

A New Synthetic Approach to Asymmetric Amphiphilic ABA' Block Copolymers by ATRP and Click Reactions

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ABSTRACT: Well-defined asymmetric amphiphilic ABA' block copolymers composed of poly(ethylene oxide) monomethylene ether (MPEO) with different molecular weights as A or A' block and poly(styrene) (PS) as B block were synthesized by the combination of atom transfer radical polymerization (ATRP) and click reactions. First, bromine-terminated diblock copolymer poly(ethylene oxide) monomethylene ether-*block*-poly(styrene) (MPEO-PS-Br) was prepared by ATRP of styrene initiated with macroinitiator MPEO-Br, which was prepared from the esterification of MPEO and 2-bromoisobutyryl bromide. Then, the azido-terminated diblock copolymers MPEO-PS-N₃ were prepared through the bromine substitution reaction with sodium azide. Propargyl-terminated MPEO with a different molecular weight was prepared under the basic condition from propargyl alcohol and *p*-toluenesulfonyl-terminated MPEO,

which was prepared through the esterification of MPEO and *p*-toluenesulfonylchloride using pyridine as solvent. Asymmetric amphiphilic ABA' block copolymers, with a wide range of number-average molecular weights from 1.92×10^4 to 2.47×10^4 and a narrow polydispersity from 1.03 to 1.05, were synthesized via a click reaction of the azido-terminated diblock copolymers and the propargyl-terminated MPEO in the presence of CuBr and 1,1,4,7,7-pentamethyldiethylenetriamine (PMDETA) catalyst system. The structures of these ABA' block copolymers and corresponding precursors were characterized by NMR, IR, and GPC. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 111: 560–565, 2009

Key words: atom transfer radical polymerization; block copolymers; poly(ethylene oxide) monomethylene ether; click reaction

INTRODUCTION

Amphiphilic block copolymers have attracted great interest in both fundamental and applied research because of their unique chain architecture and physical properties.^{1,2} They can not only self-assemble into highly ordered supramolecular structures including spherical, vesicular, cylindrical, planar geometries, etc.,^{3–11} but also have many potential applications including drug delivery, nanoreactors, and templates for the synthesis of mesoporous materials and nanoparticles.^{12–17} Among these amphiphilic block copolymers, these copolymers consisting of poly(ethylene oxide) (PEO) block play an important role. There is a reason that PEO possesses outstanding biological and physical-chemical properties including hydrophilicity, nontoxicity, and biocompatibility, so as to be

widely used in biomedical research and application.^{12,13} Especially mentioned, amphiphilic linear ABA triblock copolymers consisting of PEO as the hydrophilic block are very popular. For example, commercially available poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide) (PEO-PPO-PEO) triblock copolymers have been studied extensively in terms of their phase behavior and potential applications.^{17,18} To date, many well-defined amphiphilic ABA block copolymers consisting of PEO blocks have been synthesized using different polymerization methods, including living ionic polymerization,^{19,20} atom transfer radical polymerization (ATRP),^{21,22} and others.^{23–27} Generally, "living ionic" polymerizations are limited because of some rigorous conditions, such as strictly low temperature, water-free and oxygen-free reactions systems with a high level of monomer purification.²⁸ Compared with living ionic polymerizations, ATRP offers a powerful method for the controlled manipulation of macromolecular architecture because of polymerization of a wide variety of monomers, tolerance of a wide range of functional groups, and very facile preparation of block copolymers with a narrow polydispersity index.^{21,22}

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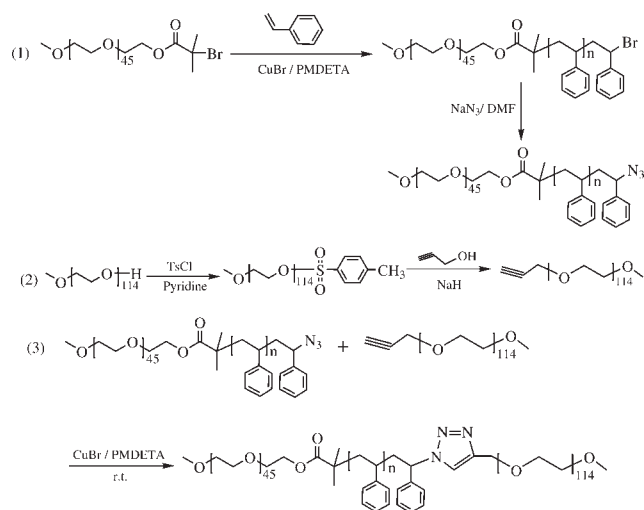
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Although there are many reports about amphiphilic ABA block copolymers composed of PEO as A block,^{19,24–27} to the best of our knowledge, there have been few reports concerning the synthesis of asymmetric amphiphilic ABA' block copolymers composed of MPEO with different molecular weights as A or A' block. At the same time, there is a growing demand of novel structural block copolymers with PEO blocks for the development of new application areas. A new approach was carried out for the synthesis of asymmetric amphiphilic ABA' block copolymers by the combination of ATRP and click reactions in this article. It is well known that the click reaction, defined by Sharpless and co-workers,²⁹ has been widely applied in polymers synthesis^{29–32} and advanced architectural designs^{33–36} because of its quantitative yields, mild reaction condition, and tolerance of a wide range of functional groups. First, bromine-terminated diblock copolymer poly(ethylene oxide) monomethylene ether-*block*-poly(styrene) (MPEO-PS-Br) with different molecular weights was prepared by ATRP and converted into azido-terminated MPEO-PS-N₃. The propargyl-terminated MPEO with a different molecular weight was prepared under the basic condition from propargyl alcohol and *p*-toluenesulfonyl-terminated MPEO, which was obtained through the esterification of MPEO and *p*-toluenesulfonyl chloride using pyridine as solvent. Asymmetric amphiphilic ABA' block copolymers were finally synthesized via a click reaction of the azido-terminated diblock copolymers and the propargyl-terminated MPEO in the presence of CuBr/PMDETA catalyst system. The synthesis of the ABA' block copolymers is shown in Scheme 1.

EXPERIMENTAL

Materials

Styrene (St, Shanghai Chemical Reagent, A.R. grade) was passed through a basic alumina column to remove the inhibitor and then distilled over CaH₂ *in vacuo* before use. CuBr (Shanghai Chemical Reagent, A.R. grade) was purified by stirring in glacial acetic acid overnight, filtered, washed with ethanol, and then dried in a vacuum oven at 60°C overnight. Tetrahydrofuran (THF, Shanghai Chemical Reagent, A.R. grade) was dried by refluxing over sodium. Poly(ethylene oxide) monomethylene ether (MPEO₄₅-OH and MPEO₁₁₄-OH mean degree of polymerization = 45 and 114, respectively.) was purchased from Aldrich. Sodium azide (NaN₃, Acros, 99%), 1,1,4,7,7-pentamethyldiethylenetriamine (PMDETA, Aldrich, 99+%), propargyl alcohol (Aldrich, 99%), sodium hydride (Acros, 60% dispersion in mineral oil), 2-bromoisobutyryl bromide (Acros, 98%), *p*-toluenesulfonyl chloride (TsCl, A.R. grade), *N,N*-



Scheme 1 Synthesis of ABA' block copolymers.

dimethylformamide (DMF, A.R. grade), pyridine (A.R. grade), and other solvents were purchased from Shanghai Chemical Reagent Company and purified by conventional procedures if needed. The macroinitiator MPEO₄₅-Br was prepared according to a published procedure³⁷: $M_n(\text{GPC}) = 3.2 \times 10^3 \text{ g mol}^{-1}$, $M_w/M_n = 1.05$.

Synthesis of MPEO₄₅-PS-Br by ATRP

MPEO₄₅-PS-Br was prepared by bulk polymerization. This was a typical bulk polymerization as follows: A Schlenk tube was charged with 0.32 g (0.1 mmol) of MPEO₄₅-Br ($M_n = 3.2 \times 10^3 \text{ g mol}^{-1}$), 5.0 g (48.0 mmol) of degassed St, 14.3 mg (0.1 mmol) of CuBr, 17.3 mg (0.1 mmol) of PMDETA, and a magnetic bar. The reaction mixture was degassed with three freeze-pump-thaw cycles. The tube was then sealed under vacuum and immersed in a thermostatic oil bath at 90°C for 4 h. The reaction was stopped and quickly cooled down to room temperature with cool water. The mixture was further diluted with THF, removed copper salts through a plugged column of neutral aluminum oxide, and precipitated in a large volume of cold methanol. The sample was purified by reprecipitating three times from THF to methanol and dried under vacuum overnight at 50°C. Yield: 67%, $M_n(\text{GPC}) = 1.06 \times 10^4 \text{ g mol}^{-1}$, $M_w/M_n = 1.08$.

Synthesis of MPEO₄₅-PS-N₃

The procedure for the transformation of MPEO₄₅-PS-Br into MPEO₄₅-PS-N₃ was adapted from the literature.³¹ Typically, 0.5 g (0.047 mmol) of MPEO₄₅-PS-Br ($M_n = 1.06 \times 10^4 \text{ g mol}^{-1}$), 4.6 mg (0.07 mmol) of NaN₃, and 10 mL of DMF were added in a round-bottom flask. The mixture solution was stirred with

a magnetic bar at room temperature overnight before removal of DMF by rotary evaporation. The solid was dissolved in methylene chloride and the undissolved solid was removed by filtration. Most of methylene chloride was removed by rotary evaporation, precipitated into cool methanol, filtered, and dried at room temperature in a vacuum oven for 48 h. Yield: 85%, $M_n(\text{GPC}) = 1.07 \times 10^4 \text{ g mol}^{-1}$, $M_w/M_n = 1.07$.

Synthesis of propargyl-terminated MPEO₁₁₄

The synthesis of propargyl-terminated MPEO₁₁₄ is briefly described as follows: In clean dry round-bottom flask, 10.0 g (2.0 mmol) of MPEO₁₁₄ was dissolved in 100 mL of anhydrous pyridine, and the solution was stirred in an ice bath under nitrogen. Three grams (20.0 mol) of *p*-toluenesulfonyl chloride was added in several portions, and the mixture was stirred at this temperature for 4 h. Subsequently, the reaction mixture was allowed to warm to room temperature with continued stirring for 24 h. The solution was evaporated by rotary evaporation. The crude produce was dissolved in 50 mL CH₂Cl₂, filtered, and precipitated into an excess amount of ethyl ether. The *p*-toluenesulfonyl-terminated MPEO₁₁₄ was recrystallized in absolute ethanol two times, filtered, and dried at room temperature in a vacuum oven for 48 h. Yield: 92%. $M_n(\text{GPC}) = 8.5 \times 10^3 \text{ g mol}^{-1}$, $M_w/M_n = 1.02$

A clean dry round-bottom flask was charged with 0.4 g (10.0 mmol) of 60% sodium hydride and 50 mL of dry THF. Propargyl alcohol (0.56 g, 10.0 mmol) was added dropwise to a sodium hydride suspension and stirred for 10 h. The solution of 5.0 g (1.0 mmol) of *p*-toluenesulfonyl-terminated MPEO₁₁₄ in 50 mL of dry THF was added dropwise to the above mixture and stirred for 24 h at room temperature. The undissolved solid was removed by filtration. The solution was then concentrated by rotary evaporation and precipitated into an excess amount of ethyl ether. The propargyl-terminated MPEO₁₁₄ was recrystallized in absolute ethanol two times, filtered, and dried at room temperature in a vacuum oven for 48 h. Yield: 90%. $M_n(\text{GPC}) = 8.0 \times 10^3 \text{ g mol}^{-1}$, $M_w/M_n = 1.03$.

Synthesis of MPEO₄₅-PS-MPEO₁₁₄ by a click reaction

A typical procedure for the click reaction was as follows: 0.26 g (0.024 mmol) of MPEO₄₅-PS-N₃ ($M_n = 1.07 \times 10^4 \text{ g mol}^{-1}$), 0.19 g (0.024 mmol) of propargyl-terminated MPEO₁₁₄ ($M_n = 8.0 \times 10^3 \text{ g mol}^{-1}$), 143.0 mg (1.0 mmol) of CuBr, and 10 mL of DMF were added into a round-bottom flask equipped with a magnetic stirring bar. The flask was capped

with a rubber plug and purged with N₂ for 30 min. One hundred seventy three milligrams (1.0 mmol) of PMDETA was then added by using a degassed syringe. The mixture was stirred overnight at room temperature. The product was precipitated in the mixture solvent (volume ratio = 2 methanol/1 ethyl ether) and purified by reprecipitating three times from THF to the mixture solvent and dried at room temperature in a vacuum oven for 48 h. Yield: 85%. $M_n(\text{GPC}) = 1.92 \times 10^4 \text{ g mol}^{-1}$, $M_w/M_n = 1.03$.

Characterization

Molecular weights M_n and polydispersity M_w/M_n were measured on a gel permeation chromatograph (Waters 150C) equipped with three Waters Styragel columns (10³, 10⁴, and 10⁵ Å) and RI detector using THF as an eluent at 35°C. The column system was calibrated by a set of monodispersed standard polystyrenes. ¹H-NMR spectra were obtained on a 500 Bruker NMR instrument using CDCl₃ as solvent, tetramethyl silane as the internal standard. Fourier transform infrared (FTIR) spectra were recorded on a Perkin-Elementer Spectrum one spectrometer.

RESULTS AND DISCUSSION

The asymmetric amphiphilic ABA' block copolymers MPEO₄₅-PS_{*n*}-MPEO₁₁₅ (*n* = 1–3, designated the sample ID) were synthesized by the combination of ATRP and a click reaction according to Scheme 1. The molecular characteristics of all ABA' block copolymers and their precursors were determined by GPC and summarized in Table I. Generally, polymers prepared by ATRP have the well-defined chain-length, the low polydispersity index, and the halide end-group.^{21,22} The halide end-group can be modified and novel polymers can be prepared.^{31–34} The precursors with the terminal bromine, MPEO₄₅-PS-Br, were prepared from the ATRP of St with the macroinitiator MPEO₄₅-Br and then converted into azido-terminated MPEO₄₅-PS-N₃ by reacting with NaN₃ in DMF. Figure 1 displays the ¹H-NMR spectra of the MPEO₄₅-PS₁-Br, MPEO₄₅-PS₁-N₃, propargyl-terminated MPEO₁₁₄, and MPEO₄₅-PS₁-MPEO₁₁₄, respectively. From Figure 1(A), the proton signal of the α position to the terminal bromine was at 4.30–4.60 ppm [Fig. 1(A: g)]. This indicates that the diblock copolymer has the bromine terminal group.³¹ After the terminal bromine group of MPEO₄₅-PS₁-Br was substituted with an azido group, the proton signal of the α position shifted to 3.80–4.00 ppm [Fig. 1(B: h)], which corresponded to the proton of the α position to the terminal azido group,³¹ and no residual peak was found at 4.30–4.60 ppm. The characteristic resonances originating from the MPEO₄₅ block at 3.35–3.77 [Fig. 1(A: b)]

TABLE I
Characterization of Polymers

Polymer	^a GPC		¹ H-NMR		
	M_n (10^4 g mol ⁻¹)	M_w/M_n	PEO ₄₅ (wt %)	PS (wt %)	MPEO ₁₁₄ (wt %)
MPEO ₄₅	0.31	1.05			
MPEO ₄₅ -Br	0.32	1.05			
^b MPEO ₁₁₄	0.80	1.03			
MPEO ₄₅ -PS ₁ -Br	1.06	1.08	35.3	64.7	
MPEO ₄₅ -PS ₁ -N ₃	1.07	1.07	34.8	65.2	
MPEO ₄₅ -PS ₁ -MPEO ₁₁₄	1.92	1.03	16.0	40.8	43.2
MPEO ₄₅ -PS ₂ -Br	1.45	1.07	23.0	77.0	
MPEO ₄₅ -PS ₂ -N ₃	1.47	1.08	21.6	78.4	
MPEO ₄₅ -PS ₂ -MPEO ₁₁₄	2.32	1.05	13.3	52.9	33.8
MPEO ₄₅ -PS ₃ -Br	1.59	1.07	21.3	78.7	
MPEO ₄₅ -PS ₃ -N ₃	1.61	1.06	20.9	79.1	
MPEO ₄₅ -PS ₃ -MPEO ₁₁₄	2.47	1.05	11.9	56.9	31.2

^a Determined by GPC in THF with calibrated PS standards.

^b MPEO₁₁₄ was propargyl-functional.

and 3.39 ppm [Fig. 1(A: a)] assigned to $-\text{CH}_2\text{CH}_2\text{O}-$ and $-\text{OCH}_3$, respectively, the PS block at 6.60 and 7.07 ppm [Fig. 1(A: d)] assigned to phenyl moieties are still presented in the spectrum of MPEO₄₅-PS₁-N₃. Figure 2 is IR spectra of MPEO₄₅-PS₁-MPEO₁₁₄ and its precursors.

The characteristic absorption peak of the terminal azido group at 2090 cm^{-1} [Fig. 2(B)] was observed on the IR spectrum of the MPEO₄₅-PS₁-N₃ because of the substitution reaction. By GPC analysis, the synthesis of the MPEO₄₅-PS-N₃ precursors involved no molecular weight reduction because narrow symmetrical signals were observed at the same position

as the starting MPEO₄₅-PS-Br precursors (Fig. 3). These suggested that the substitution reaction was highly efficient. From the results of ¹H-NMR, IR, and GPC, the precursors MPEO₄₅-PS-N₃ were successfully synthesized.

The structural characteristic of propargyl-terminated MPEO₁₁₄ has been determined by ¹H-NMR, IR, and GPC analysis. The characteristic signals of $\text{HC}\equiv\text{C}-$, $\text{HC}\equiv\text{C}-\text{CH}_2-$, and $-\text{OCH}_3$ appeared at 2.47 [Fig. 1(C: i)], 4.22, [Fig. 1(C: j)] and 3.39 ppm in ¹H-NMR spectrum of the propargyl-terminated MPEO₁₁₄, respectively. Furthermore, by GPC analysis, the molecular weight of the propargyl-terminated MPEO₁₁₄ did not reduce and the polydispersity

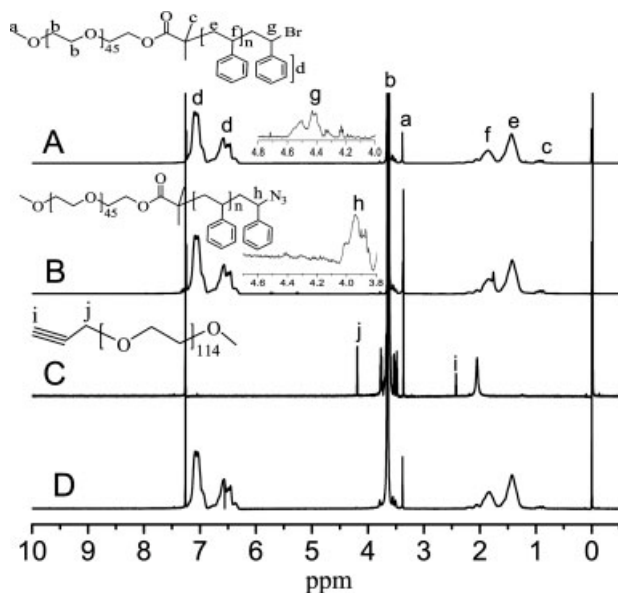


Figure 1 ¹H-NMR spectra of (A) MPEO₄₅-PS₁-Br, (B) MPEO₄₅-PS₁-N₃, (C) propargyl-terminated MPEO₁₁₄, and (D) MPEO₄₅-PS₁-MPEO₁₁₄ in CDCl₃.

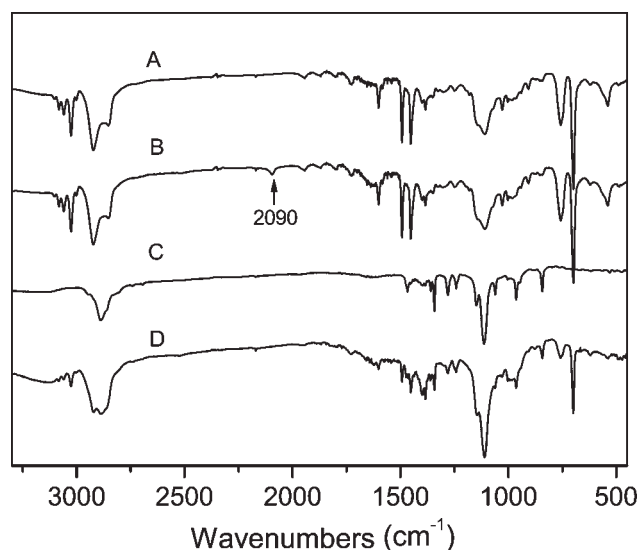


Figure 2 IR spectra of (A) MPEO₄₅-PS₁-Br, (B) MPEO₄₅-PS₁-N₃, (C) propargyl-terminated MPEO₁₁₄, and (D) MPEO₄₅-PS₁-MPEO₁₁₄.

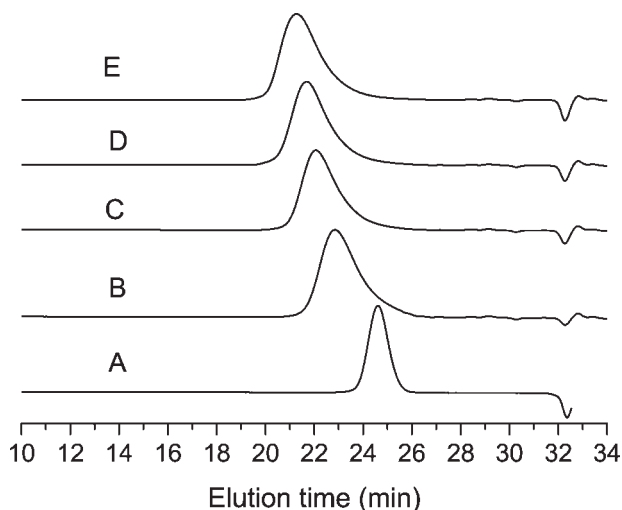


Figure 3 GPC curves of (A) MPEO₄₅-Br, (B) MPEO₄₅-PS₁-N₃, (C) MPEO₄₅-PS₁-MPEO₁₁₄, (D) MPEO₄₅-PS₂-MPEO₁₁₄, and (E) MPEO₄₅-PS₃-MPEO₁₁₄.

index was much lower (Table I). Therefore, the synthesis of the propargyl-terminated MPEO₁₁₄ was successful.

Finally, using a click reaction, the azido-terminated precursors MPEO₄₅-PS-N₃ and the propargyl-terminated MPEO₁₁₄ were reacted to obtain corresponding ABA' block copolymers MPEO₄₅-PS-MPEO₁₁₄ in the presence of CuBr/PMDETA catalyst system in DMF at room temperature. From the ¹H-NMR spectrum of the MPEO₄₅-PS₁-MPEO₁₁₄ [Fig. 1(D)], the broad peaks of phenyl moieties at 6.30–7.20 ppm and those at 3.35–3.77 ppm from MPEO block can be observed. The characteristic absorption peak of the terminal azido group at 2090 cm⁻¹ from MPEO₄₅-PS₁-N₃ segment disappeared in the IR spectrum of MPEO₄₅-PS₁-MPEO₁₁₄ [Fig. 2(D)]. Figure 3 shows the GPC curves of the ABA' block copolymers and the precursors of MPEO₄₅-PS₁-MPEO₁₁₄. The symmetrical unimodal peaks are observed in Figure 3, which shift to higher molecular weight region with the PS block contents of the ABA' block copolymers from 40.8 to 56.9%. By the combination of ¹H-NMR and GPC measurements, in our research system, with increasing the molecular weight of ABA' block copolymers from 1.92 × 10⁴ to 2.47 × 10⁴, MPEO₄₅ and MPEO₁₁₄ segment contents changed from 16.0 to 11.9% and from 43.2 to 31.2%, respectively. The ABA' block copolymers MPEO₄₅-PS-MPEO₁₁₄ were purified by reprecipitating three times from THF to the mixture solvent. After isolation and purification, there were no peaks of their corresponding precursors in the GPC curves of the products (Fig. 3). The ABA' block copolymers were successfully synthesized via a click reaction in the presence of CuBr/PMDETA catalyst system in DMF at room temperature.

CONCLUSIONS

A new approach for preparation of asymmetric amphiphilic ABA' block copolymers through the combination of ATRP and click reactions was presented in this article. The asymmetric amphiphilic ABA' block copolymers were composed of MPEO₄₅, MPEO₁₁₄, and PS with different molecular weights as A, A' block, and B block, respectively. ATRP was used to synthesize AB block copolymers MPEO₄₅-PS, and the bromine end-groups were modified and converted into the azido end-groups. The A' block, MPEO₁₁₄ was introduced into the AB block copolymers MPEO₄₅-PS by a click reaction. Therefore, the well-defined asymmetric amphiphilic ABA' block copolymers with the number-average molecular weights from 1.92 × 10⁴ to 2.47 × 10⁴ and a narrow polydispersity from 1.03 to 1.05 were successfully synthesized. According to the synthetic approach, many novel asymmetric amphiphilic ABA' block copolymers can be designed and prepared by changing B block. These works are in progress and will be reported in the future.

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