order Markoff process: Values of constants are the same as those appearing in Figure 6. The curves are identified via the notations 1 for mmm, 2 for mmr, 3 for mrr, 4 for mrm, 5 for rrr, and 6 for rmr.

The relations between triads (or tetrads) and X are shown in Figure 6 (or Figure 7). As in the case of simple Markoff processes, the sequence structures of vinyl polymers vary with reaction parameter X at the beginning of polymerization and then monotonically approach their respective limits. This is the usual behavior for second-order Markoff processes. If the polynomial ($s^3 + c_1s^2 + c_2s + c_3$) has a pair of complex roots, eq 4.35 remains a real expression because the conjugate parts of the complex roots will be cancelled by one another. However, trigonometric functions will appear in the expression and they will cause a fluctuation of the sequence structures of the polymer during the initial period of polymerization, as those of polydienes for the first-order Markoff process (see Figure 4, ref 10).

According to L'Hôpital's rule, eq 4.39–41 lead to

$$\lim_{X\to 0} P_{mmm} = aK\alpha/[(a + c)K\alpha + (f + e)Ku + (g + d)\nu(1 - K) + (b + h)\beta(1 - K)] = k_mk_{mm}k_{mmm}/[k_mk_{mm}(k_{mmm} + k_{mmr}) + k_mk_{mr}(k_{mrr} + k_{mrm}) + k_rk_{rm}(k_{rmr} + k_{rmm}) + k_rk_{rr}(k_{rrr} + k_{rrm})] \tag{4.42}$$

$$\lim_{X\to 0} P_{mmr} = [k_mk_{mm}k_{mmr} + k_rk_{rm}k_{rmm}]/[k_mk_{mm}(k_{mmm} + k_{mmr}) + k_mk_{mr}(k_{mrr} + k_{mrm}) + k_rk_{rm}(k_{rmr} + k_{rmm}) + k_rk_{rr}(k_{rrr} + k_{rrm})] \tag{4.43}$$

$$\lim_{X\to\infty} P_{mmm} = ak_{111}/[(a + c)k_{111} + (f + e)k_{222} + (g + d)k_{333} + (h + b)k_{444}] \tag{4.44}$$

$$\lim_{X\to\infty} P_{mmr} = [ck_{111} + dk_{333}]/[(a + c)k_{111} + (f + e)k_{222} + (g + d)k_{333} + (h + b)k_{444}] \tag{4.45}$$

Relevant expressions for other tetrads can be obtained from these results via the reciprocal method. As well, two additional expressions for vector triads can be obtained

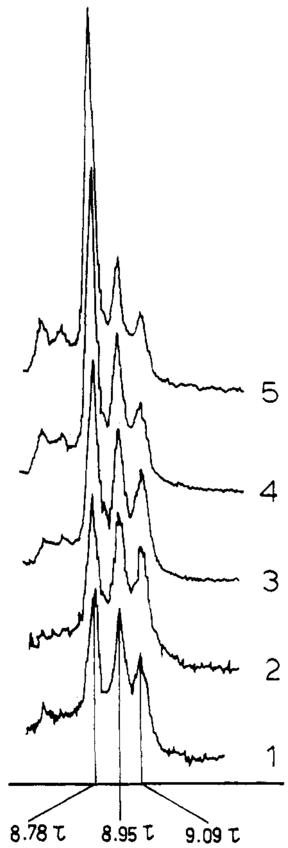


Figure 8. Typical spectra for PMMA: Reaction times (minutes) for the various runs are (1) 15, (2) 30, (3) 60, (4) 120, and (5) 240; conversions (%) of the various runs are (1) 16, (2) 21, (3) 27, (4) 64, and (5) 76; for reaction conditions, see Figure 11.

from eq 3.19a and a set of expressions for vector tetrads can be obtained from eq 4.39c and 40b, each by employing the reciprocal method. Under steady-state conditions, we can obtain the conditional probability starting from the vector probabilities:

$$\lim_{X\to\infty} P_{mr/m} = \frac{\lim\limits_{X\to\infty} P_{m\vec{r}m}}{\lim\limits_{X\to\infty} P_{\overrightarrow{mr}}} = \frac{\lim\limits_{X\to\infty} P_{mrm}}{\lim\limits_{X\to\infty} P_{\overrightarrow{mr}}} = \frac{k_{mrm}}{k_{mrm}+k_{mrr}} \tag{4.46}$$

$$\lim_{X\to\infty} P_{mr/r} = \frac{\lim\limits_{X\to\infty} P_{m\vec{r}r}}{\lim\limits_{X\to\infty} P_{\overrightarrow{mr}}} = \frac{k_{mrr}}{k_{mrm}+k_{mrr}} \tag{4.47}$$

The other conditional probabilities can be obtained by the reciprocal method. Equations 4.46 and 4.47 show that, as for first-order Markoff processes in the paper, the results from kinetics at the steady-state stage are in agreement with those from statistics. The statistical treatment can thus be used correctly only in the case of long polymer chains.

5. Experimental Section

The polymerization of methyl methacrylate was carried out in specially constructed vessels. The preparation and titration of n-BuLi and sodium naphthalene and the purification of monomer and solvent followed methods described in ref 11-13. The ^{1}H NMR spectra of PMMA samples were measured on a JEOL PS-100 spectrometer at 100 MHz, with $CDCl_3$ as solvent containing a small amount of tetramethylsilane as internal standard. Instrument conditions were as follows: spectral width, 1 KHz; probe temperature, 30 °C. Analyses of the spectra have been discussed in ref 7. Typical spectra of PMMA are shown in Figure 8. (The experimental work has been carried out in the People's Republic of China.)

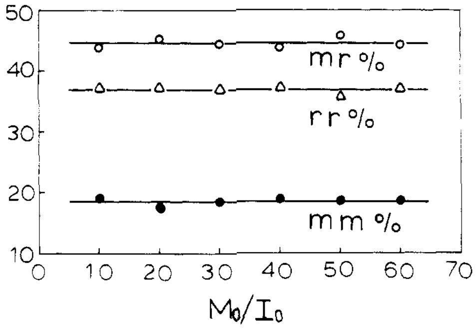


Figure 9. Relation between triad concentration and M_0/I_0; polymerized in THF at −78 °C with sodium naphthalene as catalyst; M_0 = 0.806 mol/L; 100% conversion.

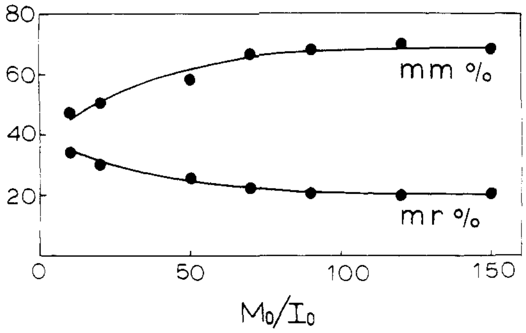


Figure 10. Effect of M_0/I_0 on the sequence structures of PMMA initiated by n-BuLi in toluene at −78 °C; M_0 = 1.128 mol/L; 100% conversion.

6. Results and Discussion

The sequence structures of PMMA initiated by sodium naphthalene in THF with different initial concentration ratios of monomer to initiator (M_0/I_0) are shown in Figure 9. The abscissa of Figure 9 can be changed into X by setting $Y = 1$ in eq 2.13 at quantitative conversion. It is clear that Figure 9 is in agreement with Figure 2, so that the relative polymerization is certainly describable as a Bernoulli process. Amerik et al.[14] reached the conclusion that the polymerization of MMA in THF with butyllithium as initiator obeys Bernoulli statistics by using the criterion that $\rho = 2[m][r]/[mr]$ attains the value unity for Bernoulli statistics. They also obtained a horizontal line relationship between sequence structures and monomer concentration (Figure 2 in ref 14) that is parallel to ours. It can happen that ρ deviates from unity because there are systematic experimental errors. It is therefore safer to use either the present criterion (see Figures 2 and 9) or both. It is worth mentioning that even at the start of polymerization, there is a non-steady-state for Bernoulli processes of polymerization of dienes,[15] so that the present criterion for a process to obey Bernoulli statistics is not suitable for polydienes.

The sequence structures of PMMA initiated by n-BuLi in toluene with different M_0/I_0 have been shown in Figure 10, and those of PMMA initiated by n-BuLi in mixed solvents (THF/toluene = 10/90 by molar ratio) with different reaction times have been illustrated in Figure 11. These figures are different from Figures 9 and 2; obviously the relative polymerizations are not describable as Bernoulli processes. Since Figures 10 and 11 are in accord with Figures 4 and 6, the relative polymerizations may be describable as Markoff processes. Peat and Reynolds[16] reported that the PMMA prepared in THF with n-BuLi as an initiator exhibited Bernoulli characteristics, while the second polymer, prepared in toluene rather than THF, showed either second-order Markoff or Coleman–Fox[3] behavior. Bovey[2] also favored the second-order Markoff

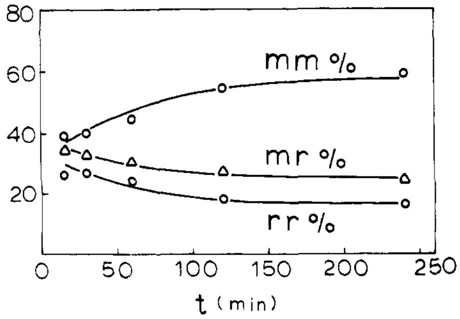


Figure 11. Relation between reaction time and sequence structure of PMMA initiated by *n*-BuLi at −21 °C. Molar ratio of solvents, THF/toluene = 10/90; M_0 = 0.972 mol/L; I_0 = 1.39 $\times 10^{-2}$ mol/L.

(or two sites) model for PMMA prepared in toluene. Müller et al.[17] claimed that the tacticity of PMMA in THF with Ce$^+$ as counterion assumes a first-order Markoff process.

According to our kinetic description, the sequence structures may fluctuate at the start of initiation for certain second-order Markoff processes, but this is not a necessary condition. To judge the order of the Markoff process, the decision equations in ref 6 are recommended. Our kinetic description is not intended to reject most statistics and/or other possible mechanisms but is intended to add some new ideas to this important topic. Because of the resolving power of the apparatus employed for the measurements, we have insufficient data to check our results for the order of the Markoff process. To use the decision equations in Tables II and III of ref 6, additional data for tetrads and pentads would be required.

7. Conclusions

From the above discussion, it can be seen that a non-steady-state stage exists at the beginning of the polymerization of vinyl polymers for both first- and second-order Markoff processes and, as a consequence, during this stage the configurational sequence structures of the products depend upon polymerization parameters. By contrast, for a Bernoulli process, once the vinyl monomer is initiated, there is no non-steady-state stage during polymerization. We thus obtain a simple method for judging the polymerization mechanism. The criterion for a Bernoulli process is that the plot of its sequence structures against any polymerization parameter (e.g., reaction time t, monomer conversion Y, X, and so on) during the whole reaction process be a horizontal line. If the polymerization does not satisfy this criterion, it should likely be ranked as a Markoff process.

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The Internal Modes of Polystyrene Single Coils Studied Using Dynamic Light Scattering

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ABSTRACT: Dynamic light scattering (DLS) has been used to examine the internal dynamics of polystyrene in cyclohexane at 34.5 °C (Θ solvent) and in toluene at 25 °C. Different procedures for evaluating the contribution from the internal modes to the decay time spectrum are used and compared: (a) fit to double-exponential function; (b) maximum entropy analysis (MAXENT); (c) CONTIN. It is found that the first internal mode (τ_1) is lower than the theoretical value given by the non-free-draining (Zimm) model for Gaussian chains.

Introduction

Dynamic light scattering is a powerful technique with suitable space and time resolution for the investigation not only of the overall movements of polymers in solution but also of the internal dynamics of the single coil, if the radius of gyration is not small compared to the wavelength of the light source used.

For dilute solutions of large polymers, Pecora[1] expressed the spectrum of the scattered light in terms of normal modes, using the so-called bead-spring model for flexible

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