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Cooperative Relaxations in Condensed Macromolecular Systems. 3. Computer-Simulated Melts of Cyclic Polymers

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ABSTRACT: Computer simulations of dense systems with cyclic chains are demonstrated with the application of a motion mechanism based on cooperative rearrangements within closed dynamic loops. Systems of close-packed cyclic chains with lengths between 16 and 512 monomer units are generated on a cubic lattice with all sites occupied. Static properties of cyclic chains in equilibrated states of the systems are analyzed in terms of predictions based on Gaussian statistics and are compared with properties of linear chains simulated in analogous systems. Monomer motions and self-diffusion of cyclic chains are characterized in comparison with diffusion of equivalent linear chains. Results indicating comparable diffusion coefficients of long cyclic and linear chains are shown.

Introduction

Much effort has been devoted to the study of the chain conformation and dilute solution behavior of ring molecules.[1-6] The experimental evidence[7-12] seems to confirm that the chain statistics of the rings and their solution behavior are well predicted by theoretical treatments. On the other hand, there are only a few studies of concentrated systems containing ring molecules,[13-16] and the theory of ring molecules in condensed systems is only fragmentary.[17,18,21] The problem of the dynamics of ring molecules in melts seems to be, however, of particular interest because the experimentally observed behavior of ring chains relative to their linear analogues can be hardly understood in terms of existing models related to the flow behavior of linear chains.

Recent theories of flow behavior of dense polymer systems model the motion of chains as reptation along curvilinear "tubes" formed by constraints of the surrounding matrix.[19,20] A straightforward interpretation of the reptation model implies that a closed cyclic chain cannot reptate since it has no chain ends. Additional motion mechanisms have therefore been suggested to justify diffusion of cyclic chains in a matrix of linear chains and in a network of fixed obstacles. A "tube renewal" mechanism due to the migration of chain ends in the surroundings and a restricted ring reptation mechanism have been considered by Klein.[21] Neither of them, however, can describe correctly the experimentally observed diffusion of ring molecules in matrices of linear chains.[28] A third mechanism called once-threaded ring diffusion along a linear chain is suggested in addition to the former two to fit the experimentally observed data.[28] To our knowledge there is no theoretical treatment of the dynamics of ring molecules in a matrix of similar rings.

The experimental evidence of the behavior of rings in melts[14,15] shows that short rings exhibit slightly higher melt viscosities than the linear molecules of the same length, while long cyclic chains have somewhat lower viscosities than their linear analogues. There is a crossover at a chain length of about 100 monomer units. In the whole range of molecular weight the viscosities of cyclic and linear chains are, however, very similar. These results are generally in contradiction with theoretical predictions[17] based on the reptation mechanism, which suggests that the self-diffusion coefficients of rings should be much lower and consequently the viscosities considerably higher than for their linear analogues.

In the two former articles of this series[22,23] a new motion mechanism for polymer chains in condensed systems has been introduced. The mechanism has been successfully applied to simulation of self-diffusion in melts of linear chains.[23] In this article results of simulation of melts of ring molecules are presented. In simulated model systems we analyze both the static properties and the self-diffusion of cyclic chains with various lengths. The results obtained for cyclic chains are compared with analogous results for linear chains.

Motion Mechanism and Generation of "Molten" Systems

The motion mechanism applied here is the same as that described in the two former articles of this series.[22,23] According to this mechanism the elementary motion in a system completely filled with chains occurs by cooperative (simultaneous) rearrangements within closed dynamic loops. One or a few chains can take part in such a rearrangement. Each rearrangement involves local movements of chain segments along chain contours. However, the motion can be transferred from one chain to another by a position-exchange mechanism. In the areas where the position exchange occurs, the chains change their local conformations and local positions with respect to each other.

In the simulation we consider cyclic chains consisting of N monomer units on the cubic lattice. The chains fill the space completely, which means that all lattice sites are occupied. The system has periodic boundary conditions with a repeat unit of 32 lattice sites. In the system's initial state, ordered structures of cyclic chains are generated as illustrated in Figure 1 for chains of length $N = 64$ (one plane from the three-dimensional model system is shown in this figure). When longer chains are considered, they are folded within planes perpendicular to the plane shown.

The mechanism of motion within closed loops in application to the system of chains on the cubic lattice has already been described.[22,23] Nevertheless, for clarity we describe again some main routes by which the rearrangements are realized. For more details the reader is referred to the two former articles. The algorithm according to which the rearrangements are sought and performed is described here in relation to Figure 2, in which a sequence of necessary steps leading to the rearrangement is shown. We start for simplicity with a suitable local configuration of three chain segments A, B, and C as shown in Figure 2a. Let us assume that an imaginary searching point looking for position-exchange possibilities starts to move along segment A. The searching point is denoted in the figure by an arrow indicating its position and direction of motion. If the kink on segment A is found with another chain segment locally parallel to its top, the position ex-

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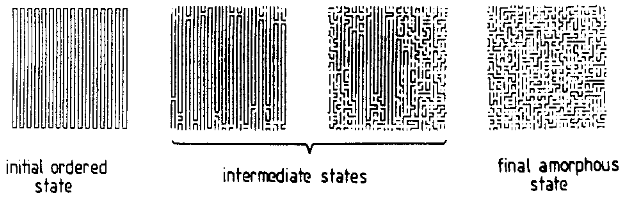

Figure 1. Illustration of the simulated melting process in a model system with cyclic chains of length $N = 64$.

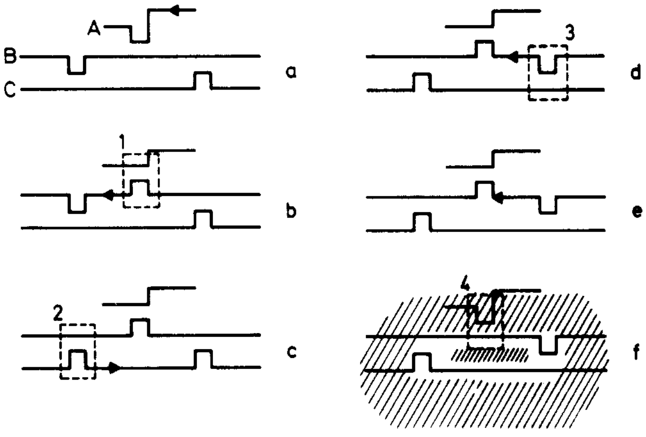

Figure 2. Schematic illustration of the procedure of searching of mobile loops (for detailed description see text).

change can be performed, leading to the new local configuration within the area denoted in Figure 2b by the dashed rectangle. Within the position-exchange area the kink on chain segment A is replaced by the kink on segment B. This involves a negative chain-length defect on chain A while chain B becomes longer for the moment. The searching point is now transferred to chain B and moves along it as shown in Figure 2b. The next possibility for position exchange can be found in this way on chain B leading, when the position exchange is made, to the local state shown in Figure 2c, within rectangle 2. At this position exchange the searching point leaves chain B and is transferred to chain C. Note that the chain-length defect of chain B is cancelled by the last position exchange. The searching point moves further along chain C to the next possibility for position exchange. In this example the searching point comes back to chain B at position-exchange 3 (Figure 2d). In the situation shown in Figure 2e the searching point recognizes that it has come to a place where it already has been. This makes closure of the loop of rearrangements possible by performing position-exchange 4. This also cancles chain-length defects on chains A and B.

By the above procedure motion within the closed loop (nonhatched area in Figure 2f) is achieved without altering the neighborhood, which is assumed to be filled completely with other chains (hatched area in Figure 2f). Systems with cyclic chains have no chain ends. Therefore the assumed mechanism of position exchange considers only replacement of a kink on a chain by a new kink formed on another chain or another part of the same chain as shown in the example. All choices that the imaginary point has to make in searching mobile loops (choice of starting point, choice of direction of searching when a new chain is entered, etc.) are made at random. The overall length of paths of the searching point is taken as a measure of time. Results presented in this article have been calculated with a Cray computer.

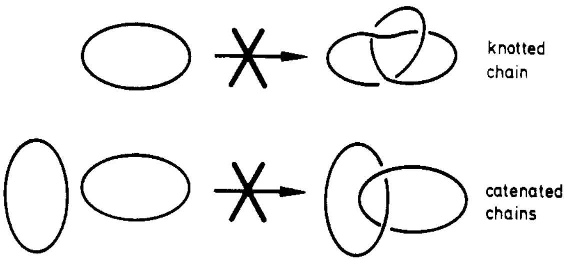

Figure 3. Illustration of nonphysical processes forbidden in the systems studied.

The temporary chain-length defects that appear in the above-described loop searching algorithm are only related to the way in which the motion possibilities are searched by the computer program. Physically the motion along the loop should be regarded as a synchronized rearrangement during which the identity of all contributing chains is completely preserved. The states before and after each closed-loop rearrangement are considered as neighboring states in the configurational-state space. Unstable intermediate states are not those that appear in the loop searching algorithm but are those that can be achieved by simultaneous small displacements of chain segments along the loop toward a new quasistable position as has been shown in the example presented in Figure 1 in the former article.[23] Such an intermediate state can certainly be realized without breaking of chains and without forming temporary chain-length defects. They are accompanied only by conformational changes within chain segments along the loop.

In application to dynamic problems each closed-loop rearrangement is considered as a stochastic kinetic step appearing randomly in space wherever the motion is possible and in time intervals proportional to the length of searching paths necessary to find the possibility of motion. This determines a time scale that ensures equal rates of short time displacements of monomers in systems with various chain lengths.[23] Each elementary motion is reversible as long as the local configuration is not changed by another rearrangement. No restrictions are imposed on loop lengths in the simulation of athermal systems.

At the moment questions concerning ergodicity as well as questions related to the proper weighting of various configurational states in our model cannot be answered uniquely. In a number of tests, however, no indications have been found that would suggest that these conditions are not satisfied in our model. Results of these tests, performed on systems with linear chains, can be summarized as follows: (1) The same equilibrium states of a system (characterized by the orientation factor, the content of gauche conformations, and the mean radius of gyration of chains) can be achieved from extremely different initial states (for example, from a completely ordered initial state[22] or from a state obtained by cutting longer equilibrated chains). (2) Stable equilibrium states can be obtained for which constant parameters have been observed over periods of time much longer than the longest relaxation times in the system (end-to-end vector relaxation). (3) In equilibrium the ratio of trans-to-gauche conformations is equal to the ratio of the a priori probabilities of these conformations.

Performing closed-loop motions in a system with ordered cyclic chains involves a kind of "melting" of the initial structure, illustrated in Figure 1 by a series of cross sections through the three-dimensional system with chains of length $N = 64$. The chains change their conformations and spatial positions, but they remain invariant with respect to their lengths and individual topological states. If the chains in the initial state are not catenated and not knotted, they remain uncatenated and unknotted under influence of the

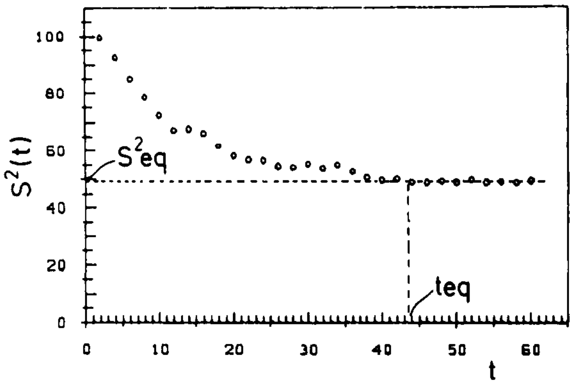

Figure 4. Relaxation of the mean-square radius of gyration of cyclic chains during the melting process.

rearrangements considered. This means that such nonphysical processes as those illustrated in Figure 3 are excluded.

During the "melting" process the following quantities characterizing the systems are monitored: (1) mean-square radius of gyration

$$s^2(t) = \frac{1}{n_k}\sum_{n=1}^{k} s_n^2(t) \tag{1}$$

(2) fraction of "gauche" conformations (noncollinear bonds)

$$g(t) = \frac{n_g(t)}{n_g(t) + n_t(t)} \tag{2}$$

and (3) orientation parameter

$$f(t) = {}^3\!/_2 n_b^{-2}[(n_x(t) - \bar{n})^2 + (n_y(t) - \bar{n})^2 + (n_z(t) - \bar{n})^2] \tag{3}$$

where t is CPU time ($t = 0$ is assumed for the initial ordered state), n_k is the number of chains in the system ($n_k = 32^3/N$), s_n is the radius of gyration of the nth chain, n_t is the number of trans (collinear) and n_g the number of gauche (bent) conformations in the system, n_b is the overall number of bonds, and $\bar{n} = n_b/3$. As an example, the typical time dependence of the radius of gyration for the system with cyclic chains of length $N = 512$ is shown in Figure 4. It is seen that the mean-squared radius of gyration of chains relaxes in the melting process from the value characteristic of the oriented initial state to some equilibrium value that fluctuates only slightly at times $t > t_{eq}$. The same type of behavior can be observed for the orientation parameter and for the fraction of gauche conformations. Time-averaged values (for $t > t_{eq}$) of the above quantities are listed in Table I for model systems with various chain lengths. In all cases values of $\langle f\rangle$ close to 0 and values of $\langle g\rangle$ close to 0.8 are achieved, which means that systems obtained are isotropic and the chains may be regarded as ideally flexible.[24,25]

Comparison of Equilibrium Properties of Linear and Cyclic Chains

The basis for characterization of equilibrium properties of polymer chains is the knowledge of the distribution $W(r_{ij})$ for a pair of chain elements i and j in the chain. This distribution determines, for example, the mean-square radius of gyration $\langle s^2\rangle$ or the particle-scattering factor. For chains having Gaussian statistics it is given by

$$W(r_{ij}) = \frac{3}{2\pi n a^2}\exp\left(-\frac{3r_{ij}^2}{2na^2}\right) \tag{4}$$

Table I
Static Properties at Model Systems with Cyclic Chains in Comparison with Dimensions of Linear Chains

N	$10^{-3}\langle f\rangle$	g	$\langle s_N^2\rangle_c$	$\langle s_N^2\rangle_c$ in solv	$\langle s_N^2\rangle_l$	$\langle s_N^2\rangle_l/\langle s_N^2\rangle_c$
16	0.25	0.791	2.16		4.06	1.88
32	0.34	0.790	4.20	≃5.3	8.35	1.98
64	0.17	0.792	7.85		16.30	2.07
128	0.19	0.792	14.70		33.60	2.28
256	0.13	0.792	26.50	≃40	68.00	2.56
512	0.20	0.791	48.8		126.5	2.59

where $n = |j - i|$ and a is the segment length. Such a distribution manifests itself in characteristic properties of chains,[26] especially for linear chains:

$$\langle r_{ij}^2\rangle_l = na^2 \tag{5}$$

$$\langle R_N^2\rangle_l = Na^2 \tag{6}$$

$$\langle s_N^2\rangle_l = {}^1\!/_6 Na^2 \tag{7}$$

where R_N is the end-to-end distance and s_N is the radius of gyration of the chain with length N. The index l denotes quantities related to linear chains.

Ring closure introduces constraints that change the Gaussian character of chains. In the case of end-to-end closed chains the resulting distribution can be found in a simple way.[26] The vector $\mathbf{r}_{ij}$ spans two subchains a an b of lengths n and $N - n$, respectively. The corresponding distribution $W_c(r_{ij})$ is then the convolution of respective distributions $W_a(r_{ij})$ and $W_b(r_{ij})$ that gives the following result:[26]

$$W_c(r_{ij}) = \frac{3}{2\pi\mu a^2}\exp\left(-\frac{3r_{ij}^2}{2\mu a^2}\right) \tag{8}$$

where

$$\mu = n - n^2/N \tag{9}$$

Based on this distribution, some characteristic properties of ring chains can be derived in analogy to those given by eq 5–7:

$$\langle r_{ij}^2\rangle_c = (n - n^2/N)a^2 \tag{10}$$

$$\langle s_N^2\rangle_c = {}^1\!/_{12} Na^2 \tag{11}$$

Index c denotes here quantities related to cyclic chains. The $\langle r_{ij}^2\rangle_c$ in 10 exhibits a parabolic dependence on n with $r_{ij} = 0$ at $n = 0$ and $n = N$ and with a maximum at $n = N/2$ given by

$$\langle r_{ij}^2\rangle_{max} = N/4 \tag{12}$$

Such behavior of $\langle r_{ij}\rangle$ for cyclic chains is in evident contrast to the linear dependence predicted for linear chains by eq 5.

The comparison of radii of gyration for linear and cyclic chains shows that[1]

$$\langle s_N^2\rangle_l/\langle s_N^2\rangle_c = 2 \tag{13}$$

The above predictions based on Gaussian statistics of chains can be compared with the properties of simulated chains. In Figure 5 the normalized mean-square distance between elements i and j ($\langle r_{ij}^2\rangle/\langle R_N^2\rangle$) is plotted versus the normalized length of chain between these elements (n/N) for simulated systems with various chain lengths. Systems with linear chains shown for comparison were described in the previous article. Linear and parabolic dependencies are observed for linear and cyclic chains,

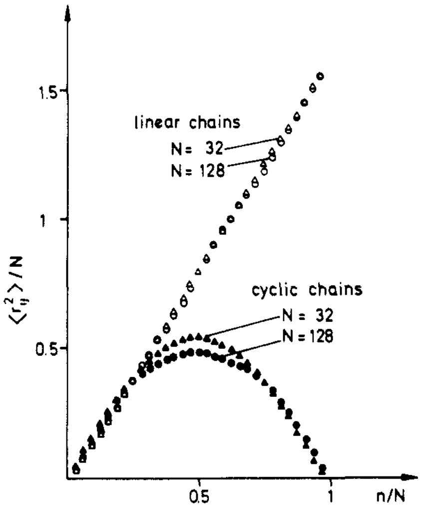

Figure 5. Normalized mean-square distance between elements i and j versus normalized length of chain between these elements for simulated linear and cyclic chains of various length.

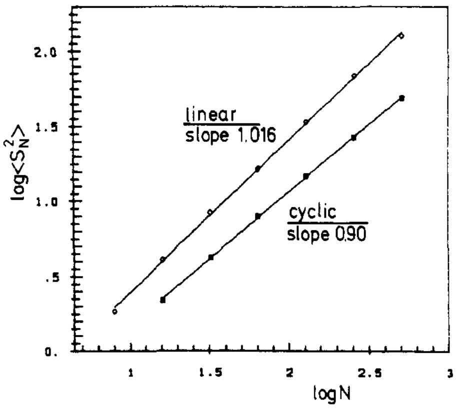

Figure 6. Chain-length dependence of the mean-square radius of gyration for linear and cyclic chains.

respectively, which is in qualitative agreement with predictions given by eq 5 and 10. The conformation of cyclic chains is, however, dependent on the chain length. The values of $\langle r_{ij}^2 \rangle_c$ are in agreement with the predictions of eq 12 only for short cyclic chains. Longer cyclic chains seem to be slightly collapsed in comparison with the prediction according to Gaussian statistics.

Similar conclusions can be drawn from comparison of radii of gyration of linear and cyclic chains. In Figure 6 the chain-length dependencies of the radius of gyration for linear and cyclic chains are shown in a double logarithmic plot. In both cases linear dependencies are observed, which means that the results can be described by a power law;

$$\langle s_N^2 \rangle \sim N^{\nu} \tag{14}$$

The exponents ν are, however, different for cyclic and linear chains; values $\nu = 0.90$ and $\nu = 1.016$, respectively, are assumed. As a consequence of this, the ratio $\langle s_N^2 \rangle_l / \langle s_N^2 \rangle_c$ increases with chain length and assumes values much higher than 2 for longer chains, as shown in Table I. Taking into account that the simulated linear chains satisfy quite well the theoretical predictions independently of the chain length, the above result indicates that long cyclic chains in the condensed system have smaller dimensions than those predicted on the basis of Gaussian statistics.

So far as we know there are no experimental results related to dimensions of ring molecules in the molten state. On the other hand, quite good agreement between relation 13 and experimental observations has been found for ring molecules in a Θ solvent. The radius of gyration of computer-simulated isolated rings has also been found to be 2 times smaller than the radius of gyration of equivalent linear chains.[27]

In view of this, the reason for the effect of collapsed cyclic chains observed in our systems can be supposed to be of topological nature. It is clear that if in the condensed system of ring molecules such processes as those shown in Figure 3 are not possible, the chains are topologically constrained because they cannot cross each other. In this way the ring chains cannot assume all possible conformations, especially those that would lead to formation of catenated chains, and therefore the rings behave as being under the "pressure" of these topological restrictions. Such an effect is certainly a property peculiar to a melt consisting of ring molecules only. Ring molecules in a solvent or even dispersed in a melt of linear chains find themselves in a quite different topological situation. For proof of this, a computer experiment has been performed in which ring chains equilibrated at first in a condensed state have been "dissolved" by cutting most of the chains in the system into dimers and by subsequent relaxation of the remaining ring chains by performing motions according to the same mechanism as that applied for a condensed system. Such "experiments" have been performed for two systems with chain lengths $N = 32$ and $N = 256$. In both cases the concentration of remaining ring chains was 1.56%. A distinct increase of squared radius of gyration averaged over time has been observed in such diluted systems in comparison with the radius of gyration of rings in condensed systems (see Table I). However, obtaining precise average values of the radius of gyration of diluted rings requires relatively long calculation times (longer than those used for the data presented) because of the low concentration of chains. This means that the effect of chain expansion in a solvent is demonstrated here only qualitatively but probably will be considered in further studies with higher precision.

The behavior of ring molecules in the melt like those observed here has been recently suggested by Cates and Deutsch,[29] who presented arguments that the noncatenated ring polymers may have statistics intermediate between those of collapsed and Gaussian chains for which the chain-length scaling exponents are $\nu = {}^2/_3$ and $\nu = 1$, respectively. Our value $\nu = 0.9$ obtained for noncatenated ring polymers in a simulated melt lies well within these bounds.

Self-Diffusion of Cyclic Chains

The condensed equilibrated systems of cyclic chains characterized in the preceding paragraph have been used as initial states for the observation of motion of whole chains and of single monomers when the closed-loop rearrangements in the system have been performed. A chosen sequence of states of a single chain of length $N = 64$ observed during its diffusion in the system filled completely with identical chains is shown in Figure 7. The trajectory of the moving chain can be estimated by following the numbers describing subsequent states. Dimensional fluctuations and various conformational states assumed by the chain when moving can be observed.

For characterization of the mobility of monomers and the diffusion of whole chains, the following quantities have been monitored as a function of time: (1) mean-square displacement of monomers in laboratory coordinates

$$g_m(t) = \frac{1}{N} \langle \sum_{i=1}^{N} [r_i(t) - r_i(0)]^2 \rangle \tag{15}$$

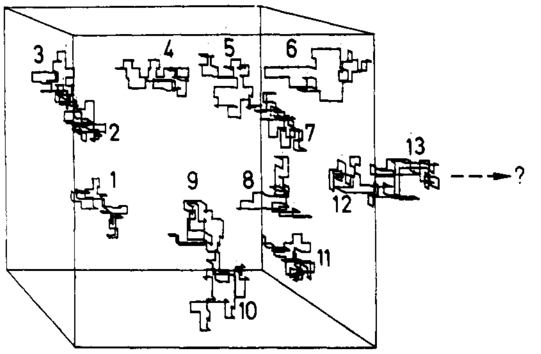

Figure 7. Illustration of the motion of a cyclic chain of length $N = 64$. Subsequent states are numbered.

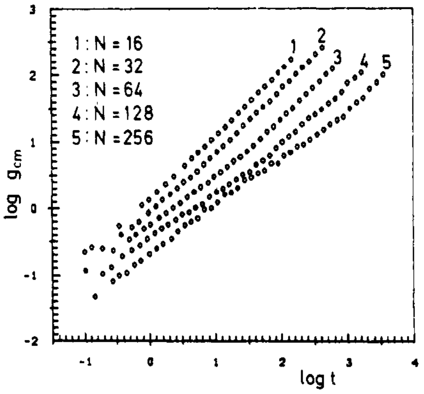

Figure 8. Time dependences of mean-square center-of-mass displacements for cyclic chains with various lengths.

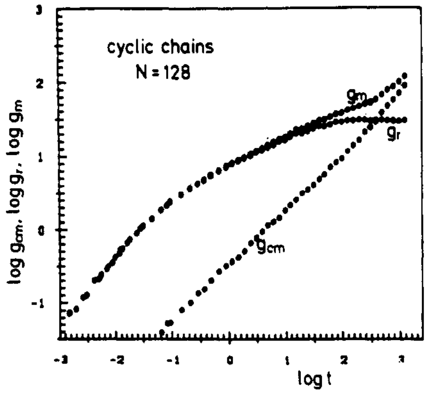

Figure 9. Comparison of time dependences of g_m, g_r, and g_{cm} for cyclic chains of length $N = 128$.

(2) mean-square displacement of monomers in center-of-mass coordinates

$$g_r(t) = \frac{1}{N}\langle\sum_{i=1}^{N}[r_i(t) - R_{cm}(t) - r_i(0) + R_{cm}(0)]^2\rangle \quad (16)$$

and (3) mean-square center-of-mass displacement

$$g_{cm}(t) = \langle[R_{cm}(t) - R_{cm}(0)]^2\rangle \quad (17)$$

where $R_{cm}(t)$ and $r_i(t)$ are positions at time t of the center-of-mass and of the ith monomer, respectively. The averaging is performed over all chains in the system.

The time dependences of g_{cm} for systems with various chain lengths are shown in Figure 8, and the displacement of the center of mass is compared with monomer displacements g_m and g_r in Figure 9 for chain length $N = 128$. Qualitatively the same behavior is observed here as that described in the previous article for linear chains. The center of mass follows the Fickian type of diffusion at long times. The behavior of monomers is split into two regimes characteristic of short and long times. In both these regimes the mean-square displacement of monomers in a laboratory coordinate system is proportional to time. At very short times it characterizes the Brownian type of motions of single monomers, and at long times it tends to coincide asymptotically with displacements of the center of mass. A crossover is observed at intermediate times when the mean-square displacement of monomers is smaller or comparable with the radius of gyration of chains. For comparison the same dependencies determined previously for linear chains are shown in Figure 10. It can be seen that displacements of monomers in the center-of-mass coordinates for cyclic chains are almost identical with displacements of central monomers of equivalent linear chains. An important property of our simualtions is that the short time scale monomer displacements are identical for chains with various lengths and, as a comparison of dependencies from Figures 9 and 10 shows, are also identical for linear and cyclic chains. This fact is related to choice of time scale, which is the same for all systems as described in the previous article.[23]

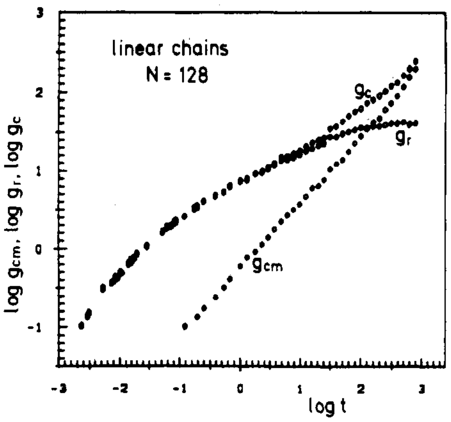

Figure 10. Comparison of time dependences of g_m, g_r, and g_{cm} for linear chains of length $N = 128$.

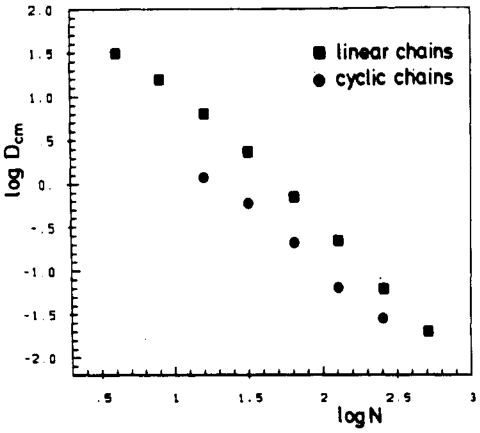

Figure 11. Center-of-mass diffusion constants as a function of chain length for linear and cyclic chains.

The diffusion constants of the center of mass are determined as

$$D_{cm} = \lim_{t\to\infty}[g_{cm}(t)/t] \quad (18)$$

The chain-length dependence of the center-of-mass diffusion constant of cyclic chains is shown in Figure 11 together with the respective dependence for linear chains. Within the whole range of chain lengths considered, the diffusion constants for cyclic chains are smaller than for linear chains. Values of the ratio $D_{cm}(\text{linear})/D_{cm}(\text{cyclic})$ are given in Table II. This ratio decreases with increasing

Table II
Ratio of Diffusion Constants for Linear and Cyclic Chains

N	D_{cm}(linear)/D_{cm}(cyclic)	N	D_{cm}(linear)/D_{cm}(cyclic)
16	5.40	128	3.22
32	3.83	256	2.44
64	3.37		

chain length as also can be seen from dependencies shown in Figure 11. Unfortunately, it is not possible from the present data to estimate the asymptotic behavior of cyclic chains at $N \rightarrow \infty$. We expect a small constant value of the ratio D_{cm}(linear)/D_{cm}(cyclic) at this limit. Considering that the diffusion constants for the linear chains are decreasing with chain length faster at the longest chain lengths considered than those for the ring chains, the possibility that the linear chains can become slightly slower than their cyclic analogues at the limit $N \rightarrow \infty$ cannot be excluded. In any case, the results presented here indicate that the mechanism of motion based on cooperative rearrangements within closed loops leads to comparable mobilities of linear and cyclic chains with the ratio of diffusion constants decreasing with increasing chain length. The larger difference in diffusion constants for short chains can be attributed to large concentrations of chain ends in systems with linear chains, which change considerably the density of position-exchange possibilities. Calculations for systems with longer chains are certainly necessary. This would demand, however, calculation times that are not available to us at the moment.

Conclusions

Results presented in this article demonstrate that application of the mechanism of cooperative motions within closed loops to ordered systems with cyclic chains filling the space completely involves a kind of "melting" process leading to equilibrated states in which cyclic chains are randomly coiled but slightly collapsed in comparison to Gaussian chains. The last effect is attributed to topological constraints imposed on cyclic chains by noncrossability and close packing.

The translational diffusion of cyclic chains in such systems is also demonstrated. The analysis of monomer displacements shows that the behavior of cyclic chains is qualitaively the same as that observed previously for systems with linear chains. The diffusion constant of the center of mass of short cyclic chains is found to be remarkably smaller than that for linear chains of equivalent length. With increasing chain length, however, the ratio of diffusion constants decreases, so that the rates of self-diffusion of linear and cyclic chains can be regarded as comparable.

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Theory of Thermoelastic Properties for Polymer Glasses

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ABSTRACT: We derive expressions for the extensional elastic moduli as functions of temperature and pressure by a generalization of the equation of state theory. Our previous efforts in this direction were confined to the low-temperature region, where the characteristic free volume function, defined by theory, is effectively frozen. We proceed now to higher temperatures, where the temperature and pressure dependence of this function play a decisive role. The static Young's and shear modulus and the Poisson ratio are computed, based solely on equation of state information. This is illustrated by means of applications to poly(vinyl acetate) glasses at low and elevated pressures and for different formation histories. Further comparisons with experimental results are presented for poly(methyl methacrylate). A unified treatment of static compressional and elongational properties thus exists, at present for the linear regime of deformations. We conclude with an outline of possible extensions.

1. Introduction

In recent years the configurational thermodynamic or quasi-thermodynamic properties of amorphous polymers in the melt and glassy states have been receiving intensive experimental and theoretical attention. Quantitatively successful formulations for single and multiconstituent systems were obtained. They are based on a lattice model which incorporates a particular structure function and

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