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ORIGINAL CONTRIBUTION

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Influence of solution conditions on formation of amphiphilic hyperbranched polyanion/ linear polycation multilayer films

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Abstract Amphiphilic hyperbranched polyester (P2) consisting of a hydrophobic core, surrounded by aromatic carboxylic acids, is self-assembled into aggregates in aqueous solution at pH region of 3.8–4.7 and in THF–water mixed solution at THF/water volume ratio of 1/100–1/10. With P2 in both aqueous and THF–water mixed solution as polyanion and linear poly(diallydimethylammonium chloride) (PDAC) as polycation, self-assembled films were successfully formed by layer-by-layer dipping. The solution condition of P2, including the pH of aqueous solution and the THF/water volume ratio, affected not only the absorption behavior of P2 but also the surface morphology and hydrophilicity of the films with P2 as the outmost layer. At lower pH or higher THF/water volume ratio the aggregation of P2 in solution was enhanced, thus resulting in higher adsorption rate for P2, more rough and less hydrophilic surface for the films.

Keywords Amphiphilic hyperbranched polymer · Self-assembly film · Solution condition · Surface morphology · Surface hydrophilicity

Introduction

Electrostatic adsorption self-assembly is a convenient technique to fabricate polyelectrolytes into ultrathin films with well-defined nano-microstructures on various substrates, such as quartz, silica, clay, and even colloidal particles [1–3]. By dipping the substrates into polycation and polyanion solutions, alternately, electrolytes in the solution would adsorb onto the substrate surface layer-by-layer (LBL), hence this technique is also noted by LBL dipping [4]. Since the first report about LBL in 1991 [1], various kinds of polyelectrolytes, including amphiphilic polymers were used in this process and the parameters affecting the adsorption behaviors have been reviewed [5]. On the other hand, hydrophobic polyelectolytes, including block polyelectolytes, associating polyelectolytes, and polysoaps were found to form self-assembled aggregates in solution due to their amphiphilic structures [6]. The addition of salt or change in pH of the aqueous solution was possible to affect the micellar morphology of charged diblock copolymers [7–9]. Moreover, the selective solvent for one of the blocks in an amphiphilic diblock copolymer could also affect the aggregation behavior [10, 11]. Through change of the solution conditions, the growth and architecture of the polyelectrolyte multilayers were controlled to a large extent [12, 13].

Much recently, dendritic molecules, including dendrimers and hyperbranched polymers, were used as polyelectrolytes to form self-assembled films by LBL dipping due to their unusual chemical and physical properties arising from branching architectures and large number of end-groups. Ultrathin films formed from poly(aminoamine) (PAMAM) dendrimer and poly(sodium *p*-styrenesulfonate) (PSS) via sequential deposition were reported [14, 15]. Multilayer films comprising of a generation 3.0 dendrimer and NLO-active polyanion PAZO were formed by ionic self-assembly [16]. Self-assembled films with fluorescence properties were obtained from hyperbranched conjugated poly(phenylene vinylene) (SPPV) through the covalent bond linkage [17]. In our pervious articles, ionizable hyperbranched polyesters were used as polyanions to form self-assembled films with linear polycations [18, 19]. However, to our knowledge, the influence of solution conditions of hyperbranched polymers on formation of self-assembled film has not been investigated.

Recently, we observed that an amphiphilic hyperbranched polyester was able to aggregate into spherical micelles in DMF–water mixed solution [20]. In this study, based on the same polymer (defined as P2), the influence of solution conditions, including solution pH and THF/water volume ratio on the aggregation behavior of P2 was investigated. With P2 as polyanion and linear poly(diallydimethylammonium chloride) (PDAC) as polycation, self-assembled films were formed by LBL dipping. The influence of solution condition on the adsorption behavior of P2, the surface morphology, and hydrophilicity of the films were investigated.

Experimental

Materials and characterization

A 20% solution of PDAC (MW: 200,000–350,000) was purchased from Aldrich. Initial polymer (P1) and modified polymer (P2) were prepared by a procedure mentioned in Qiu et al. [20] with the number average molecular weights (M_n) of 1,280 and 1,695, and the polydispersity of 1.15 and 2.02, respectively. All the other reagents were of analytic grade and were used without further purification. ^{1}H NMR spectrum of P2 was measured on BBI-300 with d_6-DMSO as the solvent.

Formation of aggregates in aqueous solution

The solution temperature for the formation of aggregates was kept at 25 ± 1°C. P2 was dissolved initially in NaOH aqueous solution at pH of 11.0 and concentration of 0.2 g/l. After adjusting to pH 4.5 by hydrochloric acid, the solution was analyzed by dynamic light scattering (DLS) on a Zetasizer 3000HS instrument at an angle of 90°.

Formation of aggregates in THF–water mixed solution

P1 and P2 were separately dissolved in THF to a concentration of 1.60 g/l. Following this, 0.15 ml of the solution was dropped into 15 ml deionized water under ultrasonication (50 W). After 2 h stabilization, several drops of phosphotungstic acid in 2 wt% aqueous solution were added for staining. The samples placed on carbon-coated grids were imaged on a transmission electron microscopy (TEM, H-800). In addition, 1.5 ml of the same P2 THF solution was dropped into 15 ml water to form a solution at THF/water volume ratio of 1/10. The solution of P2 at THF/water volume ratios of 1/10 and 1/100 were measured by DLS.

Multilayer fabrication with P2 in aqueous solution

The solution temperature was kept at 25 ± 1°C during the formation of self-assembled films. PDAC was diluted to a 0.1 mmol/l concentration with Milli-Q water (resistance > 18 MΩcm) and used as polycation. P2 was dissolved in Milli-Q water with a 0.2 g/l concentration and used as polyanion. Suitable amount of NaOH was added to increase the solubility of polyanions. The solution was adjusted by hydrochloric acid to various pH. Quartz slides were used as adsorption substrates and were treated by the methods mentioned in Qiu et al. [18]. A freshly treated quartz slide was alternately dipped in DPAC and P2 aqueous solutions for 10 min each. After each dipping, the slide was washed with excess Milli-Q water for 2 min and dried in air stream.

Multilayer fabrication with P2 in THF–water mixed solution

According to the volume ratio of THF/water, suitable amount of P2 was dissolved in THF–water mixed solution to a constant concentration of 0.2 g/l. Assembly films were fabricated from PDAC and P2 in THF–water mixed solution by the method mentioned above.

Characterization of self-assemble films

The assembling procedure for multilayer formation on quartz slides was monitored by UV–vis spectrometer (Perkin-Elmer Lambda Bio-40). The contact angle for water of the assembled films was measured with a contact angle measuring device (Dataphysics, OCA-20). The surface morphology of the films was viewed by Atomic Force Microscopy (AFM, Nanoscope IIIa, tapping Mode).

Results and discussion

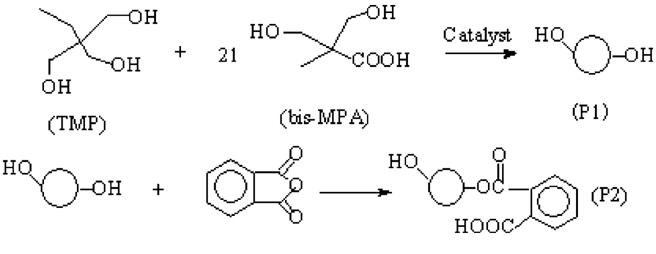
Synthesis and characterization

The synthetic procedure for initial and modified hyperbranched polymers was outlined in Scheme 1. P1 was synthesized from 2,2-bis(methylol) propionic acid (bis-MPA) and tris(methylol) propane (TMP) at a molar ratio of 21/1 by pseudo one-step synthesis method as reported by Malmström [21]. With triethylamine as the catalyst, P1 was further reacted with phthalic anhydride in refluxing acetone for 4 h to yield P2 with some terminal aromatic carboxylic acid groups. These two polymers were characterized in detail in our previous article [20]. In this study, the substitution degree of hydroxyl groups by aromatic carboxylic acid groups was calculated by ^{1}H NMR.

Figure 1 is the ^{1}H NMR spectrum of P2. The peaks at 7.55–7.71 ppm are responding to aromatic protons with a total intensity of 3.906. The peaks at 0.97–1.23 ppm are responding to $-CH_3$ with a total intensity of 4.356. In the FT-IR spectrum of P1, the characteristic adsorption band for carboxylic acid was not found. Hence it could be considered that all bis-MPA had been reacted into P1. According to the molar ratio between bis-MPA and TMP, the ratio between hydroxyl groups and methyl groups in P1 is 24/22. With the ^{1}H NMR intensity of $-CH_3$ as an internal standard, the substitution degree was calculated to be 61.2%. Due to the irregular reaction of hydroxyl groups in P1, both the molecular weight and the polydispersity of P2 are higher than those of P1.

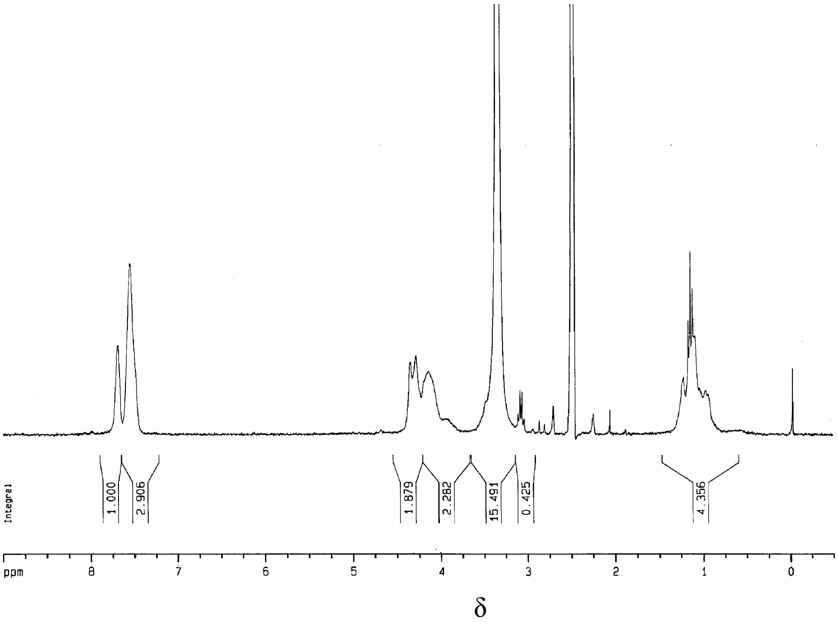
Aggregation behavior in solutions

Due to the existence of some aromatic carboxylic acid groups, P2 was completely dissolved in NaOH aqueous solution at pH 11.0. The solution pH was decreased gradually by hydrochloric acid until precipitate was formed at pH 3.7. At pH region of 11.0–4.8, the solution was transparent and colorless. DLS measurement of the solution indicated that no micelle was formed at this pH region. However, at a narrow pH region of 4.7–3.8, the solution turned to translucent and slightly blue. DSL measurement of the solution at pH 4.5 indicated that micelles were formed with their *z* average size (D_z) and volume average size (D_v) of 151.5 and 124.0 nm, respectively. It indicated that the solution pH is important in controlling the hydrophilic–hydrophobic balance and the molecules could self-assembly into aggregate within an adequate pH region. On the contrary, P1 was completely insoluble in water due to the lack of hydrophilicity.



Scheme 1 Synthetic procedure for P1 and P2

Fig. 1 ^{1}H NMR spectrum of P2



In addition, both P1 and P2 could be dissolved in THF. So THF could be regarded as a good solvent for the interior core. The THF solutions of P1 and P2 were separately dropped into large amount of water under ultrasonic vibration. After staining by phosphotungstic acid, the samples placed on carbon-coated copper grids were observed by TEM. From the photographs in Fig. 2, no typical morphology is noticed in the P1 system. But for P2 system, clear spherical particles with average diameter of about 100 nm are shown even though the size distribution is wide. Such morphology should be attributed to the amphiphilic structure of P2. In THF–water solution, the interior hydrophobic chains prefer to aggregate together into micelle core with the help of THF, which is stabilized by hydrophilic carboxylic acid groups. According to our recent study, the hyperbranched polymer with higher M_w/M_n can form aggregates in solution with wider size distribution [22]. So the wide-size distribution for P2 aggregates could be attributed to the irregular molecular structure of P2.

The THF–water solution of P2 was further measured by DLS to demonstrate the formation of micelles. The results shown in Table 1 indicate that the solution composition has some influence on the size and size distribution of the micelles. Increasing the volume ratio of THF/water from 1/100 to 1/10, both the size and the size distribution (expressed by D_v/D_n) increased. This result implies that the aggregation of the molecules was enhanced by increasing the content of THF in the solution, which should be due to the decreasing in ionizing degree of carboxylic acid groups in the solution with a decreased polarity. Meanwhile, as a result of DSL measurement, no micelle was formed for P1 in THF–water mixed solution.

Table 1 Influence of solution composition on the size and size distribution of P2 aggregates formed in THF–water mixed solution

THF/water volume ratio	D_z	D_v	D_n	D_v/D_n
1/100	250.1	270.4	164.9	1.64
1/10	371.2	371.4	187.5	1.98

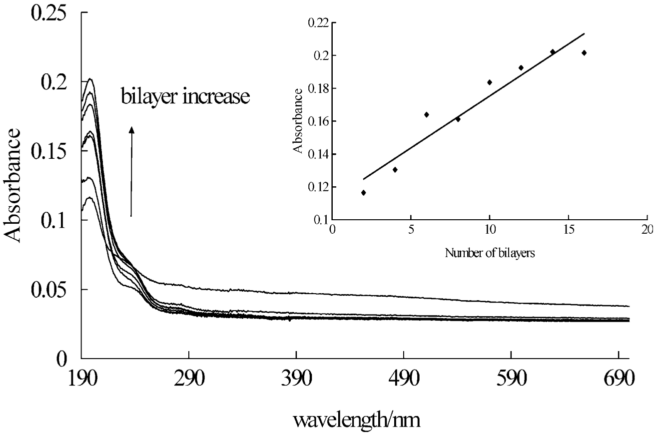
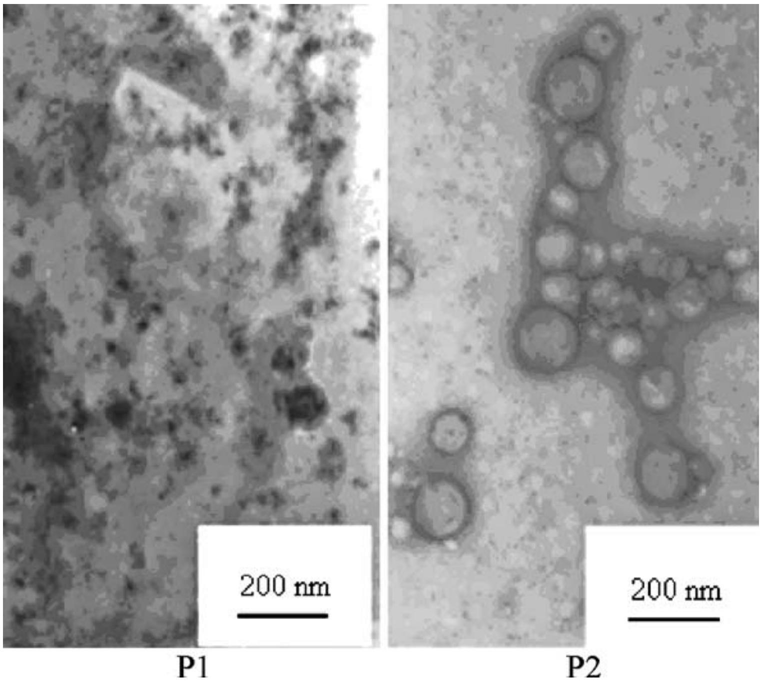


Fig. 3 The growth of bilayer with P2 in aqueous solution at pH 5.5

Fig. 2 Morphology of P1 and P2 in THF–water mixed solution at THF/water volume ratio of 1/100



P1

P2

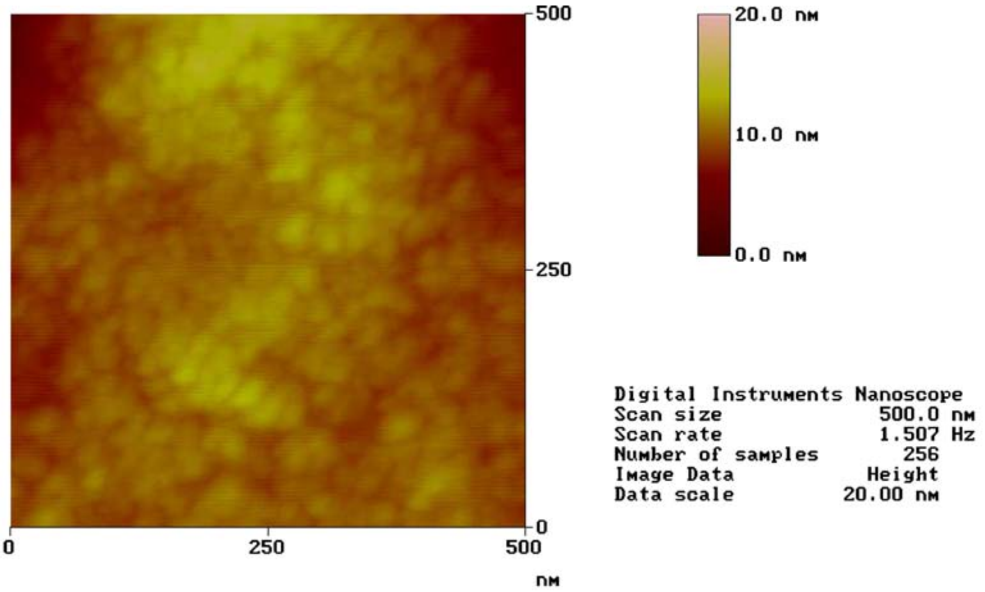
Table 2 Influence of pH of P2 aqueous solution on the absorbance at 196 nm and contact angle of the assembled films

pH of P2 aqueous solution	4.1	5.1	6.1	7.7	> 8.0
Absorbance at 196 nm (a.u.)	1.53	0.95	0.40	0.22	< 0.12
Contact angle for water (°)	54.8	54.6	53.8	49.4	–

Formation of self-assembled films with P2 in aqueous solution

It has been reported that the pH of the dipping solution of weak polyelectrolytes has significant influence on the growth and architecture of the polyelectrolyte multilayer [12]. As one kind of weak polyacid, P2 in aqueous solution was used as polyanion to form self-assembled films by LBL dipping with PDAC as polycation. Because P2 showed strong absorption in UV–vis spectrum, and PDAC did not, the building course of the assembled film on quartz slide could be monitored by UV–vis spectrometry. A typical UV–vis spectrum for the assembled film is shown in Fig. 3. The increase of the absorbance at 196 nm indicated the growth of the film thickness. The linear relation between the absorbance and the number of bilayers indicated that the thickness

Fig. 4 Influence of pH of P2 aqueous solution on the surface morphology of the assembled films with P2 as the outmost layer



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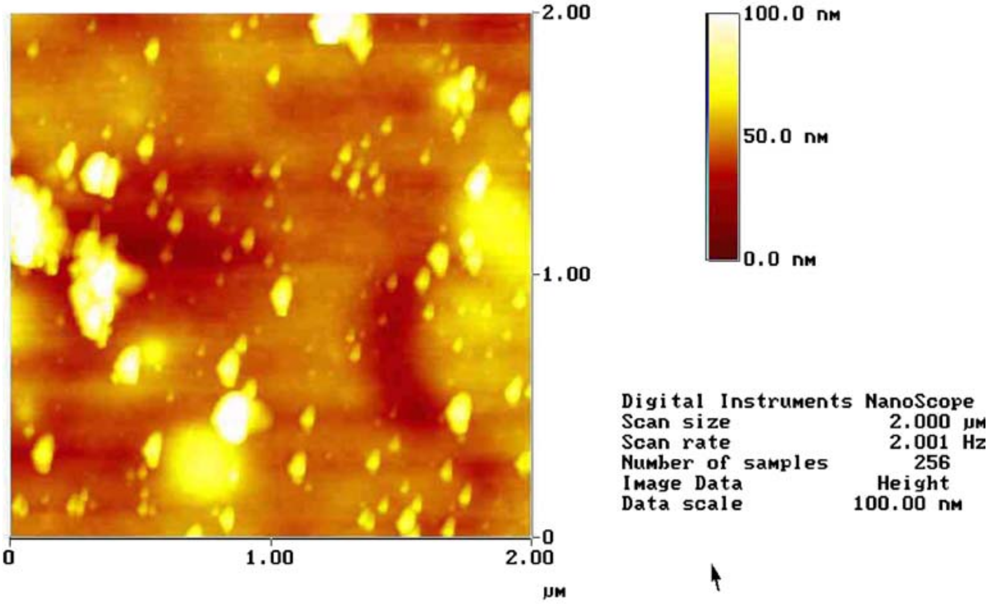
Scan rate 1.507 Hz
Number of samples 256
Image Data Height
Data scale 20.00 nm

pH= 5.5



Digital Instruments NanoScope
Scan size 2.000 µm
Scan rate 2.001 Hz
Number of samples 256
Image Data Height
Data scale 100.00 nm

pH=4.5

of every bilayer was nearly the same. So these two polyelectrolytes with opposite charges could self-assembly into multilayer structure driven by electrostatic adsorption. The maximum absorption intensity at 196 nm could be used to determine the loading amount of P2 on the film.

A series of self-assembled films in eight numbers of monolayers with P2 as the outmost layer were formed from PDAC and P2 in aqueous solution at various pH. The influence of solution pH on the absorbance of P2 on the film is shown in Table 2. It is noticed that the absorbance decreased gradually on increasing the solution pH. So in addition to electrostatic adsorption, the hydrophilic–hydrophobic balance of the polymer chains can affect the assembly behavior as well [12, 23]. The high absorbance for the film formed from P2 at pH 4.1 implies that the formation of aggregates in solution is in favor of adsorption of P2 molecules. Meanwhile, the contact angle of the films was measured to study the surface hydrophilicity. The results in Table 2 indicate that the contact angle decreased slightly on improving the solution pH. Since the slide was washed with Milli-Q water for sufficient time after each dipping, the change in contact angle could be related to the surface feature of the films rather than the ionizing degree of carboxylic acid groups in P2.

The surface of the films formed from PDAC and P2 in pH 5.5 and pH 4.5 aqueous solutions were further imagined by AFM. From Fig. 4a, it could be distinguished that the film formed at pH 5.5 possesses a rather smooth surface consisting of many tiny particles in an average diameter of about 20 nm. However, at pH 4.5 there are some pits on the surface as shown in Fig. 4b, which means a rough surface is formed. So the film surface can be changed from highly flat to rough state on decreasing the solution pH. The different surface morphologies should be related to the different adsorption fashion of P2. From DSL measurement, P2 molecules existed in solution as non-aggregating form at pH 5.5 due to the high static repulsion force of ionizing carboxylic acid groups, which also meant that the molecules have stretching conformation. During the fabrication of P2 monolayer, the molecules were absorbed onto the film as monomolecular form. So the molecules got onto the film slowly and arranged well with each other. In this case, a regular surface was formed. However, at pH 4.5, P2 molecules could aggregate together into micelles due to the hydrophilic–hydrophobic balance. During the formation of P2 monolayer, the molecules were absorbed onto the film mainly as micellar form. The irregular interaction between PDAC molecules on preformed layer and P2 micelles also makes the micelles accumulating irregularly on the film. So both the adsorption of P2 molecules and the surface roughness became high while increasing the solution aggregation of the molecules. Furthermore, the surface hydrophilicity seemed to decrease while increasing the surface roughness of the film.

Formation of self-assembled films with P2 in mixed solution

Self-assembled films were also formed from PDAC and P2 in THF–water mixed solution at various THF/water volume ratios. Figure 5 indicates that the absorption spectra of typical PDAC/P2 multilayers varied with bilayer growth. The linear relation between the absorbance at 205 nm and the number of bilayers indicated that assembled film was also formed with P2 in THF–water mixed solution. The influence of THF/water volume ratio on the adsorption amount of P2 is shown in Table 3. The absorbance at 205 nm was found to increase with increasing the content of THF in the solution. Considering the DLS results, the higher adsorbing amount of P2 at higher THF/water volume ratio should be related to the enhancement in solution aggregation of the molecules. From Table 3, it is also shown that the contact angle of the films increased at higher content of THF in the solution. It is worth mentioning that a large difference in contact angle resulted by changing the solution composition. The contact angle for the film

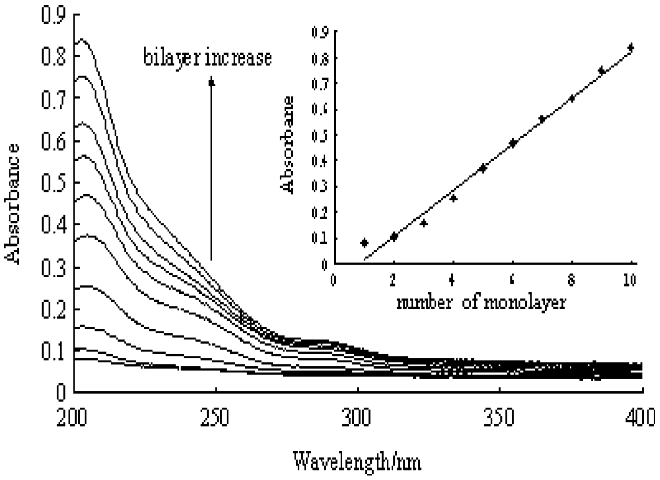


Fig. 5 The growth of bilayer in THF–water mixed solution at THF/water volume ratio of 1/50

Table 3 Influence of THF/water volume ratio on the absorbance at 205 nm and contact angle of the assembled films

THF/water volume ratio	1/100	1/50	1/40	1/10
Absorbance at 205 nm (a.u.)	0.14	0.16	0.20	0.23
Contact angle for water (°)	41	58	61	63

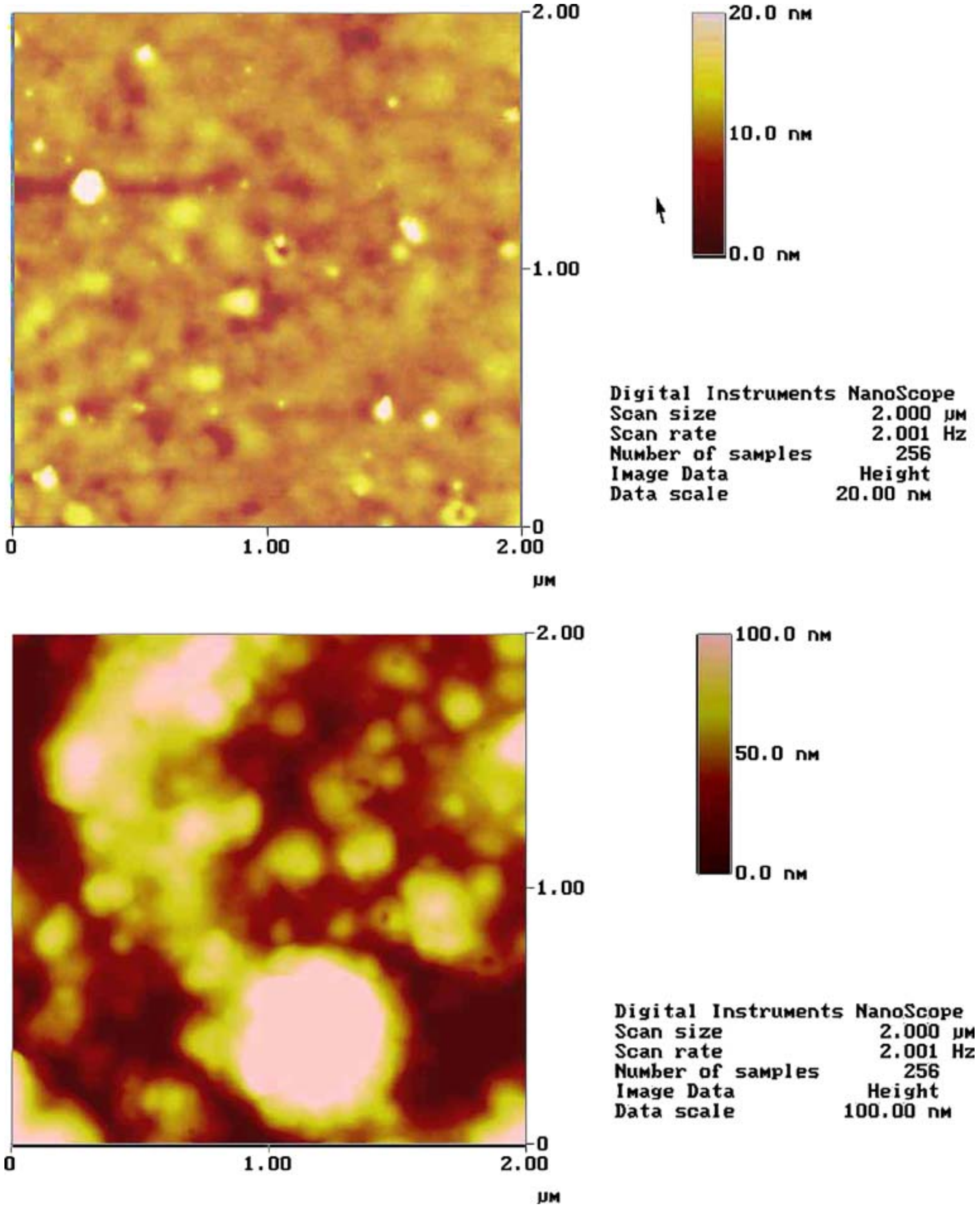


Fig. 6 AFM photography of the assembled film with P2 as the outmost layer formed from PDAC and P2 in THF–water mixed solution at THF/water volume ratio of (**a**) 1/100 and (**b**) 1/10

formed at THF/water volume ratio of 1/10 is 22° higher than that formed at THF/water volume ratio of 1/100.

The assembled films with P2 as the outmost layer formed at THF/water volume ratio of 1/100 and 1/10, respectively, were further observed by AFM and the results were shown in Fig. 6. At THF/water volume ratio of 1/100, a rather flat surface covered nearly entirely by P2 molecules was noticed. However, at THF/water volume ratio of 1/10, some large and deep pits were noticed on the film surface. So the surface roughness was affected by THF/water volume ratio. The different surface morphologies should also be attributed to the different adsorption fashion of P2 molecules. Based on DSL measurement, the aggregation of the molecules was enhanced and larger micelles were formed at higher content of THF. In this case, the adsorption of P2 molecules on the assembled film was also enhanced. In addition, the higher surface roughness obtained at higher THF content should be related to both the irregular accumulation of larger micelles and the strong hydrophobic association of the molecules even on the film. The change in contact angle in Table 3 at various THF/water volume ratios could also be attributed to the change in surface roughness of the films because the micro- and nanostructured rough surface of a film can affect the contact angle greatly [24].

From the above results, it is interesting to note that through controlling the solution aggregation behavior of amphiphilic hyperbranched polymer by solution pH or solution composition, the adsorption behavior of the polymer, both the surface morphology and the hydrophilicity of the assembled films were adjusted to a large extent.

Conclusion

At adequate solution condition, amphiphilic hyperbranched molecules (P2) were able to aggregate into micelles in both aqueous solution and in THF–water mixed solution. Self-assembled films were successfully formed by LBL dipping from PDAC and P2 in these two solutions. At lower pH or higher THF/water volume ratio, higher adsorption rate for P2, more rough and less hydrophilic surface for the films was obtained, which were attributed to the aggregation enhancement of P2 in the solutions.

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