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Tadpole-Shaped Amphiphilic Block−Graft Copolymers Prepared via Consecutive Atom Transfer Radical Polymerizations

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ABSTRACT: Tadpole-shaped (or rod−coil) block−graft copolymers, consisting of a pentafluorostyrene polymer (PFS) block and a glycidyl methyacrylate polymer (PGMA) block with grafted poly(*tert*-butyl acrylate) (PtBA) side chains, or PFS-*b*-(PGMA-*g*-PtBA) copolymers, were synthesized by consecutive atom transfer radical polymerizations (ATRP's). The process involved (i) synthesis of PFS via ATRP, (ii) synthesis of well-defined PFS-*b*-PGMA via ATRP, (iii) coupling of the bromoacid initiators with the glycidyl methacrylate units in the PGMA block to generate the PFS-*b*-PGMA macroinitiators, and (iv) ATRP-mediated graft copolymerization with *tert*-butyl acrylate to generate the PFS-*b*-(PGMA-*g*-PtBA) copolymer. Hydrolysis of the PtBA side chains in the block−graft copolymer into the acrylic acid polymer (PAAC) side chains gave rise to an amphiphilic PFS-*b*-(PGMA-*g*-PAAC) macromolecule with a brush-shaped hydrophilic head (rod) and a hydrophobic tail (coil). The copolymers were characterized by composition analysis, gel permeation chromatography (GPC), thermogravimetric analyses (TGA), nuclear magnetic resonance (NMR) spectroscopy, and X-ray photoelectron spectroscopy (XPS). The macromolecular architecture of the copolymer was suggested by atomic force microscopy (AFM) images and micelle formation.

Introduction

Recently, interest in the synthesis of polymers with well-defined structure and macromolecular architecture has increased substantially.[1] Polymers with unique structures, such as block,[2,3] graft,[4,5] star,[6,7] gradient,[8] hyperbranced,[9] and comb[10,11] structures, have found applications in colloids stabilization, crystal growth modification, induced micelle formation, and intelligent drug carrier systems.[1,12−14] Polymers with unique architectures, such as star polymers, palm-tree-shaped polymers, dumbbell-shaped polymers, and dendritic polymers, were synthesized by conventional radical polymerizations, cationic and anionic polymerizations, ring-opening polymerization, and coordination polymerization.[12] Recent progress in controlled living radical polymerization, especially in atom transfer radical polymerization (ATRP), has provided a powerful tool of synthesizing well-defined polymers and for macromolecular design.[15−17] Most importantly, the tolerance of functional groups and impurities makes ATRP a versatile tool for synthesizing complex polymer molecules.

Amphiphilic block copolymers with immiscible segments in each macromolecule have unique solution and associative properties.[18−22] Micelle and reverse micelle formation of amphiphilic block copolymers in selected solvents has been well studied because the colloidal systems can be applied as nanoreservoirs in controlled drug delivery, gene therapy, and phase transfer catalysis,[18] as templates for the fabrication of nanostructured hybrids[13] and nanoparticles,[23] and as reaction media for biocatalyst in liquid phase.[24,25] Block copolymers containing ionic or polyelectrolyte segments possess unique and attractive properties.[14] Fluorinated polymers exhibit high-temperature resistance, excellent chemical inertness, and low surface energy.[26,27] Arising from their excellent physicochemical properties, fluoropolymers are potentially useful as barrier materials and biomaterials.[28−30]

Rod−coil (or tadpole-shaped) block−graft amphiphilic copolymers with a hydrophobic head and a hydrophilic tail have been synthesized by metallocene-initiated polymerization of macromonomers[31] and ATRP of macronomers from macroinitiators.[32−36] Block copolymers of pentafluorostyrene with styrene[37] and highly fluorinated styrene with styrene[38] were prepared by ATRP for application as low surface energy materials. Acrylic acid cannot be polymerized directly by ATRP because the carboxylic acid groups interact with the Cu catalysts. Thus, a block copolymer of acrylic acid is usually prepared by hydrolysis of the corresponding *tert*-butyl acrylate block copolymer from ATRP.[39−42] In this work, well-defined and tadpole-shaped block−graft amphiphilic macromolecules with a hydrophilic head of controllable dimension, consisting of designed length and number of poly(acrylic acid) (PAAC) brushes, and a hydrophobic poly(pentafluorostyrene) (PFS) tail of controlled length were synthesized by consecutive ATRP's (Scheme 1). The process involved (i) synthesis of PFS via ATRP, (ii) block copolymerization with glycidyl methacrylate (GMA) via ATRP to give the PFS-*b*-PGMA copolymer, (iii) immobilization of the bromoacid initiators on the GMA units of the PGMA block to generate the PFS-*b*-PGMA macroinitiators, and (iv) ATRP-mediated graft copolymerization with *tert*-butyl acrylate (tBA) to generate the PFS-*b*-(PGMA-*g*-PtBA) copolymer. Hydrolysis of the PFS-*b*-(PGMA-*g*-PtBA) block−graft copolymer converted the PtBA side chains into PAAC side chains to produce an amphiphilic PFS-*b*-(PGMA-*g*-PAAC) macromolecule.

Experimental Section

Materials. The monomers 2,3,4,5,6-pentafluorostyrene (FS, 99%), glycidyl methacrylate (GMA, 97%), and *tert*-butyl acrylate (*t*BA, 99%) were purchased from Aldrich Chemical Co. of

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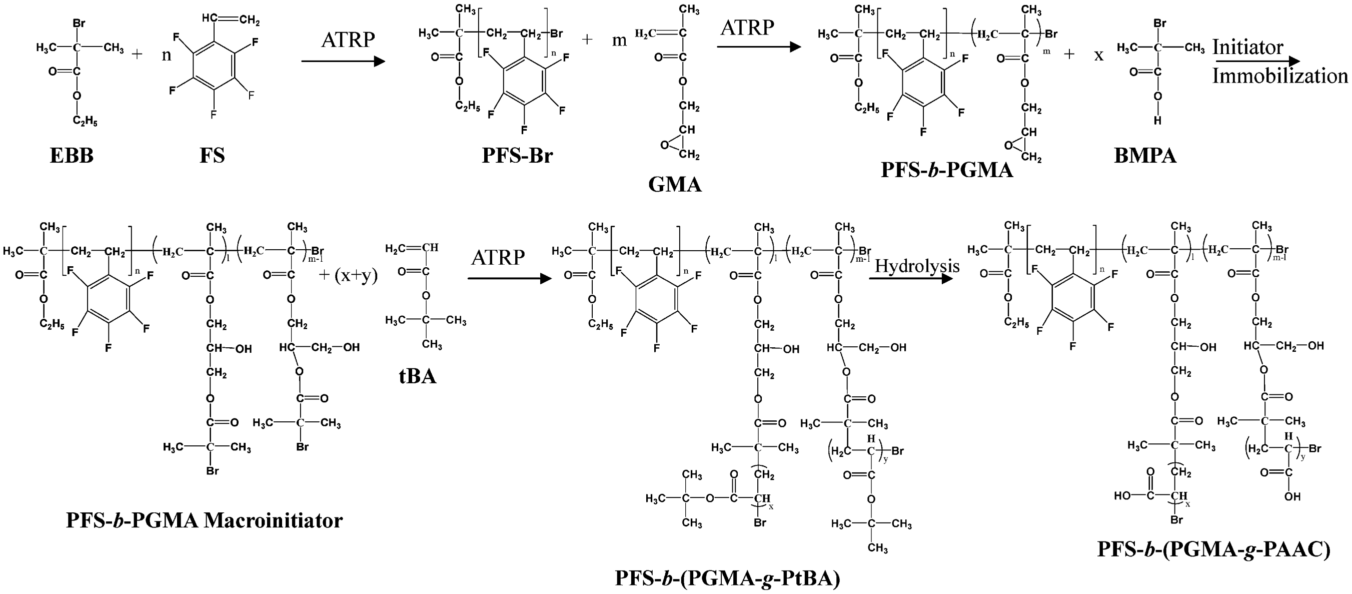
Scheme 1. Consecutive Atom Transfer Radical Polymerizations (ATRP's) for the Preparation of the Block−Graft Amphiphlic Macromolecule of Poly(pentafluorostyrene)-*block*-(poly(glycidyl methacrylate)-*graft*-poly(acrylic acid)) (PFS-*b*-(PGMA-*g*-PAAC)[a]



[a] EBB = ethyl 2-bromoisobutyrate, FS = pentafluorostyrene, PFS-Br = bromine-terminated PFS macroinitiator, GMA = glycidyl methacrylate, PFS-*b*-PGMA = poly(pentafluorostyrene)-*block*-poly(glycidyl methacrylate), BMPA = 2-bromo-2-methylproionic acid, tBA = *tert*-butyl acrylate, and PFS-*b*-(PGMA-*g*-PtBA) = poly(pentafluorostyrene)-*block*-(poly(glycidyl methacrylate)-*graft*-poly(*tert*-butyl acrylate)).

Milwaukee, WI. They were used after removal of the inhibitors in a ready-to-use disposable inhibitor-removal column (Aldrich). Analytical grade tetrahydrofuran (THF) was purchased from Tedia Co., Fairfield, OH. Copper(I) bromide (CuBr, 99%, Aldrich) was purified with acetic acid.[43] 2-Bromo-2-methylpropionic acid (BMPA, 98%), ethyl 2-bromoisobutyrate (EBB, 98%), 2,2′-bipyridine (bpy, 99%), *N,N,N′,N′,N″*-pentamethyldiethlyenetriamine (PMDETA, 99%), trifluoroactetic acid, and tetrabutylammonium hydroxide (TBAH, 99%) were also purchased from Aldrich Chemical Co. and were used as received. High-purity argon was used in all reactions.

Synthesis of the Poly(pentafluorostyrene) (PFS) Macroinitiators. A dry Pyrex test tube equipped with a magnetic stirrer was charged with 0.029 g (0.2 mmol) of CuBr and 5.7 mL (0.04 mol) of FS. The reaction mixture was degassed by bubbling argon through the solution for 20 min, after which 0.141 g (0.9 mol) of bpy ligand (0.141 g, 0.9 mmol) was added dropwise into the mixture under an argon atmosphere. The reaction mixture was flushed with argon for another 10 min. Finally, 29.4 μL (0.2 mmol) of EBB initiator was added, and the test tube was fitted tightly with a rubber stopper under an argon atmosphere. Polymerization was carried out under continuous stirring at 110 °C. After 80 min, the reaction mixture turned viscous, and the reaction was stopped by diluting with THF. The catalyst complex was removed from the reaction mixture by passing it through an alumina column. The PFS homopolymer was precipitated in an excess volume of methanol. The resulting polymer was filtered and dried in vacuo overnight. About 4.6 g of white powders (yield ~ 60%, $M_n = 2.5 \times 10^4$ g/mol) was obtained.

Synthesis of the PFS-*b*-PGMA Diblock Copolymers. A dry Pyrex test tube equipped with a magnetic stirrer was charged with 0.5 g of PFS ($M_n = 2.5 \times 10^4$ g/mol) and 1 mL of THF. The PFS macroinitiator was thus expected to assume a more fully extended conformation in THF, minimizing steric hindrance to the active chain end. GMA (0.55 mL, 4.0 mmol) was then added. The mixture was degassed by bubbling argon through it for 15 min. After degassing, the catalyst, 6 mg (0.04 mmol) of CuBr, was added carefully into the reaction mixture. The latter was degassed by bubbling argon through it for another 15 min. Finally, 10 μL (0.04 mmol) of PMDETA ligand was added, and the test tube was sealed under an argon atmosphere with a rubber stopper. The reaction mixture was stirred at 60 °C for 60 min. The reaction mixture was then diluted with THF and passed through an alumina column to remove the metal complex. The resulting copolymer (PFS-*b*-PGMA) was precipitated in hexane, filtered, and dried by pumping overnight under reduced pressure. About 0.51 g of white powders ($M_n = 2.9 \times 10^4$ g/mol) was obtained. The block copolymerization was also carried out with reaction time of 90 and 150 min.

Immobilization of the Bromoacid Initiators onto PFS-*b*-PGMA. A dry 25 mL round-bottom flask equipped with a magnetic stirrer was charged with 0.5 g of the PFS-*b*-PGMA copolymer ($M_n = 2.9 \times 10^4$g/mol, containing 20.6 mol % GMA units) and 10 mL of THF. BMPA (0.1 g, 1.2 times in molar excess relative to the concentration of GMA repeat units in the copolymer) and TBAH (0.062 g, half the amount of BMPA) were then added under vigorous stirring. The flask was subsequently fitted with a condenser and stirred at 80 °C for 24 h. When the solvent was cooled to room temperature, the product was precipitated in methanol. The filtered product was rinsed thoroughly with ethanol to remove the BMPA residue in the polymer. The macroinitiator was finally obtained after drying overnight under reduced pressure. The macroinitiator had a M_n of 3.0×10^4 g/mol and degree of functionalized ([bromoester]/[GMA] ratio) of about 1.08. The [bromoester]/[GMA] ratio was determined from the sensitivity factor corrected bromine and carbon X-ray photoelectron spectroscopy (XPS) core-level spectral area ratios.

Synthesis of the PFS-*b*-PGMA-*g*-P*t*BA Block−Graft Copolymers. The macroinitiator (0.6 g, $M_n = 3.0 \times 10^4$ g/mol) was dissolved in a test tube containing 1 mL of THF. tBA (3.6 mL, 0.025 mol) was then added. The reaction mixture was degassed with argon for 15 min. The CuBr catalyst (0.072 g, 0.5 mmol) was added carefully into the mixture, and the reaction mixture was degassed for another 15 min. Finally, the ligand PMDETA (110 μL, 0.5 mmol) was added, and the reaction tube was sealed under an argon atmosphere. The reaction was carried out at 80 °C, instead of 60 °C, for 180 min. The increase in reaction temperature improved the ATRP-mediated graft polymerization rate of the second acrylate. THF was added to stop the reaction, and the catalyst complex was removed by passing the reaction mixture through an alumina column. The product was precipitated in hexane, filtered, and then dried overnight under reduced pressure.

Table 1. Preparation of Poly(pentafluorostyrene) (PFS) and Poly(pentafluorostyrene)-*block*-poly(glycidyl methacrylate) (PFS-*b*-PGMA) Block Copolymers by Atom Transfer Radical Polymerization (ATRP)

sample	[monomer]/ [initiator]	reaction time (min)	M_n (g/mol)	polydispersity (PDI)	PGMA content NMR[c] mol %	GPC[d] mol %	TGA[e] mol %	repeat units [FS]:[GMA]	theor mol wt (g/mol)
PFS[a]	200:1	80	2.5×10^4	1.16				129:0	
PFS-*b*-PGMA1[b]	200:1	60	2.9×10^4	1.26	20.6	17.8	12.8	129:28[f] (34)[g]	3.0×10^4 [g]
PFS-*b*-PGMA2[b]	200:1	90	3.0×10^4	1.20	26.1	21.3	17.5	129:35 (46)	3.2×10^4
PFS-*b*-PGMA3[b]	200:1	150	3.3×10^4	1.24	34.3	30.3	31.7	129:56 (67)	3.5×10^4

[a] Prepared from a molar ratio of [FS]:[EBB]:[CuBr]:[bpy] = 200:1:1:3 at 110 °C for 80 min. FS = pentafluorostyrene, EBB = 2-bromoisobutyrate, and bpy = 2,2′-bipyridine. [b] The copolymer was synthesized using PFS as the macroinitiator and a molar feed ratio [GMA]:[PFS-Br]:[CuBr]:[PMDETA] = 200:1:1:1 at 60 °C for 60 min. GMA = glycidyl methacrylate, PFS-Br = bromine-terminated poly(pentafluorostyrene) macroinitiator, and PMDETA = *N,N,N′,N′,N″*-pentamethyldiethlyenetriamine. [c] The content of PGMA was determined from the area ratio of the methylidyne protons in the epoxy group (f in the ^{1}H NMR spectrum of Figure 1a) and the methylene and methylidyne protons (b and c in the ^{1}H NMR spectrum of Figure 1a) in the main chain. [d] The content of PGMA was calculated from $(M_{n[PFS-b-GMA]} - M_{n[PFS]})/M_{n[PFS-b-PGMA]}$. [e] The PGMA content calculated from the first major weight loss in TGA of the PFS-*b*-PGMA copolymer. [f] Determined from GPC results. Molecular weights of FS = 194 g/mol and GMA = 142 g/mol. [g] Determined from NMR results. Molecular weights of FS = 194 g/mol and GMA = 142 g/mol.

About 1.2 g of white powders was obtained ($M_n = 6.6 \times 10^4$ g/mol, PDI = 1.41, with 55 wt % PtBA content).

Hydrolysis of the PFS-*b*-(PGMA-*g*-P*t*BA) Copolymers. A dry 25 mL round-bottom flask equipped with a magnetic stirrer was charged with 0.5 g of the PFS-*b*-(PGMA-*g*-P*t*BA) copolymer ($M_n = 6.6 \times 10^4$ g/mol) and 5 mL of THF. Trifluoroacetic acid (5 times in molar excess relative to the amount of *tert*-butyl acrylate repeat units in the copolymer, or about 0.03 mol) was added. The reaction mixture was stirred continuously at room temperature for 36 h. The product was precipitated in hexane, filtered, and dried overnight by pumping under reduced pressure. About 0.3 g of white powders was obtained.

Polymers Characterization. The structures of PFS-*b*-PGMA, bromoacid coupled PFS-*b*-PGMA macroinitiators, PFS-*b*-(PGMA-*g*-PtBA), and PFS-*b*-(PGMA-*g*-PAAC) were characterized by ^{1}H NMR spectroscopy on a Bruker ARX 300 MHz spectrometer, using $CDCl_3$ as the solvent in 1000 scans and a relaxation time of 2 s. Gel permeation chromatography (GPC) was performed on an HP 1100 HPLC, equipped with a HP 1047A refractive index detector and a PLgel MIXED-C 300 × 7.5 mm column (packed with 5 μm particles of different pore sizes). The column packing allowed the separation of polymers over a wide molecular weight range of 200−3 000 000. THF was used as the eluent at a low flow rate of 1 mL/min at 35 °C. Polystyrene standards were used as the references. XPS measurements were carried out on a Kratos AXIS HSi spectrometer (Kratos Analytical Ltd., Manchester, England) with a monochromatized Al Kα X-ray source (1486.6 eV photons). The X-ray source was run at a reduced power of 150 W (15 kV and 10 mA). The samples were mounted on the standard sample studs by means of double-sided adhesive tapes. The core-level spectra were obtained at the photoelectron takeoff angle (with respect to the sample surface) of 90°. The pressure in the analysis chamber was maintained at 10^{-8} Torr or lower during sample measurements. Surface elemental stoichiometries were determined from the spectral area ratios, after correcting with the experimentally determined sensitivity factors, and were reliable to within ±10%. The thermal properties of the polymers and copolymers were measured by thermogravimetric analyses (TGA). The samples were heated to 900 °C at a heating rate of 10 °C/min under a dry nitrogen atmosphere in a Du Pont Thermal Analyst 2100 system, equipped with a TGA 2050 thermal gravimetric analyzer.

The surface morphology of the film was studied by atomic force microscopy (AFM), using a Nanoscope IIIa AFM from Digital Instruments Inc. About 0.01 g of the PFS-*b*-(PGMA-*g*-PAAC) copolymer ($M_n = 6.4 \times 10^4$ g/mol) was dissolved in 50 mL of THF. The solution was spin-coated on a clean Si(100) substrate at 2000 round/min until the solvent had evaporated completely. In each case, an area of 1 μm × 1 μm was scanned using the tapping mode. The drive frequency was 330 ± 50 kHz, and the voltage was between 3 and 4 V. A drive amplitude of 300 mV, a set point of 3.34 μV, and a scan rate of 1.0 Hz were used.

About 0.05 g of the PFS-*b*-(PGMA-*g*-PAAC) copolymer ($M_n = 6.4 \times 10^4$ g/mol) was dissolved in 50 mL of THF with stirring. About 50 mL of doubly distilled water was added slowly, with stirring, over a period of 3 h using a syringe pump. The mixture was stirred for an additional 2 h to yield a micelle suspension. The micelle suspension was then transferred into a cellulose dialysis membrane tubing (Sigama-Aldrich Chem. Co., St. Louis, MO). The latter was placed in a 1 L beaker filled with deionized water and dialyzed for about 2 days under gentle stirring. Field emission scanning electron microscopy (FESEM) measurements were carried out on a JEOL JSM-6700 field emission scanning electron microscope (FESEM) at an accelerating voltage of 1−5 kV and an object distance of 2 mm. The micelle solution was spin-coated on a clean Si(100) substrate at 1000 round/min until the solvent had evaporated completely. A thin layer of platinum was sputtered onto the sample surface prior to the FESEM measurement.

Results and Discussion

Synthesis of PFS and PFS-*b*-PGMA Block Copolymer. Pentafluorostyrene (FS) polymerizes readily in the bulk at 110 °C under ATRP conditions. The average molecular weight of the FS polymer (PFS) can be regulated by changing the monomer-to-initiator ratio or by controlling the extent of monomer conversion. In this work, PFS homopolymers with different molecular weights were synthesized by changing the [FS]/[initiator] ratio. Earlier studies had suggested that the end-group functionality was well-preserved in the polymer when the conversion of monomer was keep below 95%.[15] Thus, in this work, the ATRP of FS was keep below 90% conversion in order to obtain PFS macroinitiators (PFS-Br) with well-preserved end-group functionality. The PFS-Br macroinitiator, obtained from an [FS]/[EBB initiator] ratio of 200 (Table 1), was used for the subsequent block copolymerization.

PFS and poly(glycidyl methyl acrylate) (PGMA) block copolymers (PFS-*b*-PGMA) were subsequently prepared via ATRP of glycidyl methacrylate (GMA) from the PFS-Br macroinitiators. PFS-*b*-PGMA copolymers with different PGMA contents were synthesized by controlling the degree of GMA conversion. Table 1 summarizes the GPC results of PFS-*b*-PGMA block copolymers, obtained via ATRP of GMA from the PFS-Br macroinitiators ($M_n = 2.5 \times 10^4$ g/mol, $M_w/M_n = 1.16$) at a [GMA]/[PFS-Br] ratio of 200, as a function of polymerization time. With the increase in reaction time from 60 to 150 min, the number-average molecular weight (M_n) of the PFS-*b*-PGMA copolymer increases from 2.9×10^4 to 3.3×10^4 g/mol, while the polydispersity index (PDI) remains at around 1.2.

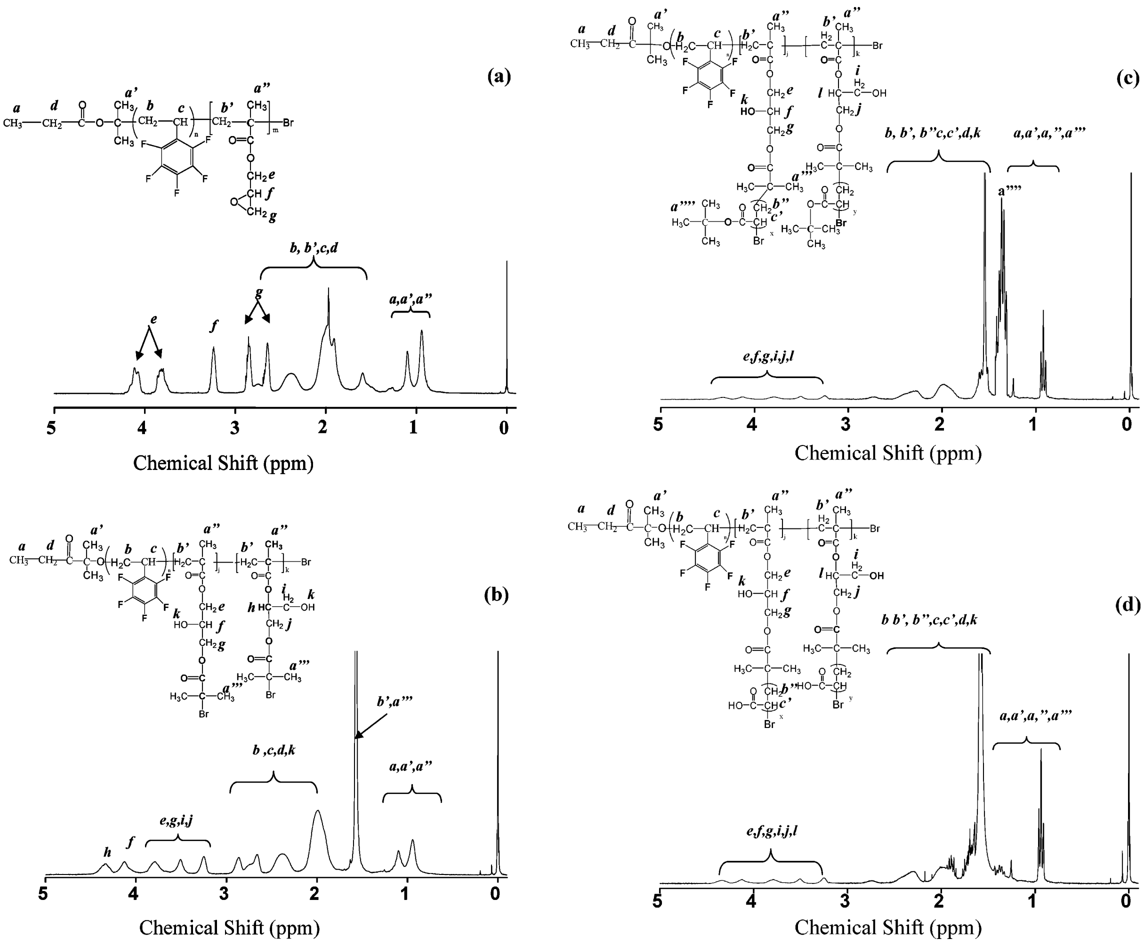


Figure 1. 300 MHz ^{1}H NMR spectra of (a) the poly(pentafluorostyrene)-*b*lock-poly(glycidyl methacrylate) (PFS-*b*-PGMA) copolymer with a [FS]:[GMA] = 129:34 (PFS-*b*-PGMA1 in Table 1), (b) the corresponding macroinitaitor with a [bromoester]:[GMA] = 1.08 (macroinitiator1 in Table 2), (c) the poly(pentafluorostyrene)-*block*-(poly(glycidyl methacrylate)-*graft*-poly(*tert*-butyl acrylate)) (PFS-*b*-(PGMA-*g*-PtBA)) copolymer with a 16 tBA repeat units (PFS-*b*-(PGMA-*g*-PtBA)1 in Table 3), and (d) the corresponding amphiphilic poly(pentafluorostyrene)-*block*-(poly(glycidyl methacrylate)-*graft*-poly(acrylic acid)) PFS-*b*-(PGMA-*g*-PAAC) copolymer hydrolyzed from PFS-*b*-(PGMA-*g*-PtBA)1.

The chemical structure of the PFS-*b*-PGMA block copolymer was characterized by ^{1}H NMR spectroscopy. Figure 1a shows the ^{1}H NMR spectrum of the PFS-*b*-PGMA copolymer (PFS-*b*-PGMA1 in Table 1, $M_n = 2.9 \times 10^4$ g/mol, PDI = 1.26). The chemical shifts at 0.9−1.7 ppm are attributable to the methyl protons of ethyl 2-bromoisobutyrate initiator and PGMA. The chemical shifts at 1.8−2.9 ppm are attributed to the methylene protons of aliphatic $-CH-CH_2$ of PFS and $-CH_2-C$ of PGMA. The chemical shifts in the region of 2.6−4.2 ppm are associated with the methylidyne protons of glycidyl groups of PGMA. The ^{1}H NMR results are thus consistent with the presence of both PFS and PGMA blocks in the copolymer structure. The GMA content in the PFS-*b*-PGMA copolymer can be determined from the ^{1}H NMR spectrum, using the area of the methylidyne protons in the epoxy group (f in Figure 1a) and the areas of the methylene and methylidyne protons (b and c in Figure 1a) in the main chain. The NMR-derived compositions of the copolymers are given in Table 1.

Curves a and b in Figure 2 are the GPC traces of the PFS homopolymer (PFS-Br) and the PFS-*b*-PGMA block copolymer (PFS-*b*-PGMA1 in Table 1), respectively. The PFS prepared by ATRP has a M_n of about 2.5×10^4 g/mol and a PDI of about 1.16. After block copolymerization, the M_n of the PFS-*b*-PGMA has increased to about 2.9×10^4 g/mol, while the PDI increases slightly to 1.26. The PGMA content in the PFS-*b*-PGMA block copolymer can be calculated from the GPC results. For the PFS-*b*-PGMA1 copolymer with a PGMA content of about 16.8 mol % (13.7 wt %), there are about 129 FS repeat units and about 28 GMA repeat units in the block copolymer. The copolymer compositions derived from GPC results are shown in Table 1. The higher value of GMA content obtained from NMR (Table 1) than that from GPC probably arose from the difference in hydrodynamic volume of PGMA and the PS standards used for GPC measurements. The chemical composition of the PFS-*b*-PGMA block copolymer was studied by XPS (see Supporting Information). The XPS-derived molar ratio of the [*C*H] + [*C*−C] species to the [O−C=O] + [*C*−F] (aromatic) species for the PFS-*b*-PGMA1 copolymer was about 0.44, comparable to the theoretical ratio of 0.48 for the copolymer ([FS]:[GMA] = 129:34, Table 1). The PGMA content in the PFS-*b*-PGMA copolymer can also be estimated from the thermogravimetric analysis (TGA) results (see Supporting Information). The extent of the initial weight loss (12.8 mol %), associated with the PGMA content of the PFS-*b*-PGMA1 block copolymer, is comparable to the PGMA content deduced from GPC results (17.8 mol % or NMR results 20.6 mol %). The copolymer composition estimated from the TGA results is also included in Table 1.

Immobilization of ATRP Initiators on the PFS-*b*-PGMA Block Copolymers. The ATRP initiators were immobilized onto the PFS-*b*-PGMA block copoly-

Table 2. Immobilization the Atom Transfer Radical Polymerization (ATRP) Initiator on the Poly(pentafluorostyrene)-*block*-poly(glycidyl methacrylate) (PFS-*b*-PGMA) Copolymers

			degree of functionalization		
sample	M_n (g/mol)	polydisdpersity (PDI)	[Br]/[C][d] (mol %)	[bromoester]/[GMA][e]	theor mol wt (g/mol)
macroinitiator1[a]	3.0×10^4	1.23	2.0	1.08	3.7×10^{4}[f]
macroinitiator2[b]	3.2×10^4	1.22	2.7	1.18	4.1×10^4
macroinitiator3[c]	3.5×10^4	1.25	3.1	0.93	4.5×10^4

[a] Prepared from PFS-*b*-PGMA1 in Table 1 with a GMA and BMPA molar feed ratio of about 1.2 in THF at 80 °C for 24 h. GMA = glycidyl methacrylate and PMBA = 2-bromo-2-methylpropionic acid. [b] Prepared from PFS-*b*-PGMA2 in Table 1 with a GMA and BMPA molar feed ratio of about 1.2 in THF at 80°C for 24 h. [c] Prepared from PFS-*b*-PGMA3 in Table 1 with a GMA and BMPA molar feed ratio of about 1.2in THF at 80°C for 24 h. [d] Determined from XPS results. [e] The molar ratio of bromoester in the macroinitiator molecule to the GMA content of the corresponding PFS-*b*-PGMA copolymer. [f] The theoretical molecular weight of the macroinitiator was calculated from the degree of functionalization of the corresponding poly(pentafluorostyrene)-*block*-poly(glycidyl methacrylate) (PFS-*b*-PGMA) copolymer.

Table 3. Characterization of Poly(pentafluorostyrene)-*block*-(poly(glycidyl methacrylate)-*graft*-poly(*tert*-butyl acrylate)) (PFS-*b*-(PGMA-*g*-PtBA)) and Poly(pentafluorostyrene)-*block*-(poly(glycidyl methacrylate)-*graft*-poly(acrylic acid)) (PFS-*b*-(PGMA-*g*-PAAC)) Copolymers

	PFS-*b*-(PGMA-*g*-PtBA)						PFS-*b*-(PGMA-*g*-PAAC)				
sample	react time (min)	M_n (g/mol)	PDI	PtBA content[b] (wt %)	tBA repeat units[c]	tBA repeat units[d]	M_n (g/mol)	PDI	PAAC content[e] (wt %)	AAC repeat units[f]	AAC repeat units[g]
PFS-*b*-(PGMA-*g*-PtBA)1[a]	180	6.6×10^4	1.41	55	10	16 (1.1×10^5)[h]	5.0×10^4	1.38	40	10	16 (7.6×10^4)[h]
PFS-*b*-(PGMA-*g*-PtBA)2[a]	360	8.6×10^4	1.38	65	16	28 ($1.6 \times 10^{5)}$	6.4×10^4	1.39	53	17	28 ($1.1 \times 10^{5)}$
PFS-*b*-(PGMA-*g*-PtBA)3[a]	600	9.5×10^4	1.42	69	18	36 (1.9×10^5)	7.1×10^4	1.42	58	20	36 (1.3×10^5)

[a] Prepared from amolar ratio of [tBA]:[macroinitiator1$_{\text{Table 2}}$]:[CuBr]:[PMDETA] = 1200:1:24:24 in THF at 80°C for 180 min. tBA = *tert*-butyl acrylate and PMDETA = *N*,*N*,*N*′,*N*′,*N*″-pentamethyldiethlyenetriamine. [b] The content of PtBA was calculated from $(M_{n[\text{PFS}-b-(\text{PGMA}-g-\text{PtBA})]} - M_{n(\text{macroinitiator1})})/M_{n[\text{PFS}-b-(\text{PGMA}-g-\text{PtBA})]}$. [c] The average number of tBA repeat units in each side chain was calculated base on the fact that all the GMA repeat units had coupled with the bromoester, a [FS]:[GMA] ratio of 129:28 (Table 1) and molecular weight of tBA = 128 g/mol. [d] The average number of tBA repeat units in each side chain was calculated from the relative proton areas of tertiary butyl group of PtBA (a″″ in the ^{1}H NMR spectrum of Figure 1c) and the methyl and methylidyne groups of epoxy. [e] The content of PAAC was calculated from $(M_{n[\text{PFS}-b-(\text{PGMA}-g-\text{PAAC})]} - M_{n(\text{macroinitiator1})})/ M_{n[\text{PFS}-b-(\text{PGMA}-g-\text{PAAC})]}$. [f] The average number of acrylic acid (AAC) repeat units in each side chain was calculated as in footnote *c*, except that the molecular weight of AAC (72 g/mol) was used. [g] The average number AAC repeat units in each side chain was calculate as in footnote *d*, except that all the tBA units had been hydrolyzed into AAC units. [h] Theoretical molecular weights of the block−graft copolymer.

mers through the TBAH-catalyzed addition reaction of 2-bromo-2-methylpropionic acid (PMBA) and the epoxy ring of the GMA units in the PFS-*b*-PGMA copolymers. The results are summarized in Table 2. The structure of the resulting macroinitiators was first studied by ^{1}H NMR spectroscopy. Figure 1b shows the ^{1}H NMR spectrum of the macroinitiator prepared from PFS-*b*-PGMA1 in Table 1. The chemical shift at about 1.7 ppm is associated with the methyl protons of the bromoester groups. The shifts in the region of 2.8−4.5 ppm (e, f, g, h, I, j, and k) are attributable to the protons resulting from the reaction of the epoxy group with the carboxylic acid group. The NMR results thus indicate that the initiator has been successfully immobilized onto the PFS-*b*-PGMA block copolymer. It is difficult to quantify the extent of esterification from NMR results because the methyl protons of the bromoester group overlap with the methylene protons of PGMA in the main chain.

The chemical composition of the PS-*b*-PGMA macroinitiators was also studied by XPS (see Supporting Information). The amounts of the bromoinitiator immobilized, defined as the number of bromoester groups/GMA moiety and calculated from the XPS-derived [Br]/[C]$_{\text{total}}$ molar ratio, are shown in Table 2. Under the given conditions, almost all of the epoxy groups have reacted with PMBA. In addition, one epoxy group may react simultaneous with two bromoester units[34] to give rise to a [bromoester]/[GMA] ratio slightly greater than 1 in some macroinitiators (Table 2). The coupling of the PMBA molecules with the epoxy groups is also supported by the GPC results. Curve c in Figure 2 shows the GPC trace of the macroinitiator1. The M_n has increased slightly to 3.0×10^4 g/mol, while the PDI remains at around 1.2, in comparison with that of the starting PFS-*b*-PGMA1 copolymer (curve b in Figure 2).

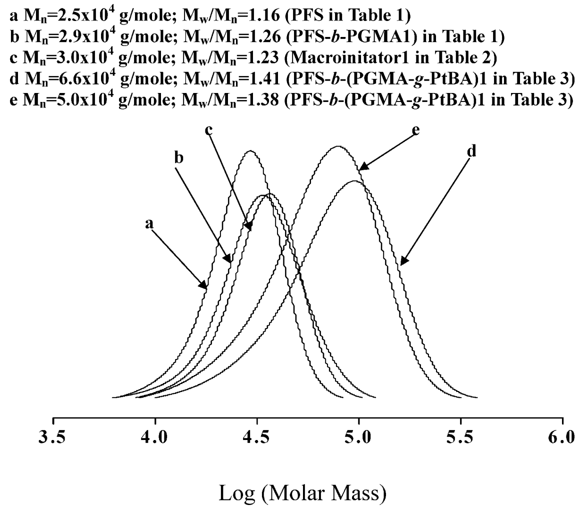


Figure 2. GPC tracesof the (a) the pristine poly(pentafluorostyrene) (PFS) homopolymer (PFS in Table 1), (b) the poly(pentafluorostyrene)-*b*lock-poly(glycidyl methacrylate) copolymer (PFS-*b*-PGMA1 copolymer in Table 1), (c) the corresponding macroinitiator1 in Table 2, (d) the poly(pentafluorostyrene)-*block*-(poly(glycidyl methacrylate)-*graft*-poly(*tert*-butyl acrylate)) copolymer (PFS-*b*-(PGMA-*g*-PtBA)1 in Table 3), and (e) the corresponding amphiphilic poly(pentafluorostyrene)-*block*-(poly(glycidyl methacrylate)-*graft*-poly(acrylic acid)) (PFS-*b*-(PGMA-*g*-PAAC)) copolymer hydrolyzed from PFS-*b*-(PGMA-*g*-PtBA)1.

Synthesis of PFS-*b*-(PGMA-*g*-PtBA) and PFS-*b*-(PGMA-*g*-PAAC) Block−Graft Copolymers. Acrylic acid (AAC) cannot be polymerized directly by ATRP because of the interaction of the carboxylic acid groups with the Cu catalyst.[15,21] Thus, the amphiphilic PFS-*b*-(PGMA-*g*-PAAC) block graft copolymer was prepared by hydrolysis of the *tert*-butyl acrylate (tBA) polymer (PtBA) side chains of the FPS-*b*-(PGMA-*g*-PtBA) copolymers. PFS-*b*-(PGMA-*g*-PtBA) copolymers with PtBA brushes (side chains) of different lengths were synthesized by controlling the degree of tBA conversion. Table 3 shows the GPC results of PFS-*b*-(PGMA-*g*-PtBA) block copolymers, synthesized via ATRP of tBA from macroinitiator1 in Table 2 at a molar feed ratio of about 1200, as a function of reaction time. With the increase in reaction time from 180 to 600 min, the number-average molecular weight (M_n) of PFS-*b*-(PGMA-*g*-PtBA) increases from 6.6×10^4 to 9.5×10^4 g/mol, while the polydispersity index (PDI) remains at about 1.4. The growth of the PtBA side chains is thus consistent with a controlled or "living" process.

The chemical structure of the PFS-*b*-(PGMA-*g*-PtBA) block−graft copolymers and the resulting PFS-*b*-(PGMA-*g*-PAAC) amphiphilic macromolecules were characterized by ^{1}H NMR spectroscopy. Parts c and d of Figure 1 show the ^{1}H NMR spectra of PFS-*b*-(PGMA-*g*-PtBA)1 in Table 3 and the resulting amphiphilic PFS-*b*-(PGMA-*g*-PAAC) macromolecule, respectively. The chemical shift at about 1.4 ppm is attributable to the methyl protons of tertiary butyl group ($C(CH_3)_3$ of the PtBA (Figure 1c). The length of PtBA side chains can also be determined from the relative proton areas of the tertiary butyl group of PtBA (a'''' in Figure 1c) and the methyl and methylidyne groups of epoxy. The higher DP of PtBA obtained from the NMR results than that from the GPC results (Table 3) can probably be accounted by the fact that the hydrodynamic volume of the densely grafted sample would be much smaller than the random coil equivalent of the polystyrene standards. The almost complete disappearance of the chemical shift at 1.4 ppm in Figure 1d is consistent with the hydrolysis of PFS-*b*-(PGMA-*g*-PtBA) to PFS-*b*-(PGMA-*g*-PAAC). The chemical composition of the PFS-*b*-(PGMA-*g*-PtBA) and PFS-*b*-(PGMA-*g*-PAAC) copolymers was again studied by XPS (see Supporting Information). For example, the presence of PtBA in the PFS-*b*-(PGMA-*g*-PtBA)1 copolymer in Table 3 is confirmed by the increase in peak intensity ratio of ([CH] + [*C*−C]) to ([O−*C*=O] + [*C*−F]) to about 1.8, from only about 0.5 for the starting macroinitiator1. The subsequent decrease of the ratio to about 0.94 after hydrolysis suggests that the PFS-*b*-(PGMA-*g*-PtBA) block−graft copolymer has been successfully hydrolyzed into the amphiphilic PFS-*b*-(PGMA-*g*-PAAC) block−graft copolymer.

Curves d and e in Figure 2 show the GPC traces of PFS-*b*-(PGMA-*g*-PtBA)1 in Table 3 and the corresponding PFS-*b*-(PGMA-*g*-PAAC) copolymer. After the ATRP of tBA, the M_n of PFS-*b*-(PGMA-*g*-PtBA)1 block−graft copolymer has reached 6.6×10^4 g/mol, in comparison to a M_n of 3.0×10^4 g/mol for the macroinitiator1 of Table 2. The PDI has also increased to about 1.41 from 1.23. The M_n of the PFS-*b*-(PGMA-*g*-PAAC) copolymer hydrolyzed from PFS-*b*-(PGMA-*g*-PtBA)1 in Table 3 decreases to 5.0×10^4 g/mol, while the PDI remains at around 1.4. The hydrolysis of PFS-*b*-(PGMA-*g*-PtBA) into PFS-*b*-(PGMA-*g*-PAAC) was also revealed by the TGA results (see Supporting Information). For the PFS-*b*-(PGMA-*g*-PAAC) block copolymer hydrolyzed from PFS-*b*-(PGMA-*g*-PtBA)1 in Table 3, the PFS content increases to about 55 wt % from about 40 wt % prior to hydrolysis. The result is consistent with the fact that the *tert*-butyl groups in the PFS-*b*-(PGMA-*g*-PtBA) copolymer have been removed during the hydrolysis.

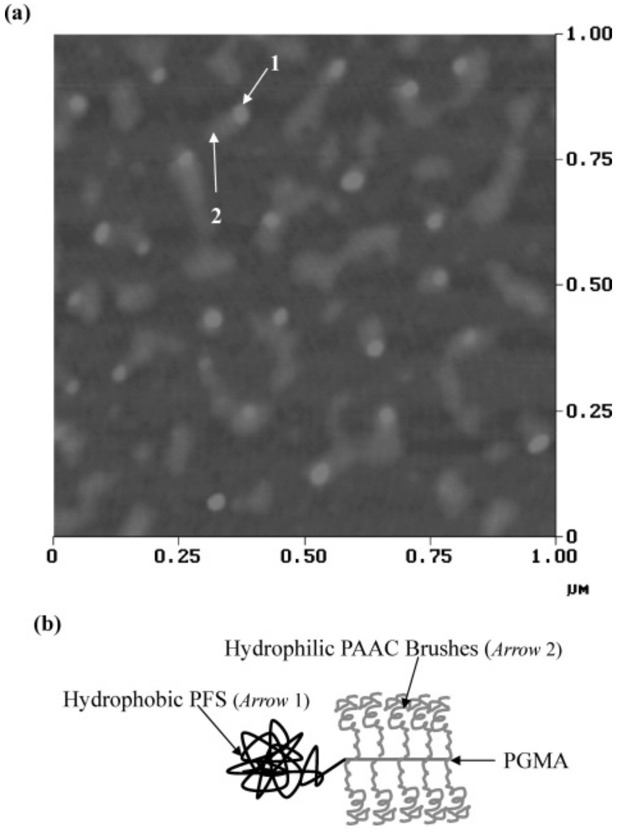


Figure 3. (a) AFM image of the rod−coil poly(pentafluorostyrene)-*block*-(poly(glycidyl methacrylate)-*graft*-poly(acrylic acid)) (PFS-*b*-(PGMA-*g*-PAAC)) (hydrolyzed from PFS-*b*-(PGMA-*g*-PtBA)2 in Table 3 with a [FS]:[GMA]:[AAC] = 129:34:28) copolymer assembly on the oxide-covered Si(100) surface. The overall size of the image is approximately 1 μm × 1 μm and (b) the plausible macromolecular structure of the poly(pentafluorostyrene)-*block*-(poly(glycidyl methacrylate)-*graft*-poly(acrylic acid)) (PFS-*b*-(PGMA-*g*-PAAC)) copolymer on the Si(100) surface.

AFM Characterization of the Tadpole-Shaped PFS-*b*-(PGMA-*g*-PAAC) Block−Graft Copolymer. The resulting rod−coil amphiphilic copolymers are should exhibit novel solution properties and naonostructures. The macromolecular architecture was studied by AFM. Figure 3a shows an AFM tapping mode image of the PFS-*b*-(PGMA-*g*-PAAC) block−graft copolymer (PFS-*b*-(PGMA-*g*-PAAC)2 in Table 3) macromolecules dispersed on an oxide-covered Si(100) substrate surface. According to the GPC and NMR results, the copolymer sample has a hydrophobic tail consisting of about 129 FS repeat units and a rod-shaped hydrophilic head comprising about 34 GMA repeat units and 34 PAAC bristles (side chains), each with a length of about 28 AAC repeat units. The bright spot (arrow 1) at the end of each cylindrical brush is probably associated with a PFS coil. The coils have dimensions on the order of 25−30 nm. The cylindrical brush (arrow 2) is probably associated with the aggregate of hydrophilic PGMA-*g*-PAAC blocks of the macromolecules on the hydrophilic SiO_x surface. The plausible structure of a PFS-*b*-(PGMA-*g*-PAAC) block−graft macromolecule on the Si-

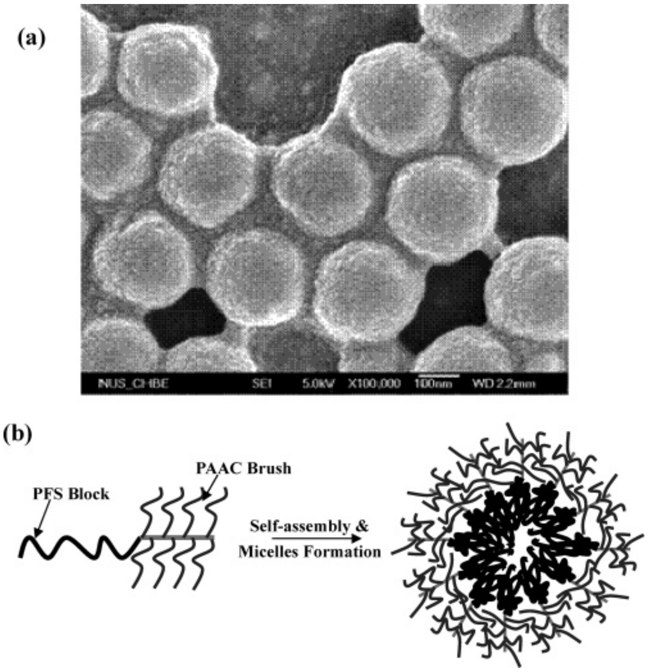


Figure 4. (a) FESEM image of the micelles from 1 g/L solution of the poly(pentafluorostyrene)-*block*-(poly(glycidyl methacrylate)-*graft*-poly(acrylic acid)) copolymer (PFS-*b*-(PGMA-*g*-PAAC)2 in Table 3 with a [FS]:[GMA]:[AAC] = 129:34:28) and (b) the plausible mechanism of micelle formation from the copolymer.

(100) surface is shown Figure 3b. On the hydrophilic (oxide-covered) Si(100) surface, the hydrophilic PGMA-*g*-PAAC block of the PFS-*b*-(PGMA-*g*-PAAC) copolymer assumes a more extended conformation. Under the driving force of surface tension and good polymer−substrate interaction, the hydrophilic PGMA-*g*-PAAC block also has a feather-like appearance. Thus, the AFM image of the macromolecular assembly on the Si(100) surface is consistent with the presence of a rod−coil structure in the present amphiphilic block−graft copolymers.

Micelles Formation. The tadpole-shaped amphiphilic PFS-*b*-(PGMA-*g*-PAAC) block copolymer, consisting of a hydrophilic PGMA-*g*-PAAC block and a hydrophobic PFS coil, provides possibility for unique micellar formation in aqueous media. The size and shape of the micelles formed from the PFS-*b*-(PGMA-*g*-PAAC) block-graft copolymers were studied by FESEM. Figure 4a shows the surface morphology of the micelles formed from a 1 g/L aqueous solution of the PFS-*b*-(PGMA-*g*-PAAC)2 copolymer ($M_n = 6.4 \times 10^4$ g/mol). Each molecule has 129 FS repeat units and 34 PAAC bristles (side chains), consisting of about 28 AAC repeat units. The micelles are well-defined, spherical, and uniform in size and have a diameter in the range of 180−200 nm. The plausible process for the micelle formation is shown in Figure 4b. The driving force for the micelle formation from the amphiphilic copolymer probably involves strong repulsion between the highly hydrophilic PGMA-*g*-PAAC block and the high hydrophobic PFS coil.[44] In the THF solution, the entire amphiphilic tadpole-shaped copolymer molecule remains well extended. During the process of micelle formation or with increasing water content, the hydrophilic PGMA-*g*-PAAC will become even more extended, while the PFS segments associate hydrophobically by phase inversion to reduce the contact area with the mixed solvent. Thus, well-defined spherical micelles, which assume the conformation of the lowest Gibbs free energy, are formed. The diameter of the micelle is determined by the chain length of the hydrophobic hydrocarbon block.[45] Thus, the well-defined uniform micelles observed can be attributed to the well-defined amphiphilic macromolecular structure of the PFS-*b*-(PGMA-*g*-PAAC) block−graft copolymer obtained via the consecutive ATRP's.

Conclusions

Tadpole-shaped block−graft copolymers or rod−coil amphiphilic macromolecules, PFS-*b*-(PGMA-*g*-PAAC), have been successfully prepared via consecutive ATRP's. The PFS-*b*-(PGMA-*g*-PAAC) macromolecules have a hydrophilic "head", comprised of a PGMA-*g*-PAAC cylindrical "brush" (rod), and a PFS hydrophobic tail (coil). The length of the hydrophilic head and the length of the PAAC bristles can be regulated by controlling the monomer-to-initiator feed ratio or the degree of monomer conversion during each ATRP. This multiple-ATRP approach allows the design and synthesis of macromolecules with specific and interesting architectures. For instance, a rod−coil block−graft amphiphilic copolymer with a hydrophobic head and a hydrophilic tail can be expected from the reversal of the polymerization sequence. The amphiphilic nature of the macromolecules may further allow the fabrication of functional materials with unique morphologies, such as porous membranes[46] and micelle/inverse micelle systems,[47] via a simple phase inversion process. The formation of well-defined and uniform micelles from the present well-defined block-graft copolymers was demonstrated.

Supporting Information Available: C 1s XPS core-level spectra and TGA curves of the PFS-*b*-PGMA, PFS-*b*-(PGMA-*g*-PtBA), and PFS-*b*-(PGMA-*g*-PAAC) copolymers. This material is available free of charge via the Internet at http://pubs.acs.org.

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