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# Amphiphilic polymer brushes with alternating PCL and PEO grafts through radical copolymerization of styrenic and maleimidic macromonomers

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## Abstract

Synthesis of a novel amphiphilic polymer brush with a sequence of alternating poly(ε-caprolactone) (PCL) and poly(ethylene oxide) (PEO) side chains through grafting-through approach is reported. This strategy consists of two steps: first, a PCL macromonomer carrying maleimide functional group (MI-PCL) and a PEO macromonomer with vinylbenzyl group (St-PEO) were prepared; then a conventional radical copolymerization of the MI-PCL and the St-PEO macromonomers was carried out to obtain the proto-type polymer brush. The reactivity ratios of two macromonomers were studied and the alternating sequence structure was proved.

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*Keywords:* Copolymerization; Block copolymers; Grafted polymers

## 1. Introduction

So-called cylindrical polymer brush is a polymer backbone being densely grafted with many polymeric side chains. Owing to the strong steric repulsion between crowded branches, the main chain is extended greatly and the whole polymer displays a wormlike morphology [1]. Because the individual molecule is "huge" which may reach as long as several hundred nanometers, the polymer brush has attracted a great attention recently. Many potential applications in nanomaterials and nanotechnologies related with one dimension are expected [2]. Several approaches, including grafting through, grafting from, and grafting onto approach, have been used to synthesize polymer brushes as summarized in a recent review article [1]. Recently, one-pot approach, simultaneous formation of the main chains and side chains, has been also reported [3].

Among all the polymer brushes, Janus-type or proto-type polymer brush with two different grafts distributed along the backbone is very interesting. Such polymer brush may undergo unusual intramolecular microphase separation [4], and shows the potential to segregate lengthwise. Random radical copolymerization of two macromonomers has been reported to produce such polymer brushes [4,5]. However, the grafting sequence cannot be precisely controlled by this way and the reactivity ratios of two macromonomers have not been studied. Therefore, the two branches may be tethered statistically and polymer brush composition may not be homogenous. Such heterografted polymer brushes with untailored structure would affect their behavior of molecular self-assembly. So far few efforts have been paid to control the sequence of hetero-branches. Ishizu et al. have studied the copolymerization of vinylbenzyl-terminated polystyrene (PS-VB) and maleate-terminated poly(ethylene oxide) monomethyl ether (PEO-MM) initiated by 2,2′-azobisisobutyronitrile (AIBN) [6]. However, the copolymerization reactivity data did not support an accurate alternation due to phase separation. They also have improved

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the branch sequence through introduction of Lewis acid during radical copolymerization of PS-VB and methacryloyl-terminated poly(ethylene oxide) methyl ether [7]. More recently, this group has prepared a proto-type polymer brush containing alternating PS and PMMA side chains through conventional copolymerization of PS-VB macromonomer and maleimide derivative combined with atom transfer radical polymerization of methyl methacrylate (MMA) [8].

It is known that the amphiphilic block copolymer of PEO and PCL has been extensively studied for the application of drug encapsulation and delivery [9]. This is because the PEO-*b*-PCL block copolymer may organize into polymer micelles in water whereas the PCL segments form a hydrophobic core. Moreover, PCL is a nontoxic biodegradable polymer, which can be biodegraded into soluble nontoxic oligomers, while PEO is a hydrophilic and nonimmunogenic nontoxic water-soluble polymer. Both of them are biocompatible materials and are widely used in the drug delivery systems. Therefore, a combination of PEO and PCL segments in a different structure would be important for drug delivery application. It has been reported that the amphiphilic brush copolymers consisting of *statistically* arranged PCL and PEO side chains can form ‘‘core-surface cross-linked micelles’’ (nanoparticles) in water [5]. Such particles are expected to be superior to the micelles formed by linear block copolymer analogues because the backbones of the polymer brushes act as crosslinkers on the hydrophobic core (PCL) surface to greatly enhance the stability of the micelles.

Herein, synthesis of a novel amphiphilic proto-type polymer brush with an alternating poly(ε-caprolactone) (PCL) and poly(ethylene oxide) (PEO) side chains is reported by using grafting-through strategy (Scheme 1). MI-PCL and St-PEO were prepared first, and then the hybrid polymer brush was obtained through conventional radical copolymerization of two macromonomers. The reactivity ratios of the two macromonomers were determined and the alternating structure of the synthesized polymer brushes was expected. This research may allow us to control the sequence of poly(comacromonomers) without using additives and also supply an amphiphilic comb like block copolymer with well-defined grafts for studying the self-assembling properties.

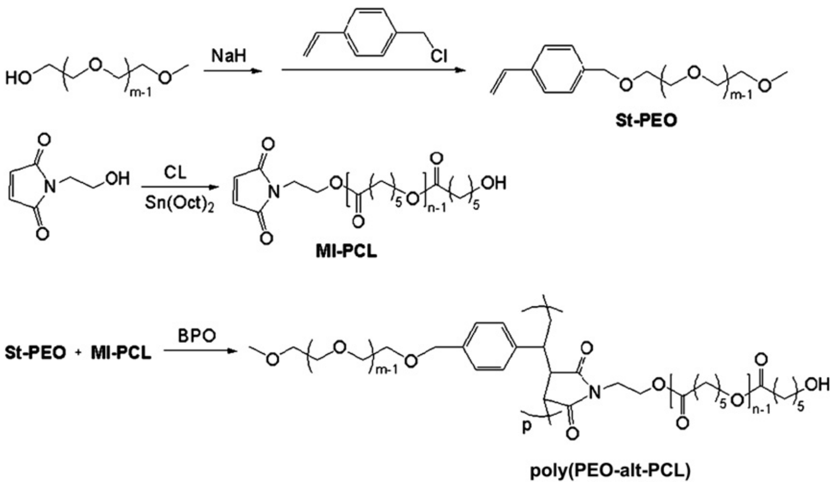
## 2. Experimental

### 2.1. Materials

ε-Caprolactone (ε-CL; Acros 99%) was dried over $CaH_2$ and distilled and stored under $N_2$ prior to use. Crude benzoyl peroxide (BPO) (10 g) was dissolved in chloroform (40 mL) and the insoluble impurity was filtered off. The filtrate was then added into cold methanol (100 mL) and white crystals were collected and dried. *N*-(2-Hydroxyethyl) maleimide (HEMI) and CuBr were prepared according to the literature, respectively [10,11]. Tetrahydrofuran (THF; Beijing Chemical Corporation, AR) was distilled over Na prior to use. *p*-Chloromethyl styrene (*p*-CMS; Fluka >90%), NaH (Aldrich), PEO monomethyl ether ($M_n = 750$; Acros), stannous(II) 2-ethylhexanoate ($SnOct_2$) (Sigma) and other reagents were commercial chemicals and used as received.

### 2.2. Measurements

Gel permeation chromatography (GPC) analysis was performed on two systems. System 1 is composed of a Waters 515 HPLC pump, a Waters 2414 differential refractometer and a combination of Styragel® HT-2, HT-4 and HT-5, of which effective molecular weight range is 100–10,000, 500–30,000 and 5000–600,000, respectively. THF was used as eluent at a flow rate of 1.0 mL/min at 35 °C. PS standards were used for the calibration. System 2 was equipped with a Postnava PN 1011 pump, a 5-μm mixed-bed C column (Polymer Lab), and a Precision PD 2100 detector system, including an RI detector, a two-angle static laser light scattering (TALLS) detector at 15 and 90°, and a dynamic laser light scattering detector, with THF as the eluent at a flow rate of 1 mL/min at 25 °C. $^1H$ NMR spectra were recorded on a Varian 400-MHz spectrometer in $CDCl_3$, or a mixture of $CDCl_3$ and $(CD_3)_2CO$ at room



Scheme 1. Synthesis of amphiphilic alternating polymer brush Poly(PEO-*alt*-PCL).

temperature. Infrared spectra were recorded on a Nicolet AVATAR 330 FT-IR spectrometer.

### *2.3. Synthesis of St-PEO*

PEO monomethyl ether (15.0 g, 20 mmol; DP = 17) was azeotropically dried by toluene. After most of the toluene was removed by distillation, dry THF (120 mL) was added under $N_2$ atmosphere and the mixture was placed in an ice bath. After NaH (1.6 g, 40 mmol; containing ∼40% oleic acid) was added to the mixture under stirring, *p*-CMS (4.73 mL, 30 mmol) in dry THF (30 mL) was dropped slowly to the suspension and the mixture was kept stirring overnight under $N_2$ atmosphere. THF was evaporated and $H_2O$ was added into the residue cautiously. The water layer was extracted with $CH_2Cl_2$ (4 × 50 mL), and the collected $CH_2Cl_2$ layer was dried with anhydrous $Na_2SO_4$. After filtration, most of the $CH_2Cl_2$ was evaporated off and the residue was precipitated in cold petroleum ether twice, dried under vacuum and kept under refrigeration. Pale yellow viscous solid, 15 g. Yield: 83%.

### *2.4. Synthesis of MI-PCL*

Typical procedure for synthesis of MI-PCL I: To a flame dried ampoule, HEMI (0.84 g, 6 mmol), ε-CL (8.86 mL, 80 mmol), $Sn(Oct)_2$ (32.4 mg, 0.08 mmol) and a magnetic stir bar were added. After three freeze-vacuum-thaw cycles, the mixture was sealed by flame in the ampoule under vacuum and placed in an oil bath at 120 °C for 26 h under stirring. The ampoule was cooled to room temperature and the product was taken out, dissolved with $CH_2Cl_2$ and precipitated in petroleum ether twice. White powders: 9.7 g. Yield: ∼100%. $M_w/M_n = 1.14$ (determined by GPC with a RI detector). $M_{n,NMR} = 1740$.

### *2.5. Copolymerization of St-PEO and MI-PCL*

A typical procedure: to a Schlenk flask with a stir bar, St-PEO (0.435 g, 0.50 mmol), MI-PCL I (0.800 g, 0.50 mmol) and BPO (12.1 mg, 0.05 mol) were charged. After three cycles of vacuum and backfill with $N_2$, degassed toluene (10 mL) was added through a syringe. The flask with reaction mixture was then placed in an oil bath at 60 °C with stirring for 3 days. A sample of 50–100 μL was taken from the reaction mixture and diluted with THF to 1 mL for GPC tests. The product was precipitated in petroleum twice and dried under vacuum.

### *2.6. Determination of reactivity ratios of St-PEO and MI-PCL*

To determine the reactivity ratios of the macromonomers, a series of copolymerization reactions with different molar feed ratios of St-PEO and MI-PCL were carried out under the same conditions as the procedure for synthetic purpose but stopped at low conversion of the macromonomers. Samples were taken directly from the reaction mixtures and tested by GPC. So, the yields of each reaction were obtained by comparing the calibrated integrations of the copolymers to the total calibrated integrations of the copolymers and the residual macromonomers. Peak integration calibration was done as the following: the copolymer, the MI-PCL and the St-PEO of equal weight were mixed together and tested by GPC. The ratio of the integrations of the three peaks on the GPC curve was 1.00:0.42:0.83 for the copolymer, the MI-PCL and the St-PEO. The yield of a polymerization reaction was calculated by the equation: integration of the copolymer/(integration of the copolymer + integration of residual MI-PCL/0.42 + integration of residual St-PEO/0.83). The molar ratios of two macromonomer units contained in the copolymer were determined by $^1$H NMR spectra by comparing the integrated proton areas of PEO and PCL segments as discussed in the following section.

## 3. Results and discussion

### *3.1. Synthesis of St-PEO and MI-PCL*

St-PEO and MI-PCL were synthesized through the procedure shown in Scheme 1. The method for preparation of St-PEO was reported in the literature [12] while the MI-PCL was obtained by ring-opening polymerization of ε-CL initiated by HEMI. As shown in Fig. 1, the GPC traces of two macromonomers given by GPC 1 with a RI detector were monomodal with low molecular weight distribution ($M_w/M_n$), 1.04 for St-PEO and 1.14 for MI-PCL I, respectively.

$^1$H NMR spectrum of St-PEO is demonstrated in Fig. 2. The peaks labeled as a, b and c are from the protons of styrene group, and other labeled peaks can be assigned to the corresponding protons as depicted in the structure in Fig. 2. The styrene functionality of St-PEO was determined by the $^1$H NMR spectrum to be approximately 100% by comparing the peak areas of b (one of the C=C bond protons at 6.60–6.80 ppm) and e (protons in PEO chains at 3.40–3.75 ppm) with the number average molecular weight value ($M_n = 750$) of the PEO precursor. The $M_n$ of the St-PEO was calculated

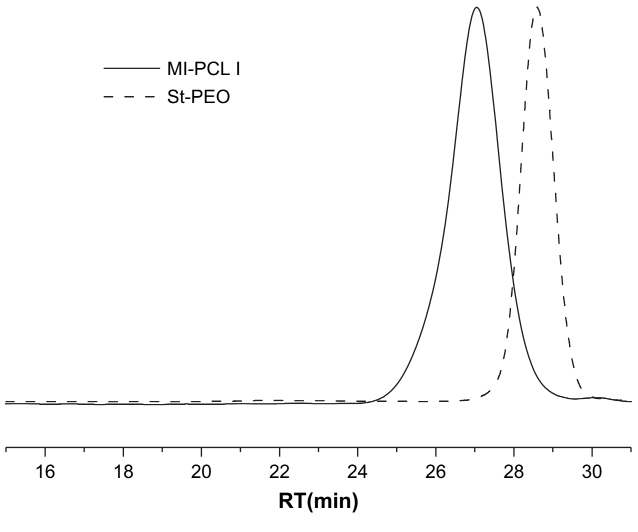


Fig. 1. GPC (System 1) curves of St-PEO ($M_w/M_n = 1.04$) and MI-PCL I ($M_w/M_n = 1.14$) with IR detector.

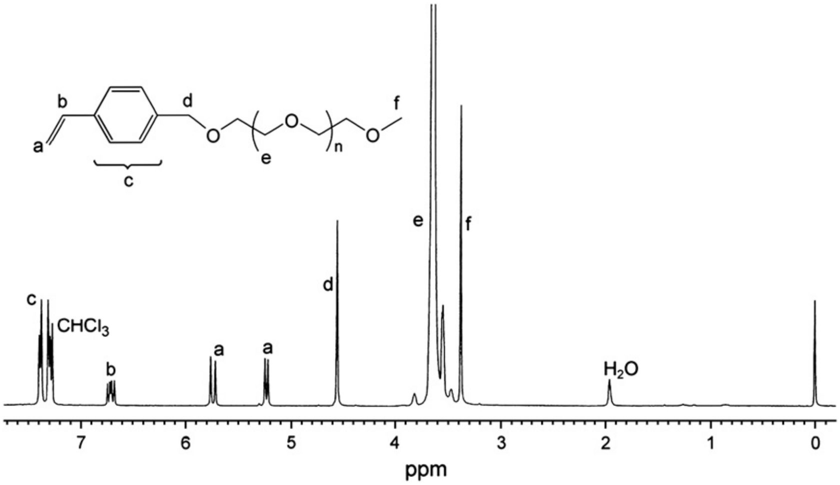


Fig. 2. $^1$H NMR spectrum of macromonomer St-PEO in CDCl$_3$.

to be 870. $^1$H NMR spectrum of MI-PCL I is also shown in Fig. 3. By comparing the peak areas of a (double C=C protons from maleimide group at 6.57 ppm) and d (protons on the carbons adjacent to the carbonyl group in PCL at 2.25 ppm) in Fig. 3, MI-PCL I was determined to contain 14 CL units with a number average molecular weight $M_{n,NMR} = 1740$. Another macromonomer, MI-PCL II containing 18 CL units with a number average molecular weight $M_{n,NMR} = 2200$, was also prepared according to the same procedure. In contrast to the relative molecular weight from GPC analysis that is calibrated with linear PS standards, the absolute molecular weights are obtained by the end group analysis using $^1$H NMR spectra. Therefore, we applied the data of $M_{n,NMR}$ for further analysis.

### 3.2. Copolymerization of St-PEO and MI-PCL

Copolymerization reactions of St-PEO and MI-PCL were carried out under conventional polymerization conditions with BPO or AIBN as initiators. The reaction conditions and results are summarized in Table 1. Poly(PEO-*alt*-PCL) I, II and III were copolymers of St-PEO and MI-PCL I (Entries 1, 2 and 3 in Table 1, respectively) under different monomer concentration, while Poly(PEO-*alt*-PCL) IV was from the copolymerization of St-PEO and MI-PCL II terminated at a short reaction time (Entry 4 in Table 1). The molar feed ratios of the macromonomers in the parallel reactions were kept 1:1. It has been reported that high macromonomer concentration and long reaction time are preferred to get a polymacromonomer with a higher degree of polymerization (DP) [13]. This criterion was found to be applicable for the copolymerization of St-PEO and MI-PCL by comparing the polymerization reaction conditions and the results in Table 1. A copolymer brush, Poly(PEO-*alt*-PCL) III with a DP$_w$ of 310, estimated with absolute molecular weights given by the GPC 2 equipped with light scattering detectors, was obtained by the reaction with a total macromonomer concentration of 0.25 mol/L for 66 h (Entry 3 in Table 1).

GPC traces of the obtained poly(comacromonomer)s without purification by the System 1 are collected in Fig. 4. Because these samples for GPC traces were obtained directly from the reaction mixtures without purification (except the Entry 4), the residual macromonomers could be seen on these curves. By comparing the calibrated peak integrations of the poly(comacromonomer)s and those of macromonomers, the

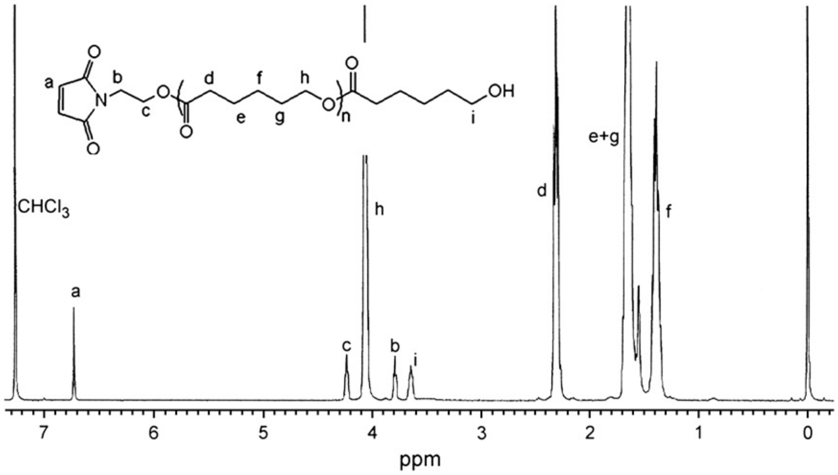


Fig. 3. $^1$H NMR spectrum of macromonomer MI-PCL in CDCl$_3$.

Table 1
Conventional radical copolymerization of St-PEO and MI-PCL

| Entry | Polymers | Temp. (°C) | Time (h) | Yield[e] (%) | $M_w/M_n$[f] | $M_{w,LS}$[g] (kDa) | $DP_{w,backbone}$[h] |
|---|---|---|---|---|---|---|---|
| 1 | Poly(PEO-*alt*-PCL) I[a] | 60 | 72 | 92.6 | 1.26 | 57 | 44 |
| 2 | Poly(PEO-*alt*-PCL) II [b] | 60 | 72 | 89.1 | 1.25 | 122 | 93 |
| 3 | Poly(PEO-*alt*-PCL) III[c] | 60 | 66 | 93.8 | 1.19 | 404 | 310 |
| 4 | Poly(PEO-*alt*-PCL) IV[d] | 50 | 24 | 37.7 | 1.48 | 27 | 18 |

[a] Feed ratio: [St-PEO]/[MI-PCL I]/[BPO] = 1:1:0.1, $[M]_{0,total}$ = 0.1 mol/L, in toluene.
[b] [St-PEO]/[MI-PCL I]/[BPO] = 1:1:0.04, $[M]_{0,total}$ = 0.1 mol/L, in toluene.
[c] [St-PEO]/[MI-PCL I]/[BPO] = 1:1:0.05, $[M]_{0,total}$ = 0.25 mol/L, in toluene.
[d] [St-PEO]/[MI-PCL II]/[AIBN] = 1:1:0.01, $[M]_{0,total}$ = 0.25 mol/L, in THF.
[e] Entries 1–3, calculated by comparing the calibrated integration of the copolymer brush and the integration of all the peaks (including residual macromonomers) from the GPC curve of the reaction mixture after termination of the reaction; Entry 4, obtained by precipitation in methanol and there was loss during filtration.
[f] Main peak values obtained by the GPC 1 with RI detector.
[g] By GPC System 2 with a TALLS detector.
[h] $M_{n,LS}/(M_n$ of St-PEO + $M_{n,NMR}$ of MI-PCL).

total conversion of the macromonomers (for Entries 1–3) was estimated as shown in Table 1. It is noteworthy that the conversions of the macromonomers are rather high compared to the results reported in the literature [4,6,7]. This advantage is owing to the copolymerization nature of St and MI that is prone to give the product with high molecular weights. Moreover, a plot of the absolute molecular weight versus retention time for Poly(PEO-*alt*-PCL) II given by GPC-MALLS (System 2) is shown in Fig. 5. We may learn that the molecular weight of poly(comacromonomer) decreased linearly with increase in retention time, indicating the heterografted polymer follows a GPC separation mechanism.

The formation of Poly(PEO-*alt*-PCL) was further confirmed through the characteristic resonances of $^1$H NMR spectrum as shown in Fig. 6. The resonances of the protons of PCL and PEO side chains are observed, which are almost the same as in their macromonomer precursors. However, it is noteworthy that the resonances of those protons, like benzene protons b, methylene protons a and ethylene protons c, d in the product, which are close to the backbones, had been greatly broadened. This indicates that the poly(comacromonomer) backbone is quit stiff due to the bulky and densely grafted side chains. The number ratio of the PEO and PCL macro-grafts obtained by comparing the peak area at 3.5–3.7 ppm from PEO to that at 2.2–2.4 ppm from PCL is 1:1.1 (number of PEO side chains/number of PCL side chains = [2 × $DP_{MI-PCL}$ × Integration area of the peak at 2.2–2.4 ppm]/[4 × $DP_{St-PEO}$ × Integration area of the peak at 3.5–3.7 ppm]). This result demonstrates that Poly(PEO-*alt*-PCL) II contains almost the same number of PEO and PCL side chains.

A typical IR spectrum of the copolymerization product (Poly(PEO-*alt*-PCL) II) is shown in Fig. 7. It shows the expected absorbance peaks from both PCL and PEO chains, such as the absorbance at 3695–3120 cm$^{-1}$ assigned from O–H in PCL, at 1728 cm$^{-1}$ from C=O in PCL, at 1700 cm$^{-1}$ (small and overlapped) from maleimide units, at 1106 cm$^{-1}$ from C–O–C in PEO, at 1506 cm$^{-1}$ and 840 cm$^{-1}$ from aromatic rings, etc.

### 3.3. Reactivity ratios of St-PEO and MI-PCL

It has been proved that styrene and maleimide have a strong tendency to form the alternating copolymer [14]. But this characteristic feature has not been proved when both styrene and

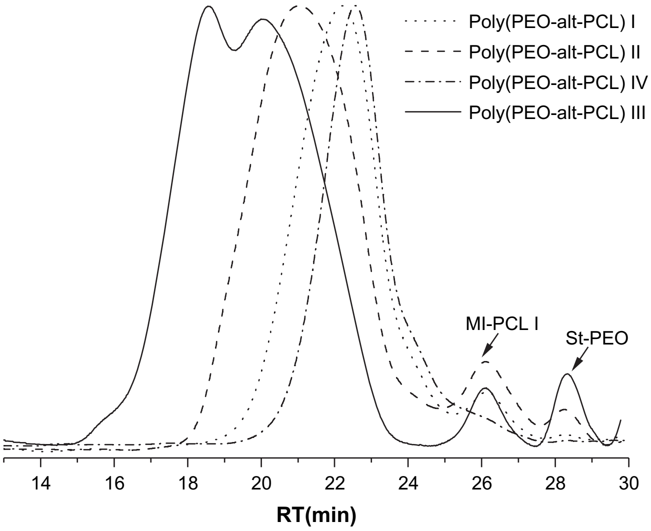


Fig. 4. GPC curves of the polycomacromonomers (System 1). For reaction conditions see Table 1.

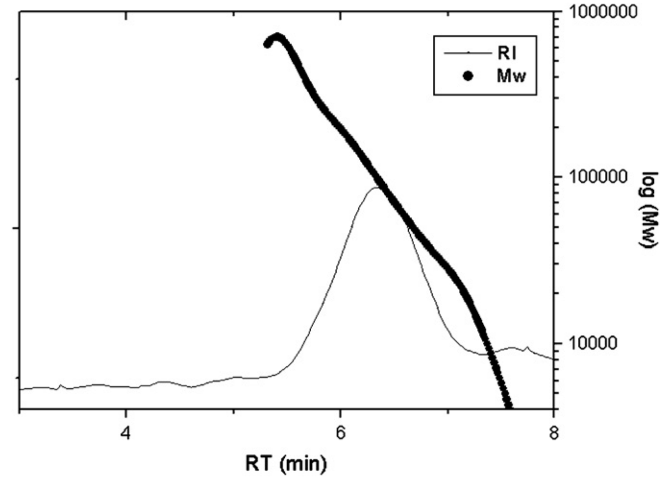


Fig. 5. GPC trace and molecular weight development of Poly(PEO-*alt*-PCL) II obtained by GPC-MALLS (System 2).

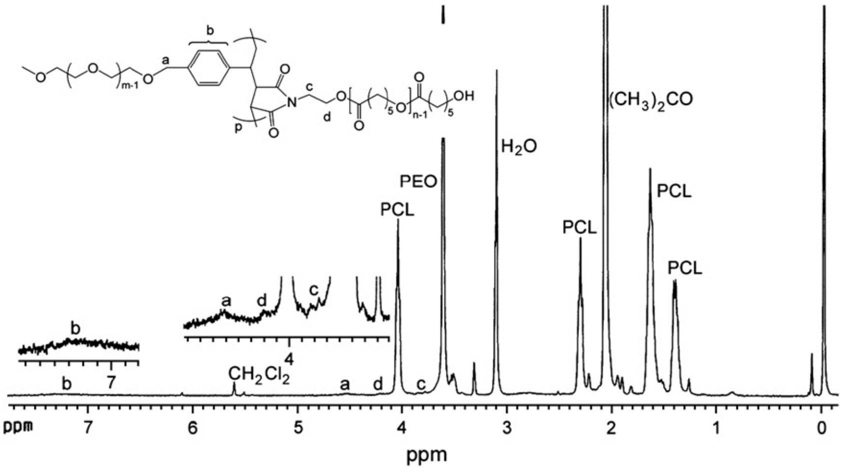


Fig. 6. $^1$H NMR spectrum of Poly(PEO-*alt*-PCL) II in CDCl$_3$/(CD$_3$)$_2$CO 1:3 (v:v). For reaction conditions see Table 1.

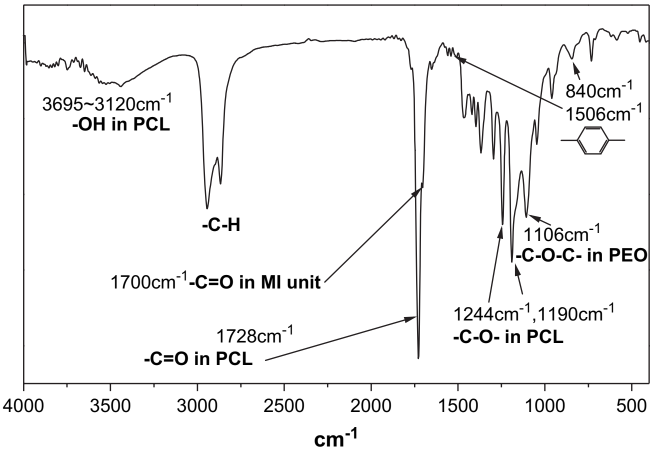


Fig. 7. IR spectrum of Poly(PEO-*alt*-PCL) II.

Table 2
Determination of reactivity ratios of MI-PCL I and St-PEO[a]

| Entry | [M$_1$]$_0$/[M$_2$]$_0$ | Conv.(%) | *X* | d[M$_1$]/d[M$_2$][b] | *Y* | *G* | *F* |
|---|---|---|---|---|---|---|---|
| 1 | 50/50 | 16.5 | 1.00 | 0.244/0.248 | 0.98 | −0.0204 | 1.02 |
| 2 | 20/80 | 9.3 | 0.25 | 0.321/0.443 | 0.73 | −0.0948 | 0.082 |
| 3 | 80/20 | 1.5 | 4.00 | 2.02/1.56 | 1.29 | 0.899 | 12.40 |
| 4 | 35/65 | 17.2 | 0.54 | 0.310/0.347 | 0.89 | −0.0667 | 0.33 |
| 5 | 65/35 | 2.8 | 1.86 | 0.164/0.144 | 1.14 | 0.227 | 3.03 |

[a] $G = r_1F - r_2$, where $G = X(Y-1)/Y$, $F = X^2/Y$, $X = [M_1]_0/[M_2]_0$, $Y = d[M_1]/d[M_2]$.

[b] d[M$_1$]/d[M$_2$] = number of M$_1$ units/number of M$_2$ units contained in the copolymer.

maleimide units are contained in macromonomers as functionalities. To identify the alternating copolymerization nature of present two macromonomers and prove the alternating microstructure of the copolymer brushes, the reactivity ratios of two macromonomers, St-PEO and MI-PCL, were investigated. The equation below put forward by Fineman and Ross [15] was used here to calculate the reactivity ratios: $G = r_1F - r_2$, where $G = X(Y-1)/Y$, $F = X^2/Y$, $X = [M_1]_0/[M_2]_0$, $Y = d[M_1]/d[M_2]$; $r_1$ and $r_2$ refer to the reactivity ratios of M1 and M2, respectively. In this study, M$_1$ and M$_2$ refer to MI-PCL I and St-PEO, respectively. Conversions of the copolymerization reactions were calculated from GPC tests with integration calibration. The *X* was determined by the feed ratio; *Y* was obtained by $^1$H NMR analysis as described in previous section. All the data are summarized in Table 2.

Based on the data in Table 2, a straight line as shown in Fig. 8 was obtained when *G* was plotted against *F*. From this line, $r_1$ and $r_2$ were determined to be 0.08 and 0.08, respectively. These reactivity ratios of the macromonomers are very close to the reported values [14] ($r_1 = r_2 = 0.1$) of the corresponding small monomers. These data demonstrate that the copolymerization of MI-PCL and St-PEO accords to a typical alternating copolymerization. Therefore, PCL and PEO side chains are tethered along the backbone with an alternating sequence. It was reported that a random copolymer brush was obtained by radical copolymerization of PS-VM and PEG-MM, because the reactivity ratios of PS-VM and PEO-MM were 0.765 and 0.064, respectively [6]. The reason was attributed to the phase separation of the copolymerization. Thus the current St and MI system can be a convenient way to obtain alternating copolymer brushes through ‘‘grafting-through’’ method.

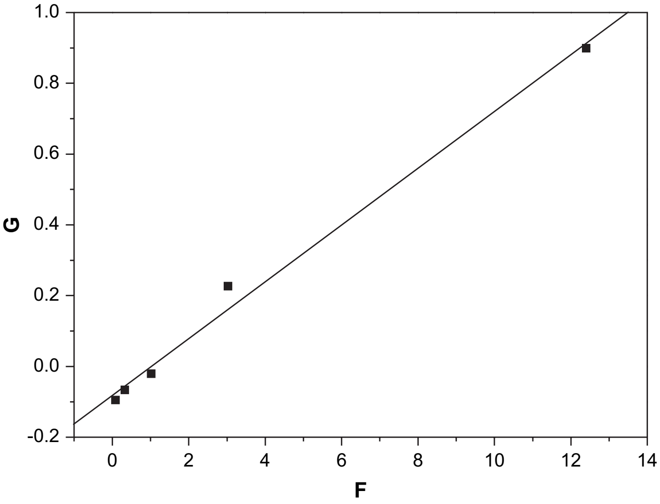


Fig. 8. *G* plotted against *F* for determination of reactivity ratio.

## 4. Conclusion

Amphiphilic grafted polymer brushes with alternating PCL and PEO side chains have been synthesized through radical copolymerization of the two macromonomers, St-PEO and MI-PCL. The reactivity ratios of the two macromonomers were determined to be close to their corresponding functional St and MI small molecules, and an alternating structure of the polymer brushes was proven. This result may be important for developing various well-controlled amphiphilic polymer brushes and to prepare segmented polymer objects. Furthermore, one OH is present at the end of PCL branch and this allows us to further introduce the functionalities.

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