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Motion of Star-Branched Chains in Polymer Networks: A Monte Carlo Study

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SUMMARY: A simple model of branched polymers in confined space is developed. Star-branched polymer molecules are built on a simple cubic lattice with excluded volume and no attractive interactions (good solvent conditions). A single star molecule is trapped in a network of linear polymer chains of restricted mobility. The simulations are carried out using the classical Metropolis algorithm. Static and dynamic properties of the star-branched polymer are determined using various networks. The dependence of the longest relaxation time and the self-diffusion coefficient on chain length and network properties are discussed and the proper scaling laws formulated. The possible mechanism of motion is discussed. The differences between the motion of star-branched polymers in such a network are compared with the cases of a dense matrix of linear chains and regular rod-like obstacles.

Introduction

In this paper we have studied a simple lattice model of star-branched polymers in a matrix of long linear ones using the Monte Carlo method. The star-branched polymers were chosen because not only are they good models for theoretical considerations, but, what is more important, they can also be synthesized and studied in real experiments. The mechanism of motion of such polymers in dense systems is still far from understood.1-2) The algorithm used in the present study was developed especially for star-branched polymers3) and used previously for free chains, melts, adsorbed and confined chains.4-8) It is efficient for isolated chains even in the presence of an impenetrable surface, as well as for dense systems.

Theoretical predictions,9) assuming that the 'arm retraction' mechanism dominates in dense systems, are that the diffusion coefficient D scales with the chain length N as $D \sim N^{-\beta}e^{-\alpha N}$. Some simulations have been made, but they were concerned with star-branched polymers in a system of fixed obstacles.10-11) They confirmed the above scaling law, finding that $D \sim N^{2}e^{-0.37N}$. On the other hand, extensive simulations of star polymers in a matrix of long linear

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chains led rather to a scaling law similar to those in melts of linear chains (with an exponent close to −2).4)

In our simulations we employed a star polymer molecule with $f = 3$ arms of equal length n emanating from a common origin called the branching point. The total number of beads in the molecule was $N_s = f(n - 1) + 1$. The chains were constructed on a simple cubic lattice with the excluded volume effect present. The system was athermal, i.e., no long-range attractive and local potentials were present. A few star-branched chains ($M_s = 4$ chains) were immersed in a dense matrix of long linear chains (every linear chain consisted of $N_l = 800$ beads). The number of linear chains M_l was selected to maintain constant density of the system $\varphi = 0.5$; the density was defined as the total number of polymer beads to the total number of beads in the Monte Carlo box: $\varphi = (M_l \cdot N_l + M_s \cdot N_s) / L^3$. The partially frozen linear chains modeled the polymer network. Each linear chain in the melt was pinned every n_p beads12). This implied that these chains could move locally (oscillate) but could not diffuse.

We used the classical Metropolis scheme in order to sample efficiently the configurational space and to calculate parameters describing the chain's size and dynamic properties. The initial configuration of the model chain underwent a series of local micromodifications where positions of a few beads (segments) were randomly changed. It was proved that a proper set of such modifications allows a chain to get to any point in the phase space. We used a set of motions which was developed and successfully used previously for linear chains; the detailed description of the elementary motions was given elsewhere.3,5) The micromodifications were: (i) two-bond chain end motion, (ii) two-bond kink motion, (iii) three-bond kink motion, (iv) three-bond 90° crankshaft motion. Star-branched chains underwent the additional (v) branching point collective motion.

Results and Conclusions

We performed a series of simulations for star polymers with n = 32, 50, 100, 200, and 400 beads in an arm. The distance between pinned beads of linear chain n_p changed from 200 to 12. The actual size of a polymer chain we described as usually by the mean-square center-to-end distance $\langle R^2 \rangle$ and the mean-square radius of gyration $\langle S^2 \rangle$. The scaling of these parameters was close to that characteristic for dense polymer melts: $\langle R^2 \rangle \sim (N_s - 1)^{0.97 \pm 0.03}$ and $\langle S^2 \rangle \sim (N_s - 1)^{0.97 \pm 0.02}$. The ratio $\langle S^2 \rangle / \langle R^2 \rangle$ was constant and equal to 0.40.

The short-time dynamics characterized the relaxation processes within the chain. We investigated the autocorrelation function of the center-to-end vector, **R**. The longest relaxation times, τ_R, were calculated as in ref.3,5) For long distances between pinned linear matrix chains ($n_p = 100$), the longest relaxation times scaled as $\tau_R \sim (N_s - 1)^{2.66\pm0.03}$. For the network with $n_p = 50$ $\tau_R \sim (N_s - 1)^{2.75\pm0.01}$. This scaling behavior is qualitatively the same as that found for a mobile matrix of linear chains.4)

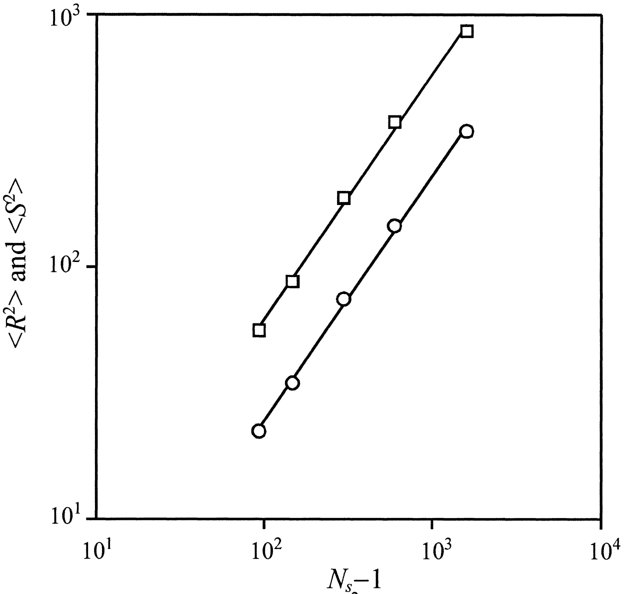

Fig. 1: The mean-square center-to-end distance, $<R^2>$, and the mean-square radius of gyration, $<S^2>$, as a function of total chain length, N_s ($n_p = 100$).

The long-time dynamics of the system was studied in terms of chain diffusion. The self-diffusion coefficient was extracted from the center-of-mass autocorrelation function $g_{cm}(t)$ according to Einstein's formula $D = g_{cm}(t) / 6t$ + const, valid for sufficiently long times, where $g_{cm} > 2 \cdot <S^2>$. For long distances between pinned linear matrix chains ($n_p = 100$), the diffusion coefficients scale as $D \sim (N_s - 1)^{-1.86\pm0.04}$. This negative exponent was much higher than that obtained for star polymers in a mobile matrix of long linear chains4) (−1.52) and for melts of linear chains13) (−1.53). For the network model with $n_p = 50$ the scaling was $D \sim (N_s - 1)^{1.98\pm0.06}$.

The mechanism of chain motion can be elucidated from the scaling behavior of autocorrelation functions. The presence of the $t^{1/4}$ regime in the single bead autocorrelation function $g(t)$ suggests some kind of reptation-like motion as the arm-retraction mode, even for networks with short chains ($n_p = 12$).

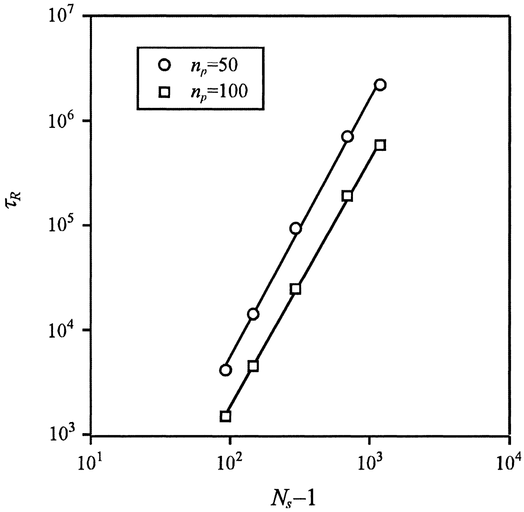

Fig. 2: The longest relaxation time, τ_R, as a function of total chain length, N_s, for two model networks.

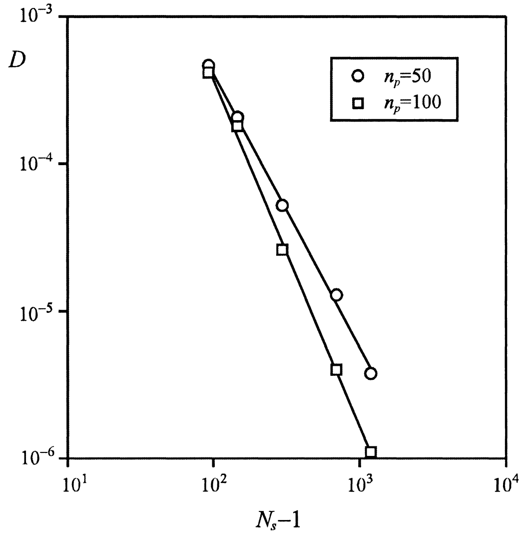

Fig. 3: The self-diffusion coefficient, D, as a function of total chain length, N_s, for networks.

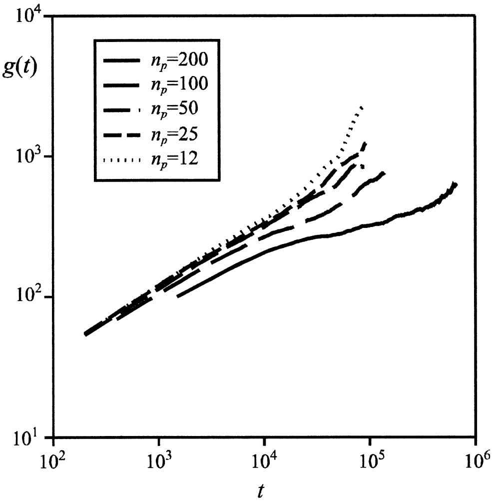

Fig. 4: The single bead autocorrelation function, *g*(*t*), for a selection of networks.

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