



# Synthesis and characterization of graft copolymers with poly(epichlorohydrin-co-ethylene oxide) as backbone by combination of ring-opening polymerization with living anionic polymerization



Tingting Tang, Xiaoshan Fan, Ying Jin, Guowei Wang\*

State Key Laboratory of Molecular Engineering of Polymers, Department of Macromolecular Science, Fudan University, Shanghai 200433, China

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## ABSTRACT

Series of graft copolymers with [Poly(epichlorohydrin-co-ethylene oxide)] [Poly(ECH-co-EO)] as backbone and polystyrene (PS), poly(isoprene) (PI) or their block copolymers as side chains were successfully synthesized by combination of ring-opening polymerization (ROP) with living anionic polymerization. The Poly(ECH-co-EO) with high molecular weight ( $M_n = 3.3 \times 10^4$  g/mol) and low polydispersity index (PDI = 1.34) was firstly synthesized by ring-ROP using ethylene glycol potassium as initiator and triisobutylaluminium (*i*-Bu<sub>3</sub>Al) as activator. Subsequently, by “grafting onto” strategy, the graft copolymers Poly(ECH-co-EO)-*g*-PI, Poly(ECH-co-EO)-*g*-PS and Poly(ECH-co-EO)-*g*-(PI-*b*-PS) were obtained using the coupling reaction between living PI<sup>-</sup>Li<sup>+</sup>, PS<sup>-</sup>Li<sup>+</sup> or PS-*b*-PI<sup>-</sup>Li<sup>+</sup> species capped with or without 1,1-diphenylethylene (DPE) agent and chloromethyl groups on poly(ECH-co-EO). By model experiment, the addition of DPE agent was confirmed to have an important effect on the grafting efficiency at room temperature. Finally, the target graft copolymers and intermediates were characterized by SEC, <sup>1</sup>H NMR, MALLS and FTIR in detail, and thermal behaviours of the graft copolymers were also investigated by DSC measurement.

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## 1. Introduction

Recently, much attention has been paid to graft polymers due to their wide applications in different areas, from complex materials to biomedical materials [1–7]. In order to the target graft polymers, various polymerization mechanisms, such as “living” anionic polymerization, nitroxide mediated radical polymerization (NMRP) [8], atom-transfer radical polymerization (ATRP) [9], reversible addition fragmentation transfer polymerization (RAFT) [10], single-electron transfer-mediated living radical polymerization (SET-LRP) [11,12], ring-opening polymerization (ROP) and others in a “living”/controlled manner, have been commonly used in the synthetic process by combination with “grafting from”, “grafting onto” or “grafting through” strategies [13–19], as well as with some efficient modification methods. Typically, variations of the composition, length, polydispersity index (PDI) of backbones and side chains, as well as the grafting density, have great impacts on physical properties of graft polymers [20,21]. Worth noting is that, the backbones of graft polymers are always consisted by polystyrene (PS) [22–24],

poly(acrylic acid) (PAA) [25], poly(hydroxyethyl methacrylate) (PHEMA) [26], poly( $\epsilon$ -caprolactone) (PCL) [27–29] and so on. However, poly(ethylene oxide) (PEO) is rarely constructed into the backbone of graft polymers, which is a classical soft segment in the investigation of multi-constitution polymers and might bring the polymers with special properties due to the good solubility both in water and organic solvents.

Graft polymers with PEO backbone were first synthesized by Xie et al. using styrene-capped PEO macromonomer [30]. In our previous work, we explored another method to synthesize functional PEO from ethoxyethyl glycidyl ether (EEGE) or 4-glycidyl-2,2,6,6-tetramethylpiperidyl-1-oxyl (GTEMPO) monomers, and various graft polymers or sun-shaped polymers with PEO backbone have been realized from the PEO pendant with hydroxyl groups or TEMPO groups [31–44]. However, the monomers for functional PEO backbone are always limited by complicated synthetic procedure of epoxides with substituent groups, and the molecular weight of PEO backbone are limited below 20,000 g/mol because of the side reactions in ROP of these epoxides.

Alternatively, the multifunctional polyethers with high molecular weight can be realized by polymerization of epichlorohydrin (ECH) monomers and used as a candidate main chain to graft

\* Corresponding author. Tel.: +86 21 65643049.

E-mail address: [gwwang@fudan.edu.cn](mailto:gwwang@fudan.edu.cn) (G. Wang).

polymers. Poly(epichlorohydrin) (PECH) and the copolymers contained ECH units, which can be regarded as attaching chloromethyl to the PEO backbone, are a class of functional polymeric materials with specific characteristics for applications in various domains [45]. For example, the poly(epichlorohydrin-co-ethylene oxide) [Poly(ECH-co-EO)] is a commercial elastomer, which is widely used as fuel hoses, air ducts, seals, diaphragms and solid electrolyte [45]. Using ATRP mechanism, Yagci et al. synthesized the poly(epichlorohydrin-g-methyl methacrylate) (PECH-g-PMMA), poly(epichlorohydrin-g-styrene) (PECH-g-PS) and (PECH-*b*-PS)-g-PMMA [46,47]. With Poly(ECH-co-EO) as backbone, the Poly(ECH-co-EO)-g-PMMA was also obtained. Regrettably, as the primary chlorine and second chlorine were usually inert [48,49], not all chloromethyl groups could be activated to initiate the ATRP and the grafting efficiencies were usually below 30%. Additionally, the PECH backbone was modified and the graft polymer PECH-g-PS was obtained by photopolymerization by Ismail et al. [50]. Using living anionic polymerization mechanism, Barrie et al. synthesized the PECH-g-PS by coupling living species onto PECH. However, their results showed that the PECH would suffer base cleavage or photochemical degradation in the presence of *n*-butyl lithium or PS<sup>-</sup>Li<sup>+</sup> anions [51,52], and the halogen-metal exchange reaction would affect the coupling reaction and low grafting efficiency was accompanied [53–57]. Especially, the above used PECH and Poly(ECH-co-EO) were usually obtained with low molecular weight and high PDIs. Thus, the synthesis of PECH or copolymers contained ECH units with controlled molecular weight and low polydispersity indexes (PDIs), as well as its application into the graft polymers are still challenge works to polymer chemists.

In this paper, poly(epichlorohydrin-co-ethylene oxide) [Poly(ECH-co-EO)] with high molecular weight ( $M_n = 3.3 \times 10^4$  g/mol) and low PDI (PDI = 1.34) was synthesized by ROP of epichlorohydrin and ethylene oxide using ethylene glycol potassium as initiator and triisobutylaluminium (*i*-Bu<sub>3</sub>Al) as activator. The graft copolymers were then obtained by coupling reaction between the chloromethyl groups and living polystyrene (PS) or poly(isoprene) (PI) species capped with or without 1,1-diphenylethylene (DPE) agent. Because of good nucleophilicity and relatively weak basicity, the addition of DPE agent was confirmed as a better choice to high grafting efficiency on Poly(ECH-co-EO). In order to confirm this hypothesis, the model experiment, in which the poly(epichlorohydrin)-(*n*-butyl) [Poly(ECH-co-EO)-Bu] and poly(epichlorohydrin)-(DPE-*n*-butyl) [Poly(ECH-co-EO)-(DPE-Bu)] were

synthesized, and the efficiency of halogen substitution were studied. The model experiment could be regarded as a solid evidence for the DPE enhancing grafting efficiency of coupling reactions (Scheme 1).

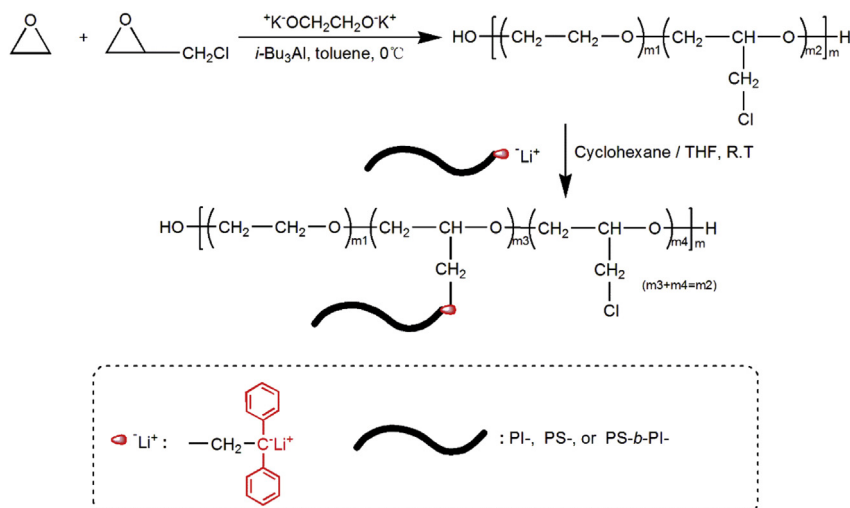
## 2. Experimental

### 2.1. Materials

Ethylene oxide (EO, Sinopharm Chemical Reagent Co., Ltd (SCR), 98%) was dried with calcium hydride (CaH<sub>2</sub>) for 48 h and then distilled before use. Styrene (St, >99.5%) was washed with 10% NaOH aqueous solution followed by water three times successively, dried over CaH<sub>2</sub> and distilled under reduced pressure. Epichlorohydrin (AR, Shanghai Chemical Reagent Co., Ltd) and 1,1-diphenylethylene (DPE, Merck Millipore Chemicals Co., Ltd) were dried over CaH<sub>2</sub> and distilled under reduced pressure just before use. Isoprene (>99%, Tokyo Chemical Industry Co., Ltd), toluene (AR, 99.5%, Shanghai DaHe Chemical Reagent Co., Ltd) and cyclohexane (AR, 99.5%, Shanghai DaHe Chemical Reagent Co., Ltd) were distilled from CaH<sub>2</sub> just before use. Tetrahydrofuran (THF, SCR, 99%) were refluxed over sodium wire, then distilled from sodium naphthalenide solution. Triisobutylaluminium (*i*-Bu<sub>3</sub>Al, 1.1 M in toluene, Aldrich), petroleum ether (60–90 °C, Jiangsu QiangSheng Functional Chemical Reagent Co., Ltd), *n*-butyllithium (*n*-Bu<sup>-</sup>Li<sup>+</sup>, 1.6 M in hexane, Amethyst Chemicals) and methanol (CH<sub>3</sub>OH AR, 99.5%, Shanghai LingFeng Chemical Reagent Co.) were used as received. Ethylene glycol (99.0%, SCR) was dried by azeotropic distillation with toluene. Diphenylmethylpotassium (DPMK) solution was freshly prepared by the reaction of potassium naphthalenide with diphenylmethane in THF according to the literature [58], and the concentration was 0.55 mol/L. All other reagents and solvents were purchased from SCR and used as received except for declaration.

### 2.2. Characterization

Size-exclusion chromatography (SEC) was performed on an Agilent 1100 with a G1310A pump, a G1310A refractive-index detector and a G1314A variable-wavelength detector with THF as eluent at a flow rate of 1.0 mL/min at 35 °C. One 5 μm LP gel column (molecular range 500–2 × 10<sup>4</sup> g/mol) and two 5 μm LP gel mixed bed columns (molecular range 200–3 × 10<sup>6</sup> g/mol) were calibrated



Scheme 1. The synthetic procedure of graft copolymers.

by polystyrene (PS) standards.  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra were obtained at a DMX500 MHz spectrometer with  $\text{CDCl}_3$  as solvent. Fourier Transform Infrared (FTIR) spectra were recorded at room temperature using a Nicolet 6700 spectrometer in the range  $4000\text{--}400\text{ cm}^{-1}$  with  $4\text{ cm}^{-1}$  resolution. Samples were prepared by dissolving in THF and tested with a diamond ATR accessory. Elemental analysis of Poly(ECH-co-EO) samples were carried out for hydrogen and carbon elements on VARIO EL III (Elementar). Differential Scanning Calorimetry (DSC) experiments were performed on a TA Q2000 thermal analysis system. Samples were first heated from  $-80$  to  $130\text{ }^\circ\text{C}$  at a heating rate of  $10\text{ }^\circ\text{C}/\text{min}$  under nitrogen atmosphere, then cooling to  $-80\text{ }^\circ\text{C}$  at  $10\text{ }^\circ\text{C}/\text{min}$  after stopping at  $130\text{ }^\circ\text{C}$  for 2 min, and finally heating to  $130\text{ }^\circ\text{C}$  at  $10\text{ }^\circ\text{C}/\text{min}$  after stopping at  $-80\text{ }^\circ\text{C}$  for 2 min. The glass transition temperature ( $T_g$ ) was taken as the inflection point of the glass transition step on the last heating.

### 2.3. Synthesis of backbone [poly(epichlorohydrin-co-ethylene oxide)] [Poly(ECH-co-EO)]

The Poly(ECH-co-EO) was prepared by ROP of epichlorohydrin and EO monomers. Typically, into a 500 mL dry ampoule with a magnetic stirrer inside, the ethylene glycol (0.12 mL, 2.4 mmol), DPMK (7.00 mL, 0.5 mol/L), epichlorohydrin (40 mL, 0.51 mol), EO (20 mL, 0.26 mol) and toluene (350 mL) were sequentially charged. Then, the ampoule was placed into a  $0\text{ }^\circ\text{C}$  ice bath and  $i\text{-Bu}_3\text{Al}$  (20 mL, 22.0 mmol) solution was injected quickly, and the solution was kept at  $0\text{ }^\circ\text{C}$  and stirred for 24 h. After termination by methanol (4.0 mL), the solvent was evaporated. The products was again dissolved in THF and precipitated into petroleum ether ( $60\text{--}90\text{ }^\circ\text{C}$ ) for three times. The final viscous product Poly(ECH-co-EO) was dried in vacuum at  $40\text{ }^\circ\text{C}$  for 12 h till to a constant weight.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , TMS),  $\delta$  (ppm): 3.50–4.00 (m,  $-\text{CH}_2\text{CH}_2\text{O}-$ ,  $-\text{CH}_2\text{CH}(\text{CH}_2\text{Cl})-$ ).  $M_n(\text{SEC}) = 3.33 \times 10^4\text{ g/mol}$ , PDI = 1.34. FTIR: 733, 907, 1065, 1460, 2857  $\text{cm}^{-1}$ . Elemental analysis: C, 45.59%; H, 6.98%.

### 2.4. Synthesis of graft copolymers [Poly(ECH-co-EO)]-g-PI and [Poly(ECH-co-EO)]-g-PS

The graft copolymers [Poly(ECH-co-EO)]-g-PI and [Poly(ECH-co-EO)]-g-PS were obtained by coupling reaction between chloromethyl groups on poly(ECH-co-EO) and the living species  $\text{PI}^- \text{Li}^+$  or  $\text{PS}^- \text{Li}^+$  capped with or without DPE agent, respectively. Taking the preparation of [Poly(ECH-co-EO)]-g-PI as an example, isoprene (15.0 mL, 150 mmol), cyclohexane (200 mL) and THF (10 mL) were charged into a 500 mL dry ampoule under nitrogen atmosphere. Then,  $n\text{-Bu}^- \text{Li}^+$  solution (6.4 mL, 10 mmol) was injected by a syringe under magnetic stirring, and the yellow macroanions of  $\text{PI}^- \text{Li}^+$  was produced. After 5.0 h, the DPE (2.16 g, 12 mmol) agent was added to cap the macroanions, and the solution turned into deep red immediately. After another 2.0 h, the backbone of Poly(ECH-co-EO) (1.10 g, 0.033 mmol) purified with three azeotropic distillation cycles by toluene was introduced into the ampoule, and the viscosity of solution increased rapidly. Finally, the reaction was terminated by methanol, and the unreacted homopolymer of PI was removed by fractional precipitation using dichloromethane ( $\text{CH}_2\text{Cl}_2$ )/methanol as solvent/precipitant system. The final product [Poly(ECH-co-EO)]-g-PI was dried under vacuum at  $40\text{ }^\circ\text{C}$  for 12 h till to a constant weight. Under the case of coupling reaction without the addition of DPE agent, the yellow macroanions of  $\text{PI}^- \text{Li}^+$  were used to couple with Poly(ECH-co-EO) directly, and the other procedure was similar to the above.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , TMS),  $\delta$  (ppm): 3.50–4.00 (m,  $-\text{CH}_2\text{CH}_2\text{O}-$ ,  $-\text{CH}_2\text{CH}(\text{CH}_2-)-$ ), 4.95 (d,  $-\text{CH}=\text{CH}_2$ ), 4.41–4.78 (s,  $-\text{C}(\text{CH}_3)=\text{CH}_2$ ), 4.78–5.17 (t,  $-\text{CH}=\text{C}(\text{CH}_3)-$ ), 5.54–5.84 (t,  $-\text{CH}=\text{CH}_2$ ), 6.94–7.30 (m,  $-\text{C}_6\text{H}_5$ ).  $M_n(\text{SEC})$ , [Poly(ECH-co-EO)]-g-

$\text{PI} = 6.72 \times 10^4\text{ g/mol}$ , PDI = 1.34. FTIR: 3068, 2922, 2854, 1642, 1494, 1443, 1373, 1101, 1031, 1001, 884, 753, 698  $\text{cm}^{-1}$ .

Similarly, the graft copolymers [Poly(ECH-co-EO)]-g-PS were obtained by changing the above isoprene monomers as styrene monomers.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , TMS),  $\delta$  (ppm): 3.50–4.00 (m,  $-\text{CH}_2\text{CH}_2\text{O}-$ ,  $-\text{CH}_2\text{CH}(\text{CH}_2-)-$ ), 6.14–7.41 (m,  $-\text{C}_6\text{H}_5$ ).  $M_n(\text{SEC})$ , [Poly(ECH-co-EO)]-g-PS =  $6.85 \times 10^4\text{ g/mol}$ , PDI = 1.32. FTIR: 3082, 3058, 3025, 2923, 2854, 1943, 1870, 1802, 1744, 1600, 1492, 1451, 1375, 1245, 1105, 1029, 905, 841, 755, 697  $\text{cm}^{-1}$ .

### 2.5. Synthesis of graft copolymers [Poly(ECH-co-EO)]-g-(PI-b-PS)

The synthetic procedure of graft copolymers [Poly(ECH-co-EO)]-g-(PI-b-PS) with block polymer as side chains was similar to that of [Poly(ECH-co-EO)]-g-PI and [Poly(ECH-co-EO)]-g-PS, except that the living species  $\text{PI}^- \text{Li}^+$  or  $\text{PS}^- \text{Li}^+$  were replaced by  $\text{PI-b-PS}^- \text{Li}^+$ . The  $\text{PS-b-PI}^- \text{Li}^+$  were obtained by sequential introduction of styrene and isoprene monomers, and the unreacted block polymers of  $\text{PS-b-PI}$  were also removed by fractional precipitation using  $\text{CH}_2\text{Cl}_2$ /methanol as solvent/precipitant system. The final products were dried under vacuum at  $40\text{ }^\circ\text{C}$  for 12 h till to a constant weight. [Poly(ECH-co-EO)]-g-(PI-b-PS)  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , TMS),  $\delta$  (ppm): 3.50–4.00 (m,  $-\text{CH}_2\text{CH}_2\text{O}-$ ,  $-\text{CH}_2\text{CH}(\text{CH}_2-)-$ ), 4.95 (d,  $-\text{CH}=\text{CH}_2$ ), 4.41–4.78 (s,  $-\text{C}(\text{CH}_3)=\text{CH}_2$ ), 4.78–5.17 (t,  $-\text{CH}=\text{C}(\text{CH}_3)-$ ), 5.54–5.84 (t,  $-\text{CH}=\text{CH}_2$ ), 6.94–7.30 (m,  $-\text{C}_6\text{H}_5$ ). FTIR: 3448, 3064, 3025, 2922, 1943, 1870, 1801, 1774, 1640, 1601, 1491, 1458, 1375, 1096, 1029, 1001, 883, 754, 699  $\text{cm}^{-1}$ .  $M_n(\text{SEC})$ , [Poly(ECH-co-EO)]-g-(PI-b-PS) =  $1.66 \times 10^5\text{ g/mol}$ , PDI = 1.42.

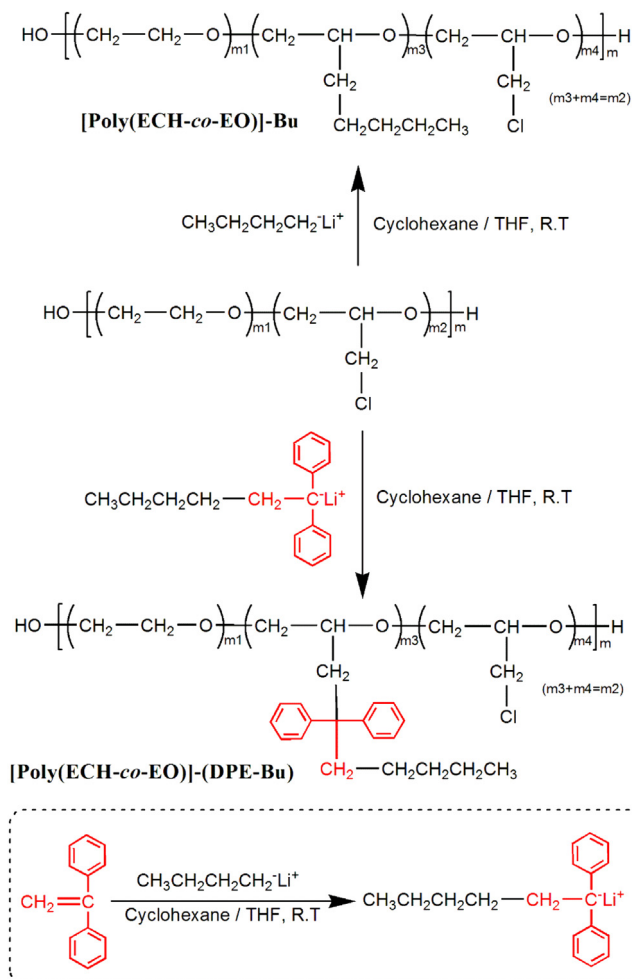
### 2.6. Model experiments by reactions between Poly(ECH-co-EO) and $\text{Bu}^- \text{Li}^+$ or $\text{Bu-DPE}^- \text{Li}^+$

To verify the influence of DPE agent on coupling reaction, the model experiments between Poly(ECH-co-EO) and  $\text{Bu}^- \text{Li}^+$  or  $\text{Bu-DPE}^- \text{Li}^+$  were carried out for polymers [Poly(ECH-co-EO)]-Bu or [Poly(ECH-co-EO)]-(DPE-Bu), respectively (Scheme 2). The  $\text{Bu-DPE}^- \text{Li}^+$  was obtained by direct addition of  $\text{Bu}^- \text{Li}^+$  into DPE solution, and the dry Poly(ECH-co-EO) was reacted with  $\text{Bu}^- \text{Li}^+$  or  $\text{Bu-DPE}^- \text{Li}^+$  directly. After the reaction was terminated by methanol, the small molecules were removed by precipitation in  $\text{CH}_2\text{Cl}_2$ /methanol system. The final products were dried under vacuum at  $40\text{ }^\circ\text{C}$  for 12 h till to a constant weight. [Poly(ECH-co-EO)]-Bu,  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , TMS),  $\delta$  (ppm): 0.70–0.96 (t,  $-\text{CH}_3$ ), 0.96–1.43 (m,  $-\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2-$ ), 3.50–4.00 (m,  $-\text{CH}_2\text{CH}_2\text{O}-$ ,  $-\text{CH}_2\text{CH}(\text{CH}_2-)-$ ).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , TMS),  $\delta$  (ppm): 14.28 ( $-\text{CH}_3$ ), 22.91 ( $-\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ ), 29.98 ( $-\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ ), 43.89 ( $-\text{CH}_2\text{Cl}$ ), 69.59–71.13 ( $-\text{CHCH}_2\text{O}-$  &  $-\text{CH}_2\text{CH}_2\text{O}-$ ), 78.99–79.26 ( $-\text{CHCH}_2\text{O}-$  &  $-\text{CH}_2\text{Cl}$ ). [Poly(ECH-co-EO)]-(DPE-Bu),  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , TMS),  $\delta$  (ppm): 0.68–1.00 ppm (m,  $-\text{CH}_3$ ), 1.00–1.38 (m,  $-\text{CH}_2$ ), 1.60–2.47 (m,  $-\text{CH}_2-(\text{Ph})_2$ ), 3.50–4.00 (m,  $-\text{CH}_2\text{CH}_2\text{O}-$ ,  $-\text{CH}_2\text{CH}(\text{CH}_2-)-$ ).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , TMS),  $\delta$  (ppm): 14.38 ( $-\text{CH}_3$ ), 22.80, 24.02 ( $-\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ ), 32.83 ( $-\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ ), 38.67, 40.32 ( $-\text{CH}_2\text{C}(\text{Ph})_2\text{CH}_2-$ ), 41.95 ( $-\text{CH}_2\text{C}(\text{Ph})_2-$ ), 51.13 ( $-\text{CH}_2\text{Cl}$ ), 69.13, 70.81, 74.27 ( $-\text{CH}_2\text{CH}_2\text{O}-$  &  $-\text{CH}_2\text{CH}(\text{CH}_2\text{Cl})\text{O}$ ), 76.48 ( $-\text{CH}(\text{CH}_2\text{C}(\text{Ph})_2)\text{CH}_2\text{O}-$ ), 78.39, 79.13 ( $-\text{CH}_2\text{CH}(\text{CH}_2\text{Cl})\text{O}$  &  $-\text{CH}(\text{CH}_2\text{C}(\text{Ph})_2)\text{CH}_2\text{O}-$ ).

## 3. Results and discussion

### 3.1. Synthesis and characterization of Poly(ECH-co-EO)

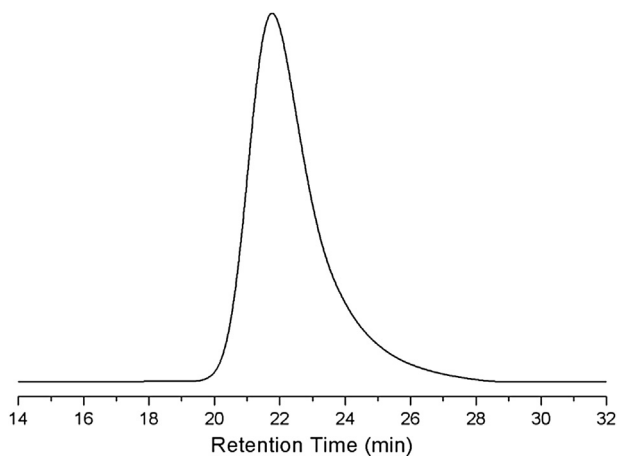
The Poly(ECH-co-EO) was synthesized by ROP of epichlorohydrin and EO monomers using ethylene glycol potassium as initiator and  $i\text{-Bu}_3\text{Al}$  as activator. Fig. 1 showed the SEC trace of Poly(ECH-co-



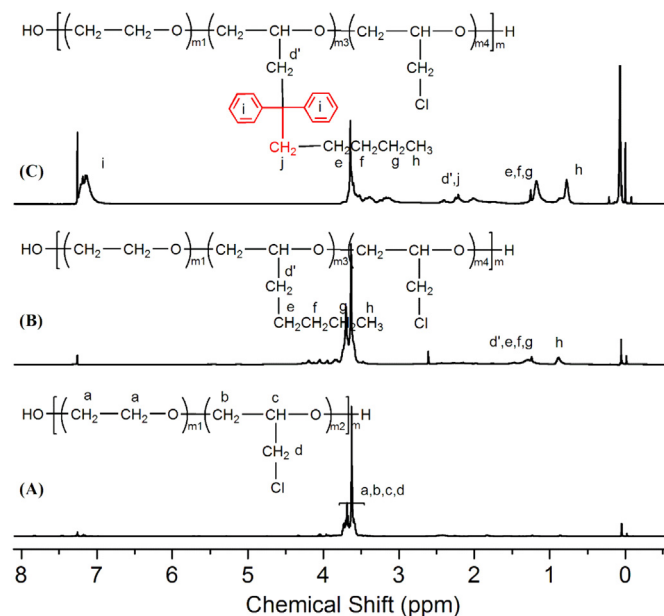
**Scheme 2.** The synthetic procedure of [Poly(ECH-co-EO)]-Bu and [Poly(ECH-co-EO)]-(DPE-Bu).

EO), the monomodal peak and low PDI could be regarded as a solid evidence for the successful polymerization procedure.

The composition of Poly(ECH-co-EO) was confirmed by  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra, respectively. In  $^1\text{H}$  NMR spectrum of Poly(-ECH-co-EO) (Fig. 2(A)), the characteristic resonance signals for methylene protons on ethylene oxide unit ( $-\text{CH}_2\text{CH}_2\text{O}-$ ) could be observed at 3.50–4.00 ppm, and the signals of methylene protons



**Fig. 1.** SEC trace of Poly(ECH-co-EO) ( $M_n = 3.33 \times 10^4$  g/mol, PDI = 1.34).



**Fig. 2.** The  $^1\text{H}$  NMR spectra of Poly(ECH-co-EO) (A) [Poly(ECH-co-EO)]-Bu (B) [Poly(-ECH-co-EO)]-(DPE-Bu) (C) ( $\text{CDCl}_3$ , TMS).

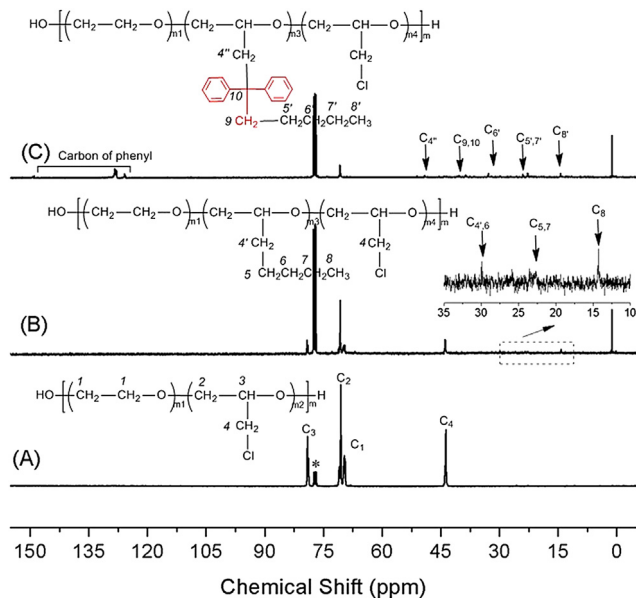
and methine proton on epichlorohydrin unit ( $-\text{CH}_2\text{CH}(\text{CH}_2\text{Cl})-$ ) were overlapped and assigned in the same region. The  $^{13}\text{C}$  NMR spectrum of Poly(ECH-co-EO) was shown in Fig. 3(A), the resonance signal of methylene carbon ( $-\text{CH}_2\text{Cl}$ ) on epichlorohydrin unit connected to chlorine was assigned at 44.04 ppm, and signals of methine carbon ( $-\text{CHO}-$ ) and methylene carbon ( $-\text{CH}_2\text{O}-$ ) on EO unit were assigned at 78.99 ppm, 70.72 ppm, respectively. Also, according to the elemental analysis, the molar percentage ( $M_{\text{ECH}}\%$ ) of epichlorohydrin units on Poly(ECH-co-EO) was calculated as 42.6%.

The Poly(ECH-co-EO) was also characterized by FTIR (Fig. S1, Supporting Information). The adsorption peak at  $733\text{ cm}^{-1}$  and  $907\text{ cm}^{-1}$  could be associated with the stretching vibration of C–Cl bond on epichlorohydrin units, and the peak at  $1460\text{ cm}^{-1}$  and  $1065\text{ cm}^{-1}$  could be regarded as the asymmetric bending vibration of methylene group and the characteristic absorption peak of stretching vibration of C–O bond, respectively. Meanwhile, the stretching vibration peak of methylene and methine groups could be concentrated at  $2857$  and  $2972\text{ cm}^{-1}$ . Thus, the above information comprehensively confirmed the successful synthesis of Poly(-ECH-co-EO).

### 3.2. Synthesis and characterization of graft copolymers

The coupling reactions between living  $\text{PI}^-\text{Li}^+$  or  $\text{PS}^-\text{Li}^+$  species (end-capped with or without DPE agent) with chloromethyl groups on Poly(ECH-co-EO) were proceeded for graft copolymers [Poly(ECH-co-EO)]-g-PI and [Poly(ECH-co-EO)]-g-PS. As shown in Fig. S2 and S1 (Supporting Information), when living species were coupled with chloromethyl groups directly, the SEC traces of graft polymers always shifted to the low molecular weight region. However, when living species were capped with DPE agent, there was a dramatically increase of molecular weight of graft copolymers.

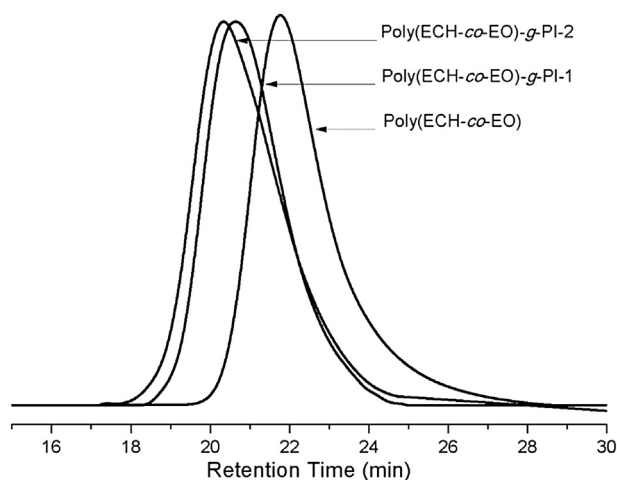
After fractional precipitation to remove the excess PI or PS homopolymers, the pure graft copolymers [Poly(ECH-co-EO)]-g-PI (Fig. 4) and [Poly(ECH-co-EO)]-g-PS (Fig. 5) with low PDIs were obtained. By changing the molecular weight of living species, series of graft copolymers were obtained. Comparing the SEC curve of Poly(ECH-co-EO) with that of graft copolymers, we could observe



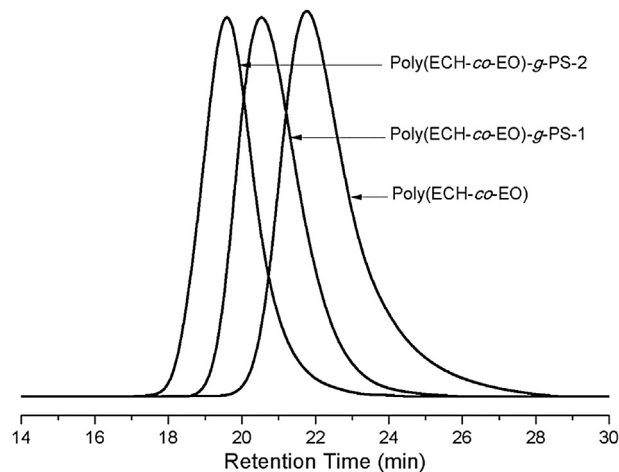
**Fig. 3.** The <sup>13</sup>C NMR spectra of Poly(ECH-co-EO) (A), [Poly(ECH-co-EO)]-Bu (B) and [Poly(ECH-co-EO)]-(DPE-Bu) (C) (CDCl<sub>3</sub>). (Peaks symbolled by \* could be attributed to the carbon signals of CDCl<sub>3</sub>).

that the SEC curves of graft copolymer shift to the lower elution time, which could be regarded as one of the evidence for the successful coupling reaction.

From the <sup>1</sup>H NMR spectrum for [Poly(ECH-co-EO)]-g-PS (Fig. 6(B)), except for the characteristic resonance signals at 3.50–4.00 ppm for protons (–CH<sub>2</sub>CH<sub>2</sub>O–, –CH<sub>2</sub>CH(CH<sub>2</sub>–)O–) on Poly(ECH-co-EO), the characteristic resonance signals for aromatic protons (–C<sub>6</sub>H<sub>5</sub>) on PS segment at 6.94–7.30 ppm were also discriminated clearly, which proved the successful introduction of PS side chain onto Poly(ECH-co-EO) backbone. Similarly, from the <sup>1</sup>H NMR spectrum for [Poly(ECH-co-EO)]-g-PI (Fig. 6(C)), the occurrence of resonance signals for the methine protons (–CH=CH<sub>2</sub>) on 1,2-addition units at 5.70 ppm, methylene protons (–(CH<sub>3</sub>)C=CH<sub>2</sub>) on 3,4-addition units at 4.49–4.77 ppm, methylene protons (–CH=CH<sub>2</sub>) on 3,4-addition units and methine protons (–CH=C(CH<sub>3</sub>)–) on 1,4-addition units at 4.77–5.16 ppm proved the successful addition of PI onto Poly(ECH-co-EO) backbone.

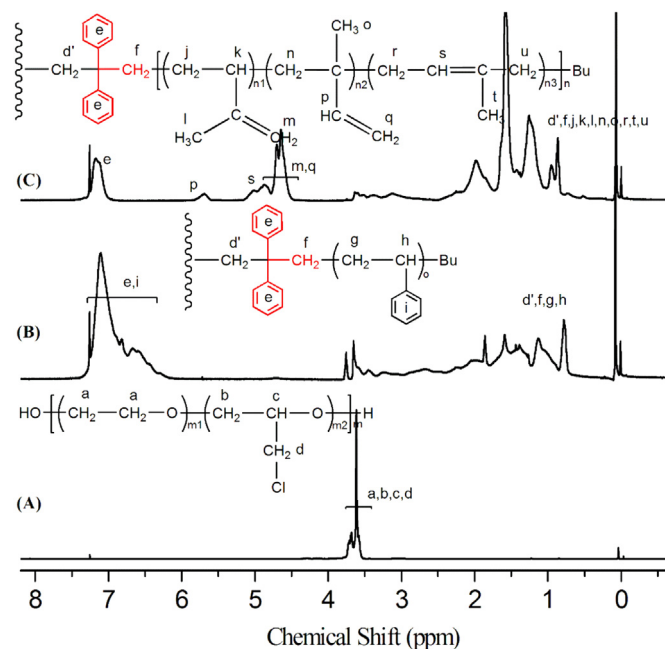


**Fig. 4.** SEC traces of Poly(ECH-co-EO) ( $M_n = 3.33 \times 10^4$  g/mol, PDI = 1.34), [Poly(ECH-co-EO)]-g-PI-1 ( $M_n = 6.72 \times 10^4$  g/mol, PDI = 1.34), [Poly(ECH-co-EO)]-g-PI-2 ( $M_n = 7.16 \times 10^4$  g/mol, PDI = 1.42).



**Fig. 5.** SEC traces of Poly(ECH-co-EO) ( $M_n = 3.33 \times 10^4$  g/mol, PDI = 1.34), [Poly(ECH-co-EO)]-g-PS-1 ( $M_n = 6.85 \times 10^4$  g/mol, PDI = 1.32), [Poly(ECH-co-EO)]-g-PS-2 ( $M_n = 1.47 \times 10^5$  g/mol, PDI = 1.36).

According to our previous works [59,60] and <sup>1</sup>H NMR spectrum of PI segment, the molar ratio of 1,2-addition (N<sub>1,2-a.</sub>), 1,4-addition (N<sub>1,4-a.</sub>) to 3,4-addition (N<sub>3,4-a.</sub>) isoprene units could be determined as 13.1/45.1/41.8 under our experimental conditions. In addition, the signals of aromatic protons (–C<sub>6</sub>H<sub>5</sub>) from DPE moiety could be clearly discriminated at 6.94–7.30 ppm, which was different from the case in spectrum for [Poly(ECH-co-EO)]-g-PS because the signals of aromatic protons (–C<sub>6</sub>H<sub>5</sub>) from DPE moiety and PS segment were seriously overlapped. However, in both spectra for [Poly(ECH-co-EO)]-g-PS and [Poly(ECH-co-EO)]-g-PI, the resonance signals of protons (–CH<sub>2</sub>CH<sub>2</sub>O–, –CH<sub>2</sub>CH(CH<sub>2</sub>–)O–) on backbone could not be assigned and integrated accurately, as the signals on backbone were significantly immobilized by the outer PS or PI side chains. The similar phenomenon was also reported in literatures [61–63].



**Fig. 6.** The <sup>1</sup>H NMR spectra of Poly(ECH-co-EO) (A) and graft polymers [Poly(ECH-co-EO)]-g-PS (B), [Poly(ECH-co-EO)]-g-PI (C) (CDCl<sub>3</sub>, TMS).

In order to get graft copolymers with block side chains, we also synthesized the block macroanions first by sequential LAP of styrene and isoprene monomers using  $n\text{-Bu}^-\text{Li}^+$  as initiator, and the macroanions  $\text{PS-}b\text{-PI}^-\text{Li}^+$  were capped with DPE agent and reacted with chloromethyl groups on Poly(ECH-*co*-EO) for [Poly(ECH-*co*-EO)]-*g*-(PI-*b*-PS). The SEC traces of these graft copolymers with block side chains were shown in Fig. 7. From the  $^1\text{H}$  NMR spectrum of [Poly(ECH-*co*-EO)]-*g*-(PI-*b*-PS) (Fig. 8), the characteristic resonance signals for aromatic proton ( $-\text{C}_6\text{H}_5$ ) on PS chain at 6.30–7.50 ppm and that of protons on PI segment between 4.41 and 5.90 ppm could all be well discriminated.

As the complicated structure and compositions, the accurate molecular weight of graft copolymers could not be directly obtained by SEC and  $^1\text{H}$  NMR measurements. Finally, the static light scattering was adopted, and the total molecular weights of graft copolymers were listed in Table 1. Based on the obtained actual molecular weight of side chains and the total molecular weight of graft copolymers, the grafting efficiencies was evaluated. Meanwhile, the FTIR spectra of [Poly(ECH-*co*-EO)]-*g*-PI and [Poly(ECH-*co*-EO)]-*g*-PS were also shown in Fig. S1 (Supporting Information). Taking [Poly(ECH-*co*-EO)]-*g*-PI as an example, we could get the characteristic signal of olefin C–H stretching vibration of [Poly(-ECH-*co*-EO)]-*g*-PI at  $3068\text{ cm}^{-1}$ , and C=C stretching vibration at  $1642\text{ cm}^{-1}$ , which confirmed the successful introduction of PI. Unlike the work by Barrie [51], the absence of characteristic peak for  $-\text{CHO}$ ,  $-\text{C}=\text{O}$  or  $-\text{C}\equiv\text{C}-$  in spectrum demonstrated that there was no cleavage in our coupling reaction, which could also be proved by the increasing of molecular weight after coupling reaction observed by SEC measurement.

### 3.3. Confirmation of coupling reactions between chloromethyl groups and living species

As described in above Section, when Poly(ECH-*co*-EO) was used as main chain, the addition of DPE agent had an important effect on the grafting efficiency of graft copolymers. Thus, the model experiment was carried out to [Poly(ECH-*co*-EO)]-Bu or [Poly(ECH-*co*-EO)]-(DPE-Bu) by coupling reactions between Poly(ECH-*co*-EO) and  $n\text{-Bu}^-\text{Li}^+$  or  $n\text{-Bu-DPE}^-\text{Li}^+$ , respectively (Scheme 2), and the detailed mechanism was further investigated.

The  $^1\text{H}$  NMR spectra of Poly(ECH-*co*-EO), Poly(ECH-*co*-EO)-Bu and Poly(ECH-*co*-EO)-(DPE-Bu) (Fig. 2) were all clearly discriminated and used to determine the coupling efficiencies (E. F.) of

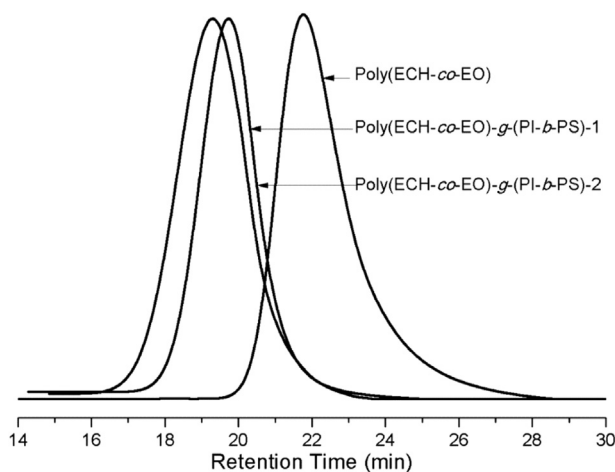


Fig. 7. SEC traces of Poly(ECH-*co*-EO), [Poly(ECH-*co*-EO)]-*g*-(PI-*b*-PS)-1 ( $M_n = 1.66 \times 10^5$  g/mol, PDI = 1.42), [Poly(ECH-*co*-EO)]-*g*-(PI-*b*-PS)-2 ( $M_n = 2.25 \times 10^5$  g/mol, PDI = 1.49).

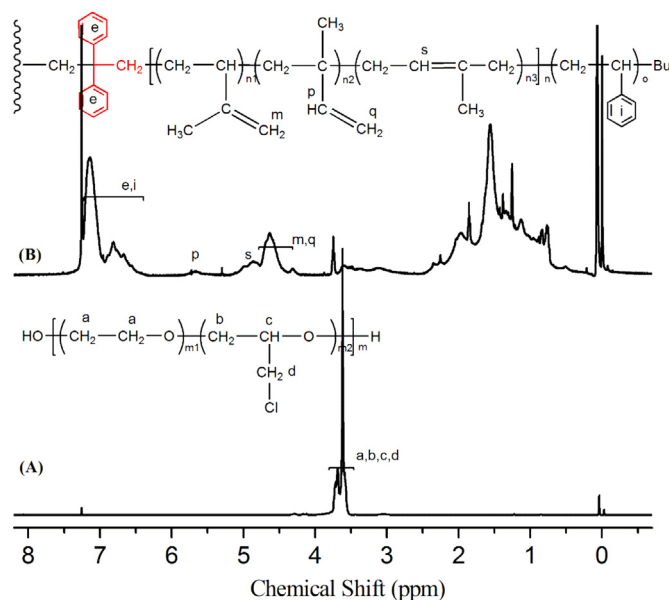


Fig. 8. The  $^1\text{H}$  NMR spectra of Poly(ECH-*co*-EO) (A) and graft copolymers [Poly(ECH-*co*-EO)]-*g*-(PI-*b*-PS) (B) ( $\text{CDCl}_3$ , TMS).

$n\text{-Bu}^-\text{Li}^+$  and  $n\text{-Bu-DPE}^-\text{Li}^+$ . For [Poly(ECH-*co*-EO)]-Bu (Fig. 2(B)), the E. F.<sub>[Poly(ECH-*co*-EO)]-Bu</sub> was calculated using Formula 1:

$$\text{E. F.}_{[\text{Poly}(\text{ECH-}i\text{co-EO})\text{-Bu}] = \frac{A_{d+e+f+g}/8}{M_{\text{ECH}\%} \times A_{a+b+c+d}/5} \times 100\% \quad (1)$$

Here,  $A_{d+e+f+g}$  represented the integral area of corresponding methylene protons in Fig. 2(B), and  $A_{a+b+c+d}$  represented the integral area of protons on Poly(ECH-*co*-EO).  $M_{\text{ECH}\%}$  was the molar percentage of epichlorohydrin units on Poly(ECH-*co*-EO). The obtained E. F.<sub>[Poly(ECH-*co*-EO)]-Bu</sub> was 22.1%. And the E. F.<sub>[Poly(ECH-*co*-EO)]-(DPE-Bu)</sub> was calculated using Formula 2 (Fig. 2(C)):

$$\text{E. F.}_{[\text{Poly}(\text{ECH-}i\text{co-EO})\text{-(DPE-Bu)}] = \frac{A_i/10}{M_{\text{ECH}\%} \times A_{a+b+c+d}/5} \times 100\% \quad (2)$$

Here,  $A_i$  represented the integral area of aromatic protons on DPE unit in Fig. 2(C), and the others were the same as defined before. The obtained E. F.<sub>[Poly(ECH-*co*-EO)]-(DPE-Bu)</sub> was about 80.5%, which was much higher than of E. F.<sub>[Poly(ECH-*co*-EO)]-Bu</sub>.

From  $^{13}\text{C}$  NMR spectra of both Poly(ECH-*co*-EO)-Bu and Poly(-ECH-*co*-EO)-(DPE-Bu) (Fig. 3(B) and (C)), it was confirmed that the Chlorine–Lithium exchange would not occur in this system because the unreacted chlorine atoms on backbone were remained untouched (signals at 43.89 ppm). On the other hand, unlike the works reported by Majid et al. [51,52,64], no characteristic signals of  $-\text{CHO}$ ,  $-\text{C}=\text{O}$  or  $-\text{C}\equiv\text{C}-$  were observed in  $^{13}\text{C}$  NMR spectrum of Poly(ECH-*co*-EO)-Bu or Poly(ECH-*co*-EO)-(DPE-Bu), instructing that no apparent backbone cleavage occurred in our system.

Thus, the above results confirmed that the DPE end-capping was an efficient method for grafting living anionic species onto Poly(-ECH-*co*-EO). These results probably due to the appropriate nucleophilicity and lower activity of the carbanion in  $n\text{-Bu-DPE}^-\text{Li}^+$  brought by relative higher hindrance of DPE (compared with  $n\text{-Bu}^-\text{Li}^+$ ), which was in favour of the coupling reaction. Similar strategy were also adopted by other groups, for example, the grafting efficiencies on chloromethylated PS [65] or poly(-chloroethyl vinyl ether) (PCEVE) [66] were improved by end-

**Table 1**  
The data of backbone and graft copolymers.

Samples	Graft copolymers				Side chains		
	$M_n, SEC^a$ ( $\times 10^4$ g/mol)	PDI	dn/dc <sup>b</sup> (mL/g)	$M_w, MALLS^c$ ( $\times 10^5$ g/mol)	$M_n, SEC^a$ ( $\times 10^3$ g/mol)	Number of side chains	Grafting efficiency <sup>d</sup> (G. E. %)
Poly(ECH-co-EO)	3.33	1.34	0.075	0.48	—	—	—
[Poly(ECH-co-EO)]-g-PI-1	6.72	1.34	0.13	1.63	1.24	92	29.0
[Poly(ECH-co-EO)]-g-PI-2	7.16	1.42	—	—	2.29	—	—
[Poly(ECH-co-EO)]-g-PS-1	6.85	1.32	0.17	1.34	0.75	114	40.0
[Poly(ECH-co-EO)]-g-PS-2	14.70	1.36	0.18	3.89	2.30	166	52.4
[Poly(ECH-co-EO)]-g-(PI- <i>b</i> -PS)-1	16.60	1.42	0.15	4.62	1.76	235	74.1
[Poly(ECH-co-EO)]-g-(PI- <i>b</i> -PS)-2	22.50	1.49	—	—	4.76	—	—

<sup>a</sup> Determined by SEC, the samples were calibrated by PS standards and using THF as eluent.

<sup>b</sup> Obtained by Optilab rEX (Wyatt) in the offline mode.

<sup>c</sup> Determined by static light scattering in THF at 25 °C.

<sup>d</sup> Calculated by the Formula: G.E. = Number of side chains/Number of ECH units  $\times$  100%.

capping polystyryllithium or polyisopryllithium with DPE before the coupling reaction. Differently, the successful results was also obtained in this work when the main chain was replaced as Poly(ECH-co-EO).

### 3.4. Thermal behaviours of Poly(ECH-co-EO) and graft copolymers

To investigate the thermal properties of Poly(ECH-co-EO) and graft copolymers, the DSC (Fig. 9) measurement was performed. Clearly, only one glass transition temperature ( $T_g$ ) was shown on each curve. Typically, the  $T_g$  of Poly(ECH-co-EO) occurred at  $-41.1$  °C. However, when the PI was introduced as the branches,  $T_g$  of Poly(ECH-co-EO)-g-PI-1 moved to the higher temperature of  $6.3$  °C though the reported  $T_g$  of PI homopolymers was rather low ( $-40$ – $-73$  °C) in literature [67]. Similarly, the  $T_g$  of Poly(ECH-co-EO)-g-PI-2 occurred at  $2.4$  °C. This increased  $T_g$  of graft copolymer in our work could be explained by the steric hindrance of the relatively high density PI branches. When PS was introduced as branches,  $T_g$ s of Poly(ECH-co-EO)-g-PS-1 and Poly(ECH-co-EO)-g-PS-2 occurred at  $60.1$  °C and  $82.0$  °C, respectively, which were lower than the  $T_g$  ( $90.0$  °C) value of PS homopolymer reported in literature [68]. As for the [Poly(ECH-co-EO)]-g-(PI-*b*-PS), although the  $T_g$  ( $38.2$  °C) of Poly(ECH-co-EO)-g-(PI-*b*-PS)-1 was a little higher than  $T_g$  ( $42.2$  °C) of Poly(ECH-co-EO)-g-(PI-*b*-PS)-2, both  $T_g$ s were between the values of  $T_g$  of Poly(ECH-co-EO)-g-PS and  $T_g$  of Poly(-ECH-co-EO)-g-PI. Thus, these results confirmed that the

compositions and architecture had important effect on physical properties of graft copolymers, and further confirmed that the graft copolymers were actually successfully synthesized in our work.

## 4. Conclusions

The Poly(ECH-co-EO) with high molecular weight and relatively narrow distribution was successfully synthesized by ROP mechanism using ethylene glycol potassium as initiator and *i*-Bu<sub>3</sub>Al as activator. Meanwhile, the graft copolymers, Poly(ECH-co-EO)-g-PI, Poly(ECH-co-EO)-g-PS, and Poly(ECH-co-EO)-g-(PI-*b*-PS) were got at room temperature through the coupling reaction between chloromethyl groups and macroanions capped with DPE. From model experiment, it was confirmed that DPE could increase the grafting efficiency at room temperature. This work provided another versatile method for the synthesis of graft copolymers with PEO as backbone.

## Acknowledgements

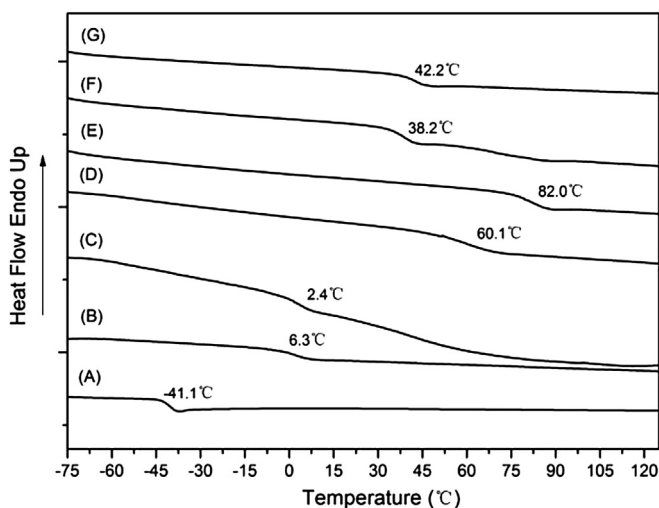
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## Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.polymer.2014.05.066>.

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**Fig. 9.** The DSC analysis of Poly(ECH-co-EO) (A) [Poly(ECH-co-EO)]-g-PI-1 (B) [Poly(-ECH-co-EO)]-g-PI-2 (C) [Poly(ECH-co-EO)]-g-PS-1 (D) [Poly(ECH-co-EO)]-g-PS-2 (E) [Poly(ECH-co-EO)]-g-(PI-*b*-PS)-1 (F) [Poly(ECH-co-EO)]-g-(PI-*b*-PS)-2 (G).

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