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ARTICLE TYPE

Synthesis and Characterization of Novel Barbwire-like Graft Polymers Poly(ethylene oxide)-*g*-Poly(ϵ -caprolactone)₄ by Grafting From Strategy

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A novel barbwire-like graft polymers PEO-*g*-PCL₄ were synthesized by combination of ring opening polymerization (ROP), Glaser coupling with thiol-yne addition reaction via “grafting from” strategy. Typically, the precursor (PEO-Diyne-PEO)_s with high molecular weight was obtained by Glaser coupling of Alkyne-PEO-Alkyne, which was prepared by modification of HO-PEO-OH with propargyl bromide. After the diyne groups on PEO was transferred into hydroxyl groups by efficient thiol-yne addition reaction with mercaptoethanol, the macroinitiator [PEO-(OH)₄-PEO]_s was obtained and the graft polymers PEO-*g*-PCL₄ were synthesized by ROP of ϵ -caprolactone monomers. The structure of graft polymers was confirmed by GPC, MALDI-TOF MS, ¹H NMR, and TGA measurements in detail, and the crystallization behavior of graft polymers was also comprehensively investigated by DSC, WAXD, and POM instruments.

Introduction

In recent years, a variety of polymers with complicated architectures and compositions have been realized by certain synthetic route via the combination of living/controlled polymerization mechanisms and efficient coupling methods. The increasing attention on these complicated architectures is mainly due to their unique physical properties and versatile applications, such as biomedical materials,^{1, 2} composite materials,³ nanotechnology,⁴ and supra-molecular science.⁵ Among these complicated architectures, the graft polymers are synthesized by connecting multiple side chains onto a certain main chain. Usually, for graft polymers, there are many parameters can be modulated, such as the length, structures and compositions of main chains and side chains, the grafting density and so on. For example, the structures of side chains and main chains of graft polymers can be designed as block,⁶ hyper-branched,⁷ V-shaped,^{8,9} star-shaped,^{10,11} dendrimer-like,¹²⁻¹⁴ and so on, and the compositions can be chosen from poly(isoprene)(PI),^{15, 16} poly(ethylene oxide) (PEO),¹⁷ polystyrene (PS),¹⁸⁻²⁰ poly(acrylic acid) (PAA),²¹ poly(hydroxyethyl methacrylate) (PHEMA),^{22,23} poly(ϵ -caprolactone) (PCL),²⁴ poly(dimethylaminoethyl methacrylate) (PDMAEMA),²⁵ and so on. With the variations of above parameters, the graft polymers with certain applications can be easily realized. Importantly, during the synthetic procedure to graft polymers, the designing and synthesizing of main chains is always the key step. The main chains not only provide controlled grafting sites and grafting density, but also embed the properties of main chains into the final graft polymers. However, in literatures, the length between adjacent grafting sites in graft polymers is always modulated by several monomer units. In such case, the properties of main chains are always difficult to be

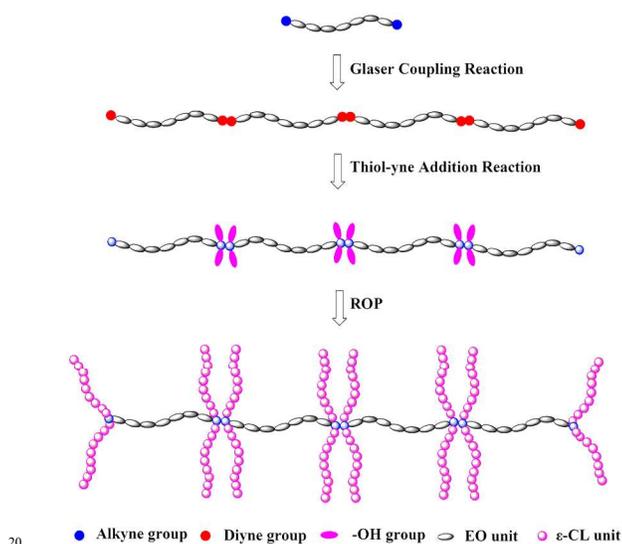
discriminated or even can be neglected because of the serious restriction and surrounding of side chains to the main chains.

Alternatively, using the living anionic polymerization and coupling reaction between living species and chlorosilane agent, Mays *et al* synthesized some novel graft polymers PI-*g*-PS or PS-*g*-PS, in which the grafting sites are separated by PI or PS segments with certain length.²⁶⁻²⁸ After these pioneering work, by combination of Williamson reaction, anionic polymerization and living / controlled radical polymerization, Plamper *et al* also synthesized some similar graft polymers PEO-*g*-PDMAEMA, in which the grafting sites are separated by PEO segment.²⁵ Actually, the graft polymers with grafting sites regularly separated by a certain polymeric segment and star-shaped polymers as side chains are rarely reported except for the above two examples. These graft polymers are termed as barbwire-like, threaded star-shaped, pearl necklace, multi-graft, centipede or multiple dumbbells polymers, which can be regarded as that the core of star-shaped polymers are sequentially linked by a common linear polymer. Because of the existence of main chain segments with a certain length in graft polymer, the properties of main chains could be well expressed in final graft polymers. For example, from the results of Mays', it had been shown that the mechanical properties of barbwire-like polymers can be well controlled by modulating the length of spaced segment on main chains. However, until recently, the synthesis of the above so-called barbwire-like polymers and the related progresses are rather limited and need to be further developed.

On the other hand, from the viewpoint of compositions, PEO is a classical soft segment in multi-constitution polymers, and might endow the polymers with special properties due to its good solubility both in water and organic solvents.²⁹⁻³¹ The polymers

contained PEO segment showed potential applications in high energy density lithium batteries, electronic devices³² and drug delivery systems.³³ Also, the PCL segment have been extensively used as an important biomaterial for a wide variety of drug delivery carriers and biomedical devices because of its biodegradability and biocompatibility,³⁴ as well as composite material because of its versatile mechanical properties and miscibility toward some commodity polymers including polyethylene and polypropylene. Thus, the polymers contained PEO or PCL segments are important in theory and applications.

Herein, considered the above progresses, we aim to synthesize some novel barbwire-like graft polymers PEO-g-PCL₄, in which the grafting sites are specially spaced with a certain length of PEO segments and the PCL segments with controlled length are introduced as side chains. In synthetic route, the ring-opening polymerization (ROP) mechanism, Glaser coupling and thiol-yne addition reaction are well combined (Scheme 1). Furthermore, the crystallization behaviors of graft polymer PEO-g-PCL₄ are also investigated.



Scheme 1. The illustration of barbwire-like graft polymers PEO-g-PCL₄ and the synthetic procedure.

Experimental

Materials

The difunctional HO-PEO-OH was synthesized in our lab according to previous work³⁵ by using ethylene glycol and diphenylmethyl potassium (DPMK) as co-initiator system. ϵ -Caprolactone (99 %, Aldrich) and propargyl bromide (98 %, Aldrich) were purified by distillation from calcium hydride (CaH₂) under reduced pressure and stored at -20 °C before use. Toluene was purified by direct distillation from CaH₂. Tetrahydrofuran (THF, 99 %) was refluxed and distilled from potassium naphthalenide solution. Tin(II)bis(2-ethylhexanoate) (Sn(Oct)₂, 95 %, Sigma) was dissolved in dry toluene (18 mg/mL). N,N,N',N',N''-pentamethyldiethylenetriamine (PMDETA, 99 %, Aldrich) was used as received. All other reagents and solvents

were purchased from Sinopharm Chemical Reagent Co., Ltd (SCR) and used as received except for declaration.

Characterization

Gel permeation chromatographic (GPC) measurement of homopolymer PEO was performed in 0.1 M NaNO₃ 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 (molecular weight ranges from 0 to 5×10⁴ and 5×10⁴ to 8×10⁶ g/mol) were calibrated with PEO standards. The absolute molecular weight of homopolymer PEO was performed by GPC measurement through three Waters Styragel columns (pore size 10², 10³ and 10⁴ Å), calibrated by narrow polystyrene standards, and equipped with three detectors: a DAWN H ELEOS (14–154°)(Wyatt multiangle laser light scattering detector, He-Ne 632.8 nm), ViscoStar (Wyatt), and Optilab rEX (Wyatt). THF was used as the eluent at a flow rate of 1.0 mL/min at 35 °C. GPC measurement of graft polymers PEO-g-PCL₄ was carried out at 35 °C using LiBr-added DMF ([LiBr]=15 mM) as eluent with a flow rate of 1.0 ml/min. The system was calibrated with linear PMMA standards. ¹H NMR and ¹³C NMR spectra were recorded on a Bruker (500 MHz) spectrometer in CDCl₃ solvent with tetramethylsilane (TMS) as internal reference. The matrix-assisted laser desorption / ionization time-of-flight mass spectroscopy (MALDI-TOF MS) measurement was performed using a Perspective Biosystem Voyager-DESTR MALDI-TOF MS (PE Applied Biosystems, Framingham, MA). Matrix solution of dithranol (20 mg/mL), polymer (10 mg/mL) and cationizing salt of sodium trifluoroacetate (10 mg/mL) in THF were mixed in the ratio of matrix: cationizing salt: polymer=10:1:2, and 0.8 μ L of mixed solution was deposited on the sample holder. The differential scanning calorimetry (DSC) analysis was carried out on a DSC Q2000 thermal analysis system (Shimadzu, Japan). Samples were first heated from -20 to 120 °C at a heating rate of 10 °C min⁻¹ under nitrogen atmosphere, then cooled to -20 °C at -10 °C min⁻¹ after stopping at 120 °C for 3 min, and finally heating to 120 °C at 10 °C min⁻¹ after stopping at -20 °C for 3 min. The thermal gravimetric analysis (TGA) curves were obtained using a Perkin Elmer Pyris 1 at a heating rate of 10 °C min⁻¹ under nitrogen atmosphere. X-ray diffraction (XRD) measurements were carried out using an XPert PRO (PANalytical) with Cu K α (1.541 Å) radiation (40 kV, 40 mA). Samples were exposed at a scanning rate of 2 θ =5 °C/min between 2 θ values of 10° to 30°. Crystal growth was observed under a polarized optical microscope (POM, Leica, DM 2500P).

Synthesis of Functional PEO with Two Terminal Alkyne Groups (Alkyne-PEO-Alkyne) by Propargylation

The functional Alkyne-PEO-Alkyne was synthesized by modification of HO-PEO-OH with propargyl bromide. First, HO-PEO-OH (3,800 g/mol, 15.00 g, 3.95 mmol) dried by azeotropic distillation with toluene was added into a 500 mL round bottom flask. After the HO-PEO-OH was dissolved in dry THF (200 mL), sodium hydride (NaH, 2.00 g, 83.30 mmol) was added. Then the

ampoule was placed into an ice bath, propargyl bromide (9.20 mL, 126.00 mmol) was added dropwise during 2.0 h and the reaction was continued for another 22 h at room temperature. Finally, the THF solvent was removed by rotary evaporation, and the product was extracted with CH_2Cl_2 , and then the organic layer was dried over MgSO_4 before purification by precipitation into anhydrous ethyl ether by three times. The obtained Alkyne-PEO-Alkyne was dried under vacuum at 45°C for 24 h. ^1H NMR (CDCl_3) δ (ppm): 3.50-3.75 ($-\text{OCH}_2\text{CH}_2\text{O}-$), 4.20 ($-\text{OCH}_2\text{C}\equiv\text{CH}$), 2.45 ($-\text{C}\equiv\text{CH}$). ^{13}C NMR (CDCl_3) δ (ppm): 58.4 ($-\text{OCH}_2\text{C}\equiv\text{CH}$), 70.5 ($-\text{OCH}_2\text{CH}_2-$), 77.1 ($-\text{C}\equiv\text{CH}$), 79.6 ($-\text{C}\equiv\text{CH}$). $M_n(\text{NMR})=5,000$ g/mol, $M_n(\text{MALDI-TOF MS})=4,600$ g/mol, $M_n(\text{GPC})=3,800$ g/mol, PDI=1.20.

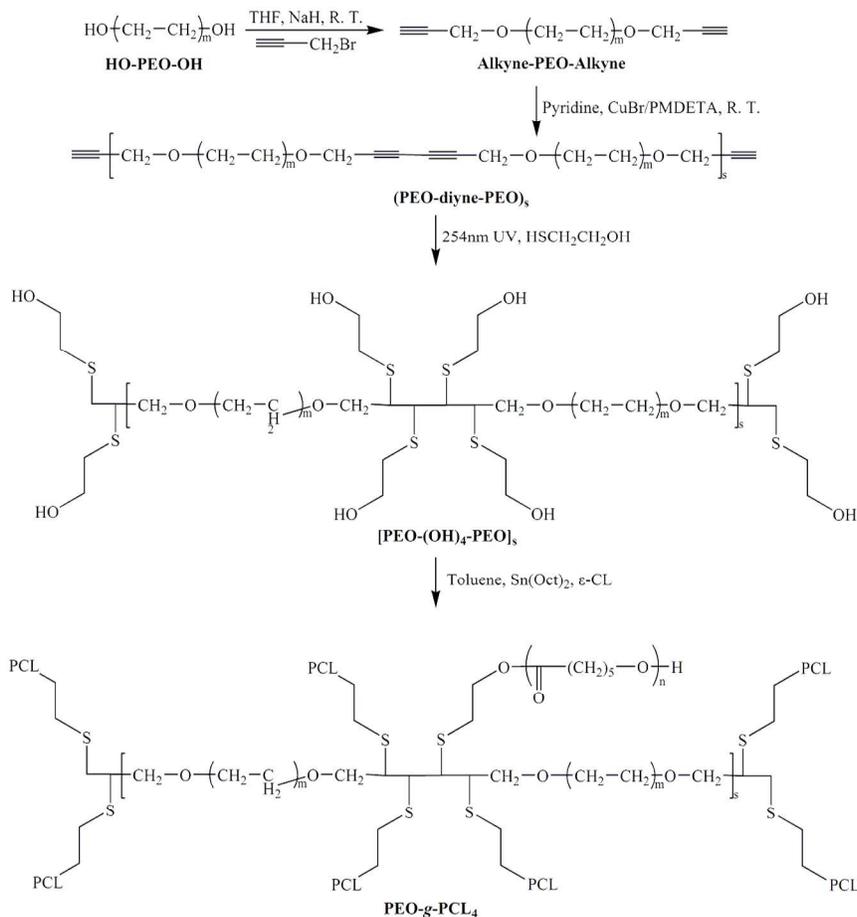
Synthesis of Precursor (PEO-Diyne-PEO)_s Contained Diyne Groups by Glaser Coupling Reaction

Typically, Alkyne-PEO-Alkyne (10.00 g, 2.56 mmol), pyridine (400 mL), CuBr (0.74 g, 5.12 mmol), and PMDETA (1.00 mL, 5.12 mmol) were sequentially added into a 500 mL round bottom flask. The system was proceeded at room temperature in air atmosphere for five days. Finally, the solution was concentrated and the crude products were purified by passing through a neutral alumina column using CH_2Cl_2 as eluent to remove the copper catalyst. After the product was recovered by precipitation into anhydrous ethyl ether, the obtained (PEO-Diyne-PEO)_s was dried

under vacuum at 45°C for 24 h. ^1H NMR (CDCl_3) δ (ppm): 3.50-3.75 ($-\text{OCH}_2\text{CH}_2\text{O}-$), 4.20 ($-\text{OCH}_2\text{C}\equiv\text{C}-$). ^{13}C NMR (CDCl_3) δ (ppm): 58.4 ($-\text{OCH}_2\text{C}\equiv\text{CH}$), 70.5 ($-\text{OCH}_2\text{CH}_2-$, $-\text{C}\equiv\text{C}-$). $M_n(\text{GPC})=33,000$ g/mol, PDI=1.52, $M_w, \text{MALLS}=58,200$ g/mol.

Synthesis of Macroinitiator [PEO-(OH)₄-PEO]_s by Thiol-yne Addition Reaction

The macroinitiator [PEO-(OH)₄-PEO]_s was obtained by thiol-yne addition reaction between (PEO-diyne-PEO)_s and mercaptoethanol. In a typical example, (PEO-Diyne-PEO)_s (2.00 g, 1.00 mmol alkyne groups), 2,2-dimethoxy-2-phenylacetophenone (DMPA) (10.00 mg, 0.04 mmol), mercaptoethanol (2.00 mL, 27.00 mmol) and 40 mL DMF were added into a 50 mL quartz glass vial and degassed by purging with nitrogen for 3.0 min. Then, the system was irradiated with UV (254 nm) for 24 h. After the evaporation of DMF solvent under reduced pressure, the crude product was re-dissolved in CH_2Cl_2 and precipitated into anhydrous ethyl ether for three times, and the obtained [PEO-(OH)₄-PEO]_s was dried under vacuum at 45°C for 24 h. ^1H NMR (CDCl_3) δ (ppm): 3.50-3.75 ($-\text{OCH}_2\text{CH}_2\text{O}-$), 3.90-3.92 ($\text{HOCH}_2\text{CH}_2-$), 2.88 ($-\text{SCH}_2\text{CH}_2-$). ^{13}C NMR (CDCl_3) δ (ppm): 32.3 ($-\text{SCH}_2\text{CH}_2\text{OH}$), 45.2 ($\text{OCH}_2\text{C}(\text{S})\text{C}(\text{S})-$), 62.6 ($-\text{SCH}_2\text{CH}_2\text{OH}$), 70.5 ($-\text{OCH}_2\text{CH}_2-$, $-\text{OCH}_2\text{C}(\text{S})\text{C}(\text{S})-$). $M_n(\text{GPC})=33,000$ g/mol, PDI=2.65.



Scheme 2. The synthetic procedure of barbwire-like graft polymers PEO-g-PCL₄ and their precursors.

Synthesis of Barbwire-like Graft Polymers PEO-g-PCL₄ by ROP Mechanism

By ROP mechanism, the graft polymer PEO-g-PCL₄ was obtained using [PEO-(OH)₄-PEO]_s as macroinitiator. The [PEO-(OH)₄-PEO]_s (0.50 g, 0.5 mmol hydroxyl groups) dried by azeotropic distillation with toluene, freshly distilled ε-CL (2.0 mL, 0.018 mol) and Sn(Oct)₂ solution (5.0 mL, 0.25 mmol, 0.5 equiv. with respect to the hydroxyl groups) were sequentially added into a 100 mL ampoule. After three freeze-thaw cycles at the temperature of liquid nitrogen, the system was charged with nitrogen and the reaction was performed at 110 °C for 12 h. The final graft polymer (PEO-g-PCL₂) was obtained by direct precipitation into petroleum ether (30-60 °C) and dried under vacuum at 45 °C for 24 h. ¹H NMR (CDCl₃) δ (ppm): 1.20–1.65 (-CH₂CH₂CH₂CH₂C(=O)O- on PCL segment), 2.20–2.41 (-CH₂C(=O)O- on PCL), 3.55–3.95 (-CH₂CH₂O- on PEO segment), 3.96–4.13 (-CH₂OC(=O)- on PCL segment). M_{n(NMR),PEO-g-PCL4}=477,000 g/mol. M_{n(GPC), (PEO-g-PCL4)}=88,000 g/mol, PDI=2.25.

Results and Discussion

Synthesis and Characterization of Macroinitiator [PEO-(OH)₄-PEO]_s

The macroinitiator [PEO-(OH)₄-PEO]_s with high molecular weight and controlled functional groups was obtained by sequential propargylation reaction, Glaser coupling reaction and thiol-yne addition reaction (Scheme 2).

The functional Alkyne-PEO-Alkyne was first prepared by end group transformation of HO-PEO-OH with propargyl bromide in the presence of NaH. As shown in our previous work³⁶ or literature³⁷, this system could give the polymer with high efficiency of functionalization. From the ¹H NMR spectrum of Alkyne-PEO-Alkyne (Fig. 1), except for the resonance signals of protons (-OCH₂CH₂-) detected at 3.50-3.75 ppm, the characteristic resonance signals attributed to alkynyl protons (-C≡CH) and methylene protons (-OCH₂C≡CH) on propargyl group were discriminated at 2.44 and 4.21 ppm, respectively. From the ¹³C NMR spectrum of Alkyne-PEO-Alkyne (Fig. 5), the resonance signals of carbons (-C≡CH) and (-OCH₂C≡CH) were detected at 79.6 ppm and 58.4 ppm, respectively, and the signals corresponded to carbons (-OCH₂CH₂-) were detected at

70.5 ppm. However, the signal of carbon (-C≡CH) was overlapped with that of CDCl₃ at 77.1 ppm and could not be discriminated. Also, the MALDI-TOF MS was another versatile measurement to characterize the functionalization of polymers. Fig. 2 showed the MALDI-TOF MS of HO-PEO-OH and the corresponding Alkyne-PEO-Alkyne. Both the mass spectra of HO-PEO-OH and Alkyne-PEO-Alkyne presented the uniform series of peaks spaced with EO units (44.4 Da). Theoretically, the series of molecular masses for HO-PEO-OH can be expressed as equation: MW=M_R+44.0×n+23.0, and that for Alkyne-PEO-Alkyne can be expressed as equation: MW=M_R+44.0×n+(39.0-1.0)×2+23.0, where M_R denoted to the molecular weight of initiator residue, 44.0, 39.0, 23.0 and 1.0 were the mass of EO monomer unit, introduced propargyl group, sodium ion and that of a proton, respectively. Obviously, the m/z difference between peaks of HO-PEO-OH with the corresponding peaks of Alkyne-PEO-Alkyne should be equal to 76.0. From Fig. 2, for example, there was an m/z difference of 76.3 from peak 4568.3 to that of 4644.6, which was rather close to the calculated value of 76.0. Thus, the MALDI-TOF MS further confirmed that the successful modification of PEO ends, and the high efficiency of functionalization of PEO ends would be the prerequisite to the following high molecular weight of precursor (PEO-Diyne-PEO)_s.

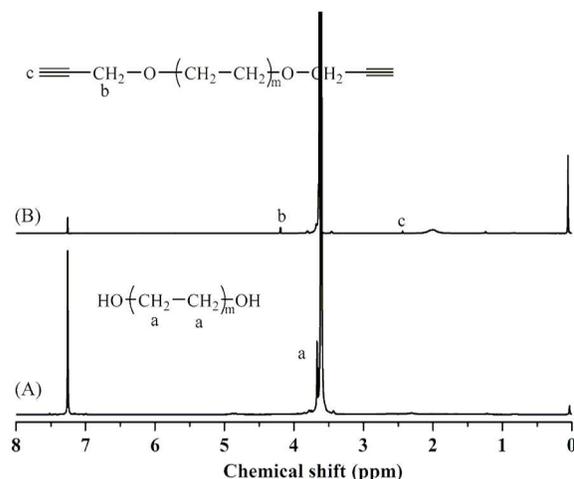


Fig. 1 The ¹H NMR spectra of HO-PEO-OH (A) and Alkyne-PEO-Alkyne (B) (in CDCl₃).

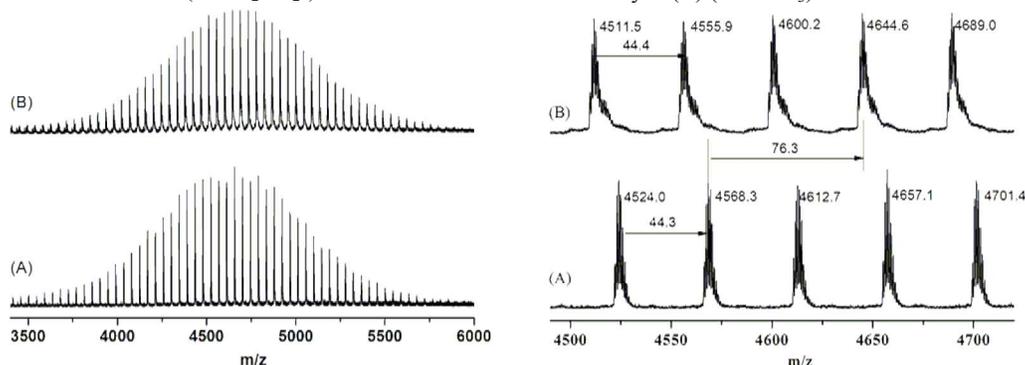


Fig. 2 The MALDI-TOF MS of HO-PEO-OH (A) and Alkyne-PEO-Alkyne (B).

For precursor (PEO-Diyne-PEO)_s, the efficient Glaser coupling reaction was adopted. Actually, the Glaser coupling between alkyne-alkyne groups have been widely used in organic chemistry,³⁸ and very recently, this reaction was also employed in the preparation of various polymeric structures.³⁹⁻⁴² In our previous work, we found that the 1,3-diynes were produced by terminal alkynes and CuBr/PMDETA catalyst system with good yields at room temperature and air atmosphere.⁴³ Based on this efficient reaction, various cyclic polymers have been successfully synthesized with high cyclization efficiency (close to 100%).⁴⁴⁻⁵⁰ Herein, the linear PEO with high molecular weight was also achieved by using this Glaser coupling reaction. The GPC trace of coupled product was shown in **Fig. 3**. From the ¹H NMR spectrum of (PEO-Diyne-PEO)_s (**Fig. 4**), there was almost no obvious change except that the signal of alkynyl protons (-C≡CH) at 2.44 disappeared. Also, compared with the ¹³C NMR spectrum of Alkyne-PEO-Alkyne (**Fig. 5**), the resonance signal of carbon (-C≡C-) at 79.6 ppm was shifted to 70.5 ppm (-C=C-) and overlapped with those on PEO main chain in ¹³C NMR spectrum of (PEO-Diyne-PEO)_s. Both the NMR spectra comprehensively confirmed the happening of Glaser coupling reaction. According to the absolute molecular weight of (PEO-Diyne-PEO)_s obtained by GPC measurement equipped with a multi-angle laser light scattering detector, the degree of Glaser (DG) coupling reaction could be calculated. As shown in **Table 1**, the DG was decreased with the increase of the molecular weight of precursor HO-PEO-OH.

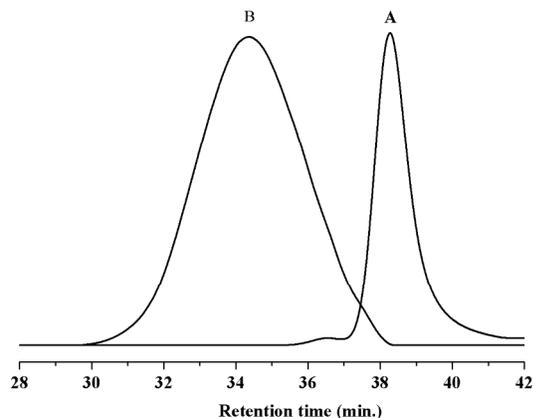


Fig. 3 The GPC traces of HO-PEO-OH (A, $M_n=3,800$ g/mol, PDI=1.20) and (PEO-Diyne-PEO)_s (B, $M_n=33,000$ g/mol, PDI=1.52) (in H₂O eluent).

Subsequently, the macroinitiator [PEO-(OH)₄-PEO]_s was obtained by another efficient thiol-yne addition reaction between 1,3-diyne structures and excess mercaptoethanol, in which the DMF was used as solvent and DMPA was used as photoinitiator under 254 nm UV irradiation. In literatures,⁵¹⁻⁵⁵ the thiol-yne reaction was usually happened on the terminal alkyne groups under 365nm UV irradiation, and rarely work was reported on the 1,3-diyne structures. In this work, we found that there was no any reaction happened on 1,3-diyne when 365nm UV irradiation was adopted, however, this reaction could be carried out smoothly under higher irradiation energy (254nm UV). From the ¹H NMR

spectrum of [PEO-(OH)₄-PEO]_s (**Fig. 4**), the characteristic resonance signal attributed to methylene protons (-OCH₂C≡CH) connected to the triple bond disappeared completely. Furthermore, the ¹³C NMR spectrum in **Fig. 5** also gave the information that the thiol-yne addition reaction was successful. The resonance signal of carbon (-OCH₂C≡C-) at 58.4 ppm were shifted to 70.5 ppm (-OCH₂C(-S-)C(-S)-) and overlapped with those on PEO main chain, and the signals of carbons on introduced groups (-SCH₂CH₂OH) were also detected at 32.3ppm and 62.6 ppm, respectively. Thus, the results from NMR spectra actually confirmed that the each 1,3-diyne had been successfully transformed into hydroxyl groups.

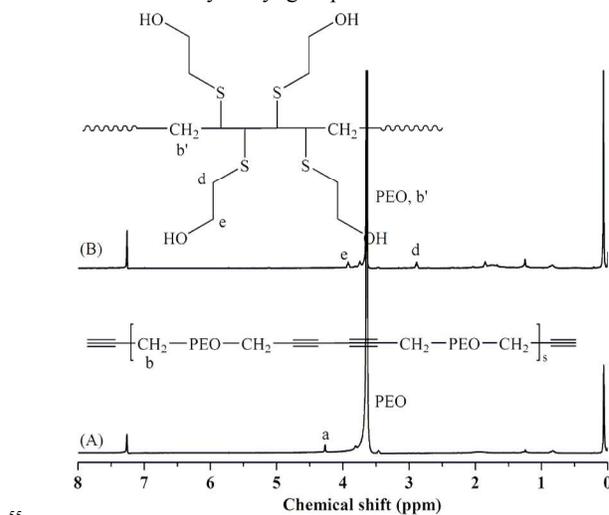


Fig. 4 The ¹H NMR spectra of (PEO-Diyne-PEO)_s (A) and [PEO-(OH)₄-PEO]_s (B) (in CDCl₃).

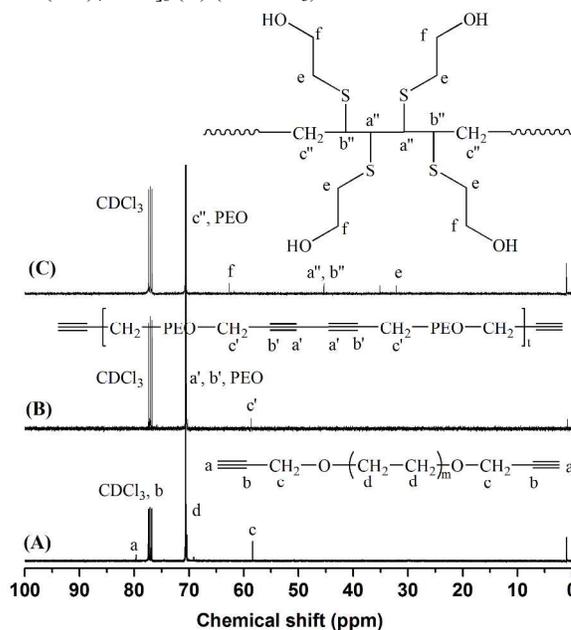


Fig. 5 The ¹³C NMR spectra of Alkyne-PEO-Alkyne (A) (PEO-Diyne-PEO)_s (B) and [PEO-(OH)₄-PEO]_s (C) (in CDCl₃).

Table 1. Data for (PEO-Diyne-PEO)_s and their precursors.

Entry	Samples	M _{n,GPC} (g/mol) ^a	PDI ^a	M _{n,MALDI-TOF MS} ^b (g/mol)	M _{w,MALLS} ^c (g/mol)	DG (Degree of Glaser coupling reaction) ^d
I	HO-PEO-OH	1,800	1.09	2,300		
	(PEO-Diyne-PEO) _s	48,000	1.32		69,800	30
II	HO-PEO-OH	3,800	1.20	4,600		
	(PEO-Diyne-PEO) _s	33,000	1.52		58,200	13
III	HO-PEO-OH	5,500	1.09	6,000		
	(PEO-Diyne-PEO) _s	31,500	1.75		51,800	9

^a Determined by GPC using PEO as standard and H₂O as eluent. ^b Determined by MALDI-TOF MS measurement. ^c Determined by GPC equipped with the multi-angle laser light scattering detector. ^d Determined by the Formula: $DG = M_{w,MALLS,(PEO-Diyne-PEO)_s} / M_{n,MALDI-TOF MS,HO-PEO-OH}$

5 Synthesis and Characterization of Barbwire-like Graft Polymers PEO-g-PCL₄

Using the above [PEO-(OH)₄-PEO]_s as macroinitiator and Sn(Oct)₂ as catalyst, the PCL side chains were introduced onto PEO main chain by “grafting from” strategy (Scheme 2).

Typically, because the Sn(Oct)₂ could react fast with hydroxyl groups to form tin(II) alkoxide initiating species reversibly, the ROP of ε-CL monomers can be proceeded in a living style.⁵⁶ The GPC result of graft polymer PEO-g-PCL₄ was shown in Fig. 6, which gave a monomodal peak. Fig. 7 showed the typical ¹H NMR spectrum of PEO-g-PCL₄, besides the characteristic resonance signals at 3.55-3.95 ppm (-CH₂CH₂O-) for PEO segment, the appearance of the resonance signals at 2.20-2.41 ppm (-CH₂C(=O)O-) and 3.96-4.13 ppm (-CH₂OC(=O)-) for PCL segment confirmed that the synthetic procedure of PEO-g-PCL was successful. According to ¹H NMR spectrum, the weight percentage (W_{NMR,PCL}%) of introduced PCL segment can be evaluated by Formula 1 (Table 2):

$$W_{NMR,PCL} \% = \frac{(A_f/2) \times 114}{(A_o/4) \times 44 + (A_f/2) \times 114} \times 100\% \quad (1)$$

Where, A_a and A_f were the integral area of resonance signals at 3.55-3.95 ppm and 2.20-2.41 ppm, respectively. The value of 114 and 44 were the molecular weight of ε-CL and EO monomer units, respectively.

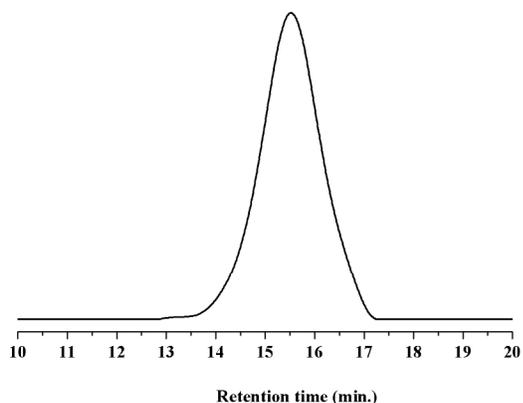


Fig. 6 The GPC trace of graft polymer PEO-g-PCL₄ (in DMF eluent).

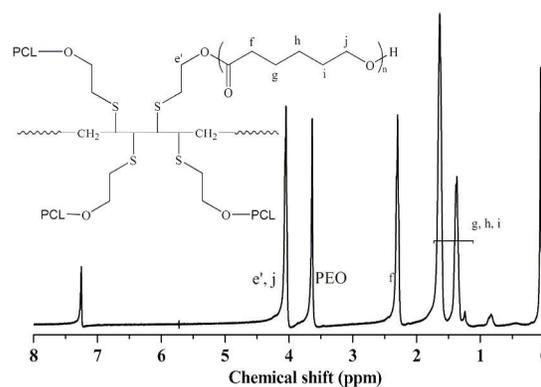


Fig. 7 The ¹H NMR spectrum of graft polymer PEO-g-PCL₄ (in CDCl₃).

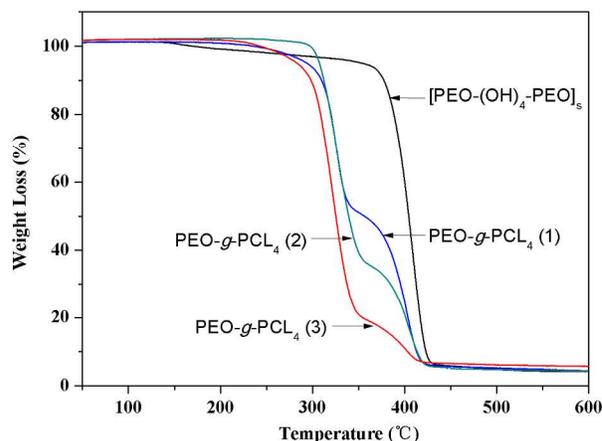


Fig. 8 TGA curves (10 °C min⁻¹) of macroinitiator [PEO-(OH)₄-PEO]_s and graft polymer PEO-g-PCL₄ under N₂ atmosphere.

Alternatively, because the PEO and PCL segments could be decomposed at different temperatures, thus, the accurate compositions of PEO and PCL segments in graft polymers could also be well evaluated by TGA measurement. From Fig. 8, we could observe that the macroinitiator [PEO-(OH)₄-PEO]_s decomposed at 400 °C. When PCL segments were introduced into graft polymers, the first stage appeared at 330 °C was ascribed to the decomposition of PCL segment, while the second stage

appeared at 390 °C was ascribed to that of PEO segment. In all TGA curves, these two stages all have an obvious inflection points and the weight percentage ($W_{TGA,PCL}$) of introduced PCL

segments could be well discriminated (**Table 2**). The obtained values were all rather coincided with that of the corresponding $W_{NMR,PCL}$.

Table 2. Data for graft polymers PEO-g-PCL₄ by using sample in Entry II as precursor.

Entry	$M_{n,GPC}^a$ (g/mol)	PDI ^a	$W_{NMR,CL}^c$ (%)	$W_{TGA,CL}^d$ (%)	T_m^e (°C)		T_c^f (°C)	
					PEO	PCL	PEO	PCL
[PEO-(OH) ₄ -PEO] _s					56.69		41.91	
PEO-g-PCL ₄ (1)	40,000	2.58	50.9	51.2	47.45		28.16	
PEO-g-PCL ₄ (2)	93,000	2.18	68.5	67.3	34.70	54.96	7.41	30.70
PEO-g-PCL ₄ (3)	88,000	2.25	83.5	85.2		56.00		33.13

^a Determined by GPC using PMMA as standard and DMF as eluent for graft polymers. ^b Determined by GPC using PEO as standard and H₂O as eluent. ^c Calculated from **Formula 1** according to ¹H NMR spectra. ^d Calculated according to TGA curves. ^e T_m denotes the melting point of PEO or PCL segments in the second heating run. ^f T_c denotes the crystallization temperature of PEO or PCL segments in the cooling run.

Investigation on Crystallization Behavior of Graft Polymers PEO-g-PCL₄

Typically, the PEO and PCL segments are all characteristic crystalline and biodegradable polymers, which had been well studied in literatures.^{57, 58} For crystalline polymers, the crystallization behavior would seriously affect their biodegradability.⁵⁹⁻⁶¹ Thus, in this contribution, the crystallization behavior of this novel barbwire-like graft copolymers PEO-g-PCL₄ were also well investigated by XRD, DSC and POM instruments.

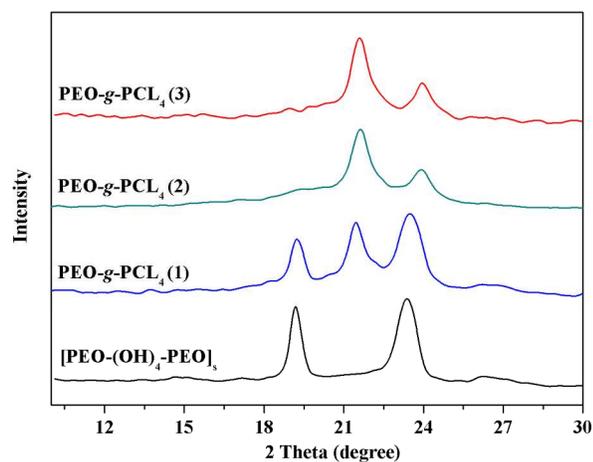


Fig. 9 XRD patterns of graft polymers PEO-g-PCL₄.

First, the XRD instrument was a very efficient method to determine the crystalline structure of polymers. According to the literatures, the linear PCL showed two intensive diffraction peaks at 21.6° and 23.9°^{62,63} and the linear PEO showed two intensive diffraction peaks at 19.1° and 23.3°, respectively.⁶⁴ Also, the architecture of polymers almost had no effect on their diffraction peaks in XRD measurement. Thus, from the XRD patterns, we could easily determine the crystalline compositions of graft polymers. From **Fig. 9**, we can observe that, for macroinitiator [PEO-(OH)₄-PEO]_s, the characteristic diffraction peak

corresponding to PEO crystallite could be discriminated at 19.1°. When PCL segments were grafted onto PEO main chain (PEO-g-PCL₄ (1)), besides the diffraction peak at 19.1°, a new characteristic diffraction peak corresponding to PCL crystal also appeared at 21.6°, which confirmed that both PEO and PCL were crystallized. With the increase of PCL content, in the sample PEO-g-PCL₄ (2) and PEO-g-PCL₄ (3), the signals to PEO crystal could not be discriminated anymore, while the strong signals attributed to the PCL crystalline were well observed.

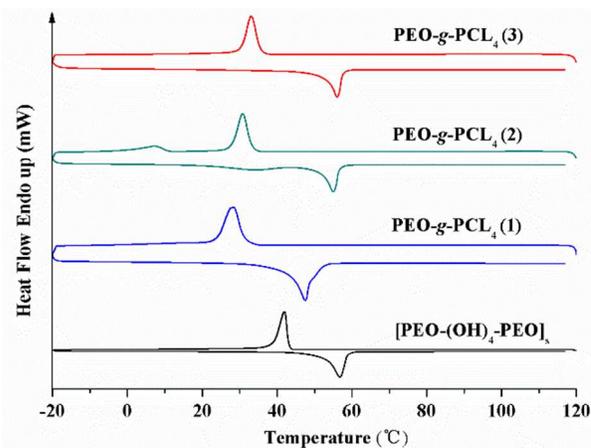


Fig. 10 DSC curves (10 °C min⁻¹) of macroinitiator [PEO-(OH)₄-PEO]_s and graft polymers PEO-g-PCL₄ in the cooling run and the second heating run.

From DSC instrument, the crystallization behaviors of macroinitiator [PEO-(OH)₄-PEO]_s and graft polymers PEO-g-PCL₄ were also investigated (**Fig. 10**). In order to eliminate the effect of thermal history, the crystallization temperature (T_c) was obtained from the cooling run, and the melting temperature (T_m) was obtained from the second heating run. According to the literature, the T_m and T_c of linear PCL were observed at 57.3 °C and 28.9 °C, while the T_m and T_c were observed at 59.5 °C and 37.8 °C, respectively.⁶⁵ Herein, for [PEO-(OH)₄-PEO]_s, the T_m and T_c was observed at 56.69 °C and 41.91 °C, respectively. After the PCL segment was introduced onto PEO main chain, for

sample PEO-g-PCL₄ (**1**), the T_m and T_c were dramatically decreased to 47.45 °C and 28.16 °C. By combination with XRD results, we can conclude that the PEO and PCL segment formed the cocrystal structure and only one T_m or T_c was discriminated. However, when the content of PCL segment was increased to 67.3 % for sample PEO-g-PCL₄ (**2**), the crystalline structure of PEO segment also disappeared and that of PCL segment became the dominant part. The almost negligible T_m or T_c appeared at 34.70 °C and 7.41 °C were inferred as that of PEO segment, while the increased and well discriminated T_m or T_c at 54.96 °C and 30.70 °C were ascribed to PCL part, respectively. When the content of PCL segment was further increased to 85.2 % for sample PEO-g-PCL₄ (**3**), the T_m or T_c of PCL segment were increased to 56.00 °C and 33.13 °C, respectively. Thus, all these DSC results were rather coincided with that from XRD patterns. Obviously, with the increase of PCL length on side chains, the PEO main chain was surrounded and restricted, and the crystalline structure was transformed and dominated by PCL part.

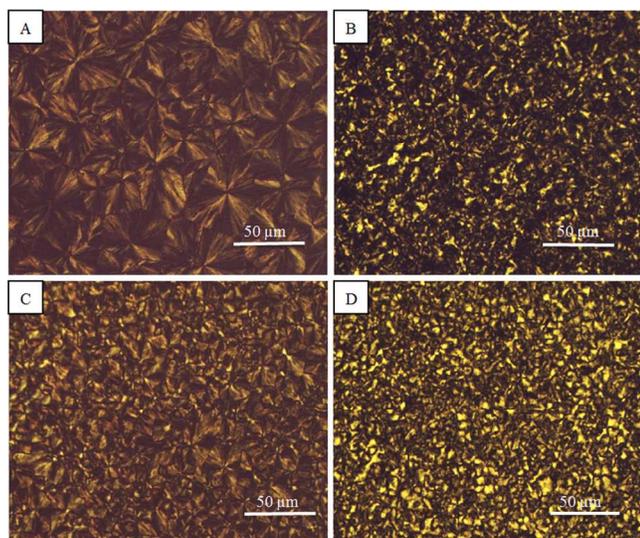


Fig. 11 The optical microscopy images of [PEO-(OH)₄-PEO]_s (A), PEO-g-PCL₄ (**1**) (B), PEO-g-PCL₄ (**2**) (C), and PEO-g-PCL₄ (**3**) (D).

Finally, the detailed crystalline structure of graft polymers were also monitored and confirmed by POM instrument. From **Fig. 11**, we could observe that the [PEO-(OH)₄-PEO]_s formed the larger spherulite, while all the graft polymers formed the smaller spherulite. Especially, the more PCL content designed into graft polymer (from 51.2 % of PEO-g-PCL₄ (**1**) to 85.2 % of PEO-g-PCL₄ (**3**)), the smaller size of spherulite formed, which was rather accorded with the literatures that the PCL segment was usually crystallized in a relatively slow rate and tend to form the smaller crystalline structure.⁶⁶⁻⁶⁸ The results from POM instrument further verified the conclusions from DSC and XRD instruments.

According to the literatures,⁶⁹⁻⁷⁴ for the copolymer of PCL-*b*-PEO, PEO-*b*-PCL-*b*-PEO or PCL-*b*-PEO-*b*-PCL with the simplest topology, it was reported that the crystallization behavior of these copolymers depend on the length of each block. For example, the

PEO segment in PCL-*b*-PEO could still crystallize even when its weight fraction was only 14.0 %. However, in this contribution, the signals corresponded to the crystallization of PEO segment could not be discriminated anymore by the above XRD, DSC and POM instruments when the weight fraction of PEO segment was lowered to 14.8 % (PEO-g-PCL₄ (**3**)). Obviously, all the above results confirmed that the architecture and compositions of copolymers actually have separate effects on their physical properties.

Conclusions

By combination of ROP mechanism, Glaser coupling with thiol-ene addition reaction, the biodegradable and biocompatible amphiphilic graft polymers PEO-g-PCL₄ were successfully synthesized via the grafting from strategy. This novel versatile method might be further used to synthesize plenty of barbwire-like graft polymers by modulating the compositions of main chains and side chains. Also, by means of DSC, XRD, and POM instruments, the crystallization behaviors of graft polymers PEO-g-PCL₄ were investigated and compared, and the results gave the conclusion that the architecture and compositions of copolymers could give separate effects on physical properties.

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Notes and references

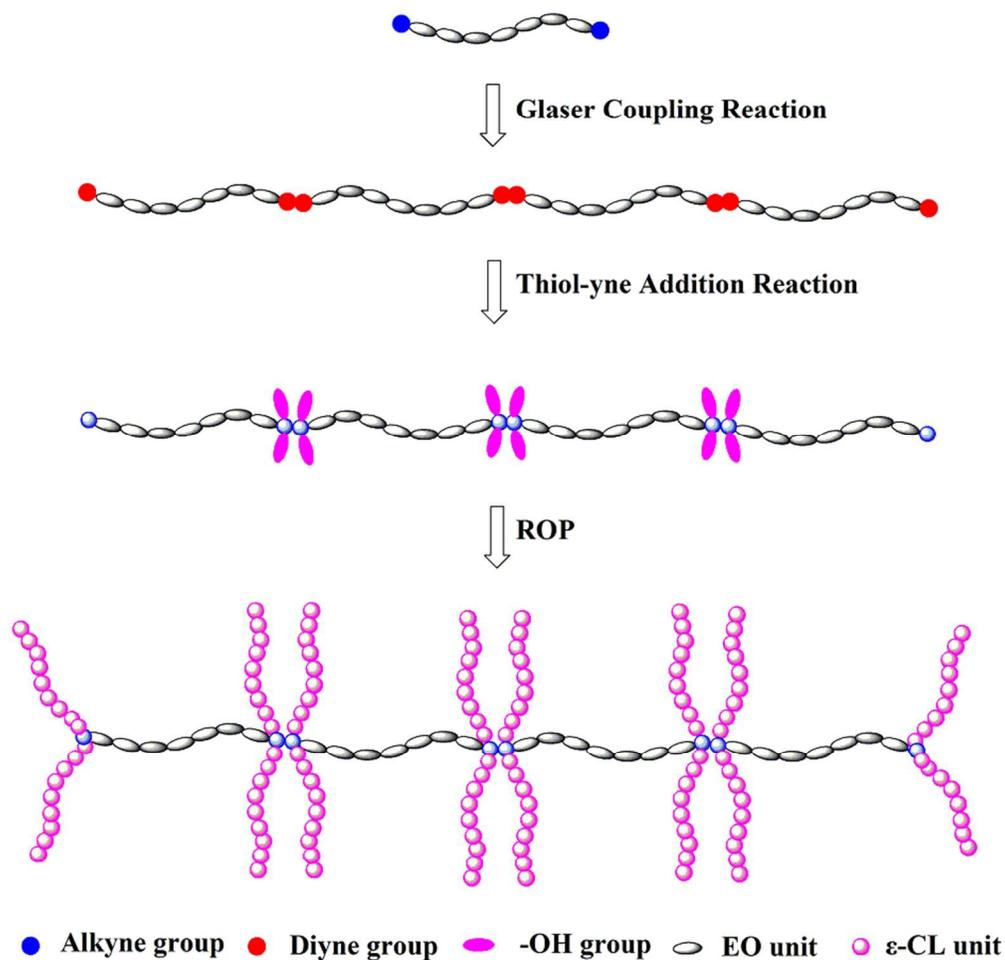
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331x318mm (72 x 72 DPI)