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PAPER

Morphological Transition Difference of Linear and Cyclic Block Copolymer with Polymer Blending in Selective Solvent by Combining Dissipative Particle Dynamics and All-atom Molecular Dynamics Simulation Based on ABEEM Polarizable Force Field

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This study describes theoretical simulations of morphological transition for linear and cyclic block copolymers with polymer blending. Mesoscopic dissipative particle dynamics simulation with reliable interaction parameters from all-atom molecular dynamics simulation based on ABEEM polarizable force field, can reproduce self-assembly behavior well and morphological transition observed by experiments.

Introduction

Block copolymers are fascinating materials constituted by two or more blocks of different homopolymers chains linked by covalent bonds. According to their architectures, block copolymers can be divided into linear copolymers, star-like copolymers, comb-like copolymers, H-shaped copolymers, cyclic copolymers and so on.[1] Due to various blocks that possess different physical and chemical properties, the block copolymers exhibit superior performance. A remarkable property of block copolymers is their ability to self-assemble in bulk or solution into a variety of ordered structures from micelles to vesicles with characteristic dimensions between 1 and 100 nm.[2]

Self-assembly of block copolymers has received great interest in recent years. Previous studies have indicated that self-assembly of block polymers is dominated by diverse factors, such as the length of block copolymer, the order of blocks, molecular architecture, composition, solvent selection, pH, ionic strength, temperature and so on. Besides, polymer blending has been of great interest in the polymer industry during the past three decades because it provides a convenient way to develop novel materials. A major advantage is that it is a time and cost effective route to commercialization of products compared with the synthesis of an entirely new polymer. Therefore, the blending of polymers has been studied widely in experiments. The blending of polymer assembly and fullerenes C_{60}[3] and carbon nannotube[4] have been also studied by experimetal and theoretical methods and access lots of emergent properties.

One of the greatest challenges in theoretical simulations is to understand the basic principles that govern soft condensed matter systems, such as polymer solutions and melts, colloidal suspensions, and various biological processes. Experimental studies of these complex systems are often complemented by numerical simulations of model systems, which can provide a great deal of information not easily accessible by experiments. Therefore simulations have become invaluable aids in the design of new materials suited to particular applications. All-atom based molecular dynamics simulation has come into wide use for material design. In general, however, such an atomistic approach is problematic since many intriguing processes in soft matter systems are not dictated by microscopic details but rather take place at mesoscopic length and time scales, which are beyond the practical capabilities of all-atom molecular dynamics simulation. Although a possible molecular structure can be simulated by the atom-based simulation, it is not realistic to predict the mesoscopic structure defined on the scale of 0.1-10μm, for example the morphology of polymer blend and composite, which often dominates actual material properties. In such cases, it is necessary to model soft matter systems by viewing them from a larger perspective than from a microscopic point of view. In practical terms, this means that one has to design ways to simplify the underlying systems as much as possible, while still retaining the key properties governing the processes of interest. Coarse-grained dynamics simulation is a practical method for studying biological systems in large system size and long time scale. Coarse-grained method can improve computation efficiency by reducing detailed information of atomic structures and interactions. The power of coarse-grained simulation methods lies in that mesoscale processes can be probed without losing sight of the chemical details from which the collective interactions arise. Complicated collective processes such as fusion, domain formation, and protein self-assembly can be probed on the microsecond timescale, something unachievable with more detailed all-atom models.

One of those coarse-grained methods that have enjoyed considerable success in recent studies is the so-called dissipative particle dynamics (DPD),[5] where the coarse-grained beads represent momentum-carrying sections of a fluid, subjected to viscous and frictional forces, in addition to conservative forces. By its construction, DPD can reach mesoscopic length and time scales at a relatively inexpensive computational effort. It is a very promising method for mesoscopic studies of soft matter, and recently has attracted considerable interest in studies of polymer microphase separation.

Although current coarse-grained models used in DPD are becoming very powerful in understanding some phenomena, the models are mostly qualitative rather than quantitative in their predictions. Illustrative of this fact is the use of dimensionless units to measure the length, time, and energy scales. When a link is made to realistic systems, the mapping onto physical measures is done in hindsight. There is a lack of a direct link between the model parameters and real molecular parameters. Typically some experimental observables are used as criteria to set the simulation parameters.[6] Moreover, one needs to spend considerable effort in developing parameters based upon the phenomenological features that one wants to preserve in the simulation.[7] It is pointed out that it is challenging to find out the correspondence between microscale and mesoscale. If this correspondence relation is found, it can be used to deduce the interaction parameter in DPD from molecular dynamics simulation rather than macroscopic observable physical quantity.[8] Ideally, one would like to derive the conservative force parameter from detailed atomistic interactions. In 1997, Groot and Warren[9] made an important contribution on this front by establishing a relation between a simple functional form of the conservative repulsion in DPD and the Flory-Huggins parameter theory. There are established theories in polymer science, which link the Flory-Huggins parameter to solubilities and mixing energies of polymeric components. The latter can be obtained either from atomistic simulations or from experiments. However, the solubility parameters available by experimental methods are limited.[10] Thus, the Groot and Warren's work provides a sound basis for which the conservative repulsion used in DPD can be derived starting from an atomistic description. The combination of mesoscopic DPD and all-atom molecular dynamics is essential. The questions are: Can a coarse-grained model be specifically parameterized from all-atom model to simulate a realistic system in advance and then can it be used to make quantitative predictions? Can this combination reproduce experimental polymer properties such as solubility parameters and the self-assembled morphologies observed by experiments? There exist such trial studies in previous work, but these all-atom molecular dynamics are based on non-polarizable force field. As indicated, the accurate description of nonbonded interaction in nonpolarizable force field is at the expense of the transferability of the nonbonded parameters. Nowadays it is necessary to combine DPD with all-atom molecular dynamics based on polarizable force field. The obtained cohesive energy and solubility parameter values will depend sensitively on the quality of the force field.[11, 12] A force field of high quality should be adopted in all-atom molecular dynamics simulations under this condition.

There exist various architectures for polystyrene (PS)-polyisoprene (PI) block copolymers.[13] Among all these, the self-assembly of linear and cyclic PS_{290}-PI_{110} block copolymers has been widely studied in experiments. Previous experiments have shown their self-assembly in selective solvents such as n-heptane, n-hexane, DMF and DMA and in non-selective solvent such as THF, and so on. However, the theoretical studies are mainly limited to their self-assembly in bulk. The self-assembly in selective solvents is little involved. Although block copolymers can self-assemble into various morphologies in bulk, the introduction of solvent and other polymers will complicate self-assembled morphologies accessible and access novel nanostructures with emergent properties. Experiments on the self-assembly of linear and cyclic PS_{290}-PI_{110} block copolymers demonstrated that the existence of PS homopolymer in solution drives the morphological transition from spherical to cylindrical micelles for linear copolymers, while from cylindrical micelle to vesicle for cyclic copolymers.[14] Another study demonstrated the addition of linear copolymers into cyclic ones has a profound effect on the self-assembled morphology.[15] However, a complete picture of the mechanisms governing the self-assembly in solution has been not achieved yet.

In this article, the self-assembly behavior of linear and cyclic block copolymers in PI-selective solvent n-heptane is studied. The effect of polymer blending is examined. Here, we carry out a series of simulations by combining mesoscopic DPD and all-atom molecular dynamics based on ABEEM polarizable force field. ABEEM has shown its prominent performance and fine parameter transferability. ABEEM can present well the nonbonded interaction in the system, especially for the electrostatic interaction.[16] As far as we all know, it is the first try to combine mesoscopic DPD with all-atom molecular dynamics based on polarizable force field.

Theoretical methods

The DPD method, originally developed by Hoogerbrugge and Koelman,[17] is a coarse-grained particle-based dynamics simulation technique. It can capture effectively the hydrodynamics of complex fluids at larger length and time scales than all-atom molecular dynamics method. This method has been successfully applied to the assembly of block copolymers.[18] Details of DPD method are given by Español and Warren[19] and Groot and Warren[9]. The combination of DPD and all-atom molecular dynamics based on non-polarizable force filed refers to previous study.[20] All the details of all-atom molecular dynamics simulations and dissipative particle dynamics simulations used in this paper are given in Electronic Supplementary Information (ESI).

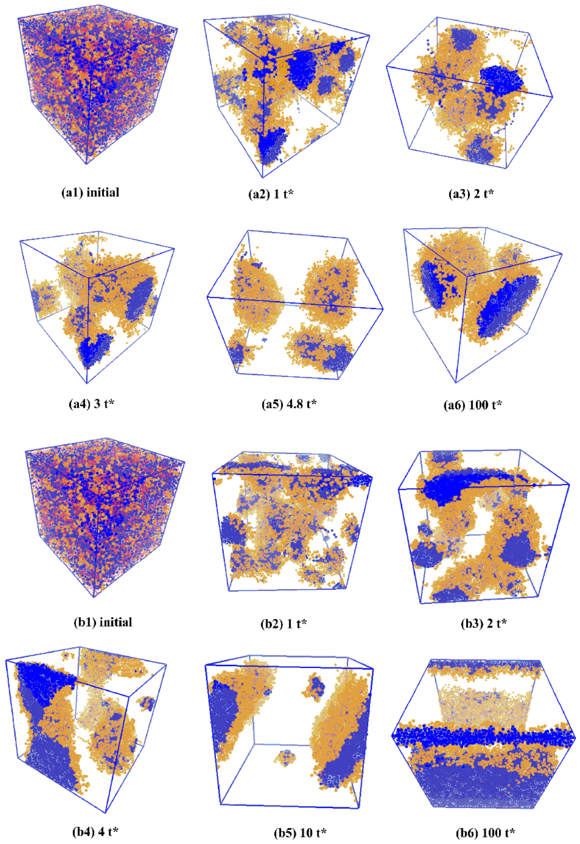
Results and discussion

As an initial step, all-atom molecular dynamics simulations were carried out to obtain cohesive energies and solubility parameters, which are vital to the success of DPD simulations. The solubility parameters obtained from MD simulations are compared with those from experimental methods, in order to check if the ABEEM polarizable force field can accurately reflect the material properties for PS, PI and n-heptane in our simulation model. The solubility parameters obtained from molecular dynamics simulations are $\delta(PS)=17.88(J/cm^3)^{1/2}$, $\delta(PI)=14.65(J/cm^3)^{1/2}$ and $\delta(\text{n-heptane})=14.43(J/cm^3)^{1/2}$, respectively. These are in good agreement with accessible experimental values, in which $\delta(PS)=16.6\sim20.2(J/cm^3)^{1/2}$,[21] $\delta(PI)=16(J/cm^3)^{1/2}$,[22] and $\delta(\text{n-heptane})=15.17\ (J/cm^3)^{1/2}$.[23] Based on the solubility parameters obtained, we can obtain Flory-Huggins parameter $\chi(PS\text{-}PI)=3.79$. Compared with the value 3.7 obtained by all-atom molecular dynamics simulation based on non-polarizable force field in previous study,[24] which has been considered to be well consistent with the experimental value, the Flory-Huggins parameter here is more close to experimental result 3.812.[25] The derivation between simulation and experimental χ can attribute primarily to that the polymers used in simulations are relatively short compared to real samples.[26] Other Flory-Huggins parameters χ and the interaction parameters α_{ij} are obtained from all-atom molecular dynamics simulations and are listed in Table S1 (ESI†). Thus, the interaction parameters in DPD can be obtained and are listed in Table S2 (ESI†). These interaction parameters are applied to subsequent DPD simulations. The quality of this atomistic study, of course, depends on the adopted force field. In order to assure reliable calculation, the use of a high quality force field and the validation of the cohesive energy by comparison with known experimental values are indispensable. By using realistic χ

parameters in cooperating with atomistic simulation, a reliable mesoscopic structure will be predicted by DPD simulation.[27]

The difference of linear and cyclic block copolymers in architecture will result in distinct self-assembly morphologies. Several snapshots of the formation of micelle by linear (a) and cyclic (b) block copolymers are shown in Fig. 1. The system includes linear or cyclic PS-PI block copolymer and n-heptane with the volume ratio of 1:4 (similarly hereinafter, if not stated specially). To show aggregate morphologies clearly, the solvent heptane molecules are not displayed similarly hereinafter unless stated specially.

As shown in Fig. 1a, all linear diblock copolymer components are distributed randomly in n-heptane at the beginning of the simulation. With the evolution of the simulation, some polymer molecules aggregate and form small clusters first, subsequently the small clusters emerge and turn into large aggregates. The solvophobic PS blocks are distributed inside the micelle forming a hydrophobic core, while the solvophilic PI blocks spread around the surface forming a protective shell. Spherical micelles with stable structures are obtained when the system achieves balance. The aggregate morphology does not change significantly with extra simulation steps. Therefore 10^6 steps are sufficient for achieving simulation equilibrium in this system.


(a1) initial (a2) 1 t* (a3) 2 t*

(a4) 3 t* (a5) 4.8 t* (a6) 100 t*

(b1) initial (b2) 1 t* (b3) 2 t*

(b4) 4 t* (b5) 10 t* (b6) 100 t*

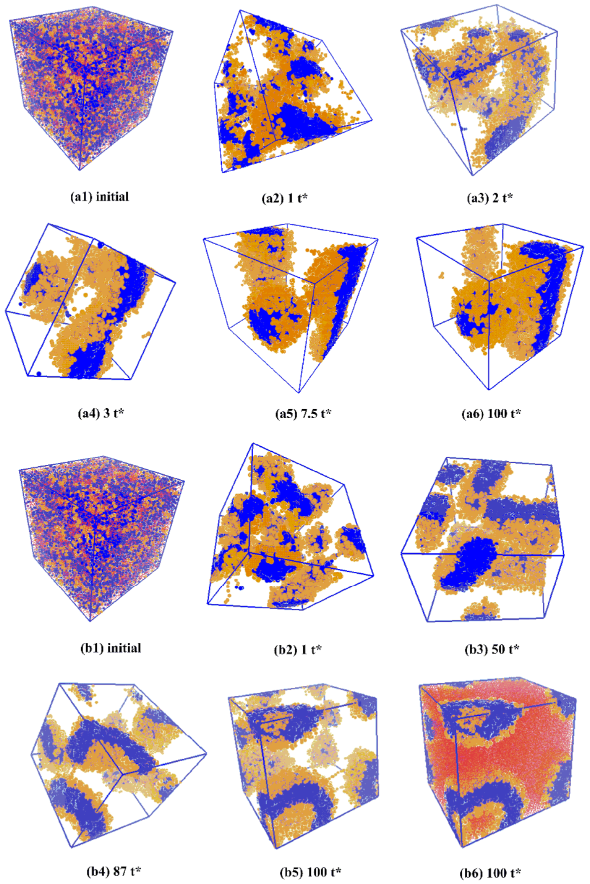
Fig. 1 Simulation snapshots of aggregates self-assembled from (a) linear and (b) cyclic PS_{290}-PI_{110} diblock copolymer in heptane in a certain simulation step. $t^*=10^4$ DPD time steps. Blue (black in the black/white version): PS segments; orange (gray in the black/white version): PI segments. The solvents are omitted for clarity.

Whereas the cyclic block copolymers with the same composition will self-assemble into cylindrical micelles under the same condition. Fig. 1b shows that some polymer molecules initially aggregate into small clusters, and then they merge and evolve into large aggregates. Later, these aggregates grow into large worm-like micelles after about 2t* (with $t^* = 10^4$ DPD time steps) (Fig. 1b3). With the evolution of time, the worm-like micelles turn into compressed cylindrical micelle.

Consistent with experimental results, linear PS-PI diblock copolymers self-assemble into spherical micelle in n-heptane, while the cyclic structures self-assemble into cylindrical micelle. However, the self-assembled morphologies will change evidently with the addition of PS homopolymers as observed in the experiments. In our simulation, we adopt the blending ratio of the PS homopolymers similar to that of experiments. As is shown in Fig. 2, we can observe the morphological transition occurred in the linear (a) and cyclic (b) block copolymers due to the addition of PS homopolymers.

Fig. 2 presents the dynamical formation process of cylindrical micelle (a) and vesicle (b). Because of the solvophobicity of PS blocks, the microphase separation occurs. After about 2t* (Fig. 2a3), the worm-like cylindrical micelles are formed. With the elapse of time, worm-like micelle turns into perfect cylindrical micelles. Here, the volume fraction of PS homopolymers is 5%.

However, the cyclic block copolymers will self-assemble into vesicle with the addition of PS homopolymers under the same condition. Fig. 2b shows the morphological transition due to the introduction of PS homopolymers into cyclic block copolymers. Here, the volume fraction of PS homopolymers is 2%. At first, the large aggregates evolve from small ones, which are formed due to different affinity to solvents. Later, these large aggregates grow into disc-like micelles. These disc-like micelles bend and further turn into vesicle.


(a1) initial (a2) 1 t* (a3) 2 t*

(a4) 3 t* (a5) 7.5 t* (a6) 100 t*

(b1) initial (b2) 1 t* (b3) 50 t*

(b4) 87 t* (b5) 100 t* (b6) 100 t*

Fig. 2 Simulation snapshots of aggregates self-assembled from (a) linear and (b) cyclic PS_{290}-PI_{110} diblock copolymer blended with PS homopolymers in heptane in a certain simulation step. $t^*=10^4$ DPD time steps. Blue (black in the black/white version): PS segments;

orange (gray in the black/white version): PI segments. The solvents are omitted for clarity.

The morphological transition of linear or cyclic block copolymer self-assembled structures due to the addition of PS homopolymers further illustrates the importance of architecture in self-assembled morphologies.

In fact, the self-assembled morphologies of cyclic block copolymers will change with the addition of linear block copolymers. Previous experiments demonstrated that the self-assembled morphology of cyclic block copolymers would change from cylindrical micelle to spherical micelle. In our simulation, this phenomenon is also observed. The concentration is 0.1 for polymers and the mixing volume ratio is 1:1 (50% volume fraction for linear block copolymers). The morphological transition due to the addition of linear block copolymers is shown in Fig. 3.

The addition of linear block copolymers has a dominant role in self-assembled morphologies of cyclic block copolymers. However low the volume fraction of linear block copolymers is, the self-assembled morphologies tend to be spherical micelles. From the simulations above, we can find that the addition of linear block copolymers does have a significant effect on self-assembled morphologies of cyclic block copolymers. In actual simulations, we also probe the self-assembled morphologies with the addition of different volume fractions of linear block copolymers, such as 5%, 10%, 15%, 20%, 25%, 30%, 35%, 40%, 45%, 55%, 60%, 65%, 70%, 75%, 80%, 85%, 90%, 95%. These simulations also present the same effect of linear block copolymers on the self-assembled morphologies of cyclic block copolymers.

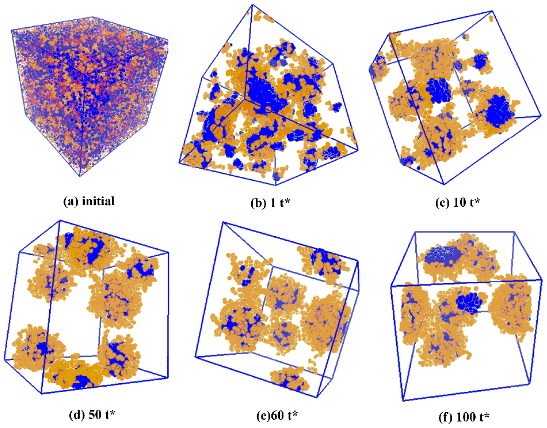

(a) initial (b) 1 t* (c) 10 t*
(d) 50 t* (e)60 t* (f) 100 t*

Fig. 3 Simulation snapshots of aggregates self-assembled from cyclic PS_{290}-PI_{110} diblock copolymers blended with linear PS_{290}-PI_{110} diblock copolymers in heptane in a certain simulation step. $t^*=10^4$ DPD time steps. Blue (black in the black/white version): PS segments; orange (gray in the black/white version): PI segments. The solvents are omitted for clarity.

Conclusions

DPD combined with all-atom molecular dynamics simulations based on ABEEM polarizable force field is applied to study the self-assembly of linear and cyclic PS_{290}-PI_{110} diblock copolymers in n-heptane. The effect of architecture and blending is probed. The model is able to capture the relevant features, governing the self-assembly of diblock copolymers in solution, reproducing the morphological transition observed in the experiments. It is prospective to serve as a guide to the control of morphological transition in the experiments. The solubility parameters thus obtained reflect well the compatibility among different species and are comparable to experimental data. As far as we all know, this is the first try to combine DPD simulations and all-atom molecular dynamics simulations based on a polarizable force field. The results obtained indicate that ABEEM polarizable force field presents a good description of the nonbonded interaction in the system not at the cost of sacrificing the transferability of parameters, which often occurs in non-polarizable force fields.[28] In this way, the combination of DPD and molecular dynamics based on polarizable force field provides a desirable way to bridge the gap between atomistic and mesoscopic simulation. The key interaction parameters in DPD simulation can be obtained from all-atom molecular dynamics simulation. This combination not only accesses larger length scale and longer time scale, but also overcomes the disadvantage of lacking atomic details and microscopic basis in mesoscopic modelling.

This work is to study the effect of the architecture and polymer blending on the self-assembly properties in solution. The self-assembly behavior of cyclic diblock copolymers is compared with those of their linear precursors. It is obvious that the architecture and polymer blending play a significant role in self-assembly morphology of polymers. The effect of other factors, such as solvent (selective or non-selective, mixtures, et al), temperature, solution concentration et al., will be investigated further in future studies.

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Notes and references

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Electronic Supplementary Information (ESI) available: Simulation details and additional data and movies. See DOI: 10.1039/c000000x/

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