Dibromomaleimide Derivative as an Efficient Polymer Coupling Agent for Building Topological Polymers

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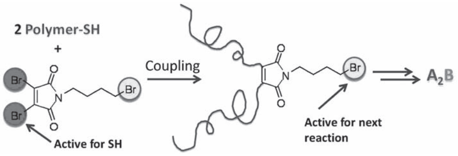
The dibromomaleimide derivative, *N*-(4-bromobutyl)-dibromomaleimide (dBMIB), is found to be a highly efficient coupling agent to dimerize thiol-terminated hydrophilic polymers by substituent reaction. When mono-thiol poly(ethylene oxide) (PEO_{45}-SH) is mixed with dBMIB in an equivalent molar feed in water, a dimer of PEO_{45} with a maleimide unit located at the chain center, $(PEO_{45})_2$MIB, is obtained quantitatively. The dBMIB is also used to dimerize thiol-terminated poly(*N*-(2-acryloyloxyethyl) pyrrolidone) and poly(*N*,*N*-dimethyl acrylamide). Moreover, the butylene bromide of $(PEO_{45})_2$MIB is transferred into a butylene azide, which is allowed to react with alkynyl-terminated polystyrene to give a A_2B miktoarm star polymer via a copper-catalyzed azide–alkyne cycloaddition coupling reaction.



1. Introduction

Efficiently building topological polymer has been a long term interest of synthetic polymer chemistry. In recent years, various topological polymers have been prepared attributed to the development of controlled polymerization and click chemistry. The controlled radical polymerization using functional monomers and initiators may be conducted and thus synthetic methodologies of star polymers, hyperbranched polymers, cyclic polymers, and molecular bottle brushes have been rapidly developed.[1,2] Also the click chemistry, ideally as a type of quantitative coupling reactions being conducted at a mild condition, has supplied a strong pushing force to the polymer synthesis.[3] Click chemistry has been widely applied in polymer chemistry to build well-defined polymer chain architectures.[3] The most important click reaction applied in polymer synthesis is the copper-catalyzed azido–alkyne coupling reaction (CuAAC), which occurs at an equivalent molar feed and, in general, undergoes quantitatively.[4] Also the Michael addition,[5] thiol-ene and thiol-yne addition,[6,7] and Diels-Alder cycloaddition[8] have been applied for polymer synthesis. However, some click chemistry is still not that efficient and an excess of one reactant is needed sometimes.[6,7]

Recently, Baker and co-workers[9] reported that bromomaleimides undergo very efficient, clean, and selective substitution reaction with the thiol group of cysteines. They have investigated the reactions of bromomaleimides with the cysteine unit of proteins and proved that this is a very useful reaction for protein modification and bioconjugation.[10,11] They also studied efficient conjugation of proteins by inserting the dibromomaleimide terminal polymers at the –S–S– units.[12–14] The results showed that the substitution was rapid and quantitative under a mild condition, which possessed the characters of an idea

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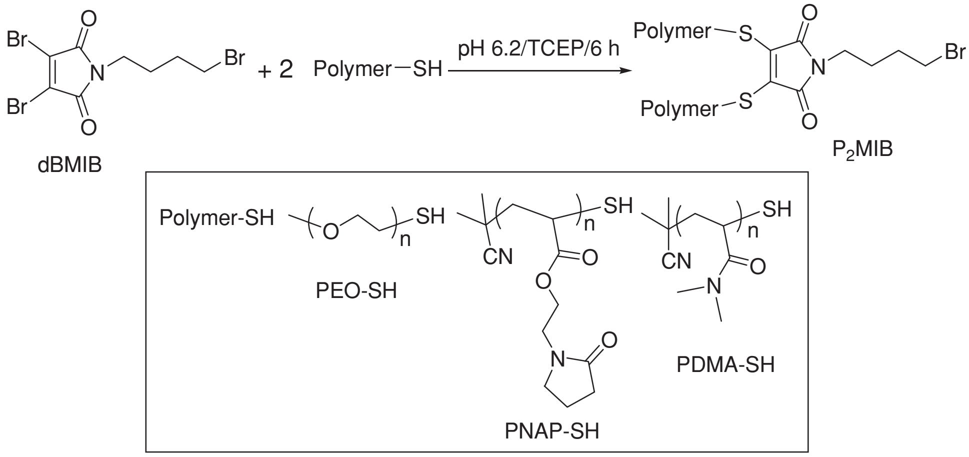


Scheme 1. dBMIB as a coupling agent to couple two thiol-terminated polymers into a polymer dimer.

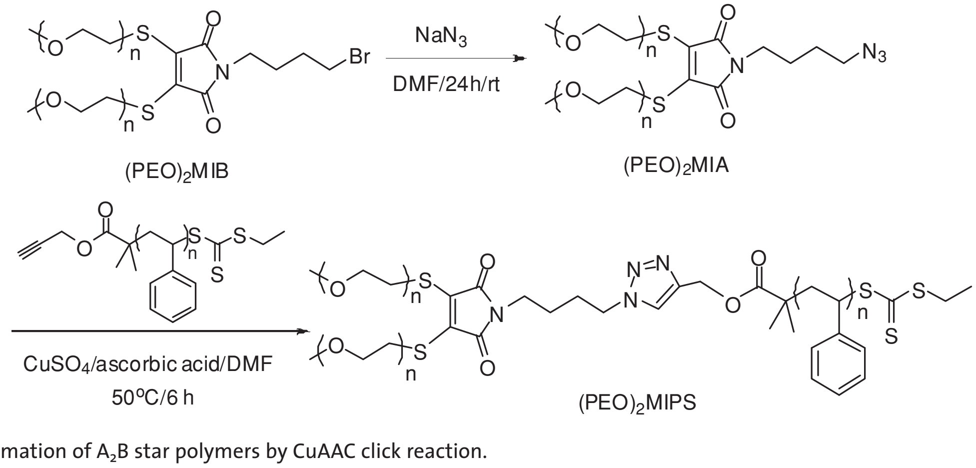
click reaction. Very recently, Robin et al.[15] have prepared well-defined polymers bearing a dibromomaleimide terminal by controlled radical polymerization and then further modified the terminal by substituting bromide groups.

Inspired by this interesting reaction, we explore the application of dibromomaleimide as a highly efficient polymer–polymer coupling agent for topological polymer engineering. Herein, we report that *N*-(4-bromobutyl)-dibromomaleimide (dBMIB) may couple two thiol-terminated synthetic polymers very efficiently into a polymer dimer with a doubled molecular weight as shown in Scheme 1. The results indicate that a simple dibromo-functionalized molecule may joint two bulky chains quantitatively, which is remarkable. Moreover, as shown in Scheme 2, the bromobutylene unit located at the chain center may be transferred into an azido unit and thus may couple a third polymer chain using CuAAC reaction, affording a A_2B star polymer.

2. Experimental Section

2.1. Characterization

NMR spectra were acquired in CDCl3 on a Bruker DMX-400 spectrometer at 400 MHz for ^1H NMR and 100 MHz for ^{13}C NMR, and the chemical shifts were given in δ values from tetramethylsilane (TMS) as an internal standard. Matrix-assisted laser desorption and ionization time-of-flight (MALDI-TOF) mass spectrometry was performed on a Bruker Biflex III spectrometer equipped with a 337 nm nitrogen laser. Polydispersity index of polymers, $\overline{M}_w/\overline{M}_n$, was obtained by size-exclusion chromatography (SEC) equipped with a Waters 515 pump, a Waters 2414 refractive index detector, and a combination of Styragel columns HT2, HT4, and HT5, the effective molecular weight range being 100-10 k, 5 k-600 k, and 50 k-4000 k. Analysis was carried out in DMF with LiBr (1 g L^{-1}) running at a flow rate of 1.0 mL min^{-1} and 50 °C. Polystyrene standards were used for the calibration. FTIR spectrometer equipped with a deuterated triglycine sulfate detector and KBr optics and controlled by OMNIC software. The spectra were collected at 32 scans with a resolution of 4 cm^{-1}.



Scheme 2. Formation of A_2B star polymers by CuAAC click reaction.

2.2. Materials

Maleimide (98%; Lyntech), 1,4-dibromobutane (99%; Alfa), sodium azide (AR; Beijing Chemical Co.), and tris(2-carboxyethyl) phosphine (TCEP, 98%; Alfa) were used without further purification. Tetrahydrofuran (THF) was distilled from sodium/benzophenone before use. Acetone, dioxane, *N,N*-Dimethylformamide (DMF), and *N,N*-dimethyl acrylamide (DMA) were dried over $\mathrm{CaH_2}$ and distilled before use. Furan-protected maleimide **1**,[16] thiol poly(ethylene oxide) ($\mathrm{PEO_{45}}$-SH),[17] 2-cyanoprop-2-yl(4-fluoro) dithiobenzoate (CPFDB),[18] alkynyl-functionalized chain transfer agents,[19] and *N*-(2-acryloyloxyethyl)pyrrolidone (NAP)[20] were synthesized according to the literatures.

2.3. Synthesis and Polymerization

2.3.1. Synthesis of *N*-(4-bromobutyl)-dibromomaleimide (2)

Preparation of 2. A solution of furan-protected maleimide **1** (1.65 g, 10 mmol) in acetone (10 mL) was added dropwise to a solution of 1,4-dibromobutane (3.24 g, 15 mmol) and $\mathrm{K_2CO_3}$ (0.69 g, 5 mmol) in acetone (20 mL). The reaction mixture was further refluxed overnight. After cooling the mixture to ambient temperature, the solvent was removed under reduced pressure. The residue was dissolved in 150 mL of $\mathrm{CH_2Cl_2}$ and washed with 3 × 100 mL of water. The organic layer was dried over $\mathrm{MgSO_4}$ and filtered. Removal of the solvent under reduced pressure. The residue was then dissolved in 30 mL of toluene and refluxed 10 h. Removal of the solvent under reduced pressure gave a yellow residue that was further purified by flash chromatography on a silica gel column (ethyl acetate:petroleum ether = 1:2, $R_\mathrm{f} = 0.6$) in 75% yield. ^{1}H NMR ($\mathrm{CDCl_3}$), δ (ppm): 1.70-1.80 (m, 2H, $\mathrm{CH_2C}\mathit{H_2}\mathrm{CH_2CH_2Br}$), 1.80-1.90 (m, 2H, $\mathrm{CH_2CH_2C}\mathit{H_2}\mathrm{CH_2Br}$), 3.35-3.45 (t, 2H, $\mathrm{CH_2CH_2CH_2C}\mathit{H_2}\mathrm{Br}$), 3.50-3.60 (t, 2H, $\mathrm{C}\mathit{H_2}\mathrm{CH_2CH_2CH_2Br}$), 6.70 (s, 2H, $\mathrm{C}\mathit{H} = \mathrm{C}\mathit{H}$).

Preparation of dBMIB. Bromine (3.2 g, 20 mmol) was added dropwise to a solution of **2** (1.1 g, 5 mmol) in DMF (20 mL) under an argon atmosphere. The reaction mixture was stirred for 3 d. The solvent was then removed under reduced pressure. The residue was dissolved in 150 mL of $\mathrm{CH_2Cl_2}$ and washed with 3 × 100 mL of water. The organic layer was dried over $\mathrm{MgSO_4}$ and filtered. Removal of the solvent under a reduced pressure gave a yellow residue that was further purified by flash chromatography on a silica gel column (ethyl acetate:petroleum ether = 1:3, $R_\mathrm{f} = 0.7$) in 50% yield. ^{1}H NMR ($\mathrm{CDCl_3}$), δ (ppm): 1.70-1.80 (m, 2H, $\mathrm{CH_2C}\mathit{H_2}\mathrm{CH_2CH_2Br}$), 1.80-1.90 (m, 2H, $\mathrm{CH_2CH_2C}\mathit{H_2}\mathrm{CH_2Br}$), 3.35-3.45 (t, 2H, $\mathrm{CH_2CH_2CH_2C}\mathit{H_2}\mathrm{Br}$), 3.60-3.70 (t, 2H, $\mathrm{C}\mathit{H_2}\mathrm{CH_2CH_2CH_2Br}$). ^{13}C NMR ($\mathrm{CDCl_3}$) δ (ppm): 170.72, 134.09, 36.81, 32.63, 29.70, 27.16. Elemental analysis: Calcd ($\mathrm{C_8H_8NO_2Br_3}$): C, 24.65; H, 2.07; N, 3.59. Found: C, 24.68; H, 2.19; N, 3.53.

2.3.2. Synthesis of $\mathrm{PDMA_{56}}$

A mixed solution of DMA (3.472 g, 35 mmol), CPFDB (0.15 g, 0.63 mmol), AIBN (10.2 mg, 0.063 mmol), and dioxane (3.5 g) was degassed via three freeze-thaw-pump cycles. After stirring for 3 h at 60 °C, the reaction was terminated by exposing system to air and the mixture was diluted with THF. The solvent was precipitated into an excess of ether. After drying overnight in a vacuum oven at room temperature, the light red product was obtained with monomer conversion of 86.8%. The $\overline{M}_\mathrm{n}$ and DP were calculated by ^{1}H NMR and $\overline{M}_\mathrm{w}/\overline{M}_\mathrm{n}$ was obtained by SEC ($\overline{M}_\mathrm{n} = 5700$, DP = 56, $\overline{M}_\mathrm{w}/\overline{M}_\mathrm{n} = 1.05$).

2.3.3. Synthesis of $\mathrm{PNAP_{31}}$

A mixed solution of NAP (6.02 g, 32.9 mmol), CPFDB (0.24 g, 1.01 mmol), and AIBN (16.4 mg, 0.1 mmol) in DMF (1.2 g) was degassed via three freeze-thaw-pump cycles. After stirring for 5 h at 60 °C, the reaction was terminated by exposing system to air and the mixture was diluted with THF. The solvent was precipitated into an excess of ether. After drying overnight in a vacuum oven at room temperature, the light red product was obtained with monomer conversion of 95.5%. The $\overline{M}_\mathrm{n}$ and DP were calculated by ^{1}H NMR and $\overline{M}_\mathrm{w}/\overline{M}_\mathrm{n}$ was obtained by SEC ($\overline{M}_\mathrm{n} = 5900$, DP = 31, $\overline{M}_\mathrm{w}/\overline{M}_\mathrm{n} = 1.10$).

2.3.4. Synthesis of $\mathrm{PDMA_{56}}$-SH and $\mathrm{PNAP_{31}}$-SH

The thiol-polymers were obtained by the aminolysis of corresponding polymers by RAFT polymerization according to the literature.[21] A general process was described as follows: 0.1 mL of hydrazine hydrate was added to a solution of $\mathrm{PDMA_{56}}$ or $\mathrm{PNAP_{31}}$ by RAFT polymerization (1 g) in DMF (1 mL). The reaction mixture was stirred 0.5 h, and then precipitated into an excess of ether. After drying overnight in a vacuum oven at room temperature, the white products were obtained.

2.3.5. Synthesis of $\mathrm{(PEO_{45})_2MIB}$

$\mathrm{PEO_{45}}$-SH (400 mg, 0.2 mmol) and TCEP (28.5 mg, 0.1 mmol) were dissolved in 16 mL of phosphate buffer (pH 6.2, 50 × 10^{-3} M). dBMIB (38.7 mg, 0.1 mmol) in 4 mL of DMF was added to the solution and the solution was stirred for 6 h. DMF and inorganic salts were removed by dialysis. Then, water was then removed under reduced pressure at room temperature to give white solid products.

2.3.6. Synthesis of $\mathrm{(PDMA_{56})_2MIB}$ and $\mathrm{(PNAP_{31})_2MIB}$

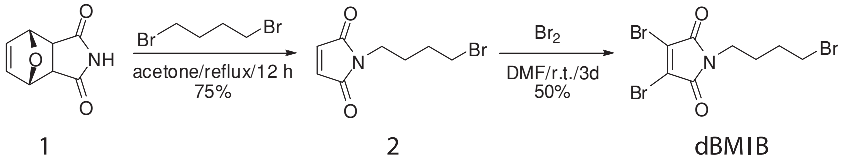
These polymers were prepared using a similar procedure that used for polymer $\mathrm{(PEO_{45})_2MIB}$ while $\mathrm{PDMA_{56}}$-SH (1.14 g, 0.2 mmol) and $\mathrm{PNAP_{31}}$-SH (1.18 g, 0.2 mmol) were added instead of $\mathrm{PEO_{45}}$-SH.

2.3.7. Synthesis of $\mathrm{(PEO_{45})_2MIA}$

To a solution of $\mathrm{(PEO_{45})_2MIB}$ (130 mg, 0.03 mmol) in DMF (1 mL), $\mathrm{NaN_3}$ (20 mg, 0.3 mmol) was added. After stirring at room temperature overnight, the solution was precipitated into an excess of ether. The collected solid was dried overnight under vacuum at room temperature.

2.3.8. Synthesis of Alkynyl-Terminated $\mathrm{PS_{48}}$

A mixed solution of St (5.2 g, 50 mmol), alkynyl-functionalized chain transfer agent (87.5 mg, 0.33 mmol), and AIBN (5.4 mg, 3.3 × 10^{-2} mmol) was degassed via three freeze-thaw-pump cycles. After stirring for 7 h at 60 ºC, the reaction was terminated by exposing system to air and the mixture was diluted with THF. The product was precipitated into an excess of ether. After drying



Scheme 3. Synthesis of dibromomaleimide dBMIB.

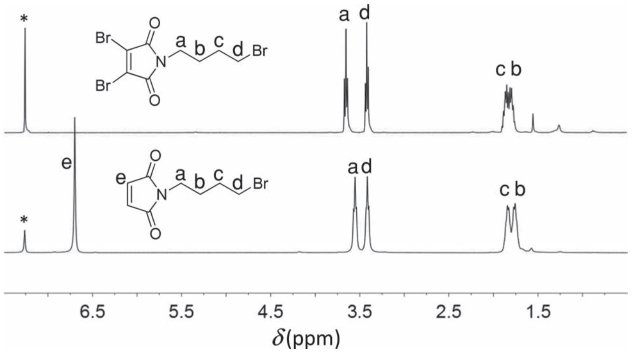


Figure 1. ^{1}H NMR spectra of 2 and dBMIB in $CDCl_3$ (the response of solvent protons is marked with ∗).

overnight in a vacuum at room temperature, the light yellow product was obtained with monomer conversion of 31%. The $\overline{M}_n$ and DP were calculated by ^{1}H NMR and $\overline{M}_w/\overline{M}_n$ was obtained by SEC ($\overline{M}_n = 5000$, DP = 48, $\overline{M}_w/\overline{M}_n = 1.08$).

2.3.9. Synthesis of $(PEO_{45})_2MIPS_{48}$

A solution of $(PEO_{45})_2MIA$ (86 mg, 0.02 mmol of azido unit), alkynyl PS_{48} (110 mg, 0.022 mmol), and ascorbic acid (1.8 mg, 0.01 mmol) in 2 mL of DMF was degassed via three freeze-thaw-pump cycles. $CuSO_4$ (2.5 mg, 0.01 mmol) was introduced into the glass ampule under a N_2 atmosphere. After stirring for 6 h at 50 °C, the reaction was terminated by exposing system to air and the mixture was diluted with THF. The product was precipitated into an excess of ether. After dried overnight in a vacuum at room temperature, white solids were obtained.

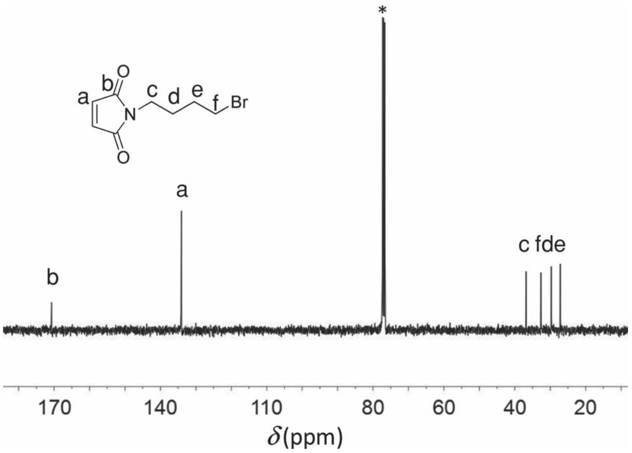


Figure 2. ^{13}C NMR spectrum of dBMIB in $CDCl_3$ (the response of solvent carbon is marked with ∗).

3. Results and Discussion

3.1. Synthesis of Coupling Agent dBMIB

The dBMIB was synthesized by a two-step procedure shown in Scheme 3. Furan-protected maleimide **1** was reacted with 1,4-dibromobutane followed by refluxing, giving N-(4-bromobutyl)maleimide **2** in high yield. The product dBMIB was obtained by a bromination of maleimide **2** with bromine at a mild condition according literature.[22] As demonstrated by ^{1}H NMR spectra of **2** and dBMIB (Figure 1), the chemical shift at 6.69 ppm from the proton resonance of vinyl protons of **2** disappeared after bromination. Due to the presence of Br linked with vinyl group, the chemical shifts of methylene protons near the maleimide moved 0.1 ppm to lower high field, while others remained nearly unchanged after reaction. The structure of dBMIB was further confirmed by ^{13}C NMR analysis as given in Figure 2 and elementary analysis in "Section 2."

3.2. Coupling Reaction of dBMIB and PEO_{45}-SH

If two thiol polymers may be coupled to one dBMIB molecule, the obtained adduct would have a doubled molecular weight. PEO_{45}-SH was chosen first to react with dBMIB.

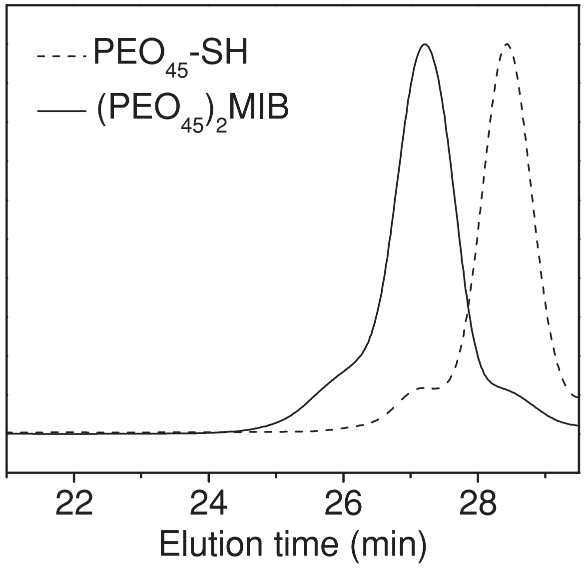


Figure 3. SEC traces of PEO_{45}-SH and $(PEO_{45})_2MIB$ with DMF as eluent.

Table 1. SEC characterization of the thiol polymers and their adducts with dBMIB.[a)]

Entry	Before reaction		After reaction	
	$\overline{M}_n$	$\overline{M}_w/\overline{M}_n$	$\overline{M}_n$	$\overline{M}_w/\overline{M}_n$
PEO_{45}-SH	12k	1.02	20k	1.02
$PDMA_{56}$-SH	26k	1.06	55k	1.10
$PNAP_{31}$-SH	24k	1.10	33k	1.10

[a)] Run in DMF calibrated by polystyrene standards.

Tris(2-carboxyethyl)phosphine (TCEP) was added to suppress oxidation of SH to form disulfide bonds. The reaction was conducted at an equivalent molar feeding ratio of functionalities, [PEO-SH]:[dBMIB] = 2:1, at room temperature for 6 h in a buffer solution of pH 6.2. SEC traces of PEO_{45}-SH and the mixture after reaction were shown in Figure 3. It may be found that a new peak at 27.2 min appeared whereas the peak of PEO_{45}-SH dropped greatly. Relative to polystyrene standards the $\overline{M}_n$ of the new peak doubled that of PEO_{45}-SH (Table 1), indicating the reaction underwent very efficiently. One may notice that there was a small peak at the eluent time of 28.3 min of the product. It could be a small amount of PEO_{45}-SH or mono-substituted adduct due to the weighting error.

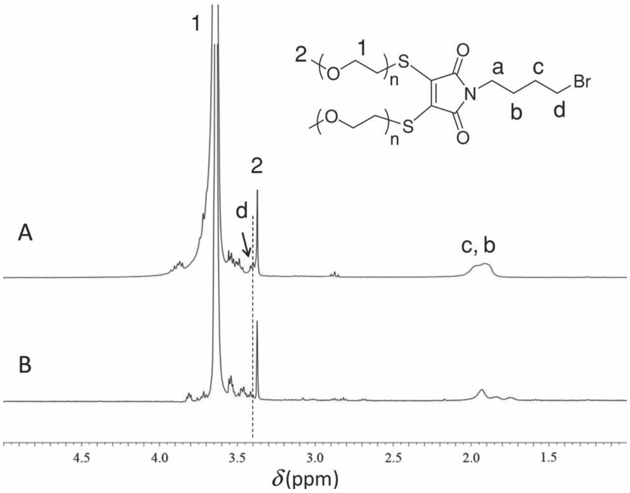


Figure 4. ^{1}H NMR spectra of (A) $(PEO_{45})_2$MIB and (B) $(PEO_{45})_2$MIA in $CDCl_3$.

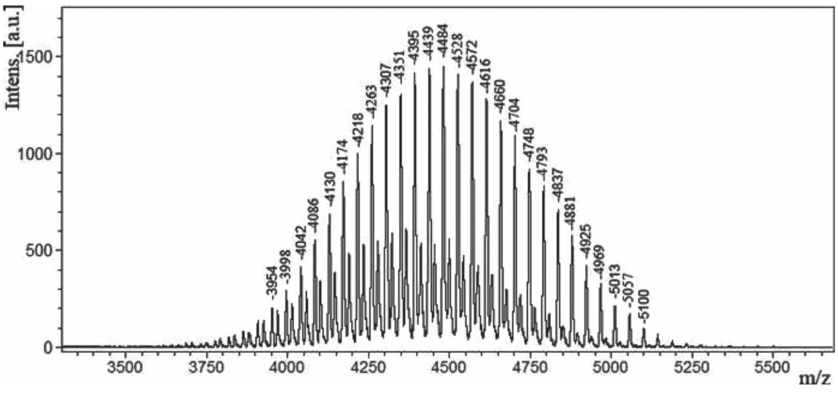


Figure 5. MALDI-TOF mass spectrum of $(PEO_{45})_2$MIB in linear mode.

The structure of $(PEO_{45})_2$MIB was characterized by ^{1}H NMR and MALDI-TOF mass spectra. As shown in Figure 4A, the protons of ethylene units and methyl terminal of PEO gave characteristic resonances at 3.63 and 3.35 ppm, respectively. One may notice a small slit peak at 3.40 ppm, which should be attributed to the proton **d** of the dBMIB unit near bromine. But due to the overlapped with methyl protons of PEO, it is impossible to get an accurate integration to evaluate the molecular weight. A precise molecular weight of the coupled products was supplied by the MALDI-TOF mass spectrum as shown in Figure 5. A series of peaks in region of 4000–5000 Dalton with an interval of 44 Dalton (EO unit) was observed, which doubled the molecular weight of PEO_{45}-SH. One selected peak at 4307 *m/z* agreed with the calculated value of molecule with 90 EO units (90 × 44.02 (C_2H_4O) + 2 × 15.01 (CH_3) + 2 × 32.06 (S) + 229.99 ($C_8H_8O_2NBr$) + 22.99 = 4308.92 (Na^+)). Therefore, the product was proved to be $(PEO_{45})_2$MIB, the adducts of PEO_{45}-SH and dBMIB.

Then, two different thiol-terminated polymers, $PNAP_{31}$-SH and $PDMA_{56}$-SH, were used to react with dBMIB. The two thiol terminal polymers were prepared by aminolysis of corresponding polymers given by RAFT-mediated radical polymerization with 2-cyanoprop-2-yl(4-fluoro) dithiobenzoate (CPFDB) as chain transfer agent according literatures.[21,23] Herein, we adopted hydrazine hydrate as a nucleophile and antioxidant to suppress the side reaction. The $\overline{M}_w/\overline{M}_n$ given from SEC calibrated by polystyrene standards and the DPs calculated by ^{1}H NMR through monomer conversion were listed in Table 1. The SEC curves of reaction products between $PDMA_{56}$-SH or $PNAP_{31}$-SH and dBMIB were shown in Figure 6 and Figure 7 and their relative molecular weights were also doubled as shown in Table 1. It may be observed that the SEC traces of the products are symmetric and no remain peaks at longer retention time can be found. Therefore, the coupling two thiol polymer chains to one dBMIB are indeed efficiently.

3.3. Synthesis of Miktoarm Star Polymer, $(PEO_{45})_2MIPS_{48}$

Since maleimide derivatives may bear various functionalities, we had introduced one bromoalkyl unit to check its further viability for building polymer topology. We studied using $(PEO_{45})_2$MIB

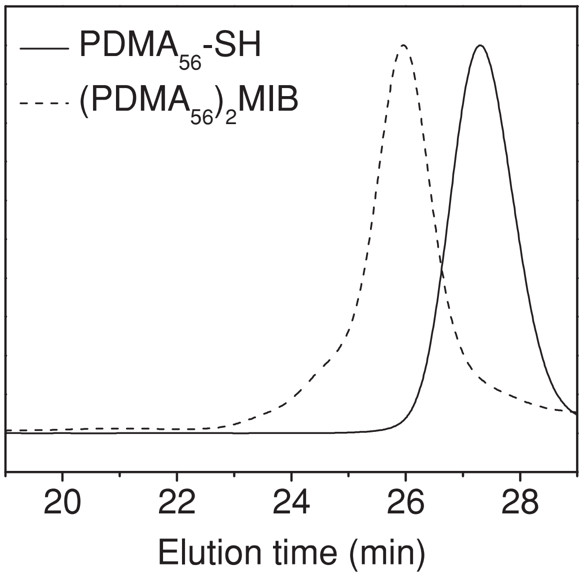


Figure 6. SEC traces of $PDMA_{56}$-SH and $(PDMA_{56})_2$MIB with DMF as eluent.

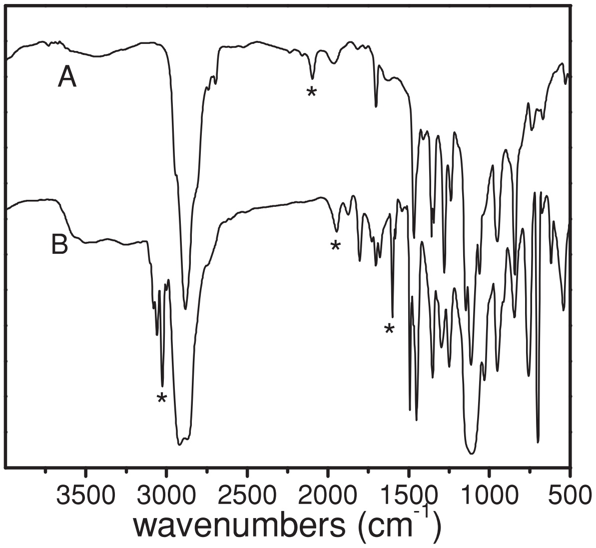


Figure 8. FTIR spectra of (A) $(PEO_{45})_2$MIA and (B) $(PEO_{45})_2MIPS_{48}$.

to prepare A_2B star polymer as an example as shown in Scheme 2. The Br group of $(PEO_{45})_2$MIB was converted into azide group by reacting with NaN_3 to given $(PEO_{45})_2$MIA. As comparison shown in Figure 4A and B, the proton resonance of the methylene **d** that linked with Br was disappeared after reaction, implying occurrence of substituent reaction. Introduction of the azido unit was also demonstrated by IR spectrum in Figure 8A by appearance of a characteristic peak of azido at 2100 cm^{-1}. Then $(PEO_{45})_2$MIA was coupled with an alkynyl- terminated PS_{48} given by RAFT polymerization by CuAAC coupling reaction. As shown in Figure 9, the eluent peak of the product $(PEO_{45})_2MIPS_{48}$ moved to a shorter retention time, indicating increase of molecular weight attributed to the introduction of PS segment. Occurrence of the CuAAC reaction was also confirmed by disappearance of azido units in IR spectrum (Figure 8B). The presence of PS segment was supported by the appearance of characteristic vibrations of PS at 3023, 1944, and 1600 cm^{-1}. The star polymer product was also characterized by ^{1}H NMR spectrum. As shown in

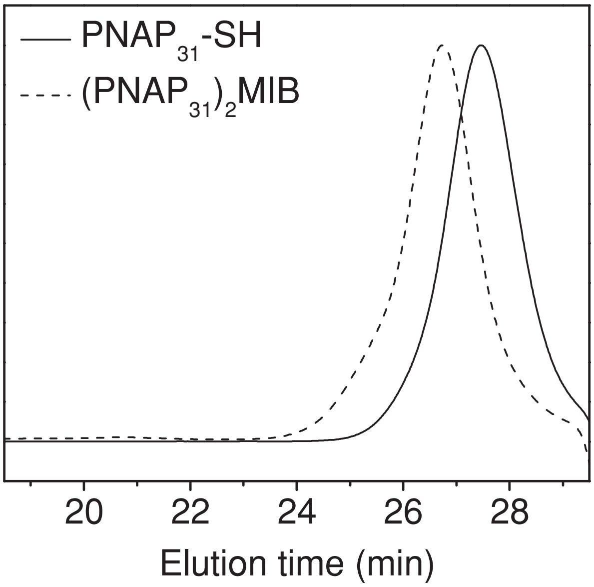


Figure 7. SEC traces of $PNAP_{31}$-SH and $(PNAP_{31})_2$MIB with DMF as eluent.

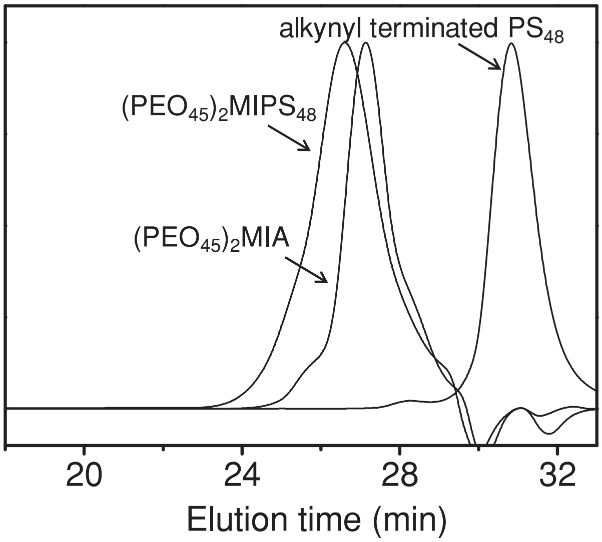


Figure 9. SEC traces of $(PEO_{45})_2$MIA and $(PEO_{45})_2MIPS_{48}$ with DMF as eluent.

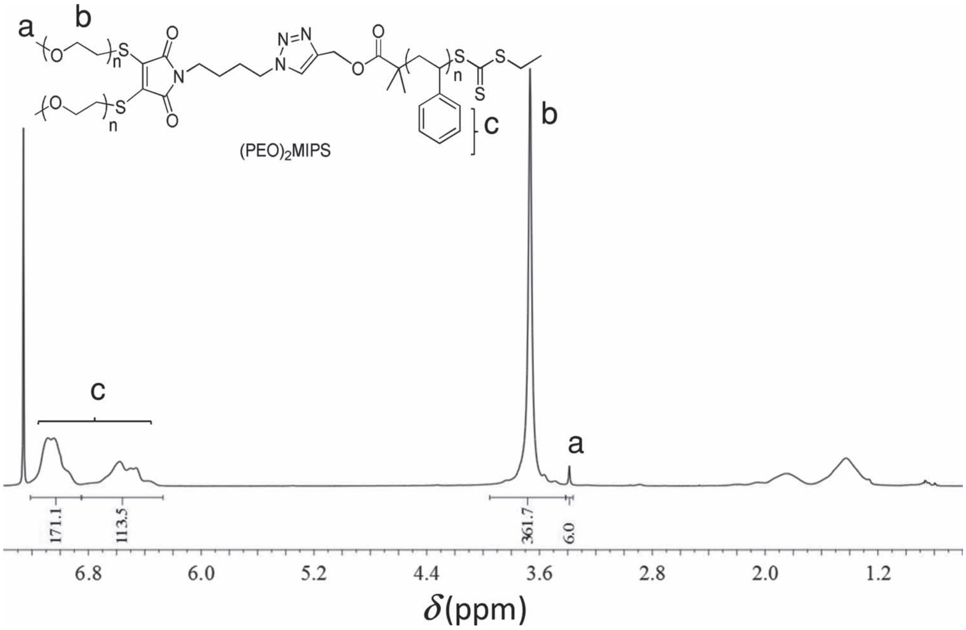


Figure 10. ^{1}H NMR spectrum of star polymer $(PEO_{45})_2MIPS_{48}$.

Figure 10, the responses of the protons from phenyl units and EO units can be found at the regions of 6.3–7.2 ppm and 3.4–3.8 ppm. The ratio of response areas from PS to PEO, 0.77, accords to the theoretical value, $48 \times 5/45 \times 2 \times 4 = 0.67$, demonstrating that the coupling PS to $(PEO_{45})_2MIA$ occurred quantitatively.

4. Conclusion

In summary, we have shown that the dibromomaleimide can be an excellent agent to couple two water-soluble polymer chains with a thiol terminal under a mild condition in aqueous phase. As a result, the polymers are dimerized and the maleimide unit is located at the center of newly formed chains. Thus, the dibromomaleimide derivative shows a promising application in building polymer architecture.

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