Cationic Polymerization of Styrene with *N*-Benzyl Pyridinium Salt. Isolation of Polymeric Cationic Species and Its Application to Block Copolymer Synthesis

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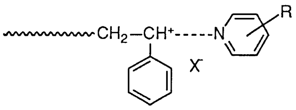
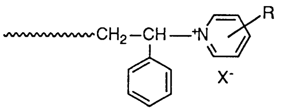
A polymeric cationic species (**III**) could be isolated in the cationic polymerization of styrene with an *N*-benzyl pyridinium salt (MBCP) by adding the corresponding pyridine (OCP). **III** is considered to be a terminated end which is active enough to initiate the cationic polymerization since it has still an *N*-benzyl pyridinium salt structure. Therefore, **III** could initiate the cationic polymerization of epoxides to give the block copolymers of styrene and epoxides.

Benzyl group-containing onium salts such as sulfonium, quaternary ammonium, and pyridinium salts have been reported to serve as good cationic initiators for various monomers.[1-15] It is conceived that, for example, in the cationic polymerization of cyclic ethers with *N*-benzyl pyridinium salts an eliminated pyridine moiety interacts with the propagating cationic end.[15] When styrene is used as a monomer, cationic end species present in the polymerization system may have the following pyridine-coordinated polymeric carbo-cation (**I**) and/or polymeric pyridinium ion (**II**).


I


II

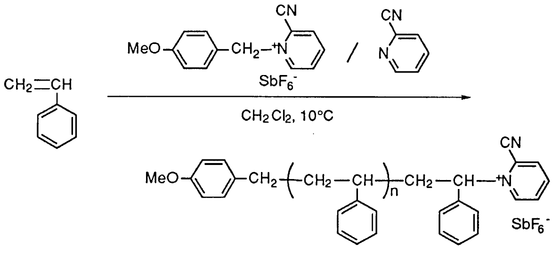
It is quite significant to isolate the cationic species, which will be stable if they hold the pyridinium salt structure **II**, since it can be regarded as a living propagating end or a terminated end. Furthermore, block copolymers will be expected to be able to be prepared by the cationic polymerizations of epoxides with the isolated polymeric cationic species (**II**), because **II** is also an *N*-benzyl pyridinium salt, i.e. a benzyl cation has been reported to be an initiating species in the cationic polymerization of propylene oxide with *N*-(*p*-methoxybenzyl)-*o*-cyanopyridinium hexafluoroantimonate (MBCP).[15]

Cationic polymerization of styrene[12] ([C]=1 M, in CH_2Cl_2) with MBCP[13,15] (10 mol%) proceeded at 10°C to give 74% conversion for 14 h (Table 1, run 1). Methanol-insoluble polystyrene (PSt) was obtained in 68% yield. Although the pyridinium salt structure ($\nu_{\text{Sb-F}}$ = 660 cm^{-1}) in the obtained PSt could be confirmed by IR, it was characterized insufficiently because of its high molecular weight. In order to obtain the polymeric cationic species with low molecular weight, the polymerization was attempted in the presence of *o*-cyanopyridine (OCP), a terminating agent (eq 1). Because the attack of OCP to the cationic species (e.g. **I**) might be competitive with that of monomer styrene, the progress of the polymerization was retarded and molecular weight of the PSt was lowered, as the amount of the added OCP increased (Table 1).[15] From the polymerization mixture (Table 1, run 3), PSt with low molecular weight was collected, i.e. monomer, uninitiated MBCP, and PSt with high molecular weight range were cut off by recycling preparative GPC (polystyrene gel, chloroform solvent) followed by precipitation with hexane to afford **III** with a limited range of molecular weight as yellow powders in 33% yield.

Table 1. Effects of OCP on the molecular weight and dispersity of PSts in the cationic polymerization of styrene

Run	OCP %	Time h	Conv^a %	Yield^b %	$\overline{\text{Mn}}^c$	$\overline{\text{Mw}}/\overline{\text{Mn}}^c$
1	0	14	74	68	4800	2.73
2	1	36	44	37	1500	1.53
3	5	63	53	33^d	800	1.20
4	10	200	40	-	600	1.11

Solvent: CH_2Cl_2; Concentration of styrene was fixed to 1 M.
a Determined by proton NMR based on styrene.
b Methanol-insoluble polymers.
c Estimated by GPC based on polystyrene standards before precipitation.
d Separated yield by recycling preparative GPC followed by precipitation with hexane.



III
(eq 1)

IR (Figure 1) and NMR (Figure 2) spectra of **III** showed characteristic absorptions based on the polystyrene and pyridinium salt structure, especially 660 cm^{-1} corresponding to SbF_6^- group in IR and δ = 9.3-7.8 ppm corresponding to *o*-cyanopyridinium salts in ^1H NMR. Degree of polymerization estimated from the ^1H NMR (mean value determined using both the initiation and termination end signals) and from EA[16] data was 5.2 (n=4.2, the calculated $\overline{\text{Mn}}$=1002). Thus, the polymeric cationic species could be isolated and its structure was identified as **III**.

III was used as a cationic initiator for polymerization of glycidyl ethers such as *t*-butyl glycidyl ether (TBGE) to obtain a block copolymer (eq 2). The bulk polymerization proceeded smoothly at 60 °C and conversion reached 20 and 50 mol% with

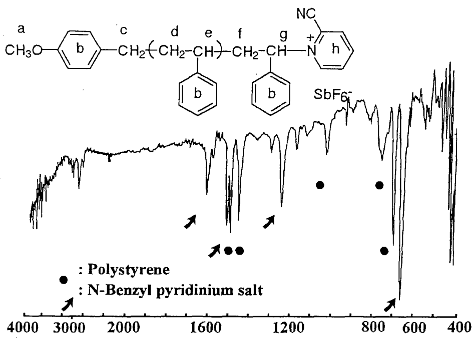


Figure 1. IR spectrum of **III**.

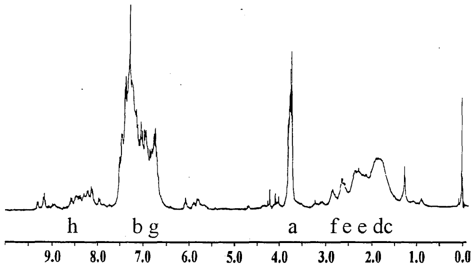


Figure 2. 300 MHz ^{1}H NMR spectrum of **III**.

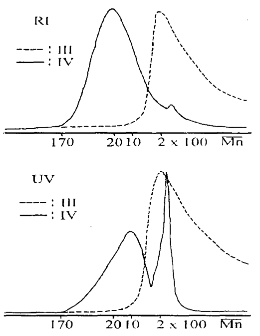
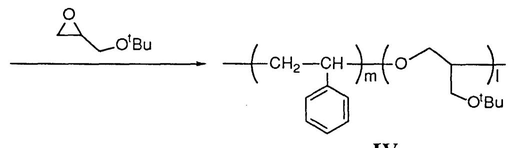


Figure 3. GPC trace of **III** and **IV**.

3 mol% of **III** for 2 and 8 h, respectively. In both cases, the obtained polymers showed new peaks in higher molecular weight region in both RI and UV detections of GPC. These new peaks support strongly that the obtained polymers consist of block copolymers of styrene and TBGE, and conversion of **III** was about 30% judging from the area of **III** and **IV** at UV detector of GPC even for 8 h. That is, at 60 °C it may be considered to be insufficient for the synthesis of block copolymer due to the lower initiation activity of **III**. In order to increase the initiation efficiency of **III**, the polymerization was conducted at 120 °C.

Polymerization proceeded rapidly and the conversion of TBGE reached 100% for 5 min. Figure 3 shows the GPC chart of the hexane-insoluble block copolymer. The composition ratio l/m calculated by the ^{1}H NMR was ca. 7.

III



IV (eq 2)

As shown in GPC chart of **III** and **IV**, the copolymerization resulted in the clear shift of the peak of **III** to a higher molecular weight region in both UV and RI detections which were responded each other. In UV detection, rather big peak of free OCP could be observed at lower molecular weight region, based on its big molar absorption at 253.7 nm. Since homopoly(TBGE) is transparent to UV, comparison of the two detections may suggest the competitive formation of homopoly(TBGE) from slightly different shape of the two peaks. Although it is not ruled out, another explanation can be made. Namely, the difference can be accounted for by the necessity that UV-sensitive groups (aromatic and pyridinium salt groups) are concentrated in the low molecular weight block copolymer which is formed in the final stage of polymerization at low concentration of TBGE. Therefore, concentration of UV-sensitive groups may be much higher in low molecular weight copolymer than in high molecular weight copolymer, in accordance with the GPC results.

In this study, the polymeric cationic species could be isolated in the cationic polymerization of styrene with an *N*-benzyl pyridinium salt by adding the corresponding pyridine. This species is considered as a terminated end with pyridinium salt and is active enough to initiate the cationic polymerization of an epoxide to easily obtain the corresponding block copolymer of styrene and epoxide.

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16 Anal. Calcd for $C_{55.6}H_{54.6}F_6N_2OSb$: H, 5.49; C, 66.63; N, 2.80 %. Found: H, 5.74; C, 66.57; N, 2.72 %.