

Synthesis of Poly(epichlorohydrin-g-methyl methacrylate) Graft Copolymers by the Combination of Cationic and Atom Transfer Radical Polymerization

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ABSTRACT: Poly(epichlorohydrin) possessing chloromethyl side groups in the main chain was used in the atom transfer radical polymerization of methyl methacrylate and styrene to yield poly(epichlorohydrin-g-methyl methacrylate) and poly(epichlorohydrin-g-styrene graft copolymers). The polymers were characterized by ^1H NMR spectroscopy,

gel permeation chromatography, differential scanning calorimetry, and fractional precipitation method. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 102: 2725–2729, 2006

Key words: cationic polymerization; ATRP; poly(epichlorohydrin); graft copolymer; styrene; methyl methacrylate

INTRODUCTION

Atom transfer radical polymerization (ATRP) yielding polymers with molecular weights predetermined by the ratio of the concentrations of consumed monomer to introduced initiator and with low polydispersities was discovered in 1995.^{1–4} ATRP is based on a fast, dynamic equilibrium established between the dormant species (alkyl halides) and active species (radicals), with transition metal complexes acting as reversible halogen atom transfer reagents, which keeps a very low radical concentration in the reaction system, and therefore, results in negligible radical termination and controlled polymerization.⁵ Various alkyl halides and pseudohalides as well as compounds with weak hetero atom halogen bonds can be used as ATRP initiators.^{2–7} Various types of monomers have also been polymerized by ATRP: styrenes,⁸ acrylates,^{2,9,10} methacrylates,^{1,3,11} and acrylonitrile.¹² Copper-mediated ATRP is one of the most extensively studied systems.^{13,14} Not only copper but also other transition metals have been used as efficient catalyst.^{15–20} The activity of the catalyst depends on the nature of the ligands. Multidentate nitrogen ligands such as aromatic nitrogens,^{1–7} imine-type nitrogens,^{8,9} and aliphatic nitrogens^{10,11} work very well for copper-mediated ATRP by providing the desired reactivity.²¹ Sulfur, oxygen, or phosphorus ligands are reported to be effective in ATRP catalyzed by copper.²¹ By using functional polymers possessing appropriate alkyl ha-

lide along the backbone as macroinitiators, it is possible to obtain graft copolymers with a well-controlled structure. Several polymers having alkyl groups such as ethylene-propylene-diene terpolymer,²² poly(vinyl chloride),²³ poly(styrene-*b*-ethylene-*co*-propylene) copolymers,²⁴ poly(isobutylene-*co*-*p*-methyl styrene-*co*-*p*-bromomethyl styrene),²⁵ polyethylene,²⁶ poly(ethylene-*co*-vinyl acetate),²⁷ poly[4-methylstyrene-*co*-4-(bromomethyl)styrene],²⁸ and poly(dimethylsiloxane).²⁹

In the present work, a poly(epichlorohydrin) (PECH) macroinitiator was synthesized by the cationic polymerization of epichlorohydrin (ECH) using HBF_4 as catalyst. PECH macroinitiator was then used as halogen source in the ATRP of styrene or methyl methacrylate to yield poly(epichlorohydrin-g-styrene) (PECH-g-PS) and poly(epichlorohydrin-g-methyl methacrylate) (PECH-g-PMMA) graft copolymers.

EXPERIMENTAL

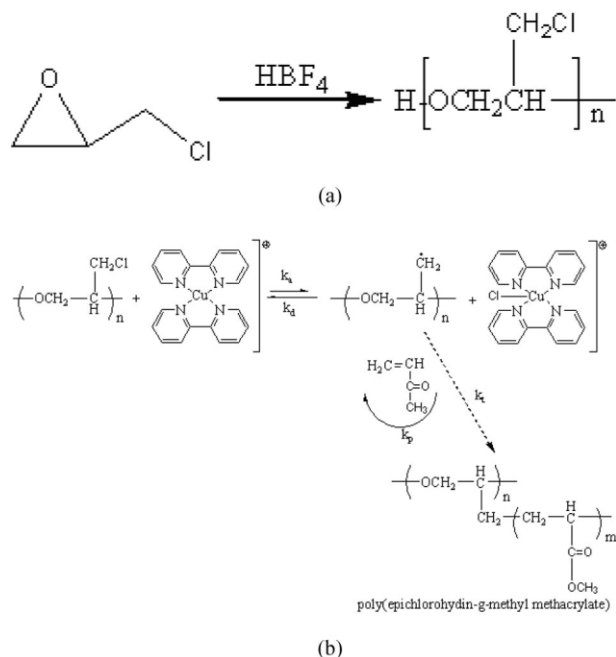
Materials

Methyl methacrylate was procured from Merck and purified by conventional procedure. 2,2'-bipyridine (bpy) (Aldrich), CuCl (Aldrich), HBF_4 in diethyl ether (Merck) were used as purchased. ECH (Merck) was dried over calcium hydride and then purified by distillation.

Cationic polymerization of EPCH

CH_2Cl_2 (100 mL) and 11.5 g of 57% HBF_4 were placed into a flask equipped with a magnetic stirrer, an addition funnel, and nitrogen bypass. To this system,

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Scheme 1. (a) Cationic polymerization of ECH and (b) Atom transfer radical polymerization of MMA.

158.1 g of ECH in 50 mL of CH_2Cl_2 was added in 5 h. A viscous liquid was obtained after drying and evaporation of organic phase (123.05 g, 77.80 yield of PECH).

Graft copolymerization via ATRP

The dry schlenk tubes containing the reaction mixture of monomer, PECH, CuCl, and bpy were degassed by vacuum and nitrogen and sealed under vacuum. Then the tubes were immersed in a silicone oil bath thermostat at 110°C . At a certain interval, schlenk tube was cooled to quench the polymerization. The schlenk tube content was diluted with THF. The solution was filtered and precipitated with methanol to yield the polymer product.

TABLE I
ATRP of Styrene in the Presence of CuCl/bpy Catalyst at 110°C

Run	PECH (g)	Polym. time (h)	Graft copolymer			
			Yield (g)	M_n	M_w/M_n	T_g ($^\circ\text{C}$)
HPP-2	0.850	24	2.03	33,549	1.36	104.22
HPP-3	0.489	24	0.85	45,728	1.25	104.27
HPP-5	1.220	24	0.74	17,483	1.54	90.84
HPP-8	0.500	18	0.73	39,280	1.46	84.56
HPP-9	0.500	12	0.40	25,767	1.28	85.68

[CuCl]: 0.41 mmol, [bpy]: 0.768 mmol, and [styrene]: 2.86 g using PECH as macroinitiator. T_g : -23°C , M_n : 1320 g/mol for poly(epichlorohydrin).

TABLE II
ATRP of Methyl Methacrylate in the Presence of CuCl/bpy Catalyst at 110°C

Run	MMA (g)	Graft copolymer			
		Yield (g)	M_n	M_w/M_n	T_g ($^\circ\text{C}$)
IH-1	1.5	0.726	76,565	1.57	92.05
IH-2	2.0	1.165	94,659	1.51	95.69
IH-5	3.5	1.045	71,765	1.33	90.78

[CuCl]: 0.41 mmol, [bpy]: 0.768 mmol, and [PECH]: 0.488 g. Polymerization time: 16 h.

Characterization

^1H NMR spectra of graft copolymers were recorded on a Bruker-200 NMR spectrometer using CDCl_3 as a solvent. Differential scanning calorimetry (DSC) curves were obtained using a Perkin-Elmer Pyris-1 differential calorimeter in the temperature range from 20 to 200°C , at a heating rate of $20^\circ\text{C}/\text{min}$, in nitrogen atmosphere. The measurements were repeated using a maximum temperature of 200°C for graft copolymers. Typically 4–5-mg sample has been used. Gel permeation chromatography (GPC) chromatograms were

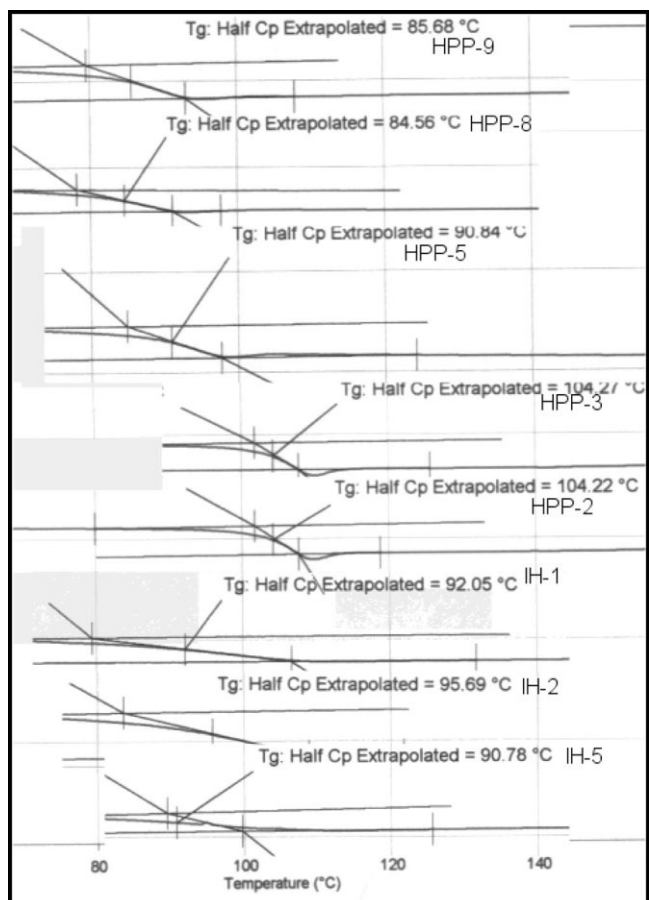


Figure 1 DSC curves of graft copolymers.

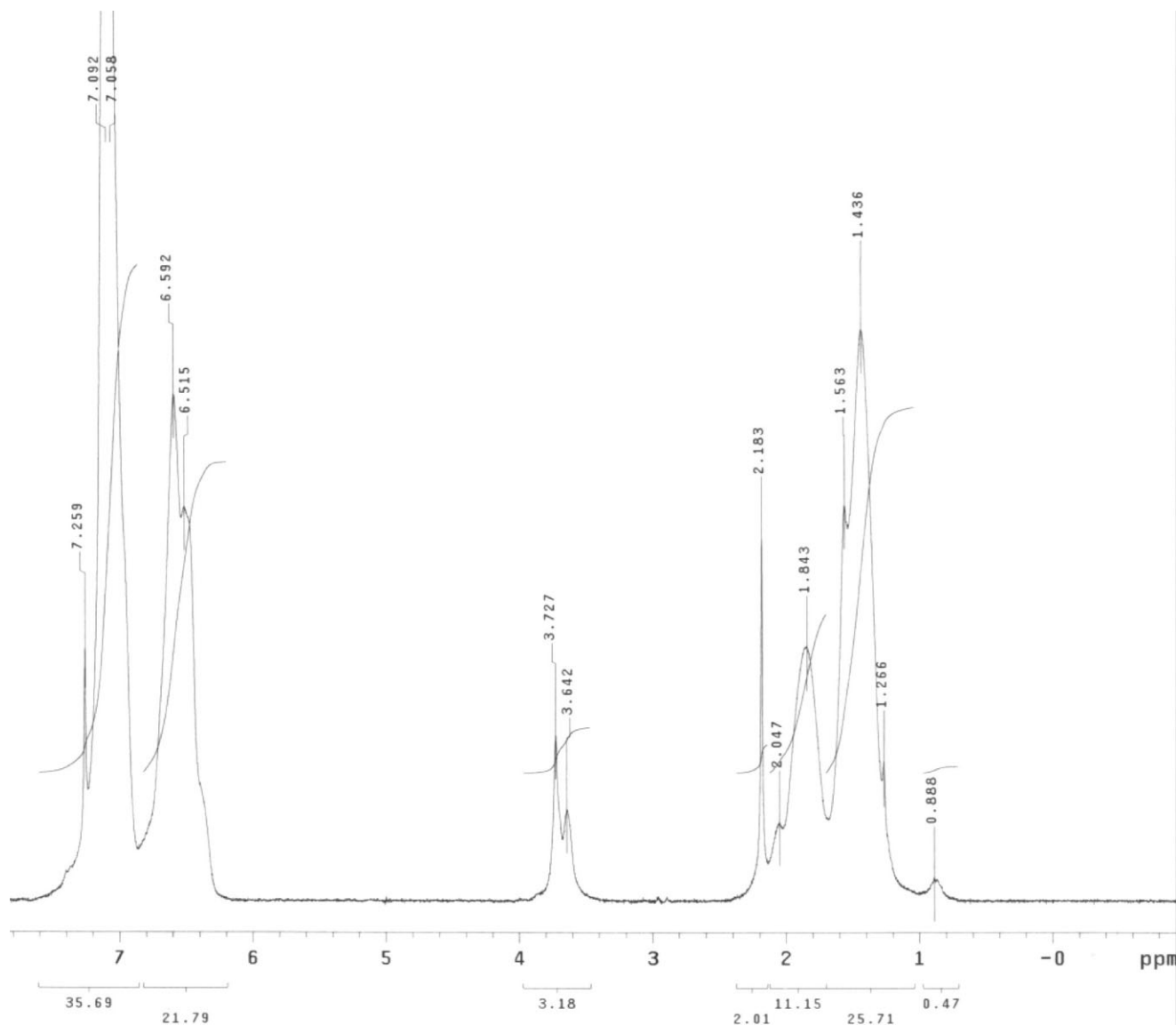


Figure 2 ^1H NMR spectrum of PECH-g-PS graft copolymer.

obtained using a Waters 410 instrument with THF as the solvent at a flow rate of 1 mL/min.

RESULTS AND DISCUSSION

Synthesis of PECH

Cationic polymerization of ECH was carried out by slow addition of ECH to a solution of HBF_4 . Reaction scheme may be represented as follows (Scheme 1a)

Graft copolymerization via ATRP

Styrene or methyl methacrylate were polymerized using CuCl/bpy ATRP initiating system in the presence of PECH to yield PECH-g-PMMA graft copolymers. Reaction pathways can be represented as (Scheme 1b)

The ATRP of methyl methacrylate with CuCl/bpy as the catalyst was carried out at 110°C . The results of the polymerization of styrene and methyl methacrylate in the presence of PECH using the CuCl/bpy as catalyst are shown in Tables I and II. As can be seen, M_n of the copolymers (run HPP-3, 8–9) increased linearly with the polymerization time, which indicates that this polymerization proceeds via the living radical mechanism. The increased amount of PECH in the reaction mixture leads to formation of a higher number of active centers. For this reason, more growing macroradicals are formed in the reaction system, they have shorter polystyrene segments, which is confirmed by a decrease in molecular weights of the graft copolymers (Table I, run: HPP-2,3,5). The increasing monomer concentration caused a decrease in the yield

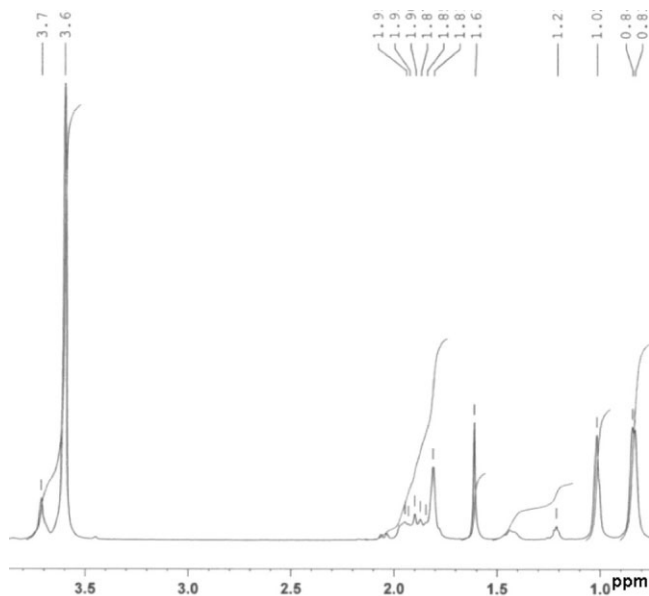


Figure 3 ^1H NMR spectrum of PECH-g-PMMA graft copolymer.

and molecular weight of the copolymers, as shown in Table II. This is probably due to chain transfer. Flory³⁰ has explained the kinetics of the chain transfer where the reactivity of a radical can be transferred to another species, i.e., monomer solvent, the growth of the chain previously bearing the free radical being thereby terminated.

Characterization of graft copolymers

The glass transition temperatures were measured to analyze the phase behavior of the graft copolymers. The experiments were performed for PECH-g-PS and PECH-g-PMMA. Glass transition temperature of PS and PMMA homopolymers are 100 and 105°C. PECH, was amorphous elastomer, exhibiting a glass transi-

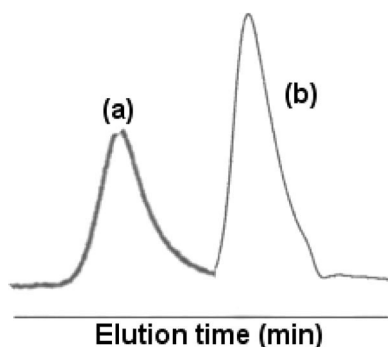


Figure 4 GPC curves of (a) PECH-g-PMMA (Table II, run HPP-2), $M_n = 33,549$ g/mol and (b) PECH, $M_n = 1050$ g/mol.

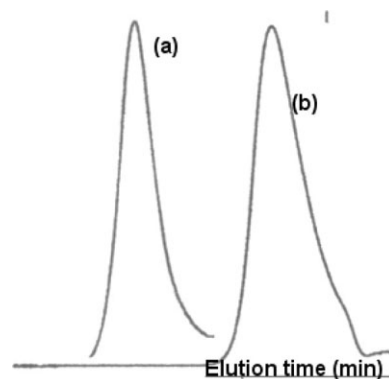


Figure 5 GPC curves of (a) PECH-g-PMMA (Table II, run IH-2), $M_n = 94,659$ g/mol and (b) PECH, $M_n = 1050$ g/mol.

tion temperature at -23°C . The glass transition temperatures of the graft copolymers are given in Table I. The results obtained indicate that T_g values of graft copolymers were different from their homopolymers, depending on the composition of the copolymers. This is one evidence of the graft copolymer formation. The typical DSC heating thermograms of graft copolymers are depicted in Figure 1. It can be seen that all the polymers were amorphous, with glass transition temperatures (T_g) ranging from 85 to 105°C, and no crystal melting peaks were found. The structure of the graft copolymers was analyzed by ^1H NMR (illustrated in Figs 2 and 3). As shown in Figure 2, signals are observed at 1.25–2.18 ppm, originating from the methylene and methine protons of the main chain, and a signal observed at 6.46–7.26 ppm was assigned to the aromatic protons. Figure 3 shows ^1H NMR spectrum of PECH-g-PMMA graft copolymer, which exhibits signals at 0.83–1.21 ppm (CH_3), 1.61–1.95 ppm (backbone CH_2 and CH), and 3.6 ppm (OCH_3). Graft copolymer formation was also demonstrated by GPC. Chromatograms recorded with initial PECH and graft copolymers is shown in Figures 4 and 5. These chromatograms indicate a unimodal molecular weight distribution in both cases and an increase in the molecular weight as result of graft copolymerization.

CONCLUSIONS

PECH-g-PS and PECH-g-PMMA graft copolymers could be prepared by a sequential two-step method without any modification of the initiating site, using transformation from cationic polymerization to ATRP. PECH obtained by the cationic polymerization of ECH was used as macroinitiator for the ATRP of styrene and methyl methacrylate to yield graft copolymers.

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