Different diffusion behavior of cyclic chains under confinement

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Abstract

Molecular dynamics simulations of merging process of two isolated cyclic chains and that of linear chains have been performed, in order to find the difference between the two kinds of chain in bulk and in vacuum, where surface of the system restrains thousands of configurations showing up. Analysis indicates that in such confinement the chain ends at most moments float on the surface layer, and their mobility is much larger than the mean value of all atoms in linear chains, or that in cyclic chains. Comparison of the merging processes of cyclic chains and their linear counterparts was intensively carried out by several means of analyzing the trajectory files in statics and in dynamics. It was found that the segments of cyclic chains showed almost the same behavior of motion with that of linear chains. This is different diffusion behavior from that in bulk systems, where the cyclic chain has much higher diffusion rate. This modeling therefore indicates that in these confined systems because of the surface energy, the end groups are involuntarily kept on the surface, and lost the capacity of leading chain reptation through the other polymer chains, which is possibly the origin that the difference of diffusion behavior between the linear chain and the cyclic chain in the bulk almost disappears in the case of the confinement.
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1. Introduction

The onset of entanglements of polymer chains is one of the subjects of fundamental importance in polymer science because the structure of entanglement network formed by long chains establishes the unique viscoelastic property of polymers. Of all the theoretical approaches to the dynamics of entangled linear polymer molecules, the theory of de Gennes [1] and Doi and Edwards [2] has been most widely referred to and has been verified for a range of polymer systems. In their theory, the topological constrains on the motion of a reference chain due to the interactions with its neighbors are replaced by a curvilinear 'tube', along which the reference chain is assumed to move like a snake. Hence, the relaxation of constrains occurs mainly at the chain ends. A cyclic chain, on this basis, since it has no 'free chain ends', cannot reptate. Accordingly, the motion of cyclic chains in melt might be quite different from that of their linear counterparts. A number of investigations on melted or condensed cyclic polymers have been reported in recent two decades, experimentally [3–9] and by simulation [10–12], not always leading to completely consistent results. General conclusion emerging from the studies of simulation is that the dimension of cyclic polymers is smaller than that of linear ones and cyclic chains have higher diffusion coefficients than their linear counterparts at high molecular weight. Some explanations indicated that the more compact cyclic chains have less interpenetration that leads to fewer entanglements and faster dynamics [11–13].

Although, the investigation of bulk system is very important, there are still many systems in practical applications in which polymer chains are confined, not in unperturbed state anymore, such as the polymer film on matrix, the particles aggregated in poor dilute solution at low temperature. The formation of these systems also provides some insight into the onset of entanglements. However, experimentally, detailed information about chain motions in these formation processes, in which entanglements occur, is much difficult to be observed. Molecular dynamics (MD) provides a useful implement to understand it at atomistic level. We aimed to investigate the details of interpenetration of polymer chains, which is directly related

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to the formation of entanglements, in a microscopic view by MD. In previous work [14], the merging process of two linear isolated polyethylene globules in vacuum, or in a confined space, was studied, and was found to have two stages, the wetting stage and the interpenetration stage, the former being driven by surface free energy, and the later by the conformational entropy of the system. In the interpenetrating process, it was found that ends always floated on the surface of the system.

In the present study, we examined two isolated cyclic chains in a merging process in vacuum by using MD. Since the surface of the system restricts the emergence of many conformational states, therefore, the chains studied are like under a kind of confined space. Several means were used to measure their structures and dynamic behaviors. Comparing with their linear counterparts, different feature from that in bulk for the linear chain and the cyclic chain was found.

2. Model and details of the simulation

Polyethylene (PE) chains were used in the present simulation, each of which consists of 300 CH_2 (more than the critical entanglement molecular weight, about 4000, i.e. 280 CH_2). The groups of CH_2 were approximated to united atoms, as used in many studies [14–18]. The simulation was performed using Cerius 2 in an O2 workstation. The force field parameters came from Dreiding II [19], and potential terms involve bond stretching, bond-angle bending potential, torsional and van der Waals interactions. A truncated Lennard–Jones potential was used for all the non-bonded interactions between CH_2 groups separated by more than three bonds and the cut-off distance was 9 Å. The canonical (constant NVT) Nose–Hoover method was used. The integration time step was 2 fs and the relaxation constant for the heat bath variable was 0.1 ps. The simulations were performed in vacuum. In order to get the system reach equilibrium as soon as possible, the temperature was set at 600 K, much higher than the temperature of glass transition of PE, so the mobility of chain segments is quite high, which speeds up the coming of the equilibrium of the system.

In MD simulation, the initial structure is very important to get reasonable results. In this work, each of isolated linear chains was obtained from MD run of a PE chain in all trans conformation in the conditions described above. When the total energy, as well as the radius of gyration (R_g) turned to be constant values, the chain collapsed into a contact globule. The globule obtained has remarkably different size of coils from that in bulk [14]. The mass centers of two such globules was separated about 25 Å (the most near edge distance of the two globules was about 5 Å), and the structure was used as the initial one of the merging process of two isolated linear chains. The difference of two isolated cyclic chains initial structure from that of linear one was that, each of globules was obtained from a cyclic PE chain—the end connecting with the head, not all trans

conformation anymore. But the steps and conditions were same as in the linear ones. The time length of the MD runs both for the merging process of two linear chains and for that of the cyclic ones was 18 ns.

3. Results and discussion

3.1. The location and the mobility of chain ends

The globules merging process of cyclic chains, which just as that of the linear chains in previous work [14], firstly experienced the wetting stage—the two globules becoming closer to and touching each other and aggregating into a new one, then the interpenetration stage. As the primary difference of the topological structure in both cases is that the linear chains have chain ends, but the cyclic ones do not. During the merging process the location of the chain ends in the system and the mobility of the ends were evaluated after the first wetting stage. We report the results below.

3.1.1. Location of the chain ends

The snapshots of structure of the linear chains trajectory file were intensively analyzed in the present study. The chain ends were found kept floating on the surface as the detailed information shown in Figs. 1 and 2. Fig. 1 displays the end location distribution along the radius from mass center of the system. It notes that all the ends were basically apart from mass center more than 10 Å, and mostly located at about 15 Å. Moreover, Fig. 2 shows the density profile of the system along the radius from the mass center (average of time after the system reaching equilibrium) and it indicates that the surface layer starts from the position about 10 Å from the systemic mass center. The two figures make it clear that the ends of linear chains floated on the surface layer at most moments, which was also observed in other simulation studies [17,18,20].

3.1.2. The mean square displacement (MSD)

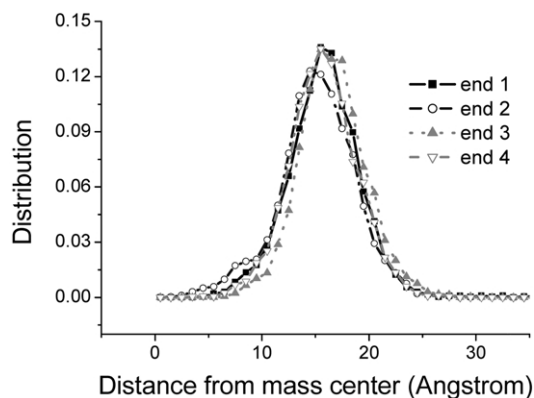The mean square displacement (MSD) is a statistical

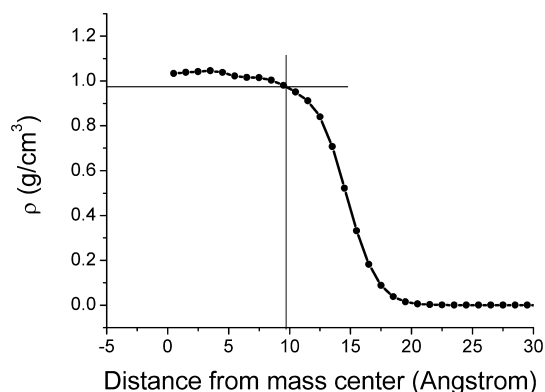Fig. 1. The locational distribution of end groups from the mass center of system along radius.

Fig. 2. The local density profile of linear chains system from the mass center of system along radius.

means to evaluate the mobility of particles, which is defined by

$$g_1(\tau) = \langle |R_i(\tau) - R_i(0)|^2 \rangle \qquad (1)$$

Where τ denotes the correlation time, and R_i stands for the coordinate vector of the ith atom. For MSD is an equilibrium statistical quantity, in this work, the data used to calculate derived from the collective records after 4000 ps, at which moment the merging process has reached the equilibrium. We made an average of MSD measurements for three atoms bond-connected, locating either at the chain end, or at the mid of the linear chains. The other two MSD measurements of all atoms in cyclic chains and that in linear chains were also undertaken. Results from the four measurements are shown in Fig. 3, which shows that the mobility of atoms at chain ends is much larger than that of mid ones in linear chains, and also much larger than the average value of all atoms in both the linear chains and the cyclic chains. The quite similar result was found in a study of Lyulin et al. [21], where MD simulation of bulk polystyrene was performed and showed that at high temperature, the mobility of chain ends was larger than that of the middle groups and of the average of all groups in the chains. It interprets the structural character that the chain ends always float on surface of the system. Since the ends have larger mobility, they thus always search for some place
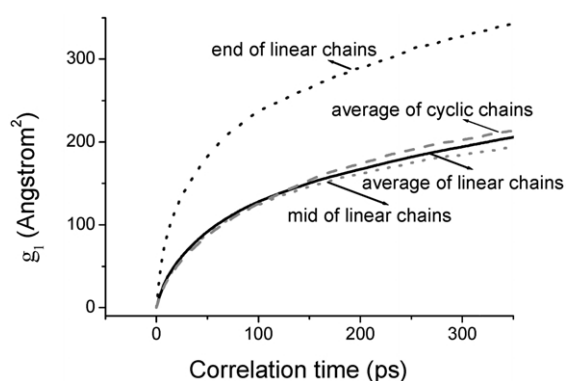
where confinement is less. The surface layer obviously is the most suitable location for the ends. Fig. 3 also shows that although the linear chains have such mobile end groups, the average mobility of all the atoms in linear chains is not very different from that in cyclic chains. It is obvious that contribution of the ends to the mobility of whole linear chains in the system studied is not so significant.

3.2. Structural characters

In this section, the structure characters in the merging processes were investigated by three means—the distance between the mass centers of two chains, the radius of gyration (R_g) of each chain, and the radial distribution function (RDF).

The variations of distance between the mass centers of two chains versus time for linear chains and for cyclic chains were shown in Fig. 4, which describes structure evolution in the merging processes. For both cases, although fluctuating acutely, the mass centers come close to each other evidently until 3500 ps or so. In this stage, more and more segments of two isolated globules touch one another. The two curves coming to overlap each other in this stage indicates that rate of closing up for two cyclic chains does not behave considerably different from that of linear chains. After 3500 ps, the distance between two mass centers fluctuated around 3 Å for cyclic and linear chains, and shows that the system came into a quasi equilibrium. The large fluctuation arises from the high simulation temperature, which makes the segments move more rapidly around ergodically most probable configurations.

The measurement of distance between mass centers roughly indicates the degree of interpenetration between two globules. With an enhancement of segments from different chains touching each other, either chain occupies more space of system, accordingly dimension gains larger changes. The size of each chain was characterized in term of the R_g (radius of gyration), as shown in Fig. 5, where (a) for linear chains and (b) for cyclic chains. One may find that the R_g measured, 12 Å, is different from that in bulk. Usually a 300 CH_2 chain should possess a R_g of ~ 28 Å in bulk. This is

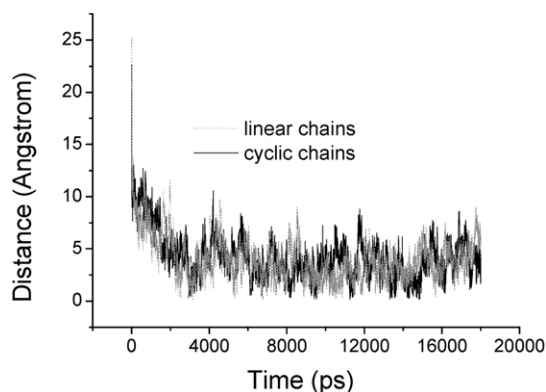Fig. 3. The mean square displacement of different atoms.

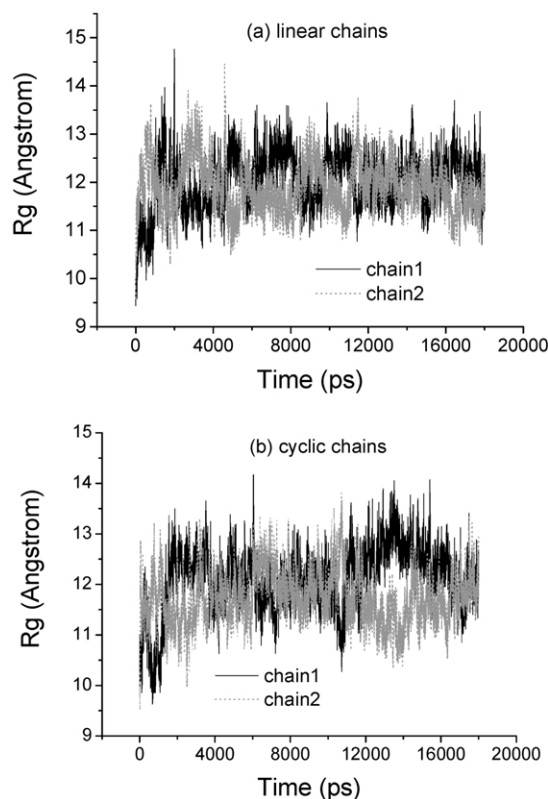Fig. 4. The distance between mass centers of two chains versus time.

Fig. 5. The R_g of each chain variation with time evolution.

because in vacuum or in a poor solvent the surface energy plays great influence and single chain or pauci chains always condense into globule. The average value of R_g of each chain during the dynamic equilibrium (after 4000 ps of the run) was about 12 Å, either for linear chains or cyclic ones. Fig. 5 also says something qualitative that although the R_g fluctuated acutely (as mentioned above, the temperature 600 K speeds up the movement of chain segments) for both cases, the R_g of linear chains varied a little more frequently than that of cyclic ones, which possibly means that the relaxation of the mobile ends leads to the variety of the chain structure a little more easy. But the distinction is not very obvious.

The two evaluation methods above characterize the properties of system in the length scale of chain coil. To investigate the difference of the two cases in more detail, we turn to inter-chain RDF, which is defined as

$$G_{AB}(r) = \frac{N_{AB}(r)}{(N_A N_B - N_{AB})4\pi r^2 dr} \qquad (2)$$

Where N_A, N_B, respectively, stands for the number of atoms in chain 1 and chain 2, N_{AB} denotes the number of atoms common to both chain 1 and 2, and in this study, it equates 0. Inter-chain RDF describes the more microscopic statistical information, the probability distribution of an atom in one chain finding another atom in another chain in various dimensions. When analyzing the variety of inter-chain RDF with the evolution of simulation time, it was

found that the first peak, which was located at about 5 Å for both linear and cyclic chains, growing up with time until around 3500 ps for both cases. In bulk amorphous polymers, segments are densely packed with each other, with the typical inter-chain separation for polyethylene being about 5 Å [22,23]. On this basis, the intensity of the first peak of inter-chain RDF can be used to characterize the extent of neighboring between different chains, i.e. the degree of interpenetration. Fig. 6 shows the intensity of the first peak of inter-chain RDF versus time for both cases. It indicates that until around 3500 ps both for linear and cyclic chains, the balanced plateau is met, which means the systems reaching dynamic equilibrium. It is consistent with the characterization of the distance between two mass centers in Fig. 4, although as mentioned above, they are two means in different length scale. Fig. 6 displays that the variety of linear chains interpenetrating structure is quite close to that of cyclic ones.

In other simulations of bulk system [11–13], the more compact structure for cyclic chains was observed. However, in our study, where chains were confined in small space under the influence of the surface energy, the two cases (cyclic and linear chains) displayed the same equilibrium microscopic structure character, which supports Taylor et al. prediction [24] that a cyclic chain in collapsed state becomes nearly identical to linear one.

3.3. Dynamic properties

The analysis of structure characterization indicates little difference for linear chains and cyclic chains in the penetration processes. To compare the dynamic properties in two cases, we monitored two kinds of time correlation functions from data collected after 4000 ps. One is for the mean square radial displacement of the chain segments from
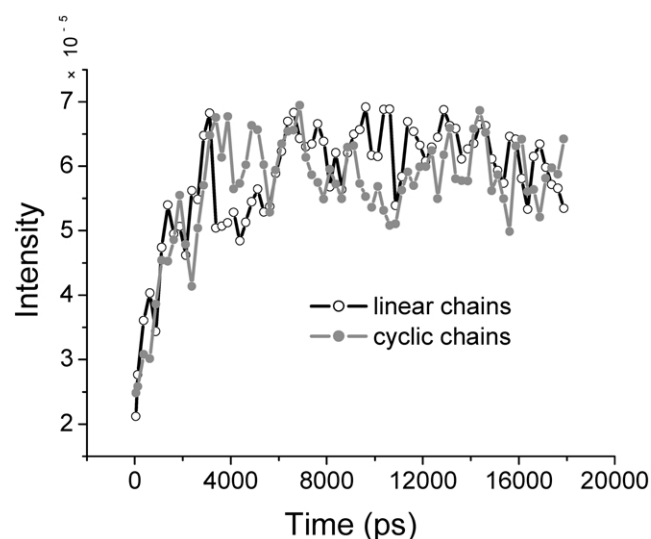

Fig. 6. The first peak intensity of inter-chain radius distribution function versus time.

the center-of-mass, and the other is for the orientation dynamics of local chain segments. The former, which had been used in many other studies [10,12,13], illuminates the statistic motive behavior of the segments in chain toward the mass center. It is defined as follows

$$g_2(\tau) = \langle |R_i(\tau) - R_c(\tau) - R_i(0) + R_c(0)|^2 \rangle / 2 \qquad (3)$$

where R_c denotes the coordinate vector of the mass center of the chain. The results are presented in Fig. 7. Before about 120 ps (correlation time), the linear chain data seem a little larger than the cyclic ones, but the distinction is negligible, and after 120 ps, the two curves almost superpose, which means that the motion of monomers toward the chain mass center in cyclic chains is very similar to that of their linear counterparts, i.e. the diffusion behaviors for both cases are similar. This is a different feature from those in bulk system.

The measurement of the mean square radial displacement interested us to consider whether the mobility of the local chain segments for cyclic chains is also similar with that for linear ones, therefore, we calculated the orientation dynamics of local chain segments, specifically, the time correlation function for arbitrary unit vector u defined by

$$M(\tau) = \langle u(\tau) \cdot u(0) \rangle \qquad (4)$$

with u standing for three kinds of unit vectors a, b and c (see Fig. 8) embedded in the polymer backbone. The a, b, c are defined for segments by

$$a_i = (l_i + l_{i+1}) / |l_i + l_{i+1}| \qquad (5)$$

$$b_i = l_i \times l_{i+1} / |l_i \times l_{i+1}| \qquad (6)$$

$$c_i = a_i \times b_i / |a_i \times b_i| \qquad (7)$$

where l_i or l_{i+1} are the vectors along the ith or the $i + 1$th bond. Vector a, 'chain axis' vector, is a good indicator of the direction of the polymer backbone. This method had been used by Takaucki et al. [25] and in their work, the local chain motion in bulk amorphous polymers was investigated by MD simulation, the result showed a strong dependence of the relaxation on the direction of the vector on a longer time scale, and the surrounding chains acts as a rigid 'pipe'
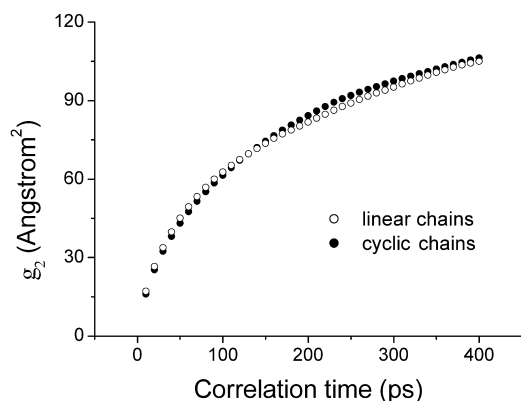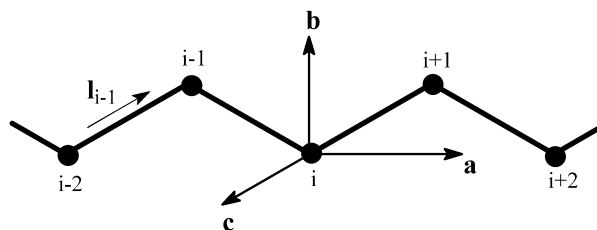

Fig. 8. The definition of unit vectors a, b and c embedded in the polymer backbone.

constraining the relaxation of the chain axis (vector a). In the present work, the globule of the two combined chains is not the same as the bulk amorphous polymer, but the similar motional behavior of local chain segments was observed. As shown in Fig. 9, the chain axis (vector a) itself slowly changes its direction according to the relaxation of the local structure, while in the perpendicular directions (vectors b and c), the relaxation of the local chain is very rapid. Just as mentioned by Takaucki [25], the orientation of the chains observed should be distinguished from the concept of the tube in the reptation model [1], in which the time scale and the spatial scale for the motion being considered are all much greater than that in the motion being evaluated here. Comparing the measurements of the linear chains and the cyclic ones, the little distinction shows that through the window here: the local chain motions for these two cases are nearly identical.

From the analysis above, it can be seen that not only in structure but also in dynamics the two processes display similarly. This is different from the observation that cyclic chains diffuse faster than their linear counterparts in bulk [11–13]. We think that in the confined system, the compact globule consisting of only a few chains, the surface energy plays a more important role. As a result, the ends of linear chains always float on the surface layer, thus appear no more significant to lead the inter-penetration process as well as in bulk amorphous polymer systems. Consequently, almost the same motion behaviors were observed for linear and cyclic system. These simulations would be significant for understanding the film forming process from polymer particles
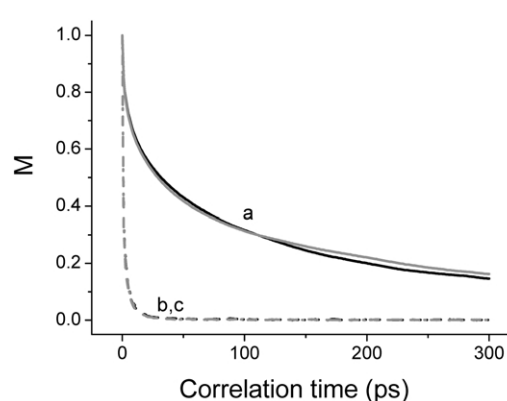

Fig. 7. The mean square displacement of monomers in the center of mass frame of chain.

Fig. 9. The time correlation function of unit vector a, b and c. Light gray: linear chains; black: cyclic chains.

and the aggregating process of polymer chains in dilute poor solution, as well as other relative phenomena.

4. Conclusions

We have performed the MD simulations of merging process of two isolated cyclic chains and that of linear chains, each of which containing 300 CH_2 (united atoms), in order to find the difference between the two kinds of chains in bulk and in the confined space. The analysis of the end-group location indicates that at most moments, the ends float on the surface layer, and their mobility is much larger than the mean value of all atoms in linear chains, or that in cyclic chains. Comparison of the merging processes of cyclic chains and their linear counterparts was intensively carried out by several means of analyzing the trajectory files in structure and in dynamics. No significant distinction was observed in all the analyses, and the segments of cyclic chains showed almost the same behavior of motion with that of linear chains. This is different diffusion behavior from that in bulk systems [11–13]. This modeling therefore indicates that in these confined systems the end groups always move on the surface under the great influence of surface energy, and lost the capacity of leading chain reptation through the other polymer chains, which is possibly the origin that the difference of diffusion behavior between the linear chain and the cyclic chain shown in the bulk almost disappears in the case of the confinement.

Acknowledgements

References

[1] de Gennes PG, Scaling concepts in polymer physics, Ithaca: Cornell University Press; 1979.
[2] Doi M, Edwards SF. The theory of polymer dynamics. Oxford: Clarendon Press; 1986.
[3] Dogson K, Higgins J. In: Semlyen JA, editor. In cyclic polymers. London: Elsevier; 1986.
[4] Roovers J. Macromolecules 1985;18:1359.
[5] Mckenna GB, Hostetter BJ, Hadjichristidis N, Fetters LJ, Plazek DJ. Macromolecules 1989;22:1834.
[6] Ttead SF, Kramer EJ, Hadziioannou G, Antonietti M, Sillescu H, Lutz P, Strazielle C. Macromolecules 1992;25:3942.
[7] Cosgrove T, Griffiths PC, Hollingshurst J, Richards RDC, Semlyen JA. Macromolecules 1992;25:6761.
[8] Orrah DJ, Semlyen JA, Ross-Murphy SB. Polymer 1988;29:1452.
[9] Orrah DJ, Semlyen JA, Ross-Murphy SB. Polymer 1988;29:1455.
[10] Muller M, Wittmer JP, Cates ME. Phys Rev E 1996;53:5063.
[11] Brown S, Szamel G. J Chem Phys 1998;108:4705.
[12] Brown S, Szamel G. J Chem Phys 1998;109:6184.
[13] Ozisik R, von Meerwall ED, Mattice WL. Polymer 2002;43:629.
[14] Liang T, Zhang Z, Li T, Yang X. Polymer 2004;45:1365.
[15] Sundararajan PR, Kavassalis TA. Macromolecules 1997;30:5172.
[16] Yang X, Qian R. Macromol Theory Simul 1996;5:75.
[17] Chang J, Han J, Yang L, Jaffe RL, Yoon Do Y. J Chem Phys 2001; 115:2831.
[18] Xia TK, Landman U. J Chem Phys 1994;101:2498.
[19] Mayo SL, Olafson BD, Goddard WA. J Phys Chem 1990;94:8897.
[20] Harris JG. J Phys Chem 1992;96:5077.
[21] Lyulin AV, Michels MAJ. Macromolecules 2002;35:1463.
[22] Rigby D, Reo RJ. J Chem Phys 1988;89:5280.
[23] Takeuchi H. J Chem Phys 1990;93:4490.
[24] Taylor MP, Mar JL, Lipson JEG. J Chem Phys 1998;109:6184.
[25] Takeuchi H, Reo R. J Chem Phys 1991;94:7446.