CHEMISTRY LETTERS, pp. 1861-1864, 1989.

Quaternary Ammonium Salts as Useful Cationic Initiators. Specially Enhanced Activity by Cyano Group Situated at o-Position of Pyridine Ring of N-Benzylpyridinium Salts

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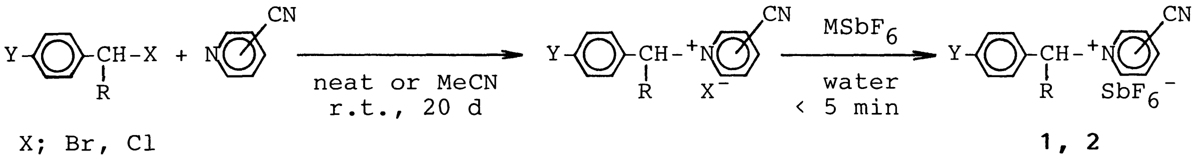
1-Phenethyl and p-methoxybenzyl o-cyanopyridinium hexafluoroantimonates were synthesized, which showed much higher initiation activity than the corresponding p-cyano derivatives in the cationic polymerization of glycidyl phenyl ether.

We have first reported that quaternary ammonium and pyridinium salts such as benzyl p-cyanopyridinium hexafluoroantimonate (**1a**) serve as thermally latent cationic initiators for the polymerizations of cyclic monomers (bicycloorthoester and epoxide)[1,2] and a vinyl monomer (styrene).[3] The most significant feature of these initiators involves thermal latency as well as easy-handling owing to their chemical stability and less hygroscopic nature. In our extensive study, activity control of the initiators on the basis of structure-activity relationship has been the next target, which would provide important insights into the molecular design of this type of cationic initiators. Although **1a** initiated cationic polymerization of glycidyl phenyl ether (GPE) above 120 °C, the activity of **1a** fairly increased by devising a chemical modification, i.e. an introduction of electron-releasing substituents onto a benzylic carbon and a benzene ring (**1b** and **1c**).[4] The activity change by the structural modification studied so far may be accounted for mainly by an electronic effect.

In this paper, synthesis of 1-phenethyl and p-methoxybenzyl o-cyanopyridinium hexafluoroantimonates (**2b** and **2c**)[5,6] and their highly enhanced activities as cationic initiators are described.

New initiators, **2b** and **2c** were prepared by the reaction of o-cyanopyridine with corresponding benzyl halides followed by exchanging the counter anions with SbF_6^- in water (Eq. 1) according to the previously reported method.[3]



(1)

1, **2**

	2b	**2c**	**1a**	**1b**	**1c**
Y	H	OMe	H	H	OMe
R	Me	H	H	Me	H
CN	o-	o-	p-	p-	p-
M	K	K	Na	Na	Na

First, the activity of **2** was evaluated in the bulk polymerization of GPE.7) Interestingly the polymerization of GPE with 1 mol% of **2c** rapidly proceeded at 60 °C within 1 min. The conversion, yield, number-average molecular weight ($\overline{Mn}$), and molecular distribution dispersion ($\overline{Mw}/\overline{Mn}$, $\overline{Mw}$: weight-average molecular weight) in this polymerization were 89%, 74%, 4200, and 2.4, respectively. Even at room temperature, the conversion reached 44% for 2 h. Among various quaternary ammonium salt type initiators examined so far,1-4) **2c** is the first initiator that causes the polymerization of GPE at such a low temperature. This result is clearly contrast to the fact that **1c**, the corresponding p-cyano derivative of **2c**, does not initiate the polymerization up to 60 °C at all, even if 3 mol% of **1c** is used. The conversion at room temperature eventually went up to ca. 80% for 23 days (Fig. 1), although the rate of the bulk polymerization considerably decreased over ca. 50% conversion, due to the increasing viscosity of the polymerization system.

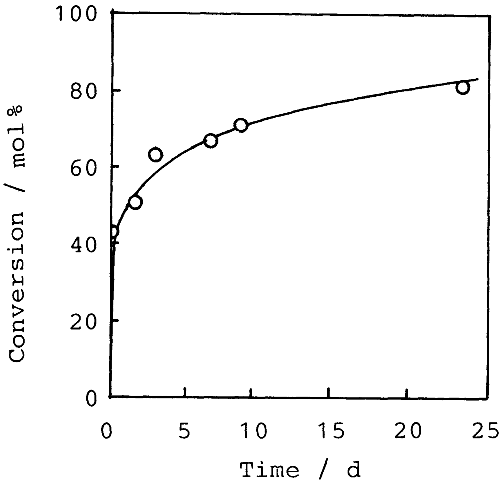


Fig. 1. Time-conversion curve of the bulk polymerization of GPE with 1 mol % of **2c** at room temperature.

In order to estimate the activity of **2** in comparison with that of **1**, the bulk polymerization of GPE was carried out at 40-80 °C using a reduced amount of **2** (0.1 mol% to 0.3 mol%). The results obtained in the limited polymerization time (2 h), are listed in Table 1. With **2c**, the conversion of GPE and the yield of polyGPE increased as the temperature increased up to 60 °C, but decreased at 80 °C. At high concentration (0.3%) of **2c**, the conversion, yield, and $\overline{Mn}$ dropped down, probably due to the high concentration of the cationic species liberated by heating

2c via S_N1 or S_N2 mechanism. Inspection of data (Table 1) unambiguously suggests the extremely high activity of **2c** compared with **1c**, the magnitude of the enhancement can be estimated as ca. 100 times.

Table 1. Bulk polymerization of GPE with **1b**,**1c**, **2b**, and **2c** for 2 h

Initiator	Amount	Temp	Conv.a)	Yieldb)	$\overline{Mn}$c)	$\overline{Mw}/\overline{Mn}$c)
	mol%	°C	%	%		
1c	3.0	40	0.0	-	-	-
	3.0	60	1.0	0.0	750	NDe)
	3.0	80	17.0	ND	1200	ND
	1.0	80	15.0	4.2	ND	ND
	1.0	100	59.4	34.6	4000	1.39
1b	3.0	60	0.3	ND	ND	ND
	3.0	80	7.9	ND	ND	ND
	1.0	80	1.5	ND	ND	ND
	1.0	100	31.8	10.5	5000	1.21
2c	1.0	r.t.	44.3	ND	2700	1.47
	0.1	40	49.2	40.7	5400	1.76
	0.1	60	68.4	53.1	4900	1.91
	0.1	80	64.4	43.4	4500	1.79
	0.1	60	68.8d)	57.8d)	5000d)	1.91d)
	0.3	60	65.6	29.8	4700	2.03
2b	0.1	60	66.4	46.0	5600	1.98

a) Estimated by NMR. b) Yields of insoluble polymers in methanol. c) Data before precipitation, estimated by GPC based on polystyrene standard. d) Data for 4 h
e) ND: not determined.

Similarly, the activity of **2b** was very high, though it was slightly lower than that of **2c**. The relative activity order of **2b** and **2c** was parallel to that of **1b** and **1c**.4) The slightly higher $\overline{Mn}$ value (5600) in case of **2b** than that of **2c** (4900) may be accounted for by the lower concentration of the initiation species.

Thus, considerable lowering of the initiation temperature has been accomplished by the transference of a cyano group from p- to o-position on the pyridine ring, and we have obtained the highly activated quaternary ammonium type of initiators capable of initiating the cationic polymerization of GPE even at room temperature. Although **2b** and **2c** are too active to be latent thermal initiators, they can preferably be regarded as useful cationic initiators which are stable, non-hygroscopic, and easy to handle.

The profound activation by o-cyano group may be explained by an electronic effect of the pyridine ring from pk_a data of p- and o-cyanopyridines (1.90 and -0.26 respectively) in the initiation8) and the propagation step. However, it may presumably be suggested that in addition to the electronic effect, a steric effect of the o-cyano group should be operative, especially in the propagation step, where of importance is the degree of interaction between a propagating end and cyanopyridines. The detailed studies for the activity enhancement by o-cyano substitution and for the whole polymerization mechanism are in progress and will be described elsewhere.

References

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2) H. Uno, T. Takata, and T. Endo, Macromolecules, 22, 2502 (1989).

3) H. Uno, T. Takata, and T. Endo, Chem. Lett., 6, 935 (1988).

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5) A solution of phenethyl bromide (7.40 g, 40 mmol) and o-cyanopyridine (2.08 g, 20 mmol) was stirred at room temperature for 20 days. This reaction mixture was extracted with ether/water. $KSbF_6$ (5.5 g, 20 mmol) was added to the aqueous layer in one portion. A white precipitate was 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, -CH-), 2.50-2.25 (d, 3 H, CH_3-); Anal. Found: H, 2.79; C, 37.66; N, 6.20%. Calcd for $C_{14}H_{13}F_6N_2Sb$: H, 2.94; C, 37.79; N, 6.29%.

6) A solution of p-methoxybenzyl chloride (7.84 g, 50 mmol) and o-cyanopyridine (5.21 g, 50 mmol) in acetonitrile (8 mL) was stirred at room temperature for 20 days. Acetonitrile was evaporated and the residue was extracted with ether/water. $KSbF_6$ (13.7 g, 50 mmol) was added to the aqueous layer in one portion. A white precipitate was collected and recrystallized from methanol. Yield 1.71 g (7.4%); 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 (m, 4 H, py-), 7.77-6.87 (q, 4 H, ph-), 6.20 (s, 2 H, -CH_2-), 3.83 (s, 3 H, CH_3O-). Anal. Found: H, 2.91; C, 36.13; N, 5.92%. Calcd for $C_{14}H_{13}F_6N_2OSb$: H, 2.82; C, 36.48; N, 6.08%.

7) Since the initiators, **2b** and **2c**, were soluble in GPE at room temperature, the polymerization proceeded homogeneously.

8) Benzylic cation is suggested as a reasonable initiation species.2)

(Received July 28, 1989)