

## Photo-Induced Cationic Ring-Opening Polymerization of 4-Methylene-2-styryl-1,3-dioxolane by Benzylsulfonium Salt

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Received February 28, 2001

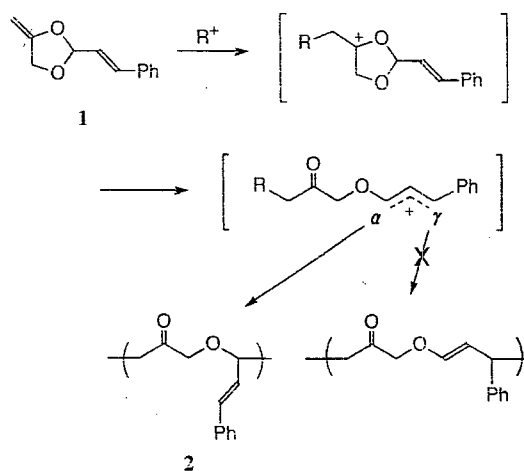
**Abstract :** One of the approaches to obtain functional polymer is polymerization of a monomer having two functional groups. Although polymerization of a monomer having two different types of functional group is general, the author has been interested in the polymerization of a monomer having two similar types of functional group. This work shows the preparation and selective polymerization of 4-methylene-2-styryl-1,3-dioxolane having two similar reactive double bonds via cationic polymerization at ambient temperature. Cationic ring-opening polymerization of 4-methylene-2-styryl-1,3-dioxolane using benzylsulfonium salt as a photo-initiator quantitatively afforded high molecular weight of poly(keto-ether).

### Introduction

Although polymerization of monomer having two polymerizable carbon-carbon double bonds usually produces crosslinked insoluble polymers, useful reactive and/or functional polymers may be synthesized from such monomers by selective polymerization of one of these double bonds.<sup>14</sup> We have reported successful cationic polymerization of unsaturated 1,3-dioxolane **1** having two polymerizable double bonds at  $-78^{\circ}\text{C}$  to afford poly (keto-ether)s **2** consisting saturated main chain and pendent double bond as shown in Scheme I.<sup>5-7</sup> However, this polymerization produced insoluble polymer in common solvents at ambient temperature resulting from the production of cross-linked product by further reaction of active carbenium with the pendent double bonds under vigorous conditions.

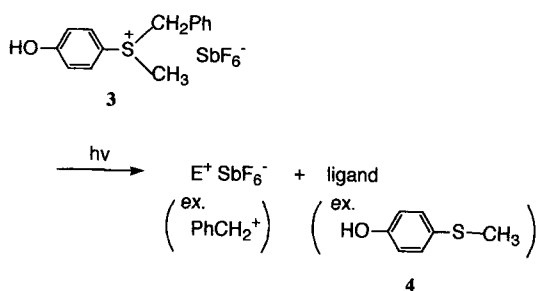
Recently, considerable attention has been focused on latent initiators<sup>8</sup> that can generate reactive species to initiate polymerization by appropriate stimulation such as irradiation and heating. We have reported that benzyl onium salts, such as sulfonium, ammonium, pyridinium, and phosphonium salts, acted as efficient cationic latent initiators polymeriz-

ing several monomers.<sup>9-15</sup> In some cases, generation of the benzyl cation in the initiation process was observed and the release of the corresponding nucleophile was simultaneously accompanied as shown in Scheme II.<sup>9,10</sup> Thus, it was successful to the polymerization using the nucleophile as a stabilizer of the terminal cation.<sup>16</sup> Sulfonium salt **3** is a useful latent initiator cationic polymerization by not only heating<sup>17</sup> but also irradiation.<sup>18</sup> In some cationic polymerization systems initiated by **3**, decomposition of **3** into the benzyl cation poly-



Scheme I

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merizing 4-(methylthio)phenol **4** was confirmed.<sup>17,19</sup>

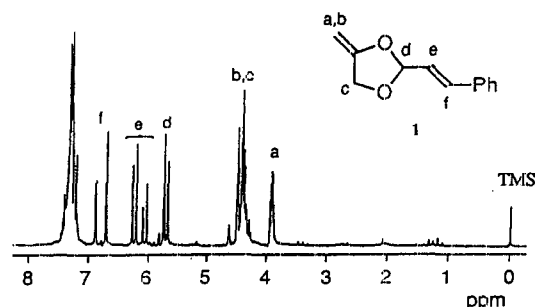
In this communication, we will report the results for successful photo-induced initiation of **1** using **3**, followed by cationic polymerization using a latent initiator as a novel method to suppress side reactions (e.g., chain-transfer reaction) at ambient temperature.

## Experimental

**Materials.** Sulfonium salt **3** was purchased from Sanshin Chemical Co. and used without further purification. Dichloromethane was used after distillation from phosphorus pentoxide.

**4-Chloromethyl-2-styryl-1,3-dioxolane (7).** A solution of 70 g (0.53 mol) of cinnamaldehyde, 62.4 g (0.5 mol) of 3-chloro-1,2-propanediol, and 3.4 g (1.8 mmol) of *p*-toluenesulfonic acid monohydrate was refluxed in 160 mL of benzene to remove the water by a Dean-Stark decantator. After no more water was distilled off, 5 g (4.9 mmol) of triethylamine was added to the reaction mixture. The solution was washed with aqueous sodium bicarbonate solution, followed by washing with distilled water. After the organic layer was dried by  $MgSO_4$ , benzene was removed at reduced pressure. The remaining black oil was distilled to obtain 79.6 g (62%) of 4-chloromethyl-2-styryl-1,3-dioxolane as colorless oil; bp 128°C/0.7 mmHg.

**4-Methylene-2-styryl-1,3-dioxolane (1).** 18.8 g (0.1 mol) of 4-chloromethyl-2-styryl-1,3-dioxolane in 100 mL of tetrahydrofuran (THF) was added dropwise into a solution of 24.7 g (0.22 mol) of potassium *tert*-butoxide in 100 mL of THF at 0°C for 1 h, the reaction mixture was poured into



**Figure 1.**  $^1H$ -NMR spectra of **1** ( $CDCl_3$ , 90 MHz).

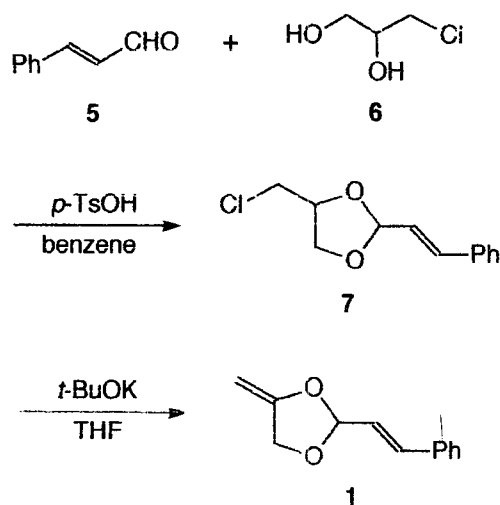
water, and was extracted with ether. The organic layer was combined, washed with water, and evaporated under reduced pressure before distillation to obtain 15.0 g (80%) of **1** as colorless oil; bp 111°C/1 mmHg

$^1H$ -NMR (90 MHz,  $CDCl_3$ ):  $\delta$ 7.47-7.07(m, 5H), 6.79(d, 1H), 6.15(dd, 1H), 4.60-4.25(m, 3H), 4.00-3.80(m, 1H) ppm (Figure 1).

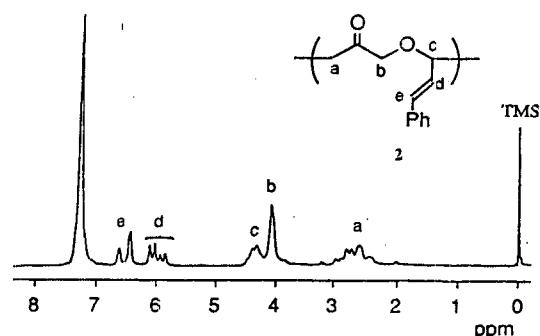
**Photo-Induced Polymerization of 1.** A solution of 0.50 g (4.0 mmol) of **5** in 7 mL of dry dichloromethane was added into 1.0 mL solution of **3** in dichloromethane ( $2 \times 10^{-5}$  mol/L, 0.5 mol %). The reaction tube (Pyrex) was flushed with argon and was irradiated with a 300 W high-pressure mercury arc lamp at room temperature (>300 nm). After the reaction was quenched by the addition of pyridine, the reaction mixture was evaporated to dry under reduced pressure. Monomer conversion was determined by its residual weight after evaporation. The crude product was dissolved in dichloromethane (5 mL), the solution was then 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 **2**.

## Results and Discussion

4-Methylene-2-styryl-1,3-dioxolane **1** was prepared by acetalization of cinnamaldehyde **5** with 3-chloro-1,2-propanediol **6** catalyzed by *p*-toluenesulfonic acid, followed by dehydrochlorination with potassium *tert*-butoxide as shown in Scheme III. The overall yield was 50% based on the incipient amount of raw reagents used.



The cationic photopolymerization of **1** with **3** was carried out at ambient temperature by irradiation under several conditions. The results are summarized in Table I. The results for the cationic polymerizations initiated by methanesulfonic acid without irradiation are also shown in Table I. Although polymerization of **1** by **3** did not occur without irradiation, rapid polymerization proceeded by irradiation. The resulting polymer is completely soluble in dichloromethane. Since the hexafluoroantimonate anion exhibits very low nucleophilicity, it was found that the cross-linking reaction accompanying the cationic photopolymerization of **1** was effectively suppressed by the



**Figure 2.**  $^1\text{H-NMR}$  spectra of **2**( $\text{CDCl}_3$ , 90 MHz).

use of latent initiator **3** under irradiation. Electrophilic active counter can attack at both corresponding  $\alpha$ - and  $\gamma$  position in the case of cationic photopolymerization of **1**. However, phenyl group and counter ion generated from **3** after irradiation prevent the active counter from addition into  $\gamma$  position. Figure 2 shows the  $^1\text{H-NMR}$  spectra of the polymer obtained. As the area ratio of aromatic protons and olefinic protons was 5:2, it was confirmed that the polymer consisted of only single unit bearing pendent double bond group **2**. When **1** was used as a monomer with **3**, the number average molecular weight ( $\overline{M}_n$ ) and polydispersity ( $\overline{M}_w/\overline{M}_n$ ) gradually increased with conversion as shown in Table I.

**Possible Mechanism of Photo-induced Cationic Polymerization.** The latent initiator **3** decomposed by irradiation seems to generate some cationic species and counter ligands. The benzyl

**Table I. Cationic Polymerization of 1 with 3 under Irradiation<sup>a</sup>**

Run	Initiator(mol%)	Temp.	Time	Conv. <sup>b</sup>	Yield <sup>c</sup>	$\overline{M}_n(\overline{M}_w/\overline{M}_n)^d$
		°C	min	%	%	
1	$\text{CH}_3\text{SO}_3\text{H}(2)^e$	-78	90	100	94	12000(2.06)
2	$\text{CH}_3\text{SO}_3\text{H}(2)^e$	rt.	5	100 <sup>f</sup>	--	
3	<b>3</b> <sup>e</sup>	rt.	180	0	0	
4	<b>3</b>	rt.	5	48	32	6700(1.32)
5	<b>3</b>	rt.	30	87	72	12800(2.07)
6	<b>3</b>	rt.	60	100	94	18000(2.94)

<sup>a</sup>Irradiation with a 300 W high-pressure mercury lamp through a pyrex filter in dichloromethane.

<sup>b</sup>Estimated by weight after evaporation. <sup>c</sup>*n*-Hexane-insoluble part.

<sup>d</sup>Estimated by GPC calibrated with polystyrene standards.

<sup>e</sup>Without irradiation. <sup>f</sup>Cross-linked polymer.

cation is the most plausible cationic species and the sulfide **4** is the most plausible nucleophilic ligand. Thus a cationic species generated on photolysis added to the vinyl ether group of monomer **1**, and the following isomerization afforded terminal oxyallyl cation. The counter ligand generated at the initiation step may interact with oxyallyl cation to stabilize it. This stabilization prevents the nonselective attack of the terminal cation on the less reactive olefins arising from steric hindrance even at ambient temperature. Since the latent initiators are stable without suitable stimulation, control of cationic polymerizations of highly reactive monomer may be easily performed using latent initiators even at ambient temperature.

### Summary

Photo-induced cationic ring-opening polymerization of **1** quantitatively afforded high molecular weight of poly(keto-ether) **2** which consisted of single unit even at ambient temperature. The introduction of latent initiator shows not only complete suppression of side reaction but also complete regioselectivity.

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