Registry No. MnT4NMPyP, 123962-95-8; MnPP, 123933-64-2; H_2O, 7732-18-5.

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(*p*-Methoxybenzyl)- and (α-Methylbenzyl)-*p*-cyanopyridinium Hexafluoroantimonates: Activated Latent Thermal Catalysts

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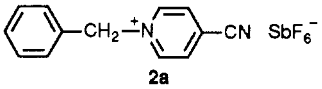
ABSTRACT: (*p*-Methoxybenzyl)- and (α-methylbenzyl)-*p*-cyanopyridinium hexafluoroantimonates (**2b**, **2c**) were synthesized by the reaction of *p*-cyanopyridine and corresponding benzyl halides followed by exchange of the counteranion with SbF_6^-. Both salts showed much higher catalytic activities than benzyl-*p*-cyanopyridinium hexafluoroantimonate (**2a**) in the cationic polymerization of glycidyl phenyl ether (**1**). The thermally latent effectiveness of these catalysts, in promoting efficient polymerization of **1** at 100–120 °C but not below 60 °C, was demonstrated.

Introduction

External stimulation-induced polymerization is of special interest in control of the initiation of polymerization. Photoinduced cationic polymerization for epoxy resins with triaryl sulfonium salts has been studied by Crivello and his co-workers.[1] It has been shown by Pappas et al. and Endo et al. that sulfonium salts can be excellent latent thermal catalysts in the curing and polymerization of epoxy resins,[2] spiro ortho carbonates,[3] bicyclo ortho esters,[4] and styrene.[5] We have extended the idea of latent catalysts to quaternary ammonium salts and recently found that quaternary ammonium salts such as benzyl-*p*-cyanopyridinium hexafluoroantimonate (**2a**) serve as thermally latent cationic catalysts in the polymerization of a cyclic ether [1-phenyl-4-ethyl-2,6,7-trioxabicyclo[2.2.2]octane][5] and a vinyl monomer (styrene)[6] as well. The merit of these salts is their chemical stability and ease of handling owing to their low hygroscopicity. Although **2a** is the most active catalyst among various quaternary ammonium salts, we have examined, so far, further activation of **2a** is required because of its rather high initiating temperature (>120 °C). Meanwhile, for the availability and the practical use of ammonium salts as latent catalysts, it is also important to synthesize a variety of quaternary ammonium salts with a variety of activities based on their molecular design.


2a

For this purpose, we have devised some chemical modifications of **2a** by introducing electron-releasing substituents onto the benzene ring and benzylic carbon. In this

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paper, synthesis of new substituted benzyl-*p*-cyanopyridinium salts and their enhanced catalytic activities are described.

Experimental Section

Materials. Commercially available extra pure grade benzyl chloride, α-methylbenzyl bromide, and *p*-methoxybenzyl chloride (Tokyo Kasei Kogyo) were used without purification. *p*-Cyanopyridine (Tokyo Kasei Kogyo) was purified by recrystallization from methanol. Solvents were distilled after removal of incorporated water by usual methods and stocked over molecular sieves (4A).

Measurements. Melting points of the catalysts synthesized were measured by a Yanaco micro melting point apparatus. FT-IR spectra were obtained with a Jasco FT/IR-3. ^{1}H NMR spectra were recorded on a JEOL PMX-60 SI spectrometer, using tetramethylsilane (TMS) as an internal standard. Molecular weight and molecular weight dispersion (MWD; $\overline{M}_w/\overline{M}_n$) were determined by gel permeation chromatography (GPC) on a Toyo Soda HPLC CCCP & 8000 system with a data processor, equipped with three polystyrene gel columns (TSK gel, G2000H, G2500H, and G3000H), using tetrahydrofuran as an eluent, a flow rate of 1.0 mL/min, polystyrene calibration, and refractive index (RI) and ultraviolet (UV) detectors.

Synthesis of Benzyl-*p*-cyanopyridinium Hexafluoroantimonate (2a).[6] A mixture of benzyl chloride (6.13 g, 48.4 mmol) and *p*-cyanopyridine (5.01 g, 48.1 mmol) in methanol (80 mL) was stirred at 45 °C for 4 days. Methanol was evaporated, and the residue was extracted with ether/water (100 mL/30 mL). $NaSbF_6$ (13.0 g, 50 mmol) was added to the aqueous layer in one portion. A white precipitate was collected and recrystallized from ethanol: yield 5.18 g (25.0%); mp 156.0–157.0 °C; IR (KBr) 1640, 1455, 760, 720, 700, 660 cm^{-1}; ^{1}H NMR (CD_3CN) δ 9.10–8.83 (d, 2 H, py-), 8.55–8.15 (br, 2 H, py-), 7.50 (s, 5 H, Ph-), 5.76 (s, 2 H, $-CH_2-$). Anal. Calcd for $C_{13}H_{11}F_6N_2Sb$: H, 2.57; C, 36.23; N, 6.50. Found: H, 2.50; C, 35.95; N, 6.55.

Synthesis of (α-Methylbenzyl)-*p*-cyanopyridinium Hexafluoroantimonate (2b). A mixture of α-methylbenzyl bromide (3.71 g, 20.1 mmol) and *p*-cyanopyridine (2.08 g, 20.0 mmol) in acetonitrile (30 mL) was stirred at room temperature for 3 days. Acetonitrile was evaporated, and the residue was extracted with ether/water (100 mL/30 mL). $NaSbF_6$ (5.20 g, 20.0 mmol) was added to the aqueous layer in one portion. A white precipitate was collected and recrystallized from methanol: yield 1.12 g (12.6%); mp 108.5–109.5 °C; IR (KBr) 1639, 1454, 767, 705, 659 cm^{-1}; ^{1}H NMR (CD_3CN) δ 9.05–8.78 (d, 2 H, py-), 8.43–8.10 (br, 2 H, py-), 7.45 (s, 5 H, Ph-), 6.33–5.87 (q, 1 H, -CH-), 2.23–1.93 (d, 3 H, CH_3-). Anal. Calcd for $C_{14}H_{13}F_6N_2Sb$: H, 2.94; C, 37.79; N, 6.29. Found: H, 2.89; C, 37.59; N, 6.12.

Synthesis of (*p*-Methoxybenzyl)-*p*-cyanopyridinium Hexafluoroantimonate (2c). A mixture of *p*-methoxybenzyl chloride (3.26 g, 20.9 mmol) and *p*-cyanopyridine (2.09 g, 20.1 mmol) in acetonitrile (30 mL) was stirred at room temperature for 4 days. Acetonitrile was evaporated, and the residue was extracted with ether/water (100 mL/30 mL). $NaSbF_6$ (5.20 g, 20.0 mmol) was added to the aqueous layer in one portion. A yellow precipitate was collected and recrystallized from ethanol: yield 1.80 g (19.4%); mp 157.5–158.5 °C; IR (KBr) 1643, 1610, 1589, 1259, 1238, 1033, 771, 714, 655 cm^{-1}; ^{1}H NMR (CD_3CN) δ 9.00–8.75 (d, 2 H, py-), 8.45–8.15 (br, 2 H, py-), 7.63–6.85 (q, 4 H, Ph-), 5.81 (s, 2 H, $-CH_2-$), 3.81 (s, 3 H, CH_3O-). Anal. Calcd for $C_{14}H_{13}F_6N_2OSb$: H, 2.84; C, 36.48; N, 6.08. Found: H, 2.84; C, 36.16; N, 5.89.

Polymerization of Glycidyl Phenyl Ether (1) with 2. General Method. A homogeneous mixture of 1 (0.30 g) and one of the initiators (2) in an ampule tube was cooled, evacuated, and sealed off. After the tube was heated in an oil bath, the reaction mixture was dissolved in methylene dichloride (1 mL) and the resulting solution was poured into methanol (50 mL) to precipitate the polymer. After the methanol layer was removed by decantation, the residual viscous polymer was collected and dried under vacuum. The methanol layer was evaporated to give the soluble polymer in methanol. Structures of the polymers were confirmed by IR and ^{1}H NMR spectra.

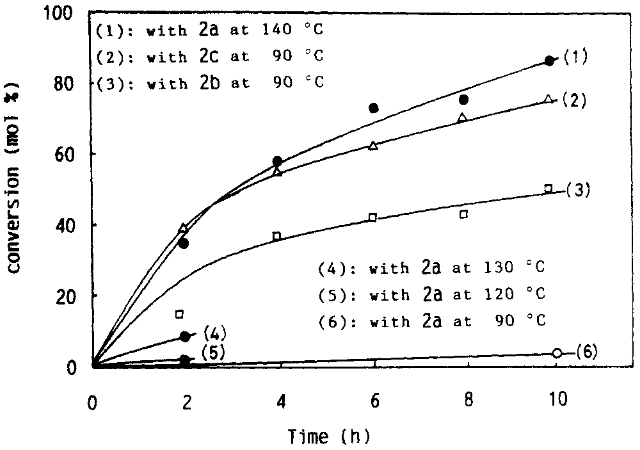


Figure 1. Time–conversion curves of the bulk polymerization of 1 with 3 mol % of **2a**–**2c**.

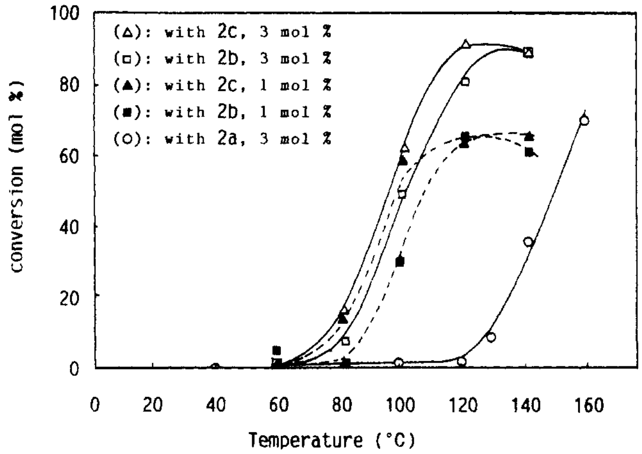
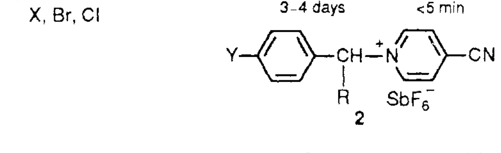


Figure 2. Effect of temperature and concentration on the polymerization of 1 with **2a**–**2c** (1 or 3 mol %) for 2 h.

Results and Discussion

Synthesis of Catalysts. Benzyl- (**2a**), (α-methylbenzyl)- (**2b**), and (*p*-methoxybenzyl)-*p*-cyanopyridinium hexafluoroantimonates (**2c**) were prepared by the reaction of *p*-cyanopyridine with an equimolar amount of the corresponding benzyl halides followed by exchange of counteranion with SbF_6^- in water (eq 1).[6]



(1)

catalyst	Y	R	mp, °C	total yield, %
2a	H	H	156.0–157.0	25.0
2b	H	Me	108.5–109.5	12.6
2c	OMe	H	157.5–158.5	19.4

The Menschutkin reaction proceeded sluggishly in each case, especially with α-methylbenzyl chloride (for **2b**), probably due to steric hinderance of the methyl group. At higher temperature (in refluxing methanol), elimination predominated over substitution, giving only trace of **2b**. Therefore, α-methylbenzyl bromide was selected, and the solvent was changed to acetonitrile in order to prevent a back-reaction caused by deposition of the prod-

Table I
Bulk Polymerization of 1 with 2a–2c (3 mol %)

	2a (at 140 °C)				2b (at 90 °C)				2c (at 90 °C)			
time, h	conv,[a] %	yield,[b] %	$\overline{M}_n$[c]	$\overline{M}_w/\overline{M}_n$[c]	conv,[a] %	yield,[b] %	$\overline{M}$[c]	$\overline{M}_w/\overline{M}_n$[c]	conv,[a] %	yield,[b] %	$\overline{M}_n$[c]	$\overline{M}_w/\overline{M}_n$[c]
2	36 2.7[d] 9.3[e]	8.9			16	3.6	5400	1.2	41	12	4100	1.3
4	57	22	2500	1.4	37	10	5100	1.2	55	25	3600	1.3
6	72	29	2300	1.4	41	9.9	5100	1.3	60	30	3300	1.5
8	74	45	2500	1.5	42	14	5100	1.2	68	30	4100	1.4
10	85 2.5[f]	52	2600	1.3	50	19	4900	1.3	73	35	4000	1.4

[a] Determined by NMR before precipitation. [b] Yields of the insoluble polymers in methanol. [c] Data for the insoluble polymers, estimated by GPC based on polystyrene standard. [d] At 120 °C. [e] At 130 °C. [f] At 90 °C.

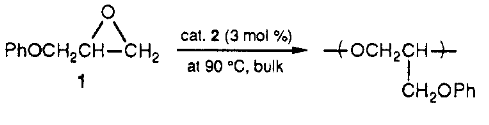
Table II
Effects of Polymerization Temperature and Concentration of Catalyst on the Bulk Polymerization of 1 with 2a–2c for 2h[a]

		2a				2b				2c[b]			
temp, °C	cat, mol %	conv, %	yield, %	$\overline{M}_n$	$\overline{M}_w/\overline{M}_n$	conv, %	yield, %	$\overline{M}_n$	$\overline{M}_w/\overline{M}_n$	conv, %	yield, %	$\overline{M}_n$	$\overline{M}_w/\overline{M}_n$
60	1									6.6	0		
	3	0				0.3				1.0	0	750[c]	
80	1					1.5				15	4.2		
	3	0.6				7.9				17		1200[d]	
100	1					32	11	5000	1.2	59	35	4000	1.4
	3	2.0				50	26	3700	1.3	62	0	1700[c]	
120	1					66	37	4900	1.5	64	34	4300	1.5
	3	2.7				80	54	3600	1.6	91	26	3800[e]	1.4
130	3	9.3											
140	1					61	25	4500	1.5	65	30	4400	1.5
	3	36	8.9	800[c]		87	46	3100	2.1	87	37	2700	1.6
160	3	70	35	2300	1.5								

[a] Yield, $\overline{M}_n$, and $\overline{M}_w/\overline{M}_n$ for the methanol-insoluble polymers. $\overline{M}_n$ and $\overline{M}_w/\overline{M}_n$ were determined by GPC based on polystyrene standard. [b] In the case of 3 mol % of **2c**, the obtained polymerization mixture was dissolved in 6 mL of methylene dichloride and then precipitated into 120 mL of methanol. [c] $\overline{M}_n$ of methanol-soluble polymer. [d] Peak top value of main peak. [e] $\overline{M}_n$ of soluble polymer was 1300.

uct as a precipitate. By these changes, **2b** was obtained in 12.6% yield, whereas with use of *p*-methoxybenzyl chloride **2c** was prepared in 19.4% yield. The structures of these catalysts were determined by IR, NMR, and elemental analyses.

Polymerization. The activity of the catalysts was evaluated in the bulk polymerization of glycidyl phenyl ether (**1**) with 3 mol % of **2a–2c**. Since the catalysts (**2a–2c**) were soluble in the monomer at temperatures above 60 °C, the polymerization system was homogeneous. All of the catalysts served as polymerization initiators to afford a polymer of **1**. The polymer was precipitated with methanol after determination of the conversion of **1** by NMR. Both insoluble and soluble polymers were confirmed by NMR and IR to have the well-known polyether structure (eq 2). The soluble part consisted of unreacted **1** and low molecular weight polymer with $\overline{M}_n$ < ca. 2000. The insoluble polymer had a $\overline{M}_n$ ranging from 2000 to 5000.



(2)

As indicated in the time–conversion curves of Figure 1, the order of catalyst activity was clearly **2c** > **2b** ≫ **2a**. At 90 °C, **2a** initiated very slow polymerization of **1** for 10 h (conversion 2.5%). Although polymerizations with **2b** and **2c** proceeded smoothly, **2c** was more active than **2b**. Polymerization with **2a** required higher temperatures than 130 °C in order to compete with **2b** or **2c**. In the detailed data shown in Table I, the yield of methanol-insoluble polymer increased with an increase in conversion, but the molecular weight of the insoluble polymer was independent of conversion or yield. In polymerization with **2a**, the $\overline{M}_n$ value for the insoluble polymer was low (2300–2600), probably due to a rapid transfer reaction, caused by the high polymerization temperature (140 °C). The difference in $\overline{M}_n$ between **2b** and **2c** can be attributed to the different concentration of initiation species formed during the polymerization. That is, the actual concentration of initiation species generated from **2b** is lower than that of **2c**.

Figure 2 shows the effects of temperature and concentration of **2** on the polymerization of **1** for 2 h in the temperature range of 60–160 °C. The relation between temperature and conversion (Figure 2 and Table II) indicates the important thermal latency of the catalysts. The fact that the rate of polymerization rapidly increased above 80 °C for both **2b** and **2c** and 130 °C for **2a**, whereas little or no polymerization proceeded below 60 °C (**2b**, **2c**) and 120 °C (**2a**), demonstrates that these catalysts are latent thermal catalysts. In accordance with the results of Figure 1, polymerizations with **2b** and **2c** proceeded much more efficiently than those with **2a**. From the difference in the polymerization temperature shown in Figure 2, it is roughly estimated that **2b** and **2c** are 20–30 times more active than **2a** in terms of conversion.

In the polymerization with **2b** or **2c** for 2 h at 120 °C, conversions reached to 80–90% with 3 mol % of catalyst and ca. 65% with 1 mol % of catalyst. However, at 140 °C, the yield, $\overline{M}_n$, or $\overline{M}_w/\overline{M}_n$ decreased, and with 3 mol % of **2a** satisfactory results were not obtained even at 140 °C (Table II). Lower conversion observed with the use of 1 mol % catalyst is clearly due to a lower concentration of initiating species, and it is confirmed by the

Macromolecules 1990, 23, 434-441

$\overline{M}_n$ values of the resulting insoluble polymers, which were higher with 1 mol % catalyst than with 3 mol % catalyst.

Considerable lowering of the initiation temperature by introduction of α-methyl (**2b**) and *p*-methoxy (**2c**) substituents seems to be attributable to the high efficiency of the initiation step of the polymerization with **2b** or **2c**. This is because both the structure of the propagating species and the rate of the polymerization (k_p) are expected to be the same in these three cases, and, therefore, the concentration of the cationic species liberated by heating **2b** or **2c** (via S_N1 or S_N2 process) should be much higher than that from **2a**. In fact, benzylic carbocations formed from **2b** and **2c** are strongly stabilized by the inductive and resonance effects of their substituents, and hence both **2b** and **2c** generate the cationic species even at a lower temperature than that for **2a**.

On the other hand, the fact that maximum conversion (ca. 65%) with 1 mol % catalyst is less than that with 3 mol % catalyst (ca. 90%) would indicate the occurrence of some termination reactions. One termination mechanism might be reaction of the propagating oxonium salts with liberated *p*-cyanopyridine to form the very stable pyridinium salt which is no longer an effective catalyst.

Thus, activation-aided modification of a benzyl group of **2a** resulted in the synthesis of **2b** and **2c** with highly enhanced catalytic activities and good thermal latency in comparison with **2a**. This catalyst activation by introduction of a cation-stabilizing group is in good accord with the results of the substituent effects observed in the polymerization of a bicyclo ortho ester with substituted benzyl sulfonium salts reported by Endo et al.[4a]

In conclusion, we have synthesized new pyridinium salts as highly activated latent thermal catalysts, (*p*-methoxybenzyl)- (**2c**) and (α-methylbenzyl)-*p*-cyanopyridinium hexafluoroantimonates (**2b**). These are stable, soluble in monomer, easy to handle, and show much higher catalytic activities than benzyl-*p*-cyanopyridinium hexafluoroantimonate (**2a**) in the cationic polymerization of glycidyl phenyl ether (**1**) as a model cationically polymerizable monomer.

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Registry No. 1 (homopolymer), 25265-27-4; 1 (SRU), 100629-24-1; **2a**, 116146-28-2; **2b**, 124156-72-5; **2c**, 123173-67-1; benzyl chloride, 100-44-7; *p*-cyanopyridine, 100-48-1; α-methylbenzyl bromide, 585-71-7; *p*-methoxybenzyl chloride, 824-94-2.

Thermal Oxidation of Blends of Polystyrene and Poly(vinyl methyl ether)

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ABSTRACT: Thermal oxidation of blends of polystyrene and poly(vinyl methyl ether) was studied at 80, 110, and 140 °C. The oxygen uptake by PS was negligible, but PVME oxidized rapidly. The induction period of oxidation of PVME was lengthened by the presence of PS in the blend. Phase separation occurred shortly before the end of the induction period, and the steady-state rate of oxidation of the blend was proportional to the PVME content. The molecular weight of PVME decreased more slowly in the blend as PS content increased. At the same time, PS also underwent chain scission. It was believed that reaction between PVME radicals and PS took place during the induction period to result in less reactive PS radicals. When low-molecular-weight polystyrene was blended with PVME, the mixtures remained homogeneous throughout the oxidation reaction. The induction periods became longer and oxidation rates slower than the values for the corresponding PS blends.

I. Introduction

Although polymer blends have become an important class of materials, our knowledge of their chemical stability is inadequate. There is scattered information in the literature about thermal degradation of heterogeneous blends[1] and thermal or photo oxidation of rubber-modified polystyrene.[2-4] But the oxidation of miscible polymer blends has received only occasional attention.[5]

In the study of oxidation of mixtures of small molecules, Russell found that the rates of oxidation were not additive.[6,7] A decrease in the rate of oxidation to below the value for either component was observed when a small amount of the more easily oxidized tetralin was added to cumene. It was concluded that tetralyperoxy radical terminated much more readily than cumylperoxy radical, and a lower rate of oxidation of the mixture resulted from the lowered steady-state concentration of peroxy radicals. The purpose of the present investigation is to study whether the oxidative rates of miscible blends obey the additivity rule. Departure from the additive rule would suggest cross-propagation or cross-termination reactions in the blend. By cross-propagation, we mean the reaction of oxy or peroxy radical A with polymer B to form

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