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Communications to the Editor

Arenesulfonates as Non-Salt-Type Latent Thermal Initiators for Cationic Polymerization

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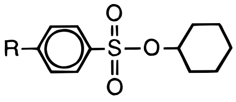
Introduction. External stimulation-induced polymerization is of special interest to control the initiation step of polymerization. Several onium salts having low nucleophilic counteranions are known to serve as efficient latent initiators in cationic polymerization. It has been shown by Endo et al. that sulfonium and pyridinium salts can be excellent latent thermal catalysts in the curing and polymerization of epoxy resins,[1] spiro ortho carbonates,[2] bicyclo ortho esters,[3] styrene,[4] and glycidyl phenyl ether.[5] However, from the viewpoint of material properties, these onium salts are poorly soluble in organic solvents and monomers, and some inorganic salts remain in the obtained polymeric materials. To improve the solubility of the latent initiator in ordinary organic compounds, it is necessary to design a novel latent initiator without salt structure. We have already reported polymerization of aziridines with *N*-substituted phthalimide[6] and that of olefins with carboxylic acid ester.[7] The designed arenesulfonates may be expected to serve as latent initiators in cationic polymerization because of their susceptibility to thermal heterolytic cleavage of the ester carbon−oxygen bond and the easy control of the thermal activity of the ester moiety by varing the component arenesulfonic acids. Cationic polymerization of vinyl monomers has generally been conducted at less than 30 °C due to the high reactivity of carbenium ions that participate in the chain propagation, and isomerization or transfer reactions proceed easily even at that temperature.[8−10] Cationic polymerization of vinyl monomers with arenesulfonate as a thermally latent catalyst has never been reported. In this paper, cationic polymerization of isobutyl vinyl ether (IBVE) with cyclohexyl arenesulfonates (**a**−**c**) is described to examine their thermal latency in the initiation.



a : R = NO_2
b : R = H
c : R = Me

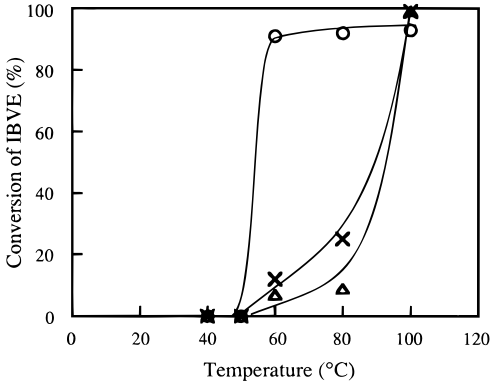
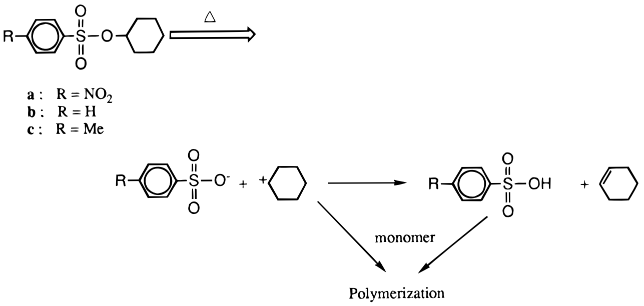


Figure 1. Effect of temperature on the conversion of IBVE in bulk polymerization of IBVE with **a**−**c** [**a**−**c**/IBVE = 0.01 (mole ratio); reaction time, 12 h]. (○) Cyclohexyl *p*-nitrobenzenesulfonate (**a**); (×) cyclohexyl benzenesulfonate (**b**); and (△)-cyclohexyl *p*-toluenesulfonate (**c**).

Scheme 1



Results and Discussion. Arenesulfonate derivatives (**a**−**c**) were selected as the candidate compounds for use as novel thermal latent initiators on the basis of the idea that they should readily undergo thermoinitiated heterolytic cleavage of the carbon−oxygen bond to give cationic and anionic species. It is advantageous that the thermal activity of the arenesulfonate may be easily controlled by varying the component of the sulfonate (Scheme 1). It has been known that cyclohexyl arenesulfonates decompose cleanly at moderate temperature to give cyclohexene in high yield.[11] Polymerization of IBVE will be initiated either by carbocationic species or by protic species, as shown in Scheme 1. Cyclohexyl arenesulfonates themselves may be finally transformed to the corresponding arenesulfonic acid and cyclohexene by thermal stimulation. The thermal behavior of **a** was confirmed by keeping **a** at 90 °C in benzene-d_6. In the thermal reaction of **a**, transformation of **a** into *p*-nitrobenzenesulfonic acid and cyclohexene was observed by ^{1}H NMR. Signals assignable to cyclohexene (5.7 ppm) and *p*-nitrobenzenesulfonic acid (9.25 ppm) increased with a decrease of **a** (4.50 ppm).[12] This result was the same as that in the polymerization system.

Arenesulfonate derivatives (**a**−**c**) were prepared by reaction of cyclohexanol with arenesulfonyl chlorides in pyridine at 0 °C.[13] The ability of **a**−**c** as thermally latent initiators was examined at 20−100 °C in bulk

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Table 1. Bulk Polymerization of IBVE with Arenesulfonates[a]

			high molecular weight polymer			low molecular weight polymer		
initiator	temp (°C)	conv (%)[b]	$\bar{M}_n$[c]	$\bar{M}_w/\bar{M}_n$[c]	yield (%)[d]	$\bar{M}_n$[c]	$\bar{M}_w/\bar{M}_n$[c]	yield (%)[d]
a	60	91	20000	2.4	50	800	1.5	41
	80	92	11000	3.3	31	800	1.5	61
	100	93	15000	2.3	35	500	1.7	58
b	60	12				400	1.0	12
	80	25				500	1.1	25
	100	99	9500	1.2	6	800	1.4	93
c	60	7				600	1.1	7
	80	9				800	1.5	9
	100	99				1300[e]	5.8	99

[a] Conditions of polymerization: initiator, 1 mol %; 12 h. [b] Determined by ^{1}H NMR. [c] Estimated by GPC (polystyrene standards). [d] Estimated by GPC area %. [e]Could not be estimated by GPC area % because of the overlap of the higher and lower molecular weight portions.

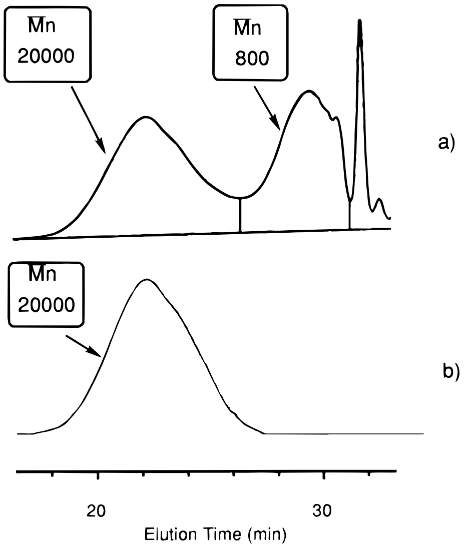
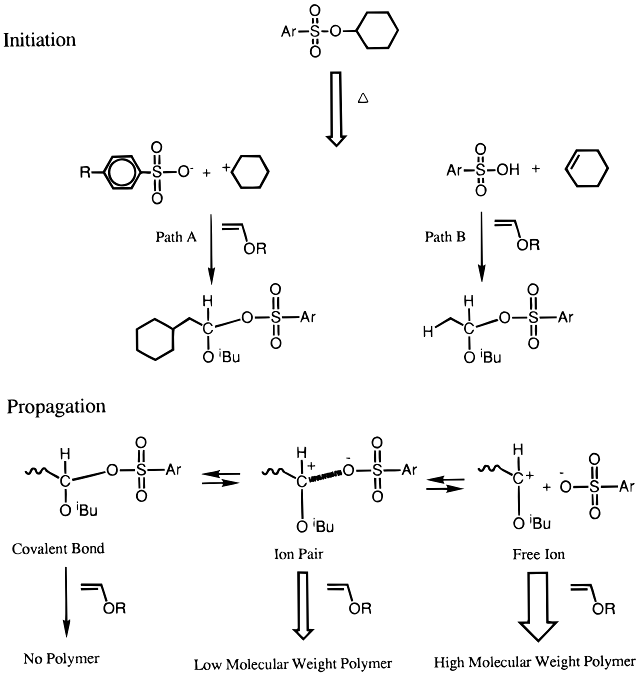


Figure 2. GPC curves of polyIBVE obtained by the polymerization with **a** (1 mol %) at 60 °C for 12 h. (a) Crude polymerization mixture. (b) Higher molecular weight part isolated by reprecipitation with methanol.

Scheme 2



for 12 h in the cationic polymerization of IBVE with 1 mol % of **a**−**c**. Without initiator, IBVE was not consumed upon heating at 100 °C for 12 h (Figure 1).

Figure 1 shows the effect of temperature on the polymerization of IBVE. The relation between temperature and conversion indicates the typical thermal latency of **a**−**c**. The rate of the polymerization rapidly increased above 60 °C for **a** and above 80 °C for **b** and **c**, whereas no polymerization proceeded below 50 °C (for **a**−**c**). As indicated by the temperature−conversion curves in Figure 1, the order of catalytic activity was clearly **a** ≫ **b** > **c** . The introduction of an electron-withdrawing substituent onto the benzene ring (p-NO_2) considerably lowered the initiation temperature. This is due to the higher stability of the sulfonate anion formed in the initial ionization and the higher acidity of sulfonic acid formed by the pyrolysis. As the control experiment, the polymerization of IBVE with **a** and p-nitrobenzenesulfonic acid was carried out in CH_2Cl_2 (0.5 M) at 40 °C for 24 h. p-Nitrobenzenesulfonic acid initiated the polymerization even at 40 °C in 100% conversion to afford the polymer with $\bar{M}_n = 4400$ and $\bar{M}_w/\bar{M}_n = 2.66$. This polymer showed a bimodal GPC curve (GPC area % of the higher molecular weight portion was 69.5%). However, **a** did not initiate the polymerization at 40 °C, which suggested the arenesulfonates served as latent thermal catalysts in the polymerization of IBVE.

Since **a**−**c** were soluble in IBVE at room temperature, the polymerization proceeded homogeneously. Table 1 summarizes the results of the polymerization.

Possible initiation species may be a carbocation (path A) from C−O bond cleavage or a proton (path B) from eliminated arenesulfonic acid (Scheme 2). Path B is supported not only by the presence of the signal for cyclohexene in the ^{1}H NMR spectrum of the polymerization system but also by the formation of polyIBVE in the polymerization of IBVE with benzenesulfonic acid at 100 °C in bulk for 1 min (conversion, 100%; yield, 47%; the $\bar{M}_n$ and $\bar{M}_w/\bar{M}_n$ were 1000 and 2.36, respectively). All polyIBVEs consisted of two different contributors to the molecular weight, as shown by their bimodal GPC curves (Figure 2). The higher molecular weight polymer was isolated by reprecipitation with methanol. The isolated yield was nearly equal to the GPC area % of the higher molecular weight portion of crude polyIBVE. These results suggest that two independent propagating species will participate in the polymerization. The propagating species that produces the higher molecular weight portion of the polymer may be more ionically dissociated than the other. These behaviors are known in the traditional cationic polymerization of olefins with trifluoromethanesulfonic acid.[14,15] Consequently, the mechanism in Scheme 2 seems plausible.

In conclusion, arenesulfonate derivatives (**a**–**c**), which are easily soluble in the monomer at room temperatureare, are found to be thermally latent initiators in the cationic polymerization of IBVE in bulk below 100°C. Among these initiators, cyclohexyl *p*-nitrobenzenesulfonate (**a**) showed the highest catalytic activity.

Supporting Information Available: ^{1}H NMR spectra of the reaction mixture in the thermal decomposition of **a** at 90 °C in C_6D_6 (1 page). Ordering information is given on any current masthead page.

References and Notes

(1) (a) Asahi Denka Kogyo, K. K. Jpn. Kokai Tokkyo Koho, 56-152,833, 1981. (b) Pappas, S. P.; Hill, L. H. *J. Coat. Technol.* **1981**, *53*, 43. (c) Pappas, S. P.; Feng, H. B. In *Cationic polymerization and Related Process*; Goethals, E. J., Ed.; Academic: New York, 1984; pp 325–333. (d) Morio, K.; Murase, H.; Tsuchiya, H.; Endo, T. *J. Appl. Polym. Sci.* **1986**, *32*, 5727.

(2) (a) Endo, T.; Arita, H. *Makromol. Chem., Rapid Commun.* **1985**, *6*, 137. (b) Endo, T.; Sato, H.; Takata, T. *Macromolecules* **1988**, *20*, 1416. (c) Takata, T.; Endo, T. *Macromolecules* **1988**, *21*, 900.

(3) (a) Endo, T.; Uno, H. *J. Polym. Sci., Polym. Lett. Ed.* **1985**, *23*, 359. (b) Uno, H.; Takata, T.; Endo, T. *J. Polym. Sci., Part A: Polym. Chem.* **1989**, *27*, 1675.

(4) (a) Uno, H.; Endo, T. *J. Polym. Sci., Part B: Polym. Lett.* **1988**, *26*, 453. (b) Uno, H.; Takata, T.; Endo, T. *Macromolecules* **1989**, *22*, 2502.

(5) Lee, S. B.; Takata, T.; Endo, T. *Macromolecules* **1990**, *23*, 431.

(6) Takata, T.; Menceloglu, Y. Z.; Endo, T. *J. Polym. Sci., Part A: Polym. Chem.* **1992**, *30*, 501.

(7) Moriguchi, T.; Nakane, Y.; Takata, T.; Endo, T. *Macromolecules* **1995**, *28*, 4334.

(8) (a) Higashimura, T. *Cationic Polymerization*; Kagaku Dojin: Kyoto, 1971 (in Japanese). (b) Pepper, D. C. *J. Polym. Sci., Polym. Symp.* **1975**, *50*, 51. (c) Kennedy, J. P. *Carbocationic Polymerization*; Wiley Interscience: New York, 1982.

(9) (a) Higashimura, T.; Kishiro, O. *J. Polym. Sci., Polym. Chem. Ed.* **1974**, *12*, 967. (b) Higashimura, T. *Polym. Prepr., Am. Chem. Soc. Div. Polym. Chem.* **1979**, *20*, 161.

(10) (a) Cotrel, R.; Sauvet, G.; Vairon, J. P.; Sigwalt, P. *Macromolecules* **1976**, *9*, 931. (b) Subira, F.; Sauvet, G.; Vairon, J. P.; Sigwalt, P. *J. Polym. Sci., Polym. Symp.* **1976**, *56*, 221.

(11) Corey, E. J.; Posner, G. H.; Nash, J. J. *J. Org. Chem.* **1989**, *54*, 389.

(12) See supporting information.

(13) Tipson, R. S. *J. Org. Chem.* **1944**, *9*, 235.

(14) Pepper, C. *Makromol. Chem.* **1974**, *175*, 1077.

(15) (a) Masuda, T.; Higashimura, T. *J. Polym. Sci., Part B: Polym. Lett.* **1971**, *9*, 783. (b) Masuda, T.; Higashimura, T.; Sawamoto, M. *Makromol. Chem.* **1976**, *177*, 2981. (c) Sawamoto, M.; Masuda, T.; Higashimura, T. *Makromol. Chem.* **1976**, *177*, 2995. (d) Sawamoto, M.; Masuda, T.; Higashimura, T.; Kobayashi, S.; Saegusa, T. *Makromol. Chem.* **1977**, *178*, 389. (e) Higashimura, T.; Sawamoto, M. *Adv. Polym. Sci.* **1984**, *62*, 50

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