Mesoscopic Simulation of Polystyrene-b-Poly(acrylic acid) Using Dissipative Particle Dynamics Method

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Self-assembly morphologies of polystyrene-b-poly(acrylic acid) (PS-b-PAA) in aqueous solution were studied at various polymer concentrations and hydrophilic/hydrophobic chain length ratios using dissipative particle dynamics (DPD) computer simulation technique. It has been found that spherical and cylindrical structures could be obtained at various concentrations. Seen from the internal distribution, the micelle core was formed by aggregation of the hydrophobic PS blocks, while the hydrophilic PAA chains distributed on the outer surface of the micelle. With the growth of the hydrophilic PAA chains, more shell chains wrapped the core. This work provides deeper insight into the microstructure of polymeric micelles, which might guide the molecular design and experimental preparation of novel polymeric micelles with controlled structures.

Keywords: Polystyrene-b-Poly(acrylic acid), Dissipative Particle Dynamics, Mesoscopic Simulation, Self-Assembly.

1. INTRODUCTION

It is well-known that amphiphilic block copolymers can self-assemble into core–shell micelles in selective solvents. Therefore, amphiphilic block copolymer micelles have been widely applied in the areas of drug delivery carriers, diagnostic reagents (MRI contrast agents, quantum dots), targeted therapy and so on.¹ Several studies have revealed that various aggregated morphologies could be prepared by altering chain length, block copolymer composition, solvent composition, concentration, temperature, additive, etc.²–⁸ For instance, Eisenberg et al. synthesized a series of polystyrene-b-poly(acrylic acid) (PS-b-PAA) block copolymers. The resulting copolymers displayed a variety of morphologies such as spherical, cylindrical, vesicular, lamellar and so on.⁹–¹¹ Although most characteristics of the amphiphilic block copolymer micelles can be investigated by transmission electron microscopy (TEM), SAXS (small angle X-ray scattering), NMR (nuclear magnetic resonance), dynamic light scattering (DLS), and fluorescence spectroscopy,¹²–¹⁴ it is rather difficult for researchers to investigate their transformations, exact internal structures, and distributions by experiments.¹⁵ Thus, it is essential to understand the microstructures and morphological developments of them by computer simulation, which is a powerful tool that can complement experimental works in a wider parameter space.

We have thus used the new dissipative particle dynamics (DPD) simulation technique to investigate the self-assembly of PS-b-PAA. DPD simulation is a coarse-grained simulation method initially devised by Hoogerbrugge and Koelman¹⁶,¹⁷ in 1992. It was subsequently reformulated and slightly modified by Espanol and Warren.¹⁸ It is effective and precise to simulate soft beads interacting through a simple, pair-wise potential that preserves the hydrodynamic modes of the fluid. In 1997, Groot and Warren¹⁹,²⁰ established the relationship between repulsion parameter and Flory–Huggins parameter, which led DPD simulation method widely applied in the study of mesostructures of complex systems, such as surface surfactants, drug delivery systems, and block copolymers.²¹–²⁴

In this paper, DPD simulation technique was employed to investigate the self-assembly behaviors of PS-b-PAA micelles with various concentrations and hydrophilic/hydrophobic chain length ratios. The aggregated morphologies and internal distributions of the micelles were observed. The results will provide valuable structural information that may contribute to the future rational design and synthesis of novel block copolymer micelles.
2. SIMULATION METHOD

2.1. DPD Simulation Theory

DPD is a mesoscale simulation method. It can simulate fluid with coarse-grained models over longer length and time scales. A series of soft beads that represent groups of atoms or fluids interact with each other. The total non-bonded force acting on a DPD bead \( i(f_i) \) is given by a sum of a conservative force \( (F_{ij}^C) \), a dissipative force \( (F_{ij}^D) \), and a random force \( (F_{ij}^R) \). Each \( f_i \) is pair wise additive\(^{20}\):

\[
f_i = \sum_{j\neq i} (F_{ij}^C + F_{ij}^D + F_{ij}^R)
\]

The three forces are given by:

\[
\begin{align*}
F_{ij}^C &= \begin{cases} 
  a_{ij}(1 - \gamma_{ij})\tilde{r}_{ij} & \gamma_{ij} < 1 \\
  0 & \gamma_{ij} > 1 
\end{cases} \\
F_{ij}^D &= \begin{cases} 
  -\gamma a_o^D(\gamma_{ij})(\tilde{r}_{ij}\tilde{v}_{ij})\tilde{r}_{ij} & \gamma_{ij} < 1 \\
  0 & \gamma_{ij} > 1 
\end{cases} \\
F_{ij}^R &= \begin{cases} 
  \sigma a_o^R(\gamma_{ij})\tilde{r}_{ij} & \gamma_{ij} < 1 \\
  0 & \gamma_{ij} > 1 
\end{cases}
\]

The repulsion parameter \( a_{ij} \) depends on the underlying atomistic interactions and is related to the Flory-Huggins \( (\chi_{ij}) \) parameters. Groot and Warren proposed the relationship between repulsion parameter \( a_{ij} \) and Flory-Huggins parameter \( \chi_{ij} \):\(^{10}\)

\[
a_{ij} \approx a_i + 3.27\chi_{ij}
\]

where \( a_i \) is the interaction parameter between beads of the same type, it can be calculated according to Eq. (4):\(^{20}\)

\[
a_i = 75k_BT/\rho
\]

where \( k_B \) is the Boltzmann constant and \( T \) is the system temperature. The particle density \( \rho \) has been used in DPD simulation, and the cut-off radius is \( r_c = k_BT \). Therefore the repulsion parameter \( a_{ij} = 25 \times \chi_{ij} \) parameter between pairs of beads can be calculated from solubility parameters:\(^{25}\)

\[
\chi_{ij} = (\delta_i - \delta_j)^2V_{ref}/kT
\]

where \( \delta_i \) and \( \delta_j \) are the solubility parameters of a pair of interacting beads, \( V_{ref} \) is the average molar volume of two beads, \( k \) is Boltzmann constant, and \( T \) is the system temperature. Solubility parameters could be calculated from molecular dynamics (MD) simulation in Materials Studio 5.0 software (Accelrys Inc.) based on COMPASS force field at 298 K.

2.2. Simulation Models and Parameters

The molecular structure and coarse-grained model of PS-b-PAA is presented in Figure 1. One water molecule is treated as an individual bead W. PS-b-PAA molecular is represented by two types of beads. We just take each PS or PAA unit a bead, which make the polymer a chain of beads. In the block copolymer model, each PAA repeat unit is represented by one PAA bead, and each PS repeat unit is represented by one PS bead. So if the model is PS\(_{50}\)-PAA\(_{100}\), it is taken as 50 PS beads connecting 100 PAA beads. A sample has been provided in Figure 1.

DPD simulations were runned with Materials Studio 5.0 software (Accelrys Inc.). In our simulations, solubility parameters \( \delta \), \( V_{ref} \), interaction parameters \( a_{ij} \) of all the beads in DPD simulation system are listed in Tables I–III. The size of simulation cubic cell was set as \( 20 \times 20 \times 20r_3 \) with periodic boundary condition. Each cell contained 24,000 DPD beads, and the spring constant \( C \) was set as 4.0. To reach dynamic equilibrium, 100,000 DPD steps have been adopted with a time step of 0.05 ns. The temperature was set constant at 298 K.
3. RESULTS AND DISCUSSION

3.1. Effect of Concentration on the Self-Assembly Morphologies

In this research, we first set chain length ratio constant and changed polymer concentration. Then we changed chain length ratio with an unaltered concentration 10% in order to study influencing factors better. Figure 2 shows the self-assembly morphologies of PS$_{50}$-PAA$_{100}$ in aqueous solution at different polymer concentrations. In this figure, green beads represent the hydrophobic PS blocks, while red ones are hydrophilic PAA blocks. In order to observe the aggregation morphologies of the polymers clearly, the water beads are hidden. Legends of these beads are same in the following figures. 100,000 DPD steps were used for this research because micelles collided and fused each other continuously from the beginning to 60,000 steps, after 100,000 steps, one stable micelle was observed and it could get thermodynamic equilibrium. As can be seen from Figures 2(a)–(c), PS$_{50}$-PAA$_{100}$ could aggregate into spherical micelles at low concentration (below 15%). Moreover, the size of the sphere micelle increased with increasing polymer concentration, the spherical micelle formed at 15% concentration was larger than that at 10% and 5% concentration. The reason for aggregation into spherical micelles is that the hydrophobic PS blocks are easier to collide and joint together with the polymer content increases. However, with further increase of the polymer content, cylindrical structure could be observed at the concentration of 20% (Fig. 2(d)). The above observations reveal that the concentration level of the polymer plays an important role in the self-assembly.

3.2. Effect of Hydrophilic/Hydrophobic Chain Length Ratio on the Self-Assembly Morphologies

Besides concentration, the self-assembly behaviors of PS-b-PAA in aqueous solution with various hydrophilic/hydrophobic chain length ratios were also investigated. In this section, we set the concentration as 10% unchangeably, keep the PS chain length unchanged and regulate...
the PAA chain length. The simulation results are shown in Figure 3. All polymers with various hydrophilic/hydrophobic chain length ratios could form spherical micelles at the concentration of 10%. When the PAA chain length increased from 5 to 100, in the case of PS\(_{50}\)-PAA\(_{5}\) (Fig. 3(a)), PS\(_{50}\)-PAA\(_{10}\) (Fig. 3(b)), PS\(_{50}\)-PAA\(_{25}\) (Fig. 3(c)), PS\(_{50}\)-PAA\(_{50}\) (Fig. 3(d)), and PS\(_{50}\)-PAA\(_{100}\) (Fig. 3(e)), with the growth of the hydrophilic PAA chain length, more and more red PAA chains were wrapped on the surface of the micelle. This is because the PS blocks are hydrophobic and lipophilic, they have the tendency to be spontaneous aggregated in aqueous solution. While the PAA blocks contain non-polar carbon chain and hydrophilic carboxyl groups (COOH), hydrophilic groups (carboxyl group) spread into water medium, the hydrophobic groups (carbon chain) of PAA segments are adsorbed on the surface of PS matrix, resulting in a stable core–shell micelle.

The simulation results indicate that the self-assembly behaviors of PS-\(b\)-PAA can be tunable by adjusting the PAA chain length. In addition, when the PAA block is shorter, some parts of the PS core are exposed to water. It is possible in real experiments, but such micelles will not mingle in experiments, because in experiments, PS\(_{200}\)-\(b\)-PAA\(_{21}\) and PS\(_{500}\)-\(b\)-PAA\(_{50}\) can form spherical micelle. In their experiments, only when the ratio of PS:PAA is higher than 10:1, micelles will mingle and form other shapes such as rod, vesicle and so on.\(^9\)\(^10\) In our simulation, the ratio of PS:PAA is 10:1, 5:1, 2:1, 1:1, and 1:2, they are all lower than 10:1, so micelles will not mingle.

In order to investigate the internal microstructures and distributions of the above micelles, cross-section views of PS-\(b\)-PAA micelles with various PAA chain lengths at the concentration of 10% were observed. As can be seen from Figure 4, PS-\(b\)-PAA micelles exhibited a clear core–shell

![Fig. 4. Cross-section views of PS-\(b\)-PAA micelles with various PAA chain lengths at the concentration of 10%: (a) PS\(_{50}\)-PAA\(_{5}\); (b) PS\(_{50}\)-PAA\(_{10}\); (c) PS\(_{50}\)-PAA\(_{25}\); (d) PS\(_{50}\)-PAA\(_{50}\); and (e) PS\(_{50}\)-PAA\(_{100}\).](image1)

![Fig. 5. TEM images of PS-\(b\)-PAA micelles compare with DPD simulation results (a) PS\(_{200}\)-PAA\(_{21}\) in experiment; (b) PS\(_{200}\)-PAA\(_{21}\) in experiment; (c) PS\(_{200}\)-PAA\(_{21}\) in DPD simulation.](image2)
structure. It was apparent that the hydrophobic PS blocks aggregated to form the micelle core, while the hydrophilic PAA chains distributed on the surface of the micelle core to form the shell, providing a protective layer between the core and water. With the growth of the hydrophilic PAA chain length, from PS$_{50}$-PAA$_5$ (Fig. 4(a)), PS$_{50}$-PAA$_{10}$ (Fig. 4(b)), PS$_{50}$-PAA$_{25}$ (Fig. 4(c)), PS$_{50}$-PAA$_{50}$ (Fig. 4(d)), to PS$_{50}$-PAA$_{100}$ (Fig. 4(e)), more and more shell chains were distributed on the outer surface of the micelle. Such distributions appeared to result in a more stable spherical micelle. Figure 5 shows the TEM images of PS-b-PAA micelles compare with DPD simulation results (a) PS$_{500}$-PAA$_{50}$ in experiment; (b) PS$_{200}$-PAA$_{21}$ in experiment; (c) PS$_{50}$-PAA$_{5}$ in DPD simulation. The simulation results are in coincidence with the spherical structure of PS-b-PAA micelles through TEM observation by Eisenberg et al.$^{9,10}$

4. CONCLUSIONS
In summary, the results show that DPD computer simulation is a powerful tool to understand the self-assembly behaviors of PS-b-PAA under the influences of concentration and hydrophilic/hydrophobic chain length ratio. The aggregation morphology of PS-b-PAA micelle was depending on the concentration. In addition, the internal distribution of the PS-b-PAA micelle could be regulated by the PAA chain length. This study provides us mesoscopic-level information for developing novel polymeric micelles with controlled structures.

References and Notes

Received: 13 November 2013. Accepted: 16 December 2013.