On the Stereoregularity of Vinyl Polymer Chains. II

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ABSTRACT: Increased chemical shift discrimination at 220 MHz has made it possible to observe and assign pentad sequences in the α-methyl proton spectrum of poly(methyl methacrylate). This in turn permits the testing of consistency with second-order Markov statistics and also allows a more searching examination of the Coleman–Fox two-state mechanism. A polymer prepared with a Grignard initiator at $-78°$ and known from previous tetrad sequence intensity measurements to deviate from first-order Markov statistics is found to approximate second-order Markov statistics but to fit a two-state mechanism within experimental error. The configuration of this polymer is consistent with a propagation mechanism in which 80% of the polymer is produced under the influence of a counterion which directs almost exclusive *m* (*i.e.*, isotactic) monomer placement; the remainder of the polymer is generated by an uncomplexed anionic growing chain end at which *r* placement predominates, as in free radical propagation.

Previous discussions of configurational probabilities in vinyl polymer chains could be related to experimental observations of sequences of three[1–3] or at most four[4–13] monomer units.

Recently, observations of poly(methyl methacrylate) at 220 MHz[14,15] have revealed fine structure in the *i*, *h*, and *s* α-methyl peaks (to be designated *mm*, *mr*, and *rr* hereafter)[6] which undoubtedly arises from discrimination of *pentad* sequences of monomer units. It is obvious that if one can identify and measure the frequencies of these pentad sequences, one will have a deeper insight into the configurational statistics of the chains and into the propagation mechanism producing them. In particular, as has been shown,[6] one can test consistency with second-order Markov statistics and can (at least in principle) gives the Coleman–Fox two-state propagation mechanism[16,17] a more searching examination.

In Figures 1a and 2a are shown the 220-MHz spectra of the α-methyl and β-methylene protons of a predominantly syndiotactic poly(methyl methacrylate) prepared with a free radical initiator, designated polymer I. It is assumed that the propagation is a Bernoulli-trial process,[1–3,5,6,15] and that the triad, tetrad, and pentad probabilities are therefore given by the curves of Figure 4, 5, and 6, respectively, in ref 15. This enables the peaks of Figure 1a to be assigned to tetrad sequences on the basis of their relative areas, which were determined with the aid of a Du Pont Model 310 curve resolver. The assignments are as shown in the figure. The *meso* tetrads appear as approximately AX quartets; the centers of the doublets may be taken as the chemical shifts without significant error. It is believed that the less shielded proton in the *meso* methylene groups is the "*erythro*" proton, *i.e.*, that which is the fully extended conformation would be on the same side of the zigzag plane as the ester group.[15,18–20] The more shielded proton is designated "*threo*." The *mrr* tetrad is in principle heterosteric[5,6,15] and in fact exhibits widely differing chemical shifts in the poly(vinyl chloride) spectrum.[15,21,22] In Figure 1a a small difference in chemical shift is evident from the shape of the peak, in agreement with the observation of Lim, *et al.*;[9] the outer lines of the AB quartet are too weak to distinguish. The *mmm* tetrad, which is expected (see below) to appear downfield from the *mmr* resonances, is likewise too weak to see.

In the α-methyl spectrum of polymer I (Figure 1a), splitting of the *mm*, *mr* and *rr* peaks into pentad fine

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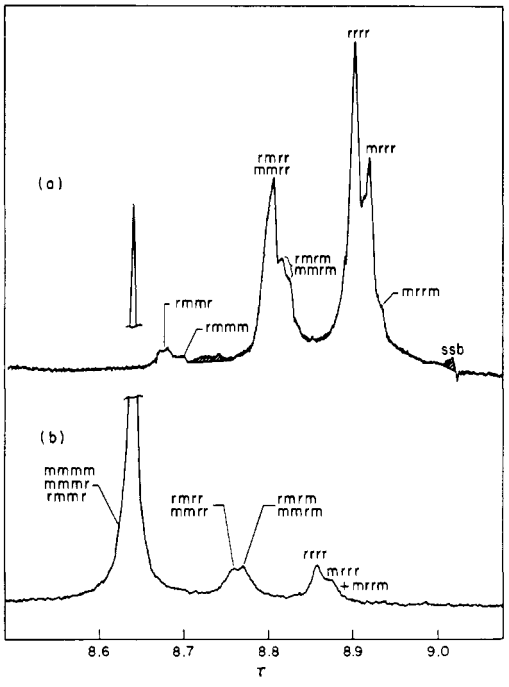

Figure 1. (a) α-Methyl proton spectrum of predominantly syndiotactic poly(methyl methacrylate) (polymer I), observed at 220 MHz (*ca.* 10% w/v solution in chlorobenzene at 135°); (b) α-methyl proton spectrum of predominantly isotactic poly(methyl methacrylate) (polymer II), same conditions as a. "Ssb" designates spinning side band.

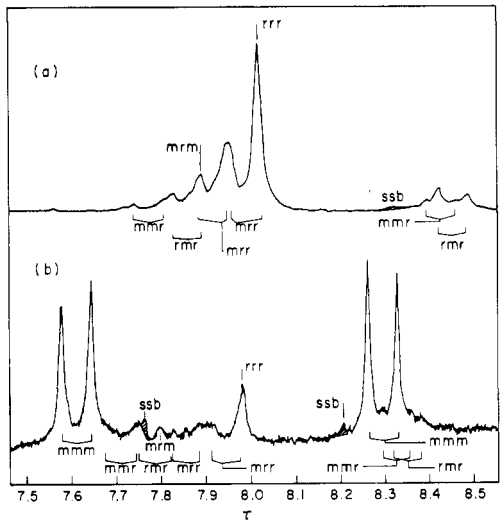

Figure 2. (a) β-Methylene proton spectrum of predominantly syndiotactic poly(methyl methacrylate) (polymer I), observed at 220 MHz (*ca.* 10% w/v solution in chlorobenzene at 135°); (b) β-methylene proton spectrum of predominantly isotactic poly(methyl methacrylate) (polymer II), same conditions as a. In these spectra, the doublet components of the *mmr*, *rmr*, and *mrr* quartets are connected by slanting lines which intersect at the chemical shift. "Ssb" designates spinning side band.

structure can be clearly seen. The assignments shown are the most logical and consistent set that we could arrive at, but their correctness cannot be rigorously proved. In Table I, the experimental triad, tetrad, and pentad intensities are compared to those expected for Bernoulli-trial propagation with a P_m of 0.24. The agreement is within the probable experimental error.

TABLE I
BERNOULLI MODEL FITTING FOR POLYMER I
Dyad (*m*): 0.24
(*r*): 0.76

		Obsd	Bernoulli trial, P_m = 0.24
Triad			
	(*mm*)	0.04	0.06
	(*mr*)	0.36	0.36
	(*rr*)	0.60	0.58
Tetrad			
	(*mmm*)	*Ca.* 0.00	0.01
	(*mmr*)	0.07	0.09
	(*rmr*)	0.19	0.20
	(*mrm*)	0.04	0.04
	(*mrr*)	0.23	0.23
	(*rrr*)	0.43	0.44
Pentad			
	(*mmmm*)	*Ca.* 0.00	0.003
Peak 2	(*mmmr*)	0.02	0.02
Peak 1	(*rmmr*)	0.05	0.03
Peak 3	(*rmrr*) + (*mmrr*)	0.25	0.27
Peak 4	(*rmrm*)	0.06	0.07
Peak 5	(*mmrm*)	0.02	0.02
Peak 6	(*rrrr*)	0.40	0.39
Peak 7	(*mrrr*)	0.14	0.16
Peak 8	(*mrrm*)	0.05	0.03

In Figures 1b and 2b are shown the α-methyl and β-methylene proton spectra of a predominantly isotactic poly(methyl methacrylate) prepared in toluene with phenylmagnesium bromide initiator, designated polymer II. (This polymer appears also in Figure 12 of ref 5 and Figure 3a of ref 15.) We assume that the proton shieldings, while they may be (and in fact are) slightly altered when the predominant stereochemistry is altered,[23] will remain in the same order for tetrad and pentad sequences. (It is obvious that they do so for triad sequences.) The assignments in Figures 1b and 2b are then essentially the same as in Figures 1a and 2a. The *mmm* tetrad resonance, not discernible in Figure 2a, is now the dominant feature of the methylene spectrum. The much weaker AX spectra of the *mmr* and *rmr* sequences are difficult to see in Figure 2b; although clearer in the original spectra, relative intensities cannot be accurately measured. The "*threo*" doublets are more clearly resolved than the "*erythro*" and are the basis of the measurement. The measured triad, tetrad, and pentad intensities are given in Table II.

It may be noted that, assuming the correctness of the tetrad peaks assignments, there is a consistent trend in the chemical shifts of both *m* and *r* methylene protons: shielding increases as the number of *r* neighbors is increased from zero to one to two. In the absence of information concerning the local conformations of the chains, it is difficult to draw any conclusion from this observation.

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TABLE II
MODEL FITTING FOR POLYMER II
Dyad (*m*): 0.82
(*r*): 0.18
Triad (*mm*): 0.75
(*mr*): 0.14
(*rr*): 0.11

	Obsd	First-order Markov $P(m/r) = 0.085$ $P(r/m) = 0.39$	Second-order Markov	Coleman–Fox
Tetrad				
(*mmm*)	0.70	0.69	0.70	0.70
(*mmr*)	0.09	0.13	0.09	0.09
(*rmr*)	0.03	0.006	0.03	0.02
(*mrm*)	0.04	0.03	0.04	0.04
(*mrr*)	0.06	0.09	0.06	0.06
(*rrr*)	0.07	0.07	0.07	0.08
Pentad				
Peak 1 (*mmmm*), (*mmmr*), (*rmmr*)	0.75	0.75	0.77	0.74
Peak 2 (*rmrr*), (*mmrr*)	0.07	0.09	0.06	0.07
Peak 3 (*rmrm*), (*mmrm*)	0.07	0.05	0.08	0.08
Peak 4 (*rrrr*)	0.07	0.04	0.05	0.07
Peak 5 (*mrrr*), (*mrrm*)	0.04	0.07	0.05	0.05

Interpretation

In ref 5 and 6 we have discussed the fitting of spectral data to first-order Markov and Coleman–Fox two-state propagation mechanisms. In this paper we extend this treatment to include pentad frequencies and their fitting to possible second-order Markov and two-state mechanisms. The two-state and first-order Markov models have been defined and discussed in ref 6; we shall adopt the basic notation used there, but will find it desirable to employ some additional notation.

1. Markov Models. For convenience, we designate the eight conditional probabilities of the second-order Markov model as

$$\begin{aligned} P(mm/m) &= \alpha & P(mm/r) &= \bar{\alpha} \\ P(mr/m) &= \beta & P(mr/r) &= \bar{\beta} \\ P(rm/m) &= \gamma & P(rm/r) &= \bar{\gamma} \\ P(rr/m) &= \delta & P(rr/r) &= \bar{\delta} \end{aligned} \tag{1}$$

where $P(mm/m)$ is the probability of a monomer adding in *m* fashion to a chain ending in *mm*, and so on. There are actually four independent probabilities, since

$$\begin{aligned} \alpha + \bar{\alpha} &= 1 \\ \beta + \bar{\beta} &= 1 \\ \gamma + \bar{\gamma} &= 1 \\ \delta + \bar{\delta} &= 1 \end{aligned} \tag{2}$$

This model reduces to the first-order Markov model when $\alpha = \gamma$ and $\beta = \delta$. Putting

$$s = \bar{\alpha}\bar{\beta} + 2\bar{\alpha}\delta + \gamma\delta \tag{3}$$

we find that the observable dyad through pentad frequencies are

$$\begin{aligned} (m) &= (\bar{\alpha} + \gamma)\delta/s \\ (r) &= (\bar{\beta} + \delta)\alpha/s \end{aligned} \tag{4}$$

$$\begin{aligned} (mm) &= \gamma\delta/s \\ (mr) &= 2\bar{\alpha}\delta/s \\ (rr) &= \bar{\alpha}\bar{\beta}/s \end{aligned} \tag{5}$$

$$\begin{aligned} (mmm) &= \alpha\gamma\delta/s \\ (mmr) &= 2\bar{\alpha}\gamma\delta/s \\ (mrm) &= \bar{\alpha}\beta\delta/s \\ (mrr) &= 2\bar{\alpha}\bar{\beta}\delta/s \\ (rmr) &= \bar{\alpha}\bar{\gamma}\delta/s \\ (rrr) &= \bar{\alpha}\bar{\beta}\bar{\delta}/s \end{aligned} \tag{6}$$

$$\begin{aligned} (mmmm) &= \alpha^2\gamma\delta/s = (mmm)^2/(mm) \\ (mmmr) &= 2\alpha\bar{\alpha}\gamma\delta/s = (mmm)\,(mmr)/(mm) \\ (mmrm) &= 2\bar{\alpha}\beta\gamma\delta/s = 2(mmr)(mrm)/(mr) \\ (mmrr) &= 2\bar{\alpha}\bar{\beta}\gamma\delta/s = (mmr)(mrr)/(mr) \\ (mrmr) &= 2\bar{\alpha}\beta\bar{\gamma}\delta/s = 4(mrm)(rmr)/(mr) \\ (mrrm) &= \bar{\alpha}\bar{\beta}\delta^2/s = (mrr)^2/4(rr) \\ (mrrr) &= 2\bar{\alpha}\bar{\beta}\delta\bar{\delta}/s = (mrr)(rrr)/(rr) \\ (rmmr) &= \bar{\alpha}^2\gamma\delta/s = (mmr)^2/4(mm) \\ (rmrr) &= 2\bar{\alpha}\bar{\beta}\bar{\gamma}\delta/s = 2(mrr)(rmr)/(mr) \\ (rrrr) &= \bar{\alpha}\bar{\beta}\bar{\delta}^2/s = (rrr)^2/(rr) \end{aligned} \tag{7}$$

The following expressions are also useful

$$\begin{aligned} \alpha &= \frac{(mmm)}{(mm)} & \bar{\alpha} &= \frac{(mmr)}{2(mm)} \\ \beta &= \frac{2(mrm)}{(mr)} & \bar{\beta} &= \frac{(mrr)}{(mr)} \\ \gamma &= \frac{(mmr)}{(mr)} & \bar{\gamma} &= \frac{2(rmr)}{(mr)} \\ \delta &= \frac{(mrr)}{2(rr)} & \bar{\delta} &= \frac{(rrr)}{(rr)} \end{aligned} \tag{8}$$

In ref 5 it was shown on the basis of tetrad and triad frequencies that the polymer shown in Figures 1b and 2b does not conform to first-order Markov statistics. This is further demonstrated by comparison of observed and predicted intensities in Table II. The values in column three are calculated for values of $P(m/r)$ and $P(r/m)$, indicated at the top of column three, deduced from triad frequencies and eq 6 and 7 of ref 5. (The values of $P(m/r)$ and $P(r/m)$ differ slightly from those given in ref 5 because they are obtained by analysis of the 220-MHz spectrum; they are probably more accurate than the previous values obtained from the 60-MHz spectrum.)

To test for conformity to second-order Markov statistics, the eight conditional probabilities are calculated from triad and tetrad intensities using eq 8. The

$$\begin{aligned} \alpha &= 0.94 & \bar{\alpha} &= 0.06 \\ \beta &= 0.56 & \bar{\beta} &= 0.44 \\ \gamma &= 0.63 & \bar{\gamma} &= 0.37 \\ \delta &= 0.28 & \bar{\delta} &= 0.64 \end{aligned}$$

values obtained are a further test of first-order Markov statistics since, as we have seen, $\alpha = \gamma$ and $\beta = \delta$ if these apply. It is clear that this is not the case. From the method of calculation it is necessary that $\beta + \bar{\beta} = 1$ and $\gamma + \bar{\gamma} = 1$, so this agreement does not consti-

tute a test of second-order Markov statistics. The fact that $\alpha + \bar{\alpha} = 1$ and $\delta + \bar{\delta} \simeq 1$ does constitute a valid test, however. A further test is indicated in column four of Table II, in which pentad intensities, calculated from eq 7, are listed. The agreement with experimental values is quite good except that the predicted ratio of the *rrrr* to the *mrrr–mrrm* peak is lower than experimental observation. The pentad test is, unfortunately, not as conclusive as might be wished because only five peaks can be resolved out of a possible ten.

2. Coleman–Fox. In Table VI of ref 6 the constants of the Coleman–Fox two-state propagation model[16,17] are expressed in terms of triad and tetrad frequencies. To these relationships we now add the following

$$\begin{gathered}(mmmm)(mm) - (mmm)^2 = AM^2 \\ (mmmr)(mm) - (mmm)(mmr) = -2AM^2 \\ 4(rmmr)(mm) - (mmr)^2 = 4AM^2 \\ (mmrm)(mr) - 2(mmr)(mrm) = 4AMR \\ (rmrm)(mr) - 4(rmr)(mrm) = -4AMR \\ (mmrr)(mr) - (mmr)(mrr) = -4AMR \\ (rmrr)(mr) - 2(mrr)(rmr) = 4AMR \\ 4(mrrm)(rr) - (mrr)^2 = 4AR^2 \\ (mrrr)(rr) - (rrr)(mrr) = -2AR^2 \\ (rrrr)(rr) - (rrr)^2 = AR^2\end{gathered} \tag{9}$$

where $A = ax$, $M = bx$, and $R = cx$ (a, b, c, and x are defined as in ref 6, 16, and 17). It will be recalled that in this model, propagation in each state is assumed to proceed by a Bernoulli-trial process. Let m_1 ($= k_{1i}/k_1$) be the probability of isotactic placement in state 1 and m_2 ($= k_{2i}/k_2$) the probability of isotactic placement in state 2; here, k_{1i} and k_{2i} are the rate constants for isotactic placement in states 1 and 2, respectively, and k_1 and k_2 are the total propagation rates in each state. The quantity w_1 is defined as

$$w_1 = \frac{\lambda_a k_1}{\lambda_a k_1 + \lambda_b k_2} \tag{10}$$

and will be seen to represent the fraction of polymer produced in state 1, λ_a and λ_b being the rate constants for the transitions state 2 → state 1 and reverse, respectively (previously erroneously defined[6] *vice versa*). In Appendix 1 it is shown how m_1, m_2 and w_1 can be obtained from experimental values for (m) and the triad probabilities. For polymer II, we find

$$\begin{aligned} w_1 &= 0.81 \\ m_1 &= 0.96 \\ m_2 &= 0.21 \end{aligned}$$

State 1 is arbitrarily taken as that in which isotactic placement predominates. In the last column of Table II, the tetrad and pentad frequencies calculated from these parameters are shown. The agreement with experimental observation is at least as good as that of the second-order Markov model. It is in fact rather better for peaks four and five, the relative magnitudes of which are, as we have seen, not correctly predicted by the second-order Markov model.

It should be noted that the two-state model, although it reduces to first-order Markov statistics when only m placements are possible in one state and only r placements in the other, cannot reduce identically to second-order Markov statistics. It may, however, approach closely, as in the present case.

The experimental error in measuring intensities being probably ±0.01 even for the smaller peaks, this result cannot be said to provide conclusive evidence for the two-state model. The parameters obtained, however, are very reasonable. They imply that about 80% of the polymer is produced under conditions such that isotactic placement is nearly exclusively preferred; the rest of the time, isotactic placement has the probability characteristic of a free radical or uncomplexed anionic chain end. In this second state, the metal counterion exerts no steric control, possibly because it is complexed with residual ether introduced with the Grigard reagent.[6,15,20]

Appendix 1

To Obtain Coleman–Fox Constants from Experimental Data. As defined in the main portion of this paper, m_1 and m_2 are the probabilities of isotactic placement in state 1 and state 2, respectively, of the propagating chain end; the fraction of the total polymer which is produced in state 1 is

$$w_1 = \lambda_a k_1/(\lambda_a k_1 + \lambda_b k_2) \tag{A1-1}$$

where $k_1 = k_{1i} + k_{1s}$ and $k_2 = k_{2i} + k_{2s}$, as defined above and in ref 6, 16, and 17; λ_a and λ_b have also been defined in the last section of this paper. From the defining relationships[6,16,17]

$$p = (m) = (\lambda_a k_{1i} + \lambda_b k_{2i})/(\lambda_a k_1 + \lambda_b k_2)$$

$$a = \frac{\lambda_a \lambda_b k_1 k_2}{(\lambda_a k_1 + \lambda_b k_2)^2}\left(\frac{k_{1i}}{k_1} - \frac{k_{2i}}{k_2}\right)^2$$

$$b = k_{1i}k_{2i}/k_1k_2$$

$$c = k_{1s}k_{2s}/k_1k_2$$

we obtain a quadratic equation in m the roots of which are m_1 and m_2; a/c, b/c and p are quantities obtainable from experiment and treated here as constants

$$m^2\left[\frac{a}{c} + p + (1-p)\frac{b}{c}\right] - m\left[\frac{a}{c} + \frac{b}{c} + p^2\left(1 - \frac{b}{c}\right)\right] + p(1-p)\frac{b}{c} = 0 \tag{A1-2}$$

From m_1 and m_2 we can then obtain w_1 from

$$p = w_1 m_1 + (1 - w_1)m_2 = (m) \tag{A1-3}$$

For polymer II, we find

$$\begin{aligned} a/c &= 2.9 \\ b/c &= 6.7 \\ w_1 &= 0.81 \\ m_1 &= 0.96 \\ m_2 &= 0.21 \end{aligned}$$

The physical significance of the last three quantities is discussed in the last section of the main body of the paper.

Appendix 2

Proof that the Two-State Coleman-Fox Model is Reversible. In ref 6 we have introduced the concept of reversibility of propagation mechanisms. A third-order Markov model that will generate the pure polymer ...*rrmrmmrrmrmm*... (with repeat period six) cannot

generate the same polymer in the reversed direction. This asymmetry can be exhibited by third- and higher order Markov models; to each such model corresponds a reversed model which generates the same polymers in the reversed direction. Also, to each such model and to each n there corresponds a reversible Markov model which generates polymers having the same n-*ad* proportions, and that are statistically completely indistinguishable from their reversals. It seems desirable to to use only Markov models of this kind so long as observational data cannot distinguish the direction of chain growth.

The two-state Coleman-Fox model is not of finite Markov order, and the question arises as to whether it is reversible. We show below that it is, so that the polymers it generates are indistinguishable from their reversals. The model involves the parameters λ_a, λ_b, $k_1 = k_{1i} + k_{1s}$, $k_2 = k_{2i} + k_{2s}$ mentioned above. It is very convenient to use vector and matrix algebra to express the properties of the model. We put

$$t = \lambda_a k_1 + \lambda_b k_2$$
$$d = t + k_1 k_2$$

and define the 2×2 matrices

$$U_m = \begin{pmatrix} k_{1i}/k_1 & 0 \\ 0 & k_{2i}/k_2 \end{pmatrix} \qquad U_r = \begin{pmatrix} k_{1s}/k_1 & 0 \\ 0 & k_{2s}/k_2 \end{pmatrix}$$

$$D = \begin{pmatrix} 1 - \lambda_a k_1/d & \lambda_b k_2/d \\ \lambda_a k_1/d & 1 - \lambda_b k_2/d \end{pmatrix} \qquad T = \begin{pmatrix} \lambda_a k_1/t & 0 \\ 0 & \lambda_b k_2/t \end{pmatrix}$$

For any n + 1-*ad*, $q = q_1 q_2 \ldots q_n$ (where each q_j is either m or r) we define the 1×2 vector

V_q = [Prob(chain ends in q, and is in state 1), Prob(chain ends in q, and is in state 2)]

Under this model, the proportional frequency of q will be

$$[q] = \text{Prob(chain ends in } q) = V_q 1'$$

where 1 is the 1×2 vector (1,1) and (1′ is its transpose).

The power of this notation, using matrix multiplication, becomes clear when we observe that

$$\begin{matrix} V_{qm} = V_q D U_m & V_{qr} = V_q D U_r \\ V_m = 1 T U_m & V_r = 1 T U_r \end{matrix} \qquad \text{(A2-1)}$$

Now consider any n + 1-*ad*, $q_1 q_2 \ldots q_n$. From eq A2-1 we have

$$[q_1 q_2 \ldots q_n] = V_{q_1 q_2 \ldots q_n} 1' = 1 T U_1 D U_2 D U_3 \ldots D U_n 1' \qquad \text{(A2-2)}$$

where each U_j is U_m or U_r according as q_j is m or r. For the reversed n + 1-*ad* we have

$$[q_n q_{n-1} \ldots q_1] = 1 T U_n D U_{n-1} \ldots D U_1 1' \qquad \text{(A2-3)}$$

To show that these are equal, transpose eq A2-3 and use the facts that $U_m = U_m'$, $U_r = U_r'$, $TU_m = U_m T$, $TU_r = U_r T$, $TD = D'T$. This gives

$$\begin{aligned} \text{(A2-3)} &= 1 U_1 D' U_2 \ldots U_{n-1} D' U_n T 1' \\ &= 1 U_1 D' U_2 \ldots U_{n-1} D' T U_n 1' \\ &= 1 U_1 D' U_2 \ldots U_{n-1} T D U_n 1' \\ &= 1 U_1 T D U_2 \ldots U_{n-1} D U_n 1' \\ &= \text{(A2-2)} \end{aligned}$$

Thus $q_1 \ldots q_n$ and $q_n \ldots q_1$ are equally probable under the two-state Coleman-Fox model. However, the three-state version of the model will not be reversible, in general.

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The Influence of Stereoregularity on the Glass Transition Temperatures of Vinyl Polymers

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ABSTRACT: Correlation of available data for glass transition temperatures of mono- and disubstituted vinyl polymers, $(CH_2CXY)_n$, leads to the conclusion that steric configuration affects T_g only when X ≠ Y and neither X or Y is hydrogen. Conversely, T_g is independent of configuration when hydrogen is one of the substituents. A basis for this observation can be developed in terms of the Gibbs–DiMarzio theory if it is postulated that (a) the effect of configuration in disubstituted polymers is intramolecular and is brought about by changes in the flex energy of the isomers, and (b) changes in T_g due to side-chain modification are strictly intermolecular. Using the Simha–Boyer constant of 0.113 for the product $T_g\Delta\alpha$ (where $\Delta\alpha$ is the difference in the volume expansion coefficient above and below T_g), the unoccupied volumes at T_g and the flex energy differences for the syndiotactic and isotactic poly(methyl methacrylates) were calculated. The above postulates imply that the configuration-induced difference in T_g in the poly(alkyl methacrylates) should be constant. This appears to be approximately true, but cannot be properly verified as yet because the completely syndiotactic polymers have not been prepared.

Since the development of techniques for the synthesis of stereoregular vinyl polymers, there has been interest in studying the effect of steric configuration on the physical and mechanical properties of these substances. In the present paper we wish first to draw attention to some correlations of the effect of molecular structure and configuration on the glass transition temperatures, T_g, of certain classes of such polymers, second to provide a theoretical basis for these observations, and third to attempt quantitative predictions