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Communications

tert-Amine Group-Containing *N*-Benzyl Quaternary Ammonium Salts as Advanced Thermally Latent Cationic Initiators

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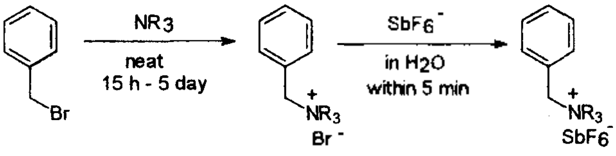
Many interests have been focused on onium salts such as sulfonium and iodonium salts which induce cationic species by external stimulation such as photoirradiation or heating in the field of coating because initiation step of cationic polymerization could be controlled.[1-15]

Endo *et al.* and Lee *et al.* have reported that *N*-benzyl group-containing quaternary ammonium salts **1** serve as thermally latent cationic initiators in the bulk polymerization of cyclic ethers[16-20] and a vinyl monomer.[21,22] Benzyl cation was found to be an initiating species and the eliminated *tert*-amine moieties to act as terminating species in the initiation and propagation step of the cationic polymerization of glycidyl phenyl ether (GPE)[20] and styrene.[22]

Meanwhile, it is necessary to control activity, thermal latency and/or molecular weight for variety needs in fields of cationic polymerizations. For example, an active initiator can lower the initiation temperature and a highly latent initiator can enhance the pot-life and reduce the polymerization time of a monomer. Especially, pyridine-terminated polystyrene having lower molecular weight, a polymeric initiator, was needed in our recent work for the synthesis of polystrene-block-polyether.[22] For this purpose, several *tert*-amine group-containing *N*-benzyl quaternary ammonium salts **2** were examined in the bulk polymerization of GPE, a model compound of an epoxy resin.

In this paper, synthesis, activity, and thermal latency of **2** in comparison with **1** are to be described in the bulk polymerization of GPE.

1 and **2** were synthesized according to the similar method reported (Eq. 1).[17-22]



1 or **2** (1)

The Menschutkin reaction proceeded smoothly according to their nucleophilicity to give the corresponding quaternary ammonium bromides as white precipitates due to their less solubility in benzyl bromide. Yields were increased with increasing reaction time and negligible byproducts were detected by NMR. The structures of these initiators were confirmed by IR, ^{1}H NMR, and elemental analysis to have the corresponding *t*-amine group-containing mono-*N*-benzyl quaternary ammonium salts (Table 1).

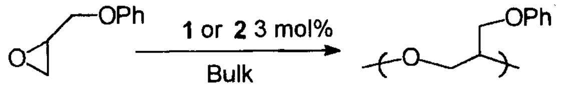
The bulk polymerization of GPE with 3 mol% of **1** or **2** proceeded in homogeneous solution since all the initiators were soluble in the monomer at temperatures above 40 °C. The polymer was precipitated from methanol after determination of the conversion of GPE by ^{1}H NMR. Both insoluble and soluble polymers were confirmed by ^{1}H NMR, IR to have the well-known polyether structure (Eq. 2).

Activity (based on temperatures at 50% conversion) and thermal latency (the slope of temperature-conversion curve)

Table 1. Summary of the physical properties of **1** and **2**

Initiator	NR_3	pK_a[a]	yield (mol %)	mp (°C)	^{1}H NMR (δ_{CH_2} ppm)	IR $\nu_{Sb\text{-}F}$ (cm^{-1})	EA			
								C	H	N
1a	2-cyanopyridine	– 0.26	51	121-124	6.29	659	Calcd	36.23	2.57	6.50
							Found	36.01	2.43	6.34
1b	4-cyanopyridine	1.9	68	156-157	6.20	660	Calcd	36.23	2.57	6.50
							Found	35.95	2.50	6.55
2a	4-N,N-dimethyl-aminopyridine	8.68	54	132-133	6.10	655	Calcd	37.45	3.81	6.24
							Found	37.28	3.80	6.20
2b	4,4'-dipyridyl	4.82	75	156-158	6.10	656	Calcd	42.27	3.13	5.79
							Found	41.95	3.04	5.72
2c	pyrazine	0.6	73	143-144	6.18	662	Calcd	32.45	2.70	6.88
							Found	32.70	2.74	6.91
2d	quinoxaline	0.72	41	146-148	6.66	667	Calcd	39.39	2.74	6.13
							Found	39.69	2.84	6.16

[a] pK_a value of the corresponding protonated ammonium salt[23]



(2)

of **2** compared with **1** was evaluated from temperature-conversion curves shown in Figure 1. Conversion, yield, $\overline{Mn}$, and $\overline{Mw}/\overline{Mn}$ of the methanol-insoluble polyGPE were summarized in Table 2. All of the salts **1** and **2** except **2a**, which did not initiate the polymerization even at 220 °C for 2 h, served as thermally latent cationic initiators in the bulk polymerization of GPE since they showed initiator activity above normal condition such as room temperature.

Tert-amine group-containing *N*-benzyl quaternary ammonium salts showed very interesting results, similar and different tendencies, compared with pyridinium salts. For example, similar tendencies are as follows: As shown in Figure 1 and Table 2, the order of activity was evaluated as **1a** > **2c** ≅ **2d** > **1b** > **2b** > **2a** and was reversely proportional to the pK_a value of the corresponding *t*-amine ($-0.26 < 0.6 \cong 0.72 < 1.9 < 4.82 < 8.68$, respectively). Conversion and yield tended to increase and $\overline{Mn}$s were to decrease with increasing reaction temperature. This tendency was in good accordance with that in cases of pyridinium salts though comparing the activities of them is difficult due to their different thermal latency.

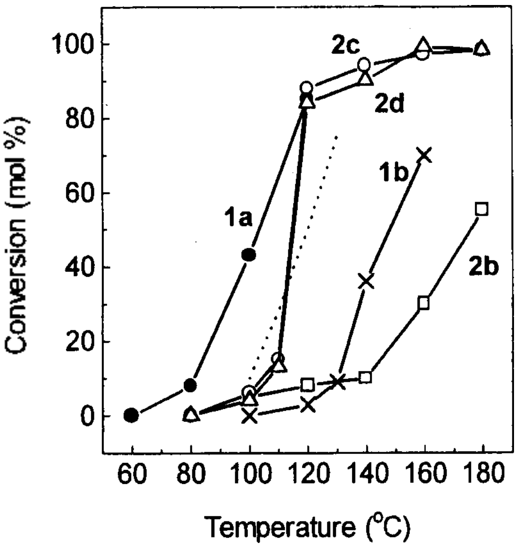


Figure 1. Temperature-conversion curves of the bulk polymerization of GPE with 3 mol % of **1** or **2** for 2h.

Different tendencies are as follows: The order of thermal latency as shown in Figure 1 was evaluated as **2c** ≅ **2d** > **1a** ≅ **1b** > **2b**. Precisely speaking, pyrazinium **2c** and qui-

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

Initiator	temperature (°C)	conversion[a] (mol %)	Yield[b] (mol %)	$\overline{Mn}$[c]	$\overline{Mw}/\overline{Mn}$[c]
1a	80	8	6	3700	1.5
	100	43	29	4600	1.6
	120	85	60	4600	2.1
1b	120	3	–	–	–
	130	9	–	–	–
	140	36	9	800	–
	160	70	35	2300	1.5
2b	100	5	0	800[d]	1.1[d]
	120	8	0	600[d]	1.3[d]
	140	10	0	800[d]	1.7[d]
	160	30	0	600[d]	1.4[d]
	180	55	0	600[d]	1.6[d]
2c	80	0	–	–	–
	100	6	–	–	–
	110	15	2	1400	1.4
	120	88	71	1900	2.4
	140	94	73	1800	3.0
	160	97	89	1700	2.4
	180	98	83	1600	2.6
2d	100	4	–	1100[d]	1.8[d]
	110	13	9	1100	1.8
	120	84	71	3100	3.3
	140	90	73	2400	3.3
	160	99	73	2200	5.7
	180	98	98	2100	3.9

[a] Determined by ^{1}H NMR. [b] Methanol-insoluble polyGPE. [c] Methanol-insoluble polyGPE estimated by GPC. [d] Methanol-soluble polyGPE.

noxalinium salts **2d** showed much enhanced thermal latency, while dipyridylium salt **2b** showed much reduced thermal latency in comparison with pyridinium salts **1**. $\overline{M}$ns of the obtained polyGPE at 160 °C in cases of **2c** and **2d** (1700 and 2200) were lower than those in case of **1b** (2300) in spite of the fact that the basicities of the corresponding pyrazine and quinoxaline moieties (pK_a=0.6 and 0.72) are lower than that of 4-cyanopyridine (pK_a=1.9).

The enhanced thermal latency, the higher slope of temperature-conversion curve of **2c** or **2d** compared with that of **1a** or **1b** seems to be attributed to the effective suppression of initiation step of the polymerization since the higher slope is caused by relatively lower conversions at 100 and 110 °C and higher conversions at 120 °C compared with those expected in cases of pyridinium salts. The expected conversions at 100, 110, and 120 °C were about 10, 35 and 50%, respectively judging from the fact that log k/k_o (k: polymerization rate constant for a initiator, k_o: polymerization rate constant for a reference initiator) is propotional to the pK_a difference[24] of the corresponding *t*-amine moiety and is reversely propotional to temperature difference.[18,22] For example, temperature differences at each conversion in case of **2c** and **1b** are expected to be about 30 °C [50 °C × (1.9-0.6)/[1.9-(− 0.26)]=30] since that in case of **1b** and **1a** is about 50 °C. Therefore the expected temperature-conversion curve of **2c** will be the dot-line shown in Figure 1.

The lower conversions than were expected at 100 and 110 °C can be explained by the rapid reverse reaction of the liberated benzyl cation and pyrazine moiety to prevent the attack of monomer (suppress the initiation) due to its bidentate structure. It seems reasonable that terminating probability of bidentate pyrazine moiety is two times higher than that of monodentate pyridine moiety if their basicities are the same. Higher conversion at 120 °C seems to be attributed to too high initiation rate and insufficient heat removal in this exothermic bulk polymerization. Therefore, the suppression effect might be negligible compared with the effect of high initiation rate. These phenomena can be compared to a super heated state (low conversions at 100 and 110 °C) and bumping (higher conversion at 120 °C).

The lower $\overline{M}$ns at 160 °C (1700 and 2200, respectively; where expected $\overline{M}$n was about 4000) in cases of **2c** and **2d** than that (2300) in case of **1a** in spite of their lower basicity of the corresponding *t*-amines (pK_a=0.6 and 0.72, respectively) seems to be attributed to the enhanced terminating power of bidentate pyrazine moiety compared with monodentate 4-cyanopyridine in the propagation step of the polymerization as described above. Slightly higher $\overline{M}$ns in case of **2d** than that in case of **2c** seems to be the retardation of termination due to the steric hindrance of quinoxaline in spite of its higher basicity. Though we can not rule out the effect of initiator concentration and of transfer reaction at high temperatures, however, they can be negligible comparing with the effect of terminating probability (the estimated decrease of $\overline{M}$n is about 2000). That is, decrease of $\overline{M}$n at higher temperatures (high initiator concentration and/or transfer reaction) is not so high (about 300) as shown in Table 2.

The reduced thermal latency in case of **2b**, seems to be attributed to the too high basicity of the corresponding 4,4'-dipyridyl (pK_a=4.82). That is, the rate of termination might be as high as that of propagation, and therefore lower $\overline{M}$n (600) could be obtained.

In conclusion, we have first tried and succeeded in control of the thermal latency and $\overline{M}$n in addition to the control of activity in the cationic polymerization of GPE by precise control of initiation and propagation step through a chemical modification of *tert*-amine moiety of *N*-benzyl group containing quaternary ammonium salts. Overall mechanistic study in pyrazinium salts and their application to block copolymer synthesis will be reported in near future.

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