Research Article

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Synthesis of aminated polystyrene and its self-assembly with nanoparticles at oil/water interface

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Abstract: The influence of density of amino groups, nanoparticles dimension and pH on the interaction between end-functionalized polymers and nanoparticles was extensively investigated in this study. PS-NH₂ and H₂N-PS-NH₂ were prepared using reversible addition–fragmentation chain transfer polymerization and atom transfer radical polymerization. Zero-dimensional carbon dots with sulfonate groups, one-dimensional cellulose nanocrystals with sulfate groups and two-dimensional graphene with sulfonate groups in the aqueous phase were added into the toluene phase containing the aminated PS. The results indicate that aminated PS exhibited the strongest interfacial activity after compounding

with sulfonated nanoparticles at a pH of 3. PS ended with two amino groups performed better in reducing the water/toluene interfacial tension than PS ended with only one amino group. The dimension of sulfonated nanoparticles also contributed significantly to the reduction in the water/toluene interfacial tension. The minimal interfacial tension was 4.49 mN/m after compounding PS-NH₂ with sulfonated zero-dimensional carbon dots.

Keywords: aminated polystyrene, nanoparticles, interfacial tension, self-assembly, O/W interface

1 Introduction

Nanoparticles (NPs) with a responsive behavior to external forces, e.g., magnetic fields (1), electric fields (2) and ultraviolet radiation (3), have been widely studied for their ability of self-assembly at oil/water (O/W) interfaces. It was also found that the formulation of NPs and end-functionalized polymers, which can be individually used as surfactants, can strengthen the O/W interfacial activity (4) by forming complex NPs/surfactants structures driven by electrostatic structures. The orderly assembly of NPs/surfactants at the O/W interface improves the compatibility between the O/W phases, allowing promising applications in fields including medical pharmaceuticals (5), food processing (6), enhanced oil recovery (7) and inkjet printing (8).

The O/W interfacial energy can be regulated by the pH of the aqueous solution, the molecular weight, the concentration of the end-functionalized polymer and the external electric field (9). Huang et al. (10) investigated the effect of pH on the *in situ* formation of NPs (carboxylated polystyrene, PS-COOH)/surfactants (aminated polydimethylsiloxane, PDMS-NH₂) and found an optimal pH of 4.66. Liu et al. (4) used CNCs and PS-NH₂ ($M_w = 1.5k$, 2.5k, 13k, 25k, 40k) as NPs in water and as the surfactant in toluene, respectively, and reached the conclusion that the molecular weight of PS-NH₂ exerted a considerable influence on the interfacial behavior of NPs/surfactants. When $M_w = 1.5k$, PS-NH₂, interacting with CNCs, reduced

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the O/W interfacial tension to below 7 mN/m. As the M_w increased, the interfacial activity of NPs/surfactants decreased; the O/W interface was seldom affected when the M_w was higher than 25k. The molecular weight of PS-NH₂ also influenced the formation process of NPs/surfactants. Although PS-NH₂ ($M_w = 13k$) and PS-NH₂ ($M_w = 2.5k$) exhibited a similar ability to reduce the O/W interfacial tension in the presence of CNCs, it took a longer time for the former/CNCs to reach interfacial equilibrium. The assembly of carboxylated SiO₂ as NPs in water and PDMS-NH₂ as the surfactant in silicon oil also reduced the O/W interfacial tension, according to Chai *et al.* (11). The introduction of salt increased the ionic strength of water and further decreased the O/W interfacial tension. The observation result of in situ AFM indicated that the addition of NaCl enhanced the packing density of NPs at the O/W interface and therefore improved the assembly of NPs/surfactants. Toor *et al.* (12) used carboxylated silica as NPs in water and PDMS-NH₂ as surfactants in silicone oil to investigate the effect of polymer concentration on the interfacial properties. The interfacial activity of NPs/surfactants benefited from the increase in polymer concentration, and the interfacial tension was reduced to less than 10 mN/m. They also demonstrated that PDMS-NH₂ exhibited little interfacial activation in the absence of carboxylated NPs (13). Cui *et al.* (14) used PS-COOH as NPs in water and PDMS-NH₂ in silicone oil as the surfactants. By analyzing the shape of the droplets, the authors revealed the formation process of NPs/surfactants at the O/W interface in an external electric field, including the diffusion of NPs and surfactants to the O/W interface as well as the electrostatic interaction mechanism.

The above research achieved a considerable reduction in O/W interfacial tension via a series of methods. Most of the end-functionalized polymers reported in these papers were aminated. Adjusting the pH of water had a profound influence on both the protonation of amino groups and the electrostatic interaction between oppositely charged groups of NPs and polymers. However, the effect of two terminal functionalized polymers on the assembly of NPs/surfactants, and the relationship between the dimension of NPs and the interaction between NPs and end-functionalized polymers were not discussed in the previous papers. In addition, to the best knowledge of the authors, little research has been done on the simulation of the arrangement of NPs/surfactants in the O/W interface.

To reveal the influence of the number of amino groups in end-functionalized polymers and the dimension of NPs, two kinds of aminated PS and three kinds of NPs (zero-dimensional sulfonated carbon dots (CDs-SO₃H)), one-dimensional sulfated cellulose nanocrystals (CNCs-OSO₃H) and two-

dimensional sulfonated graphene oxides (GOs-SO₃H) were used to test the O/W interfacial tension in this study. Molecular simulations on the interaction between aminated PS and sulfonated carbon dots were also carried out to reveal the assembly of NPs/surfactants at the O/W interface.

2 Materials and methods

2.1 Sample preparation

Triethylamine, 1-butanethiol, *N*-(bromomethyl)phthalimide, tributylstannane, potassium phthalimide, 2,2'-bipyridine, citric acid and sulfanilic acid were purchased from TCI and used as received. Copper(I) bromide was obtained from Aldrich and was purified by stirring in acetic acid, washed with ethanol and then stored in argon. Aladdin provided 2,2'-azobis(2-methylpropionitrile) (AIBN), which was recrystallized twice from methanol. Carbon disulfide and chloroform were purchased from Aladdin and distilled three times. Styrene from Aladdin was passed through basic alumina (100–200 mesh) to remove inhibitors. Sulfonated CNCs (diameter of 5–20 nm, length of 100–200 nm) in aqueous solutions and GOs-SO₃H (diameter of 1.2–4.0 μm, thickness of 0.8–6.6 nm) were obtained from Shanghai Science & Nanotechnology Co., Ltd (China) and Shandong Jincheng Graphene Technology Co., Ltd (China), respectively. Other agents were purchased from Aladdin and used as received.

2.2 Synthesis

2.2.1 Synthesis of PS-NH₂ by reversible addition-fragmentation chain transfer polymerization (RAFT)

2.2.1.1 Synthesis of chain transfer agent (1)

The compound was synthesized following the procedures reported by Postma (15). A mixture of carbon disulfide (6.07 g, 0.0797 mol) and 1-butanethiol (3.57 g, 0.0396 mol) in chloroform (25 mL) was prepared with stirring, and triethylamine (8.21 g, 0.0811 mol) was then added. The reaction lasted for 3 h at room temperature, and *N*-(bromomethyl)phthalimide (9.59 g, 0.0399 mol) was then added in portions for over 0.5 h. The mixture was stirred at room temperature for 16 h. Chloroform (20 mL) was added and the organic layers were washed successively with water, H₂SO₄, water and brine. Then, the organic layers were dried over magnesium sulfate, and the solvent was subsequently filtered and removed

Figure 1: ^1H NMR spectra of **2a**, **2b** and **2c**; all bands have been characterized in previous papers (15).

to provide a crude solid that was crystallized from methanol. Yield = 11.87 g (88.28%).

2.2.1.2 Synthesis of modified PS via RAFT (**2a**)

Styrene (30.42 g, 0.2925 mol), chain transfer agent **1** (2.85 g, 0.0088 mol) and AIBN (1.71 g, 0.0104 mol) were added into a three-neck flask. The flask was sealed and pumped to vacuum ($\approx 10^{-3}$ Torr), and the mixture was purged with argon for 30 min. The mixture was stirred at 60°C for various durations (4, 8, 12, 24 h). After the reaction, the mixture was cooled to room temperature and added to methanol to obtain yellowish modified PS. The ^1H NMR spectrum of **2a** is shown in Figure 1.

2.2.1.3 Removal of trithiocarbonate (**2b**)

Modified PS **2a** (3.03 g), tributylstannane (5.24 g), AIBN (0.39 g) and toluene (20 mL) were added to a three-neck flask. The flask was purged with argon (20 min) three times and heated in an oil bath at 70°C for 3 h. After the mixture was cooled to room temperature, it was concentrated by rotary evaporation. The concentrated solution was poured into methanol to obtain the product **2b**. The product was dried at 50°C under vacuum ($\approx 10^{-3}$ Torr).

2.2.1.4 Synthesis of PS- NH_2 (**2c**)

Modified PS **2b** (1.35 g), hydrazine hydrate (0.34 g) and DMF (25 mL) were added to a three-neck flask. The

reaction was carried out with stirring at 80°C for 12 h in the protection of argon. The mixture was added into methanol. The precipitate was washed with deionized water and then with brine, and its color changed from yellow to white. Finally, the product **2c** was obtained. The chemical structures of **2a**, **2b** and **2c** were characterized by ^1H NMR, and the spectra are shown in Figure 1.

2.2.2 Synthesis of $\text{H}_2\text{N-PS-NH}_2$ by atom transfer radical polymerization (ATRP)

2.2.2.1 Synthesis of PS via ATRP (**3a**)

The synthesis of PS via ATRP was carried out following a previous paper (16). CuBr (0.83 g, 0.0058 mol), styrene (15 g, 0.1442 mol), 2,2'-bipyridine (1.78 g, 0.0114 mol) and *N*-(bromomethyl)phthalimide (2.35 g, 0.0098 mol) were added into a three-neck flask. The flask was purged with argon (20 min) three times and was then heated in an oil bath at 110°C for various durations (1.5, 3 h). The mixture was cooled to room temperature, diluted with THF (25 mL) and passed through a neutral alumina column to remove the copper catalyst. Then, the product was precipitated from methanol and dried under vacuum ($\approx 10^{-3}$ Torr).

2.2.2.2 Synthesis of di-phthalimide-ended PS (**3b**)

A mixture of potassium phthalimide (2.13 g), PS **3a** (2.51 g) and DMF (30 mL) was heated at 80°C for 12 h

Figure 2: ^1H NMR spectra of **3a**, **3b** and **3c**; A: Ar-H, B: Ph-CH-Br, C: phthalimide- CH_2 .

under argon. Then, the mixture was added to water, and the product **3b** was prepared by filtration (17).

2.2.2.3 Synthesis of $\text{H}_2\text{N-PS-NH}_2$ (**3c**)

Product **3b** (1.83 g), hydrazine hydrate (1.05 g) and DMF (25 mL) were added to a three-neck flask. The mixture was stirred at 80°C for 16 h under argon. The mixture was added to methanol, and the precipitate was washed with deionized water and brine. Then, $\text{H}_2\text{N-PS-NH}_2$ **3c** was obtained. The chemical structures of **3a**, **3b** and **3c** were characterized by ^1H NMR, and the spectra are shown in Figure 2.

2.2.3 Synthesis of $\text{CDs-SO}_3\text{H}$

Citric acid (8.01 g) was added to deionized water (100 mL). The mixture was sonicated and transferred to a hydrothermal kettle. The reaction was carried out at 200°C for 5 h. The mixture was cooled to room temperature and centrifuged at 10,000 rpm for 20 min. The supernatant was mixed with sulfanilic acid (1.25 g). The ultrasonic dispersion was uniformly placed in a hydrothermal kettle at 135°C for 5 h. After being cooled to room temperature, the mixture was purified in a dialysis bag (500–1,000 D) for 48 h and lyophilized for 24 h. Finally, a reddish brown solid ($\text{CDs-SO}_3\text{H}$) was obtained (18).

2.3 Characterization

^1H NMR and ^{13}C NMR measurements were conducted on a Bruker-AVANCE III 400M spectrometer using CDCl_3 as the solvent.

Gel permeation chromatography (GPC) analyses were performed on a Waters 1515 instrument equipped with a MIXED 7.5×50 mm PL column, two MIXED-C 7.5×300 mm columns and a differential refractive index detector. Tetrahydrofuran (THF, HPLC grade) was used as the eluent at 35°C with a flow rate of 1 mL min^{-1} .

The O/W interfacial tension was measured by a KRÜSS DSA25 using the pendant drop method. $\text{CDs-SO}_3\text{H}$ (10 mg/mL, pH = 3, 9), $\text{CNCs-OSO}_3\text{H}$ (10 mg/mL, pH = 2, 3, 4, 5, 6, 9) and $\text{GOs-SO}_3\text{H}$ (10 mg/mL, pH = 2, 3, 4, 5, 6, 9) were added to deionized water as the aqueous phase, and PS-NH_2 (1 mg/mL) and $\text{H}_2\text{N-PS-NH}_2$ (1 mg/mL) were dissolved in toluene as the oil phase. When the aqueous droplet contacted the oil phase, the interfacial tension was measured and the time was marked as 0 s. The intervals of the subsequent tests were recorded every 15 s in the first 1 min and every 30 s after that. The experiments were carried out at 25°C .

2.4 Molecular dynamics (MD) simulation

MD methods were used to simulate the interface between $\text{H}_2\text{N-PS-NH}_2$ in the toluene phase and $\text{CDs-SO}_3\text{H}$ in the

Figure 3: Model used in the MD simulations.

water phase. The molecular model used in this study is illustrated in Figure 3, which is a large periodic unit cell with dimensions of $100 \times 100 \times 124$ Å. In each unit cell, there are 19 $\text{H}_2\text{N-PS-NH}_2$ molecules, 19 $\text{CDs-SO}_3\text{H}$ molecules, 2,000 toluene molecules and 10,000 H_2O molecules. To simplify the model, we used positively charged $\text{NH}_3^+(\text{CH}_2\text{-CHC}_6\text{H}_5)_6\text{-NH}_3^{2+}$ to represent the $\text{H}_2\text{N-PS-NH}_2$ molecules. We also used C_{60} spheres to simulate quantum dots; therefore, the $\text{CDs-SO}_3\text{H}$ are represented by negatively charged $\text{C}_{60}(\text{SO}_3^-)_7$. Both the toluene and the water phases were set to be electronically neutral by adding counterions of Cl^- and H_3O^+ . These two phases were sandwiched by two layers of graphene, and a vacuum space of 24 Å was added between the graphene layers to minimize electrostatic interactions between neighboring images in the z -direction.

MD simulations were performed in the constant-volume and constant-temperature (NVT) ensemble with a Nosé-Hoover thermostat at 298 K (19). A cutoff radius of 15.5 Å and time step of 1 fs were used. The universal forcefield was used in this work (20). During the simulations, the graphene layers were fixed.

3 Results and discussion

The molecular weight and polydispersity (PDI) of PS-NH_2 and $\text{H}_2\text{N-PS-NH}_2$ are summarized in Table 1. The

gravimetric conversion rate of aminated PS increased with the reaction time, and the PDI was well controlled.

Three NPs, $\text{CDs-SO}_3\text{H}$, $\text{CNCs-OSO}_3\text{H}$ and $\text{GOs-SO}_3\text{H}$, were used to interact with PS-NH_2 and $\text{H}_2\text{N-PS-NH}_2$ and form the assembly of NPs/surfactants.

By adjusting the pH of the aqueous phase toward acidity, the amino groups of PS underwent protonation ($-\text{NH}_3^+$), while the sulfonate groups ($-\text{SO}_3^-$) and sulfate groups ($-\text{OSO}_3^-$) underwent deprotonation. The positively charged PS in the toluene phase interacted with the negatively charged NPs in the aqueous phase, resulting in a high concentration of NP-surfactants at the interface and a low O/W interfacial tension.

In order to investigate the effect of pH on the interfacial activity of NP-surfactants, a series of $\text{CNC-OSO}_3\text{H}$ aqueous solutions (10 mg/mL, pH = 2, 3, 4, 5, 6, 9) were prepared to mix with a toluene solution. The O/W interfacial tension between $\text{CNC-OSO}_3\text{H}$ aqueous solutions (pH = 3) and pure toluene was approximately 35 mN/m, which is close to the interfacial tension of water/toluene, indicating that $\text{CNCs-OSO}_3\text{H}$ alone had no interfacial activity, as shown in Figure 4e. When amino-terminated PS (1 mg/mL) was added to the toluene solution, the interfacial tension decreased significantly with the decrease in pH, indicating that the $\text{CNCs-OSO}_3\text{H}$ and the polymers arranged as NPs/surfactants via electrostatic interaction at the O/W interface. In the case of the $\text{CNCs-OSO}_3\text{H}$ and $\text{H}_2\text{N-PS-NH}_2$ ($M_n \approx 0.9\text{k}$), the interfacial tension was lowered to 5.36 mN/m at pH = 3.

Table 1: Molecular weight and polydispersity of aminated PS

	[St]/[I]	Time (h)	Conv. (%)	M_n^{Calc} (Daltons)	M_n^{GPC} (Daltons)	M_w^{GPC} (Daltons)	PDI
PS-NH ₂	33.16	4	7.93	610	518	622	1.20
PS-NH ₂	33.16	8	41.05	1,752	2,127	2,528	1.21
PS-NH ₂	33.16	12	65.82	2,606	2,970	3,611	1.23
PS-NH ₂	33.16	24	77.61	3,013	3,256	3,920	1.20
H ₂ N-PS-NH ₂	14.71	1.5	47.15	961	931	1,138	1.22
H ₂ N-PS-NH ₂	14.71	3	78.65	1,443	2,371	2,844	1.20

$$M_n^{\text{Calc}} = \frac{[\text{St}]}{[\text{I}]} \times \text{Conv} \times 104 + (\text{molecular weight of RAFT or ATRP agent}).$$

A considerable decline in O/W interfacial tension could be observed when the pH decreased from 6 to 5, as amino groups protonated in the presence of an increasing amount of H⁺. However, as the pH decreased from 3 to 2, the O/W interfacial tension increased as a result of the suppression of the dissociation of -SO₃H. Similar phenomena could be observed in the compounding of the CNCs-OSO₃H and PS-NH₂ (Figure 4a-d). The O/W interfacial tension of the GOs-SO₃H with aminated PS at different pH values was also observed (shown in Supporting Information).

The results indicate that the pH of the aqueous solutions exerted a significant effect on the formation rate and interfacial activity of NP-surfactants. At pH = 9, amine groups were rarely protonated, and their interaction with negatively charged groups on the NPs through the electrostatic force was not intensive, thus failing to exhibit high interfacial activity. As the pH decreased, the protonation of amine groups increased dramatically, resulting in a strengthening interaction between positively charged surfactants and negatively charged NPs. NPs/surfactants assembled and deformed the O/W interface, and the interfacial tension decreased. Meanwhile, it can be observed that the O/W interfacial tension reached a minimum at pH = 3.

The reason for this observation may be that, although the ratio of primary amino protonation at pH = 2 is higher than that at pH = 3, the lower pH also inhibits the ionization of negatively charged groups in NPs partially combined with H⁺ rather than NH₃⁺, leading to a slight decrease in interfacial activity, as the pK_a of methanesulfonic acid ranged from 2.4 to 2.5.

Similarly, the number of amino groups and the molecular weight of the polymers also have a significant influence on the interfacial tension. PS-NH₂ ($M_n \approx 0.5\text{k}$, 2.1k, 2.9k, 3.2k) and H₂N-PS-NH₂ ($M_n \approx 0.9\text{k}$, 2.3k) also reduced the O/W interfacial tension with NPs (CDs-SO₃H, CNCs-OSO₃H, GOs-SO₃H) in the aqueous phase at pH = 3, as shown in Figure 5.

PS-NH₂ ($M_n \approx 0.5\text{k}$) reduced the O/W interfacial tension to approximately 6 mN/m, interacting with

CDs-SO₃H. Similar behaviors had been observed in the interaction between H₂N-PS-NH₂ ($M_n \approx 0.9\text{k}$) and CDs-SO₃H, and the O/W interfacial tension was reduced to approximately 4.5 mN/m. H₂N-PS-NH₂ also exhibited a better performance than PS-NH₂ when CNCs-OSO₃H and GOs-SO₃H were used as NPs.

The percentage of amine groups in PS-NH₂ can be calculated using Eq. 1, in which m is the molar mass of the monomer unit and M_n is the number-average molecular weight of PS-NH₂ determined by GPC.

$$[\text{NH}_2] = \frac{1}{m} \times \frac{M_n}{10^6} \quad (1)$$

As the molecular weight increases, the percentage of amine groups decreases. In the case of PS-NH₂ ($M_n \approx 0.5\text{k}$), the percentage of amine groups is 18.56 µg/g; as for PS-NH₂ ($M_n \approx 3.2\text{k}$), this figure decreases to 2.95 µg/g. Therefore, this demonstrates that the higher the content of amino groups in aminated PS, the lower the O/W interfacial tension. In addition, although H₂N-PS-NH₂ ($M_n \approx 0.9\text{k}$) has a higher M_n than PS-NH₂ ($M_n \approx 0.5\text{k}$), the former can prevent the deformation of the drop while interacting with CDs-SO₃H, thereby reaching a lower O/W interfacial tension (9).

The dimension of NPs (CDs-SO₃H of zero dimensions, CNCs-OSO₃H of one dimension, GOs-SO₃H of two dimensions) also affected the O/W interfacial tension, as shown in Figure 6.

The formation of CD-SO₃H/surfactants appears faster than those of CNC-OSO₃H/surfactants and GO-SO₃H/surfactants. The former also performed better in the O/W interfacial tension than the latter. These results reveal that NPs of various dimensions had a different morphology at the O/W interface in the presence of aminated PS. The spherical CDs-SO₃H had a diameter of approximately 2.71 nm; the rod-like CNCs-OSO₃H had a diameter of 5–20 nm and a length of 100–200 nm; and the lamellar GOs-SO₃H had a diameter of 1.2–4.0 µm and a thickness of 0.8–6.6 nm. Considering the effect of NP dimension on the

Figure 4: Aminated PS (1 mg/mL) compounded with CNCs-OSO₃H (10 mg/mL) at various pHs. (a) PS-NH₂ ($M_n \approx 0.5k$); (b) PS-NH₂ ($M_n \approx 2.1k$); (c) PS-NH₂ ($M_n \approx 2.9k$); (d) PS-NH₂ ($M_n \approx 3.2k$); (e) H₂N-PS-NH₂ ($M_n \approx 0.9k$); (f) H₂N-PS-NH₂ ($M_n \approx 2.3k$).

arrangement efficiency of NPs/surfactants at the interface, the CDs-SO₃H (0 dimension) had a more compacted structure with surfactants than the CNCs-OSO₃H and GOs-SO₃H.

To gain a better understanding of the interaction between NPs and aminated PS in the O/W interface and their final assembly, a MD simulation was performed for a total time length of 100 ps (Video 1 in supporting files). The evolution of the structure of the phase interface over

time can be observed in the snapshots shown in Figure 7. For clarity, only H₂N-PS-NH₂ and CD-SO₃H molecules are shown, while solvent molecules are hidden. It can be found that when the time is 0 ps, the NPs in the aqueous phase aggregated with each other, and only few moved to the interface.

With the increase in the simulation time, H₂N-PS-NH₂ in toluene and CDs-SO₃H in the aqueous phase attracted each other by the electrostatic force, and more NPs moved to

Figure 5: Aminated PS (1 mg/mL) compounding with NPs (10 mg/mL) at pH = 3: (a) CDs-SO₃H; (b) CNCs-OSO₃H; (c) GOs-SO₃H.

the interface and combined with H₂N-PS-NH₂ to form NPs/surfactants. Eventually, it can be observed that both H₂N-PS-NH₂ and CD-SO₃H molecules were concentrated on the phase interface and approached each other under the influence of the electrostatic attractions. At 100 ps, the assembly of H₂N-PS-NH₂ and CD-SO₃H reached a thermodynamic equilibrium, driving by the electrostatic force, which indicates that these two substances have a strong tendency to arrange in an orderly aggregation in the O/W interface.

Results of the MD simulation should not be interpreted as a conclusion that the NPs/surfactants interface can be formed and reach an equilibrium state in a short timescale such as 100 ps. In fact, in the starting point ($t = 0$ ps) of the MD simulations, part of NPs and surfactant molecules had already aggregated around the phase interface. Therefore, the MD simulation suggests that the system of the phase interface can return to the equilibrium state after a small perturbation. The MD simulation result can serve as a proof of the thermodynamic stability of the NPs/surfactants interface which will be reached in a short time, but not a reflection of the

dynamic process of phase interface formation in the macroscopic timescale.

4 Conclusions

In this study, PS-NH₂ with different molecular weights was synthesized by RAFT followed by chemical modification. H₂N-PS-NH₂ was prepared by ATRP and then modified by the Gabriel method. The factors determining the O/W interfacial tension of the compounding between aminated polystyrene and nanoparticles include the pH of aqueous phase, molecular weight of aminated PS, the density of amine groups and NPs dimension. The grafting density of amine groups in polystyrene and the dimension of nanoparticles play important roles, other than the pH and the molecular weight of functionalized polymers suggested by previous works (7,9), in adjusting the O/W interfacial tension. The compounding of H₂N-PS-NH₂ ($M_n \approx 0.9k$) with CDs-SO₃H at pH = 3 exhibited the highest efficiency to reduce the O/W interfacial tension to 4.49 mN/m, which is a

Figure 6: NPs (10 mg/mL) compounding with aminated PS (1 mg/mL) at pH = 3. (a) PS-NH₂ ($M_n \approx 0.5k$); (b) PS-NH₂ ($M_n \approx 2.1k$); (c) PS-NH₂ ($M_n \approx 2.9k$); (d) PS-NH₂ ($M_n \approx 3.2k$); (e) H₂N-PS-NH₂ ($M_n \approx 0.9k$); (f) H₂N-PS-NH₂ ($M_n \approx 2.3k$).

significant improvement compared with previous results (5,7,20). The results suggest that the density of amine groups has a positive correlation with the performance of aminated PS. NPs with a smaller dimension also contribute to the lowering of O/W interfacial tension. The molecular simulation results of the evolution of the distribution of NPs and aminated PS at the O/W interface revealed that CD-SO₃H and H₂N-PS-NH₂ reach a distribution equilibrium within a considerably short time. The simulation of the evolution of NPs/surfactants interaction at the O/W interface showed that the equilibrium was reached after 100 ps, and this result indicated that the orderly NPs/surfactants assembly contributed to the thermostability of

the O/W interface and makes the latter return to the equilibrium state quickly after a small perturbation. Our next simulation research includes changing the concentration of NPs and surfactants, as well as prolonging the duration.

The fast and significant reduction in O/W interfacial tension induced by NPs/surfactants assembly could be applied in both enhanced oil recovery and inkjet printing. Based on the results of this study, we plan to carry out further research on both increasing the number of amino groups in PS and decreasing the size of CD-SO₃H, aiming at lowering the O/W interfacial tension by more than an order of magnitude.

Figure 7: MD simulation of H₂N-PS-NH₂ compounding with CDs-SO₃H; (a) 0 ps; (b) 3 ps; (c) 10 ps; (d) 25 ps; (e) 50 ps; (f) 100 ps.

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