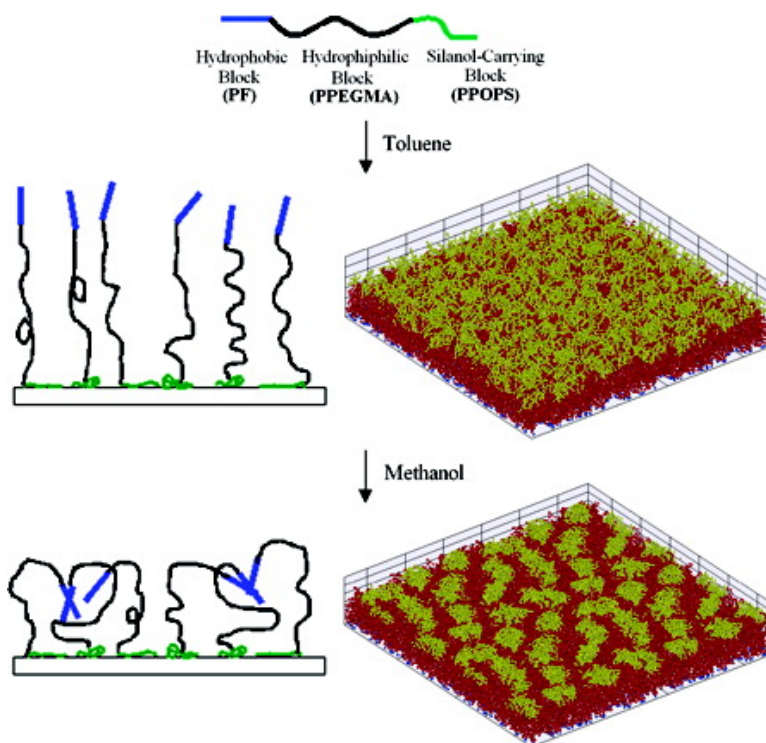


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Theoretical and Experimental Studies on the Surface Structures of Conjugated Rod–Coil Block Copolymer Brushes

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A combined theoretical and experimental investigation of conjugated rod–coil block copolymer brushes is reported. The theoretical study for the surface structures of rod–coil block copolymer brushes was established based on the simulation method of dissipative particle dynamics. The effects of solvent stimuli, grafting density, and rod–coil block ratio of the polymer brushes on the surface structures were examined. The rod blocks of polymer brushes were found to be well-dispersed on the surface in their good solvents. On the other hand, aggregative domains of the rod blocks were formed in their poor solvents with the conformations of isolated islands or worm-like structures depending on the grafting density of the polymer brushes. The aggregative domains tend to stay on top of the coil blocks for small rod-to-coil block ratio. However, the submergence of the aggregative domains into the coil blocks is thermodynamically preferred for large enough rod-to-coil block ratio. New multifunctional amphiphilic rod-coil block copolymers, poly-[2,7-(9,9-di-*n*-hexylfluorene)]-block-poly-[poly(ethylene glycol) methyl ether methacrylate]-block-poly-[3(triisopropoxysilyl)propyl methacrylate] (**PF-b-PPEGMA-b-PPOPS**), with two different block ratios were synthesized and used to prepare the corresponding polymer brushes via the grafting- method. The effects of stimuli factors on the surface structures characterized by the atomic force microscopy images were consistent with the theoretical results. Furthermore, the photophysical properties of **PF-b-PPEGMA-b-PPOPS** brushes were significantly varied by the solvent stimuli. The emission peaks originated from the aggregation and/or excimer formation of **PF** blocks were observed after methanol treatment. The photoluminescence intensity and its efficiency were well correlated to the surface structure and the methanol content in mixed solvents. Our study demonstrates how the surface structures and photophysical properties of rod–coil block copolymer brushes response to environmental stimuli.

Introduction

Polymer brushes have been recognized as a fascinating synthetic target because of their ability in surface modification and potential applications in many fields.^{1–18} The chemical characteristics of polymer segments give thermal and solvent

stabilities in various environments and processing conditions, which are potential for certain applications such as switching membranes, sensors, and cell growth control.^{19–26} Two primary approaches for preparation of polymer brushes are grafting-to and grafting-from methods.¹⁵ The grafting-to method means that polymers are anchored onto surface via chemical bond formation between reactive groups on the surfaces and reactive end-groups in the polymer backbones. The grafting-from method, or commonly known as “surface-initiated polymerization”, utilizes the initiators bound to surfaces to prepare polymer brushes from monomers. It is a powerful alternative to control the functionality, density, and thickness of polymer brushes with almost molecular precision. However, conjugated polymer rod–coil brushes via surface-initiated polymerization have seldom been explored because of the synthetic difficulty of conjugated backbones.

Rod–coil block copolymers consisting of a π -conjugated polymer as the rod and a flexible block as the coil are an unique and interesting class of nanomaterials because it opens the way for the tuning of both molecular organization and optical properties of these materials by controlling their aggregation structures.^{27–32} Several fluorene-based rod–coil and coil–rod–coil block

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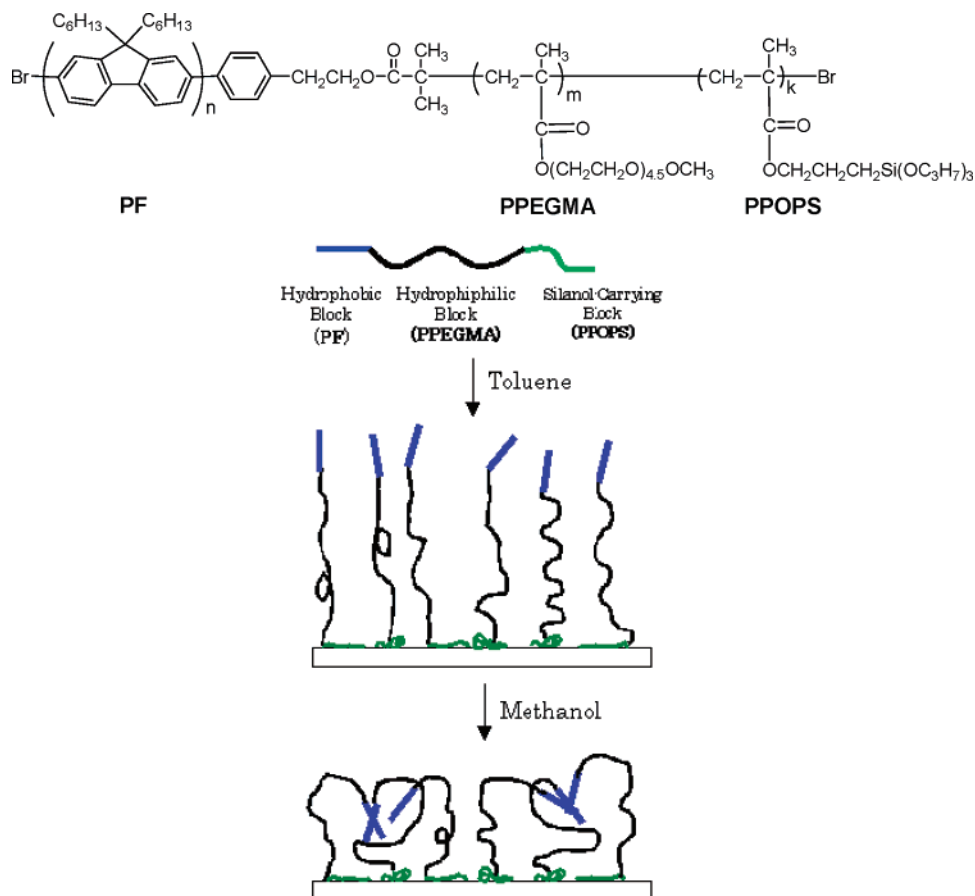


Figure 1. Chemical structure of the amphiphilic triblock copolymer, **PF-b-PPEGMA-b-PPOPS**, and the corresponding polymer brush under solvent stimuli.

copolymers have been reported because they exhibit high thermal and chemical stability and high fluorescence quantum yields in both solution and solid state.^{33–38} The equilibrium properties of polymer brushes, such as surface structures and optical properties, are determined by the environmental stimuli (solvent stimuli for example), polymer chain length, and grafting density. Therefore, it is worthwhile to investigate the relationship between the optoelectronic characteristics and the surface structures of polyfluorene-based rod-coil block copolymer brushes. In consideration of the synthetic difficulty of conjugated backbones via surface-initiated polymerization, the grafting-to method might be a possible approach for the formation of polyfluorene-based rod-coil block copolymer brushes.

In this study, a combined theoretical and experimental investigation of conjugated fluorene based rod-coil block copolymer brushes is reported. The equilibrium properties of

polymer brushes in various solvents have been studied by Monte Carlo (MC) simulations,³⁹ molecular-dynamics (MD),^{40,41} and dissipative particle dynamics (DPD).^{42–46} Because the DPD method has the ability to treat a wider range of length and time scales compared to atomistic simulations due to the consideration of soft forces, it is used for the present study. In this work, the effects of solvent stimuli, grafting density, and rod-coil block ratio of the polymer brushes on the surface structures were investigated. The resulting surface structures can then be compared with the experimental works. Two new rod-coil block copolymer brushes were prepared, as shown in Figure 1. The block copolymer, poly-[2,7-(9,9-di-*n*-hexylfluorene)]-b-poly-[poly(ethylene glycol) methyl ether methacrylate]-b-poly-[3-(tri-propoxysilyl)propyl methacrylate] (**PF-b-PPEGMA-b-PPOPS**), contains a polyfluorene (**PF**) as the hydrophobic, fluorescent rod block, poly-[poly(ethylene glycol) methyl ether methacrylate] (**PPEGMA**) as the hydrophilic coil block, and poly-[3-(tri-propoxysilyl)propyl methacrylate] (**PPOPS**) as the reactive block for anchoring the polymer onto glass or silicon substrates. Then, the block copolymers were assembled onto a glass substrate with the silanol groups anchored on the surface. The surface

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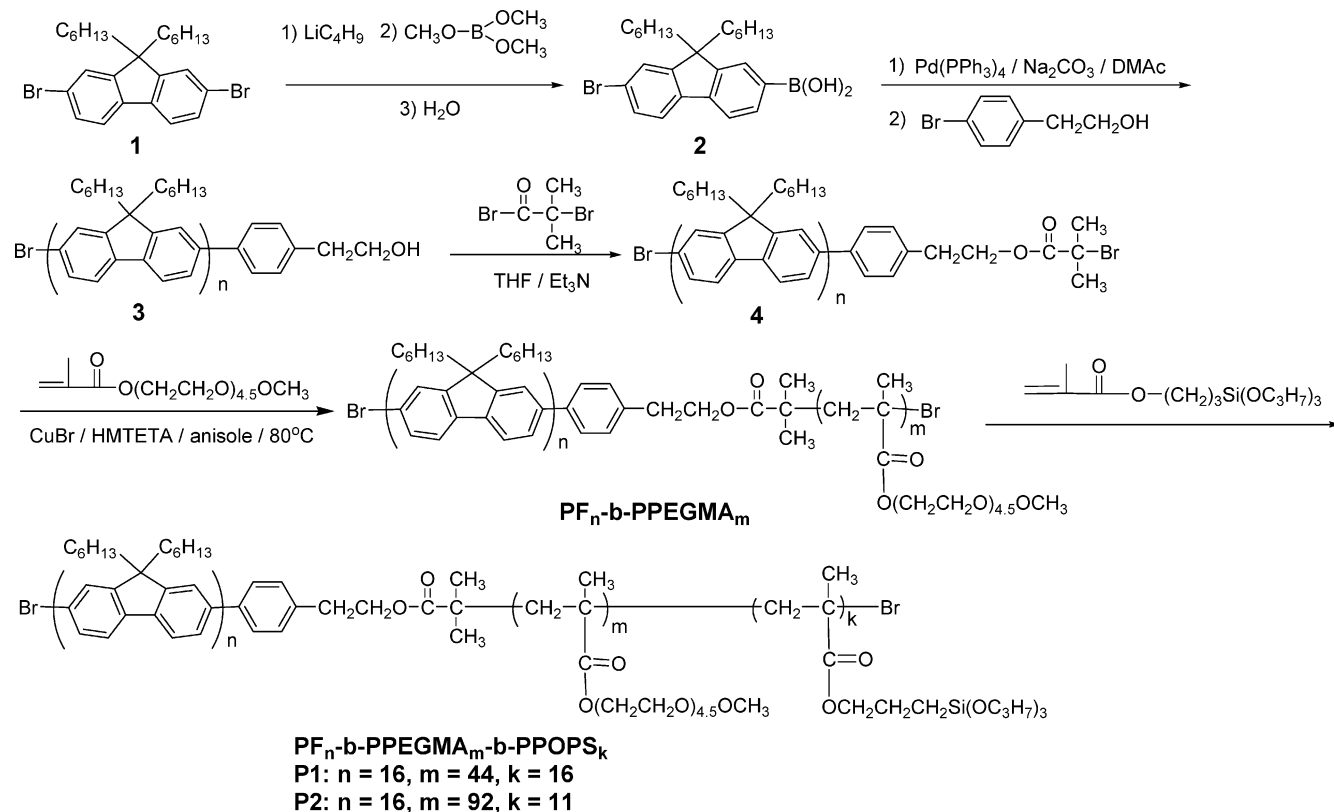
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Scheme 1. Synthetic Scheme of PF-b-PPEGMA-b-PPOPS



structures and photophysical properties of the polymer brushes were investigated by treating with toluene (good solvent for both the **PF** and **PPEGMA** blocks) and then with methanol (poor solvent for **PF** blocks, whereas good solvent for **PPEGMA** blocks). The present study demonstrates how the surface structures and photophysical properties of rod–coil block copolymer brushes response to environmental stimuli.

Theoretical Methodology

DPD Simulation Method. The simulation method used to study the surface structures of rod–coil block copolymer brushes was based on the DPD.^{47,48} The DPD is a mesoscopic simulation technique that can be used to study systems over greater length and time scales than are accessible in classical atomistic simulations like MC and MD. It has been successfully used to study morphologies and physical properties of polymer systems. The polymer model and simulation details are described as follows.

Model and Parameters for Rod–Coil Block Copolymer Brushes. In our system (volume $V = L_x \times L_y \times L_z$ with N particles), the polymer brush is modeled as a copolymer with sections of rod and coil blocks. The end-beads of the coil blocks are attached to an impenetrable surface at $z = 0$. The lengths of the rod and coil blocks are represented by n_A and n_B , respectively. The total number of particles in the system is $N = N_S + N_P(n_A + n_B)$ in which N_S and N_P are the numbers of solvent particles and polymer brushes. We define grafting (surface) density $\rho_S = N_P/(L_x \times L_y)$. Like MD, the DPD particles obey Newton's equation of motion. In addition to the three different pairwise-additive forces (conservative, dissipative, and random forces) considered in DPD simulations, the spring force (F^S) and angle force (F^θ) describing the chemical bonding and angle bending effects of

the polymer chain are also taken into account in this system and are given by

$$F_{ij}^S = c(\mathbf{r}_{ij} - 0.7) \quad (1)$$

and

$$F_{ij}^\theta = \begin{cases} k_\theta(\theta - \pi)^2 & \text{(for rod)} \\ 0 & \text{(for coil)} \end{cases} \quad (2)$$

In this work, we have chosen $c = 100$ and $k_\theta = 20$.

Our system volume is set to be $V = L_x \times L_y \times L_z = 30 \times 30 \times L_z$, and the total number density ($\rho = N/V$) is 3. The depth of the system, L_z , ranges from 15 to 25 depending on the length of the polymer brush. The length of the rod block is fixed at 5 (i.e., $n_A = 5$) and n_B varies from 5 to 30. In other words, the block ratio of rod to coil ranges from 1:1 to 1:6. The effect of different degrees of grafting on the surface structures also is studied and the grafting density (ρ_S) spans from 0.1 to 1.0.

The conservative force F^C for nonbonded beads is a soft repulsive force and the repulsion parameter a_{ij} is the maximum repulsion between particles i and j . Groot and Warren⁴⁷ showed that the repulsion parameter of 25 corresponds to a highly compatible pair. As the repulsion parameter increases, the compatibility between i and j particles decreases. In our study, a_{AS} , a_{BS} , and a_{AB} represent the maximum repulsive forces between rod block and solvent particle, coil block and solvent particle, and rod and coil blocks, respectively. We chose $a_{AS} = 26$ to symbolize the solvophilic nature of the rod block and $a_{AS} = 40$ to denote the solvophobic character of the rod block. The a_{BS} and a_{AB} were set to be 26 and 40, respectively, indicating good solvent condition for the coil block and incompatible characteristics between rod and coil blocks. The masses of the particles, the cutoff radius r_c , and $k_B T$ were put at 1 for simplicity. A

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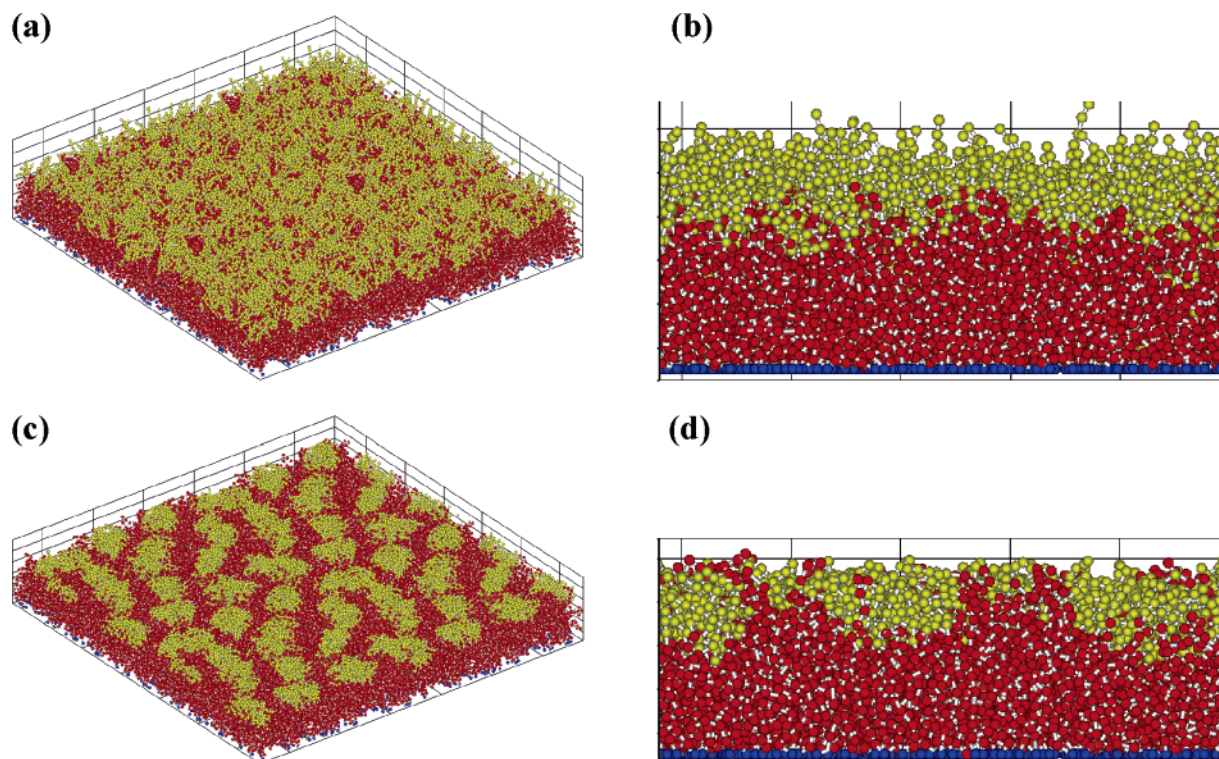


Figure 2. Simulated surface structures of rod-coil block copolymer brushes with the parameters of $\rho_S = 0.7$, $n_A = 5$, $n_B = 20$, $a_{BS} = 26$, and $a_{AB} = 40$: (a) top view (for $a_{AS} = 26$); (b) side view (for $a_{AS} = 26$); (c) top view (for $a_{AS} = 40$); and (d) side view (for $a_{AS} = 40$). The yellow and red spheres correspond to the rod and coil blocks, respectively. The blue spheres are the anchoring points of the copolymers on the surface. The system volume is set to be $V = L_x \times L_y \times L_z = 30 \times 30 \times 20$.

modified version of the velocity-Verlet algorithm was adapted with a time step of $\Delta t = 0.05$ and $\lambda = 0.65$.⁴⁹

Experimental

Materials. 2,7-Dibromofluorene, 2-bromophenethyl alcohol, 2-bromoisobutyryl bromide, 1,1,4,7,10,10-Hexamethyltriethylenetetramine (HMTETA, 97%), tetrakis(triphenylphosphine)palladium(0), *N,N*-dimethylacetamide (DMAc), anisole, and sodium carbonate were purchased from Aldrich and were used without purification. CuBr (Aldrich) was washed with acetic acid and then ether and then was dried under vacuum. Poly(ethylene glycol) methyl ether methacrylate (PEGMA, Aldrich, $M_n \approx 300$) was purified by distillation under vacuum before use. Tetrahydrofuran (THF) and ether were distilled from sodium/benzophenone under nitrogen. 3-(Tripropoxysilyl)propyl methacrylate (POPS),⁵⁰ 2,7-dibromo-9,9-di-*n*-hexylfluorene (**1**),⁵¹ and 2-bromo-9,9-di-*n*-hexylfluoreneboronic acid (**2**)⁵⁰ were prepared according to known procedures.

Synthesis. The preparation of the triblock copolymer is shown in Scheme 1.

α -[4-(2-Hydroxyethyl)phenyl]- ω -bromo-2,7-(9,9-dihexylfluorene) (**3**). 1.0 g (2.18 mmol) of compound **2**, 1.34 g of sodium carbonate, and 42 mg (0.037 mmol) of tetrakis(triphenylphosphine)palladium(0) were dissolved in 10 mL of anhydrous *N,N*-dimethylacetamide (DMAc). The solution was degassed and flushed with argon three times. After heating (120 °C) and vigorously stirring the mixture for 30 h, 1.5 mL (7.5 mmol) of 2-bromophenethyl alcohol was added as an end capping reagent. Heating overnight at 120 °C followed by reprecipitation of the reaction mixture into 300 mL of methanol afforded a solid. The solid was washed with water and then was dissolved into 5 mL of methylene chloride and was precipitated into 200 mL of methanol to afford 630 mg of polymer **3**. M_n (GPC) = 2700, $M_w/M_n = 1.80$. M_n (NMR) = 5500. The degree

of polymerization (DP) of polyfluorene is 16 based on the NMR result. ¹H NMR (300 MHz, CDCl₃): $\delta = 0.60$ –0.98 and 1.05–1.31 (s, b, 352H), 2.05–2.26 (m, 64H), 2.92 (t, 2H), 3.94 (t, 2H), 7.34–7.39 (m, 2H), 7.42–7.60 (m, 2H), 7.58–7.92 (m, 100H).

α -{4-[2-(2-Bromo-2-methylpropoxy)ethyl]phenyl}- ω -bromo-2,7-(9,9-dihexylfluorene) (**4**). 1.0 mL of 2-bromoisobutyryl bromide was added dropwisely to a solution of 620 mg of **3** and 2.0 mL of triethyl amine in 10 mL of dry THF, and the reaction mixture was stirred at room temperature for 24 h. After the mixture was poured into 200 mL of cold methanol, a solid was obtained. The solid then was redissolved into 5 mL of THF and reprecipitated into 200 mL of cold methanol to afford 590 mg of white powder with yield of 94%. M_n (GPC) = 2800, $M_w/M_n = 1.81$. M_n (NMR) = 5600. The DP of polyfluorene is 16. ¹H NMR (300 MHz, CDCl₃): $\delta = 0.60$ –0.98 and 1.05–1.31 (s, b, 352H), 1.96 (s, 6H), 2.05–2.26 (m, 64H), 3.04 (t, 2H), 4.36 (t, 2H), 7.34–7.39 (m, 2H), 7.42–7.60 (m, 2H), 7.58–7.92 (m, 100H).

Poly-[2,7-(9,9-di-*n*-hexylfluorene)]-*b*-*poly*-[*poly*(ethylene glycol) methyl ether methacrylate]-*b*-*poly*-[3(tripropoxysilyl)propyl methacrylate] (**PF-b-PPEGMA-b-PPOPS**, **P1** and **P2**). The amphiphilic triblock copolymers of **PF-b-PPEGMA-b-PPOPS** were prepared by atom transfer radical polymerization (ATRP)⁵² as shown in Scheme 1. In detail, 180 mg (~0.03 mmol) of **PF** macroinitiator **4** and 8.7 mg of CuBr (0.06 mmol) were added into a Schlenk tube and then vacuumed for 10 min. Under nitrogen atmosphere, a solution of PEGMA [450 mg (~1.5 mmol) for **P1**; 900 mg (~3 mmol) for **P2**] and 17.1 μ L (0.06 mmol) of HMTETA in 6 mL of anisole was added into the Schlenk tube. The mixture was degassed three times and then filled with Argon. After stirring at ambient temperature for 30 min, the Schlenk tube was immersed into an oil bath at 80 °C for 5 h. A small amount of the polymerization mixture was taken out from the polymerization mixture for the determination of conversion. ¹H NMR result shows the conversion is >95%. Then, 498 mg (1.5 mmol) of degassed POPS was added into the polymerization tube via microsyringe. The polymerization was continuously kept at 80

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°C overnight. After being cooled down to room temperature, the mixture was passed through an Al_2O_3 column to remove the copper and then was precipitated into an excess amount of ether resulting in a **PF-b-PPEGMA-b-PPOPS** triblock copolymer. The gas permeation chromatography (GPC) trace after the sequential addition of POPS shows a shift of the peak position to a higher molecular weight region, showing the successful preparation of the functional triblock copolymer. Through the controlling of the polymerization times and feed ratios of PPOPS or PPEGMA to **PF**, two triblock copolymers (**P1**, and **P2**) were synthesized. The ^1H NMR spectra of the purified triblock block copolymers indicate the DPs of PPEGMA and POPS of **P1** are 44 and 16, respectively, and those of **P2** are 92 and 11, respectively. The rod–coil block ratios (**PF/PPEGMA**) of **P1** and **P2** are about 1:3 and 1:6, respectively. M_n (GPC) M_w/M_n and M_n (NMR) of **P1** and **P2** are 13200, 1.52, and 24400, and 18600, 1.36, and 37100, respectively. Because the **PF** macroinitiator was obtained through a step-growth polymerization approach, the prepared **PF** macroinitiator has a high polydispersity of 1.81. The considerable decrease of polydispersity of the diblock copolymer **PF-b-PPEGMA** compared with that of the **PF** macroinitiator should be attributed to the well-defined PPEGMA chains existing in the copolymers through the ATRP process. Similar phenomenon was observed by Lu et al.⁵³ Details such as the ^1H NMR spectra and the GPC traces of **PF** macroinitiator, **P1** and **P2** are given in the Supporting Information.

Self-Assembly of Triblock Copolymers on Oxidized Surfaces and Solvent Stimuli. The polymer brushes were prepared by using a new surface-reactive method developed by Thomas et al.¹⁴ Glass substrates were cleaned by water followed by acetone. And then, the substrates were immersed into Piranha solution ($\text{H}_2\text{O}_2/\text{H}_2\text{SO}_4$ with 70:30 volume ratio) for 40 min. After washed by water, methanol, and then dried in vacuum oven for 2 h, the oxidized substrates were immersed in a toluene solution with a concentration of polymer ranging from 5 to 20 mg/mL and a small amount ($\sim 20 \mu\text{L}/\text{mL}$) of triethylamine as catalyst for 24 h at room temperature followed by repeated rinsing and ultrasonic washing with toluene three times. Finally, the films were Soxhlet extracted with CH_2Cl_2 for 46 h to remove any possible physical adsorbed polymers on the surfaces. To investigate the responses corresponding to environmental stimuli, the polymer brushes were immersed into either toluene (good solvent of both the PPEGMA block and the **PF** block) or methanol (good solvent of PPEGMA block but nonsolvent for **PF** block) for 30 min at room temperature and then were dried under a flow of clean air before characterization.

Characterization. ^1H NMR spectra were measured by using a Bruker 300 instrument spectrometer operating at 300 MHz with tetramethylsilane internal standard as a reference for chemical shifts. Molecular weights of polymers were determined by using a Lab Alliance RI2000 instrument (two column, MIXED-C and D from Polymer Laboratories) connected with one refractive index detector from Schambeck SFD GmbH. All GPC analyses were performed on polymer/THF solution at a flow rate of 1 mL/min at 40 °C and calibrated with polystyrene standards.

Atomic force microscopy (AFM, NanoScope III, Digital Instrument) equipped with an integrated silicon tip/cantilever with resonance frequency ~ 240 kHz in height and phase image models were utilized for observation of morphologies. The AFM topographies showed no evidence of tip-induced modification during successive scans. X-ray photoelectron spectroscopy (XPS) was analyzed by using Surface Science Instruments (X-Probe). Photoluminescence (PL) spectra were recorded on a Fluorolog-3 spectrofluorometer (Jobin Yvon).

Results and Discussion

Theoretical Investigation on the Surface Structures of Rod–Coil Block Copolymer Brushes. Molecular simulation is an alternative approach to gain more direct and microscopic-level information than experiments. The building of mesoscale

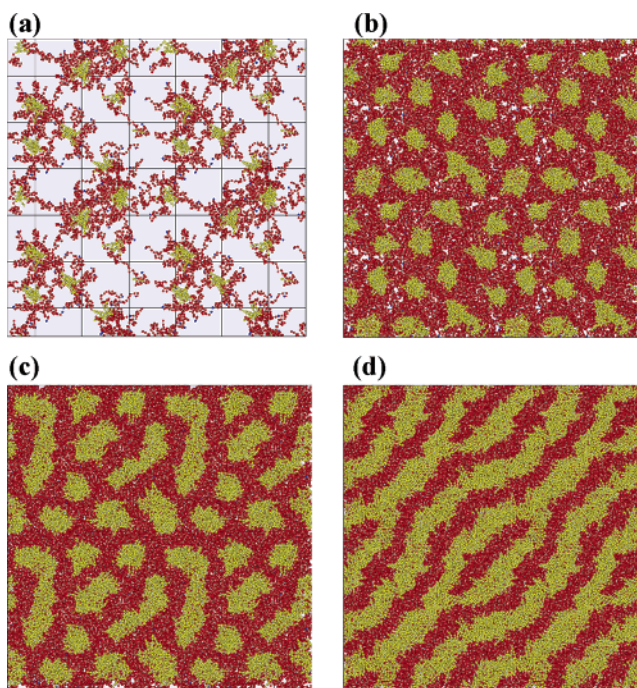


Figure 3. Top views of the surface structures of rod–coil block copolymer brushes with the parameters of $n_A = 5$, $n_B = 20$, $a_{AS} = 40$, $a_{BS} = 26$, and $a_{AB} = 40$: (a) $\rho_S = 0.1$; (b) $\rho_S = 0.5$; (c) $\rho_S = 0.7$; (d) $\rho_S = 0.9$. The system volume is set to be $V = L_x \times L_y \times L_z = 30 \times 30 \times 20$.

surface structures of the rod–coil block copolymer brushes with the use of classical molecular dynamics at atomic resolution is a challenge at present owing to the length and time scales at which these phenomena can occur. However, mesoscale simulations such as dissipative particle dynamics can overcome this deficiency. In this paper, DPD is performed to explore the effects of solvent stimuli, grafting density, and block ratio on the morphologies of surface structures formed by rod–coil block copolymer brushes. The results are complementary to the experimental observations.

The Effect of Solvent Stimuli on the Surface Structures of Rod–Coil Block Copolymer Brushes. It is well known that the compatibility between solvents and polymeric solutes can greatly influence the resulting morphologies of the systems. Two scenarios were considered here: first, the solvents were compatible to both the rod and coil blocks of the rod–coil copolymer and second, the solvents became incompatible to the rod blocks. The systems evolved to significantly different surface structures as shown in Figure 2a,c. The yellow and red spheres correspond to the particles in the rod and coil blocks, respectively. The blue spheres are the anchoring points of the rod–coil copolymers on the surface. For the polymer brushes immersed in common good solvents (Figure 2a), the rod blocks are well dispersed on the surface because of the good compatibility between the rod blocks and the solvents. On the other hand, aggregative domains of the rod blocks are observed in Figure 2(c). The incompatibility between the rod blocks and the solvent particles drives the rod blocks into forming aggregates to reduce the contacts between rod blocks and solvents. In doing so, the free energy of the system decreases and a thermodynamically stable structure is developed.

From the side views of the systems, the rod blocks of the polymers extend themselves into the good solvents (Figure 2b). On the other hand, the rod blocks back away from the solvents and even hide within the coil blocks to avoid contact with the

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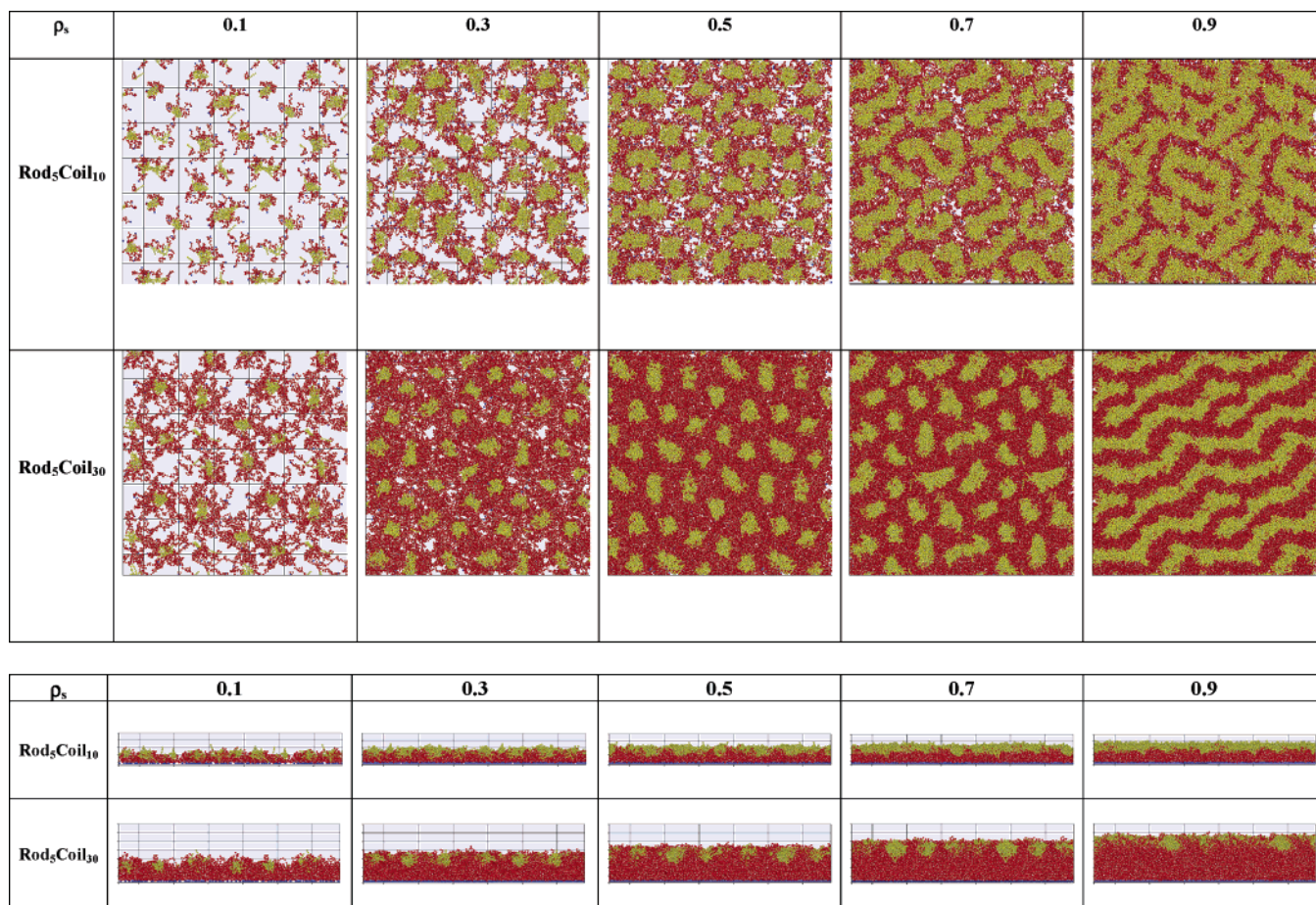


Figure 4. Simulated surface structures of rod-coil block copolymer brushes with the parameters of $n_A = 5$, $a_{AS} = 40$, $a_{BS} = 26$, $a_{AB} = 40$, $\rho_S = 0.1$ – 0.9 and $n_B = 10$ and 30 . (a) Top view and (b) side views. The system volume is set to be $V = L_x \times L_y \times L_z = 30 \times 30 \times L_z$. L_z are 15 and 25 for $n_B = 10$ and 30 , respectively.

solvents (Figure 2d). The surface layer of the former is clearly thicker than that of the latter.

The Effect of Grafting Density on the Surface Structures of Rod-Coil Block Copolymer Brushes. The surface structure of polymer brushes also is influenced by the steric hindrance between polymer chains. Thus, the grafting density of polymer brushes on the surface becomes an important factor for determining the surface structures of the polymer brushes. Our study found that the resulting surface structures show no distinguished variation with different grafting densities if the polymer brushes are in the good solvents for both the rod and coil blocks. The only difference is the surface coverage. Nevertheless, the surface structures are greatly affected by the grafting density if the polymer brushes are immersed in the poor solvents for the rod blocks. Figure 3 shows the surface structures of the rod-coil block copolymer brushes with rod-to-coil block ratio of 1:4 ($n_A = 5$; $n_B = 20$) and grafting density of 0.1–0.9 in the poor solvent for the rod blocks. The rod blocks form a series of small isolated islands on the surface when the grafting density is as small as $\rho_S = 0.1$, as shown in Figure 3a. The size of these isolated islands increases with increasing grafting density ($\rho_S = 0.5$). Then, worm-like conformation is revealed from the interconnection of these isolated islands as the grafting density increases to 0.7 (Figure 3c). Finally, the worms begin to intertwine and networklike surface structures disclose ($\rho_S = 0.9$).

The Effect of Block Ratio on the Surface Structures of Rod-Coil Block Copolymer Brushes. Two different rod-to-coil block ratios, 1:2 ($n_A = 5$; $n_B = 10$), and 1:6 ($n_A = 5$; $n_B = 30$), were simulated under different solvent stimuli and grafting densities

to illustrate the effect of block ratio on the surface structures. Again, the resulting surface structures show no distinguished differences with different block ratios if the polymer brushes are in the good solvent for both the rod and coil blocks. However, it does reveal evident influence on the surface structures in the case of the poor solvent for the rod blocks. Figure 4 demonstrates the surface structures and their corresponding side views of the rod-coil block copolymer brushes with rod-to-coil block ratio of 1:2 and 1:6 ($n_B = 10$ and 30) and at different grafting densities. As the grafting density increases, the surface structures vary from isolated islands to wormlike conformation and finally the networklike configuration for all the polymer brushes with different block ratio. However, the increase in the length of the coil blocks delays the onset of the wormlike conformation. For example, as shown in Figure 4a at $\rho_S = 0.7$, the system with $n_B = 30$ has aggregates shaped like isolated islands but for system with $n_B = 10$, the worms are noticeably interconnected.

It also is interesting to find that the isolated islands tend to float on the top of the coil blocks if the length of the coil blocks is short because of the limited movement of coil blocks as shown in Figure 4b for $\rho_S = 0.5$ and $n_B = 10$. As n_B increases, the flexible coil blocks start to cover the islands. Finally, the aggregations formed by the rod blocks are entirely surrounded by the flexible coil blocks (for $\rho_S = 0.5$ and $n_B = 30$). The flexible coil blocks, which are compatible with the solvent particles, protect the solvophobic aggregates from the energetically unflavored contacts with the solvents. The submergence of the aggregative domains into the coil blocks is thus thermodynamically preferred. However, for brushes with short coil blocks,

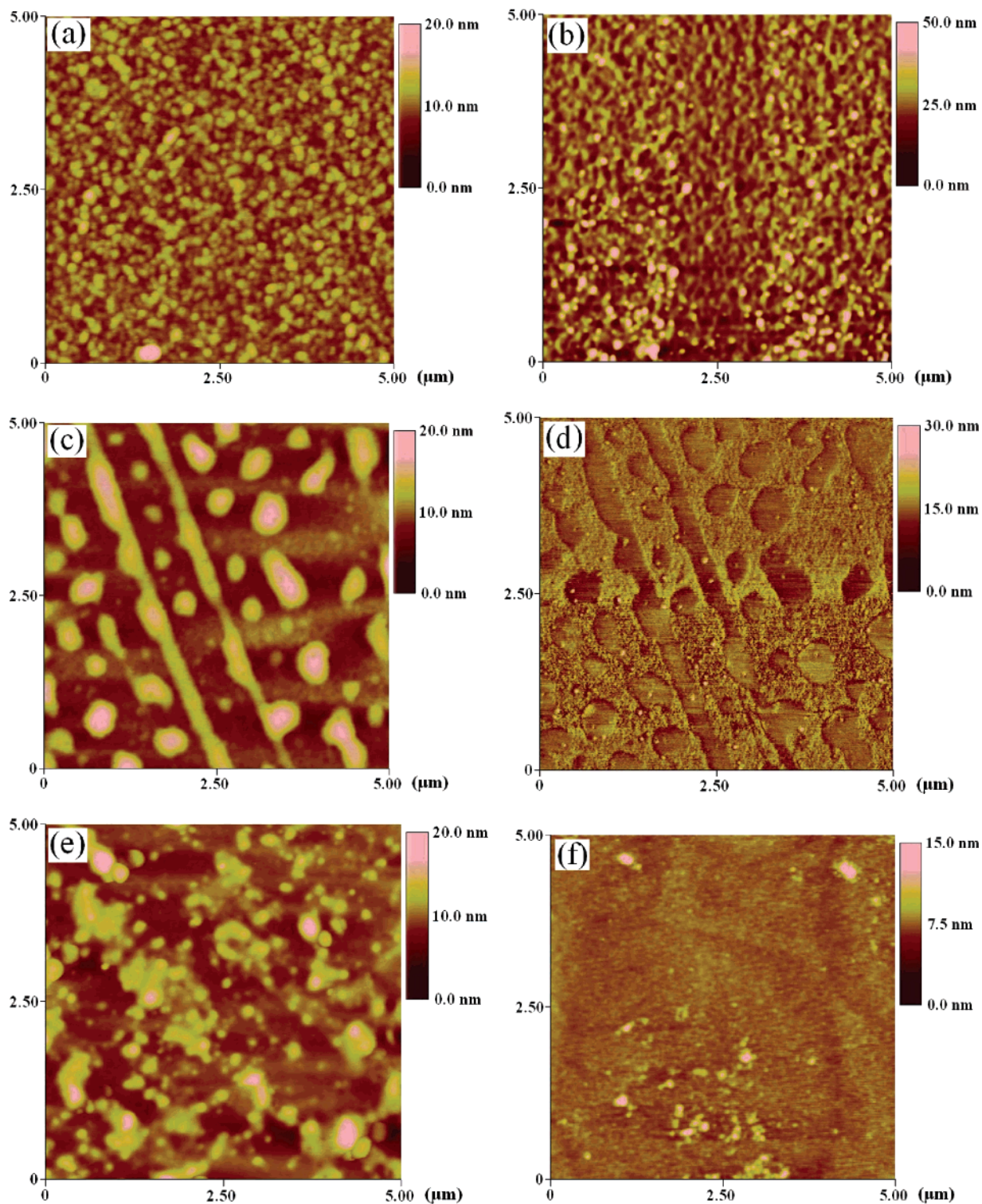


Figure 5. AFM images ($5 \times 5 \mu\text{m}$) of the polymer brushes after solvent treatment. (a) and (b): **PB2-1** after toluene treatment; (c) and (d): **PB2-1** after methanol treatment; (e) and (f): **PB2-2** and **PB2-3** after methanol treatment. (a), (c), (e), and (f) are height images; (b), and (d) are phase images.

the attempt to cover the aggregates will lead to significant stretch of the coil blocks. By doing so, the entropy of the system will be greatly reduced. When the gain in energy cannot compensate the loss in the entropy, the floating island conformations emerge. The system suffers less entropic loss as n_B increases and the energetic effect becomes the dominant factor. Therefore, the aggregates reside within the solvophilic coil blocks.

Experimental Results of PF-*b*-PPEGMA-*b*-PPOPS Rod–Coil Block Copolymer Brushes. *Surface Structures of the PF-*

b-PPEGMA-*b*-PPOPS Polymer Brushes. The polymer brushes of **P1** are named as **PB1-1**, **PB1-2**, and **PB1-3** corresponding to the concentration of polymer solution equals to 20, 10, and 5 mg/mL, respectively. Similarly, the polymer brushes of **P2** are named as **PB2-1**~**PB2-3**. The thickness (5–6 nm in dry state) of the tethered block copolymer was nearly independent of concentrations. This observation is in accordance with the results of Thomas et al., indicating the brush layer set up a self-limiting barrier to prevent further diffusion of the rod–coils to surface.¹⁴

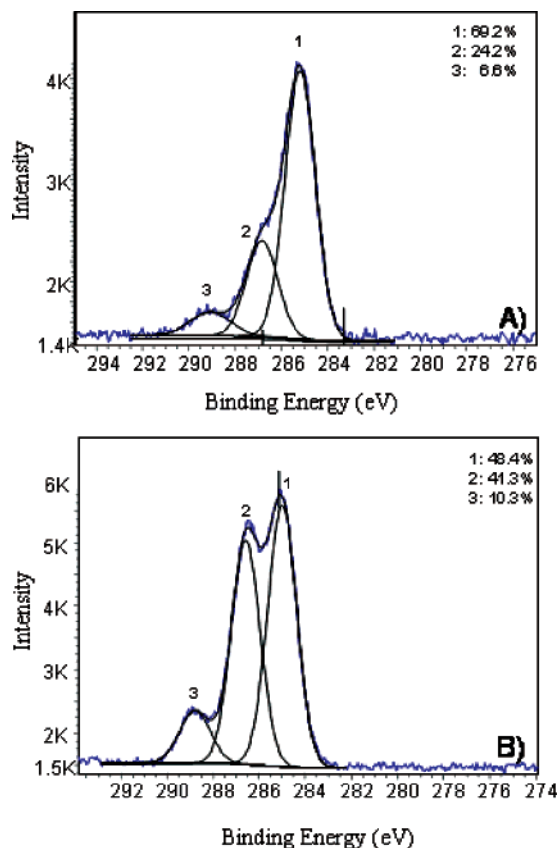


Figure 6. XPS results of the carbon (C_{1s}) in the **PB2-1** brush treated with toluene (A) and with methanol (B). 1, Hydrocarbon; 2, ester carbon of $-\text{CH}_2\text{O}-$; 3, carbonyl carbon (e.g., $-\text{COO}-$).

Tapping mode AFM was utilized to examine surface structures of the polymer brushes. Representative AFM images of polymer brushes **PB2-1**~**PB2-3** are given in Figure 5. Figure 5a,b are the height and phase images, respectively, of the polymer brush **PB2-1** after the toluene treatment. The surface is relatively smooth; the roughness is 1.45 nm in which roughness is defined as root-mean-square of height deviations taken from the mean area plan. The phase image (Figure 5b) provides additional information on the surface structure. The contrast in the phase image reflects the differences in hardness between different phases. Considering that the glass transition (T_g) of the polyfluorene^{54,55} (about 60 °C) is much higher than that of **PPEGMA**⁵⁶ (~ -60 °C), bright regions are assigned to the **PF** phase because of its relative hardness as compared to the **PPEGMA** phase at room temperature. Figure 5b shows that after the toluene treatment both the **PF** and **PPEGMA** phases are present on the surface, which is reasonable because toluene is a good solvent for both **PF** and **PPEGMA** blocks. Figure 5c,d are the height and phase images, respectively, of the polymer brush **PB2-1** after the methanol treatment. In Figure 5c, the height image indicates that the surface becomes relatively rough with a roughness of 6.97 nm. Note that methanol is a good solvent for **PPEGMA** block but a poor solvent for **PF** block. The **PPEGMA** blocks are swollen with methanol resulting in its moving up to the surface, whereas the **PF** blocks are possibly covered by the **PPEGMA** resulting in its falling down to the substrate. Both effects lead to opposite movement of the blocks and, hence, aggregated islands of **PF** blocks with large dimension and even interconnected, wormlike

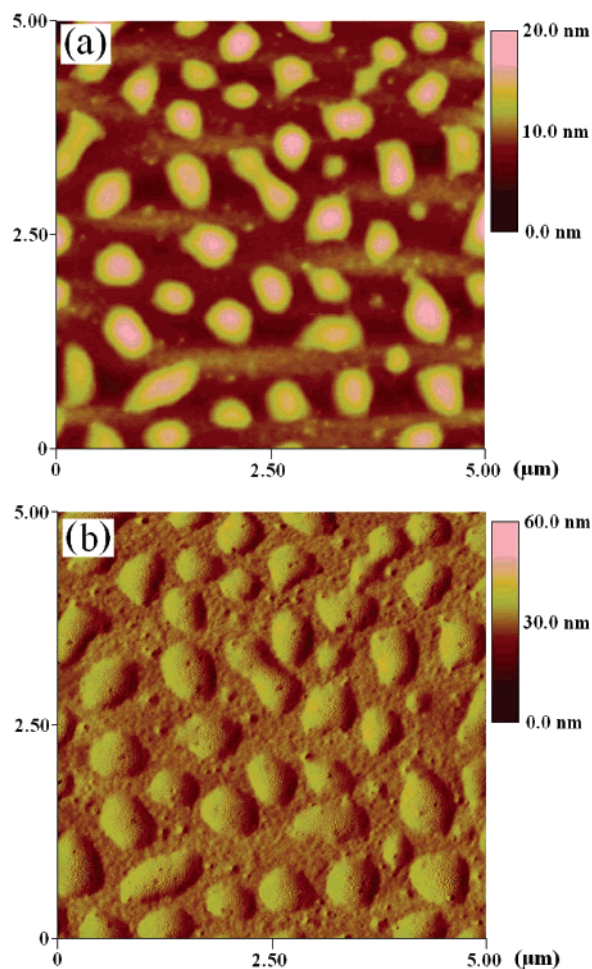


Figure 7. AFM images ($5 \times 5 \mu\text{m}$) of **PB1-1** after methanol treatment. (a) Height image; (b) phase image.

structures are formed. Figure 5d shows less contrast in the phase image of **PB2-1** after methanol treatment as compared to that after toluene treatment. The possible explanation of the reduced contrast is that some of the **PPEGMA** blocks form a layer around the aggregated domains of **PF** blocks. The variation of surface structures of **PB2-1** affected by solvent stimuli can be further qualitatively verified by XPS as shown in Figure 6. The ratio of the C_{1s} of $-\text{CH}_2\text{O}-$ group at 287.2 eV to the total C_{1s} peak intensity increases significantly from 24 to 41% after treating with methanol, implying that the $-\text{CH}_2\text{O}-$ side-group of **PPEGMA** block on the surface becomes richer in content after methanol treatment.

Figure 5e,f are the height images of the polymer brushes **PB2-2** and **PB2-3** after the methanol treatment, respectively. The surface roughness of **PB2-2** and **PB2-3** is 5.63 and 0.75 nm, respectively. As shown in the height images of polymer brushes **PB2-1**~**PB2-3**, the surface coverage estimated from the ratio bright region in height images increases from about 5% of **PB2-3** to about 50% of **PB2-1** indicating that the grafting density of polymer brushes increases with increasing concentration of the polymer solution used to prepare the polymer brush. It can be seen that the size of the aggregated domains of **PF** blocks increases with increasing grafting density. Finally, some interconnected wormlike structures are formed on the surface of polymer brush **PB2-1**. The variation of surface structure with grafting density is exactly the same as the theoretical prediction as shown in Figure 3.

Figure 7a,b are the height and phase images of the polymer brush **PB1-1** after methanol treatment, respectively. The height images of the polymer brushes **PB1-1** and **PB2-1** after methanol

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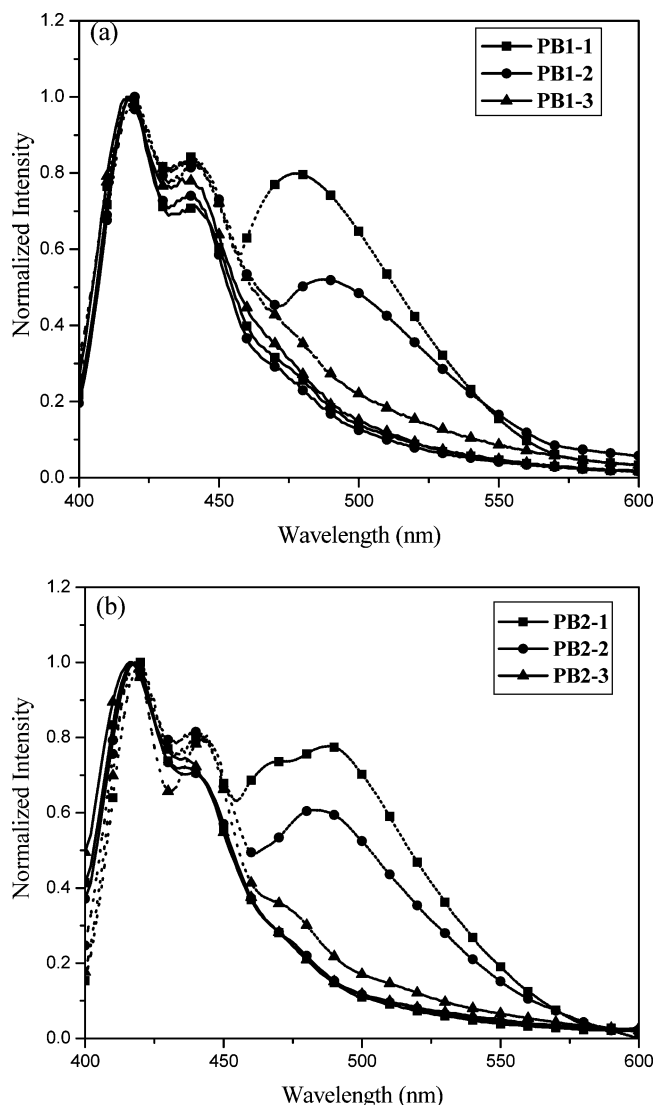


Figure 8. Photoluminescence spectra of polymer brushes (a) **PB1-1**~**PB1-3** and (b) **PB2-1**~**PB2-3** after toluene treatment (solid lines) and methanol treatment (dot lines) excited at the wavelength of 380 nm.

treatment show similar sizes of aggregated domains of **PF** blocks and similar roughness (6.49 nm for **PB1-1**; 6.97 nm for **PB2-1**). However, Figures 5d and 7b suggest significant difference in phase contrast between the surface structures of these two polymer brushes after methanol treatment. As shown in Figure 7b, the bright regions of aggregated **PF** domains on polymer brush **PB1-1** are attributed to the difference of hardness between **PF** and **PPEGMA** phases. On the other hand, small phase contrast as shown in Figure 5d suggests that most of the aggregated **PF** domains might be covered by a layer of **PPEGMA** blocks. The possible reason resulting in the difference is the different rod–coil block ratios of **P1** and **P2**. As we discussed in the theoretical analysis, the aggregated domains are on the top of the coil blocks if the polymer chain length of the coil blocks is short because of the limited movement of coil blocks. This is consistent with the phase image of polymer brush **PB1-1** because of the short coil blocks of **P1** (rod/coil = 1:3). As the polymer chain length of the coil blocks extends, the isolated islands start to be covered by the flexible coil blocks, which explains the small phase contrast in Figure 5d where the copolymer with longer coil blocks (**P2**, rod/coil = 1:6) was used. The results of AFM images suggest that the surface structures of the studied polymer brushes are in

Table 1. Photoluminescence Characteristics of **PF-b-PPEGMA-b-PPOPOS** Brushes

polymer brush	conc (mg/mL) ^a	solvent treatment		λ _{max} ^{PL} (nm)	PL efficiency ^b
		T, toluene;	M, methanol		
PB1-1	20	T		418, 441	1.00
		M		418, 440, 478	0.86
PB1-2	10	T		418, 439	0.79
		M		420, 442, 488	0.67
PB1-3	5	T		418, 437	0.48
		M		418, 440	0.40
PB2-1	20	T		417, 438	0.78
		T/M = 5:1		417, 440, 475 ^c	0.71
		T/M = 1:1		418, 440, 475 ^c	0.66
		T/M = 1:5		418, 440, 486	0.57
		M		420, 442, 488	0.51
PB2-2	10	T		417, 439	0.62
		M		418, 440, 482	0.43
PB2-3	5	T		417, 437	0.34
		M		418, 442, 475 ^c	0.25

^a Concentration of the polymer solution used to prepare the polymer brush. ^b Relative PL efficiencies with the integrated PL intensity of polymer brush **PB1-1** after toluene treatment as unity. ^c Emission shoulder.

response to the solvent stimuli and also are determined by the grafting density and the chemical structures of the amphiphilic rod–coil block copolymers.

Photophysical Properties of the PF-b-PPEGMA-b-PPOPOS Polymer Brushes. Figure 8 represents the PL spectra of polymer brushes **PB1-1**~**PB1-3** and **PB2-1**~**PB2-3** after toluene treatment and methanol treatment excited at the wavelength of 380 nm of which the corresponding emission peaks are summarized in Table 1. All the polymer brushes after toluene treatment show two fluorescence emission peaks around 420 and 440 nm, which are typical emission peaks of polyfluorene. After methanol treatment, dramatic fluorescence spectral changes were observed except for **PB1-3**. Additional emission shoulders around 475–488 nm were observed. Furthermore, this additional shoulder shows increasing intensity with increasing grafting density in both polymer brushes **PB1-1**~**PB1-2** and **PB2-1**~**PB2-3**. Such a result clearly indicates that the **PF** blocks aggregate and possibly form excimers in the polymer brushes.⁵⁷ Although the appearance of such excimer emission is very common for **PF** polymers upon heating,⁵⁷ our findings suggest that the formation of excimers may be facilitated in **PF** aggregates with tight intermolecular packing only through the solvent stimuli. Therefore, the fluorescence results are in good accordance with the AFM studies as described above. The absence of this additional shoulder for **PB1-3** is probably attributed to limited mobility because of the short chain length of flexible **PPEGMA** blocks and the low grafting density that in turn prevent the formation of aggregated **PF** domains.

Figure 9 represents the PL spectra of polymer brush **PB2-1** after treatments with mixed solvents of toluene and methanol excited at the wavelength of 380 nm of which the corresponding emission peaks are summarized in Table 1. The additional shoulders due to the aggregation of **PF** blocks show increasing intensity with increasing methanol ratio of mixed solvents. The PL spectra clearly suggest that the surface structures of amphiphilic rod–coil block copolymer brushes are very sensitive to solvent stimuli.

The relative PL efficiencies of these polymer brushes after different treatments were calculated by assuming the integrated PL intensity of polymer brush **PB1-1** after toluene treatment as

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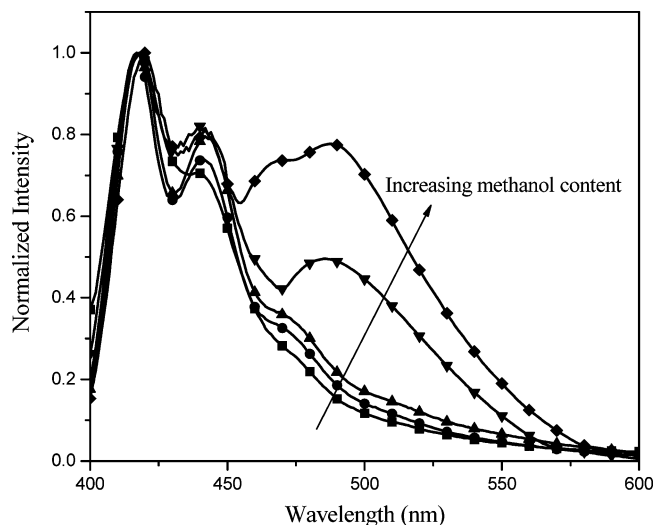


Figure 9. Photoluminescence spectra of polymer brush, **PB2-1**, after treatment with mixed solvent of toluene and methanol excited at the wavelength of 380 nm.

unity. The corresponding PL efficiencies are listed in Table 1. The PL efficiencies of polymer brushes **PB1-1**~**PB1-3** and **PB2-1**~**PB2-3** decreases with decreasing grafting density after the treatment with both toluene and methanol due to the decrement of fluorescent **PF** blocks on the surface. The higher PL efficiencies of the polymer brushes based on **P1** than those based on **P2** under the conditions of similar grafting density and after the same solvent treatment are attributed to the higher block ratio of **PF** in the backbone of **P1**. The PL efficiency of the polymer brush after methanol treatment is generally lower than that of toluene treatment because the aggregation in the former results in excimer formation and reduces the efficiency. Besides, the degree on the reduction of PL efficiency after methanol treatment as compared to that after toluene treatment is higher for **PB2** than that of **PB1** (e.g., from 0.78 to 0.51 for **PB2-1** and from 1 to 0.86 for **PB1-1**). This probably is resulting from the coverage of aggregated **PF** domains with flexible **PPEGMA** blocks due

to the longer **PPEGMA** blocks of **P2**. The PL spectra and the relative PL efficiencies suggest that the photophysical characteristics of the studied polymer brushes can be correlated to their surface structures and the chemical structures of the amphiphilic rod-coil block polymers. The present study could be further explored to helical polymer brushes by incorporating chiral coil blocks, which then generate biomimetic assembling structures and emit polarized light.⁵⁸

Conclusion

The simulated surface structures by DPD method showed that the aggregation of the rod blocks was triggered by their poor solvents, and the conformation of the aggregation was affected by the grafting density and the block ratio of the polymer brushes. The aggregative domains tend to stay on top of the surface as n_B is small and submerge into coil blocks as n_B increases. The resulting surface structure is a compromise between the energetic and entropic effects. For the justification of our theoretical model, two new rod-coil block copolymers, **PF-b-PPEGMA-b-PPOPS**, and their corresponding polymer brushes were synthesized by the grafting- method. The experimentally observed surface effects of solvent stimuli, grafting density, and rod-coil block ratio on the surface structure were in a good agreement with the theoretical results. The photophysical characteristics of the polymer brushes also were consistent with their surface structures. The present study demonstrates that the surface structures and photophysical properties of rod-coil block polymer brushes could be manipulated by solvent quality, grafting density, and rod-coil block ratio.

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Supporting Information Available: ¹H NMR spectra, GPC diagrams, and corresponding molecular weights of **PF** macroinitiator and **PF-b-PPEGMA-b-PPOPS**. This material is free of charge via the Internet at <http://pubs.acs.org>.

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