Cyclohexene Oxide Mid-Chain Functional Macromonomer of Poly(ε-caprolactone): Synthesis, Characterization, and Photoinitiated Cationic Homo- and Copolymerization

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ABSTRACT: In this study, a novel well-defined epoxy mid-chain functional macromonomer of poly(ε-caprolactone) (PCL) has been synthesized by ring-opening polymerization (ROP) of ε-caprolactone (ε-CL) and epoxidation on workup with 3-chloroperoxybenzoic acid. The ROP of ε-CL monomer in bulk at 110°C, by means of a dihydroxy functional initiator namely, 3-cyclohexene-1,1-dimethanol in conjunction with stannous-2-ethylhexanoate, ($Sn(Oct)_2$), yielded a well-defined PCL with a cyclohexene mid-chain group. The epoxidation of the cyclohexene (CH) mid-chain group of PCL was performed using 3-chloroperoxybenzoic acid. GPC, IR, and ^{1}H-NMR analyses revealed that a low-polydispersity macromonomer of PCL with the desired cyclohexene oxide (CHO) functionality at the mid-chain was obtained. The photoinduced cationic polymerizations of this macromonomer yielded comb-shaped and graft copolymers. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 123: 2567–2573, 2012

Key words: ring-opening polymerization; functionalization of polymers; macromonomers; photopolymerization; graft copolymers

INTRODUCTION

The design and synthesis of polymers bearing reactive functional groups are of great scientific and industrial importance. Various materials with polymerizable functional groups have been synthesized as precursors of block and graft copolymers, star polymers, and polymer networks.[1] Many studies on varied type of macromonomers and their applications have been reported in recent years.[2–5] Macromonomers are linear polymers or oligomers carrying polymerizable functional groups at their chain end(s) with molecular weight ranging from several thousands to several tens of thousands.[1,6,7] With the changing of chemical structure of the polymer chain and end group, the chemical reactivity of macromonomers would be different. Several methods have been described for making macromonomers[8,9]: (1) end capping of a living polymer (termination method), (2) initiation of living polymer (initiation method), (3) transformation of any functional end group, and (4) polyaddition to introduce monomer functionalities. The resulting macromonomers typically have a monomer functionality bonded with one polymeric chain. There have been many publications on preparing macromonomers by applying above techniques via various methods including anionic, cationic, and radical polymerizations, as well as chemical modifications of polymer ends.[5,6,10–13]

The most practical and convenient strategy to synthesize designed polymers based on poly(ε-caprolactone) (PCL) is ring opening polymerization (ROP) initiated by metal alkoxides.[14,15] Tin octoate, $Sn(O(O)CCH(C_2H_5)C_4H_9)_2$, in short $Sn(Oct)_2$ is the most widely used initiator for the ROP of ε-Caprolactone (ε-CL).[16,17] In particular, when used in conjunction with hydroxyl functional compounds or prepolymers, telechelics, macromonomers, graft polymers, linear, and star-shaped block copolymers or networks can be obtained[18–24] via corresponding alkyl octoate formation. Polymers or macromonomers based on PCL prepared by using $Sn(Oct)_2$ catalyst via ROP methods have predetermined molecular weights and low polydispersities.

olymerization of macromonomers with end- or mid-chain monomer functionalities has produced either brush polymers[25–27] or graft copolymers with interesting structural features.[2,28,29] Three general methods have been used in the preparation of graft polymers: "grafting onto" (attachment of side chains to the backbone), "grafting from" (grafting side

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chains from the backbone), and "grafting through" (polymerization of macromonomers).[28,30–32] Each of these methods has some advantages and limitations. In the work described herein, we employed the grafting-through process with macromonomers in photoinitiated cationic polymerization. We have previously synthesized novel well-defined end-functional macromonomers of PCL[33] via transformation of vinyl end group of PCL to cyclohexene oxide (CHO) and polystyrene[34] via cyclohexene oxide (CHO) functional an initiator. These homopolymer-based macromonomers were used in so-called free radical promoted cationic polymerization to yield comb-shaped and graft copolymers. It occurred to us that such macromonomers (having CHO end or mid-chain functional group) might be particularly useful for photoinitiated cationic polymerization, because photochemically generated cationic species are quite reactive toward these groups.

In this study, we report for the first time to the best of our knowledge, the synthesis of CHO mid-chain functional a macromonomer based on PCL by ROP of ε-CL and epoxidation on workup with 3-chloroperoxybenzoic acid. This PCL-based macromonomer has a potential to be used in photoinduced cationic polymerization for obtaining comb-shaped and graft copolymers.

EXPERIMENTAL

Materials

ε-Caprolactone (ε-CL) (Aldrich, USA) and cyclohexene oxide (CHO) (Aldrich, USA) were distilled over calcium hydride (CaH_2) and stored in a refrigerator under nitrogen before use. The compounds 3-cyclohexene-1,1-dimethanol (Aldrich, USA), 3-chloroperoxybenzoic acid (Aldrich, USA), and sodium bicarbonate ($NaHCO_3$) (Merck Darmstadt, Germany) were used as received. The compound **2**,2-dimethoxy-2-phenyl acetophenone (DMPA) (Irgacure 651), the photoinitiator, was purchased from Ciba Specialty Chemicals and used as received without further purification. Dichloromethane (CH_2Cl_2) (Lab-scan, Gliwice, Poland), methanol (Lab-scan, Gliwice, Poland), diphenyliodonium hexafluorophosphate ($Ph_2I^+PF_6^-$) (Fluka, USA), and all other solvents and chemicals were used as received.

Synthesis of poly(ε-caprolactone) with cyclohexene mid-chain group (CH-PCL)

The ring-opening polymerization (ROP) of ε-CL was carried out in bulk at 110°C. The procedure is as follows: Monomer (ε-CL) (6.18 g, 54.1 mmol), 3-Cyclohexene-1,1-dimethanol (0.19 g, 1.35 mmol), and stannous octoate (2.74 g, 6.76 mmol) were added under nitrogen in previously dried and nitrogen-purged a schlenk tube equipped with a magnetic stirring bar. After 3 days, the tube was immersed into ice-water bath immediately to stop the polymerization. Then, the sample in the tube was diluted with CH_2Cl_2 and precipitated into 10-fold excess of cold methanol. The polymer with cyclohexene (CH) mid-chain group was collected after filtration and drying at room temperature in a vacuum for 2 days. The conversion was calculated gravimetrically.

Yield: 4.84 g, 78%, $M_{n\ GPC} = 3000$, $M_w/M_n = 1.25$. ^{1}H-NMR (400 MHz, $CDCl_3$, δ/ppm): 5.64, 5.56 (m, 2H, C*H*═C*H* of cyclohexene ring), 4.04–4.00 (t, 2H, ─CH_2─O─), 3.94–3.83 (m, 2H, ─CH_2─O─CO─), 3.62–3.59 (t, 2H, ─CH_2─OH), 2.28–2.25 (t, 2H, ─CO─CH_2), 2.11–1.89 (m, 6H, methylene protons of cyclohexene ring), 1.65–1.55 (m, 4H, ─CO─CH_2─CH_2─CH_2─CH_2─CH_2─O─), and 1.40–1.31 (m, 2H, ─CO─CH_2─CH_2─CH_2─CH_2─CH_2─O─).

Synthesis of cyclohexene oxide mid-chain functional macromonomer of PCL (CHO-PCL)

Epoxidation of the cyclohexene mid-chain group of poly(ε-caprolactone) (CH-PCL) was performed under inert atmosphere at 0°C. The above obtained polymer (CH-PCL) ($M_{n\ GPC} = 3000$) (2 g), sodium bicarbonate (0.34 g, 4 mmol), and 50 mL CH_2Cl_2 were added into a 250-mL three-necked round-bottom flask fitted with a condenser, a magnetic stirrer, nitrogen inlet–outlet, and an addition funnel containing 3-chloroperoxybenzoic acid (0.35 g, 2 mmol) and 20 mL CH_2Cl_2 mixture. The flask was placed in an ice-water bath. The solution of 85% 3-chloroperoxybenzoic acid was added dropwise over a period of 2 h under nitrogen. Then, the mixture was allowed to reach room temperature and stirred at that temperature overnight. The solution was washed three times with water. Finally, the solution was dried with $MgSO_4$, and the solvent was removed by rotary evaporator. The solid product was dissolved in CH_2Cl_2 and poured into 10-fold excess of cold methanol. Cyclohexene oxide (CHO) mid-chain functionalized poly(ε-caprolactone) macromonomer (CHO-PCL) was collected after filtration and drying at room temperature in a vacuum for 2 days. The conversion was calculated gravimetrically.

Yield: 2 g, 100%, $M_{n\ GPC} = 3050$, $M_w/M_n = 1.25$. ^{1}H-NMR (400 MHz, $CDCl_3$, δ/ppm): 4.05–4.02 (t, 2H, ─CH_2─O─), 3.92–3.83 (t, 2H, ─CH_2─O─CO─), 3.64–3.61 (m, 2H, ─CH_2─OH), 3.18–3.09 (m, 2H, C*H*─O─C*H*, epoxide protons), 2.30–2.27 (t, 2H, ─CO─CH_2), 1.68–1.55 (m, 4H, ─CO─CH_2─CH_2─CH_2─CH_2─CH_2─O─), and 1.42–1.30 (m, 2H, ─CO─CH_2─CH_2─CH_2─CH_2─CH_2─O─).

TABLE I
Photoinitiated Cationic Polymerization of CHO-PCL Macromonomer (200g L^{-1}, Mn = 3050) in the Presence of $Ph_2I^+PF_6^-$ (5×10^{-3} mol L^{-1}) at Room Temperature in CH_2Cl_2, t = 5h

Run	Photoinitiaton type	Activator (mol L^{-1})	Wavelength (λ, nm)	M_n	M_w/M_n
1	Direct	—	300	7450	1.75
2	Promoted	DMPA (5×10^{-3})	350	9100	1.55
3	Sensitized	Anthracene (5×10^{-3})	350	11200	1.81

Photopolymerization

Photopolymerizations were carried out both in bulk and solution. Appropriate solutions of macromonomers containing calculated amounts of other components, shown in Tables I and II, were placed in pyrex or quartz tubes and degassed with nitrogen before irradiation by a merry-go-round type photoreactor equipped with 16 lamps emitting light nominally at λ = 300 or λ = 350 nm and a cooling system. At the end of the given time (Tables I and II again), the polymers were poured into cold methanol, filtered, dried, and weighed. Conversions were determined gravimetrically.

Characterization

Fourier transform infrared (FTIR) spectra were recorded on a Perkin–Elmer spectrum RXI FTIR spectrophotometer. ^{1}H-NMR spectra were measured on a Bruker 400 MHz spectrometer with $CDCl_3$ as the solvent and tetramethylsilane as the internal standard at ambient temperature. Gel permeation chromatography (GPC) analyses were performed with a setup consisting of an Agilent 1100 RI apparatus equipped with two Waters Ultrastyragel columns (HR series 4E and 5E), with THF as the eluent at a flow rate of 0.4 mL/min and a refractive index detector. The universal calibration method was applied for the CH-PCL and CHO-PCL using the following viscosimetric relationship[35]:

$$M_{n\,\mathrm{PCL}} = 0.259\, M_{n\,\mathrm{PSt}}^{1.073}$$

RESULTS AND DISCUSSION

The cyclohexene oxide (CHO) mid-chain functional macromonomer of PCL was prepared in two steps. First, ROP of ε-CL monomer has been performed using 3-cyclohexene-1,1-dimethanol as initiator and tin(II) 2-ethylhexanoate ($Sn(Oct)_2$) as catalyst. $Sn(Oct)_2$ is frequently used a catalyst in the ROP of ε-CL via coordination-insertion mechanism.[16] In view of the reported role of hydroxyl groups as initiators in ring-opening polymerization, this reaction was expected to produce a polymer containing a cyclohexene (CH) functional group in the middle of the chain derived from the initiator. Then, the epoxidation of precursor (CH-PCL) using 3-chloroperoxybenzoic acid under inert atmosphere at 0°C results in a new CHO functional macromonomer of PCL. The overall reactions for synthesis of PCL with cyclohexene (CH) and cyclohexene oxide (CHO) mid-chain functional group were depicted in Scheme 1.

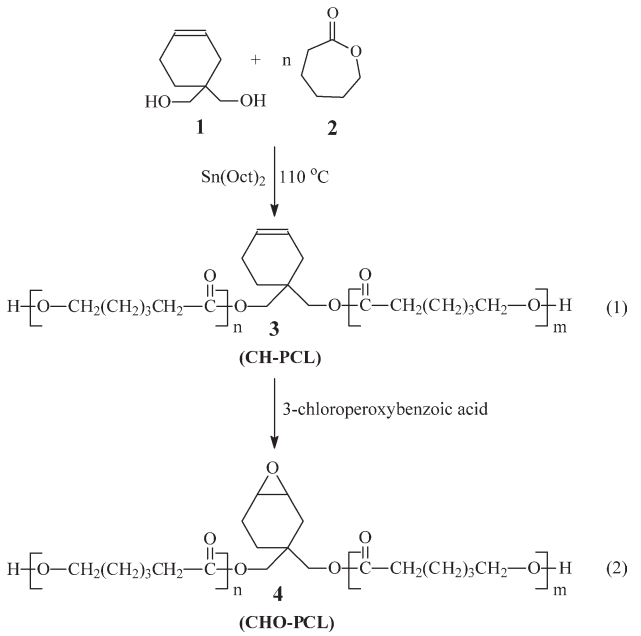
Figure 1(a,b) show the GPC traces of PCL before and after epoxidation process. The GPC molecular weight of the polymer obtained before and after epoxidation reaction does not so much change and molecular weight distribution of the polymers remain the same. The M_n and M_w/M_n of CH-PCL (M_n = 3000, M_w/M_n = 1.25) and CHO-PCL (M_n = 3050, M_w/M_n = 1.25) fit very well with each other. As can be clearly seen from Figure 1(b), the GPC trace of CHO mid-chain functional macromonomer of PCL is still unimodal and narrow, indicating that polymerization was performed in a controlled manner and no chain destruction occurred during the epoxidation process.

In addition, the theoretical molecular weights of the CH-PCL ($M_{n\ \mathrm{theo}}$ = 3710) and the CHO-PCL

TABLE II
Photoinitiated Cationic Polymerization of CHO-PCL Macromonomer (200 g L^{-1} with M_n = 3050) with Cyclohexene Oxide (CHO) Monomer in the Presence of $Ph_2I^+PF_6^-$ (5×10^{-3} mol L^{-1}) at Room Temperature in CH_2Cl_2, λ = 300 nm

Run	CHO (mol L^{-1})	Irradiation time (min)	Yield[a] (%)	M_n	M_w/M_n	Copolymer composition[b] (mol, %) PCL	PCHO
4	3.30 (0.5 mL)	35	63	3800	2.08	23	77
5	4.95 (1 mL)	25	60	3770	1.76	16	84
6	5.94 (1.5 mL)	20	45	3700	1.98	10	90
7[c]	9.90 (1 mL)	10	35	4000	1.90	15	85

[a] CHO conversion.
[b] Calculated from ^{1}H NMR spectra of samples.
[c] Bulk.



Scheme 1 Synthesis of cyclohexene oxide mid-chain functional macromonomer of poly(ε-caprolactone).

($M_{n\ \mathrm{theo}} = 3726$) samples calculated by the following equations fit very well with the one calculated by NMR ($M_{n\ \mathrm{NMR}} = 3800$) from the relative intensity of the **a** and **b** protons of cyclohexene (CH) or cyclohexene oxide (CHO) mid-chain group and methylene protons of PCL.

$$M_{n\,\mathrm{CHO-PCL}} = M_{n\,\mathrm{CH-PCL}} + M_{\mathrm{O}}$$

where $M_{n\ \mathrm{CH\text{-}PCL}}$ and $M_{n\ \mathrm{CHO\text{-}PCL}}$ are the theoretical molecular weight of CH-PCL and CHO-PCL, respectively, and M_O is the molecular weight of oxygen. The theoretical molecular weight of CH-PCL ($M_{n\ \mathrm{CH\text{-}PCL}}$) is calculated by the following equation:

$$M_{n\,\mathrm{CH-PCL}} = [M]_0/[I]_0 \times M_{\varepsilon\mathrm{-CL}} \times C\% + M_{\mathrm{I}}$$

where $[M]_0$ and $[I]_0$ are the initial molar concentrations of monomer (ε-CL) and initiator (3-cyclohexene-1,1-dimethanol), $C\%$ is the % conversion of monomer (ε-CL) to polymer (CH-PCL), and $M_{\varepsilon\text{-CL}}$ and M_I are the molecular weights of the monomer and initiator, respectively.

The ^{1}H-NMR spectra of the PCL's with cyclohexene and cyclohexene oxide mid-chain groups display the signals characteristic of the corresponding segments (Fig. 2). As can be clearly seen, the **a** and **b** protons of double bond at 5.64 and 5.56 ppm, respectively, observed in the spectrum of CH-PCL [Fig. 2(a)] completely disappeared in the spectrum of CHO-PCL [Fig. 2(b)]. Instead, the new signals at 3.18 and 3.09 ppm were assigned to the protons of the CHO moiety. Moreover, the FTIR spectral

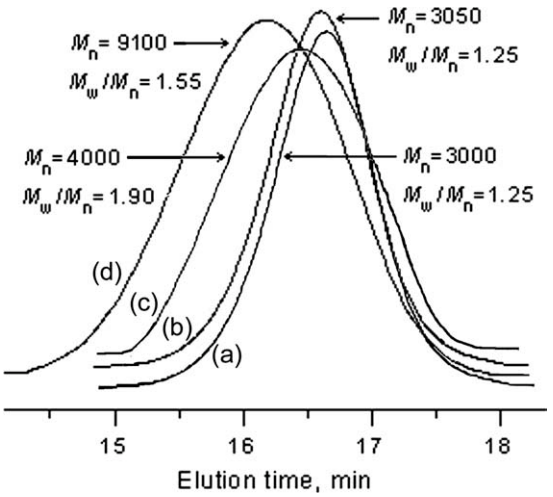


Figure 1 GPC traces of CHO-PCL (**a**), CH-PCL (**b**), PCHO-PCL graft copolymer (Table II, Run 7) (**c**), and PCHO-PCL comb-shaped polymer (Table I, Run 2) (**d**).

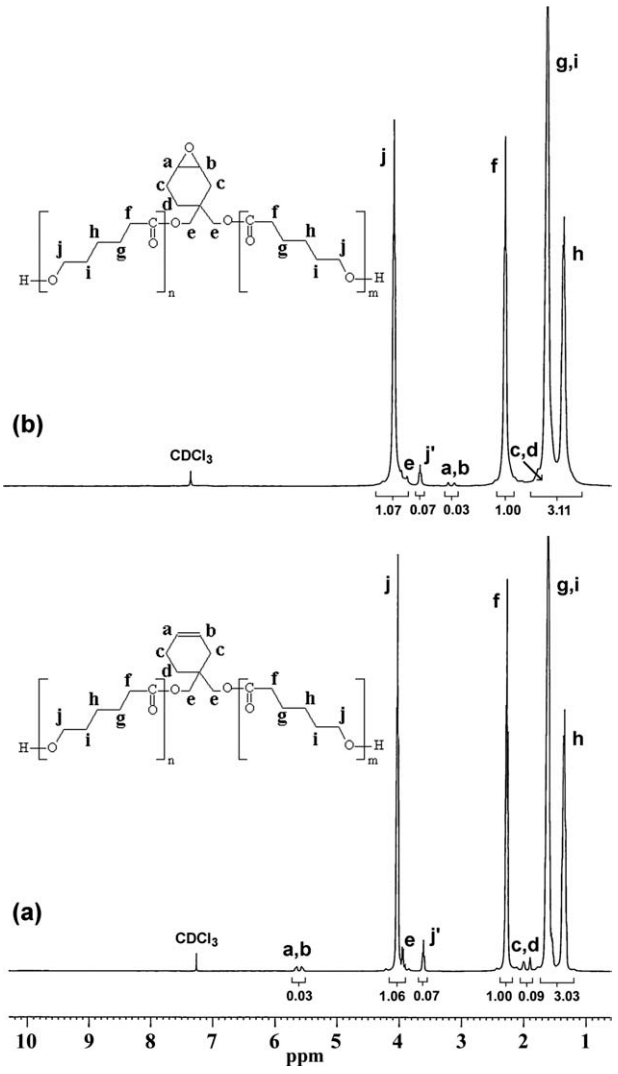


Figure 2 ^{1}H-NMR spectra of cyclohexene (**a**) and cyclohexene oxide (**b**) mid-chain functional poly(ε-caprolactone) in $CDCl_3$.

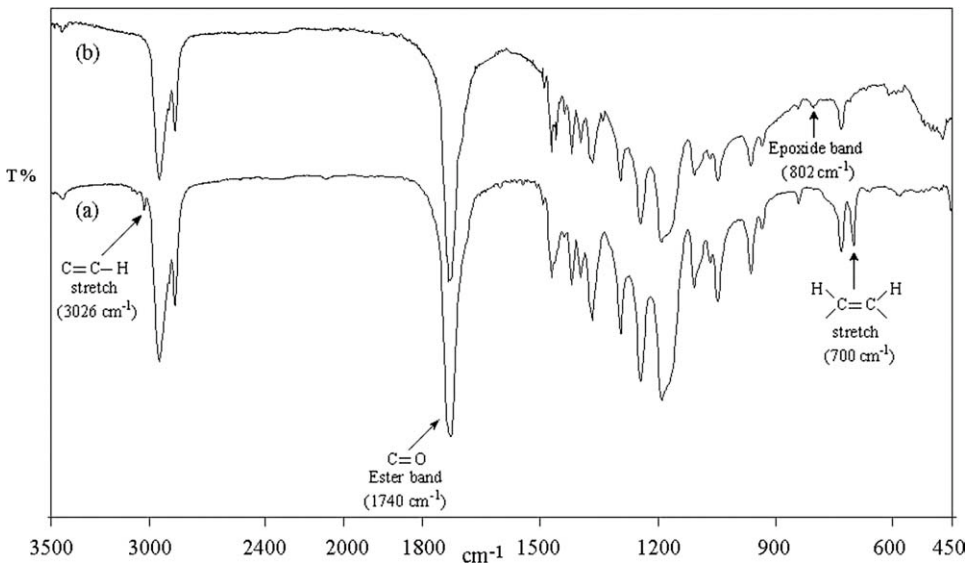


Figure 3 FTIR spectra of cyclohexene (**a**) and cyclohexene oxide (**b**) mid-chain functional poly(ε-caprolactone).

analysis also supports this result (Fig. 3). For example, the peak at 3026 cm^{-1} and 700 cm^{-1} due to the C═C—H and H—C═C—H, respectively, of CH-PCL stretching vibration completely disappeared in the case of CHO-PCL, and a new peak at 802 cm^{-1}, which was assigned to the epoxide band was clearly observed. All these results indicated successful epoxidation and the formation of the new CHO mid-chain functional macromonomer of PCL.

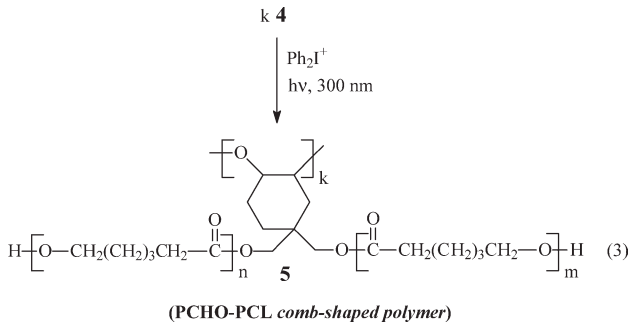
The obtained CHO-PCL was used as precursor in the photoinitiated cationic polymerization. Table I shows the types of photoinitiation used in our work. As can be seen from Scheme 2, homopolymerization of macromonomers provides comb-shaped polymers with a very high branch density.[8,9]

All the types of photoinitiation systems yielded polymers with high conversion (>99%) and basically the same structure. As expected, the molecular weight and molecular weight distribution of the obtained polymers were slightly higher than those of the macromonomer [Fig. 1(d)]. Photoinitiated cationic polymerization by direct irradiation of the iodonium salt at 300 nm presents some limitations for the potential use of PCL macromonomers because of their overlapping tail absorptions. Therefore, we have also employed indirect ways, namely free radical promoted and electron transfer photosensitization, to provide working conditions for photoinitiated cationic polymerization at a broad wavelength range.

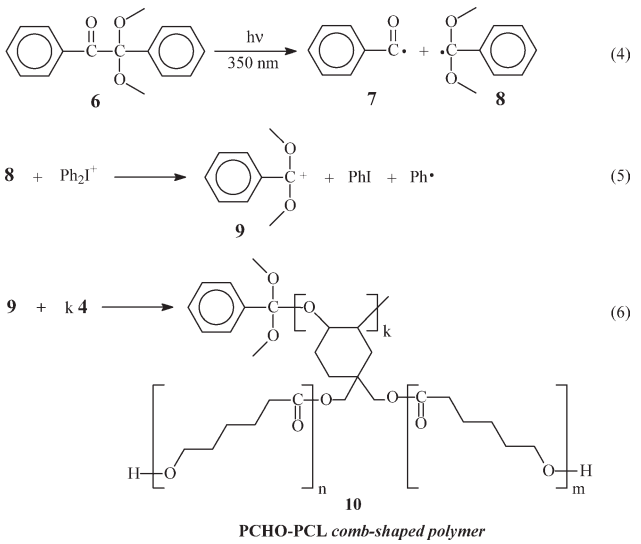
In the radical-promoted cationic polymerization, DMPA was used as the radical source. The photolysis of DMPA results in α-cleavage and 2,2-dimethoxy benzyl (strong electron donor) and benzoyl (electron withdrawing) radicals are formed. When irradiated in the presence of an onium salt such as diphenyl iodonium at 350 nm where onium salt is transparent, the light is absorbed only by DMPA. The photochemically generated 2,2-dimethoxy benzyl radicals reduce the iodonium salt to yield corresponding carbocations[36] capable of initiating cationic polymerization of the macromonomer. The overall reaction mechanisms were depicted in Scheme 3.

Figure 4(b) shows the ^{1}H-NMR spectrum of the poly(cyclohexene oxide)-poly(ε-caprolactone) comb-shaped polymer (Table I, Run 2). Not only the specific signals of PCHO and PCL segments are visible but also absorptions belonging to the rest of the initiator fragment.

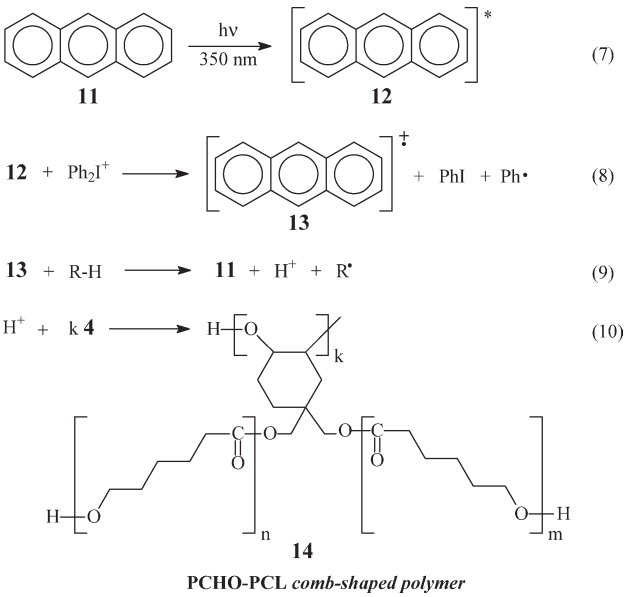
In earlier studies on photoinitiated cationic polymerization using anthracene as a sensitizer, it was shown that the electron transfer, governed by energetic and thermodynamic considerations, was the dominant process. The magnitude of the free ΔG energy for the electron transfer should have been 10 kJ mol^{-1}. The ΔG value (−193 kJ mol^{-1}) suggests that electron transfer from singlet anthracene to iodonium ions is quite favorable.[36] Anthracene radical cation or Brønsted acid formed from the hydrogen



Scheme 2 Synthesis poly(cyclohexene oxide)-poly(ε-caprolactone) comb-shaped polymer.



Scheme 3 Photolysis of 2,2-dimethoxy-2-phenyl acetophenone in the presence of diphenyliodonium salt.



Scheme 4 Photolysis of anthracene in the presence of diphenyliodonium salt.

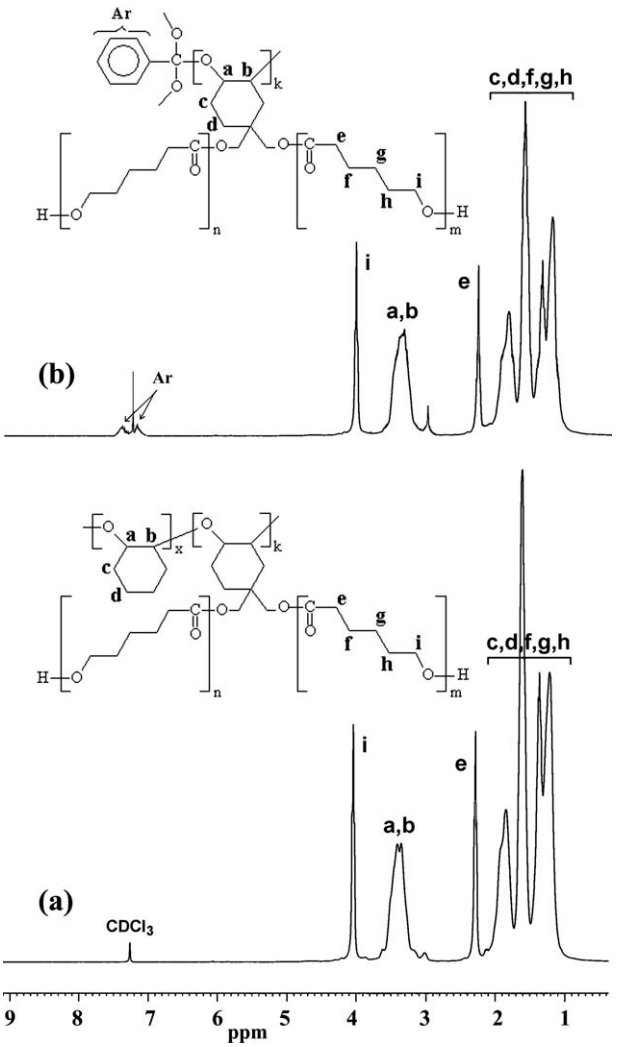


Figure 4 ^{1}H-NMR spectrum of PCHO-PCL graft (Table II, Run 4) (**a**) and comb shaped (Table I, Run 2) (**b**) polymer in $CDCl_3$.

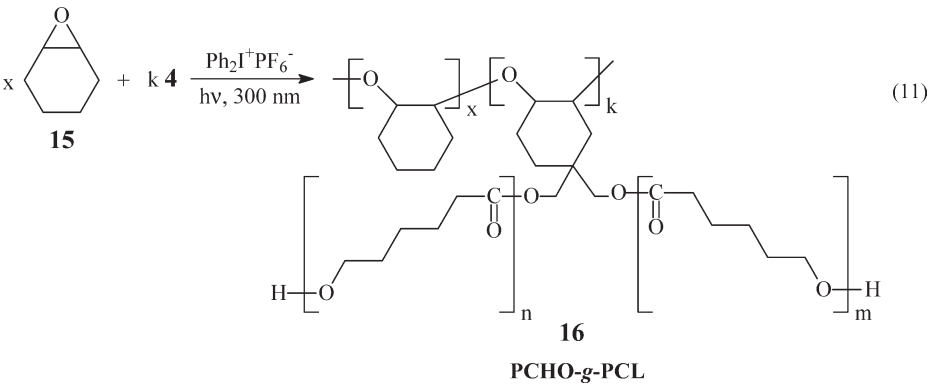
abstraction reaction may initiate the cationic polymerization of the macromonomer as shown in Scheme 4.

Poly(ε-caprolactone) (CHO-PCL) was also used as a comonomer in the copolymerization with CHO monomer under similar conditions to those applied for the polymerization of the CHO-PCL macromonomer itself. Using CHO-PCL macromonomer as the comonomer allowed for a rather simple incorporation of PCL side chains into poly(cyclohexene oxide) (PCHO) backbone. In this way, poly(cyclohexene oxide)-poly(ε-caprolactone) graft copolymer (PCHO-*g*-PCL) with random sequences of the following structure was formed (Scheme 5).

Typical results concerning photochemically induced cationic copolymerization of CHO with CHO-PCL macromonomer at room temperature are shown in Table II. As can be seen, the concentration of the CHO comonomer influences the composition of the graft copolymer. The composition of the copolymers PCHO-*g*-PCL was determined from ^{1}H-NMR spectrum [Fig. 4(a)] using the integrated peak ratio of the **e** protons of ε-caprolactone (2.35–2.20 ppm) in the PCL segment to the OCHCHO protons (**a** and **b**) in the PCHO segment (3.45–3.20 ppm). The content of PCL units in a copolymer *X* (mol %) was calculated using the following formula:

$$X_{\mathrm{PCL}} = \frac{(I_{2.35-2.20}/4)}{(I_{2.35-2.20}/4) + (I_{3.45-3.20}/2)} \times 100$$

where $I_{2.35-2.20}$ is the integral of the **e** proton signals at 2.35–2.20 ppm, and $I_{3.45-3.20}$ is the integral of the OCHCHO proton signals at 3.45–3.20 ppm.



Scheme 5 Synthesis of poly(cyclohexene oxide)-*g*-poly(ε-caprolactone).

The graft copolymer structures were assigned by means of ^{1}H-NMR and GPC spectral measurements. Figure 1(c) shows the GPC chromatogram of the poly(cyclohexene oxide)-poly(ε-caprolactone) graft copolymer (PCHO-*g*-PSt) that was formed (Table II, Run 7). Notably, no peak relating to the residual homopolymer was detected. Figure 4(a) shows the ^{1}H-NMR spectrum of the PCHO-*g*-PSt (Table II, Run 4). As can be seen from the spectrum, specific signals of both PCHO and PCL segments of graft copolymer at 3.45–3.20 ppm of O**C**H—**C**HO and 2.35–2.20 ppm of CO—C$\mathbf{H_2}$— (PCL), respectively, are visible.

CONCLUSIONS

A new cyclohexene mid-chain functional polymer of poly(ε-caprolactone) (CH-PCL) was synthesized by ring-opening polymerization (ROP) method. The epoxidation of the CH-PCL using 3-chloroperoxybenzoic acid formed a novel well-defined PCL macromonomer possessing CHO mid-chain group (CHO-PCL). The obtained CHO-PCL macromonomer was employed in photoinitiated cationic (co)polymerization using diphenyliodonium salt. Photoinitiation cationic homopolymerization of macromonomers can be efficiently achieved by using the iodonium salt at 300 nm as well as at wavelengths of about 350 nm with the aid of sensitizers and free radical sources. In each case, poly(cyclohexene oxide)-poly(ε-caprolactone) comb-shaped polymer was obtained. CHO-PCL macromonomer was also used as a comonomer in the photoinitiated cationic copolymerization with CHO monomer. In this way, poly(cyclohexene oxide)-poly(ε-caprolactone) graft copolymer with random sequences was formed.

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