Cationic Double Isomerization Polymerization of 4-Methylene-2-phenyl-2-styryl-1,3-dioxolane Catalyzed by Acidic Silica Gel

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ABSTRACT: Cationic polymerization of 4-methylene-2-phenyl-2-styryl-1,3-dioxolane (**1**) was carried out. Monomer **1** was very sensitive to acid, and even the glass surface afforded polymer **2**. Acidic glass or silica gel was also a good catalyst for the formation of the high $\bar{M}_n$ polymer ($\bar{M}_n$ = 54 000−340 000). The polymerization proceeded through selective cationic double isomerization (ring-opening/allyl isomerization) and gave a 1,7-addition polymer. Polymer **2** can be degraded by water or amine.
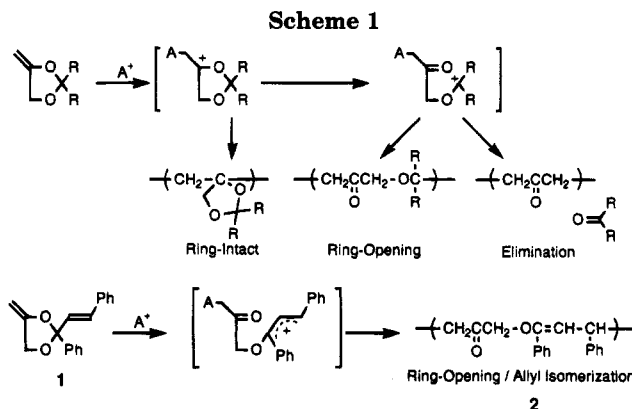
Introduction

Cationic ring-opening polymerization of 4-methylene-1,3-dioxolanes proceeds through several reaction modes, such as ring-intact, ring-opening, elimination, and other unsettled behaviors.[1−6] Thus, the structure of the resulting polymers is very complicated. Recently, we have found that the cationic polymerization of 4-methylene-2-phenyl-2-styryl-1,3-dioxolane (**1**) can afford a selective 1,7-addition polymer (**2**) through the ring-opening/allyl isomerization mode, as shown in Scheme 1.[7] The polymerization behavior can be explained for the stabilization of allyl cation with two phenyl groups and one alkoxy group. In our previous study, it was found that trifluoroacetic acid, trifluoromethanesulfonic acid, and boron trifluoride etherate could catalyze the polymerization of **1** with high conversion. However, the number average molecular weights ($\bar{M}_n$'s) of the polymers were very low (1700−3200), estimated by GPC based on the polystyrene standard. Recently, we found the acid-pretreated glass vessel or silica gel could afford a higher molecular weight polymer ($\bar{M}_n$ = 54 000−340 000) and polymer **2** was degraded by water at ambient temperature. Herein we wish to report this remarkable silica gel catalyzed polymerization and the hydrolysis behavior of the polymer **2**.

Experimental Section

Measurements. IR spectra were recorded on a Hitachi I-5020 FT-IR spectrophotometer. NMR spectra were obtained on a JEOL JNM-EX270 (270 MHz) spectrometer. Molecular weights were determined by a gel permeation chromatograph (GPC) based on standard polystyrenes using a JASCO TR-IROTAR-III system equipped with Shodex KF-800P and KF-80M columns at 40 °C in tetrahydrofuran.

Materials. Monomer **1** was prepared by a previous method.[7] Other reagents were obtained commercially and used as received.

Catalyst and Vessels. The catalyst silica gel (Merck, silica gel 60 (70−230 mesh)) was pretreated by dipping in H_2O_2/concentrated H_2SO_4 (1:10) for 12 h, then washing with distilled water and methanol, and drying at 80 °C for 1 h under reduced pressure. Reaction vessel A was a Pyrex glass tube pretreated

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Scheme 1

by dipping in H_2O_2/concentrated H_2SO_4 (1:10) for 12 h and then washing with a large amount of distilled water and methanol. Reaction vessel B was also pretreated in a manner similar to that of vessel A, followed by washing with NaHCO₃-saturated aqueous solution, distilled water, methanol/triethylamine (200:1), and methanol. Reaction vessel C was also pretreated in a manner similar to that of vessel B with potassium *tert*-butoxide/methanol (0.1 g/mL) instead of NaHCO₃-saturated aqueous solution.

Polymerization. Polymerization was carried out in vessel A or B under a N₂ atmosphere. After a specified time, CH₂Cl₂/Et₃N (10:1) was added to quench, and catalyst was filtered off through pressed cotton. Polymer was collected as an insoluble powder in MeOH/Et₃N (200:1).

Results and Discussion

Homopolymerization of 1. Cationic polymerization of **1** was carried out in bulk. The results are summarized in Table 1. Reaction glass vessels had been dipped in a H_2O_2/concentrated H_2SO_4 mixture to decompose any organic contaminants. The polymerization took place both in non-neutralized vessel A and in neutralized vessels B and C. In vessel A, monomer **1** without any additives converted to polymer **2** in 36% yield although the vessel had been washed with a large amount of distilled water (run 1). On the other hand, the polymerization was depressed in neutralized vessel B under the same conditions, yielding polymer **2** in only 3% yield (run 6). It means that monomer **1** is very sensitive to acid and the pretreatment of the vessel by acid gives the catalysis activity to the glass surface, which cannot be quenched without neutralization. The initiation species might be protons of residual sulfuric acid or silicic acid of the glass surface.

Table 1. Cationic Polymerization of 1

run	vessel[a]	temp, °C	time, h	amt of catalyst, wt %	yield,[b] wt%	high area[c] $\bar{M}_n$	high area[c] $\bar{M}_w/\bar{M}_n$	all area[c] $\bar{M}_n$	all area[c] $\bar{M}_w/\bar{M}_n$
1	A	80	48		36	212 000	2.7	58 000	8.9
2	B	80	12	10	62	54 000	2.4	6 000	14.3
3	B	25	12	10	60	189 000	2.3	15 000	18.9
4	B	25	6	10	59	305 000	2.0	11 000	2.7
5	B	25	6	2	44	343 000	1.8	12 000	22.0
6	B	80	48		3	133 000	3.0	83 000	4.6
7[d]	C	80	48		trace				

[a] A: washed with H_2O_2/H_2SO_4 and water. B: same as A followed by $NaHCO_3$, Et_3N treatment. C: same as A followed by *t*-BuOK treatment. [b] Insoluble parts in methanol. [c] Estimated by GPC (based on standard polystyrene). [d] Yield of **6**: 28%.
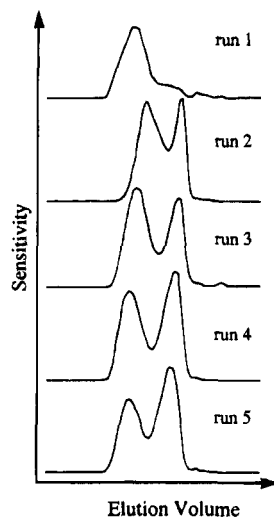

Figure 1. GPC curves of polymer **2**.

Using vessel C which was washed by potassium *tert*-butoxide in methanol, monomer **1** converted to 4,5-dihydro-5,7-diphenyl-3(2*H*)-oxepinone (**6**) in 28% yield and a few polymers that could not be collected as an insoluble part in methanol (run 7). It indicated that treatment of the vessel by a strong base could also depress the polymerization but might cause a side reaction.

When the stirring was not vigorous, the active surface of the vessel was overlaid with the polymer obtained and most of the monomer could not be converted. In order to disperse the active site, acid-pretreated silica gel was used for a catalyst instead of the acidic surface of the vessel. As soon as silica gel was added into the monomer, particles of the white silica gel turned red-orange. Each polymerization system in runs 2–5 became viscous in 1–2 h and then solidified. It showed the acidic silica gel also acts as the catalyst and affords polymers in higher conversions (44–62%).

The structure of the polymers obtained in Table 1 was of the 1,7-addition type, confirmed by ¹H and ¹³C NMR and IR spectroscopy coincident with the reported spectra.[7] It means that polymerization occurs through a double isomerization (ring-opening/allyl isomerization) mode. GPC curves for all the polymers were bimodal, shown in Figure 1. The bimodal products could be fractionated by GPC; then it is confirmed that the ¹H NMR spectrum of each fraction agrees with the spectrum of the original polymer. It means the each fraction has the same structure but only $\bar{M}_n$ is different. Higher $\bar{M}_n$ area peaks indicated $\bar{M}_n$ values of 50 000–340 000, which were unprecedentedly high values as compared with previous polymers $\bar{M}_n$ values obtained from other 4-methylene-1,3-dioxolanes.[1-6]

A derivative of monomer **1**, 4-methylene-2-phenyl-1,3-dioxolane (**3**) was also polymerized by the silica gel

**Scheme 2**
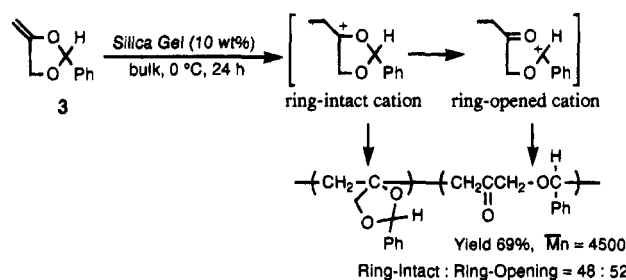
Table 2. Solution Polymerization of 1[a]

run	solvent, (concn, mol L⁻¹)	temp, °C	time, h	yield,[b] wt %	$\bar{M}_n$[c]	$\bar{M}_w/\bar{M}_n$[c]
8	CH_2Cl_2 (10)	25	1	86	6000	2.6
9	CH_2Cl_2 (1)	25	2	68	4100	1.8
10	dioxane (10)	25	1	46	1500	1.7
11	dioxane (10)	80	1	2	400	2.1
12	dioxane (1)	80	1	0		

[a] Stirred in vessel B with 10 wt % silica gel under N_2. [b] Insoluble parts in methanol. [c] Estimated by GPC (based on standard polystyrene).

under bulk conditions, but the $\bar{M}_n$ value of the polymer obtained was not beyond 5000 (Scheme 2). It means the silica gel does not always convert 4-methylene-1,3-dioxolanes to high $\bar{M}_n$ polymers. Ring-opening isomerization of **1** may proceed more smoothly than isomerization of **3** because the ring-opened diphenylallyl cation of **1** is more stabilized than the ring-opened benzyl cation of **3**. It seems that quick ring-opening isomerization depresses a chain transfer reaction due to the β-proton elimination of the ring-intact cation.

Although polymer **2** was also obtained from solution polymerization, GPC profiles of the polymers showed unimodal curves in a lower $\bar{M}_n$ area below 6000 (Table 2). It means that the dilution of the monomer might depress the formation of high $\bar{M}_n$ polymer. From the bimodal GPC profile of polymer **2** obtained from bulk polymerization it was assumed that the polymerization took place through plural paths such as a reaction on the surface of the catalyst particle and a reaction remote from the particle. If the formation of the high $\bar{M}_n$ polymer resulted from an on-surface reaction, disappearance of the higher $\bar{M}_n$ peak in solution polymerization could be explained by absorption of the solvent to silica gel which decreases the local concentration of the monomer around the silica gel surface.

Generally, in cationic polymerization, rigorous purity of the monomer is required to exclude the chain transfer reaction caused by contaminants such as water. Monomer **1** was simply purified by alumina column chromatography because **1** could not be distilled without isomerization to **6**.[8] The reasons monomer **1** afforded a high $\bar{M}_n$ polymer in spite of the simplified purification
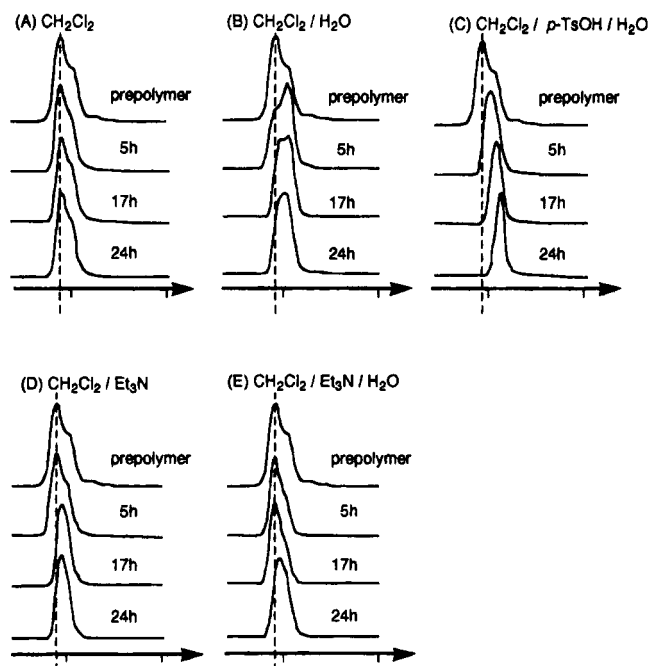
Figure 2. GPC curves of polymer **2** treated by (A) dichloromethane, (B) dichloromethane/water, (C) dichloromethane/ *p*-toluenesulfonic acid/water, (D) dichloromethane/triethylamine, and (E) dichloromethane/triethylamine/water.

Table 3. Cationic Polymerization of Various Monomers[a]

run	monomer[b]	yield,[c] wt %	$\bar{M}_n{}^d$	$\bar{M}_w/\bar{M}_n{}^d$
13	BVE	14	600	14.4
14	St	13	600	7.2
15	PO	0		

[a] Stirred for 12 h in vessel B with 10 wt % silica gel under N_2 at 25 °C. [b] BVE, butyl vinyl ether; St, styrene; PO, propylene oxide. [c] Insoluble parts in methanol. [d] Estimated by GPC (based on standard polystyrene).

might be attributable to (1) absorption of residual water by silica gel, (2) low nucleophilicity of the polysilicate counteranion, and/or (3) high polymerizability of **1** itself. As shown in Table 3, the silica gel was not an especially good catalyst for common monomers such as vinyl ether, styrene, and epoxide. Therefore absorption of chain transfer reagents and/or low nucleophilicity of the counteranion seemed to be only partly responsible for formation of the high $\bar{M}_n$ polymer. Since monomer **1** was very sensitive to acid, the main reason might be the high polymerizability of **1** itself.

Stability of Polymer 2. Thermal stability and properties of polymer **2** were examined by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). Polymer **2** exhibited a degradation temperature where 10% weight was lost (T_d) at 271 °C. The glass transition temperature (T_g) of the polymer was 61 °C.

Although polymer **2** was stable in dry CH_2Cl_2, treatment with a CH_2Cl_2—water mixture shifted the higher $\bar{M}_n$ peak to the low molecular weight area (Figure 2, Table 4). It means that polymer **2** is hydrolytically degradable. This degradation was accelerated by *p*-toluenesulfonic acid. IR spectra of the resulting polymers treated by acidic water showed a characteristic absorption at 1668 cm^{-1} that was assignable to the aromatic ketone of the terminal benzoyl of **4**. Therefore this reaction would be caused by the hydrolysis of a vinyl ether moiety (Scheme 3).
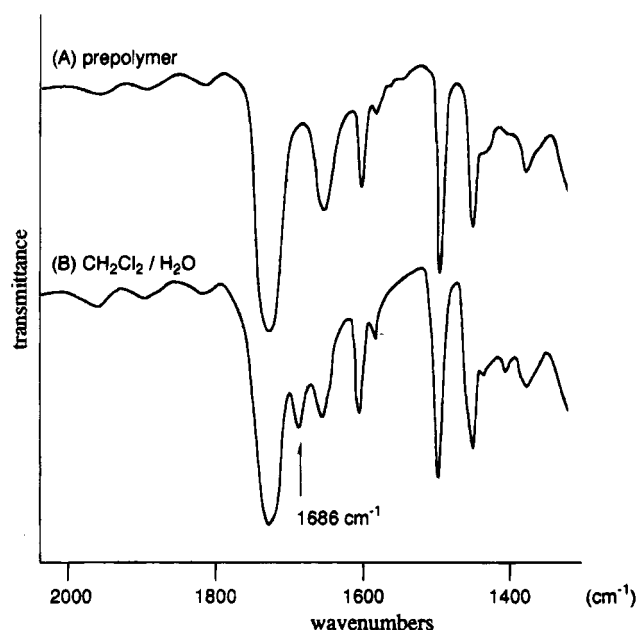
Figure 3. IR spectra of the polymers: (A) prepolymer; (B) after treatment with dichloromethane/water.
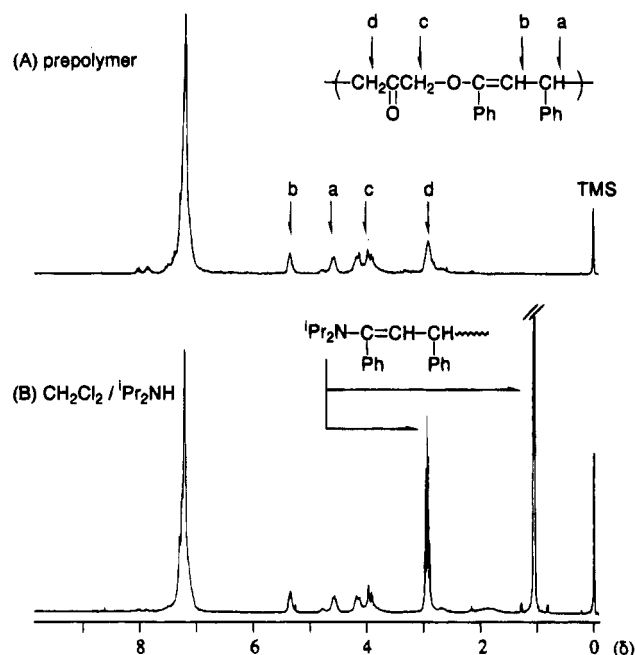
Figure 4. ^1H NMR spectrum of the polymers: (A) prepolymer; (B) after treatment with dichloromethane/diisopropylamine.

Table 4. Degradation of Polymer 2[a]

run	condition[b]	$\bar{M}_w$ at 24 h[c]
16	CH_2Cl_2	40 000
17	CH_2Cl_2/H_2O	14 000
18	$CH_2Cl_2/p\text{-TsOH}/H_2O$	1 800
19	CH_2Cl_2/Et_3N	19 000
20	$CH_2Cl_2/Et_3N/H_2O$	23 000

[a] Stirred 100 mg of prepolymer **2** (M_w = 84 000) at 25 °C. [b] CH_2Cl_2, 5 mL; H_2O, 1 mL; *p*-TsOH H_2O, 19 mg; Et_3N, 10 mg. [c] Estimated by GPC (based on standard polystyrene).

Similar degradation of **2** was obtained by amine treatment. However, there was no absorption of the aromatic ketone in the resulting IR spectra. Their ^1H NMR spectra indicated the presence of an ethyl group; therefore diethylamine, which was a contaminant in triethylamine, might add to the polymer, causing cleavage of vinyl ether bonding to afford **5** (Scheme 3). When

Scheme 3

Scheme 4
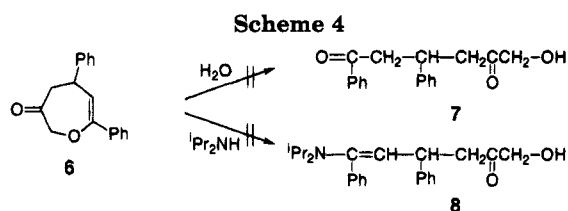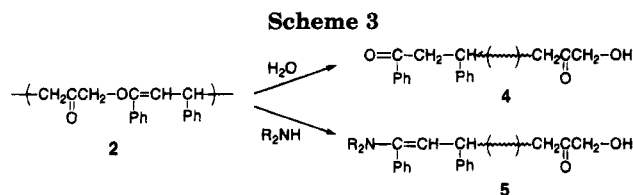
polymer **2** was treated with diisopropylamine instead of triethylamine, the ^{1}H NMR spectrum of the resulting polymer showed a diisopropylamino group that never disappeared by repeating precipitation, and its IR spectrum showed no absorption of the aromatic ketone. These findings indicate that the polymer degraded by amine might have an enamine terminal.

Except for additional peaks of the terminal structure, the NMR spectra of the polymers isolated from hydrolysis at 24 h hardly differed from the spectra of the original polymer. The monomeric products **7** and **8** were not detected even with the reaction time prolonged for a few weeks. For model reaction of the degradation, solvolyses of **6** took place under the same conditions. Although **6** was treated with *p*-toluenesulfonic acid or diisopropylamine in dichloromethane at 25 °C for 24 h, **6** was retained and the linear monomeric compounds **7** and **8** were not detected (Scheme 4). Therefore this reaction is not suitable for the model reaction of polymer degradation. It was explained by an assumption that vinyl ether bonding in the 7-membered ring of **6** was more stable and tolerant than the bonding in the linear polymer although the repeating unit has the same structure.

Additionally, it was confirmed that polymer **2** showed a continuative shift of GPC curves during degradation without production of new peaks that were assignable to **6** and similar macrocyclic oligomers. It means the degradation mechanisms exclude a back-biting reaction to afford cyclic compounds from the terminal of the polymer.

Summary

The present paper can demonstrate the cationic polymerization of 4-methylene-2-phenyl-2-styryl-1,3-dioxolane (**1**) catalyzed by acidic silica gel. Since the monomer is very sensitive to acid, even the glass surface can polymerize the monomer. Acidic glass or silica gel is a good catalyst to produce the high $\bar{M}_n$ polymer. Polymerization proceeds through selective cationic double isomerization (ring-opening/allyl isomerization) and gave a 1,7-addition polymer including ketone and vinyl ether moieties in the main chain. It is also found that the polymer obtained can be degraded by water at the vinyl ether moiety to form a terminal benzoyl. The degradation of the polymer is accelerated by acid. Amines also degrade the polymer to afford an amine adduct terminal instead of benzoyl.

References and Notes

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