Hydrazinium Salts as Novel Thermally Latent Brönsted Acid-Inducing Initiators

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1,2-Substituted-1,1-dimethylhydrazinium hexafluoroantimonates and their derivatives, $R^2(Me)_2N^+NHC(O)R^1\ SbF_6^-$ (**2**) served as thermally latent cationic initiators in the bulk polymerization of glycidyl phenyl ether. Their initiation temperatures were controlled at 40-140 °C by chemical modification on R^1 and R^2 of **2**. Active species of **2** were suggested to be proton.

Much interests have been focused on onium salts in the field of coating and photoresist because they induce cationic species by external stimulations such as photoirradiation or heating to cure cationically curable resins or to decompose the cured resins.

Crivello and his co-workers[1] reported those triaryl sulfonium salts and diaryl iodonium salts serve as photo-induced cationic initiators in the polymerization of epoxy resins. It has shown by Pappas et al. and Endo et al. that several sulfonium salts serve as thermally latent cationic initiator in the curing and polymerization of epoxy resins,[2] cyclic ethers,[3] and vinyl monomers.[4] We have found that N-benzyl group-containing quaternary ammonium salts and pyridinium salts serve as thermally latent cationic initiators in the cationic polymerization of cyclic ethers[5] and a vinyl monomer.[6] Benzyl cation was demonstrated to be initiating species and therefore these salts were regarded as the precursors of Lewis acids.[7] The significant features of these initiators are thermal latency and easy handling due to their less hygroscopicity than other Lewis or Brönsted acids.

Meanwhile, it is necessary to develop Brönsted acid-inducing thermally latent cationic initiators for the variety needs in fields of cationic polymerizations or of acid catalyzed organic reactions.[8] For this purpose, several hydrazinium salts (**2**) were examined for thermally latent cationic initiators in the bulk polymerization of glycidyl phenyl ether (GPE), a model compound of an epoxy resin.

In this paper, synthesis, thermal latency, and relationship between structure and activity of **2** in addition to the real initiation species, are described.

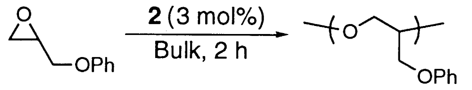
2 were synthesized by exchanging the corresponding halide ions (**1**), which were synthesized from 1,1-dimethylhydrazine according to the reported methods,[9] with hexafluoroantimonate anion,[10] (Eq. 1).

$$(CH_3)_2NNH_2 \xrightarrow[\text{i), iii) in benzene} \quad \text{ii) in } H_2O]{\text{i) } R^1COCl \quad \text{ii) aq. NaOH (- HCl)} \quad \text{iii) } R^2X} R^2(CH_3)_2N^+NHCOR^1\ X^- \quad \mathbf{1}\ \text{(X: Cl, Br, I)}$$

$$\mathbf{1} \xrightarrow[\text{in } H_2O]{NaSbF_6} \underset{\mathbf{2}}{R^2(CH_3)_2N^+NHCOR^1\ SbF_6^-} \qquad (1)$$

			Yield
2a	$R^1=CH_3$,	$R^2=C_6H_5CH_2$	64%
2b	$R^1=C_6H_5$,	$R^2=C_6H_5CH_2$	90%
2c	$R^1=p\text{-}NO_2\text{-}C_6H_4$,	$R^2=C_6H_5CH_2$	92%
2d	$R^1=p\text{-}NO_2\text{-}C_6H_4$,	$R^2=p\text{-}CH_3O\text{-}C_6H_4CH_2$	80%
2e	$R^1=C_6H_5$,	$R^2=CH_3$	55%

Polymerization of GPE with 3 mol% of **2** was conducted in an ampule tube at an elevated temperature. **2** were slightly soluble in GPE at room temperature, however, all of **2** were soluble at elevated polymerization temperatures. Thus, the polymerization proceeded homogeneously. The conversion was determined by ^1H NMR and the structure of the polymer was confirmed by FT-IR and ^1H NMR to have well-known polyether structure, (Eq. 2).



(2)

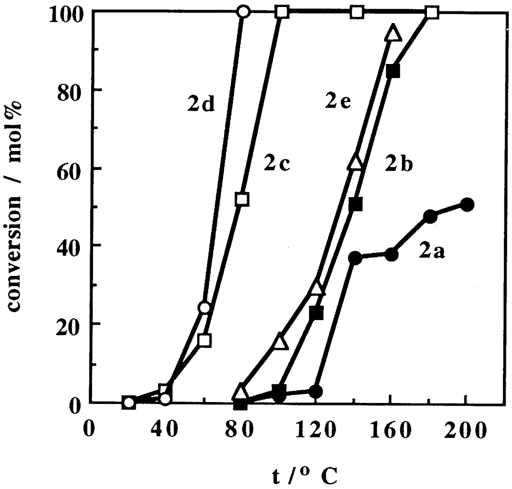


Figure 1. Thermal latency and relationship between structure and activity of hydrazinium salts (**2**, 3 mol%) in the bulk polymerization of GPE for 2 h.

Thermal latency and activity were evaluated from temperature-conversion curves of the cationic polymerization of GPE with 3 mol% of **2**. As shown in Figure 1, **2a**-**e** did not initiate the polymerization below 120 °C, 100 °C, 40 °C, 40 °C, and 80 °C, whereas the polymerization rapidly proceeded above

Table 1. Bulk polymerization of GPE with 3 mol % of **2** for 2 h

In.	2a			2b			2c			2d			2e		
temp (°C)	conv (%)	$\overline{Mn}$	$\overline{Mw}/\overline{Mn}$	conv (%)	$\overline{Mn}$	$\overline{Mw}/\overline{Mn}$	conv (%)	$\overline{Mn}$	$\overline{Mw}/\overline{Mn}$	conv (%)	$\overline{Mn}$	$\overline{Mw}/\overline{Mn}$	conv (%)	$\overline{Mn}$	$\overline{Mw}/\overline{Mn}$
40							3	650	1.30	1	-	-			
60							16	900	2.35	24	700	1.57			
80							52	800	1.79	100	800	3.12	3	-	-
100	2	-	-	3	-	-	100	800	2.01				16	1700	1.56
120	3	-	-	23	-	-							30	1500	1.61
140	37	2000	1.70	51	800	1.73	100	-	-				62	1500	1.87
160	38	1100	2.01	85	700	1.74							95	1500	2.00
180	48	1200	2.10	100	1400	1.50	100	-	-						
200	51	1100	1.86												

140 °C, 120 °C, 60 °C, 60 °C, and 100 °C, respectively. These results indicated that these were thermally latent initiators.

The order of activity was evidently **2d** > **2c** >> **2e** > **2b** > **2a** as shown in Figure 1. The enhancements of the activities of **2d**, **2c**, **2e**, and **2b** compared with that of **2a** were roughly estimated about 512, 256, 8, and 4 times, respectively judging from the fact that a reaction rate increases 2 times as increasing 10 °C of reaction temperature. That is, the temperature differences of **2d**, **2c**, **2e**, and **2b** from **2a** at the same conversions of GPE were roughly estimated 90 °C, 80 °C, 30 °C, and 20 °C, respectively. Inspection of Figure 1, activity of **2** tended to be largely increased by substituting R^1 with electron-withdrawing groups (**2c**-**2b** and **2b**-**2a**) and slight changes were detected by substituting R^2 (**2d**-**2c** and **2e**-**2b**). These enhancements of activity seemed to be reverse-proportional to the basicity of the corresponding aminimides (**3**) which are believed to be liberated by heating **2**, (Eq. 3).

Conversion, number-average molecular weight ($\overline{Mn}$), and dispersity ($\overline{Mw}/\overline{Mn}$, $\overline{Mw}$: weight-average molecular weight) of polymerization mixtures before precipitation were summarized in Table 1. As shown in Table 1, conversion tended to be increased as increasing polymerization temperature, however, $\overline{Mn}$ and $\overline{Mw}/\overline{Mn}$ were independent of polymerization temperature or conversion. $\overline{Mn}$s were ranged from 650 to 2000.

In order to predict the initiating species of **2**, the corresponding hydrazium salts (**1**) were titrated with 0.1 N sodium hydroxide aqueous solution. Aminimides (**3**) were obtained almost quantitatively and all of them did not initiated the polymerization of GPE up to 140 °C. These results suggested that **2** are not anionic initiators but cationic initiators and the initiating species are proton.

$$\mathbf{1} \xrightarrow[\text{OH}^-]{\text{- HX}} \underset{\mathbf{3}}{R^2(CH_3)_2N^+N^-COR^1} \qquad (3)$$

			Yield
3a	R^1=CH_3,	R^2=$C_6H_5CH_2$	90%
3b	R^1=C_6H_5,	R^2=$C_6H_5CH_2$	79%
3c	R^1=p-NO_2-C_6H_4,	R^2=$C_6H_5CH_2$	76%
3d	R^1=p-NO_2-C_6H_4,	R^2=p-CH_3O-$C_6H_4CH_2$	76%
3e	R^1=C_6H_5,	R^2=CH_3	82%

Thus, we found out a new class of cationic initiators which induce Brönsted acid by heating. Activity of these salts can be easily controlled by chemical modification of R^1 and R^2 of **2**. Moreover, these are easy to handle due to their stability against humidity and alcoholic solvents. The detailed studies for the whole mechanism and for the activity control of the hydrazinium salts are in progress and will be described elsewhere in near future.

References and Notes

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10 Structures of **2** were confirmed by ^{1}H NMR, FT-IR, and EA to have hydrazinium salts structures.