Benzylpyrazinium Salts as Thermally Latent Initiators in the Polymerization of Glycidyl Phenyl Ether: Substituent Effect on the Initiator Activity and Mechanistic Aspects

Moon Suk Kim,[†] Kyu Wan Lee,[‡] Takeshi Endo,[§] and Sang Bong Lee*[,‡]

Nanobiomaterials Laboratory and Advanced Chemical Technology Division, Korea Research Institute of Chemical Technology, P.O. Box 107, Yuseong, Daejeon 305-600, Korea, and Department of Polymer Science and Engineering, Yamagata University, 4-3-16 Jonan, Yonezawa, Yamagata 992-8510, Japan

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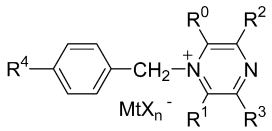
Introduction

"Latent initiators" show no activity under normal condition but form active species to initiate polymerization by only certain external stimulation like heating and photoirradiation. Latent initiation is one of the most promising candidates for controlled polymerizations. The approach of one component system using the premixed mixture of the monomers and latent initiators could offer an excellent processability, which are very important in industrial fields.[1] Therefore, the chemistry of latent initiators has been greatly expanding due to its successful application to industrial fields such as paints, inks, adhesives, epoxy molding compounds, and photoresists using thermosetting materials like epoxy resin and multifunctional vinyl ethers.[2]

Crivello et al. have developed various onium salts such as diaryliodonium and triarylsulfonium salts as latent photoinitiators.[3] Endo et al. and Yagci et al. have also developed several benzylsulfonium[4] and benzylpyridinium salts[5] as thermal-latent and photolatent initiators for the polymerization of styrene, vinyl ethers, and epoxides. In addition, the mechanism studies for the benzylonium salts have been comparably well established in the thermal-induced polymerization using a benzyl cation as initiating species and the sulfide or pyridine as terminating species.[4,5] Namely, monomers such as epoxides rapidly attacked a benzyl cation formed by the thermal stimulation of benzylsulfonium or benzylpyridinium salts and subsequently formed propagating cationic species, which was capable of chain propagation by successive reaction with monomer. However, the sulfide or pyridine released from the salts could attack propagating species to terminate the polymerization through competitive attack with monomer, and the attack ability could become dominant when the monomer concentration decreased. The order of the initiator activity was increased by the introduction of an electron-donating group in the para position of the benzyl and electron-withdrawing group in the sulfide or pyridine. Through detailed studies, some initiators have been already industrialized in practical applications.

Scheme 1



	1	2	3	4	5	6
R^0	H	H	H	H	H	H
R^1	H	H	CH_3	H	H	H
R^2	H	CH_3	CH_3	CH_3	CN	H
R^3	H	H	H	CH_3	H	H
R^4	H	H	H	H	H	OCH_3
MtX_n^-	SbF_6^-					

	7	8	9
R^0, R^1, R^2, R^3, R^4	H		
MtX_n^-	AsF_6^-	PF_6^-	BF_4^-

Ideally, latent initiators will initiate polymerization at only the desired temperature range. They should be stable indefinitely below threshold temperature but generate the initiating species and polymerize rapidly without inhibition or retardation of polymerization above the temperature, indicating high latency of latent initiator. Initiators with high latency can enhance pot life and reduce the polymerization time of a monomer. The high latency is therefore important to establish further utilization of latent initiators in the industrial fields. Pappas et al. have reported that the rapid increase of latency above a threshold temperature could be obtained by combining the large activation energy for forming initiating species and the polymerization rate increase according to increasing the temperature.[6] They suggested that the larger activation energy for initiation of thermally latent initiators, e.g., benzylsulfonium or benzylpyridinium salts, might be depend on the cleavage of the bond between a heteroatom and a carbon atom.

To design latent initiators with high latency, we have employed benzylpyrazinium salts based on bidentate pyrazine. This article deals with thermal latency, activity, and mechanistic aspects of benzylpyrazinium salt derivatives with electron-donating or -withdrawing groups at the benzyl group or pyrazine in the polymerization of glycidyl phenyl ether (GPE).

Results and Discussion

Initiator Synthesis. The Menschutkin reaction of benzyl bromide derivatives with various pyrazine derivatives proceeded to give the corresponding benzyl quaternary ammonium bromides as white precipitates due to less solubility in corresponding benzyl bromide derivatives. The benzylpyrazinium hexafluoroantimonate (**1**), benzyl-3-methylpyrazinium hexafluoroantimonate (**2**), benzyl-2,5-dimethylpyrazinium hexafluoroantimonate (**3**), benzyl-3,5-dimethylpyrazinium hexa-

[†] Nanobiomaterials Laboratory, Korea Research Institute of Chemical Technology.

[‡] Advanced Chemical Technology Division, Korea Research Institute of Chemical Technology.

[§] Yamagata University.

* Corresponding author: Tel 82-42-860-7613; e-mail sangbl@krict.re.kr.

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Table 1. Structures and Characteristic of Benzylpyrazinium Salts

salt no.	structure	MtX_n^-	yield (%)	mp (°C)	IR	elemental analysis	C	H	N
1	$R^0, R^1, R^2, R^3, R^4 = H$	SbF_6^-	85	136.8−137.6	3137, 1454, 1164, 760, 709, 659	calcd	32.45	2.70	6.88
						found	32.70	2.74	6.91
2	$R^2 = CH_3$ $R^0, R^1, R^3, R^4 = H$	SbF_6^-	77	90.7−91.8	3154, 1502, 1468, 1179, 749, 705, 669	calcd	34.21	3.09	6.65
						found	34.24	2.76	6.65
3	$R^1, R^2 = CH_3$ $R^0, R^3, R^4 = H$	SbF_6^-	70	93.5−96.3	3130, 1497, 1164, 757, 659	calcd	35.88	3.48	6.44
						found	36.02	3.36	6.30
4	$R^2, R^3 = CH_3$ $R^0, R^1, R^4 = H$	SbF_6^-	92	88.7−89.9	3116, 1476, 1178, 762, 723, 660	calcd	35.88	3.48	6.44
						found	35.80	3.37	6.46
5	$R^2 = CN$ $R^0, R^1, R^3, R^4 = H$	SbF_6^-	38	157.1−162.8	3123, 1469, 1154, 1125, 744, 653	calcd	33.34	2.31	9.72
						found	33.13	2.35	9.70
6	$R^4 = OCH_3$ $R^0, R^1, R^2, R^3 = H$	SbF_6^-	54	102−105.3	3127, 1613, 1260, 1150, 1026, 662	calcd	32.97	2.98	6.41
						found	33.15	2.96	6.46
7	$R^0, R^1, R^2, R^3, R^4 = H$	AsF_6^-	75	145.2−146.9	3131, 1446, 1172, 1153, 748, 696	calcd	36.65	3.08	7.77
						found	36.29	3.23	7.98
8	$R^0, R^1, R^2, R^3, R^4 = H$	PF_4^-	86	139.1−140.8	3152, 1455, 1183, 1162, 869, 843, 561	calcd	41.75	3.48	8.86
						found	42.14	3.45	8.92
9	$R^0, R^1, R^2, R^3, R^4 = H$	BF_4^-	36	118.9−120.2	3149, 1453, 1155, 1066, 756, 707	calcd	51.20	4.26	10.85
						found	51.60	4.34	10.70

fluoroantimonate (**4**), benzyl-3-cyanopyrazinium hexafluoroantimonate (**5**), *p*-methoxybenzylpyrazinium hexafluoroantimonate (**6**), benzylpyrazinium hexafluoroarsenate (**7**), benzylpyrazinium hexafluorophosphate (**8**), and benzylpyrazinium tetrafluoroborate (**9**) obtained by anion-exchange reaction with the corresponding counteranions. The structures of **1**−**9** were confirmed by ^{1}H NMR, IR, and elemental analysis (Table 1). Only the monoquarternized structure by one nitrogen atom in pyrazine was identified by ^{1}H NMR and elemental analysis, probably due to radical decrease in nucleophilicity of another nitrogen atom after monoquarternization. In the IR spectrum, the characteristic signals assignable to hexafluoroantimonate (SbF_6), hexafluoroarsenate (AsF_6), hexafluorophosphate (PF_6), and tetrafluoroborate (BF_4) as the corresponding counteranion of pyrazinium salts appeared at 660, 696, 843, and 1066 cm^{-1}, respectively.

Polymerization of GPE Using Benzylpyrazinium Salts. GPE was polymerized in bulk using **1**−**6** at 30−190 °C for 2 h. The polymerization proceeded homogeneously throughout the reaction because **1**−**6** were completely soluble in GPE at ambient temperature. Figure 1 shows the temperature−conversion curves of

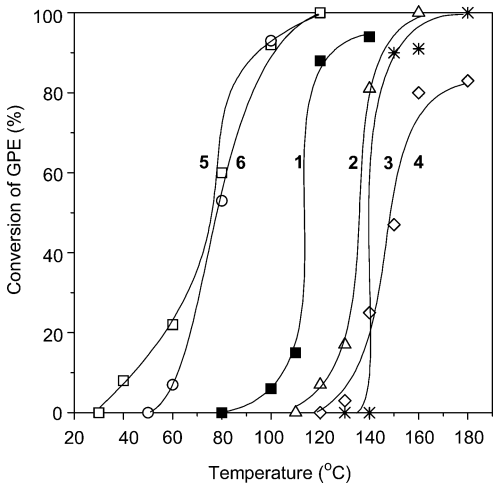
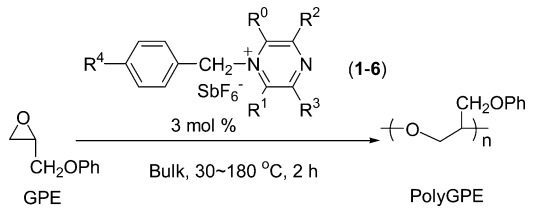


Figure 1. Temperature−conversion relationships in the bulk polymerization of GPE with pyrazinium salts **1**−**6** (3 mol %) in 2 h.

Scheme 2



the polymerization. No polymerization of GPE took place with **1** below 80 °C, whereas it proceeded rapidly above the temperature. The salts **2**−**4** with methyl substitute as electron-donating group into the pyrazine ring did not initiate the polymerization below 110−140 °C, but it converted to afford polyGPE above those temperatures. GPE did not react with **5** and **6** below 30 and 50 °C but proceeded rapidly above those temperatures, respectively. The pyrazinium salts **1**−**6** served as thermally latent initiators in the polymerization of GPE. The salts **1**−**6** as latent initiators initiated within only a narrow temperature range to polymerize GPE in high conversion. The introduction of an electron-donating methyl substituent in the pyrazine group decreased the initiator activity, while an electron-withdrawing cyano substituent in the pyrzaine group decreased the initiation temperature. An electron-donating methoxy substituent in benzyl group decreased the initiation temperature. This indicates that the initiation temperature depends on the bond cleavage between a nitrogen atom and a carbon atom due to the influence of electron density change for benzyl and pyrazine group. Therefore, the activity of pyrazinium salts can be controlled by the electronic modification of the benzyl and pyrazine group.

Table 2 shows the M_n of the polymers obtained with the pyrazinium salts. The molecular weight of polymer seemed to be affected by the nucleophilicity and steric hindrance of pyrazine derivatives as terminating species. Namely, the molecular weight of the polymer obtained with **1** as an initiator was higher than that of **2** and **4** and lower than that of **5**, suggesting that the terminating ability of pyrazine group increased by methyl substituent and decreased by cyano substituent. In the case of **3** with two methyl substituents, the terminating ability probably decreased due to its sterically hindered structure. This result demonstrates that

Table 2. Polymerization of GPE with Benzylpyrazinium Salts 1−6 (3 mol %) for 2 h

initiator	temp (°C)	conv[a] (%)	M_n [b]	M_w/M_n [b]	initiator	temp (°C)	conv[a] (%)	M_n [b]	M_w/M_n [b]
1	110	15			**4**	140	25		
	120	88	1900	2.38		150	47	1300	1.95
	140	94	1800	2.99		160	80	1200	1.85
						180	83	1400	1.72
2	130	17							
	140	81	1600	2.44	**5**	40	8		
	160	100	1600	3.46		60	22	4500	1.23
						80	60	4500	1.39
3	140	0				100	92	5100	1.80
	150	90	3500	1.53					
	160	91	3400	1.57	**6**	60	8		
	180	100	3000	1.46		80	53	1500	2.08
						100	93	2500	2.25
						120	100	2200	3.09

[a] Determined by ^{1}H NMR. [b] Estimated by GPC based on polystyrene standards.

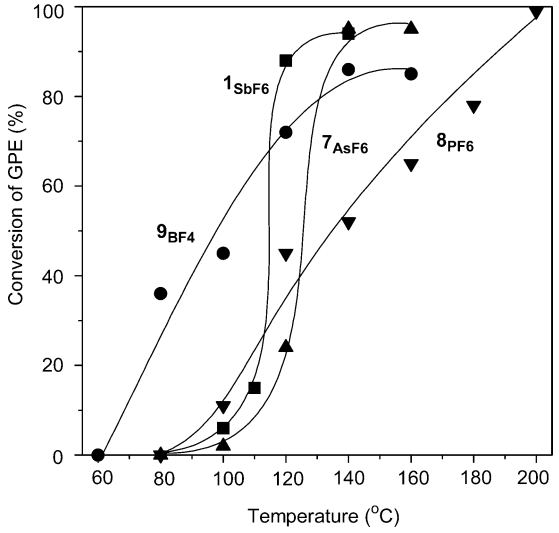
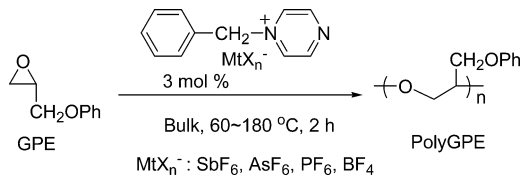


Figure 2. Temperature−conversion relationships in the bulk polymerization of GPE with pyrazinium salts **1** and **7**−**9** (3 mol %) in 2 h.

Scheme 3



the pyrazine moieties play an important role not only in initiation but also in propagation.

The polymerization of GPE was also carried out with the salts **7**−**9** having different counteranions at 80−190 °C for 2 h.[7] As shown in Figure 2, the activity order of initiators is $\mathbf{9}_{BF_4} > \mathbf{8}_{PF_6} > \mathbf{1}_{SbF_6} > \mathbf{7}_{AsF_6}$ below 110 °C, while the order changed to $\mathbf{1}_{SbF_6} > \mathbf{7}_{AsF_6} > \mathbf{9}_{BF_4} > \mathbf{8}_{PF_6}$ in the high conversion region above 140 °C. The change of activity might be contributed by the variation between cleavage energy in the initiation and the different propagation rates in propagation step, probably due to the different nucleophilicity of the counteranions.

Mechanistic Study. *p*-Methoxybenzylpyrazinium hexafluoroantimonate (**6**) was chosen to examine the initiating species. The thermal polymerization of **6** in the presence of ethylene oxide (EO) was carried out at 100 °C for 2 h using nitromethane-d_3 in a sealed NMR sample tube. Figure 3 illustrates the change of the ^{1}H NMR spectra of the reaction mixture of **6** and EO. A new signal *s* assignable to benzyl protons polymerized

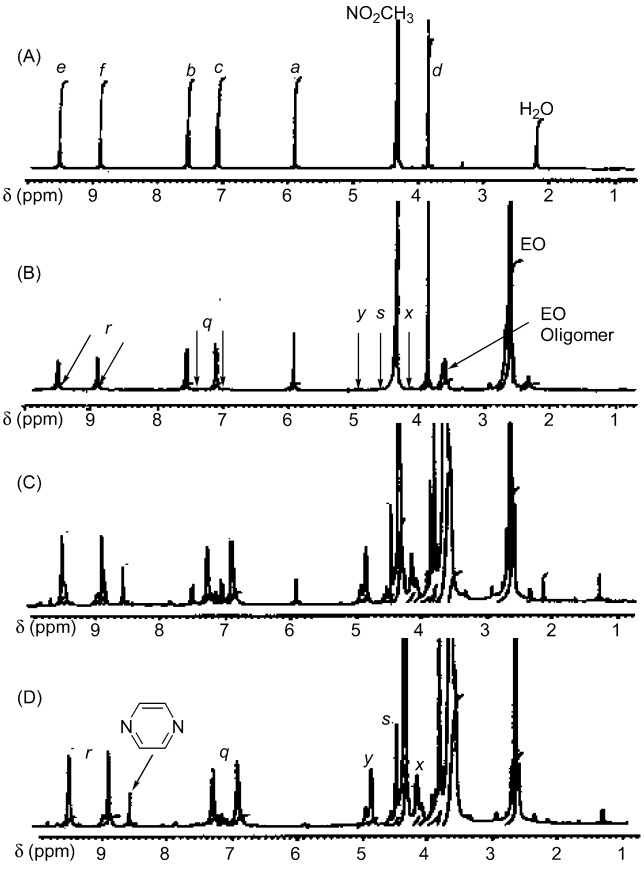
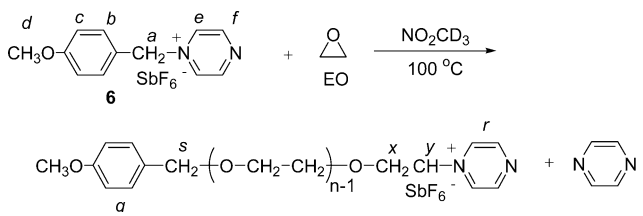


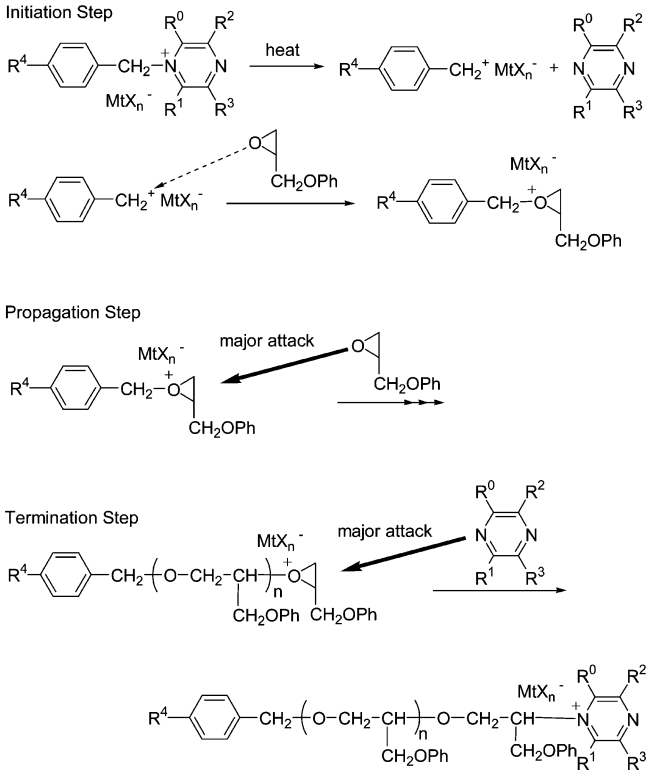
Figure 3. Thermal polymerization of EO with *p*-methoxybenzylpyrazinium hexafluoroantimonate **6**. ^{1}H NMR (300 MHz) spectra of (A) **6**, after heating in nitrobenzene-d_5 at 100 °C for (B) 2, (C) 30, and (D) 120 min. Initial concentrations of EO and **6** were 11 and 0.015 M, respectively.

Scheme 4



through initiation of **6** appeared at 4.55 ppm, and the integration increased simultaneously with decreasing integration of *a*, which completely disappeared after 2 h. This strongly indicates that the initiating species is a benzyl cation. In addition, a new signal of EO oligomer

Scheme 5



appeared at around 3.6 ppm after 2 min reaction, and its integration increased with the reaction time, along with decreasing the EO integration.[8] New signals *r* assignable to pyrazine acted as terminating species, *q* assignable to benzene acted as initiating species, and *y*, *x* assignable to methylene protons of EO oligomer end-terminated by pyrazine appeared at 9.30, 8.98, 7.48, 6.71, 4.95, and 4.18 ppm, respectively. Their integration also increased as the reaction time increased. In contrast, the signal at 8.6 ppm was assignable to a pyrazine (ca. <10%), which did not terminate the propagation cation, probably due to the backbiting reaction forming cyclic EO oligomers like 1,4-dioxane. This result indicates clearly that the pyrazine group acted as the terminating species.

Scheme 5 represents a plausible mechanism for the polymerization. The benzylpyrazinium salts thermally decompose to generate benzyl cationic initiating species, which is coordinated by counteranions, along with a pyrazine. In the initial propagation step, monomers attack a propagating cationic species, in preference to pyrazine as terminating species. When the monomer concentration decreased, pyrazine released from the salts could attack predominantly propagation species to terminate the polymerization.

In summary, the benzylpyrazinium salts **1**−**9** successfully served as thermally latent initiators in the polymerization of GPE. The polymerization of GPE with the salts **1**−**6** as latent initiators performed at the comparably narrow temperature range to give high conversion. The activities of the benzylpyrazinium salts were affected by the substituents into the benzene and pyrazine ring. The introduction of an electron-donating methyl substituent in the pyrazine group decreased the initiator activity, while an electron-withdrawing cyano substituent in the pyrzaine group and an electron-donating methoxy substituent in the benzyl group increased the initiator activity. It was confirmed that the activity of pyrazinium salts could be controlled by the electronic modification of the benzyl and pyrazine group. The initiating and terminating species by the NMR experiment were identified as the benzyl cation and pyrazine, respectively.

Experiments

Materials. Benzyl bromide (98%), pyrazine (99%), 2-methylpyrazine (99%), pyrazinecarbonitrile (99%), 2,5-dimethylpyrazine (98%), 2,6-dimethylpyrazine (98%), sodium hexafluoroantimonate (technical purity grade), sodium hexafluoroarsenate, potassium hexafluorophosphate (98%), and sodium tetrafluoroborate (98%) were purchased from Aldrich (Milwaukee, WI) and used as received without further purification. Glycidyl phenyl ether (GPE, Aldrich) was dried and distilled over calcium hydride before use.

Measurements. ^{1}H NMR spectra were recorded with a SYKES disk 7000 300 MHz FT/NMR spectrometer using tetramethylsilane (TMS) as an internal standard in acetone-d_6. IR spectra were measured with a JASCO FT/IR-3 spectrophotometer. Melting points (mp) were measured by a Thomas-Hoover capillary melting point apparatus. Number- and weight-average molecular weights (M_n and M_w) and polydispersity ratios (M_w/M_n) were estimated by gel permeation chromatography (GPC) on a Waters 2690, equipped with two consecutive polystyrene gel columns [PLgel, 5 μm, 500 Å (500−30 000: molecular weight of exclusion limit) and PLgel mixed B, 10 μm (500 000-10 000 000: molecular weight of exclusion limit)] at 40 °C, using THF as an eluent with a flow rate of 1.0 mL/min by polystyrene calibration and with refractive index detectors (Waters 410RI). Elemental analyses were carried out with a Perkin-Elmer 240C CHN.

Synthesis of Benzyl Pyrazinium Hexafluoroantimonate (1). Pyrazine (23.8 g, 0.3 mol) was added to benzyl bromide (440 g, 2.92 mol) at room temperature. The mixture was stirred for 48 h. A precipitated product was filtered and washed with benzene several times. A solution of aqueous $NaSbF_6$ (109 g, 0.4 mol) was added to a solution of the resulting solid in water. After stirring for 5 min, a white precipitate was filtered and washed with ether several times. It was crystallized from methanol to give 90.1 g (2.49 mol, 85%) of a white crystal; mp 136.8−137.6 °C. IR (KBr, cm^{-1}): 3137, 1454, 1164, 760, 709, 659 (SbF_6). ^{1}H NMR (acetone-d_6): δ 9.68 (s, 2H, $C_2H_2N^+$), 9.36 (s, 2H, C_2H_2N), 7.72 (m, 2H, $-C_6H_5$), 7.52 (m, 3H, $-C_6H_5$), 6.21 (s, 2H, $-CH_2$). Anal. Calcd for $C_{11}H_{11}N_2SbF_6$: C, 32.45; H, 2.70; N, 6.88. Found: C, 32.70; H, 2.74; N, 6.91.

Synthesis of Benzylpyrazinium Salts (2−9). Compounds **2**−**9** were synthesized from benzyl bromide derivatives and pyrazine derivatives, followed by the reaction of corresponding counteranions in the similar manner with **1**. The detailed results are summarized in the Supporting Information.

Polymerization. Typical procedure: initiator **1** (24.4 mg, 0.06 mmol) was fed into a glass tube. The tube was closed with a three-way stopcock, and a cycle of vacuum−nitrogen was repeated three times to remove oxygen. GPE (301 mg, 2 mmol) was fed into the glass tube with a syringe under nitrogen. The tube was sealed under vacuum using the freeze−thaw technique and heated at a set temperature in an oil bath. After 2 h, the tube was cooled into a dry ice−acetone bath, and the reaction mixture was diluted with chloroform (0.5 mL). The mixture was then poured into methanol (50 mL) to precipitate a polymer. The polymer was separated from the supernatant decantation and dried in vacuo. The monomer conversion was determined by ^{1}H NMR spectroscopy before precipitation with methanol, and the molecular weight of the polymer was determined by GPC. The obtained polymer was identified to be polyGPE. ^{1}H NMR ($CDCl_3$): δ 7.99−7.65 (m, 5H, $-C_6H_5$), 4.80−3.25 (m, 5H, $-OCH_2CH(CH_2Ph)-$). IR (NaCl, cm^{-1}): 3036, 2930, 2876, 1599, 1495, 1244, 1132, 1044, 754, 661.

Supporting Information Available: Detailed synthesis data corresponding to experimental parts and polymerization

data (Table S1). This material is available free of charge via the Internet at http://pubs.acs.org.

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(7) The data of the polymerization including M_n and M_w/M_n are summarized in the Supporting Information (Table S1).

(8) The obtained ethylene oxide oligomers gave the M_n of 600 and showed the signal assignable to the hexafluoroantimonate moiety at 660 cm^{-1} in IR.

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