Synthesis of Conductive Core−Shell Nanoparticles Based on Amphiphilic Starburst Poly(*n*-butyl acrylate)-*b*-poly(styrenesulfonate)

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Received December 7, 2007; Revised Manuscript Received May 29, 2008

ABSTRACT: A synthetic route for highly stable electrically conductive core−shell nanoparticle was developed. It involves the synthesis of multiarmed poly(*n*-butyl acrylate-*b*-polystyrene) (PBA-*b*-PS) starburst block copolymers via the atom transfer radical polymerization method from polyfunctional initiators under very dilute condition using *n*-butyl acrylate and styrene as monomers, sequentially. Both NMR and gel permeation chromatography analyses reveal that the as-synthesized copolymers had a well-controlled molecular weight with a polydispersity of below 1.2. Then, the outer PS shell of the star copolymer was converted into hydrophilic poly(*p*-styrenesulfonate) with acetyl sulfate to generate amphiphilic PBA-*b*-PSS unimolecular micelles. The ^{1}H NMR spectrum confirmed that a sulfonation of almost 100% was reached without hydrolysis of the side butyl ester chain on PBA blocks. Finally, the oxidative propagation of 3,4-ethylenedioxythiophene (EDOT) on the PSS chains was carried out by counterion-induced polymerization to produce a stable aqueous dispersion of star-shaped PBA-*b*-PSS/PEDOT complex, which can be visualized as a conducting core−shell nanoparticle. The obtained products were characterized by FT-IR and UV−vis spectroscopy. All thin films prepared by casting from 4-, 6-, and 12-armed complexes exhibited excellent flexibility and strong adhesion to glass substrate; their conductivities were determined by the four-point probe method to be 6.7, 4.9, and 6.8 mS/cm, respectively.

Introduction

Polymeric micelles have been extensively studied in recent years because of their wide range of applications in medicine and biotechnology.[1] In particular, polymeric micelles have been developed as drug and gene delivery carriers for various therapeutical purposes.[2] However, since the formation of polymeric micelles is a thermodynamic process, micelles are quite sensitive to fluctuations in the surrounding environment and easily dissociate into free chains at concentrations below the critical micelle concentration (cmc). Alternatively, hyperbranched polymers with covalently bonded core and shell architectures can be regarded as "unimolecular" polymeric micelles (UPM) with excellent stability in dilute solution because the chemical structure is firmly connected and is independent of concentration.[3] UPM is frequently prepared using either dendrimer or a star-shaped polymer as the core moiety and by sequentially modifying its chain ends with functional blocks to form a core−shell structure.[4] Herein, the use of a star-shaped polymer as core typically simplifies preparation since fewer synthetic steps are required. The star-shaped polymer can be synthesized using either the arm-first or the core-first strategy, and the latter has been widely developed because the crowding effect of the incoming polymer arms at the reactive sites on the core molecule can be greatly reduced and living polymerization technique can be adopted to grow the polymer chain in a highly controlled manner.[5] Atom transfer radical polymerization (ATRP) is one of the most useful living/controlled radical polymerizations because the dynamic equilibrium of the transfer of halogen atoms between the dormant polymer chain and the ligand is such that the polymerization can be effectively controlled to produce polymers that bear predictable molecular weights and low polydispersity.[6] Therefore, versatile polymer-based architectures, such as block copolymers, graft copolymers, and even star-shaped copolymers, can be easily created.[7] Recently, we demonstrated an easy route for synthesizing well-defined C_{60}-anchored star-shaped polymers via the effective cycloaddition of C_{60} with malonate ester-bearing star-shaped poly(*tert*-butyl acrylate) (PtBA), which was prepared using the ATRP technique.[8]

Conductive core−shell particles have attracted considerable interest because they exhibit excellent processability and a very low conductivity percolation threshold—normally of only 5−20 wt % of conjugated polymers—enabling the mechanical and optical properties of the composite to be optimized by the use of maximum amount of core material.[9] Accordingly, they can be used in effective anticorrosive and antistatic coatings.[10] These particles are usually prepared by coating sterically stabilized latex, such as polystyrene, poly(methyl methacrylate), and polyurethane, with a thin layer of conducting polymers via in situ oxidative polymerization.[11] However, once the dimensions of the latex particle drop from the submicron scale to the nanoscale, the formation of a stable colloidal dispersion after the surface has been coated with a conducting polymer becomes difficult. Given this concern, UPM is highly suitable for the preparation of conducting core−shell "nanoparticles" because of its nanoscale dimensions and remarkable stability in solution. Another interesting route for synthesizing stable electroactive nanoparticle involves the use of starlike block copolymer as a template and stabilizer to incorporate metal particles formed in situ into its matrix.[12] However, the reports on the preparation of conductive all-organic core−shell nanoaprticles based on starburst polymers or dendrimers are still rare.[13] This work demonstrates a new route for preparing electroactive core−shell nanoparticles using an amphiphilic starburst block copolymer as a template. Scheme 1 depicts this novel conducting nanoparticle. First, well-defined star-shaped poly(*n*-butyl acrylate)-*b*-polystyrene (PBA-*b*-PS) was synthesized by ATRP. Then, a gentle sulfonation reaction converts oleophilic star-shaped PBA-*b*-PS to hydrophilic star-shaped poly(*n*-butyl acrylate)-*b*-poly(styrenesulfonate) (PBA-*b*-PSS). Since amphiphilic star-shaped PBA-*b*-PSS has a hydrophobic PBA core and a hydrophilic PSS shell favors the formation of UPM structure in water, the oxidative propagation of 3,4-ethylenedioxythiophene (EDOT) was carried out along each PSS chain through counterion-

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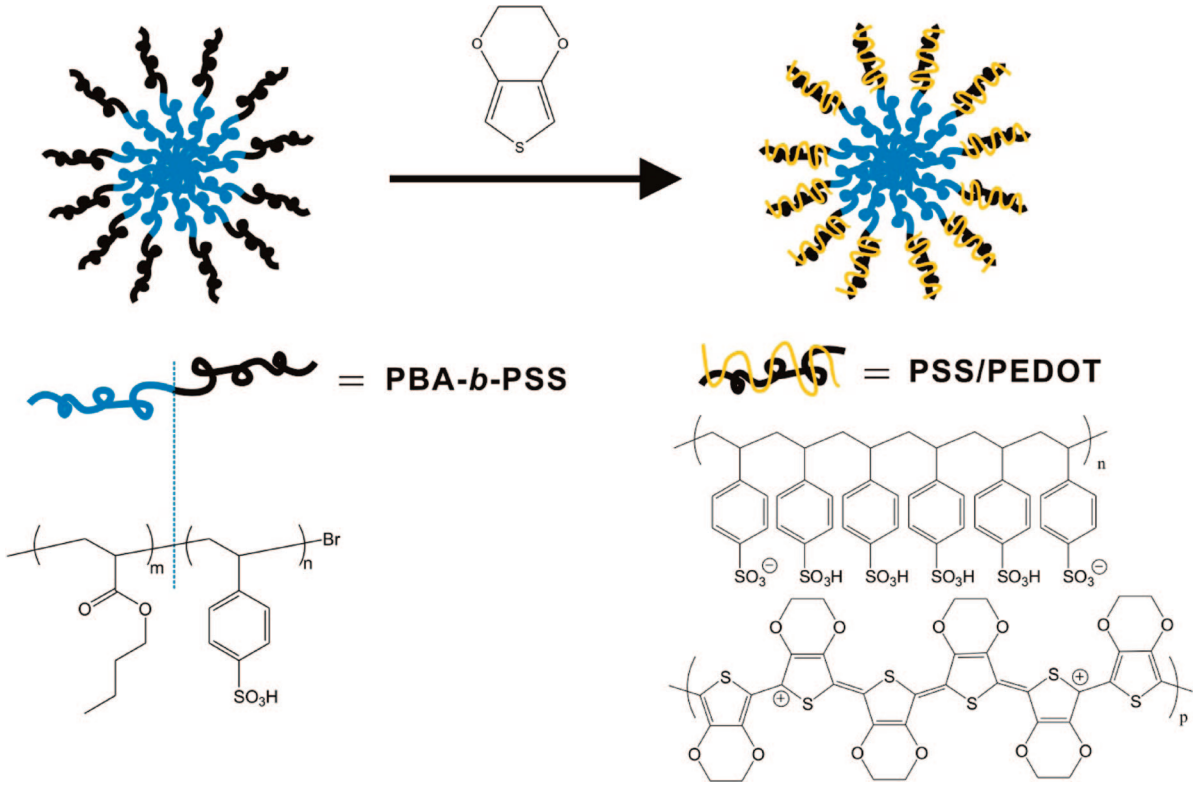
10.1021/ma7027243 CCC: $40.75
Published on Web 07/12/2008

Scheme 1. Schematic Illustration of Starburst Poly(*n*-butyl acrylate)-*b*-poly(styrenesulfonate)/Poly(3,4-ethylenedioxythiophene) (PBA-*b*-PSS/PEDOT) as a Conductive Core−Shell Nanoparticle



induced polymerization.[14] Consequently, poly(3,4-ethylenedioxythiophene) (PEDOT) was generated and became entangled with PSS chains to produce a stable shell structure, which covalently bonded to the inner PBA core.

Experimental Section

Materials and Instruments. 2-Bromoisobutyryl bromide, pentaerythritol (tetraol), dipentaerythritol (hexaol), copper(I) bromide, *N*,*N*′,*N*′,*N*″,*N*″-pentamethyldiethylenetriamine (PMDETA), and ammonium persulfate (APS) were all obtained as high-purity reagent-grade chemicals (>99%) from Acros and used without further purification. 3,4-Ethylenedioxythiophene (EDOT; >98%) was purchased from Bayer and used as received. Dendritic [G#2] polyol with 12 hydroxyl peripherals was prepared as described in the literature.[15] All organic solvents were AR grade and purchased from either TEDIA or Mallinckrodt. Dichloromethane, dichloroethane (DCE), and pyridine were dried over calcium hydride under N_2 before use. Tetrahydrofuran (THF) and ether were distilled over sodium under N_2 in the presence of benzophenone as the indicator prior to use. The *n*-butyl acrylate (BA; >99%) and styrene (99%) monomers were purchased from Acros and extracted three times with 5% aqueous NaOH and then washed with distilled water. After they were dried over $CaCl_2$ and the drying agent was filtered off, the BA monomer was distilled in vacuo, stored in a Schlenk flask, and degassed over three freeze−pump−thaw cycles prior to use.

Gel permeation chromatography (GPC) was conducted at 40 °C using two Jordi DVB mixed-bed columns (250 × 10 mm; suitable for separating polymers with molecular weights from 1×10^2 to 1×10^7 g mol^{-1}) for the organic phase and at 35 °C using two Shodex 803 HQ columns (300 × 8 mm; suitable for separating polymers with molecular weights from 1×10^2 to 1×10^6 g mol^{-1}) for the water phase on a JASCO instrument that was equipped with UV−vis and refractive index (RI) detectors connected in series. THF and 20% acetonitrile in water with 0.05 M sodium nitrate were used as the eluent at flow rates of 1.0 and 0.5 mL/min for organic and aqueous systems, respectively. Thirteen linear polystyrene samples (Aldrich) with molecular weights from 7×10^2 to 2×10^6 g mol^{-1} and six linear poly(styrenesulfonate) (Polymer Standards Service) samples with molecular weights from 1×10^3 to 4×10^5 g mol^{-1} were used as standards to establish the calibration curves for organic and water phase systems, respectively. ^{1}H (400 MHz) and ^{13}C (100 MHz) nuclear magnetic resonance (NMR) spectra were recorded using a Bruker Spectrospin spectrometer at room temperature using $CDCl_3$, DMSO-d_6, or CD_3OD as the solvent; the solvent signal was adopted as an internal standard. Ultraviolet−visible absorption (UV−vis) spectra and Fourier-transform infrared absorption (FT-IR) spectra were recorded on a Hitachi U-3410 spectrometer and on a JASCO FT/IR 480 spectrometer, respectively. Dynamic light scattering measurements were carried out on Zetasizer Nano-S (Malvern Instruments) at room temperature.

Synthesis of Tetra-, Hexa-, and Dodecabromo-Functionalized Initiators. A round-bottomed flask that contained polyol (tetraol: 2.40 g, 20.0 mmol; hexaol: 2.54 g, 10.0 mmol; dendritic [G#2] dodecaol: 1.00 g, 0.74 mmol) and pyridine (20 mL) was cooled to 0 °C using an ice/water bath. Then, 1.5 equiv of 2-bromoisobutyryl bromide relative to the hydroxyl end group on the polyols was added dropwise. The reaction mixture was stirred for 12 h and allowed to warm to room temperature. After the solvent had been removed by rotary evaporation, the mixture was transferred to a separation funnel with 100 mL of CH_2Cl_2 and extracted using 3 × 50 mL of 1 M $NaHSO_4$, 3 × 50 mL of 10% Na_2CO_3, and 3 × 50 mL of brine, consecutively. The organic phase was dried over $MgSO_4$ and filtered; the solvent was evaporated. The obtained crude product was then crystallized from methanol, yielding multibromo-functionalized initiators as white solids. ^{1}H NMR (400 MHz) was adopted to characterize the chemical structures of these polyfunctional initiators. Their chemical structures are shown in Scheme 2. Furthermore, the number of bromo end groups on each initiator was estimated from the ratio of the area under the resonance peak of the methyl protons on 2-bromoisobutyryl moieties (δ = 1.94) to that of the protons (4Br: $-CH_2OCO$, δ = 4.34; 6Br: $-CH_2OCO$, δ = 4.29; 12Br: $-ArH$, δ = 7.11, 6.99) on the core initiators in the corresponding ^{1}H NMR

Scheme 2. Chemical Structures of Tetra-, Hexa-, and Dodecabromo-Functionalized Initiators for Atom Transfer Radical Polymerization

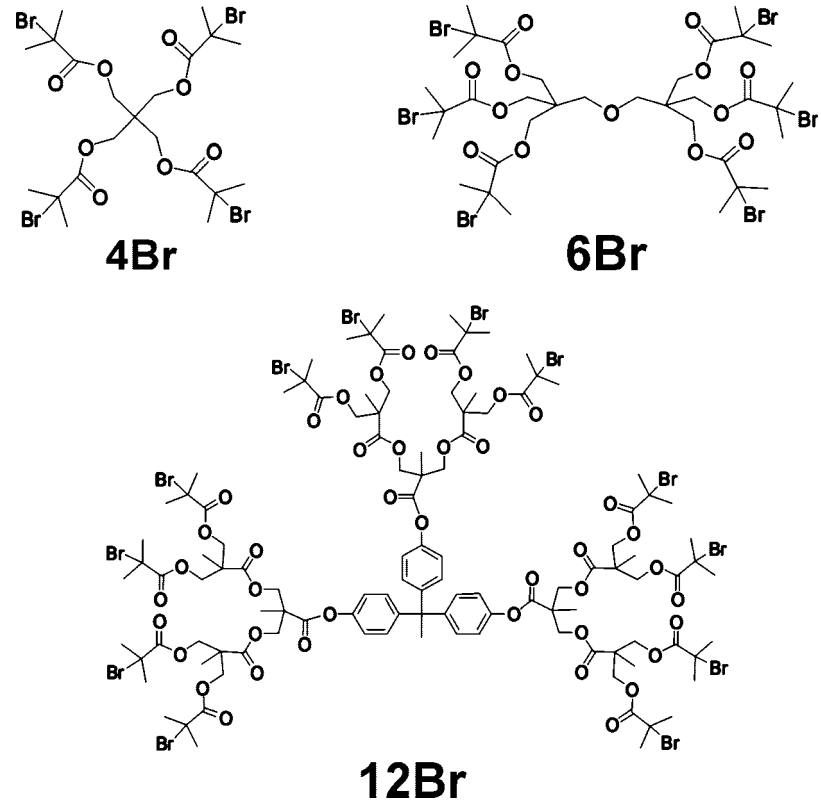


Table 1. Molecular Weight Characteristics of Star-Shaped Poly(*n*-butyl acrylate) (PBA)

	parent polymer			recovered polymer[c]		
	$M_{n,GPC}$[a]	$M_{n,NMR}$[b]	M_w/M_n	$M_{n,GPC}$[c]	M_w/M_n[c]	weight loss (%)[d]
4-armed	20 200	20 600	1.09	20 900	1.12	1.4 (1.6)
6-armed	24 600	26 800	1.12	24 000	1.10	1.7 (1.8)
12-armed	26 000	32 900	1.11	23 900	1.12	3.1 (2.9)

[a] Determined via gel permeation chromatography analysis with RI detector in THF; low-dispersed polystyrenes were used as calibration standards. [b] The number-average molecular weights (M_n) were calculated from the number-average degree of polymerization (DP_n) of each arm; $M_{n,NMR} = (DP_{per\ arm} \times 128.17 \times n) + M_i$, where 128.17 and M_i stand for the molar mass of *n*-butyl acrylate (BA) and initiator, respectively; *n* stands for the arm numbers. [c] The samples for GPC measurement were recovered from a heat treatment at 250 °C for 10 min. [d] The weight loss was determined by comparing the weight of sample before and after heating it at 250 °C for 10 min; the data in parentheses denotes the weight percentage of bromo end groups on star-shaped PBA.

Table 2. Molecular Ueight Characteristics of Star-Shaped Poly(*n*-butyl acrylate)-*b*-polystyrene (PBA-*b*-PS)

	run	$M_{n,GPC}$[a]	$M_{n,NMR}$[b]	M_w/M_n
4-armed	1	36 360	63 300	1.11
	2	45 500	64 800	1.12
	3	51 800	68 100	1.15
6-armed	1	50 500	77 900	1.10
	2	62 600	86 200	1.09
	3	74 100	89 900	1.10
12-armed	1	47 750	81 600	1.07
	2	62 700	101 600	1.08
	3	68 250	132 900	1.07

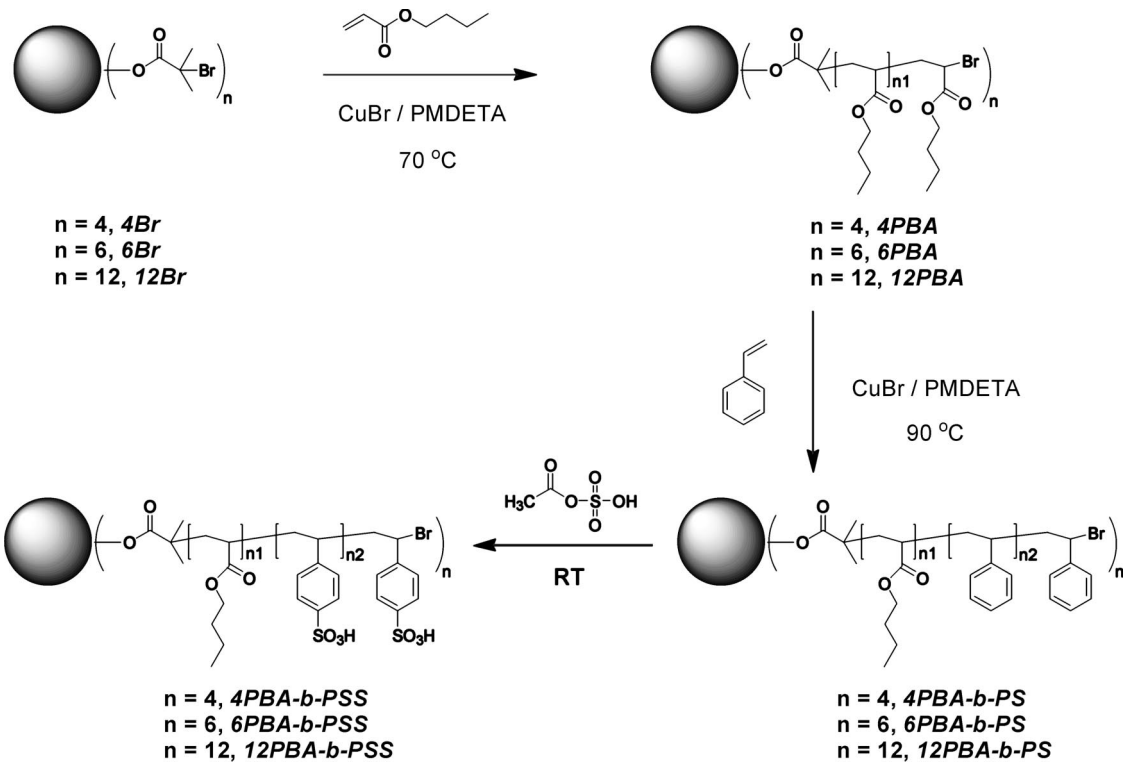
[a] Determined via gel permeation chromatography (GPC) analysis with RI detector in THF; low-dispersed polystyrenes were used as calibration standards. [b] $M_{n,NMR} = (DP_{n1} \times 128.17 + DP_{n2} \times 104.15) \times n + M_i$, where DP_{n1} and DP_{n2} stand for the number-average degree of polymerization of BA and styrene of each arm; 128.17, 104.15, and M_i stand for the molar mass of BA, styrene, and initiator, respectively; *n* stands for the arm numbers.

spectrum. It was determined to be 4.0, 6.0, and 12.1 for tetra-, hexa-, and dodecabromo-functionalized molecules, respectively, revealing an extent of acylation of almost 100%. ^{1}H NMR ($CDCl_3$, 400 MHz) of **4Br**: δ = 4.34 (s, 8H, $-CH_2OCO$), 1.95 (s, 24H, $-C(CH_3)_2$); **6Br**: δ = 4,29 (s, 12H, $-CH_2OCO$), 3.60 (s, 4H, $-OCH_2C$), 1.94 (s, 36H, $-C(CH_3)_2$); **12Br**: δ = 7.11 (d, 6H, $-ArH$), 6.99 (d, 6H, $-ArH$), 4.42 (d, 24H, $-CH_2OCO$), 4.33 (d, 12H, $-CCH_2O$), 2.16 (s, 3H, $-CH_3$), 1.90 (s, 72H, $-C(CH_3)_2$), 1.44 (s, 9H, $-CH_3$), 1.36 (s, 18H, $-CH_3$).

Preparation of 4-, 6-, and 12-Armed Poly(*n*-butyl acrylate) (PBA). A round-bottomed flask that contained multibromo-functionalized initiator (**4Br**: 366 mg, 0.50 mmol; **6Br**: 571 mg, 0.50 mmol; **12Br**: 625 mg, 0.20 mmol), PMDETA (346 mg for **4Br**; 519 mg for **6Br**; 415 mg for **12Br**), and CuBr (286 mg for **4Br**; 429 mg for **6Br**; 343 mg for **12Br**) was purged with N_2. Deoxygenated acetone (10 mL) and BA (30 mL) were added, after which the solution was placed in an oil bath, whose temperature was thermostatically maintained at 70 °C; the solution was vigorously stirred. The polymerization was conducted for 4 h to obtain 4-, 6-, and 12-armed polymers, **4PBA**, **6PBA**, and **12PBA**. Following the reaction, the mixtures were diluted with a small amount of CH_2Cl_2 and passed through a short column that was packed with silica gel, celite powder, and neutral alumina for complete removal of catalyst. The solutions were then precipitated twice in a large excess of 10% H_2O/methanol with vigorous stirring. The precipitates were collected using a centrifuge and vacuum-dried to yield final products as pale yellow liquids. The molecular weight characteristics of these star polymers are listed in Table 1.

Preparation of 4-, 6-, and 12-Armed Poly(*n*-butyl acrylate)-*b*-polystyrene (PBA-*b*-PS). A round-bottomed flask that contained macroinitiator (**4PBA**: 400 mg, 0.05 mmol; **6PBA**: 400 mg, 0.02 mmol; **12PBA**: 280 mg, 0.01 mmol), PMDETA (13.8 mg for **4PBA**; 20.8 mg for **6PBA**; 20.8 mg for **12PBA**), and CuBr (11.4 mg for **4PBA**; 17.2 mg for **6PBA**; 17.2 mg for **12PBA**) was purged with N_2. Styrene (17 mL for **4PBA**; 15 mL for **6PBA** and **12PBA**) was added, and the solution was then placed in an oil bath whose temperature was thermostatically

Scheme 3. Synthetic Pathway of 4-, 6-, and 12-Armed Poly(*n*-butyl acrylate)-*b*-poly(styrenesulfonate)



maintained at 90 °C; the solution was vigorously stirred. Polymerization was performed for 1, 2, and 3 h to obtain target polymers with various molecular weights. Following the reaction, the mixtures were diluted with a small amount of CH_2Cl_2 and passed through a short column that was packed by silica gel, Celite powder, and neutral alumina to remove the catalyst completely. The solutions were then precipitated twice in a large excess of 10% H_2O/methanol with vigorous stirring. The precipitates were collected using a centrifuge and vaccuum-dried to yield **4PBA-*b*-PS, 6PBA-*b*-PS**, and **12PBA-*b*-PS** as white solids. The molecular weight characteristics of these starburst block copolymers are listed in Table 2.

Preparation of 4-, 6-, and 12-Armed Poly(*n*-butyl acrylate)-*b*-poly(styrenesulfonate) (PBA-*b*-PSS). A sulfonation agent, acetyl sulfate (1.008 mol/L), was prepared according to the published procedure, based on Makowski's method.[16] Acetic anhydride (10.2 mL, 0.108 mmol) and sulfuric acid (3.6 mL, 0.064 mmol) were mixed thoroughly in distilled DCE (49.8 mL) in an ice bath and then used as a stock solution without further purification. A round-bottomed flask was charged with star-shaped PBA-*b*-PS (**4PBA-*b*-PS**: 228 mg, 3.51 μmol; **6PBA-*b*-PS**: 380 mg, 4.95 μmol; **12PBA-*b*-PS**: 156 mg, 2.05 μmol) and distilled DCE (5 mL) and then purged with N_2. As-prepared acetyl sulfate (5 mL) was then added, and the reaction mixture was vigorously stirred for 24 h at room temperature. After the reaction had been terminated by adding 5 mL of methanol, the volatile was removed by rotary evaporation. The crude products were dissolved in H_2O/methanol (9:1, v/v) mixed solution and then dialyzed for 48 h to remove small impurities and organic solvents. The final aqueous solutions were dried in vacuo at 50 °C to yield star-shaped PBA-*b*-PSS as cellophane-like solids.

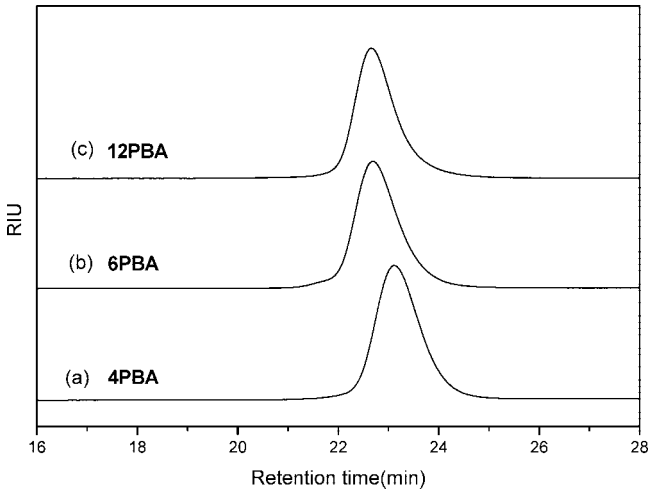


Figure 1. Gel permeation chromatograms of (a) 4-armed, (b) 6-armed, and (c) 12-armed poly(*n*-butyl acrylate) that were synthesized by atom transfer radical polymerization at 70 °C for 4 h. Feeding molar ratios of catalytic complex (CuBr/PMDETA) to tetra-, hexa-, and dodecabromo-functionalized initiators were set to 4, 6, and 12, respectively.

Preparation of 4-, 6-, and 12-Armed Poly(*n*-butyl acrylate)-*b*-poly(styrenesulfonate)/Poly(3,4-ethylenedioxythiophene) (PBA-*b*-PSS/PEDOT). A round-bottomed flask was charged with star-shaped PBA-*b*-PSS (**4PBA-*b*-PSS**: 31.0 mg, 0.48 μmol; **6PBA-*b*-PSS**: 85.0 mg, 1.15 μmol; **12PBA-*b*-PSS**: 45 mg, 0.62 μmol) and then purged with N_2. Deoxygenated distilled water (40 mL) was added, and then the solution was vigorously stirred until the polymers had completely dissolved. Freshly distilled EDOT (14.6 mg for **4PBA-*b*-PSS**; 66.0 mg for **6PBA-*b*-PSS**; 24.0 mg for **12PBA-*b*-PSS**) and APS (23.4 mg for **4PBA-*b*-PSS**; 106 mg for **6PBA-*b*-PSS**; 38.0 mg for **12PBA-*b*-PSS**) were added, and the reaction mixture was stirred for 24 h at room temperature. Membrane dialysis of the mixture overnight against distilled water removed excess EDOT and APS, and a blue powder of star-shaped PBA-*b*-PSS/PEDOT complex was obtained by lyophilization.

Results and Discussion

Synthesis and Characterization of Star-Shaped Poly(*n*-butyl acrylate)-*b*-poly(styrenesulfonate) (PBA-*b*-PSS). As presented in Scheme 3, tetrabromo- and hexabromo-functionalized initiators were synthesized by the simple acylation of corresponding tetraol and hexaol with 2-bromoisobutryl bromide and a promoting base. Dodecabromo-functionalized initiator was

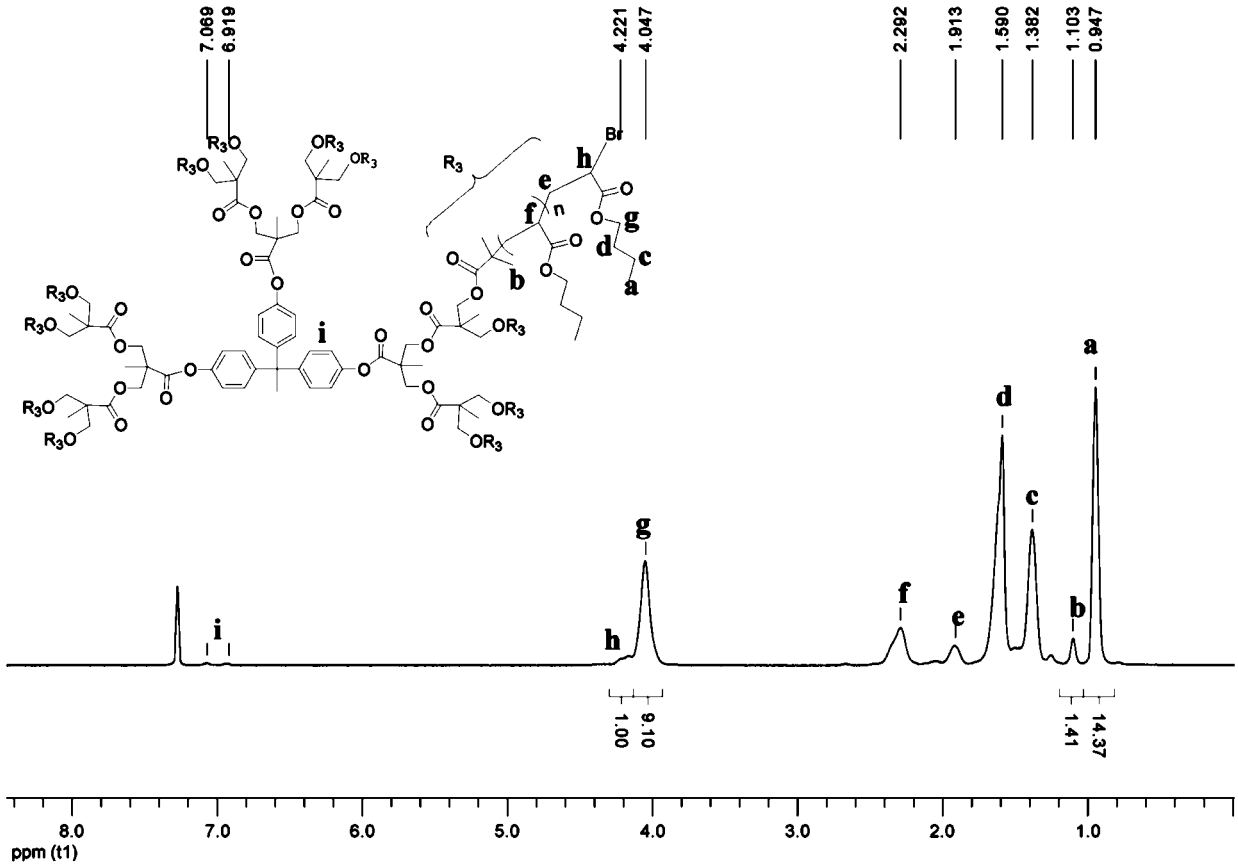


Figure 2. ^{1}H NMR spectrum of 12-armed poly(*n*-butyl acrylate) in $CDCl_3$.

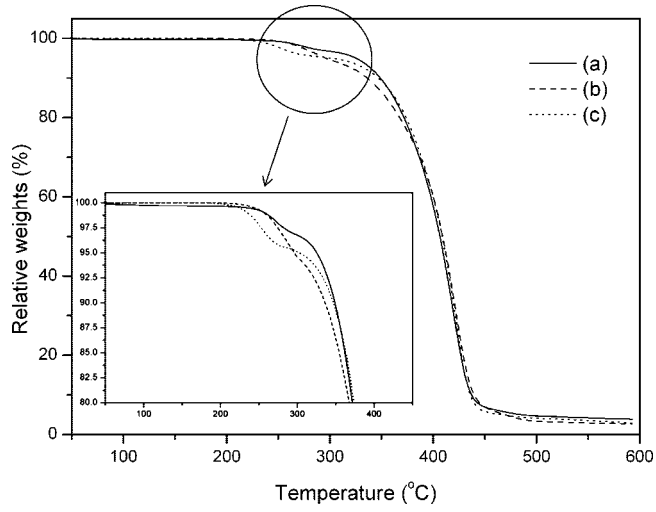


Figure 3. Thermogravimetric analyses of (a) 4-armed, (b) 6-armed, and (c) 12-armed poly(*n*-butyl acrylate). The inset zooms in the weight loss on the temperature range 200−300 °C. The measurements were carried out at a heating rate of 10 °C /min under a nitrogen atmosphere.

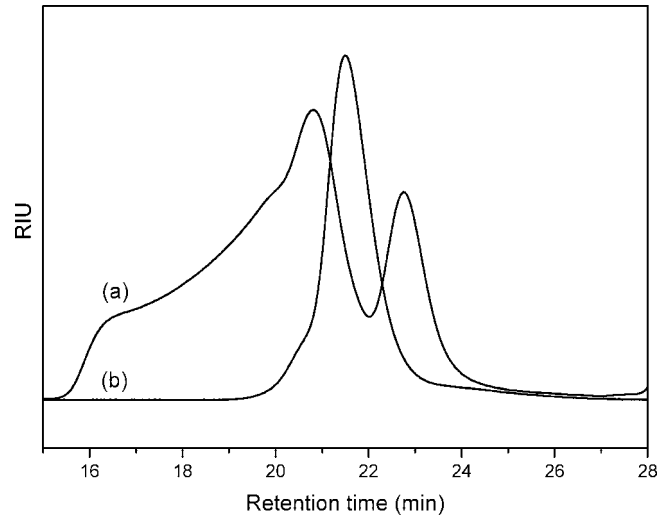


Figure 4. Gel permeation chromatograms of 4-armed poly(*n*-butyl acrylate)-*b*-polystyrene that were synthesized by atom transfer radical polymerization using 4-armed bromo-terminated poly(*n*-butyl acrylate) as macroinitiator at 90 °C for 4 h at feeding molar ratios of monomer to initiator of (a) 450 and (b) 4500.

derived in the same manner from dendritic [G#2] polyol, which was synthesized following the method described in the literature.[15] Then star-shaped PBA with 4, 6, or 12 arms was obtained by the ATRP of BA monomer in the presence of CuBr/PMDETA complex from the corresponding initiators. The feeding molar ratios of the catalytic complex to tetrabromo-, hexabromo-, and dodecabromo-functionalized initiators were set to 4, 6, and 12, respectively, to maintain sufficient catalytic power at each active site on the multifunctional initiators and to control the propagation of the monomers on each arm of the star-shaped polymers. All GPC chromatograms of these star-shaped PBA, shown in Figure 1, revealed a single symmetric peak and nearly monodispersed molecular weights, indicating well-controlled chain growth during ATRP. Herein, the number-averaged molecular weights (M_n) of these polymers were determined from both GPC chromatograms, using linear polystyrene as a standard, and ^{1}H NMR spectra, calculating from the peak area ratio of methylene protons (δ = 4.05 ppm) on the butyl ester side chain to the peripheral methyl protons (δ = 1.10 ppm) on the core initiators. Figure 2 presents an example

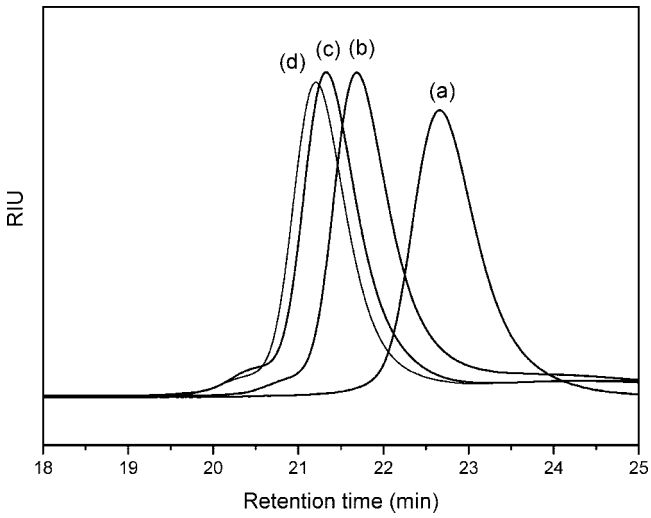


Figure 5. Gel permeation chromatograms of (a) 12-armed poly(*n*-butyl acrylate) macroinitiator and corresponding 12-armed poly(*n*-butyl acrylate)-*b*-polystyrene copolymers after polymerization time of (b) 1 h (4%), (c) 2 h (5%), and (d) 3 h (6%). The value in parentheses represents the monomer conversion.

^{1}H NMR spectrum of 12-armed PBA. Table 1 presents the molecular weights of 4-, 6-, and 12-armed PBA, determined by both GPC and NMR methods. Notably, the GPC method often underestimates the M_n values of branched polymers, such as dendrimers and star-shaped polymers, because they have a more globular architecture than linear polymers, causing the molecules are smaller than random-coiled polystyrene standards.[8,17] Although the M_n values determined in this study by both methods reveal acceptable discrepancies, the M_n values determined by the NMR method for all star-shaped polymers are still closer to the target values calculated from the monomer conversion at a defined propagation time. This fact also reveals that the ATRP of BA from the multifunctionalized initiators was well-controlled.

Thermogravimetric analysis (TGA) was performed to compare the thermal stability of star-shaped PBA with that of linear PBA (M_n: 25 000); the results for all samples plotted in Figure 3 clearly show a major weight loss at around 400 °C, which results from the thermal degradation of PBA segments either on linear or star-shaped polymers. Interestingly, zooming in on the temperature range 200−300 °C of the degradation curves of 4-, 6-, and 12-armed PBAs revealed slight weight losses (ca. 1−3%); conversely, commercial linear PBA exhibited no such weight loss. Moreover, GPC analyses verified that the structures of star-shaped PBA were intact because the changes in M_n values and molecular weight distributions upon heating the sample to 250 °C were negligible. Therefore, the slight weight losses of these star-shaped polymers according to TGA analyses may mainly correspond to the thermolysis of carbon−halogen bonds at the ends of the polymeric chains. After heating the multiarmed PBA samples to 250 °C for 10 min, the observed weight losses were very close to the calculated weight percentages of the bromo end groups on corresponding multiarmed PBA (Table 1).

Since TGA results confirmed that the active halogen groups were still present at the chain ends of star-shaped PBA after BA polymerization, they can be further used as initiators for the propagation of the second monomer, styrene, by ATRP to yield a starburst PBA−PS block copolymer. The feeding molar ratios of monomer to the macroinitiators were held at around 4500, 6600, and 12 000 for 4-, 6-, and 12-armed PBA, respectively. In other words, every PBA arm was fed with 1000−1200 styrene monomers, which range of amounts was about 10 times the amount required theoretically to be fed for the synthesis of the star copolymer with the desired molecular weight. GPC analyses (Figure 4) show a substantial increase in the molecular weight distribution after the introduction of the PS block into the 4-armed PBA when the molar ratio of styrene to PBA was less than 4500. As the ratio was increased to 4500, the propagation of the second block can be well-controlled by ATRP, such that the generated 4-armed PBA-*b*-PS exhibit almost monodispersed molecular weight because the styrene monomer also acts as a solvent, and the use of a large amount of styrene reduces the concentration of the persistent radicals at each chain end of the star and increases the distance between the molecules, effectively suppressing intermolecular radical combination, star−star coupling. At a cost of lower propagation rate, extremely dilute conditions improve the ATRP manipulation of PS block from star-shaped macroinitiators even in the case of a 12-armed PBA. GPC traces of 12-armed PBA-*b*-PS following the polymerization of styrene for various times, displayed in Figure 5, indicate an increase in molecular weight while the chromatogram retains a single elution peak with a polydispersity of under 1.2. A monomer conversion value of less than 15% was required for both 4- and 6-armed systems to yield star-shaped PBA-*b*-PS copolymers with a symmetric Gaussian distribution of molecular weights and a polydispersity of under 1.2; however, a much lower value of less than 5% was needed for a 12-armed star because of high possibility of star−star coupling termination for highly branched molecules. Additionally, the degree of polymerization (DP) of the PS block on star-shaped copolymers was also estimated from the ratio of the area under the peak that corresponded to the aromatic protons on the PS block (Figure 6a, peak A) to that of the peak of the methylene protons on the PBA block (Figure 6a, peak B) in the ^{1}H NMR spectrum. Figure 6a depicts an example of 12-armed PBA-*b*-PS. Table 2 presents the M_n values and polydispersties (M_w/M_n) of all star-shaped copolymers calculated from both NMR and GPC methods.

The conversion of hydrophobic PS segments on three star-shaped copolymers (4-armed PBA-*b*-PS: run 2; 6- and 12-armed PBA-*b*-PS: run 1 in Table 2) into hydrophilic PSS was carried out by a gentle sulfonation reaction at room temperature, based on Makowski's method.[16] A sulfonating agent, acetyl sulfate, was freshly prepared by adding concentrated sulfuric acid to a solution of acetic anhydride in cold dichloroethane and then applied in situ to sulfonate the styrene block on 4-, 6-, and 12-armed PBA-*b*-PS to yield starburst PBA-*b*-PSS. Figure 6b presents an example of ^{1}H NMR analysis of 12-armed PBA-*b*-PSS. The absence of any marked change in the intensity of the peak that corresponds to *n*-butyl protons on PBA at 4.2 ppm clearly demonstrates the intact structure of BA following the treatment with acetyl sulfate. The appearance of the signal at $\delta = 7.6$ ppm proved the formation of styrenesulfonate and resulted from the downfield shift of the meta protons on the aromatic rings due to the electron-withdrawing effect of adjacent sulfonate group. Moreover, the extent of sulfonation (f) of the PS block can be determined from the ratio of the area under the peak of the meta protons (Figure 6b, peak C) on the sulfonated aromatic rings to the sum of areas of the peaks of the meta and para protons (Figure 6b, peak D) on the unsulfonated aromatic rings.[18] Deuterated methanol instead of D_2O was selected as the solvent in the NMR analyses because it effectively dissolves both blocks in amphiphilic star-shaped copolymers, such that each group of aromatic protons on either PSS or PS moieties can be identified. Based on the near disappearance of peak D, the f values of 4-, 6-, and 12-armed copolymers all reach 90−100%. Consequently, these star-shaped block copolymers are highly dispersed in water and are amphiphilic because of the ionic PSS shell and the lipophilic PBA core.

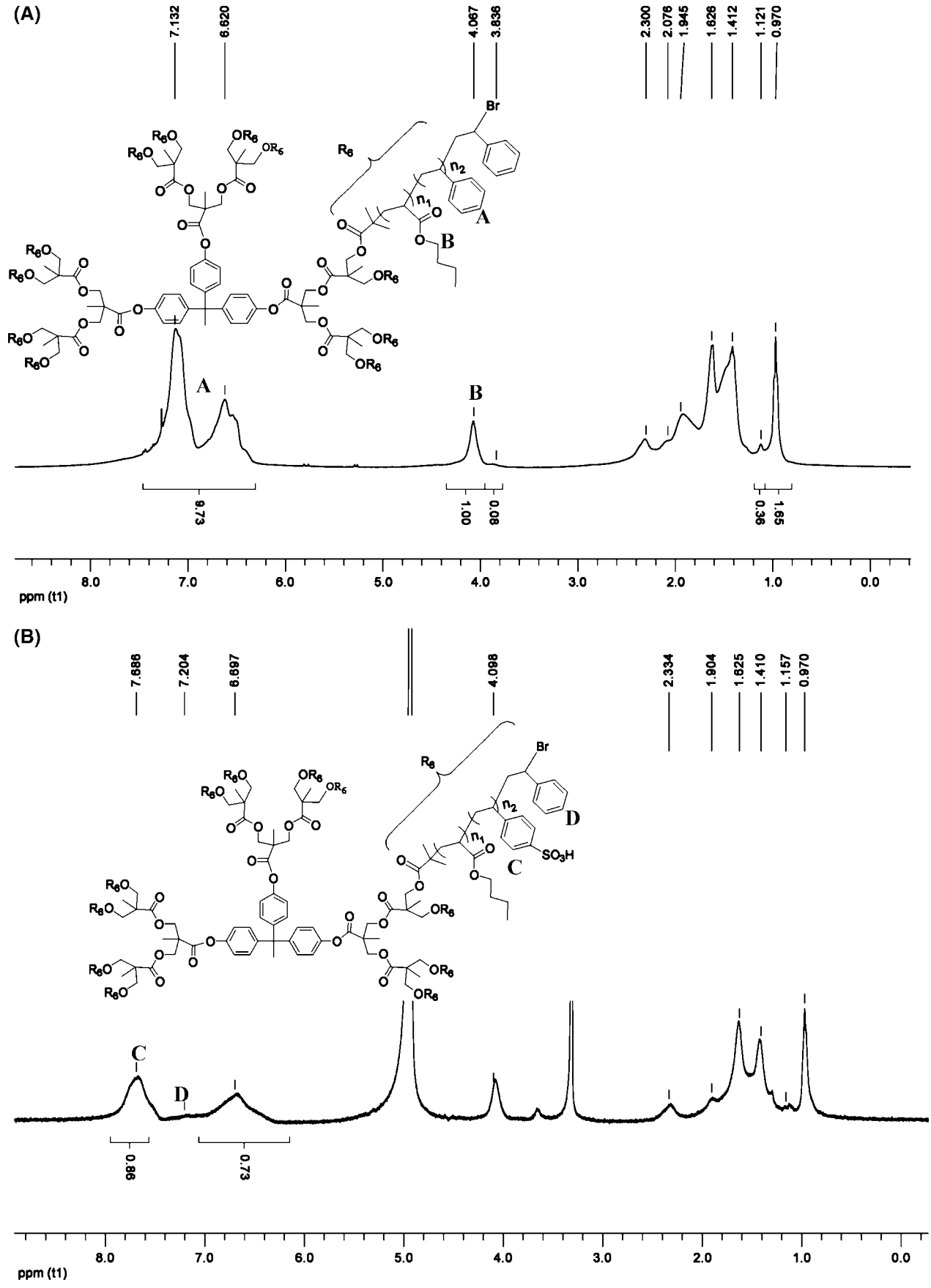


Figure 6. (a) ^{1}H NMR spectrum of 12-armed poly(*n*-butyl acrylate)-*b*-polystyrene in $CDCl_3$. (b) ^{1}H NMR spectrum of 12-armed poly(*n*-butyl acrylate)-*b*-poly(styrenesulfonate). The near disappearance of peak D indicates a complete sulfonation of polystyrene blocks.

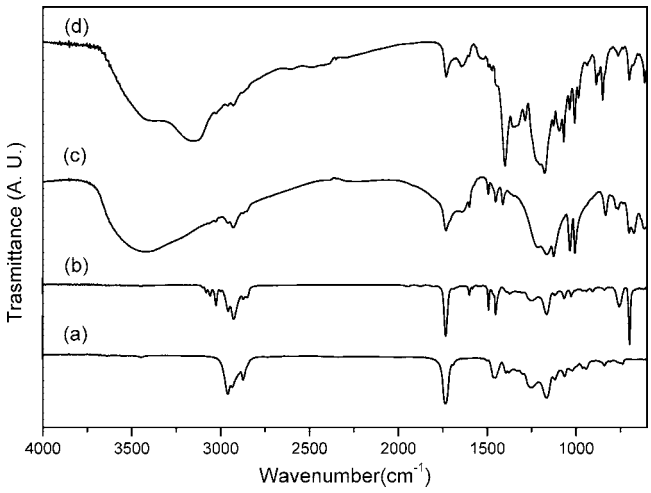


Figure 7. FT-IR spectra of 12-armed (a) poly(*n*-butyl acrylate), (b) poly(*n*-butyl acrylate)-*b*-polystyrene, (c) poly(*n*-butyl acrylate)-*b*-poly(styrenesulfonate), and (d) poly(*n*-butyl acrylate)-*b*-poly(styrenesulfonate)/poly(3,4-ethylenedioxythiophene).

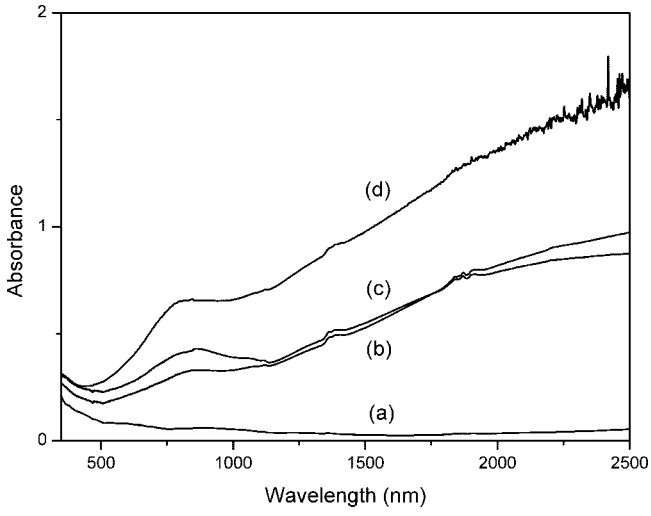


Figure 8. UV−vis absorption spectra of (a) glass substrate and thin films of (b) 4-armed, (c) 6-armed, and (d) 12-armed poly(*n*-butyl acrylate)-*b*-poly(styrenesulfonate)/poly(3,4-ethylenedioxythiophene).

Preparation of Star-Shaped Poly(*n*-butyl acrylate)-*b*-poly(styrenesulfonate)/Poly(3,4-ethylenedioxythiophene) (PBA-*b*-PSS/PEDOT) as Conductive Core−Shell Nanoparticle. The counterion-induced polymerization of conjugated monomer, such as aniline or 3,4-ethylenedioxythiophene (EDOT), was performed using anionic polyelectrolyte as a codopant and steric stabilizer; this synthetic scheme takes advantage of the preferential electrostatic alignment of the ionic monomer on the counterionic template to minimize branching and promote the linear chain growth of conjugated polymer.[19] In this study, star-shaped PBA-*b*-PSS bears a lipophilic PBA core and an anionic PSS shell and can therefore be regarded as not only a unimolecular polymeric micelle but also an anionic macrotemplate for the propagation of EDOT using the counterion-induced polymerization technique. After oxidative treatment of ammonium persulfate (APS), EDOT monomers first form the radical cations on the thiophenic ring and then polymerize along the anionic PSS chains through electrostatic induction. The fact that a colorless solution of star-shaped PBA-*b*-PSS turned into dark blue without precipitation reveals the formation of stable star-shaped PBA-*b*-PSS/PEDOT complex. The blue powder obtained by the lyophilization of the clear complex solution remains highly soluble in water, suggesting that these star-shaped complexes behave as a single system rather than two separated species. No precipitation was observed after the thus-prepared samples were stored under ambient conditions for 3 months. Figure 7 presents an example of FT-IR characterization of the 12-armed PBA, PBA-*b*-PS, PBA-*b*-PSS, and PBA-*b*-PSS/PEDOT complex. The characteristic absorption band at 1730 cm^{-1} is assigned to the C═O stretching mode of butyl ester on the PBA core, and that at 1180 cm^{-1} corresponds to the S═O stretching mode of sulfonated aromatic rings on the PSS shell. The formation of PEDOT was supported by the presence of the absorption bands at 1094 and 1176 cm^{-1}, corresponding to the C−O−C stretching in the ethylenedioxy group, and the bands at 1345 and 1532 cm^{-1}, corresponding to the C−C or C═C stretching of thiophene ring. Moreover, the UV−vis spectra of these star-shaped complexes (Figure 8) clearly exhibit strong and increasing absorption starting from about 500 nm and extending to the near-IR region, resulting from the polaron and bipolaron transitions of the PSS-doped PEDOT.

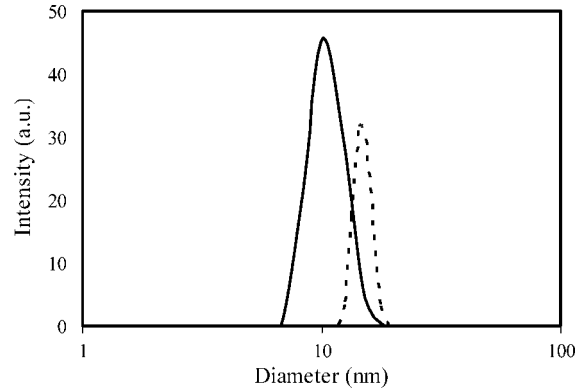


Figure 9. Size distribution plots of poly(*n*-butyl acrylate)-*b*-poly(styrenesulfonate) (solid line) and poly(*n*-butyl acrylate)-*b*-poly(styrenesulfonate)/poly(3,4-ethylenedioxythiophene) (dashed line) in water at a concentration of 5×10^{-3} wt %. Measurements were made by dynamic light scattering at room temperature.

Dynamic light scattering measurements were conducted to determine the particle size of multiarmed PBA/PSS and PBA/PSS−PEDOT in water. The diameters of 4-, 6-, and 12-armed PBA−PSS in water were found to be 17.1, 15.8, and 11.5 nm, respectively, and increased to 19.4, 18.5, and 15.2 nm, after they were entangled with PEDOT. Figure 9 plots the size distributions of 12-armed PBA/PSS and PBA/PSS−PEDOT. Additionally, electrical conductivity measurements were made using the four-point probe method, and the conductivities of 4-, 6-, and 12-armed PBA-*b*-PSS/PEDOT complexes were determined to be 6.7, 4.9, and 6.8 mS/cm, respectively. Furthermore, the elastomeric PBA core enables the as-synthesized star polymer-based conductive nanoparticle dispersion to be simply cast on a glass substrate to prepare a uniform and cellophane-like film with noteworthy flexibility and excellent adhesion to the substrate.

Conclusions

A series of novel conducting core−shell-like nanoparticles were successfully synthesized by the oxidative polymerization of EDOT using well-defined 4-, 6-, and 12-armed PBA-*b*-PSS copolymers as anionic templates, which were prepared via the ATRP of *n*-butyl acrylate and then styrene from tetra-, hexa-, and dodecabromo-functionalized initiators, respectively, followed by the sulfonation of the PS segments into PSS with acetyl sulfate. By holding the feeding ratios of styrene monomer to PBA macroinitiator at 4500, 6600, and 12 000 for 4-, 6-, and 12-armed stars, respectively, the undesired intermolecular coupling was effectively reduced to ensure that the ATRP was

performed as a well-controlled process and at a moderate reaction rate to yield starburst block copolymers with a preset molecular weight and a polydispersity of less than 1.2 because the monomers also acted as a solvent to increase the distance between star molecules. Additionally, treating the starburst PBA-*b*-PS with acetyl sulfate at room temperature leads to the nearly complete sulfonation of PS but preserves the structure of butyl ester on PBA blocks to form amphiphilic macromolecules. These thus-synthesized star-shaped PBA-*b*-PSS/PEDOT complexes not only disperse highly in water but also combine the elasticity of the PBA core and the electrical conductivity of PSS/PEDOT shells. A cellophane-like film with remarkable flexibility, excellent adhesion to the substrate, and adequate conductivity can be easily prepared by simple casting without secondary doping. Further investigations of the imaging of single 12-armed PBA-*b*-PSS/PEDOT complex and the self-assembly of such complexes into an ordered array are now underway.

Acknowledgment. The authors thank the National Taiwan University and National Science Council of Republic of China, Taiwan, for financially supporting this research.

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MA7027243