# Synthesis and Self-Assembly of Amphiphilic Star-Block Copolymers Consisting of Polyethylene and Poly(ethylene glycol) Segments

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**ABSTRACT:** We report on the synthesis and self-assembly in water of well-defined amphiphilic star-block copolymers with a linear crystalline polyethylene (PE) segment and two or three poly(ethylene glycol) (PEG) segments as the building blocks. Initially, alkynyl-terminated PE (PE-≡) is synthesized via esterification of pentynoic acid with hydroxyl-terminated PE, which is prepared using chain shuttling ethylene polymerization with 2,6-bis[1-(2,6-dimethylphenyl) imino ethyl] pyridine iron (II) dichloride/methylaluminoxane/diethyl zinc and subsequent in situ oxidation with oxygen. Then diazido- and triazido-terminated PE (PE-$(N_3)_2$ and PE-$(N_3)_3$) are obtained by the click reactions between PE-≡ and coupling agents containing triazido or tetraazido, respectively. Finally, the three-arm and four-arm star-block copolymers, PE-$b$-$(PEG)_2$ and PE-$b$-$(PEG)_3$, are prepared by click reactions between PE-$(N_3)_2$ or PE-$(N_3)_3$ and alkynyl-terminated PEG. The self-assembly of the resultant amphiphilic star-block copolymers in water was investigated by dynamic light scattering, transmission electron microscopy, and atomic force microscopy. It is found that, in water, a solvent selectively good for PEG blocks; these star-block copolymer chains could self-assemble to form platelet-like micelles with insoluble PE blocks as crystalline core and soluble PEG blocks as shell. The confined crystallization of PE blocks in self-assembled structure formed in aqueous solution is investigated by differential scanning calorimetry. © 2013 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 129: 2216–2223, 2013

## INTRODUCTION

Block copolymers have attracted a great deal of interest in physical chemistry and polymer science owing to their precise supramolecular structures in bulk or solution[1–4] and potential various applications.[3–9] However, perhaps due to the ease of preparation, most attention has focused on coil–coil block copolymers. Incorporating crystalline moieties into block copolymers has been demonstrated to increase morphology richness in the self-assembly process.[10–12] Compared to bulk situation, self-assembly of crystalline block copolymers in selective solvent is attracting increasing interests. The final micelle structure can be tuned by introducing crystalline block. Linear crystalline polyethylene (PE) is a common material that can crystallize due to its regular chain structure. Up to now, most work related to self-assembly of PE-containing block copolymers has focused on bulk or blends, which imposes narrow limits to the self-assembly morphology.[10,11] Therefore, introducing crystalline core-forming PE into self-assembly micelles not only provides more information about micelle morphology with crystalline core but also allows

the studies on confined crystallization of PE in a special micelle confinement. Moreover, these nanosized micelles have potential applications in incorporating hydrophobic chemicals.[13,14] Recently, self-assembly of PE-based copolymers in selective solvent has been reported. Worm-like and disk-shaped micelles were usually formed.[15–20] However, only linear block copolymers are focused, star-block copolymers consisting of chemically different chains emanating from a central junction point are seldom concerned. The change in the chain architecture of block copolymers may dramatically affect the self-assembling behavior and micellar morphology. There are only a few reports on the micelle solution of PE-containing block star-block copolymers. Fujita et al.[15] studied self-assembly behavior of polyethylene-$b$-poly(ethylene glycol) (PE-$b$-PEG) star copolymers. However, the relatively wide molecular weight distributions of the star copolymers used in their study caused the coexistence of multiple micellar morphology in the self-assembly of one star copolymer.

In this work, we report a convenient route for preparation of novel amphiphilic three-arm and four-arm star-block copolymers,

PE-$b$-(PEG)$_2$ and PE-$b$-(PEG)$_3$ with narrow molecular weight distributions. At first, alkynyl end-terminated PE (PE–≡) was synthesized via esterification of pentynoic acid with monohydroxyl-terminated PE (PE-OH), which was prepared using chain shuttling ethylene polymerization (CSEP) with 2,6-bis[1-(2,6-dimethylphenyl) imino ethyl] pyridine iron(II) dichloride/methylaluminoxane (MAO)/diethyl zinc (ZnEt$_2$) and subsequent *in situ* oxidation with oxygen. Then, the PE chains were end capped with two or three azido groups by click reactions between PE-≡ and coupling agents containing triazido or tetraazido groups. Finally, the resultant PE-$b$-(PEG)$_2$ and PE-$b$-(PEG)$_3$ star-block copolymers were prepared by click reactions between PE-(N$_3$)$_2$, PE-(N$_3$)$_3$, and alkynyl-terminated PEG (PEG-≡). Furthermore, the self-assembly of PE-$b$-(PEG)$_2$ and PE-$b$-(PEG)$_3$ star-block copolymers in water was investigated by dynamic light scattering (DLS), transmission electron microscopy (TEM), and atomic force microscopy (AFM). The confined crystallization of PE blocks in nanosized micelle cores were studied by differential scanning calorimetry (DSC).

## EXPERIMENTAL

### Materials

Pentaerythritol (>98%) was purchased from Aldrich, Shanghai, China and recrystallized from water. Monohydroxyl-terminated PEG (PEG-OH, $M_n = 1000$) was obtained from Fluka, Guangzhou, China and dried by azeotropic distillation with anhydrous toluene under nitrogen prior to use. ZnEt$_2$ was purchased from Alfa Aesar, Tianjing, China as a 1.0 mol/L solution in hexane. Toluene was refluxed over sodium/benzophenone. $N,N'$-dimethylformamide (DMF) was distilled over CaH$_2$ under vacuum. Dichloromethane (CH$_2$Cl$_2$) was distilled from P$_2$O$_5$. Pentynoic acid (98%), $N,N'$-dicyclohexylcarbodiimide (DCC, 98%), 4-dimethylaminopydine (DMAP, 98%), sodium azide (99%), triphenylphosphine (99%), copper(I) bromide were all purchased from Aldrich, Shanghai, China and used as received. Other reagents if not specified were purchased from Sinopharm Chemical Regent, Shanghai, China and used as received. 2,6-Bis[1-(2,6-dimethylphenyl) imino ethyl] pyridine iron (II) dichloride was synthesized according to the literature,[20] MAO was prepared by partial hydrolysis of trimethylaluminum in toluene at 0–60°C with Al$_2$(SO$_4$)$_3$·18H$_2$O as the water source. The initial [H$_2$O]/[Al] in molar ratio was 1.3.

### Synthesis of PE-OH

Toluene (100 mL), MAO (0.23 g, [Al] = 3.75 mmol), and ZnEt$_2$ (2.5 mL, 2.5 mmol) were introduced to a 300 mL steel reactor equipped with a mechanical stirrer and a temperature probe. The mixture was saturated with ethylene, then 2,6-bis[1-(2,6- dimethylphenyl) imino ethyl] pyridine iron (II) dichloride (3.0 mg, 5.0 $\mu$mol) in 10 mL toluene was added to start the polymerization. The pressure of ethylene was kept at 2.5 MPa. After 30 min, the mixture was warmed to 100°C, and dry oxygen was bubbled for 2 h. Following the oxidation reaction, the mixture was poured into acidic methanol to precipitate the product. After filtration, it was washed with methanol and dried under vacuum at 60°C overnight, and a white powder was obtained.

### Synthesis of PE-CH$_2$OCOCH$_2$CH$_2$C≡CH (PE-≡)

To a 150 mL round bottom flask, 80 mL anhydrous toluene, PE-OH (1.4 g, [OH] = 1.5 mmol), pentynoic acid (1.5 g, 15 mmol), and a small amount of HfCl$_4$·2THF were added. The reaction mixture was refluxed for 24 h. After reaction, the mixture was cooled, poured into methanol to precipitate the product. The obtained white powder was dried under vacuum at 60°C overnight.

### Synthesis of PEG-CH$_2$OCOCH$_2$CH$_2$C≡CH (PEG-≡)

PEG-OH (5.0 g, [OH] = 5.0 mmol) was dissolved in 50 mL CH$_2$Cl$_2$ in a 100 mL round bottom flask. Pentynoic acid (2.5 g, 25.0 mmol) and DMAP (0.06 g, 0.5 mmol) were then added to the solution. After stirring for 5 min, DCC (5 g, 25 mmol) in 15 mL CH$_2$Cl$_2$ was slowly added in an ice bath. The mixture was allowed to stir at room temperature overnight. After the reaction, the mixture was filtrated and the solution was concentrated, precipitated into cold ether. The above dissolution–precipitation cycle was repeated for three times. PEG-≡. The obtained white powder was dried under vacuum overnight at room temperature.

### Synthesis of Pentaerythritol Tetrakis($p$-toluenesulfonyl)

4.2 g (6.25 mmol) pentaerythritol was slowly added into the 40 mL pyridine solution of $p$-toluenesulfonyl chloride (20.0 g, 25 mmol) at 0°C for 2 h. The reaction mixture was then stirred at room temperature overnight, then 25 mL cold water was added and stirred for a further 3 h before precipitation into cold water. The crude product was recrystallized from ethanol to give pentaerythritol tetrakis($p$-toluenesulfonyl) as a white powder.

### Synthesis of Pentaerythritol Tetraazide

Pentaerythritol tetrakis($p$-toluenesulfon-yl) (8.0 g, 10.0 mmol) and sodium azide (6.5 g, 100 mmol) were added into 60 mL DMF and stirred at 80°C for 12 h. The reaction mixture was concentrated to dryness under vacuum, dissolved in 60 mL diethyl ether, washed with water. The combined organic layer was dried over MgSO$_4$, concentrated to dryness under vacuum to yield a white solid.

### Synthesis of 2,2-Bis(bromomethyl)-3-bromo-propan-1-ol

Pentaerythritol (12.8 g, 94.0 mmol) was dissolved in the mixture of 10 mL acetic acid and 50 mL 40 % HBr aqueous solution, and the mixture was heated under reflux. After 24 h, 50 mL 40% HBr aqueous solution and 23 mL H$_2$SO$_4$ were added, the resulting solution was then heated under reflux for a further 24 h. Then the mixture was cooled, the lower liquid layer was separated, dissolved in 50 mL CH$_2$Cl$_2$, washed with water, dried over MgSO$_4$. The solvent was removed and the residue was purified by column chromatography (EtOAC : hexane = 1 : 10) to give the product as a white solid.

### Synthesis of Pentaeythritol Triazide

NaN$_3$ (8.4 g, 120.0 mmol) was added to 50 mL DMF solution of 2, 2-bis(bromomethyl)-3- bromo-propan-1-ol (7.2 g, 20.0 mmol). The reaction mixture was heated to 100°C for 12 h. Then mixture was concentrated to dryness under vacuum, dissolved in 100 mL diethyl ether, washed with water. The combined organic layers were then dried over MgSO$_4$ and concentrated to dryness under vacuum to yield a slightly yellow oil.

### Synthesis of Diazido-Terminated PE (PE-(N$_3$)$_2$)

PE-≡ (0.8 g, 0.8 mmol alkynyl groups), pentaeythritol triazide (3.68 g, 16 mmol), and 15 mL toluene were added into a

Schlenk tube. The mixture was purged with $N_2$ for 30 min, then 15 mg $Cu(PPh_3)_3Br$ was added under nitrogen. The tube was sealed, heated to 85°C for 12 h. After reaction, the mixture was poured into methanol, the precipitation was washed with methanol, dried under vacuum at 40°C overnight to give a white powder.

### Synthesis of Triazido-Terminated PE (PE-$(N_3)_3$)
The synthesis procedures of PE-$(N_3)_3$ was similar to that of PE-$(N_3)_2$, except that pentaeythritol tetraazide (4.22 g, 20.0 mmol) was used.

### Synthesis of PE-$b$-$(PEG)_2$
PE-$(N_3)_2$ (0.10 g, $[N_3]$= 0.24 mmol), PEG-≡ (0.33 g, 0.30 mmol alkynyl groups), and 10 mL toluene were added to a Schenk tube. The mixture was purged with $N_2$ for 30 min, 20.0 mg $Cu(PPh_3)_3Br$ was then added. The tube was sealed and heated to 85°C for 24h. After the reaction, the mixture was poured into cold hexane, and the precipitation was then extracted with hot acetone. The acetone soluble fraction was collected and poured into cold hexane. The obtained white solid was then dispersed into 20 mL double distilled water and dialyzed against water for 5 days using a dialysis bag (cut-off $M_w$ = 5000). In the end, the dispersion was freezing dried for 3 days to yield a white solid.

### Synthesis of PE-$b$-$(PEG)_3$
The synthesis and postpurifications of PE-$b$-$(PEG)_3$ were similar to those of PE-$b$-$(PEG)_2$, except that PE-$(N_3)_3$ (0.10 g, $[N_3]$ = 0.34 mmol) and acetylated PEG (0.41 g, 0.4 mmol) were used.

### Self-Assembly of Amphiphilic Star-Block Copolymers in Water
Typically, 20 mg star-block copolymer and 2 mL water were placed in a 10 mL heavy wall flask. The mixture was degassed by five times freeze-pump-thaw cycles and left under nitrogen. The mixture was then heated above the melting temperature of PE block (120°C) for 1 h and was allowed to cool down slowly to 20°C in about 2 h. The stock micelle solution was left at room temperature for 5 days. The stock micelle solution was diluted to other concentrations if needed.

### Measurements
$^1$H NMR (300 MHz) spectra were recorded in $CDCl_3$ on a Varian Unity Inova 300 spectrometer. Molecular weight and molecular weight distribution ($M_w/M_n$) were determined by gel permeation chromatography (GPC) against narrow molecular weight distribution polystyrene standards on a Waters 2414 refractive index detector Water 150 C at 135°C with 1,2,4-trichlorobenzene as solvent. Fourier transform infrared (FTIR) spectra were recorded on a Brucker VECTOR-22 IR spectrometer. The spectra were collected at 64 scans with a spectral resolution 4 cm$^{-1}$.

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 angle was fixed to be 90°. The samples were placed in an index-matching decaline bath with temperature control within ± 0.2°C. Each solution passed through a 0.45 $\mu$m Polytetrafluoroethene (PTFE) filter to remove dust. The data were analyzed by CONTIN algorithm,

while the hydrodynamic radius ($R_h$) and size polydispersity of the particles were obtained by a cumulant analysis of the experimental correlation function.

TEM observations were performed on a TEM (Philips TECNAI) with an accelerating voltage of 100 kV. A drop of micelle solution was dropped onto a carbon-coated copper grid. After a few minutes, the excess solution was blotted away with filter paper, and the samples were dried at room temperature. No staining agent was used.

AFM was performed on SPA300HV Probe station (Japan) in tapping mode, and scan rate was 2.0 Hz. 10 $\mu$L of the micelle solution was dipped onto a mica wafer and dried at 25°C for 48 h before the test.

DSC experiments were carried out on a Perkin-Elmer Pyris 1 instrument. For micelle solution, high-pressure stainless-steel hermetic pans were chosen to avoid the evaporation of solvent during heating at high temperatures. The concentration of micelle solution was about 2 wt %. Typically, about 30 mg sample including solvent was encapsulated into the tightly sealed pans. DSC heating and cooling scans were performed at 5°C/min.

## RESULTS AND DISCUSSION

### Synthesis and Characterization of PE-$b$-$(PEG)_2$ and PE-$b$-$(PEG)_3$ Star-Block Copolymers
As shown in Scheme 1, chain shuttling ethylene polymerization was conducted with 2,6-bis[1-(2,6-dimethylphenyl) imino ethyl] pyridine iron (II) dichloride/MAO as catalyst and $ZnEt_2$ as chain shuttling agent to produce linear PE-OH according to our previous report.[21] In this case, at a ratio of Fe : Al : Zn = 1 : 750 : 500, a white product was obtained. $^1$H NMR of PE-OH is shown in Figure 1(a). By comparing the integration areas of $a$ and $c$ peaks (0.89 and 3.62 ppm), the efficiency of hydroxyl termination could be estimated to be about 80%. On the basis of the 80% functionality, the molecular weight of PE-OH in terms of the proportion of integration areas of $b$ and $c$ peaks (0.89 and 1.25 ppm) was 800. GPC analysis of the PE-OH reveals a monomodal and symmetric elution peak, $M_w$ = 1100 and $M_w/M_n$ = 1.12 (Figure 3).

PE-$CH_2OCOCH_2CH_2C{\equiv}CH$ (PE-≡) was easily obtained by esterification of PE-OH with pentynoic acid using $HfCl_4\cdot2THF$ as catalyst. The $^1$H NMR of PE-$CH_2OCOCH_2CH_2C{\equiv}CH$ is shown in Figure 1(b). The signals of the methylene protons adjacent to the hydroxyl group at 3.62 ppm completely disappears. Alternatively, a new signal of methylene protons adjacent to the ester group is observed at 4.05 ppm. Furthermore, the signal
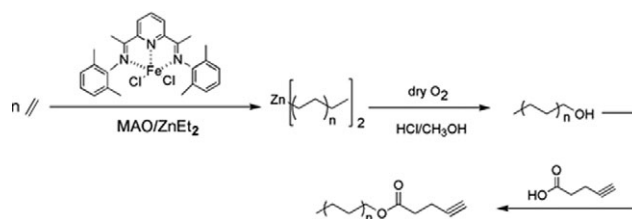


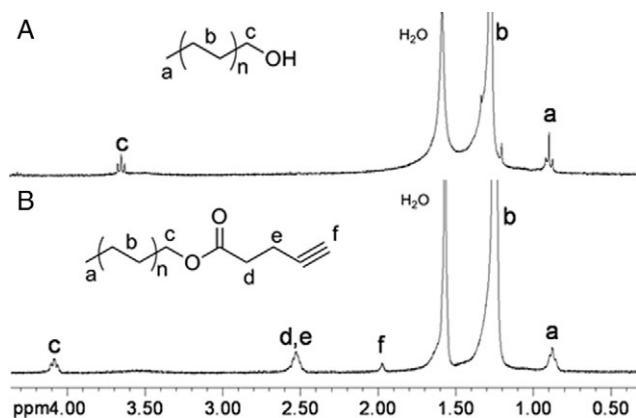**Scheme 1.** Synthetic route used for the synthesis of PE-$COCH_2CH_2C{\equiv}CH$.

**Figure 1.** $^1$H NMR spectra for PE-OH (A) and PE-PE-COCH$_2$CH$_2$C≡CH (B).

assigned to the hydrogen on the alkynyl appears at 1.95 ppm. These results indicate that the efficiency of the esterification is almost 100%. So 80% of the PE chains are capped with alkynyl group. PEG-CH$_2$OCOCH$_2$CH$_2$C≡CH (PEG-≡) was also synthesized by quantitative esterification with PEG-OH and pentynoic acid in the presence of DCC/DMAP. As shown in Figure 2, successful conversion to alkynyl end groups is confirmed by $^1$H NMR in terms of the appearance of the signal at 1.95 ppm assigned to the hydrogen on alkynyl.

PE-(N$_3$)$_2$ and PE-(N$_3$)$_3$ were obtained by click reaction of PE-≡ with an large excess of pentaerythritol triazide and pentaerythritol tetraazide. To make sure only one azido group participates in the click reaction, a large excess of the coupling agent was used (20 equiv.). The click reaction was performed at 85°C in toluene for 12 h to make sure the complete end group transformation. Figure 3(a) shows the GPC traces of PE-(N$_3$)$_2$ and PE-(N$_3$)$_2$. The elution peaks are monomodal without any shoulder at the higher molecular weight region, which suggest that the coupling reaction between alkynyl terminated PE and azido terminated PE does not occur during the end group transformation. Figure 4 shows the $^1$H NMR spectra of PE-(N$_3$)$_2$ and
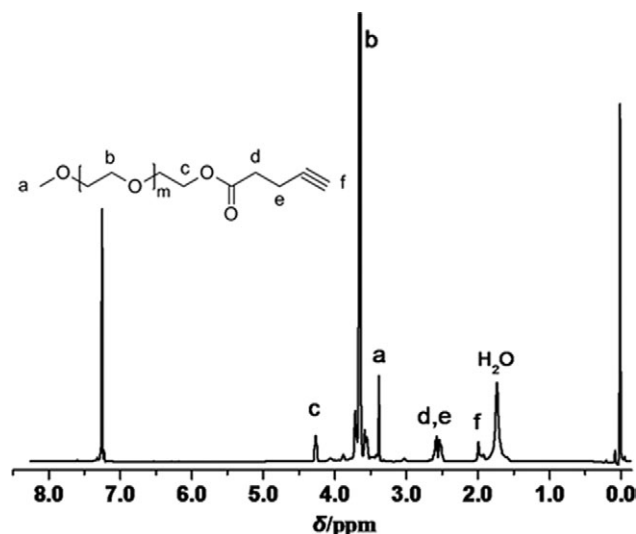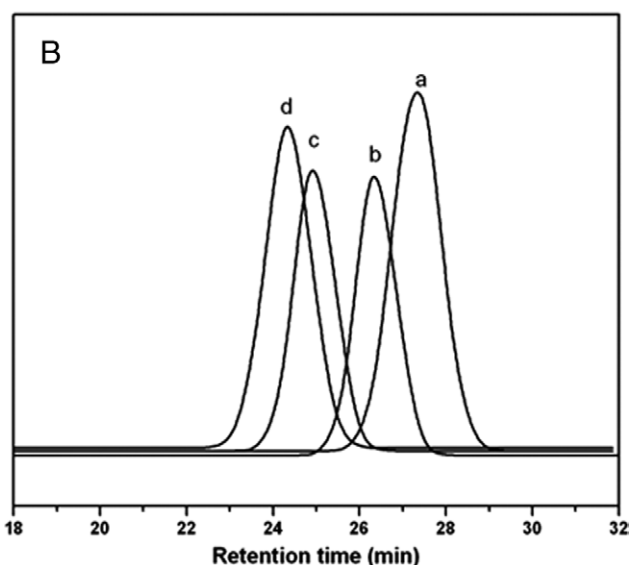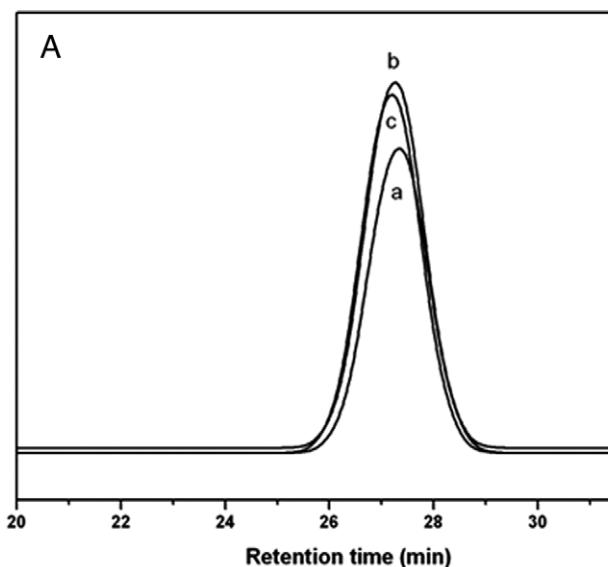


**Figure 2.** $^1$H NMR spectrum for PEG-CH$_2$OCOCH$_2$CH$_2$C≡CH.



**Figure 3.** GPC traces of the samples. (A): a, PE-OH; b, PE-(N$_3$)$_2$; c, PE-(N$_3$)$_3$ and (B): a, PE-OH; b, PEG; c, PE-b-(PEG)$_2$; d, PE-b-(PEG)$_3$.

PE-(N$_3$)$_3$. The signals of hydrogen on the alkynyl at 1.95 ppm completely disappear and new signals of methine proton in the triazole ring are observed at 7.62 ppm. Furthermore, the signals assigned to the methylene protons in the neighborhood of the triazole ring and the azido group locate at 4.25 ppm and 3.42 ppm, respectively. These results further support the successful preparation of PE-(N$_3$)$_2$ and PE-(N$_3$)$_3$.

Finally, PE-b-(PEG)$_2$ and PE-b-(PEG)$_3$ star-block copolymers were obtained by click reaction between PEG-≡ and PE-(N$_3$)$_2$ or PE-(N$_3$)$_3$ (Scheme 2). An excess of PEG-≡ was used to ensure the complete consumption of PE-(N$_3$)$_2$ and PE-(N$_3$)$_3$. A typical coupling reaction between PEG-≡ and PE-(N$_3$)$_2$ or PE-(N$_3$)$_3$ was performed with Cu(PPh$_3$)$_3$Br as catalyst in toluene at 85°C for 24 h. As PE was insoluble in hot acetone due to its nonpolarity, the crude products were extracted with acetone to remove PE homopolymer. Then pure PE-b-(PEG)$_2$
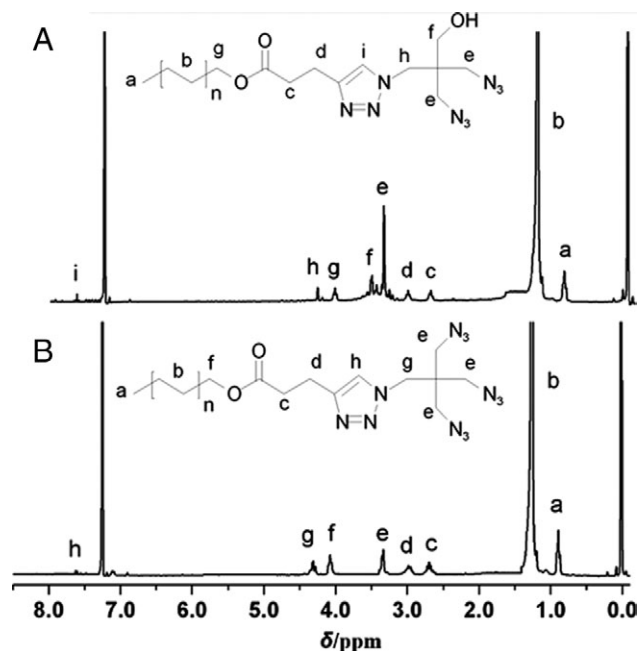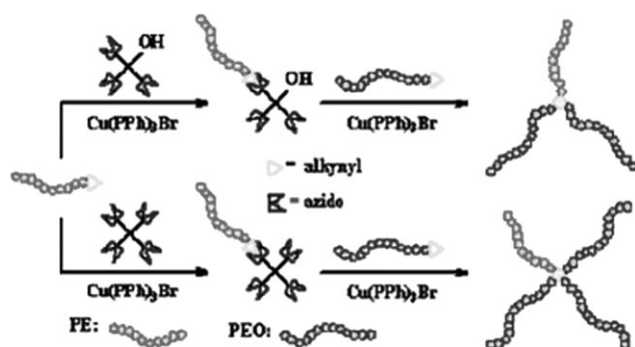
**Figure 4.** $^1$H NMR spectra for the PE-(N$_3$)$_2$ (A) and PE-(N$_3$)$_3$ (B).



**Figure 5.** IR spectra of a, PE-(N$_3$)$_2$; b, PE-$b$-(PEG)$_2$; c, PE-(N$_3$)$_3$; d, PE-$b$-(PEG)$_3$.

and PE-$b$-(PEG)$_3$ were obtained by dialysis against water with a dialysis bag (molecular cut-off 5000) to remove excess PEG-≡. Figure 5 shows the FTIR spectra of the final products, compared to PE-(N$_3$)$_2$ and PE-(N$_3$)$_3$, the spectra reveal the complete disappearance of the characteristic azido group absorption peak at 2100 cm$^{-1}$. These indicate that all PE-(N$_3$)$_2$ and PE-(N$_3$)$_3$ are consumed in the click reaction with PEG–≡. GPC analysis further supported the successful preparation of the PE-$b$-(PEG)$_2$ and PE-$b$-(PEG)$_3$ star-block copolymers. As shown in Figure 3(b), the GPC traces of the PE-$b$-(PEG)$_2$ and PE-$b$-(PEG)$_3$ are monomodal with narrow molecular weight distributions ($M_w = 5100$, $M_w/M_n = 1.08$ for PE-$b$-(PEG)$_2$ and $M_w = 6100$, $M_w/M_n = 1.10$ for PE-$b$-(PEG)$_3$). Compared to their precursors, the elution peaks clearly shift toward higher molecular weight region. Both resultant star-block copolymers were also characterized by $^1$H NMR. Figure 6 reveals the $^1$H NMR spectra of the PE-$b$-(PEG)$_2$ and PE-$b$-(PEG)$_3$, respectively. The characteristic resonance peaks of —CH$_2$CH$_2$— repeating unit in PE block appear at 1.25 ppm and the characteristic signal of —CH$_2$CH$_2$O— in PEG block

locate at 3.65 ppm. In addition, the characteristic resonance peaks of the methine proton in triazole are also observed at 7.96 ppm. The peak integral ratios between PE block and PEG



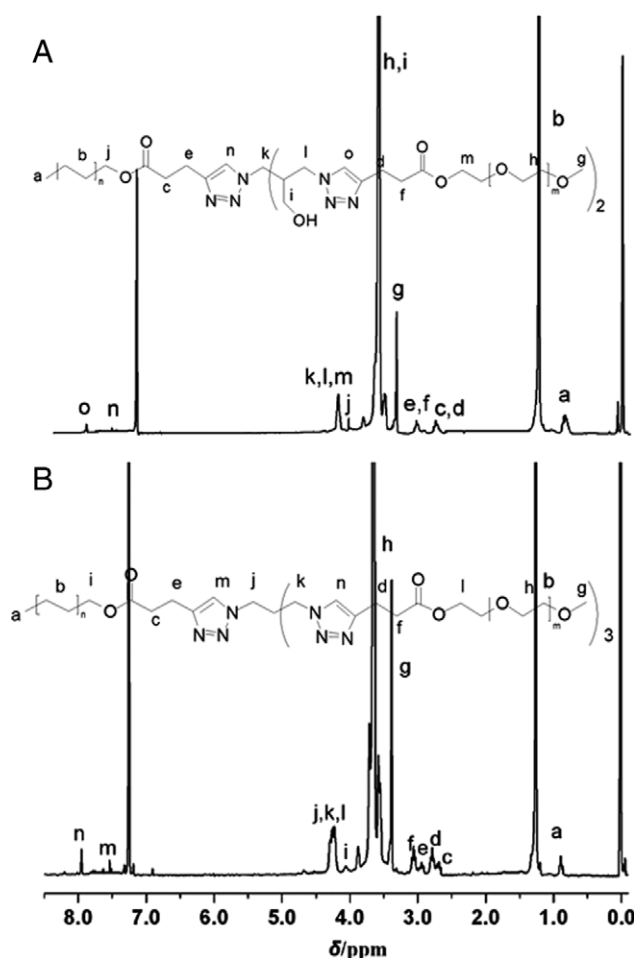**Scheme 2.** Synthetic route for the synthesis of PE-$b$-(PEG)$_2$ and PE-$b$-(PEG)$_3$ via click chemistry.



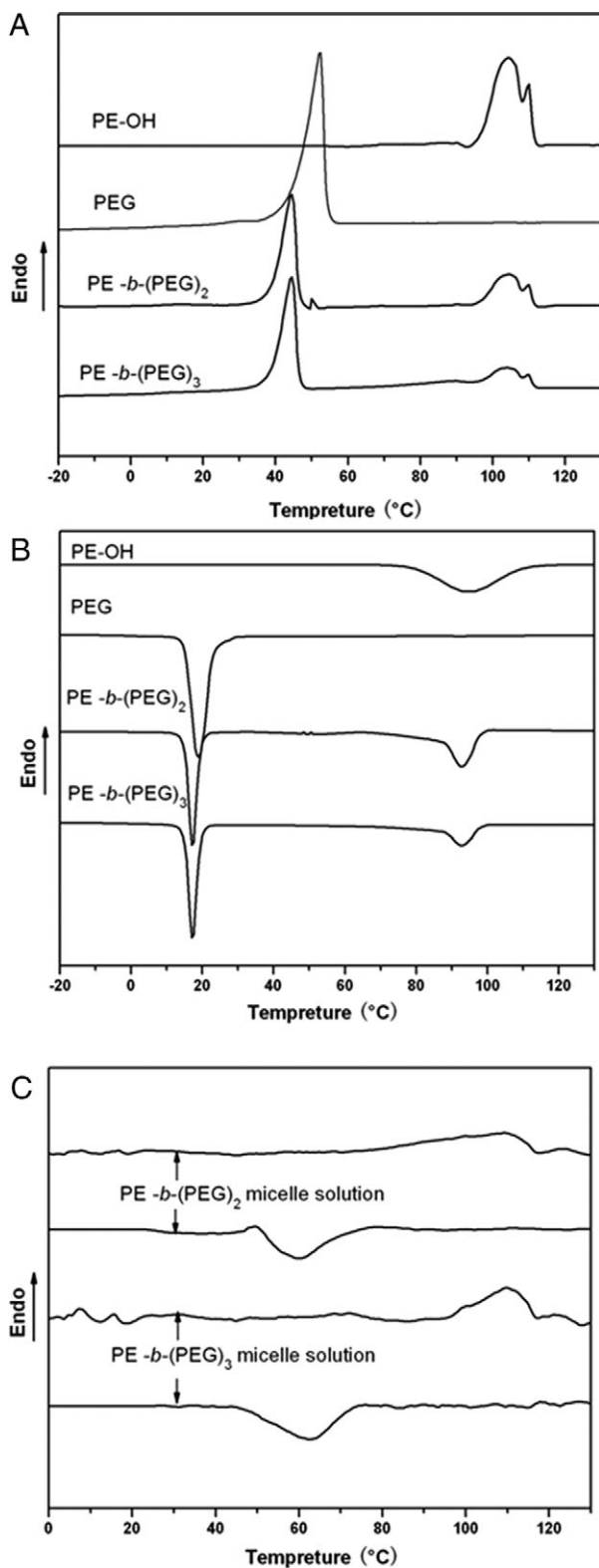**Figure 6.** $^1$H NMR spectra for PE-$b$-(PEG)$_2$ (A) and PE-$b$-(PEG)$_3$ (B).

**Figure 7.** DSC second heating (A), cooling curves (B) of bulk sample and second heating and cooling curves of micelle solution (C).

blocks agree quite well with the relative block lengths. The $M_w$ of PE-b-(PEG)$_2$ and PE-b-(PEG)$_3$ were also calculated according to their $^1$H NMR spectra, the $M_n = 2800$ for PE-b-(PEG)$_2$

and $M_n = 3900$ for PE-b-(PEG)$_3$. So based on the above results, well-defined PE-b-(PEG)$_2$ and PE-b-(PEG)$_3$ star-block copolymers were prepared by click chemistry.

## Self-Assembly of PE-b-(PEG)$_2$ and PE-b-(PEG)$_3$ Star-Block Copolymers in Water

It should be emphasized that the self-assembly of crystalline PE-containing block copolymers always requires a high temperature near to or above the $T_m$ of PE blocks. Therefore, the self-assembly of PE-b-(PEG)$_2$ and PE-b-(PEG)$_3$ star-block copolymer in water which was a selective solvent for PEG was accomplished at 120°C which was above the $T_m$ of PE blocks. The mixture of the star-block copolymer and water was first heated to 120°C and kept at the temperature for 1 h. The solution was then cooled slowly to 20°C. Upon heating, the dispersion appeared a slight bright blue which corresponded to the characteristic of micelle solution and no obvious change was observed in the cooling process. To get insight of the influence of core crystallization on the micellar morphology, the obtained micelle solution was first subjected to DSC analysis to explore the melting and crystallization behavior of PE block in micelle cores. As shown in Figure 7, PE block exhibits $T_m$ about 105°C for both star-block copolymers in the micelle solution, which is near to the bulk sample. The lower $T_m$ of PE block is due to the relatively lower molecular weight. Furthermore, it can be clearly seen that in the micelle solution, the $T_c$ of PE block is 65°C which is much lower than bulk (90°C). The large supercooling implies that PE undergoes confined crystallization within the micelle core. Consequently, a homogeneous nucleation should be the dominant nucleation mechanism.[10,17] This phenomenon was also observed in bulk[2,3,22] and dispersions,[17,23] in which the number of microdomains of PE per unit volume was much higher than the number destiny of heterogeneous nuclei. Then the micellar structure with crystalline PE core was investigated. First, the size of the formed micelle was determined by DLS as shown in Figure 8. The average hydrodynamic radius ($\langle R_h \rangle$) determined by DLS at 20°C and $C = 0.5$ mg/mL for both star-block copolymers show a clear aggregations of the polymer chains, as the $\langle R_h \rangle$ is 70 nm and 82 nm for PE-b-(PEG)$_2$ and
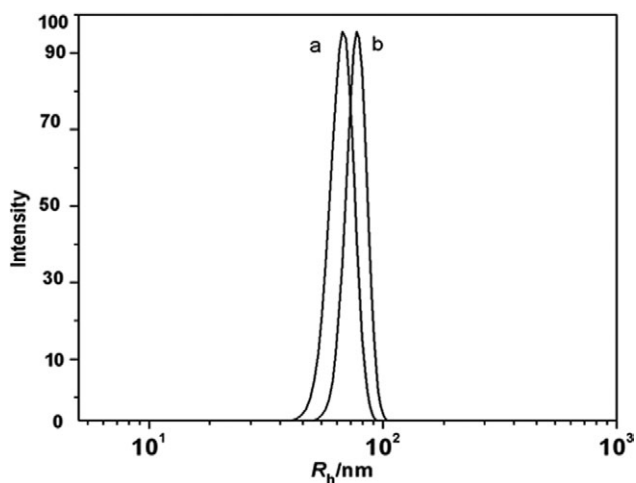


**Figure 8.** $R_h$ distributions of the micelles of a, PE-b-(PEG)$_2$ and b, PE-b-(PEG)$_3$ self-assembled in water at 20°C.
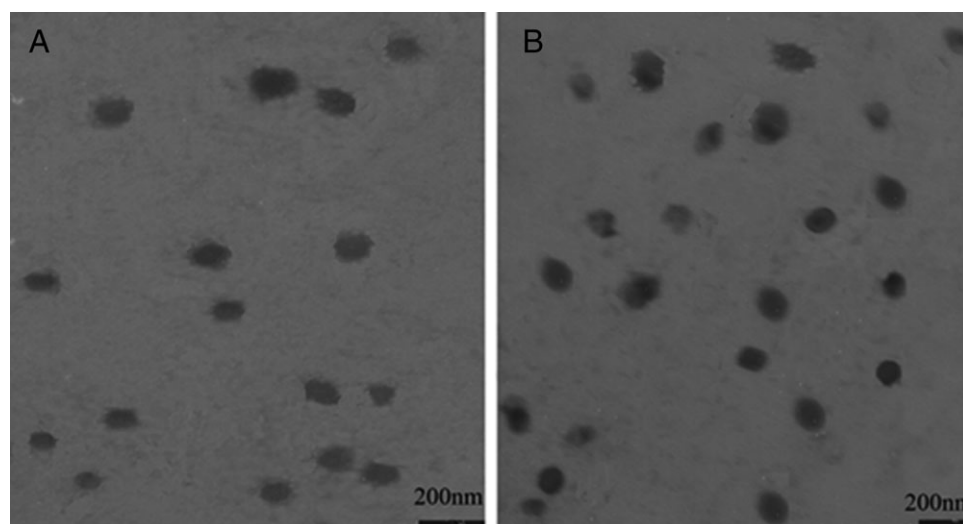
**Figure 9.** TEM images of the micelles of PE-*b*-(PEG)$_2$ (A) and PE-*b*-(PEG)$_3$ (B) self-assembled in water at 20°C.

PE-*b*-(PEG)$_3$, respectively, much larger than the individual chains. Figure 9 shows the TEM micrographs of these micelles. Near spherical micelles with an average diameter of 120 nm for PE-*b*-(PEG)$_2$ and 150 nm for PE-*b*-(PEG)$_3$ are clearly observed. Note that TEM observes the micelle dimensions in the dry state, whereas DLS reflects the average dimensions of micelles in wet as described in Experimental section, which contains the dominant contribution of hydrated PEG coronas. Consequently, the micelle sizes estimated from TEM images were systematically smaller than those obtained by DLS due to shrinkage in the solid state. The morphology of the micelles was further characterized by AFM, which allowed visualization of the 3D structures. As shown in Figure 10, micelles with lateral size 120–160 nm and height of 20 nm are detected in height images. Although AFM could slightly overestimate the lateral size because of the tip-broadening effect, the finding of a height much lower than the lateral size of dried micelle still suggests self-assembling into platelet-like structures.[24,25] Formation of platelet-like micelle with a crystalline micelle core was previously found in other self-assembly of crystalline block copolymers due to the crystallization of the core-forming

blocks,[14,18,24,25] In this case, the driving force for the platelet-like micelles formation in water is the strong insolubility and crystallization character of PE blocks, as well as the repulsions between two or three PEG blocks in one star-block copolymer chain. It strike a balance between solvent–core interface energy and repulsion among the swollen corona chains.

## CONCLUSIONS

Amphiphilic PE-*b*-(PEG)$_2$ and PE-*b*-(PEG)$_3$ star-block copolymers were prepared via a combination of CSEP and click chemistry. First, PE-≡ with narrow molecular weight distribution was effectively synthesized by CSEP and postfunctionalization. Then, PE-≡ was further modified by pentaerythritol triazide and pentaerythritol tetraazide via click reactions to yield PE-(N$_3$)$_2$ and PE-(N$_3$)$_3$. The resultant star-block copolymers were yielded by click reaction between PE-(N$_3$)$_2$ or PE-(N$_3$)$_3$ and PEG–≡. The obtained amphiphilic star-block copolymers could self-assemble to form platelet-like micelles in water with crystallized PE core and soluble PEG blocks as shell. In the micelle cores, PE blocks undergone confined crystallization at a large supercooling.

**Figure 10.** AFM height images of the micelles of PE-*b*-(PEG)$_2$ (A) and PE-*b*-(PEG)$_3$ (B) self-assembled in water at 20°C.

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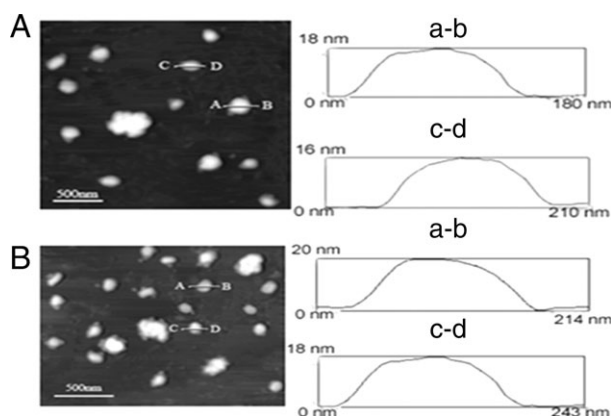
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