

Solubilization and Polymer Analogous Reactions of Polyepichlorohydrin in Ionic Liquids

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ABSTRACT: Polyepichlorohydrin containing reactive chloromethyl side groups was found to be highly soluble in polar ionic liquids containing halide anions such as 1-*n*-butyl-3-methyl imidazolium chloride, 1-*n*-ethyl-3-methyl imidazolium bromide, and 1-*n*-hexyl-3-methyl imidazolium chloride, whereas it was insoluble in less polar ionic liquids such as 1-*n*-butyl-3-methyl imidazolium tetrafluoroborate and 1-*n*-butyl-3-methyl imidazolium hexafluorophosphate. The reaction of polyepichlorohydrin with thiolates and thiol compounds in the polar ionic liquids as reaction media produced polyoxyethylenes with thio-

ether side groups in very high conversions and yields. When polyepichlorohydrin was reacted with sodium 1*H*,1*H*,2*H*,2*H*-perfluorinated decanethiolate in 1-*n*-hexyl-3-methyl imidazolium chloride at 70°C and the product was separated through centrifugation, the ionic liquid could be used more than four times, and high conversions (>70 mol %) and yields (>62 wt %) were maintained. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 114: 132–138, 2009

Key words: fluoropolymers; modification; recycling

INTRODUCTION

Ionic liquids have significant potential for applications in green chemistry, particularly as green solvents for separation processes and as reaction media for organic reactions including catalysis.^{1,2} Recently, the application of ionic liquids has also been extended to the synthesis of polymers. For example, ionic liquids are used as green reaction media for the preparation of polymers through radical polymerization, ionic polymerization, polycondensation processes, and dispersion polymerization starting from the corresponding monomers.^{3,4} Polymer analogous reactions are also useful for preparing polymers when the functional groups in the starting polymers are substituted to obtain the products.⁵ Homogeneous path reactions are usually desired in these reactions to control the degree of substitution and to effectively impart various functional groups into the reactive polymers.⁶ Cellulose, which has two primary hydroxyl groups and one secondary

hydroxyl group per monomeric unit, is soluble in several ionic liquids, and these hydroxyl groups have been successfully functionalized (acetylation) through the homogeneous synthesis of a polymer analogous reaction with ionic liquids as green reaction media.^{7,8} Besides this example, however, there are no other reports of using polymer analogous reactions with ionic liquids as reaction media, despite the advantages of ionic liquids, including increased reaction rates and yields, enhancement of selectivity, and recycling. Furthermore, there are only limited studies on the solubility behavior of reactive functional polymers in ionic liquids, except for polymers containing hydroxyl groups.⁹ The development of homogeneous solution systems for reactive polymers in ionic liquids could increase the use of green synthetic pathways. Here, we investigated the solubility of some reactive functional polymers bearing chloromethyl groups, hydroxyl groups, and hydrosilyl groups in ionic liquids, and then we studied the polymer analogous reactions using a reactive polymer, polyepichlorohydrin, which is soluble in ionic liquids.

Additional Supporting Information may be found in the online version of this article.

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EXPERIMENTAL

Materials

Epichlorohydrin (Aldrich) was dried over calcium chloride (OCI Co., Ltd., Seoul, Korea) and then

fractionally distilled from calcium oxide. Methylene chloride and methanol were refluxed over calcium hydride and freshly distilled under a nitrogen atmosphere before use. Chloroform (CHCl₃) and tetrahydrofuran (THF) were refluxed over calcium chloride and sodium benzophenone, respectively, and freshly distilled under a nitrogen atmosphere before use. *N,N*-Dimethylacetamide (DMAc) and ethanol were dried over molecular sieves (4 Å). 1*H*,1*H*,2*H*,2*H*-Perfluorinated decanethiol (Aldrich), 1*H*,1*H*,2*H*,2*H*-perfluorinated octanethiol (Aldrich), 1*H*,1*H*,2*H*,2*H*-perfluorinated hexanethiol (Aldrich), benzenethiol (Aldrich), decanethiol (Aldrich), triphenylcarbenium hexafluorophosphate (Aldrich), sodium (Aldrich), *d*-trifluoroacetic acid (Aldrich), *m*-chloroperoxybenzoic acid (*m*-CPBA; Acros, Geel, Belgium), poly(vinyl alcohol; Aldrich), poly(4-vinyl phenol; Aldrich), poly(chloromethyl styrene; Aldrich), poly(ethylene glycol; Aldrich), poly(methylhydrosiloxane; Aldrich), and ionic liquids (C-TRI, Hwaseong-si, Korea) were used without further purification. The water contents of the ionic liquids were not greater than 400 ppm, and the residual chloride contents after anion exchange were not greater than 40 ppm.

Analysis

¹H-NMR spectra (500 MHz) were measured in CDCl₃ or a CDCl₃/1,1,2-trichlorotrifluoroethane mixture with a Bruker Avance 500 (Germany). The molecular weight of polyepichlorohydrin was obtained with a Viscotek gel permeation chromatograph with a diffractometer as a detector (Houston, TX). THF was used as a solvent, and monodisperse polystyrenes were used as standards. The molecular weight of poly(oxy[[2-(perfluorooctyl)ethyl]thiomethyl]ethylene) (H2F8TP) was determined by gel permeation chromatography in 1,1,2-trichlorotrifluoroethane at 30°C on a Waters apparatus equipped with refractive-index detection (Milford, MA). Monodisperse polydimethylsiloxanes (Scientific Polymer Products, Inc., New York, NY) were used as standards.

Solubility of the polymers in ionic liquids

Dissolution experiments were carried out with several polymers. The polymer samples were added to the ionic liquids (10 g) without pretreatment in glass vials and heated with gentle stirring on a heating plate (70°C). The test time for dissolution was limited to a maximum of 24 h. If a residue of the insoluble material was present after 24 h when 0.1 g of the polymer was added to the ionic liquid (10 g), we considered the tested polymer to be insoluble. When the polymer was soluble without any residue, the dissolution experiment was repeated with the addition of more polymer (0.1 g).

Synthesis

Preparation of polyepichlorohydrin

Triphenylcarbenium hexafluorophosphate (0.05 g, 0.13 mmol) was added to a stirred solution of epichlorohydrin (5.0 g, 54.04 mmol) in 3.78 mL of methylene chloride under a nitrogen atmosphere. This reaction mixture was stirred at 0°C for 72 h. The product was purified by precipitation from a THF solution into methanol twice and then was dried *in vacuo* at room temperature for 72 h. This product was obtained in a 33 wt % yield after purification steps (fractional precipitation). The number-average molecular weight and polydispersity index of the polymer, measured with gel permeation chromatography, were 10,000 and 1.4, respectively.

¹H-NMR of polyepichlorohydrin (CDCl₃, δ): 3.72 (m, 5H).

Polymer analogous reactions of polyepichlorohydrin with various sodium thiolates in 1-*n*-butyl-3-methyl imidazolium chloride ([bmim][Cl]; reaction 1 in Fig. 1)

The following procedure was used for the polymer analogous reactions using [bmim][Cl] as the reaction medium. The reaction of polyepichlorohydrin with benzenethiol in [bmim][Cl] is given as an example.

Benzenethiol (0.134 mL, 0.97 mmol) was added to a stirred solution of sodium methoxide (58 mg, 1.07 mmol) in methanol (10 mL). After 30 min of stirring at room temperature, methanol was removed with a rotary evaporator, and the residue was dried *in vacuo* for 3 h to remove the extra methanol to afford sodium benzenethiolate. A solution of polyepichlorohydrin (76 mg, 0.82 mmol) in [bmim][Cl] (10 g) was transferred into the sodium benzenethiolate (128 mg, 0.97 mmol). The reaction mixture was stirred at 100°C for 24 h and then poured into a water/methanol mixture. Viscous polymer products were oxidized with *m*-CPBA to facilitate further Soxhlet purification and NMR measurements for the calculation of the conversion. No residual ionic liquid was detected from NMR measurements, and the degree of conversion (mol %) was calculated by a comparison of the multiplet at 7.90 ppm (2H) from

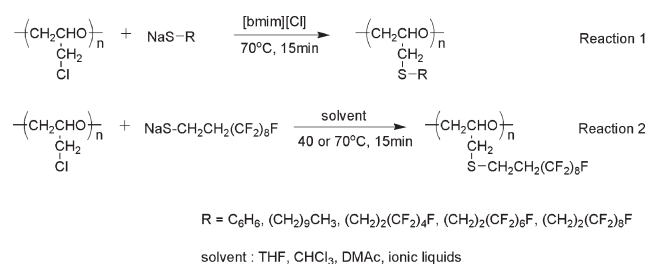


Figure 1 Reaction scheme of the polymers.

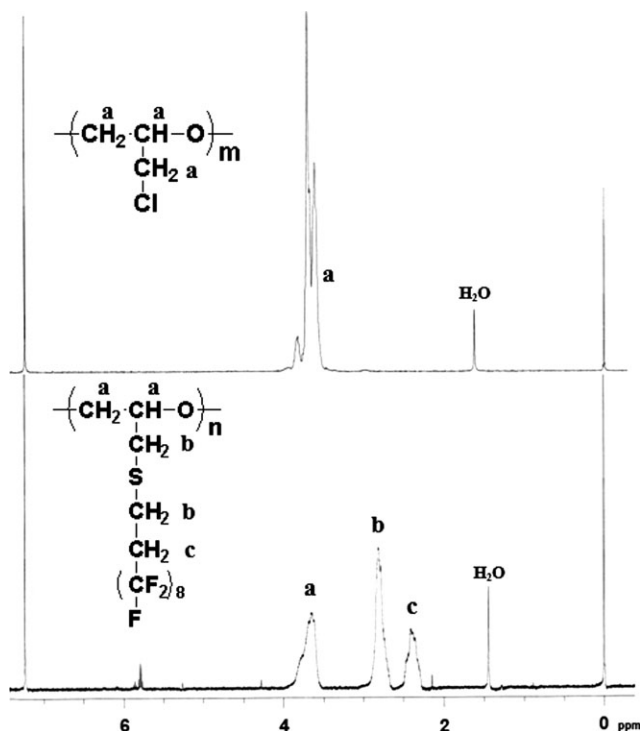


Figure 2 NMR spectra of (a) polyepichlorohydrin and (b) H2F8TP.

the benzene ring and the multiplet at 3.53 ppm (5H) from the backbone, which included the contribution of residual polyepichlorohydrin. The weight-average molecular weight of the products was 2 or 3 times larger than that of the starting polymer, polyepichlorohydrin. The product was obtained in a yield of 30 wt % with 99 mol % conversion.

$^1\text{H-NMR}$ of poly[oxy(phenylsulfonylmethyl)ethylene] (CDCl_3 , δ): 3.53 (m, 5H), 7.56 (m, 3H), 7.90 (m, 2H).

The same reaction conditions were used for the preparation of poly[oxy(decylthiomethyl)ethylene], poly[oxy{[2-(perfluorobutyl)ethyl]thiomethyl}ethylene], and poly[oxy{[2-(perfluorohexyl)ethyl]thiomethyl}ethylene], except that decanethiol, 1*H*,1*H*,2*H*,2*H*-perfluorinated hexanethiol, and 1*H*,1*H*,2*H*,2*H*-perfluorinated octanethiol were used instead of benzenethiol. The conversions and yields were always greater than 98 mol % and 56 wt %, respectively.

$^1\text{H-NMR}$ of poly[oxy(decylsulfonylmethyl)ethylene] (CDCl_3 , δ): 0.86 (m, 3H), 1.27 (m, 14H), 1.80 (m, 2H), 3.02 (m, 2H), 3.29 (m, 2H), 3.66 (m, 2H), 4.10 (m, 1H). $^1\text{H-NMR}$ of poly[oxy{[2-(perfluorobutyl)ethyl]sulfonylmethyl}ethylene] (CDCl_3 /trifluoroacetic acid-*d* mixture, δ): 2.66 (m, 2H), 3.46 (m, 6H), 4.29 (m, 1H). $^1\text{H-NMR}$ of poly[oxy{[2-(perfluorohexyl)ethyl]sulfonylmethyl}ethylene] (CDCl_3 /trifluoroacetic acid-*d* mixture, δ): 2.68 (m, 2H), 3.48 (m, 6H), 4.28 (m, 1H).

Preparation of H2F8TP in various solvents (reaction 2 in Fig. 1).

1*H*,1*H*,2*H*,2*H*-Perfluorinated decanethiol (464 mg, 0.97 mmol) was added to a stirred solution of sodium methoxide (58 mg, 1.07 mmol) in methanol (10 mL). After 30 min of stirring at room temperature, methanol was removed with a rotary evaporator, and the residue was dried *in vacuo* for 3 h to remove the extra methanol to afford sodium 1*H*,1*H*,2*H*,2*H*-perfluorinated decanethiolate. A solution of polyepichlorohydrin (76 mg, 0.82 mmol) in [bmim][Cl] (10 g) was transferred into the sodium 1*H*,1*H*,2*H*,2*H*-perfluorinated decanethiolate. The reaction mixture was stirred at 70°C for 15 min and then poured into a water/methanol mixture. The precipitate was further purified by several precipitations from 1,1,2-trichlorotrifluoroethane into methanol. After further extraction with methanol for 12 h with a Soxhlet extractor, the polymer was dried overnight under a higher vacuum. This product was obtained in a yield of 80 wt % with 100 mol % conversion. The same procedure was used for the reaction of polyepichlorohydrin with sodium 1*H*,1*H*,2*H*,2*H*-perfluorinated decanethiolate with other solvents such as THF, CHCl_3 , DMAc, and ionic liquids. Conversions and yields with other solvents are summarized later in Figure 3 and Table II. When DMAc was used as a solvent at 70°C, the product contained more than 50 mol % byproducts, whereas when [bmim][Cl] was used, it did not contain any byproduct, and a higher conversion and a higher yield were obtained (see the supporting information).

$^1\text{H-NMR}$ of H2F8TP (CDCl_3 /1,1,2-trichlorotrifluoroethane mixture, δ): 2.39 (m, 2H), 2.73 (m, 2H), 2.81 (m, 2H), 3.64 (m, 3H).

RESULTS AND DISCUSSION

Table I shows the solubility behavior of the polymers tested at 70°C through the addition of polymer samples to ionic liquids in glass vials with gentle

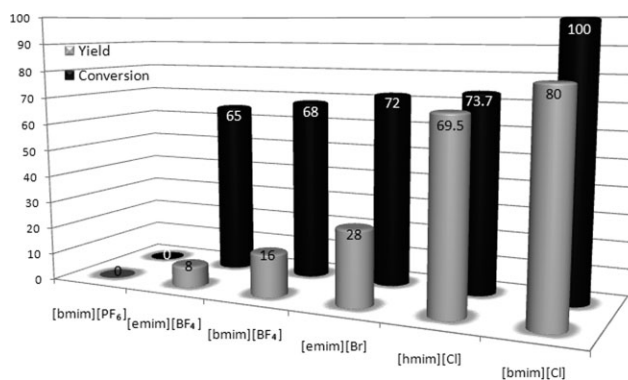


Figure 3 Conversions and yields obtained from reaction 2 with ionic liquids at 70°C.

TABLE I
Solubility of Some Functional Polymers in Ionic Liquids at 70°C

Polymer	Ionic liquid	Solubility
Cellulose (DP = 223)	[bmim][Cl]	3 wt %
	[bmim][BF ₄]	Insoluble (phase separation)
	[bmim][PF ₆]	Insoluble (phase separation)
PVA ($M_w = 31,000$ – $50,000$)	[bmim][Cl]	10 wt %
	[bmim][BF ₄]	Insoluble (phase separation)
	[bmim][PF ₆]	Insoluble (phase separation)
PVP ($M_w = 20,000$)	[bmim][Cl]	25 wt %
	[bmim][BF ₄]	>33 wt %
	[bmim][PF ₆]	Insoluble (phase separation)
PECH ($M_w = 15,000$)	[bmim][Cl]	>33 wt %
	[bmim][BF ₄]	Insoluble (cloudy dispersion)
	[bmim][PF ₆]	Insoluble (cloudy dispersion)
PCMS ($M_w = 40,000$)	[bmim][Cl]	3 wt %
	[bmim][BF ₄]	Insoluble (phase separation)
	[bmim][PF ₆]	Insoluble (phase separation)
PEG ($M_v = 14,000$)	[bmim][Cl]	Insoluble (cloudy dispersion)
	[bmim][BF ₄]	>33 wt %
	[bmim][PF ₆]	>33 wt %
PMHS ($M_n = 1,700$ – $3,200$)	[bmim][Cl]	Insoluble (phase separation)
	[bmim][BF ₄]	Insoluble (phase separation)
	[bmim][PF ₆]	Insoluble (phase separation)

DP = degree of polymerization; M_n = number-average molecular weight; M_w = weight-average molecular weight; M_v = viscosity-average molecular weight; PCMS = poly (chloromethyl styrene); PECH = polyepichlorohydrin; PEG = poly(ethylene glycol); PMHS = polymethylhydrosiloxane; PVA = poly(vinyl alcohol); PVP = poly(4-vinyl phenol).

stirring with a magnetic stirring bar. The test time for dissolution was limited to a maximum of 24 h. If the residue of insoluble material was present after 24 h, we considered the tested polymer to be insoluble. Some ionic liquids with chloride ions such as [bmim][Cl], having high hydrogen-bond basicity and polarity,¹⁰ have been known to dissolve cellulose because the hydrogen-bonding network in the polymer can be broken by the chloride ions.¹¹ On the other hand, cellulose is not soluble in less polar 1-*n*-butyl-3-methyl tetrafluoroborate ([bmim][BF₄]) or 1-*n*-butyl-3-methyl hexafluorophosphate ([bmim][PF₆]).⁹ Other polymers with intermolecular hydrogen bonding, such as poly(vinyl alcohol) and poly(vinyl phenol), are also highly soluble in the [bmim][Cl] ionic liquid; 10 wt % poly(vinyl alcohol) and 25 wt % poly(vinyl phenol) homogeneous [bmim][Cl] solutions could be prepared. Poly(ethylene glycol), composed of less polar oxyethylene backbone units, is not soluble in [bmim][Cl] but is soluble in less polar ionic liquids such as [bmim][PF₆] and [bmim][BF₄]. Polymethylhydrosiloxane, a common starting polymer for the polymer analogous reaction to prepare functional silicon polymers,¹² is not soluble in [bmim][Cl], [bmim][PF₆], or [bmim][BF₄], probably because polymethylhydrosiloxane does not have any polar groups like other reactive polymers. The solubilities of polyepichlorohydrin and poly(chloromethyl styrene), which have polar and reactive chloromethyl side groups, were also tested.

Interestingly, although the chloromethyl group is less polar than the hydroxyl group, these polymers are soluble in polar [bmim][Cl] but are not soluble in less polar [bmim][PF₆] and [bmim][BF₄].

On the basis of these solubilization results, we studied the polymer analogous reactions of polyepichlorohydrin using ionic liquids as the reaction media because it showed high solubility in [bmim][Cl] and formed a dispersion in [bmim][BF₄] and [bmim][PF₆]. Polyepichlorohydrin is often a starting polymer in polymer analogous reactions because the chloromethyl side group can be easily substituted by various nucleophilic compounds in organic solvents to produce polymer systems with important functionalities such as liquid crystallinity, barrier properties, and curing ability.^{13–17} Polyepichlorohydrin was reacted with thiolate anions to obtain polymers with thioether linkage groups. Because thioether compounds are very important in biological and chemical processes,¹⁸ a variety of procedures for their synthesis have been developed. Mostly, thioether compounds are produced by the reaction of low-molecular-weight organic halides with thiolate anions with volatile organic solvents as the reaction media. However, a novel green procedure using ionic liquids for their synthesis was developed recently, and this new process has been found to have significant advantages, such as clean reactions and high yields.^{19–22} We also found such

TABLE II
Synthesis of H2F8TP (Reaction 2) with
Various Solvents

Solvent	Reaction temperature (°C)	Conversion (mol %)	Yield (wt %)
[bmim][Cl] ^a	70	100	80 ^c
[emim][Br] ^a	70	72	32 ^c
[hmim][Cl]	40	68	64 ^c
	70	74	70 ^d
[bmim][BF ₄]	40	36	7 ^c
	70	68	16 ^c
[emim][BF ₄]	40	Trace	Trace
	70	65	8 ^c
[bmim][PF ₆]	40	Trace	Trace
	70	Trace	Trace
DMAc	40	67	69 ^c
	70	— ^b	— ^b
CHCl ₃	40	Trace	Trace
THF	40	Trace	Trace

^a The melting points of the ionic liquids were higher than 40°C.

^b The product contained more than 50 mol % byproducts (disulfide).

^c The resulting polymer was separated from the reaction mixture through the reprecipitation process with methanol as a nonsolvent.

^d The resulting polymer was separated from centrifugation.

advantages from the reaction of polyepichlorohydrin with thiolate anions in ionic liquids.

Thiolate compounds are generally used for the reaction of organic halides to produce thioether compounds.^{23–25} Therefore, we performed polymer analogous reactions of polyepichlorohydrin with thiolate anions such as sodium benzene thiolate, sodium decanethiolate, sodium 1*H*,1*H*,2*H*,2*H*-perfluorinated hexanethiolate, sodium 1*H*,1*H*,2*H*,2*H*-perfluorinated octanethiolate, and sodium 1*H*,1*H*,2*H*,2*H*-perfluorinated decanethiolate at 70°C (reaction 1 in Fig. 1) with [bmim][Cl] as a reaction medium without any additional base or catalyst. The conversions of chloromethyl groups in polyepichlorohydrin to thioether groups were always greater than 80 mol %, with a short reaction time of 15 min. Furthermore, when polyepichlorohydrin was reacted with benzenethiol, which is known to be much less nucleophilic than the thiolate compounds, relatively high conversions (>65 mol %) from polyepichlorohydrin to polyoxyethylene containing benzenethiomethyl side groups were still observed. When polyepichlorohydrin was reacted with benzenethiol with various organic solvents including THF and DMAc, the reaction did not occur.

To further understand the effects of ionic liquids on the reactivity, selectivity, yields, and conversions in the polymer analogous reaction, various media, including ionic liquids and volatile organic solvents, were used for the reaction of polyepichlorohydrin (reaction 2 in Fig. 1). We intentionally chose sodium

1*H*,1*H*,2*H*,2*H*-perfluorinated decanethiolate as a reactant to obtain fluorinated polyoxyethylenes because they are useful for low-surface-energy coating materials.^{26,27} The conversions were obtained by a comparison of the NMR peak integration of chloromethyl groups and that of attached side groups (Fig. 2), and yields are given as the ratio of the mass of the product obtained after purification to the mass of the product calculated under the assumption that all polyepichlorohydrin chloromethyl groups reacted with the corresponding thiolate reagent (Table II). The conversions and yields of the reactions in THF and CHCl₃ were very low because both the perfluorinated anion and fluorinated polyoxyethylene were not soluble.²⁷ With the polar, aprotic DMAc as the reaction medium at 40°C, a higher conversion of 67 mol % and a yield of 69 wt % could be obtained, probably because the perfluorinated anion was partially soluble in these solvents. Attempts were made to reach higher conversions with organic solvents in this polymer analogous reaction through changes in the feed ratio and reaction temperature, but higher conversions could not be achieved.²⁸ For example, when the reaction temperature was increased to 70°C with DMAc, this produced byproducts composed mostly of disulfides because of the coupling reactions of the thiolate anions.²⁹ When the same reaction was performed with ionic liquids with halide anions, higher conversions and yields were achieved; even 100 mol % conversion was obtained when [bmim][Cl] was used at 70°C. Therefore, ionic liquids with chloride anions show enhanced reactivity and improved selectivity for the polymer analogous reaction of polyepichlorohydrin with the perfluorinated thiolate anion. One possible explanation is that ionic liquids with halide anions could act like phase-transfer catalysts such as tetrabutyl phosphonium bromide.³⁰ Previously, it was reported that the ionic liquid could act as both a reaction medium and a catalyst (a phase-transfer catalyst in heterogeneous reactions) to improve the reactivity and selectivity in low-molecular-weight organic synthesis (a nucleophilic substitution reaction).^{19–22} When less polar ionic liquids such as [bmim][BF₄], 1-*n*-ethyl-3-methyl imidazolium tetrafluoroborate ([emim][BF₄]), and [bmim]

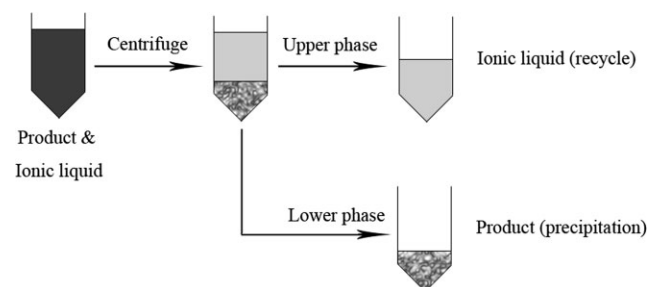


Figure 4 Scheme of the recycling process.

TABLE III
Reuse of Ionic Liquids in the Synthesis
of H2F8TP (Reaction 2)

Solvent	Reaction temperature (°C)	Conversion (mol %)	Yield (wt %)
[hmim][Cl] ^{1st}	70	74	70 ^a
[hmim][Cl] ^{2nd}	70	73	62 ^a
[hmim][Cl] ^{3rd}	70	78	68 ^a
[hmim][Cl] ^{4th}	70	>70	>70 ^{a, b}

^a The resulting polymer was separated by centrifugation and then washed with water.

^b The product contained small amounts of byproducts (disulfide).

[PF₆]⁻ were used as the reaction media of the polymer analogous reactions of polyepichlorohydrin, yields were generally low because the starting polymer, polyepichlorohydrin, and the product, a fluorinated polyoxyethylene, were not soluble in these ionic liquids and formed only cloudy dispersions; therefore, the separation of the starting polymer and the product was very tough. Therefore, the conversions with [bmim][BF₄]⁻ and [emim][BF₄]⁻ at 70°C were relatively high (>65 mol %), whereas the yield for the final product was less than 16 mol %. Figure 3 clearly shows the effect of the anion on the reaction. As the polarity of the ionic liquids increased (PF₆⁻ < BF₄⁻ < Br⁻ < Cl⁻), the conversion and yield obtained from reaction 2 increased.

We also tested the possibility of recycling ionic liquids in the polymer analogous reaction of polyepichlorohydrin with sodium 1*H*,1*H*,2*H*,2*H*-perfluorinated decanethiolate used to produce fluorinated polyoxyethylene. In the recycling experiment, we separated the fluorinated polyoxyethylene from the reaction mixture by centrifugation to avoid the use of any organic solvents in the purification process (Fig. 4). We tried to use polar ionic liquids such as [bmim][Cl], 1-*n*-ethyl-3-methyl imidazolium bromide ([emim][Br]), and 1-*n*-hexyl-3-methyl imidazolium chloride ([hmim][Cl]), which produced high yields and conversions, whereas [bmim][Cl] and [emim][Br] could not be used because they are solid at room temperature. Therefore, polyepichlorohydrin was reacted in [hmim][Cl] at 70°C, and then the product could be separated through centrifugation because [hmim][Cl] is a liquid at room temperature. The recovered ionic liquid was reused under the same reaction conditions for a second recycling reaction. The third and fourth recycling reactions were also performed with the ionic liquid separated from the former recycling reactions. High conversions (>73 mol %) and yields (62 wt %) were retained after the recycling experiments using [hmim][Cl]. In Table III, [hmim][Cl]^{1st}, [hmim][Cl]^{2nd}, [hmim][Cl]^{3rd}, and [hmim][Cl]^{4th} indicate the first, second, third, and fourth recycling reactions, respectively. Although the

fourth and later recycling steps still produced the fluorinated polyoxyethylene in high yields and conversions, small amounts of a disulfide byproduct were produced (confirmed by the NMR analysis), and the amount of the byproduct increased as the number of recycling reactions increased. Because unreacted thiolate ions in the reaction mixtures could produce these disulfides, further purification processes such as reprecipitation could help to obtain a pure polymer product when an ionic liquid is reused more than three times. We also confirmed the stability of ionic liquids during the recycling process because ionic liquids with halide anions are less stable than other ionic liquids containing non-nucleophilic anions such as PF₆⁻ or BF₄⁻.³¹ The NMR spectra of the recovered solvents (see the supporting information) indicated no evidence of ionic liquid degradation after three reuses.

CONCLUSIONS

Fluorinated polyoxyethylenes were successfully prepared from polyepichlorohydrin in high yields and conversions through polymer analogous reactions using ionic liquids with halide anions as the reaction media. There are many obvious advantages, including the selectivity and simplicity of the methodology, the ease of product isolation, and the potential for recycling, that are not possible with organic solvent systems. For example, 100 mol % conversion from polyepichlorohydrin to fluorinated polyoxyethylene was achieved and high yields and conversions were maintained with recycled ionic liquids; this is not possible with organic solvents. Because of the solubility of functional polymers in ionic liquids, these ionic liquids have the potential to be used as alternatives to common volatile solvents for polymer synthesis through polymer analogous reactions. We expect polymer analogous reactions using ionic liquids as both reaction media and catalysts to reveal new possibilities for polymer synthesis processes involving ionic liquids, and such work is in progress in this laboratory.

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