(40) (a) Williams, G.; Watts, D. C. *Trans. Faraday Soc.* **1970**, *66*, 80. (b) Shlesinger, M. F.; Montroll, E. W. *Proc. Natl. Acad. Sci. U.S.A.* **1984**, *81*, 1280.

(41) Kovacs, A. J.; Hutchinson, J. M.; Aklonis, J. J. In *The Structure of Non-Crystalline Materials*; Gaskell, P. H., Ed.; Taylor and Francis: London, 1977.

(42) O'Reilly, J. M.; Bair, H. E.; Karasz, F. E. *Macromolecules* **1982**, *15*, 1083.

(43) O'Reilly, J. M.; Connelly, R. *Thermochim. Acta* **1985**, *86*, 231.

(44) Tribone, J. J., unpublished results.

(45) Plazek, D. J.; Ngai, K. L.; Rendell, R. W. *Polym. Eng. Sci.* **1984**, *24*, 1111.

(46) McCrum, N. G. *Polym. Commun.* **1984**, *25*, 2; *Polymer* **1984**, *25*, 309.

(47) Brawer, S. A. *J. Chem. Phys.* **1984**, *81*, 954.

(48) Karasz, F. E.; MacKnight, W. J. *Macromolecules* **1968**, *1*, 537.

(49) (a) Williams, M. L.; Landel, R. F.; Ferry, J. D. *J. Am. Chem. Soc.* **1955**, *77*, 3701. (b) Vogel, H. *Phys. Z.* **1921**, *22*, 645. Fulcher, G. S. *J. Am. Ceram. Soc.* **1925**, *8*, 339. Tammann, G.; Hesse, G. *Z. Anorg. Allg. Chem.* **1926**, *156*, 245. (c) Angell, C. A.; Smith, D. L. *J. Phys. Chem.* **1982**, *86*, 3845.

(50) Adam, G.; Gibbs, J. H. *J. Chem. Phys.* **1965**, *43*, 139.

(51) Scherer, G. W. *J. Am. Ceram. Soc.* **1984**, *67*, 504.

Effect of Finite Chain Length on the Helix/Coil Coexistence Behavior of Polymers: Poly(oxymethylene)†

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Received December 31, 1985

ABSTRACT: Monte Carlo calculations were performed on poly(oxymethylene) chains using the rotational isomeric state model. The end-to-end distribution function was found to exhibit bimodal behavior, characteristic of a helix/coil coexistence, over a range of temperature and chain length. The first-order gauche distribution (P_G) and the second-order gauche pair distribution (P_{GG}) did not show any bimodality. The sequence length distribution, however, did show pronounced bimodality. The transition-like behavior was found to become sharper and shifts to lower temperature with a logarithmic dependence on the chain length. Thus the helix/coil coexistence behavior is a finite chain effect, with the transition temperature approaching 0 K for the infinite system. As expected, an external force on the ends of the chain was found to shift the coexistence temperature to higher temperatures. These results can be understood by analogy with the one-dimensional Ising model.

Introduction

Poly(oxymethylene) (POM) is an interesting polymer because it is an example of a synthetic chain in which the gauche state has a significantly lower energy than the trans state. This energy difference, which is thought to be due to attractive interactions between CH_2 and O groups, is estimated to be −1.4 kcal/mol on the basis of semiempirical conformational energy calculations and dipole moment measurements.[1-4] The preference for gauche configurations, coupled with severe repulsive interactions for alternate gauche bonds of opposite sign, gives POM a strong tendency to form helical sequences.[1]

Distribution functions for POM chains were computed previously[5] from Monte Carlo simulations for rotational isomeric state chains. The tendency toward helix formation was manifested by a curious bimodal shape for the end-to-end distribution function. This "bimodality", which increases as the temperature is lowered, is suggestive of a helix/coil transition. Such a phenomenon cannot be a true phase transition, of course, since the rotational isomeric state model is a one-dimensional, Ising-like model,[6] for which no thermodynamic phase transition can exist at finite temperature. Rather it is a pseudo-first-order coexistence behavior which occurs due to finite size effects.

The purpose of the present investigation is to examine the configurational statistics of POM in more detail in order to gain a further understanding of this helix/coil coexistence behavior observed in the end-to-end distribution function. In addition, we have computed various internal sequence distributions for POM from computer simulations of rotational isomeric state chains. We also examine the influence of an external field on the end-to-end distribution function. In a broader context, the present study is representative of the variety of physical behavior that can occur in polymer chains of moderate length.

Monte Carlo Simulations

The Monte Carlo scheme here uses a modified Metropolis[7] algorithm to compute the average $\langle X \rangle$ of some observable variable X_i which depends on the chain configuration.[8] $\{\phi\}_i$ represents the set $\{\phi_1 ... \phi_N\}_i$ of possible rotational states (t, g^+, g^-) for a specific chain i of N repeat units. For a canonical ensemble, $\langle X \rangle$ takes the form

$$\langle X \rangle = \sum_i X_i \Omega_i / \sum_i \Omega_i \qquad (1)$$

where the subscript refers to a specific set of many possible configurations $\{\phi\}_i$. The coefficient Ω_i is the Boltzmann factor for the configuration i.

Using the conventional rotational isomeric state[1] formalism for POM, we can define two statistical weight matrices for a pair of bonds.

$$\mathbf{U}_a = \begin{pmatrix} 1 & \sigma & \sigma \\ 1 & \sigma & \sigma\omega_a \\ 1 & \sigma\omega_a & \sigma \end{pmatrix} \qquad (2a)$$

$$\mathbf{U}_b = \begin{pmatrix} 1 & \sigma & \sigma \\ 1 & \sigma & \sigma\omega_b \\ 1 & \sigma\omega_b & \sigma \end{pmatrix} \qquad (2b)$$

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† Supported by the U.S. Department of Energy under Contract No. DE-AC04-76DP00789 and the National Science Foundation (J.E.M.) through Grant DMR79-18903-03 (Polymers Program, Division of Materials Research).

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Rotational states are taken to occur at $\phi = 0, \pm 115°$ and are designated as trans and gauche +/−, respectively. In this notation, an a-bond pair is taken as the pair of bonds flanking an O atom in POM, whereas the b-bond pair flanks the CH_2 group. Using Flory's notation,[1] we employed the following energy parameters: $E_\sigma = -1.4$ kcal/mol, $E_{\omega_a} = \infty$, and $E_{\omega_b} = 1.5$ kcal/mol. The corresponding Boltzmann factors are defined as $\sigma = \exp(-E_\sigma/RT)$ etc. These parameters were chosen to be in agreement with the conformational energy calculations of Abe and Mark[3] and with dipole moment measurements on POM.[4] E_σ is the energy of having a gauche bond following a trans. The negative value reflects the fact that in POM, the gauche configuration is the preferred state. The E_ω's reflect the high energies associated with having a consecutive pair of gauche bonds of opposite sign. The weighting factor Ω_i for the ith chain configuration can then be calculated from the product of the individual factors in eq 2,

$$\Omega_i = \prod_k U_{\zeta n;k} \tag{3}$$

for the specific chain configuration $\{\phi\}_i$. $U_{\zeta n;k}$ refers to the appropriate matrix element for state ζ for ϕ_{k-1} and state n for bond angle ϕ_k. When k is odd the $\mathbf{U}_a$ matrix is used, whereas k even refers to the $\mathbf{U}_b$ matrix.

In the usual Metropolis scheme, each chain configuration i would be generated so that it was proportional to Ω_i. For convenience, in this paper, we instead generate the chains according to a normalized weighting factor P_i defined as

$$P_i = \prod_k U_{\zeta n;k} / \sum_n U_{\zeta n;k} \tag{4}$$

where each row in the $\mathbf{U}$ matrix is normalized to unity. This allows each chain to be generated sequentially by choosing random numbers defining the state of each bond from $i = 3$ to N. By convention, we take bonds 1 and 2 to be in the trans configurations. Thus each X_i needs to be multiplied by Ω_i/P_i in order to correct for the non-Boltzmann generation scheme. The relevant averages are then computed from the relation

$$\langle X \rangle = \sum_i X_i(\Omega_i/P_i) / \sum_i \Omega_i/P_i \tag{5}$$

As in the usual Metropolis Monte Carlo scheme, this method allows the preferential sampling of the lower energy configurations contributing to the Boltzmann average in eq 1.

In addition to the Monte Carlo calculations, an approximate analytic technique has been applied to calculate local, scalar distribution functions. The technique is based on the availability of the exact rotational isomeric state partition function[1] and a steepest descent approximation. The method is restricted to the calculation of one bond and two nearest-neighbor bond probability distributions. Closed-form expressions can be derived for arbitrary temperature, chain length, and energy parameters. As an example, the normalized gauche distribution function is given by

$$P_G(N_G) = \langle \sum_j \delta_{j,g\pm} \rangle \tag{6}$$

where the sum is over all bonds and the Kronecker delta $\delta_{j,g\pm}$ simply tests whether bond j is in the gauche state. By employing a continuum integral representation of the Kronecker delta, followed by a change of variables, eq 6 can be expressed as

$$P_G(N_g) = Z_N^{-1} \sigma^{N_g} \int_{-i\infty}^{+i\infty} \frac{dx}{i} \exp(xN_g) Z_N(\sigma = e^{-x}) \tag{7}$$

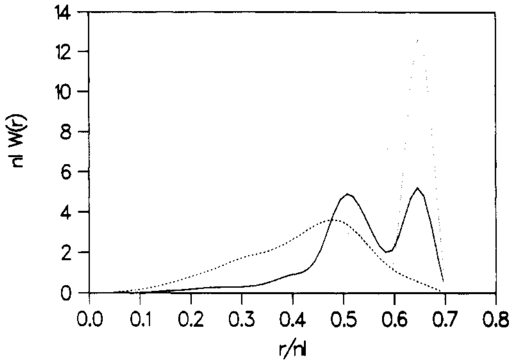

Figure 1. Monte Carlo generated end-to-end distribution function $W(r)$ for POM chains of 40 bonds at various temperatures: 300 K (dashed); 200 K (solid); 150 K (dotted). The area under the curves is normalized to unity. Note that the ordered-phase contribution increases as the temperature is lowered.

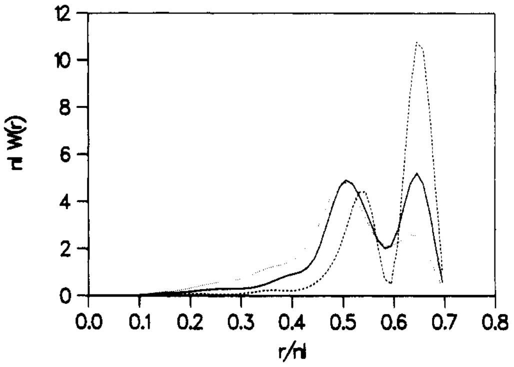

Figure 2. Monte Carlo generated end-to-end distribution function $W(r)$ for POM chains at $T = 200$ K for various chain lengths: $N = 20$ (dashed); $N = 40$ (solid); $N = 60$ (dotted). Note that the ordered-phase contribution increases as the chain length decreases.

where Z is the partition function and i is the imaginary unit. The above integral is of the Laplace inversion form and can be approximately evaluated via the method of steepest descents.[9] The result is a closed-form analytic formula which becomes increasingly accurate as the number of bonds gets larger. Analogous analytic results can be derived for the other one- and two-bond distribution functions. Detailed derivations will be presented elsewhere.[10]

End-to-End Distribution

The end-to-end distribution functions $W(r)$ were generated for POM chains[8] according to the above scheme. The range of r/nl from 0 to 1 was divided into intervals of 0.05 where n is the number of bonds of length l. The number of chains having end-to-end distances in the various intervals were averaged according to eq 5 to give a histogram of the distribution. A smooth curve was then drawn through the points using a cubic-spline, least-squares technique. The results are shown in Figure 1 for a chain of 40 units at various temperatures and in Figure 2 at various chain lengths.

It can be seen from Figure 1 that below 300 K, for a chain of 40 bonds, the end-to-end distribution W shows two distinct maxima. As the temperature is lowered, the peak at $r/nl \sim -0.65$ increases sharply. This corresponds to a 9_5 helix ($r/nl = 0.623$) as mentioned previously.[5] It can be seen from Figure 2 that as the chain length decreases at fixed temperature, the helical peak of the distribution also increases.

In previous studies[11,12] on poly(ethylene) (PE) and poly(dimethylsiloxane) (PDMS), no bimodality of this type was observed over the temperature and chain length range

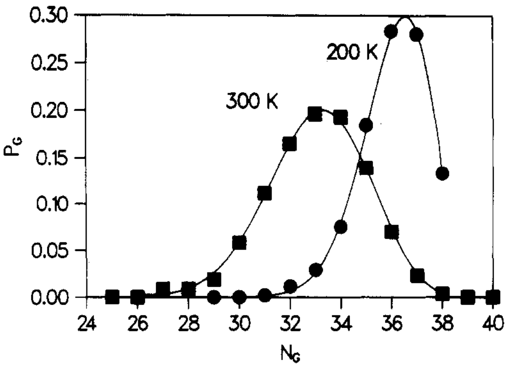

Figure 3. Probability P_G of having N_G gauche bonds of the same sign for a POM chain of 40 bonds. Points are from Monte Carlo calculations: 300 K (squares); 200 K (circles). Solid curves represent the steepest descents approximation. No bimodal behavior is observed. The ordered state occurs at N_G = 38.

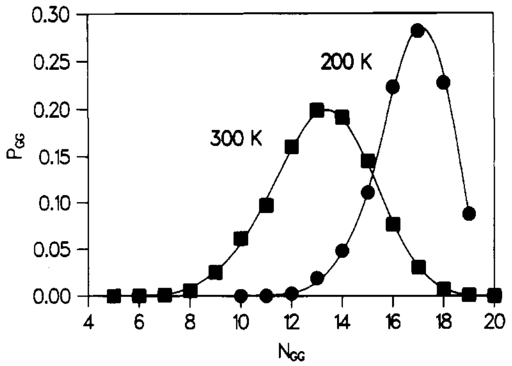

Figure 4. Probability P_{GG} for POM of having N_{GG} consecutive b-bond pairs with gauche states of the same sign. Points are from Monte Carlo calculations: 300 K (squares); 200 K (circles). Solid curves represent the steepest descents approximation. No bimodal behavior is observed. The ordered state occurs at N_{GG} = 19.

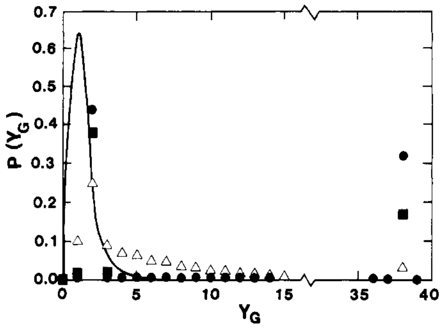

Figure 5. Monte Carlo generated probability $P(Y_G)$ of having Y_G consecutive gauche bonds of the same sign for a chain of 40 bonds. The points are for POM chains at various temperatures: 125 K (circles); 150 K (squares); 250 K (triangles). The solid curve is for a random chain of 40 bonds obtained from Monte Carlo simulation with zero energies. Note the pronounced bimodality as the temperature is lowered. The ordered state occurs at Y_G = 38.

studied. When these results were used to estimate the force–extension behavior of a PDMS network,[11,12] the force was a monotonically increasing function of the extension ratio. If the present results were used to predict the network behavior of a POM network of short chains, however, nonmonotonic behavior would be observed. Because the force is related to the derivative of the distribution function,[11] the force–extension curve would show a behavior reminiscent of the "van der Waals loops" seen in the *PVT* curves of gases.[13] More generally, the bimodal behavior of POM calculated here resembles a helix/coil transition. The transition, however, is not sharp as can be seen from Figures 1 and 2. Similar behavior is well-known in the case of polypeptides and nucleic acids[14] where the interaction is somewhat longer range. The present behavior of POM is analogous to the pseudo-first-order transition phenomenon that occurs for the magnetization in finite, one-dimensional, Ising-like spin models. In these cases short-range, nearest-neighbor interactions in finite chains can lead to coexistence type behavior between ordered and disordered phases.

Sequence Distributions

In addition to the end-to-end distribution, we also obtained various internal sequence distributions according to the Monte Carlo scheme outlined. Our purpose was twofold. First, the end-to-end distance is a long-range, three-dimensional vectorial property, whereas the internal sequence distributions are scalar, one-dimensional quantities that characterize short-range correlations. An interesting question is whether such internal probability distributions are also capable of exhibiting bimodality. Second, the internal sequence distributions are relevant to many experimental probes. Because they describe the local structure, properties such as the electronic absorption and vibrational spectra can be sensitive to the qualitative form of these distributions.

Figure 3 shows the probability P_G of having N_G gauche bonds of the same sign on a POM chain of 40 bonds. Likewise, Figure 4 shows the probability P_{GG} of having N_{GG} adjacent pairs of gauche b-bonds of the same sign. The points represent the Monte Carlo results, whereas the curves were obtained with the steepest descents approximation mentioned earlier. Excellent agreement between the Monte Carlo and the steepest descents calculations was obtained above 200 K.

Unlike the case of the end-to-end distribution, those internal gauche distributions do not show a bimodal shape. Instead, the curves merely shift smoothly to the ordered state as the temperature is lowered with subsequent narrowing. A range of rotational isomeric state parameters, besides those of POM, was also explored and in no case could we resolve more than a single peak in the P_G and P_{GG} distributions.

Quite different behavior is observed, however, from higher order or longer range sequence distributions. We define $P(Y_G)$ as the probability of having Y_G consecutive gauche bonds of the same sign on a chain. This is a collective distribution function in the sense that it probes correlations over all length scales. This is in contrast to the two gauche distributions considered above. We obtained this sequence length distribution function by determining the g^+ or g^- sequence lengths within each Monte Carlo generated chain. A given chain, of course, may have many gauche sequences of different lengths. The individual chain distributions were then averaged according to eq 5. This distribution function is shown in Figure 5 for POM at various temperatures. Figure 6 depicts the effect of chain length.

It can be seen from these figures that the sequence length distribution, $P(Y_G)$, shows a dramatic bimodality which clearly shows the existence of a helix and a coil-like state. (Similar behavior was previously found analytically by Nagai.[15]) As in the case of the end-to-end distribution, the sequence length distribution shows an increase in the ordered phase as the temperature or the chain length is decreased.

That the higher order distributions $P(Y_G)$ and $W(r)$ show bimodality while the local distributions do not is not that surprising. In all distributions, the helical peak is due to the highly favored energies at low temperatures. The

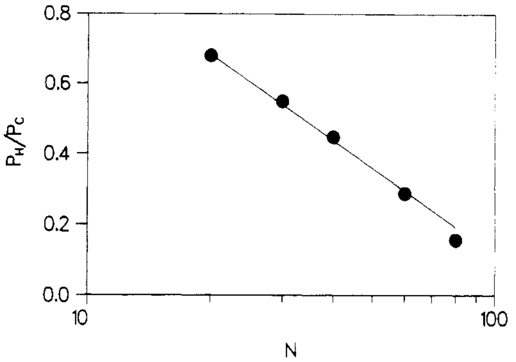

Figure 6. Ratio of the helix probability ($Y_G = 38$) to the coil probability ($Y_G = 2$) as a function of chain length N. The points are from Monte Carlo calculations of $P(Y_G)$ for POM chains at $T = 150$ K. Note the approximate logarithmic dependence of this ratio as a function of chain length.

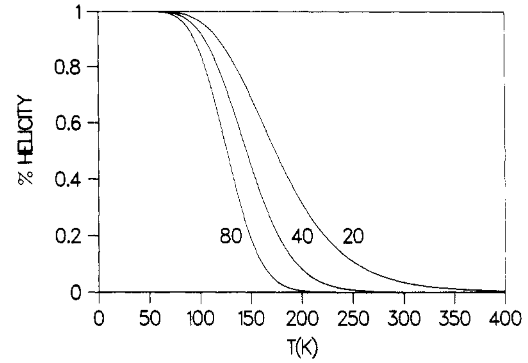

Figure 7. Percent helicity calculated from eq 8 in the text for various lengths of POM chains.

coil-like peak in the higher order distributions is due to the much higher entropy of the more disordered states. The entropy increase with disorder, however, is much less for the local distribution functions. In fact, the increase is too gradual to produce the second maximum.

Discussion

It can be shown that the rotational isomeric state model[1] of a polymer chain can be recast in the language of a one-dimensional, Ising-like model.[6] For the case of three rotational isomeric states, as in the case for many polymer chains, the model is equivalent to a one-dimensional, spin one, Potts model in an external field.[6] For the two-state Ising model, it can be analytically shown that the nearest-neighbor 2-spin distribution functions do not exhibit bimodality. Therefore, by analogy, the results shown in Figures 3 and 4 are not surprising. The magnetization,[13] m, however, does show bimodal behavior in the Ising model. It is expected that the analogue of m in the rotational isomeric state model

$$m = N_{G+} - N_{G-}$$

would also show bimodality in its distribution. Since m is not physically meaningful in the polymer problem, this distribution was not evaluated. However, as seen in Figures 5 and 6, the sequence length distribution displays coexistence between the fully ordered, helical state and the highly disordered configuration in a fashion reminiscent of the Ising magnetism behavior.

As pointed out in the Introduction, it is well-known[13] that a one-dimensional model of the Ising type cannot have a true thermodynamic phase transition for $T > 0$ K, provided the range of the interaction potential is finite. Thus it is obvious that the "helix/coil transition" observed here for POM cannot be a true thermodynamic transition. Nevertheless, depending on parameters, a coexistence between an ordered and disordered phase can occur over a fairly narrow temperature range. This same behavior has been studied extensively in polypeptide chains.[14] In the case of those molecules, the "pseudo-first-order transition" usually occurs at higher temperatures than for POM. This is due to the longer range, strong H-bond interactions present in polypeptides.[14] In contrast, the POM transition-like behavior arises from the modest size of the chains with short-range interactions.

The coexistence behavior observed here can be viewed as a freezing out of the lowest energy state. For POM, this ground state happens to coincide with the helical configuration and is twofold degenerate (i.e., g^+ or g^-). We can define an order parameter f_0 as the fraction of helicity. For POM using the rotational isomeric state model, we have simply

$$f_0 = 2\sigma^{N-2}/Z_N \tag{8}$$

for a chain of N bonds. Z_N is the configurational partition function which can be evaluated exactly[1] for the rotational isomeric state model.

$$Z_N = \Gamma_1\lambda_1^{N/2-1} + \Gamma_2\lambda_2^{N/2-1} \tag{9a}$$

$$\Gamma_{1,2} = 0.5\left[1 \pm \frac{1 + 4\sigma + \sigma^2\beta(4 - \alpha)}{[(1 - \sigma^2\alpha\beta)^2 + 8\sigma(1 + \alpha\sigma)(1 + \beta\sigma)]^{1/2}}\right] \tag{9b}$$

$$\lambda_{1,2} = 0.5[(1 + 4\sigma + \sigma^2\alpha\beta) \pm [(1 - \sigma^2\alpha\beta)^2 + 8\sigma(1 + \alpha\sigma)(1 + \beta\sigma)]^{1/2}] \tag{9c}$$

where α and β are given by

$$\alpha = 1 + \omega_a$$

$$\beta = 1 + \omega_b$$

A plot of the helical fraction f_0 is shown for POM in Figure 7 for various chain lengths. Note that the curves shift to lower temperature and become sharper as N increases. This clearly demonstrates that finite size effects are the source of the bimodality.

We can make a crude estimate of the onset T_c of the coexistence region by expanding eq 8 and 9 for low temperatures. In this limit, σ becomes large compared to ω_a and ω_b. This expansion leads to the result

$$f_0 = \frac{2\sigma^{N-2}}{2\sigma^{N-2} + 4(N - 3)\sigma^{N-3} + ...} \tag{10}$$

It is interesting to note that the first term in the denominator corresponds to the ground state, the second term to the first excited state, and so on. The first excited state consists of all gauche chains with a single trans defect. Taking $f_0 = 0.5$ as the midpoint of the transition, we can obtain an estimate of T_c from eq 10.

$$T_c \sim -E_\sigma/R \ln [2(N - 3)] \tag{11}$$

Thus we see that the coexistence temperature approaches zero with a logarithmic dependence on chain length. Such behavior is analogous to the critical Ising model temperature in one dimension. The true transition for the infinite system occurs at $T = 0$ as expected for an Ising model. Nevertheless, since $-E_\sigma$ for POM is large, helix/coil coexistence occurs at reasonably high temperatures for short chains.

By analogy with magnetic spin problems, the coexistence temperature would be expected to be influenced by an external field. Consider the case in which a tensile force

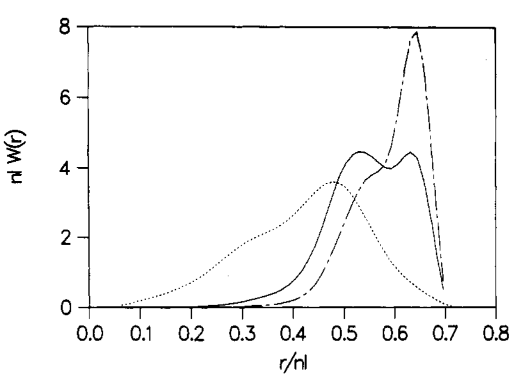

Figure 8. Effect of an external tension f applied in the direction of the end-to-end vector of a POM chain of 40 bonds at 298 K. The curves are from Monte Carlo calculations for various values of fr_0/kT: 8.32 (chain dash); 5.20 (solid); 0 (dashed).

f is applied to the ends of a POM chain in the direction of the end-to-end vector. The Hamiltonian will then be increased by an amount fr/kT, and the end-to-end distribution function $W_f(r)$ becomes

$$W_f(r) = \frac{W(r)\exp(fr/kT)}{\int W(r)\exp(fr/kT)\,\mathrm{d}r} \qquad (12)$$

where W is the zero-field result.

Using the previously generated Monte Carlo results with eq 12, we can then see the effect of this external field. These results are shown in Figure 8 for various values of the field $f\langle r^2\rangle_0{}^{1/2}/kT$, where $\langle r^2\rangle_0$ is the mean square end-to-end distance of the chain in the absence of an external field. As expected, we see that the contribution of the ordered phase increases markedly as the force increases. In fact, as can be seen in Figure 8, it is possible to induce a helix/coil coexistence even though the temperature is above T_c in the absence of the external field.

We have seen in this paper that the bimodal structure of the distribution curves is a consequence of the "freezing out" of the low-energy helical configurations in the finite polymer chain. When the ground state corresponds to the extended or rodlike configuration, then similar rod/coil coexistence behavior can be expected at low temperature. This would include polymers like polyethylene, where the transplanar configuration is the ground state, as well as certain stereoregular vinyl chains.[16]

One can speculate on the possible experimental consequences of the behavior we have discussed here. POM is known to be a highly crystalline polymer in the bulk state with crystalline structures consisting of helices.[2] The melting point is quite high (~175 °C) and the polymer is insoluble in most solvents.[17] As a result, few studies have been performed on POM melts or solutions.[14] In view of the tendency to induce a helix/coil coexistence with an external force, one might expect some unusual hydrodynamic effects in solution or the melt, particularly for elongational flows. If one could prepare an amorphous network from a chain of the type discussed here, unusual stress–strain behavior would be anticipated. The tendency of the network chains to undergo a helix/rod transition could play a role in strain-induced crystallization, well-known in networks like natural rubber. Finally, in amorphous melts the intramolecular structure of the flexible polymer has important consequences for the intermolecular packing. In general, there is a self-consistent coupling of the intra- and intermolecular structure. Consequently, since a bimodal end-to-end distribution implies two qualitatively distinct polymeric shapes, intermolecular reorganization or phase separation may occur with decreasing temperature due to steric interactions between the polymer chains.

References and Notes

(1) Flory, P. J. *Statistical Mechanics of Chain Molecules*; Interscience: New York, 1969.
(2) Flory, P. J.; Mark, J. E. *Makromol. Chem.* **1964**, *75*, 11.
(3) Abe, A.; Mark, J. E. *J. Am. Chem. Soc.* **1976**, *98*, 6468.
(4) Achida, T.; Kurita, Y.; Kubo, M. *J. Polym. Sci.* **1956**, *19*, 365.
(5) Curro, J. G.; Mark, J. E. *J. Chem. Phys.* **1985**, *82*, 3920.
(6) Binder, K. *Phase Transitions and Critical Phenomena*; Academic: New York, 1983.
(7) Teller, E. *J. Chem. Phys.* **1953**, *21*, 1087.
(8) We acknowledge Dr. L. DeBolt, University of Cincinnati, for pointing out an inconsistency in the Monte Carlo method used in ref 5. The correct method used here gives minor differences in the distributions shown in ref 5. The conclusions given in ref 5, however, remain unchanged.
(9) Wyld, H. W. *Mathematical Methods for Physics*; Addison-Wesley: Reading, MA, 1979.
(10) Schweizer, K. S., to be submitted to *Macromolecules*.
(11) Mark, J. E.; Curro, J. G. *J. Chem. Phys.* **1984**, *79*, 5705.
(12) Curro, J. G.; Mark, J. E. *J. Chem. Phys.* **1984**, *80*, 4521.
(13) Stanley, H. E. *Introduction to Phase Transitions and Critical Phenomena*; Oxford University Press: Oxford, 1971.
(14) Poland, D.; Scheraga, H. A. *Theory of Helix-Coil Transitions in Biopolymers*; Academic: New York, 1970.
(15) After submission of this paper, W. H. Stockmayer brought to our attention the work of Nagai (*Nagai*, K. *J. Chem. Phys.* **1961**, *34*, 887). Using a two-state model for a polypeptide chain, Nagai showed analytically that the helical sequence distribution for finite chains can exhibit bimodality. This is qualitatively similar to our results for $P(Y_G)$ shown in Figure 5.
(16) Mark, J. E.; Curro, J. G., submitted to *Macromolecules*.
(17) Stockmayer, W.; Chan, L. L. *J. Polym. Sci., Part A-2* **1966**, *4*, 437.