Micelles Possessing Mixed Cores and Thermoresponsive Shells Fabricated from Well-Defined Amphiphilic ABC Miktoarm Star Terpolymers

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ABSTRACT: Amphiphilic ABC miktoarm star terpolymers consisting of polystyrene, poly(ε-caprolactone), and poly(*N*-isopropylacrylamide) arms, PS(-*b*-PNIPAM)-*b*-PCL, were synthesized via a combination of atom transfer radical polymerization, ring-opening polymerization (ROP), and click chemistry. Difunctional PS bearing an alkynyl and a primary hydroxyl moiety at the chain end, PS-*alknyl-OH*, was prepared by reacting azido-terminated PS with an excess of 3,5-bis(propargyloxy)benzyl alcohol (BPBA) under click conditions. The subsequent ROP of ε-caprolactone using PS-*alknyl-OH* macroinitiator afforded PS(-*alkynyl*)-*b*-PCL copolymer bearing an alkynyl moiety at the diblock junction point. Target PS(-*b*-PNIPAM)-*b*-PCL amphiphilic ABC miktoarm star terpolymers were then prepared via click reaction between PS(-*alkynyl*)-*b*-PCL and an excess of azido-terminated PNIPAM (PNIPAM-N_3). The removal of excess PNIPAM-N_3 was accomplished by "clicking" onto alkynyl-functionalized Wang resin. All the intermediate and final products were characterized by gel permeation chromatography, ^{1}H NMR, and FTIR. In aqueous solution, the obtained amphiphilic ABC miktoarm star terpolymer self-assembles into micelles possessing mixed PS/PCL cores and thermoresponsive shells, which were further characterized by dynamic laser light scattering and transmission electron microscopy. © 2009 Wiley Periodicals, Inc. J Polym Sci Part A: Polym Chem 47: 1636–1650, 2009
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INTRODUCTION

The supramolecular self-assembly of amphiphilic block copolymers in aqueous solution have been extensively investigated in the past decade.[1–6] Previous studies in this field mainly focused on structural characterization and morphology control of self-assembled aggregates from linear-shaped AB or ABC block copolymers,[7–9] as well as exploring their applications as drug nanocarriers, biomineralization template, colloidal stabilizer, and rheology modifier.[10,11] Although less attention has been paid to the self-assembly of nonlinear-shaped amphiphilic block copolymers in aqueous solution, it is well accepted that chain architectures (topology) of block copolymers can play an important role in determining their self-assembly behavior both in solution and bulk states.[12–15]

When three types of polymer sequences are arranged in a nonlinear fashion, the simplest

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form would be ABC miktoarm star terpolymers. In the context of their supramolecular self-assembly in aqueous solution, notable examples have been published by Lodge and coworkers.[16–18] They synthesized miktoarm star terpolymers consisting of hydrophilic poly(ethylene oxide) (PEO), hydrophobic perfluorinated polyether, and hydrogenated polybutadiene arms and investigated their self-assembly in dilute aqueous solution. Interestingly, depending on the relative block lengths, a variety of morphologies ranging from discrete multicompartment micelles, extended worm-like structures with segmented cores, polygonal bilayer sheets, and laterally nanostructured vesicles have been observed, taking advantage of the miktoarm star topology and the intrinsic incompatibility between perfluorinated polyether and hydrogenated polybutadiene within hydrophobic cores or bilayers.[16–18]

Concerning the synthesis of miktoarm star terpolymers, the first few examples typically rely on anionic polymerization, which requires the strict control of molar ratios between reactive species.[14,19–22] Huang and coworkers[23–25] and Jérôme and coworkers[26,27] successful prepared a series of miktoarm star terpolymers via a combination of anionic polymerization and ring-opening polymerization (ROP). On the other hand, the invention of controlled radical polymerizations, such as nitroxide-mediated radical polymerization (NMP), atom transfer radical polymerization (ATRP), and reversible addition-fragmentation chain transfer polymerization, has considerably facilitated the synthesis of miktoarm star terpolymers. A variety of miktoarm star terpolymers have been synthesized employing a combination of controlled radical polymerization techniques and ROP.[24,28–39]

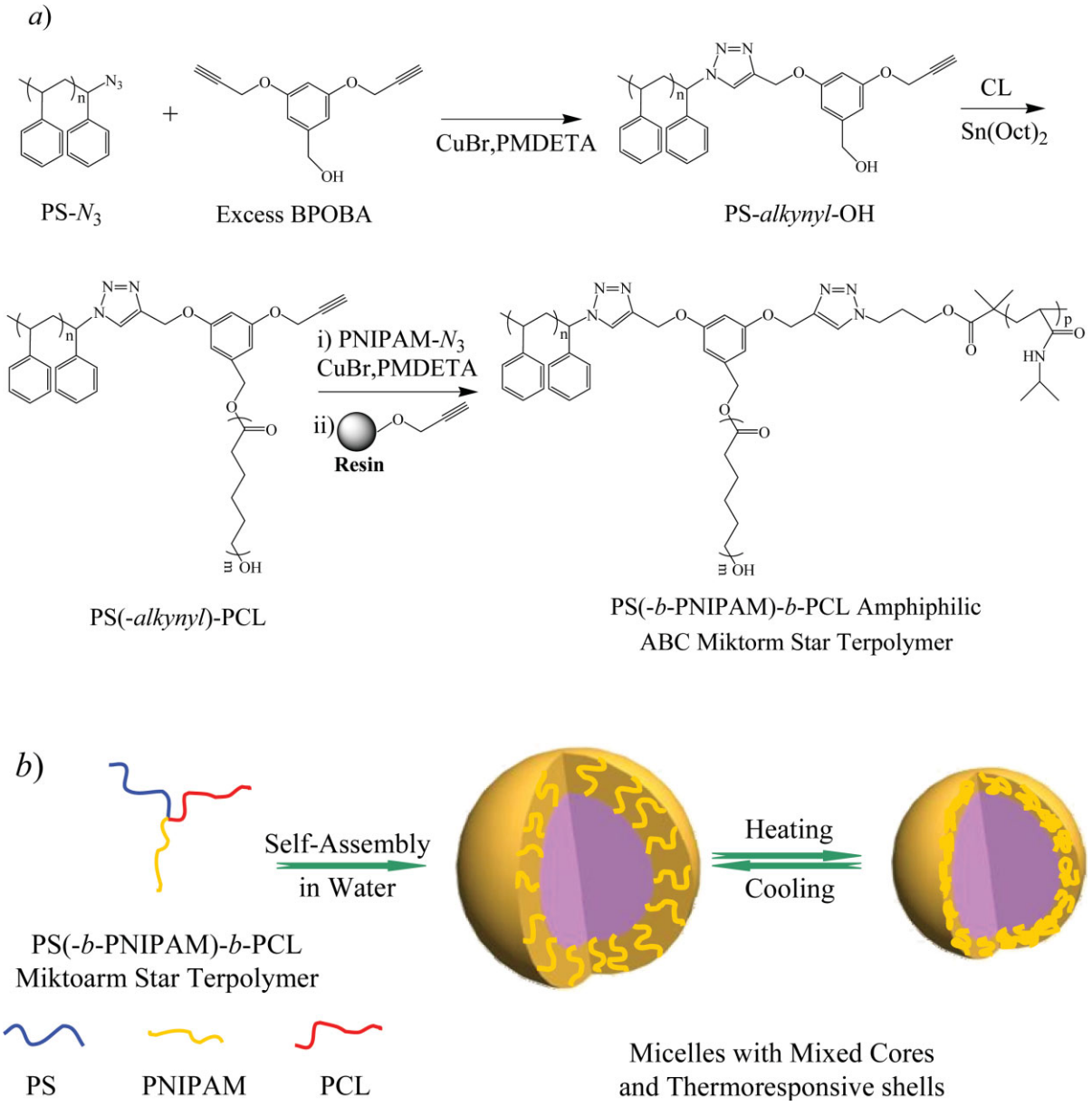
In the past few years, the concept of click chemistry invented by Sharpless and coworkers[40–42] has also been incorporated into the synthesis of miktoarm star terpolymers, serving as a highly efficient coupling technique between well-defined polymer precursors.[43–50] Tunca and coworkers[51] reported the synthesis of miktoarm star terpolymer consisting of polystyrene (PS), poly(methyl methacrylate) (PMMA), and poly(*t*-butyl acrylate) or PEO arms via a combination of NMP, ATRP, and click reaction. They also succeeded in preparing miktoarm star terpolymers of poly(ε-caprolactone) (PCL), PS, and PMMA arms in a one-pot manner, taking advantage of the compatibility between reaction conditions of NMP, ROP, and click reaction.[52]

It should be noted that the aforementioned examples mainly focused on the synthetic aspect. Our research interests partially involve the controlled synthesis of responsive block copolymers and their supramolecular self-assembly in aqueous solution. Herein we report the synthesis of amphiphilic miktoarm star copolymer, PS(-*b*-PNIPAM)-*b*-PCL, consisting of PS, PCL, and thermoresponsive poly(*N*-isopropylacrylamide) (PNIPAM) arms by coupling ATRP, ROP, and click techniques [Scheme 1(a)]. In aqueous solution, it self-assembles into core-shell nanoparticles consisting of mixed PS/PCL cores and thermoresponsive PNIPAM coronas [Scheme 1(b)]. Dynamic laser light scattering (LLS) and transmission electron microscopy (TEM) were further employed to characterize the micellar structure and thermoresponsive collapse of PNIPAM coronas.

EXPERIMENTAL

Materials

N-Isopropylacrylamide (NIPAM) (97%; Tokyo Kasei Kagyo) was purified by recrystallization from a mixture of benzene and *n*-hexane (1/3, v/v). ε-Caprolactone (ε-CL, 99%; Acros) was vacuum-distilled from CaH_2 just prior to use. Styrene (St, 99.5%; Beijing Chemical Factory) was successively washed with aqueous NaOH (5.0 wt %) and water and then distilled over CaH_2 at reduced pressure. *N*,*N*,*N*′,*N*″,*N*″-Pentamethyldiethylenetriamine (PMDETA), tris(2-aminoethyl)amine (TREN), copper(I) bromide (98%), propargyl bromide (80% solution in toluene), tin(II) 2-ethylhexanoate ($Sn(Oct)_2$, 95%), α-bromoisobutyryl bromide, (1-bromoethyl)benzene, and Wang resin (1.47 mmol/g) were purchased from Aldrich and used as received. Sodium azide (NaN_3, 99%) and sodium hydride (NaH, 60% suspension in oil) were purchased from Alfa Aesar and used without further purification. Tetrahydrofuran (THF, 99.5%) and toluene (99.5%) were refluxed and distilled over sodium benzophenone until a purple color was obtained. Triethylamine and dichloromethane (CH_2Cl_2) were dried with CaH_2 and distilled at reduced pressure. Methyl 3,5-dihydroxybenzoate, 3-chloro-1-propanol, *N*,*N*-dimethylformamide (DMF), 2-propanol, and all other chemicals were purchased from Sinopharm Chemical Reagent Co. and used as received. Tris(2-(dimethylamino)ethyl) amine (Me_6TREN), 3,5-bis(propargyloxy)benzyl alcohol (BPBA), and



Scheme 1. (a) Synthetic schemes employed for the preparation of PS(-*b*-PNIPAM)-*b*-PCL amphiphilic ABC miktoarm star terpolymer via a combination of ATRP, ROP, and click reactions. (b) Schematic illustration of the fabrication of micelles with mixed PS/PCL cores and thermoresponsive coronas from PS(-*b*-PNIPAM)-*b*-PCL amphiphilic ABC miktoarm star terpolymer.

3-azidopropyl 2-bromoisobutyrate (APBIB) were synthesized according to the literature procedures.[53–55]

General schemes employed for the synthesis of PS(-*b*-PCL)-*b*-PNIPAM miktoarm star terpolymers are shown in Scheme 1(a), which involve consecutive click reactions and ROP steps. Table 1 summarizes the structural parameters of all intermediate and final products.

Alkynyl-Functionalized Wang Resin[56]

Alkynyl-functionalized Wang resin was synthesized as follows. Commercial Wang resin (5 g, 7.35 mmol) was dispersed in 40 mL dry DMF under stirring. After cooling to 0 °C, NaH (467 mg, 11.7 mmol) was added into the reaction flask. The reaction mixture was stirred at 0 °C for 50 min followed by the addition of propargyl bromide

Table 1. Summary of Structural Parameters of All Intermediate and Final Products

Samples	$[M]_0$:[Initiator]:[Catalyst]	Conversion (%)	DP_{NMR}[a] (PS/PNIPAM/PCL)	$M_{n,GPC}$[b] (kDa)	M_w/M_n[b]
PS_{43}-*Br*[c]	200:1:1	21	44/0/0	4.7	1.05
PS_{43}-N_3[d]			43/0/0	4.7	1.05
PS_{43}-*alkynyl-OH*[e]			43/0/0	4.8	1.05
PS_{43}(-*alkynyl*)-*b*-PCL_{55}[f]	250:4.5:1	99	43/0/55	12.2	1.05
$PNIPAM_{52}$-N_3[g]	55:1:1	95	0/52/0	4.3	1.15
$PNIPAM_{84}$-N_3[g]	90:1:1	93	0/84/0	6.8	1.19
PS_{43}(-*b*-$PNIPAM_{52}$)-*b*-PCL_{55}[h]			43/52/55	14.5	1.05
PS_{43}(-*b*-$PNIPAM_{84}$)-*b*-PCL_{55}[h]			43/84/55	16.2	1.10

[a] Determined by ^{1}H NMR.
[b] Determined by GPC analysis in THF at a flow rate of 1.0 mL/min.
[c] ATRP of St was carried out using (1-bromoethyl)benzene as initiator and CuBr/PMDETA as catalysts in anisole at 80 °C for 4 h.
[d] The nucleophilic substitution of terminal Br end group in PS-*Br* with NaN_3 was conducted in DMF at room temperature for 24 h.
[e] PS-*alkynyl-OH* was prepared by click reaction of PS-N_3 with an excess of BPBA in DMF at 80 °C for 1.5 h.
[f] The ROP of ε-CL was carried out using PS-*alkynyl-OH* as macroinitiator and $Sn(Oct)_2$ as catalysts in toluene at 90 °C for 24 h.
[g] The ATRP of NIPAM was carried out using APBIB as the initiator and CuCl/Me_6TREN as catalysts in 2-propanol at 30 °C.
[h] PS_{43}(-*b*-$PNIPAM_{52}$)-*b*-PCL_{55} and PS_{43}(-*b*-$PNIPAM_{84}$)-*b*-PCL_{55} were prepared via the click reaction of PS(-*alkynyl*)-*b*-PCL with an excess of $PNIPAM_{52}$-N_3 and $PNIPAM_{84}$-N_3, respectively.

(1.6 g, 13.4 mmol) under N_2 atmosphere. After 12 h, the suspension was filtrated and thoroughly washed with THF and methanol. After drying in a vacuum oven overnight at 50 °C, alkynyl-functionalized Wang resin was obtained with quantitative yield. Fourier transform infrared (FTIR) analysis revealed the presence of characteristic alkynyl signals at ~2100 cm^{-1}.

Synthesis of Azido-Terminated PS

Into a Schlenk tube equipped with a magnetic stirring bar, St (10.42 g, 0.1 mol), (1-bromoethyl)-benzene (93 mg, 0.5 mmol), PMDETA (87 mg, 0.5 mmol), and anisole (5 mL) were added. The flask was degassed by three freeze–pump–thaw cycles, back-filled with N_2, and then placed in an oil bath thermostated at 80 °C. After ~5 min, CuBr (72 mg, 0.5 mmol) was introduced into the reaction mixture under protection of N_2 flow to start the polymerization under N_2 atmosphere. After 4 h, the monomer conversion was determined to be ~21% as judged by ^{1}H NMR. The reaction tube was quenched into liquid nitrogen, exposed to air, and diluted with CH_2Cl_2. After passing through a column of neutral alumina to remove the copper catalysts and removing all the solvent by a rotary evaporator, the residues were dissolved in CH_2Cl_2 and precipitated into an excess of methanol to remove residual monomers. The above dissolution–precipitation cycle was repeated for three times. After drying in a vacuum oven overnight at room temperature, PS-*Br* was obtained as white powder (2.1 g, yield: 20%; $M_{n,GPC}$ = 4.7 kDa; M_w/M_n = 1.05).

^{1}H NMR ($CDCl_3$, δ, ppm): 7.6–6.3 (Ar*H* of PS chain), 4.5 (—CH_2CH(Ph)Br), 2.4–1.2 (—CH_2CH(Ph)— of PS chain), 1.1 (CH_3CH(Ph)—). FTIR (cm^{-1}): 1601, 1489, 1453.

The degree of polymerization (DP) of PS-*Br* was calculated to be 43, which is in reasonable agreement with that determined from ^{1}H NMR analysis [DP_{NMR} = 44; Fig. 1(a)]. The polymer was denoted as PS_{43}-*Br*.

PS_{43}-*Br* (1.5 g) and sodium azide (1.0 g) were dissolved in 5 mL DMF. The reaction mixture was stirred for 24 h at room temperature. The mixture was precipitated into an excess of methanol and filtered. The collected sediments were dissolved in CH_2Cl_2 and passed through a silica gel column, followed by precipitation into methanol. After drying in a vacuum oven overnight at room temperature, azido-terminated PS (PS-N_3) was obtained as a white powder (1.4 g, yield: 93%; $M_{n,GPC}$ = 4.7 kDa; M_w/M_n = 1.05). The polymer was denoted as PS_{43}-N_3.

^{1}H NMR ($CDCl_3$, ppm, δ): 7.6–6.3 (Ar*H* of PS chain), 3.9 (—CH_2CH(Ph)N_3), 2.4–1.2 (—CH_2CH

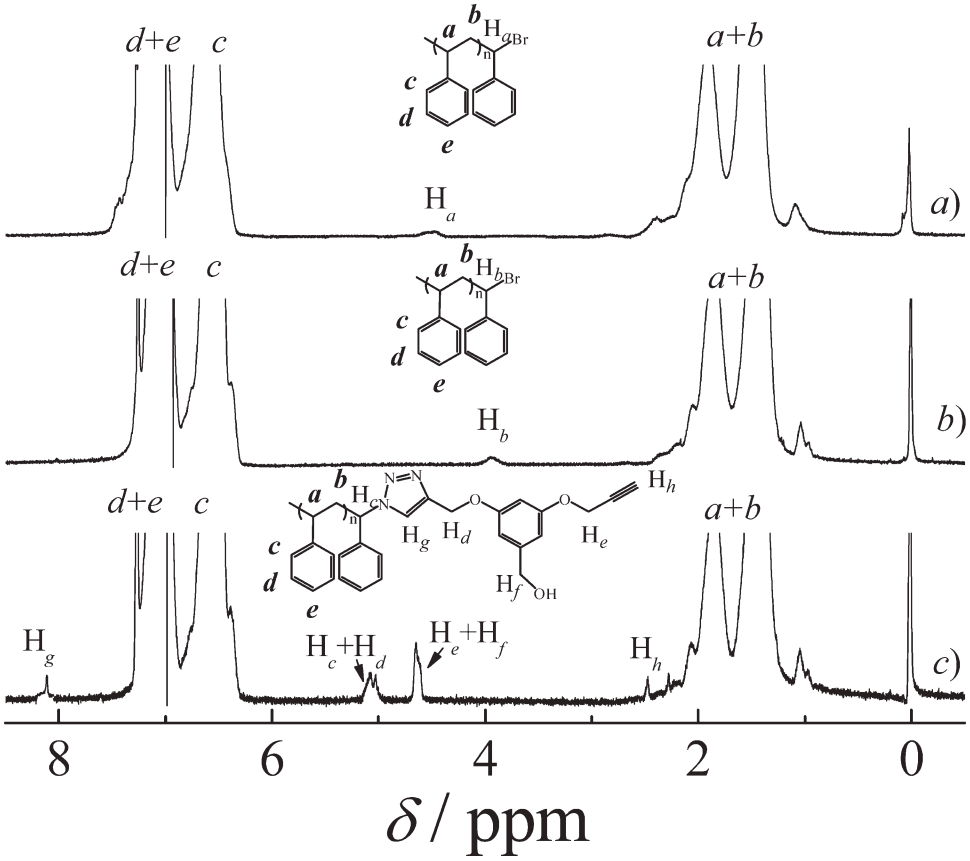


Figure 1. ^{1}H NMR spectra recorded for (a) PS_{43}-*Br*, (b) PS_{43}-N_3, and (c) PS_{43}-*alkynyl-OH* in $CDCl_3$.

(Ph)— of PS chain), 1.1 (CH_3CH(Ph)—). FTIR (cm^{-1}): 2096 (—N_3), 1601, 1489, 1453.

Synthesis PS-*alkynyl-OH*

Into a 20-mL Schlenk tube equipped with a magnetic stirring bar, PS-N_3 (1.39 g, 0.3 mmol), BPBA (3.24 g, 15.0 mmol), PMDETA (0.65 g, 3.75 mmol), and 15 mL DMF were added. After one brief freeze–thaw cycle, CuBr (0.54 mg, 3.75 mmol) was introduced under protection of N_2 flow. The reaction tube was carefully degassed by three freeze–pump–thaw cycles, sealed under vacuum, and placed in an oil bath thermostated at 80 °C. After stirring for 1.5 h, the mixture was exposed to air, diluted with THF, and passed through a basic alumina column to remove copper catalysts. After removing the solvents, the residues were dissolved in THF and precipitated into an excess of methanol. The above dissolution–precipitation cycle was repeated for three times. After drying in a vacuum oven overnight at room temperature, PS-*alkynyl-OH* was obtained as a white solid (1.36 g, yield: 93%; $M_{n,GPC}$ = 4.8 kDa; M_w/M_n = 1.05).

^{1}H NMR ($CDCl_3$, δ, ppm): 8.1 (methine proton in 1,2,3-triazole), 7.6–6.3 (Ar*H* of PS chain), 5.2–4.9 (—CH_2CH(Ph)—1,2,3-triazole and —OCH_2— 1,2,3-triazole), 4.7–4.5 (HC≡CCH_2O and PhCH_2 OH), 2.5 ($OCH_2C{\equiv}CH$), 2.4–1.2 (—CH_2CH(Ph)— of PS chain), 1.1 (CH_3CH(Ph)—). FTIR (cm^{-1}): 1601, 1489, 1453.

Preparation of PS(-*alkynyl*)-*b*-PCL Block Copolymer by ROP of ε-CL

PS(-*alkynyl*)-*b*-PCL with an alkynyl moiety at the diblock junction was prepared via the ROP of ε-CL monomer using $Sn(Oct)_2$ as the catalyst. To a previously flamed Schlenk tube equipped with a magnetic stirring bar, PS-*alkynyl-OH* (0.22 g, 0.045 mmol), ε-CL (0.29 g, 2.5 mmol), $Sn(Oct)_2$ (0.2 mL, 20 g/L solution in dry toluene, 0.01 mmol), and dry toluene (1.5 mL) were added. The reaction tube was carefully degassed by three freeze–pump–thaw cycles, sealed under vacuum,

and placed in an oil bath thermostated at 90 °C. After 24 h, the reaction mixture was dissolved in THF, precipitated into an excess of methanol. After filtration, the sediments were dissolved in THF and precipitated into an excess of methanol, the above dissolution–precipitation cycle was repeated for three times. After drying in a vacuum oven overnight at room temperature, PS(-*alkynyl*)-*b*-PCL was obtained as a white powder (0.41 g, yield: 76%; $M_{n,GPC}$ = 12.2 kDa; M_w/M_n = 1.05). The actual DP of PCL block was calculated to be 55 based on ^{1}H NMR analysis. Thus, the obtained diblock copolymer was denoted as PS_{43}(-*alkynyl*)-*b*-PCL_{55}.

^{1}H NMR ($CDCl_3$, δ, ppm): 8.1 (methine proton in 1,2,3-triazole), 7.6–6.3 (Ar*H* of PS chain), 5.1–4.9 (—CH_2CH(Ph)—1,2,3-triazole, —OCH_2—1,2,3-triazole, and PhCH_2OCO—), 4.6 (HC≡CCH_2OPh), 4.1–3.8 (—COOCH_2CH_2— of PCL chain), 3.6 (—CH_2CH_2OH), 2.4–2.2 (—CH_2CH_2COO— of PCL chain), 2.4–1.2 (—CH_2CH(Ph)— of PS and —$COOCH_2CH_2CH_2CH_2CH_2$— of PCL), 1.1 (CH_3CH(Ph)—). FTIR (cm^{-1}): 1727, 1601, 1489, 1453.

Preparation of Azido-Terminated PNIPAM

Azido-terminated PNIPAM (PNIPAM-N_3) was prepared by ATRP of NIPAM using APBIB as the initiator. A typical procedure was as follows. Into a three-neck flask equipped with a magnetic stirring bar, NIPAM (6.22 g, 55 mmol), Me_6TREN (0.23 g, 1.0 mmol), APBIB (0.25 g, 1.0 mmol), and 2-propanol (12 mL) were added. The mixture was degassed by two freeze–pump–thaw cycles. After the flask was thermostated at 30 °C, CuCl (99 mg, 1.0 mmol) was introduced under the protection of N_2 flow to start the polymerization. The solution turned dark green and apparently more viscous as polymerization proceeded. After 5 h, the monomer conversion was determined to be 95% as judged by ^{1}H NMR. The polymerization was quenched with $CuCl_2$, exposed to air, and diluted with 20 mL THF. The reaction mixture was passed through a silica gel column to remove the copper catalysts. After removing the solvents by a rotary evaporator, the residues were dissolved in THF and precipitated into an excess of diethyl ether. The above dissolution–precipitation cycle was repeated for three times. The final product was dried in a vacuum oven, yielding a white solid (5.5 g, yield: 85%; $M_{n,GPC}$ = 4.3 kDa; M_w/M_n = 1.15).

^{1}H NMR ($CDCl_3$, δ, ppm): 6.9–5.9 (CON*H*CH—), 4.2–3.8 (—CONHC*H*$(CH_3)_2$), 3.4 (—$CH_2CH_2N_3$), 2.5–0.9 (CH_2CHCO and CONHCH $(CH_3)_2$). FTIR (cm^{-1}): 2101 and 1650.

The actual DP of PNIPAM block was determined to be 52 by ^{1}H NMR analysis in $CDCl_3$. Thus, the polymer was denoted as $PNIPAM_{52}$-N_3. Following similar procedures employed for the preparation of $PNIPAM_{52}$-N_3, $PNIPAM_{84}$-N_3 (yield: 83%; $M_{n,GPC}$ = 6.8 kDa; M_w/M_n = 1.19) was also synthesized in 2-propanol at a feed ratio of NIPAM/Me_6TREN/CuCl/APBIB = 90/1/1/1.

Synthesis of PS(-*b*-PNIPAM)-*b*-PCL Amphiphilic ABC Miktoarm Star Terpolymer

The synthesis of PS(-*b*-PNIPAM)-*b*-PCL miktoarm star terpolymers was accomplished by the click coupling between PS(-*alkynyl*)-*b*-PCL diblock copolymer and PNIPAM-N_3 using CuBr as the catalyst (Scheme 1), and a typical procedure was as follows. PS_{43}(-*alkynyl*)-*b*-PCL_{55} (0.223 g, 0.02 mmol) and $PNIPAM_{52}$-N_3 (0.246 g, 0.04 mmol) were dissolved in DMF (5 mL) containing PMDETA (4 mg, 0.02 mmol). After one brief freeze–pump–thaw cycle, CuBr (3 mg, 0.02 mmol) was introduced under the protection of N_2 flow. The reaction tube was then carefully degassed by three freeze–pump–thaw cycles and placed in an oil bath thermostated at 60 °C. After 14 h, alkynyl-functionalized Wang resin (0.2 g, 0.294 mmol alkynyl groups) was added. The suspension was stirred for another 6 h at 60 °C under N_2 atmosphere. After diluting the suspension with THF and passing through a neutral alumina column to remove copper catalysts and resin, the eluents were evaporated to dryness. The residues were dissolved in THF and precipitated into an excess of *n*-hexane. The above dissolution–precipitation cycle was repeated for three times. After drying in a vacuum oven overnight at room temperature, ABC miktoarm star terpolymer, PS_{43}(-*b*-$PNIPAM_{52}$)-*b*-PCL_{55}, was obtained as a white solid (0.147 g, yield: 85%; $M_{n,GPC}$ = 14.5 kDa; M_w/M_n = 1.05).

Following similar procedures as employed for the preparation of PS_{43}(-*b*-$PNIPAM_{52}$)- *b*-PCL_{55}, PS_{43}(-*b*-$PNIPAM_{84}$)-*b*-PCL_{55} ABC miktoarm star terpolymer was also synthesized ($M_{n,GPC}$ = 16.2 kDa; M_w/M_n = 1.10). Table 1 summarizes the structural parameters of all intermediate and final products.

Preparation of Micellar Solutions

Ten micrograms of amphiphilic ABC miktoarm star terpolymer, PS_{43}(-*b*-$PNIPAM_{52}$)-*b*-PCL_{55}, was

dissolved in 1 mL of DMF. Under vigorous stirring, 9 mL of deionized water was added via syringe pump at a flow rate of 0.2 mL/min. After the addition was completed, the dispersion was left stirring for another 5 h. DMF was then removed by dialysis [molecular weight (MW) cutoff: 14 kDa] against deionized water for 24 h. Fresh deionized water was replaced approximately every 6 h. Stock solutions with a characteristic bluish tinge were typically obtained. The micellar solution exhibited no macroscopic phase separation upon standing at room temperature for more than 3 months, suggesting the formation of stable aggregates.

Characterization

Nuclear Magnetic Resonance Spectroscopy

All ^{1}H NMR spectra were recorded at 25 °C on a Bruker AV300 NMR spectrometer (resonance frequency of 300 MHz for ^{1}H NMR) operated in the Fourier transform mode. $CDCl_3$ was used as the solvent.

Gel Permeation Chromatograph

Molecular weights and molecular weight distributions were determined by gel permeation chromatography (GPC) equipped with Waters 1515 pump and Waters 2414 differential refractive index detector (set at 30 °C). It employs a series of three linear Styragel columns HT2, HT4, and HT5 and an oven temperature of 45 °C. The eluent was THF at a flow rate of 1.0 mL/min. A series of low polydispersity PS standards were employed for the GPC calibration.

FTIR Spectroscopy

All FTIR spectra were measured on a Bruker Vector 22 Fourier transform infrared spectrometer using the KBr disk method.

Differential Scanning Calorimetry Thermograms

Differential scanning calorimetry (DSC) was carried on a DSC TA-60WS thermal analysis system (Shimadzu, Japan). Samples were first heated from 20 to 200 °C at a heating rate of 10 °C/min under nitrogen atmosphere, followed by cooling to 20 °C at the rate of 10 °C/min after stopping at 200 °C for 3 min, and finally heating to 200 °C at the rate of 10 °C/min. Glass transition temperature (T_g) and the melting temperature (T_m) were determined as the midpoint and the peak maximum of the transition of the second heating sequence, respectively.

Laser Light Scattering

A commercial spectrometer (ALV/DLS/SLS-5022F) equipped with a multiple tau digital time correlator (ALV5000) and a cylindrical 22 mW Uniphase He-Ne laser ($\lambda_0 = 632$ nm) as the light source was employed for dynamic LLS measurements. Scattered light was collected at a fixed angle of 90° for duration of ~10 min. Distribution averages and particle size distributions were computed using cumulants analysis and CONTIN routines. All data were averaged over three measurements.

Transmission Electron Microscopy

TEM observations were conducted on a JEM-100SX electron microscope at an acceleration voltage of 100 kV. The sample for TEM observations was prepared by placing 10 μL of micellar solution on copper grids coated with thin films of Formvar and carbon successively. No staining was required.

Temperature-Dependent Turbidimetry

The temperature-dependent optical transmittance of the aqueous micellar solution of PS_{43}(-*b*-$PNIPAM_{52}$)-*b*-PCL_{55} (3.0 g/L) at a wavelength of 700 nm was acquired on a Unico UV/vis 2802PCS spectrophotometer with a thermostatically controlled cuvette holder and the heating rate was 0.2 °C/min.

RESULTS AND DISCUSSION

ABC miktoarm star terpolymer can be regarded as two different types of polymer sequences covalently attached to the terminal of the third type of polymer chain. In this work, the target amphiphilic miktoarm star terpolymer consisting of PS, PCL, and PNIPAM arms was prepared via a combination of ATRP, ROP, and click reaction [Scheme 1(a)]. The synthesis started with the preparation of difunctional PS bearing one primary hydroxyl and one alkynyl moieties, PS (-*alkynyl*)-*OH*; these two functional groups were then utilized for the subsequent ROP of ε-CL and

click reaction with azido-terminated PNIPAM, respectively. It should be noted that Tunca and coworkers have successfully prepared miktoarm star terpolymers via combinations of NMP, click reaction, and ROP or ATRP) techniques.[51,52] These different techniques allow different monomer sequences to be incorporated into target molecules. The trifunctional core molecule is crucial for the successful design, and we chose BPBA as the core molecule for the synthesis of PS(-*b*-PNIPAM)-*b*-PCL amphiphilic ABC miktoarm star terpolymer.

Synthesis of PS-*alkynyl-OH*

PS-*Br* precursor was obtained by the ATRP of St monomer using (1-bromoethyl)benzene as the initiator and CuBr/PMDETA as catalysts. This polymerization system has been proved successful for St monomer; moreover, a high degree of end Br group in PS-*Br* can be achieved if monomer conversions were kept relatively low. In our case, the monomer conversion was controlled to be ~21%. The theoretical DP of PS-*Br* was then calculated to be 42, which generally agrees with that determined from GPC (43, using PS standards). For such relatively low-MW PS, the DP can also be calculated from ^{1}H NMR analysis [Fig. 1(a)] by comparing the integration areas of resonance signal at δ = 4.5 ppm (—CH_2CH(Ph)Br) to that at 6.3–7.5 ppm (Ar*H*). The obtained DP_{NMR} was 44. This confirmed that the end-group functionality is close to be quantitative, which is quite crucial in subsequent reactions (Scheme 1).

The nucleophilic substitution of terminal Br end-group in PS-*Br* with NaN_3 was conducted in DMF at room temperature. Quantitative conversion to PS-N_3 was confirmed by ^{1}H NMR results (Fig. 1). After azidation, resonance signal of terminal methine proton in PS-*Br* at δ = 4.5 ppm completely shifted to δ = 3.9 ppm in PS-N_3, which should be ascribed to the methine proton (—CH_2CH(Ph)N_3). A comparison of the FTIR spectra of PS-*Br* and PS-N_3 revealed the presence of a new absorbance peak at 2094 cm^{-1} for PS-N_3, which is characteristic of azide groups. Moreover, the azidation reaction resulted in essentially no changes in the GPC elution peaks for PS-*Br* and PS-N_3 precursors, suggesting that the PS main chains were unaffected. It should be noted that the aforementioned observation agrees quite well with that reported by Vogt and Sumerlin.[57]

The difunctional PS-*alkynyl-OH* bearing one alkynyl and one primary hydroxyl moiety at the chain terminal was obtained by the click reaction of PS-N_3 with an excess of BPBA. Previously, Vogt and Sumerlin[57] prepared PS-based macromonomers via click reacting PS-N_3 with propargyl methacrylate. In the current case, an excess of BPBA was used to ensure that only one propargyl group in BPBA participates in the click reaction with PS-N_3. Monteiro and coworkers[43] have investigated the reaction of PS-N_3 with an excess of tripropargylamine and successfully obtained PS terminated with dialkynyl functionality, which were further employed for the synthesis of AB_2 miktoarm star polymers. The click reaction between PS-N_3 and an excess of BPBA was conducted in DMF at 80 °C using CuBr/PMDETA catalysts. After purification, quantitative chain end transformation was confirmed by ^{1}H NMR analysis [Fig. 1(c)]. We can clearly observe the complete disappearance of resonance signal at δ = 3.9 ppm, —CH_2CH(Ph)N_3 in PS-N_3, after click reaction. Moreover, the appearance of new resonance signals at 8.1 and 4.6–5.2 ppm can also be well ascribed [Fig. 1(c)]. From the FTIR spectrum of PS-*alkynyl-OH* [Fig. 2(c)], it was clearly evident that the characteristic azide absorbance peak at 2094 cm^{-1} completely disappeared, when compared with that of PS-N_3. It should be noted that the alkynyl functionality also exhibits absorbance peak at ~2100 cm^{-1}; however, it was too weak to be clearly discerned in the IR spectrum of PS-*alkynyl-OH*. GPC elution peak of PS-*alkynyl-OH* [Fig. 3(c)] revealed a discernible but slight shift to higher MW side compared with those of PS-*Br* and PS-N_3, accompanied with the increase of M_n

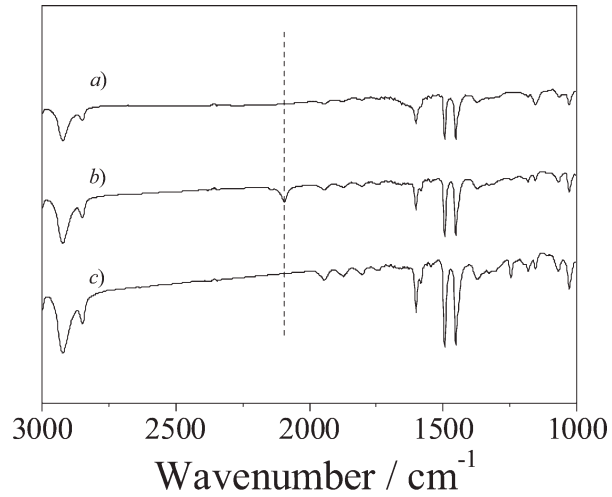


Figure 2. FTIR spectra recorded (a) PS_{43}-*Br*, (b) PS_{43}-N_3, and (c) PS_{43}-*alkynyl-OH*.

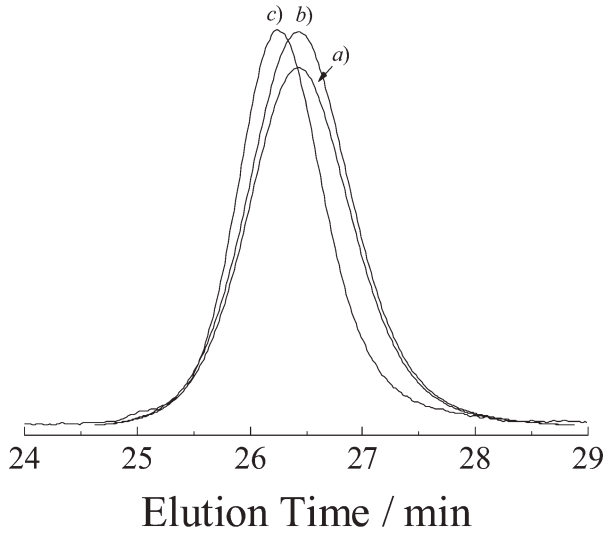


Figure 3. THF GPC traces obtained for (a) PS_{43}-*Br*, (b) PS_{43}-N_3, and (c) PS_{43}-*alkynyl-OH*.

from 4.7 to 4.8 kDa after click functionalization. It should be noted that the elution peak of PS-*alkynyl-OH* was monomodal and quite symmetric, indicating that the click coupling of PS-N_3 by BPBA was negligible. This was reasonable considering that the alkynyl functionality in BPBA is in large excess relative to azido moiety in PS-N_3 (100:1*M* ratio). PS_{43}-*alkynyl-OH* was then employed for the subsequent ROP of ε-CL and click reaction with azido-terminated PNIPAM [Scheme 1(a)].

Synthesis of PS(-*alkynyl*)-*b*-PCL by ROP

PS(-*alkynyl*)-*b*-PCL possessing an alkynyl moiety at the diblock junction was obtained by the ROP of ε-CL in toluene at 90 °C using PS-*alkynyl-OH* as the initiator and $Sn(Oct)_2$ as the catalyst. The monomer conversion typically went to nearly 100% after 24 h under our conditions. ^{1}H NMR spectrum of PS(-*alkynyl*)-*b*-PCL was shown in Figure 4(b), together with the peak assignments. Compared with that of PS-*alkynyl-OH* [Fig. 4(a)], the NMR spectrum of PS(-*alkynyl*)-*b*-PCL revealed the presence of resonance signals characteristic of PS and PCL blocks, and all signals were assigned. From ^{1}H NMR, the number-average molecular weight of PS(-*alkynyl*)-*b*-PCL can be calculated based on the equation: $M_{n,NMR} = I_{4.1}$ DP_{PS} $M_{n,St}/I_{6.3–6.8} + M_{n,PS}$, where $I_{4.1}$ and $I_{6.3–6.8}$ are the integration areas of peak i (4.1 ppm, 2H, —COOCH_2— in PCL block) and peak c (6.3–6.8 ppm, 2H; Ar-*H* of PS block, ortho-position), respectively. DP_{PS} and $M_{n,St}$ are the DP of PS sequence and the molecular weight of St monomer, respectively. The DP of PCL block was then determined to be 55, which agrees quite well with the theoretical DP calculated from feed ratios.

Typical GPC trace of PS(-*alkynyl*)-*b*-PCL was shown in Figure 5(c). Compared with that of PS-*alkynyl-OH*, the elution peak of PS(-*alkynyl*)-*b*-PCL clearly shifted to the higher molecular weight side. Moreover, the elution peak was narrow disperse and quite symmetric and shows no tailing at the lower molecular weight side, indicating a complete consumption of PS-*alkynyl-OH* macroinitiator. GPC analysis gave an M_n of 12.2 kDa and an M_w/M_n of 1.05 for PS(-*alkynyl*)-*b*-PCL. Typical FTIR spectra of PS-*alkynyl*-OH and PS(-*alkynyl*)-*b*-PCL are shown in Figure 6. A comparison of them revealed the new appearance of carbonyl-stretching band at 1727 cm^{-1}, which is characteristic of PCL sequence.

Synthesis of PS(-*b*-PNIPAM)-*b*-PCL ABC Miktoarm Star Terpolymer via Click Coupling

In subsequent steps, azido-terminated PNIPAM was synthesized, and the click reaction of PS (-*alkynyl*)-*b*-PCL with PNIPAM-N_3 facilely afforded PS(-*b*-PNIPAM)-*b*-PCL (Scheme 1). Acrylamido monomers were initially considered to be difficult to be polymerized in a controlled manner by ATRP technique. Teodorescu and Matyjaszewski,[58,59] Brittain et al.,[60] and Masci et al.[61] reported several examples for the ATRP of acrylamido monomer. The most successful synthesis came from the Stöver research group, who employed 2-propanol as the solvent and CuCl/Me_6TREN as the catalysts.[62] Previously, Haddleton and coworkers reported the preparation of azido-terminated PMMA by ATRP using APBIB as the initiator, indicating that terminal azide moiety does not interfere with ATRP polymerization.[54] In this study, we employed APBIB as the initiator and CuCl/Me_6TREN as the catalysts for the ATRP of NIPAM in 2-propanol at 30 °C. THF GPC analysis of PNIPAM-N_3 revealed a monomodal elution peak, giving an M_n of 4.3 kDa and an M_w/M_n of 1.15 [Fig. 5(a)]. The actual DP of PNIPAM was determined to be 52 by ^{1}H NMR analysis in $CDCl_3$. Moreover, FTIR spectrum of PNIPAM-N_3 clearly revealed the presence of absorbance peak at ~2100 cm^{-1} [Fig. 6(a)], which is characteristic of the terminal azide group.

The click reaction between PS_{43}(-*alkynyl*)-*b*-PCL_{55} diblock copolymer and $PNIPAM_{52}$-N_3

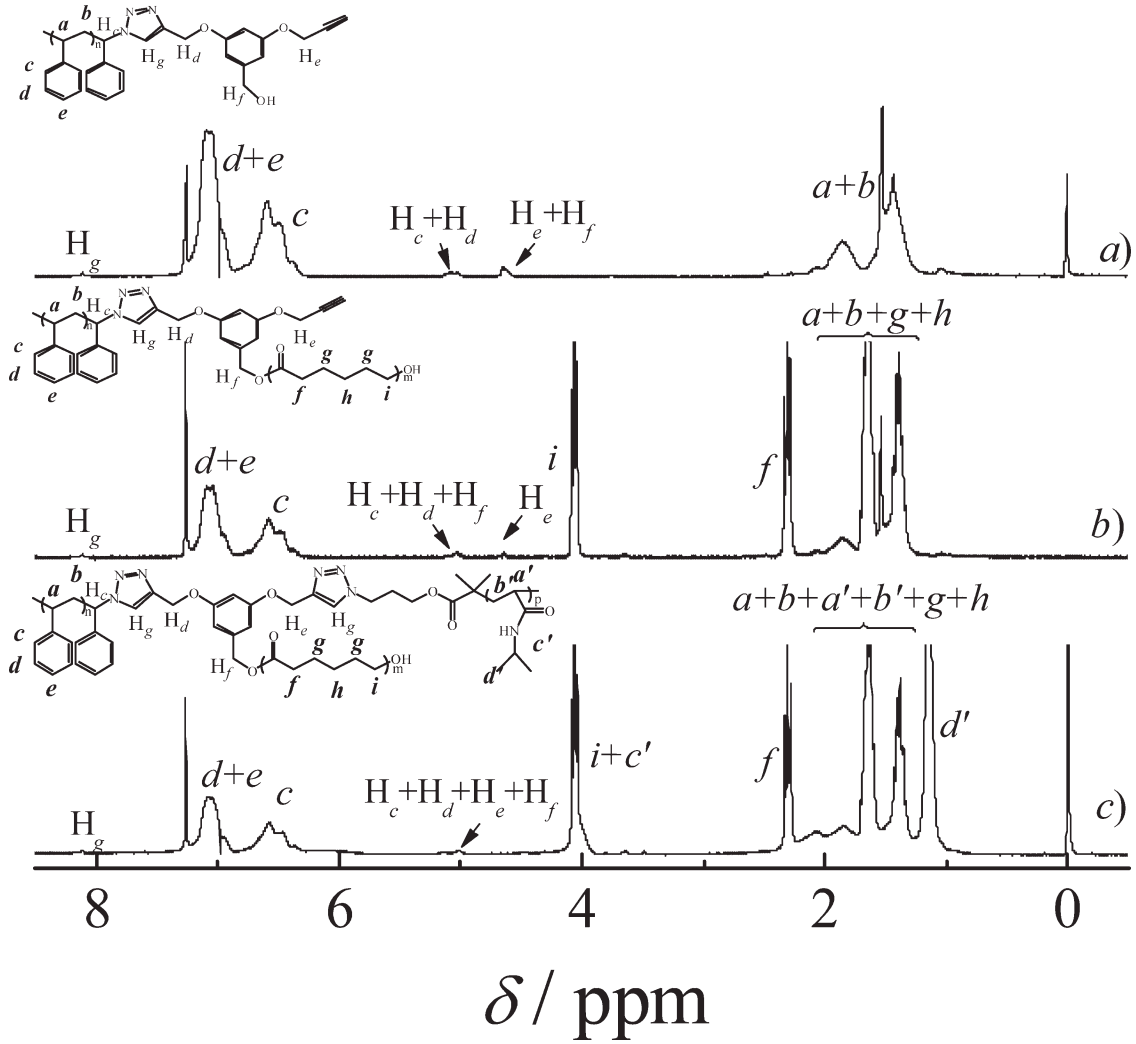


Figure 4. ^{1}H NMR spectra recorded for (a) PS_{43}-*alkynyl*-*OH*, (b) PS_{43}(-*alkynyl*)-*b*-PCL_{55}, and (c) PS_{43}(-*b*-$PNIPAM_{52}$)-*b*-PCL_{55} amphiphilic ABC miktoarm star terpolymer in $CDCl_3$.

afforded the target ABC miktoarm star terpolymer, PS(-*b*-PNIPAM)-*b*-PCL (Scheme 1). To ensure the complete consumption of alkynyl moieties of PS_{43}(-*alkynyl*)-*b*-PCL_{55}, an excess of $PNIPAM_{52}$-N_3 was used. The removal of excess of $PNIPAM_{52}$-N_3 was accomplished by clicking onto alkynyl-functionalized resin, followed by the subsequent simple filtration step.[56]

The purified click coupling product was characterized by ^{1}H NMR, GPC, and FTIR. ^{1}H NMR spectrum of PS(-*b*-PNIPAM)-*b*-PCL amphiphilic ABC miktoarm star terpolymer displayed characteristic resonance signals at 7.2–6.3, 2.38, and 1.14 ppm, which can be ascribed to Ar-*H* of PS, —COOCH_2— of PCL, and —CH(CH_3)$_2$ of PNIPAM sequences, respectively [Fig. 4(c)]. Relative integral ratios between these characteristic peaks agreed quite well with the DPs of the three blocks of PS_{43}(-*b*-$PNIPAM_{52}$)-*b*-PCL_{55}. This strongly supported that all alkynyl groups of PS_{43}(-*alkynyl*)-*b*-PCL_{55} have participated in the click reaction with $PNIPAM_{52}$-N_3.

GPC analysis of PS_{43}(-*b*-$PNIPAM_{52}$)-*b*-PCL_{55} exhibited a monomodal and symmetric peak, giving an M_n of 14.5 kDa and an M_w/M_n of 1.05 (Fig. 5). The absence of a shoulder peak at the lower molecular weight side confirmed that excess $PNIPAM_{52}$-N_3 has been successfully removed via clicking onto alkynyl-functionalized Wang resin. On the other hand, the elution peak of the miktoarm star terpolymer clearly shifted to the higher molecular weight side, when compared with PS_{43}(-*alkynyl*)-*b*-PCL_{55} and $PNIPAM_{52}$-N_3 precursors. This indicated the incorporation of a

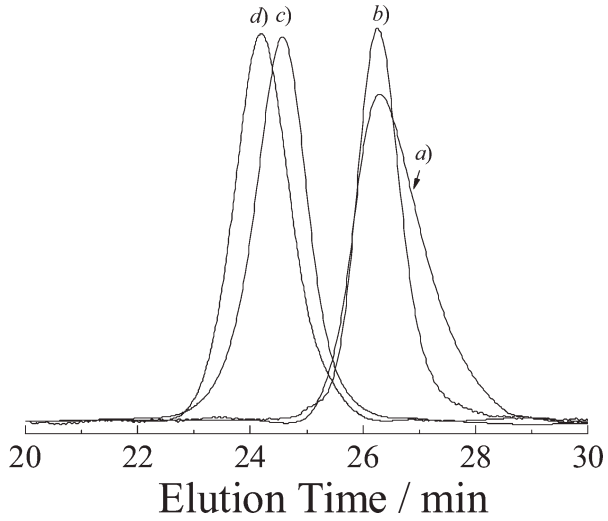


Figure 5. THF GPC traces recorded for (a) PNIPAM$_{52}$-N_3, (b) PS$_{43}$-*alkynyl-OH*, (c) PS$_{43}$(-*alkynyl*)-*b*-PCL$_{55}$, and (d) PS$_{43}$(-*b*-PNIPAM$_{52}$)-*b*-PCL$_{55}$ amphiphilic ABC miktoarm star terpolymer.

third polymer sequence into the diblock architecture. However, compared with the elution peak shift between PS$_{43}$-*alkynyl-OH* and PS$_{43}$(-*alkynyl*)-*b*-PCL$_{55}$, the peak shift from PS$_{43}$(-*alkynyl*)-*b*-PCL$_{55}$ to PS$_{43}$(-*b*-PNIPAM$_{52}$)-*b*-PCL$_{55}$ was relatively small. This can be explained by the miktoarm star topology of PS$_{43}$(-*b*-PNIPAM$_{52}$)-*b*-PCL$_{55}$, which tends to give smaller hydrodynamic volume when compared with that of linear triblock copolymers with comparable MW. This phenomenon has also been observed previously concerning the synthesis of other miktoarm star terpolymers.

FTIR spectrum of PS$_{43}$(-*b*-PNIPAM$_{52}$)-*b*-PCL$_{55}$ was shown in Figure 5(d). Compared to those of PNIPAM-N_3 and PS(-*alkynyl*)-*b*-PCL, we can observe the disappearance of the characteristic azide absorbance peak at $\sim$2100 cm^{-1} in the IR spectrum of PS$_{43}$(-*b*-PNIPAM$_{52}$)-*b*-PCL$_{55}$. On the other hand, absorbance peaks characteristic of PS, PCL, and PNIPAM blocks are clearly evident. Based on results shown earlier, we can conclude that we have successfully obtained amphiphilic ABC miktoarm star terpolymer, PS$_{43}$(-*b*-PNIPAM$_{52}$)-*b*-PCL$_{55}$, via a quite controlled and well-defined manner. Following similar procedures, PS$_{43}$(-*b*-PNIPAM$_{84}$)-*b*-PCL$_{55}$ was also prepared. Detailed synthetic conditions and structural parameters for all intermediate and final products are summarized in Table 1.

Glass transition temperature (T_g) and melting temperature (T_m) are two basic physical parameters of synthetic polymers.[30,63–67] The thermal behavior of PS$_{43}$-*alkynyl-OH*, PS$_{43}$(-*alkynyl*)-*b*-PCL$_{55}$, and PNIPAM$_{52}$-N_3 precursors as well as PS$_{43}$(-*b*-PNIPAM$_{52}$)-*b*-PCL$_{55}$ ABC miktoarm star terpolymer was investigated by DSC measurements (Fig. 7). For PS$_{43}$-*alkynyl-OH* and PNIPAM$_{52}$-N_3 [Fig. 7(a,c)], T_g values were determined to be 88.9 and 130.5 °C, respectively. PS$_{43}$(-*alkynyl*)-*b*-PCL$_{55}$ diblock precursor exhibited a peak melting temperature (T_m) of 57.3 °C ascribed to the PCL segments, whereas the glass transition of PS segment could not be clearly discerned

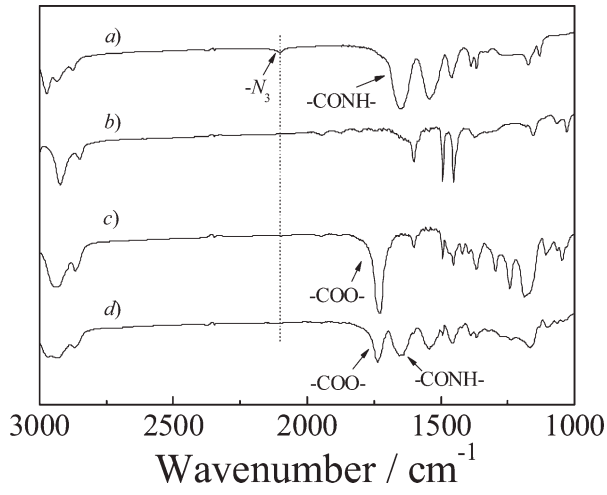


Figure 6. FTIR spectra obtained for (a) PNIPAM$_{52}$-N_3, (b) PS$_{43}$-*alkynyl-OH*, (c) PS$_{43}$(-*alkynyl*)-*b*-PCL$_{55}$, and (d) PS$_{43}$(-*b*-PNIPAM$_{52}$)-*b*-PCL$_{55}$ amphiphilic ABC miktoarm star terpolymer.

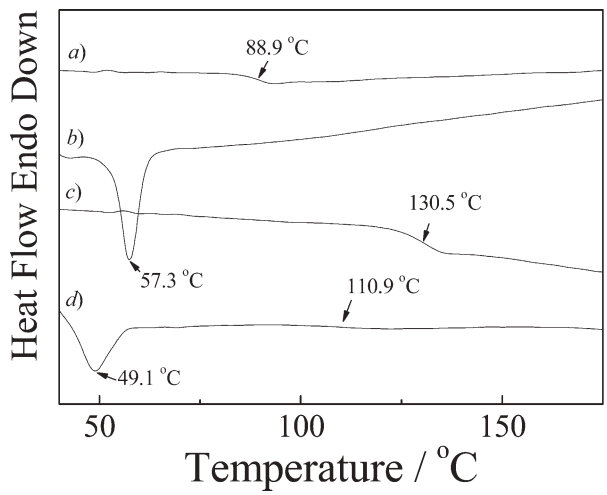


Figure 7. DSC thermograms recorded for (a) PS$_{43}$-*alkynyl-OH*, (b) PS$_{43}$(-*alkynyl*)-*b*-PCL$_{55}$, (c) PNIPAM$_{52}$-N_3, and (d) PS$_{43}$(-*b*-PNIPAM$_{52}$)-*b*-PCL$_{55}$ amphiphilic ABC miktoarm star terpolymer.

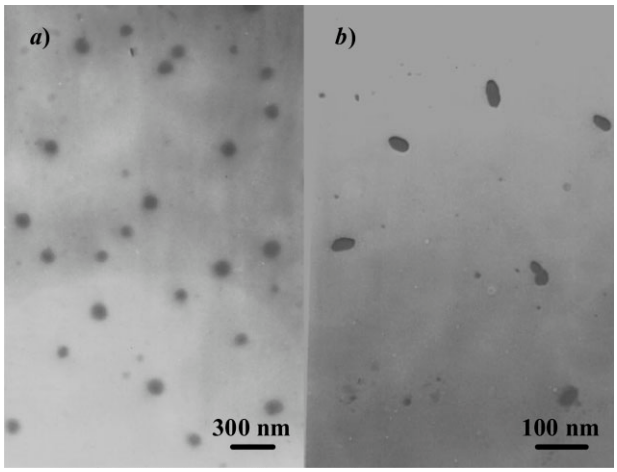


Figure 8. TEM image obtained by drying aqueous micellar solutions of (a) PS_{43}(-*b*-$PNIPAM_{52}$)-*b*-PCL_{55} and (b) PS_{43}(-*b*-$PNIPAM_{84}$)-*b*-PCL_{55} amphiphilic ABC miktoarm star terpolymers.

[Fig. 7(b)]. For PS_{43}(-*b*-$PNIPAM_{52}$)-*b*-PCL_{55} miktoarm star terpolymer, we can clearly discern one glass transition (T_g = 110.9 °C) and one melting peak (T_m = 49.1 °C), which can be ascribed to those of PNIPAM and PCL segments, respectively. Compared to those of $PNIPAM_{52}$-N_3 and PS_{43} (-*alkynyl*)-*b*-PCL_{55} diblock precursors, the lower T_g and T_m values of PS_{43}(-*b*-$PNIPAM_{52}$)-*b*-PCL_{55} can be ascribed to the miktoarm star topology.

Supramolecular Self-Assembly of PS(-*b*-PNIPAM)-*b*-PCL in Aqueous Solution and Thermoresponsive Collapse of PNIPAM Coronas

The obtained miktoarm star terpolymer contains hydrophobic PS and PCL arms, as well as the well-known thermoresponsive PNIPAM arm. PNIPAM homopolymer dissolves in cold and dilute aqueous solution but becomes insoluble at 32 °C because of the lower critical solution temperature (LCST) phase transition behavior.[62,68] PS(-*b*-PNIPAM)-*b*-PCL can not be directly dissolved in water, a cosolvent approach was then employed for the preparation of self-assembled aggregates in aqueous solution. Typical organic solvents such as THF or acetone cannot be used as the cosolvent because of cononsolvency behavior of PNIPAM sequences in THF/water and acetone/water mixture.[69,70] DMF was chosen as the cosolvent, because PNIPAM is soluble in the whole range of DMF/water mixture.[71]

Based on chemical intuition, PS(-*b*-PNIPAM)-*b*-PCL in aqueous solution is expected to self-assemble into micelles consisting of PS/PCL mixed cores and thermoresponsive PNIPAM coronas [Scheme 1(b)]. In the context of linear triblock copolymers, Kriz et al. investigated the micellar solution of poly(2-ethylhexyl acrylate-*b*-methyl methacrylate-*b*-acrylic acid) (PEHA-*b*-PMMA-*b*-PAA) in D_2O by NMR, SANS, and LLS. They concluded that narrowly distributed spherical micelles with PEHA inner and PMMA outer cores and PAA coronas were formed.[72] Some intermixing between the layers was observed at the inner-core/outer-core and outer-core/corona interface. The inner PEHA core can encapsulate small amounts of hydrophobic solvents, such as cyclohexane. For PS(-*b*-PNIPAM)-*b*-PCL, the covalent linkage of PS, PCL, and PNIPAM block to a common junction point will preclude the formation of micelles with inner-core/outer-core/corona micelle structures. However, we expect that PS/PCL within the micellar core will exhibit considerable microphase separation because of their intrinsic incompatibility and the possible crystallization of PCL segments.[66,73] Additional work to investigate this in detail is currently underway. It should be noted that interesting systems concerning microphase separation within mixed cores of micelles self-assembled from miktoarm star terpolymers have been previously reported by Lodge and coworkers.[16,18]

Figure 8 shows TEM images of micelles prepared from PS_{43}(-*b*-$PNIPAM_{52}$)-*b*-PCL_{55} and PS_{43}(-*b*-$PNIPAM_{84}$)-*b*-PCL_{55} miktoarm star terpolymers. Figure 8(a) revealed the presence of spherical nanoparticles with diameters in the

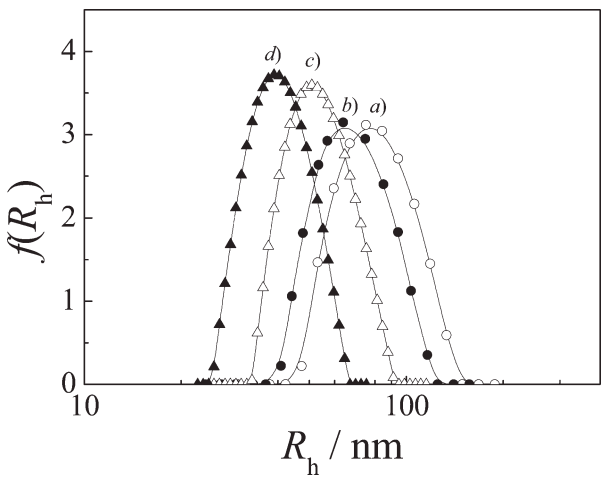


Figure 9. Hydrodynamic radius distributions, $f(R_h)$, obtained for 2.0×10^{-5} g/mL aqueous micellar solutions of PS_{43}(-*b*-$PNIPAM_{52}$)-*b*-PCL_{55} at 25 °C (a) and 45 °C (b) and PS_{43}(-*b*-$PNIPAM_{84}$)-*b*-PCL_{55} at 25 °C (c) and 45 °C (d).

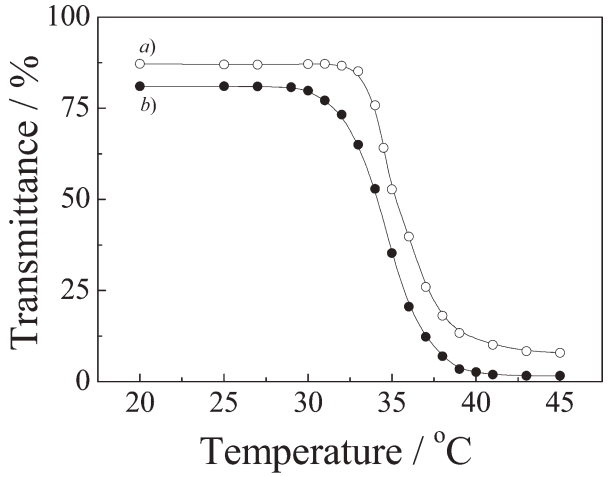


Figure 10. Temperature dependence of the optical transmittance at 700 nm obtained for aqueous micellar solutions of (a) PS_{43}(-*b*-$PNIPAM_{84}$)-*b*-PCL_{55} and (b) PS_{43}(-*b*-$PNIPAM_{52}$)-*b*-PCL_{55} at a concentration of 3.0 g/L.

range of 70–110 nm for micelles prepared from PS_{43}(-*b*-$PNIPAM_{52}$)-*b*-PCL_{55}. For PS_{43}(-*b*-$PNIPAM_{84}$)-*b*-PCL_{55}, slightly ellipsoidal nanoparticles can be observed [Fig. 8(b)]. Compared to that of PS_{43}(-*b*-$PNIPAM_{52}$)-*b*-PCL_{55}, smaller nanoparticles formed from PS_{43}(-*b*-$PNIPAM_{84}$)-*b*-PCL_{55} can be ascribed to the larger DP of water-soluble PNIPAM arm.

Figure 9 shows temperature-dependent hydrodynamic radius distributions, $f(R_h)$, of micelles prepared from PS_{43}(-*b*-$PNIPAM_{52}$)-*b*-PCL_{55} and PS_{43}(-*b*-$PNIPAM_{84}$)-*b*-PCL_{55} in aqueous solution at a concentration of 2.0×10^{-5} g/mL. For PS_{43}(-*b*-$PNIPAM_{52}$)-*b*-PCL_{55}, R_h of micelles ranges from 40 to 150 nm with an intensity-average hydrodynamic radius, $\langle R_h \rangle$, of 75 nm at 25 °C. Upon heating to 45 °C, R_h is in the range of 35–130 nm with $\langle R_h \rangle$ of 65 nm. Similarly, micelles prepared from PS_{43}(-*b*-$PNIPAM_{84}$)-*b*-PCL_{55} also exhibits thermoresponsive size shrinkage upon heating, with the $\langle R_h \rangle$ decreasing from 51 nm at 25 °C to 38 nm at 45 °C. The decrease of micellar size should be ascribed to the collapse of PNIPAM coronas at elevated temperatures because of the LCST phase behavior of PNIPAM. It is worthy of noting that micelles with swollen and collapsed PNIPAM coronas exhibit mono-modal size distributions with polydispersity indexes, μ_2/Γ^2, typically less than 0.12 over the temperature range of 25–45 °C.

Figure 10 shows temperature dependence of optical transmittance at a wavelength of 700 nm obtained for the micellar solutions of PS_{43}(-*b*-$PNIPAM_{52}$)-*b*-PCL_{55} and PS_{43}(-*b*-$PNIPAM_{84}$)-*b*-PCL_{55} in water at a concentration of 3.0 g/L. Compared with that of LLS measurement, a much higher concentration was employed for transmittance measurements to obtain enough detection sensitivity. In the range of 15–30 °C, optical transmittance of micellar solutions prepared from PS_{43}(-*b*-$PNIPAM_{52}$)-*b*-PCL_{55} and PS_{43}(-*b*-$PNIPAM_{84}$)-*b*-PCL_{55} remained at ~81 and 87%, respectively. Above 30 and 33 °C, the optical transmittance of micellar solutions of PS_{43}(-*b*-$PNIPAM_{52}$)-*b*-PCL_{55} and PS_{43}(-*b*-$PNIPAM_{84}$)-*b*-PCL_{55} decreased abruptly to <10%, respectively. This should be ascribed to the thermoresponsive aggregation of micelles possessing mixed PS/PCL cores and PNIPAM coronas above the phase transition temperatures.

CONCLUSIONS

Amphiphilic ABC miktoarm star terpolymers, PS(-*b*-PNIPAM)-*b*-PCL, were synthesized via a combination of ATRP, ROP, and click reaction. First, PS-*alknyl-OH*, was prepared by reacting PS-N_3 with an excess of BPBA under click conditions. The subsequent ROP of ε-CL using PS-*alknyl-OH* macroinitiator afforded PS(-*alkynyl*)-*b*-PCL copolymer. The target PS(-*b*-PNIPAM)-*b*-PCL amphiphilic ABC miktoarm star terpolymer was then successfully prepared via click reaction between PS(-*alkynyl*)-*b*-PCL and PNIPAM-N_3. In aqueous solution, the obtained amphiphilic ABC miktoarm star terpolymers self-assembled into micelles possessing mixed PS/PCL cores and PNIPAM shells. The shells showed thermoresponsive collapse upon heating through the LCST of PNIPAM. This work represents the first example of a thermoresponsive core-shell nanoparticle fabricated from amphiphilic ABC miktoarm star terpolymers.

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