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Synthesis and characterization of cyclohexene oxide functional polystyrene macromonomers by ATRP and their use in photoinitiated cationic polymerization

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ABSTRACT

In this study, a novel well-defined macromonomer of epoxy end-functionalized polystyrene was synthesized by atom transfer radical polymerization (ATRP). The compound 3-cyclohexenylmethyl-2-bromopropanoate was synthesized by the condensation of 3-cyclohexene-1-methanol with 2-bromopropanoyl bromide. Subsequently, the epoxidation of the obtained 3-cyclohexenylmethyl-2-bromopropanoate using 3-chloroperoxybenzoic acid results in a new epoxy functional ATRP initiator. The ATRP of styrene (St) in bulk at 110 °C, by means of this initiator in conjunction with the cuprous complex Cu(I)Br/bipyridine, yields a well-defined macromonomer of polystyrene with an epoxy end group. GPC, IR, and ^{1}H NMR analyses revealed that a low-polydispersity polystyrene with the desired functionality at the end of the chain was obtained. The photoinduced cationic polymerization of this macromonomer yielded graft and block copolymers.

1. Introduction

Recently, the attention of both academic and industrial fields has been attracted to the design and synthesis of materials with novel properties. Various polymers with end-functional groups have been synthesized as precursors of block and graft copolymers, star polymers, and polymer networks [1]. Macromonomers are linear polymers or oligomers carrying polymerizable functional groups at their chain end(s). The chain end(s) can include unsaturated groups, which can participate in radical or ionic polymerizations, heterocycles active in ring-opening polymerizations, and functional groups that can participate in polycondensation reactions. Depending on the type of end-functionality, the polymerization of macromonomers results in graft copolymers or networks. There have been many publications on preparing macromonomers via various methods including anionic, cationic, and radical polymerizations, as well as chemical modifications of polymer ends [1–7].

In recent years, there have been many developments in the synthesis of functional polymers with controlled architecture and site-specific functionality by applying controlled radical polymerization (CRP) techniques [8–13]. One of the most powerful and versatile methods in CRP is atom transfer radical polymerization (ATRP) because of its relatively mild reaction conditions, the availability of appropriate monomers, initiators, and catalysts, and in particular its versatility in the synthesis of polymers with predictable molecular weights, low polydispersities, specific functionalities and various architectures [14–18]. Due to the radical nature of ATRP, a wide range of functional monomers can be polymerized, yielding polymers with pendant functional groups. Therefore, various functional monomers including styrenes, (meth)acrylates and others have been (co)polymerized in a controlled fashion by ATRP [10,19,20].

We have previously prepared types of functional polymers of poly(ε-caprolactone) [21,22], polystyrene [23,24], and poly(methyl methacrylate) [25] that have the potential to initiate light-induced free radical polymerization by CRP techniques such as ring-opening polymerization and ATRP. These polymers were also used in so-called free radical promoted cationic polymerization to yield block copolymers of structurally different monomers such as cyclohexene oxide (CHO) and ε-caprolactone (CL). There are many reports on the use of photoinitiated cationic polymerization for the preparation of block copolymers [26–32]. However, the corresponding graft copolymerization via a similar photoinduced process has received little study [33,34]. It occurred to us that the macromonomer method involving CHO end-functional polymers might be particularly useful because photochemically generated

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cationic species are quite reactive towards these groups. In this article, we present the results of a study of the preparation of CHO end-functional macromonomers via ATRP of styrene monomer using a new CHO-functional initiator and a Cu(I)Br/bipyridine catalyst system.

2. Experimental

2.1. Materials

Styrene (St) (Fluka) and cyclohexene oxide (CHO) (Aldrich) were distilled over calcium hydride (CaH_2) and stored in a refrigerator under nitrogen before use. The compounds 3-cyclohexene-1-methanol (Aldrich), 2-bromopropanoyl bromide (Aldrich), 3-chloroperoxybenzoic acid (Aldrich), and sodium bicarbonate ($NaHCO_3$) (Merck) 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) pyridine (Lab-scan), diphenyliodonium hexafluorophosphate ($Ph_2I^+PF_6^-$) (Fluka), CuBr (Aldrich), 2,2′-bipyridine (Merck) and all other solvents and chemicals were used as received.

2.2. Synthesis of 3-cyclohexenylmethyl-2-bromopropanoate (CH–Br)

For this synthesis, 3-cyclohexene-1-methanol (5.02 mL, 44.6 mmol), pyridine (5.40 mL, 66.9 mmol), and 30 mL dry CH_2Cl_2 were added to a two-necked round-bottom flask fitted with a magnetic stirrer, nitrogen inlet–outlet and an addition funnel containing 2-bromopropanoyl bromide (7.07 mL, 66.90 mmol) and 5 mL dry CH_2Cl_2. The flask was placed in an ice-water bath. The solution of 2-bromopropanoyl bromide was added dropwise over a period of 1 h under nitrogen. The mixture was stirred at 0 °C for 30 min. The mixture was then allowed to reach room temperature and stirred at that temperature overnight. The solution was washed with 0.2 N HCl and several times with water. Finally, the solution was dried with $MgSO_4$, and the solvent was removed by vacuum distillation. A yellowish liquid product was obtained. Yield: 9.97 g, 91%.

$C_{10}H_{15}O_2Br$: (247,131): Calcd. C, 48.60%; H, 6.07%, Found: C, 48.12%; H, 6.01%. ^1H NMR (acetone-d_6, δ/ppm): 5.92–5.52 (m, 2H, *H*C═C*H*), 4.75–4.41 (q, 1H, C*H*–Br), 4.28–3.82 (m, 2H, OC*H*$_2$), 2.16–1.96 (m, 1H, OCH$_2$C*H*), 1.84–1.65 (d, 3H, C*H*$_3$CH), 1.51–1.16 (m, 6H, methylene protons of cyclohexene oxide group). FT-IR (cm^{-1}): 3024 (C═**C**–**H** stretch), 1739 (**C**═**O** ester band), 1651 (**C**═**C** stretch).

2.3. Synthesis of cyclohexene oxide (CHO) functional ATRP initiator (CHO–Br)

Epoxidation of the 3-cyclohexenylmethyl-2-bromopropanoate was performed under inert atmosphere at 0 °C. The obtained 3-cyclohexenylmethyl-2-bromopropanoate (4 g, 16.18 mmol), sodiumbicarbonate (5.437 g, 64.72 mmol), 3-chloroperoxybenzoic acid (5.58 g, 32.37 mmol) and 20 mL of dry CH_2Cl_2 were added into a 100-mL three-necked round-bottom flask fitted with a condenser, a magnetic stirrer, and a nitrogen inlet–outlet. The flask was placed in an ice-water bath and stirred for 30 min. Then, the mixture was allowed to reach room temperature and stirred at that temperature for 2 h. After the reaction, the reaction mixture was added into 100 mL of water, and then extracted several times with CH_2Cl_2. Finally, the solution was dried with $MgSO_4$, and the solvent was removed by vacuum distillation. A yellowish oily product was obtained. Yield: 2.25 g, 53%.

$C_{10}H_{15}O_3Br$: (263,130): Calcd. C, 45.64%; H, 5.70%, Found: C, 45.12%; H, 5.54%. ^1H NMR (acetone-d_6, δ/ppm): 4.73–4.42 (q, 1H, C*H*–Br), 4.41–3.86 (m, 2H, OC*H*$_2$), 3.23–3.00 (m, 2H, C*H*–O–C*H*, epoxide protons), 2.24–1.94 (m, 1H, OCH$_2$C*H*), 1.82–1.62 (d, 3H, C*H*$_3$CH), 1.60–1.00 (m, 6H, methylene protons of cyclohexene oxide group). FT-IR (cm^{-1}): 1739 (**C**═**O** ester band), 920 (epoxide band),

2.4. Synthesis of cyclohexene oxide end-functional macromonomer of polystyrene by atom transfer radical polymerization (CHO-PSt)

A Schlenk tube equipped with a magnetic stirrer was used. The system was vacuumed and back-filled with nitrogen several times. The catalyst (CuBr), ligand bipyridine (bpy), initiator (CHO–Br), and monomer (St) were introduced under inert atmosphere. The tube was placed in an oil bath warmed at 110 °C and stirred at that temperature. After a given time (see Table 1), the mixture was diluted with THF and poured into ten-fold methanol. The macromonomer (CHO-PSt) was collected after filtration and dried at 40 °C in vacuum overnight. In order to remove the complex salt from the polymer, it was redissolved in THF and passed through an alumina column, followed by precipitation in methanol.

^1H NMR (acetone-d_6, δ/ppm): 7.52–6.39 (m, 5H, Ar–*H*), 4.60 (q, 1H, C*H*–Br), 3.84–3.63 (m, 2H, OC*H*$_2$), 3.23–3.00 (m, 2H, C*H*–O–C*H*,

Table 1
Synthesis of CHO end-functional macromonomers of PSt by ATRP[a] using CHO–Br as initiator.

Run	$[I] \times 10^{-2}$ (mol L^{-1})	Time (min)	Conversion (%)	$M_{n\ theo}$	$M_{n\ GPC}$[b]	M_w/M_n	$M_{n\ H\ NMR}$
1	9.7	180	45	4500	3650	1.21	4200
2	28.9	90	39	1490	1590	1.27	1920
3	57.9	60	59	1160	970	1.24	1025

[a] Temperature 110 °C, $[St]_0$ = 8.75 mol L^{-1}(in bulk), [*I*]:[CuBr]:[Bpy] = 1:1:3.
[b] Determined by GPC according to PSt standards.

Table 2
Photoinitiated cationic polymerization of CHO-PSt macromonomer[a].

Run	Photoinitiaton type	Activator (mol L^{-1})	Wavelength (λ, nm)	M_n	M_w/M_n
1	Direct	–	300	3940	1.60
2	Promoted	DMPA (5810^{-3})	350	4110	1.44
3	Sensitized	Anthracene (5×10^{-3})	350	6200	1.75

Conversions were calculated using the following formula: Conv.% = $(W - W_0)/W \times 100$; where W and W_0 are the total polymer obtained and unreacted macromonomer.
[a] Macromonomer: 200 g L^{-1} with M_n = 1590; onium salt, $Ph_2I^+PF_6^-$: 5×10^{-3} mol L^{-1}; temperature: room temperature; solvent: CH_2Cl_2; irradiation time: 5 h; conversions: >99%.

Table 3
Photoinitiated cationic polymerization CHO-PSt macromonomer with cyclohexene oxide (CHO) monomer[a].

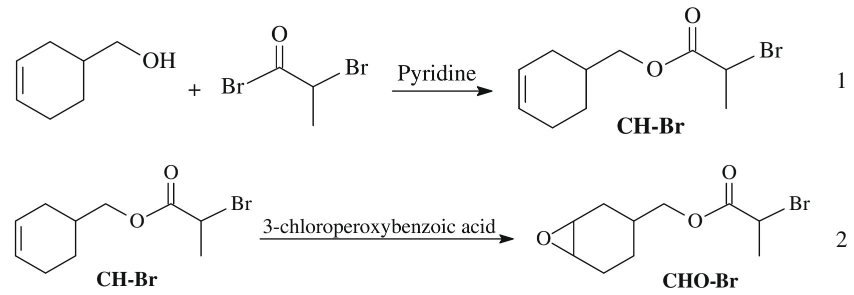
Run	CHO (mol L^{-1})	Irradiation time (min)	Yield[b] (%)	M_n	M_w/M_n	Copolymer composition[c] (mol, %) PSt PCHO
1	0.85	70	52	6800	1.75	69 31
2	1.65	60	50	4700	1.89	65 35
3	4.95	45	45	3200	1.90	21 79
4	6.60	25	23	2500	2.14	19 81
5[d]	9.90	20	37	4600	1.95	23 77

[a] Macromonomer: 200 g L^{-1} with $M_n = 1590$; onium salt, $Ph_2I^+PF_6^-$: 5×10^{-3} mol L^{-1}; temperature: room temperature; solvent: CH_2Cl_2; irradiation wavelength: $\lambda = 300$ nm.

[b] CHO conversion.

[c] Calculated from ^1H NMR spectra of samples.

[d] Bulk.



Scheme 1. Synthesis of cyclohexene oxide (CHO) functional ATRP initiator.

epoxide protons), 2.20–1.81 (m, 3H, OCH_2CH, CH_3CH and Ar–CH), 1.80–1.21 (m, 10H, methylene protons of cyclohexene oxide group and styrene segment in polymer chain).

2.5. Photopolymerization

Photopolymerizations were carried out both in bulk and solution. Appropriate solutions of macromonomers containing calculated amounts of other components, shown in Tables 2 and 3, were placed in Pyrex or quartz tubes and degassed with nitrogen prior to irradiation by a merry-go-round type photoreactor equipped with 16 lamps emitting light nominally at $\lambda = 300$ or $\lambda = 350$ nm and a cooling system. At the end of the given time (see Tables 2 and 3 again), the polymers were poured into cold methanol, filtered, dried, and weighed. Conversions were determined gravimetrically.

2.6. Characterization

Fourier transform infrared (FT-IR) spectra were recorded on a Perkin–Elmer spectrum RXI FT-IR spectrophotometer. ^1H NMR spectra were measured on a Bruker 250 MHz spectrometer at ambient temperature. Gel permeation chromatography (GPC) chromatograms were obtained using a Waters instrument equipped with a R410 differential refractometer and 600E pump and with THF as the eluent, at a flow rate of 1.0 mL/min. Molecular weights were calculated using monodisperse polystyrene standards.

3. Results and discussion

It has been shown that CuBr/bipyridine complex is very effective for ATRP in conjunction with alkyl halides [15]. The objective of this work was to design an initiator with cyclohexene oxide (CHO) containing alkyl bromide, so as to produce CHO end-func-

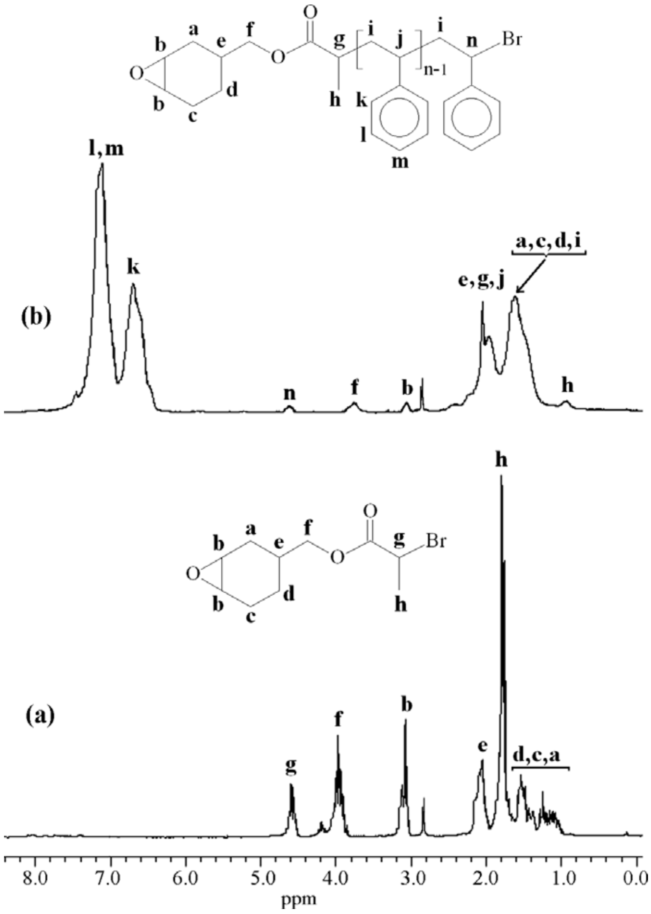


Fig. 1. ^1H NMR spectra of CHO–Br (a) and CHO-PSt (Table 1, run 2) (b) in acetone-d_6.

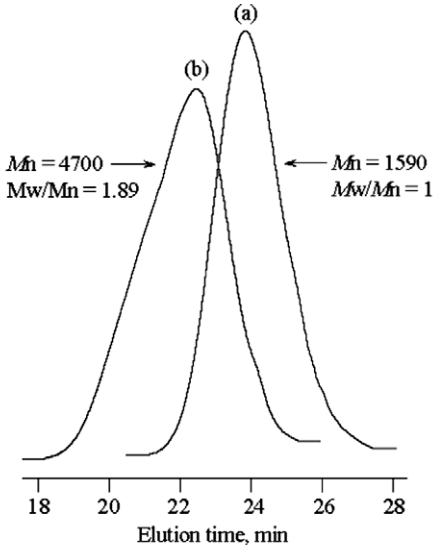


Fig. 2. GPC traces of polystyrene (Table 1, run 2) (a) and poly(cyclohexene oxide)-g-polystyrene (Table 3, run 2) (b).

tionalized polystyrenes and subsequently use them as a precursor for photoinitiated cationic polymerization. The ATRP initiator was prepared in two steps, as shown in Scheme 1. In the first step, 3-cyclohexenylmethyl-2-bromopropanoate (CH–Br) was synthesized by the condensation of 3-cyclohexene-1-methanol with 2-bromopropanoyl bromide. In the second step, the epoxidation of obtained CH–Br using 3-chloroperoxybenzoic acid results in a new CHO-functional ATRP initiator (CHO–Br).

The structures of initiators with cyclohexene and cyclohexene oxide end groups (CH–Br and CHO–Br) were confirmed by elemental analyses and spectroscopic investigations. The ^{1}H NMR spectra of the CH–Br (see supporting information) and of the CHO–Br (Fig. 1a) display the signals characteristic of the corresponding segments. The characteristic peak at 5.92–5.52 ppm observed in the spectrum of CH–Br was ascribed to the protons at the double bond (–C*H*═C*H*–) of the cyclohexene ring. The other characteristic resonances originating from the CH–Br compound at 4.75–4.41 ppm, 4.28–3.82 ppm, 2.16–1.96 ppm, 1.84–1.65 ppm, and 1.51–1.16 ppm, assigned to the –C*H*–Br, –OC*H*$_2$–, –OCH$_2$C*H*–, –C*H*$_3$CH–, and –C*H*$_2$– groups, respectively, were still present in the ^{1}H NMR spectrum of CHO–Br (Fig. 1a). As can be clearly seen from the ^{1}H NMR spectra of related compounds, only the peak observed at 5.92–5.52 ppm due to the vinyl protons completely disappeared in the spectrum of CHO–Br (Fig. 1a). Instead, new signals appeared at 3.23–3.00 ppm, which were assigned to the protons of the CHO moiety. Moreover, the FT-IR spectral analysis also supports this result (see supporting information). For example, the peak at 1651 cm^{-1} due to the C═C stretch and the peak at 3024 cm^{-1} due to the C═C–H stretching vibration observed in the spectrum of CH–Br spectrum completely disappeared in the spectrum of CHO–Br, and a new peak at 920 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-functional ATRP initiator.

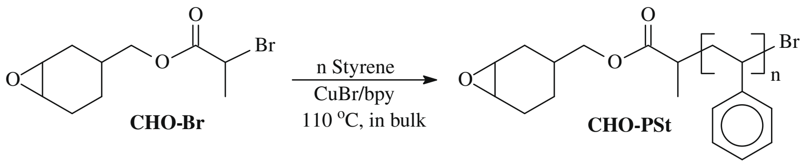
The ATRP of styrene (St) was performed in bulk at 110 °C by means of an ATRP initiator (CHO–Br) in conjunction with a cuprous complex Cu(I)Br/bpy. In view of the reported role of halide groups as initiators in ATRP, this reaction was expected to produce a polymer containing a cyclohexene oxide (CHO) group on one chain end (CHO-PSt) derived from the initiator as shown in Scheme 2.

As can be seen from Table 1, the measured and calculated M_n values are in good agreement, indicating that the photoinitiator added to the solution generates one growing end. By modifying the initiator concentration and the polymerization time, CHO end-functional macromonomers with various molecular weights and low polydispersities were obtained. A control experiment in the absence of styrene monomer was performed under similar ATRP conditions in order to check whether the epoxide group (CHO) remained intact during the ATRP processes. After 2 h of reaction time, the product was isolated and characterized. The spectral characterization (FT-IR and ^{1}H NMR spectral measurements) of the product obtained after ATRP clearly showed the same results as CHO–Br before ATRP. This result indicated that the CHO end group was not affected under polymerization conditions.

The theoretical molecular weights ($M_{n\,\text{theo}}$) of the CHO-PSt samples were calculated by the following equation:

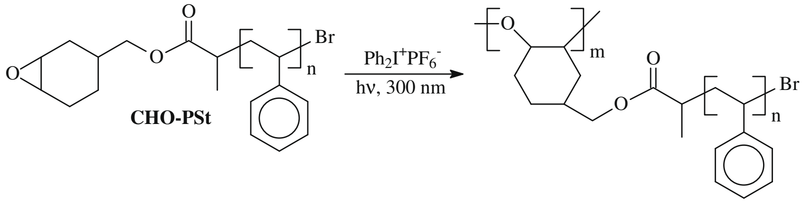
$$M_{n\,\text{theo}} = [M]_0/[I]_0 \times M_{n\,\text{St}} \times \text{Conversion} + M_{n\,\text{CHO-Br}}$$

where $[M]_0$ and $[I]_0$ are the initial molar concentrations of monomer and initiator (CHO–Br), and $M_{n\ \text{St}}$ and $M_{n\ \text{CHO-Br}}$ are the molecular weights of the monomer (styrene) and initiator, respectively. The molecular weights ($M_{n\ \text{H NMR}}$) can be calculated from the ratio of aromatic protons of styrene in the CHO-PSt polymer to b protons of the cyclohexene oxide end group in the ^{1}H NMR spectrum. The equation is shown below:



3

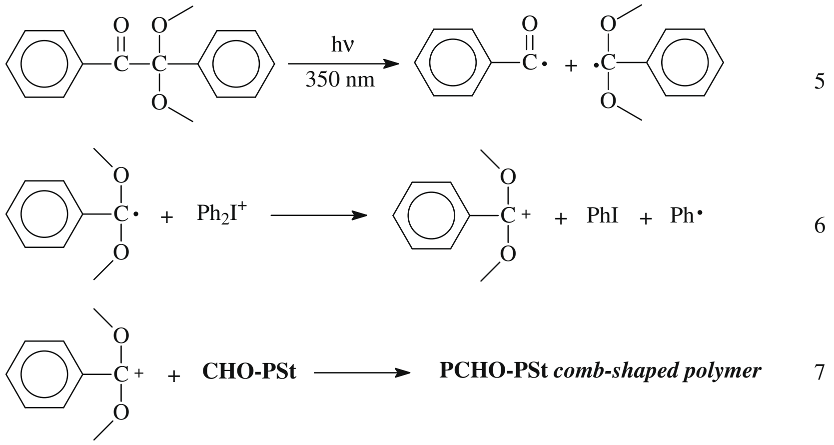
Scheme 2. Synthesis of cyclohexene oxide (CHO) end-functional polystyrene macromonomer.



4

PCHO-PSt ***comb-shaped polymer***

Scheme 3. Photoinitiated cationic polymerization of polystyrene macromonomer.



Scheme 4. Photolysis of 2,2-dimethoxy-2-phenyl acetophenone in the presence of diphenyliodonium salt.

$$M_{n\ \mathrm{H\ NMR}} = \frac{(I_{7.52-6.39/5})}{(I_{3.23-3.00/2})} \times M_{n\ \mathrm{St}} + M_{n\ \mathrm{CHO-Br}}$$

where $I_{7.52-6.39}$ is the integral of the signals at 7.52–6.39 ppm, $I_{3.23-3.00}$ is the integral of the signals at 3.23–3.00 ppm, $M_{n\ \mathrm{St}}$ is the molecular weight of styrene and $M_{n\ \mathrm{CHO-Br}}$ is the molecular weight of CHO–Br.

Fig. 2a shows the GPC trace of cyclohexene oxide end-chain functional macromonomer (CHO-PSt). It is unimodal and narrow, indicating that polymerization was performed in a controlled manner and that no side reactions occurred during the ATRP process.

In the ^{1}H NMR spectrum of the macromonomer (CHO-PSt) (Table 1, run 2) can be found not only the specific signals of polystyrene (PSt) but also absorptions belonging to the rest of the initiators. As can be clearly seen from that spectrum, the epoxy end group of the polymer was conserved under the polymerization conditions (Fig. 1b).

The obtained CHO end-functional macromonomers were used as precursors in the photoinitiated cationic polymerization. Table 2 shows the types of photoinitiation used in our work. As can be seen from Scheme 3, homopolymerization of macromonomers provides comb-shaped polymers with a very high branch density [35,36].

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 (Scheme 3). Although the conversions are so high, the molecular weights of the polymers are quite low. This is probably due to the chain entanglement and steric hindrances of high branch polymers obtained during photoinitiation. These effects prevent the initiator from reaching the macromonomer's active site to initiate polymerization and leads to short chains even at very long reaction times. Photoinitiated cationic polymerization by direct irradiation of the iodonium salt at 300 nm presents some limitations for the potential use of PSt macromonomers because of their overlapping tail absorptions. Therefore, we have also employed indirect ways, namely free radical promoted 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, as shown in Scheme 4. The photolysis of DMPA results in α-cleavage and 2,2-dimethoxy benzyl (strong electron donor), and benzoyl (electron withdrawing) radicals are formed according to reaction 5. 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 [37] (reaction 6) capable of initiating cationic polymerization of the macromonomer.

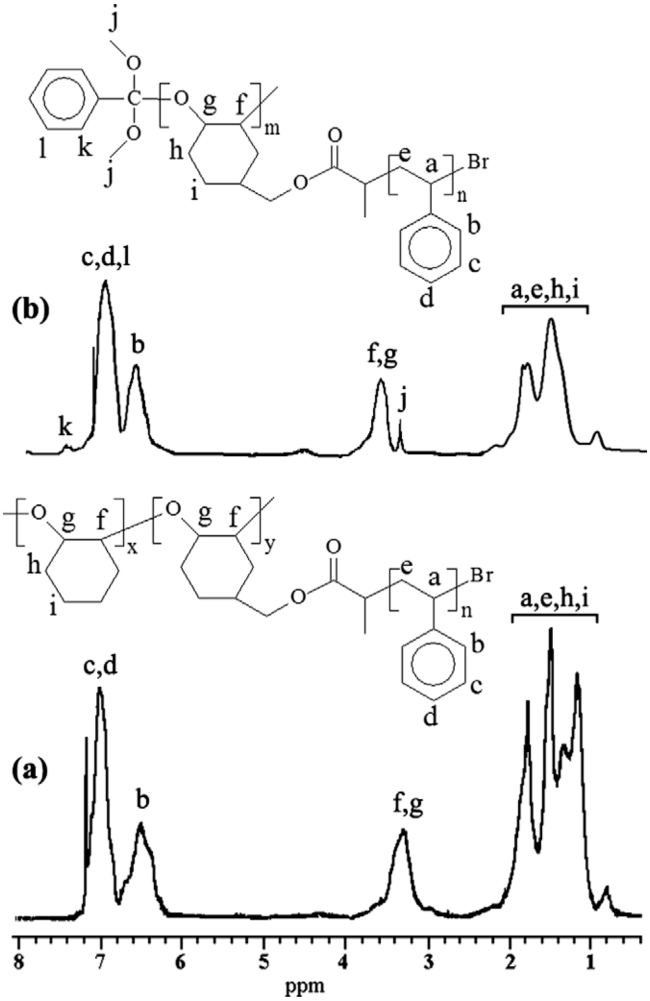
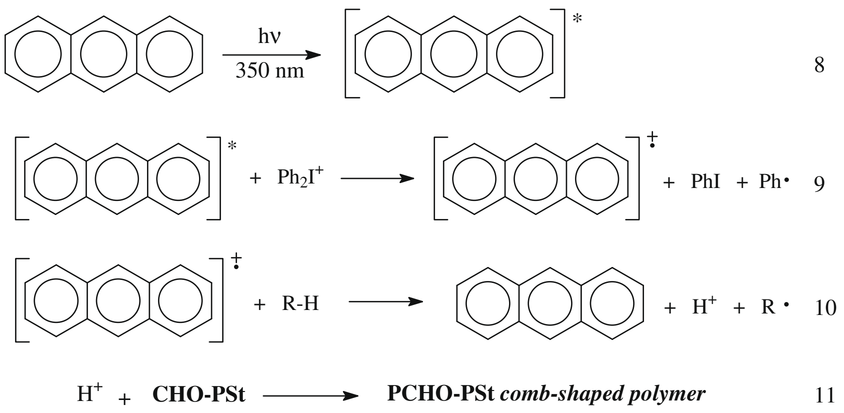
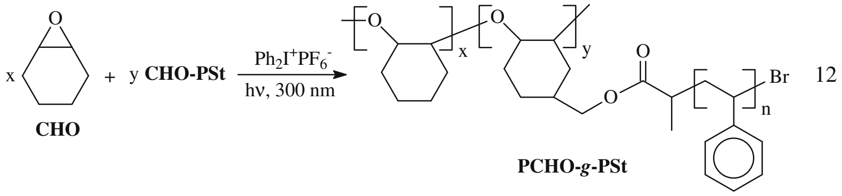


Fig. 3. ^{1}H NMR spectra of poly(cyclohexene oxide)-polystyrene graft copolymer (Table 3, run 2) (a) and poly(cyclohexene oxide)-polystyrene comb-shaped polymer (Table 2, run 2) (b) in CDCl$_3$.



Scheme 5. Photolysis of anthracene in the presence of diphenyliodonium salt.



Scheme 6. Synthesis of poly(cyclohexene oxide)-*g*-polystyrene.

Fig. 3b shows the ^1H NMR spectrum of the poly(cyclohexene oxide)-polystyrene comb-shaped polymer (Table 2, run 2). Not only the specific signals of PCHO and PSt 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 [37]. Anthracene radical cation or Brønsted acid formed from the hydrogen abstraction reaction may initiate the polymerization (Scheme 5).

Polystyrene macromonomer (CHO-PSt) was used as a comonomer in the copolymerization with CHO under similar conditions to those applied for the polymerization of the CHO-PSt macromonomer itself. Typical results concerning photochemically induced cationic copolymerization of CHO with CHO-PSt macromonomer at room temperature are shown in Table 3. As can be seen, the concentration of the CHO comonomer influences the composition of the graft copolymer. The composition of the copolymers PCHO-g-PSt was determined from ^1H NMR spectra using the integrated peak ratio of the aromatic protons of styrene (6.25–7.20 ppm) in the PSt segment to the OCHCHO protons in the PCHO segment (3.36 ppm). The content of PSt units in a copolymer X (mol %) was calculated using the following formula:

$$X_{PSt} = \frac{(I_{7.20-6.25}/5)}{(I_{7.20-6.25}/5) + (I_{3.36/2})} \times 100$$

where $I_{7.20-6.25}$ is the integral of the aromatic proton signals at 7.20–6.25 ppm, and $I_{3.36}$ is the integral of the OCHCHO proton signals at 3.36 ppm.

Using CHO-PSt macromonomer as the comonomer allowed for a rather simple incorporation of PSt side chains into poly(cyclohexene oxide) (PCHO) backbone. In this way, poly(cyclohexene oxide)-polystyrene graft copolymer with random sequences of the following structure (PCHO-g-PSt) was formed (Scheme 6).

Fig. 3b shows the GPC chromatogram of the graft copolymer (PCHO-*g*-PSt) that was formed. Notably, no peak pertaining to the residual homopolymer was detected. The graft copolymer structures were also assigned by means of NMR spectral measurements. As can be seen the ^1H NMR spectrum of the graft copolymer displays typical signals at 3.36 ppm of OCHCHO (PCHO) and 7.20–6.25 ppm of aromatic protons (PSt).

4. Conclusions

A new ATRP initiator with a CHO-functional group (CHO–Br) was synthesized by epoxidation of 3-cyclohexenylmethyl-2-bromopropanoate in the presence of 3-chloroperoxybenzoic acid. The ATRP of styrene monomer using CHO–Br initiator formed a well-defined PSt macromonomer possessing CHO end groups. The obtained CHO end-functional PSt macromonomer was employed in photoinitiated cationic (co)polymerization using diphenyliodonium salt. Photoinitiation of cationic polymerizations 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.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.reactfunctpolym.2009.09.010.

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