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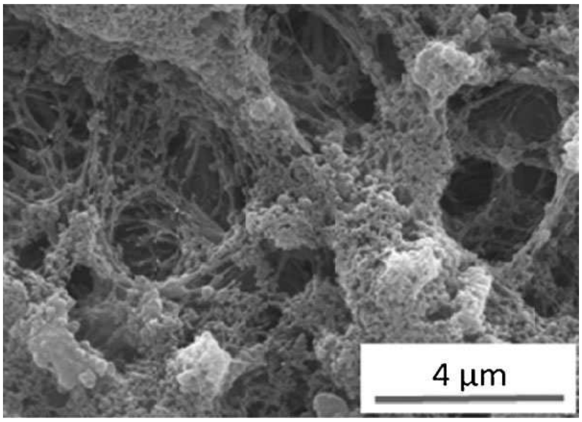
Spherical Comb Copolymer Micelles and their Application in the Construction of Superhydrophobic Surfaces

Zhe Cui, Jianfu Ding,* Ludmila Scoles, Qingjun Wang, Qingmin Chen

A comb copolymer with a fluorinated FPAE main chain and narrowly dispersed PMS graft chains has been prepared. The micellization behavior of this copolymer in a methanol/acetone mixture was studied. DLS studies showed hydrodynamic diameters of the micelles between 50 and 80 nm, while the diameters of dry micelles were ≈40 nm in TEM images. Micelle films with an interesting porous composite structure of nanofibers bearing micelle particles on the surface have been prepared by double coating the micelle solution. Superhydrophobicity with a WCA of 165° and a sliding angle of 3° was observed. As comb copolymers can adjust their molecular weight and block length independently, materials with a high physical strength and controllable morphological structure can be obtained.



Introduction

Superhydrophobic surfaces with high water repelling properties including a contact angle larger than 150° and a sliding angle smaller than 10° have attracted much interest because of its significance in fundamental research and many applications,[1] such as self-cleaning,[2,3] anti-biofouling,[4] non-stick[5] and low friction[6] surfaces. Previous works show that low surface energy and micro-/nano-binary structure (MNBS) are two essential factors to achieve superhydrophobic surfaces.[7,8] A lot of techniques have been utilized to prepare such surfaces,[8–10] but most of them are expensive associated with a complicate processing, which is undesirable for practical use. Facile processing of superhydrophobic surfaces is still a hot issue that a lot of researchers are working on.

It is well-known that block and graft copolymers are able to construct nanostructures in bulk or in a block selective solvent by self-assembly due to the combination effects of the phase separation of different blocks and the restriction from the chemical linkage between them. Polymer micelles formed in a block selective solvent have received a lot of attention because of their essential core/shell structure,[11] which is very useful for many applications, such as solubilizers,[12] drug carriers[13] and so on. The uniform size distribution of the micelle particles also allows them to assemble higher order structures.[14] These properties also give researchers inspiration to fabricate superhydrophobic surfaces. Xu's group has assembled surfaces with a high

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water repellency from block copolymer micelle solutions.[15–18] Chang's group also utilized the self-assembly of pincushion-like micelle particles of poly(vinylphenol)-*block*-polystyrene (PVPh-*b*-PS) to produce superhydrophobic surfaces.[19] Hong et al. produced multifunctional films with tunable superhydrophobicity via the layer-by-layer deposition of positively charged polystyrene-*block*-poly(4-vinylpyridine) (PS-*b*-P4VP) and negatively charged polystyrene-*block*-poly(acrylic acid) (PS-*b*-PAA) micelles onto colloidal particles.[20] Since the molecular weight of a block copolymer is not adjustable independently with the block length, which determines the morphological structure of the self-assembled materials, the physical strength and durability of the formed materials are usually restricted. Apparently this shortcoming can be overcome by graft copolymers, which allow the molecular weight and block length to be adjusted independently. However, the application of micelles from graft copolymers in the preparation of superhydrophobic surface has not been reported previously.

In this work, we synthesized a fluorinated comb copolymer poly(arylene alkylene ether)/poly(α-methylstyrene) (FPAE-PMS), and studied its micelle formation behavior in methanol/acetone mixtures using dynamic light scattering (DLS) and transmission electron microscopy (TEM). Finally we coated the micelle solution on a substrate to construct films with binary nano-/micro-structures. The film exhibits excellent water repelling properties.

Experimental Part

Materials

4,4'-dihydroxybenzophenone (99%), *t*-butyldimethylsilyl chloride, imidazole (>99%), *N*,*N*-dimethylformamide (DMF), α-methylstyrene ($\geq$99%) and *sec*-butyllithium (*s*-BuLi; 1.4 M in cyclohexane) were obtained from Aldrich and used as received. Tetrahydrofuran (THF) for anionic polymerizations was distilled from purple benzophenone/sodium under dry argon. 1*H*,1*H*,6*H*,6*H*-perfluoro-1,6-hexanediol and decafluorobiphenyl were purchased from Oakwood Products Inc. and used as received. Anhydrous dimethyl acetamide (DMAc) was used for condensation polymerizations. All the purifications and chemical reactions were performed under a dry argon atmosphere using standard Schlenk techniques. All the other solvents and reagents (obtained from Aldrich) were reagent grade and were used as received.

Characterization

The molecular weights of the polymers were determined by size exclusion chromatography (SEC) using a Viscotek SEC system, which consisted of a Viscotek VE1122 HPLC pump coupled with a Viscotek TDA Triple detector and a Viscotek 2501 UV detector operated at 260 nm. A set of ViscoGEL columns (G4000H and G5000H) was used and calibrated using polystyrene standards in THF. NMR spectra were recorded in acetone-d_6 using a Varian Unity Inova spectrometer at a resonance frequency of 400 MHz for ^{1}H NMR and 376 MHz for ^{19}F NMR. DSC measurements were performed on a TA Instruments DSC 2920 using a heating rate of 10 $^\circ C \cdot min^{-1}$ under nitrogen. A Brookhaven model 9025 light scattering instrument equipped with a 632.8 nm He-Ne laser was utilized to perform DLS analyses. The data were analyzed by the cumulant method to obtain hydrodynamic diameters d_h and polydispersity (K_2/K_1^2).[21] In this test, 1.0 mL of FPAE-PMS solution in acetone was first filtered through a 0.1 μm poly(tetrafluoroethylene) (PTFE) filter (Whatman Co.) into a quartz light scattering cell. Then, an additional amount of acetone followed by a calculated amount of methanol were filtered into the cell to obtain a desired methanol/acetone (M/A) ratio and a concentration of 0.3 $mg \cdot mL^{-1}$. DLS data were collected every 5 min after the solution was prepared. TEM observations were completed on a Philips CM20 instrument operated at 120 kV. The TEM samples were prepared by spraying the micelle solution onto carbon coated copper grids using a home-made spray gun. The surface structures of the micelle films were observed using scanning electron microscopy (SEM, JAM-840A, JEOL). Samples were sputter-coated with a thin Au layer prior to the SEM tests. The contact and sliding angles of the films were measured with a FTA 200 contact-angle meter (Folio Instruments) by dropping a 10 μL water droplet on the top. In addition, a home-made tilting stage was used to measure sliding angles. All the data were the average value of five original data points from the tests. An optical microscope (Leitz DMRD, Leica) was utilized to observe the trace of the water droplet left on the prepared film.

Preparation of the Fluorinated Comb Copolymer

The comb copolymer was prepared following a previously reported procedure,[22,23] which is outlined in Scheme 1. Briefly, a poly(α-methylstyrene) (PMS) macromonomer with an average degree of polymerization (DP) of 22 ($\overline{M}_n = 2800$ Da) and a polydispersity index (PDI) of 1.04 was first prepared using an anionic polymerization. Then the obtained PMS macromonomer (2.880 g, 1.03×10^{-3} mol of bisphenol end unit), 1*H*,1*H*,6*H*,6*H*-perfluoro-1,6-hexanediol (2,129 g, 8.12×10^{-3} mol), perfluorobiphenyl (3.088 g, 9.24×10^{-3} mol), CsF (4.26 g, 28×10^{-3} mol, pre-dried by heating at 150 °C for 30 min under a vacuum) and anhydrous DMAc (60 mL) were added into a 100 mL round-bottom flask, The mixture was gently purged with argon under vacuum and then stirred at 22 °C. The reaction was stopped after 6 h by centrifuging the solution to remove the salt. The supernatant was then dropped into methanol with stirring to precipitate the polymer. The resulting fibrous white powder was collected and washed with methanol and then vacuum dried to give 7.03 g of product (yield 91%). The n/m ratio was 7.9:1 (design) and 7.8:1 (calculated from ^{19}F NMR), $\overline{M}_n = 53\,500$ Da, PDI = 2.41.

^{1}H NMR (acetone-d_6): $\delta = 7.6$–6.5 (m, aromatic protons of PMS), 5.17 (t, $J = 13.4$ Hz, 4H, $-CH_2-$ in the diol unit), 2.2–0.0 (m, aliphatic proton of PMS). ^{19}F NMR (acetone-d_6): $\delta = -121.9$ [m, 8F, F^d (see Scheme 1)], -124.4 (m, 8F, F^c), 141.3 (m, 8F, F^a), -157.2 (m, 8F, F^b).

Preparation and Characterization of the Micelle Films

7.5 mg of the copolymer was dissolved in 1.0 mL of acetone, and then 0.5 mL of methanol was slowly added into the solution with agitation to form a micelle solution with a concentration of

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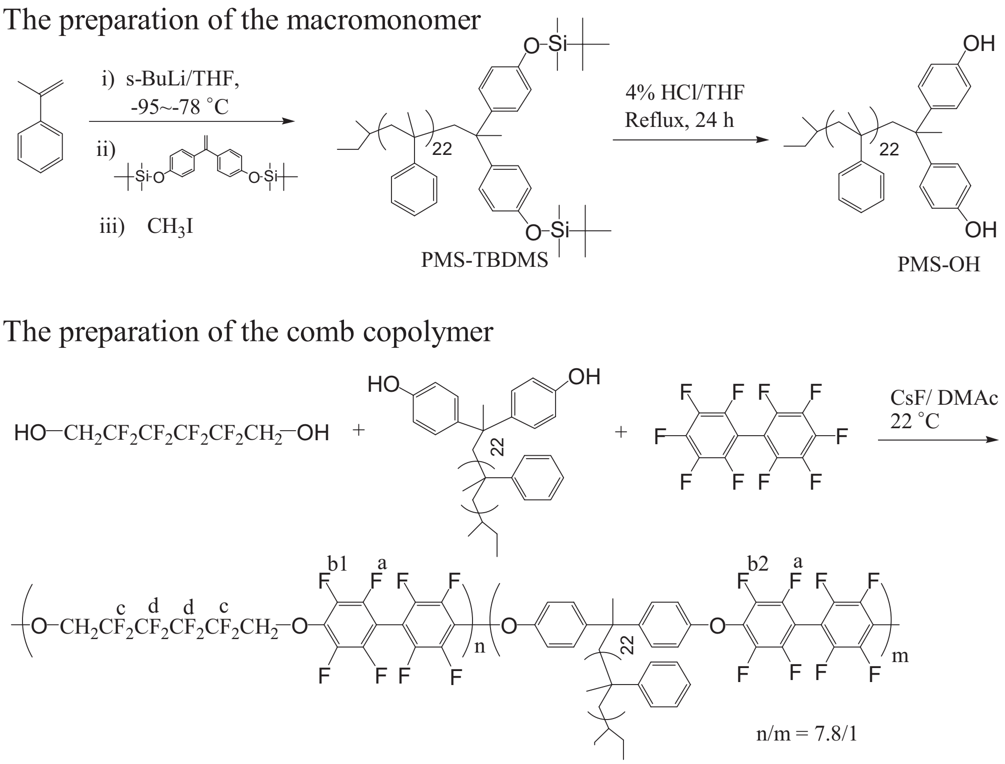

■ *Scheme 1.* Preparation of the FPAE-PMS comb copolymer.

5.0 mg · mL^{-1} and an M/A ratio of 2/4. Single layer films with a thickness of ≈3 μm were prepared by drop-coating the micelle solution on silicon wafers or glass plates and the solvents were evaporated freely in air at room temperature. For the purpose of promoting the superhydrophobicity of the surface, double layer films were also prepared, where the first layer was prepared by drop-coating the micelle solution on the substrate followed by baking at ≈140 °C for 5 min to obtain a transparent film with a thickness of ≈5 μm. Then the second layer was coated on the top of the first layer in the same manner as used to coat the single layer film to give a double layer film with a total thickness of ≈8 μm.

Results and Discussion

Material Preparation and Characterization

The FPAE-PMS comb copolymer was designed to comprise a highly fluorinated polyether main chain and narrow dispersed PMS graft chains for the purpose of the formation of micelle particles in a selective solvent, where PMS graft chains formed the core and FPAE main chain formed the corona. The narrow dispersion of the side chain length (PDI = 1.04) will offer the polymer a capability to form uniform nanospheres with a narrow size distribution in a micelle solution by self-assembly, and the high molecular weight of the copolymer will ensure a high physical strength of the formed materials.

The n/m ratio of the copolymer was designed to be 7.9/1, so that the copolymer contained 38 wt.-% of the PMS graft chain by considering its DP = 22. This ratio was confirmed by comparing the integral intensity of the aromatic proton peaks at around 7.0 ppm and that of the aliphatic proton peak of the diol unit at 5.17 ppm in the ^{1}H NMR spectrum in acetone-d_6 (Figure 1). This ratio is found to be 17/4, which results in 38.2 wt.-% of the PMS content in the copolymer, very close to the designed value.

This result was also confirmed by ^{19}F NMR spectroscopy (Figure 2), where the peaks were assigned using the labels defined in Scheme 1. The resonance of the *meta*-fluorine of the biphenyl units was split into a strong peak at $\delta = -157.2$ and a weak peak at $\delta = -155.5$, corresponding to the two different adjacent units, diol and PMS bisphenol. Therefore, the intensity ratio of these two peaks in fact represents the n/m ratio, which was found to be 7.8/1, resulting in 38.3 wt.-% of the PMS content. This value is in good agreement with that from ^{1}H NMR measurements, and perfectly matched the design, indicating all the monomers were completely incorporated during the polymerization. It is interesting to note that the peak of the *ortho*-fluorine of the biphenyl unit at $\delta \approx 141$ was split into four peaks with intensity ratios of 1/7.8/7.8/7.8^2. This is also attributed to the existence of the two different adjacent units of the biphenyl. The formed triads could have four different combinations, AA, AB, BA, and BB (A represents for PMS bisphenol, and B for diol). They resulted in four peaks in the spectrum. From the previous discussion, we know the A/B ratio is 1/7.8, consequently the intensity ratio of these four

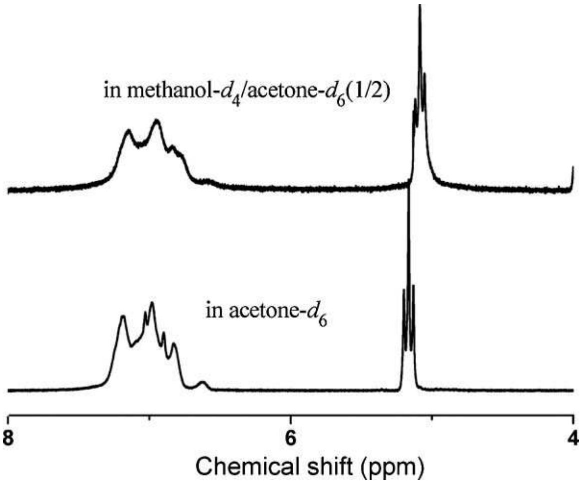

Figure 1. ^{1}H NMR spectra of the FPAE-PMS in acetone and in a micelle solution.

peaks equals AA/AB/BA/BB = 1/7.8/7.8/7.8^2. The expanded spectrum of these peaks in the inset of Figure 2 confirmed these ratios. The thermal behavior of the polymer was studied by DSC. Figure 3 shows a melting peak at 187 °C, indicating a certain crystallization capability of the comb copolymer, which should come from the FPAE main chain. However, the heat of this peak is only about 18% of the main chain homopolymer and the T_m is about 32 °C lower (18.3 J · g^{-1}, 219 °C for the FPAE homopolymer),[24] indicating the crystallization of the main chain in the copolymer was significantly depressed by the graft structure.

Micelle Particle Formation in Methanol/Acetone Mixtures

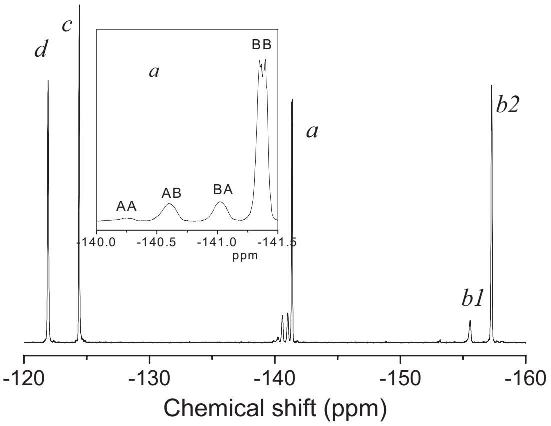

Figure 2. ^{19}F NMR spectra of the FPAE-PMS in acetone-d_6.

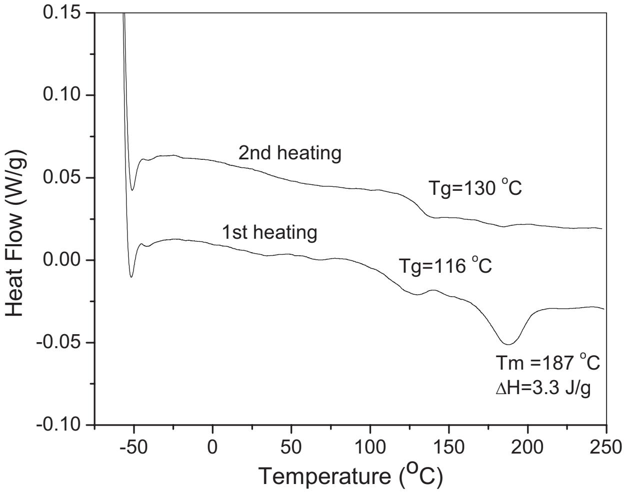

Figure 3. DSC curves of the first and second heating scan of the comb copolymers.

The micelle solutions of this comb copolymer were prepared in M/A mixtures, which acted as a block selective solvent when the M/A volume ratio was in the range of 1/4 to 4/4. Acetone is a good solvent for FPAE main chains, but a relatively poor one for PMS graft chains, while methanol is a poor solvent for both. When the copolymer is dissolved in acetone, PMS graft chains contract to some extent while FPAE main chains stretch in the solution. The addition of methanol will aggravate the collapse of the graft chains to form a core, while the main chains form a corona layer of a micelle particle. 38 wt.-% of PMS content makes the copolymer possibly form spherical micelle particles in a block selective solvent. The NMR test was used to confirm the formation of the micelle particles. The NMR spectra of the comb copolymer in an acetone-d_6 and in a micelle solution (methanol-d_4/acetone-d_6, 2/4) are compared in Figure 1, which were collected in the following sequence. First, the spectrum in acetone-d_6 (Figure 1(a)) was collected, and then methanol-d_4 in half quantity of acetone-d_6 was added into the NMR tube and mixed completely. A bluish micelle solution was formed inside the tube. The ^{1}H NMR spectrum was collected again [Figure 1(b)]. To eliminate the influence of the concentration change to the peak intensity, the two spectra were normalized to the integral intensity of the acetone peak at $\delta = 2.05$. It was observed that the peak of the methylene proton of the diol unit at $\delta \approx 5.15$ slightly broadened with a slightly reduced integral intensity (0.226 versus 0.245) in the micelle solution, indicating the mobility of the main chain slightly reduced. While the aromatic proton band at $\delta \approx 7.0$ from PMS graft chain became much broader than in acetone-d_6, meanwhile, the integral intensity of this band reduced by about 40% (0.528 versus 0.888). This result indicates that the mobility of the PMS graft chain is significantly reduced in the micelle solution. This phenomenon only can be explained by the formation of micelle particles with the core formed by the PMS graft chains and the corona formed by the FPAE main chains. However, this result also indicates that the graft chains in the core still have mobility to some extent in the micelle solution, attributed to a high swelling ratio of the core. The

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^{19}F NMR spectrum of the micelle solution (not shown) was also collected and compared with the spectrum in acetone-d_6. It only showed a slightly peak broadening, indicating the fluorine containing main chain was well dispersed in the solution to form a corona layer.

Dynamic light scattering (DLS) was used to monitor the formation of the micelle particles, where the hydrodynamic diameter d_h and polydispersity K_2/K_1^2 of the micelle particles at different times after the micelle solution was prepared were detected. The change of d_h as a function of the time at M/A ratios of 1/4, 2/4, 3/4 and 4/4 is presented in Figure 4. It can be clearly seen that the formation of the micelle particles follows two different patterns in this M/A range. When the M/A ratio was 1/4, a steady increase in particle size with time was found; this means that the micelle solution was not stable and that aggregation was occurring. The initial particle size was above 130 nm, about double the size under the other three M/A ratios, indicating the core of the micelle particles in the solution is highly swelled. Under this condition, the core formed by the graft chain was not firm enough to hold the whole polymer chain. In addition, with the highly stretched main chain in the corona, it increased the potential to aggregate nearby particles together to form clusters. Under this M/A ratio, the K_2/K_1^2 value is $\approx$0.2, about double the value for the other three ratios, showing a much higher size distribution of the particles due to the continuous aggregation of the particles.

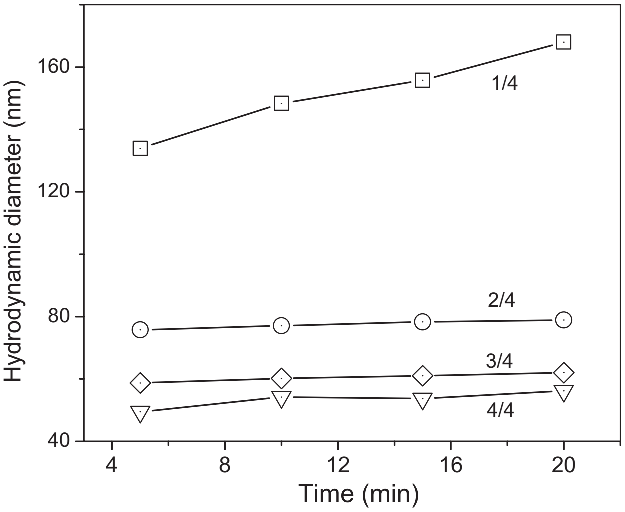

Figure 4. The variation of d_h values of micelle particles with time after the micelle solution was prepared in methanol/acetone mixture at M/A of 1/4, 2/4, 3/4, and 4/4. The concentration of the copolymer in each micelle solution was 0.3 mg · mL^{-1}.

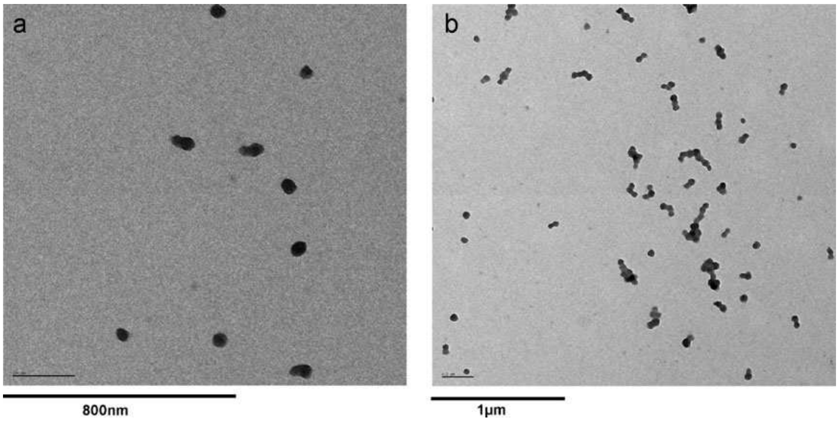

Figure 5. TEM images of micelle particles prepared at a concentration of 0.19 mg · mL^{-1} and M/A of 4/4.

When the M/A ratio increased to 2/4, 3/4 and 4/4, the solvent is getting poorer. This resulted in a less swelled core to stabilize the structure of the micelle particles. Under these ratios, the d_h values and the polydispersities of the micelle particles became stable 10 min after the micelle solutions were prepared. The d_h values were 77, 60 and 55 nm for M/A ratios of 2/4, 3/4 and 4/4, respectively, and the polydispersities were all around 0.1, meaning a narrow size distribution. This indicates that 10 min is necessary for the micelle solution to reach equilibrium in this M/A range. After this, the micelle solutions showed good stability. The size difference of the micelle particles under the different M/A ratios is associated with the variation of the swollen ratio of the particles. With the increase of the methanol content, the mixture solvent became poorer for both the graft PMS chain and the FPAE main chain. It obviously reduced the hydrodynamic size of the micelle particles. The TEM observations of the micelle particles prepared from the solutions confirmed this result. No apparent difference in size was found from the dry particle samples of the solutions at M/A ratios of 2/4, 3/4 and 4/4. Figure 5 displays a TEM image of the micelle particles prepared from the solution (0.19 mg · mL^{-1}) at an M/A ratio of 4/4. It shows a narrow size distribution of the micelle particles with a diameter of $\approx$40 nm. This result is in agreement with the DLS observations by considering the swelling of the micelle particles in the solution. A further study in detail of the TEM image in Figure 5(a) shows that the spherical micelle particles are not perfectly round. They have more or less irregular shapes. This structural feature is significantly different from what is observed for the micelle particles of block copolymers. Though this phenomenon is rarely reported, we believe that this irregular surface morphology represents the true surface structure of the micelle particles from graft copolymers. In these micelle particles, the graft chains with uniform chain length form the core and the main chains form the corona, so that the core size of the micelle particles is well controlled by the narrow dispersed length of graft chain, which results in a narrow size distribution of micelle particles. However, the thickness of the corona layer at different positions on the surface of a particle is dependent on the length of individual main chain segments defined by two adjacent graft points. Although its average value is determined by the n/m ratio (see Scheme 1), the length of the individual segments has a very wide distribution for a graft copolymer because of the randomly dispersed graft points in the main chain. It will result in a large variation of the thickness of the corona layer and lead to an irregular shape for the dry micelle particles.

Hydrophobicity of the Micelle Films

The capability of the micelle solution for the formation of superhydrophobic surfaces was tested. The micelle solution was drop-coated on a silicon wafer or a glass plate and the solvents were evaporated freely in air at room temperature to form a film with a thickness of ≈3 μm. The film showed a white color, indicating a porous bulk structure. An SEM image of the surface in Figure 6(a) shows a relative smooth surface on a μm scale but rough on a nanometer scale. The film was comprised of loosely packed micelle particles accompanied with small cracks. This structure was formed by the aggregation of micelle particles during the solvent evaporation. It should be noted that the solvent in the micelle solution is a mixture of methanol and acetone (1:2, v/v). Acetone is a more volatile solvent than methanol. The free solvent evaporation in air will make the solvent become poorer in the micelle solution. It is beneficial to maintain the core/shell micelle particle structure, meanwhile to aggregate the particles onto the substrate to form a porous film as indicated by the SEM image in Figure 6(a).The hydrophobicity of the film was tested by water contact angle and sliding angle measurements. The tests revealed a water contact angle (WCA) of 140°. However, the water droplet tightly stuck on the surface, meaning a sliding angle larger than 90°. It indicates this surface is at the Wenzel regime,[25] i.e., water can penetrate into the film. This result was checked by an optical microscopy test, where the trace of water in the film was examined. Therefore, a water droplet (5 μL) containing a small amount of red dye, Rhodamine 590, was placed on the surface of the film. It was then removed after 5 min by gently touching with a piece of a filter paper. The top and bottom surface of the film was observed by microscopy in a reflection mode. Figure 7 (a1) and (a2) show the images of the top and bottom surface of the film, respectively. The top view picture clearly shows a complete stain of the red dye, indicating a close contact of water with the film surface. Furthermore, three cyclic stain areas were also observed on the bottom view picture, indicating water penetrating through the film in these areas. This made the film act as a Wenzel surface.[25] This behavior might be attributed to the existence of cracks in the film, as observed in Figure 6(a), which allowed the water reach and spread on the polymer-glass interface due to the hydrophilic property of the glass substrate to make the water droplet pin on the surface tightly. To improve the water repelling property, we attempted to eliminate the influence from cracks by inserting a dense copolymer layer between the micelle film and substrate to screen off the hydrophilic substrate. Therefore a double layer film was prepared by depositing a second micelle layer on a dense first micelle layer. The first layer was prepared by drop-coating a 5 μm thick micelle film on a substrate, followed by annealing at 140 °C for 5 min. On the formed transparent film, the second micelle layer of 3 μm thick was then coated in the same manner as used to coat the single layer film. Surprisingly the formed double layer film appeared more porous than the single layer film under naked eyes. An SEM image of the double layer film revealed a different morphological structure compared to the single layer film. Figure 6(b) shows that this sample possessed a honeycomb structure comprising nanofibers decorated by micelle particles on the surface. This structure possesses a higher roughness than that of the single layer film in Figure 6(a). The formation of the fiber-like structure is unusual. It is possibly converted from the spherical micelle particles during the solvent evaporation. In some conditions, spherical micelle particles are able to convert to nanofibers by self assembly,[26] but it is a slow process and the formed fibers have a diameter close or larger than the size of the

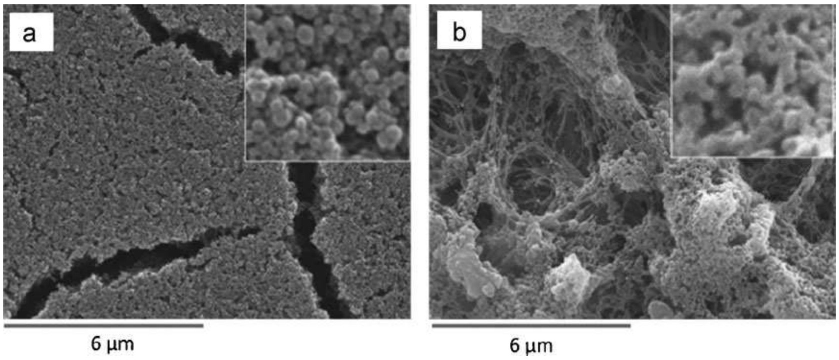

Figure 6. SEM image of (a) the micelle film (≈3 μm) prepared by drop-coating the micelle solution; (b) the composite film prepared by drop-coating the second micelle layer on the top of the annealed first micelle layer (≈5 μm). The inserted pictures are images at a larger magnification of a 1 × 1 μm² area.

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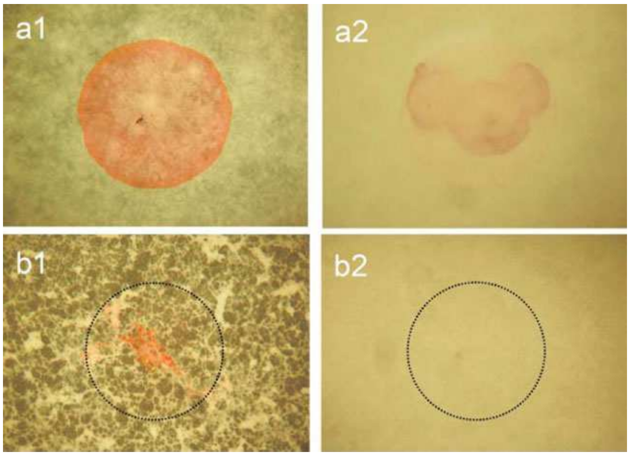


Figure 7. Front view (1) and back view (2) images of a water droplet (containing trace of Rhodamine 590) stain of the polymer films coated on glass surface. a) single layer film (≈3 μm) coated from the micelle solution; b) double layer film by coating the micelle solution on the top of an annealed micelle film (≈8 μm), the dot circle represents the contact line of the water droplet (magnification: 50×).

spherical particles. However, Figure 6(b) shows a much smaller diameter of the fibers than spherical particles. Therefore this sphere/fiber conversion is unlikely in the present test. Moreover, as mentioned above, the solvent evaporation will make the solvent in the micelle solution poorer, making it much more difficult for the micelle particles to change size and shape. Another possibility is that the nanofibers were formed from the annealed bottom micelle layer. It should be noted that the polymer in the corona layer is the FPAE, which has a high crystallization tendency. Therefore, during the annealing of the bottom micelle layer, a dense film with certain crystallinity was formed, which is beneficial to protect the film from being damaged by the solvent used for the second layer coating. When the second micelle layer was coated on top of this annealed layer, this semi-crystalline structure allowed the solvent to attack the amorphous region of the film, while tending to hold the film structure. The combination of these effects produced a honeycomb nanofiber structure, as shown in Figure 6(b). This assumption was confirmed by the SEM image of an annealed micelle film shown in Figure 8, where the annealed micelle film was treated with a methanol/acetone mixture (1/2, v/v) in the same way as coating the micelle solution. Honeycomb structures with nanofibers formed inside the cells can be clearly seen. Therefore, when the solvent mixture was replaced with micelle solution, along with the formation of the fiber structure, the micelle particles aggregated on the nanofiber surface to form the composite structure, as shown in Figure 6(b). It is worth noting that using a film of the main chain homopolymer to replace the annealed first micelle layer in this test produced a similar composite structure, indicating the crystal structure of the bottom layer is important in forming the porous fibrous structure.

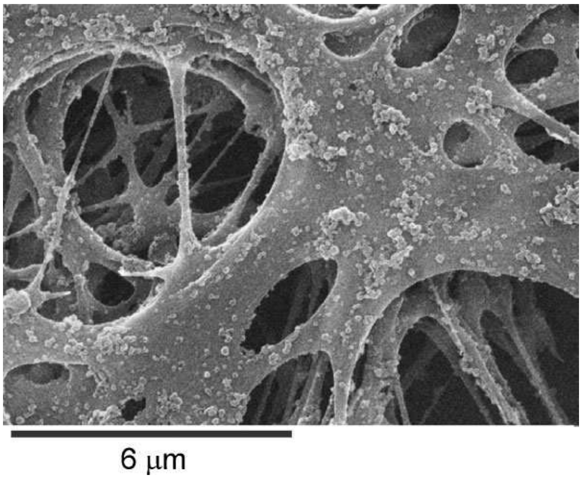
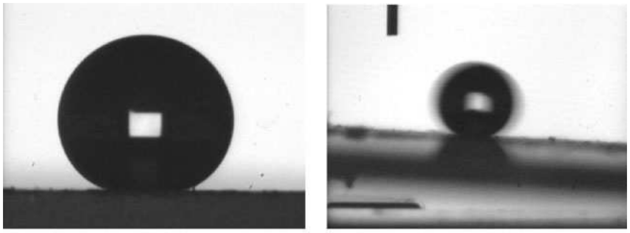


Figure 8. SEM image of the honeycomb structure formed from an annealed micelle film by treating with a mixture solvent of methanol/acetone (1/2, v/v).


CA 165.5°±3.0°

SA around 3°

Figure 9. The hydrophobicity test of the double layered micelle film.

The obtained double layer film displayed an excellent superhydrophobic property with a WCA of 165° and a sliding angle of 3° (Figure 9). The water contact test by microscopy shown in Figure 7(b1) and (b2) indicates the water droplet does not closely contact the film, and no water penetrates through the film either. This result indicates the surface is at the Cassie regime.[27]

Conclusion

Spherical micelle particles were prepared from the fluorinated graft copolymer FPAE-PMS in methanol/acetone mixtures, where micelle particles were formed, with the FPAE main chain forming a corona and the PMS graft chain forming the core. DLS showed that when the M/A ratio reached above 2/4, the micelle particles were stable and uniform. The hydrodynamic diameter of the particles was about 78 nm in the solvent with a M/A ratio of 2/4, and decreased with increasing methanol content. The micelle solution became unstable when the M/A ratio went below 2/4 or above 4/4. A TEM study showed that the particle size was around 40 nm with a narrow size distribution in the M/A range of 2/4 to 4/4, independent of the solvent composition. Superhydrophobic films were prepared by double coating the micelle solution. The film has a binary nano-/micro-honeycomb structure, where the cells of the honeycomb were filled with nanofibers and the surface was covered with micelle particles. The films exhibited excellent superhydrophobicity with a WCA of 165° and a sliding angle of 3°. This process provides a practical and promising method for fabricating large scale highly water repellent polymeric surfaces.

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