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Citation: *The Journal of Chemical Physics* **109**, 6169 (1998); doi: 10.1063/1.477245

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Shape of star-branched polymers at various solvent conditions. A computer simulation study

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(Received 13 April 1998; accepted 9 July 1998)

Monte Carlo simulations of a simple cubic lattice model of star-branched polymers were made. The solvent conditions (temperature) were varied in a wide range and the total chain length was up to 800 beads. The analysis of a shape of branched macromolecules was performed by means of the gyration tensor principal moments and asphericity factor. The changes of shape parameters during the transition from a random coil to a collapsed globule have been determined. In high temperatures, the instantaneous shape of the branched chain is more symmetric than that for linear chains. The shape of one star arm is very similar to that of the entire polymer. In lower temperatures, the collapsed model chain forms an isotropic globule. The shape of inner and outer parts of the star polymers is discussed. © 1998 American Institute of Physics. [S0021-9606(98)51838-7]

INTRODUCTION

During the last decade, enormous progress was made in the experimental studies of branched polymers. Star-branched macromolecules, which are the simplest models of branched chains, were synthesized and studied by means of many sophisticated techniques, which enabled one to measure precisely parameters of interest.¹ Along with the experimental studies, many theoretical works concerning properties of star polymers were also made.²⁻⁴

The description of the shape of the polymer chain was a main goal of many theoretical studies for the last 20 years, which started with the pioneering works of Solc and Stockmayer.^{5,6} They defined an “equivalent ellipsoide” which was built of components of the squared radius of gyration. The instantaneous shape of polymer chains described by these components was far away from the sphere. The ratio of these principal components was calculated for a random-flight chain model and was found to be 11.7:2.7:1. The influence of temperature on these components has been determined by means of the Monte Carlo simulation of lattice models of linear polymer chains.⁷ These were found rather independent on the chain length (at least in the range of $N = 50$ to 500 beads) as well as on the kind of lattice [simple cubic vs face-centered-cubic (fcc) lattices]. At high temperatures (good solvent conditions), the chain was more asymmetric than in the random-flight model. The model chain became more symmetrical along with the decrease of temperature, although the changes of the instantaneous shape were rather surprisingly small. Recent Monte Carlo simulations of Tanaka and Mattice⁸ of simple cubic lattice model chains with polymer-polymer interactions allowed one to determine precisely the shape of the linear polymer chain. The ratio of the principal components of the tensor of inertia was found to vary from 15:3:1 (an athermal chain), to

11:2.6:1 (theta conditions), and finally 1.9:1.4:1 in the low-temperature collapsed and almost symmetrical globule. The shape of the macromolecule can also be described by a single parameter called the asphericity parameter δ . It takes value 1 for a one-dimensional rod and 0 for a spherical object. The detailed discussion of δ is given in the Results and Discussion section.

Star-branched polymers are considered to be more packed and spherical than linear ones having the same molecular weight. This was proved for these branched macromolecules by Solc⁹ and by Mattice,¹⁰ who studied models of stars with $f=3$ and 4 arms without the excluded volume on the simple cubic lattice and of the rotameric state model, respectively. Solc found that for 3-arm stars the ratio of principal components of the tensor of inertia was 8.5:2.8:1, which shows that the star-branched molecules are more spherical than linear chains. They^{9,10} also found that a higher number of arms led to a more symmetric structure. Batoulis and Kremer¹¹ performed Monte Carlo simulation of long athermal star-branched polymers on face-centered lattice using a different simulation algorithm (the dimerization technique). Besides the detailed description of static and dynamic properties of stars, they also determined their shape. They found the asphericity of star-branched polymers $\delta=0.344$, compared with a value of 0.550 obtained for linear chains. They also showed that the asphericity of star polymers depends strongly on the number of arms: the higher the number of arms the more spherical polymer coil is formed. Zifferer and Olaj¹² have shown that there is no difference in the shape of polymer chain on various lattices (tetrahedral, simple cubic, face-centered cubic, and body-centered cubic) and in continuous space if sufficiently long chain is considered.

Recently, Zifferer¹³ performed MC simulations of very long ($N \approx 15000$) star polymers with different numbers of arms (f up to 96). He found that the asphericity and shape factors do not scale simply with the number of arms. Zifferer¹⁴ has performed the study of the shape of the linear

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as well as the star-branched polymer near the theta conditions using the pivot algorithm on a tetrahedral lattice for a different number of arms and chain length. The interactions between the nearest neighbors have been introduced and the simulations were performed from good solvent conditions to the theta point. The results have been extrapolated to the infinite lengths of chains. It has been found that the asphericity factor δ decreases for linear chains along with the decrease of temperature. The opposite result has been achieved for star-branched molecules—the growth of δ along with the decrease of temperature from athermal conditions to the theta point was clearly explained as the result of the interactions between arms satisfying the excluded-volume effect. In a very recent series of papers, Zifferer¹⁵ has studied the behavior of the asphericity δ^* along with the changes of the chain length, as well as the distribution of the bond length of the molecule. Also, the analysis of the correlation between δ^* and other parameters describing the shape and the size of the molecule has been performed. An interesting result of Zifferer¹² shows that for star-branched molecules the asphericity increases along with the increase of the chain length, while for the linear molecules the opposite effect has been observed.

Bishop and Clarke¹⁶ studied off-lattice models of star-branched polymers by means of the Brownian dynamics method. The method applied allowed the study of the asphericity of star-branched polymers in three different regimes: excluded volume, Θ , and collapsed. It was confirmed that star polymers are more symmetrical compared with linear ones, and that the low-temperature collapsed polymeric globules are almost symmetrical. Results of Bishop and Clarke were close to those of Batoulis and Kremer,¹¹ in spite of the fact that quite different models and simulation techniques were used. Results of recent off-lattice Monte Carlo simulations¹⁷ gave values of asphericity factor very close to those of lattice models (0.360 for star-branched polymers without the excluded volume and 0.345 with the excluded volume). Asphericity of two-dimensional star-branched polymers was also determined using the same method.¹⁸ Stars without the excluded volume were less spherical and stars with the excluded volume were more spherical than their counterparts in three dimensions.

The dynamical properties concerning the shape of star-branched chains were the subject of works by Kovac and co-workers.^{19,20} They simulated short (N up to 85 beads) star polymers using the cubic lattice bond fluctuation model. They found 3-arm stars more symmetrical than in previous studies:^{5,6} the ratio of the principal moments of the tensor of inertia was 5:2:1. Shape fluctuations were determined from the behavior of the autocorrelation function of the principal moments. They found that scaling of the longest relaxation times of these parameters is not dependent on the number of arms, and exponents varied from 0.54 to 1.08. In their second paper²⁰ they studied the influence of the concentration on star-branched polymer shape fluctuation.

In this work, which is the study of the influence of temperature on the shape of macromolecules, we investigated the simple model of a star-branched polymer with the low number of branches ($f=3$). Model chains were embedded to

the simple cubic lattice and the classical dynamic Monte Carlo (DMC) algorithm was used. A detailed analysis of static and dynamic properties and their temperature dependence on single star polymer (infinite dilution) has been published elsewhere.^{21–24} Some initial results concerning dynamic properties of polymer melt containing star-branched chains were also published.²⁵ Here we want to point out some most interesting results concerning the shape of the star-branched polymers at various temperatures.

DESCRIPTION OF THE MODEL

The general assumptions of the model used in this paper have been presented and discussed in detail elsewhere,^{22,23} so only the main features will be given below. The model polymer chains form a star-branched structure: f linear chains, called branches, emanate from a common origin (a branching point). Every arm consists of the same number n of polymer beads connected by $n-1$ segments. The total number of beads in the entire star-branched polymer $N=f(n-1)+1$. We assumed that the number of arms is constant and equal three ($f=3$). Model chains are confined to a simple cubic lattice and thus only vectors, which are permutations of $[\pm 1, 0, 0]$, are allowed. We introduced a contact potential, which can be written in a form,

$$V(r_{ij}) = \begin{cases} \infty & \text{for } r_{ij} < 1 \\ \varepsilon < 0 & \text{for } r_{ij} = 1 \\ 0 & \text{for } r_{ij} > 1, \end{cases} \quad (1)$$

where ε is energy (in kT units), and r_{ij} is a distance between nonbonded polymer beads i and j . The parameter is assumed to have a negative value, which implies that we have attractive forces in the model system. This is a potential of mean force where all kinds of interactions are included and averaged over all positions of solvent molecules. The reference state ($\varepsilon=0$) corresponds to the situation in which there is no distinction between polymer–polymer and polymer–solvent interactions. As a measure of the temperature we took $T^* = -kT/\varepsilon = -1/\xi$, which is also referred to as the reduced temperature.

Thus the total energy of a linear polymer chain on a simple cubic lattice can be written in the following form:

$$E_{\text{total}} = \sum_{i=1}^{N-3} \sum_{j=i+3}^N V(r_{ij}), \quad (2)$$

where $V(r_{ij})$ is the energy of a pair of beads ij calculated according to Eq. (1). Beads that are adjacent along the chain contour are assumed to not be interacting. Because of the assumption that we deal with homopolymers, one can assign the same energy to every bead–bead contact. We did not introduce any local interaction potential; all conformational states had the same energy (assumed to be zero). Hence our model chains are fully flexible.

The initial configuration of a model chain underwent a series of local micromodifications where positions of a few segments were randomly changed. These moves are: two-bond motion, three-bond motion, three-bond crankshaft motion, chain end modifications, and a branching point collec-

TABLE I. Values of squared principal moments of the equivalent ellipsoid and the asphericity factor for stars of arm length $N=49$, 199, and 799 at different reduced temperatures T^* .

$1/T^*$	$N=49$					$N=199$					$N=799$				
	L_1^2	L_2^2	L_3^2	δ^*	δ	L_1^2	L_2^2	L_3^2	δ^*	δ	L_1^2	L_2^2	L_3^2	δ^*	δ
0	8.95	3.36	0.97	0.332	0.327	51.24	18.05	5.42	0.337	0.348	258.5	93.71	28.42	0.338	0.331
0.2	7.90	2.75	0.89	0.342	0.343	36.03	13.08	4.34	0.330	0.330	174.6	60.03	20.85	0.341	0.340
0.3	7.01	2.42	0.84	0.340	0.342	29.06	9.75	3.54	0.351	0.355	99.52	34.02	13.06	0.343	0.345
0.4	6.07	2.09	0.80	0.330	0.340	17.76	6.19	2.69	0.303	0.339	22.50	11.43	6.96	0.160	0.173
0.5	4.98	1.79	0.76	0.325	0.315	8.93	4.07	2.28	0.207	0.207	13.60	8.76	6.11	0.062	0.065
0.6	4.14	1.53	0.72	0.288	0.298	6.29	3.46	2.13	0.116	0.121	11.62	7.95	5.72	0.050	0.050
0.7	3.37	1.38	0.70	0.253	0.255	5.36	3.21	2.08	0.089	0.090	8.38	7.97	7.38	0.038	0.039
0.8	2.82	1.30	0.69	0.206	0.200	4.84	3.06	2.07	0.073	0.073	9.76	7.36	5.62	0.030	0.030
1.0	2.34	1.18	0.69	0.159	0.156	4.37	2.90	2.04	0.056	0.058	9.05	7.08	5.65	0.022	0.021

tive motion.²² The transition to a new conformation is accepted according to the classical asymmetric Metropolis scheme,

$$P(\text{old} \rightarrow \text{new}) = \begin{cases} \exp\left(-\frac{E_{\text{new}} - E_{\text{old}}}{kT}\right) & \text{for } E_{\text{new}} > E_{\text{old}}, \\ 1 & \text{for } E_{\text{new}} \leq E_{\text{old}} \end{cases} \quad (3)$$

where $P(\text{old} \rightarrow \text{new})$ is a probability of the transition from an “old” to a “new” conformation, and E_{old} and E_{new} are the total energies of “old” and “new” conformations, respectively. After the acceptance (or rejection) of a new conformation, the procedure was repeated by a random selection of next test move out of a set of possible moves.

We performed a series of simulations of a chain consisting of the given number of segments. All calculations were carried out in the Monte Carlo cubic box of the edge length equal to 100, which is quite sufficient to avoid any interaction of the simulated molecule with its image, since the periodic boundary condition algorithm was used. We started from a randomly chosen chain conformation and then we made a series of simulation runs. In a single run we maintained the temperature to be constant. In order to equilibrate the chain under consideration we performed an additional Monte Carlo simulation run at the same temperature before the collection of the simulation data was started. In lower temperatures we applied the thermalization procedure in which from time to time the temperature has been moderately raised in order to avoid trapping a polymer chain in local energy minima.

RESULTS AND DISCUSSION

The simulations were performed for three chain lengths $N=49$, 199, and 799 beads; the single arm consisted of $n=17$, 67, and 267 chain beads, respectively. The temperature was varied in a wide range from good solvent conditions to a collapsed globule state: the reduced temperature T^* was between 5 and 1. Also, the athermal chains, i.e., chains without the attractive part of the potential, were simulated and the results obtained are given for comparison as the limiting values for infinitely high temperature. The results for a given

temperature are the averages obtained from several (usually more than 20) trajectories, which lasted up to 10^7 time units each.

The instantaneous shape of the polymer chain is usually described in two ways. The first is based on a concept that shows the macromolecule as an “equivalent” ellipsoid which is characterized by its three orthogonal components of the square radius of gyration taken along the principal axes of inertia of the object—this has been introduced by Solc and Stockmayer.^{5,6} Let the symmetric tensor of the second kind,

$$\mathbf{S} = \begin{vmatrix} S_{xx} & S_{xy} & S_{xz} \\ S_{yx} & S_{yy} & S_{yz} \\ S_{zx} & S_{zy} & S_{zz} \end{vmatrix}, \quad (4)$$

have the elements defined as follows:

$$S_{xx} = \frac{1}{N} \sum_i (x_i - x_{\text{CM}})^2, \quad (5)$$

$$S_{xy} = \frac{1}{N} \sum_i (x_i - x_{\text{CM}}) \cdot (y_i - y_{\text{CM}}) \text{ etc.,}$$

where the summation goes over all coordinates of the chain beads and the subscript CM denotes the coordinates of the center of mass of the system. The trace of the tensor \mathbf{S} is equal to the squared radius of gyration $S^2 = \text{tra}(\mathbf{S}) = S_{xx} + S_{yy} + S_{zz}$. The principal moments of the equivalent ellipsoid are the eigenvalues L_1^2, L_2^2, L_3^2 obtained by the diagonalization of the tensor \mathbf{S} . In this paper the eigenvalues are listed in decreasing order $L_1^2 \geq L_2^2 \geq L_3^2$. These ordered principal moments were averaged over numerous chain conformations obtained during the simulation process. Values of average principal moments are collected in Table I. The ratio of the principal components $L_1^2:L_2^2:L_3^2$ in a good solvent is approximately 8:3:1, which is in good agreement with values 8.35:2.75:1 found by Bishop and Clarke¹⁶ for off-lattice chains and shows that the molecules have the elongated, beanlike shape. Our simulation results are also in a good agreement with Monte Carlo simulation results of Solc,⁹ who found the proportion 8.5:2.8:1 for the random-flight star-branched chain. The cooling of the model star-branched polymer leads to diminishing the differences between the principal components of the radius of inertia, and at low

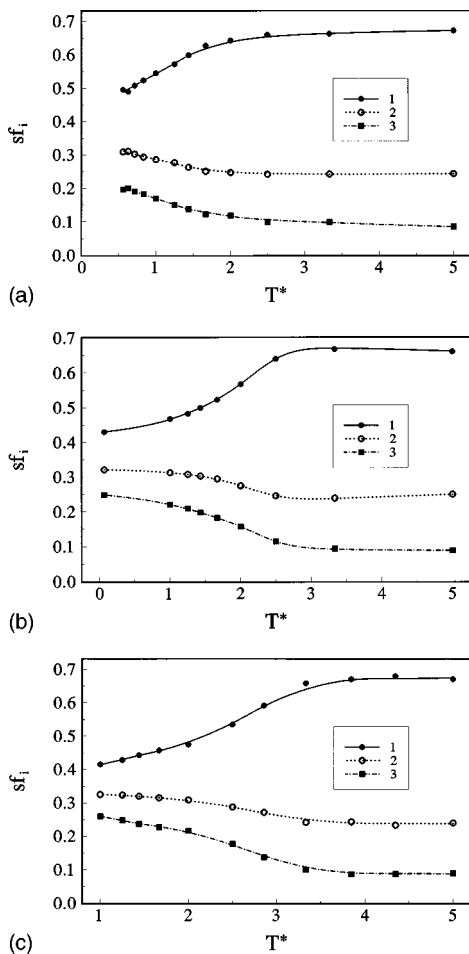


FIG. 1. Plot of average shape factors sf_i vs the reduced temperature T^* for different chain lengths: $N=49$ (a), $N=199$ (b), and $N=799$ (c).

temperatures the proportions approach the limiting value 1:1:1, which is characteristic for a symmetrical object.

We also used the normalized principal moments (shape factors) $sf_i = L_i^2/S^2$ in order to compare the results obtained for chains containing different numbers of beads. In Fig. 1 we present the values of shape factors vs the reduced temperature T^* . One can observe that the three curves exhibit some plateau at high temperatures, and then each shape factor starts to approach the value of 1/3, which shows the tendency to form the symmetrical spherelike globule. One can notice that at high temperatures the values of sf_i do not depend on the length of the star-branched polymer chain, as it has been reported by Zifferer and Olaj.¹² On the other hand, the course of sf_i during the cooling of the system depends on the chain length: the longer the chain the more pronounced the changes in shape during the coil-to-globule transition.

The second method of describing the shape of the molecules is the use of one parameter characterizing the asymmetry of the molecule. This has been introduced by Rudnick and Gaspari²⁶ and by Aronowitz and Nelson²⁷ and called an asphericity parameter δ^* and is defined as follows:

$$\delta^* = \left\langle \frac{\sum_{i>j} (L_i^2 - L_j^2)^2}{2 \cdot (\sum_{i=1}^3 L_i^2)^2} \right\rangle. \quad (6)$$

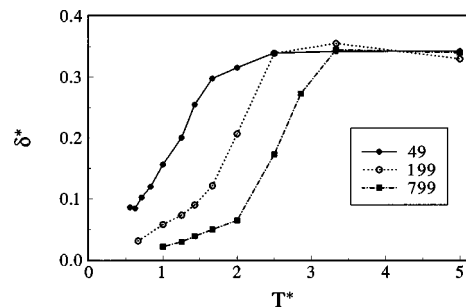


FIG. 2. Plot of the average asphericity factor δ^* vs the reduced temperature T^* for different chain lengths N (see legend).

For rodlike molecules, δ^* takes value 1 and vanishes for the molecules of spherical symmetry. Because it is difficult to calculate the average defined in Eq. (6) analytically, researchers often use the ratio,

$$\delta = \frac{\langle \sum_{i>j} (L_i^2 - L_j^2)^2 \rangle}{\langle 2 \cdot (\sum_{i=1}^3 L_i^2)^2 \rangle}. \quad (7)$$

We have calculated δ^* and δ for all the lengths of the chains in various temperatures. The values of δ^* and δ are collected in Table I. For all the chain lengths, the values of δ^* and δ are almost identical in good solvent conditions ($T^* > 3.3$). At the collapsed globule regime, the differences between δ^* and δ are more pronounced for shortest chains and fluctuate within the range ± 0.01 . In the vicinity of the coil-to-globule transition temperature, the δ^* is smaller than δ , the maximum difference between δ^* and δ in this region is 4%. The temperature dependence of the parameter δ^* has been plotted on Fig. 2 for various chain lengths. As one can see, the two different regimes of the behavior of this parameter of the star-branched polymer can be distinguished. The first range covers the temperature range in which the molecules are in a form of a random coil immersed in the solvent. Values of the asphericity factor for linear random-flight chains without the excluded volume can be estimated analytically as 0.525 (value 0.534 was obtained by ϵ expansion²⁷). For star-branched polymers in three-dimensional space, the following formula was derived for the random-flight chain model in the limit of infinite chain:²⁸

$$\delta = \frac{150f^{-1} - 140f^{-2}}{135 - 120f^{-1} + 4f^{-2}}. \quad (8)$$

For stars containing $f=3$ arms, Eq. (8) yields $\delta \approx 0.36$. Our simulations of athermal branched polymer chains give very close results $\delta=0.33$ (for chains with $N=49$ beads), $\delta=0.35$ (for chains with $N=199$ beads), and $\delta=0.33$ (for chains with $N=799$ beads). Simulations of other models of star-branched polymers gave similar results: Batoulis and Kremer¹¹ found on fcc lattice $\delta=0.34$ (the value obtained from Fig. 10 of Ref. 11) and Bishop *et al.*¹⁷ found for the off-lattice model $\delta=0.35$.

In a wide range of temperatures from athermal ($T^* = \infty$) to temperatures in the vicinity of Θ -point, δ^* remains almost constant (within the experimental error estimated from ten independent runs as ± 0.01). At the Θ -temperature (3.3), where the polymer has some features of random-flight

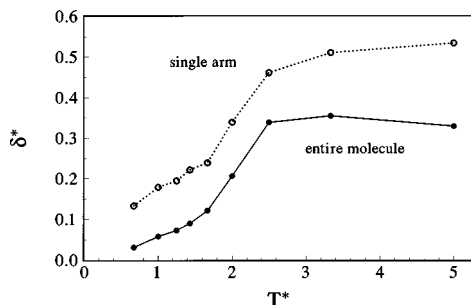


FIG. 3. Comparison of the dependence of the average asphericity factor δ^* on the reduced temperature T^* for a single arm and the entire molecule of total length $N=199$.

chain, $\delta^*=0.34$ – 0.35 , which is close to theoretical predictions listed above. At a certain temperature the values of the asphericity factor start to decrease rapidly with the decrease of temperature and approach values close to 0. Besides the large intervals between the points, one can observe that the decrease of δ^* starts just above the values of temperature at which the coil-to-globule transition takes place ($T_c = 1.2, 2.1$, and 2.8 for the total length 49, 199, and 799 respectively).²⁴ Since the depression of δ^* takes place in the region of $T > T_c$, we may speculate that it can be caused by some kind of rearrangement of the polymer molecule just before the coil-to globule transition takes place.

At the temperature $T^*=1$ asymmetry, $\delta^*=0.16$ for $N=49$, 0.06 for $N=199$, and 0.02 for $N=799$, which was rather expected. This shows that the low-temperature globules formed by the macromolecules under consideration are symmetrical. Comparing the curves for the chains of different length one can see that for longer chains the highly symmetrical globule is formed at higher temperature than for the case of shorter chains.

The coil-to-globule transition in which the shape of the molecule changes is a process in which all arms of the star-branched molecules take part and the resulting change of the shape does not reflect any specific behavior of a single arm. We have investigated the changes of the shape of the single arm in this process. In order to do so we have calculated δ^* for each arm separately and then the results have been averaged over all arms. The results of the example for the molecule containing $N=199$ beads have been plotted in Fig. 3. As one can see, the plots for a single arm and for the entire polymer are similar. The collapse of the star-branched polymer and of its arm begin at the same temperature. As one can observe, the values of δ^* for the entire molecule are systematically about 0.1 less than those for the averaged arm in the whole range of T^* . This is an interesting result, especially for the collapsed system. It shows that in the collapsed state, an arm of the star-branched molecule remains, in some sense, a prolonged object, despite the fact that the entire polymer molecule is highly spherical. It can be a result of the existence of the hard core in the center of the molecule, where the fragments of the polymer arms form a dense packed structure in the vicinity of the branching point. As it has been discussed in previous papers, the number of interactions between the arms is much larger in the hard core of the polymer than in other fragments of the polymer. Thus the

core of the polymer forms a spherelike and hardly impenetrable structure which extends up to about ten beads counted from the branching point along the chain length. The existence of the core can force the single arm to stay in the asymmetric form rather than to obtain the spherelike shape since all three arms form a dense packed structure (at least in the center of the star). These arms interpenetrate themselves, as was shown elsewhere, and thus the chain, as the whole is more symmetric. The effect of the differences in δ^* between the single arm and the whole molecule can also be explained, in part, by the influence of the chain length (the arm consists only of 1/3 of the total number of segments). Comparing the plots for a single arm and the entire molecule one can easily observe that the latter exhibits a slight increase from $T^*=5.0$ to the theta temperature. This behavior is quite different than that of the single arm, exhibiting continuous decrease of δ^* , and is in perfect agreement with the results of Zifferer¹⁴ discussed in the first section of this paper.

The results discussed above give the information about the instantaneous shape of the entire star-branched chain and of a single arm. From our previous simulations^{22–24} we know that most of the star-branched polymers' properties are different for inner and outer parts of a chain. In order to give some insight into a shape of specified parts of a polymer we present Fig. 4. In this figure we plotted the partial asphericity factor δ_i^* calculated as follows: the calculations were performed using the same equation [Eq. (6)] for the first i (as counted from the branching point) beads of the molecule. Thus for small values of i , δ_i^* characterizes the shape of the most inner parts of the chain. The larger i , the closer is δ_i^* to the overall δ^* value; for $i=n$ one has $\delta_i^* = \delta^*$. The results are presented for different solvent conditions: a good solvent, Θ conditions, and a collapsed globule regime. From Fig. 4 one can notice that for low i , $\delta_i^* \approx 0.3$ and does not depend on the chain length as well as on the temperature. It means that the structure of the most inner parts of the molecule which are close to the branching point remain unchanged and are defined by the lattice properties, namely the dense packing of segments. For a good solvent condition as well as for the Θ point, the changes in δ_i^* are small, and in fact, after a slight initial growth, δ_i^* remains constant. The opposite behavior of δ_i^* is observed for a collapsed globule regime, ($T^*=1$) where δ_i^* decreases monotonically from 0.3. Except in the case of the shortest chain, the shape of the molecules becomes almost spherical ($\delta_i^* \approx 0.1$) after 1/3 of the total beads contribute to δ_i^* . The further adding of the next 2/3 of the total number of beads does not significantly change the isotropy of the globule. One can notice that at the collapsed globule regime the beads located near the branching point from an asymmetric structure (δ_i^* close to 0.3). During the process of the collapse of the chain, the beads, which are more distant from the branching point, fill the "holes" in the globule formed by the beads located near the branching point that leads to the globular, more isotropic structure. This behavior is more pronounced in the case of longer chains ($N=199$ and $N=799$).

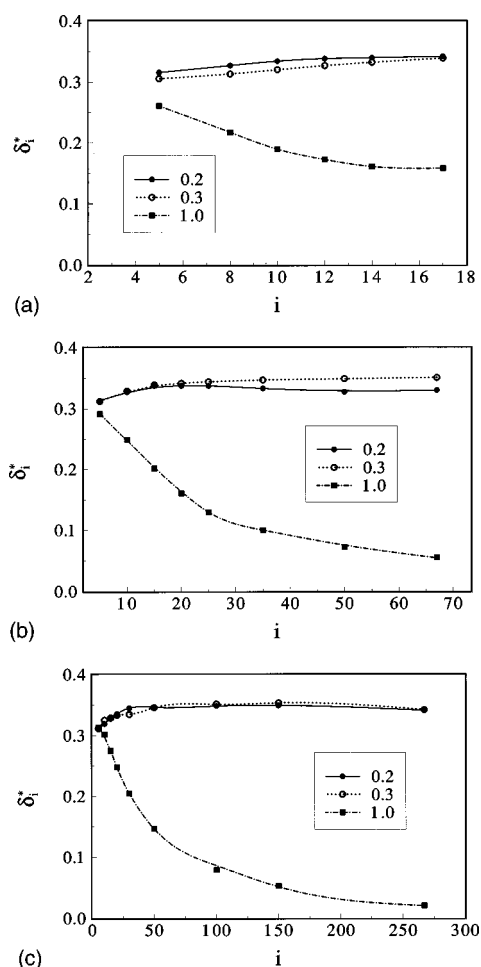


FIG. 4. Plot of the average asphericity factor δ_i^* vs the number of bead i (see text for details) for different chain lengths: $N=49$ (a), $N=199$ (b), and $N=799$ (c). The values of $1/T^*$ are given in the legend.

CONCLUSION

We performed a series of Monte Carlo simulations of star-branched polymer models on a simple cubic lattice. The changes of the instantaneous shape of the polymer during the annealing of the system have been studied. It was shown that at high temperatures the molecules form the elongated coils, which, during the cooling process, become more symmetrical after the collapse to a globule. The parameters characterizing the shape of the entire polymer differ from those, which describe the inner parts of the macromolecule. As it was shown, the dense core of the star-branched polymer does not change its shape during the annealing process. The observed changes of the asphericity parameter of the entire polymer are caused mostly by the changes in the structure (dense packing) of the arms of the star, since they exhibit more flexibility and mobility than the inner core of the polymer.

Star-branched polymers exhibit a more spherical shape in a good solvent than their linear counterparts. This is probably caused by a different distribution of polymer segments in the inner part of a polymeric random coil. In a star polymer there exists a dense spherical core formed in the vicinity of the branching point, and therefore the remaining outer parts of arms behave almost like linear chains (the number of interarmal contacts is rather small).

The annealing of the branched polymer molecule leads to the diminishing of its size but the shape remains almost unchanged in a wide range of temperatures. Thus, the star-branched polymer at the Θ temperature is only slightly more spherical than in the athermal system. The further annealing leads to the formation of a dense globule. In this state a star polymer becomes almost symmetrical. Its arms are now entangled (a high number of interarmal contacts is observed) and the entire polymer exhibits properties of an inner core. Comparing the star-branched molecules to linear chains, the asphericity parameters of the latter are more symmetrical at good solvent conditions. The collapsed globules of both types of molecules are symmetrical.

ACKNOWLEDGMENT

A partial support of this work by the University of Warsaw Grant No. BST-512/34/96 is gratefully acknowledged.

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