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Bimodal Distribution of Relaxational Modes for the Helix-Coil Transition in Poly(oxymethylene)

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ABSTRACT: The helix-coil transition in poly(oxymethylene) has been investigated by using the recently developed dynamic rotational isomeric state (DRIS) model and the related matrix multiplication technique. The conditional probability $P_\tau(\mathrm{h/h})$ that a chain originally in the perfect helical form will preserve its state unchanged at a later time τ is evaluated for various chain lengths and temperatures. The transition to the coiled structure in an originally fully ordered helix is found to exhibit a bimodal relaxation, indicated by a plateau in the time decay curves of the conditional probabilities, before restoration of equilibrium distribution. This intermediate quasi-steady state preceding full relaxation is attributed to an equilibrium between perfect helices and chains possessing a single defect in the form of a trans bond, interrupting sequences of gauche bonds of the same sign.

I. Introduction

Poly(oxymethylene) (POM) chains present interesting configurational properties manifested by their strong tendency to form helical sequences.[1] POM may be considered as a prototype of macromolecules in which the most probable rotational isomeric state taken on by skeletal bonds is the gauche state, in contrast to the widely studied polyethylene chains where the trans state is preferred. From experimental evidence and semiempirical energetic considerations, it is established that, in POM, the marked preference for the gauche state, supplemented by the highly repulsive second-order interactions precluding the occurrence at successive bonds of gauche states of opposite sign, leads to the propagation of either left-handed or right-handed helical forms over several units along the chain. The symmetry of the rotation potential guarantees that helices of both handedness occur with equal probability.

Recently, the helix-coil coexistence in POM has been investigated by Monte Carlo simulations based on the rotational isomeric state formalism.[2,3] Accordingly, the distribution function for the end-to-end distance in relatively short chains exhibits a distinct bimodality, which becomes particularly pronounced as the temperature is lowered. This feature is attributed to the existence of a helix and coillike state, in parallel with Nagai's analytical work[4] on helical sequence distribution in finite polypeptide chains.

Clearly, those studies rely on equilibrium considerations, and, to our knowledge, no theoretical investigation of the time dependence of helix-coil transitions in POM chains has been performed so far. The relatively simple chemical structure and the striking configurational properties of that chain at equilibrium are most inviting for a theoretical analysis of its conformational stochastics. The recently developed dynamic rotational isomeric state (DRIS) model,[5,6] originally introduced by Jernigan,[7] is readily amenable to such a treatment. The DRIS model presents two main advantages for this analysis: First, it permits the incorporation of real chain structural and conformational characteristics, which has proven to successfully account for the specific equilibrium properties of individual chains, into the treatment of chain dynamics. Second, the matrix multiplication scheme employed therein is a very efficient and convenient method readily adaptable to various chains and dynamic properties.[8,9] Thus, the purpose of the present work is to explore the time dependence of the passage from helical to disordered structure in POM chains through the use of the DRIS formalism. This analysis is expected to assess the applicability and the limitations of the DRIS model in relation to a definitely distinct class of polymeric chains, on the one hand, and to furnish some insights into the dynamics of helix-coil transitions, on the other.

A brief recapitulation of the DRIS formalism will be presented in the next section, together with its application to the phenomenon of helix-coil transitions in POM. Calculations will be given in the third section, which will then be succeeded by the discussion and concluding remarks.

II. Model and Assumptions

Following the basic postulates underlying the rotational isomeric state model of equilibrium statistics, for a chain of N bonds, a given configuration $\{\Phi\}$ is characterized by a set $\{\alpha\beta\gamma\delta...\}$ of $N-2$ rotational isomeric states corresponding to each internal skeletal bond. The conformational dynamics treated in the present work will refer to transitions of the type $\{\Phi\}\rightarrow\{\Phi\}'$. Other degrees of freedom, such as bond length oscillations and/or bond angle vibrations, will not be considered inasmuch as their contribution to relaxation in POM is of minor effect compared to the much softer modes associated with bond torsional mobility. Thus for the case of ν isomeric states accessible to each of the $N-2$ internal bonds, an ensemble of $\nu^{2(N-2)}$ transitions is treated. Mean dynamic properties associated with conformational transitions are evaluated by assigning a stochastic weight $\Omega_\tau[\{\Phi\};\{\Phi\}']$ to each specific transition occurring at time τ. On the basis of bond interdependence restricted to first neighbors along the chain, as in conventional Markov chains, $\Omega_\tau[\{\Phi\};\{\Phi\}']$ is given by

$$\Omega_\tau[\{\Phi\};\{\Phi\}'] = \prod_{i=2}^{N-1} \upsilon_i(\alpha\beta;\alpha'\beta') \tag{1}$$

where $\upsilon_i(\alpha\beta;\alpha'\beta')$ represents the stochastic weight corresponding to the transition $\alpha\beta \rightarrow \alpha'\beta'$ effectuated at time τ by the pairs of bonds $(i-1, i)$, each skeletal bond being indexed from 1 to N. $\upsilon_i(\alpha\beta;\alpha'\beta')$ may be determined from

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time-dependent probabilities according to

$$\upsilon_i(\alpha\beta;\alpha'\beta') = p_i(\alpha\beta;\alpha'\beta')/p_{i-1}(\alpha;\alpha') \qquad (2)$$

Here the symbol $p_i(\alpha\beta\gamma...;\alpha'\beta'\gamma'...)$, in general, indicates the time-delayed probability of the joint occurrence of isomeric states $\{\alpha\beta\gamma...\}$ and $\{\alpha'\beta'\gamma'...\}$, within a time interval τ, for the group of bonds $(i, i-1, i-2, ...)$. Following the approach recently developed,[5-7] $p_i(\alpha\beta;\alpha'\beta')$ is found from

$$p_i(\alpha\beta;\alpha'\beta') = c_i(\alpha'\beta'/\alpha\beta)p_i^\circ(\alpha\beta) \qquad (3)$$

where $p_i^\circ(\alpha\beta)$ is the equilibrium probability of state $\{\alpha\beta\}$ for bonds $(i-1, i)$ directly determined from the Boltzmann weight of the corresponding state in the ensemble of ν^2 isomeric pairs, and the conditional probability $c_i(\alpha'\beta'/\alpha\beta)$ for the indicated transition is an element of the $\nu^2 \times \nu^2$ transition probability matrix $\mathbf{C}_i(\tau)$ for the interdependent pairs of bonds $(i-1, i)$. The latter reads[5-7]

$$\mathbf{C}_i(\tau) = \exp\{-\mathbf{A}_i\tau\} = \mathbf{B}_i \exp\{-\mathbf{\Lambda}_i\tau\}\mathbf{B}_i^{-1} \qquad (4)$$

Here $\mathbf{A}_i$ is the transition rate matrix governing the kinetics of pair transitions, and $\mathbf{B}_i$ and Λ_i are the respective matrices of eigenvectors and eigenvalues resulting from the diagonalization $\mathbf{A}_i = \mathbf{B}_i\mathbf{\Lambda}_i\mathbf{B}_i^{-1}$ of $\mathbf{A}_i$. Kramers' type expressions are adopted for the rate constants in $\mathbf{A}_i$ with the activation energies therein estimated from two-dimensional conformational energy maps constructed as a function of adjacent bond torsional angles. The front factor in the rate constant expressions reflects the viscous resistance opposing the motion. In previous work, either a mean-field approach based on an inverse linear proportionality on effective friction coefficient, regardless of the size and type of moving unit,[5-7] or a more refined treatment of viscous drag considering the dependence on the size of the moving unit accompanying a given bond rotation[10] has been adopted. Detailed calculations based on the second approach demonstrate that the so-called "size effect" has the consequence of shifting the relaxation spectrum to lower frequency ranges without significant alteration of the shape of the distribution. In the present work we will adopt the former approach inasmuch as our immediate concern is the qualitative understanding of the origin and mechanism of relaxation in chains undergoing helix–coil transition phenomenon, which is inherently due to specific structural and conformational characteristics, irrespective of the retarding or perturbing effect of frictional resistance.

The summation of the stochastic weights $\Omega_\tau[\{\Phi\};\{\Phi\}']$ over all initial and final configurations leads to the time-dependent partition function $Z(\tau)$

$$Z(\tau) = \sum_{\{\Phi\}}\sum_{\{\Phi\}'}\Omega_\tau[\{\Phi\};\{\Phi\}'] \qquad (5)$$

which normalizes the stochastic weights to yield the time-dependent joint probabilities $\mathbf{P}_\tau[\{\Phi\};\{\Phi\}']$ of occurrence of configurations $\{\Phi\}$ and $\{\Phi\}'$ with a time delay of τ, as

$$\mathbf{P}_\tau[\{\Phi\};\{\Phi\}'] = \Omega_\tau[\{\Phi\};\{\Phi\}']/Z(\tau) \qquad (6)$$

A convenient mathematical method of evaluating $Z(\tau)$ is the matrix multiplication scheme developed[8] as an extension of the equivalent methods of the linear Ising model. Accordingly, stochastic weight matrices $\mathbf{V}_i(\tau)$ of the form

$$\mathbf{V}_2(\tau) = \begin{bmatrix} p_2(\zeta;\zeta') & 0 & 0 & 0 \\ 0 & p_2(\zeta;\eta') & 0 & 0 \\ 0 & 0 & p_2(\eta;\zeta') & 0 \\ 0 & 0 & 0 & p_2(\eta;\eta') \end{bmatrix} \qquad (7)$$

and

$$\mathbf{V}_i(\tau) = \begin{bmatrix} \upsilon_i(\zeta\zeta;\zeta'\zeta') & \upsilon_i(\zeta\zeta;\zeta'\eta') & \upsilon_i(\zeta\eta;\zeta'\zeta') & \upsilon_i(\zeta\eta;\zeta'\eta') \\ \upsilon_i(\zeta\zeta;\eta'\zeta') & \upsilon_i(\zeta\zeta;\eta'\eta') & \upsilon_i(\zeta\eta;\eta'\zeta') & \upsilon_i(\zeta\eta;\eta'\eta') \\ \upsilon_i(\eta\zeta;\zeta'\zeta') & \upsilon_i(\eta\zeta;\zeta'\eta') & \upsilon_i(\eta\eta;\zeta'\zeta') & \upsilon_i(\eta\eta;\zeta'\eta') \\ \upsilon_i(\eta\zeta;\eta'\zeta') & \upsilon_i(\eta\zeta;\eta'\eta') & \upsilon_i(\eta\eta;\eta'\zeta') & \upsilon_i(\eta\eta;\eta'\eta') \end{bmatrix} \qquad (8)$$

for $3 \le i \le N-1$ are defined[8,9] for the simplest case of two states ζ and η accessible to each bond. Those matrices are combined following the scheme

$$Z(\tau) = \mathbf{J}^{\mathrm{T}}[\sum_{i=2}^{N-1}\mathbf{V}_i(\tau)]\mathbf{J} \qquad (9)$$

where $\mathbf{J} \equiv$ col (1, 1, ..., 1), $\mathbf{J}^{\mathrm{T}} \equiv$ row (1, 1, ..., 1). The organization of the elements of $\mathbf{V}_i(\tau)$ according to eqs 7 and 8 ensures the suitable juxtaposition of required terms in the serial multiplication above. It is understood that, for POM in which three states trans (t), gauche$^+$ (g$^+$), and gauche$^-$ (g$^-$) are accessible to each bond,[1] stochastic weight matrices and row or column vectors of order $\nu^2 = 9$ are adopted. The extension of eqs 7 and 8 to this case is straightforward.

It should be noted that $Z(\tau)$ equates to unity, provided that $p_{i-1}(\alpha;\alpha')$ in eq 2 is replaced by[5]

$$p_{i-1}(\alpha;\alpha') = \sum_{\zeta}\sum_{\zeta'}p_i(\alpha\zeta;\alpha'\zeta') \qquad (10)$$

The summations in eq 10 are performed over all initial (ζ) and final (ζ') states assumed by bond i. Such an equality in terms of time-delayed 1-bond and 2-bond probabilities is reminiscent of the relationship between the respective singlet and doublet equilibrium probabilities, and the resulting serial multiplication in eq 2 may be viewed as an extension of the equilibrium doublet closure approximation[11] to time-dependent probabilities. Alternately, $p_{i-1}(\alpha;\alpha')$ at a given time may be evaluated from the diagonalization of the $\nu \times \nu$ transition rate matrix corresponding to single *independent* bonds, following the scheme described above (for the case of interdependent pairs), by eqs 3 and 4. In this case, $Z(\tau) \neq 1$ and the deviation increases with the strength of secondary interactions responsible for neighbor dependence. Clearly, for the particular case of chains subject to independent bond rotational potentials, both approaches yield $Z(\tau) = 1$, as the identity $p_i(\alpha\beta;\alpha'\beta') = p_{i-1}(\alpha;\alpha')\, p_i(\beta;\beta')$ implies.

The transition of interest within the framework of the present study will be the disruption of the helical order as a function of time. In relatively short chains as those treated below, the helix structure embodies almost the whole of the chain as demonstrated by the recent probability distribution analysis of the size of helical sequence: The ordered state is predicted to occur at Y_g = number of consecutive gauche bonds = 38 for POM chains of 40 bonds.[3] Relying on this feature, we will confine our attention to the time evolution of an originally fully ordered configuration. More precisely, in terms of the mathematical notation introduced above, we will investigate the time decay of $\mathbf{P}_\tau[\{\Phi\}_h;\{\Phi\}_h]$ where $\{\Phi\}_h$ stands for a sequence of all g$^+$ and/or g$^-$ states assumed by the $N-2$ internal bonds of POM. Let us suppose that we consider one type of chirality, say $\{\Phi\}_h = \{g^+g^+g^+...g^+\}$, for instance. Then $\mathbf{P}_\tau[\{\Phi\}_h;\{\Phi\}_h]$ reads

$$\mathbf{P}_\tau[\{\Phi\}_h;\{\Phi\}_h] = Z(\tau)^{-1}\mathbf{J}^{\mathrm{T}}[\sum_{i=2}^{N-1}\mathbf{V}_i^*(\tau)]\mathbf{J} \qquad (11)$$

where the asterisk of $\mathbf{V}_i^*(\tau)$ indicates that, in the corresponding stochastic weight matrix, all elements are equated to zero except for the element $v_i(g^+g^+;g^+g^+)$, which corresponds to the joint configuration under study. Naturally, $\mathbf{P}_\tau[(\Phi)_h;\{\Phi\}_h]$ decays from the equilibrium probability $\mathbf{P}_0\{\Phi\}_h$ of the ordered structure to $(\mathbf{P}_0\{\Phi\}_h)^2$ at long times. For stationary processes where the transition rate matrix is constructed on the basis of the principle of detailed balance, the probability of a given configuration remains constant and equal to its equilibrium value, for all times, i.e., $\mathbf{P}_0\{\Phi\}_h = \mathbf{P}_\tau\{\Phi\}_h = \mathbf{P}_\infty\{\Phi\}_h$.

Inasmuch as our objective is to concentrate on the dynamic aspects of the relaxation phenomenon, the initial and final asymptotic values, which are dictated by equilibrium statistics, will be excluded from consideration upon normalization of the time decay curves in the range [0, 1]. For brevity we will indicate the helical configuration of either chirality by the symbol "h" and the corresponding normalized transition probability $\overline{P_\tau(h/h)}$ will be found from

$$\overline{P_\tau(h/h)} = [\mathbf{P}_\tau[\{\Phi\}_h;\{\Phi\}_h] - \mathbf{P}_\infty[\{\Phi\}_h;\{\Phi\}_h]]/[\mathbf{P}_0[\{\Phi\}_h;\{\Phi\}_h] - \mathbf{P}_\infty[\{\Phi\}_h;\{\Phi\}_h]] = [\mathbf{P}_\tau[\{\Phi\}_h;\{\Phi\}_h] - \mathbf{P}_0\{\Phi\}_h^{\,2}]/[\mathbf{P}_0\{\Phi\}_h - \mathbf{P}_0\{\Phi\}_h^{\,2}] \quad (12)$$

Here the overbar indicates that the transition probability is normalized. It will be omitted when the transition probability is not normalized; i.e., it simply equates to

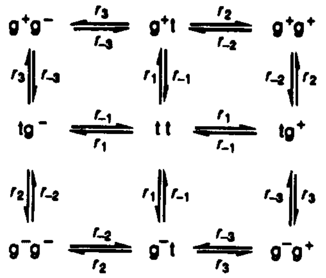
$$P_\tau(h/h) = \mathbf{P}_\tau[\{\Phi\}_h;\{\Phi\}_h]/\mathbf{P}_0[\{\Phi\}_h] \quad (13)$$

III. Calculations

Kinetic Scheme and Energy Parameters. As may be deduced from the above presentation, the assignment of stochastic weights to specific types of rotational transitions relies on the construction of a representative transition rate matrix governing pairwise interdependent conformational kinetics. In previous work, two-dimensional conformational energy maps has been examined to establish the type and rates of rotations accessible to interdependent bonds, in polyethylene,[5] poly(ethylene oxide),[6] and various polyesters.[12] In general, molecular mechanics treatments, coupled with related experimental findings, furnish sufficient information on the stable isomeric states and their relative *equilibrium* probabilities of occurrence. An analogous approach may be undertaken for the estimation of the probable isomeric transitions and their relative rates; i.e., the heights of the saddles between isomeric minima may be estimated from molecular mechanics considerations and if necessary readjusted to achieve best agreement with experiments.

For poly(oxyalkanes), it is known that there is some discrepancy between the predictions of conventional energetic considerations and the energy parameters best fitting experimental measurements.[1,13] In this respect, the gauche states are asserted to be subject to nearest-neighbor interactions much more favorable than those theoretically deduced. Bearing in mind that a realistic estimation of isomeric minima depth and barrier heights in POM naturally suffer from the same limitations, the following values were adopted in the present work: Using conventional notation for energy parameters,[1] we take $E_\sigma = -1.4$ kcal/mol, $E_\omega = 1.7$ kcal/mol, and $E_\psi = 0$. The activation energies E_i associated with the rate constants r_i (i = 1–3) of the kinetic Scheme I are taken as $E_1 = E_2 = 3.5$ kcal/mol and $E_3 = 4.3$ kcal/mol. Those values are selected to be of comparable magnitude to those previously adopted for PE[5] and poly(oxyethylene),[6] as the similarities in the chemical and geometrical structures imply. The activation energies for the reverse transitions associated with r_{-i} (i = 1–3) are automatically fixed from the knowledge of isomeric minima depths. The preexponential factor in the rate constants is taken as 0.277/ps, as in previous works.[5,10] We note that the most important energy parameter E_σ, which leads to an overwhelmingly large population of gauche bonds, is valid for a chain in the unperturbed state[2,3] and is susceptible to changes in the presence of specific solvent effects. POM is formed of two distinct types of bond pairs, (CO, OC) and (OC, CO), differing mainly in the secondary interactions prevailing in the g^+g^- state, which assumes the respective values $E_\omega = \infty$ and 1.5 kcal/mol. Present calculations indicate, however, that their conformational behavior may be satisfactorily accounted for by adopting the representative value $E_\omega = 1.7$ kcal/mol, for both pairs. Nevertheless the theory presented above is readily applicable to a chain with several distinct types of consecutive bond pairs, inasmuch as bond serial number is explicitly accounted for, in eqs 8–11.

Scheme I



Transition Probabilities. The transition rate matrix $\mathbf{A}_i$ associated with the above kinetic scheme is explicitly given in ref 5. This matrix consists, as usual, of negative diagonal elements accounting for the escape from a given state and positive off-diagonal terms for the interstate passages such that each column sums up to zero. Similarity transformation of $\mathbf{A}_i$ followed by the application of eqs 2–4 leads to the required elements $v_i(\alpha\beta;\alpha'\beta')$ of the stochastic weight matrices. $p_{i-1}(\alpha;\alpha')$ in eq 2 is found with the use of eq 10. This approach is preferred over the alternative adoption of independent bond joint probabilities, due to the fact that the former approximation of evaluating singlet time-delayed probabilities on the basis of the doublet time-delayed probabilities allows for the close preservation of the Boltzmann distribution of equilibrium configurational probabilities during the whole time span of the stochastic process of conformational transitions. The resulting stochastic weight matrices are combined in eqs 11 and 12 to yield the desired quantity $\overline{P_\tau(h/h)}$, which expresses the normalized probability that an initially fully ordered structure will conserve its state unchanged at a later time τ. Repeating the same procedure for various times yields the time dependence of the transition probabilities.

Results. Calculations have been performed for various chain lengths, over a wide range of temperature. Equilibrium considerations reveal that oligomeric POM chains with $20 \leq N \leq 80$ exhibit a transition from helical to coil-like state at about 250 K. The transition becomes sharper and shifts to lower temperature, as the chain length increases. This prediction follows from the sharp decrease in the equilibrium fractional helicity in chains investigated around those conditions.[3] Accordingly, we confined our attention to the same region for the possible occurrence of some abrupt change in conformational dynamics accompanying the change in equilibrium probabilities. That such a change has to take place is inherently implied by the principle of detailed balance. The instantaneous

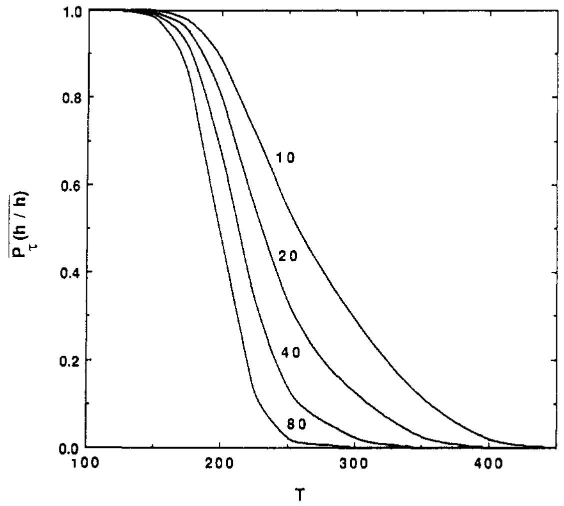


Figure 1. Instantaneous values of the normalized transition probabilities $\overline{P_\tau(h/h)}$, evaluated at τ = 10 ns, as a function of temperature. The number of bonds in each POM chain is noted for each curve.

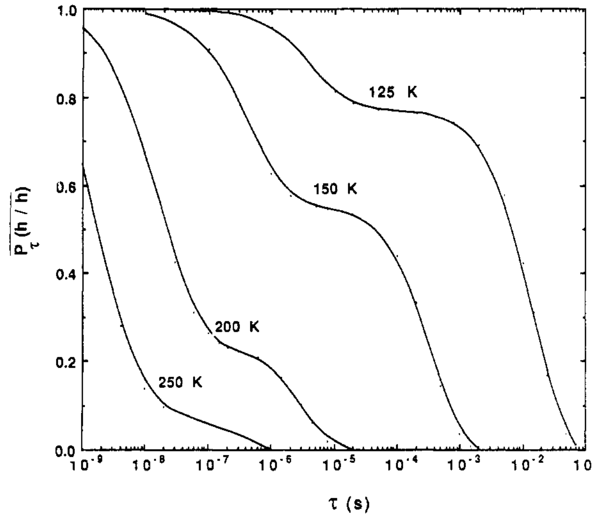


Figure 2. Time decay of $\overline{P_\tau(h/h)}$ for a POM chain with N = 40, at the four temperatures identified for each curve.

$\overline{P_\tau(h/h)}$ values at τ = 10 ns have been plotted in Figure 1 as a function of temperature, for the four cases of N = 10, 20, 40, and 80. The striking similarity between the curves in Figure 1 and the curves of the equivalent equilibrium probabilities in Curro et al.[3] is in fact in parallel with the expected behavior. Such a close correlation between chain statistics and dynamics was also emphasized in previous work[9] where the familiar even-odd end effect for conformational probabilities was observed from both standpoints.

In general, the decay of $\overline{P_\tau(h/h)}$ with time is found to be spread over a time interval that may be quite long at low temperature. In order to gain a better understanding of the mechanism of conformational relaxation in this specific direction, we choose to plot $\overline{P_\tau(h/h)}$ against the logarithm of time. Such an approach, common to treatments of viscoelastic properties,[14] is found to yield interesting results in the present study. Figure 2 displays the variation of $\overline{P_\tau(h/h)}$ with log τ for the case of N = 40. Curves are drawn for T = 125, 150, 200, and 250 K. At each temperature there is a relatively fast transition to some intermediate quasi-steady state, followed by the full relaxation at long times. The generation of the intermediate quasi-steady state is particularly apparent at low temperatures.

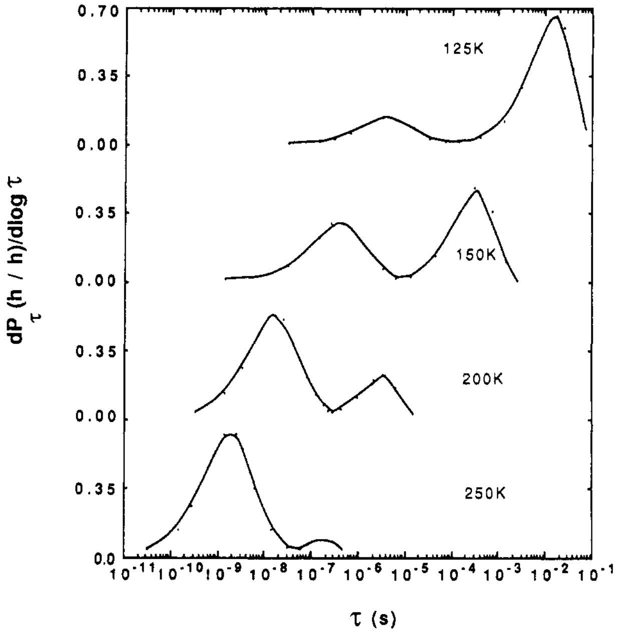


Figure 3. Relaxation spectra at four temperatures for the POM with N = 40. The ordinate is shifted by $d\overline{P_\tau(h/h)}/d\log\tau = 0.7$ for successive temperatures.

The shape of the curves in Figure 2 is reminiscent of a typical biexponential relaxation phenomenon: two modes with relaxation times located at the two inflection points of a given curve govern its time decay. In the present case, the frequency spectrum of relaxational modes contributing to the investigated conformational transition may in fact be obtained from the slope of the transition probability curves. Differentiation of the curves in Figure 2 with respect to log τ yields the family of curves depicted in Figure 3. The bimodal character of the relaxation spectrum is clearly apparent from those plots. In all cases, the disruption of helical order occurs with the contribution of two distinct types of modes, with mean frequencies separated by about 2–3 orders of magnitude.

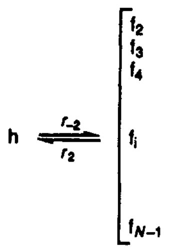
It is observed that the effect of an increase in temperature is 2-fold: First, a general shift to lower times (or higher frequencies) is brought about. Second, the relative contribution of the two types of relaxational modes is smoothly inverted. Thus the slowest mode is the one almost fully dominating relaxation at lower temperature whereas at higher T its contribution almost vanishes, as follows from the examination of the curves for T = 125 and 250 K, respectively.

IV. Discussion and Conclusions

In the present work, the DRIS model has been employed to explore the dynamics of the helix–coil transition in POM. A recent helical size distribution study confirms that the ordered form is perpetuated over several units without interruption and that in oligomeric chains it embodies the whole molecule.[3] Accordingly, helix–coil transition is identified with the disruption of helical order in an originally fully ordered chain via all possible conformational transitions. Thus, we consider the stochastic process of relaxation of a set of fully ordered chains to the equilibrium distribution of various configurations.

Although the above description of the helix–coil transition may seem similar to the classical two-state model for the passage between ordered and disordered states, the significant departure is clearly apparent upon exam-

Scheme II



ination of the resulting probability decay curves as a function of time. In contrast to a single-exponential decay characteristic of a simple two-state model, the disruption of helical order is found to result from the contribution of two distinct relaxation regimes, with mean correlation times differing by about 2 or 3 orders of magnitude. This feature is portrayed in Figure 3. It should be noted that, in the stochastic process under study, a large number and variety of pathways are involved so that the relaxation is definitely multiexponential. However, the aggregation of the modes about two centers is particular to POM.

The present bimodal character of the relaxational spectrum deserves special attention. For a better understanding of the origin of the plateau observed in the transition probabilities depicted in Figure 2, we considered the types of conformational transitions possibly responsible for the establishment of a quasi-steady state before full relaxation. The fact that the plateau becomes more pronounced at lower temperature suggests that it results from a metastable equilibrium between *low-energy conformations*. Inasmuch as those conformations become highly probable at low T, the dynamic behavior is necessarily predominated by the passages between them. Clearly, helices are the most probable conformations over a wide range of temperature. They are succeeded by chains including a single trans defect interrupting gauche bonds of the same sign. If we confine our attention to the group of bonds of a given chirality, there are mainly $N - 2$ conformations with a single trans bond, competing with the perfect helical structure. All of the other conformations, which may be roughly classified as coils, are of secondary importance, at low T. The plateau in the transition probabilities may thus be attributed to the equilibrium between those most probable conformations.

For a verification of this hypothesis, we consider the $N - 2$ transitions of the form in Scheme II between a helix h of a given chirality, say $\{g^+g^+g^+g...g^+\}$ and the conformations f_i in which all bonds are in the state g^+ except for the ith bond, which is in the trans state. From statistical mechanical considerations, for a system where h and f_i ($i = 2, N - 1$) are the only accessible configurations, the respective equilibrium probabilities equate to

$$P_0^*(\mathrm{h}) = \frac{\sigma}{\sigma + (N-2)}$$

$$P_0^*(f_i) = \frac{1 - P_0^*(\mathrm{h})}{N-2} \qquad (14)$$

where $\sigma = \exp\{-E_\sigma/RT\}$ and the asterisk is used to distinguish the above equilibrium probabilities that are prevailing in the reduced set of configurations from those of the whole ensemble of ν^{N-2} configurations. The time evolution of the transition probability $P^*(\mathrm{h/h})$, for that particular case, is given by

$$P_\tau^*(\mathrm{h/h}) = P_0^*(\mathrm{h}) + [1 - P_0^*(\mathrm{h})] \exp\{-[r_2 + (N-2)r_{-2}]\tau\} \qquad (15)$$

The resulting time decay curves for $T = 125$, 150, and 175 K are shown in Figure 4, by the curves identified with the label (b). For comparison the $P(\mathrm{h/h})$ curves obtained from eq 15 are drawn in the same graph and indicated by the label (a). It should be noted that the $P(\mathrm{h/h})$ curves displayed in Figure 4 are not normalized and converge asymptotically to the equilibrium probability $P_0(\mathrm{h})$ of helices of a given chirality. Otherwise, they are identical with $P_\tau(\mathrm{h/h})$ shown in Figure 2. From the examination of the two groups of curves in Figure 4, it is seen that the mechanism described by Scheme II is definitely responsible for the occurrence of the plateau in the transition probabilities. This is particularly apparent at $T = 125$ K and explains to a good approximation the evolution to the quasi-steady intermediate state at 150 and 175 K. As the temperature increases, Scheme II and the corresponding eq 14 are no longer applicable due to the increased population of chains with coiled structure that compete more effectively with the h and f_i states to give rise to full relaxation following some lowering of the plateau.

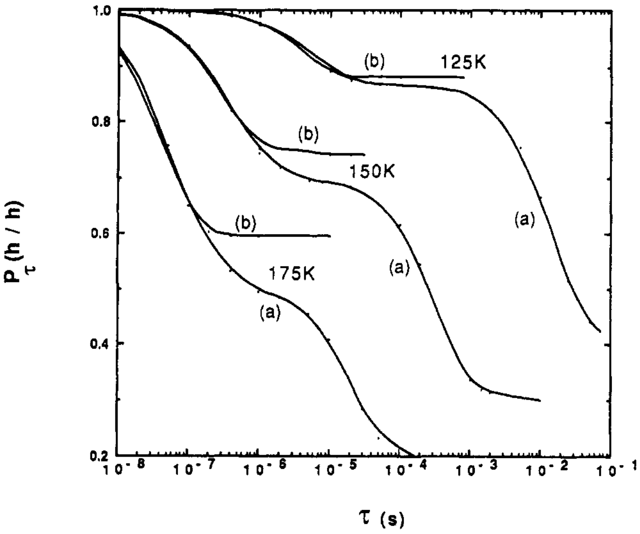


Figure 4. Time decay of transition probabilities (a) $P_\tau(\mathrm{h/h})$ given by eq 13, for the whole set of conformations and (b) $P_\tau^*(\mathrm{h/h})$ given by eq 15, for the reduced set of the most probable conformations. The comparison confirms the validity of the simplified Scheme II for interpreting the intermediate plateau. The curves are drawn for the three indicated temperatures.

It is noted that in the helix–coil transition of relatively short polypeptide chains, Cerf draws attention to such sequential processes where the transition occurs in two or more steps.[15] As an example, the well-defined sequence of steps experimentally observed in the base pairing of oligonucleotides is explained with the aid of a population analysis giving the relative fractions of the helix species present at equilibrium,[16] in parallel with the present study.

A dynamic property that may be measured by dielectric and/or spectroscopic techniques is the orientational autocorrelation function. The bimodal relaxation mechanism is directly reflected upon the time decay of the internal orientational autocorrelation function $\langle \mathbf{m}(0)\cdot\mathbf{m}(\tau)\rangle$ of a vectorial property $\mathbf{m}$ rigidly moving with the chain. The latter may be readily evaluated following the procedure recently outlined.[9] Figure 5 displays the decay of $\langle \mathbf{m}(0)\cdot\mathbf{m}(\tau)\rangle$ with time, for the particular case of the vector $\mathbf{m}$ affixed along the x, y, and z components of the

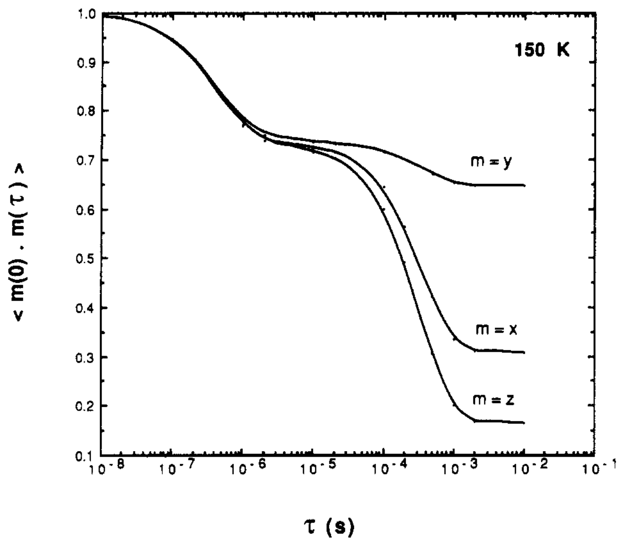


Figure 5. Time decay of the internal orientational autocorrelation function $\langle \mathbf{m}(0)\cdot\mathbf{m}(\tau)\rangle$ of a vector **m** along the x, y, and z components of the conventional local coordinate system[1] associated with the central bond in a POM chain with $N = 40$, at 150 K, expressed in the frame of the first bond of the oligomer.

conventional local coordinate system[1] of the central bond in a POM chain with $N = 40$, at 150 K, expressed in the frame of the first bond of the oligomer.

It should be mentioned that we focused our attention on the interrelation between the equilibrium conformational statistics and the relaxational dynamics of oligomeric POM chains. In addition to specific conformational characteristics, it is known that chain dynamics is affected by two additional factors, the viscous drag and the chain connectivity extending beyond first neighbors. Both of them are responsible for the localization of the motion through some cooperative process. The latter becomes particularly important in the case of relatively shallow potential energy surfaces where the distortion of chain geometry from isomeric minima is easily afforded whereas diffusion is the rate-controlling mechanism. However, in POM oligomers we have the opposite situation, i.e., strong preference for specific states as apparent from substantial differences in isomeric minima vs rather short chains to be subjected to significant resistance due to either friction or connected tails. Thus, we deliberately choose to use a mean-field approach to account for the effective friction coefficient, and we neglect the perturbations in relaxation paths caused by those external and/or large-scale effects, assuming that hopping the saddle points in the configurational space is the rate-determining step. We note, however, that, in a detailed comparative study of relaxation of different chain lengths, a practical approach introduced by Paul and Mazo,[17] and applied to the helix–coil transition,[18] could be to assign position-dependent friction coefficients to each bond along the chain, thus reflecting the reduced mobility of interior bonds and longer chains. Such a refinement may be easily incorporated into the present calculation method since bond serial index is kept in the formulation. The latter may be of interest in the future, provided that experimental evidence invites such a quantitative analysis.

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