

THE COLLAPSE OF POLYETHYLENE RINGS ON AN ATTRACTIVE SURFACE*

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Abstract Polymers exhibit extended structures at high temperatures or in good solvents and collapsed configurations at low temperatures or in poor solvents. This fundamental property is crucial to the design of materials, and indeed has been extensively studied in recent years. In this paper, the collapse of polyethylene rings on an attractive surface was investigated by using molecular dynamics simulations. It is found that the collapse of ring chains on the attractive surface is of distinct difference from their free counterparts, where the collapse becomes more continuous and a one-stage instead of two-stage collapse can be identified by the specific heat. Some hairpin-like crystal structures are found at low temperatures, which are induced by the adsorption interaction of polymer-surface. For a given chain length, the results were further compared with those of the adsorbed linear chains. Due to the topological constraint of ring chains, the number of hairpin structures is clearly less than that of the linear chains. These numerical simulations may provide some new insights into the folding of ring polymers under adsorption interactions.

Keywords: Molecule dynamics simulations; Polyethylene rings; Adsorption; Collapse.

INTRODUCTION

The collapse of polymer chains as a fundamental problem in polymer physics has been of considerable interest both for theory^[1–9] and experiment^[10–17] in the past few years due to its applications in many fields. Examples include the folding of proteins, the packing of DNA molecules and the collapse of a polymer gel network as well as the complexation between two polymer chains^[18–22]. The complex phase behavior of an isolated flexible chain has been well established by Zhou *et al.*, where gas-liquid-like, liquid-solid-like and solid-solid-like polymorphic transitions were observed in their computer simulations^[23, 24]. The liquid-solid-like transformation was found to be a first-order-like transition. While in a later experiment, the coil-to-globule (CG) transition of a single synthetic polymer chain was found to be two-stage kinetics^[25]. Actually, it is still difficult to identify the dynamic and thermodynamic details of the CG transition by experiments.

However, through extensive studies by computer simulations, our understanding of the CG transition has been enriched significantly. It is demonstrated that many factors affect the CG transition process, such as polymer stiffness^[26–28], hydrophobic-polar (HP) sequence^[29, 30], confinement^[31] and so on. As the conformation sampling of polymers at low temperatures is difficult to be sufficient due to local minimum in the free energy, some novel sampling approaches are developed, *e.g.*, the Wang-Landau sampling with suitable Monte Carlo trial

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moves^[32]. Meanwhile, some theoretical models are proposed to predict the CG transition temperature^[33].

Although our knowledge about the CG transition has been increased remarkably, unfortunately, most of previous reports have focused on linear chains^[26–33], and the collapse behaviors for polymers with more complex molecular architecture are still poorly understood. It is long known that ring polymers differ from their linear counterparts by the topological constraints which force a ring polymer conformation to stay within the topological state of preparation. In fact, most of the short genomes as well as plasmids are circular, yielding an even stronger constraint for the polymer's shape. To obtain a complete picture for any circular or double-strand DNA^[34–36], it is desirable to understand the shape effect of ring polymers. For example, Alim and Frey presented a detailed study concerning the shape of a single semiflexible polymer ring over a large range of flexibility^[37]. While Su *et al.* showed very different CG transition behaviors of polyethylene rings from their linear counterparts^[38]. This is because the polyethylene chain is a relatively stiff polymer, compared with the flexible square-well and Lennard-Jones chains.

On the other hand, linear polymers can exhibit different thermodynamic properties when they are adsorbed onto a solid surface^[39, 40], yielding to unique collapse behaviors^[41, 42]. Meanwhile, the visual observations of linear polyelectrolytes at solid-liquid interfaces during the CG transitions are also accessible by recent experiments^[43–45]. Previously, we investigated the collapse of polyethylene linear chains on an attractive surface and found some hairpin structures at low temperatures^[46]. As the ring polymers have stronger topological constraints than their linear counterparts, it will be more interesting to consider the collapse of ring polymers adsorbed on surfaces. Herein, we use molecular dynamics (MD) simulations to study the collapse of polyethylene rings adsorbed on an attractive surface, where the final hairpin structures are found to be different from those of the linear ones.

Model and Simulation Details

Similar to our previous work^[38, 46] the united-atom (UA) force field for the polyethylene ring chains is used in the present study, and it regards each CH₂ group as a monomer. The potential between chain monomers contains four parts: the bond-stretching U_{bond} for two adjacent monomers, the bond-bending U_{bend} among three adjacent monomers, the torsion U_{dih} among four adjacent monomers, and the 12-6 Lennard-Jones U_{nonbond} between monomers divided by at least three bonds. The bond-stretching interaction U_{bond} is defined as:

$$U_{\text{bond}} = \sum_{i=2}^n \frac{1}{2} k_s (r_i - r_0)^2 \quad (1)$$

where k_s is the harmonic spring constant, and set as $k_s = 265443$ kJ/(mol nm²). $r_0 = 0.153$ nm is the equilibrium bond length. r_i denotes the bond length between monomers $i-1$ and i . The bond-bending interaction U_{bend} is given by:

$$U_{\text{bend}} = \sum_{i=3}^n \frac{1}{2} k_\theta (\cos \theta_i - \cos \theta_0)^2 \quad (2)$$

where $k_\theta = 502.42$ kJ/mol is the bond-bending constant and $\theta_0 = 1.920$ rad is the equilibrium bond angle. θ_i represents the bond angle between two adjacent bonds $i-1$ (the bond between monomers $i-2$ and $i-1$) and i (the bond between monomers $i-1$ and i). The torsion interaction U_{dih} can be expressed as:

$$U_{\text{dih}} = \sum_{i=4}^n \frac{1}{2} [k_\phi^1 (1 - \cos \phi_i) + k_\phi^2 (1 - \cos 2\phi_i) + k_\phi^3 (1 - \cos 3\phi_i)] \quad (3)$$

where ϕ_i is the dihedral angle between the $(i-3, i-2, i-1)$ and $(i-2, i-1, i)$ planes. $k_\phi^1 = 6.70$ kJ/mol, $k_\phi^2 = -3.63$ kJ/mol, and $k_\phi^3 = 13.57$ kJ/mol represent the torsion angle constant, respectively. The non-bonded interaction of 12-6 Lennard-Jones potential is

$$U_{\text{nonbond}} = \sum \frac{1}{2} \epsilon \left[\left(\frac{\sigma}{r_{ij}} \right)^{12} - 2 \left(\frac{\sigma}{r_{ij}} \right)^6 \right] \quad (4)$$

where r_{ij} denotes the distance between two non-bonded monomers that are divided by at least three bonds, and the cutoff distance used here is 0.9 nm. $\sigma = 0.45$ nm is a constant that represents the position with minimum interaction energy. ϵ is a constant which depends on the type of the interacting groups (CH_2 or CH_3), where $\epsilon(\text{CH}_2 - \text{CH}_3) = 0.3912$ kJ/mol, $\epsilon(\text{CH}_3 - \text{CH}_3) = 0.9481$ kJ/mol, and $\epsilon(\text{CH}_2 - \text{CH}_2) = 0.6090$ kJ/mol. The adsorption interaction between chain monomers and the surface is defined as^[46]:

$$U_a = \sum_{i=1}^n w \left[\left(\frac{z_w}{z_i} \right)^9 - \left(\frac{z_w}{z_i} \right)^3 \right] \quad (5)$$

where $z_w = 0.45$ nm is a constant, and z_i represents the perpendicular distance between the chain monomer i and the surface. w denotes the strength of adsorption, and is changed from 18.84 kJ/mol to 43.96 kJ/mol. More details about the integration of Langevin equation as well as the simulated annealing techniques can be found in our previous study^[38].

RESULTS AND DISCUSSION

To elucidate the conformational transitions of ring chains on the attractive surface, we first calculated the mean-square radius of gyration $\langle S^2 \rangle$ for $N = 60$, shown as a function of temperature in Fig. 1. For comparison, we also give the results of free case, where $\langle S^2 \rangle$ is subjected to a sudden decrease with the decrease of temperature, indicating the CG transition. More details about the collapse of free polyethylene rings can be found in a recent work^[38]. In contrast, $\langle S^2 \rangle$ varies inversely for the adsorbed rings. Due to the chain-surface interactions, the chain can not achieve extended structures as the free case, where $\langle S^2 \rangle$ has smaller values at high temperatures. While at low temperatures, due to the chain stiffness^[26–28], the chain forms hairpin-like crystal structures with a larger $\langle S^2 \rangle$, similar to the linear chain^[46]. In the polyethylene chain model, the bond-bending and torsion potentials should increase the chain stiffness. Thus, the polyethylene ring can be considered as a more stiff polymer, where for the free case, the collapse behavior^[38] is found to be very different compared to flexible rings, such as square-well^[47] and Lennard-Jones^[48] systems. We also note that the values of $\langle S^2 \rangle$ are slightly dependent on the adsorption strength.

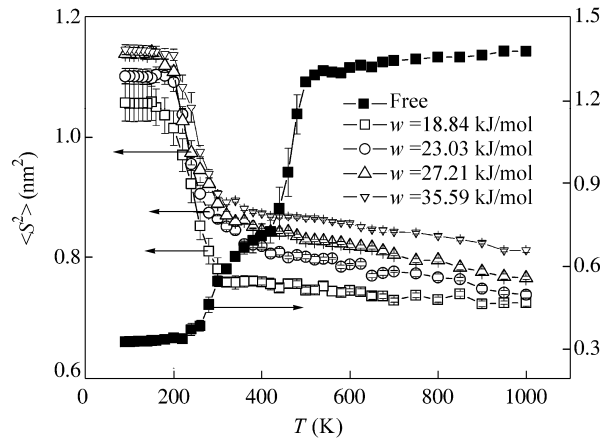


Fig. 1 Temperature dependence of the mean-square radius of gyration $\langle S^2 \rangle$ for a single polyethylene ring chain of $N = 60$ beads under different adsorption interactions of w , and for a free chain of same length (Error bars are shown for ten data points.)

To further understand the structural transformation, we show in Fig. 2 the shape factor $\langle \delta^* \rangle$ as a function of temperature, where we also plotted the typical structures in the inset. The shape factor can be defined as^[38]:

$$\langle \delta^* \rangle = 1 - 3 \frac{L_1^2 L_2^2 + L_2^2 L_3^2 + L_1^2 L_3^2}{(L_1^2 + L_2^2 + L_3^2)^2} \quad (6)$$

where L_1^2 , L_2^2 , L_3^2 are the principal components of the squared radius of gyration $S^2 = L_1^2 + L_2^2 + L_3^2$. The value of $\langle \delta^* \rangle$ varies between 0 (globule) and 1 (rod). At high temperatures, the values of $\langle \delta^* \rangle$ for the free chain are 0.25, implying an oblate structure that may be obtained only for a sufficient stiff ring chain in Monte Carlo simulation^[37]. While the adsorbed chain forms a random ring-coil structure with larger magnitude of $\langle \delta^* \rangle$. With the decrease of temperature, the free chain collapses into the 8-like structure suddenly, and then the globular structure finally. However, for the adsorbed chain, $\langle \delta^* \rangle$ increases monotonously and continuously with the decrease of temperature. Finally, at low temperatures, $\langle \delta^* \rangle$ attains a saturation value of about 0.8, denoted by a rectangle shape. Clearly, for the adsorbed chains, the collapse becomes a less intensive one-stage process, instead of a two-stage one for the free chains, which will be further illustrated in the following.

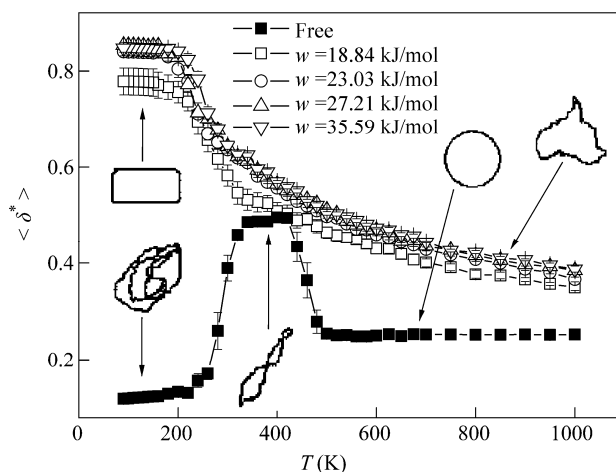


Fig. 2 Temperature dependence of the shape factor $\langle \delta^* \rangle$ for a single polyethylene ring chain of $N = 60$ beads under different adsorption interactions of w , and for a free chain of same length (Error bars are shown for ten data points.)

Additional information of the collapse transition can be provided by the energetic properties of the ring chains. The total energy $\langle U \rangle$ and adsorption energy $\langle U_a \rangle$ as a function of temperature are given in Fig. 3. For the free chain, the total energy decreases with decreasing the temperature as a whole, but there is an energy barrier near $T = 450$ K, due to abrupt U-turns of the conformation^[38]. For the adsorbed chain, the energy barrier vanishes, indicating a more continuous or second-order-like phase transition. The adsorption energy also decrease as a whole with decreasing the temperature, where a critical region of $T = 200$ – 300 K is in consistent with $\langle S^2 \rangle$ and $\langle \delta^* \rangle$.

It is still difficult to identify the exact critical temperatures of phase transitions from those variables like polymer size and energy. On the other hand, the actual collapse transition temperature can be determined from the specific heat C_v , shown as a function of temperature in Fig. 4. For the free chain there is a strong peak at high temperature of $T = 440$ K as well as a low temperature peak at $T = 260$ K, representing gas-liquid-like and liquid-solid-like transitions, respectively, according to previous studies^[23, 24]. But a further comparison with previous square-well^[47] and Lennard-Jones^[48] ring chains indicates that the phase transition nature is completely different for the gas-liquid-like transition^[38]. The heat curves become very different for adsorbed ring chains, and they are more smooth or continuous than that of the free chain. It can be observed that there is only one peak in

each heat curve, and the peaks are at $T = 220, 240, 240$ and 260 K for $w = 18.84, 23.03, 27.21$ and 35.59 kJ/mol, respectively. Hence, there should be a one-stage transition for adsorbed ring chains, *i.e.*, a coil-hairpin-like transition instead of a two-stage transition for the free chain.

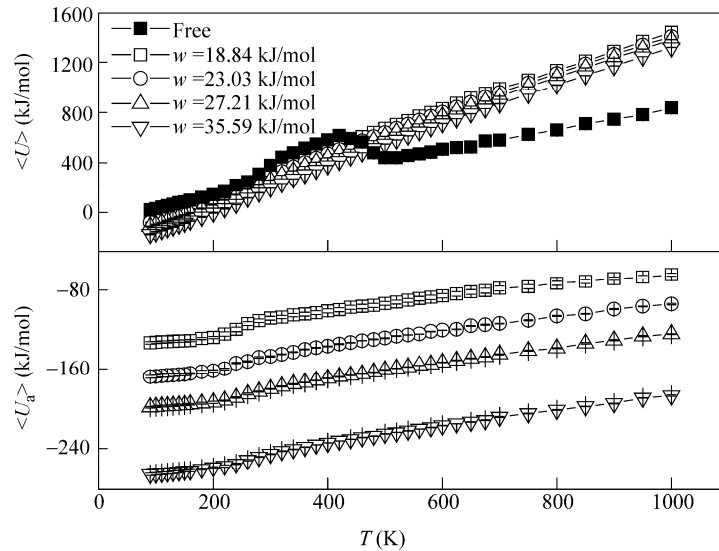


Fig. 3 Temperature dependence of the total energy $\langle U \rangle$ and the total adsorption energy $\langle U_a \rangle$ for a single polyethylene ring chain of $N = 60$ beads under different adsorption interactions of w , and temperature dependence of the total energy $\langle U \rangle$ for a free chain of same length (Error bars are shown for ten data points.)

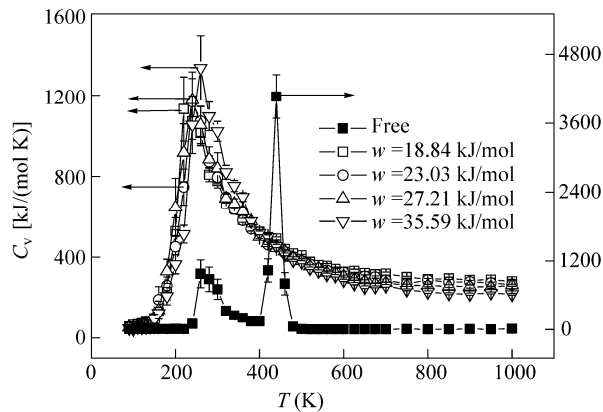


Fig. 4 Temperature dependence of the heat capacity $\langle C_v \rangle$ for a single polyethylene ring chain of $N = 60$ beads under different adsorption interactions of w , and for a free chain of same length (Error bars are shown for ten data points.)

We finally plotted the x - y coordinates of chain monomers at high and low temperatures, respectively, shown in Fig. 5. At high temperatures, the chain exhibits a loosely closed structure that differs from the oblate structure for the free chain in Fig. 2. At low temperatures ring chains are in closed hairpin-like structures resembling a rectangle, where with the increase of adsorption strength, the rectangle becomes more perfect.

To consider the finite-size effect, additional simulations for $N = 120$ and 180 are also conducted. As we focus on different structural transitions between short and long chains, it is unnecessary to present all the figures as $N = 60$ again. Selectively, we give the shape factor as a function of temperature for $N = 120$ in Fig. 6. As seen, the behavior of $\langle \delta^* \rangle$ for the free chain is similar to that of $N = 60$ in Fig. 2. The values of $\langle \delta^* \rangle$ are 0.25, 0.45,

0.083 at high temperatures, intermediate temperatures and low temperatures, respectively, representing oblate, 8-like and globular structures, respectively. Hence the collapse process of $N = 120$ should be similar to that of $N = 60$, but higher temperatures are needed for longer chains to reach oblate states. Detailed discussion about the finite-size effect for the free chains can be found elsewhere^[38]. For the adsorbed chain, compared with $N = 60$ in Fig. 2, the behaviors of $\langle \delta^* \rangle$ for $N = 120$ become very different. For weak adsorptions of $w = 18.84$ and 23.03 kJ/mol, $\langle \delta^* \rangle$ falls in low values at low temperatures, indicating globular structures, where some local hairpin-like structures can be observed in Fig. 7(a). While for $w = 35.59$ and 43.96 kJ/mol, $\langle \delta^* \rangle$ is at high values, standing for hairpin-like structures, also demonstrated in Fig. 7(a).

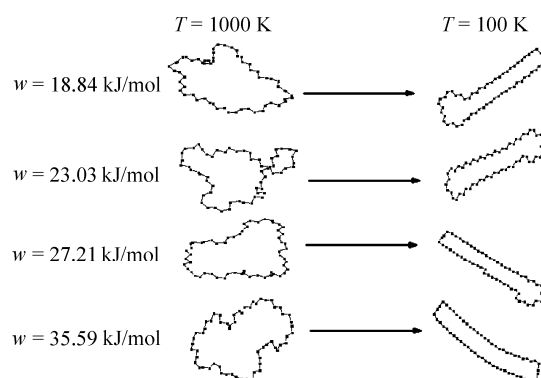


Fig. 5 The possible conformational transition for the adsorbed 60-bead polyethylene ring chain under different adsorption interactions of w (The structures are plotted by x - y coordinates.)

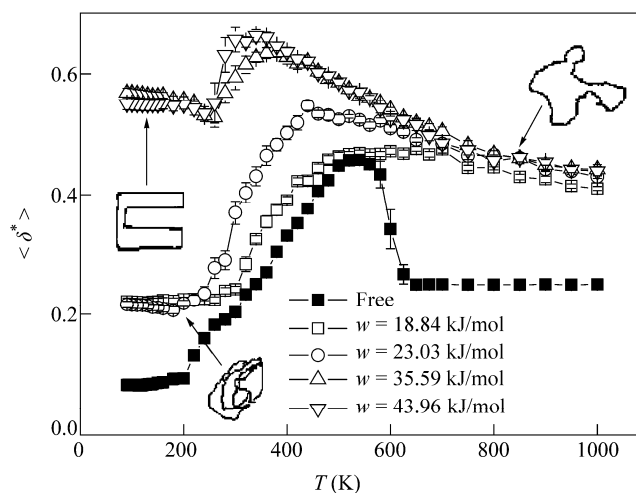


Fig. 6 Same as Fig. 2 but for 120-bead polyethylene rings under different adsorption interactions of w

For comparison, we also plot the structures of the 120-bead linear chains in Fig. 7(b), which have been discussed in our previous work^[46]. As can be seen, the linear chain can form three possible hairpin structures at low temperatures, while there is only one for the ring chain. This difference is clearly due to the topological constraint of ring chains. As the two ends of linear chains are free, they can form more kinds of hairpin structures. For both the linear and ring chains, the collapse becomes more continuous, and there should be one-stage collapse for the adsorbed case instead of two-stage one for the free case. The results of $N = 180$ is similar to $N = 120$, thus we only give the structural transition snapshot in Fig. 8. As a conclusion of the finite-size

consideration, the collapse process of $N = 120$ is different from $N = 60$, and stronger adsorption is needed for $N = 120$ to form crystal structures at low temperatures, while the difference between $N = 120$ and $N = 180$ is not appreciable.

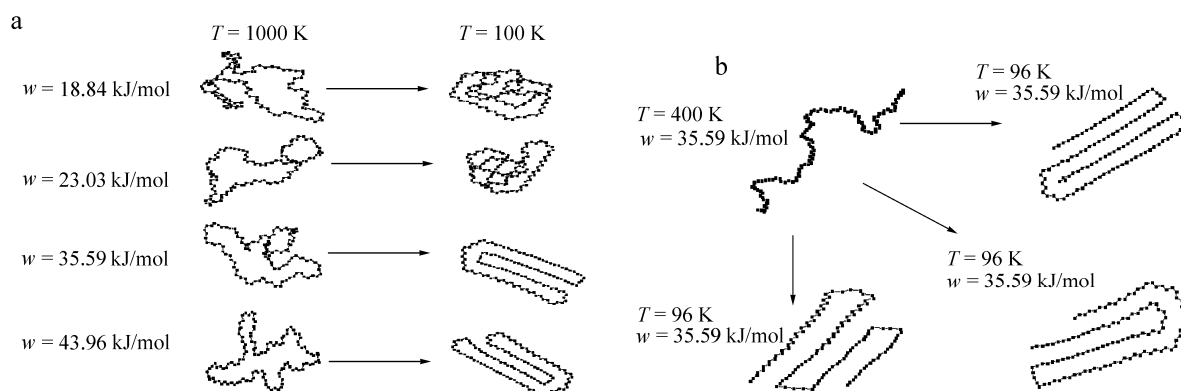


Fig. 7 The structural transition for 120-bead polyethylene (a) ring and (b) linear chains under different adsorption interactions

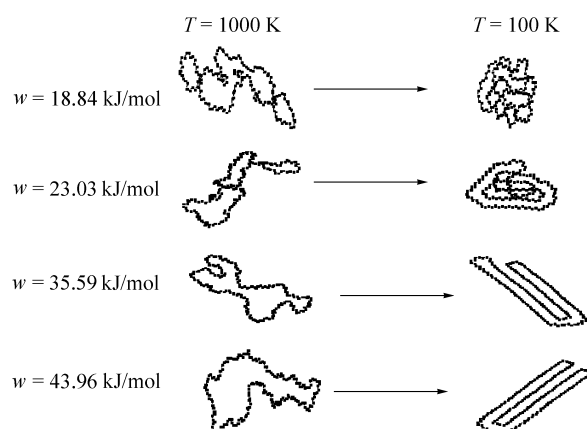


Fig. 8 Same as Fig. 7(a) but for 180-bead polyethylene rings

CONCLUSIONS

In summary, the influence of chain length and surface adsorption on the collapse of single polyethylene ring chains adsorbed on an attractive surface is investigated. Molecular dynamics simulations as well as annealing techniques are used to simulate the systems. A series of measurements of the total energy, the adsorption energy, the heat capacity, the mean-square radius of gyration, and the shape factor as a function of temperature are made with different adsorption interactions to characterize the systems. The chain forms hairpin-like crystal structures at low temperatures, which should be determined by the chain-surface adsorption. Compared with adsorbed linear chains, the topological constraint of ring chains leads to less hairpin structures. For both the ring and linear chains, the collapse on the attractive surface is thoroughly different from their free counterparts, where the collapse becomes more continuous and a one-stage collapse instead of a two-stage collapse can be identified by the specific heat. Our study provides some new insights into the folding of ring polymers on an attractive surface, which should be helpful to illustrate the collapse of circular double-strand DNAs on solid interfaces.

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