

2-(Multimethoxyphenyl)-4-methylene-1,3-dioxolane: (III) Polymerization of 2-(2,4-Dimethoxyphenyl)-4-methylene-1,3-dioxolane with Various Cationic Catalysts

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The 2-(2,4-dimethoxyphenyl)-4-MDO (**2**) underwent polymerization with ring opening as well as cyclization reaction in the presence of various cationic catalysts such as boron trifluoride, trifluoromethanesulfonic acid, *p*-toluenesulfonic acid, hydrochloric acid and trifluoroacetic acid. They afforded a mixture of the ring-opened poly(keto ether) and 3(2H)-dihydrofuranone derivative. Both the methylene group and oxygen atom of 1,3-dioxolane ring were participated in the reaction with cationic catalyst. The contents of the polymer and cyclization product were variable according to the acid strength of the cationic catalysts.

Introduction

The free-radical and cationic ring-opening polymerization of 4-methylene-1,3-dioxolane (4-MDO) derivatives, for instance, 2-phenyl-4-MDO,^{1,2} 2-styryl-4-MDO^{3,4} and 2,2-diphenyl-4-MDO,⁵ were recently studied. A number of 4-methylene-1,3-dioxolane derivatives, which polymerized at the double bond with the retention and ring-opening of the dioxolane ring, have been reported.^{6,7} On the other hand, ring-opening polymerization with simultaneous double-bond migration occurred in some 4-MDO derivatives.⁸⁻¹¹ The extent of formation of the keto ether sequence depends on the substituent, polymerization catalyst, polarity of solvent, and polymerization temperature. In the polymers of 2-substituted 4-MDOs, the keto ether lies between 40-90%.^{12,13}

Recently, it was widely known that the polymerization of 4-MDO derivatives proceeded via mixed modes of vinyl ring-opening, ring-opening *via* double bond and elimination reaction.^{1,3,5,8} More recently, 4-MDO derivatives were reported to undergo intramolecular cyclization reaction to form 3(2H)-dihydrofuran derivatives by cationic catalyst.¹⁴⁻¹⁷ The content of the cyclization reaction was variable according to the substituents as well as the acid strength of cationic catalysts. Especially, it is of interest that the protonating rate and ability to olefin and oxygen atom lead to the different contents of polymerization and cyclization product.

This report deals with the acid catalyzed polymerization and cyclization reaction of 2-(2,4-dimethoxyphenyl)-4-methylene-1,3-dioxolane in the presence of various cationic catalysts.

Experimental Section

Methylene chloride was purified by distillation over sodium metal after drying over calcium hydride. 2-(2,4-Dimethoxyphenyl)-4-MDO was prepared by the dehydrochlorination reaction of 4-chloromethyl-2-(2,4-dimethoxyphenyl)-1,3-dioxolane (**1**) and potassium *t*-butoxide.^{16,18} Acetic acid and trifluoroacetic acid were purified by conventional purification method. Hydrochloric acid was generated by reaction of

sodium chloride and sulfuric acid and dried by passing through anhydrous sulfuric acid. Boron trifluoride diethyl etherate (Aldrich Chem. Co.) and *p*-toluenesulfonic acid were used without further purification.

FT-IR spectra were obtained with a Midac Model M-1200 spectrophotometer and the positions of the absorption band are reported in cm⁻¹. ¹H NMR spectra were obtained with a Varian Gemini 2000 spectrometer. The chemical shifts are recorded in ppm from tetramethyl silane as an internal standard. ¹³C NMR spectra were performed with a Varian Gemini 2000 spectrometer. Elemental analyses were obtained with a Yanaco MT-3 CHN-Analyzer.

Gel-permeation chromatography (GPC) data were obtained with a Waters HPLC using three columns (μ -Styragel 10², 10³ and 10⁴ Å), calibrated with polystyrene standards, in tetrahydrofuran as eluent at 254 nm.

Representative acid-catalyzed polymerization of 2-(2,4-dimethoxyphenyl)-4-MDO derivatives. A solution of **2** (0.5 g, 5.5 mmol) in 4 mL of purified methylene chloride was placed in a septum rubber-capped glass tube in a dry nitrogen atmosphere. The tube was then cooled to -30 °C and 14.25 μ L (5 mol%) of boron trifluoride etherate solution was injected. After 4 h, the reaction mixture was quenched with excess triethylamine and washed with distilled water several times. The crude mixture was poured into a large amount of cold *n*-hexane. The solid powdery product was dried at 50 °C for 12 h under vacuum. Other cationic polymerization with acetic acid, trifluoroacetic acid, trifluoromethanesulfonic, *p*-toluenesulfonic acid, and hydrochloric acid were carried out by the similar methods as described above. Hydrochloric acid catalyst was prepared by dissolving hydrochloric acid gas in methylene chloride.

Poly2: FT-IR 2960-2940 (aromatic C-H), 2840 (aliphatic C-H), 1718 (C=O), 1220, 1120, 1020 (C-O) cm⁻¹. ¹H NMR (CDCl₃) δ 6.6 (br m; 2H, aromatic protons), 5.0 (m; 1H, -O-CH(Ph)-CH₂-), 3.8-3.6 (br m; 2H, -CO-CH₂-O-), 3.7 (2 s, 6 H, CH₃O-), 2.3 (br; 2H, -CO-CH₂-). ¹³C NMR (CDCl₃) δ 205.0 (-C=O-), 152.1, 151.8, 140.2, 128.6, 126.4 (aromatic C's), 78.9 (-O-CH(Ph)-), 74.3 (-O-CH₂-CO-), 58.2, 57.2 (-OCH₃), 47.1 (-CO-CH₂-). Anal. Calcd for C₁₅H₁₄O₄: C,

64.80; H, 6.30. Found: C, 65.41; H, 6.18.

2-(2,4-Dimethoxyphenyl)-3-(2H)dihydrofuranone (3): FT-IR 2970-2940 (aromatic C-H), 2840 (aliphatic C-H), 1757 (C=O), 1264, 1138, 1026 (C-O) cm^{-1} . ^1H NMR (CDCl_3) δ 6.9-6.7 (s; 2H, aromatic protons), 5.4 (t; 1H, $-\text{O}-\text{CH}(\text{Ph})-\text{CH}_2-$), 4.2-3.6 (s; 2H, $-\text{O}-\text{CH}_2-\text{CO}-$), 3.8 (2 s, 6H, $\text{CH}_3\text{O}-$), 2.8-2.4 (m; 2H, $-\text{CO}-\text{CH}_2-$). ^{13}C NMR (CDCl_3) δ 214.0 ($-\text{CO}-$), 157.8, 152.4, 138.2, 114.4 (aromatic C's), 78.8 ($-\text{O}-\text{CH}(\text{Ph})-$), 68.4 ($-\text{O}-\text{CH}_2-\text{CO}-$), 58.1, 57.7 ($-\text{OCH}_3$), 44.2 ($-\text{CO}-\text{CH}_2-$). Anal. Calcd for $\text{C}_{12}\text{H}_{14}\text{O}_4$: C, 64.80; H, 6.30. Found: C, 64.35; H, 6.21.

Results and Discussion

2-(2,4-Dimethoxyphenyl)-4-methylene-1,3-dioxolane (**2**) was selected for the cationic polymerization. The monomer **2** is very reactive, therefore spontaneous polymerization occurred at higher temperature than 125 $^\circ\text{C}$. It possessed a great tendency to polymerize because of the sensitivity to acid moiety.

The results and conditions of polymerization including molecular weight data are summarized in Table 1.

Protonic acids and Lewis acids are potential sources of proton, but the abilities of protonation to the double bond were quite different. It is of interest to compare the amount of ring opening polymerization and cyclization reaction of 2-(2,4-dimethoxyphenyl)-4-MDO according to the acid strength ($\text{p}K_a$) of cationic catalysts.¹⁴

The monomer **2** was polymerized in methylene chloride with 5 mol% of cationic catalysts such as boron trifluoride, trifluoromethanesulfonic acid, trifluoroacetic acid, hydrochloric acid, *p*-toluenesulfonic acid, and acetic acid at -30 $^\circ\text{C}$ for 4 h. The resulting polymerization mixture was quenched with excess triethylamine after completion of polymerization and purified by washing with water, followed by precipitation into cold *n*-hexane.

The chemical structure of polymerization product was characterized by ^1H NMR, ^{13}C NMR, and IR spectroscopy, and was further checked by elemental analysis. The contents of ring-opened polymer and cyclization product were deter-

mined by the ratio of the integration of ^1H NMR peak centered at 7.2 ppm and 5.4 ppm assignable to phenyl and cyclized benzyl proton in 2-(2,4-dimethoxyphenyl)-3(2H)-dihydrofuranone. On the other hand, benzyl proton of the ring-opened poly(keto ether) exhibited at 4.9-5.0 ppm.

When 2-(2,4-dimethoxyphenyl)-4-MDO was polymerized with boron trifluoride diethyl etherate at -30 $^\circ\text{C}$, a white powdery crosslinked polymer was obtained after precipitation. The IR spectrum of the polymer obtained from **2** showed 1718 cm^{-1} indicating the presence of ring opened ketone group. In the ^1H NMR spectrum of the soluble portion in CDCl_3 , the peak at 5.0 ppm assignable to ring-opened benzyl proton was observed. And also characteristic methylene peaks of poly(keto ether) were showed at 3.6-3.9 ppm. From these results **2** underwent a 92% of ring-opening polymerization with boron trifluoride.

Trifluoromethane sulfonic acid (triflic acid) was also adopted for the cationic catalyst. Similarly, monomer **2** polymerized with a 83% of ring-opening in the presence of triflic acid. Although triflic acid is stronger acid than boron trifluoride, the content of ring-opened polymer is relatively lower than that of boron trifluoride. This observation may be due to the heterogeneity of the polymerization mixture. Sometimes triflic acid is partially soluble in methylene chloride to form heterogeneous mixture because of the strong hydrogen bond of the triflic acid.¹⁸ The stronger protonic acid than hydrochloric acid gave a crosslinked polymer, which is caused by the electrophilic substitution reaction¹² of the electron rich aromatic ring during the polymerization.

Trifluoroacetic acid having $\text{p}K_a$ value 0.2 was much less effective than the corresponding triflic acid.¹⁹ As to the cationic polymerization of **2** with trifluoroacetic acid in methylene chloride solution at -30 $^\circ\text{C}$, the reaction mixture gave a white powdery polymer after precipitation into *n*-hexane. Polymerization mixture of **2** gave 45% of distillate and 52% of the solid residue with 5 mol% of trifluoroacetic acid. IR spectra of the polymer showed a strong absorption band at 1718 cm^{-1} , which is attributable to ring-opened ketone linkage and absorption bands at 1294, 1203, and 1105 cm^{-1} attributable to an ether linkage. In contrast the IR spectrum

Table 1. Conditions and Results of Polymerization of 2-(2,4-Dimethoxyphenyl)-4-methylene-1,3-dioxolane Derivatives^a

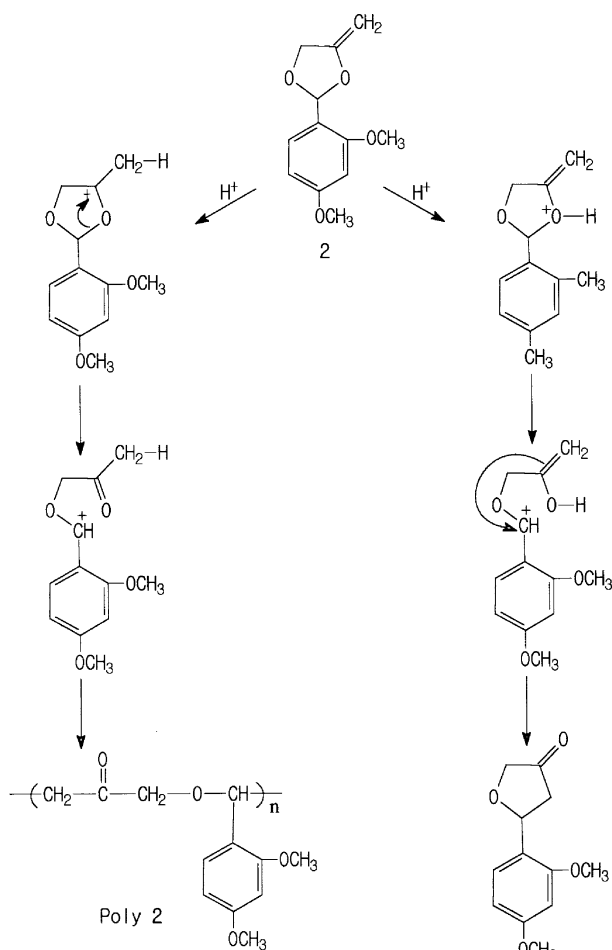
No	Catalyst	Solvent	Temp ($^\circ\text{C}$)	Yield ^b (%)	MW	MWD	Cyclization		Polymer
							Content (%) ^c		
1	$\text{BF}_3\text{OEt}_2^d$	CH_2Cl_2	-30	89	-	-	15	85	
2	$\text{CF}_3\text{SO}_3\text{H}^e$	CH_2Cl_2	-30	86	-	-	17	83	
3	CF_3COOH	CH_2Cl_2	-30	63	11,000	2.8	42	58	
4	HCl^f	CH_2Cl_2	-30	76	-	-	28	72	
5	<i>P</i> -TsOH	CH_2Cl_2	-30	56	12,000	3.2	40	60	
6	CH_3COOH	CH_2Cl_2	-30	9	-	-	-	9	
7	BF_3OEt_2	CH_3NO_2	-30	40	4,800	2.1	63	37	
8	BF_3OEt_2	Toluene	-30	26	6,400	1.8	32	24	
9	BF_3OEt_2	Toluene	0	42	6,700	2.5	42	38	
10	BF_3OEt_2	Toluene	40	37	4,500	2.8	47	36	

^aPolymerization was carried out with 5 mol% of catalyst. ^bYields were measured gravimetrically. ^cRing-opened polymer and cyclization contents were determined by the NMR integration or gravimetrically. ^dInsoluble polymer was obtained.

of the cyclization product obtained from the distillate show a strong absorption band at 1759 cm^{-1} indicating the presence of the cyclic carbonyl group. The presence of a multiplet peak at 5.4 ppm corresponding to cyclized benzyl proton indicated that **2** underwent cyclization reaction. ^{13}C NMR spectrum also showed a peak at 214 ppm assignable to carbonyl carbon indicating that some of **2** undergo cyclized intramolecularly to form 2-(2,4-dimethoxyphenyl)-3(2*H*)-dihydrofuranone. The similar polymerization behaviors were observed between *p*-toluenesulfonic acid and trifluoroacetic acid as indicated in Table 1. Note that the two acids possess a similar pK_a value.¹⁹

Hydrochloric acid is strong protonic acid. When **2** was polymerized with hydrochloric acid in methylene chloride solution at $-30\text{ }^\circ\text{C}$, polymerization mixture of **2** gave a 28% of distillate and 72% of the solid residue with 5 mol% of hydrochloric acid.

In the case of the cationic polymerization of **2** with acetic acid, only a small amount of polymerization and cyclization product including the trace of elimination product were obtained. Thus the conversion of the ring-opening polymerization and the cyclization reaction is very low. This result was caused by the weak acidity of acetic acid (pK_a value 4.8). However, it gave a 30-35% yield of polymer and



Scheme 1

cyclization product at $60\text{ }^\circ\text{C}$.

As to the monomer in the presence of boron trifluoride, for 4 h at $-30\text{ }^\circ\text{C}$ even in nonpolar solvent toluene (DN, 2.5) monomer **2** gave a 40% of polymerization product but more polar solvent nitromethane having DN (35.9) afforded a polymerization product in high yield. In nitromethane solvent, polymerization proceeded with ring-opening, but the high yield of polymer without crosslinking was observed. The conversion of **2** and the yield of polymer increased as the reaction temperature was raised, but the crosslinked gell was observed at $40\text{ }^\circ\text{C}$.

Polymerization of 2-(2,4-dimethoxyphenyl)-4-MDO derivatives may proceed more rapidly than other 2-phenyl-4-MDO. The methoxy groups as an electron donating group can make a benzyl acetal carbon and oxygen atom more electron-rich. Especially, the methoxy substituents at both *ortho*- and *para*-position in **2** make it possible that the ring-opening is more favored by forming stable intermediates as shown in Scheme 1.

In every case, ^1H NMR spectra of the obtained polymers corresponded reasonably well to those of poly(keto ether) previously reported. A typical ^1H NMR spectra of the poly(keto ether), cyclization product 2-(2,4-dimethoxyphenyl)-3(2*H*)-dihydrofuranone, and their mixtures are shown in Figure 1. The intensities of the characteristic aldehyde peak was weak, which indicates that the reaction proceeded with ring opening and accompanied by elimination reaction. The elimination content was calculated to be using the gas chromatography.

As mentioned previously, the modes of cationic polymerization are dependent upon the kind of cationic catalyst. The content of the ring-opened polymer increased slightly as the acid strength increased.

Cationic initiator was competitively reacted with double

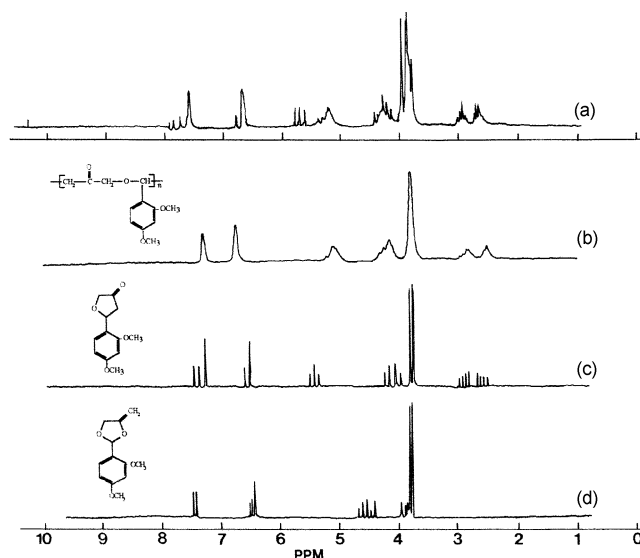


Figure 1. ^1H NMR spectra obtained from (a) the mixture of cationic polymerization, (b) poly(keto ether), (c) 2-(2,4-dimethoxyphenyl)-3(2*H*)-dihydrofuranone and (d) 2-(2,4-dimethoxyphenyl)-4-methylene-1,3-dioxolane.

bond and oxygen atom of the 4-MDO ring during the polymerization. The cyclization reaction may be initiated through an electrophilic addition reaction of oxygen atom to give the corresponding oxonium intermediate, which was intramolecularly cyclized to form 2-(2,4-dimethoxyphenyl)-3(2H)-dihydrofuranone.

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