

Synthesis of Poly(epichlorohydrin-*g*-methyl methacrylate) and Poly(epichlorohydrin-*g*-styrene) Graft Copolymers by a Combination of Cationic and Photopolymerization Methods

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ABSTRACT: Poly(epichlorohydrin-*g*-styrene) and poly(epichlorohydrin-*g*-methyl methacrylate) graft copolymers were synthesized by a combination of cationic and photoinitiated free-radical polymerization. For this purpose, first, epichlorohydrin was polymerized with tetrafluoroboric acid (HBF₄) via a cationic ring-opening mechanism, and, then, polyepichlorohydrin (PECH) was reacted ethylhydroxymethyl dithio sodium carbamate to obtain a macrophotoinitiator. PECH, possessing photolabile thiuram di-

sulfide groups, was used in the photoinduced polymerization of styrene or methyl methacrylate to yield the graft copolymers. The graft copolymers were characterized by ¹H-NMR spectroscopy, differential scanning calorimetry, and gel permeation chromatography. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 107: 1604–1608, 2008

Key words: graft copolymers; photopolymerization; cationic polymerization; macrophotoinitiator

INTRODUCTION

Iniferters are initiators that induce radical polymerization that proceeds via initiation, propagation, primary radical termination, and transfer to initiator. Since Otsu et al.^{1–3} proposed the iniferter concept and discovered the living radical polymerization of vinyl monomers in homogeneous systems, many photoiniferters and thermal iniferters have been prepared and used for vinyl monomer polymerizations to efficiently synthesize polymers with well-defined structures (e.g., block, graft, star, and telechelic polymers); there are many review articles. (Methacryloyl ethylenedioxycarbonyl) benzyl *N,N*-diethyldithiocarbamate was synthesized and used as a monomer iniferter to develop a novel, photopatternable grafting technology by Ning et al.⁴ This molecule functions as both a methacrylic monomer and a photoiniferter (photoinitiator–transfer agent–terminator). Poly(ethylene glycol) (PEG) macroiniferters, which are prepared by the end capping of PEG mono methyl ethers with a benzyl *N,N*-diethyldithiocarbamate group at one end, were irradiated with UV light in the presence of styrene to yield poly(ethylene glycol-*b*-styrene) block copolymers by Nakayama et al.⁵ A macroiniferter with photolabile thiuram disulfide groups and PEG segments was prepared by the solution polyconden-

sation of bis(2-hydroxyethyl) thiuram disulfide with adipoyl chloride and PEG in the presence of triethyl amine.⁶ The macroiniferter obtained was used in the photoinduced polymerization of methyl methacrylate (MMA) to yield active poly(methyl methacrylate-*b*-ethylene glycol) block copolymers by Cakmak.⁶ Toluene diisocyanate based polyurethane iniferters containing tetraphenylethane groups between polyurethane blocks were prepared by the reaction of isocyanate-terminated prepolymers and 1,1,2,2-tetraphenyl-1,2-ethanediol.⁷ When these iniferters were decomposed in the presence of styrene, polyurethane–polystyrene (PS) multiblock copolymers were obtained through a living radical mechanism.⁷ Different types of iniferters, such as thiuram disulfides,^{8,9} dithiocarbamates^{10,11} and tetraphenylethane derivatives,^{12,13} can initiate living radical polymerization.

This article describes the synthesis and molecular characterization of new polymeric photoiniferters based on polyepichlorohydrin (PECH) bearing thiuram disulfide groups along the chain. PECH with photolabile groups was used in the photoinduced radical polymerization of styrene or MMA to yield poly(epichlorohydrin-*g*-styrene) (PECH-*g*-PS) or poly(epichlorohydrin-*g*-methyl methacrylate) (PECH-*g*-PMMA) graft copolymers.

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EXPERIMENTAL

Epichlorohydrin (ECH), 2-ethyl amino ethanol, carbon disulfide, tetrafluoroboric acid (54%), styrene,

TABLE I
Photopolymerization of MMA at 30°C

Run	Initiator (g)	MMA (g)	Time (h)	Yield (g)	M_n (g/mol)	M_w/M_n
1	0.5	1.5	4	0.213	53,550	1.85
2	0.5	1.0	4	0.253	56,429	1.70
3	0.5	2.0	4	0.285	61,008	1.96
4	0.5	2.5	4	0.300	67,274	2.09

and MMA were from E. Merck (Darmstadt, Germany). Styrene and MMA were purified and distilled by a conventional procedure. 2-Ethyl ethanol dithiosodium carbamate was synthesized in a reaction between CS_2 , 2-ethyl ethanol amine, and NaOH according to a method reported in the literature.¹⁴

Synthesis of PECH

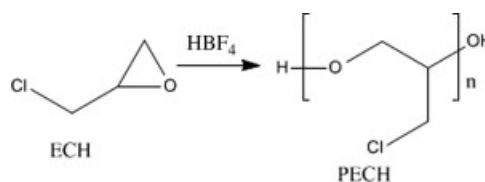
CH_2Cl_2 (30 mL) and 57% tetrafluoroboric acid (HBF_4) (10 g) were placed into a flask equipped with a magnetic stirrer, an addition funnel, and a nitrogen bypass. To this system, 96 g of ECH was added over 3-h periods. The reaction content was then poured in 1 L of water to remove the inorganic materials, and the organic phase was separated. A viscous liquid was obtained after drying with MgSO_4 and evaporation of the organic phase (23.0 g or a 36% yield of ECH).

Number-average molecular weight (M_n) = 887 g/mol; weight-average molecular weight (M_w)/ M_n = 1.6.

$^1\text{H-NMR}$ (ppm): 4.07–4.12 (HOCH_2), 1.36–1.36 (HOCH_2), 3.69–3.60 (CHO), 3.97–3.72 (OCH_2).

Synthesis of the macrophotoinitiator (MPI)

The reaction between PECH and 2-ethyl ethanol dithiosodium carbamate was carried out in a 250-mL flask equipped with a reflux condenser, magnetic stirrer, and thermometer. To this system, 19.0 g of PECH, 2.87 g of 2-ethyl ethanol dithiosodium carbamate, and 4.0 g of benzyl triethyl ammonium chloride were added; these were dissolved in a mixture of dimethylformamide and tetrahydrofuran (1 : 4 v/



Scheme 1

v) and refluxed at 60°C for 3 h. The reaction mixture was then cooled to room temperature. The same purification procedure for the synthesis of PECH was applied.

Yield = 11.52 g. M_n = 1057 g/mol; M_w/M_n = 1.37.

$^1\text{H-NMR}$ (ppm): 4.10–3.60 ($\text{OCH}_2\text{CH}-\text{CH}_2$) and ($\text{N}-\text{CH}_2\text{CH}_2\text{OH}$), 2.97 ($\text{N}-\text{CH}_2\text{CH}_3$), 3.05 ($\text{N}-\text{CH}_2\text{CH}_2\text{OH}$), 1.35–1.30 ($\text{N}-\text{CH}_2\text{CH}_3$).

Photopolymerization

The photopolymerization of styrene and MMA was carried out in a quartz tube at 30°C under irradiation with a 400-W high-pressure mercury lamp at a distance of 10 cm. Monomer was added to a given amount of PECH photoinitiator in a quartz tube. The tube content was purged by nitrogen. After polymerization for a given time, the contents of the tube were poured into a 10-fold excess of methanol to isolate the graft copolymer. The yield of the polymer was determined by gravimetry. The results of the graft polymerization of MMA and styrene are shown in Tables I and II, respectively.

Measurements

$^1\text{H-NMR}$ spectra were measured in CDCl_3 in a Bruker (Fällanden, Switzerland) 400-MHz spectrometer. Gel permeation chromatography (GPC) chromatograms were obtained with a Waters (Milford, MA) 410 instrument with tetrahydrofuran as the eluent at a flow rate of 1.0 mL/min and with a Waters Styragel HT6E+HR2 column. The GPC was calibrated with a PS standard. Differential scanning calorimetry

TABLE II
Photopolymerization of Styrene at 30°C

Run	Initiator (g)	Styrene (g)	Time (h)	Yield (g)	M_n (g/mol)	M_w/M_n
5	0.5	2.5	8	0.037	24,788	1.80
6	0.5	2.0	8	0.085	24,873	1.64
7	0.5	1.5	8	0.080	22,512	1.67
8	0.5	2.0	19	0.280	30,894	1.85
9	1.0	4.0	6	0.030	27,098	1.65
10	1.0	4.0	12	0.031	30,043	1.78
11	1.0	4.0	18	0.035	31,199	1.86
12	1.0	4.0	24	0.280	31,469	1.86

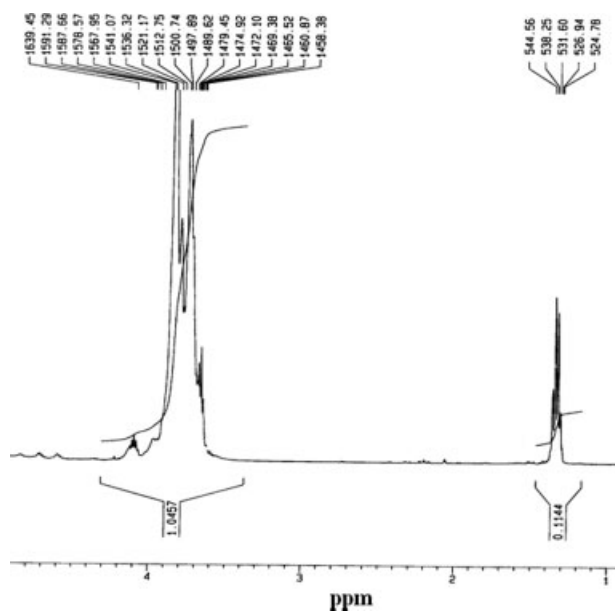


Figure 1 $^1\text{H-NMR}$ spectrum (CDCl_3) of PECH.

(DSC) curves were obtained using a PerkinElmer (Waltham, MA) Pyris-1 differential calorimeter in the temperature range 20–200°C at a heating rate of 20°C/min under a nitrogen atmosphere. The measurements were repeated with a maximum temperature of 200°C for the graft copolymers. Typically, 4–5 mg of sample was used.

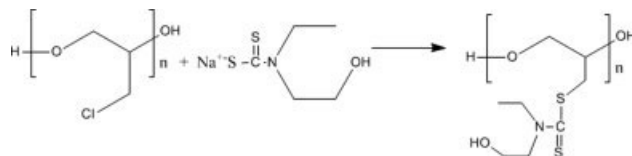
RESULTS AND DISCUSSION

Synthesis of PECH

PECH was prepared according to the reaction sequence shown in Scheme 1 and was characterized by $^1\text{H-NMR}$ and GPC measurements. The NMR spectrum of PECH in Figure 1 shows the characteristic signals at 4.07–3.60 ppm for the PECH protons.

Synthesis of MPI

The PECH photoinitiator with dithiocarbamate (DTC) at the side chain was prepared according to the reaction sequence shown in Scheme 2 by the reaction of PECH with dithio sodium carbamate salt. The NMR spectrum of the PECH photoinitiator in Figure 2 shows characteristic signals at 4.10–3.60 ppm ($-\text{CH}_2-$, $-\text{CH}_2\text{Cl}-$, $-\text{CH}-$ protons of PECH).



Scheme 2

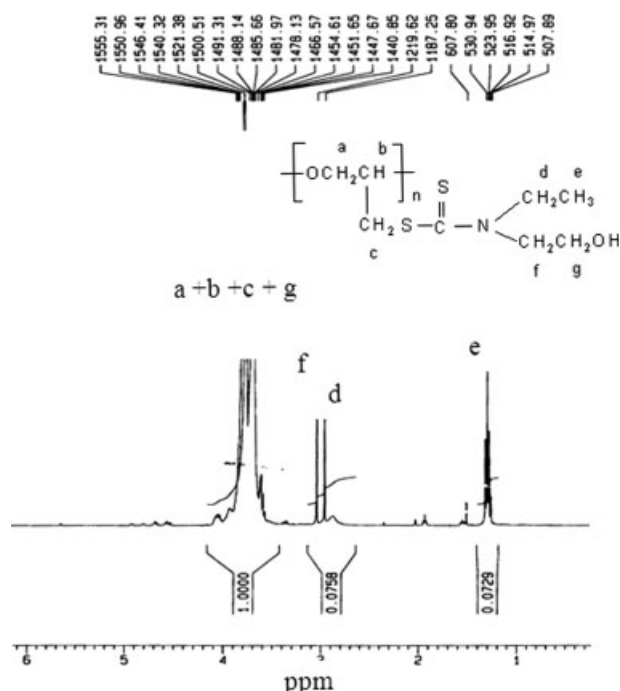
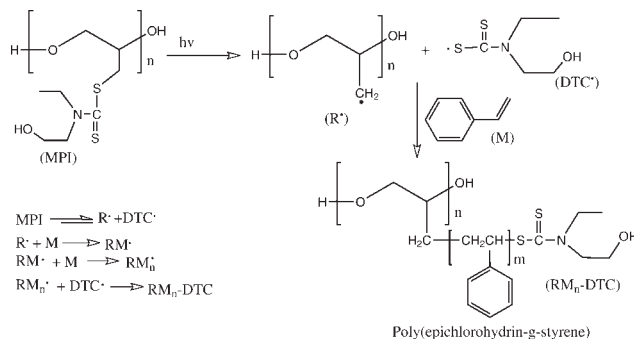


Figure 2 PECH reacted with ethyl-hydroxymethyl dithio sodium carbamate (in CDCl_3).

Photopolymerization

PECH with a thiuram disulfide group in the side chain was used in the photopolymerization of MMA and styrene. The photopolymerization reaction of styrene may be represented in Scheme 3. Scheme 3 is depicted according to the mechanism of a classical quasilinging radical photopolymerization process as originally proposed by Otsu and Matsumoto.³ The reactions shown in Scheme 3 were involved in the polymerization process; then, quasilinging polymerization occurred with equilibrium between propagating (active) and nonpropagating (terminated) species in the absence of permanent termination. The reaction between the growing chain (RM_n^\cdot) and dithiocarbamate radical (DTC^\cdot) was photochemically reversible (through a photodissociation of the DTC end



Scheme 3

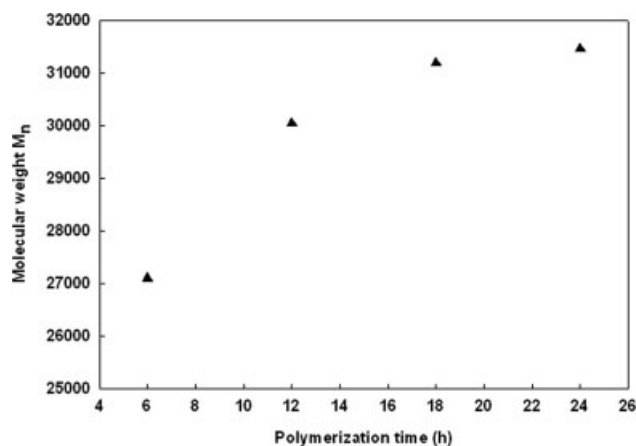


Figure 3 Dependence of M_n on the polymerization time for the living graft polymerization of styrene. See Table II for the conditions.

groups), which led to the living character of the polymerization, which is achieved provided that the exchange between the reactive species and the dormant species is fast in comparison with the propagation. Other features of a true living system, such as accurately controlled molecular weights and low polydispersities, could not be obtained because a thiocarbamate radical can also initiate polymerization. During the course of polymerization, we observed that the molecular weights of the polymers increased with irradiation time. The quasiling nature of the system was confirmed by the increasing molecular weight with polymerization time (Table II runs 6, 8, and 9–12). As shown in Figure 3, the increase in the

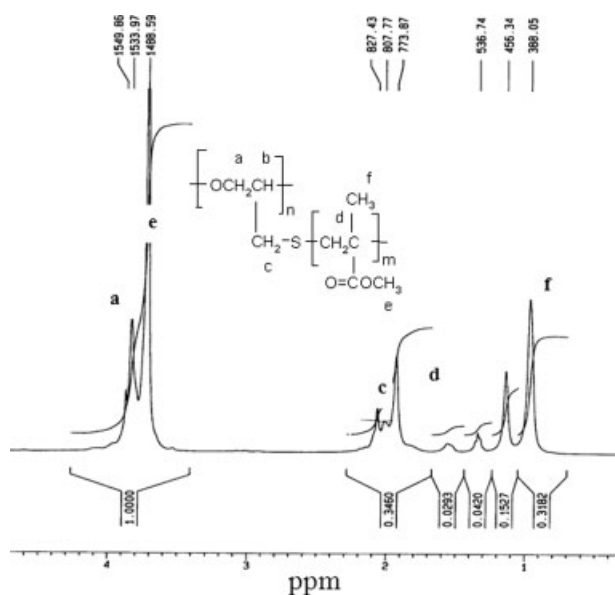


Figure 4 $^1\text{H-NMR}$ (CDCl_3) spectrum of the PECH-g-PMMA graft copolymer (Table I, run 3).

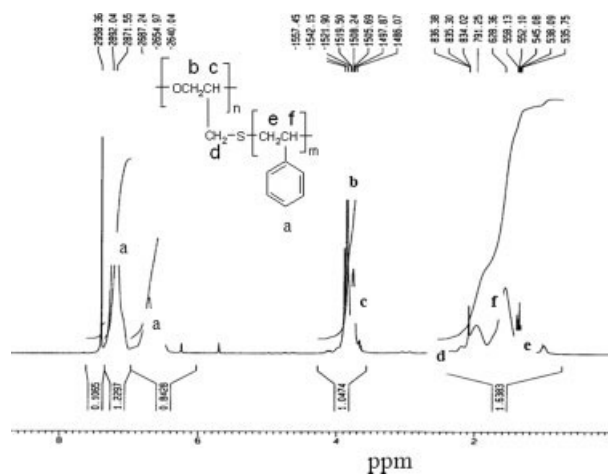


Figure 5 $^1\text{H-NMR}$ spectrum (CDCl_3) of the PECH-g-PS graft copolymer (Table II, run 6).

molecular weight as a function of polymerization time was linear.

Characterization of the products

Tables I and II give the results of several polymerizations with the MPis with thiuram disulfide groups. To confirm the structure of the graft copolymers obtained, a $^1\text{H-NMR}$ spectrometer was used. The $^1\text{H-NMR}$ spectrum of the PECH-g-PMMA graft copolymer shown in Figure 4 (Table I, run 3) showed characteristic signals at 3.8 ppm ($-\text{OCH}_2-$ protons of PECH) and 3.4 ppm [$-\text{OCH}_3$ protons of poly(methyl methacrylate) (PMMA) segments]. The formation of a PECH-g-PS graft copolymer was also supported by $^1\text{H-NMR}$. As shown in Figure 5 (Table II, run 6), $-\text{OCH}_2-$ and $-\text{S}-\text{CH}_2-$ protons appeared in the 3.8–3.7-ppm region, respectively, in addition to peaks around 7 ppm for aromatic protons. Graft copolymer formation was also evidenced by GPC. Chromatograms recorded with initial PECH with photolabile groups and graft copolymers are

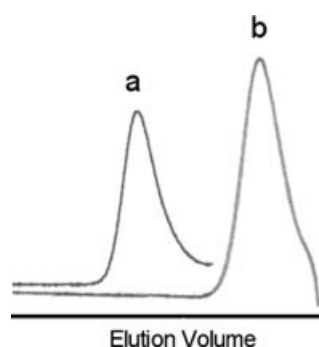


Figure 6 GPC curves of the (a) PECH-g-PMMA graft copolymer (Table I run 3; $M_n = 61,008$ g/mol) and (b) MPI ($M_n = 1057$ g/mol).

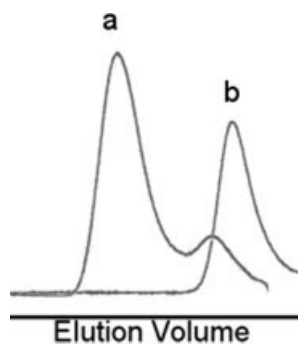


Figure 7 GPC curves of the (a) PECH-g-PS graft copolymer (Table II, run 12; $M_n = 31,191$ g/mol) and (b) MPI ($M_n = 1057$ g/mol).

shown in Figures 6 and 7. These chromatograms indicated the unimodal molecular weight distribution in both cases and an increase in the molecular weight as result of graft copolymerization. Furthermore, GPC showed no additional peaks of non-reacted PECH homopolymer, which was apparently removed by the precipitation procedure. The glass-transition temperatures (T_g 's) of PS and PMMA homopolymers were 100 and 105°C, respectively. PECH was an amorphous elastomer, exhibiting a T_g at -23°C . The T_g 's of the graft copolymers are shown in Figures 8 and 9. The results obtained indicate that T_g values of graft copolymers were different from their homopolymers. This is evidence of the graft copolymer formation. The typical DSC heating thermograms of the graft copolymers are depicted in Figures 8 and 9. All of the polymers were amorphous, and no crystal melting peaks were found.

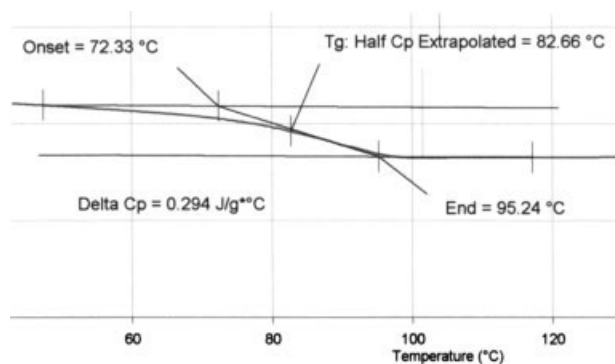


Figure 8 DSC curve of the PECH-g-PMMA graft copolymer (Table I, run 3). C_p , heat capacity.

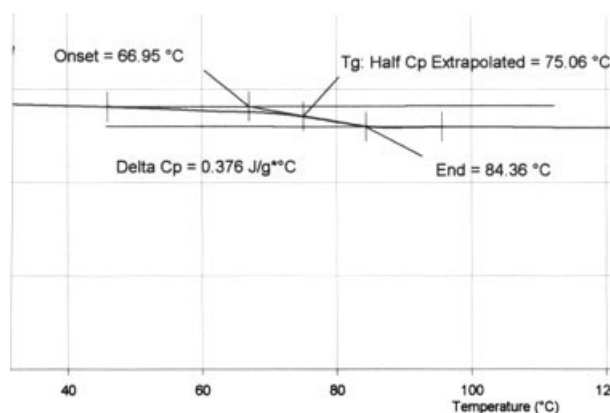


Figure 9 DSC curve of the PECH-g-PS graft copolymer (Table II, run 12). C_p , heat capacity.

CONCLUSIONS

The living photopolymerization of styrene and MMA with PECH with photolabile groups in bulk was successfully carried out. Graft copolymers were obtained with broad polydispersities ($M_w/M_n = 1.78\text{--}2.09$) as determined by GPC. A broad molecular distribution is a drawback of the macroiniferter system.

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