Notes

Synthesis and the Initiator Activity of Fluorenyltriphenylphosphonium Salts in the Cationic Polymerization of Epoxide. Novel Thermally Latent Initiators

Tatsuya Toneri, Ken-ichi Watanabe, Fumio Sanda, and Takeshi Endo*

Research Laboratory of Resources Utilization, Tokyo Institute of Technology, Nagatsuta-cho, Midori-ku, Yokohama 226-8503, Japan

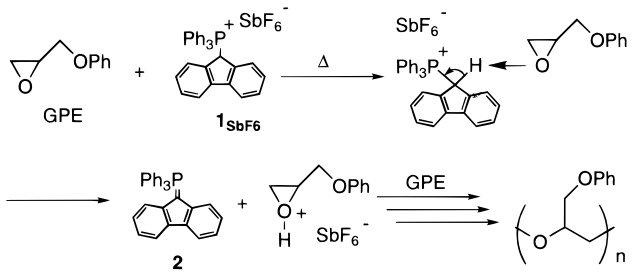
Received August 11, 1998
Revised Manuscript Received November 25, 1998

Introduction

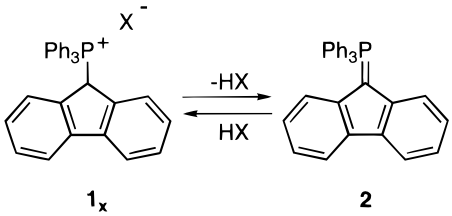
In cationic polymerizations and cross-linking reactions, catalysts that function as initiators solely by heating or photoirradiation are useful as "latent catalysts". They have been utilized in various fields of materials such as adhesive, packings, and paints, since they can control the initiation step of polymerization or curing. These initiators must be inert under ambient conditions but should be transformed into activated species to initiate the reaction by appropriate external stimulations such as heating and photoirradiation. We have developed several benzylsulfonium,[1] benzylpyridinium,[2] benzylammonium,[3] and phosphonium[4] salts having low nucleophilic counteranions as thermally latent and photolatent initiators for the polymerizations of styrene and epoxides. Among these latent initiators, only benzylphosphonium salts release proton as an active species, which is different from other benzylonium salts releasing benzyl cation as the active species,[1] because the phosphonium salts easily release a proton to form the corresponding stable ylides. The chemistry of phosphonium salts has been widely investigated, and they have been utilized for organic synthesis as useful intermediates. Phosphonium salts show more variety of reactivities compared with the corresponding pyridinium and ammonium salts, because of the participation of the d-orbital. In a preceding communication,[4d] we have reported that fluorenyltriphenylphosphonium hexafluoroantimonate (**1**$_{SbF_6}$) can serve a thermally latent initiator capable of initiating cationic polymerization of glycidyl phenyl ether (GPE) (Scheme 1).

Although the polymerization of GPE could not proceed below 110 °C, it rapidly took place above 120 °C. The fluorenyltriphenylphosphonium salt (**1**$_{SbF_6}$) showed a dramatically higher activity than benzyltriphenylphosphonium hexafluoroantimonate, probably due to the higher acidity of **1**$_{SbF_6}$ than that of the corresponding benzyltriphenylphosphonium salt. The high acidity of **1**$_{SbF_6}$ may be ascribed to the delocalization effect of the negative charge on the fluorene ring.[5] Suppression of termination by the liberated ylide may be based on the lower nucleophilicity of the stable fluorenyltriphenylphosphonium ylide (**2**) (Scheme 2).

Scheme 1



Scheme 2

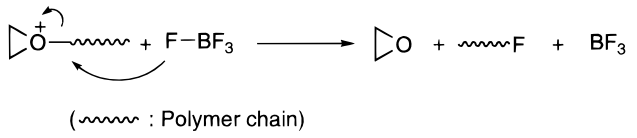


As is often the case with cationic polymerization of epoxides, the propagating oxonium cation transforms into a covalent species to terminate the polymerization (Scheme 3).

Scheme 3

Therefore, counterions with lower nucleophilicities such as BF_4^-, SbF_6^-, PF_6^-, and AsF_6^- are favorable for the cationic polymerization. BF_4^- reacts with a strong electrophilic agent as a special case to form a fluorinated polymer as shown in Scheme 4.[6]

Scheme 4



We report here the details of synthesis and activity of some fluorenyl triphenylphosphonium salts with different counteranions (SbF_6^-, BF_4^-, PF_6^-, and AsF_6^-) as an initiator for the polymerization of GPE.

Results and Discussion

Synthesis of Initiators. The phosphonium salts **1**$_{SbF_6}$, **1**$_{AsF_6}$, **1**$_{PF_6}$, and **1**$_{BF_4}$ were synthesized by the reaction of 9-bromofluorene and triphenylphosphine, followed by the counteranion exchange with the corre-

* To whom all correspondence should be addressed.

10.1021/ma981275q CCC: $18.00
Published on Web 02/03/1999

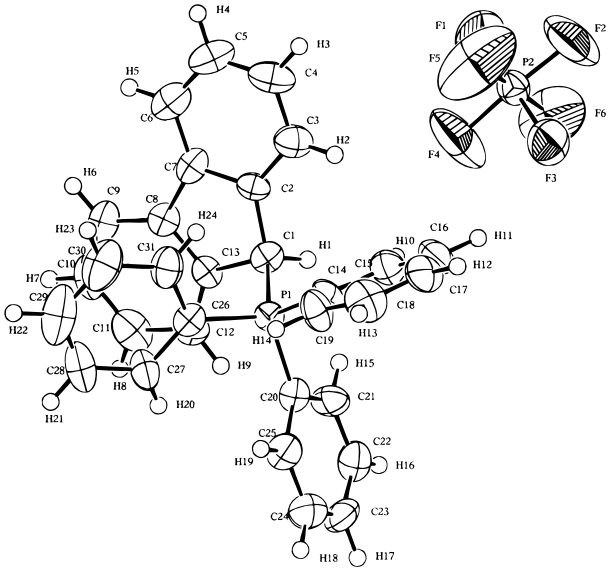
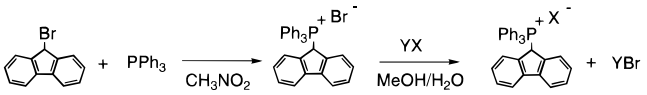


Figure 1. ORTEP drawing of $\mathbf{1}_{\mathbf{PF_6}}$.

sponding inorganic salts (YX) according to the modified method of the literature as shown in Scheme 5.[7] Figure

Scheme 5

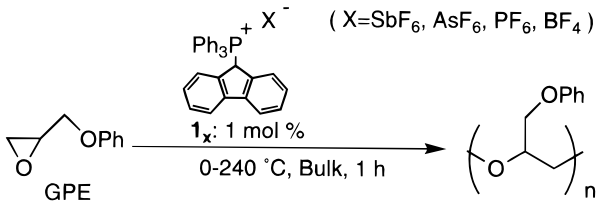


$\mathbf{1}_{\mathbf{SbF6}}$: X=$SbF_6$, Y=K, $\mathbf{1}_{\mathbf{AsF6}}$: X=$AsF_6$, Y=Na, $\mathbf{1}_{\mathbf{PF6}}$: X=$PF_6$, Y=K, $\mathbf{1}_{\mathbf{BF4}}$:X=$BF_4$, Y=K

1 shows the molecular structure of $\mathbf{1}_{\mathbf{PF_6}}$ obtained by single-crystal X-ray analysis. The interatomic distances between the fluorenyl methine protons and carbons of $\mathbf{1}_{\mathbf{PF_6}}$[8] and $\mathbf{1}_{\mathbf{BF_4}}$[9] were 0.98 and 1.12 Å, respectively. This would be related to the order of acidity of the fluorenyl methine protons ($\mathbf{1}_{\mathbf{BF_4}} > \mathbf{1}_{\mathbf{PF_6}}$).

Polymerization. Polymerization of GPE was carried out in the presence of $\mathbf{1}_{\mathbf{X}}$ at the temperature ranging from 0 to 190 °C for 1 h (Scheme 6, Table 1). The

Scheme 6



conversion of GPE was estimated by the ^{1}H NMR spectrum of the crude polymerization mixture. Figure 2 illustrates the temperature−conversion relationships in the polymerization of GPE in the presence of 1 mol % $\mathbf{1}_{\mathbf{X}}$, suggesting that GPE could not be converted into the polymer below 100 °C, whereas it rapidly polymerized above 110 °C. All of the salts $\mathbf{1}_{\mathbf{X}}$ served as thermally latent initiators in the polymerization of GPE. The counteranion X and polymerization temperature little affected the molecular weight of the obtained polymer. In the case of $\mathbf{1}_{\mathbf{BF_4}}$, the obtained polymer showed a bimodal GPC curve.[10] As shown in Figure 2, the initiator activity was on the order of $\mathbf{1}_{\mathbf{BF_4}} > \mathbf{1}_{\mathbf{SbF_6}} > \mathbf{1}_{\mathbf{PF_6}} > \mathbf{1}_{\mathbf{AsF_6}}$ in a low-conversion region (<10%), while the order changed to $\mathbf{1}_{\mathbf{SbF_6}} > \mathbf{1}_{\mathbf{BF_4}} > \mathbf{1}_{\mathbf{PF_6}} > \mathbf{1}_{\mathbf{AsF_6}}$ in a high-conversion region.

Table 1. Polymerization of GPE with Fluorenyltriphenylphosphonium Salt ($\mathbf{1}_{\mathbf{X}}$)[a]

init (X)	temp (°C)	conv[b] (%)	M_n (M_w/M_n)[c]
SbF_6	110	0	
	120	26	2300 (1.2)
	130	73	3700 (1.4)
	140	84	4100 (1.4)
	150	89	4100 (1.4)
	160	100	4100 (1.4)
BF_4	120	0	
	130	12	2400 (1.1)[d]
	140	22	2600 (1.1)[d]
	160	26	2500 (1.1)[d]
	180	39	2600 (1.1)[d]
	190	35	2800 (1.1)[d]
PF_6	120	0	
	130	7	2700 (1.1)
	140	8	2900 (1.1)
	160	15	2700 (1.2)
	180	22	2600 (1.1)
	190	25	2500 (1.4)
AsF_6	140	0	
	160	3	2300 (1.1)
	180	7	2200 (1.1)
	190	13	2600 (1.4)

[a] Conditions; initiators: 1.0 mol % vs GPE for 1 h. [b] Determined by ^{1}H NMR. [c] Estimated by GPC based on polystyrene standards. [d] Bimodal peak was observed, whose area ratio between high- and low-molecular-weight parts was 1.7:1.0.

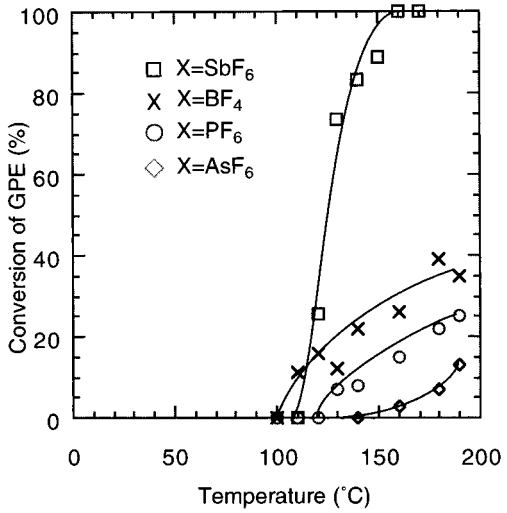


Figure 2. Temperature−conversion relationships in the polymerization of GPE in bulk with 1 mol % $\mathbf{1}_{\mathbf{SbF_6}}$, $\mathbf{1}_{\mathbf{AsF_6}}$, $\mathbf{1}_{\mathbf{PF_6}}$, and $\mathbf{1}_{\mathbf{BF_4}}$ for 1 h.

The initiation species should be a fluorenyl methine proton in this polymerization as illustrated in Scheme 1.[4d] If this mechanism is operative, we may find a tendency between the ^{1}H NMR chemical shifts of $\mathbf{1}_{\mathbf{X}}$ and the activities. The ^{1}H NMR signals of the fluorenyl methine protons of the phosphonium salts $\mathbf{1}_{\mathbf{BF_4}}$, $\mathbf{1}_{\mathbf{SbF_6}}$, $\mathbf{1}_{\mathbf{AsF_6}}$, and $\mathbf{1}_{\mathbf{PF_6}}$ were observed at 7.05, 7.02, 7.01, and 7.00 ppm in acetone-d_6 (0.02 mol/L), respectively, indicating the highest acidity of $\mathbf{1}_{\mathbf{BF_4}}$, which agreed with the order of the initiator activity of $\mathbf{1}_{\mathbf{X}}$ in a low-conversion region. The acidity of the fluorenyl methine proton would decide the initiator activity of $\mathbf{1}_{\mathbf{X}}$ in the low-conversion region. Namely, only $\mathbf{1}_{\mathbf{BF_4}}$ with the largest acidity could initiate the polymerization of GPE at 110 °C. No apparent tendency could be observed between the ^{13}C NMR chemical shifts[11] of the fluorenyl methine carbons or ^{31}P NMR chimical shifts[12] of the phosphines and the initiator activity of $\mathbf{1}_{\mathbf{X}}$. Molecular orbital (MO)

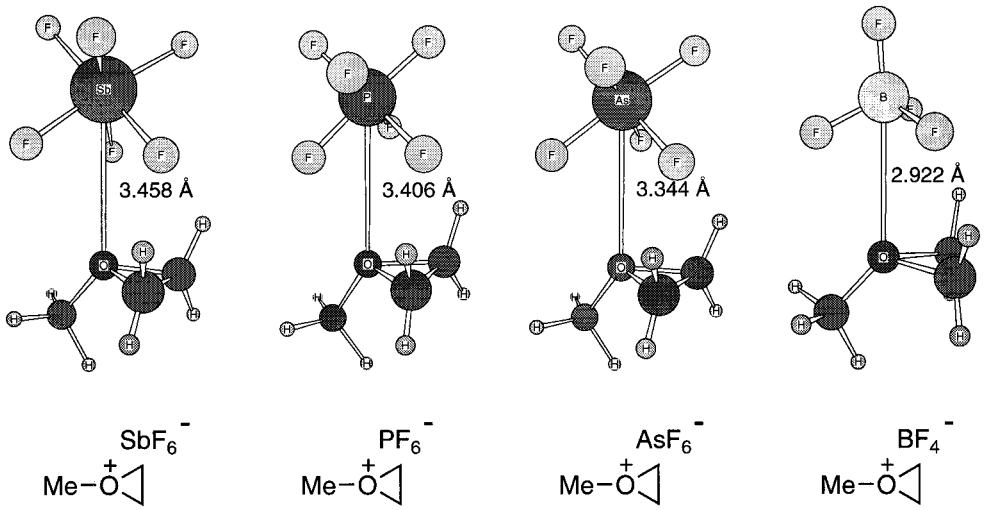


Figure 3. Structures of the oxonium cations formed by the addition of ethylene oxide with $\mathbf{Me^+SbF_6^-}$, $\mathbf{Me^+PF_6^-}$, $\mathbf{Me^+AsF_6^-}$, and $\mathbf{Me^+BF_4^-}$. Geometries were fully optimized by Biosym/MSI Dmol 950, DNP basis.

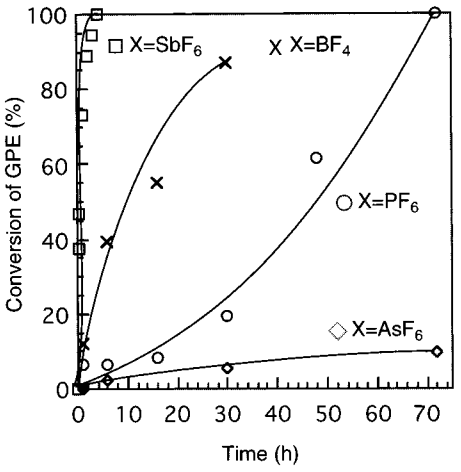


Figure 4. Time–conversion relationships in the polymerization of GPE in bulk with 1 mol % $\mathbf{1_{SbF_6}}$, $\mathbf{1_{AsF_6}}$, $\mathbf{1_{PF_6}}$, and $\mathbf{1_{BF_4}}$ at 130 °C.

calculations were carried out to examine the interionic distance between the oxonium cation of the propagating polymer end and the counteranion. Oxonium cations, formed by the addition of methyl cation to ethylene oxide, were used as the models of the propagating end to simplify the calculation. Figure 3 illustrates the conformers fully optimized by the ab initio method based on density functional theory. The interionic distance was on the order of $SbF_6^- > PF_6^- > AsF_6^- > BF_4^-$, which should reflect the order of nucleophilicities of the counteranions. A counteranion with a longer distance to the oxonium cation shows a lower nucleophilicity, which is favorable for the propagation step.

Figure 4 illustrates the time-conversion relationships in the polymerization of GPE in bulk with 1 mol % $\mathbf{1_X}$ at 130 °C. It was confirmed that the initiator activity of $\mathbf{1_X}$ was on the order of $\mathbf{1_{SbF_6}} > \mathbf{1_{BF_4}} > \mathbf{1_{PF_6}} > \mathbf{1_{AsF_6}}$, which agreed with the result of the temperature–conversion relationship in Figure 2. This order may be the result of the acidity of the fluorenyl methine proton and the nucleophilicity of the counteranion, which influence the reaction rates of the initiation and propagation steps, respectively. The initiator $\mathbf{1_{BF_4}}$ has a counteranion with the largest nucleophilicity, but its fluorenyl methine proton has the largest acidity. By the compensation of these two factors $\mathbf{1_{BF_4}}$ might show the second largest activity as described above.

Summary

We have synthesized four fluorenyltriphenylphosphonium salts ($\mathbf{1_X}$) and examined the polymerization of GPE with $\mathbf{1_X}$ to examine the effect of counteranion on the activity of $\mathbf{1_X}$. All the phosphonium salts were stable against water and air and served as a thermally latent initiator in the polymerization. The activity of $\mathbf{1_X}$ was on the order of $\mathbf{1_{SbF_6}} > \mathbf{1_{BF_4}} > \mathbf{1_{PF_6}} > \mathbf{1_{AsF_6}}$. From the ^{1}H NMR and ab initio calculation, it might be suggested that this order was the result of the acidity of the fluorenyl methine proton and the nucleophilicity of the counteranion. It has become possible to control the rates of initiation and propagation by selecting the counteranion. The present work may contribute as a basis for designing novel thermally latent initiators possessing precisely controlled activity.

Experimental Section

Measurements. The X-ray crystallographic data for $\mathbf{1_{PF_6}}$ and $\mathbf{1_{BF_4}}$ were collected on a Rigaku AFC5R diffractometer with graphite monochromated Mo–Kα radiation ($\lambda = 0.710\,69$ Å) and a 12 kW roating anode generator. The data were collected at a temperature of 23 ± 1 °C using the ω–2θ scan techniqe to a maximum 2θ value of 55.0°. The structure was solved by direct methods[13] and expanded using Fourier techniques.[14] Some nonhydrogen atoms were refined anisotropically, while the rest were refined isotropically. NMR spectra (^{1}H, ^{13}C, and ^{31}P) were recorded with JEOL JNM-EX-90 and JNM-EX-400 spectrometers using tetramethylsilane as an internal standard in acetone-d_6. In ^{31}P NMR spectroscopy, 85% H_3PO_4 was used as an external standerd. IR spectra were measured with a JEOL JIR-5300 spectrophotometer. Molecular weights (M_n and M_w: number- and weight-average molecular weights) and polydispersity ratios (M_w/M_n) were estimated by gel permeation chromatography on a Tosoh HPLC HLC-8020 system, equipped with three consecutive polystyrene gel columns (TSKgels G5000HXL, G4000HXL, G2500HXL), using LiBr solution in DMF (5.8 mM) as an eluent with a flow rate of 1.0 mL/min by polystyrene calibration, and refractive index and ultraviolet detectors. Elemental analyses were carried out with a Yanaco type MT-5 CHN and SX-Elements microanalyzer YS-10.

Synthesis of Fluorenyltriphenylphosphonium Hexafluoroantimonate ($\mathbf{1_{SbF_6}}$). Fluorenyltriphenylphosphonium bromide was synthesized by the reaction of 9-bromofluorene and triphenylphosphine according to the reported method.[7] To a solution of $KSbF_6$ (6.50 g, 23.64 mmol) in H_2O (50 mL) was

added a solution of fluorenyltriphenylphosphonium bromide (4.00 g, 7.88 mmol) in methanol (500 mL) at room temperature. After the mixture was stirred at room temperature for 0.5 h, a precipitate was collected by filtration and washed with methanol and ether. The precipitate was recrystallized from a solution of ethanol−acetonitrile (22:1, volume ratio) and dried under vacuum. Yield 68%, mp 266.0−267.0 °C. ^{1}H NMR (acetone-d_6,0.02 M): δ = 7.95−7.24 (m, 23H, Ph, Flu), 7.02 (d, J = 15.6 Hz, 1H, CH) ppm. ^{13}C NMR (acetone-d_6,0.02 M): δ = 143.42, 135.94, 134.58, 131.00, 130.67, 128.71, 127.49, 121.87, 118.85, 118.01, 41.83 ppm. IR (KBr): 2924, 1460, 723, 688, 661, 536 cm^{-1}. Anal. Calcd for $C_{31}H_{24}PSbF_6$: H, 3.65; C, 56.14; F, 17.19. Found: H, 3.89; C, 56.20; F, 17.30.

Synthesis of Fluorenyltriphenylphosphonium Hexafluoroarsenate ($\mathbf{1}_{\mathbf{AsF_6}}$). The title compound was synthesized by the reaction of fluorenyltriphenylphosphonium bromide with $NaAsF_6$ in a similar manner with $\mathbf{1}_{\mathbf{SbF_6}}$. Yield 42%, mp 292.0−293.0 °C. ^{1}H NMR (acetone-d_6,0.02 M): δ = 7.94−7.24 (m, 23H, Ph, Flu), 7.01 (d, J = 16.0 Hz, 1H, CH) ppm. ^{13}C NMR (acetone-d_6,0.02 M): δ = 143.42, 135.92, 134.58, 130.72, 130.69, 128.73, 127.47, 121.89, 118.85, 118.01, 41.79 ppm. IR (KBr): 2884, 1441, 799, 754, 534 cm^{-1}. Anal. Calcd for $C_{31}H_{24}PAsF_6$: H, 3.92; C, 60.40; F, 18.49. Found: H, 3.90; C, 60.50; F, 18.49.

Synthesis of Fluorenyltriphenylphosphonium Hexafluorophosphate ($\mathbf{1}_{\mathbf{PF_6}}$). The title compound was synthesized by the reaction of fluorenyltriphenylphosphonium bromide with KPF_6 in a similar manner with $\mathbf{1}_{\mathbf{SbF_6}}$. Yield 45%, mp 289.0−291.0 °C. ^{1}H NMR (acetone-d_6,0.02 M): δ = 7.94−7.24 (m, 23H, Ph, Flu), 7.00 (d, J = 16.0 Hz, 1H, CH) ppm. ^{13}C NMR (acetone-d_6,0.02 M): δ = 143.42, 135.92, 134.58, 131.02, 130.69, 128.75, 127.47, 121.89, 118.85, 118.01, 41.81 ppm. IR (KBr): 2909, 1439, 839, 743, 721, 687 cm^{-1}. Anal. Calcd for $C_{31}H_{24}P_2F_6$: H, 4.23; C, 65.04; F,19.91. Found: H, 4.51; C, 65.29; F, 19.67.

Synthesis of Fluorenyltriphenylphosphonium Tetrafluoroborate ($\mathbf{1}_{\mathbf{BF_4}}$). The title compound was synthesized by the reaction of fluorenyltriphenylphosphonium bromide with KBF_4 in a similar manner with $\mathbf{1}_{\mathbf{SbF_6}}$. Yield 56%, mp 294.0−297.0 °C. ^{1}H NMR (acetone-d_6,0.02 M): δ = 7.95−7.24 (m, 23H, Ph, Flu), 7.05 (d, J = 16.0 Hz, 1H, CH) ppm. ^{13}C NMR (acetone-d_6,0.02 M): δ = 143.42, 135.97, 134.60, 131.00, 130.67, 128.71, 127.50, 121.87, 118.89, 118.03, 41.79 ppm. IR (KBr): 2913, 1439, 1065, 743, 720, 687 cm^{-1}. Anal. Calcd for $C_{31}H_{24}PBF_4$: H, 4.70; C, 72.40; F, 14.78. Found: H, 4.59; C, 72.32; F, 14.94.

Polymerization of GPE. Typical Procedure. GPE (333 mg, 2.21 mmol) and an initiator ($\mathbf{1}_{\mathbf{SbF_6}}$, 14.69 mg, 0.02 mmol; $\mathbf{1}_{\mathbf{AsF_6}}$, 13.70 mg, 0.02 mmol; $\mathbf{1}_{\mathbf{PF_6}}$, 12.70 mg, 0.02 mmol; or $\mathbf{1}_{\mathbf{BF_4}}$, 11.40 mg, 0.02 mmol) were placed into a polymerization ampule containing a small magnetic stirrer. The ampule was cooled, evacuated, and sealed off. The ampule was heated at a desired temperature. After heating for a set time, the ampule was cooled immediately with liquid nitrogen. After warming to room temperature, the conversion of GPE was estimated by ^{1}H NMR of the crude polymerization mixture. The reaction mixture was dissolved in dichloromethane (1 mL), and the solution was poured into methanol (100 mL) to precipitate a polymer. After the methanol was removed by decantation, the isolated polymer was dried at room temperature under vacuum.

Molecular Orbital Calculations. All computations were done on a Silicon Graphics Indigo 2 with use of Biosym/MSI DMol 950, DNP basis. All calculations were done with full optimization of all geometrical variables (bond lengths, bond angles, and dihedral angles).

References and Notes

(1) (a) Morio, K.; Murase, H.; Tsuchiya, H.; Endo, T. *J. Appl. Polym. Sci.* **1986**, *23*, 5727. (b) Uno, H.; Takata, T.; Endo, T. *Chem. Lett.* **1988**, 935. (c) Endo, T.; Kikkawa, A.; Uno, H.; Sato, H.; Hiza, M.; Takata, T. *J. Polym. Sci., Polym. Lett. Ed.* **1989**, *27*, 73. (d) Hamazu, F.; Akashi, S.; Koizumi, T.; Takata, T.; Endo, T. *J. Polym. Sci., Polym. Chem. Ed.* **1991**, *29*, 1675. (e) Kikkawa, A.; Takata, T.; Endo, T. *J. Polym. Sci., Polym. Chem. Ed.* **1991**, *29*, 1089. (f) Hamazu, F.; Akashi, S.; Koizumi, T.; Takata, T.; Endo, T. *Makromol. Chem., Rapid Commun.* **1992**, *13*, 203.

(2) (a) Lee, S.-B.; Takata, T.; Endo, T. *Macromolecules* **1990**, *23*, 431. (b) Lee, S.-B.; Takata, T.; Endo, T. *Macromolecules* **1991**, *24*, 2689. (c) Nakano, S.; Endo, T. *J. Polym. Sci., Part A: Polym. Chem.* **1996**, *34*, 475.

(3) (a) Nakano, S.; Endo, T. *Prog. Org. Coatings* **1993**, *22*, 287. (b) Nakano, S.; Endo, T. *J. Polym. Sci., Part A: Polym. Chem.* **1995**, *33*, 505. (c) Nakano, S.; Endo, T. *Prog. Org. Coatings* **1996**, *28*, 143.

(4) (a) Takuma, K.; Takata, T.; Endo, T. *Macromolecules* **1993**, *26*, 862. (b) Takuma, K.; Takata, T.; Endo, T. *Makromol. Chem., Rapid Commun.* **1993**, *14*, 203. (c) Takuma, K.; Takata, T.; Endo, T. *J. Photopolym. Sci. Technol.* **1993**, *6* (1), 67. (d) Toneri, T.; Sanda, F.; Endo, T. *J. Polym. Sci., Part A: Polym. Chem.* **1998**, *36*, 1957.

(5) (a) Hudson, R. F. *Chem. Br.* **1971**, *7*, 287. (b) Ramirez, F.; Levy, S. *J. Am. Chem. Soc.* **1957**, *79*, 67.

(6) Eastmond, G. C., Ledwith, A., Russo, S., Sigwalt, P., Eds. *Comprehensive Polymer Science*: Pergamon Press: Oxford, 1989; Vol. 6, p 711.

(7) Pinck, L. A.; Hilbert, G. E. *J. Am. Chem. Soc.* **1947**, *69*, 723.

(8) X-ray data of $\mathbf{1}_{\mathbf{PF_6}}$: triclinic, $P\bar{1}$(no. 2), a = 11.282(5) Å, b = 12.57(1) Å, c = 10.791(6) Å, α = 107.08(6)°, β = 108.94(4)°, γ = 92.18(6)°, V = 1368(1) Å^3, Z = 2, D_{calc} = 1.389 g cm^{-3}, F(000) = 588, μ(Mo−Kα) = 2.19 cm^{-1} for monochromated Mo−Kα radiation (λ = 0.710 69 Å). The structure was solved by the direct method and refined by full matrix least-squares calculations. $R(R_w)$ = 0.060 (0.063) for 1702 reflections with $I > 3\sigma(I)$ among 6289 unique reflections.

(9) X-ray data of $\mathbf{1}_{\mathbf{BF_4}}$: triclinic, $P\bar{1}$(no. 2), a = 10.789(5) Å, b = 12.59(1) Å, c = 10.448(6) Å, α = 107.06(5)°, β = 108.04(4)°, γ = 93.25(7)°, V = 1273(1) Å^3, Z = 2, D_{calc} = 1.341 g cm^{-3}, F(000) = 532, μ(Mo−Kα) = 3.12 cm^{-1} for monochromated Mo−Kα radiation (λ = 0.710 69 Å). The structure was solved by the direct method and refined by full matrix least-squares calculations. $R(R_w)$ = 0.078 (0.078) for 2618 reflections with $I > 3\sigma(I)$ among 4564 unique reflections.

(10) This result may be explained by the interaction between the counteranion and the propagation species, because the initiator $\mathbf{1}_{\mathbf{BF_4}}$ has a counteranion with the largest nucleophilicity.

(11) δ values of fluorenyl methine carbon of $\mathbf{1}_{\mathbf{BF_4}}$, $\mathbf{1}_{\mathbf{SbF_6}}$, $\mathbf{1}_{\mathbf{AsF_6}}$, and $\mathbf{1}_{\mathbf{PF_6}}$ in the ^{13}C NMR spectra were 41.79, 41.81, 41.79, and 41.81 ppm in acetone-d_6 (0.02 M), respectively.

(12) δ values of phosphine of $\mathbf{1}_{\mathbf{BF_4}}$, $\mathbf{1}_{\mathbf{SbF_6}}$, $\mathbf{1}_{\mathbf{AsF_6}}$, and $\mathbf{1}_{\mathbf{PF_6}}$ in the ^{31}P NMR spectra were 30.84, 30.75, 30.75, and 30.76 ppm in acetone-d_6 (0.02 M), respectively.

(13) Sheldrick, G. M., Kruger, C., Goddard, R., Eds. *Crystallographic Computing*: Oxford University Press: New York, 1985; Vol. 3, p 175.

(14) Beurskens, P. T.; Admiraal, G.; Beurskens, G.; Bosman, W. P.; Garcia-Granda, S.; Gould, R. O.; Smits, J. M. M.; Smykalla, C. The DIRDIF program system, Technical Report of the Crystallography Laboratory, University of Nijmegen, The Netherlands, 1992.

MA981275Q