

A STEERED MOLECULAR DYNAMICS SIMULATION ON THE ELASTIC BEHAVIOR OF ADSORBED STAR POLYMER CHAINS*

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Abstract Elastic behavior of 4-branched star polymer chain with different chain length N adsorbed on attractive surface is investigated using steered molecular dynamics (SMD) simulation method based on the united-atom (UA) model for branched alkanes. The simulation is realized by pulling up the chain *via* a linear spring with a constant velocity $v = 0.005$ nm/ps. At the beginning, the chain lies extensionally on adsorbed surface and suffers continuous deformations during the tensile process. Statistical parameters as mean-square radii of gyration $\langle S^2 \rangle_{xy}$, $\langle S^2 \rangle_z$, shape factor $\langle \delta \rangle$, describing the conformational changes, sectional density $\langle \text{den} \rangle$ which gives the states of the chain, and average surface attractive energy $\langle U_a \rangle$, average total energy $\langle U \rangle$, average force $\langle f \rangle$ probed by the spring, which characterize the thermodynamic properties, are calculated in the stimulant process. Remarkably, distinguishing from the case in linear chains that there only exists one long plateau in the curve of $\langle f \rangle$, the force plateau in our study for star chains is multiple, denoting different steps of desorption, and this agrees well with the experimental results in essence. We find during the tensile process, there are three characteristic distances Z_c , Z_t and Z_0 from the attractive surface, and these values vary with N . When $Z = Z_c$, the chain is stripped from the surface, but due to the form of wall-monomer interaction, the surface retains weak influence on the chain till $Z = Z_c$. From $Z = Z_t$, parameters $\langle U_a \rangle$, $\langle U \rangle$ and $\langle f \rangle$ respectively reach a stable value, while the shape and the size of the chain still need adjustments after Z_t till Z_0 to reach their equilibrium states. Specifically, for short chain of $N = 41$, Z_t and Z_0 are incorporated. These results may help us to deepen the knowledge about the elastic behavior of adsorbed star polymer chains.

Keywords: Steered molecular dynamics; Elastic behavior; Star polymer chain.

INTRODUCTION

In the recent past, various features or behaviors of star-shaped polymers such as the conformations, the aggregates and the equilibrium/non-equilibrium phase behaviors have been widely investigated, both experimentally^[1–15] and theoretically^[16–45]. The reason for this is threefold. First, from a technical point of view, star polymers are important for several industrial applications^[1]. One example is hydrogenated polyisoprene star polymers, which are used as viscosity index modifiers in oil industry applications due to their excellent shear stability. Further, commercial star polymers are brought into action in coating materials, as binders in toners for copying machines, and in several pharmaceutical and medical applications^[1]. Second, from an experimental point of view, the recent synthesis by Roovers and co-workers^[2, 3] of regular star polymers with various possible numbers of arms made it possible to explore the physics of well-defined model systems, which are monodisperse in both the number of arms and the degree of polymerization. Important examples are polyisoprene stars with arm number $F = 8$, and 18^[4] and polybutadiene stars with $F = 32$, 64 and 128^[3], both synthesized by anionic polymerization. Third, star polymers constitute an important soft-condensed matter system, linking the fields of

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polymer physics and colloid physics, thus also attracting interest from a purely theoretical point of view. Star polymers with small arm numbers ($F=1$ and 2) resemble linear polymers. Thus their configurations show a considerable asphericity^[16–18], although their chain-averaged number density of monomers, $\phi(r)$, is spherically symmetric around the center of mass of the polymer. With increasing arm number F , the asphericity of the stars has been shown to decrease considerably^[19–27], leading to “stiff” spherical particles in the limit of high F . It is essentially in this limit that a description of star polymers as sterically stabilized colloidal particles holds.

Many phenomena or processes in physics, chemistry, biology and material science, such as colloidal dispersions^[46], polymer adhesive^[47], biocompatibility^[48], protein molecules on solid interfaces^[49–52] and chromatographic separation^[53], are related to the adsorption of a polymer chain on a surface. Then studies on the adsorption of a polymer are necessary. The structure and adsorption behavior of a linear polymer chain has been well studied^[54–61]. However, the behavior of star polymer chains is a more challenging problem than that of linear polymer chains, and star polymers are hybrids between polymer-like entities and colloidal particles establishing an important link between these different systems. Although there have been many investigations performed in the field of star polymers, simulation studies for elastic dynamics of adsorbed star polymers are scarce. We now focus our attention on this subject, which has relevance to extensive practical applications, for example, it is important in surface adhesion, surface protection, wetting, stabilization of colloids and in numerous biological applications. Additionally, our work is based on steered molecular dynamics (SMD) method and united-atom (UA) model, the motions and the potentials in which make the simulation more realistic. The novel SMD simulation technique usually applies external forces to manipulate biomolecules or polymer chains in order to probe mechanical functions and provides specific atomic-level descriptions for their elastic properties and conformational structures. It links directly to the experiments and has the advantage over the Monte Carlo method that non-equilibrium processes can be studied. The method and the model will be detailedly explained below in the second section.

MODEL AND METHOD

United-atom Model

In our simulation, a united-atom (UA) model^[62, 63] suitable for branched molecules is adopted. The united-atom model combines each carbon and its bonded hydrogen atoms, CH_x , into a single interaction site, called as a monomer in this paper. This reduces the number of interaction sites compared to explicit atom models where all H atoms are included. The advantage of this model with significantly reduced number of degrees of freedom is that longer chains or larger systems can be explored within the computational limit. In the past 20 years, the united-atom model has been optimized constantly and used with alternative form in both Monte Carlo simulation^[64, 65] and molecular dynamics simulation^[66–69]. The united-atom model introduced in this paper is fit for branched molecules.

In this model, total potential V_{tot} consists of five parts, respectively defined as below:

The dispersion forces between all pairs of monomers are most commonly modeled using the Lennard-Jones (LJ) pair potential,

$$V(r_{ij}) = 4\varepsilon_{ij} \left[\left(\frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^6 \right] \quad (1)$$

where r_{ij} , ε_{ij} and σ_{ij} are the separation, LJ well depth and LJ size, respectively, for the pair of monomers i and j . The LJ parameters for interactions between different monomers are listed in Table 1. Unlike interactions are computed using standard Lorentz-Berthelot combining rules:

$$\sigma_{ij} = \frac{1}{2}(\sigma_{ii} + \sigma_{jj})$$

$$\varepsilon_{ij} = \sqrt{\varepsilon_{ii}\varepsilon_{jj}}$$

For intra-molecular pairs the LJ potential is only applied if they are further than three covalent bonds apart.

Table 1. Interaction parameters for all CH_x groups^[62]

	van der Waals		Angle triplet		Dihedral quadruplet (kJ/mol)			
	ε	σ (nm)	θ_0	k_{bend}	a_0	a_1	a_2	a_3
C	0.0041	0.640						
CH	0.0828	0.468						
CH ₂	0.3814	0.395						
CH ₃	0.8130	0.373						
CH _x —C—CH _y			109.47	517.52				
CH _x —CH—CH _y			112.00	517.52				
CH _x —CH ₂ —CH _y			114.00	517.52				
CH _x —C—CH ₂ —CH _y					3.8262	11.4785	0	−15.3047
CH _x —CH—CH ₂ —CH _y					3.2783	7.4242	1.8555	−14.6404
CH _x —CH ₂ —CH ₂ —CH _y					8.3933	16.7782	1.1333	−26.3048

Covalent bonds between nearest neighbor carbons are modeled by a simple harmonic potential around a finite average distance l_0 ,

$$V_{\text{bond}}(r) = \frac{1}{2} k_{\text{bond}} (r - l_0)^2 \quad (2)$$

The constant k_{bond} is set to the experimental value 3.76×10^5 kJ/(mol·nm²) and the bond length $l_0 = 0.154$ nm regardless of the number of hydrogens bound to a particular carbon.

To respect the angular geometry of nearest- and next-to-nearest neighbor carbons a harmonic bending potential between three neighboring sites is introduced:

$$V_{\text{bend}}(\theta) = \frac{1}{2} k_{\text{bend}} (\theta - \theta_0)^2 \quad (3)$$

The elasticity parameters k_{bond} and the equilibrium angles θ_0 for the various neighbor triplets are listed in Table 1.

Furthermore to incorporate the effect of transitional potential barriers between anti and gauche conformations and different population densities of these states, a rotational potential for the dihedral angle Φ between nearest neighbor chain-like quadruplets a, b, c, d is introduced.

$$V_{\text{rot}}(\Phi) = \sum_{i=0}^3 a_i \cos^i(\Phi) \quad (4)$$

Table 1 contains the parameters a_i for the various quadruplet combinations of sites. The dihedral angle Φ is defined as the angle of neighboring vectors $(\vec{c} - \vec{b}) \times (\vec{b} - \vec{a})$ and $(\vec{d} - \vec{c}) \times (\vec{c} - \vec{b})$, related to three neighboring bonds $(\vec{b} - \vec{a})$, $(\vec{c} - \vec{b})$ and $(\vec{d} - \vec{c})$.

$$\cos(\Phi) = \left(\frac{(\vec{c} - \vec{b}) \times (\vec{b} - \vec{a})}{\|(\vec{c} - \vec{b}) \times (\vec{b} - \vec{a})\|} \right) \cdot \left(\frac{(\vec{d} - \vec{c}) \times (\vec{c} - \vec{b})}{\|(\vec{d} - \vec{c}) \times (\vec{c} - \vec{b})\|} \right) \quad (5)$$

The adsorption of the surface is realized with a 9-3 LJ potential between each monomer and the surface, which is defined as^[70]:

$$V_{\text{surface}}(z) = w \left[\left(\frac{z_w}{z} \right)^9 - \left(\frac{z_w}{z} \right)^3 \right] \quad (6)$$

here z_w is set to 0.45 nm, and z represents the perpendicular distance from the surface, and w is a parameter of adsorptivity. For the star chains studied here, we take a strong adsorptive parameter of $w = 25.0$ kJ/mol.

Molecular Dynamics Method

SMD method has been successfully presented before in our work^[71, 72]. A schematic illustration of using SMD

method to pull an adsorbed star chain of total monomers $N = F \cdot n + 1$ away from the surface is shown in Fig. 1. In the schematic plan, $F = 4$ is the number of branches, and n is the number of monomers in every branch. To perform our simulation, monomers in the star chain should be numbered clearly, and here we number the center monomer of the star as 0 and monomers in four branches as $1-n$, $(n+1)-2n$, $(2n+1)-3n$ and $(3n+1)-4n$, respectively. An ideal linear spring (force probe) is attached to one branched end (*i.e.*, n) of the chain. Star chains will undergo more complicated process of tension than their linear counterparts. The stiffness of the spring is $k_0 = 945$ pN/nm, and the force in the spring is given by Hook's law, *i.e.*, $f = k_0(z_a - z_b)$, where z_a and z_b are the perpendicular displacements of the two end points of the spring, respectively. The perpendicular distance between the end of the chain attached to the spring and the surface is denoted by z . In the molecular dynamics simulation, the positions and velocities of each monomer in the polyethylene chain are determined by solving the Newton's equation:

$$m_i \frac{d^2 \vec{r}_i}{dt^2} = \vec{F}_i = -\nabla_i V + \begin{cases} \vec{f} & i = n \\ 0 & i \neq n \end{cases} \quad (7)$$

where m_i , $\vec{r}_i$ and $\vec{F}_i$ respectively denotes the mass of monomer i , the position vector of monomer i , and the force on monomer i . V denotes the total potential as discussed above, and $\vec{f}$ is a force acted by the spring to one branched end of the chain. In the meantime, Beeman's algorithm^[73] is used to update the positions and the velocities,

$$\vec{r}_i(t + \Delta t) = \vec{r}_i(t) + \vec{v}_i(t)\Delta t + \frac{4\vec{F}_i(t) - \vec{F}_i(t - \Delta t)}{6m} \Delta t^2 \quad (8)$$

and

$$\vec{v}_i(t + \Delta t) = \vec{v}_i(t) + \frac{2\vec{F}_i(t + \Delta t) + 5\vec{F}_i(t) - \vec{F}_i(t - \Delta t)}{6m} \Delta t \quad (9)$$

where $\vec{v}_i$ denotes the velocity of monomer i and Δt denotes the time step. In this work, the time step is 1 fs. In order to keep the temperature constant, the velocities of all monomers are scaled by a factor

$$\lambda = (1 + \frac{\Delta t}{t_T} (\frac{T}{T_c} - 1))^{\frac{1}{2}} \quad (10)$$

where T_c is the current kinetic temperature; T denotes the desired temperature; t_T is a preset time constant. Berendsen^[74] have found that a suitable relaxation time is $t_T = 0.4$ ps. In this work, the system temperature is fixed at $T = 280$ K.

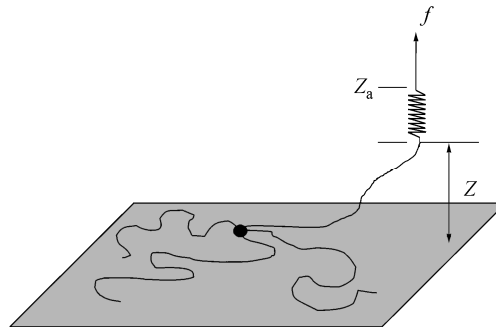


Fig. 1 A schematic illustration of using SMD method to pull an adsorbed star chain away from the surface

To begin, we randomly spread a star chain on the surface. In order to reach thermal equilibrium, 1×10^7 molecular dynamics (MD) steps are implemented first in the vacuum. Then the chain is pulled up gradually *via* the linear spring and full MD data are recorded. To obtain the exact statistical results, we repeat the above

process 1000 times with different initial configurations.

RESULTS AND DISCUSSION

Here we discuss the results for pulling a single 4-branched star polymer chain of different chain lengths away from an attractive surface with a constant velocity of $v = 0.005$ nm/ps. The velocity employed in this work is about 2 orders of magnitude lower than the velocity generally used in reported SMD simulations. Some statistical properties such as the size, the shape, the sectional density and thermodynamic properties of the chain are calculated during the elongation process.

Chain Size and Shape

The size and the shape of polymer chains can be described by mean-square radii of gyration $\langle S^2 \rangle_{xy} (\times 10^{-2} \text{ nm}^2)$, $\langle S^2 \rangle_z (\times 10^{-2} \text{ nm}^2)$ and the shape factor $\langle \delta \rangle$.

Some conformational properties of the star chain can be presented by the calculation of mean-square radius of gyration $\langle S^2 \rangle$, parallel and perpendicular mean square radii of gyration $\langle S^2 \rangle_{xy}$ and $\langle S^2 \rangle_z$, which are defined as:

$$\langle S^2 \rangle_{xy} = \langle \frac{1}{N+1} \sum_{i=0}^N (x_i - x_{c.m.})^2 + (y_i - y_{c.m.})^2 \rangle \quad (11)$$

$$\langle S^2 \rangle_z = \langle \frac{1}{N+1} \sum_{i=0}^N (z_i - z_{c.m.})^2 \rangle \quad (12)$$

$$\langle S^2 \rangle = \langle S^2 \rangle_{xy} + \langle S^2 \rangle_z \quad (13)$$

where (x_i, y_i, z_i) is the coordinate of the i -th monomer in a chain and $(x_{c.m.}, y_{c.m.}, z_{c.m.})$ is the position of the mass center of a chain. The angular brackets $\langle \rangle$ denotes thermodynamic average. We plot mean-square radii of gyration per monomer $\langle S^2 \rangle_{xy}/N$ and $\langle S^2 \rangle_z/N$ as a function of Z in Figs. 2 and 3 for star polymer chains with total monomers $N = F \cdot n + 1 = 41, 81$ and 121 , respectively. Dividing by N is for the comparability among the chains with different chain length. In this paper, four-arm ($F = 4$) chains with different n are considered. Horizontal ordinate Z is defined as:

$$Z = \frac{z}{N} \quad (14)$$

where $z (\times 10^{-1} \text{ nm})$ is the perpendicular distance between one branched end of the star chain attached to the spring and the surface. While z increases, Z also increases at the same time, and then the chains with different length N can easily be compared in the process of elongation. Without force applied, the chain is adsorbed on the surface completely, and so $\langle S^2 \rangle_{xy}/N$ for all chains with different chain length has the maximum value, while $\langle S^2 \rangle_z/N$ approaches 0 in this case. As Z increases, for $N = 41$, $\langle S^2 \rangle_{xy}/N$ first decreases to a minimal value occurring at a characteristic distance $Z_c = 0.71$, and then increases again till a stable value at $Z_0 = 0.95$. Associated with the analysis of other parameters which will be discussed below in detail, we can conclude that $Z_c = 0.71$ is the stripped point for the chain with $N = 41$. On the other hand, $\langle S^2 \rangle_z/N$ in Fig. 3 shows the opposite behavior that first increases to a maximal value occurring at about $Z_c = 0.71$, and then decreases again till a stable value. For $N = 81$ and 121 , the change of $\langle S^2 \rangle_{xy}/N$ as Z increases seems more challenging that there exists another extreme point at $Z_t = 0.8$ and 0.75 between Z_c and Z_0 for $N = 81$ and 121 respectively. Characteristic values for $N = 81$ and 121 are $Z_c = 0.68$, $Z_0 = 1.24$ and $Z_c = 0.66$, $Z_0 = 1.1$. Within allowable deviation, similar behavior could be found between chains with $N = 81$ and 121 , while the chain with $N = 41$ has some short chain effect. The significance represented by Z_c , Z_t and Z_0 can be revealed from the following analysis. In these figures, we take $N = 81$ for example to mark out Z_c , Z_t and Z_0 . The behavior of $\langle S^2 \rangle_z/N$ for $N = 81$ and 121 is similar to the case for $N = 41$ that drops rapidly after Z_c to a stable value, indicating that the chain folds rapidly due to its inherent restoring force after stripping from the surface. For a certain chain, we can see that stable

values approximately fit a relationship of $\langle S^2 \rangle_z \approx \langle S^2 \rangle_{xy}/2$, and account for the dimension of the star polymer chain without any adsorption.

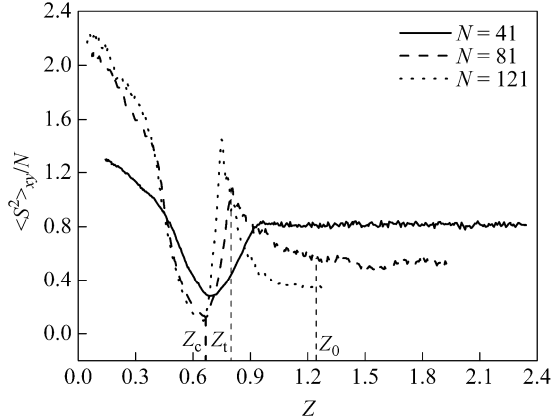


Fig. 2 Parallel mean-square radius of gyration per monomer $\langle S^2 \rangle_{xy}/N$ as a function of Z for 41-monomer, 81-monomer, and 121-monomer star molecular chains with 4 arms
The pulling velocity is $v = 0.005$ nm/ps.

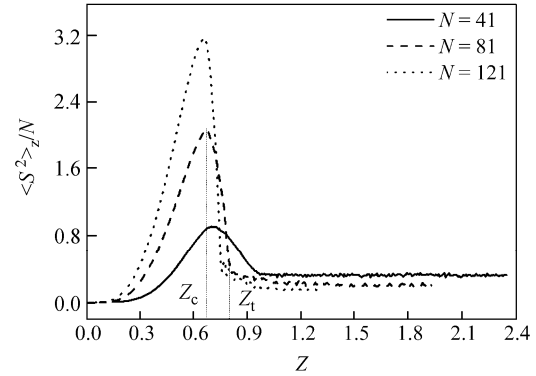


Fig. 3 Perpendicular mean-square radius of gyration per monomer $\langle S^2 \rangle_z/N$ as a function of Z for 41-monomer, 81-monomer, and 121-monomer star molecular chains with 4 arms
The pulling velocity is $v = 0.005$ nm/ps.

In order to investigate the shape of a star polymer chain, we consider the radius of gyration tensor S , which is defined as:

$$S = \frac{1}{n \cdot F + 1} \sum_{i=0}^{n \cdot f} S_i S_i^T = \begin{pmatrix} S_{xx} & S_{xy} & S_{xz} \\ S_{yx} & S_{yy} & S_{yz} \\ S_{zx} & S_{zy} & S_{zz} \end{pmatrix} \quad (15)$$

where $S_i = \text{col}(x_i, y_i, z_i)$ denotes the position of monomer i in a frame of reference with its origin at the center of mass. The tensor S can be diagonalized with three eigenvalues of L_1^2 , L_2^2 , and L_3^2 ($L_1^2 \leq L_2^2 \leq L_3^2$). Solc and Stockmayer^[16, 17] first studied the ratio of the parameters $\langle L_1^2 \rangle : \langle L_2^2 \rangle : \langle L_3^2 \rangle$ to characterize the shape of a flexible polymer chain in their Monte Carlo simulation and obtained the ratio of 1:2.7:11.7 based on a random walk of 100 bonds in a simple cubic lattice. According to the three eigenvalues for the tensor S , a new parameter^[75, 76] characteristic of the shape of chains may be obtained by combining the reduced components of S^2 to a single quantity that varies between 0 and 1:

$$\langle \delta \rangle = 1 - 3 \left\langle \frac{L_1^2 L_2^2 + L_2^2 L_3^2 + L_1^2 L_3^2}{(L_1^2 + L_2^2 + L_3^2)^2} \right\rangle \quad (16)$$

when $\langle \delta \rangle = 0$, 0.5 or 1, the shape of the chain corresponds to a sphere, a prolate spheroid or a rod, respectively. In Fig. 4, $\langle \delta \rangle$ of chains with different N behaves similarly with Z that first decreases to a minimum value and then turns to increase to a maximum value at the characteristic distance Z_c . Z_c for $N = 41$, 81 and 121 equals 0.71, 0.68 and 0.66 respectively, which is consistent with the case in Figs. 2 and 3. When $Z > Z_c$, $\langle \delta \rangle$ decreases again and then becomes a constant value $\langle \delta \rangle = 0.25$ beginning from $Z_0 = 0.91$, $\langle \delta \rangle = 0.23$ beginning from about $Z_0 = 1.24$ and $\langle \delta \rangle = 0.10$ beginning from $Z_0 = 1.1$ for $N = 41$, 81 and 121 respectively. From the statistical data, we find that values of $\langle \delta \rangle$ increase with the increase of N before the chain is divorced from the attractive surface, while constant $\langle \delta \rangle$ unaffected by the surface has the contrary sequencing with N . This information is interesting and useful. At the beginning, the chain lies on the surface, and its shape is elongated due to the strong attractive interactions between the chains and the surface. When the star chain begins to be pulled away from the surface, space allows the chain to fold itself, and then a sphere is formed. In the plots, one phenomenon is

noticeable that for short chain of $N = 41$, $\langle\delta\rangle$ at this state is even smaller than constant $\langle\delta\rangle$ at the final stage. The reason may be that the combined action of surface potential and intrachain potential at this state enables short chains such as $N = 41$ to fold more tightly. With Z increasing again, the sphere is elongated and a prolate shape along z direction is formed at $Z = Z_c$. After $Z = Z_c$, the chain begins to be divorced from the surface and folds itself to form a sphere unaffected by the surface at $Z = Z_0$. $\langle\delta\rangle$ of star chains is generally smaller than that of linear chains^[77], which shows the fact that star polymers are more globular than linear ones.

Sectional Density

Parameter $\langle\text{den}\rangle$ denotes the average density of monomers per layer above the attractive surface and can exhibit the particle distribution with its changes during the tensile process. Take $N = 41$ for example, and the results are plotted in Fig. 5. Here horizontal ordinate z is the perpendicular distance between one branched end of the star chain attached to the spring and the surface. In the early stage, the chain is still strongly adsorbed by the surface, so most of the monomers centralize between $z = 0.55$ nm and 0.75 nm, with insignificant response to pulling. Curves are similar to δ function, and the peak descends slightly with pulling in this stage. Further pulling will lead the chain to be desorbed gradually, and at $t = 900$ ps and 1800 ps, the chain has been unaffected by the surface completely, so symmetrical distribution of $\langle\text{den}\rangle$ mainly depends on intrachain potentials. As a matter of fact, we can summarize from both above and below analysis that for the chain with $N = 41$, $z_c = 2.9$ nm ($z_c = Z_c \times N$), namely $t = 600$ ps is the stripped point, while $z_0 = 3.9$ nm, namely $t = 672$ ps is the just point after which the chain begins to be free of the surface completely. Therefore, at $t = 600$ ps, the surface still exists some effect on the chain so that in Fig. 5 the left dimension under the curve of $\langle\text{den}\rangle$ with $t = 600$ ps is larger than the right counterpart.

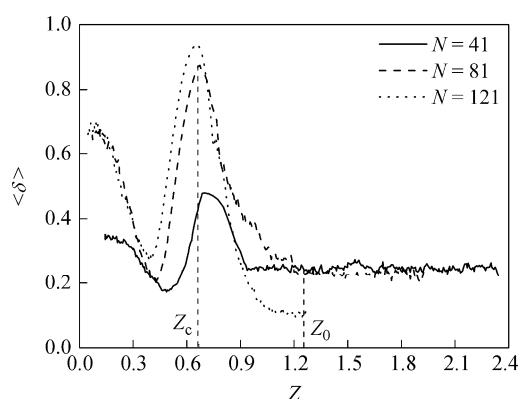


Fig. 4 The shape factor $\langle\delta\rangle$ as a function of Z for 41-monomer, 81-monomer, and 121-monomer star molecular chains with 4 arms. The pulling velocity is $v = 0.005$ nm/ps.

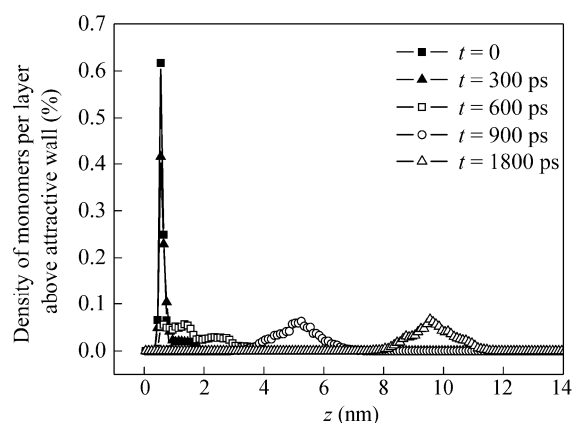


Fig. 5 Density distribution of monomers during the tensile process for a 41-monomer star molecular chain. The pulling velocity is $v = 0.005$ nm/ps.

Thermodynamic Properties

The merit of SMD is that the force can be measured directly during the pulling process, and the linear spring acted on the chain is similar to the probe in AFM or SMFS. Single-molecule force spectroscopy (SMFS), based on atomic force microscopy (AFM), has become a versatile platform for investigating intermolecular and intramolecular interactions^[78–84]. Here, our results of the force obtained by the spring agrees well in essence with the experiment of the adhesion force between PDDA chain and the surface using SMFS^[84]. However, the object in our simulation is star polymer chains with four branches, so the force plateau is multiple, which can be seen from Fig. 6 visually. $N = 41$, 81 and 121 are considered. In the cases of $N = 81$ and 121, $\langle f \rangle/N$ first increases abruptly and keeps a plateau of constant force around 3 pN for $N = 81$ till about $Z = 0.3$ and 2 pN for $N = 121$ till $Z = 0.3$, when one branch of the star chains is pulled away from the surface; then $\langle f \rangle/N$ increases abruptly again and achieve a second plateau of constant force around 9 pN for $N = 81$ and 6 pN for $N = 121$ till Z_c . So Z_c is the stripped point. For certain N , the value of the second plateau is approximate three times that of the first

one, indicating the coinstantaneous pulling of the other three branches. When $Z > Z_c$, $\langle f \rangle/N$ decreases and then becomes zero at $Z_t = 0.8$ for $N = 81$ and $Z_t = 0.75$ for $N = 121$ as the chain leaves the surface completely. The force plateau indicates the role of the surface adsorption during the elongation process. However, the case of short chain with $N = 41$ is some specific. In the plot of $\langle f \rangle/N$ - Z for $N = 41$, there exist three plateaus and the second one is extra compared with the cases of $N = 81$ and 121 , the cause of which can be explained associated with the phenomenon occurred in shape factor $\langle \delta \rangle$ in Fig. 4. In the tensile process, molecular chains are stretched not only in contour, but also in bond length and bond angle.

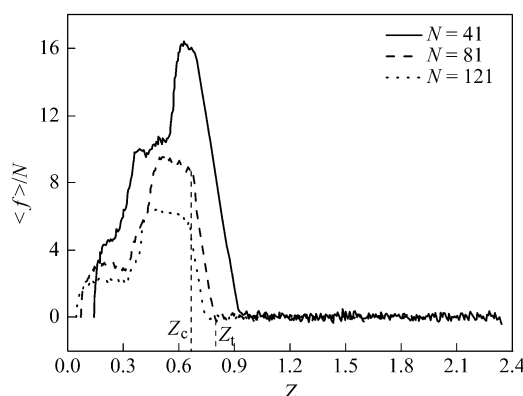


Fig. 6 Average force probed by the spring $\langle f \rangle/N$ as a function of Z for 41-monomer, 81-monomer, and 121-monomer star molecular chains with 4 arms
The pulling velocity is $v = 0.005$ nm/ps.

Thermodynamic properties are also characterized by the average attractive energy $\langle U_a \rangle$ (kJ/mol) and the average total energy $\langle U \rangle$ (kJ/mol). Plots of $\langle U_a \rangle/N$ and $\langle U \rangle/N$ as a function of Z are presented in Fig. 7 and Fig. 8. In Fig. 7, $\langle U_a \rangle/N$ increases steadily from negative values to zero as Z increases, monitoring the status of adsorption. Different slope coefficients of the ascending curve denote the different steps of desorption. $\langle U_a \rangle$ is about 104.5 kJ/mol almost independent of N at the stripped point Z_c , and this means although the star polymer chain is stripped from the attractive surface at this point, the surface retains weak influence on the chain due to the form of wall-monomer interaction. When $Z = Z_t$, $\langle U_a \rangle$ becomes 0 and the chain is unaffected by the surface completely at this point. By now, the significance of Z_c and Z_t is distinct. Moreover, the shape and the size of the chain still need adjustments after Z_t till Z_0 , which can be seen in Figs. 2, 3 and 4. While for short chain of $N = 41$, Z_t and Z_0 is incorporated.

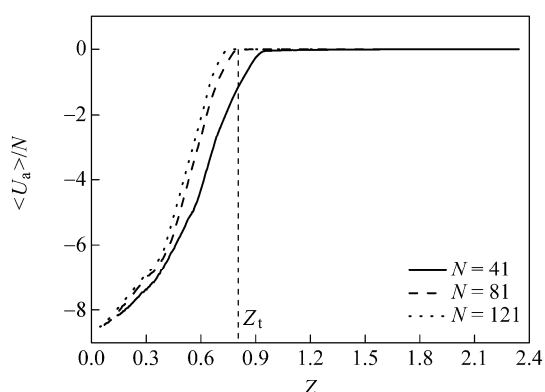


Fig. 7 Average attractive energy $\langle U_a \rangle/N$ as a function of Z for 41-monomer, 81-monomer, and 121-monomer star molecular chains with 4 arms
The pulling velocity is $v = 0.005$ nm/ps.

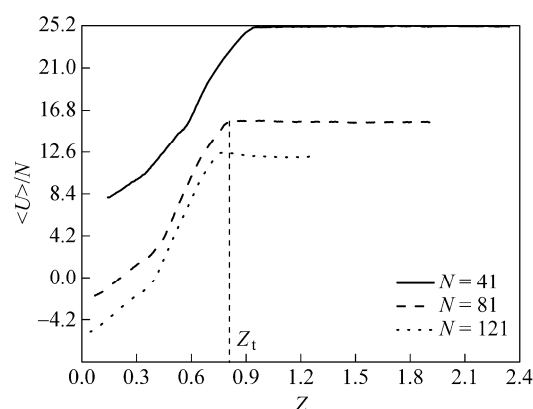


Fig. 8 Average total energy $\langle U \rangle/N$ as a function of Z for 41-monomer, 81-monomer, and 121-monomer star molecular chains with 4 arms
The pulling velocity is $v = 0.005$ nm/ps.

On the other hand, the total energy is the sum of the adsorption energy, the kinetic energy of all monomers, the intrachain potential energies related to bond length, bond angle, torsion angle, and non-bonded energy. In Fig. 8, the curve for $\langle U \rangle / N$ has a similar behavior to the curve for $\langle U_a \rangle / N$, reason of which may be that the change of the total energy during the elongation process is mainly contributed from the change of the adsorption energy.

CONCLUSIONS

In this paper, we perform SMD simulation to pull a star polymer chain away from an attractive surface in the vacuum. Different N is considered. Statistical structural parameters such as mean-square radii of gyration and shape factor are calculated. Chain first lies extensionally on adsorbed surface, and when the chain begins to be pulled away from the surface, space allows the chain to fold itself, so a sphere is formed. With Z increasing again, the sphere is elongated and a prolate shape is formed at $Z = Z_c$. After $Z = Z_c$, the chain begins to be divorced from the surface and folds itself to form a sphere unaffected by the attractive surface at $Z = Z_0$. Star polymers are more globular than linear ones. Parameter $\langle \text{den} \rangle$ denotes the average density of monomers per layer above the attractive surface and can exhibit the particle distribution with its changes during the tensile process. Thermodynamic parameters such as Helmholtz free energy A and total energy $\langle U \rangle$ are usually studied. Different slope coefficients in the plots of average total energy $\langle U \rangle / N$ as a function of Z denote different steps of desorption, respectively corresponding to different plateaus in the curve of $\langle f \rangle / N - Z$. This result agrees well with the experimental results in essence. During the tensile process, Z_c , Z_t and Z_0 are three characteristic distances from the attractive surface, and these values vary with N . When $Z = Z_c$, the chain is stripped from the surface, but due to the form of wall-monomer interaction, the surface retains weak influence on the chain till $Z = Z_t$. From $Z = Z_t$, parameters $\langle U_a \rangle$, $\langle U \rangle$ and $\langle f \rangle$ respectively reach a stable value, while the shape and the size of the chain still need adjustments from Z_t till Z_0 to reach their equilibrium states. Specifically, for short chain of $N = 41$, Z_t and Z_0 is concurrent. Some conclusions obtained in our simulation agree well with the available experimental results, while the others may provide some insights into the related processes and further experimental investigations.

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