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Thermoinitiated Cationic Polymerization of Styrene with a Pyridinium Salt

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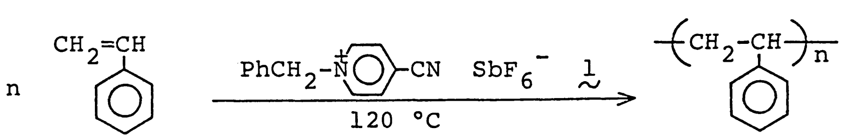
N-Benzyl-*p*-cyanopyridinium hexafluoroantimonate behaved as a thermally latent catalyst to initiate the cationic polymerization of styrene at 120 °C leading to polystyrene possessing a bimodal molecular weight distribution.

Cationic polymerization of vinyl monomers have generally been conducted at low temperature($<$30 °C) due to high reactivity of carbenium ions that participate in chain propagation, and isomerization or transfer reaction easily proceeds even at that temperature.1-3)

Meanwhile, we have recently found that benzyl-substituted sulfonium salts4) and quaternary ammonium salts5) are available as thermally latent cationic catalysts, which can liberate apparently benzyl cation by thermolysis (120 °C) and initiate the cationic polymerization of cyclic ethers. However, cationic polymerization of vinyl monomers with onium salts as thermally latent catalysts has never been reported.6) In order to make sure their availability for wide range of cationically polymerizable monomers, it needs to examine their catalytic activity in the polymerization of vinyl monomers.

In the present paper, we wish to describe the polymerization of styrene at a high temperature using an ammonium type thermally latent catalyst, *N*-benzyl-*p*-cyanopyridinium hexafluoroantimonate (**1**).7)



When styrene was polymerized in bulk in the presence of **1** (3 mol%) and catechol (50 ml% vs. styrene) at 120 °C for 24 h, styrene was completely consumed and methanol-insoluble polystyrene was obtained in 22% yield along with methanol-soluble polystyrene (76% yield).8) In the control experiment without catalyst **1**, a small amount of low molecular weight polystyrene9) (12% yield,10) $\overline{M}_n < 500$ by GPC11)) was obtained even in the presence of 50 mol% of catechol (Table 1, run 1). However, no positive radical polymerization did take place under the conditions because neither methyl methacrylate (MMA) nor acrylonitrile

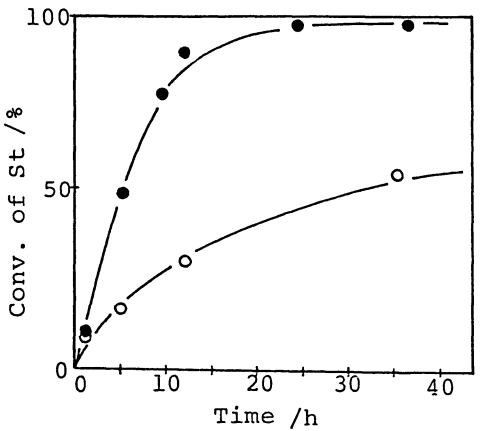


Fig. 1. Time-conversion curves of polymerization of styrene with 1 in bulk at 120 °C. 1: (●) 3 mol%; (○) 0.5 mol%

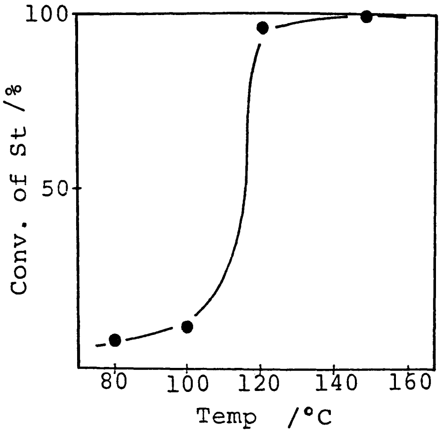


Fig. 2. Effect of temperature on conversion of styrene in the polymerization with 1 (3 mol%) in bulk for 24 h.

(AN) was polymerized at all at 120 °C in the presence of 1 (3 mol%) and catechol (50 mol%).[12,13] Thus, all the experiments done in this study were carried out in the presence of 50 mol% catechol, and thereby most of polystyrene obtained (more than 88%) was derived from the cationic polymerization with 1.

Figure 1 shows time-conversion curves in which styrene was perfectly consumed in 24 h in a higher concentration of 1 (3 mol%) but incompletely in a lower one (0.5 mol%). Then, effect of temperature, i.e. thermal latency of 1 was studied (Fig. 2).[8] Temperature dependence on the catalytic activity of 1 for styrene was very similar to that for a bicycloorthoester.[5] That is, the polymerization proceeded quantitatively over 120 °C, whereas no or very small amount of styrene was consumed at 100 °C and below. Thus, clear thermal latency of 1 was confirmed.

Table 1 summarizes the results of the polymerizations under various catalyst concentrations. The molecular weight distribution (MWD) of polystyrene obtained without precipitation was bimodal in any case, in which two peaks appeared at higher ($\overline{\mathrm{Mn}}$ 3000-4500) and lower ($\overline{\mathrm{Mn}}$ 1000-1300) molecular weight regions in GPC. The lower molecular weight polymer was the main product (ca. 95%).

Table 1. Cationic polymerization of styrene with 1 under various catalyst concentrations[a]

	Cat. (1)	Conv.	Higher MW polymer		Lower MW polymer
Run	/mol%	/%	$\overline{\mathrm{Mn}}$(x10^3)	$\overline{\mathrm{Mw}}/\overline{\mathrm{Mn}}$	$\overline{\mathrm{Mn}}$(x10^3)
1	0	12	none	none	0.53
2	0.05	49	b)	b)	b)
3	0.1	61	2.81	1.18	1.16
4	0.5	100	4.51	1.62	1.01
5	1.0	100	3.04	1.68	1.27
6	3.0	100	4.14	1.48	1.26

a) Polymerization conditions; catechol 50 mol%, 120 °C, 24 h in bulk. b) Not measured.

Inspection of data of Table 1 reveals independence of $\overline{Mn}$ on the catalyst concentration, which is characteristic of usual cationic polymerization.

In the solution polymerization of styrene with 1 (3 mol%) at 120 °C for 24 h in chlorobenzene under the homogeneous conditions,[8)] low molecular weight polystyrene ($\overline{Mn}$ 500 and 1200) was produced (Fig. 3. A) without the formation of the higher molecular weight polymer ($\overline{Mn}$ ca. 3500) as obtained in the bulk polymerization. As shown in Fig. 3 (A), monomer concentration little affected $\overline{Mn}$. Addition of polar solvent, CH_3CN, caused formation of the higher molecular weight polymer which had MW of 15200 (Fig. 3. B). Since polystyrene with such bimodal MWD has never been found in the cationic polymerization of styrene with metal halides, the results mentioned above seem to imply that a few different kinds of propagating species simultaneously participate in the polymerization.

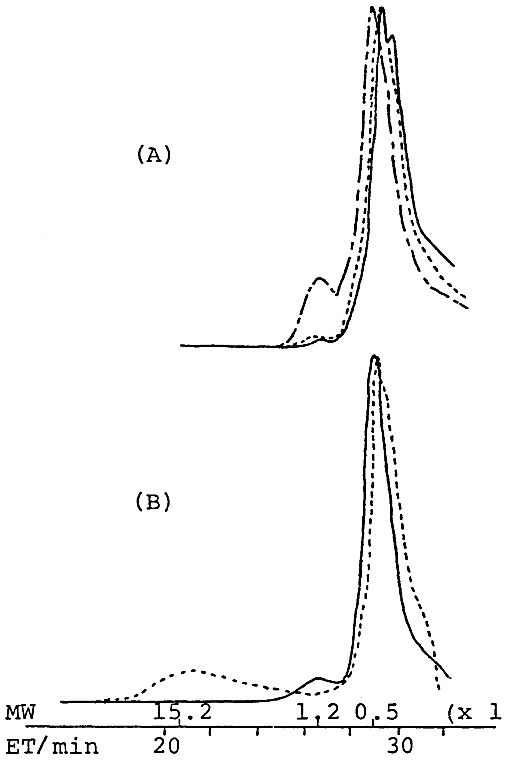


Fig. 3. Effect of monomer concentration (A) and solvent polarity (B) on MWD of polystyrene obtained by 1 at 120 °C for 24 h. (A) solvent PhCl: (—) [St]=1.2 M; (----) 10.6 M; (–·–) 21.1 M. (B) [St]=3 M: (—) CH_3CN/PhCl=0/1 (vol%); (-----) 1/1.

In summary, the present work demonstrated that styrene can be cationically polymerized with the pyridinium salt 1 at 120 °C to afford polystyrene with a bimodal MWD in a high yield.

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7) Among several N-benzyl p-substituted pyridinium hexafluoroantimonates, **1** was the most active catalyst.$^{5)}$ Preparation: A solution of benzyl chloride (1.6 g, 13 mmol) and *p*-cyanopyridine (1.0 g, 10 mmol) in methanol (20 ml) was stirred at 50 °C for 10-15 h. Methanol was evaporated and the residue was extracted with ether-water. To the aqueous layer, $NaSbF_6$ (2.6 g, 10 mmol) was added and the precipitates collected were recrystallized from ethanol. Yield 20%. mp 156-157 °C. IR(KBr); 1640, 1455, 760, 720, 700, 660 cm^{-1}. ^1H NMR(δ/CD_3CN); 8.95 (d, 2H, 2C$\underline{H}$), 8.55-8.15 (broad, 2H, 2C$\underline{H}$), 7.45 (s, 5H, Ph), 5.80 (s, 2H, C$\underline{H}_2$) ppm.

8) Styrene (0.26 g) was polymerized in a sealed tube. The polymerization was initiated by raising the temperature up to 120 °C in the presence of **1** and 50 mol% of catechol. The absence of water contaminated into the polymerization solvent (PhCl or CH_3CN) was checked by FT-IR. The polymerization was terminated by addition of ammoniacal methanol. The quenched reaction mixture was concentrated *in vacuo* and extracted with benzene-water to remove catechol, evaporated and finally vacuum dried. Conversion was determined from the polymer yield. The polymer was dissolved in 0.3 ml of tetrahydrofuran and poured into 200 ml of methanol.

9) Probably the polystyrene was radically produced, because small amount of low molecular weight copoly(styrene)(MMA) was isolated when a mixture of styrene and MMA was heated in the presence of catechol under the same conditions.

10) This yield would fairly decrease in the polymerization in the presence of the catalyst **1** since the cationic polymerization with **1** should proceed competitively with the thermal polymerization.$^{9)}$

11) Gel permeation chromatography The molecular weights and their distributions of the polymers were measured by GPC (solvent; tetrahydrofuran, 35 °C) with a Toyo Soda HPLC CCCP & 8000 system equipped with three polystyrene gel columns (TSK gel, G-2000HXL, G-2500HXL, and G-3000HXL, or G-2000HXL, G-5000HXL, and G-40000HXL).

12) To a mixture of MMA or AN (2.5 mmol) and catechol (50 mol% for monomer) in a small ampule tube was added 0.03 g (3 mol%) of **1**. The tube was cooled, degassed, and sealed off. The ampule tube was heated at 120 °C for 24 h, and the reaction mixture was dissolved in a small amount of tetrahydrofuran and the resulting solution was poured into methanol. Insoluble part in methanol was not PMMA or PAN (from IR spectra) but a complex mixture which is insoluble in any other organic solvents. Soluble part in methanol was a mixture of catechol and **1**.

13) *N*-benzyl-*N*,*N*-dimethylanilinium chloride has been reported to initiate radically the polymerization of MMA. T. Fueno, H. Okamoto, T. Tsuruta, and J. Furukawa, J. Polym. Sci., **XXXVI**, 407 (1959).

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