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## Order-Disorder Transitions in Tetrahedral Lattice Polymer Systems

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**ABSTRACT:** Monte Carlo simulations were performed on multichain, semiflexible polymer systems with excluded volume confined to a diamond lattice, and the requirements for a phase transition between a globally random and a globally anisotropic phase were explored. For chains composed of  $n = 12$  and 24 beads packed at volume fractions 0.5 and 0.75, a transition to a globally ordered phase is not observed if the attractive interactions are excluded, in agreement with recent work of Baumgartner (Baumgartner, A. *J. Chem. Phys.* 1986, 84, 1905) on square and cubic lattice multichain systems. Inclusion of attractive interactions between nonbonded nearest-neighbor pairs of beads produces an isotropic-to-anisotropic phase transition which is probably first order. The properties of the isotropic and globally ordered phases are extensively characterized, and the ability of simple mean field theory to treat the isotropic-nematic phase transition is examined.

### I. Introduction

Our recent Monte Carlo study of a tetrahedral lattice model of a polymer melt provides evidence that the presence of local stiffness in polymer chains, related to the energetic preference for trans over gauche conformational states, induces a local ordering of the chains; i.e., on a local scale, there is a tendency for polymers to pack in a parallel manner, resulting in the formation of locally ordered domains.<sup>1</sup> These domains exist over a rather broad temperature range and are loosely defined, but the domain structure becomes more apparent if attractive forces between polymer segments are introduced into the model. Moreover, in the globally isotropic phase, the subchains of a given chain participating in two such domains essentially lack orientational correlation. One would expect that as temperature decreases, the system of locally ordered but globally disordered, semiflexible polymers should exhibit a phase transition to a globally ordered phase such as was predicted by Flory<sup>2</sup> using a mean field argument. Baumgartner and Yoon<sup>3</sup> and Yoon and Baumgartner<sup>4</sup> have performed Monte Carlo studies of two-dimensional square and three-dimensional cubic lattice polymer systems very similar to the system originally considered by Flory and have observed what appeared to be a first-order transition from a random to a nematic phase that was in qualitative

agreement with the theoretical predictions. Some deviations of the simulations from Flory-Huggins-Miller-Guggenheim theory, for instance, a higher transition temperature and a smaller entropy change at the transition, were reported. In recent work, Baumgartner more carefully examined the nature of the order-disorder transition for trimers on a square lattice<sup>5</sup> and for polymers packed at high density on square and cubic lattices in Monte Carlo boxes appreciably larger than the chain length.<sup>6</sup> He found that finite-length chains lacking attractive interactions do not experience a transition between a globally isotropic and a long-range, orientationally ordered state. However, such systems form locally ordered domains whose size,  $\xi$ , is on the order of the chain length. Introduction of orientation-dependent intermolecular interactions is found to produce an isotropic-nematic phase transition in three dimensions which appears to be of first order.

In the present work, we describe the order-disorder transition in systems of tetrahedral polymers confined to a lattice. The effect of density as well as short-range, segment-segment interactions on the location and character of the phase transition is examined. While Baumgartner and Yoon<sup>3-5</sup> required a pair of adjacent nearest-neighbor bonds to be parallel in order to have an attractive interaction, in what follows, we employ the less restrictive condition of allowing an attractive interaction between any nonbonded neighboring pair of beads. Since the model and Monte Carlo (MC) procedure have been described in the preceding paper,<sup>1</sup> we omit most of the details.

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The models under consideration consist of  $N$  chains, each composed of  $n$  beads ( $n - 1$  bonds), confined to a diamond lattice. The density of the system is defined by the fraction of lattice sites occupied by polymers  $\phi = Nn/V$ , where  $V$  is the number of diamond lattice points in a MC box subject to periodic boundary conditions. No multiple occupancy of lattice sites is allowed. The conformation of each chain can be described by a sequence of  $n - 3$  conformational states, in which for each bond the trans conformation ( $t$ ) is lower in energy than the two gauche states ( $g^+$  or  $g^-$ ). The energy difference between trans and gauche states is defined as  $\epsilon_g$ . In what follows, we employ a reduced temperature scale  $T^* = k_B T / \epsilon_g$ .

Two types of systems have been modeled. In the first case, we merely exclude multiple occupancy of lattice sites to mimic a system experiencing only hard-core, repulsive steric interactions. In the second case, we add an attractive interaction  $\epsilon_a$  between nonbonded nearest-neighbor beads, taken to be proportional to  $\epsilon_g$ . The total configurational energy of the system is given by

$$E = N[\epsilon_g(n - 3)f_g + \epsilon_a n \langle \nu \rangle] \quad (1)$$

where  $f_g$  is the average fraction of gauche states and  $\langle \nu \rangle$  is the average fraction of nonbonded nearest neighbors per segment. Setting  $\epsilon_g/k_B T$  equal to zero corresponds to the infinite-temperature reference state for the system.

Computational experiments were performed as a sequence of decreasing and increasing temperature runs. At every temperature, the systems were carefully equilibrated. For the densities of the systems studied ( $\phi = 0.5$  and  $\phi = 0.75$ ),  $10^6$  iterations were sufficient to achieve good statistics. A single iteration consists of one attempt at a reptation step per polymer chain together with ten attempts to effect a three-bond kink motion at sites randomly chosen in the chain by following a standard Metropolis scheme.<sup>7,8</sup> The majority of the simulations were for chains of length  $n = 24$ , although  $n = 12$  systems were also studied.

The organization of the remainder of the paper is as follows. In the Results, section II, we first describe the global order parameter as a function of temperature. This is followed by a discussion of the temperature dependence of the heat capacity and  $\langle \nu \rangle$ . We then compare the results of the present simulation with predictions from simple mean field theory. This section finishes with a discussion of chain conformation in the isotropic and anisotropic phase. Finally, in section III we summarize the conclusions of the present work.

## II. Results

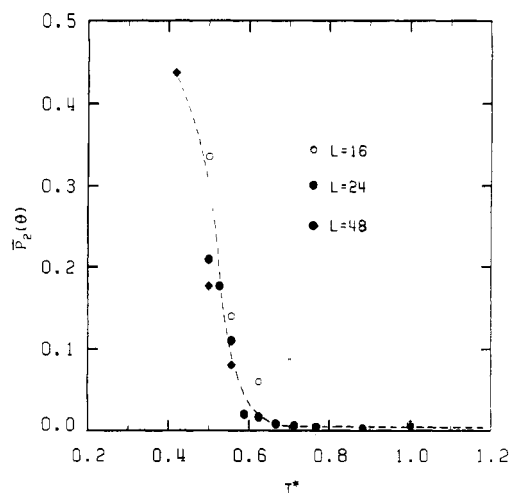
**Global Order Parameter.** Anticipating the possibility of a transition from a globally random, isotropic phase to an ordered, anisotropic one, we computed average values of the global order parameter  $\bar{P}_2(\theta)$  at each temperature, which in the absence of an external field is related to the average mutual orientation of all the polymer segments by

$$\bar{P}_2(\theta) = (3\langle \cos^2 \theta \rangle - 1)/2 \quad (2)$$

with

$$\cos \theta = (\mu_{ji} \cdot \mu_{lk}) / |\mu|^2 \quad (3)$$

where subscripts  $j$  and  $l$  enumerate vectors down the  $i$ th and  $k$ th chains, respectively. The ensemble average denoted by the angular brackets involves all the polymer segments in the MC box. The vector  $\mu_{ji}$  is defined as the sum of the two chain bond vectors adjacent in the  $j$ th bead of the  $i$ th chain (no end beads are counted). Since a single chain bond is a vector of the form  $[\pm 1/3^{1/2}, \pm 1/3^{1/2},$



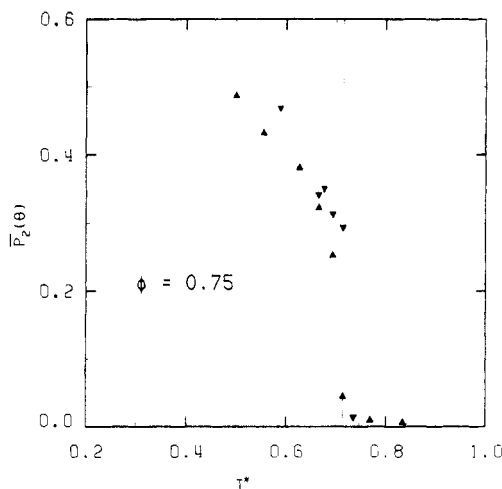
**Figure 1.** Plot of the average global order parameter,  $\bar{P}_2(\theta)$ , calculated via eq 2 vs. the reduced temperature,  $T^*$ , for a system with  $\epsilon_a = -\epsilon_g/4$  composed of chains with  $n = 12$  beads packed at a density  $\phi = 0.75$  in Monte Carlo boxes of length  $L = 16$  (open circles), 24 (solid circles), and 48 (diamonds).

$\pm 1/3^{1/2}]$ , the length of the vector  $\mu$  is equal to  $(8/3)^{1/2}$  in units of bond length. Employing  $\bar{P}_2(\theta)$  as the global order parameter gives convenient numerical values for limiting cases. Namely,  $\bar{P}_2(\theta) = 0$  for a globally random system and  $\bar{P}_2(\theta) = 1.0$  when all the tetrahedral lattice chains have parallel orientations and are in their completely extended conformations.

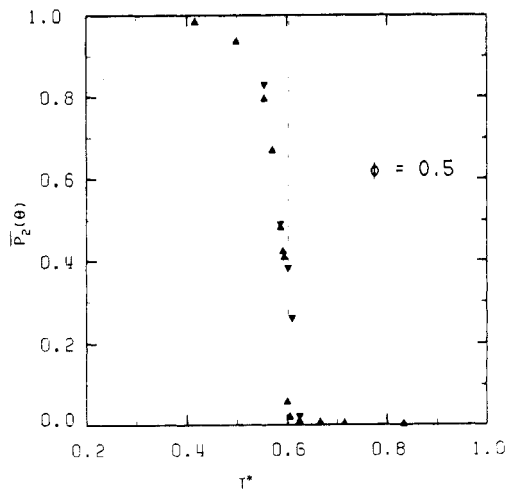
For a system composed of chains of  $n = 12$  beads packed at  $\phi = 0.75$  in a MC box of length  $L = 48$ , we find no evidence whatsoever of a global isotropic-to-anisotropic phase transition. For example, although this system exhibits considerable local ordering of parallel domains of extent  $\xi \sim n$  at temperatures below  $T^* = 0.6$ , even when  $T^* = 0.4$ ,  $\bar{P}_2(\theta) = 0.034$ . However, on setting  $\epsilon_a = -\epsilon_g/4$ , we find a global isotropic-anisotropic phase transition at  $T_t^* = 0.58$ . (See discussion below.) Thus, we find qualitatively similar behavior to that seen by Baumgartner.<sup>6</sup> To investigate the effect of MC box size on systems having attractive interactions, we plot in Figure 1  $\bar{P}_2(\theta)$  vs.  $T^*$  for a system with  $\epsilon_a = -\epsilon_g/4$  composed of chains with  $n = 12$  beads packed at  $\phi = 0.75$  in Monte Carlo boxes of length  $L = 16$  (open circles), 24 (solid circles), and 48 (diamonds). Clearly, the results of the simulation are essentially independent of MC box size. Thus, we feel confident in examining the character of the isotropic-anisotropic transition for systems containing attractive interactions by choosing MC boxes whose length is on the order of that of a single chain, thereby allowing us to study longer chain systems at higher densities. In all cases, unless otherwise stated we examine multichain systems having  $n = 24$  beads packed in a Monte Carlo box of length  $L = 24$ .

We have also performed a series of simulations with  $L = n$  on systems having  $\epsilon_a = 0$ . In qualitative accord with the results for polymers confined to a cubic lattice,<sup>4</sup> we find the abrupt growth of domains whose length  $\xi \sim n$  at and below a transition temperature  $T_t^*$ ;<sup>5</sup> concomitantly, the persistence length of a single chain becomes on the order of the chain length. In some sense, this class of simulations corresponds to the  $L \rightarrow \infty$  and  $n \rightarrow \infty$  limit. However, as the diamond lattice system having  $\epsilon_a = 0$  exhibits no global isotropic-anisotropic transition in the case  $n \ll L$ , we confine our attention in the remainder of the paper to the characterization of systems with attractive interactions,  $\epsilon_a < 0$ , that do exhibit such a transition.

In Figures 2 and 3, the computed values of  $\bar{P}_2(\theta)$  calculated via eq 2 are plotted vs. the reduced temperature  $T^*$

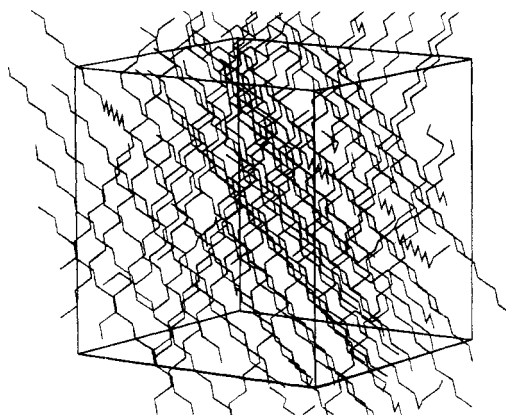


**Figure 2.** Plot of the average global order parameter,  $\bar{P}_2(\theta)$ , calculated via eq 2 vs. the reduced temperature,  $T^*$ , for a system with  $\epsilon_a = -\epsilon_g/4$  composed of chains with  $n = 24$  beads packed at density  $\phi = 0.75$  in a Monte Carlo box with  $L = 24$ . Down or up triangles indicate the direction of the temperature sequence.



**Figure 3.** Plot of the average global order parameter,  $\bar{P}_2(\theta)$ , calculated via eq 2 vs. the reduced temperature,  $T^*$ , for a system with  $\epsilon_a = -\epsilon_g/4$  composed of chains with  $n = 24$  beads packed at a density  $\phi = 0.5$  in a Monte Carlo box with  $L = 24$ . Down or up triangles indicate the direction of the temperature sequence.

for a system with  $\epsilon_a = -\epsilon_g/4$  composed of chains with  $L = n = 24$  packed at  $\phi = 0.75$  and  $\phi = 0.5$ , respectively. Sequences of both decreasing- and increasing-temperature simulations are represented in Figures 2 and 3 by triangles pointing down and up. Clearly, these systems exhibit a transition from a globally random to an ordered phase, with a correspondingly large jump in the value of the global order parameter  $\bar{P}_2$ . The vertical dashed line indicates the estimated reduced transition temperature  $T_t^*$ . The procedure used to estimate  $T_t^*$  requires some amplification. In the low-density case,  $\phi = 0.5$ , shown in Figure 3, one can observe at  $T_t^* = 0.602$  a stable random or a stable ordered phase, depending on the degree of ordering of the initial configuration (an exceptionally long series of simulations consisting of  $(3-5) \times 10^6$  iterations was made at this point). A small change in temperature of  $\pm \Delta T^* = 0.004$  leads to a very rapid ordering or disordering of the system, respectively; the abrupt change in ordering requires a much smaller number of iterations than the sampling period employed at each temperature. The higher density system,  $\phi = 0.75$ , with nearest-neighbor interactions depicted in Figure 2 behaves identically except that the two phases coexist at  $T_t^* = 0.714$ .



**Figure 4.** Representative low-temperature configuration illustrating the arrangement of the system in two layers of parallel polymers for the case  $\epsilon_a = -\epsilon_g/4$ ,  $\phi = 0.75$ , and  $T^* = 0.556$ .

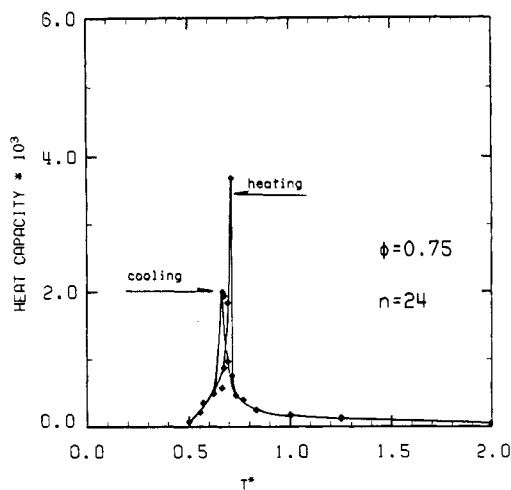
Unlike the case when  $\phi = 0.5$  shown in Figure 3 (which will be discussed in further detail later), one should note that  $\bar{P}_2(\theta)$  in Figure 2 is far from unity, the value for a perfectly ordered nematic liquid crystal. There are two reasons for this. First, at the transition the polymers are still relatively flexible and even on the local scale, ordering is not perfect. Second, in three-dimensional lattice systems in the absence of anisotropic attractive interactions and/or any external field, there is an additional degree of freedom, which allows even completely rigid rods to pack in two parallel layers. When this occurs, the order parameter embodied in eq 2 does not fully describe the "true" ordering of the model system. At the transition, the local order parameter<sup>1</sup> in the phase having long-range orientational order is substantially larger than in the disordered phase and ranges from 0.6 to 0.8, but it is still relatively far from unity.

A representative "low-temperature" configuration of chain backbones ( $\epsilon_a = -\epsilon_g/4$ ,  $\phi = 0.75$ , and  $T^* = 0.556$ ) illustrating the arrangement of the system in two layers of parallel polymers, discussed above, is shown in Figure 4. A detailed examination of a series of pictures of the ordered phase (not shown here) seems to indicate that the anisotropic phase is smectic rather than nematic. However, given the size of the Monte Carlo box employed in the simulation, whose length is essentially equal to the maximum number of bonds, we cannot tell whether or not this is an artifact of the finite box size and periodic boundary conditions. Unfortunately, to fully resolve this question would require far greater computational resources than we presently have available.

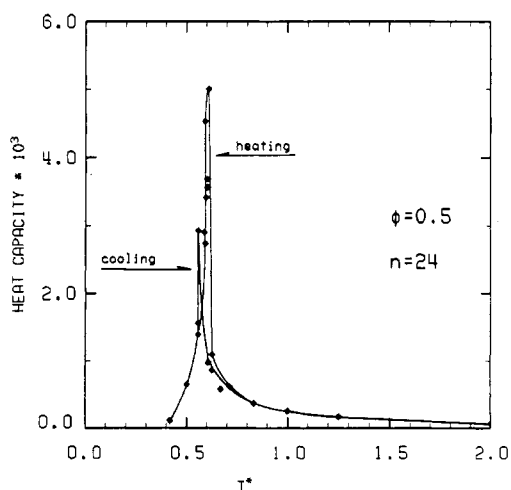
**Temperature Dependence of the Heat Capacity.** Other properties of the system can be used to confirm the transition temperatures, which we estimated from the change of the order parameter with temperature. The reduced heat capacity,  $C_v$ , per bead computed from the fluctuation of the energy of the system (given by eq 1) is one example; that is

$$C_v = (\langle E^2 \rangle - \langle E \rangle^2) / (nNk_B T^2) \quad (4)$$

In Figures 5 and 6, we show  $C_v$  vs. the reduced temperature  $T^*$  for a system packed at  $\phi = 0.75$  and  $\phi = 0.5$ , respectively, with  $\epsilon_a = -\epsilon_g/4$  (the diamonds represent points obtained from the simulation). As is clearly evident from the figures, the heat capacity profiles associated with the cooling and heating cycles are distinct; the lower temperature  $C_v$  vs.  $T^*$  peak is obtained on cooling and the higher temperature  $C_v$  vs.  $T^*$  peak is obtained on heating. The scattering of heat capacity in the vicinity of the phase transition is rather large, and the double structure of the



**Figure 5.** Plot of reduced heat capacity per bead calculated via eq 4 vs. the reduced temperature,  $T^*$ , for a system with  $n = 24$  beads,  $\phi = 0.75$ , and  $\epsilon_a = -\epsilon_g/4$ . The peak at lower (higher) temperature is associated with the cooling (heating) cycles. The diamonds represent points obtained from the simulation.



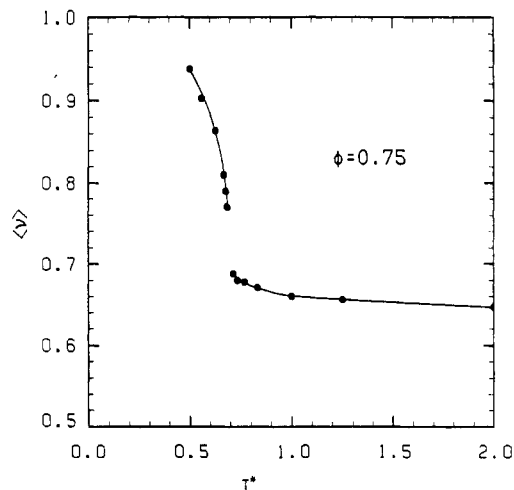
**Figure 6.** Plot of reduced heat capacity per bead calculated via eq 4 vs. the reduced temperature,  $T^*$ , for a system with  $n = 24$  beads,  $\phi = 0.5$ , and  $\epsilon_a = -\epsilon_g/4$ . The peak at lower (higher) temperature is associated with the cooling (heating) cycle. The diamonds represent points obtained from the simulation.

peaks associated with metastable states is noticeable<sup>8</sup> at both densities when  $\epsilon_a \neq 0$ . This gives good evidence for a first-order transition for systems with nearest-neighbor attractive interactions.

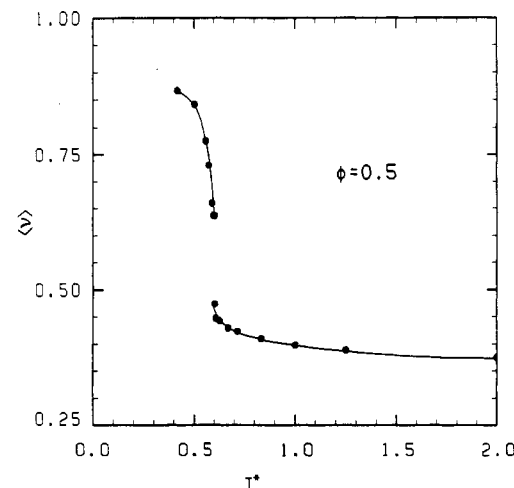
**Average Fraction of Occupied Nearest-Neighbor Sites.** For multichain diamond lattice systems having attractive interactions, we found that the character of the local structure of the system abruptly changes at the transition temperature. To demonstrate this, in Figures 7 and 8, for systems with  $\epsilon_a = -\epsilon_g/4$  having  $n = 24$ , packed at  $\phi = 0.75$  and  $\phi = 0.5$ , respectively, we display the average fraction of nearest-neighbor sites surrounding a bead that are occupied,  $\langle \nu \rangle$ , as a function of reduced temperature  $T^*$ . At high temperatures,  $\langle \nu \rangle$  changes very slowly with temperature. The  $\phi = 0.75$  system, depicted in Figure 7, gives a high-temperature ( $T^* = 2.0$ ) value for the average fraction of occupied neighbor sites ( $\nu$ ) of 0.645. This is in good agreement with the value 0.635 computed from the Miller-Guggenheim theory via<sup>9</sup>

$$\langle \nu \rangle = \frac{qz}{2n} \xi_n \quad (5)$$

In eq 5  $\xi_n = qN/(N_1 + qN)$ , where  $N$  is the number of



**Figure 7.** Average fraction of nearest-neighbor sites surrounding a bead that are occupied,  $\langle \nu \rangle$ , vs. the reduced temperature,  $T^*$ , for a system with  $n = 24$  beads,  $\phi = 0.75$ , and  $\epsilon_a = -\epsilon_g/4$ . The Miller-Guggenheim quasi-chemical approximation gives  $\langle \nu \rangle_{T=\infty} = 0.635$  (see eq 5). Flory's mean field value of  $\langle \nu \rangle = 0.75$ .



**Figure 8.** Average fraction of nearest-neighbor sites surrounding a bead that are occupied,  $\langle \nu \rangle$ , vs. the reduced temperature,  $T^*$ , for a system with  $n = 24$  beads,  $\phi = 0.5$ , and  $\epsilon_a = -\epsilon_g/4$ . The Miller-Guggenheim quasi-chemical approximation gives  $\langle \nu \rangle_{T=\infty} = 0.357$  (see eq 5). Flory's mean field value of  $\langle \nu \rangle = 0.5$ . The low-temperature value of  $\langle \nu \rangle$  agrees with that obtained by assuming close packing of chains, corrected for surface effects.

polymer chains in the system,  $N_1$  is the number of empty sites,  $z$  is the coordination number of the lattice (for a diamond lattice,  $z = 4$ ), and  $qz$  is the number of available nearest neighbors of the chain, namely,  $qz = (z - 2)n + 2$ . Equation 5 is obtained by assuming that attractive interactions can be neglected. With increasing temperature the number of nearest neighbors changes very slowly in the isotropic phase, except close to the transition. At the transition  $\langle \nu \rangle$  jumps to a higher value, which in the ordered phase exceeds Flory's mean field result<sup>9</sup> that  $\langle \nu \rangle = (z - 2)\phi/2$ ; i.e.,  $\langle \nu \rangle = 0.75$ .

In Figure 8, we examine  $\langle \nu \rangle$  vs.  $T^*$  for the lower density system,  $\phi = 0.5$  with  $\epsilon_a = -\epsilon_g/4$ . The high-temperature Monte Carlo results are slightly smaller than the Miller-Guggenheim value,  $\langle \nu \rangle = 0.357$ , calculated from eq 5. In the ordered phase as in the case of  $\phi = 0.75$ , when  $\phi = 0.5$ ,  $\langle \nu \rangle = (z - 2)\phi/2$  differs substantially from the Flory theory value of 0.5.

The analysis of the dependence of  $\langle \nu \rangle$  on temperature for the low-density system with an attractive interaction between beads allows us to rationalize the high degree of

Table I  
Order-Disorder Phase Transition Temperatures and Entropy Changes per Polymer Bead<sup>a</sup>

system	transition temp, $T_t^*$	$\Delta S/k_B$ per bead
$\phi = 0.5$ (MC)	0.602 (4) <sup>b</sup>	0.24
$\phi = 0.5$ (mean field)	0.418	0.59
$\phi = 0.75$ (MC)	0.714 (2)	0.20
$\phi = 0.75$ (mean field)	0.513	0.52

<sup>a</sup>In all cases  $\epsilon_a = -\epsilon_g/4$ . <sup>b</sup>0.602 (4) means  $0.602 \pm 0.004$ , and the error limits correspond to the limiting temperature of the metastable states or the hysteresis seen in the simulation.

ordering in this system reported in Figure 3, a discussion of which has been deferred up to now. The average fraction of nearest-neighbor occupied sites in the ordered phase significantly increases with decreasing temperature. When  $T^* = 0.4$ , the number of nearest neighbors is characteristic of a close-packed structure of polymers (taking into consideration surface effects) rather than one at the overall uniform density of  $\phi = 0.5$ . This suggests that after the transition to an ordered phase the density of the system is not uniform and that with further temperature decrease, phase segregation occurs. Since the higher density phase tries to minimize its surface area, the energetically preferred configuration of the system is a single cylindrical bundle of polymers. As a result, one observes in Figure 3 a smooth increase of the order parameter below the transition temperature up to values of  $\bar{P}_2(\theta)$  close to unity.

For the higher density case (see Figure 2), this effect is not observed for two reasons. First, the transition temperature is considerably higher, so that the relative importance of attractive interactions at the phase transition is less. Second, the density is large enough for the phase to be considered as "close packed" (taking into consideration the considerable flexibility of the chains at the transition temperature). Caution, however, should be exercised in interpreting the character of the  $\phi = 0.5$  density, highly ordered phase as a finite-size effect. One might expect that an infinite system composed of finite-length polymer chains packed on a lattice at a density  $\phi = 0.5$  to exhibit a similar bidirectional orientation of the polymers, as described above. The phenomenon of microheterogeneity, i.e., phase segregation at low temperature, should be independent of box size as long as the MC box is large enough to accommodate the chains in their expanded conformations, as is the case in the present computations.

**Comparison of Transition Temperature and Entropy with Simple Mean Field Theory.** In Table I, the Monte Carlo results for the transition to an ordered state in systems having  $n = 24$  and  $\epsilon_a = -\epsilon_g/4$  packed at  $\phi = 0.5$  and 0.75 are compared with the predictions of mean field theory. In the framework of the Flory-Huggins or the Miller-Guggenheim<sup>9</sup> theory of lattice systems, the transition temperature can be calculated by equating the configurational partition function for a system of semiflexible polymers ( $Z_{\text{random}}$ ) with that for a system of parallel all-trans, rigid molecules<sup>1</sup> ( $Z_{\text{ordered}}$ ), suitably modified for the presence of attractive interactions between nonbonded, neighboring pairs of beads. Now

$$Z_{\text{random}} = \left( \frac{nN + N_1}{N} \right)^N \left( \frac{nN + N_1}{N_1} \right)^{N_1} z^N (z - 1)^{N Z_c (n-3)N} \left( \frac{nN + N_1}{qN + N_1} \right)^{-z(qN + N_1)/2} \exp(-nN\epsilon_a \langle \nu \rangle / k_B T) \quad (6)$$

and

$$Z_{\text{ordered}} = \left( \frac{N + N_1}{N} \right)^N \left( \frac{N + N_1}{N_1} \right)^{N_1} \exp(-nN\epsilon_a \langle \nu \rangle / k_B T) \quad (7)$$

in which  $N_1$  is the number of unoccupied sites in the MC box and  $N$  is the number of polymer chains.  $Z_c$  in eq 6 is the intrachain configurational partition function that accounts for the internal rotational degrees of freedom

$$Z_c = 1 + (z - 2) \exp(-\epsilon_g / k_B T) \quad (8)$$

with  $z$ , the diamond lattice coordination number, equal to 4, and  $qz$  is defined following eq 5. In practice, if  $\epsilon_a \neq 0$ , we numerically solve for the  $T^*$  that satisfies  $Z_{\text{random}} = Z_{\text{ordered}}$ . Furthermore, the energy change per bead at the phase transition is given by

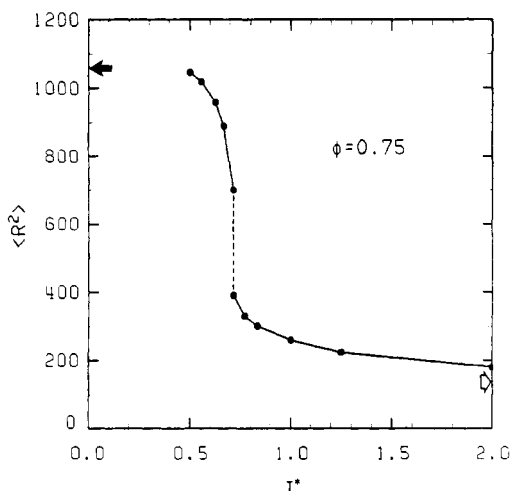
$$\Delta E_b = \epsilon_g(1 - 3/n)\Delta f_g + \epsilon_a \Delta \nu \quad (9)$$

wherein  $\Delta f_g$  is the difference in the fraction of gauche states in the ordered and disordered states (taken equal to  $-f_g$  in the disordered phase in the mean field approximation) and  $\Delta \nu$  is the change in the fraction of nonbonded nearest neighbors in the ordered and disordered states. Thus, the transition entropy per bead is given by

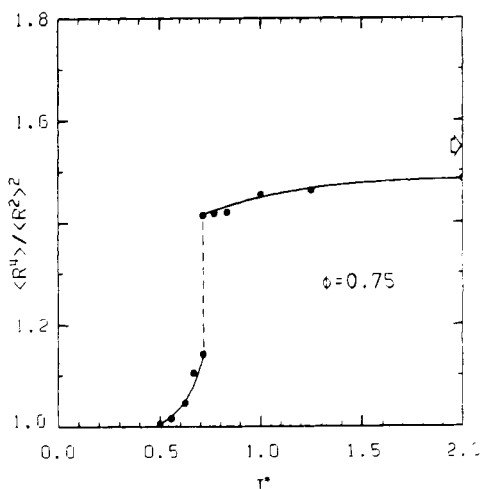
$$\Delta S / k_B = \Delta E_b / \epsilon_g T_t^* \quad (10)$$

As is clearly evident from Table I, the entropy of the transition computed from the MC data is considerably smaller than that obtained from mean field statistics, corrected for the presence of attractive interactions and employing the difference between  $\langle \nu \rangle$  in the anisotropic and isotropic phase obtained from the MC simulation (see Figures 7 and 8); for the  $\phi = 0.75$  (0.5) system,  $\Delta \nu = 0.078$  (0.16). This suggests that the systems we have studied exhibit considerably higher local ordering in the "disordered" phase<sup>1</sup> and a smaller degree of order in the "ordered" phase than for an ideal order/disorder transition characterized by Flory mean field statistics. Furthermore, the simple mean field theory does not include the possibility of an abrupt change in the character of the polymer packing on the local scale at the phase transition such as was seen in the  $\phi = 0.5$  system. On going from the isotropic to the anisotropic phase, the microheterogeneity of the ordered phase must be also taken into account. Finally, inspection of the data compiled in Table I shows that transition to an ordered phase occurs at temperatures appreciably higher than that obtained from mean field statistics.

**Polymer Conformation.** As mentioned above, the model systems studied in the present work exhibit a significant amount of ordering on the local scale in the globally isotropic phase prior to the phase transition, and subsequent to the phase transition they exhibit a considerable deviation from an ideal order in the "nematic" phase. In this section we analyze for both phases some conformational properties of a single chain. First, we examine the average conformation of the entire molecule as characterized by the mean-square end-to-end distance,  $\langle R^2 \rangle$ , and the reduced fourth moment of the distribution,  $\langle R^4 \rangle / \langle R^2 \rangle^2$ . Figure 9 shows representative behavior of the chain dimensions  $\langle R^2 \rangle$  as a function of reduced temperature  $T^*$  for a system with  $n = 24$ ,  $\phi = 0.75$ , and  $\epsilon_a = -\epsilon_g/4$ . At high temperatures,  $\langle R^2 \rangle$  is close to the value for a nonreversing random walk on a lattice, the correct model for a flexible chain at bulk density.<sup>10,11</sup> With decreasing temperature, but above  $T_t^*$ , the dimensions of the chain increase with increasing stiffening of the polymer backbone

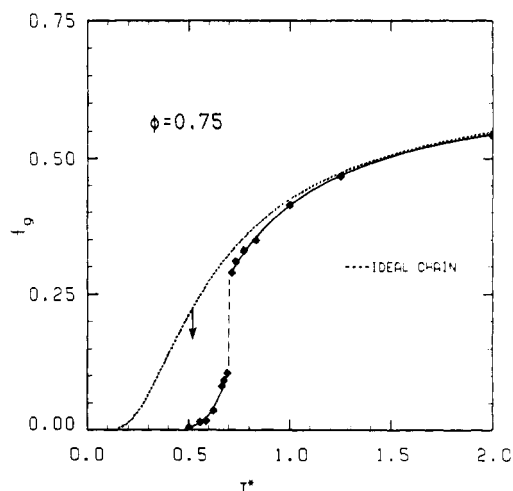


**Figure 9.** Plot of the mean-square end-to-end distance  $\langle R^2 \rangle$  vs. the reduced temperature,  $T^*$ , for a system with  $n = 24$  beads,  $\phi = 0.75$ , and  $\epsilon_a = -\epsilon_g/4$ . The open arrow denotes the value for the nonreversing random walk at  $T^* = \infty$ , and the solid arrow is the value of  $\langle R^2 \rangle$  for a fully stretched out, all-trans sequence of the molecule.

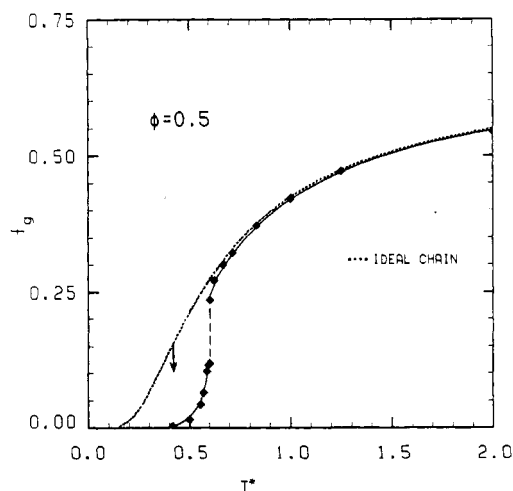


**Figure 10.** Plot of  $\langle R^4 \rangle / \langle R^2 \rangle^2$  vs. the reduced temperature,  $T^*$ , for a system with  $n = 24$  beads,  $\phi = 0.75$ , and  $\epsilon_a = -\epsilon_g/4$ . The open arrow denotes the value for a nonreversing random walk at  $T^* = \infty$ .

but lie quite close to the value obtained from ideal chain statistics.<sup>1</sup> At the phase transition the end-to-end distance increases abruptly to a value that is still appreciably smaller than that for the fully stretched out sequence of trans states (see solid arrow in Figure 9). Further decrease of the temperature results in the rapid approach to the rigid rod limit. Similar behavior can be seen in the plot of the reduced fourth moment of the end-to-end separation for the same system, in Figure 10, where  $\langle R^4 \rangle / \langle R^2 \rangle^2$  vs. reduced temperature is shown. The behavior of  $\langle R^2 \rangle$  and  $\langle R^4 \rangle / \langle R^2 \rangle^2$  vs.  $T^*$  for the  $\phi = 0.5$  system is qualitatively the same. These data also support the statement that in the isotropic phase the polymer chain can be considered as a "random coil" with a decreasing number of equivalent segments with decreasing temperature (see, for example, the results for the persistence length in ref 1 and the findings in ref 10 for the chain length dependence of  $\langle R^2 \rangle$ ). Thus, we have a picture of the isotropic-anisotropic phase transition in which there is embryonic order in the isotropic phase and where the phase transition is the point at which the length of a given subchain in the locally ordered domain abruptly increases to be on the order of the size of the entire molecule. In the anisotropic phase, the distri-



**Figure 11.** Fraction of gauche states,  $f_g$ , as a function of the reduced temperature,  $T^*$ , obtained from the MC simulation (solid curve) and ideal chain statistics (dotted curve) for a system with  $n = 24$  beads,  $\phi = 0.75$ , and  $\epsilon_a = -\epsilon_g/4$ .



**Figure 12.** Fraction of gauche states  $f_g$  as a function of the reduced temperature,  $T^*$ , obtained from the MC simulation (solid curve) and ideal chain statistics (dotted curve) for a system with  $n = 24$  beads,  $\phi = 0.5$ , and  $\epsilon_a = -\epsilon_g/4$ .

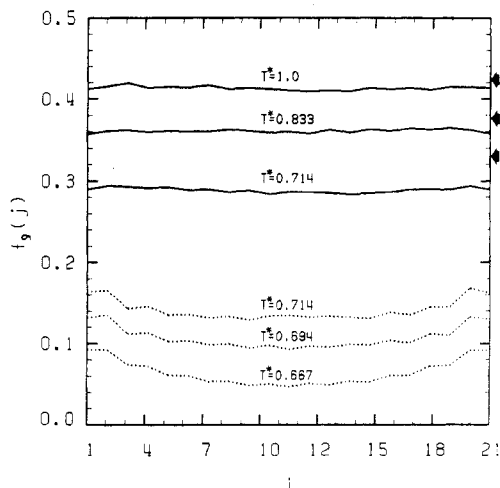
bution of end-to-end vectors is that of partially flexible rod, where the flexibility is very temperature dependent; just below the transition temperature, the deviation from rigid rod behavior is large but then rather rapidly approaches the rigid rod limit.

For systems packed at  $\phi = 0.75$  and  $0.5$ , respectively, the same deviations from an idealized ordered phase consisting entirely of an all-trans stretch can be seen in Figures 11 and 12, where the fraction of gauche states,  $f_g$ , obtained from the Monte Carlo simulations (solid curve with diamonds) is compared with that obtained from ideal chain statistics  $f_g^i$  (dotted curve). Now

$$f_g^i = \frac{(z-2)e^{-\epsilon_g/k_B T}}{1 + (z-2)e^{-\epsilon_g/k_B T}} \quad (11)$$

The fraction of gauche states in the isotropic phase is well described by an ideal chain model over a wide temperature range, until we approach close to the phase transition. With increasing density a larger deviation in  $f_g$  from  $f_g^i$  is observed. It is also clear from Figures 11 and 12 that while  $f_g$  decreases substantially at  $T_t^*$ , the anisotropic phase does not in fact consist of chains entirely in the all-trans state.

In order to further clarify the effect of the phase transition on the fraction of gauche states, we examined the



**Figure 13.** The solid (dotted) curves are plots of the probability that the  $j$ th conformational state is gauche,  $f_g(j)$ , vs.  $j$  for the globally random (ordered) system with  $n = 24$  beads,  $\phi = 0.75$ , and  $\epsilon_a = -\epsilon_g/4$  at various temperatures. The mean field results for  $f_g(j)$  obtained with eq 11 are shown by the filled arrows.

fraction of gauche states as a function of chain position, where  $f_g(j)$  is the probability that the  $j$ th conformational state is gauche. A representative example of  $f_g(j)$  vs.  $j$  is shown for a series of temperatures in Figure 13 for the system with  $\epsilon_a = -\epsilon_g/4$  comprised of  $n = 24$  beads packed at  $\phi = 0.75$ . The solid (dotted) lines denote  $f_g(j)$  vs.  $j$  for globally random (ordered) systems. The phase transition temperature  $T_t^* = 0.714$ . The mean field results for  $f_g(j)$  obtained via eq 11 for the isotropic system at  $T^* = 1.0, 0.833$ , and  $0.714$  are indicated by the filled in arrows in Figure 13. The following qualitative features hold not only for the system ( $\phi = 0.75$ ,  $\epsilon_a = -\epsilon_g/4$ ) but the other systems ( $\phi = 0.5$ ) studied as well.

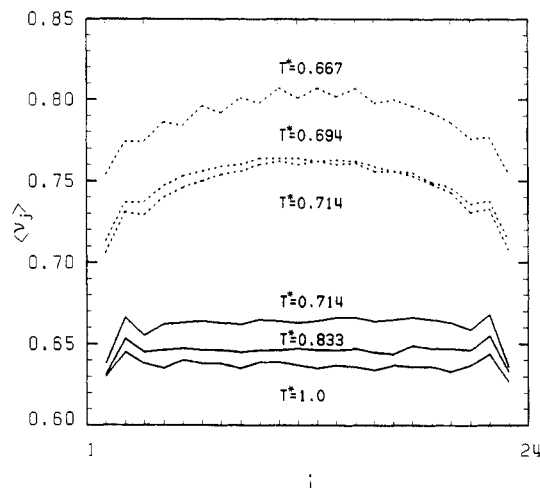
(1) Above  $T_t^*$ , the  $f_g(j)$  vs.  $j$  profiles are essentially flat, with increasing deviation from the mean field prediction the closer the temperature is to  $T_t^*$ .

(2) Below  $T_t^*$ , the profiles show a pronounced curvature, with  $f_g(j)$  rising at the chain ends.

The curvature in  $f_g(j)$  vs.  $j$  seems to be the result of a packing effect in the ordered state. To test this conjecture, we present in Figure 14  $\langle \nu_j \rangle$ , the average fraction of occupied nearest-neighbor sites surrounding the  $j$ th site, vs.  $j$  for the same polymer system as in Figure 13. Above the phase transition temperature,  $T_t^* = 0.714$ , the plot of  $\langle \nu_j \rangle$  vs.  $j$  is essentially flat, consistent with the observed flat gauche probability profiles. Below  $T_t^*$ ,  $\langle \nu_j \rangle$  has pronounced downward curvature, consistent with a lower density (and a higher fraction of gauche states) near the chain ends. Similar effects were seen for the  $\phi = 0.5$  system. Although we attempted to relate  $\langle \nu_j \rangle$  more directly to  $f_g(j)$ , all our simple attempts to do so were unsuccessful. The curvature seems to be the result of a complicated interplay of the chain-packing effects that produces a stronger effective nematic field in the middle of the chain than near the chain ends; the attempt to develop a treatment that is more successful than the simple, and apparently not too adequate, mean field theory employed here will be the focus of future work.

### III. Conclusions

By studying multichain systems of semiflexible polymers confined to a tetrahedral lattice, we have examined the conditions under which a transition from a globally isotropic random phase to an anisotropic phase (in which the polymer chains are globally oriented) can occur. In the isotropic phase, if the polymers are semiflexible, they tend



**Figure 14.** Plot of the average fraction of occupied nearest-neighbor sites surrounding the  $j$ th bead,  $\langle \nu_j \rangle$ , vs.  $j$  at various temperatures for a system with  $n = 24$  beads,  $\phi = 0.75$ , and  $\epsilon_a = -\epsilon_g/4$  in the globally disordered phase (solid curve) and globally ordered phase (dotted curve).

to pack in a locally parallel fashion, giving rise to the formation of locally ordered domains; these domains are loosely defined structures but become more apparent at higher polymer density and/or on inclusion of attractive interactions between any nearest-neighbor nonbonded pair of polymer segments. Moreover, in the isotropic phase the largest linear dimension of these domains,  $\xi$ , is appreciably less than the contour length of a single chain, and the various domains in which a given chain participates are essentially uncorrelated. For systems having attractive interactions, the isotropic-anisotropic transition seems to occur when these locally ordered domains coalesce and the persistence length of a given region of local order exceeds the length of the polymer. It appears that the phase transition is most probably first order, with the transition temperature increasing with increasing polymer density. For finite-size multichain systems lacking attractive interactions and confined to a diamond lattice, while we find that  $\xi$  abruptly increases to a value on the order of the chain size, these systems do not exhibit any long-range orientational order. The absence of an isotropic-nematic transition in this model for finite-length, dense collections of chains entirely devoid of attractive interactions seems to be a lattice effect. Similar behavior has been reported previously by Baumgartner<sup>6</sup> for multichain systems confined to square and cubic lattices.

It should be pointed out that the intrinsic character of the attractive interaction we assume differs from that employed by Baumgartner.<sup>6</sup> While Baumgartner requires a pair of parallel bonds in order to effect the attractive interaction, we assume the in principle far less restrictive requirement that any pair of nonbonded beads experience an attractive interaction. Thus, the potential as employed here is intrinsically orientation independent, whereas the Baumgartner potential is orientation dependent. In practice, however, because the chains are semiflexible, they tend to pack in locally parallel domains, and by the time the system is near the phase transition temperature, the majority of nonbonded interactions are between parallel (trans) pairs of bonds. Observe that it is the intrinsic local chain stiffness which induces the locally parallel chain domain structure and effectively produces an anisotropic attractive interaction between beads; in other words, our potential and that of Baumgartner are as a practical matter rendered essentially equivalent. Again, we point out that if local chain stiffness is absent, we do not observe either

the formation of locally ordered domains or the presence of an isotropic-anisotropic transition; this conclusion is found to hold over a broad range of values of the attractive interaction between beads.

While other results presented here qualitatively confirm the prediction of Flory's theory<sup>2</sup> modified to include attractive interactions that semiflexible polymers should undergo a phase transition from a globally disordered to a globally ordered state, there are substantial quantitative disagreements with the MC simulation results. Among other things, the simple mean field theory appreciably underestimates the transition temperature,  $T_t^*$ , and even more drastically overestimates the change in energy and entropy at  $T_t^*$ . Furthermore, it in no way addresses the microheterogeneity seen in the simulations. All of the above clearly point out that satisfactory theory of the configurational statistics of highly dense systems of semiflexible chains is not yet at hand. Such a theory must reproduce the observed local ordering of the chains in the isotropic phase, as well as features seen in the ordered phase such as the appreciable fraction of gauche states near the transition temperature and the curvature in the gauche probability profiles. The latter features seem to reflect the packing and cooperativity present in the ordered phase. Work is now in progress toward the development of this theory.

Since the qualitative features observed here seem to be independent of density insofar as these dense tetrahedral lattice polymers resemble real polymers, this work may perhaps point out some essential aspects of the semiflexible polymer liquid crystal phase transition. Nevertheless, based on the system lacking attractive interactions, substantial questions concerning the effects of the lattice re-

main and we echo Baumgartner's<sup>6</sup> concerns about the validity of conclusions based on lattice systems as applied to continuum models of semiflexible polymers at the phase transition.<sup>13-15</sup>

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## Conformational Energies and Random-Coil Configurations of Aliphatic Polyesters

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**ABSTRACT:** Values of the mean-square dipole moment ( $\mu^2$ ) of poly(oxyneopentyleneoxyadipoyl) were determined from measurements of dielectric constants and refractive indices of the polymer in benzene. The value of the dipole moment ratio at 30 °C was found to be 0.653, and its temperature coefficient  $d \ln \langle \mu^2 \rangle / dT$  amounts to  $1.7 \times 10^{-3} \text{ K}^{-1}$ . Poly(oxyneopentyleneoxyadipoyl) networks were prepared by cross-linking hydroxyl-terminated chains with an aromatic triisocyanate. Stress-strain isotherms obtained at two temperatures fit reasonably well to the Mooney-Rivlin formulation for values of the elongation ratio  $\lambda$ , lying in the range  $1.3 < \lambda < 2.5$ ; however, for values of  $\lambda > 2.5$  an anomalous increase in the modulus occurs, which was attributed to maximum extension of the chains. The temperature coefficient of the unperturbed dimensions  $10^4(d \ln \langle r^2 \rangle_0 / dT)$ , determined from thermoelastic experiments carried out on the networks, was  $0.46 \pm 0.23$ . The dipole moment ratio and the temperature coefficient of both the dipole moment and the unperturbed dimensions were critically interpreted by using the rotational isomeric state model. Good agreement between theory and experiment was obtained by assuming that the gauche states about  $\text{C}(\text{CH}_3)_2\text{-CH}_2$  bonds, which give rise to first-order  $\text{CH}_2 \cdots \text{O}$  interactions, have an energy 0.6 kcal/mol lower than the alternative trans states, and that the rotational states about  $\text{CH}_2\text{CH}_2\text{-COOCH}_2$  bonds have similar energy.

## Introduction

Dielectric properties of aliphatic polyesters with cyclohexane rings incorporated in the main chain were recently investigated.<sup>1</sup> These studies showed a sharp increase in the polarity of poly(oxymethylene-1,4-cyclohexylene-methyleneoxysebacoyl) (PCDMS) when the substitution in the cyclohexane ring changes from equatorial-equatorial (trans isomer) to equatorial-axial (cis isomer). The temperature coefficient of the unperturbed mean-square

end-to-end distance,  $d \ln \langle r^2 \rangle_0 / dT$ , was found to be large and negative for both trans and cis isomers.<sup>1</sup> The critical interpretation of the dipole moment and the temperature coefficient of both the dipole moment and the unperturbed dimensions led to the conclusion that these quantities are very sensitive to the gauche population about the  $\text{CH}_2\text{-O}$  bonds next to the equatorial substitution.

An important issue in the configurational analysis of polyesters is to elucidate the value of the conformational