

Hydrazinium Salts as Thermally Latent Initiators in the Polymerization of Glycidyl Phenyl Ether

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ABSTRACT: Novel hydrazinium salts, *N,N*-dimethyl *N*-benzyl *N'*-benzyl *N'*-benzoyl hydrazinium hexafluoroantimonate (**2**) and *N,N*-dimethyl *N*-benzyl *N'*-(2-propyl) *N'*-benzoyl hydrazinium hexafluoroantimonate (**3**) were synthesized from hydrazinium salt (**1**) with the corresponding alcohol. Their initiator activities were examined in the polymerization of glycidyl phenyl ether (GPE). The polymerization of GPE did not proceed with **2** and **3** below 60 and 100°C but proceeded rapidly above those temperatures, re-

spectively. It was found that **1–3** served as thermally latent initiators in the polymerization of GPE. The initiating species and terminating species were identified as the proton or alkyl cation and aminimide, respectively. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 95: 1439–1442, 2005

Key words: thermogravimetric analysis (TGA); initiators; cationic polymerization

INTRODUCTION

Latent initiators show no activity under normal conditions but form active species to initiate polymerization by certain external stimuli such as heat and photoirradiation. Crivello et al., Yagci et al., and Endo et al. have developed various onium salts as latent thermal and photoinitiators (i.e., diaryl iodonium and triaryl sulfonium salts,^{1,2} sulfonium,^{3,4} pyridinium,^{5–10} and phosphonium salts¹¹). One-component systems, which are very important in industrial fields, can be achieved by the use of latent initiators. Some latent initiators are now commercially available in various fields such as paints, inks, adhesives, epoxy molding compounds, and photoresists using thermosetting materials such as epoxy resin and multifunctional vinyl ethers.¹² Therefore, it is important to design more promising latent initiators as commercial products. We recently developed hydrazinium salts as latent thermal initiators in the polymerization of glycidyl phenyl ether (GPE).^{13,14} The initiator activity increased by the electron-withdrawing substituents on the hydrazinium salts. Proton was expected as the possible initiating species, but no clear evidence was established. We report the hydrazinium salts with alkyl

substitutes on proton position to elucidate the initiating species of hydrazinium salt acting as thermally latent initiators in the polymerization of GPE.

EXPERIMENTAL

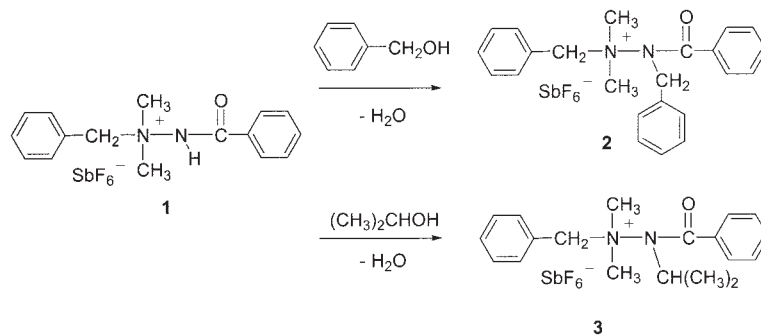
Materials

Commercially available extra-pure benzyl bromide (98%; Aldrich, Milwaukee, WI), 1,1-dimethylhydrazine (97%; TCI, Tokyo, Japan), benzoyl chloride (99%; Aldrich), and sodium hexafluoroantimonate (Aldrich) were used as received without further purification. Glycidylphenylether (GPE) (99%; Aldrich) was dried and distilled over calcium hydride before use.

Measurements

¹H-NMR spectra were recorded with a Bruker ARX-300 spectrometer, using tetramethylsilane (TMS) as an internal standard in acetone-*d*₆. IR spectra were measured with a Jasco FTIR-3 spectrophotometer. Melting points (m.p.) were measured on 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 R-401 ALC/GPC, using THF as an eluent with a flow rate of 1.0 mL/min by polystyrene calibration, and refractive

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Scheme 1

index and ultraviolet detectors. Thermal gravimetry analysis (TGA model 2950) was performed with a 2910 Modulated DSC (TA Instruments) by using a heating rate of 10°C/min in the temperature range from 25 to 500 °C. Elemental analyses were carried out with a Perkin–Elmer 240C CHN.

Synthesis of *N,N*-dimethyl *N*-benzyl *N'*-benzyl hydrazinium hexafluoroantimonate **1**

Compound **1** was prepared according to the previously reported method.^{13,14}

Synthesis of *N,N*-dimethyl *N*-benzyl *N'*-benzyl *N'*-benzyl hydrazinium hexafluoroantimonate **2**

To a solution of **1** (2.2 g, 4.5 mmol) in benzene (30 mL) was added benzyl alcohol (9.66 g, 89.4 mmol). The resulting solution was stirred at 55°C for 4 h. After the formation of water, the solution was concentrated by evaporation. It was crystallized from benzyl alcohol to give 2.1 g (3.6 mmol, 80%) of a white crystal (m.p. 80.1–82.9°C).

IR (KBr): 3519, 1676, 1457, 1277, 1007, 659 cm⁻¹. ¹H-NMR (Acetone-*d*₆): δ 7.88–7.24 (m, 10H, 2(—C₆H₅)), 5.49 (s, 2H, —CH₂—), 4.62 (s, 2H, —CH₂), 4.01 (s, 6H, 2(—CH₃)). C₂₃H₂₅N₂OSbF₆: Calcd. C, 47.53; H, 4.34; N, 4.82. Found: C, 48.17; H, 4.84; N, 4.42.

Synthesis of *N,N*-dimethyl *N*-benzyl *N'*-(2-propyl) *N'*-benzyl hydrazinium hexafluoroantimonate **3**

To **1** (1.9 g, 3.9 mmol) was added isopropyl alcohol (10 ml). The resulting solution was stirred at room temperature for 2 h. The solution was concentrated by evaporation. It was crystallized from isopropyl alcohol to give 1.8 g (3.4 mmol, 87%) of a white crystal (m.p. 133.5–135.0°C).

IR (KBr): 3518, 1670, 1457, 1276, 939, 659 cm⁻¹. ¹H-NMR (Acetone-*d*₆): δ 7.88–7.27 (m, 10H, 2(—C₆H₅)), 5.48 (s, 2H, —CH₂—), 4.01 (s, 2H, —CH₂), 3.85 (m, 1H, —CH—), 1.12 (s, 6H, 2(—CH₃)).

C₁₉H₂₅N₂OSbF₆: Calcd. C, 42.78; H, 4.72; N, 5.26. Found: C, 42.46; H, 4.62; N, 5.20.

Polymerization

The typical procedure was as follows: initiator **1** (29.3 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 by 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 washed with methanol. Then it was dried *in vacuo*. The monomer conversion was determined by ¹H-NMR spectroscopy before precipitation with methanol, and the molecular weight of the polymer was determined by GPC. The obtained polymer was identified to be poly(GPE) by ¹H-NMR and IR spectra.

RESULTS AND DISCUSSION

Initiator synthesis

The hydrazinium salt **1** was prepared according to the previously reported method.^{13,14} Salts **2** and **3** were synthesized by the reaction of hydrazinium salt and the corresponding alcohol (Scheme 1). The IR absorption signals assignable to hexafluoroantimonate (SbF₆), the corresponding counter anion of hydrazinium salts, appeared around at 660 cm⁻¹. The structures of **2** and **3** were confirmed by ¹H-NMR and element analysis.

Polymerization of GPE with hydrazinium salts

As reported previously, hydrazinium salts with various substituents served as thermally latent initiators

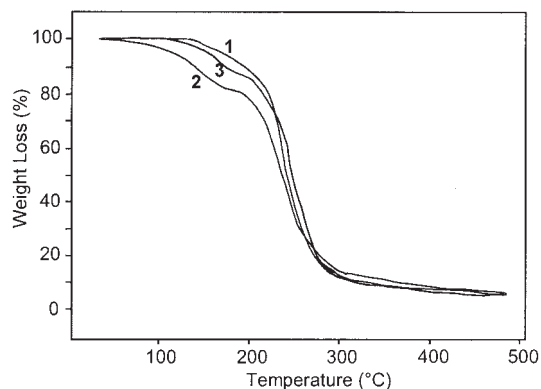


Figure 1 TGA curves of hydrazinium salts (1–3).

for the cationic polymerization of GPE. Initiation may occur by protons formed by decomposition of hydrazinium salts. In this work, hydrazinium salts with benzyl and isopropyl group on proton position was synthesized to confirm the proton as an initiating species. First, the thermal decomposition of 1–3 was monitored by TGA thermograms (Fig. 1). TGA curve shows onset temperatures of thermal dissociation at ≈ 90 and 130°C for 2, 1, and 3, respectively. Moreover, 1 showed one-step decomposition behavior, whereas 2 and 3 showed two-step decomposition, implying the thermal decomposition of benzyl and isopropyl group, along with aminimide.

Polymerization of GPE was carried out with the hydrazinium salts 1–3 (3 mol %) as initiator at 60 – 180°C for 2 h (Scheme 2). The polymerization proceeded homogeneously throughout the reaction, because 1–3 were completely soluble in GPE at ambient temperature. Figure 2 shows the temperature–conversion relationships in the polymerization. The polymerization of GPE did not proceed with 2, 1, and 3 below

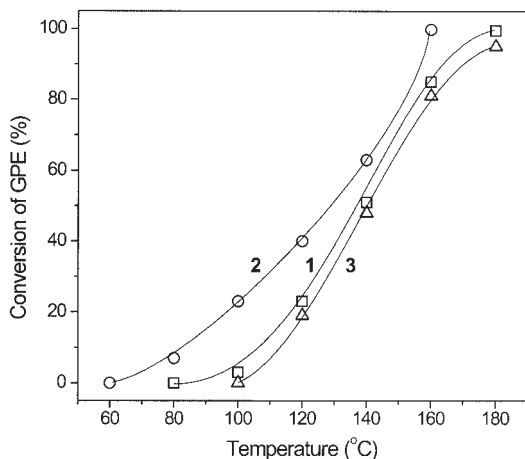
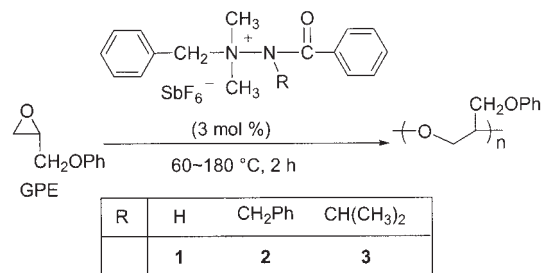


Figure 2 Temperature–conversion relationships in the polymerization of GPE with hydrazinium salts 1–3 (3 mol %) for 2 h.



Scheme 2

60 , 80 , and 100°C , respectively, but proceeded rapidly above those temperatures. The activity order of the hydrazinium salts was $2 > 1 > 3$. The hydrazinium salts 2 and 3 served as latent thermal initiators in the polymerization of GPE. The activity of initiators depends on substitutes in proton position of hydrazinium salts, implying proton or alkyl group as initiating species. The conversion increased as the temperature increased, but the obtained polymer showed the molecular weights of 700 – 3000 , probably due to some side reactions such as chain transfer and formation of cyclic oligomers.

The polymer was obtained by precipitation with methanol to remove noninitiated hydrazinium salts in the polymerization mixture, because they are completely soluble in methanol. Figure 3 shows IR spectrum of the polymer precipitated with methanol after the polymerization of GPE with 2 at 140°C . Signals assignable to the hydrazinium moiety of the terminating polymer end were observed at 1612 and 660 cm^{-1} . Thus, it was confirmed that the end group of the GPE polymer is a hydrazinium salt group (i.e., the terminating species is an aminimide). The reaction of aminimide with benzyl bromide gave a hydrazinium salt 2,

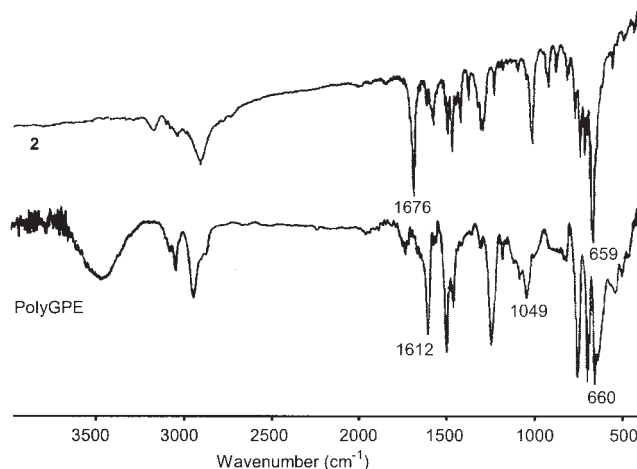
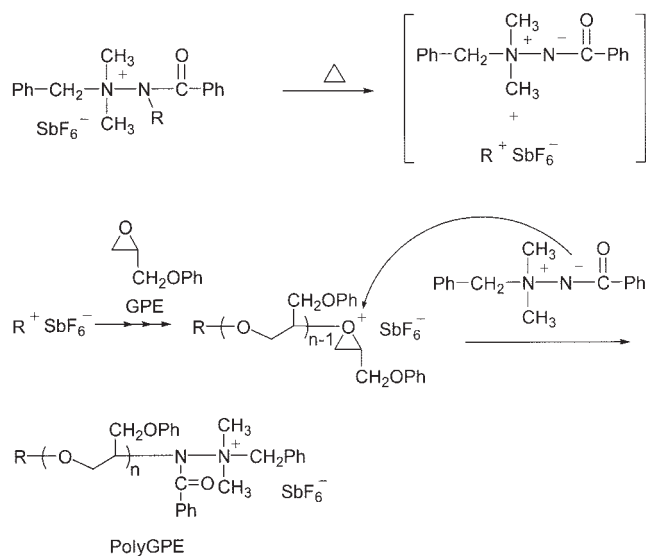


Figure 3 IR spectra of hydrazinium salt 2 and the poly(GPE) precipitated with methanol after the polymerization of GPE with 2 (3 mol %) at 140°C for 2 h.



indicating that aminimide, which formed by the thermal decomposition of the hydrazinium salts, might terminate the cationic polymerization of GPE. [Aminimide was synthesized by the titration of *N,N*-dimethyl *N*-benzyl *N'*-benzoyl bromide using a solution of 0.1N NaOH. $^1\text{H-NMR}$ (CDCl_3): δ 7.88–7.24 (m, 10H, 2($-\text{C}_6\text{H}_5$)), 5.49 (s, 2H, $-\text{CH}_2-$), 4.62 (s, 2H, $-\text{CH}_2$), 4.01 (s, 6H, 2($-\text{CH}_3$)). $\text{C}_{16}\text{H}_{18}\text{N}_2\text{O}$: Calcd. C, 75.56; H, 7.13; N, 11.01. Found: C, 75.09; H, 7.45; N, 11.32. The reaction refluxed with benzene for 5 h to afford the yield of around 60%.] Scheme 3 represents a plausible mechanism of the polymerization. The hydrazinium salts thermally decompose to generate cationic initiating species (H^+ or R^+) along with an aminimide. The

cationic initiating species afford the polymers. In the termination step, the polymerization is terminated by an aminimide.

CONCLUSION

In this article, we demonstrated that the hydrazinium salts **2** and **3** serve as thermally latent initiators in the polymerization of GPE. The activities of the hydrazinium salts were affected by the substituents on proton position. The initiation species of hydrazinium salts **1** was identified as proton by the introduction of alkyl group. Terminating species was an aminimide formed by the decomposition of hydrazinium salts.

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