Synthesis of Multiblock Copolymers by Coupling Reaction Based on Self-Assembly and Click Chemistry

WanJuan Wang, Ting Li, Ting Yu, and FangMing Zhu*

Institute of Polymer Science, School of Chemistry and Chemical Engineering, Sun Yat-Sen (Zhongshan) University, Guangzhou 510275, China

Received October 12, 2008; Revised Manuscript Received November 12, 2008

ABSTRACT: Diends-azido-terminated and diends-alkynyl-terminated poly(ethylene oxide)-*b*-poly(propylene oxide)-*b*-poly(ethylene oxide) triblock copolymers (N_3-PEO-*b*-PPO-*b*-PEO-N_3 and HC≡C-PEO-*b*-PPO-*b*-PEO-C≡CH) were respectively prepared and used together as the precursors for multiblock copolymer synthesis through coupling reaction by combination of self-assembly and click chemistry. The self-assembly of equimolar resultant triblock copolymers in water, a selective solvent for PEO, results in a core−shell structure with the insoluble and collapsed PPO blocks as the core and the soluble and swollen PEO blocks as the shell. The self-assembly concentrates and exposes the azido and alkynyl end groups on the periphery. The multiple click coupling reactions between the self-assembled diends-functionalized triblock copolymers were performed, leading to the highly efficient formation of −(−PEO-*b*-PPO-*b*-PEO−)$_n$− multiblock copolymer chains. In comparison, the click coupling reaction was also presented in *N*,*N*-dimethylformamide (DMF) solution without self-assembly. It was found that the efficiency of the coupling reaction was very low, and no long multiblock copolymer chains were produced.

Introduction

The synthesis of block copolymers, mainly di- and triblock copolymers, with various polymerization reactions has been studied extensively. In polymer synthesis chemistry, living polymerization, including living anionic, cationic, and radical polymerizations, is the commonly used methodology for preparing well-defined block copolymers with designed molecular weight and microstructure.[1] Block copolymers were also prepared by changing the polymerization mechanism, such as using macroinitiators[2−5] or macromonomers.[6−9]

In theory, multiblock copolymers could be synthesized by an alternately sequential addition of different comonomers into a living copolymerization system.[10−12] In practice, each addition of new monomer will inevitably make some living chains dead because of impurities, leading to the resultant block copolymer with lower block numbers and broad molecular weight distribution. Therefore, the sequential addition method can only be used to make copolymers with a few blocks, such as diblock or triblock copolymers. Another limitation of the sequential addition of different comonomers is their reaction compatibility; namely, each added monomer must be sufficiently reactive so that the chain can propagate. Often, a living A block can initiate comonomer B, but a living B block cannot initiate comonomer A.

In another approach, one could, in principle, prepare multiblock copolymers by coupling[13] different polymer chains diends-terminated with suitable reactive groups or by linking[13,14] diends-functionalized polymer chains using so-called difunctional linking agents in solution. However, both coupling and linking reactions are extremely ineffective when long polymer chains ($M_w > 5 \times 10^3$) are used as the precursors because most of the reactive end groups are wrapped and hidden inside the polymer chains coiled in good solvent. Moreover, for long polymer chains, the concentration of the reactive end groups is too low to have an effective coupling or linking reaction because the overall polymer concentration cannot be too high. Therefore, the essential problem is how to expose and concentrate the reactive end groups of long polymer chains, while the overall polymer concentration will not be increased.

On the other hand, it is well-known in polymer physics that A−B diblock or A−B−A triblock copolymers with a proper comonomer composition in a selective solvent can self-assemble to form polymeric core−shell-like micelles.[15−19] Such a self-assembly forces and concentrates the reactive end groups of the soluble block to stay on the periphery of each micelle, which should make the coupling or linking reaction much easier. Using such a self-assembly assisted coupling or linking concept, we have so far had a limited success in the preparation of multiblock copolymers by starting with A−B−A triblock copolymers terminated with two reactive end groups.[20−22] However, a commonly encountered drawback, when using multiple linking reaction using a linking agent, is a low yield of multiblock products due to the slow and inefficient reactions between the diends-functionalized triblock copolymer chain ends and diends-functionalized linking agent.[21,22] First, the addition of a right amount of linking agent to link each two of the reactive chain ends is always a problem, and insufficient or excessive amount of linking agent will reduce the linking efficiency. Second, highly efficient linking or coupling reactions require reactive end groups having very high activity, which are always sensitive to impurities such as moisty carbon dioxide and oxygen.[20−22] Therefore, a large amount of selective solvent for the self-assembly of triblock copolymers inevitably loses the linking reactivities because of impurities. In addition, it is difficult to ensure that the linking agents can be dissolved by the selective solvents.

As compared with linking reactions, directly self-assembly-assisted coupling reaction among diends-functionalizaed block copolymers without linking agent should overcome above shortcomings. We have reported the self-assembly assisted photocycloaddition of polystyrene-*b*-polyisoprene diblock copolymer which polyisoprene block was terminated with a photosensitive molecule, 7-chlorodimethylsilanoxy-4-methylcoumarin, which can undergo [2 + 2]- photocycloaddition under a UV irradiation.[23] However, UV irradiation technology will lead to some side reactions, such as cross-linking and degradation.

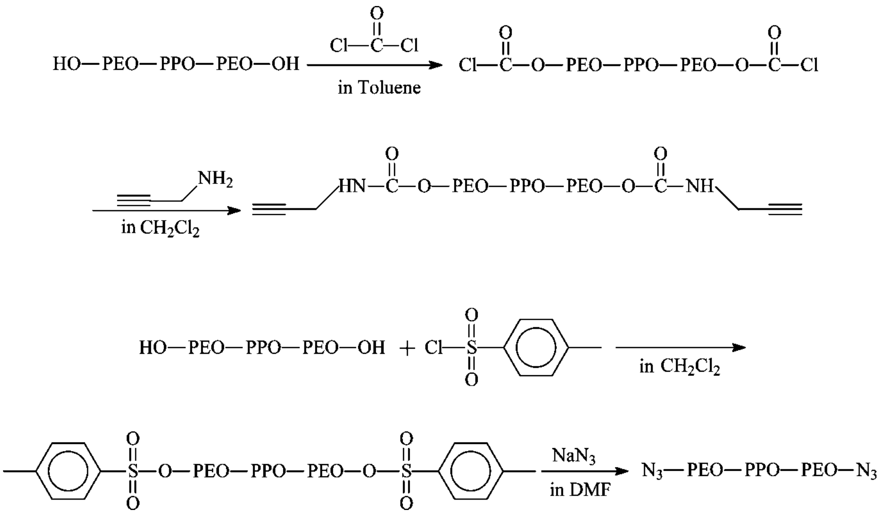
Recently, Diels−Alder reaction and atom transfer radical coupling reaction have attracted much attention in polymer chemistry, particularly in the synthesis of ABC type triblock

---

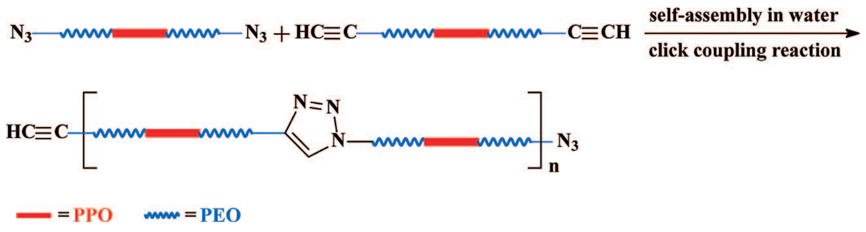
* Corresponding author: Tel (020) 84113250; Fax (020) 84114033; e-mail ceszfm@mail.sysu.edu.cn.

10.1021/ma802291w CCC: \$40.75

Scheme 1. Synthetic Route to N_3-PEO-*b*-PPO-*b*-PEO-N_3 and HC≡C-PEO-*b*-PPO-*b*-PEO-C≡CH



Scheme 2. Synthesis of −(−PEO-*b*-PPO-*b*-PEO−)$_n$− Multiblock Copolymer with Self-Assembly-Assisted Click Coupling Reactions



copolymers.[24,25] However, it is difficulty to prepare the precursor polymers end-capped with the required functional groups, and the coupling reactions are always required to proceed at higher temperature. Click chemistry has been extensively used in polymer chemistry due to the high efficiency and technical simplicity of the reaction.[26−36] Moreover, this procedure can be conducted in aqueous or organic media with little or no side reactions in a wide temperature range. Herein, we demonstrate the synthesis of multiblock copolymers by multiple coupling procedure using a combination of self-assembly and click chemistry. N_3-PEO-*b*-PPO-*b*-PEO-N_3 and HC≡C-PEO-*b*-PPO-*b*-PEO-C≡CH were self-assembled together in water used as a selective solvent to form core−shell-like micelles. Alkyne and azido were exposed and concentrated on the micellar periphery, and multiple click reactions resulted in the formation of −(−PEO-*b*-PPO-*b*-PEO−)$_n$− multiblock copolymers.

Experimental Section

Materials. Diends-hydroxy-terminated triblock copolymer HO-PEO-*b*-PPO-*b*-PEO-OH ($PEO_{100}PPO_{65}PEO_{100}$, Pluronic F127, M_w = 12 600) was purchased from Sigma and dried in vacuum at 60 °C for 24 h. *p*-Toluenesulfonyl chloride (99%, TsCl), propargylamine (99%), 1,4-dibromobutane (99%), sodiumazide (NaN_3, 99%), sodium ascorbic acid, copper sulfate, and *n*-butyllithium (2.5 mol/L solution in hexane, *n*-BuLi) were purchased from Acros and all used as received. Phosgene toluene solution (20%) was purchased from Aldrich. All solvents and other reagents if not specified were purchased from Sinopharm Chemical Reagent Co., Ltd.S.

Synthesis of 1,4-Diazobutane. 1,4-Dibromobutane (50.0 g, 0.23 mol) and NaN_3 (37.6 g, 0.58 mol) were dissolved in 80 mL of DMF and 8 mL of H_2O and stirred at 80 °C for 20 h. After cooled to room temperature, 160 mL of diethyl ether (Et_2O) was added into the reaction mixture, and then the resultant solution was washed with 4% NaCl solution four times. The organic layer was dried with anhydrous $MgSO_4$ for 24 h and concentrated to give 30.8 g (0.22 mol) of 1,4-diazidobutane (yield: 95.1%). ^1H NMR (400 MHz, $CDCl_3$, ppm): δ 3.29 (t, J = 5.8 Hz, 4H, N_3CH_2), δ 1.64 (m, J = 12.4 Hz, 4H, $CH_2CH_2CH_2CH_2$).

Synthesis of HC≡C-PEO-*b*-PPO-*b*-PEO-C≡CH. HO-PEO-*b*-PPO-*b*-PEO-OH (12.6 g, [−OH] = 2 mmol) was dissolved in dry toluene, refluxed, and dried in a vacuum to remove water. Phosgene solution (15 mL, 20% in toluene) was then added into the dried HO-PEO-*b*-PPO-*b*-PEO-OH under stirring. The reaction was allowed to proceed overnight in a fume hood. The excess phosgene was removed in vacuum. 30 mL of dichloromethane (DCM) was used to dissolve the viscous residue. Propargylamine (0.55 g, 10 mmol) was then added into the solution. The reaction was allowed to proceed for 8 h at room temperature. The product was precipitated into Et_2O three times and dried in a vacuum at 50 °C for 2 days; 10.1 g of the product was obtained. Yield: 80.5%.

Synthesis of N_3-PEO-*b*-PPO-*b*-PEO-N_3. HO-PEO-*b*-PPO-*b*-PEO-OH (12.6 g, [−OH] = 2 mmol) was dissolved in dry toluene, refluxed, and dried in a vacuum to remove water. Dry benzene (100 mL) was then added into the dried polymer with stirring under nitrogen. After the polymer solution was cooled to 5 °C, 2.5 mol/L solution of *n*-butyl lithium in hexane (1 mL, 2.5 mmol *n*-BuLi) was added rapidly while stirring. After 30 min, *p*-toluenesulfonyl chloride (0.70 g, 3.6 mmol) dissolved in 10 mL of dry benzene was added. The resultant mixture was stirred overnight at room temperature. The precipitate was filtered, and the filtrate was evaporated in vacuum until it was dry. The residue was purified by precipitation from THF to Et_2O three times, and the precipitate was filtered off. After drying in a vacuum at 50 °C for 2 days, 9.8 g of the product of TsO-PEO-*b*-PPO-*b*-PEO-OTs (pluronic tosylate) was obtained. Yield: 77.8%.

Sodium azide (1.8 g, 28 mmol) was added to a solution of pluronic tosylate (8.82 g, 0.7 mmol) in DMF (30 mL) with stirring at 80 °C and allowed to react for 18 h. After the removal of *N*,*N*-dimethylformamide (DMF) by rotary evaporation, the solid was dissolved in dichloromethane (CH_2Cl_2) and the undissolved solid was removed by filtration. The organic solution was washed twice by water before dried over anhydrous $MgSO_4$ overnight, and then the product was purified by precipitation from CH_2Cl_2 to Et_2O. After the precipitate was filtered off, it was dried in a vacuum at 50 °C for 2 days. Finally, 6.41 g of the product was obtained. Yield: 72.8%.

Self-Assembly-Assisted Click Coupling Reaction between HC≡C-PEO-*b*-PPO-*b*-PEO-C≡CH and N_3-PEO-*b*-PPO-*b*-PEO-N_3. Doubly distilled water, equimolar HC≡C-PEO-*b*-PPO-*b*-PEO-C≡CH (0.63 g, 0.05 mmol), and N_3-PEO-*b*-PPO-*b*-PEO-N_3 (0.63 g, 0.05 mmol) were introduced into a 100 mL Schlenk flask. The mixture was degassed with several cycles of vacuum pumping and argon purging. Before the click coupling reaction, the solution was stirred at 0 °C for 8 h and then further stirred at 25 °C for 8 h to make the self-assembly in water possible. The concentrations of both triblock copolymer precursors were 40 mg/mL, which is sufficiently low in order to avoid a possible intermicelle coupling reaction. The self-assembly assisted click coupling reaction was carried out when the aqueous solution of $CuSO_4 \cdot 5H_2O$ (15.5 mg, 0.062 mmol) and sodium ascorbate (22.0 mg, 0.11 mmol) used as catalyst was added. After 24 h coupling reaction, the water in the reaction solution was removed in vacuum, and CH_2Cl_2 was used to dissolve the residue. Then the solution was passed through neutral alumina column and precipitated in Et_2O in order to harvest the resultant product. After dried in a vacuum at 50 °C for 2 days, finally 0.90 g of the product was obtained. Yield: 71.4%.

Measurements. ^1H NMR (300 MHz) and ^{13}C NMR (75 MHz) spectra were recorded in $CDCl_3$ at room temperature on a Varian Unity Inova 300 spectrometer. Molecular weight and molecular weight distribution (M_w/M_n) were measured by gel permeation chromatography (GPC) against narrow molecular weight distribution polystyrene standards in THF at a flow rate of 1.0 mL/min at 35 °C with a Waters 2414 refractive index detector. Dynamic light scattering (DLS) measurements were conducted at 25 °C on a Brookhaven BI-200SM apparatus with a BI-9000AT digital correlator and a He−Ne laser at 532 nm. The stock solution (1 wt %) was first prepared and then diluted to a proper concentration for the DLS measurement. Prior to the measurement, the sample aqueous solutions were stored in refrigerator (about 0 °C) for at least 24 h to ensure complete dissolution and then remained at 25 °C for 48 h to accomplish the self-assembly. Each solution was clarified by passing through a 0.45 μm nylon filter to remove dust. The data were analyzed by CONTIN algorithm, while the hydrodynamic radius (R_h) and size polydispersity of the particles (individual chains or micelles) were obtained by a cumulant analysis of the experimental correlation function.

Results and Discussion

There have been several reports on the preparation of PEO having azido or/and alkynyl end groups from hydroxy-terminated PEO.[32−34] As shown in Scheme 1, diends-alkynyl-terminated PEO-*b*-PPO-*b*-PEO was synthesized through esterification between the hydroxyl end groups on HO-PEO-*b*-PPO-*b*-PEO-OH with phosgene and subsequent amidation by propargylamine. Quantitative conversion to alkynyl end groups was confirmed by ^1H NMR in terms of observing the appearance of the characteristic peak at 2.25 ppm assigned to the hydrogen on alkynyl (Figure 1). Moreover, the peak at 5.34 ppm corresponds to the hydrogen adjacent to the nitrogen atoms from the propargyl anmide group was detected.

N_3-PEO-*b*-PPO-*b*-PEO-N_3 was obtained through the two-step modification, the tosylation and the subsequent substitution by sodium azide of hydroxyl groups as described in Scheme 1. The precise structure of the obtained N_3-PEO-*b*-PPO-*b*-PEO-N_3 chains cannot be determined by ^1H NMR due to the overlapped peaks between chain-end methylene protons (CH_2N_3) and the $(CH_2CH_2O)_n$ protons in the backbone. Therefore, ^{13}C NMR was used to characterize the resultant triblock copolymer. In the ^{13}C NMR spectrum (Figure 2), the signal of the methylene carbon adjacent to the azido group ($CH_2CH_2N_3$) was observed at 50.5 ppm. Moreover, no signals of the methylene carbon adjacent to the hydroxyl end groups (CH_2CH_2OH δ 61.50 ppm)[37] and the methyl carbon ($C_6H_4CH_3$ δ 21.64 ppm)[32] in tosyl were detected. These results indicate the successful preparation of almost 100% diends-azido-terminated PEO-*b*-PPO-*b*-PEO derivated from HO-PEO-*b*-PPO-*b*-PEO-OH.

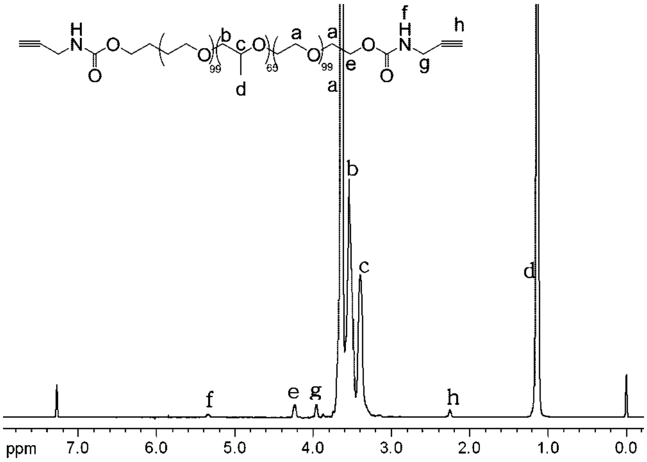


Figure 1. ^1H NMR spectrum of HC≡C-PEO-*b*-PPO-*b*-PEO-C≡CH.

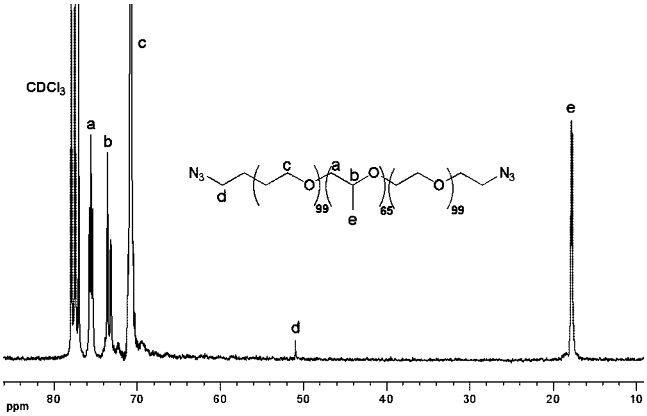


Figure 2. ^{13}C NMR spectrum of N_3-PEO-*b*-PPO-*b*-PEO-N_3.

In water, a solvent selectively good for the PEO block, such PEO-*b*-PPO-*b*-PEO at proper temperatures and concentration can form polymeric core−shell micelles with the insoluble and collapsed PPO blocks as the core and the soluble and swollen PEO blocks as the shell.[38−46] In this case, the self-assembly of the reultant PEO-*b*-PPO-*b*-PEO chains ($PEO_{100}PPO_{65}PEO_{100}$) in water was investigated by dynamic light scattering (DLS). Figure 3 shows the change of hydrodynamic radiu (R_h) as a function of temperature for the dilute PEO-*b*-PPO-*b*-PEO aqueous solution (C = 40 mg/mL). It is apparent that there is a distinct temperature (~20 °C) at which R_h increases dramatically, implicating the formation of micelles. The temperature at which this break in the curve occurs can therefore be designated as the critical micellization temperatures (CMT). When temperature is lower than the CMT, the solution contains only individual polymer chains since R_h (~4 nm) is very small, and at the CMT, individual polymer chains start to aggregate to form large core−shell micelles (R_h ~ 20 nm). Figure 4 displays the concentration dependence of the R_h of PEO-*b*-PPO-*b*-PEO at 25 °C. A distinct increase of R_h was observed at C = 20 mg/mL, which is defined as critical micellization concentration (CMC). This sharp increase in R_h clearly indicates the aggregation of individual polymer chains in solution.

Figure 5 shows a typical R_h distribution of individual PEO-*b*-PPO-*b*-PEO triblock copolymer chains (N_3-PEO-*b*-PPO-*b*-

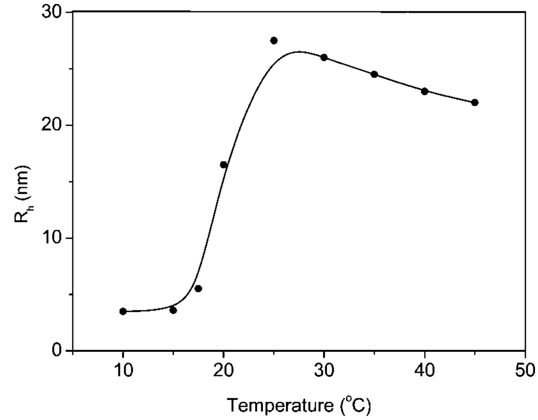


Figure 3. Change of R_h as a function of temperature for the dilute PEO-*b*-PPO-*b*-PEO aqueous solution ($C = 40$ mg/mL).

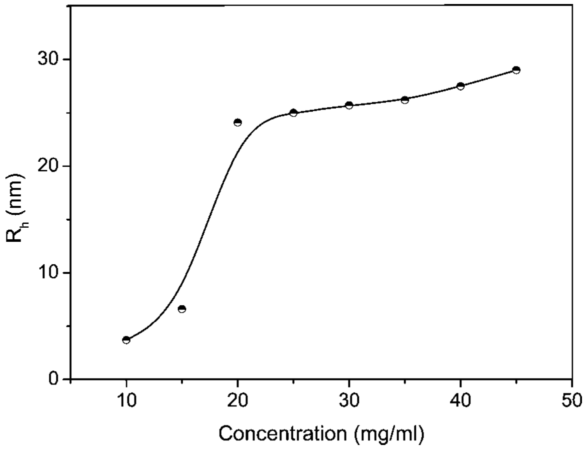


Figure 4. Concentration dependence of the R_h of PEO-*b*-PPO-*b*-PEO at 25 °C.

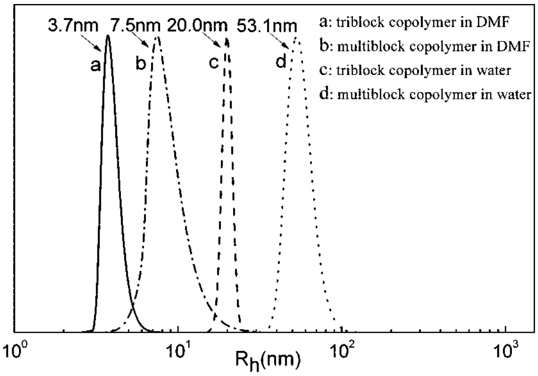


Figure 5. Typical R_h distributions of PEO-*b*-PPO-*b*-PEO triblock copolymer (in DMF and water) and multiblock copolymer (in DMF and water).

PEO-N_3 or HC≡C-PEO-*b*-PPO-*b*-PEO-C≡CH) in DMF (a good solvent for both PEO and PPO) and a typical R_h distribution of equimolar N_3-PEO-*b*-PPO-*b*-PEO-N_3 and HC≡C-PEO-*b*-PPO-*b*-PEO-C≡CH self-assembled core−shell micelles in water used as a selective solvent, where temperature = 25 °C and $C = 40$ mg/mL. The shift of the peak from 3.7 to 20.0 nm clearly revealed the self-assembly of the resultant individual triblock copolymer chains, resulting in well-defined narrowly distributed micelles. Note that only one peak located at ~20 nm was detected on the R_h distribution of PEO-*b*-PPO-*b*-PEO in water, indicating the aggregation of all the polymer chains.

It should be emphasized once more that the self-assembly concentrates and exposes the reactive ends of precursor A−B−A triblock copolymer chains on the periphery of such formed core−shell micelles, which greatly increases the efficiency of multiple coupling reaction leading to the formation −(−A−B−A−)$_n$− multiblock copolymers. In this investigation, we succeeded in obtaining −(−PEO-*b*-PPO-*b*-PEO−)$_n$− multiblock copolymers by self-assembly-assisted click coupling reaction between equimolar amount of N_3-PEO-*b*-PPO-*b*-PEO-N_3 and HC≡C-PEO-*b*-PPO-*b*-PEO-C≡CH chains in water (Scheme 2). Note that the addition of an insufficient or excessive amount of either of the two triblock copolymer precursors will reduce the coupling efficiency[20,23] because the excessive portion may act as a polymer chain terminator. So the equimolar of the two triblock copolymer precursors on the self-assembly-assisted multiple click coupling reaction will be the best choice.

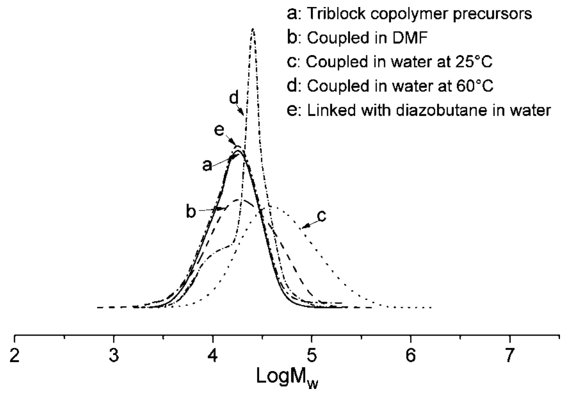


Figure 6. GPC profiles of PEO-*b*-PPO-*b*-PEO triblock copolymer precursors before and after click coupling or linking reaction in water as well as after click coupling reaction in DMF without the self-assembly.

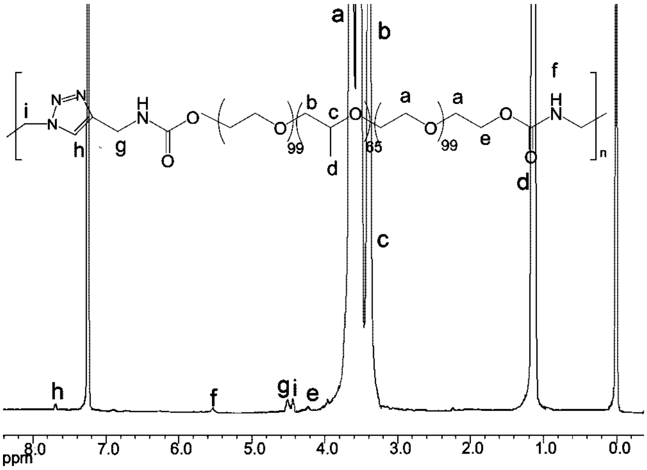


Figure 7. ^{1}H NMR spectrum of −(−PEO-*b*-PPO-*b*-PEO−)$_n$− multiblock copolymer synthesized by self-assembly-assisted click coupling reaction in water.

Such an effect can be clearly viewed in the GPC profiles of PEO-*b*-PPO-*b*-PEO precursors before and after click coupling reaction. As shown in Figure 6c, the weight-averaged molecular weight ($M_w = 7.0 \times 10^4$, $M_w/M_n = 1.7$) of the click coupling product of equimolar N_3-PEO-*b*-PPO-*b*-PEO-N_3 and HC≡C-PEO-*b*-PPO-*b*-PEO-C≡CH in water at 25 °C was about 5 times as high as the precursors' ($M_w = 1.3 \times 10^4$, $M_w/M_n = 1.3$). It suggested that the click coupling reaction presented four times in this case. Notably, no a tail peak, corresponding to the molecular weight region of the precursors, could be observed in the GPC profile of the click coupling product, proving the high efficiency of click coupling. In order to demonstrate the efficiency of self-assembly assisted click coupling, the resultant product was characterized by ^{1}H NMR (Figure 7). As compared with the ^{1}H NMR spectrum of the HC≡C-PEO-*b*-PPO-*b*-PEO-C≡CH (Figure 1), the signal at 2.25 ppm assigned to the alkynyl groups was obviously weakened after the reaction, while the protons of 1,2,3-triazole groups were clearly observed at 7.72 ppm. Figure 5 summarizes R_h distributions of PEO-*b*-PPO-*b*-PEO and $-(-$PEO-*b*-PPO-*b*-PEO$-)_n-$ synthesized by self-assembly-assisted click coupling reaction in water. Not only in DMF but also in water, both R_h of individual multiblock copolymer chains (7.5 nm) and their micelles (53.1 nm) are much larger than triblock copolymer (3.7 nm in DMF and 20.0 nm in water). In contrast, when the click coupling reactions were performed in DMF without self-assembly, the molecular weight (2.5×10^4) of the product was a slight increase (Figure 6b).

In addition, the temperature dependence on the self-assembly-assisted multiple click coupling reaction was also investigated. The results showed that the molecular weight and molecular weight distribution were almost unchanged in the temperature range of 25−45 °C. However, when the temperature for the click reaction was above 45 °C, the molecular weight of the resultant multiblock copolymer was lowered. As shown in Figure 6d, the molecular weight of the resultant multiblock copolymer is only 2.6×10^4 at 60 °C, and a tail was observed in the molecular weight region of the PEO-*b*-PPO-*b*-PEO triblock copolymer precursors. A decrease in the molecular weight of the multiblock copolymer as an increase in click temperature can be understood in terms of the decrease in the solubility of PEO in water with increasing temperature,[42] which can result in further wrap of the reactive group inside the shrunk chains.

In order to compare the reaction efficiency between self-assembly-assisted coupling and linking, after the self-assembly of HC≡C-PEO-*b*-PPO-*b*-PEO-C≡CH in water, the click linking reactions were induced by the addition of 1,4-diazobutane with $CuSO_4 \cdot 5H_2O$ and sodium ascorbate used as catalyst. It is notable that the addition of an insufficient or excessive amount of 1,4-diazobutane reduces the linking efficiency. In this study, an equimolar 1,4-diazobutane was divided into four portions, and each portion was added with a time interval of 6 h. As shown in Figure 6e, the molecular weight of linking product almost did not change, indicating that there is no significant click linking reaction assisted by self-assembly.

Conclusion

A unique methodology to efficaciously prepare multiblock copolymers has been demonstrated with self-assembly-assisted multiple click coupling reactions between diends-azido-terminated and diends-alkynyl-terminated A−B−A triblock copolymers in a selective solvent. Micellizaton of equimolar N_3-PEO-*b*-PPO-*b*-PEO-N_3 and HC≡C-PEO-*b*-PPO-*b*-PEO-C≡CH in a selective solvent water leaded to concentrate and expose the azido and alkynyl end groups, which greatly increased the click coupling efficiency. These results broaden the scope of self-assembly application and click chemistry reactions in polymer synthesis as well as will serve as a valuable guideline for the synthesis of multiblock copolymers.

Acknowledgment. The financial support of the National Natural Science Foundation of China (contract grant number: 20574088) and the Guangdong Natural Science Foundation (contract grant number: 05003263) is gratefully acknowledged.

References and Notes

(1) Lodge, T. P. *Macromol. Chem. Phys.* **2003**, *204* (2), 265–273.

(2) Mendrek, S.; Mendrek, A.; Adler, H. J.; Walach, W.; Dworak, A.; Kuckling, D. *J. Polym. Sci., Part A: Polym. Chem.* **2008**, *46* (7), 2488–2499.

(3) Mueller, L.; Jakubowski, W.; Tang, W.; Matyjaszewski, K. *Macromolecules* **2007**, *40* (18), 6464–6472.

(4) Bernaerts, K. V.; Du Prez, F. E. *Polymer* **2005**, *46* (19), 8469–8482.

(5) Coessens, V.; Pintauer, T.; Matyjaszewski, K. *Prog. Polym. Sci.* **2001**, *26* (3), 337–377.

(6) Se, K.; Hayashino, Y. *Macromolecules* **2007**, *40* (3), 429–437.

(7) Bernaerts, K. V.; Fustin, C. A.; Bomal-D'Haese, C.; Gohy, J. F.; Martins, J. C.; Du Prez, F. E. *Macromolecules* **2008**, *41* (7), 2593–2606.

(8) Patton, D. L.; Advincula, R. C. *Macromolecules* **2006**, *39* (25), 8674–8683.

(9) Castle, T. C.; Hutchings, L. R.; Khosravi, E. *Macromolecules* **2004**, *37* (6), 2035–2040.

(10) Ekizoglou, N.; Hadjichristidis, N. *J. Polym. Sci., Part A: Polym. Chem.* **2002**, *40* (13), 2166–2170.

(11) Buzdugan, E.; Ghioca, P.; Stribeck, N. *Mater. Plast.* **2000**, *37* (3), 138–144.

(12) Reuter, H.; Berlinova, I. V.; Horing, S.; Ulbricht, *J. Eur. Polym.* **1991**, *27* (7), 673–680.

(13) Yagci, Y.; Tasdelen, M. A. *Prog. Polym. Sci.* **2006**, *31* (12), 1133–1170.

(14) Rahman, M. S.; Sama, L. S.; Lee, J. S. *Macromolecules* **2007**, *40* (26), 9279–9283.

(15) Rodriguez-Hernandez, J.; Checot, F.; Gnanou, Y.; Lecommandoux, S. *Prog. Polym. Sci.* **2005**, *30* (7), 691–724.

(16) Hadjichristidis, N.; Iatrou, H.; Pitsikalis, M.; Pispas, S.; Avgeropoulos, A. *Prog. Polym. Sci.* **2005**, *30* (7), 725–782.

(17) Riess, G. *Prog. Polym. Sci.* **2003**, *20* (7), 1107–1170.

(18) Dems, A.; Strobin, G. *Makromol. Chem.* **1991**, *192* (11), 2521–2537.

(19) Chu, B. *Langmuir* **1995**, *11* (2), 414.

(20) Hong, L. Z.; Zhu, F. M.; Li, J. F.; Ngai, T.; Xie, Z. W.; Wu, C. *Macromolecules* **2008**, *41* (6), 2219–2227.

(21) Wu, C.; Xie, Z. W.; Zhang, G. Z.; Zi, G. F.; Tu, Y. F.; Yang, Y. L.; Cai, P.; Nie, T. *Chem. Commun.* **2002**, *23*, 2898.

(22) Wu, C.; Xie, Z. W.; Zhang, G. Z.; Zi, G. F. *Chin. J. Polym. Sci.* **2001**, *19*, 451–454.

(23) Zhu, F. M.; Ngai, T.; Xie, Z. W.; Wu, C. *Macromolecules* **2003**, *36* (19), 7405–7408.

(24) Durmaz, H.; Dag, A.; Altintas, O.; Erdogan, T.; Hizal, G.; Tunca, U. *Macromolecules* **2007**, *40* (2), 191–198.

(25) Lin, W. C.; Fu, Q.; Zhang, Y.; Huang, J. L. *Macromolecules* **2008**, *41* (12), 4127–4135.

(26) Jiang, X. Z.; Zhang, J. A.; Zhou, Y. M.; Xu, J.; Liu, S. Y. *J. Polym. Sci., Part A: Polym. Chem.* **2008**, *46* (3), 860–871.

(27) Fournier, D.; Du Prez, F. *Macromolecules* **2008**, *41* (13), 4622–4630.

(28) Gondi, S. R.; Vogt, A. P.; Sumerlin, B. S. *Macromolecules* **2007**, *40* (3), 474–481.

(29) Agut, W.; Taton, D.; Lecommandoux, S. B. *Macromolecules* **2007**, *40* (16), 5653–5661.

(30) Ranjan, R.; Brittain, W. J. *Macromolecules* **2007**, *40* (17), 6217–6223.

(31) Fournier, D.; Hoogenboom, R.; Schubert, U. S. *Chem. Soc. Rev.* **2007**, *36* (8), 1369–1380.

(32) Hiki, S.; Kataoka, K. *Bioconjugate Chem.* **2007**, *18* (6), 2191–2196.

(33) Gao, H. F.; Matyjaszewski, K. *J. Am. Chem. Soc.* **2007**, *129* (20), 6633–6639.

(34) Liu, X. M.; Thakur, A.; Wang, D. *Biomacromolecules* **2007**, *8* (9), 2653–2658.

(35) Gao, H. F.; Krzysztof Matyjaszewski, K. *Macromolecules* **2006**, *39* (15), 4960–4965.

(36) Vogt, A. P.; Sumerlin, B. S. *Macromolecules* **2006**, *39* (16), 5286–5292.

(37) Zalipsky, S. *Bioconjugate Chem.* **1995**, *6* (2), 150–165.

(38) Yanic, C.; Bredenkamp, M.; Jacobs, E.; Spies, H.; Swart, P. *J. Appl. Polym. Sci.* **2000**, *78* (1), 109–117.

(39) Holmqvist, P.; Alexdandridis, P.; Lindman, B. *J. Phys. Chem. B* **1998**, *102* (7), 1149–1158.

(40) Alexandridis, P.; Olsson, U.; Lindman, B. *Langmuir* **1998**, *14* (10), 2627–2638.

(41) Alexdandridis, P. *Macromolecules* **1998**, *31* (20), 6935–6942.

(42) Alexandridis, P.; Zhou, D.; Khan, A. *Langmuir* **1996**, *12* (11), 2690–2700.

(43) Alexandridis, P.; Olsson, U.; Lindman, B. *Macromolecules* **1995**, *28* (23), 7700–7710.

(44) Zhang, K.; Khan, A. *Macromolecules* **1995**, *28* (11), 3807–3812.

(45) Alexandridis, P.; Holzwarthf, J. F.; Hatton, T. A. *Macromolecules* **1994**, *27* (9), 2414–2425.

(46) Wanka, G.; Hoffmann, H.; Ulbricht, W. *Macromolecules* **1994**, *27* (15), 4145–4159.

MA802291W