Properties of Simple Models of Polymer Networks. A Monte Carlo Simulation

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Summary: A model polymer network was constructed from branched chains. Each chain was built on a simple cubic lattice forming a star-branched polymer consisting of $f = 3$ arms of equal lengths. The fragment of network under consideration consisted of 1, 2 and 3 star polymers with different topology of connections. The only potential used was excluded volume (athermal chains). The properties of the network were determined by the means of computer simulations using the classical Metropolis sampling algorithm (local micromodifications of chain conformation). The behaviour of linear chains of the same molecular weight was also studied as a state of reference. The influence of attaching the next star-branched chain to the network on its static and dynamic properties was studied. The short-time dynamic behaviour of chain fragments was determined and discussed.

Keywords: lattice models; Monte Carlo method; polymer dynamics; polymer networks; star-branched polymers

Introduction

Models of polymer networks have been a subject of extensive theoretical considerations.[1] In simple theoretical models of network one can study the dynamic properties of a network and especially of its fragments. It is of great interest to study cooperative chain motions on a scale larger than the distance between neighbouring cross-links.[2-3]

Star-branched polymer chains are interesting and non-trivial models of branched macromolecules the properties of which are studied extensively by experimental and theoretical methods.[4-5] In a series of papers we studied the static and dynamic properties of simple lattice models of star-branched polymers. The model chains were simulated at various solvent conditions,[6-7] in a dense polymer melt,[8] adsorbed on an attractive surface[9-10] and in confinement.[11] The motion of a star polymer in very naive models of polymer network was also studied.[12-13]

This simple model star-branched chain seemed to be a good starting point for studying the properties of fragments of polymer networks. Therefore, in this work we used star polymers as a component of a polymer network with a few cross-links. The main goal of this work was to

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determine the properties of the network during its formation, i.e., after adding an element with a cross-link to the existing network.

The Model and the Algorithm

Chains were built on a simple cubic lattice.[14-15] The chain had volume, i.e., it could not cross itself. No long-distance attractive potential or local stiffness was introduced. The structure of network under consideration was the following. In every star there were $f = 3$ arms of equal length n emanating from a common origin (Figure 1A). The basic element was a star branched chain consisted of $N = f \cdot n + 1$ beads. The simulated chains were put into a Monte Carlo box with edge $L = 100$ with periodic boundary conditions imposed. A pair of star chains can be connected by the ends of their arms: the scheme of such a structure is presented in Figure 1B.

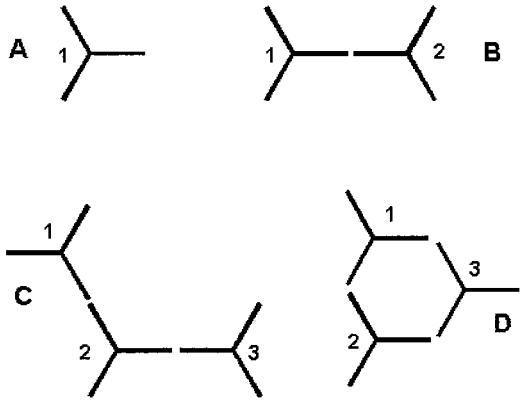

Fig. 1. An idea of the model networks under consideration. A single star-branched polymer (A), two-star system (B), linear three-star system (C) and ring three-star system (D).

The attachment of the next (third) star polymer can be made in the same way, forming two different structures: a linear one (Figure 1C) and a ring-like one (Figure 1D). The total number of beads is N in model A, $2N$ in model B and $3N$ in models C and D respectively.

We used the classical Monte Carlo algorithm based on a Metropolis scheme. In this algorithm the set of local micromodifications was used in order to sample the conformational space.[14-15] The set of elementary motions consisted of 1-bead motion, 2-bead motion, 2-bead crankshaft

motion, end of chain reorientations and collective motions of the branching point. A new conformation of a chain was chosen at random and accepted due to geometrical constraints and excluded volume.

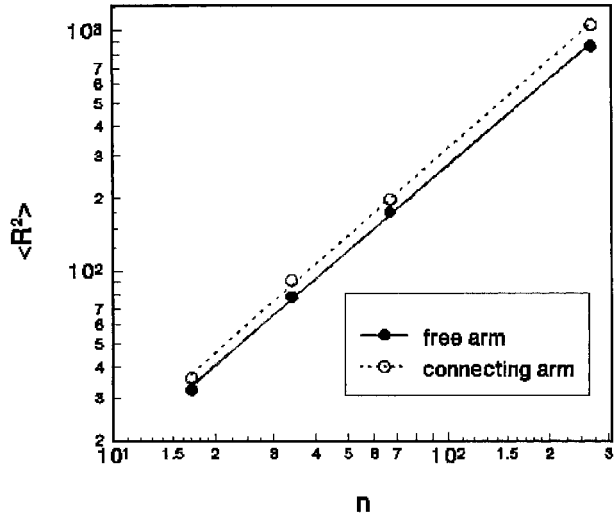

Fig. 2. Mean square cross-link-to-arm-end distance $< R^2 >$ versus the number of beads in an arm n for the model of network *B*.

Results and Discussion

The changes of the parameters describing the size of a polymer system can be seen in Figure 2 where the mean square distance $< R^2 >$ between the branching point (cross-link) and the arm-end of the star is plotted. It can be noted that the dimensions of the arms forming the network structure obey the scaling law $< R^2 > \sim n^{1.22 \pm 0.02}$ while the exponent for the scaling of the non connecting arm as well as the free star arm[14] is 1.19±0.02. The connecting arms are longer than the free ones. This scaling effect is probably caused by the short chain effect. The differences in the chain length are evident when it is recalled that the cross-link points must stay at some distance and, therefore, the connecting link cannot behave as a fully flexible coil.

The dynamics of the model system can be studied by the means of autocorrelation functions.[6-7] We define a single bead autocorrelation function *g(t)*:

$$g(\Delta t) = \left\langle [\mathbf{r}_i(t+\Delta t) - \mathbf{r}_i(t)]^2 \right\rangle \quad (1)$$

where $\boldsymbol{r}_i$ are the coordinates of the i^{th} polymer bead at times t and $t+\Delta t$ respectively.

In Figures 3-6, we present the autocorrelation functions *g(t)* versus the bead number for the single star-branched polymer (*A*), and three models of network (*B-D*). The bead numbering is as follows: we consider the longest linear chain that can be constructed in the given mode, e.g., in model *A* this chain corresponds to any pair of arms, while in the model *D* it consists of all (6) connecting arms. It can be observed that for every model the cross-links exhibit lower mobility than other parts of the chain. The free arms are much more mobile and their correlation function plot is parabolic (Rouse-like). However, for longer times the plots begin to adopt the parabolic, Rouse-like shape. The only exception is model *D*, where the long time limit is a straight line parallel to *x*-axis, as in a ring polymer chain. The different topology of model networks does not change the mobility significantly (model *C* versus model *D*).

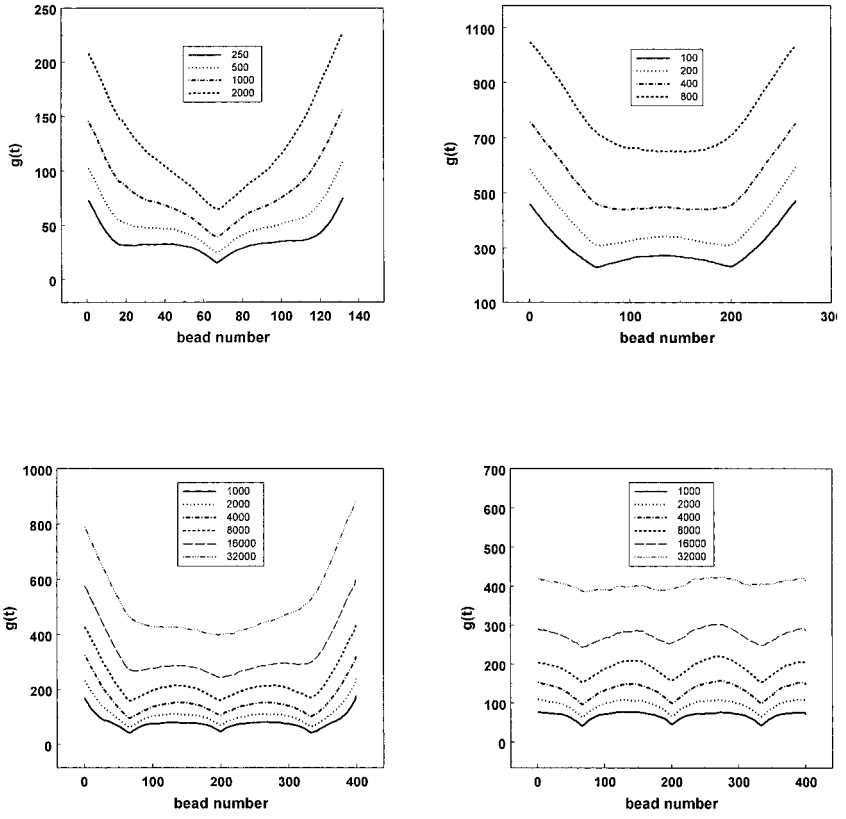

Fig. 3-6. Autocorrelation function of a single bead *g(t)* as a function of the residue number *i*. The case of a chain with $n = 67$ beads in an arm and model *A* (upper left), *B* (upper right), *C* (lower left) and *D* (lower right). The numbers given in inset give the time.

To estimate the differences in dynamics of free and connected arms the longest relaxation times were calculated for the respective vectors. The relaxation process of free arms is about 5 times faster than for connecting arms. The relaxation times in both cases scale roughly with the arm length as N^2.

The models presented and the simulation method seem to be useful in studying certain properties of polymer network. The positions of cross-links in the network can be identified by analysing the short-time scale chain mobility. The models under consideration can also be treated as components of more complicated networks for theoretical considerations.

[1] B. Erman, J. E. Mark, "*Structures and Properties of Rubberlike Networks*", Oxford University Press, New York 1997.
[2] A. A. Gurtovenko, Y. Ya. Gotlib, *Macromolecules* **1998**, 31, 5756.
[3] A. A. Gurtovenko, Y. Ya. Gotlib, *Macromolecules* **2000**, 33, 6578.
[4] G. S. Grest, L. J. Fetters, J. S. Huang, D. Richter, *Adv. Chem. Phys.* **1996**, *94*, 67.
[5] J. J. Freire, *Adv. Polym. Sci.* **1999**, *143*, 35.
[6] A. Sikorski, *Polymer* **1993**, 34, 1271.
[7] P. Romiszowski, A. Sikorski, *J. Chem. Phys.* **1998**, *109*, 2912.
[8] A. Sikorski, A. Kolinski, J. Skolnick, *Macromol. Theory Simul.* **1994**, 3, 715.
[9] A. Sikorski, *Macromol. Theory Simul.* **2001**, 10, 38.
[10] A. Sikorski, *Macromol. Theory Simul.* **2002**, 11, 359.
[11] A. Sikorski, P. Romiszowski, *J. Chem. Phys.* **2002**, 116, 1731.
[12] A. Sikorski, *Macromol. Symp.* **2001**, **171**, 57.
[13] P. Romiszowski, A. Sikorski, *Macromol. Symp.* **2001**, 171, 63.
[14] A. Sikorski, *Makromol. Chem., Theory Simul.* **1993**, *2*, 309
[15] A. Sikorski, P. Romiszowski, *J. Chem. Phys.* **1996**, *104*, 8703.