

## 2-(Multimethoxy)phenyl-4-methylene-1,3-dioxolane (I): Preparation and Cationic Polymerization of 2-(Dimethoxy)phenyl-4-MDO Derivatives

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The 4-methylene-1,3-dioxolane (4-MDO) derivatives with dimethoxyphenyl group on the 2-position of 1,3-dioxolane ring, 2-(*x,y*-dimethoxyphenyl)-4-MDO derivatives (*x,y* = 2,3 (**1b**), 2,4 (**2b**), 2,5 (**3b**) and 3,4 (**4b**)) were prepared by acetalization of the corresponding benzaldehyde with 3-chloro-1,2-propanediol, followed by dehydrochlorination. 2-(Dimethoxy)phenyl-4-MDO derivatives underwent polymerization with ring opening as well as cyclization reaction to afford a mixture of the ring-opened polymer and 3(2*H*)-dihydrofuranone derivatives with boron trifluoride as a cationic catalyst. Both the methylene group and 1,3-dioxolane ring were participated in the reaction with cationic catalyst. The key intermediate of the polymerization is a benzyl cation generated by ring opening, and the cyclization reaction proceed via proton addition to oxygen atom of 1,3-dioxolane ring.

### Introduction

There has been a continuous interest to investigate the ring-opening polymerization of  $\alpha$ -methylene-1,3-dioxolane derivatives with various catalysts such as radical,<sup>1-6</sup> cation<sup>7-10</sup> and tungsten hexachloride.<sup>11,12</sup> 4-MDO ring itself does not possess enough reactivity to polymerize with ring opening.<sup>13</sup> The polymerization of 4-MDO derivatives was reported to proceed via ring-opening, vinyl and elimination.<sup>1</sup> The extent of ring-opening depends upon the substituents at 2-position of 4-MDO ring.<sup>7</sup> By introducing radical stabilizing group such as phenyl group into 2-position of 1,3-dioxolane ring, the tendency of ring opening polymerization became enhanced.<sup>14</sup>

In the case of radical polymerization of 2-phenyl-4-MDO, the degree of ring-opening is 40-50%.<sup>1</sup> On the other hand, 4-methylene-2,2-diphenyl-1,3-dioxolane polymerizes exclusively through ring-opening, followed by elimination of benzophenone to form the polyketone.<sup>5</sup>

Recently, 4-MDO derivatives were reported to undergo intramolecular cyclization reaction to form 3(2*H*)-dihydrofuran derivatives by cationic catalyst such as boron trifluoride and tungsten hexachloride.<sup>15-17</sup>

In this paper, we report the acid catalyzed polymerization and cyclization reaction of some 2-(dimethoxyphenyl)-4-methylene-1,3-dioxolane derivatives in the presence of boron trifluoride diethyl etherate.

### Experimental Section

Methylene chloride and 1,2-dichloroethane were purified by distillation over sodium metal after drying with calcium hydride. 3-Chloro-1,2-propanediol, 2,3-dimethoxybenzaldehyde, 2,4-dimethoxybenzaldehyde, 2,5-dimethoxybenzaldehyde and 3,4-dimethoxybenzaldehyde (Aldrich Chemical Co.) were used without further purification. *tert*-Butanol was purified by distillation over calcium hydride and sodium

metal. Dowex-50W (H<sup>+</sup>, strong cation exchange resin) was used as an acetalization catalyst. Boron trifluoride diethyl etherate (Aldrich Chem. Co.) was used as a cationic catalyst.

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

Gel-permeation chromatography (GPC) data were obtained with a Waters HPLC using three columns ( $\mu$ -Stryragel 10<sup>2</sup>, 10<sup>3</sup> and 10<sup>4</sup> Å), calibrated with polystyrene standards, in tetrahydrofuran as eluent at 254 nm.

**Representative Preparation of 4-Chloromethyl-2-(dimethoxyphenyl)-1,3-dioxolane.** A mixture of 3,4-dimethoxybenzaldehyde (10.00 g, 60.0 mmol) and 3-chloro-1,2-propanediol (7.96 g, 72.0 mmol) in toluene (150 mL) was heated at 130 °C with Dowex-50W resin (0.5 g) in a 250 mL flask equipped with Dean-Stark separator. After the calculated amount of water was collected by azeotropic distillation for 24 h, the ion exchange resin was removed by filtration. After the solvent was evaporated, the reaction mixture was dissolved in methylene chloride (100 mL) and the solution was washed with water to remove the excess 3-chloro-1,2-propane diol. The solvent was evaporated and the crude product was purified by Kugelrohr distillation to give 14.0 g of **4a** as a viscous colorless liquid.

Other 4-chloromethyl-2-(dimethoxyphenyl)-1,3-dioxolane derivatives were prepared by the similar procedures described above.

**4a:** Yield 83%. bp 110 °C/0.1 mmHg. FT-IR 2955 (aromatic C-H), 2884-2860 (aliphatic C-H), 1331-1140 (C-O) cm<sup>-1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  7.6-6.8 (m, 3H, aromatic protons), 5.8-5.5 (d, 1H, acetal proton), 4.4-3.6 (m, 3H, -OCH<sub>2</sub>CH(CH<sub>2</sub>Cl)O-), 3.7 (d, *J* = 4.03 Hz, 6H, CH<sub>3</sub>O-), 3.5 (m, 2H,

-CH<sub>2</sub>Cl).

**Representative Preparation of 2-(Dimethoxyphenyl)-4-methylene-1,3-dioxolane.** A solution of **4a** (13.00 g, 50.0 mmol) in *tert*-butanol (10 mL) was added slowly to the solution of potassium (3.30 g, 60.0 mmol) dissolved in *tert*-butanol (60 mL) at 25 °C under nitrogen atmosphere. After the addition was completed, the solution was heated to 80 °C and refluxed for 24 h. The reaction mixture was cooled and *tert*-butanol was removed by evaporation. The crude product was dissolved in methylene chloride (100 mL) and washed with distilled water several times. After methylene chloride was evaporated, the resulting residue was vacuum distilled through a Vigreux column to get 8.80 g of **4b** as a colorless liquid. The purified product was confirmed by gas chromatography (GC). 2-(2,3-Dimethoxyphenyl)-4-MDO (**1b**), 2-(2,4-dimethoxyphenyl)-4-MDO (**2b**) and 2-(2,5-dimethoxyphenyl)-4-MDO (**3b**) were also prepared by the similar methods described above.

**1b:** Yield 96%. bp 110 °C/0.1 mmHg. FT-IR (cm<sup>-1</sup>) 3025-2945 (aromatic C-H), 2920-2838 (aliphatic C-H), 1686 (C=C), 1389-1060 (C-O) cm<sup>-1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 7.2-6.8 (m, 3H, aromatic protons), 6.5 (s, 1H, acetal proton), 4.7-4.4 (m, 2H, =CH<sub>2</sub>), 4.0-3.8 (m, 2H, -OCH<sub>2</sub>C(=CH<sub>2</sub>)O-), 3.8 (d, *J* = 7.5 Hz, 6H, CH<sub>3</sub>O-). Anal. Calcd for C<sub>12</sub>H<sub>14</sub>O<sub>4</sub>: C, 64.80; H, 6.30. Found: C, 65.17; H, 6.27.

**2b:** Yield 68%. bp 113 °C/0.1 mmHg. FT-IR (cm<sup>-1</sup>) 3020-2937 (aromatic C-H), 2920-2841 (aliphatic C-H), 1686 (C=C), 1312-1110 (C-O) cm<sup>-1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 7.4-6.4 (m, 3H, aromatic protons), 6.4 (s, 1H, acetal proton), 4.7-4.4 (m, 2H, =CH<sub>2</sub>), 4.2-3.8 (m, 2H, -OCH<sub>2</sub>C(=CH<sub>2</sub>)O-), 3.8 (d, *J* = 5.49 Hz, 6H, CH<sub>3</sub>O-). Anal. Calcd for C<sub>12</sub>H<sub>14</sub>O<sub>4</sub>: C, 64.80; H, 6.30. Found: C, 64.20; H, 6.30.

**3b:** Yield 82%. bp 115 °C/0.1 mmHg. FT-IR (cm<sup>-1</sup>) 3010-2940 (aromatic C-H), 2910-2835 (aliphatic C-H), 1688 (C=C), 1329-1121 (C-O) cm<sup>-1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 7.2-6.8 (m, 3H, aromatic protons), 6.5 (s, 1H, acetal proton), 4.7-4.4 (m, 2H, =CH<sub>2</sub>), 4.0-3.8 (m, 2H, -OCH<sub>2</sub>C(=CH<sub>2</sub>)O-), 3.7 (d, *J* = 8.79 Hz, 6H, CH<sub>3</sub>O-). Anal. Calcd for C<sub>12</sub>H<sub>14</sub>O<sub>4</sub>: C, 64.80; H, 6.30. Found: C, 64.96; H, 6.41.

**4b:** Yield 85%. bp 115 °C/0.1 mmHg. FT-IR (cm<sup>-1</sup>) 3015-2938 (aromatic C-H), 2925-2835 (aliphatic C-H), 1686 (C=C), 1318-1110 (C-O) cm<sup>-1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 7.2-6.8 (m, 3H, aromatic protons), 6.1 (s, 1H, acetal proton), 4.7-4.4 (m, 2H, =CH<sub>2</sub>), 4.0-3.8 (m, 2H, -OCH<sub>2</sub>C(=CH<sub>2</sub>)O-), 3.9 (d, *J* = 4.03 Hz, 6H, CH<sub>3</sub>O-). Anal. Calcd for C<sub>12</sub>H<sub>14</sub>O<sub>4</sub>: C, 64.80; H, 6.30. Found: C, 65.10; H, 6.49.

**Representative Acid-Catalyzed Reaction of 2-(Dimethoxyphenyl)-4-MDO Derivatives.** A solution of **4b** (0.5 g, 5.5 mmol) in purified methylene chloride (4 mL) was injected to a septum rubber-capped glass ampoule in a dry nitrogen atmosphere. The tube was then placed in a cooler at -30 °C and boron trifluoride etherate (14.25 μL, 5 mol%) 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 product was dried at 50 °C for 12 h under vacuum. Other monomers **1b**,

**2b** and **3b** were reacted by the similar methods as described above. The IR spectra were obtained from the polymerization mixture and the NMR spectra were taken from the products obtained after Kugelrohr distillation.

**Poly(1b):** FT-IR 2980-2940 (aromatic C-H), 2850-2834 (aliphatic C-H), 1757, 1719 (C=O), 1273, 1171, 1063 (C-O) cm<sup>-1</sup>. **1b-III:** <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 7.2-6.8 (br, 3H, aromatic protons), 5.2 (m, 1H, -O-CH(Ph)-CH<sub>2</sub>-), 3.9-3.6 (br m, 2H, -CO-CH<sub>2</sub>O-), 3.8 (d, *J* = 7.5, 6H, CH<sub>3</sub>O-), 2.6-2.4 (br, 2H, -CO-CH<sub>2</sub>-). **1c:** <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 7.2-6.8 (m, 3H, aromatic protons), 5.4 (m, 1H, acetal proton), 4.2-3.6 (m, 2H, -O-CH<sub>2</sub>-CO-), 3.8 (d, *J* = 7.5, 6H, CH<sub>3</sub>O-), 3.0-2.4 (m, 2H, -CO-CH<sub>2</sub>-).

**Poly(2b):** FT-IR 2980-2938 (aromatic C-H), 2850-2834 (aliphatic C-H), 1757 (3-(2*H*)dihydrofuranone C=O), 1715 (C=O), 1296, 1205, 1105 (C-O) cm<sup>-1</sup>.

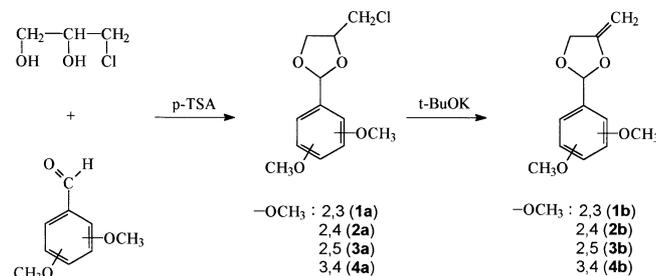
**Poly(3b):** FT-IR 3030-2938 (aromatic C-H), 2834 (aliphatic C-H), 1758, 1719 (C=O), 1250, 1217, 1044 (C-O) cm<sup>-1</sup>. **3b-III:** <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 7.0-6.4 (br m, 3H, aromatic protons), 5.0 (m, 1H, -O-CH(Ph)-CH<sub>2</sub>-), 3.8-3.4 (br m, 2H, -CO-CH<sub>2</sub>O-), 3.5 (d, *J* = 8.79, 6H, CH<sub>3</sub>O-), 2.0-1.8 (m; 2H, -CO-CH<sub>2</sub>-). **3c:** <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 7.0-6.5 (m, 3H, aromatic protons), 5.4 (m, 1H, acetal proton), 4.2-3.4 (m, 2H, -O-CH<sub>2</sub>-CO-), 3.7 (d, *J* = 8.79 Hz, 6H, CH<sub>3</sub>O-), 2.8-2.4 (m, 2H, -CO-CH<sub>2</sub>-).

**Poly(4b):** FT-IR 2970-2940 (aromatic C-H), 2836 (aliphatic C-H), 1757, 1719 (C=O), 1264, 1138, 1026 (C-O) cm<sup>-1</sup>. **4b-III:** <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 7.0-6.7 (m, 3H, aromatic protons), 4.8 (m, 1H, -O-CH(Ph)-CH<sub>2</sub>-), 3.8-3.6 (m, 2H, -CO-CH<sub>2</sub>O-), 3.8 (d, *J* = 4.03, 6H, CH<sub>3</sub>O-), 2.4-2.0 (br; 2H, -CO-CH<sub>2</sub>-). **4c:** <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 6.9-6.7 (m, 3H, aromatic protons), 5.2 (m, 1H, acetal proton), 4.2-3.6 (m, 2H, -O-CH<sub>2</sub>-CO-), 3.7 (d, *J* = 4.03 Hz, 6H, CH<sub>3</sub>O-), 2.8-2.4 (m, 2H, -CO-CH<sub>2</sub>-). <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 214.0 (-C=O-), 149.5, 118.3, 111.0, 109.0 (aromatic C's), 78.7 (-O-CH(Ph)-), 71.5 (-OCH<sub>2</sub>CO-), 79.0 (-CH(Ph)-CH<sub>2</sub>-CO-), 55.8 (OCH<sub>3</sub>), 44.2 (-CH<sub>2</sub>-CO-).

## Results and Discussion

**Preparation and Characterization of 4-MDO Derivatives.** The 4-methylene-1,3-dioxolane (4-MDO) derivatives with dimethoxyphenyl group at 2-position, 2-(2,3-dimethoxyphenyl)-4-MDO (**1b**), 2-(2,4-dimethoxyphenyl)-4-MDO (**2b**), 2-(2,5-dimethoxyphenyl)-4-MDO (**3b**) and 2-(3,4-dimethoxyphenyl)-4-MDO (**4b**) were prepared by acetalization of 2,3-dimethoxybenzaldehyde, 2,4-dimethoxybenzaldehyde, 2,5-dimethoxybenzaldehyde and 3,4-dimethoxybenzaldehyde with 3-chloro-1,2-propanediol, followed by dehydrochlorination with potassium *tert*-butoxide (*t*-BuOK) as shown in Scheme 1.

2-(Dimethoxyphenyl)-4-MDO derivatives were stable at room temperature. However, they were gradually transformed to sticky liquids at higher temperature than 125 °C. And also they were very sensitive toward acid moiety. Upon contamination, they showed a great tendency to form a sticky resinous material.



Scheme 1

The chemical structures of 2-(dimethoxyphenyl)-4-MDO derivatives were confirmed by  $^1\text{H}$  NMR and IR spectroscopy. The characteristic acetal methine protons in 4-chloromethyl-1,3-dioxolane derivatives appeared at 5.5–5.8 ppm as a doublet peak, but the acetal protons of 4-MDO monomers occurred as a singlet peak centered at 6.05 ppm. The characteristic  $=\text{CH}_2$  protons were observed between 4.7 and 4.4 ppm as a multiplet. In the IR spectra of monomers and 4-chloromethyl-2-(dimethoxyphenyl)-1,3-dioxolane derivatives, the C–O acetal and C=C absorption bands were shown at 1335–1140  $\text{cm}^{-1}$  and 1686  $\text{cm}^{-1}$ , respectively.

#### Acid Catalyzed Polymerization of 4-MDO Derivatives.

The results and conditions of polymerization are summarized in Table 1. It was already reported that the cationic polymerization of 4-MDO derivatives such as 2-styryl-4-MDO and *p*-(2-methoxyethoxy)phenyl-4-MDO gives poly(keto ether) and 3(2*H*)-dihydrofuranone via ring-opening and rearrangement.<sup>10,16,17</sup>

All the monomers, **1b–4b**, were polymerized in the presence of 5 mol% of boron trifluoride etherate as a cationic catalyst at  $-30$  °C or  $-70$  °C for 4 h. The resulting reaction mixtures were neutralized with excess triethylamine and purified by precipitation into cold *n*-hexane. Yields were relatively lower in the case of **4b** because of the high solubility of cyclization product in *n*-hexane. Therefore the extents of polymerization and cyclization had to be measured.

The chemical structure of reaction product was deter-

**Table 1.** Conditions and Results of Polymerization of 2-(Dimethoxyphenyl)-4-methylene-1,3-dioxolane Derivatives<sup>a</sup>

Mono- mer	Solvent	Temp (°C)	Yield <sup>b</sup> (%)	MW	MWD	Poly-	Cyclization
						mer	Product <sup>c</sup>
						Content (%) <sup>f</sup>	
<b>1b</b>	$\text{CH}_2\text{Cl}_2$	$-30$ °C	62	5,300	2.4	46	54
<b>1b</b>	$(\text{CH}_2)_2\text{Cl}_2$	$-30$ °C	74	7,200	2.1	60	40
<b>1b</b>	$\text{CH}_2\text{Cl}_2$	$-70$ °C	78	11,000	2.8	52	48
<b>2b<sup>d</sup></b>	$\text{CH}_2\text{Cl}_2$	$-30$ °C	80	-	-	85	15
<b>2b<sup>d</sup></b>	$\text{CH}_2\text{Cl}_2$	$-78$ °C	84	-	-	88	12
<b>3b</b>	$\text{CH}_2\text{Cl}_2$	$-30$ °C	67	4,800	2.1	37	63
<b>4b</b>	$\text{CH}_2\text{Cl}_2$	$-30$ °C	48	6,400	1.8	24	76

<sup>a</sup>Polymerization was carried out with 5 mol% of boron trifluoride etherate as a cationic catalyst. <sup>b</sup>Yields were measured gravimetrically. <sup>c</sup>The content of ring-opened polymer and cyclization product was obtained from the polymerization mixture before precipitation into *n*-hexane and was determined by the NMR integration. In the case of **2b**, the content was measured by gravimetrically. <sup>d</sup>Insoluble polymer was obtained. <sup>e</sup>3(2*H*)-dihydrofuranone derivatives.

mined by  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR and IR spectroscopy, and was further checked by elemental analysis. The contents of polymer and cyclized product were determined by the ratio of the integration of  $^1\text{H}$  NMR peak, centered at 7.2 ppm and 5.5 ppm assignable to phenyl and cyclized benzyl proton in 3(2*H*)-dihydrofuranone (**c**), respectively.

In the case of monomers **1b** and **3b**, both cyclization and polymerization proceeded. IR spectra of the reaction products obtained from **1b** and **3b** showed two absorption bands at 1757 and 1719  $\text{cm}^{-1}$  indicating the presence of the cyclic carbonyl and ring opened ketone group. In the  $^1\text{H}$  NMR spectra of the reaction products, the peaks assignable to two kinds of benzyl proton at 5.4 and 5.2 ppm were observed. And also characteristic methylene peaks of poly(keto ether) and 3(2*H*)-dihydrofuranone were shown at 3.6–3.9 and 3.6–4.2 ppm, respectively. From these spectral data, **1b** and **3b** underwent both ring-opening polymerization and cyclization reaction to afford **1b-III**, 2-(2,3-dimethoxyphenyl)-3(2*H*)-dihydrofuranone (**1c**) and **3b-III**, 2-(2,5-dimethoxyphenyl)-3(2*H*)-dihydrofuranone (**3c**), respectively.

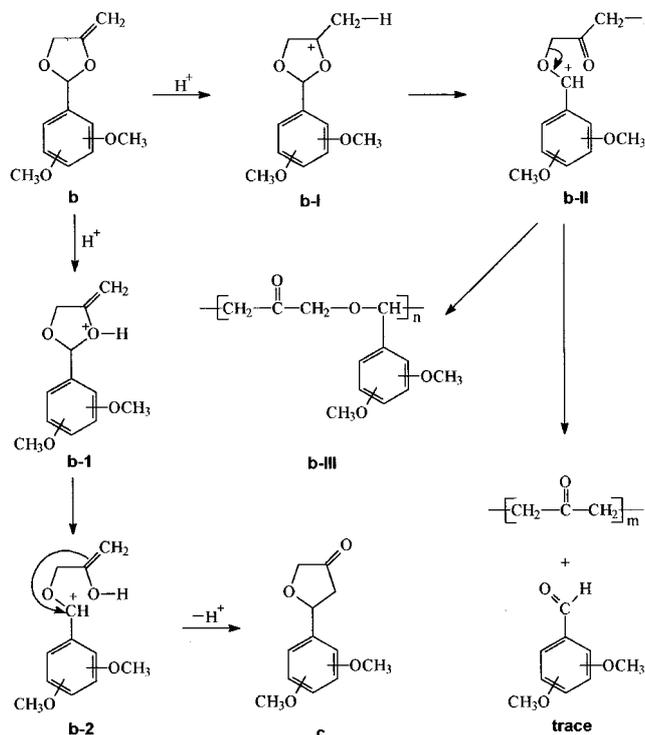
Not only the polarity but also the temperature affect the reactivity of cationic species as well as the electrophilicity of the propagating end. In order to investigate the effect of solvent polarity, the reaction of **1b** was performed in 1,2-dichloroethane instead of methylene chloride. The cyclization product was obtained in 40% yield. The rate of the proton addition to double bond was 16% higher in 1,2-dichloroethane ( $\epsilon = 10.4$ ) than in methylene chloride ( $\epsilon = 8.9$ ). Hence the polymerization was more favored than cyclization reaction.

On the other hand, when the reaction temperature was lowered to  $-78$  °C, any detectable change in the content of polymer and cyclization product was not found.

When **2b** was reacted with boron trifluoride in methylene chloride solution at  $-30$  °C, the reaction mixture gave a white powdery polymer after precipitation into *n*-hexane in 84% yield. IR spectra of the reaction mixture of **2b** showed a strong absorption band at 1719  $\text{cm}^{-1}$ , which is attributable to ring-opened ketone linkage and absorption bands at 1294, 1203 and 1105  $\text{cm}^{-1}$  attributable to an ether linkage. It might be deduced that **2b** polymerized mainly to give the corresponding poly(keto ether). Also **4b** gave 76% of distillate and 24% of the solid residue.

IR spectrum of the cyclization product obtained from **4b** showed a strong absorption band at 1759  $\text{cm}^{-1}$  indicating the presence of the cyclic carbonyl group. Multiplet peaks at 5.4 ppm assignable to cyclized benzyl proton in  $^1\text{H}$  NMR spectrum and a peak at 214 ppm assignable to carbonyl carbon in  $^{13}\text{C}$  NMR spectrum indicates that **4b** underwent intramolecular cyclization to form 2-(3,4-dimethoxyphenyl)-3(2*H*)-dihydrofuranone (**4c**). Furthermore, the mass spectrum and elemental analysis were consistent with the assigned cyclization product.

The polymers have a weight average molecular weight *M<sub>w</sub>* in the range of 11000–4800 and molecular weight distribution was in the range of 1.8–2.8. The separated polymers except **2b** were soluble in common organic solvents such as



Scheme 2

chloroform, THF, acetone, ethanol and benzene, partially soluble in methanol and insoluble in pentane and hexane. Specially, it was found that the polymer obtained from **2b** with methoxy groups at 2- and 4-positions was insoluble in common organic solvents. This result indicates that **2b** proceeded primarily in ring-opening fashion, followed by further cross-linking reaction such as electrophilic addition reaction.

The phenyl substituent at 2-position of 4-MDO ring can provide a sufficient driving force to open the 1,3-dioxolane ring by forming a stable benzyl intermediate. Polymerization of 2-dimethoxyphenyl-4-MDO derivatives may proceed more rapidly than those of 2-phenyl-4-MDO and 2-(4-methoxyphenyl)-4-MDO. The methoxy groups as an excellent electron donating group can make a benzyl acetal carbon and oxygen atom more electron-rich. Especially, the methoxy substituents of **b-II** at 2,4-position make it greatly favor the ring-opening by forming stable intermediates as shown in Scheme 2.

Also the polymerization was accompanied by elimination reaction. When the *n*-hexane-soluble portion was analyzed by gas chromatography, the eliminated compound, dimethoxy benzaldehyde could be detected in 3-5% yield, as shown in Scheme 2.

Monomers were competitively transformed to cyclization

product during the polymerization. The cyclization reaction may be initiated through electrophilic addition of oxygen atom in 4-MDO ring to give the corresponding oxonium intermediate, which underwent intramolecular cyclization by [1,3] sigmatropic reaction. This intermediate was also stabilized by the more stable benzyl cation **b-2** thereby generated.

It was of interest to compare the amount of ring opening polymerization and cyclization reaction, since the number and position of substituents could form various resonance structures.

In conclusion, we have performed a boron trifluoride catalyzed polymerization reaction in which the 2-(dimethoxy) phenyl-4-MDO derivatives rearranges, and it was revealed that the content of the cyclization product and polymer was influenced by position of substituents at phenyl group in the 4-MDO ring.

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