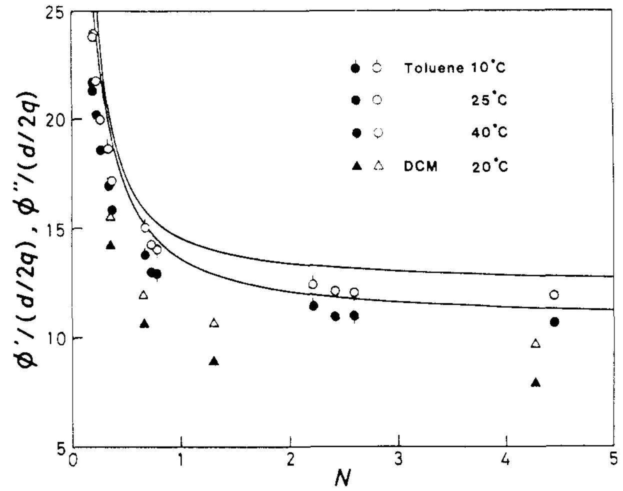

Figure 10. Plots of $\phi'/(d/2q)$ and $\phi''/(d/2q)$ versus N for PHIC in toluene and DCM: DCM at 20 °C, ▲ (ϕ'), △ (ϕ''). The other symbols are the same as those in Figures 8 and 9; solid curves, theoretical values calculated according to eq 6.

free energy inherent in the Onsager theory,[1] where all the terms in concentration higher than the third virial term in free energy are neglected. This approximation may not be accurate for such small q as that in DCM, where the critical concentrations ϕ' and ϕ'' are quite high. This problem will be discussed in a future publication in connection with solvent chemical potential data for the two PHIC solutions considered.

Registry No. PHIC, 26746-07-6.

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Effect of Lattice Coordination Number on the Dynamics of Models of Dense Polymer Systems

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ABSTRACT: Dynamic Monte Carlo simulations of both simple cubic and face-centered cubic lattice models of dense polymer systems have been performed and analyzed by studying the autocorrelation functions of the first three Rouse coordinates. A significant difference between the two lattices is found in the concentration dependence of the scaling exponent that describes the chain length dependence of the relaxation times. This difference is due to the necessity of using bead movement rules with two different length scales in the simple cubic lattice model, while in the face-centered cubic model elementary motions with a single length scale are sufficient. Implications of this result are discussed. The normal mode analysis also provides some insight into the nature of the entanglement constraint in dense polymer systems.

Introduction

The dynamics of polymer chains in entangled systems is a topic of intense recent interest. Much of the discussion centers around the validity of the reptation model introduced long ago by de Gennes.[1] The reptation model, which proposes that the constraints on the motion of a single polymer chain provided by all the surrounding chains can be modeled by a confining tube, is simple and physically appealing and provides definite predictions concerning the chain-length dependence of the relaxation time and the diffusion constant of the chain. The reptation model has been very fruitful and has received considerable experimental support.[2]

Despite these successes the reptation hypothesis remains controversial. The experimental evidence is not unambiguous. Crucial experiments such as dynamic neutron scattering either fail to see reptation or do not show it clearly.[3] Recent experiments concerning the chain-length dependence of the diffusion constant as a function of polymer concentration show a large region of behavior intermediate between the dilute solution Rouse–Zimm result and reptation.[4] Because of the difficulties in interpretation of experimental results a large amount of effort has gone into computer simulation of the dynamics of concentrated polymer systems to learn more about the details of chain motion and to see if the reptation model is reasonable.[5,6] Due to the large amounts of computer time necessary for the simulation of a multiple chain systems most workers have chosen to study lattice systems. All the lattice simulations of which we are aware have been done on one of three types of systems: a single mobile chain in a frozen regular array of obstacles or a frozen irregular matrix of other chains on either a tetrahedral or simple cubic lattice, mobile chains on a tetrahedral lattice, and mobile chains on a simple cubic lattice. The only systems that clearly show reptation are those in which a single mobile chain is allowed to move in a frozen matrix. In systems where all chains are mobile, deviations from the dilute solution Rouse behavior are seen, but clear evidence of reptation has not yet been found.

The recent multiple chain simulations of Crabb and Kovac,[7] Kolinski et al.,[8] and Kranbuehl and Verdier[9] on simple cubic lattice and tetrahedral lattice systems have shown strong deviations from Rouse-like behavior of the chain-length dependence of the relaxation times and the diffusion constant as the concentration of the system increases. The central monomer diffusion, however, does not show the behavior characteristics of reptation. It is therefore important to study the dynamics of the chains in more detail to learn more about the nature of the constraints on the motion at high concentration.

One way to do this is to study the relaxation of the normal coordinates of the chain. As the mode number of the normal coordinate increases, the length scale of the motion decreases. Studying the relaxation as a function of mode number should provide some insight into the length scale of the entanglement constraints. One can imagine two very different models for the constraints in an entangled system. In the first model the constraints operate continuously along the chain contour. One visualization of a continuous constraint is a tube. In the second model the constraint operates only at discrete points along the chain. This can be visualized as a mesh of transient cross-links. These two models qualitatively predict very different behavior for the relaxation behavior of the normal modes as a function of mode number. With a tubelike constraint one would expect all the normal modes should be affected in the same way by the constraint. With a meshlike constraint one would expect a transition from constrained chain behavior to free chain behavior at some length scale characteristic of the constraint mesh size.

Other questions that must always be asked in lattice model simulations are whether the results obtained are dependent on the coordination number of the lattice and, in a polymer system, whether the results depend on the particular elementary motions chosen. We have previously shown that for single chain simulations the dynamics are essentially independent of the lattice coordination number,[10] but for the simple cubic lattice they do depend strongly on the particular movement rules chosen.[11] The effect of lattice coordination number on chain dynamics has also been studied by Verdier and Kranbuehl for a different set of movement rules.[12] For concentrated systems the results for the tetrahedral and the simple cubic lattices are in basic agreement. Both these lattices require two different types of elementary motions to construct a proper dynamic model. For the simple cubic lattice these motions are ordinarily referred to as the normal bead motion and the 90° crankshaft motion. The first involves the motion of two bonds while the second involves three. In the tetrahedral lattice model both a three- and a four-bond motion are required. The work of Stokely et al.[13] shows that decreasing the frequency of the 90° crankshaft motion does affect the relaxation of the chain. Therefore, it is essential that simulations be done by using a lattice model in which elementary motions of only a single length scale are needed to see how important the simple suppression of the longer length scale motion is in explaining the concentration dependence of the dynamics.

To answer these questions, we have reanalyzed our simulations of multiple chain simple cubic lattice systems by computing the autocorrelation functions of the first three Rouse coordinates.[7] In addition, we have performed simulations on multiple chain systems using the face-centered cubic lattice model developed by Downey et al.[14] In the face-centered cubic lattice simulation we studied the same range of concentrations and chain lengths as in the simple lattice simulations. The face-centered cubic lattice dynamics were also studied by computing the autocorrelation functions of the Rouse coordinates. We find that the Rouse coordinates are an approximate set of normal coordinates for the chain at all concentrations. We also find that at the length scales probed by the first three modes the entanglement constraint acts in a continuous or tubelike manner. In other words, the relaxation times of all the modes are affected similarly by the increase in concentration. The chain length dependence of the relaxation times of the face-centered cubic chains shows a less dramatic increase with concentration than that seen with the simple cubic chains. These results, along with the results of Stokely et al.[13] suggest that the large deviations from Rouse-like behavior seen at high concentrations in the tetrahedral and simple cubic lattice systems can be most simply explained in terms of the suppression of the longer range elementary motion as the concentration increases. There are long-range entanglement effects in these two kinds of systems, but they are not as large suggested by previous simulation results. The qualitative difference between the face-centered cubic results and those obtained in the other two lattices serves as a reminder that we should be extremely careful when using a lattice model to represent a continuous system.

Model

Simulations were performed by using the dynamic Monte Carlo models developed by Crabb and Kovac[7] for the simple cubic lattice and by Downey et al.[14] for the face-centered cubic lattice. Chains are represented as self-avoiding walks of $N - 1$ steps on the lattice. We refer to the individual steps as bonds and the vertices as beads. The reader is referred to the original publications for the details of the models. For the simulation of multiple chain systems the chains are confined to a periodic system of size $20 \times 20 \times 20$. All simulation runs are begun from a fully equilibrated conformation. The time scale for all simu-

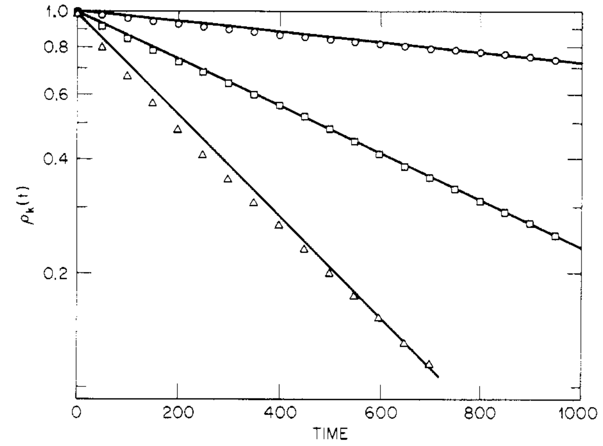

Figure 1. Semilogarithmic plot of representative normal coordinate autocorrelation functions, $\rho_k(t)$, for the modes $k = 1$ (○), $k = 2$ (□), and $k = 3$ (△) for the simple cubic lattice model. The functions shown here were determined for chains of length $N = 60$ at a concentration of 0.38 beads per lattice site. The time unit is nN attempted bead moves.

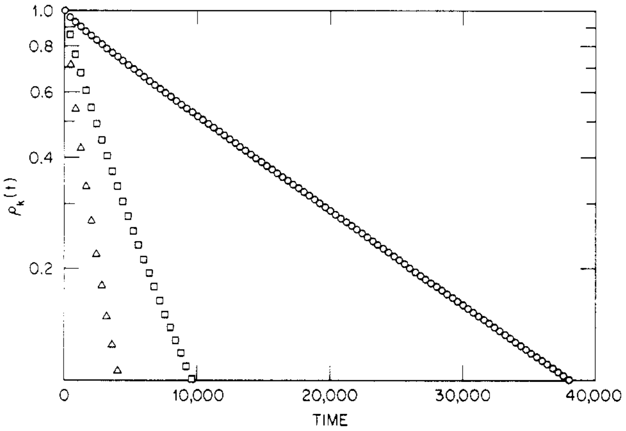

Figure 2. Semilogarithmic plot of representative normal coordinate autocorrelation functions, $\rho_k(t)$, for the modes $k = 1$ (○), $k = 2$ (□), and $k = 3$ (△) for the face-centered cubic lattice model. The functions shown here were determined for chains of length $N = 60$ at a concentration of 0.75 beads per lattice site. The time unit is nN attempted bead moves.

lations is taken to be equal to the total number of beads in the periodic system. If there are n chains in the periodic system, a single time step is taken to be nN attempted moves. We have discussed this choice for the time scale in several previous publications.

For the simple cubic lattice we performed simulations for chains of length 24, 48, and 60 beads at concentrations of 0.09, 0.19, 0.28, 0.38, and 0.75 beads per lattice site. At least four simulation runs were done for each chain length and concentration.

For the face-centered cubic lattice we performed simulations for chains of length 24, 48, and 60 beads at concentrations of 0.12, 0.24, 0.36, 0.48, 0.60, 0.75, and 0.90 beads per lattice site. To check the chain length dependences further, we also performed a simulation with chains of length 100 at a concentration of 0.75. At least six simulation runs were done for each chain length and concentration.

The simulations were analyzed by computing the autocorrelation functions of the first three Rouse coordinates of the chain. The Rouse coordinates, $\vec{u}_k(t)$, are given by the equation[15]

$$\vec{u}_k(t) = \sum_{j=1}^{N} ((2 - \delta_{kj})/N)^{1/2} \cos [(j - \tfrac{1}{2})\pi k/N]\vec{R}_j(t) \qquad (1)$$

Table I
Values of the Normal Coordinate Relaxation Times τ_k as a Function of Chain Length, N, and Concentration, c, for the Simple Cubic and Face-Centered Cubic Models (The Time Unit is Nn Bead Cycles)

c		N			
		24	48	60	100
		Simple Cubic Lattice Model			
0.99	τ_1	213	962	1720	
	τ_2	43.9	220	346	
	τ_3	16.8	89.0	182	
0.19	τ_1	230	1120	2180	
	τ_2	51.5	269	403	
	τ_3	19.2	108	177	
0.28	τ_1		1630		
	τ_2		316		
	τ_3		137		
0.38	τ_1	344	2030	3290	
	τ_2	81.1	466	702	
	τ_3	31.0	177	339	
0.75	τ_1	1220	9590	14000	
	τ_2	310	2390	3570	
	τ_3	112	1060	1540	
		Face-Centered Cubic Lattice Model			
0.12	τ_R	299	1540	2610	
	τ_1	303	1550	2650	
	τ_2	68.7	364	616	
	τ_3	28.6	152	250	
0.24	τ_R	372	1960	3270	
	τ_1	374	1970	3340	
	τ_2	84.7	452	792	
	τ_3	34.0	192	321	
0.36	τ_R	466	2440	4190	
	τ_1	471	2480	4270	
	τ_2	109	586	1010	
	τ_3	43.2	243	411	
0.36	τ_R	634	3320	5680	
	τ_1	640	3340	5840	
	τ_2	141	806	1410	
	τ_3	57.2	334	581	
0.60	τ_R	863	5070	8120	
	τ_1	875	5060	8430	
	τ_2	205	1220	2100	
	τ_3	82.4	503	857	
0.75	τ_R	1610	9200	16300	65100
	τ_1	1640	9540	17000	68900
	τ_2	393	2340	4210	16800
	τ_3	161	967	1720	7050
0.90	τ_R	5510	32600		
	τ_1	5620	33500		
	τ_2	1330	8630		
	τ_3	544	3530		

where $\vec{R}_j(t)$ is the position of the jth bead at time t. The autocorrelation functions, $\rho_k(t)$, are defined as

$$\rho_k(t) = \langle \vec{u}_k(t)\cdot\vec{u}_k(0)\rangle / \langle \vec{u}_k^{\,2}\rangle \qquad (2)$$

where the broken brackets represent an equilibrium ensemble average. The ensemble average is calculated as a time average for each individual chain. The single chain time averages are then averaged over all chains in the periodic system.

Results and Discussion

Figures 1 and 2 display typical semilogarithmic plots of the autocorrelation functions $\rho_k(t)$ for the simple cubic and the face-centered cubic lattice systems. The decay curves are quite linear, indicating that the Rouse coordinates are a good set of normal modes for the chains even in a concentrated system. As a further check we computed the mode–mode cross correlations, $\langle \vec{u}_1(t)\cdot\vec{u}_2\rangle$, for the face-centered cubic lattice and found them to be essentially zero. The relaxation times, $\tau_k(N)$, were calculated by fitting an unweighted least-squares line to the curves. The reciprocal of the slope of this line is the negative of the

Table II
Values of the Scaling Exponents α_k and γ_N as a Function of Concentration for the Simple Cubic and Face-Centered Cubic Lattice Models

Simple Cubic Lattice Model

c	α_1	α_2	α_3	γ_{24}	γ_{48}	γ_{60}
0.09	2.19	2.21	2.49	2.31	2.16	2.07
0.19	2.34	2.22	2.37	2.25	2.12	2.30
0.38	2.42	2.33	2.51	2.18	2.21	2.09
0.75	2.66	2.66	2.87	2.15	2.00	2.00

Face-Centered Cubic Lattice Model

c	α_R	α_1	α_2	α_3	γ_{24}	γ_{48}	γ_{60}	γ_{100}
0.12	2.30	2.29	2.32	2.31	2.15	2.11	2.15	
0.24	2.31	2.32	2.37	2.39	2.18	2.12	2.13	
0.36	2.32	2.33	2.36	2.39	2.17	2.11	2.13	
0.48	2.32	2.34	2.44	2.46	2.20	2.09	2.09	
0.60	2.40	2.42	2.48	2.50	2.14	2.09	2.07	
0.75	2.53	2.55	2.57	2.58	2.11	2.08	2.08	2.07
0.90	2.49	2.50	2.61	2.62	2.12	2.04		

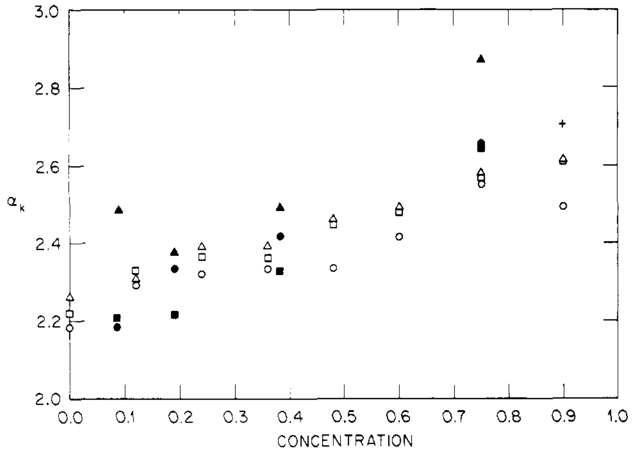

Figure 3. Plot of the scaling exponents α_k as a function of concentration for both the simple cubic (filled symbols) and the face-centered cubic lattice model (open symbols). The modes are designated by the shapes: $k = 1$ (○), $k = 2$ (□), $k = 3$ (△). The point designated by the plus sign is the value of α_R for the simple cubic lattice determined by Crabb and Kovac.[6]

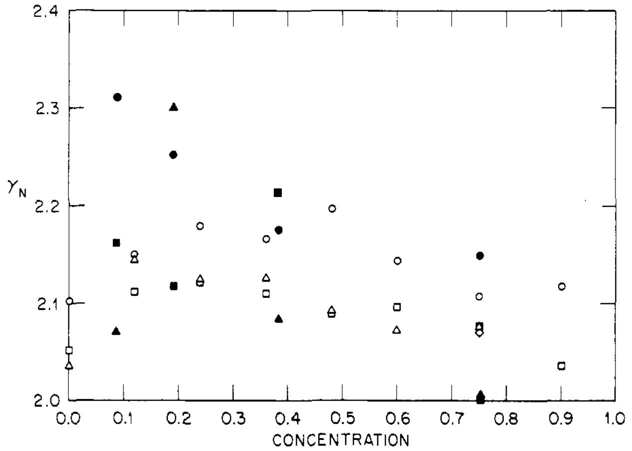

Figure 4. Plot of the scaling exponents γ_N as a function of concentration for both the simple cubic lattice model (filled symbols) and the face-centered cubic lattice model (open symbols). The values of N are designated by the shapes: $N = 24$ (○), $N = 48$ (□), $N = 60$ (△), $N = 100$ (◇).

relaxation time. The numerical values of the relaxation times are collected in Table I.

As in previous work the chain length and mode number dependence of the relaxation times were determined by making scaling plots of ln $\tau_k(N)$ versus ln $(N - 1)$ and ln k, respectively. The least-squares slopes of these scaling plots correspond to the scaling exponents α_k and γ_N defined by the relationships

$$\tau_k(N) \sim (N-1)^{\alpha_K} \tag{3}$$

$$\tau_k(N) \sim k^{-\gamma_N} \tag{4}$$

The numerical values of these scaling exponents for all the concentrations studied are collected in Table II.

In Figures 3 and 4 we have plotted the values of the scaling exponents as a function of concentration. Several observations can be made immediately. First, the values of α_k increase more slowly with concentration for the face-centered cubic lattice than for the simple cubic lattice. The difference between the two lattices would be even greater at $c = 0.9$, where unfortunately we do not have normal mode data. To indicate the difference, we have plotted the exponent α_R obtained in ref 6. (α_R is essentially equal to α_1.) Second, the values of the exponent γ_N are relatively independent of concentration. The exponent in both cases remains approximately constant at a value near 2.1. Third, for the face-centered cubic lattice the values of α_R increase with k for all concentrations. This is not observed for the simple cubic lattice, although in this case the value of α_1 is always larger than α_2 and α_3.

The weaker dependence of the scaling exponent in the face-centered cubic lattice system suggests that the dramatic rise in the exponent with concentration seen in both cubic and tetrahedral lattice systems is due to the suppression of the longer scale elementary motion, the 90° crankshaft in the cubic lattice model, and the four-bond motion in the tetrahedral lattice model, as the number of holes in the lattice decreases. This suggestion is supported by the work of Stokely et al.[13] who studied the effects of suppression of the crankshaft motion on the exponent α_R for single cubic lattice chains. (α_R is the exponent describing the chain length dependence of the end-to-end vector relaxation time, τ_R. α_R is equivalent to α_1.) The increase in the exponent α_R observed by Stokely et al. as the probability of a crankshaft motion decreases is qualitatively the same as the difference in the exponent between the simple cubic and face-centered cubic lattice results reported here if one identifies the concentration, c, with 1 minus the crankshaft probability, $(1 - P_{cs})$. In Figure 5 we reproduce Figure 1 from the paper of Stokely et al.[13] Comparison of this figure with the exponents α_1 in Figure 3 shows this similarity quite clearly.

This dramatic difference between lattices suggests that one must be careful about drawing general conclusions about melt dynamics from lattice model simulations done

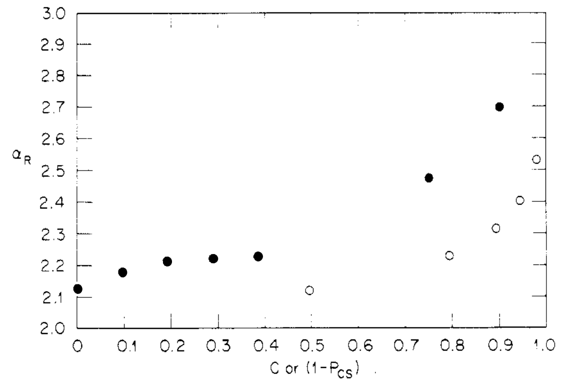

Figure 5. Plot of the scaling exponent α as a function of concentration (●) and of $1 - P_{cs}$ (○). The values of α_R as a function of concentration are taken from ref 6, and the values of α_R as a function of $1 - P_{cs}$ are taken from ref 13. This figure is the same as Figure 1 of ref 13.

on only one lattice, particularly a lattice of low coordination number. There is clearly an entanglement effect on the dynamics of lattice model chains. By entanglement effect we mean a slowing down of the chain motion due to the fact that chain contours cannot cross. This effect seems to move the scaling exponent from its dilute solution value of 2.2 to a value of about 2.5 at high concentrations. There is a second effect observed in simple cubic and tetrahedral lattice systems that might be called a free-volume effect and is due to the suppression of the longer range elementary motion with increasing concentration. This second effect might well be unique to lattice models and not observed in real physical systems. Certain conclusions concerning the origin of the glass transition and aspects of melt dynamics that have been drawn from simulations done on tetrahedral and cubic lattice models may be less general than suggested by the authors.

An important question that must be considered is whether the lattice difference is due to the short chain lengths used in this study. There are two ways of thinking about this question. The first is to observe that the suppression of the crankshaftlike motions is a short-range effect. As a short-range effect it should disappear in the limit of infinite chains. Since our results are consistent with those of Kolinski et al., who have studied considerably longer chains, we can say that the crossover to long-chain behavior, if it exists, is probably beyond current computational capabilities. The second view of this question begins with the analysis of Hilhorst and Deutch[16] of the original Verdier–Stockmayer[17] algorithm for the cubic lattice model. Hilhorst and Deutch observed that in the absence of the crankshaft motion the chain contained certain topological constraints that imposed an N^3 time scale because local extrema could only relax by diffusing to the chain ends. (This effect has been studied by using simulation methods by Kranbuehl and Verdier.[18]) If this diffusion of local extrema is important in the high-concentration regime where the crankshaft motion is partially suppressed, then the lattice dependence should persist even at infinite chain lengths. This second view of the question is supported by the work of Stokely et al. on single chains with restricted crankshaft probability, where an increase in the exponent was seen as the crankshaft probability was reduced. Our inclination is to favor the second view of the question and to regard the face-centered cubic lattice results as a more accurate representation of the effects of the excluded volume on the chain dynamics in concentrated systems.

Both the relaxation times and the exponents vary smoothly as a function of concentration. There is no indication that there is any crossover between confined chain behavior and free chain behavior in the third normal mode. This suggests that the multichain matrix acts as a continuous constraint at the length scales and on the time scales probed by our analysis. These results suggest that a continuous constraint or "tube" model is a good approximation, although the dynamics of a chain within the tube may be significantly different than those predicted by the reptation model. The absence of any crossover in behavior as a function of mode number is also consistent with a free-chain-like behavior. Since the range of chain lengths and normal modes studied was very limited, this suggestion must be regarded as very tentative. A much more extensive set of simulations would have to be performed to make any definite conclusions on this matter. The simulation results of Kolinsky et al.[8] suggest that a tube, in the sense of the reptation model, does not exist. Since they did not do the normal-coordinate analysis of their model, we cannot determine whether the picture of the dynamics that they propose is consistent with the results obtained here. We expect that there is no inconsistency because the almost free chain behavior that they see would not result in a different dynamics for the higher normal modes and so the normal mode analysis would imply a continuous constraint.

The dependence of the exponent α_k on k seen in the face-centered cubic case can be explained in terms of dependence of the excluded volume on the chain length. It has long been known that short segments of chain are more expanded than long segments. This has recently been called the blob model. Naghizadeh and Kovac[19] have recently studied the dynamics of cubic lattice chains as a function of the excluded volume and observed that the exponent α_R for the relaxation time decreased as the static excluded volume decreased in such a way that the dynamic scaling hypothesis given in eq 5 is obeyed:

$$\tau_R \sim \langle R^2 \rangle (N-1) \qquad (5)$$

In application of this to the normal modes, it is necessary only to observe that the larger the mode number the shorter the length of chain being probed and therefore the larger the effect of the excluded volume. The ordering of the exponents with mode number is strictly seen in the face-centered cubic case and approximately seen in the simple cubic case. The difference is probably due to larger statistical errors in the simple cubic data, where fewer and shorter runs were done. We expect that a more extensive and careful study of the cubic lattice would show the same effect.

Conclusions

We have studied the dynamics of the first three normal modes as a function of concentration for two different lattice models of chain dynamics. We find that the Rouse coordinates are a good set of normal coordinates for the chain at all concentrations and for both lattices. We see a strong effect of concentration on the chain dynamics in both models, but this effect is weaker in the face-centered cubic lattice model than in the simple cubic lattice model. This lattice difference seems to be due to differences in the elementary motions used in the two cases. In the simple cubic lattice it is necessary to use elementary motions with different length scales, and the longer length scale motion is preferentially frozen out as the concentration increases. In the face-centered cubic lattice all elementary motions have the same length scale, and so this effect does not appear. We have presented an argument based on the analysis of Hilhorst and Deutch to suggest that the difference between lattices will persist even at long

Macromolecules 1988, *21*, 2235–2240 **2235**

chain lengths. We therefore suggest that the face-centered cubic lattice model is the better lattice model for simulating the effects of concentration on chain dynamics.

The normal mode analysis suggests that the excluded volume constraint acts in a continuous manner at the length scales probed in this study. Since the chain lengths studied were short and only the first three normal modes were studied, this deserves further investigation. We also observed that the chain length dependence of the relaxation time increases with mode number. This effect can be explained in terms of the blob model.

Clearly these results are preliminary. Because of limited computer time only a limited number of chain lengths were studied. We feel that the basic results will be corroborated by studies on systems with longer chains. We also feel that the face-centered cubic lattice model is an excellent model for the study of a variety of problems in polymer melt dynamics.

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Distribution of Matrix Homopolymer in Block Copolymers of Spherical Morphology

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ABSTRACT: Samples made by blending deuteriated polystyrene S_d of three different molecular weights with a polystyrene–polybutadiene block copolymer SB were studied with small-angle scattering techniques using X-rays (SAXS) and neutrons (SANS). The SANS results were sensitive both to the amount of added homopolymer S_d and to its chain length. Anomalously high SANS intensities and the absence of an intraparticle scattering maximum are consistent with the exclusion of added S_d from the corona of the SB micelles, resulting in S_d enrichment of the interstitial regions.

Introduction

The study of block copolymers has proved to be a fertile area for the detailed elucidation of polymer interactions; it has been particularly fruitful in the production of information generated through the interplay between theoretical studies (see, for example, papers by Meier,[1] Helfand,[2] Leibler,[3–5] and Noolandi[6,7] and their co-workers) and experimental work, particularly small-angle scattering studies involving X-rays (SAXS) and neutrons (SANS).

One of the advantages of SANS over SAXS is the possibility of manipulating the contrast (in SANS, the nuclear scattering-length density) by selective deuteriation. This technique was exploited in previous studies[8,9] by synthesizing a polystyrene–polybutadiene diblock with the polybutadiene segment deuteriated (SB_d) to enhance the contrast between the spherical polybutadiene microdomains and the polystyrene matrix; the SANS signal was increased by a factor of 27, allowing detection of Debye–Scherrer powder peaks characteristic of cubic packing of the B_d domains[8] and accurate assessment of sphere size and interfacial thickness for a number of samples of differing molecular weight.[9] In another experiment,[10] deuteriated polystyrene–polybutadiene diblocks SB_d were blended with a normal (hydrogenous) diblock SB in such a way that the scattering-length densities of the S and B phases were matched, eliminating (inter- and intradomain) structural scattering and thus (presumably) leaving scattering from isolated B_d chains as the dominant scattering mechanism.

The present study is a further attempt to use deuteriated probe molecules to gain information about the distribution of polymer chains in a diblock system with spherical morphology—this time with the added chains in the polystyrene matrix. Samples were prepared by adding deuteriated homopolystyrene (S_d) to a solution of poly-

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