# One-Pot Synthesis of ABC Miktoarm Star Terpolymers by Coupling ATRP, ROP, and Click Chemistry Techniques

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*Received 25 December 2008; accepted 4 March 2009*
*DOI: 10.1002/pola.23388*
*Published online in Wiley InterScience (www.interscience.wiley.com).*

**ABSTRACT:** We report on the one-pot synthesis of well-defined ABC miktoarm star terpolymers consisting of poly(2-(dimethylamino)ethyl methacrylate), poly(ε-caprolactone), and polystyrene or poly(ethylene oxide) arms, PS(-*b*-PCL)-*b*-PDMA and PEO(-*b*-PCL)-*b*-PDMA, taking advantage of the compatibility and mutual tolerability of reaction conditions (catalysts and monomers) employed for atom transfer radical polymerization (ATRP), ring-opening polymerization (ROP), and click reactions. At first, a novel trifunctional core molecule bearing alkynyl, hydroxyl group, and bromine moieties, *alkynyl*(—*OH*)—*Br*, was synthesized via the esterification reaction of 5-ethyl-5-hydroxymethyl-2,2-dimethyl-1,3-dioxane with 4-oxo-4-(prop-2-ynyloxy)butanoic acid, followed by deprotection and monoesterification of *alkynyl*(—*OH*)$_2$ with 2-bromoisobutyryl bromide. In the presence of trifunctional core molecule, *alkynyl*(—*OH*)—*Br*, and CuBr/PMDETA/Sn(Oct)$_2$ catalytic mixtures, target ABC miktoarm star terpolymers, PS(-*b*-PCL)-*b*-PDMA and PEO(-*b*-PCL)-*b*-PDMA, were successfully synthesized in a one-pot manner by simultaneously conducting the ATRP of 2-(dimethylamino)ethyl methacrylate (DMA), ROP of ε-caprolactone (ε-CL), and the click reaction with azido-terminated PS (PS-$N_3$) or azido-terminated PEO (PEO-$N_3$). Considering the excellent tolerability of ATRP to a variety of monomers and the fast expansion of click chemistry in the design and synthesis of polymeric and biorelated materials, it is quite anticipated that the one-pot concept can be applied to the preparation of well-defined polymeric materials with more complex chain architectures. © 2009 Wiley Periodicals, Inc. J Polym Sci Part A: Polym Chem 47: 3066–3077, 2009
**Keywords:** block copolymers; living radical polymerization (LRP); star polymers

## INTRODUCTION

Miktoarm star polymers typically refer to star polymers with three or more arms, and at least two of which are of different monomer types.[1–13] In recent years, ever-increasing attention has been paid to the synthesis of ABC miktoarm star terpolymers because of their intriguing properties both in solution and solid states.[8,14–21] Representing the simplest form of star polymers containing more than two monomer types, ABC miktoarm star terpolymers can be considered as three different polymer chains emanated from a core junction point. Compared to linear AB diblock copolymers, the incorporation of a third type of polymer sequence in to the junction point endows ABC miktoarm star terpolymers with more diverse supramolecular self-assembling properties, resulting from the special chain topology and inherent incompatibility between three component arms.[15,16,22–28]

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Journal of Polymer Science: Part A: Polymer Chemistry, Vol. 47, 3066–3077 (2009)

Before the emergence of controlled radical polymerization (CRP) and click chemistry concepts, the synthesis of ABC miktoarm star terpolymers has mainly relied on the anionic polymerization technique, which is quite challenging considering difficulties encountered in strictly controlling molar ratios between reactive species.[1,14] In the past 10 years, the advent of CRP techniques, such as nitroxide-mediated radical polymerization (NMP), atom transfer radical polymerization (ATRP), and reversible addition-fragmentation chain transfer (RAFT) polymerization, the once formidable task of the synthesis of ABC miktoarm star polymers has been rendered much easier because of their less stringent requirements in both polymerization conditions and experimental procedures.[29,30] In this context, pioneering works has been reported by Huang and coworkers.[31,32] and Pan and coworkers.[33–37]

Recent developments in the synthesis of ABC miktoarm star terpolymers have been the introduction of click chemistry concept invented by Sharpless in 2001, affording a highly efficient and reliable coupling technique.[38–41] In 2006, Tunca and coworkers[38] reported the synthesis of ABC miktoarm star terpolymers via a combination of ATRP, ring-opening polymerization (ROP), and click reaction. In their work, poly(methyl methacrylate)-*b*-polystyrene bearing an alkynyl functionality at the diblock junction, PMMA(-*alkynyl*)-*b*-PS, was synthesized at first by consecutive ATRP and NMP, staring from a trifunctional core molecule. The subsequent click coupling between PMMA(-*alkynyl*)-*b*-PS and azido-terminated poly (*tert*-butyl acrylate) (P*t*BA) afforded PMMA(-*b*-P*t*BA)-*b*-PS ABC miktoarm star terpolymer. In another stimulating example, Monteiro and coworkers successfully prepared well-defined $AB_2$ Y-shaped and ABC miktoarm star polymers via click chemistry by employing tripropargylamine as the core molecule.[42] Recently, we further reported the synthesis of amphiphilic and double hydrophilic ABC miktoarm star terpolymers via the combination of click chemistry, ATRP, and ROP.[43,44]

Just recently, Tunca and coworkers[45] further reported the one-pot synthesis of ABC miktoarm star terpolymer by simultaneously conducting ROP, NMP, and click reactions, taking advantage of the compatibility of reaction conditions required for these three techniques. This pioneering work has rendered possible the large-scale preparation of miktoarm star polymers. Considering this promising aspect, it is highly desirable to further broaden this design principle to more diverse systems by choosing appropriate combination of available polymerization and coupling techniques.

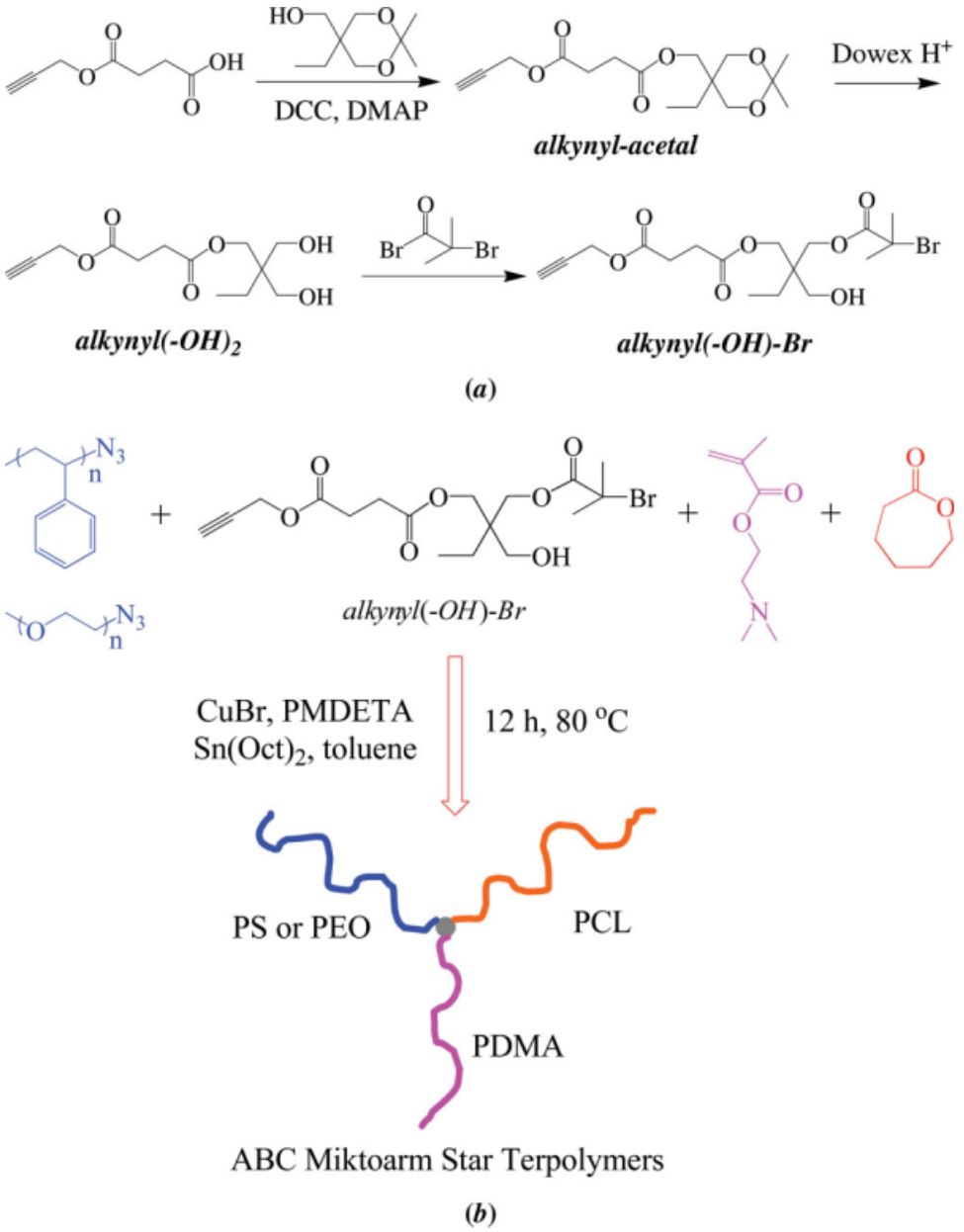
Compared to NMP, it has been well-accepted that the ATRP technique can be tolerable to more diverse vinyl monomer types.[46–48] In 1998, Hawker and his coworkers originally reported the one-step synthesis of poly(methyl methacrylate)-*b*-poly($\varepsilon$-caprolactone) (PMMA-*b*-PCL) by simultaneously conducting ROP and ATRP.[49] Later, this combination has been further applied to the synthesis of other diblock copolymers by Dumas,[50] Chang,[51] and Howdle research groups.[52–54] ATRP and click reactions typically employ the same Cu(I)-based catalysts.[55,56] Recently, Dubois and coworkers.[57] reported the one-pot synthesis of poly($\varepsilon$-caprolactone)-*b*-poly(2-(dimethylamino) ethyl methacrylate) (PCL-*b*-PDMA) by simultaneously conducting ATRP of 2-(dimethylamino)ethyl methacrylate (DMA) and clicking coupling to alkynyl-terminated PCL. Recently, the combination of ATRP and click techniques has also been applied to the one-pot synthesis of terminally or side chain-functionalized polymers.[58,59]

Considering the above examples, it is quite reasonable to speculate that the reactions required for ROP, ATRP, and click reactions are mutually compatible in terms of monomer species and catalytic mixtures. Inspired by the ideas of Tunca and coworkers[45] herein we reported the facile one-pot synthesis of ABC miktoarm star terpolymers by coupling ROP, ATRP, and click techniques (Scheme 1). Starting from a trifunctional core molecule, *alkynyl*(—*OH*)—*Br*, the simultaneous ROP of $\varepsilon$-caprolactone ($\varepsilon$-CL), ATRP of DMA, and click coupling with azido-terminated PS or poly (ethylene oxide) (PEO) successfully afforded ABC miktoarm star terpolymers, PS(-*b*-PCL)-*b*-PDMA and PEO(-*b*-PCL)-*b*-PDMA. GPC, $^1$H NMR, and FTIR were employed to verify the chemical structures of target miktoarm star terpolymers.

## EXPERIMENTAL

### Materials

Poly(ethylene oxide) monomethyl ether ($PEO_{113}$-OH, $M_n = 5.0$ kDa, $M_w/M_n = 1.06$, mean degree of polymerization, DP, is 113) was purchased from Aldrich and used as received. $\varepsilon$-Caprolactone ($\varepsilon$-CL, 99%, Acros) was vacuum-distilled from $CaH_2$ just before use. Styrene (St, 99.5%, Beijing Chemical Factory) was successively washed with




**Scheme 1.** Schematic illustration for (a) the preparation of trifunctional core molecule, *alkynyl*(—*OH*)—*Br*, and (b) one-pot synthesis of amphiphilic ABC miktoarm star copolymers via a combination of ATRP, ROP, and click chemistry.

aqueous NaOH (5.0 wt %) and water, then distilled over $CaH_2$ at reduced pressure. 2-(Dimethylamino)ethyl methacrylate (DMA) was obtained from Aldrich and was distilled over $CaH_2$ at reduced pressure, and stored at −20 °C before use. *N,N,N′,N″,N‴*-Pentamethyldiethylenetriamine (PMDETA), copper(I) bromide (98%), propargyl alcohol (99%), tin(II) 2-ethylhexanoate ($Sn(Oct)_2$, 95%), (1-bromoethyl)benzene, and 2-bromoisobutyryl bromide were purchased from Aldrich and used as received. Dowex 50WX8-200 resin ($H^+$ form) was purchased from Lancaster and used as received. Sodium azide ($NaN_3$, 99%) was purchased from Alfa Aesar and used without further purification. Tetrahydrofuran (THF) and toluene were refluxed over sodium/benzophenone and distilled before use. Triethylamine (TEA), dichloromethane ($CH_2Cl_2$), succinic anhydride, 1,1,1-trihydroxymethylpropane, *p*-toluenesulfonic acid, *N,N*-dimethylformamide (DMF), and all other chemicals were

purchased from Sinopharm Chemical Reagent and used as received. 5-Ethyl-5-hydroxymethyl-2,2-dimethyl-1,3-dioxane,[60] 4-oxo-4-(prop-2-ynyloxy)butanoic acid,[38] and azido-terminated PEO ($PEO_{113}$-$N_3$)[38] were synthesized according to literature procedures.

## Characterization

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. 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 polystyrene standards were employed for the GPC calibration. All FTIR spectra were measured on a Bruker Vector 22 Fourier transform infrared spectrometer using the KBr disk method. The spectra were collected at 64 scans with a spectral resolution of 4 $cm^{-1}$. Differential scanning calorimetry (DSC) was carried on a DSC TA-60WS thermal analysis system (Shimadzu, Japan). Samples were first cooled to −100 °C under nitrogen atmosphere, followed by heating to 120 °C at a rate of 10 °C/min. After thermostating at 120 °C for 3 min and then cooling to −100 °C, samples were heated to 120 °C at a rate of 10 °C/min. Glass transition temperatures ($T_g$) and melting temperatures ($T_m$) were determined as the midpoint and the peak maximum of associated transitions during the second heating sequence, respectively.

## Sample Synthesis

Scheme 1 shows general synthetic routes employed for the one-pot synthesis of PS(-*b*-PCL)-*b*-PDMA and PEO(-*b*-PCL)-*b*-PDMA miktoarm star terpolymers by simultaneously conducting ATRP, ROP, and click reactions.

### *Synthesis of Alkynyl-Acetal [Scheme 1(a)]*

Into a 250 mL baked round-bottomed flask, 5-ethyl-5-hydroxymethyl-2,2-dimethyl-1,3-dioxane (15.7 g, 0.09 mol), 4-oxo-4-(prop-2-ynyloxy)butanoic acid (15.6 g, 0.10 mol), and 100 mL dry $CH_2Cl_2$ were added. The reaction mixture was then cooled to 0 °C in an ice-water bath. To this solution, DCC (20.6 g, 0.10 mol) and DMAP (1.22 g, 0.01 mol) dissolved in 50 mL dry $CH_2Cl_2$ was added dropwise over a period of 1 h. After the addition was completed, the mixture was stirred at 0 °C for 1 h and then at room temperature for 12 h. After removing the insoluble salts by suction filtration, the filtrate was evaporated to dryness and further purified by silica gel column chromatography using ethyl acetate/*n*-hexane (2:1 v/v) as the eluent. After removing the solvents on a rotary evaporator, *alkynyl-acetal* was obtained as a viscous and colorless liquid (23.1 g, yield: 82%).

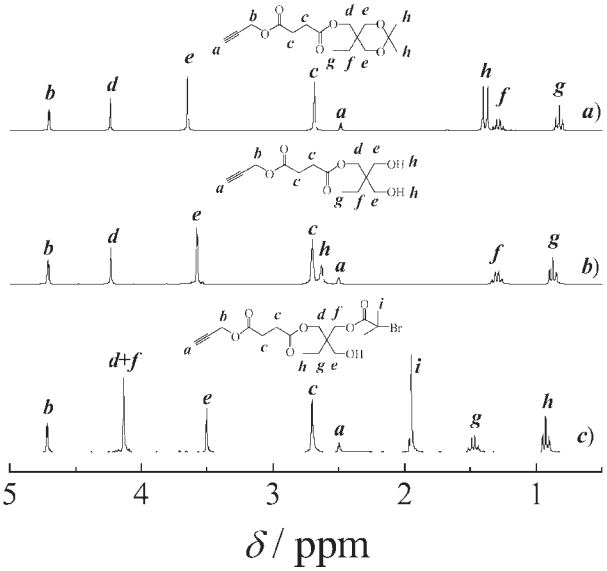



**Figure 1.** $^1$H NMR spectra recorded for (a) *alkynyl-acetal*, (b) *alkynyl*(—*OH*)$_2$, and (c) *alkynyl*(—*OH*)—*Br* in $CDCl_3$.

$^1$H NMR ($CDCl_3$, $\delta$, ppm, TMS): 4.71 (2H, —COOC$H_2$C≡CH), 4.23 (2H, —$CH_2$COOC$H_2$C—), 3.65 (4H, OC$H_2$C— in 1,3-dioxane), 2.68 (4H, OOCC$H_2$C$H_2$COO), 2.49 (1H, —C≡C*H*), 1.43-1.34 (6H, —C(C$H_3$)$_2$), 1.34-1.22 (2H, —C$H_2$CH$_3$), 0.89-0.75 (3H, —$CH_2$C$H_3$) [Fig. 1(a)]. $^{13}$C NMR ($CDCl_3$, $\delta$, ppm, TMS): 171.83 (—$CH_2$*C*OOC≡CH), 171.58 (—$CH_2$*C*OOC$H_2$C(C$H_2$)$_3$), 101.85 (—*C*(C$H_3$)$_2$), 76.75 (—COOC$H_2$*C*≡CH), 75.35 (—COOC$H_2$C≡*C*H), 66.75 (C*C*H$_2$OC(C$H_3$)$_2$), 65.52 (—C$H_2$COO*C*H$_2$C(C$H_2$)$_3$), 55.75 (—COO*C*H$_2$C≡CH), 67.85 (*C*(C$H_2$)$_4$), 29.12 (—OOCC$H_2$*C*H$_2$COOC≡*C*H), 29.03 (—OOC*C*H$_2$CH$_2$COOC≡*C*H), 26.54, (—C(*C*H$_3$)$_2$), 22.53 (—*C*H$_2$CH$_3$), 7.51 (—CH$_2$*C*H$_3$).

### *Synthesis of Alkynyl(—OH)$_2$*

The deprotection of *alkynyl-acetal* in the presence of Dowex 50WX8-200 resin afforded *alkynyl*(—*OH*)$_2$. A typical procedure was as follows. Into a 500 mL round-bottomed flask, 10.0 g Dowex 50WX8-200 resin, *alkynyl-acetal* (22.0 g, 0.07 mol), and 300 mL methanol were added, and the dispersion was stirred at 40 °C. The reaction progress was monitored by sampling at time intervals for thin layer chromatography (TLC) analysis. After ~16 h, the deprotection is 100% complete as further evidenced by the total disappearance of signal at ~102 ppm in the $^{13}$C NMR spectrum, which is unique to the quaternary carbon in acetonide moiety. After suction filtration, the filtrate was evaporated to dryness under high vacuum, affording *alkynyl*(—*OH*)$_2$ as a viscous and colorless liquid (18.8 g, yield: 99%).

$^1$H NMR ($CDCl_3$, $\delta$, ppm, TMS): 4.71 (2H, —COOC*H*$_2$C≡CH), 4.23 (2H, —CH$_2$COOC*H*$_2$C—), 3.58 (4H, —C*H*$_2$OH), 2.69 (4H, OOCC*H*$_2$C*H*$_2$COO), 2.63 (2H, CH$_2$O*H*), 2.49 (1H, —C≡C*H*), 1.34-1.22 (2H, —CH$_3$C*H*$_2$), 0.93-0.81 (3H, —C*H*$_3$CH$_2$) [Fig. 1(b)].

$^{13}$C NMR($CDCl_3$, $\delta$, ppm, TMS): 171.85 (—CH$_2$*C*OOC≡CH), 171.60 (—CH$_2$*C*OOCH$_2$C(CH$_2$)$_3$), 76.78 (—COOCH$_2$*C*≡CH), 75.35 (—COOCH$_2$C≡*C*H), 65.52 (—CH$_2$COO*C*H$_2$C(CH$_2$)$_3$), 62.52 (—*C*H$_2$OH), 55.79 (—COO*C*H$_2$C≡CH), 44.10 (*C*(CH$_2$)$_4$), 29.12 (—OOCCH$_2$*C*H$_2$COOC≡*C*H), 29.03 (—OOC*C*H$_2$CH$_2$COOC≡*C*H), 22.52 (—*C*H$_2$CH$_3$), 7.48 (—CH$_2$*C*H$_3$).

### *Synthesis of Trifunctional Core Molecule Alkynyl(—OH)—Br*

A typical procedure employed for the preparation of *alkynyl*(—*OH*)—*Br* was described below. To a dry 250 mL round-bottomed flask, *alkynyl*-(*OH*)$_2$ (6.0 g, 22 mmol), TEA (2.23 g, 22 mmol), and 100 mL dry THF were added. The mixture was cooled to 0 °C in an ice-water bath, 2-bromoisobutyryl bromide (2.9 mL, 23.5 mmol) in 20 mL dry THF was added dropwise over 1 h under nitrogen atmosphere. After the addition was completed, the reaction mixture was stirred at 0 °C for 1 h and then at room temperature for another 24 h. After removing insoluble salts by suction filtration, the filtrate was concentrated and further purified by silica gel column chromatography using ethyl acetate/*n*-hexane (1:2 v/v) as eluent. After removing all the solvents on a rotary evaporator, *alkynyl*(—*OH*)—*Br* was obtained as a viscous and colorless liquid (6.2 g, yield: 67%).

$^1$H NMR ($CDCl_3$, $\delta$, ppm, TMS): 4.72 (2H, —COOC*H*$_2$C≡CH), 4.13 (4H, —COOC*H*$_2$—), 3.50 (2H, —C*H*$_2$OH), 2.71 (4H, —OOCC*H*$_2$C*H*$_2$COO—), 2.51 (1H, —C≡C*H*), 1.95 (6H, —C(C*H*$_3$)$_2$), 1.53-1.42 (2H, —C*H*$_2$CH$_3$), 0.97-0.86 (3H, —CH$_2$C*H*$_3$) [Fig. 1(c)].

$^{13}$C NMR ($CDCl_3$, $\delta$, ppm): 172.48 (—*C*OC(CH$_3$)$_2$Br), 171.87 (—CH$_2$*C*OOC≡CH), 171.62 (—CH$_2$*C*OOCH$_2$C), 76.73 (—COOCH$_2$*C*≡CH), 75.24 (—COOCH$_2$C≡*C*H), 65.50 (—CH$_2$COO*C*H$_2$C(CH$_2$)$_3$), 64.39 (—CCOO*C*H$_2$C(CH$_2$)$_3$), 62.52 (—*C*H$_2$OH), 55.78 (—COO*C*H$_2$C≡CH), 52.46 (—CO*C*(CH$_3$)$_2$Br), 43.08 (*C*(CH$_2$)$_4$), 30.85 (—COC(*C*H$_3$)$_2$Br), 29.08 (—OOCCH$_2$*C*H$_2$COOC≡*C*H), 29.00 (—OOC*C*H$_2$CH$_2$COOC≡*C*H), 22.45 (—*C*H$_2$CH$_3$), 7.45 (—CH$_2$*C*H$_3$). ELEM. ANAL: Calc. for $C_{17}H_{25}O_7Br$: C, 48.47; H, 5.98. Found C, 48.38; H, 5.96.

### *Synthesis of Azido-Terminated Polystyrene (PS-N$_3$)*

Into a Schlenk tube equipped with a magnetic stirring bar, styrene (10.42 g, 0.1 mol), (1-bromoethyl)benzene (61 mg, 0.33 mmol), PMDETA (58 mg, 0.33 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 (48 mg, 0.33 mmol) was introduced into the reaction mixture as a solid to start the polymerization. The mixture was stirred under $N_2$ atmosphere. After ~4 h, the monomer conversion was determined to be ~19% as judged by $^1$H NMR. The reaction was terminated by quenching into liquid nitrogen, exposed to air, and diluted with $CH_2Cl_2$. After passing though a neutral alumina column to remove the copper catalysts and removing all the solvents by a rotary evaporator, the residues were dissolved in $CH_2Cl_2$ and precipitated into an excess of methanol. The above dissolution-precipitation cycle was repeated for three times. The final product was dried in a vacuum oven overnight at room temperature, affording PS-*Br* as a white powder (1.89 g, yield: 18%; $M_{n,GPC}$ = 6.4 kDa, $M_w/M_n$ = 1.06). The degree of polymerization (DP) of PS$_{60}$-*Br* was then calculated to be 60, which reasonably agrees with that determined from $^1$H NMR analysis (~61). Next, PS-*Br* (1.5 g) and sodium azide (1.0 g) were dissolved in 5 mL DMF, the reaction mixture was stirred at room temperature for 24 h. 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,

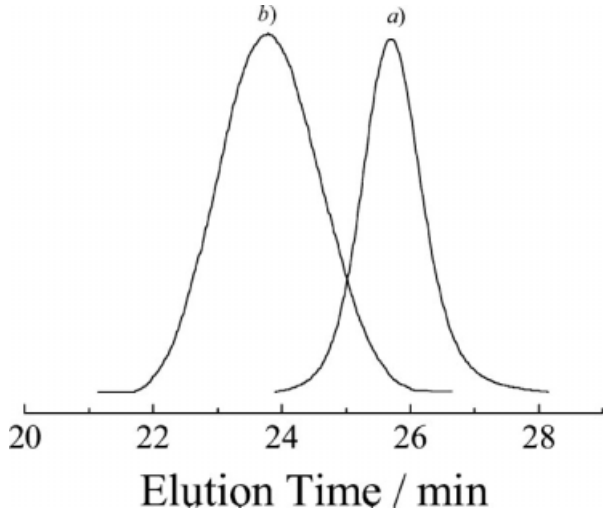



**Figure 2.** GPC traces obtained for (a) $PS_{60}$-$N_3$ and (b) $PS_{60}$(-*b*-$PCL_{71}$)-*b*-$PDMA_{47}$ ABC miktoarm star terpolymer synthesized via the one-pot technique.

followed by precipitation into an excess of methanol. The final product was dried in a vacuum oven overnight at room temperature, affording $PS_{60}$-$N_3$ as a white powder (1.45 g, yield: 97%; $M_{n,GPC}$ = 6.4 kDa, $M_w/M_n$ = 1.06) (Fig. 2). Thus, the polymer was denoted as $PS_{60}$-$N_3$.

### *One-Pot Synthesis of PS(-b-PCL)-b-PDMA and PEO(-b-PCL)-b-PDMA ABC Miktoarm Star Terpolymers*

The target miktoarm star terpolymers, PS(-*b*-PCL)-*b*-PDMA and PEO(-*b*-PCL)-*b*-PDMA, were obtained in a one-pot manner by simultaneously conducting the ATRP of DMA, the ROP of ε-caprolactone (ε-CL), and the click reaction with PS-$N_3$ or PEO-$N_3$ using CuBr/PMDETA/$Sn(Oct)_2$ as the catalytic system. A typical procedure employed for the preparation of PS(-*b*-PCL)-*b*-PDMA was described as follows. Into a Schlenk tube equipped with a magnetic stirring bar, *alkynyl(—OH)—Br* (42 mg, 0.1 mmol), DMA (0.79 g, 5 mmol), ε-CL (0.83 g, 7.3 mmol), $PS_{60}$-$N_3$ (0.64 g, 0.1 mmol), PMDETA (17 mg, 0.1 mmol), and 5 mL dry toluene were added. After one brief freeze-pump-thaw cycle, CuBr (14 mg, 0.1 mmol), and $Sn(Oct)_2$ (20 g/L in dry toluene, 0.2 mL, 0.01 mmol) were introduced under the protection of $N_2$ flow. The reaction tube was carefully degassed by three freeze-pump-thaw cycles and then placed in an oil bath thermostated at 80 °C. The reaction solution became dark green and more viscous as polymerization proceeded. After 12 h, the reaction was terminated by quenching into liquid nitrogen, exposed to air, and diluted with 20 mL THF. After passing through a silica gel column and removing all the solvents on a rotary evaporator, the residues were dissolved in THF and precipitated into an excess of *n*-hexane. The above dissolution-precipitation cycle was repeated for three times. The final product was dried in a vacuum oven overnight at room temperature, affording PS(-*b*-PCL)-*b*-PDMA miktoarm star terpolymer as a white solid (2.06 g, yield: 94%; $M_{n,GPC}$ = 18.8 kDa, $M_w/M_n$ = 1.18) (Fig. 2). The actual DPs of PCL and PDMA arms were determined to be 71 and 47 by $^1$H NMR analysis, respectively, (Fig. 3). Thus, the obtained ABC miktoarm star terpolymer was then denoted as $PS_{60}$(-*b*-$PCL_{71}$)-*b*-$PDMA_{47}$.

Followed similar procedures as employed for the preparation of PS(-*b*-PCL)-*b*-PDMA, PEO(-*b*-PCL)-*b*-PDMA ABC miktoarm star terpolymer was also synthesized using $PEO_{113}$-$N_3$ (0.1 mmol) to replace $PS_{60}$-$N_3$ and the reaction time was 8 h. $PEO_{113}$(-*b*-PCL)-*b*-PDMA was also obtained as a white solid (1.80 g, yield: 87%; $M_{n,GPC}$ = 17.6 kDa, $M_w/M_n$ = 1.20) (Fig. 5). The actual DPs of PCL and PDMA arms were also determined to be 68 and 45 by $^1$H NMR analysis, respectively, (Fig. 6). The final product was then denoted as $PEO_{113}$(-*b*-$PCL_{68}$)-*b*-$PDMA_{45}$ (Table 1).

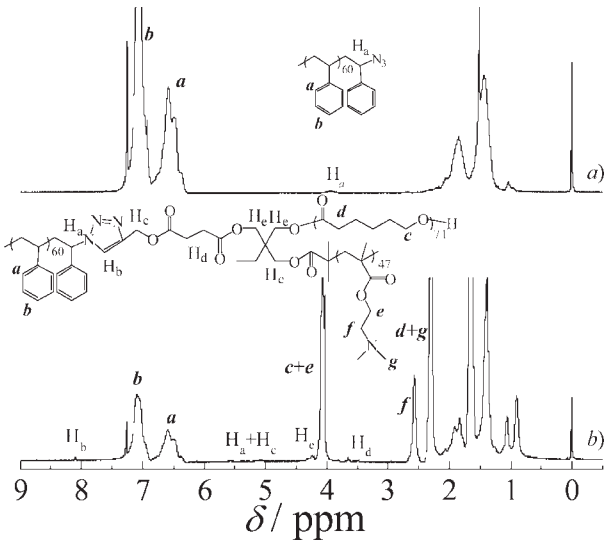



**Figure 3.** $^1$H NMR spectra recorded in $CDCl_3$ for (a) $PS_{60}$-$N_3$ and (b) $PS_{60}$(-*b*-$PCL_{71}$)-*b*-$PDMA_{47}$ ABC miktoarm star terpolymer synthesized via the one-pot technique.

**Table 1.** Summary of Structural Parameters of Polymers Synthesized in this Work

| Samples | Conversion ε-CL/DMA (%) | Yield (%) | $M_{n,theo}$ (kDa)[a] | $M_{n,NMR}$ (kDa)[b] | $M_{n,GPC}$ (kDa)[c] | $M_w/M_n$[c] |
|---|---|---|---|---|---|---|
| PS-Br[d] | / | 18 | / | 6.5 | 6.4 | 1.06 |
| PS(-*b*-PCL)-*b*-PDMA[e] | 97/94 | 94 | 22.3 | 22.3 | 18.8 | 1.18 |
| PEO(-*b*-PCL)-*b*-PDMA[f] | 93/90 | 87 | 21.7 | 21.6 | 17.6 | 1.20 |
| PCL(-*alkynyl*)-*b*-PDMA[g] | 95/92 | 90 | 15.6 | 15.5 | 14.8 | 1.16 |

[a] Theoretical molecular weights, $M_{n,theo}$, were calculated as $M_{n,theo} = MW_{initiator} + M_{n,PS\ or\ PEO} + M_{monomer1} \times DP_{n1} + M_{monomer2} \times DP_{n2}$, where $DP_n = [M]_0/[initiator] \times$ conversion.
[b] Determined by $^1$H NMR.
[c] Determined by THF GPC using PS standards and RI detector at a flow rate of 1.0 mL/min.
[d] The ATRP of St was carried out in anisole at 80 °C for 4 h using (1-bromoethyl)benzene as initiator and CuBr/PMDETA as catalysts.
[e] One-pot ROP of ε-CL, ATRP of DMA, and click reactions with PS-$N_3$ were carried out in toluene at 80 °C for 12 h with a feed ratio of [ε-CL]$_0$:[DMA]$_0$:[PS-$N_3$]: [*alkynyl*(—*OH*)-*Br*]:[CuBr]:[PMDETA]:[Sn(Oct)$_2$] = 73/50/1/1/1/1/0.1.
[f] One-pot ROP of ε-CL, ATRP of DMA, and click reactions with PEO-$N_3$ were carried out in toluene at 80 °C for 8 h with a feed ratio of [ε-CL]$_0$:[DMA]$_0$:[PEO-$N_3$]: [*alkynyl*(—*OH*)-*Br*]:[CuBr]:[PMDETA]:[Sn(Oct)$_2$] = 73/50/1/1/1/1/0.1.
[g] PCL(-*alkynyl*)-*b*-PDMA diblock copolymer was obtained in a one-pot manner by simultaneously conducting the ATRP of DMA momomer and ROP of ε-CL in toluene at 80 °C for 12 h with a feed ratio of [ε-CL]$_0$:[DMA]$_0$:[*alkynyl*(—*OH*)—*Br*]:[CuBr]:[PMDETA]:[Sn(Oct)$_2$] = 73/50/1//1/1/0.1.

### *One-Pot Synthesis of PCL(-alkynyl)-b-PDMA Block Copolymer*

PCL(-*alkynyl*)-*b*-PDMA was synthesized following similar protocols as described above for the one-pot synthesis of PS(-*b*-PCL)-*b*-PDMA miktoarm star terpolymer in the absence of PS-$N_3$. The actual DPs of PCL and PDMA segments were determined to be 69 and 46 by $^1$H NMR analysis, respectively. The final product was then denoted as PCL$_{69}$(-*alkynyl*)-*b*-PDMA$_{46}$ ($M_{n,GPC}$ = 14.8 kDa, $M_w/M_n$ = 1.16) (Table 1).

## RESULTS AND DISCUSSION

General schemes employed for the preparation of two types of ABC miktoarm star polymers were shown in Scheme 1. At first, a novel trifunctional core molecule, *alkynyl*(—*OH*)—*Br*, was synthesized, which bears alkynyl, hydroxyl group, and bromine moieties and can be employed for click chemistry, ROP, and ATRP reactions, respectively. Target miktoarm star terpolymers, PS(-*b*-PCL)-*b*-PDMA and PEO(-*b*-PCL)-*b*-PDMA, were then synthesized in a one-pot manner by simultaneously conducting the ATRP of DMA, ROP of ε-CL, and click reaction with PS-$N_3$ or PEO-$N_3$ using CuBr/PMDETA/Sn(Oct)$_2$ as the catalytic system. $^1$H NMR, GPC, and FTIR were employed to verify the chemical structures of miktoarm star terpolymers.

Synthetic scheme employed for the preparation of *alkynyl*(—*OH*)—*Br* was shown in Scheme 1(a). The esterification of 5-ethyl-5-hydroxymethyl-2,2-dimethyl-1,3-dioxane with 4-oxo-4-(prop-2-ynyloxy) butanoic acid afforded *alkynyl-acetal*. In the presence of Dowex resin ($H^+$ form), the deprotection of *alkynyl-acetal* led to the formation of *alkynyl*(—*OH*)$_2$. Figure 1 shows $^1$H NMR spectra of *alkynyl-acetal* and *alkynyl*(—*OH*)$_2$, together with the peak assignments. In comparison with the $^1$H NMR spectrum of *alkynyl-acetal* (Fig. 1a), resonance peak characteristic of acetonide moiety (1.43-1.34 ppm, C(C*H*$_3$)$_2$) totally disappeared in *alkynyl*-(*OH*)$_2$ (Fig. 1b). $^{13}$C NMR analysis further confirmed the complete deprotection of acetonide groups, as indicated by the disappearance of resonance signal at ~102 ppm assigned to the quaternary carbon in acetonide moiety.

Next, the target trifunctional core molecule, *alkynyl*(—*OH*)—*Br*, was obtained by the monoesterification of *alkynyl*-(*OH*)$_2$ with 2-bromoisobutyryl bromide and subsequent purification by column chromatography. Compared to that of *alkynyl*-(*OH*)$_2$, $^1$H NMR spectrum of *alkynyl*(—*OH*)—*Br* exhibited new signal at 1.95 ppm, which can be ascribed to methyl protons of 2-bromoisobutyrate residues. Moreover, a comparison of NMR spectra between *alkynyl*-(*OH*)$_2$ and *alkynyl*(—*OH*)—*Br* revealed that the integration area of peak *e* (3.58 ppm, —C*H*$_2$OH) relative to that of peak *b* considerably decreased after monoesterification, accompanied with the much enhanced peak at 4.13 ppm (peaks *d* and *f*). The calculated integral ratios supported the monoesterification of *alkynyl*-(*OH*)$_2$. The chemical structure of

*alkynyl*(—*OH*)—*Br* has also been confirmed by $^{13}C$ NMR and elemental analysis results.

PS-*Br* precursor was obtained by the ATRP of St monomer using (1-bromoethyl)benzene as the initiator and CuBr/PMDETA as catalyst. The monomer conversion was kept to be low (19%) to ensure the high end bromine functionality. For such relatively low MW PS, its DP can also be calculated from $^1H$ NMR analysis by comparing integration areas of resonance signal at $\delta = 4.5$ ppm (terminal methine proton, —$CH_2CH$(Ph)Br) to that of Ar-*H* ($\delta = 6.3$-7.5 ppm) of the PS main chain. The obtained $DP_{NMR}$ was 61. The theoretical DP of PS-*Br* was calculated to be 57 based on monomer conversion and feed ratios, which also generally agreed with that calculated from GPC analysis (DP = 60, $M_n = 6.4$ kDa, $M_w/M_n = 1.06$) based on PS standards. Thus, the obtained polymer was denoted as $PS_{60}$-*Br*.

The subsequent nucleophilic substitution of terminal Br moiety in PS-*Br* with $NaN_3$ in DMF at room temperature afforded azido-terminated polystyrene, PS-$N_3$. After azidation, the resonance signal of the terminal methine proton in PS-*Br* at $\delta = 4.5$ ppm completely shifted to $\delta = 3.9$ ppm (—$CH_2CH$(Ph)$N_3$) in PS-$N_3$.[61] A comparison of the FTIR spectra of PS-*Br* and PS-$N_3$ revealed the presence of a new absorbance peak at 2100 $cm^{-1}$ in the latter, which is characteristic of the terminal azide moiety. Moreover, the azidation reaction results in essentially no changes in the GPC elution peaks of PS-*Br* and PS-$N_3$. The obtained azido-terminated polymer was then denoted as $PS_{60}$-$N_3$.

Reaction schemes employed for the one-pot synthesis of target ABC miktoarm star terpolymers, PS(-*b*-PCL)-*b*-PDMA and PEO(-*b*-PCL)-*b*-PDMA, were shown in Scheme 1(b). Matyjaszewski and coworkers reported that $Sn(Oct)_2$ can be employed as the reducing agent for reverse ATRP in the presence of $CuBr_2$.[62–64] On the other hand, Chang and coworkers reported the synthesis of diblock copolymer via simultaneous ROP and ATRP in the presence of $Sn(Oct)_2$ and $CuBr_2$.[51] In this work, we observed that the ROP of ε-CL can be simultaneously conducted with the ATRP process. Using CuBr/PMDETA/$Sn(Oct)_2$ as the catalytic system, the ATRP of DMA, ROP of ε-CL, and click reactions with PS-$N_3$ or PEO-$N_3$ can be conducted in one-pot to afford target ABC miktoarm star terpolymers. Original examples of one-pot synthesis of ABC miktoarm star terpolymers, PMMA(-*b*-PCL)-*b*-PS and PEO(-*b*-PCL)-*b*-PS, were previously reported by the Tunca research group, by coupling ROP, NMP, and click reactions. In the current work, we attempt to employ the combination of ROP, ATRP, and click reaction. It is reasonable to expect that the incorporation of ATRP instead of NMP into the one-pot synthesis of miktoarm star polymers can lead to more diverse monomer types.

As the MW of PS-$N_3$ can be determined to a relatively high accuracy using THF GPC based on linear PS standards, we chose to employ an equimolar amount of *alkynyl(—OH)—Br* relative to azide residues of $PS_{60}$-$N_3$, taking advantage of the high efficiency and quantitative conversion of click reaction. Similar principle can be applied into the preparation of PEO(-*b*-PCL)-*b*-PS ABC miktoarm star terpolymers. Typical GPC elution peaks of PS(-*b*-PCL)-*b*-PDMA miktoarm star terpolymer and PS-$N_3$ precursor were shown in Figure 2. Compared to that of $PS_{60}$-$N_3$ precursor, the GPC trace of PS(-*b*-PCL)-*b*-PDMA exhibited a clear shift to higher MW region, indicating the incorporation of different polymer sequences at the chain end of PS. Moreover, the GPC trace of PS(-*b*-PCL)-*b*-PDMA was symmetric and relatively narrow-disperse. The absence of a shoulder peak at the lower MW side indicated that all $PS_{60}$-$N_3$ has participated in the click reaction with *alkynyl(—OH)—Br* and incorporated into the miktoarm star terpolymer. GPC analysis of PS(-*b*-PCL)-*b*-PDMA revealed an $M_n$ of 18.8 kDa and an $M_w/M_n$ of 1.18.

Further evidence supporting the formation of PS(-*b*-PCL)-*b*-PDMA miktoarm star terpolymer was obtained by NMR analysis. $^1H$ NMR spectra of PS-$N_3$ and PS(-*b*-PCL)-*b*-PDMA, together with the peak assignments were shown in Figure 3. Compared to that of $PS_{60}$-$N_3$, we can clearly observe the complete disappearance of resonance signal at $\delta = 3.9$ ppm (—$CH_2CH$(Ph)$N_3$ in PS-$N_3$) in the $^1H$ NMR spectrum of PS(-*b*-PCL)-*b*-PDMA. Furthermore, the appearance of a new resonance signals at 8.11 ppm (peak $H_b$) can be ascribed to proton in 1,2,3-triazole ring, confirming the successful click coupling with $PS_{60}$-$N_3$. The number-average molecular weight, $M_{n,NMR}$, of PS(-*b*-PCL)-*b*-PDMA can be calculated to be ~22.3 kDa based on the equation: $M_{n,NMR} = (I_{4.1}-I_{2.6})\ DP_{PS}\ M_{n,CL}/I_{6.3-6.8} + I_{2.6}\ DP_{PS}\ M_{n,DMA}/I_{6.3-6.8} + M_{n,PS}$, where $I_{2.6}$, $I_{4.1}$, and $I_{6.3-6.8}$ are the integration areas of peak *f* (2.6 ppm, —$COOCH_2CH_2N$— in PDMA), *c* + *e* (4.1 ppm, —$COOCH_2$— in PCL and PDMA), and peak *a* (6.3-6.8 ppm, Ar-*H* of PS block, ortho-position), respectively. $DP_{PS}$ is the degree of polymerization of PS segment. $M_{n,DMA}$, $M_{n,CL}$, and $M_{n,PS}$ are molecular weights DMA and ε-CL

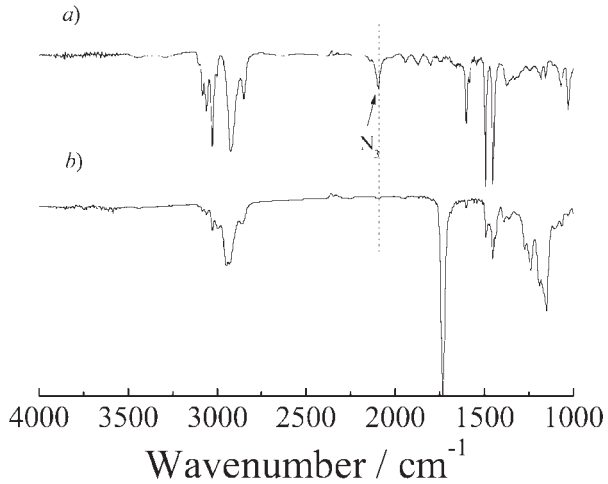



**Figure 4.** FTIR spectra recorded for (a) $PS_{60}$-$N_3$ and (b) $PS_{60}$(-*b*-$PCL_{71}$)-*b*-$PDMA_{47}$ ABC miktoarm star terpolymer synthesized via the one-pot technique.

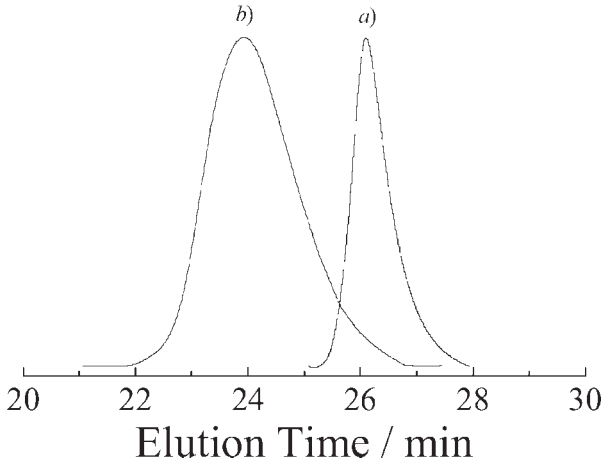



**Figure 5.** GPC traces obtained for (a) $PEO_{113}$-$N_3$ and (b) $PEO_{113}$(-*b*-$PCL_{68}$)-*b*-$PDMA_{45}$ ABC miktoarm star terpolymer synthesized via the one-pot technique.

monomers, as well as the PS segment, respectively. DP of PCL and PDMA arms was determined to be 71 and 47 from $^1$H NMR analysis. Thus, the ABC miktoarm star terpolymer was denoted as $PS_{60}$(-*b*-$PCL_{71}$)-*b*-$PDMA_{47}$.

Figure 4 shows the FTIR spectra of $PS_{60}$(-*b*-$PCL_{71}$)-*b*-$PDMA_{47}$ and $PS_{60}$-$N_3$. Compared to that of PS-$N_3$ precursor, the IR spectrum of $PS_{60}$(-*b*-$PCL_{71}$)-*b*-$PDMA_{47}$ revealed the complete disappearance of characteristic azide absorbance peak at 2100 cm$^{-1}$. This further confirmed that azide terminal moieties in $PS_{60}$-$N_3$ were all consumed. Based on the above GPC, $^1$H NMR, and FTIR results, we conclude that we have successfully obtained PS(-*b*-PCL)-*b*-PDMA ABC miktoarm star terpolymer in a one-pot manner.

Followed similar procedures employed for the synthesis of $PS_{60}$(-*b*-$PCL_{71}$)-*b*-$PDMA_{47}$, PEO(-*b*-PCL)-*b*-PDMA ABC miktoarm star terpolymer was also prepared, in which $PEO_{113}$-$N_3$ was employed instead of $PS_{60}$-$N_3$. Typical THF GPC traces of PEO(-*b*-PCL)-*b*-PDMA and $PEO_{113}$-$N_3$ precursor were shown in Figure 5. Compared to that of $PEO_{113}$-$N_3$, GPC trace of PEO(-*b*-PCL)-*b*-PDMA exhibited a clear shift to the higher molecular weight region. We can also discern a slight tailing at the lower MW side for PEO(-*b*-PCL)-*b*-PDMA, which might be explained by the fact that GPC elution peak of $PEO_{113}$-$N_3$ precursor also exhibited a slight tailing. GPC analysis gave an $M_n$ of 17.6 kDa and an $M_w/M_n$ of 1.20 for PEO(-*b*-PCL)-*b*-PDMA. The successful one-pot preparation of PEO(-*b*-PCL)-*b*-PDMA miktoarm star terpolymer has been further confirmed by $^1$H NMR and FTIR results described below.

$^1$H NMR spectra of PEO-$N_3$ and PEO(-*b*-PCL)-*b*-PDMA, together with the peak assignments were shown in Figure 6. $^1$H NMR spectrum of PEO(-*b*-PCL)-*b*-PDMA ABC miktoarm star terpolymer displayed characteristic resonance signals at 3.6, 2.6, and 1.7 ppm, which can be ascribed to —OC$H_2$C$H_2$O— in PEO, —C$H_2$C$H_2$N— in PDMA, and —COOC$H_2$— of PCL, respectively, [Fig. 6(b)]. Again, the DPs of PCL and PDMA arms were

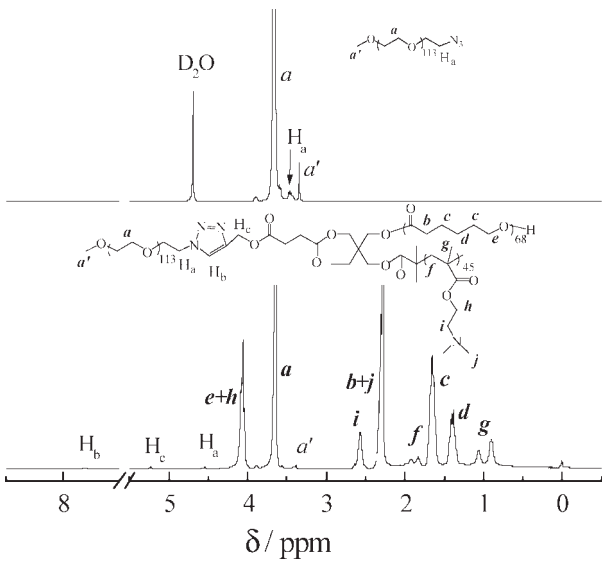



**Figure 6.** $^1$H NMR spectra recorded for (a) $PEO_{113}$-$N_3$ in $D_2O$ and (b) $PEO_{113}$(-*b*-$PCL_{68}$)-*b*-$PDMA_{45}$ ABC miktoarm star terpolymer in $CDCl_3$.

calculated to be 68 and 45, respectively, from the relative integral ratios of these characteristic peaks. The obtained polymer was denoted as $PEO_{113}$(-*b*-$PCL_{68}$)-*b*-$PDMA_{45}$. Moreover, we can clearly observe the presence of resonance signal at 7.8 ppm (peaks $H_b$), which is characteristic of the proton in 1,2,3-triazole ring.

Typical FTIR spectra of $PEO_{113}$(-*b*-$PCL_{68}$)-*b*-$PDMA_{45}$ and $PEO_{113}$-$N_3$ were shown in Figure 7. Compared to that of PEO-$N_3$, the IR spectrum of $PEO_{113}$(-*b*-$PCL_{68}$)-*b*-$PDMA_{45}$ revealed the complete disappearance of characteristic azide absorbance peak at 2100 $cm^{-1}$. FTIR results agreed quite well with that obtained from GPC analysis (Fig. 5), which exhibited the absence of a shoulder peak in the lower MW region. These results indicated that all $PEO_{113}$-$N_3$ has participated in the click reaction with *alkynyl(—OH)—Br*.

In addition, $PCL_{69}$(-*alkynyl*)-*b*-$PDMA_{46}$ block copolymer was also synthesized in a one-pot manner (Table 1). GPC analysis of $PCL_{69}$(-*alkynyl*)-*b*-$PDMA_{46}$ gave an $M_n$ of 14.8 kDa and an $M_w/M_n$ of 1.16. Compared to that of $PCL_{69}$(-*alkynyl*)-*b*-$PDMA_{46}$, $PS_{60}$(-*b*-$PCL_{71}$)-*b*-$PDMA_{47}$ and $PEO_{113}$(-*b*-$PCL_{68}$)-*b*-$PDMA_{45}$ ABC miktoarm star terpolymers exhibited considerably higher $M_n$ values (Table 1), and this further confirmed the successful preparation of miktoarm star terpolymers in a one-pot manner.

Glass transition temperatures ($T_g$) and melting temperatures ($T_m$) of $PS_{60}$(-*b*-$PCL_{71}$)-*b*-$PDMA_{47}$ and $PEO_{113}$(-*b*-$PCL_{68}$)-*b*-$PDMA_{45}$ ABC miktoarm star terpolymer were determined by DSC analysis (Fig. 8). For $PS_{60}$(-*b*-$PCL_{71}$)-*b*-$PDMA_{47}$ miktoarm star terpolymer, we can discern one melting peak ($T_m$ = 53.2 °C) for PCL segment and two glass transitions (3.1 °C for PDMA and 88.5 °C for PS segments).[65] For $PEO_{113}$(-*b*-$PCL_{68}$)-*b*-$PDMA_{45}$ miktoarm star terpolymer, we can discern two melting peak ($T_m$ = 50.2 °C and 53.0 °C) associated with PEO and PCL segments, respectively. On the other hand, the glass transition of PDMA segment is barely visible.

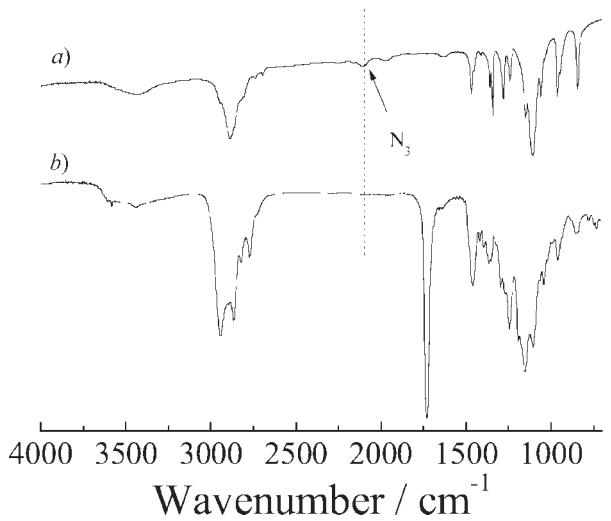



**Figure 7.** FTIR spectra recorded for (a) $PEO_{113}$-$N_3$ and (b) $PEO_{113}$(-*b*-$PCL_{68}$)-*b*-$PDMA_{45}$ ABC miktoarm star terpolymer synthesized via the one-pot technique.

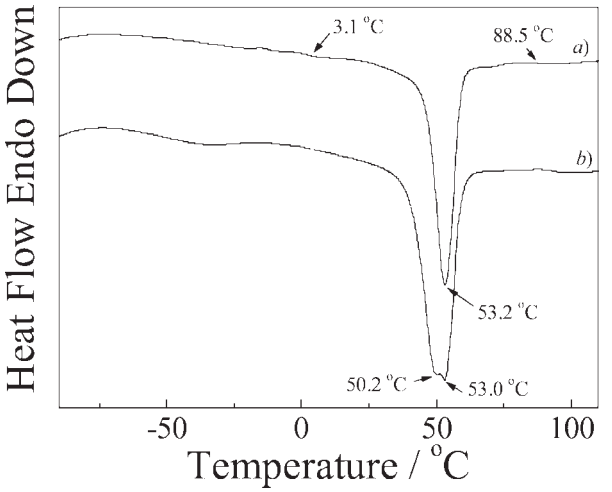



**Figure 8.** DSC thermograms recorded for (a) $PS_{60}$(-*b*-$PCL_{71}$)-*b*-$PDMA_{47}$ and (b) $PEO_{113}$(-*b*-$PCL_{68}$)-*b*-$PDMA_{45}$ ABC miktoarm star terpolymer.

## CONCLUSIONS

We report on the facile one-pot synthesis of PS(-*b*-PCL)-*b*-PDMAand PEO(-*b*-PCL)-*b*-PDMA miktoarm star terpolymers by simultaneously conducting ATRP, ROP, and click reactions using CuBr/PMDETA/$Sn(Oct)_2$ catalytic system, starting from the trifunctional core molecule *alkynyl(—OH)—Br* (Scheme 1). By varying the monomer feed ratios and reaction time/temperatures, we expect that arm lengths in target miktoarm star terpolymers can be finely tuned. This work represents a useful extension from the previous report by Tunca research group, in which a combination of ROP, NMP, and click reactions were employed. The one-pot strategy for the synthesis of ABC miktoarm star terpolymers augurs well for their large scale preparation.

The financial supports of National Natural Scientific Foundation of China (NNSFC) Projects (20534020,

20674079, and 20874092), Specialized Research Fund for the Doctoral Program of Higher Education (SRFDP), and the Program for Changjiang Scholars and Innovative Research Team in University (PCSIRT) are gratefully acknowledged.

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