Quaternary Ammonium Salts as Useful Cationic Initiators. 6.† Synthesis, Activity, and Thermal Latency of *N*-Benzylpyridinium Salts and the Role of the Pyridine Moiety

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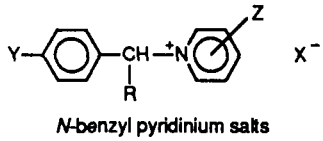
ABSTRACT: *N*-Benzyl-, *N*-(1-phenethyl)-, and *N*-(*p*-methoxybenzyl)-*o*-cyanopyridinium hexafluoroantimonate (**2a**, **2b**, and **2c**, respectively) were synthesized by the reaction of *o*-cyanopyridine (OCP) and the corresponding benzyl halide followed by exchange of the counteranion with $KSbF_6$. *N*-(*p*-Methoxybenzyl)-*m*-(methoxycarbonyl)pyridinium (**3c**), *N*-benzyl-*p*-methylpyridinium (**4a**), and *N*-benzyl-*o*-methylpyridinium hexafluoroantimonate (**5a**) were also prepared, and their initiator activities were evaluated similarly. The *o*-cyanopyridinium salts **2** showed much higher activity than the corresponding *p*-cyanopyridium salts **1** in the cationic polymerization of glycidyl phenyl ether (GPE). The activity change was attributed to the electronic and steric effect of the *o*-cyano group of pyridine. Major initiating and terminating species were found to be the *p*-methoxybenzyl cation and the pyridine moiety, respectively, by a detailed ^1H NMR study of the solution polymerization of propylene oxide (PO) with **2c** in CD_3NO_2. The pyridine moiety was suggested to interact not only with the initiator and initiating species but also with the propagating species, since the bulk and solution polymerization of GPE was strongly suppressed in the presence of extra OCP or *p*-cyanopyridine (PCP). From these results, a plausible mechanism is discussed, which involved competitive attack of monomer and liberated free pyridine group on the cationic propagating end.

Introduction

Initiators, which induce polymerization by external stimulation such as photoirradiation and heating, are extremely important in control of the initiation step of polymerization. Considerable attention has focused on several onium salts (sulfonium, iodonium, and phosphonium salts) that undergo photolysis[1] and thermolysis[2-5] to initiate radical or cationic polymerizations.

We extended the idea of latent initiators to *N*-benzyl group containing quaternary ammonium salts and found that quaternary ammonium salts such as *N*-benzyl-*p*-cyanopyridinium hexafluoroantimonate (**1a**) serve as good latent thermal initiators in the cationic polymerizations of cyclic ethers[5] and a vinyl monomer.[6] The benzyl cation is regarded as the actual initiating species formed via heterolytic C–N bond cleavage. Significant features of the pyridinium salts involve easy handling owing to their chemical stability and less hygroscopic nature, easy activity control by introducing substituents on the benzyl group and pyridine ring, and thermal latency.[7,8]



N-benzyl pyridinium salts

In our extensive study on control of the activity, α-methyl (**1b**) and *p*-methoxy (**1c**) groups placed on the benzyl group undoubtedly made the initiators 20–30 times more active than the parent salt **1a**, lowering considerably the initiation temperature. These modifications, therefore, seemed to contribute at least to the enhancement of the rate of the initiation.

This paper describes the synthesis of novel *N*-benzylpyridinium salts and evaluation of their initiator activity from the viewpoint of chemical modification of the pyridine group. Moreover, the mechanism of the cationic polymerization with *N*-benzylpyridinium salts and role of the pyridine group in the polymerization are discussed.

† Part 5 is ref 7.

Experimental Section

Materials. Commercially available extra pure grade benzyl bromide, 1-phenethyl bromide, *p*-methoxybenzyl chloride, *p*-methoxybenzyl alcohol, *o*-cyanopyridine, nicotinic acid methyl ester, *o*- and *p*-methylpyridines, and 47% hydrobromic acid (Tokyo Kasei Kogyo) were used without purification. Solvents were distilled and purified by the usual methods and stored over 4A molecular sieves.

Measurements. Melting points of the initiators synthesized were measured with a Yanaco micro melting point apparatus (Yanagimoto Seisakusho Ltd.) and were uncorrected. FT-IR spectra were obtained with a JASCO FT/IR-3. ^1H NMR spectra were recorded on a JEOL PMX-60si and an EX-90 spectrometer, using tetramethylsilane (TMS) as an internal standard. Molecular weight ($\bar{M}_w$, $\bar{M}_n$) and molecular weight distribution (MWD; $\bar{M}_w/\bar{M}_n$) were estimated by gel permeation chromatography (GPC) on a Toyo Soda HPLC CCP & 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.

***N*-Benzyl-*o*-cyanopyridinium Hexafluoroantimonate (2a).** A mixture of benzyl bromide (3.42 g, 20 mmol) and OCP (1.04 g, 10 mmol) was stirred at room temperature for 2 days. The reaction mixture was extracted with ether/water (50 mL/30 mL). $KSbF_6$ (2.74 g, 10 mmol) was added to the aqueous layer in one portion. White precipitates were collected and recrystallized from methanol: yield 0.47 g (12.0%); mp 153.0–154.5 °C; IR (KBr) 1613, 781, 764, 730, 659 cm^{-1}; ^1H NMR (acetone-d_6) δ 9.55–8.40 (m, 4 H, py), 7.52 (s, 5 H, Ph), 6.29 (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, 2.43; C, 36.01; N, 6.34.

***N*-(1-Phenethyl)-*o*-cyanopyridinium Hexafluoroantimonate (2b).**[8] A solution of 1-phenethyl bromide (7.40 g, 40 mmol) and OCP (2.08 g, 20 mmol) was stirred at room temperature for 20 days. The reaction mixture was extracted with ether/water (100 mL/50 mL). $KSbF_6$ (5.5 g, 20 mmol) was added to the aqueous layer in one portion. White precipitates were collected and recrystallized from methanol: yield 0.32 g (3.6%); mp 122–124 °C; IR (KBr) 1615, 774, 737, 700, 661 cm^{-1}; ^1H NMR (acetone-d_6) δ 9.77–8.43 (m, 4 H, py), 7.62 (s, 5 H, Ph), 7.06–6.60 (q, 1 H,

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PhCHMe), 2.50–2.25 (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, 2.79; C, 37.66; N, 6.20.

***p*-Methoxybenzyl Bromide.**[9] *p*-Methoxybenzyl alcohol (27.80 g (0.2 mol)) dissolved in benzene (60 mL) was put into a column reactor (i.d. = 2.2 cm and H = 36 cm) whose bottom was narrow enough to check the amount of water produced during the reaction (estimation of rough conversion). Then gaseous HBr generated by dropping 47% HBr (50 mL) into concentrated sulfuric acid (500 mL) was bubbled from the bottom of the reaction vessel through a capillary tube till the theoretical amount of water (3.6 mL) was separated out. The exothermic reaction took place and the reaction temperature increased. Benzene (300 mL) was added to the reaction mixture, which was neutralized with saturated $NaHCO_3$, washed with water, and dried with anhydrous $MgSO_4$. Yield 36.7 g (90.5%); purity 80% by NMR.

***N*-(*p*-Methoxybenzyl)-*o*-cyanopyridinium Hexafluoroantimonate (2c).**[8] A solution of freshly prepared *p*-methoxybenzyl bromide (27.8 g, 110 mmol) and OCP (11.8 g, 113 mmol) in acetonitrile (60 mL) was stirred at room temperature for 3 days. Acetonitrile was evaporated and the residue was extracted with ether/water (300 mL/100 mL). $KSbF_6$ (27.4 g, 100 mmol) was added to the aqueous layer in one portion. White precipitates were collected and recrystallized from methanol: yield 10.9 g (20.9%); mp 118–120 °C; IR (KBr) 1613, 1257, 1181, 784, 756, 711, 659 cm^{-1}; ^1H NMR (acetone-d_6) δ 9.50–8.40 (br, 4 H, py), 7.77–6.87 (q, 4 H, arom), 6.20 (s, 2 H, CH_2), 3.83 (s, 3 H, CH_3O). Anal. Calcd for $C_{14}H_{13}F_6N_2OSb$: H, 2.82; C, 36.48; N, 6.08. Found: H, 2.91; C, 36.13; N, 5.92.

***N*-(*p*-Methoxybenzyl)-*m*-(methoxycarbonyl)pyridinium Hexafluoroantimonate (3c).** A mixture of freshly prepared *p*-methoxybenzyl bromide (1.00 g, 5.0 mmol) and *m*-(methoxycarbonyl)pyridine (0.68 g, 4.0 mmol) in acetonitrile (3 mL) was stirred at room temperature for 12 h. Acetonitrile was evaporated and the residue was extracted with ether/water (50 mL/15 mL). $KSbF_6$ (1.37 g, 5.0 mmol) was added to the aqueous layer in one portion. White precipitates were collected and recrystallized from methanol: yield 0.59 g (24%); mp 97–98.5 °C; IR (KBr) 1744, 1639, 796, 744, 660 cm^{-1}; ^1H NMR (acetone-d_6) δ 10.05–8.10 (m, 4 H, py), 7.85–6.65 (q, 4 H, arom), 6.37 (s, 2 H, CH_2), 3.95 (s, 3 H, CH_3OCO), 3.74 (s, 3 H, $CH_3OC_6H_4$). Anal. Calcd for $C_{15}H_{16}F_6NO_3Sb$: H, 3.26; C, 36.47; N, 2.84. Found: H, 3.41; C, 36.62; N, 2.84.

***N*-Benzyl-*p*-methylpyridinium Hexafluoroantimonate (4a).** A mixture of benzyl chloride (1.27 g, 10.0 mmol) and *p*-methylpyridine (0.93 g, 10.0 mmol) was stirred at room temperature for 36 h. The mixture was extracted with ether/water (50 mL/15 mL). $KSbF_6$ (2.74 g, 10.0 mmol) was added to the aqueous layer in one portion. White precipitates were collected and recrystallized from methanol: yield 2.78 g (65.0%); mp 149.5–150.5 °C; IR (KBr) 1645, 779, 736, 701, 653 cm^{-1}; ^1H NMR (acetone-d_6) δ 8.98 (d, 2 H, py), 8.07 (d, 2 H, py), 7.47 (s, 5 H, Ph), 5.90 (s, 2 H, CH_2), 2.72 (s, 3 H, CH_3). Anal. Calcd for $C_{13}H_{14}F_6NSb$: H, 3.36; C, 37.18; N, 3.33. Found: H, 3.34; C, 37.46; N, 3.26.

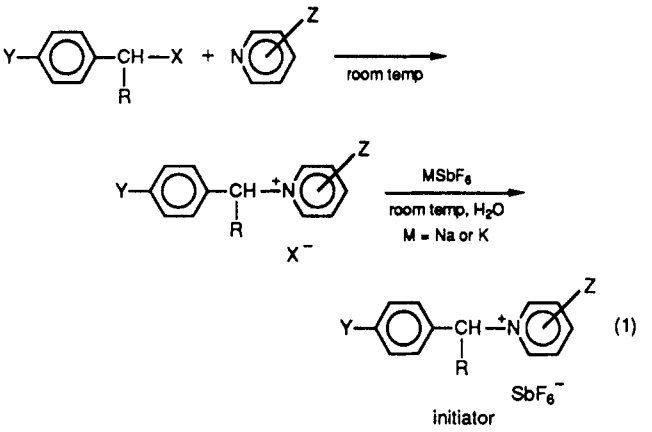
***N*-Benzyl-*o*-methylpyridinium Hexafluoroantimonate (5a).** A mixture of benzyl chloride (1.27 g, 10.0 mmol) and *o*-methylpyridine (0.93 g, 10.0 mmol) was stirred at room temperature for 7 days. The reaction mixture was extracted with ether/water (50 mL/15 mL). $KSbF_6$ (2.74 g, 10.0 mmol) was added to the aqueous layer in one portion. White precipitates were collected and recrystallized from methanol: yield 0.6 g (14.1%); mp 149.5–150.0 °C; IR (KBr) 1634, 793, 744, 703, 653 cm^{-1}; ^1H NMR (acetone-d_6) δ 9.20–7.90 (m, 4 H, py), 7.47 (s, 5 H, Ph), 6.04 (s, 2 H, CH_2), 2.97 (s, 3 H, CH_3). Anal. Calcd for $C_{13}H_{14}F_6NSb$: H, 3.36; C, 37.18; N, 3.33. Found: H, 3.23; C, 37.22; N, 3.35.

Polymerization of Glycidyl Phenyl Ether (GPE) with Pyridinium Salts: General Method. A homogeneous mixture of GPE (0.30 g) and one of the initiators 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 poured into methanol (50 mL) to precipitate polymer. After methanol was removed by decantation, the residual viscous polymer was collected and dried under vacuum. The methanol layer was evaporated to give the methanol-soluble polymer. Structures of the polymers were confirmed by IR and ^1H NMR spectra.

Polymerization of Oxiranes with Pyridinium Salts in an NMR Tube: General Method. An oxirane monomer was dropped from a well-dried syringe into a homogeneous mixture of 2c and an NMR solvent in a precooled NMR tube at ca. 5 °C with an ice-water bath. After that, the tube was sealed off and transferred to a preheated oil bath. The ^1H NMR spectrum was measured at intervals.

Results and Discussion

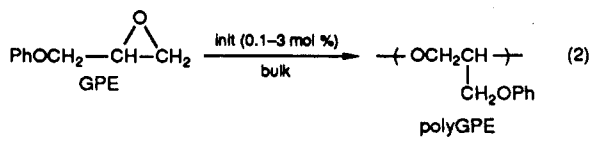
Initiators. In the structural modification of the pyridine group of 1, OCP was selected as a more promising group capable of enhancing the activity of the corresponding initiator than PCP, because either OCP has a lower nucleophilicity or higher leaving ability than PCP. Six *N*-(substituted benzyl)-*p*- and *o*-cyanopyridinium hexafluoroantimonates (1 and 2) were prepared by the reaction of cyanopyridines and benzyl halides followed by exchange of the counteranion with $KSbF_6$ in water (eq 1). Three other pyridinium salts (3c, 4a, and 5a) were also synthesized similarly.



(1)

Although 4a and 5a could be obtained by use of benzyl chloride, no or a trace amount of 2 was formed with it (2a,b). The reaction of benzyl, 1-phenethyl, and *p*-methoxybenzyl bromides with OCP gave the corresponding pyridinium salts. By efficient exchange of the counteranion with $KSbF_6$, 2a–c were obtained in purified yields of 12.0, 3.6, and 20.9%, respectively. Meanwhile, the reaction of *m*-(methoxycarbonyl)pyridine with *p*-methoxybenzyl bromide proceeded exothermically and rapidly. *N*-(*p*-Methoxybenzyl)-*p*-methylpyridinium hexafluoroantimonate was not obtained as crystals. All of the pyridinium salts used in this work were unknown compounds except 1, and their structures were determined by NMR, IR, and elemental analysis. Yields, melting points, and ^1H NMR chemical shifts of the obtained initiators are listed in Table I.

Polymerization. The activity of the initiators (2–5) was evaluated in the bulk polymerization of GPE in the presence of 0.1–3 mol % of them. Each initiator was soluble in GPE at room temperature and the reaction proceeded homogeneously. The polyGPE was precipitated with methanol after estimation of the conversion 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



(2)

molecular weight polymer with $\bar{M}_n$ < ca. 2000. The

Table I
Structure and Properties of Various Pyridinium Salts

	1a	1b	1c	2a	2b	2c	3c	4a	5a
X	Cl	Br	Cl	Br	Br	Br	Br	Cl	Cl
Y[a]	H	H	MeO	H	H	MeO	MeO	H	H
R[a]	H	Me	H	H	Me	H	H	H	H
Z[a]	*p*-CN	*p*-CN	*p*-CN	*o*-CN	*o*-CN	*o*-CN	*m*-COOMe	*p*-Me	*o*-Me
yield,[b] %	25.0	12.6	19.4	12.0	3.6	20.9	24.0	65.0	14.1
mp, °C	156.0–157.0	108.5–109.5	157.5–158.5	153.0–154.5	122.0–124.0	118.0–120.0	97.0–98.5	149.5–150.5	149.5–150.0
δ[c] ppm	6.20	6.47	6.05	6.29	6.83	6.20	6.37	5.90	6.04

[a] Substituents of pyridinium salts 1–5. [b] Isolated total yield. [c] ^{1}H NMR chemical shift of the benzyl proton in acetone-d_6.

Table II
Bulk Polymerization of GPE with Various Pyridinium Salts for 2 h

init	amt, mol %	temp, °C	conv,[a] %	yield,[b] %	$\bar{M}_n$[c]	$\bar{M}_w/\bar{M}_n$[c]
1c	1.0	80	15.0	4.2		
	1.0	100	59.4	34.6	4000[d]	1.39
2c	1.0	rt[e]	44.3		2700	1.47
	0.1	60	68.4	53.1	4900	1.91
2b	0.1	60	66.4	46.0	5600	1.98
4a	3.0	200	2.9			
5a	3.0	200	44.6		1300	2.40

[a] Determined by NMR. [b] Yield of insoluble polymer in methanol. [c] Estimated for crude product before precipitation by GPC based on polystyrene standards. [d] Methanol-insoluble polymer. [e] Room temperature.

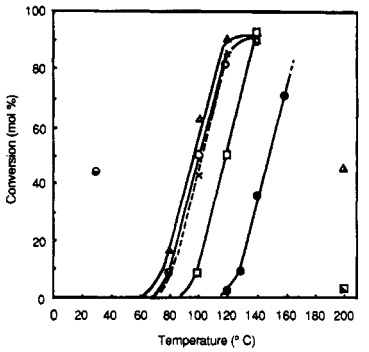


Figure 1. Effect of temperature on the bulk polymerization of GPE with several pyridinium salts (3 mol %) for 2 h: (●) **1a**; (○) **1b**; (△) **1c**; (×) **2a**; (⊖) **2c** (1 mol %); (□) **3c**; (▣) **4a**; (▲) **5a**.

insoluble polymer had $\bar{M}_n$ ranging from 2000 to 6000. Results of the polymerization with several initiators are summarized in Table II.

Figure 1 shows temperature–conversion curves of the polymerizations of GPE with several pyridinium salts at temperatures ranging from 25 to 200 °C. **2a** did not initiate the polymerization below 60 °C, whereas the polymerization rapidly proceeded above 80 °C. **2a** had about 20 times more enhanced activity than **1a** in terms of the roughly estimated temperature difference (45 °C) at the same conversion. On the other hand, **2c** initiated the polymerization at room temperature and was about 100 times more active than **1c**. This result suggests that the thermal latency of **2c** is lost due to its high activity.[8] The activity of **2b** was sufficiently higher than that of **1b** but slightly lower than that of **2c**.[8] Thus, introduction of the *o*-cyano group into pyridine nuclei causes a large enhancement of the initiator activity. Inspection of Table II supports these conclusions.

The reason for the activity enhancement by this modification can be accounted for by both electronic and steric effects of the *o*-cyano group of the pyridine group. For example, in comparison of **1c** and **3c**, in which the steric effect of the substituents is negligible, **1c** is ca. 10 times more active than **3c** in the polymerization at 100 °C. A similar tendency is observed between **1a** and **4a**. This is in good accordance with the order of pK_a of the corresponding protonated pyridines (**1c**, 1.90; **3c**, 3.13; **1a**, 1.90; **4a**, 6.00),[10] i.e., that of the leaving ability in the initiation step.

Generally, the steric effect of an ortho substituent is serious in aromatic systems, as a so-called ortho effect. In the two pyridinium salts **4a** and **5a**, which have similar pK_a values (**4a**, 6.00; **5a**, 5.96 (in the protonated forms of the pyridines)),[10] **5a** was about 15 times more active than **4a** as estimated by the conversions of GPE at 200 °C (Table II). Thus, the *o*-methyl group (steric effect coefficient E_s = −1.24)[11] accelerates the polymerization to a considerable extent only by the steric effect. If the initiator activity is predicted to be affected by only the above two effects, simple estimation of the contribution of the steric effect of the *o*-cyano group in **2c** in comparison with **1c** reveals that the electronic effect of the *o*-cyano group causes a roughly 30 times enhancement of activity. Because the E_s value of the cyano group is −0.51,[11] indicating the degree of the steric effect of the cyano group is one-fifth that of the methyl group, one would expect a 3 times enhancement of the activity from steric considerations alone. Consequently, the electronic effect seems to predominate over the steric effect on the activation by changing the cyano group from the para to the ortho position.

As mentioned above, the structure of the pyridine moiety appears to affect the initiation, although the observed conversion of the monomer results from the overall polymerization. The pyridine moiety should play an important role not only in the initiation but also in the propagation, since it is the most basic species in the polymerization system. To investigate the behavior of the pyridine moiety that is formed during the initiation step, we carried out a solution polymerization in the presence or absence of pyridines. Propylene oxide (PO) and CD_3NO_2 were selected as an epoxide and a solvent for ^{1}H NMR work in order to clarify the mechanistic features of the polymerization.

First, the polymerization of PO with 100 mol % of **2c** (0.48 M) in the absence of OCP proceeded rapidly at room temperature and was completed within 10 min. When an additional 5 equiv of PO with respect to **2c** was added to the resulting mixture, NMR signals of liberated free OCP (B3), terminated end (T), and *p*-methoxybenzyl ether (I) increased while those of **2c** decreased as the conversion of PO increased (B3, T, and I: see Figure 2). Conversion of **2c** was very low (below 5%), and NMR signals of propionaldehyde (B1) and acetone (B2) were not detected. Figure 2 shows the ^{1}H NMR spectrum after the solution polymerization of PO (6 M) with **2c** (0.48 M) at 60 °C for 10 min, where gaseous PO mixed with argon (total volume 100 mL) was slowly added to the homogeneous mixture of **2c** and CD_3NO_2 over a period of 30 min. From the integral ratio of all the pyridine groups to benzyl groups of **2c**, the conversion of **2c** was 50%. B3 peaks (corresponding to OCP) obviously increased when OCP was added to the polymerization mixture. Furthermore, when

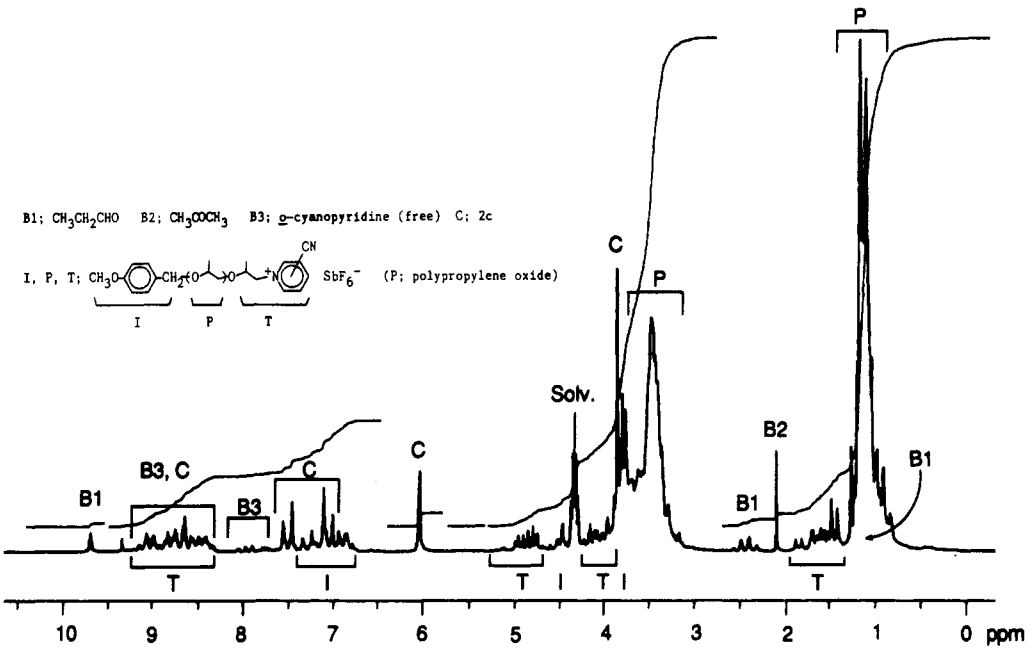


Figure 2. 90-MHz ^{1}H NMR spectrum of the solution polymerization of PO with **2c** at 60 °C in CD_3NO_2. No PO remains. Signals B1 and B2 are attributable to those of propionaldehyde and acetone, respectively, which are the cationic isomerization products of PO.

a drop of triethylamine was added, the T and C peaks disappeared immediately whereas the B3 peaks increased to be quantitative. However, the T peaks did not disappear even when excess OCP was added. These results indicate that OCP is formed in the initiation, and the T peaks would correspond to the terminated species having the *N*-alkyl-*o*-cyanopyridinium salt structure. In fact, the chemical shifts of the peaks T, P, and I appeared in the regions expected for them. Meanwhile, the fact that pyridine moiety is liberated during the polymerization supports that the initiating species is a benzyl cation.

Second, in the presence of an OCP (0.45 M), the solution polymerization of PO (0.45 M) with **2c** (0.23 M) did not proceed at all even at 60 °C, and the conversion of **2c** was 0%. When an equimolar PCP was added, conversion of **2c** to **1c** via pyridine moiety exchange was observed, which occurred independently of the presence of monomer PO. That is, the benzyl proton peak of **2c** at 6.03 ppm shifted to that of **1c** at 5.86 ppm. These results show that the liberated pyridine interacts with the initiator (**2c**) or the initiating species (i.e., benzyl cation) and possibly decreases the rate of the initiation. This anticipation is supported by the results of the bulk polymerization of GPE in the presence of OCP. As shown in Table III, addition of OCP clearly made the polymerization rate drop. Even at 100 °C in the case of **1c**, the result was almost the same. When the ratio of OCP to **2c** was over 3, the polymerization did not proceed at all. These experimental results are consistent with the actual occurrence of the efficient polymerization with **2c** under the influence of the liberated OCP. As expected, the amount of free OCP was only ca. 20% of all the liberated OCP (peaks B3, Figure 2). Most OCP liberated, therefore, would react with the propagating cationic end to give the corresponding pyridinium salt at the end of the polymerization. This pyridinium salt seems not to initiate the polymerization of PO at 60 °C. About 20% of the terminated species may be a very stable terminal six-membered oxonium salt,[12] judging from the ^{1}H NMR spectrum of the polymerization mixture (Figure 2).

In the study of the role of the pyridine moiety in the propagation, we found that $\bar{M}_n$ is higher and $\bar{M}_w/\bar{M}_n$ is wider in the methanol-insoluble polymer obtained with **2a** than that with **1b**, although the observed activity of **2a** and **1b** with respect to the conversion of GPE is almost the same (Figure 1 and Table IV). These results can be explained by assuming slower initiation and faster propagation with **2a** than with **1b**. Thus, it is conceivable that, owing to a weak interaction of the more bulky and less basic OCP with the propagating species, the propagation is accelerated, since the benzyl group does not take part in this process. Slightly lower conversion of GPE with **2a** than with **1b** in the low-conversion region is possibly due to the lower concentration of the initiating species.

Table III
Bulk Polymerization of GPE with 1 mol % of 2c and 1c in the Presence of OCP

init	OCP/init, mol/mol	temp, °C	time, h	conv,[a] %	$\bar{M}_n$[b]	$\bar{M}_w/\bar{M}_n$[b]
2c	0	rt[e]	2	44	2700	1.5
			4	62	2400	1.7
	1		2	2	930	1.5
			4	6		
	3		2	0		
	6		2	0		
1c	0	100	2	59	4000[d]	1.4[d]
	1		2	4		
	3		2	0		
	1[c]		2	0		

[a] Determined by NMR before precipitation. [b] Estimated by GPC based on polystyrene standards before precipitation. [c] In the presence of *p*-cyanopyridine instead of OCP. [d] Methanol-insoluble polymer. [e] Room temperature.

The above discussion was supported by the NMR study on the solution polymerizations of GPE with 5 mol % of **1b** and **2a** at 100 °C in CD_3NO_2. As shown in Table V, the conversion of GPE with **1b** was slightly higher than that with **2a** at 2 h. However, after 24 h, the conversion of **1b** was higher than that of **2a** while the conversion of GPE with **1b** conversely became lower than that with **2a**. These results indicate that, although the initiation rate with **2a** is smaller than that with **1b**, the propagation rate with **2a** is larger than that with **1b**. Thus, the interaction of OCP with the propagating species is weaker than that of PCP.

Table IV
Bulk Polymerization of GPE with 2a and 1b for 2 h

		init							
		2a				1b			
temp, °C	init, mol %	conv,[a] %	y,[b] %	$\bar{M}_n$[c]	$\bar{M}_w/\bar{M}_n$[c]	conv,[a] %	y,[b] %	$\bar{M}_n$[c]	$\bar{M}_w/\bar{M}_n$[c]
80	3	8	6	3700	1.5	8			
100	3	43	29	4600	1.6	50	26	3700	1.3
120	3	85	60	4600	2.1	80	54	3600	1.6
120	1	61	23	5100	1.5	66	37	4900	1.5
120	0.1	14		3200	1.5	36		3600	1.6

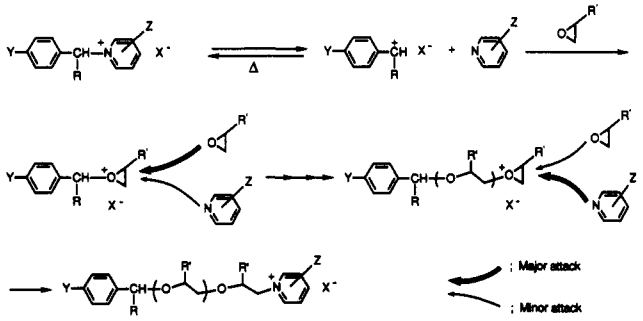
[a] Determined by NMR before precipitation. [b] Yield of methanol-insoluble polymer. [c] Estimated by GPC based on polystyrene standards.

Table V
Solution Polymerization of GPE with 5 mol % of 2a and 1b in CD_3NO_2 at 100 °C[a]

time, h	conv of 2a,[b] %	conv of GPE,[c] %	conv of 1b,[b] %	conv of GPE,[c] %
2	13	15	16	19
24	29	42	43	33

[a] Polymerization was carried out in an NMR tube, using 0.0581 g of 2a or 0.0602 g of 1b, 0.35 mL of GPE, and 0.1 mL of CD_3NO_2. [b] Determined by benzyl proton (6.03 ppm, s) for 2a and methyl proton (2.13 ppm, d) for 1b. [c] Determined by ^1H NMR.

Scheme I



According to the various results obtained above, a possible mechanism of the cationic polymerization with *N*-benzylpyridinium salts is postulated (Scheme I).

The main process of this polymerization is considered to be as follows: A benzylpyridinium salt (X = SbF_6) reaches an equilibrium with a mixture of a benzyl cation, X^-, and a pyridine by heating. The cation-stabilizing substituent on the benzyl group and the pyridinium cation destabilizing group on pyridine (or the low pK_a of the corresponding protonated pyridine) move the equilibrium to the right. In addition, substitution causing steric repulsion contributes to the cleavage of the C–N bond. Monomer, such as expoxide, reacts with the benzyl cation during the initiation. In the propagation, monomer rapidly attacks the propagation end in the initial stage, whereas competitive attack of the liberated pyridine increases as the monomer concentration decreases. The propagating end attacked by the pyridine may result in a dead cationic end that cannot initiate the polymerization any longer (i.e., termination). However, since the cationic species capable of initiating the polymerization is continuously produced from the pyridinium salt, the polymerization does not stop until the initiator is completely exhausted or the amount of the free pyridine liberated reaches about 3 times amount of the initiator unreacted, unless there is something to suppress the polymerization, such as increasing viscosity.

Thus, the activation-aided structural modification of the pyridine group of 1 based on the electronic and steric effects has resulted in the synthesis of 2 with a highly enhanced activity in both the initiation and propagation steps.

In conclusion, we have found the important mechanistic features of the polymerization with *N*-benzylpyridinium salts from the structure–activity relationship and a detailed NMR study. All pyridinium salts prepared are soluble in monomer, stable against water and air, and therefore easy to handle. Furthermore, it has become possible to control the rates of initiation and propagation by combining the correct benzyl and pyridine groups as well as by selecting an appropriate counteranion.[2d,3a,4a]

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Registry No. **2a**, 129254-45-1; **2b**, 125274-19-3; **2c**, 125274-21-7; **3c**, 132981-63-6; **4a**, 118732-50-6; **5a**, 126826-31-1; GPE, 122-60-1; GPE (homopolymer), 25265-27-4; $KSbF_6$, 16893-92-8; o-cyanopyridine, 100-70-9; benzyl bromide, 100-39-0; 1-phenethyl bromide, 103-63-9; *p*-methoxybenzyl alcohol, 105-13-5; *p*-methoxybenzyl bromide, 2746-25-0; *m*-(methoxycarbonyl)pyridine, 93-60-7; benzyl chloride, 100-44-7; *p*-methylpyridine, 108-89-4; o-methylpyridine, 109-06-8.