erties from nature's solutions to energy minimization in variously constrained phase-separating macromolecules.[18]

Acknowledgment. The financial support of the Polymers Division of the NSF through Grant DMR 84-06079 is greatly appreciated. We thank Professors L. E. Scriven (University of Minnesota) and D. A. Hoffman (University of Massachusetts) and Dr. D. B. Anderson (University of Minnesota) for helpful discussions concerning periodic minimal surfaces and Drs. H. Hasegawa and T. Hashimoto (Kyoto University) for discussions concerning the OBDD structure in linear diblock systems. E.L.T. and L.J.F. thank the organizers of the China–U.S. Bilateral Symposium on Polymer Chemistry and Physics held in Beijing, October 1979. It was at that meeting that this work had its inception.

Registry No. (Styrene)-(isoprene) (block copolymer), 25038-32-8.

References and Notes

(1) Alward, D. B.; Kinning, D. J.; Thomas, E. L.; Fetters, L. J. *Macromolecules* **1986**, *19*, 215.
(2) Alward, D. B. Ph.D. Dissertation, University of Massachusetts, 1985.
(3) Kinning, D. J.; Alward, D. B.; Thomas, E. L.; Fetters, L. J.; Handlin, D. L., Jr. *Macromolecules* **1986**, *19*, 1288.
(4) Kinning, D. J. Ph.D. Dissertation, University of Massachusetts, 1986.
(5) Hadjichristidis, N.; Guyot, A.; Fetters, L. J. *Macromolecules* **1978**, *11*, 668.
(6) Hadjichristidis, N.; Fetters, L. J. *Macromolecules* **1980**, *13*, 191.
(7) Aggarwal, S. L. *Polymer* **1976**, *17*, 938.
(8) *International Tables for X-Ray Crystallography*; Kynoch: Birmingham, England; Vol. II, p 147.
(9) Arizona State University, MULTISLICE Program. See, for example: Cowley, J. M.; Moodie, A. F. *Acta Crystallogr.* **1957**, *10*, 609.
(10) Herman, D.; Kinning, D. J.; Fetters, L. J.; Thomas, E. L., to be published.
(11) Kinning, D. J., unpublished results.
(12) Hasegawa, H.; Hashimoto, T.; Kinning, D. J.; Thomas, E. L.; Fetters, L. J., to be published.
(13) Longley, W.; McIntosh, T. J. *Nature (London)* **1983**, *303*, 612.
(14) Scriven, L. E. *Nature (London)* **1976**, *263*, 123.
(15) Delauney, C. *J. Math. Pures. Appl., Ser. 1* **1841**, *6*, 425.
(16) Anderson, D.; Davis, H. T.; Nitsche, J. C.; Scriven, L. E., to be published.
(17) Schwarz, H. A. *Gesammelte Mathematische Abhandlung*; Springer: Berlin, 1890; Vol. 1. Also see: Schoen, A. H. *NASA Tech. Note* **1970**, D-5541.
(18) Matsushita, Y.; Yamada, K.; Hattori, T.; Fujimoto, T.; Sawada, Y.; Nagasawa, M.; Matsui, C. *Macromolecules* **1983**, *16*, 10. A wagon wheel type of arrangement (Figures 2b and 3b) was observed by these authors in unannealed benzene-cast films of a styrene–(4-vinylbenzyl)dimethylamine–isoprene terpolymer.

Dynamics of a Face-Centered Cubic Lattice Model for Polymer Chains

James Patton Downey, Charles C. Crabb,† and Jeffrey Kovac*

Department of Chemistry, University of Tennessee, Knoxville, Tennessee 37996-1600.
Received January 29, 1986

ABSTRACT: The dynamic behavior of a face-centered cubic lattice model for a polymer chain was simulated with and without excluded volume using a Monte Carlo technique. The chain relaxation was analyzed with both the end-to-end vector autocorrelation function and the autocorrelation functions of the Rouse normal coordinates. In the absence of excluded volume we find almost exact agreement with the predictions of the Rouse theory. In the presence of excluded volume the N dependence of the relaxation times of the first three modes conforms quite well to scaling theory predictions. The k dependence of the relaxation times deviates from the Rouse value in the presence of excluded volume and the deviation is consistent with that seen for the cubic lattice model. The problem of the proper definition of the time scale in Monte Carlo simulations is discussed.

I. Introduction

The study of the dynamics of lattice models for polymer chains using Monte Carlo techniques was initiated long ago by Verdier and Stockmayer.[1] Probably the most interesting and important aspect of these conceptually and computationally simple simulations is their ability to explore the effects of excluded volume on the chain dynamics. Recently, there has been a lot of interest in lattice model simulations because they offer an opportunity to simulate entangled polymer systems without the expenditure of immense amounts of computer time.[2] Much of the recent effort has been focused on the study of the reptation model introduced by de Gennes.[3]

Most of the studies of the dynamic lattice models have used either a cubic[2,4,5] or a tetrahedral lattice.[6,7] Dynamic models based on these two lattices have one important feature in common. In order to create a dynamic model that is ergodic it is necessary to have a set of elementary motions involving different numbers of bonds. In the tetrahedral lattice model both a three- and a four-bond motion are required. In the cubic lattice model both the two-bond "normal bead" motion and the three-bond 90° crankshaft motion are needed to obtain reasonable dynamic behavior in the presence of excluded volume. The need for two different types of motions raises a problem with the definition of the time scale in the simulation model.

In the dynamic Monte Carlo method time is defined in terms of a "bead cycle", (although this particular term is not universally employed). A bead cycle consists of the choice of a random position on the chain, examination of the local conformation surrounding that point, identification of a particular elementary motion to be attempted, and acceptance or rejection of the proposed movement as

† Present address: Rohm and Haas Research Laboratories, Rohm and Haas Co., Bristol, PA 19007.

0024-9297/86/2219-2202$01.50/0

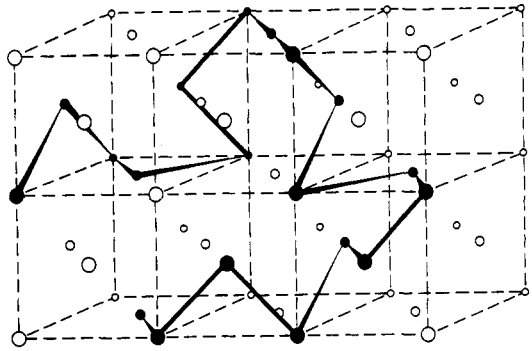

Figure 1. Representative conformation of a chain confined to a face-centered cubic lattice.

the new local configuration of the chain. The natural definition of the time scale is the number of bead cycles such that each vertex (or bead) in the chain has the opportunity to move once per time unit. For a cubic lattice chain with $(N - 1)$ bonds and N beads the time unit is ordinarily taken as N bead cycles.

This choice is sensible when the same number of beads (or bonds) are moved per bead cycle. With two different kinds of movements in the model, a problem arises. For example, should a three-bond motion be assigned the same time value as a two-bond motion? If not, what relative time value should be assigned to each? The answers to these questions are not obvious. In fact, the questions have not really been adequately discussed in the literature.

One way of studying these questions is to develop a lattice model in which this problem does not arise and to compare its behavior with either the cubic or tetrahedral lattice model. Such a model is presented in this paper, the face-centered cubic (FCC) lattice model. The FCC lattice is a twelve-choice lattice and allows enough local conformations that new bond directions can be introduced into the interior of the chain with only two-bond or one-bead motions.

In the following sections we will present the details of our Monte Carlo simulation model for face-centered cubic lattice chains and show detailed results for the dynamics of single chains with and without excluded volume. We have studied both the end-to-end vector autocorrelation function and, as a more detailed probe of the dynamics, the relaxation of the first three normal modes. We find, in the absence of excluded volume, that the chain dynamics follow the predictions of the Rouse theory[8] in both the chain length and mode number dependence of the relaxation time much more closely than in the cubic lattice model. In the presence of excluded volume the prediction of the scaling theories for the chain-length dependence of the relaxation time is followed quite closely. In addition, we find a deviation from the Rouse theory in the mode number dependence of the relaxation time. This deviation is similar to that observed in the cubic lattice model.[9]

II. Model

The polymer chain is modeled as a random walk of $N - 1$ steps of unit length on a face-centered cubic lattice. Each of the steps is referred to as a bond. The chain occupies N lattice junctions, each of which is called a bead. A representative chain configuration is shown in Figure 1. The chain is moved according to the following algorithm, which is similar to our algorithm for the cubic lattice model.[2,5,9] The initial description is for the case when excluded volume is present.

First, a bead is chosen at random. If it is an end bead there are 11 possible motions corresponding to the 11 possible locations lying one lattice unit from the next to last bead. One of these 11 positions is chosen at random and a check is made to see if the new position is already occupied. If the new position is unoccupied the end bead is moved and the cycle terminates. If the position is occupied the bead remains at its original position and the cycle is terminated.

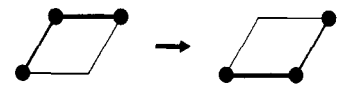

Figure 2. Elementary motion for two bonds with a bond angle of 120°.

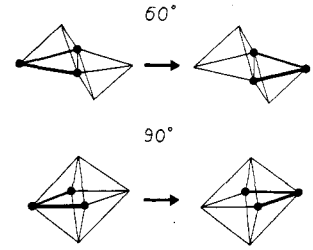

Figure 3. In-plane elementary motion for two bonds with 60° and 90° bond angles.

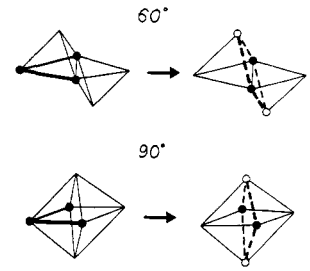

Figure 4. Out-of-plane elementary motions for two bonds with 60° and 90° bond angles.

If an interior bead is chosen, the conformation of the two adjacent bonds is determined. In the presence of excluded volume the two bonds can form four different angles: 60°, 90°, 120°, and 180°. The allowed elementary motions depend on the bond angle. If the angle is 180°, the bonds are collinear and no motion is possible. If this conformation is found the cycle is terminated. If the bonds form a 120° angle, then there is one allowed motion analogous to the normal bead motion in the cubic lattice model. This is illustrated in Figure 2. If the new position is unoccupied the bead is moved. If it is occupied, the old configuration is maintained and the cycle is terminated.

The 60° and 90° cases involve more possibilities. In both these cases there is one in-plane motion shown in Figure 3. In addition there are two out-of-plane, crankshaft-type motions. These are shown in Figure 4. It is these motions that create new bond directions in the chain interior. In both the 60° and 90° cases a random choice is made among the three possible motions. The new bead position is checked, and, if it is unoccupied, the motion is performed. If the position is occupied the original position is maintained.

If excluded volume is not present the new bead position is not checked and all motions are accepted even if the new position is occupied by one or more beads. For the end bead there are 11 new positions, one of which is chosen at random. One additional modification in the absence of excluded volume is the possibility of a 0° angle between two interior bonds. This "spike" conformation is treated in the same way as the end bead.

From time to time the coordinates of all the beads are sampled and recorded for later data analysis. The elementary time unit is taken to be N bead cycles. All the

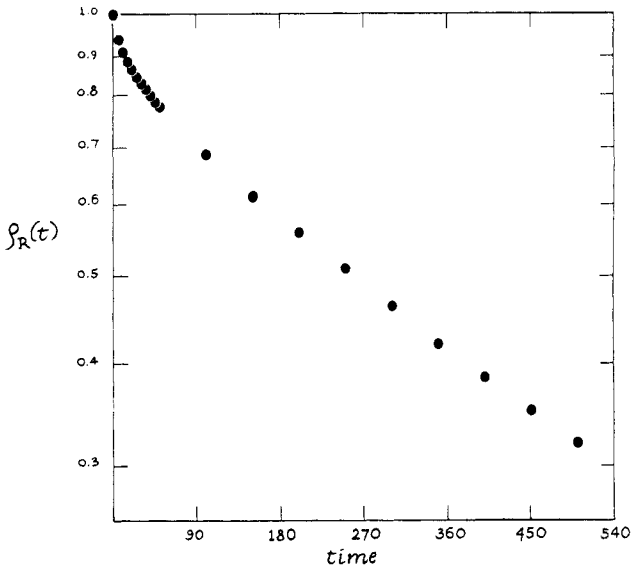

Figure 5. Semilogarithmic plot of the end-to-end vector autocorrelation function, $\rho_R(t)$, vs. t for a chain of length $N = 60$ in the absence of excluded volume.

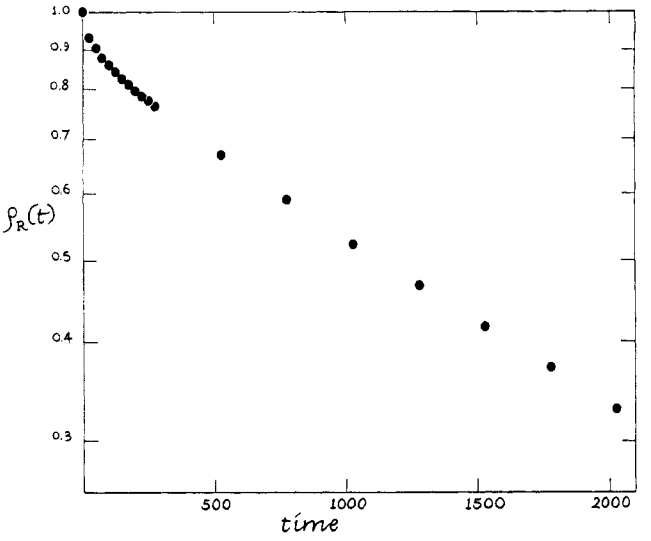

Figure 6. Semilogarithmic plot of the end-to-end vector autocorrelation function, $\rho_R(t)$, vs. t for a chain of length $N = 60$ in the presence of excluded volume.

computations were performed on our Hewlett-Packard 1000 series A900 computer using FORTRAN sources codes.

To analyze the dynamics of the chain, we used the values of the end-to-end vector $\mathbf{R}(t)$ to compute the autocorrelation function $\rho_R(t)$ defined by

$$\rho_R(t) = \langle \mathbf{R}(t)\cdot\mathbf{R}(0)\rangle / \langle R^2\rangle \quad (1)$$

where the broken brackets represent an equilibrium ensemble average. The equilibrium average was computed as a time average over a trajectory begun from a fully equilibrated chain conformation. The relaxation time τ_R was estimated by fitting a least-squares line to the linear long-time region of a semilog plot of $\rho_R(t)$ vs. time. The inverse of the relaxation time is the negative of the slope of the line.

To analyze the dynamics in more detail, we also studied the relaxation of the first three normal modes. The normal modes $\mathbf{U}_k(t)$ are given by the Rouse formula[10]

$$\mathbf{U}_k(t) = \sum_{j=1}^{N}\left(\frac{2-\delta_{k0}}{N}\right)^{1/2} \cos\left[(j-1)\pi k/N\right]\mathbf{R}_j(t) \quad (2)$$

where $\mathbf{R}_j(t)$ is the position of the jth with respect to the origin. The autocorrelation function of the kth normal mode, $\rho_k(t)$, is given by

$$\rho_k(t) = \langle \mathbf{U}_k(t)\cdot\mathbf{U}_k(0)\rangle / \langle U_k^2\rangle \quad (3)$$

The equilibrium average was again computed as a time average. The relaxation time of the kth mode, τ_k, is computed by fitting a least-squares line to a semilog plot of $\rho_k(t)$ vs. time. The negative of the relaxation time is the inverse of the slope of this line.

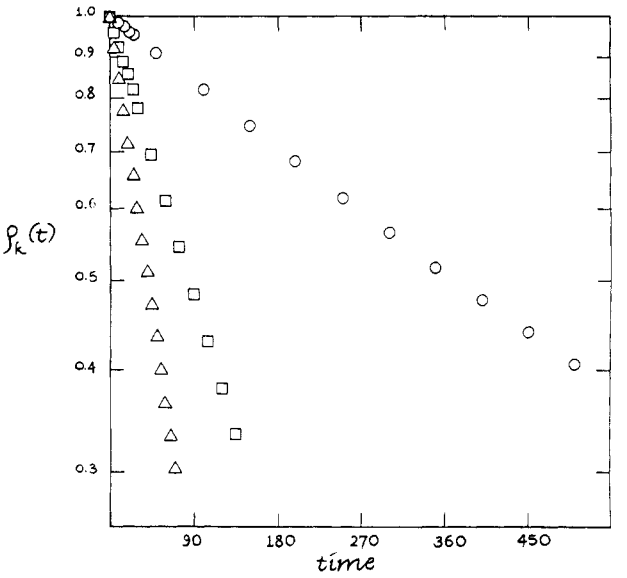

Figure 7. Semilogarithmic plot of the normal mode autocorrelation function, $\rho_k(t)$, vs. t for the modes $k = 1$ (○), $k = 2$ (□), and $k = 3$ (△) for a chain of length $N = 48$ in the absence of excluded volume.

III. Results and Discussion

Simulation runs were performed on chains of length 12, 24, 36, 48, and 60 beads both in the absence and presence of excluded volume. At least three runs were done for each case. Figures 5 and 6 show typical end-to-end vector autocorrelation functions $\rho_R(t)$. It is clear from these semilog plots that the autocorrelation function is a single exponential at long times. The relaxation times τ_R extracted from the long-time slope of the ln $\rho_R(t)$ vs. t plot are collected in Table I. These values are the averages of at least three simulation runs. Also given in Table I is the

Table I
End-to-End Vector Relaxation Times, τ_R, as a Function of Chain Length, N[a]

	τ_R	
N	no excluded volume	excluded volume
12	18.4	46.2
24	84.1	249
36	187	643
48	316	1190
60	533	2030

[a] The scaling exponents, α_R, are 1.98 with no excluded volume and 2.25 with excluded volume.

scaling exponent, α_R, obtained from a least-squares fit of a plot of ln τ_R vs. ln $(N-1)$. This slope corresponds to a scaling exponent given by the relation

$$\tau_R \sim (N-1)^{\alpha_R} \quad (4)$$

In the absence of excluded volume the value of α_R is 1.98, which is essentially identical with the Rouse value of 2. In the presence of excluded volume the value of α_R is 2.25,

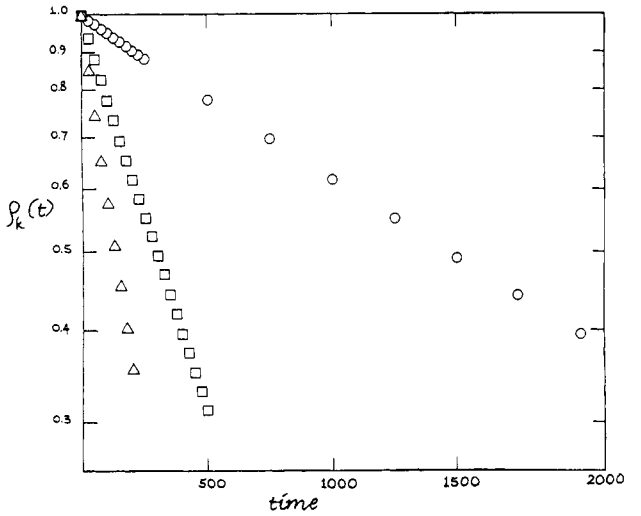

Figure 8. Semilogarithmic plot of the normal mode autocorrelation function, $\rho_k(t)$, vs. t for the modes $k = 1$ (○), $k = 2$ (□), and $k = 3$ (△) for a chain of length $N = 60$ in the presence of excluded volume.

Table II
Normal Coordinate Relaxation Times, τ_k, as a Function of Chain Length

	no excluded volume			excluded volume		
N	τ_1	τ_2	τ_3	τ_1	τ_2	τ_3
12	18.7	4.66	2.20	46.4	9.78	3.81
24	80.0	18.7	9.23	252	57.0	22.7
36	194	44.4	20.7	649	150	60.7
48	314	84.1	36.4	1220	298	125
60	552	125	58.6	2050	476	200

which is quite close to the scaling theory prediction of 2.2. The exponents obtained from the FCC model are much closer to the theoretical predictions than those obtained for the cubic lattice model.

In Figures 7 and 8 are shown representative semilog plots of the normal mode autocorrelation functions $\rho_k(t)$ for the first three modes. The semilog plots are extremely linear, indicating that the Rouse coordinates are an excellent set of normal coordinates for this model as they were for the cubic lattice model.[9] In Table II are collected the relaxation times τ_k extracted from the least-squares slopes of the ln $\rho_k(t)$ vs. t plots. These values are also averages from at least three simulation runs.

The scaling properties of the normal mode relaxation times were determined by making plots of ln τ_k vs. ln $(N - 1)$ at constant k and ln τ_k vs. ln k at constant $(N - 1)$. The slopes of these plots correspond to the scaling exponents α_k and γ_N defined by the relationships

$$\tau_k \sim (N - 1)^{\alpha_k} \tag{5}$$

$$\tau_k \sim k^{-\gamma_N} \tag{6}$$

The values of α_k and γ_N are collected in Table III. In our study of the cubic lattice model[9] we found that the higher order ($k = 2$ and $k = 3$) relaxation times for chains of length 12 did not fit the scaling relationships well. This was because the length scale of the motion being probed by the normal mode was comparable to the length scale of the crankshaft motion. Since only two-bond motions are used in the FCC model, this should be less of a problem here. We have investigated this by making two estimates of the exponment α_k in the presence of excluded volume. One includes all points in the least-squares fit. The other excludes the value for $N = 12$. Both fits give sensible values for the exponents with excellent correlation coefficients (>0.9995). The exponents that exclude the $N = 12$ point are somewhat smaller, but, considering the statistical errors involved in the Monte Carlo procedure, it is impossible to choose between the two.

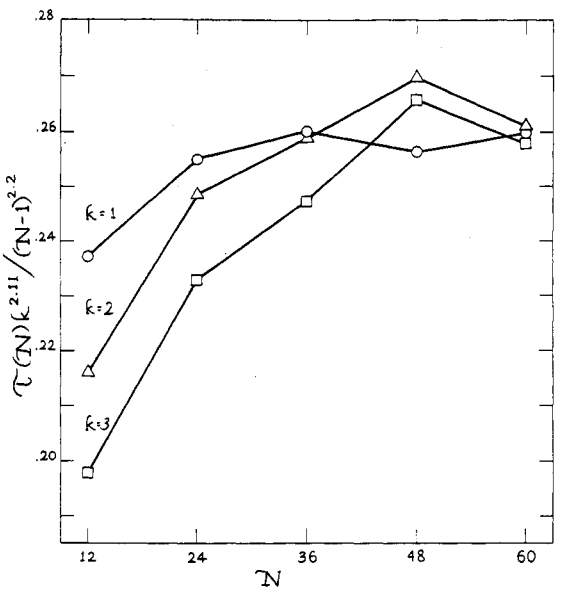

Figure 9. Plot of $[\tau_k(N)k^{2.11}/(N - 1)^{2.2}]$ vs. N for excluded-volume chains.

The values for γ_N are very close to the Rouse value of 2.0 in the non-excluded-volume case and significantly larger than 2.0 in the excluded-volume case. This is consistent with our results for cubic lattice chains. The asymptotic value for the exponent seems to be slightly smaller (2.11) for the FCC lattice chains than that found for the cubic lattice model, where the value was 2.14.[9]

To investigate the difference between the non-excluded- and excluded-volume cases further we have computed the quantities $[\tau_k(N)k^2/(N - 1)^2]$ for the non-excluded-volume case and $[\tau_k(N)k^{2.11}/(N - 1)^{2.2}]$ for the excluded-volume case. The numerical values are collected in Table IV. The values for the excluded-volume case are also plotted as a function of N and of k in Figure 9 and 10. In the excluded volume case we used the scaling theory value for α_k and then adjusted γ_N to qualitatively minimize the scatter in the values at the larger values of N. The table clearly shows that the dynamics of the FCC lattice chains are quite well described by the Rouse theory in the absence of excluded volume. When excluded volume is present

Table III
Scaling Exponents α_k and γ_N as a Function of Mode Number, k, and Chain Length, N

	α_k				γ_N	
		excluded volume				
k	no excluded volume	including $N = 12$	excluding $N = 12$	N	no excluded volume	excluded volume
1	1.99	2.25	2.21	12	1.96	2.27
2	1.97	2.32	2.27	24	1.98	2.19
3	1.95	2.37	2.33	36	2.05	2.15
				48	1.96	2.07
				60	2.05	2.12

Table IV
Values of $\tau_k k^2/(N-1)^2$ (No Excluded Volume) and $\tau_k k^{2.11}/(N-1)^{2.2}$ (Excluded Volume) as a Function of Mode Number, k, and Chain Length, N

	no excluded volume $[\tau_k k^2/(N-1)^2]$			excluded volume $[\tau_k k^{2.11}/(N-1)^{2.2}]$		
N	$k=1$	$k=2$	$k=3$	$k=1$	$k=2$	$k=3$
12	0.155	0.154	0.164	0.236	0.216	0.198
24	0.151	0.142	0.157	0.255	0.249	0.233
36	0.158	0.145	0.152	0.260	0.259	0.247
48	0.142	0.147	0.148	0.257	0.270	0.266
60	0.159	0.144	0.152	0.260	0.261	0.258

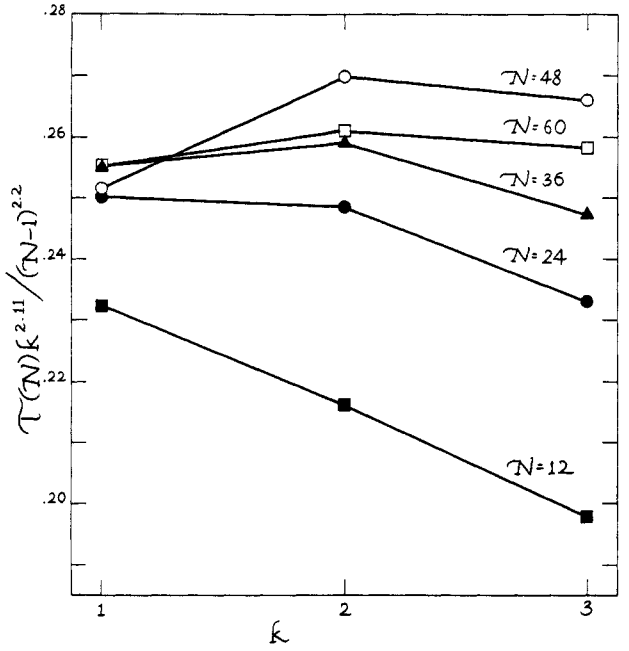

Figure 10. Plot of $[\tau_k(N)k^{2.11}/(N-1)^{2.2}]$ vs. k for excluded-volume chains.

there is a deviation from the Rouse theory in both the N dependence and the k dependence of the relaxation times. There is more scatter in the excluded-volume case, but at the longer chain lengths the relaxation times seem to be well described by the formula

$$\tau_k(N) \sim (N-1)^{2.2}/k^{2.11} \quad (7)$$

This result is consistent with our results for the cubic lattice model.[9] This strongly suggests that the deviation of γ_N from the Rouse prediction in the presence of excluded volume is a real effect that deserves further study.

IV. Comparison with the Cubic Lattice Model

There are several interesting differences between the FCC lattice model and the cubic lattice model. First, in the absence of excluded volume, the dynamic behavior of the FCC chains is much closer to the Rouse model predictions than is the behavior of the cubic lattice chains. All the exponents α_R, α_k, and γ_N are very close to 2.0 in the FCC case, while in the cubic case there are much larger deviations.[9] This may indicate that the time scale in the cubic lattice model is a function of N and k because of the involvement of the crankshaft motion. If this is true, then the FCC model also provides a better picture of the dynamics in the presence of excluded volume. Indeed, the exponents α_R and α_k do conform more closely to scaling predictions in the FCC model than in the cubic lattice model. The exponents are slightly higher than the scaling prediction of 2.2, however. Whether this is a short-chain effect, a lattice effect, statistical error, or a real deviation cannot be determined from the data presented here.

It also appears that the FCC chains approach an asymptotic "long-chain" behavior more rapidly than the cubic lattice chains. This is reasonable because the FCC chains are more flexible than the cubic chains and because the elementary motions operate on a shorter length scale (two bonds) in the FCC case. If one is interested in studying the asymptotic long-chain behavior of polymer chains using lattice models, the FCC model is probably the best alternative.

We are currently testing some of these ideas by studying the dynamics of a body-centered cubic (BCC) lattice model. This is an eight-choice lattice, on which an ergodic dynamic model can also be developed with only two-bond motions. This will allow us to study the effects of the lattice coordination number and to further explore the effect of the elementary motions on the time scale and the chain dynamics.

Acknowledgment is made to the US Department of Energy, Office of Basic Energy Sciences, Division of Materials Sciences, for partial support of this research. Acknowledgment is also made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, and to the Research Corp. for partial support of this research. The Hewlett-Packard 1000 Series A900 computer was purchased with funds provided by the National Science Foundation, the US Department of Energy, The Research Corp., and the University of Tennessee Research Incentive Program.

References and Notes

(1) Verdier, P. H.; Stockmayer, W. H. *J. Chem. Phys.* **1962**, *36*, 227.
(2) Crabb, C. C.; Kovac, J. *Macromolecules* **1985**, *18*, 1430 and references therein.
(3) de Gennes, P.-G. *J. Chem. Phys.* **1971**, *55*, 572.
(4) Kranbuehl, D. E.; Verdier, P. H. *J. Chem. Phys.* **1979**, *71*, 2662 and references therein.
(5) Gurler, M. T.; Crabb, C. C.; Dahlin, D. M.; Kovac, J. *Macromolecules* **1983**, *16*, 398 and references therein.
(6) Geny, F.; Monnerie, L. *J. Polym. Sci., Polym. Phys. Ed.* **1979**, *17*, 131.
(7) Kremer, K. *Macromolecules* **1983**, *16*, 1632.
(8) Rouse, P. E. *J. Chem. Phys.* **1953**, *21*, 1273.
(9) Dial, M.; Crabb, K. S.; Crabb, C. C.; Kovac, J. *Macromolecules* **1985**, *18*, 2215.
(10) Verdier, P. H. *J. Chem. Phys.* **1966**, *45*, 2118.