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Photo-Induced Cationic Ring-Opening Polymerization of 2-Alkenyl-4-methylene-1,3-dioxolanes by Benzylsulfonium Salt

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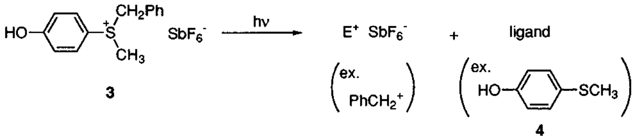
Introduction

Many functional polymers have been prepared by cationic and radical polymerizations of the 4-methylene-1,3-dioxolanes.[1−6] We have reported that the cationic polymerization of 2-alkenyl-4-methylene-1,3-dioxolane (**1**) afforded unsaturated polyketone **2** *via* quantitative ring-opening.[6−8] Further, we have found that addition of a nucleophilic compound in the polymerization system was highly effective in suppressing side reactions arising from the unsaturation of **2**.[9,10] The nucleophile acted as a ligand of the terminal cation and decreased its reactivity to depress the side reactions. It should be noted that nucleophilic compounds played an important role in the cationic living polymerization to suppress the chain-transfer reaction.[11]

Recently, considerable attention has been focused on "latent initiators"[12] that can generate reactive species to initiate polymerization by appropriate stimulation such as irradiation and heating. We have reported that benzyl onium salts, such as sulfonium, ammonium, pyridinium, and phosphonium salts, can act as efficient cationic latent initiators that polymerize various cationically polymerizable monomers.[13−19] In some cases, generation of the benzyl cation in the initiation process has been proved.[13,14] Apparently, the release of the corresponding nucleophile was accompanied by initiation, and we have succeeded in controlling the polymerization using such a nucleophile as a stabilizer of the terminal cation.[20] Sulfonium salt **3** is a useful latent initiator that initiates cationic polymerization by not only heating[21] but also irradiation.[22] In some cationic polymerization systems initiated by **3**, decomposition of **3** into the benzyl cation that initiated the cationic polymerization and 4-(methylthio)phenol (**4**) was confirmed.[21,23] On the basis of these results, our interest was focused on the polymerization of **1** with **3**, in which the side reactions were expected to be suppressed by the nucleophilic species such as **4** released from **3** in the initiation step.

We have communicated a preliminary result of photo-induced cationic polymerization of **1a** by **3**.[24] In this paper, we wish to describe details of successful photo-induced cationic polymerization of **1** using **3** and wish to emphasize that the cationic polymerization using a latent initiator can be a novel method to control the cationic polymerization to suppress side reactions (e.g., chain-transfer reaction).

Scheme 1



Results and Discussion

Photo-Induced Cationic Polymerization of 1. The cationic polymerization of **1** with **3** was carried out at ambient temperature under irradiation, and the results are summarized in Table 1. The results of the cationic polymerization initiated by methanesulfonic acid without irradiation are also shown in Table 1.

Although polymerization of **1** by **3** did not occur without irradiation, rapid polymerization proceeded by irradiation. The polymerization initiated by **3** afforded a polymer that is completely soluble in dichloromethane. When methanesulfonic acid was used as an initiator, soluble polymer was obtained at −78 °C, although completely insoluble polymer was obtained at ambient temperature. Further, when trifluoromethanesulfonic acid was used as an initiator, soluble polymer could not be obtained even at −78 °C because of the low nucleophilicity of the trifluoromethanesulfonate anion.[7,8] Since the hexafluoroantimonate anion has no nucleophilicity, the cross-linking reaction accompanying the cationic polymerization of **1** was effectively suppressed by the use of latent initiator **3** under irradiation.

^{1}H-NMR spectra of the polymers clearly showed that the expected polymer **2** was obtained.[7,8] Thus, cationic polymerization of **1** initiated by **3** under irradiation took place in the same manner as that initiated by methanesulfonic acid at −78 °C. The ratio of repeating units I and II could be estimated from ^{1}H-NMR spectra using integrations of corresponding olefin protons. The ratio of the integration of the olefin protons to that of the other protons was smaller than that expected from the unit structures I and II. Further, a decrease of olefin content was accompanied by an increase of unexpected signals around δ 1.0 ppm that appeared to be derived from a saturated unit. These results indicated that side reactions arising from unsaturation of **2** could not be completely suppressed by the nucleophile released from **3** in the initiation step.

When **1a** was used as a monomer with **3**, $\bar{M}_n$ and $\bar{M}_w/\bar{M}_n$ gradually increased with conversion. In the case of cationic polymerization of **1a** initiated by trifluoromethanesulfonic acid in the presence of nucleophilic compounds, $\bar{M}_w/\bar{M}_n$ was almost constant during the polymerization.[9] Therefore, in the case of a latent initiator system, the intermolecular cationic reaction arising from unsaturation of **2a** was accompanied by polymerization because the concentration of the counter ligand in the polymerization system was rather low. Since the ratio of x and y was about 65:35 in every run, the reactivity of units I and II toward the terminal cation should be similar. As reported previously, cationic polymerization of **1a** always afforded **2a**, whose unit ratio was 65:35 to 70:30.[8−10]

When **1b** was used as a monomer with **3**, an increase of $\bar{M}_n$ and $\bar{M}_w/\bar{M}_n$ with conversion was also observed. Further, y in **2b** decreased with conversion, while x in **2b** was almost constant. The values of x were closely

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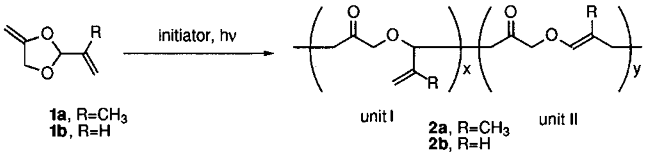
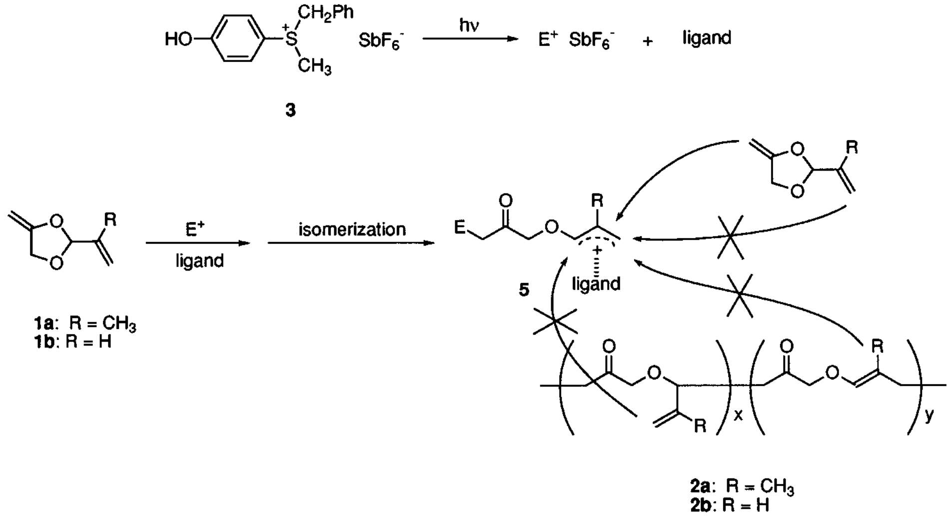
Table 1. Cationic Polymerization of 1 with 3 under Irradiation[a]



monomer	initiator	temp (°C)	time (min)	conversion[b] (%)	yield[c] (%)	$\bar{M}_n$[d]	$\bar{M}_w/\bar{M}_n$[d]	composition[e] x	y	olefin content (%)
1a	CH_3SO_3H[f]	rt	5	100	100[g]					
1a	CH_3SO_3H[f]	−78	90	100	88	4500	4.3	39	17	56
1a	**3**[f]	rt	180	0	0					
1a	**3**	rt	5	40	24	3900	1.8	57	32	89
1a	**3**	rt	30	73	64	4700	2.8	54	27	81
1a	**3**	rt	60	100	76	5000	*h*	50	23	73
1b	CH_3SO_3H[f]	rt	5	100	100[g]					
1b	CH_3SO_3H[f]	−78	960	100	78	4000	2.1	68	31	99
1b	**3**	rt	5	44	31	4300	1.8	66	27	93
1b	**3**	rt	30	71	60	5800	2.3	65	25	90
1b	**3**	rt	60	100	80	7100	2.6[h]	66	14	80

[a] Irradiation with a 300 W high-pressure mercury lamp through a Pyrex filter in dichloromethane. [b] Estimated by weight after evaporation. [c] *n*-Hexane-insoluble part. [d] Estimated by GPC calibrated with polystyrene standards. [e] Estimated by ^{1}H-NMR spectra. [f] Without irradiation. [g] Cross-linked polymer. [h] Bimodal GPC curve.

Scheme 2



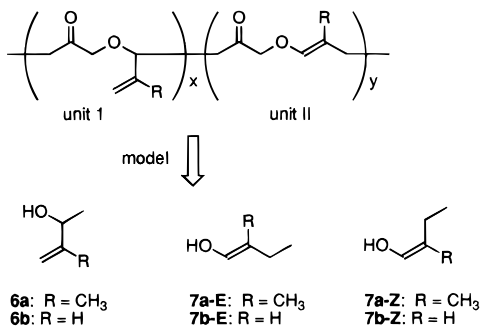
related to that of **2b** obtained by methanesulfonic acid at −78 °C, where the olefin content was 100%.[7] Since unit I of **2b** is a monosubstituted simple olefin, it is far less nucleophilic than unit II of **2b** and the olefins in **2a**. Therefore, unit I of **2b** hardly reacted with the terminal cation in these polymerization conditions. On the other hand, the cationic reaction of unit II of **2b** occurred when **3** was used as a latent initiator at ambient temperature because of the low concentration of the counter ligand. It is interesting that the cationic polymerization of **1b** with **3** afforded **2b**, whose unit ratio was almost same as that of **2a**.

Possible Mechanism of Photo-Initiated Cationic Polymerization. Latent initiator **3** decomposed by irradiation to generate some cationic species and counter ligands.[25] The benzyl cation is the most plausible cationic species, and sulfide **4** is the most plausible nucleophilic ligand, although we cannot exclude other possibilities. Thus, a cationic species generated on photolysis added to the vinyl ether group of monomer **1**, and the following isomerization afforded terminal oxyallyl cation **5**. The counter ligand generated at the initiation step may interact with **5** to stabilize it. This stabilization prevents the nonselective attack of the terminal cation on the less reactive olefins, the alkenyl group of the monomer and/or those of the polymer, even at ambient temperature. Since the latent initiators are stable without suitable stimulation, control of cationic polymerizations of highly reactive monomers may be easily performed using latent initiators.

The ratio of units I and II (65:35 to 70:30) was almost independent of the polymerization conditions.[7−10] These results suggest that the unit ratio was not controlled by the thermodynamic stability of the two unit structures. To evaluate this speculation, the heat of formation of each unit structure was calculated by the semiempirical molecular orbital method using the program MOPAC with a PM3 Hamiltonian.[26] To simplify the calculation, calculations were made for **6** and **7** as the model structure of each unit structure. Calculations were made for all possible conformers, and heats of formation of the most stable conformers are shown in Scheme 3. Isomer **6** was more stable than **7**, indicating that unit II is thermodynamically more favored, although unit I was dominant in the real polymerization system.

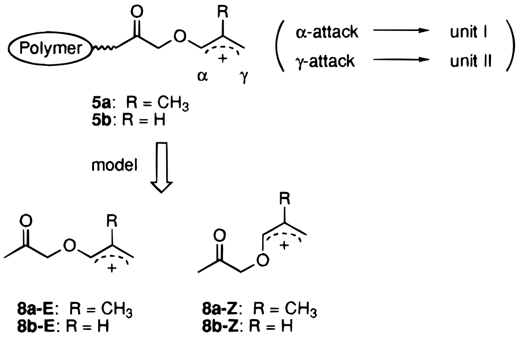
These results suggest that the unit ratio was kinetically controlled, *i.e.*, the rate of the attack of the monomer to the α- and γ-positions of the terminal cation **5**. To evaluate this speculation, molecular orbital calculation was made for **8**, which is the model cation of **5**. Calculations were attempted for all possible conformers, and coefficients of LUMO of the most stable conformer of every stereoisomer are shown in Scheme 4.

Scheme 3



model compound	Heat of formation (kcal/mol)
6a	-46.19
7a-E	-51.47
7a-Z	-51.32
6b	-37.75
7b-E	-43.61
7b-Z	-42.66

Scheme 4



model cation	coefficient of LUMO	
	α-position	γ-position
8a-E	0.7314	-0.5552
8a-Z	0.7352	-0.5529
8b-E	0.7170	-0.5688
8b-Z	0.7266	-0.5646

In every case, the coefficient of LUMO at the α-position was larger than that at the γ-position. Further, the methyl group at the β-position hardly affected the coefficient of the LUMO. These results suggest that nucleophilic attack of the monomer at the α-position of **8** as well as **5** should take place prior to that at the γ-position. Consequently, the unit ratio of **2** was independent of the polymerization condition because the regioselectivity was based on the electronic nature of the terminal oxyallyl cation **5**.

Allenyl ethers undergo cationic polymerization, where the terminal cation was the oxyallyl cation as well as **1**.[27] The resulting polymer has two repeating units, and it is very interesting that propagation by the attack of the monomer at the α-position is dominant. We can propose that the regioselectivity of the polymerization of which the terminal cation was the oxyallyl cation may be controlled by the electronic nature of the terminal cation, *i.e.*, the coefficient of LUMO.

Experimental Section

Materials. **1a** and **1b** were synthesized as reported previously.[7,8] **3** was purchased from Sanshin Chemical Co. and used without further purification.[24] Dichloromethane was used after distillation from phosphorus pentoxide.

Photo-Initiated Polymerization of 1a. To a solution of 0.50 g (4.0 mmol) of **1a** in 7 mL of dry dichloromethane was added 1.0 mL solution of **3** in dichloromethane (2×10^{-5} mol/L, 0.5 mol %). The reaction tube (Pyrex) was flushed with argon and was irradiated with a 300 W high-pressure mercury arc lamp at room temperature (>300 nm). After the reaction was quenched by the addition of pyridine, the reaction mixture was evaporated to dryness under reduced pressure. Monomer conversion was determined by its residual weight after evaporation. The crude product was dissolved in dichloromethane (5 mL), and the solution was poured into a large amount of hexane to precipitate the polymer. After the hexane layer was removed by decantation, the precipitate was dried under vacuum to obtain polymer **2a**.

Photo-Cationic Polymerization of 1b. To a solution of 0.46 g (4.0 mmol) of **1b** in 7 mL of dry dichloromethane was added 1.0 mL solution of **3** (2×10^{-5} mol/L, 0.5 mol%). Following treatment was as same as the case of **1a**.

Supporting Information Available: Figure S1, ^{1}H-NMR spectra of **2a** (1 page); Figure S2, ^{1}H-NMR spectra of **2b** (1 page); Table S1, the conformations and heat of formations of the most stable conformer of every stereoisomer of **6** and **7** (2 pages); Table S2, the conformations and coefficients of LUMO of the most stable conformer of every stereoisomer of **8** (2 pages). Ordering information is given on any current masthead page.

References and Notes

(1) Goodman, M.; Abe, A. *J. Polym. Sci., Part A: Polym. Chem.* **1964**, *2*, 3471.
(2) Yokozawa, T.; Hayashi, R.; Endo, T. *J. Polym. Sci., Part A: Polym. Chem.* **1990**, *28*, 3739.
(3) Yokozawa, T.; Hayashi, R.; Endo, T. *Macromolecules* **1992**, *9*, 2776.
(4) Park, J.; Choi, W.-M.; Kihara, N.; Endo, T. *J. Polym. Sci., Part A: Polym. Chem.* **1994**, *32*, 983.
(5) Sugiyama, J.; Yokozawa, T.; Endo, T. *J. Polym. Sci., Part A: Polym. Chem.* **1990**, *28*, 3529.
(6) Sugiyama, J.; Ueda, M.; Endo, T. *Macromolecules* **1995**, *28*, 6735.
(7) Park, J.; Yokozawa, T.; Endo, T. *Makromol. Chem.* **1993**, *194*, 2017.
(8) Park, J.; Yokozawa, T.; Endo, T. *J. Polym. Sci., Part A: Polym. Chem.* **1993**, *31*, 1141.
(9) Park, J.; Kihara, N.; Kobayashi, M.; Endo, T. *J. Polym. Sci. Part A: Polym. Chem.* **1994**, *32*, 199.
(10) Park, J.; Kihara, N.; Endo, T. *Makromol. Chem. Phys.* **1996**, *197*, 2455.
(11) Higashimura, T.; Aoshima, S.; Sawamoto, M. *Makromol. Chem., Makromol. Symp.* **1988**, *13/14*, 457.
(12) Crivello, J. V. *Adv. Polym. Sci.* **1984**, *62*, 1.
(13) Takata, T.; Endo, T. *Yuki Gosei Kagaku Kyokaishi* **1990**, *48*, 978.
(14) Sanda, F.; Endo, T. *Kobunshi* **1996**, *45*, 128.
(15) Uno, H.; Endo, T. *J. Polym. Sci., Part C: Polym. Lett.* **1985**, *23*, 359.
(16) Uno, H.; Endo, T. *Chem. Lett.* **1986**, 1869.
(17) Endo, T.; Sato, H.; Takata, T. *Macromolecules* **1987**, *20*, 1416.
(18) Morio, K.; Murase, H.; Endo, T. *J. Appl. Polym. Sci.* **1986**, *32*, 5727.
(19) Kikkawa, A.; Takata, T.; Uno, H.; Hiza, M.; Endo, T. *J. Polym. Sci., Part C: Polym. Lett.* **1989**, *26*, 73.
(20) Lee, S.-B.; Takata, T.; Endo, T. *Chem. Lett.* **1989**, 1861.
(21) Hamazu, F.; Akashi, S.; Koizumi, T.; Takata, T.; Endo, T. *J. Polym. Sci., Polym. Chem. Ed.* **1991**, *29*, 1675.
(22) Hamazu, F.; Akashi, S.; Koizumi, T.; Takata, T.; Endo, T. *Makromol Chem., Rapid Commun.* **1992**, *13*, 203.
(23) Lin, M.-P.; Kim, H.-B.; Ikeda, T.; Endo, T. *J. Polym. Sci., Part A: Polym. Chem.* **1992**, *30*, 2365.
(24) Park, J.; Kihara, N.; Ikeda, T.; Endo, T. *J. Polym. Sci. Part A: Polym. Chem.* **1993**, *31*, 1083.
(25) Saeva, F. D.; Breslin, D. T.; Luss, H. R. *J. Am. Chem. Soc.* **1991**, *113*, 5333.
(26) Stewart, J. J. P. *J. Comput. Chem.* **1989**, *10*, 209.
(27) Takahashi, T.; Yokozawa, T.; Endo, T. *Macromolecules* **1995**, *28*, 866.

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