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Synthesis of Macrocyclic Poly(ethylene oxide) and Polystyrene via Glaser Coupling Reaction

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ABSTRACT: Glaser coupling reaction of alkynyl groups was used as a new ring-closure technique to synthesize monocyclic poly(ethylene oxide) (PEO) and polystyrene (PS) successfully. The linear PEO with hydroxyl groups at both ends was prepared by ring-opening polymerization (ROP) of ethylene oxide (EO) using 2,2-dimethyl-1,3-propanediol and diphenylmethylpotassium (DPMK) as co-initiators, terminated by anhydrous methanol. The linear PS with hydroxyl groups at both ends was prepared by anionic polymerization using lithium naphthalenide as initiator and terminated by EO. The propargyl-telechelic precursors (*l*-PEO and *l*-PS) were then obtained by the reaction between hydroxyl-telechelic polymers (HO-PEO-OH and HO-PS-OH) and propargyl bromide in the presence of sodium hydride. The intramolecular cyclizations of the latter were carried out in the presence of Cu(I)Br/*N,N,N′,N″,N″*-pentamethyldiethylenetriamine (PMDETA) under mild conditions with oxygen in the air as oxidant and the efficiency was as high as nearly 100%. The cyclic PEO and PS (*c*-PEO and *c*-PS) were characterized by GPC, ^{1}H NMR, FTIR, and MALDI-TOF MS. *G* factors (ratio of the apparent peak molar masses of cyclic product to their linear precursor) derived from GPC profiles were in the range 0.63−0.80. The highly efficient Glaser coupling took place at ambient temperature and did not need oxygen removal procedures, so it was a convenient approach for nearly quantitative preparation of cyclic polymers.

Introduction

In recent years, cyclic macromolecular architectures have gained increasing interest in both fundamental polymer chemistry and supramolecular chemistry. Cyclic polymers with "endless" polymer main chains show distinctively unique characteristics and physical properties due to their closed ring topology compared to linear analogues.[1,2] Although significant advances have occurred in the development of precise synthetic strategies,[3−5] a straightforward and efficient synthetic method is still challenging.

In general, the synthetic strategies for preparation of cyclic polymers include ring-closure techniques and ring-expansion techniques. The ring-closure techniques involve cyclization of linear polymer precursors with heterodifunctional or homodifunctional end groups. The key step of this method is selecting highly efficient coupling reactions to afford the well-defined monocyclic polymer under ultradilute conditions to prevent intermolecular oligomerization.

It has been reported that "click" reaction of complementary azide and alkyne end groups is a good choice for cyclization because of its extremely high reactivity and selectivity. The combination of the "living"/controlled polymerization technique with "click" chemistry has yielded a series of macrocyclic polymers including polystyrene (PS),[6,7] poly(*N*-isopropylacrylamide),[8,9] poly(ε-caprolactone),[10] poly(δ-valerolactone),[11] and expanded crown ethers.[12] Furthermore, the "click" reaction has also been used to synthesize cyclic polymer with various architectures.[13−20] However, the typical "click" cyclization reaction requires oxygen free conditions and higher temperature (> 80 °C), which may lead to some side reactions.[21] Although recently Jacobson−Stockmayer theory has been used to improve the conditions of "click" cyclization,[22] the results have not been widely employed and oxygen removal is required. In addition, synthesizing heterodifunctional polymers is less convenient than homodifunctional ones. The existing homocoupling cyclization reactions include ring-closing metathesis reaction of allyl groups[23−27] and reversible oxidation of thiol groups,[28] but the former needs expensive catalysts (Grubbs catalyst) and the latter reaction is not efficient enough (< 90%). Moreover, the separation of intermolecular reaction products is necessary.

Recently, we found that Cu(I)Br/*N,N,N′,N″,N″*-pentamethyldiethylenetriamine (PMDETA) promotes terminal alkynes to produce 1,3-diynes with good yields using pyridine as solvent at room temperature. This Glaser coupling of terminal alkynes, as one of the most important carbon−carbon bond formation methods, has been applied in various fields of chemistry.[29] It would also be a powerful tool in the synthesis of cyclic polymers. Cyclization of propargyl-telechelic polymers via Glaser coupling might have some advantages: (1) telechelic polymer precursors can be prepared through diverse polymerization techniques from difunctional initiators, and then alkyne end groups are easy to introduce; (2) the reaction can take place under mild conditions without deoxygenation and heating; (3) the reaction can produce 1,3-diynes in excellent yields with high efficiency. Herein we report a nearly quantitative preparation of cyclic polymers via the modified Glaser coupling reaction of terminal alkynes under pseudo-ultradilute conditions. The preparation process and characterization of cyclic poly(ethylene oxide) (*c*-PEO) and cyclic PS (*c*-PS) are discussed below.

Experimental Section

Materials. Ethylene oxide [EO, CP, Sinopharm Chemical Reagent Co. (SCR)] was dried over CaH_2 for 48 h, then distilled under N_2, and stored at −20 °C before use. Styrene (St, 99%, SCR) was washed with 10% NaOH aqueous solution followed

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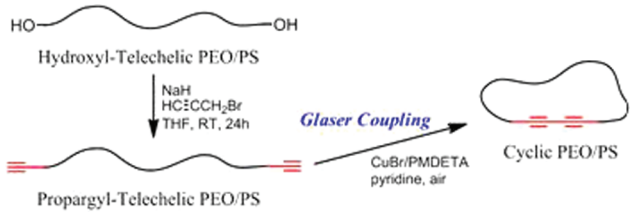
Scheme 1. Synthesis of *c*-PEO/PS by Glaser Coupling



by water three times successively, dried over CaH_2, and distilled under reduced pressure. Tetrahydrofuran (THF, >99%, SCR) were refluxed and distilled from sodium naphthalenide solution. Dimethyl sulfoxide (DMSO, 98%, SCR) was dried over CaH_2 and distilled under reduced pressure. 2,2-Dimethyl-1,3-propanediol (99%, SCR) was recrystallized from acetone and H_2O (v/v = 1:1). Copper(I) bromide [Cu(I)Br, 95%, SCR] was stirred overnight in acetic acid, filtered, washed with ethanol and ethyl ether successively, and dried *in vacuo*. Sodium hydride (NaH, 99%), propargyl bromide (>99%), and *N,N,N′,N″,N″*-pentamethyldiethylenetriamine (PMDETA, 99%) were purchased from Aldrich and used as received. All other reagents were purchased from SCR and used as received, unless otherwise noted. Diphenylmethylpotassium (DPMK) solution was freshly prepared by the reaction of potassium naphthalenide with 1,1-diphenylmethane in THF according to the literature,[30] and the concentration was 0.75 mol/L. *n*-Butyllithium (*n*-Bu^-Li^+) was prepared according to the literature[31] and analyzed by the double-titration method,[32] and the concentration was 1.57 mol/L.

Measurements. Gel permeation chromatographic (GPC) analysis of PEO was performed in 0.1 M $NaNO_3$ aqueous solution at 40 °C with an elution rate of 0.5 mL/min on an Agilent 1100 equipped with a G1310A pump, a G1362A refractive index detector, and a G1315A diode-array detector. Three TSK-gel PW columns in series (bead size: 6, 13, and 13 μm; pore size: 200, >1000, and <100−1000 Å; molecular range: $0-5\times10^4$, $5\times10^4-8\times10^6$, and $(5-8)\times10^6$ g/mol, respectively) were calibrated with PEO standard samples. GPC analysis of PS was performed in THF at 35 °C with an elution rate of 1.0 mL/min on an Agilent 1100 equipped with a G1310A pump, a G1362A refractive index detector, and a G1314A variable wavelength detector. One 5 μm LP gel column (500 Å, molecular range $500-2\times10^4$ g/mol) and two 5 μm LP gel mixed bed column (molecular range $200-3\times10^6$ g/mol) were calibrated by PS standard samples. The injection volume was 20 μL, and the concentration was 5 mg/mL. ^{1}H NMR spectra were recorded on a DMX 500 MHz spectrometer in $CDCl_3$ with tetramethylsilane (TMS) as the internal reference for chemical shifts. FTIR spectra were recorded on a Magna 550 Fourier transform infrared spectrometer instrument. The polymer samples were dissolved in dry THF and then cast onto a NaCl disk to form the film by solvent evaporation under an infrared lamp. The matrix-assisted laser desorption ionization time-of-flight mass spectrometry (MALDI-TOF MS) measurement was performed using a Perspective Biosystem Voyager-DE STR MALDI-TOF MS (PE Applied Biosystems, Framingham, MA). For PEO samples, a matrix solution of dithranol (20 mg/mL), polymer (10 mg/mL), and cationizing salt of sodium trifluoroacetate (10 mg/mL) in THF was mixed in the ratio of matrix:cationizing salt:polymer = 10:1:2, and 0.8 μL of mixed solution was deposited on the sample holder. MALDI-TOF MS analysis of PS samples was performed using the same method except that silver trifluoroacetate was used to substitute sodium trifluoroacetate. All spectra were recorded in reflectron mode, and the mass scale was calibrated externally using PS standards.

Synthesis of Hydroxyl-Telechelic PEO (HO-PEO-OH). HO-PEO-OH was obtained by ring-opening polymerization (ROP) of EO initiated by co-initiator of 2,2-dimethyl-1,3-propanediol and DPMK. The polymerization was carried out in a stainless steel kettle, and the typical procedure was as follows: a 400 mL kettle was vacuumed at 80 °C for 24 h and cooled to room temperature and then to −20 °C. A given volume of an initiator solution [2,2-dimethyl-1,3-propanediol (3.12 g, 30.0 mmol) with DPMK (12 mL, 9.00 mmol) dissolved in DMSO (120 mL)] and EO (60.0 g, 136 mmol) were introduced successively into the kettle. Subsequently, it was heated at 50 °C under stirring for 48 h. The reaction was terminated with anhydrous methanol. The reaction solution was concentrated under reduced pressure and redissolved in H_2O. The products were extracted with CH_2Cl_2, then the organic layer was dried over $MgSO_4$. After the solvents were evaporated, HO-PEO-OH was obtained by precipitation in cold ethyl ether twice and dried under vacuum at 45 °C. Yield: 56.0 g (93.3%). GPC: M_n = 1.1 kDa, PDI = 1.09. ^{1}H NMR ($CDCl_3$, δ, ppm, TMS): 0.92 (CH_3-), 3.20 ($-OCH_2C(CH_3)_2-$), 3.56−3.70 ($-CH_2CH_2O-$), calcd M_n = 2.0 kDa. MALDI-TOF MS: M_n = 1.9 kDa, PDI = 1.09.

Synthesis of Hydroxyl-Telechelic PS (HO-PS-OH). HO-PS-OH was obtained by living anionic polymerization of St initiated by lithium naphthalenide, end-capped with EO.[33] The initiator of lithium naphthalenide was first synthesized from naphthalene and lithium according to refs 31 and 34. The solution of lithium naphthalenide was analyzed by titration using hydrochloric acid (0.1 mol/L), and the concenration was 1.20 mol/L. Typically, cyclohexane (120 mL), styrene (10 mL, 87.0 mmol), and THF (4 mL) were introduced to a 400 mL ampule successively. In order to remove impurities in the ampule, *n*-Bu^-Li^+ solution was added dropwise until the mixture turned yellowish, and then lithium naphthalenide solution (4 mL, 4.80 mmol) was added rapidly. After the reaction had stirred in an ice bath for 35 min, EO (4-fold excess, 1 mL, 19.0 mmol) dissolved in THF (30 mL) was added, and the red solution changed to faint yellow. The solution was stirred for another 1 h at room temperature and terminated with acidic methanol (1 vol % HCl). After all solvents were evaporated, the product was obtained by precipitation in methanol twice and dried under vacuum at 45 °C. Yield: 4.40 g (97%). GPC: M_n = 3.8 kDa, PDI = 1.05. ^{1}H NMR ($CDCl_3$, δ, ppm, TMS): 1.25−2.01 ($-CH_2CH-$ of PS chain), 3.09−3.25 ($-CH_2CH_2OH$), 6.30−7.30 ($-C_6H_5$ of PS chain) calcd. M_n = 3.8 kDa. MALDI-TOF MS: M_n = 3.8 kDa, PDI = 1.05.

Synthesis of Propargyl-Telechelic PEO (*l*-PEO) and PS (*l*-PS). The synthesis of *l*-PEO was taken for example. Dried HO-PEO-OH (1.9 kDa, 1.50 g, 0.789 mmol) was added to a 100 mL round-bottomed flask. The polymer was dissolved in THF (30 mL), and then NaH (0.330 g, 14.0 mmol) was added. The solution was allowed to stir at 40 °C for 1 h. Then propargyl bromide (1 mL, 14.0 mmol) was added dropwise in ice bath. The solution was stirred at 25 °C for 48 h, and the pH of the solution was adjusted to 7.0 by addition of 0.1 mol/L hydrochloric solution. After THF was removed by rotary evaporation, the products were extracted with CH_2Cl_2 (100 mL × 2), and then the organic layer was dried over $MgSO_4$ before purification by precipitation into anhydrous ethyl ether three times to give yellow powder (yield: 1.30 g, 87%). ^{1}H NMR ($CDCl_3$, δ, ppm, TMS): 0.92 (CH_3-), 2.44 ($-CH_2C\equiv CH$), 3.20 ($-OCH_2C(CH_3)_2-$), 3.56−3.70 ($-CH_2CH_2O-$), 4.20 ($-CH_2C\equiv CH$), calcd M_n = 2.0 kDa. MALDI-TOF MS: M_n = 1.9 kDa, PDI = 1.09. FTIR: 3247, 2868, 1458, 1349, 1297, 1250, 1107, 950, 850 cm^{-1}.

The transformation of terminal hydroxyls of HO-PS-OH (3.8 kDa, 1.50 g, 0.395 mmol) was similar to PEO presented above. *l*-PS was obtained by precipitation into anhydrous methanol three times to give a yellow powder (yield: 1.38 g, 92%). ^{1}H NMR ($CDCl_3$, δ, ppm, TMS): 1.25−2.01 ($-CH_2CH-$ of PS chain), 2.29 ($-C\equiv CH$), 3.09−3.25 ($-CH_2CH_2O-$), 3.90−4.00 ($-OCH_2-C\equiv CH$), 6.30−7.30 ($-C_6H_5$ of PS chain) calcd M_n = 3.8 kDa. MALDI-TOF MS: M_n = 3.8 kDa, PDI = 1.05. FTIR: 3302, 3059, 3025, 2924, 2851, 1944, 1872, 1804, 1742, 1601, 1493, 1452, 1366, 1069, 1029, 907, 842, 747, 699 cm^{-1}.

Synthesis of Cyclic PEO (*c*-PEO) and Cyclic PS (*c*-PS). To a 500 mL round-bottomed flask was added pyridine (400 mL), Cu(I)Br (0.432 g, 3.00 mmol), and PMDETA (0.619 mL, 3.00 mmol), and the solution was stirred for 1 h. To a separate flask

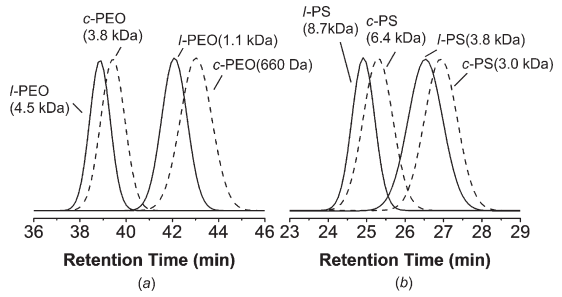


Figure 1. GPC profiles of (a) *l*-PEO and *c*-PEO and (b) *l*-PS and *c*-PS.

was added *l*-PEO (1.9 kDa, 200 mg, 0.105 mmol) dissolved in pyridine (100 mL). This solution was then added to the Cu(I)Br/PMDETA reaction solution via a peristaltic pump at a rate of 2 mL/h (2.1 μmol/h). After 2 h, the reaction solution was concentrated and redissolved in CH_2Cl_2. Then the products were purified by passing through a neutral alumina column using CH_2Cl_2 as eluent to remove the copper catalyst residues and recovered by precipitation into anhydrous ethyl ether. The obtained product was dried overnight in a vacuum oven for 24 h (yield: 86 mg, 43%). GPC: M_n = 660 Da, PDI = 1.20. ^{1}H NMR ($CDCl_3$, δ, ppm, TMS): 3.56−3.70 (−C***H***$_2$C***H***$_2$O−), 4.27 (−C***H***$_2$C≡C−C≡C−C***H***$_2$−), calcd M_n = 2.0 kDa. MALDI-TOF MS: M_n = 1.9 kDa, PDI = 1.08. FTIR: 2868, 1458, 1349, 1297, 1250, 1107, 950, 850 cm^{-1}.

The cyclization procedure for PS (3.8 kDa, 399 mg, 0.105 mmol) was similar to the synthesis of *c*-PEO. THF was used as eluent instead of CH_2Cl_2 when passing through a neutral alumina column, and the product was recovered by precipitation into anhydrous methanol (yield: 280 mg, 70%). GPC: M_n = 3.0 kDa, PDI = 1.04. ^{1}H NMR ($CDCl_3$, δ, ppm, TMS): 1.25−2.01 (−C***H***$_2$C***H***− of PS chain), 3.09−3.25 (−CH$_2$C***H***$_2$O−), 3.90−4.10 (−OC***H***$_2$C≡C−C≡C−C***H***$_2$O−), 6.30−7.30 (−C$_6$***H***$_5$ of PS chain) calcd M_n = 3.8 kDa. MALDI-TOF MS: M_n = 3.8 kDa, PDI = 1.05. FTIR: 2953, 2924, 2854, 1601, 1492, 1460, 1377, 1259, 1104, 1020, 726, 698 cm^{-1}.

Results and Discussion

Synthesis and Characterization of Linear Precursors. HO-PEO-OH was grown from hydroxyl groups of 2,2-dimethyl-1,3-propanediol after partial deprotonation (30%) by DPMK.[35] The typical synthetic procedures are described in the Experimental Section in detail. *l*-PEO were prepared by an end-group transformation reaction of HO-PEO-OH with propargyl bromide in the presence of NaH.[12] From GPC results of obtained two PEO samples (Figure 1a, solid line), the monomodal distribution curves indicated the successful polymerization of EO. The ^{1}H NMR spectrum of *l*-PEO in Figure 2b shows characteristic signals due to alkynyl protons (e) and methylene protons of the propargyl group (d) at 2.44 and 4.21 ppm, respectively. FTIR analysis of *l*-PEO (Figure 3) shows the characteristic peak at 3300 cm^{-1} (alkyne). In the MALDI-TOF MS spectrum for *l*-PEO (Figure 4, top), the series of molecular masses are expressed in the following equation: $MW_{MS} = 102.1\ (C_5H_{10}O_2) + 44.0\ (EO) \times n + 39.1$ (propargyl group) $\times 2 + 23.0$ (sodium), where n is the number of EO units. With no molecular masses of HO-PEO-OH detected in the spectrum, it was proved that the propargylation efficiency was nearly 100%.

HO-PS-OH was synthesized by living anionic polymerization of St initiated from lithium naphthalenide, and EO was employed as termination agent.[36] The propargylation of HO-PS-OH was carried out in the same manner with PEO. Figure 1b (solid lines) shows the GPC profiles of two *l*-PS samples. In Figure 5b, the ^{1}H NMR spectrum of *l*-PS exhibits the characteristic signals due to alkynyl proton (g) and methylene

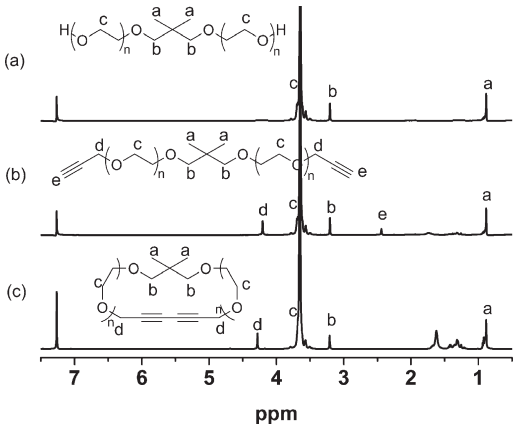


Figure 2. ^{1}H NMR (500 Hz) spectra of (a) HO-PEO-OH (b) *l*-PEO, and (c) *c*-PEO in $CDCl_3$.

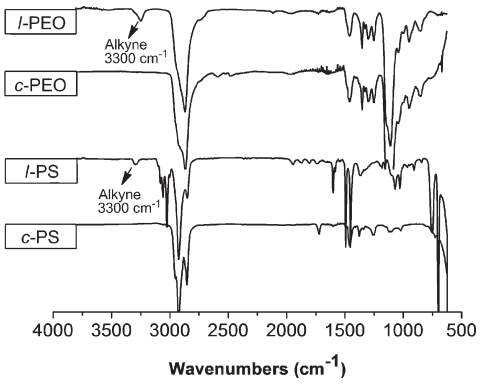


Figure 3. FTIR spectra of *l*-PEO, *c*-PEO, *l*-PS, and *c*-PS.

protons of propargyl (f) at 2.44 ppm and 3.90−4.00 ppm, respectively. FTIR analysis of *l*-PS (Figure 3) also shows the appearance of a characteristic peak at 3300 cm^{-1} (alkyne).

Synthesis and Characterization of Cyclic Polymers. The intramolecular cyclization of linear propargyl-telechelic precursors was carried out using Cu(I)Br/PMDETA as catalytic system. As good solvent to most polymers, pyridine was used here. The small amount oxygen dissolved in pyridine was acted as oxidant. Utilizing a peristaltic pump, a solution of linear presursors (0.2 mmol) in pyridine (100 mL) was added dropwise into a 400 mL volume solution of pyridine containing catalysts at ambient temperature over 48 h. The long periods of reaction time can be explained by the larger scale here versus that reported in the literature ($\leq$0.1 g, mostly).[6,13,22,27] After stirring for an additional 2 h, the reaction solution was concentrated, and the residue was dissolved in CH_2Cl_2. Then the products were purified by passing through a neutral alumina column to remove the copper catalyst residues and recovered by precipitation into corresponding solvents.

The functional groups modification and cyclization reaction for PEO with $M_{n(GPC)}$ of 1.1 and 4.5 kDa as well as PS with $M_{n(GPC)}$ of 3.8 and 8.7 kDa (Table 1) were successfully carried out. The cyclization strategy was confirmed through analyzing the linear precursors and cyclization products by GPC, ^{1}H NMR, FTIR, and MALDI-TOF MS.

The GPC profiles of *l*-PEO and *c*-PEO as well as *l*-PS and *c*-PS are presented in Figure 1. From the results of four samples, the hydrodynamic volume of cyclization products was noticeably smaller than that of their linear precursors. The unimodal GPC profiles of cyclic polymers with low PDI indicated that intermolecular reaction products were not produced as a byproduct during the cyclization process.

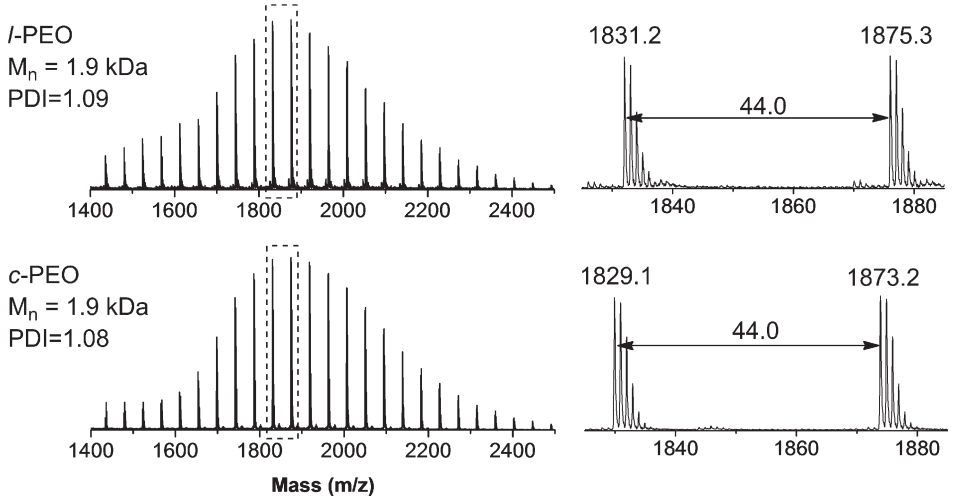


Figure 4. MALDI-TOF MS spectra of *l*-PEO and *c*-PEO.

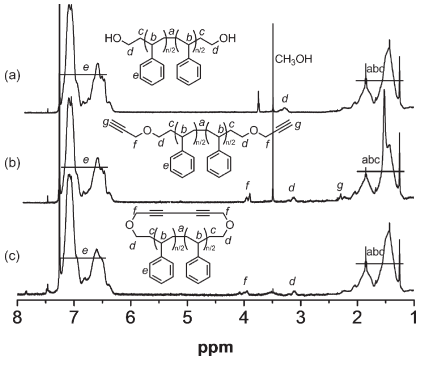


Figure 5. ^{1}H NMR (500 MHz) spectra of (a) HO-PS-OH (b) *l*-PS, and (c) *c*-PS in $CDCl_3$.

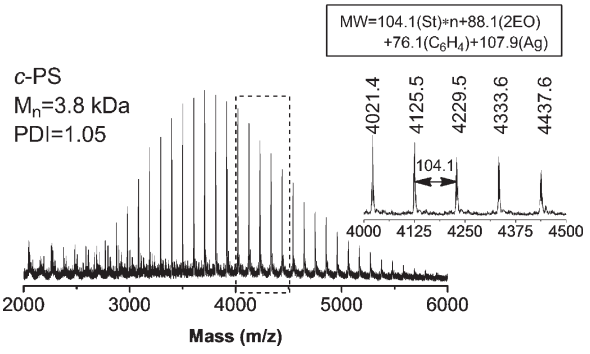


Figure 6. MALDI-TOF MS spectrum of *c*-PS (III).

Table 1. Data for *c*-PEO/PS and Their Linear Precursors

		GPC[a]				NMR[c]	MALDI[d]	
entry	polymer	M_n (kDa)	PDI	M_p (kDa)	G^b	M_n (kDa)	M_n (kDa)	PDI
I	*l*-PEO	1.1	1.09	1.2	0.63	2.0	1.9	1.09
	c-PEO	0.66	1.20	0.78		2.0	1.9	1.08
II	*l*-PEO	4.5	1.09	5.6	0.78	4.6	4.5	1.16
	c-PEO	3.8	1.12	4.4		4.6	4.5	1.19
III	*l*-PS	3.8	1.05	3.8	0.80	3.8	3.8	1.05
	c-PS	3.0	1.04	3.1		3.8	3.8	1.05
IV	*l*-PS	8.7	1.03	8.6	0.75	12	8.8	1.05
	c-PS	6.4	1.05	6.4		12	8.8	1.05

[a] Determined by GPC. The PEO samples were calibrated by PEO standards using 0.1 M aqueous $NaNO_3$ as eluent. The PS samples were calibrated by PS standards using THF as eluent. M_p is the apparent peak molar mass. [b] G is ratio of the apparent peak molar masses (M_p) derived from GPC traces of cyclic polymer to their linear precursor. [c] Determined from ^{1}H NMR by end-group analysis based on the integral area using the formulas: $M_{n(NMR)PEO} = [(A_c/4)/(A_a/6)] \times 44 + 104$, where A_a and A_c are the integral area of the corresponding protons in Figure 2a, and the values 44 and 104 are the molecular weight of EO unit and the mass of the initiator. $M_{n(NMR)PS} = [(A_e/5)/(A_d/4)] \times 104 + 90$, where A_e and A_d are the integral area of the corresponding protons in Figure 5a, and the values 104 and 90 are the molecular weight of St unit and the mass of end groups. [d] Determined from MALDI-TOF MS calculated by software Polymerix.

The G factor (M_{pc}/M_{pl}) was the ratio of the apparent peak molar mass (M_p) corresponding to the signals of cyclic and linear polymer derived from GPC profiles (see Table 1). The G values of PEO were 0.63 and 0.78, and that of PS were 0.78 and 0.80, which agreed well with data reported in the literature.[37−39] The G factor reflects the difference in solution dimensions of cyclic and linear polymer chains of identical degree of polymerization.

^{1}H NMR analysis was used to determine the end-groups transformation after cyclization process. The ^{1}H NMR spectrum of *c*-PEO (Figure 2c) shows that the signals for alkynyl proton (2.44 ppm) became invisible after cyclization. At the same time, those methylene protons adjacent to the alkyne moiety still existed, shifting from 4.21 to 4.27 ppm. Figure 5 shows the ^{1}H NMR analysis of *l*-PS and *c*-PS, in which the signals for alkynyl proton were also lost after cyclization. Further evidence for the formation of 1,3-diynes could be given by FTIR analysis. From the FTIR spectra of *c*-PEO and *c*-PS (Figure 3), the disappearance of the terminal alkyne (3300 cm^{-1}) peaks indicated a complete conversion of the alkyne end groups into 1,3-diynes as the occurrence of the Glaser coupling cyclization.

Figure 4 shows the MALDI-TOF MS spectra of *c*-PEO and its linear precursor. Both *l*-PEO and *c*-PEO presented a uniform series of peaks corresponding to EO (peak interval of 44.0 EO units). The series of molecular masses for *c*-PEO are expressed in the following equation: $MW_{MS} = 102.1$ ($C_5H_{10}O_2$) + 44.0 (EO) × n + 76.1 (1,3-diynes) + 23.0 (sodium), where n is the number of EO units. Mass spectrometry analysis matched the anticipated molecular formulas very well. For example, in the top spectrum, the peaks (assumed to be adducts with Na^+) at 1875.3 corresponded to *l*-PEO (n = 38) and the peaks in the bottom spectrum at 1873.2 corresponded to *c*-PEO (n = 38). Since *c*-PEO products were produced from the precursors, *l*-PEO, by elimination of two

hydrogens through oxidative homocoupling of terminal alkynes, their molecular weights only differed by 2 mass units, which was strongly confirmed by data from MALDI-TOF MASS spectra. The MALDI-TOF MS characterization of *c*-PS also had the same results (Figure 6).

Conclusions

In conclusion, the synthesis of well-defined cyclic PEO and PS via Glaser coupling catalyzed by Cu(I)Br/PMDETA was feasible. Linear propargyl-telechelic polymer can be easily obtained through end-groups transformation from telechelic polymers, e.g., hydroxyl-telechelic polymers with low PDI. The cyclization reactions were carried out by slow dropwise addition of linear precursor to catalyst solution at room temperature under mild conditions, leading to a near-quantitative conversion. With the high efficiency of Glaser coupling, time-consuming purification of the products was not necessary. The fact that it can be carried out under mild conditions (need no oxygen removal and heating procedures) makes the copper-catalyzed alkynyl homocoupling cyclization a valuable method for the preparation of cyclic polymers. In addition, the versatility of this approach allows a potentially wide range of polymers to be cyclized in this manner.

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