Acknowledgment. I thank Prof. L. Monnerie and Drs. R. Dejean, L. Facchini, F. Lauprêtre, and J.-L. Viovy of the Ecole Supérieure de Physique et Chimie Industrielles de Paris for stimulating discussions on the subject of this paper.

Registry No. Bisphenol A polycarbonate (SRU), 24936-68-3; (bisphenol A)·(carbonic acid) (copolymer), 25037-45-0.

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Monte Carlo Study of Local Orientational Order in a Semiflexible Polymer Melt Model

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ABSTRACT: To investigate the character of local chain packing in a globally amorphous polymer melt, Monte Carlo simulations were performed on model systems consisting of polymers confined to a diamond lattice. The necessary condition for the existence of locally ordered domains is shown to be the presence of local chain stiffness, which in these systems is manifested by the energetic preference of trans (t) over gauche (g) states. These locally parallel domains are not unique static structures but rather are defined only in a statistical sense and exist over a rather broad temperature range. The local domain structure appears to be insensitive to the molecular weight, provided that the chain length exceeds the domain size. It is also found that, to a very good approximation, within a given chain, two subchains belonging to two different domains are statistically independent. The local domain structure becomes enhanced, at fixed chain stiffness, by inclusion of attractive interactions between nonbonded nearest neighbors and/or by increasing the polymer density. The locally ordered melt is shown to be globally disordered over a broad temperature range, with the dimensions of an individual chain very close to those obtained from ideal chain statistics. Various quantities characterizing the character of local ordering in these model systems are examined, and the applicability of these results to real polymer systems is discussed.

I. Introduction

The possible existence of local orientational order in an amorphous polymer melt or glass has long been the subject of controversy. Basically, the kinds of models developed to describe local ordering can be divided into three classes, qualitatively illustrated in Figure 1: (1) the random coil model, (2) bundle models, and (3) a locally ordered domain model. For the random coil model (Figure 1A), espoused by Flory,[1] Flory argued that the dimensions of a chain in the melt should be identical with those in the Θ-solvent and therefore local orientational correlations between neighboring chains are negligible. Bundle models assert that in order to achieve the relatively high density of a melt, the chains have to pack in a locally parallel fashion.[2] These bundles may consist of highly folded regions within a given chain that are randomly oriented with respect to each other as the bead–string model of Schoon[3] (Figure 1B) or may consist of molecules that sharply fold to give the isotropic, high-density melt in which a given set of locally ordered chains maintains orientational correlation over relatively large distances as in the meander model[4–6] (Figure 1C). Finally, the locally ordered domain model is midway between classes 1 and 2.[7] Here the chains are assumed on the average to be locally parallel over a persistence length; however, there is no orientational correlation between two domains, nor are the locally parallel pieces of chains in one domain necessarily the same as those in the neighboring domain (Figure 1D). Thus, in this

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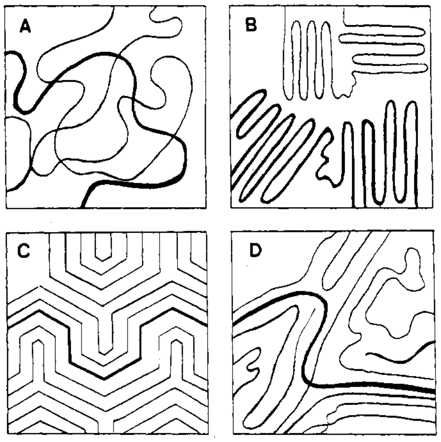

Figure 1. Schematic representation of various models of local chain packing in polymer melts: (A) isotropic random coil model; (B) bead–string model; (C) meander model; (D) locally ordered domain model. In all cases, a single test chain is represented by the heavy curve.

model the local ordering is loosely defined rather than sharply defined as in class 2. In the context of a series of Monte Carlo simulations of dense polymer systems confined to a tetrahedral lattice, it is our purpose to qualitatively investigate the possible validity of these three classes of models and to identify the conditions, if any, under which each of the various models are valid.

Before proceeding to a detailed discussion of the present simulation, it is worthwhile to summarize the successes and failures of each of the various models. We begin with the widely accepted random coil model, which predicts that the dimensions of polymer chains in the melt and a Θ-solvent are identical. Within experimental error, for a number of amorphous polymers, this conjecture has been verified by small-angle neutron scattering.[8] However, certain stiff polymers exhibit a mean square radius of gyration, $\langle s^2 \rangle$, somewhat larger than that of the unperturbed chain (for example, by about 20% for polycarbonate).[9-11] Nevertheless, the qualitative prediction that $\langle s^2 \rangle$ in the melt and in a Θ-solvent should be very close certainly holds.

The problem with the random coil model taken to its extreme limit is that it cannot account for the local orientational order in poly(methylenes) observed by depolarized Rayleigh light scattering[12-14] nor can it rationalize the presence of three intermolecular peaks in the radial distribution function measured by electron diffraction and interpreted by Kargin and co-workers to provide evidence of local ordering in the melt.[15,16] Moreover, another major objection to the random coil model is that it is impossible to pack chains at the observed experimental density unless a certain amount of local orientational order exists.[17] Motivated by these experimental observations, "bundle" models have been proposed which have in common the viewpoint that the local orientational order in the melt can be treated as a perturbation from an ideal crystal.[2-6,15-17] Thus, these models necessarily produce a relatively long-range orientational correlation between chains in the "bundle". However, a necessary corollary to these models is that $\langle s^2 \rangle$ must be at least an order of magnitude larger in the melt than in the Θ-solvent,[17] in direct contradiction to experiment. Thus, the bundle model in its simplest incarnation does not appear to be correct.

Recently, another model, which qualitatively would seem to incorporate the best features of both viewpoints, was proposed in the context of an order–disorder model of the stress–strain behavior of polymer glasses (systems whose orientational order in the absence of strain presumably is identical with that in the melt infinitesimally above T_g).[7] It was suggested that locally chains tend to align in a parallel manner (in agreement with depolarized light scattering studies and electron diffraction studies), but since there is no orientational correlation between domains (each of which is only defined in a statistical sense and whose size down a given chain is on the order of a persistence length), the chain dimensions should be close to those in a Θ-solvent. Further use has been made to this "bundle model" in qualitatively explaining the experimentally observed 180° ring flips in polycarbonate glasses.[18,19] If the packing of chains in this way is capable of achieving the high density of the melt, then it would be consistent with all known experimental facts. One major objective here is to determine the plausibility of the above description of amorphous polymer melts.

The possible existence of local orientational order seems to be predicated on the presence of local chain stiffness. It is well-known that most real polymers exhibit an energetic preference of some conformational states over others, thereby introducing an intrinsic limitation on the flexibility of the chains. While the effect of chain stiffness on the conformation of single chains in dilute solution is theoretically well understood,[20] the problem of chain conformations in a concentrated polymer solution or melt is more complicated. Using mean field statistics, Flory[21] has shown that beyond a certain critical local stiffness (as measured by the energetic preference for the trans as compared to the gauche conformation), a polymer melt should undergo a transition from an isotropic random phase to an oriented nematic phase. Baumgartner and Yoon[22] and Yoon and Baumgartner[23] have performed Monte Carlo simulations of dense, athermal polymer systems confined to a two-dimensional square lattice and a three-dimensional cubic lattice, respectively. Both systems appeared to exhibit a first-order, isotropic–nematic phase transition, in qualitative agreement with Flory's predictions. In the latter system, they see embryonic ordered regions present in the disordered state at and above the transition temperature. However, more recent work by Petschek[24] and Baumgartner[25] indicates that in the absence of attractive intermolecular interactions, semiflexibile polymers confined to a square or cubic lattice in fact do not undergo a phase transition to a globally ordered state. The apparent phase transition reported earlier was the result of finite size effects. However, locally ordered domains are strikingly evident as the chain stiffness increases. Thus, it also appears that the local ordering is intimately connected with local chain stiffness and for those systems having nonbonded attractive interactions, with the liquid crystal phase transition.

In the present Monte Carlo study, we analyze the influence of chain stiffness on conformational properties, in particular the evidence for short-range ordering in polymer systems as a function of both the density and the strength of interaction between polymer segments. We focus here explicity on the nature of local ordering in a melt of semiflexible polymers at temperatures above T_t, where the size of the locally ordered domain is on the order of the contour length of an entire chain. For systems having attractive interactions, T_t is identical with the isotropic–anisotropic phase transition temperature. The analysis of the global order–disorder transition forms the subject of the following, companion paper.[26]

The model we employ represents a compromise between the requirements of computational tractability and our desire to reproduce, as much as possible, the qualitative features of real polymers. We employ a tetrahedral lattice representation of the dense polymer system that also incorporates hard sphere–repulsive excluded volume interactions together with the possibility of a short-range, isotropic attractive force between the polymer segments. Our simulations are complementary to those of Baumgartner and Yoon[22,23] and Baumgartner,[25] who studied systems composed of n = 10–30 beads confined to square and cubic lattices at a very high volume fraction, ϕ (greater than 95%), and in which collinear (trans) and right angle (gauche) rotational states are allowed. We present results at ϕ = 0.5 and 7.5 for tetrahedral lattice systems with n = 12, 24, 48, and 98 along with the possibility of an attractive interaction between nonbonded nearest-neighbor beads. It should be reiterated that in all sample lattice models of dense polymeric systems the lattice bonds or chain segments cannot represent the simple chemically bonded units (e.g., the C–C bonds of polyethylene).[27,28] The chain segment must be considered as an effective unit which in some sense is a compromise between the average breadth of a chain molecule (i.e., excluded volume) and the "statistical" segments which depict the flexibility of a polymer chain. Hence, torsional potentials, or as used here the energy difference between a gauche and trans state, are not directly comparable to the torsional potentials of any real polymer. Perhaps it is best to view lattice models of polymers as analogous to cell models of liquids or solutions.[27] For these reasons one should not attempt to transfer quantitative results from lattice treatments of polymers to real polymeric systems but should view these and other similar simulations as computational experiments from which one can obtain *qualitative* insights.

The outline of the rest of the paper is as follows: In section II, the model and Monte Carlo procedure are described in greater detail. This is followed by a discussion of the results in section III, which consists of four subsections. Subsection A discusses the intrinsic stiffness of a polymer chain as a function of temperature in the context of the wormlike chain model.[29] Then subsection B demonstrates the existence of interchain ordering in semiflexible polymers on a local scale and examines the effect of polymer concentration and the presence of attractive interactions on such ordering. Subsection C addresses the question of global disorder and the nature and extent of the correlation between the locally ordered domains. We conclude in subsection D with a discussion of possible finite size effects on the Monte Carlo simulation results reported here. Finally, section IV summarizes the conclusions of the present paper.

II. Model and Monte Carlo Procedure

A. Model. The model system consists of a monodisperse collection of N chains, each composed of n units (beads) confined to diamond lattice sites that are connected by $n - 1$ bonds. Thus, there are three discrete allowed internal rotational states, one trans (t) state and two gauche (g^+ and g^-) states. The trans conformation is assumed to be energetically preferred. Hence there are $n - 3$ rotational degrees of freedom in a chain of length n. The statistical weights of the three rotational states of a given bond are

$$\omega_{g^+} = \omega_{g^-} = \exp(-\epsilon_g/k_BT)$$
$$\omega_t = 1 \qquad (1)$$

For convenience, we define a reduced temperature $T^* = k_BT/\epsilon_g$. Hard-core repulsive forces between polymer beads are introduced by the exclusion of multiple occupancy of all lattice sites. The short-range attractive interaction (taken to be the same for both intrachain and interchain interactions) is described in the model by the parameter ϵ_a, with $\epsilon_a = -A\epsilon_g$ (where A is a positive constant), and is only allowed between neighboring, nonbonded polymer beads. Hence the total configurational energy of the system can be expressed as

$$E = \eta\epsilon_g + \gamma\epsilon_a \qquad (2)$$

where η is the number of gauche states in the system and γ is the number of nearest-neighbor, nonbonded pairs of polymer beads. The reference state is the system with ϵ_g = 0 (or equivalently, at infinite temperature T^*, i.e., a random, athermal system).

Periodic boundary conditions were employed in the simulation. If there are N chains of length n in a Monte Carlo (MC) box of length L, one can define the volume fraction of polymer in the model system as

$$\phi = N(n/V) \qquad (3)$$

with $V = L^3/8$. The factor of 8 arises from the use of an integer representation of the bead coordinates. As a consequence, the length of a bond, l, equals $3^{1/2}$.

B. Summary of Monte Carlo Procedure. A standard asymmetric Metropolis scheme[30] was used in the simulation algorithm. The following modifications of the chain conformation were employed to sample the configuration space:[31] (i) "reptation" type motions[32] where a randomly chosen end segment is clipped off and then added to the opposite chain end in a random direction; (ii) a random rotation of a small end portion of the chain (1–2 bonds); (iii) three-bond kink motions, resulting from the permutations of the chain segments in a randomly chosen part of the chain (only a sequence containing a gauche conformation can be affected by this kind of modification—see ref 33 for further details). Each Monte Carlo cycle consists on the average of one attempt to make a reptation step and several attempts (from two to ten, depending on conditions) at kink flips per polymer chain. Reptation dynamics, in particular, provides a very efficient means of sampling broad regions of configuration space.[32] It does however suffer a defect in that it can lead to self-trapped configurations, the so-called "double-ended cul-de-sac". It is widely felt that this defect is negligible—the origin of this feeling is the mainly a posteriori checks where the results of a reptation dynamics MC simulation are compared to an analytic result (see, e.g., ref 34). We hope to further minimize such situations by including end rotations (step ii above). In particular, we checked our algorithm by performing a single-chain calculation for $\epsilon_g = \epsilon_a = 0$. This athermal result (which is published elsewhere[35] as part of a work on single-chain collapse transitions) is in very good agreement with previous analytic and numerical self-avoiding-walk calculations.

At every temperature, the simulation was run for a sufficient number of cycles to ensure proper equilibration. In most cases, due to the high acceptance ratio of the Metropolis scheme for the densities studied, 5×10^5 to 1×10^6 cycles per polymer chain were sufficient to achieve equilibration. Equilibrium information for the system was then extracted from a run lasting twice the equilibration time. The sequence of simulations as a function of temperature started from an athermal system with $\epsilon_g = 0$. At high temperatures where the properties of the system are rather insensitive to temperature, relatively large temperature increments between successive temperature states where employed. As the temperature of the system was lowered further, small temperature increments were employed in "cooling" the system. In the vicinity of T_t^*, "heating" sequences were also employed; the discussion of

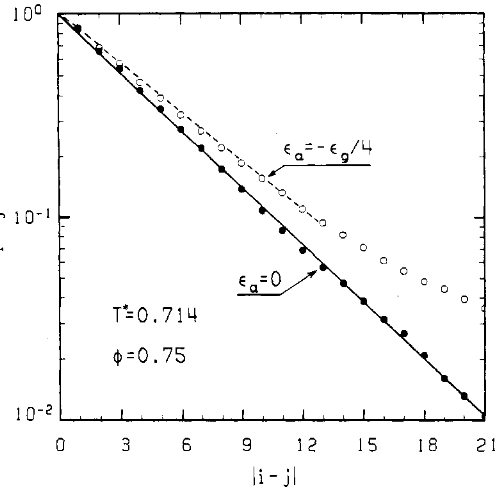

Figure 2. Plot of $\langle \mu_i \cdot \mu_j \rangle / \mu^2$ vs. $|i-j|$ for a system having $\phi = 0.75$, $n = 24$, $T^* = 0.714$, and $\epsilon_a = 0$ $(-\epsilon_g/4)$ in the filled (open) circles, respectively. The solid (dashed) curve is the linear fit to the Monte Carlo data extrapolated through $|i-j| = 0$.

the properties of the system near and below T_t^* (which we remind the reader is the phase transition temperature for systems with attractive interactions) is deferred to the following paper.[26]

In section III, we examine equilibrium data obtained from long runs (preceded by appropriate equilibration) in a decreasing temperature sequence. For the $n = 24$ ($n = 48$) systems, after every 10 (250) cycles the contribution of various properties to the equilibrium averages was calculated.

III. Results

General Considerations. The majority of results presented below are for systems composed of chains of length $n = 24$ confined in a Monte Carlo box of length $L = 24$. Thus, the direct influence of the finite size of the Monte Carlo box should be eliminated. For $n = 24$, we studied two densities, $\phi = 0.5$ and $\phi = 0.75$. To examine the role of intersegmental attraction on local domain structure at each density, ϵ_a was set equal to zero and $-\epsilon_g/4$, the latter providing attractive interactions somewhat less than are present in a Θ-solvent.[33] (We remind the reader that ϵ_g is taken as the independent energy variable.) To more completely characterize the nature of and extent of correlation in the local chain packing, a less extensive series of simulations were also undertaken for $N = 216$ chains with $n = 48$ confined to a Monte Carlo box of length $L = 48$, i.e., packed at $\phi = 0.75$, again with both $\epsilon_a = 0$ and $-\epsilon_g/4$. The latter set of results when combined with the discussion of the effect of periodic boundary conditions in subsection D leads us to conclude that the qualitative picture of local chain ordering developed below should hold for dense systems of very long chains confined to a tetrahedral lattice and, perhaps, for polymer melts in general.

A. Intrinsic Chain Stiffness. Because, in these model simulations, the polymers are confined to a diamond lattice, the well-known odd–even effect of the mutual orientation of the chain bonds is expected. To eliminate this lattice artifact the local orientation of the chain backbone is defined by averaging over two successive bonds:

$$\mu_i = \mathbf{l}_i + \mathbf{l}_{i+1} \tag{4}$$

where $\mathbf{l}_i$ is the ith bond vector. In case of wormlike chains,[29] $\langle \mu_i \cdot \mu_j \rangle$should decay exponentially with increasing distance down the chain countour $|i-j|$. Thus

$$\langle \mu_i \cdot \mu_j \rangle / \mu^2 = \exp(-|i-j|/P) \tag{5}$$

Table I
Persistence Length for Chains of n = 24 Beads as a Function of Temperature[a]

	$\phi = 0.5$		$\phi = 0.75$	
T^*	$\epsilon_a = 0$	$\epsilon_a = -\epsilon_g/4$	$\epsilon_a = 0$	$\epsilon_a = -\epsilon_g/4$
1	3.2	3.2	3.2	3.3
0.833		3.7	3.8	4.0
0.714		4.6	4.7	*5.3*
0.667	4.9	5.1	5.5	$>n^c$
0.625		*5.7*	*7.1*	
0.588		$>n^c$	$>n^b$	
0.5	8.0			
0.417	*16.5*			
0.4	$>n^b$			

[a] Calculated by employing eq 5. [b] At this value of T^* in a system lacking attractive interactions, the bundle length exceeds the chain contour length; however, these systems are still globally isotropic. [c] Below the isotropic–anisotropic phase transition temperature.

with μ^2 the equilibrium value of $\langle \mu_i \cdot \mu_i \rangle$ and which equals $^8/_3$ for diamond lattice systems in units of bond length and where P is the persistence length (expressed in units of bond length).

A representative plot of $\langle \mu_i \cdot \mu_j \rangle / \mu^2$ vs. $|i-j|$ for $\phi = 0.75$, $T^* = 0.714$, and $n = 24$ is shown in Figure 2. The lower solid curve (where there are no nearest-neighbor interactions) clearly exhibits the characteristic behavior of a wormlike chain. However, as seen in the upper, dashed curve, at the phase transition temperature $T^* = 0.714$, the value of $\langle \mu_i \cdot \mu_j \rangle$ for the globally isotropic system with nearest-neighbor interactions and having $\epsilon_a = -\epsilon_g/4$ deviates from simple wormlike chain behavior, if one considers long distance down the chain. Nevertheless, the broad range of linear behavior allows one to estimate the persistence length P even in this case. The numerical values of P as a function of temperature for $\phi = 0.5$ and $\phi = 0.75$ with and without attractive interactions are presented in Table I. For all the systems under consideration, P increases smoothly with decreasing temperature up to a transition temperature T_t^* where the persistence length P jumps abruptly to a value considerably greater than the chain length. In the vicinity of the transition temperature, all the systems exhibit a similar deviation from wormlike behavior as is the case for that with $T^* = 0.714$ and $\epsilon_a \neq 0$ displayed in Figure 2. This phenomenon as well as the effect of concentration and intersegment interaction on the observed chain stiffness (compare the data in rows four and five of Table I) strongly suggests that a cooperative change in chain packing occurs at low temperatures which, however, are still above the transition temperature to a globally ordered phase. It has been theoretically[36] demonstrated that the stiffness of a wormlike polymer dissolved in a nematic medium could be considerably greater than if it were dissolved in an isotropic solvent. Partially ordered domains or bundles could conceivably provide such a nematic environment.

B. Nature of Local Ordering of the Chains. Several questions on the character of the local ordering need to be addressed. First, what are the conditions under which local ordering of chains occurs? When such ordering exists, what is the size of a locally ordered domain? Does inclusion of attractive interactions make the local domain structure better defined? Can systems that possess significant local order be globally random? A sufficient condition for global disorder would seem to be lack of significant orientational correlation between different parts of a chain contained in two nearest-neighbor domains. If this is the case, then we would expect the dimensions of a single chain in the dense melt to be quite close to those of an ideal chain. In what follows, we address each of these

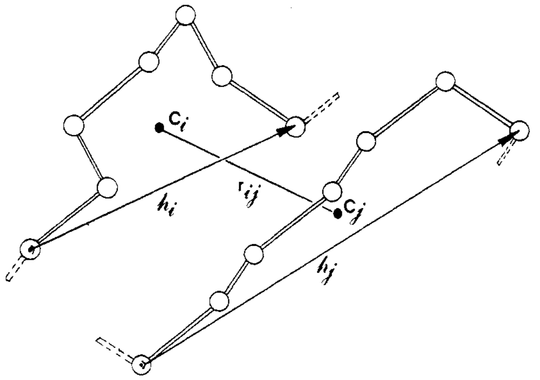

Figure 3. Geometry employed to examine the mutual orientation of subchains of various lengths as a function of their spatial distribution. The scripts i and j refer to two different subchains, $\mathbf{C}_i$ is the center of mass vector, and $\mathbf{h}_i$ is the end-to-end vector of the ith subchain, respectively. $\mathbf{r}_{ij}$ is the vector connecting the centers of mass of subchains i and j.

points in turn. We begin with systems lacking attractive interactions between polymer segments and then subsequently analyze those containing attractive interactions.

Local Interchain Orientational Correlations. In order to establish and estimate the range of local ordering in a melt of semiflexible polymers, we examined the mutual orientation of subchains of various lengths concomitant with their spatial distribution. Interchain correlations were probed via the following procedure. First, two subchains (or blobs) were extracted from randomly chosen chains. Then the distance between their centers of mass and the angle between their end-to-end vectors were measured. An example of the relevant geometry is shown in Figure 3. Subchains of length n_B equal to 3, 5, 7, 9, and 11 beads were considered. Because the end-to-end vectors for short subunits of semiflexible polymers should be, on the average, close to the local orientation of the chain backbone, the measured angle θ_{ij} between the end-to-end vectors of subchains i and j, $\mathbf{h}_i$ and $\mathbf{h}_j$ defined in Figure 3, should reflect the mutual orientation of the subchains and was computed from

$$\cos(\theta_{ij}) = (\mathbf{h}_i \cdot \mathbf{h}_j)/(|\mathbf{h}_i| \cdot |\mathbf{h}_j|) \tag{6}$$

and the degree of local ordering was measured by calculating the second Legendre polynomial

$$P_2(\theta_{ij}) = (3\langle \cos^2(\theta_{ij})\rangle - 1)/2 \tag{7}$$

where the angular brackets denote an ensemble average of $\cos^2(\theta_{ij})$ as a function of r_{ij}, the distance of separation of the centers of mass of the blobs. Discrete intervals of r_{ij} were used. The global order parameter $\bar{P}_2$ was computed from an ensemble average of the angle between the 3-bead blob vectors defined by eq 4, where the averaging involves all the vectors $\mu_{i,m}$, where i is the bead position in the chain and m is the chain number.

The radial distribution functions $g(r)$ for the separation of the centers of mass of the various subchains i and j were computed in a manner similar to the distance-dependent order parameter described above. That is

$$g(r) = \omega(r)/v_r \tag{8a}$$

with

$$v_r = \tfrac{4}{3}\pi\left(\left(r + \frac{\Delta r}{2}\right)^3 - \left(r - \frac{\Delta r}{2}\right)^3\right) \tag{8b}$$

In eq 8a, ω is the probability of finding the center of mass of blob j at a given distance from the center of mass of blob i, where the spatial increment Δr was set equal to unity (in lattice units), which is smaller than the length of a single polymer bond, l, which equals $3^{1/2}$, and v_r is the volume between $r + \Delta r/2$ and $r - \Delta r/2$. Thus, $g(r)$ is normalized to approach the value 1 when r_{ij} becomes large. However, it should be noted that although r_{ij}, the distance between the centers of mass of the blobs, takes on values from a discrete set of numbers, only a small fraction belong to the set of points on the diamond lattice. Hence, while the choice of the particular spacing of Δr is somewhat arbitrary, nevertheless it seems to be reasonable.

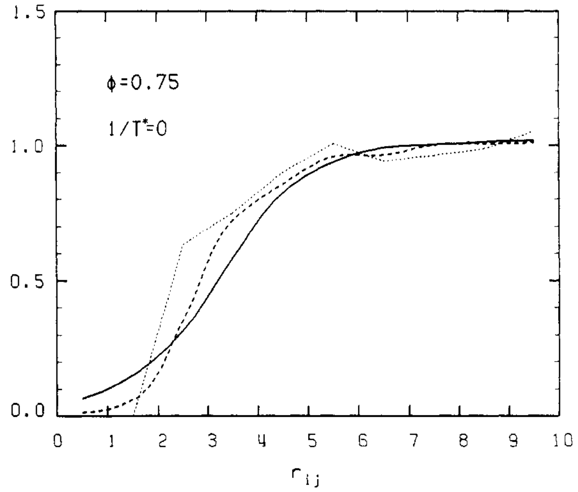

Figure 4. Plot of the radial distribution function $g(r)$, defined in eq 8, vs. r_{ij}, the center of mass separation of two subchains, for subchains of length n_B = 3, 7, and 11 in the dotted, dashed, and solid curves, respectively. In all cases, n_B = 24, ϕ = 0.75, and $T^* = \infty$; i.e., $\epsilon_a = \epsilon_g = 0$.

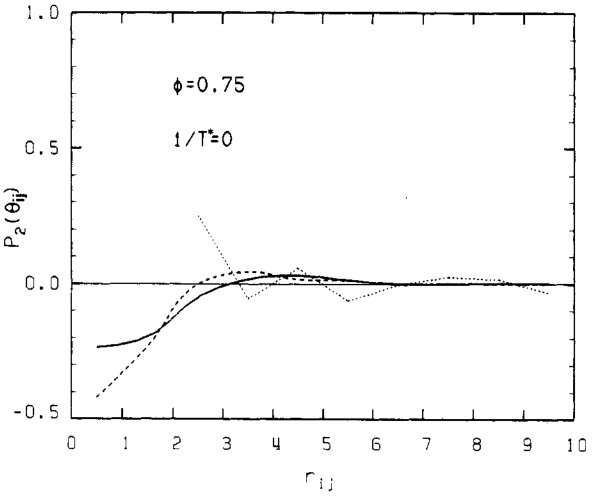

Figure 5. Plot of $P_2(\theta_{ij})$, the local order parameter defined in eq 7, vs. r_{ij}, the distance of separation of the centers of mass of two subchains, for subchains of length n_B = 3, 7, and 11 in the dotted, dashed, and solid curves, respectively. In all cases n = 24, ϕ = 0.75, and $T^* = \infty$; i.e. $\epsilon_a = \epsilon_g = 0$.

Systems without Attractive Interactions. In Figures 4 and 5, respectively, the radial distribution function $g(r)$ and the corresponding profiles for the order local parameter $P_2(\theta_{ij})$ for chains of length n = 24 and ϕ = 0.75 are plotted for subchains of length n_B = 3 (dotted curve), n_B = 7 (dashed curve), and n_B = 11 (solid curve) at the high (infinite) temperature limit for the system ($\epsilon_a = \epsilon_g = 0$). Fluctuations in the order parameter of the shortest subchain under consideration, n_B = 3, reflect the intrinsic lattice structure of the model system. For the case of longer subchains, n_B = 7 and n_B = 11, two major features should be noted. First there is a strong excluded volume

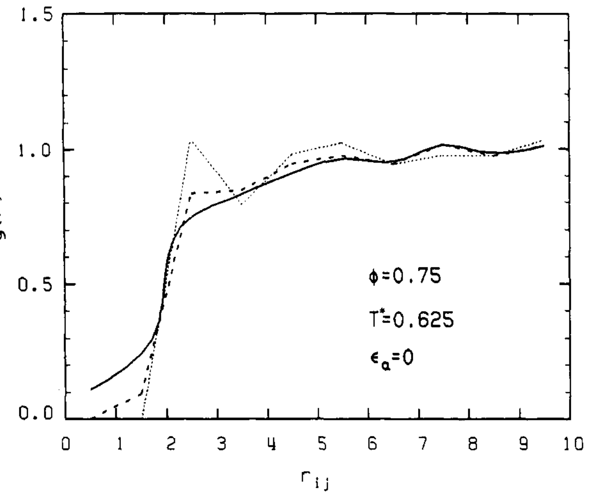

Figure 6. Plot of the radial distribution function $g(r)$, defined in eq 8 vs. r_{ij}, the center of mass separation of two subchains, for subchains of length $n_B = 3$, 7, and 11 in the dotted, dashed, and solid curves, respectively. In all cases, $n = 24$, $\phi = 0.75$, $T^* = 0.625$, and $\epsilon_a = 0$.

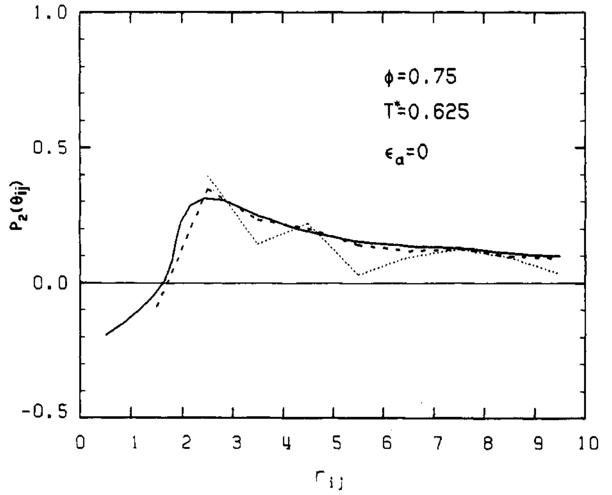

Figure 7. Plot of $P_2(\theta_{ij})$, the local order parameter defined in eq 7, vs. r_{ij}, the center of mass of two subchains, for subchains of length $n_B = 3$, 7, and 11 in the dotted, dashed, and solid curves, respectively. In all cases, $n = 24$, $\phi = 0.75$, $T^* = 0.625$, and $\epsilon_a = 0$.

effect between the pairs of subchains. This excluded volume effect extends up to distances comparable to the subchain size (that is, r_{ij} is equivalent to approximately three bond lengths) as can be seen in Figure 4. Second, when the subchains are very close to each other they tend toward a mutually orthogonal orientation (see Figure 5). At larger distances, the longer subchains exhibit an essentially random orientation with a very slight tendency toward parallelism at a distance equivalent to the blob size. Somewhat similar behavior was observed by Olaj and Zifferer[37] even on the length scale of an entire chain in their Monte Carlo studies of two interpenetrating chains.

At lower temperatures, as the flexibility of the chains decreases, the local packing changes dramatically. However, the chains still possess considerable flexibility in that the persistence length is appreciably smaller than the chain length. Representative results are shown in Figures 6 and 7 for $g(r)$ and $P_2(\theta_{ij})$ vs. r_{ij} in a system having $\phi = 0.75$, $n = 24$, and $\epsilon_a = 0$ and at a reduced temperature $T^* = 0.625$. Subchains of size $n_B = 3$, 7, and 11 are denoted by the dotted, dashed, and solid lines, respectively. In Figure 6, the effective range of the repulsive interaction drops to a value close to the chain diameter rather than the mean dimension of a blob; i.e., $g(r)$ approaches a value close to unity at a distance of a single bond length. At the same distance, as shown in Figure 7, there is a steep increase in the order parameter. The maximum value of the local orientational order parameter for blobs of $n_B = 7$ is $P_2 = 0.35$ and for $n_B = 9$ is $P_2 \cong 0.3$. Both the range of the average local orientational order parameter and the smaller interchain excluded volume effect are evidence of the strong tendency of chains to be locally parallel. On increasing the distance between subchains, this tendency decreases. Thus on the basis of the comparison of this case with the system of infinite temperature shown in Figures 4 and 5, we conclude that local chain stiffness is a necessary condition for local parallelism between chains.

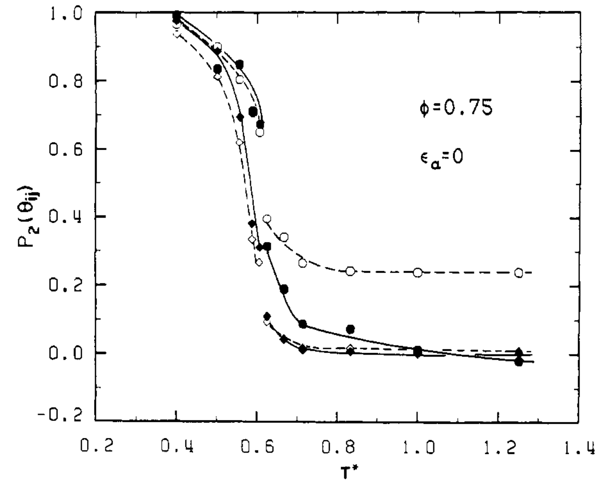

Figure 8. Plot of $P_2(\theta_{ij})$, the local order parameter calculated via eq 7, vs. T^*. The dashed line and open symbols correspond to subchains of $n_B = 3$, and the solid line and filled symbols to subchains of $n_B = 11$. The circles (diamonds) correspond to the order parameter at $r_{ij} = 3$ (10). In all cases, $n = 24$, $\phi = 0.75$, $T^* = 0.625$, and $\epsilon_a = 0$.

The relationship between increasing local chain stiffness and the increasing tendency of chains to be locally parallel is graphically demonstrated in Figure 8, where we plot $P_2(\theta_{ij})$ vs. temperature for a system at $\phi = 0.75$ and $\epsilon_a = 0$. (Decreasing temperature corresponds to increasing chain stiffness.) The dashed lines (and open symbols) correspond to the shortest blob ($n_B = 3$) and the solid lines (and filled symbols) to the longest one ($n_B = 11$). Data for subchains of size $n_B = 5$, 7, and 9 lie between the curves for $n_B = 3$ and $n_B = 11$ and have been omitted for the sake of clarity. The circles correspond to the values of the order parameter at the smaller intersubchain center of mass distance $r_{ij} = 3$ and the diamonds to the values of P_2 at the larger distance $r_{ij} = 10$.

While the local order parameter P_2 can differ appreciably from zero in the globally isotropic phase, the global order parameter $\bar{P}_2$ is close to zero over the entire range of temperatures regardless of the length of blob under consideration.[26] While there is no global isotropic-to-anisotropic transition for the system lacking attractive interactions, the short-range order parameter $P_2(\theta_{ij})$ exhibits a jump at a transition temperature $T_t^* = 0.615$, but above the transition (the right branches of the two upper curves) the degree of ordering is still significant over a wide temperature range and depends on subchain length. (At T_t^* the persistence length of a chain in the locally ordered bundle exceeds the chain contour length.) However, both above and below T_t^*, the locally ordered domains themselves are still globally disordered.

Even if one adopts a more rigid criterion and asserts that the present data only provide convincing evidence for local

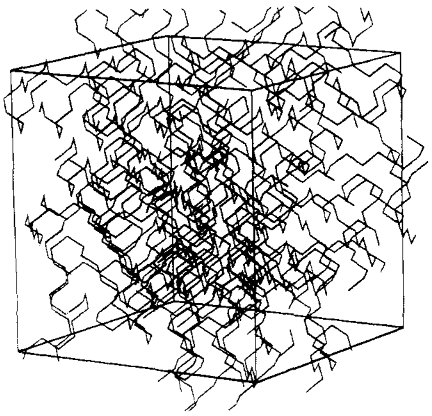

Figure 9. Representative configuration of a locally and globally random system with $\phi = 0.75$ and $\epsilon_g = 0$. See text for further details.

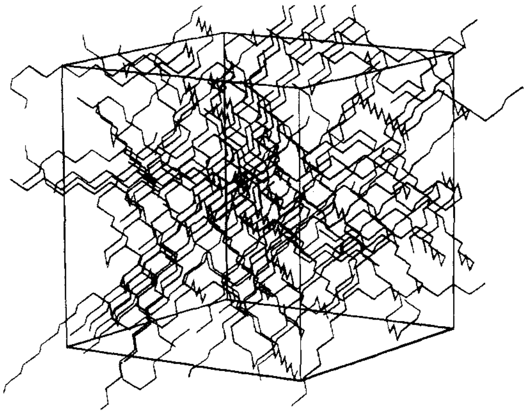

Figure 10. Representative configuration of a globally random system having appreciable local order, with $\phi = 0.75$ and $T^* = 0.625$. See text for further details.

ordering of polymer melts for temperatures below $T^* = 0.8$, the requisite stiffness necessary to effect local parallelism between chains is typical of many real polymers. However, it must be pointed out that the locally ordered domains we observe are not rigidly preserved structures. The domain or bundle structure reported here reflects the fact that semiflexible polymers on average tend to pack in a locally parallel fashion which involves several subchains and where the length of a bundle is somewhat larger than the persistence length of the polymer (see Table I).

The validity of the above statements is pictorially illustrated in Figures 9 and 10, where representative configurations of two systems, a random one ($\phi = 0.75$, $\epsilon_g = 0$) and a globally random one but with significant local order ($\phi = 0.75$, $T^* = 0.625$), are shown. For purposes of clarity, no images of the chains resulting from the periodic boundary conditions are drawn. Thus the density of the polymer on the sides of the MC box appears to be lower than in the center of the box where the pictures reflect the "true" density.

The finding that chains must be locally stiff in order to pack in a locally parallel fashion is consistent with a Monte Carlo simulation of an off-lattice model of n-alkanes in the melt performed by Vacatello and co-workers.[38] While they did not report any appreciable local ordering of chains, in fact they do observe the onset of some slight ordering at distances that correspond to an r_{ji} equal to about 2.7 in our reduced units (as shown in Figure 10 of ref 38). In the context of our results, this is not at all surprising. At the relatively high temperature, 400 K, used in their simulation, the rotational potential of n-butane that they employed does not provide the amount of chain stiffness required to induce appreciable local parallelism of chains. They compare their results to those for molten polyethylene. It should be noted that 400 K corresponds in our reduced units to a reduced temperature T^* of 1.58, where an individual polymer chain is highly flexible. Thus, Vacatello et al.[38] were in fact probing the high-temperature regime of Figure 8, where one would expect and does indeed find fairly negligible local ordering. The close correspondence between their off-lattice simulation results and the lattice simulation results reported here is highly suggestive that the qualitative effect of local ordering is likely to be a universal property of polymeric systems.

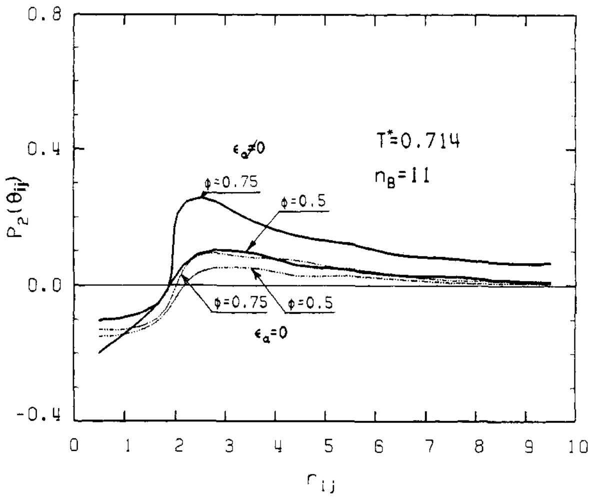

Figure 11. Plot of $P_2(\theta_{ij})$, the local order parameter calculated via eq 7, vs. r_{ij} for systems lacking attractive interactions in the lower dotted curves and for systems having $\epsilon_a = -\epsilon_g/4$ in the upper solid curves. The densities are as indicated in the figure. In all cases $n = 24$, $n_B = 11$, and $T^* = 0.714$.

Effect of Attractive Interactions and Density on Local Ordering. Attractive interactions were introduced into our model by allowing nearest-neighbor nonbonded interactions of strength ϵ_a, which in the present study are set at a value $\epsilon_a = -\epsilon_g/4$. For the range of temperatures employed here, the values of ϵ_a are usually smaller than those found at the coil–globule transition for the model of a single chain confined to a diamond lattice.[33] In other words, in the present study, in the melt, the segment–segment interactions were always slightly weaker than those in a Θ-solvent. At a constant temperature (the same chain stiffness), it is found that the inclusion of attractive interactions ($\epsilon_a \neq 0$) increases the local ordering as manifested by an increased short-range order parameter. Moreover, at a constant temperature and at fixed ϵ_a and ϵ_g, an increase in the polymer concentration also leads to an increase in the order parameter. Both these effects are illustrated in Figure 11, where for $n = 24$ and $T^* = 0.714$, the order parameter $P_2(\theta_{ij})$ for subchains of size $n_B = 11$ is plotted vs. distance for densities $\phi = 0.5$ ($\phi = 0.75$) and for two types of segment–segment interactions, $\epsilon_a = 0$ in the lower (upper) dotted curves and $\epsilon_a = -\epsilon_g/4$ in the lower (upper) solid curves. Figure 11 clearly demonstrates that at lower densities segment–segment attractions have a strong influence on the local ordering of the polymers, even in the absence of global ordering. Furthermore, as shown in Figure 12, where we plot $P_2(\theta_{ij})$ vs. r_{ij} for various temperatures, for a system having $n = 24$, $\phi = 0.5$, $n_B = 9$, and $\epsilon_a = 0$, the local parallel packing of chains is present over a wide temperature range. Finally, it should be pointed out that a melt of chains of length $n = 24$ and at $\phi = 0.75$ with unlimited chain flexibility ($\epsilon_g = 0$) but with a nonzero attractive interaction ($\epsilon_a \neq 0$) does not exhibit any tend-

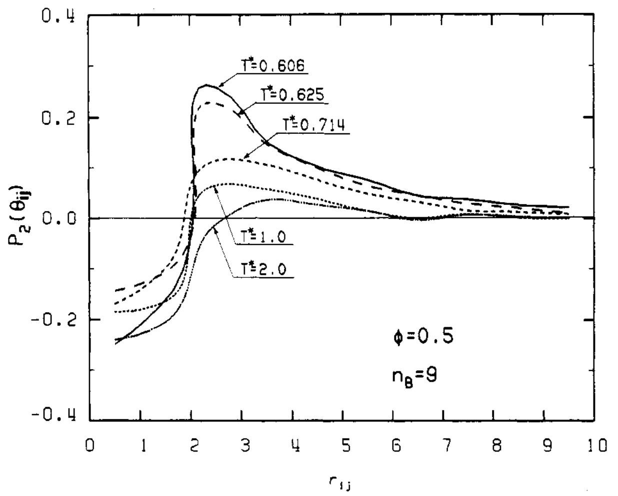

Figure 12. Plot of $P_2(\theta_{ij})$, the local order parameter calculated via eq 7, vs. r_{ij} at various temperatures for a system having $n = 24$, $\phi = 0.5$, $n_B = 9$, and $\epsilon_a = 0$.

ency toward either local or global ordering at any reasonable temperature. Thus, our conjecture that local chain stiffness is a prerequisite for the formation of locally ordered domains is confirmed.

C. Extent of Correlation between Locally Ordered Domains. In the previous subsection, the conditions under which the model predicts that chains tend to pack in a locally parallel manner were established. For chains having lengths of $n = 24$, we showed that over a substantial temperature range within a given chain, the locally ordered domains seem to persist on average for about 10 bonds down the chain and seem to have a maximum in orientational correlation at a distance of about 3 bond lengths between the centers of mass of two subchains. Proof that the ordering is local rather than global is provided by the decay of $P_2(\theta_{ij})$ with distance, by the fact that $g(r) \rightarrow 1$ as $r_{ij} \rightarrow \infty$, and by the fact that the global order parameter is close to zero for systems having attractive interactions and above the phase transition temperature and for systems lacking attractive interactions at all temperatures studied. Nevertheless, the possibility remains that down a given chain, there exists a strong orientational correlation between adjacent locally ordered domains; such correlations (as in the bead-string[3] or meander model[4-6]) could yield mean square end-to-end distances, $\langle R^2 \rangle$, appreciably greater than that predicted from ideal chain statistics. If this would turn out to be the case, it would completely eliminate the locally ordered domain model as a viable description of real polymer systems. Thus, the examination of the extent, if any, of down-chain correlation between the locally parallel domains of subchains is the focus of this subsection.

Table II
Expansion Factor[a] $(\langle R^2 \rangle / \langle R_0^2 \rangle)^{1/2}$ for Various Dense Systems of Semiflexible Polymers Composed of n = 24 Beads

	$\phi = 0.5$		$\phi = 0.75$	
T^*	$\epsilon_a = 0$	$\epsilon_a = -\epsilon_g/4$	$\epsilon_a = 0$	$\epsilon_a = -\epsilon_g/4$
2		1.0277	1.0118	1.0091
1.25		1.0122	1.0010	1.0152
1	1.0094	1.0164	1.0084	1.0205
0.833		0.9944	0.9984	1.0089
0.769			1.0140	1.0226
0.714		1.0078	1.0098	*1.0763*[c]
0.667	1.0028	1.0148	1.0542	1.4965
0.625		*1.0470*[c]	*1.1120*[b]	1.5900
0.588		1.3942	1.3970	1.5808
0.5	1.0150	1.4550	1.3907	1.4753
0.417	*1.0936*[b]	1.3476		
0.4	1.2104		1.3000	

[a] $\langle R^2 \rangle$ = Monte Carlo data; $\langle R_0^2 \rangle$, the ideal chain value is computed according to Flory's method[20] for a finite chain of length $n - 1 = 23$ bonds. (Assuming independent rotations and no excluded volume.) [b] Lowest temperature where bundle size is less than the chain length. [c] Lowest temperature for an isotropic system having attractive interactions.

Table III
Representative Properties for a System of Semiflexible Polymers Having n = 48 Packed at ϕ = 0.75

				$P_2(\theta)_{\max}$[b]	
	T^*	$\langle R^2 \rangle_{MC}$	α^2[a]	7 beads	11 beads
athermal	"∞"	299.5	1.0793	0.070	0.023
$\epsilon_a = 0$	1.0	545.6	0.9631	0.119	0.076
$\epsilon_a = 0$	0.714	772.1	0.9981	0.205	0.167
$\epsilon_a = 0$	0.625	1086.9	1.2023	0.354	0.243
$\epsilon_a = -\epsilon_g/4$	1.0	547.1	0.9658	0.137	0.098

[a] Calculated via eq 9. [b] Maximum intersubchain local order parameter, $P_2(\theta_{ij})$, for subchains of length $n_B = 7$ and $n_b = 11$, respectively.

We begin by examining, in Table II, for polymers confined to a diamond lattice having $n = 24$, $\phi = 0.5$ and 0.75, without and with attractive interactions, the expansion factor α^2 as a function of T^*. Here

$$\alpha^2 = \langle R^2 \rangle / \langle R_0^2 \rangle \qquad (9)$$

where $\langle R_0^2 \rangle$ is computed according to Flory's method[20] for an isolated chain containing $n - 1$ bonds, assuming independent rotations and no excluded volume effects. For the system having attractive interactions at all temperatures where the system is globally isotropic, α^2 is seen to be less than 1.1, and for most cases, in fact lies with 3% of unity. Similar behavior is seen for the systems lacking attractive interactions at temperatures where the size of the locally ordered domain is less than the chain length. In other words, even when packing of the chains produces appreciable local order, the average dimensions of a given chain are very close to that obtained assuming ideal (but semiflexible) chain statistics. This is consistent with the idea that the domain correlation between locally parallel domains decays with distance and that the local parallelism between chains is loosely defined rather than strictly obeyed as in a meander or bead-string model.

It might be argued that chains of length $n = 24$ are simply too short to produce appreciable deviations in α^2 from unity. In other words, perhaps at this chain length there are too few domains per molecule. To preclude this possibility, we examined 216 chains of length $n = 48$ confined to a Monte Carlo box of length $L = 48$; thus, the system is packed at a density $\phi = 0.75$. All the qualitative conclusions concerning the tendency of chains to pack in a locally parallel manner seen when $n = 24$ also hold when $n = 48$. This substantiates the notion that beyond a certain minimum chain length the formation of these locally ordered domains is essentially a local property whose characteristics are molecular weight independent. Thus, conclusions obtained here may also describe the local structure of melts of high molecular weight, semiflexible polymers.

In Table III, we present a summary of representative properties for the system of semiflexible polymers each of length $n = 48$, having a volume fraction $\phi = 0.75$. Due to the larger size of the system, the statistics for the $n = 48$ system are not as good as for the $n = 24$ system. Thus, except for the $T^* = 0.625$ results, within the statistical error of the simulation (estimated to be about 5%), α^2 is indistinguishable from unity. The value of $\alpha^2 = 1.20$ when

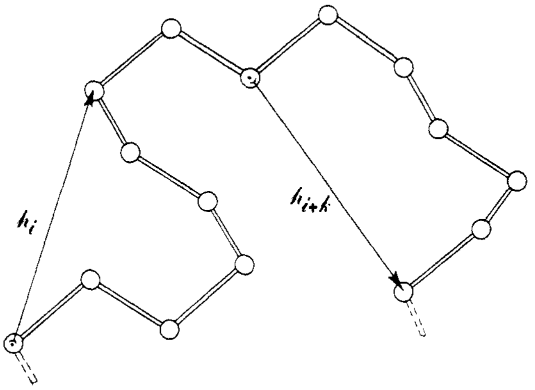

Figure 13. Geometry employed to calculate the various interdomain correlation functions. $\mathbf{h}_i$ is the end-to-end vector of a subchain containing n_B beads whose origin is at bead i.

$T^* = 0.625$ is statistically significant and reflects the same trend as in the $n = 24$ case for isotropic systems near the apparent transition temperature where the chain persistence length exceeds the contour length. Nevertheless, in all cases, α^2 is sufficiently close to unity to make the qualitative prediction that semiflexible chains in the melt essentially have dimensions quite close to those of an ideal chain, in agreement with small-angle neutron scattering experiments.[8]

The next property we examined is the extent of subchain–subchain correlation down a given chain. Such correlation may be measured by examining the ensemble average of

$$\langle \cos \theta_{i,i+k} \rangle = \langle \mathbf{h}_i \cdot \mathbf{h}_{i+k} / |\mathbf{h}_i||\mathbf{h}_{i+k}| \rangle \qquad (10)$$

as a function of the distance of separation between a subchain starting at bead i and the start of the next subchain at bead $i + k$. $\mathbf{h}_i$ and $\mathbf{h}_{i+k}$ are both defined in Figure 13. In Figures 14, parts A, B, and C, we plot $\langle \cos \phi_{i,i+k} \rangle$ vs. k for systems composed of chains having $\epsilon_a = 0$ and $\phi = 0.75$ at $T^* = 1.0$, 0.714, and 0.625, respectively, and where n_B (the length of each of the two subchains) is set equal to 3, 7, and 11 in the dashed, solid, and dotted lines, respectively. The slope of $\langle \cos \phi_{i+k} \rangle$ vs. k provides the persistence length P_b for the decay of locally ordered domain–domain correlation. For $T^* > 0.625$, apart from some initial correlation at short distances, the three sets of curves give essentially the same P_b, which equals about 3.3 when $T^* = 1$ and about 4.8 when $T^* = 0.714$. In other words, the range of correlation between pairs of locally ordered domains is very small, being on the order of a few bond lengths at most. When $T^* = 0.625$ (which is close to the apparent transition temperature T_t^* where the chain persistence length exceeds the chain contour length), there seems to be some additional orientational correlation of the shorter subchains (with $n_B = 3$ and 7) that is enforced by the local domain structure.

On the basis of the above, we conclude that these model systems are globally disordered even when significant local parallelism of the chains exists because of (a) the decay of interchain correlations with increasing separation of the subchains, (b) the fact that the global order parameter is very close to zero above the phase transition temperature (for a more detailed discussion of the transition to the ordered phase, please see the following paper),[26] (c) the observation that in the system with attractive interactions in the isotropic phase as well as in the system having $\epsilon_a = 0$ and whose bundle dimensions are smaller than the chain length, the chain dimensions as probed by $\langle R^2 \rangle$ are consistent with ideal (semiflexible) chain statistics, and (d) the fact that the correlation down the chain for the various subchain vectors decays very rapidly with increasing distance. That is, in these model systems there appears to be a loosely defined bundle structure wherein chains tend to pack in a locally parallel manner, but there is very little orientational correlation between two parts of a given chain belonging to two different locally ordered domains.

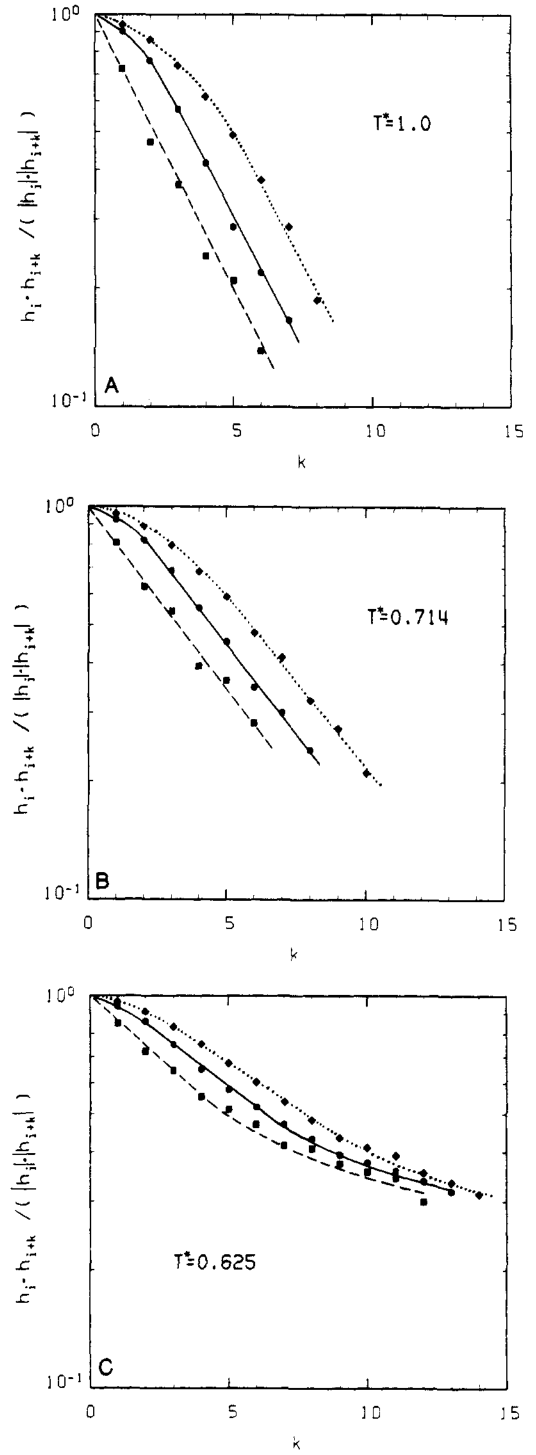

Figure 14. Parts A, B, and C present plots of $\langle \cos \theta_{i,i+k} \rangle$, defined in eq 10, vs. k for systems having $\epsilon_a = 0$, $\phi = 0.75$, and $T^* = 1.0$, 0.714, and 0.625, respectively. In each plot, $n_B = 3$, 7, and 11 in the dashed, solid, and dotted lines, respectively. See text for further details.

D. Finite-Size Effects. All of the results discussed above were obtained from computer experiments with the Monte Carlo box size equal to the chain length under consideration ($n = 24$ and $L = 24$ or $n = 48$ and $L = 48$). Hence even in the fully extended conformation, a chain

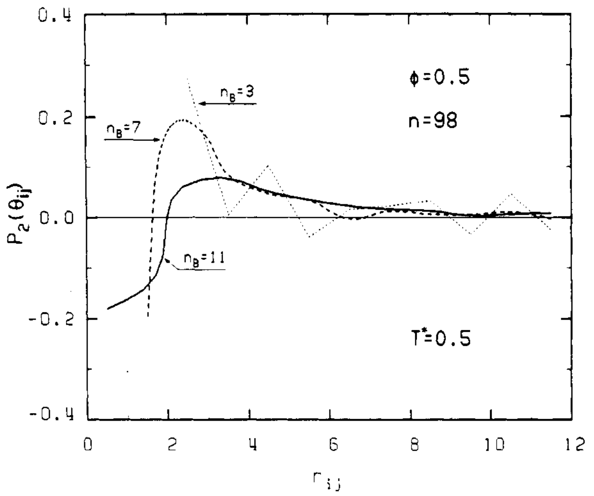

Figure 15. Plot of $P_2(\theta_{ij})$, the local order parameter calculated via eq 7, vs. r_{ij}, the distance of separation of the centers of mass of two subchains, for subchains of length n_B = 3, 7, and 11 in the dotted, dashed, and solid curves, respectively. In all cases, n = 98, ϕ = 0.5, T^* = 0.5, and ϵ_a = 0.

cannot interact with its image produced by the periodic boundary conditions. As pointed out by Baumgartner[25] this may affect the global order parameter but should leave the local domain structure unchanged. While there may still be some effects introduced by the periodicity of the system, it should not have any noticeable influence on the character of local ordering of the system. This was first checked by running a test simulation on a system composed of shorter chains, n = 12, in a MC box with L = 16, 24, and 48. Above T_t^*, all the results are essentially independent of L and the major qualitative features of this system remain the same as those seen in systems having n = 24 and n = 48. In order to further investigate the effects of chain length, some simulations were performed on systems with chains of length n = 98 confined to a Monte Carlo box of length L = 28. In Figure 15, the order parameter profiles of subchains of lengths n_B = 3 (dotted curve), n_B = 7 (dashed curve), and n_B = 11 (solid curve) are shown for the chains with n = 98 packed at a density ϕ = 0.5 in the absence of nearest-neighbor interactions and at the temperature T^* = 0.5 (a temperature far from the region where the bundle size exceeds the chain contour length). Again, the local ordering of the subchains is very similar to that seen for the shorter chains (see, for example, Figure 12), and the computed values of the order parameter at short distances do not exhibit any systematic changes when compared to systems of shorter chains discussed above. However, in this case, one cannot rely on the results obtained from the simulation for T_t^* because n is such that the possibility of the "direct" influence of periodic box size (possible interaction of images) cannot be excluded. However, the insensitivity of the character of the short-range ordering to chain length is highly suggestive of the universal occurrence of a locally ordered domain structure in concentrated solutions of semiflexible polymer chains and melts.

IV. Conclusions

Using the Monte Carlo method applied to model systems composed of polymers confined to a tetrahedral lattice, we have examined the nature of the local ordering in a polymer melt. It was found that the minimum requirement for the local parallel packing of chains in the amorphous phase is that the chains possess local stiffness. Polymers that are very flexible, i.e., which exhibit a preference for neither trans nor gauche states, are predicted to lack local orientational correlation; that is, a melt of infinitely flexible chains resembles a bowl of overcooked spaghetti. This is in qualitative agreement with the random coil model of melts espoused long ago by Flory.[1] Following introduction of local chain stiffness, however, semiflexible polymers tend to form locally ordered domains. The domains of such locally parallel collections of chains are not well-defined or unique static structures but are statistically defined, quite fuzzy dynamically fluctuating structures. Beyond a certain minimum molecular weight, the characteristics of these domains appear to be molecular weight independent. Moreover, to a good approximation within a given chain, a subchain that is part of one such locally ordered domain is statistically uncorrelated with a subchain that is a part of another locally ordered domain. Furthermore, the local ordering of semiflexible polymer chains, at a fixed chain stiffness (temperature), becomes better defined on increasing the density of the melt and/or with the introduction of an attractive interaction between polymer segments. These findings are highly suggestive that local ordering is a cooperative phenomenon. Thus, we conclude that for the model systems employed in this series of simulations, the packing of semiflexible chains in the melt is well described by the locally ordered domain model schematically depicted in Figure 1D.

Our simulation results are qualitatively consistent with the major experimental features seen in real polymer melts. On the one hand, our model systems exhibit chain dimensions very close to that predicted by ideal chain statistics, i.e. Θ-solvent dimensions, in qualitative agreement with small-angle neutron scattering results;[8] and on the other hand, they exhibit the local ordering in the melt indicated by electron diffraction[15,16] and depolarized Rayleigh light scattering studies.[12-14] Thus, insofar as this diamond lattice model system is a reasonable approximation to real melts of semiflexible polymers, a locally ordered domain structure composed of partially parallel chains is suggested to be a ubiquitous property for many polymeric systems, e.g., concentrated polymer solutions at low temperatures, polymer melts, and polymer glasses.

Acknowledgment. This research was supported in part by a grant from the Polymers Program of the National Science Foundation (No. DMR-83-03797). Acknowledgment is made to Monsanto Co. for an institutional research grant for the purchase of a μVAX-II computer on which the simulations reported here were predominantly carried out. We thank Jake Schaefer and Ed Stejskal for many helpful discussions. We also thank a referee for several suggestions that improved the presentation of our results.

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Order–Disorder Transitions in Tetrahedral Lattice Polymer Systems

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Received April 14, 1986

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.[1] 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[2] using a mean field argument. Baumgartner and Yoon[3] and Yoon and Baumgartner[4] 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[5] and for polymers packed at high density on square and cubic lattices in Monte Carlo boxes appreciably larger than the chain length.[6] 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, ξ, 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[3-5] 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,[1] we omit most of the details.

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0024-9297/86/2219-2560$01.50/0