

RSC Advances



This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. This *Accepted Manuscript* will be replaced by the edited, formatted and paginated article as soon as this is available.

You can find more information about *Accepted Manuscripts* in the [Information for Authors](#).

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard [Terms & Conditions](#) and the [Ethical guidelines](#) still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.

Simulation of Conformational Properties of End-grafted Diblock Copolymers

Hong Li^{a,b}, Bin Gong^a, Chang-Ji Qian^{b*}, Chao-Yang Li^c, Jian-Hua Huang^d, and Meng-Bo Luo^e

^a School of Computer Science and Technology, Shandong University, Jinan 250100, China

^b Department of Physics, Wenzhou University, Wenzhou 325035, China

^c Department of Physics, Hangzhou Normal University, Hangzhou 310036, China

^d Department of Chemistry, Zhejiang Sci-Tech University, Hangzhou 310018, China

^e Department of Physics, Zhejiang University, Hangzhou 310027, China

* Corresponding author. E-mail: qcj@wzu.edu.cn (C.J. Qian)

ABSTRACT

Conformational properties of end-grafted flexible diblock copolymers were studied by using Monte Carlo simulation. The copolymers, XA_nB_n and XB_nA_n , are grafted with the end X to a flat surface which attracts monomers A but repulses monomers B. Results show that the blocks A in XA_nB_n and XB_nA_n are adsorbed upon the surface at low temperature, and the adsorption of blocks A takes place roughly at the same temperature. However, the conformational size and instantaneous shape of the blocks A and B in XA_nB_n and XB_nA_n are different. The possible reasons were discussed and they were interpreted by different properties and grafting locations of the two blocks.

Keywords: Diblock copolymer; Adsorption; Conformation; Simulation

1. Introduction

Adsorption of polymers on attractive surfaces or interfaces plays an important role in various areas of technological applications and biological processes [1-6]. The conformation of adsorbed polymers can be classified into distinct types according to the adsorption strength [7-8]. It is relevant to many applications, such as gel permeation chromatography [1,2], compatibilization by copolymer [3,4], copolymer separation [5], medical implants and bioaffinity sensors [6]. The behavior of polymers near an attractive surface has been numerous studied by theory and computer simulation [8-11].

The adsorption of end-grafted homogeneous polymers on a flat attracting surface was intensively investigated [12-17]. Every monomer contacting with the surface is assigned an attraction energy E . There is a phase transition from a desorbed state at high temperatures to an adsorbed state at low temperatures beyond a critical value T_c , which is named as the critical adsorption point (CAP). The conformation of an adsorbed polymer changes from three dimensional to a quasi two dimensional

conformation at CAP. The properties of adsorption, conformational size and shape of the polymer show different behaviors at the temperature below, above, and near the CAP. At CAP, it was found that the conformational sizes, such as mean square end-to-end distance $\langle R^2 \rangle$ and mean square radius of gyration $\langle R_G^2 \rangle$, reach minimum [16]. But it is difficult to directly measure the conformational properties of a single polymer [18]. Theoretical study of a single polymer chain is important as it provides a tool for understanding the properties of polymer aggregates.

The critical adsorption and conformational properties of end-grafted AB copolymers has also been investigated [19-21]. The critical adsorption point, statistical conformational size and shape of the copolymer are the key factors to understand the behavior of copolymer, since these properties are dependent on the chain length and polymer-surface attraction [19-21]. The AB copolymer is composed of two types of monomers A and B that have different properties. Therefore AB copolymer can be modeled as a synthetic protein or DNA [22]. The properties of copolymer tethered to surface are more complex. The copolymer is usually modeled as having attractive monomers A and non-attractive monomers B. It was found that copolymer's properties depend not only on the whole chain length but also on the block size of the attractive monomers and the interaction strength [20,21]. Copolymers tend to adsorb with the attractive blocks rather flat on the surface, whereas the non-attractive block in one dangling tail (or loop) protrudes into the solution [19]. Besides, for end-grafted diblock copolymer $A_n B_n$, the adsorption and conformational properties will be also dependent on the position of non-attractive block B, i.e. on the grafted end which is near B or near A. Study the adsorption of end-grafted diblock copolymers is helpful to understand the macroscopic behaviors and structures of block-copolymer on surface [23-25].

In the present paper, we study the adsorption of two simple flexible diblock copolymers $XA_n B_n$ and $XB_n A_n$ with the end monomer X grafted to a flat surface. The conformational size and instantaneous shape of the whole copolymer and that of the blocks A or B in $XA_n B_n$ and $XB_n A_n$ are studied. We find that the adsorption property of the blocks A in both copolymers is similar, but the conformational properties are quite different for the block A and block B. As a result, properties of diblock copolymer $XA_n B_n$ are different from $XB_n A_n$. Our results show that the conformational properties of the whole copolymer as well as that of each block are dependent on the position of the non-attractive block B.

2. Model and calculation method

We use self-avoiding walk (SAW) copolymers on the simple cubic lattice with one end grafted to a flat surface. The flat surface located at $z = 0$ is assumed infinitely large and impenetrable to copolymer chain. The copolymer $XA_n B_n$ or $XB_n A_n$ has equal block length for the blocks A and B. The polymer length is defined as $N = 2n$. The graft monomer X is fixed at position (0, 0, 1), and copolymer is restricted to lie in the upper half space ($z > 0$). Each monomer occupies one site of the lattice. The bond length in copolymer can fluctuate from 1, $\sqrt{2}$ and $\sqrt{3}$ lattice unit [26-28]. We

consider that two types of monomers are different in the interaction with the surface. The interaction between the monomer A and the surface is attractive, whereas that between the monomer B and the surface is pure repulsive. Especially, every monomer locating at layer $z = 1$, namely contacting with the surface, is assigned an interaction energy $E_{AS} = -1$ for monomer A and $E_{BS} = 0$ for monomer B. We consider the case that the interaction between two non-bonded monomers are pure repulsive and is assigned as $E_{AA} = E_{BB} = E_{AB} = 0$ in the simulation. Here, we only consider a simple flat surface with short-range interactions, which is widely used in theory and simulation [11-17]. Whereas long-range interactions, such as electrostatic interactions which might be exist in real surface, are ignored in the present work.

Fluctuation of bond in polymer is due to random Brownian motion resulted from random collisions between monomers and solvent molecules. In the dynamic model, a monomer is chosen randomly and attempts to jump one lattice spacing selected randomly from one of the six directions. This jump will be accepted if the following five conditions are satisfied: (1) the new site locates at $z > 0$, (2) the new bond vector still belong to the allowed bond set, (3) self-avoidance is obeyed, (4) two bonds do not intersect, and (5) the Boltzmann factor $\exp(-\Delta E/k_B T) > p$, where $0 < p < 1$ is a random number in $(0, 1)$ and ΔE is the energy shift due to the change of monomer sites. The Boltzmann constant k_B is set unity in the simulation. In one Monte Carlo step (MCS) all monomers except the grafted end in the chain attempt to move once.

Annealing method is adopted to simulate the temperature dependence of polymer properties. Starting at a high temperature $T = 8$, we slowly decrease T with a small step ΔT . The step is chosen as small as 0.05 near T_c , while a slightly big value is chosen away from T_c . The chain changed its configurations with time. At each T , the copolymer is first equilibrated for about $2.5N^{2.13}$ MCS [15]. Then we record the conformations of polymer at every $0.1N^{2.13}$ MCS in the next $100 N^{2.13}$ MCS. The results are averaged over 1000 conformations for one independent run. And our final results are further averaged over 1000 independent runs. The simulation codes are written in *Fortran 90* with MPI.

In this work we have simulated the adsorption and conformation properties of copolymer $A_n B_n$ with different grafted points and with different block length n varied from $n = 5$ to $n = 200$. We find that the conformational properties of three representative copolymers $A_{50} B_{50}$, $A_{100} B_{100}$, and $A_{200} B_{200}$ present the similar behaviors. However the difference in the conformational properties between $X A_n B_n$ and $X B_n A_n$ increases slightly with the increase in the block length n . Therefore, in this work we take $X A_{200} B_{200}$ and $X B_{200} A_{200}$ as the main samples.

3. Results and discussions

Fig. 1 shows the mean number of surface contacts for blocks A and B at different temperatures for the diblock copolymers $X A_{200} B_{200}$ and $X B_{200} A_{200}$. The block B almost does not contact with the surface since $E_B = 0$, whereas the block A begins to be adsorbed at about $T = 1.5$ which is close to the CAP of homogeneous polymer [17]. It means that the CAPs of $X A_{200} B_{200}$ and $X B_{200} A_{200}$ are about $T = 1.5$ and the non-attractive block B has little influence on the CAP of diblock copolymers $A_n B_n$.

The difference between $XA_{200}B_{200}$ and XA_{200} is smaller than that between $XB_{200}A_{200}$ and XA_{200} , indicating that the influence of the end-grafted block B is slightly more obvious than the dangled block B. At $T > 1.7$, the block A in $XB_{200}A_{200}$ does not contact the surface anymore. The insets show the snapshots of polymer configurations at high temperature $T = 2.5$ and at low temperature $T = 0.1$. The configurations of $XA_{200}B_{200}$ and $XB_{200}A_{200}$ at $T = 2.5$ are similar. Both copolymers fully extend in the solution. But at $T = 0.1$, large difference can be found for the block B: Block B in $XA_{200}B_{200}$ behaves like an end-grafted chain whereas it in $XB_{200}A_{200}$ behaves like a ring with two end monomers B contacting with the surface. The block B stretches in the solution for $XA_{200}B_{200}$, whereas the middle part extends in solution for $XB_{200}A_{200}$. At $T = 0.1$, the contact number is $M = 200$ for both copolymers, indicating that all the monomers A lie on the surface and thus the conformation of block A is two-dimensional.

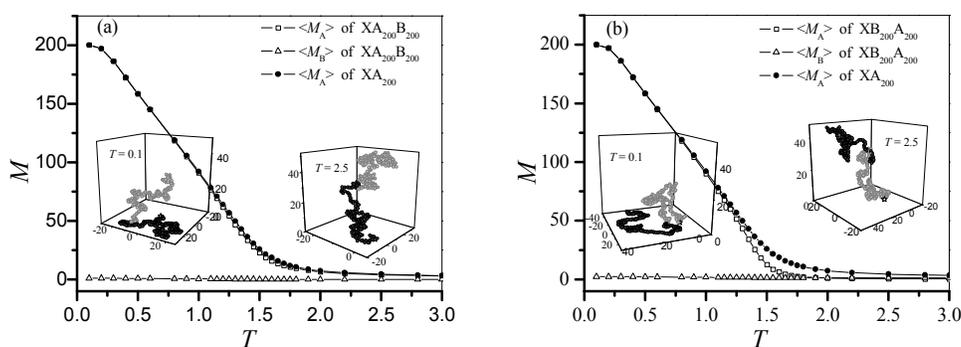


Fig. 1. The mean number of surface contacts $\langle M \rangle$ at different temperatures T for diblock copolymers $XA_{200}B_{200}$ (a) and $XB_{200}A_{200}$ (b). The dark circles present monomers A, while the gray circles present monomers B.

The square end-to-end distances R^2 and the square radius of gyration R_G^2 of a chain with length N are defined as:

$$R^2 \equiv (\vec{r}_N - \vec{r}_1)^2, \quad (1)$$

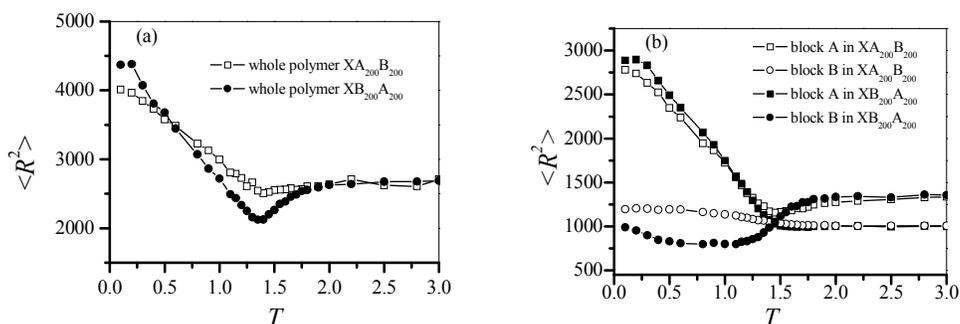
$$R_G^2 = \frac{1}{N} \sum_{i=1}^N (\vec{r}_i - \vec{r}_c)^2, \quad (2)$$

where \vec{r}_i and $\vec{r}_c = \frac{1}{N} \sum_{i=1}^N \vec{r}_i$ are the position vectors of the i th monomer and the

center of mass of the chain, respectively. The mean square end-to-end distances $\langle R^2 \rangle$ and the mean square radius of gyration $\langle R_G^2 \rangle$ are calculated at different temperatures. At the same time, the mean square end-to-end distances and the mean square radius of gyration for the block A ($\langle R_A^2 \rangle$ and $\langle R_{GA}^2 \rangle$) and the block B ($\langle R_B^2 \rangle$ and $\langle R_{GB}^2 \rangle$) are also calculated. The results are presented in Fig. 2 for $XA_{200}B_{200}$ and $XB_{200}A_{200}$. The location $T = 1.5$ at which both $\langle R_A^2 \rangle$ and $\langle R_{GA}^2 \rangle$ are minima is defined as the CAP of

the copolymer $XA_{200}B_{200}$ as the method adopted for homogeneous polymers [16]. We find that both $\langle R^2 \rangle$ s and $\langle R_G^2 \rangle$ s of $XA_{200}B_{200}$ and $XB_{200}A_{200}$ show the same behaviors. And difference between the two copolymers is only at low temperatures below CAP. The behavior of polymer conformation can be understood from the behaviors of blocks A and B.

$\langle R_A^2 \rangle$ of $XA_{200}B_{200}$ decreases with the decrease in T at high temperatures but increases with the decrease in T at low temperatures, which is consistent with the behavior of a homogeneous polymer [17]. That implies that the dangled block B has little influence on the properties of $XA_{200}B_{200}$. $\langle R_A^2 \rangle$ of $XB_{200}A_{200}$ however increases monotonically with the decrease in T . Such a difference results from that the block A of $XA_{200}B_{200}$ is initially end-grafted whereas the block A of $XB_{200}A_{200}$ is initially roughly free in the solution. At high temperature, $\langle R_A^2 \rangle$ of $XA_{200}B_{200}$ is bigger than $\langle R_A^2 \rangle$ of $XB_{200}A_{200}$. On the other hand, with the decrease of T , the block B of $XA_{200}B_{200}$ changes from a free conformation with small $\langle R_B^2 \rangle$ at high T to an end-grafted conformation with a slightly larger $\langle R_B^2 \rangle$ at low T . $\langle R_B^2 \rangle$ of $XA_{200}B_{200}$ at $T = 0.1$ is roughly the same as $\langle R_A^2 \rangle$ of $XA_{200}B_{200}$ at high temperatures. While the block B of $XB_{200}A_{200}$ changes from an end-grafted conformation at high T to a double end-grafted conformation at low T . We find $\langle R_B^2 \rangle$ of $XB_{200}A_{200}$ changes nonmonotonically with T . A minimum of $\langle R_B^2 \rangle$ is found when the polymer changes from an end-grafted conformation to a double end-grafted conformation. The properties of $\langle R_G^2 \rangle$ are similar to those of $\langle R^2 \rangle$ for these two end-grafted diblock copolymers A_nB_n . The different conformational properties of block A or block B are due to their different surface interactions and their different positions in chain.



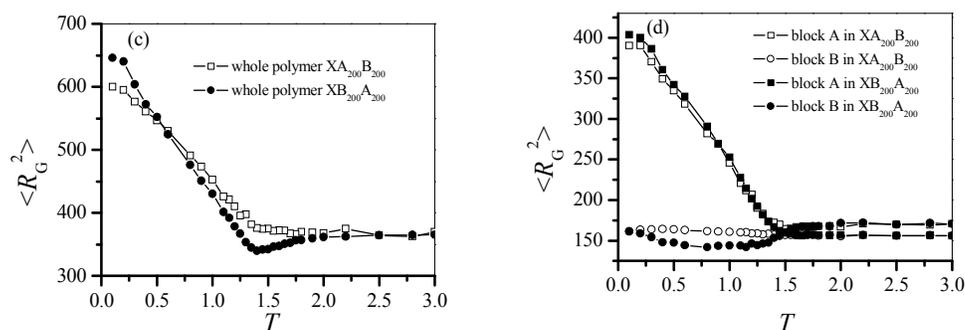


Fig. 2. The dependence of mean square end-to-end distances $\langle R^2 \rangle$ and mean square radius of gyration $\langle R_G^2 \rangle$ on the temperature T for diblock copolymer $XA_{200}B_{200}$ and $XB_{200}A_{200}$. $\langle R^2 \rangle$ of whole copolymer chain (a), the block A and the block B (b), while $\langle R_G^2 \rangle$ of whole copolymer chain (c), the block A and the block B (d).

The dependence of $\langle R^2 \rangle$ and $\langle R_G^2 \rangle$ on the chain length N of homogenous polymer is in scaling laws as $\langle R^2 \rangle \propto N^{2\nu}$ and $\langle R_G^2 \rangle \propto N^{2\nu}$ [16,26-27]. Here the exponent ν is dependent on polymer model and space dimension [29-31]. For SAW chain, $\nu = 0.588$ for a three-dimensional (3D) chain and 0.75 for two-dimensional (2D) one, respectively [29]. While in a melt of poly(ethylene terephthalate) (PET), ν is dependent on chain length [30,31]. It was found that the exponent changes from about 0.6 for short chains to about 0.5 for longer chain [30,31]. We here examine whether the scaling laws are still valid for the end-grafted diblock copolymer chain. We calculate $\langle R^2 \rangle$ and $\langle R_G^2 \rangle$ of copolymers XA_nB_n and XB_nA_n for different block lengths $n = 5, 10, 20, 25, 40, 50, 75, 100, 150, \text{ and } 200$. We find that the scaling relation is still applicable for the copolymers XA_nB_n and XB_nA_n at different temperatures above, below or near CAP. For example, the dependence of $\langle R^2 \rangle$ and $\langle R_G^2 \rangle$ on N in is presented in Fig. 3a for copolymers at low temperature $T = 0.5$ and at $T = 1.4$ near CAP. The dependence of the scaling exponent ν on the temperature T is plotted in Fig. 3b for the scaling law of $\langle R_G^2 \rangle \propto N^{2\nu}$. We find that there is a transition for the value of ν with the decrease of T . The location of the transition point is near CAP. At the temperature T above CAP, the value of ν is close to the Flory exponent 0.588 of 3D SAW chain. At T below CAP, the value of ν increases with the decrease of T . At the temperature $T = 0.5$ or below, the scaling exponent $\nu = 0.675$ is located between $\nu = 0.6$ of three dimension and $\nu = 0.75$ of two dimension, which is due to two dimensional conformation of block A adsorbed on the surface and three dimensional conformation of block B dangled in the solution. At T near CAP, the value ν of XB_nA_n is slightly smaller than that of XA_nB_n because the block B changes from an end-grafted conformation to a double end-grafted one. We find that the scaling exponent ν of $\langle R^2 \rangle \propto N^{2\nu}$ is also similar to that of $\langle R_G^2 \rangle \propto N^{2\nu}$.

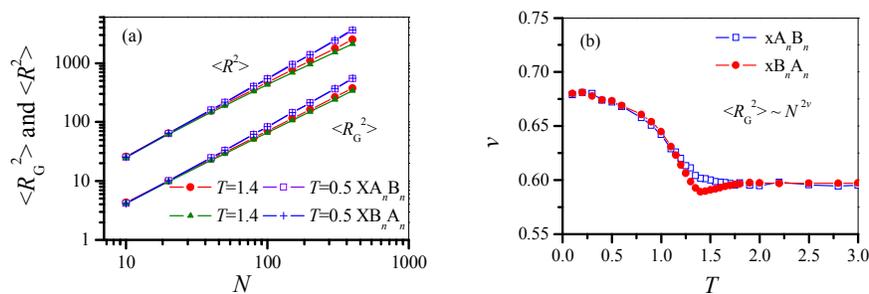


Fig. 3 (color online) The dependence of mean square end-to-end distances $\langle R^2 \rangle$ and mean square radius of gyration $\langle R_G^2 \rangle$ on chain length N (a) and the dependence of the scaling exponent ν on the temperature T (b) for two end-grafted diblock copolymers XA_nB_n and XB_nA_n .

The instantaneous shape of polymer can be expressed by the mean asphericity parameter $\langle A \rangle$ which is defined as

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

in three-dimension space. Here, L_1^2 , L_2^2 , and L_3^2 ($L_1^2 \leq L_2^2 \leq L_3^2$) are the eigenvalues of the radius of gyration tensor

$$S = \frac{1}{n} \sum_{i=1}^n s_i s_i^T = \begin{pmatrix} S_{xx} & S_{xy} & S_{xz} \\ S_{xy} & S_{yy} & S_{yz} \\ S_{xz} & S_{yz} & S_{zz} \end{pmatrix} \quad (4)$$

where $s_i = \text{col}(x_i, y_i, z_i)$ is the position of monomer i in a frame of reference with its origin at the center of mass. This parameter ranges from 0 for spherically symmetric chain conformations, to 0.25 for circular ones, and to 1 for rod-shaped ones. For a long SAW chain, the instantaneous shape is an ellipsoid with $\langle A_{\text{free}} \rangle \approx 0.44$ for polymer in dilute solution [32] and $\langle A_{\text{grafted}} \rangle \approx 0.45$ for end-grafted polymer [17].

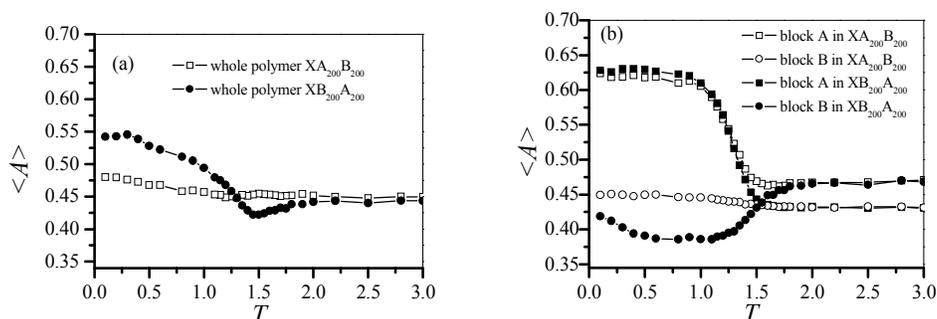


Fig. 4. The mean asphericity parameter $\langle A \rangle$ at different temperatures T for whole copolymer chain (a) and for the block A and the block B (b) in copolymers $\text{XA}_{200}\text{B}_{200}$ and $\text{XB}_{200}\text{A}_{200}$.

Fig. 4 shows the dependence of $\langle A \rangle$ on T for copolymers $\text{XA}_{200}\text{B}_{200}$ and $\text{XB}_{200}\text{A}_{200}$. Values of the mean asphericity parameter $\langle A \rangle$ are calculated for the whole copolymer $\langle A \rangle$, block A $\langle A_A \rangle$ and block B $\langle A_B \rangle$, respectively. We find that the variation of $\langle A \rangle$ is similar to that of $\langle R^2 \rangle$ and $\langle R_G^2 \rangle$, indicating that there are correlations between shape and size for each block in the copolymers as that found in homogeneous polymer [33]. $\langle A_A \rangle$ of the blocks A increases fast below $T = 1.5$, indicating the transition from 3D to 2D takes place roughly at the same temperature for both copolymers. The value of $\langle A_A \rangle$ is about 0.62 at low temperatures, indicating that the 2D conformation of block A is elliptical. The increase of $\langle A_B \rangle$ with decreasing temperature for the block B of $\text{XA}_{200}\text{B}_{200}$ shows that the block B changes to end-grafted conformation at low temperature. Whereas for the block B in $\text{XB}_{200}\text{A}_{200}$, it changes from an end-grafted conformation to a double end-grafted one. We find that $\langle A_B \rangle$ decreases at first and then increases with the decrease in temperature.

4. Conclusion

Dynamic Monte Carlo methods are carried out for the investigation of adsorption and conformational properties of diblock copolymers XA_nB_n and XB_nA_n . The conformational properties, the mean square end-to-end distance $\langle R^2 \rangle$, the mean square radius of gyration $\langle R_G^2 \rangle$ and the mean asphericity parameter $\langle A \rangle$, are dependent on temperature and the property of block. We found that at high temperature (above CAP), the conformations of the whole diblock copolymer XA_nB_n and XB_nA_n are almost the same, whereas that of block A or block B in XA_nB_n and XB_nA_n exist difference due to the different positions of A and B in the end-grafted polymer. At low temperature (below CAP), the block A is attracted to the surface, whereas the block B in XA_nB_n is an end-grafted coil and that in XB_nA_n is a loop with two ends contacted with the surface. At the intermediate temperature (near CAP), the conformational size and instantaneous shape of the whole copolymer reach a minimum, especially in XB_nA_n . Our results show that one could distinguish different types of blocks in copolymer by measuring their temperature dependence of size and shape.

Our results show that the difference in conformational properties of XA_nB_n and XB_nA_n is due to the different properties between two blocks and different positions of B. Therefore the difference will be reduced if the difference between two blocks is reduced. The cases of different block length between block A and block B are also considered for diblock copolymers XA_mB_n and XB_nA_m . However, the effect of block length A on the behavior of block B is quite interesting. If the block B is the dangled block as in XA_mB_n , the behavior of block B is roughly independent of the length of block A. Whereas if the block B is the end-grafted block as in XB_nA_m , the behavior of block B is strongly dependent on the length of block A. In this case, the block B

changes from one end grafted chain at high temperature to a loop with two ends grafted. The behavior can be also observed but the transition temperature (close to CAP) is dependent on the length of block A, since CAP increases with the length of block A [8]. Therefore, the general trend is that the effect of block A is reduced when the length of block A is decreased.

Acknowledgements

This work was supported by the National Natural Science Foundation of China under Grant Nos. 11304231, 11374255, and 21171145 and by the Zhejiang Natural Science Foundation of China under Grant No. LY14B040004.

References

- [1] E. Uliyanchenko, S. Wal and P. J. Schoenmakers, *Polym. Chem.*, 2012, **3**, 2313-2335.
- [2] B. Trathnigg, *Prog. Polym. Sci.*, 1995, **20**, 615-650.
- [3] N. Zgheib, J. L. Putaux, A. Thill, E. Bourgeat-Lami, F. D'Agosto, and M. Lansalot, *Polym. Chem.*, 2013, **4**, 607-614.
- [4] G. Pu, Y. Luo, A. Wang, and B. Li, *Macromolecules*, 2011, **44**, 2934-2943.
- [5] Y. S. Lipatov, A. E. Nesterov, T. D. Ignatova, and D. A. Nesterov, *Polymer*, 2002, **43**, 875-880.
- [6] L. A. Ruiz-Taylor, T. L. Martin, F. G. Zaugg, K. Witte, P. Indermuhle, S. Nock, and P. Wagner, *Proc. Natl. Acad. Sci. U.S.A.*, 2001, **98**, 852-857.
- [7] R.J. Roe, *J. Chem. Phys.*, 1965, **43**, 1591-1598.
- [8] E. Eisenriegler, K. Kremer, and K. Binder, *J. Chem. Phys.*, 1982, **77**, 6296-6320.
- [9] F. Wang and D.P. Landau, *Phys. Rev. Lett.*, 2001, **86**, 2050-2053.
- [10] D. P. Landau, and F. Wang, *Comput. Phys. Commun.*, 2002, **147**, 674-677.
- [11] D. T. Seaton, T. Wüst, and D. P. Landau, *Comput. Phys. Commun.*, 2009, **180**, 587-589.
- [12] H. Zhang, J. Zhu, J. He, F. Qiu, H. Zhang, Y. Yang, H. Lee, and T. Chang, *Polym. Chem.*, 2013, **4**, 830-839.
- [13] R. Decase, J. U. Sommer, and A. Blumen, *J. Chem. Phys.*, 2004, **120**, 8831-8840.
- [14] E. J. J. van Rensburg, and A. R. Rechnitzer, *J. Phys. A: Math. Gen.*, 2004, **37**, 6875-6898.
- [15] M.B. Luo, *J. Chem. Phys.*, 2008, **128**, 044912.
- [16] H. Li, C. J. Qian, and M. B. Luo, *Polymer J.*, 2010, **42**, 383-385.
- [17] H. Li, C. J. Qian, L. Z. Sun, and M. B. Luo, *Journal of Applied Polymer Science*, 2012, **124**, 282-287.
- [18] M. Vacha, and S. Habuchi, *NPG Asia Mater.*, 2010, **2**, 134-142.
- [19] O. A. Evers, J. M. H. M. Scheutjens, and G. J. Fleer, *Macromolecules*, 1990, **23**, 5221-5233.
- [20] Y. Tan, L. Fang, J. Xiao, Y. Song, and Q. Zheng, *Polym. Chem.*, 2013, **4**, 2939-2944.
- [21] S. Bhattacharya, H. -P. Hsu, A. Milchev, V. G. Rostiashvili, and T. A. Vilgis, *Macromolecules*, 2008, **41**, 2920-2930.

- [22] A. Meller, L. Nivon, E. Brandin, J. Golovchenko, and D. Branton, *Proc. Natl. Acad. Sci. U. S. A.*, 2000, **97**, 1079-1084.
- [23] G Srinivas, D. E. Discher, and M. L. Klein, *Nature Materials*, 2004, **3**, 638-644.
- [24] S. Egli, H. Schlaad, N. Bruns, and W. Meier, *Polymers*, 2011, **3**, 252-280.
- [25] J. N. L Albert, and T. H. Epps III, *Materials Today*, 2010, **13**, 24-33.
- [26] J. S. Shaffer, *J. Chem. Phys.*, 1994, **101**, 4205-4213.
- [27] H. Li, C. J. Qian, C. Wang, and M. B. Luo, *Phys. Rev. E*, 2013, **87**, 012602.
- [28] H. Li, C. J. Qian, C. Wang, and M. B. Luo, *Polymers & Polymer Composites*, 2012, **20**, 107-110.
- [29] A. Yethiraj, *Macromolecules*, 2003, **36**, 5854-5862.
- [30] Q. Wang, D. J. Keffer, S. Petrovan, J. B. Thomas, *J. Phys. Chem. B*, 2010, **114**, 786-795.
- [31] Q. Wang, D. J. Keffer, D. M. Nicholson, and J. B. Thomas, *Macromolecules*, 2010, **43**, 10722-10734.
- [32] M. B. Luo and J. H. Huang, *J. Chem. Phys.*, 2003, **119**, 2439-2443.
- [33] M. B. Luo, J. H. Huang, Y. C. Chen, and J. M. Xu, *Eur. Polym. J.*, 2001, **37**, 1587-1590.