2-(Multimethoxy)phenyl-4-methylene-1,3-dioxolane: II. Preparation and Cationic Polymerization of 2-(x,y,z-Trimethoxyphenyl)-4-methylene-1,3-dioxolane Derivatives

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2-(2,4,5-Trimethoxyphenyl)-4-methylene-1,3-dioxolane (**1b**), 2-(2,4,6-trimethoxyphenyl)-4-methylene-1,3-dioxolane (**2b**), and 2-(3,4,5-trimethoxyphenyl)-4-methylene-1,3-dioxolane (**3b**) were prepared and polymerized with boron trifluoride. Boron trifluoride catalyzed reaction proceeded *via* mainly ring-opening polymerization and cyclization reaction to yield poly(keto ether) and 3(2*H*)-dihydrofuranone. The yields of polymer and cyclized product exhibited a dependency on the position of the methoxy substituents in the benzene ring of 2-phenyl-4-methylene-1,3-dioxolane derivatives. Electrophilic attack of methylene or oxygen atom on 4-methylene-1,3-dioxolane ring were suggested for the polymerization and cyclization.

Introduction

2-Phenyl-4-methylene-1,3-dioxolane (2-P-4-MDO) derivatives have been reported to undergo radical[1-11] and cationic polymerization with various initiators such as radical, cation[12-22] and transition metal catalysts.[23-24] They underwent vinyl, ring-opening and ring-opening polymerization *via* double bond as well as elimination and cyclization reaction.[1-3,6-8] Recently, 2-(4-methoxyphenyl)-4-MDO,[20] [4-(2-methoxyethoxy)phenyl]-4-MDO[21] and 2-(x,y-dimethoxyphenyl)-4-MDO[22] derivatives have been reported to undergo cationic polymerization to give the polymers *via* a variety of polymerization modes accompanying by intra-molecular cyclization reaction.

Particularly, some electron donating methoxy groups are incorporated into the phenyl group of the 2-phenyl-4-MDO ring, hence the acetal carbon in the 1,3-dioxolane ring can be highly activated.[22] In addition, the electron-donating substituents make the double bond or/and oxygen atom of 4-MDO ring extremely reactive to the cationic species.

In the previous work, we reported the relationship between the position of methoxy substituents and cationic polymerization behavior for the series of 2-(x,y-dimethoxyphenyl)-4-MDO derivatives in the presence of boron trifluoride.[24]

The present work deals with the synthesis, characterization and polymerization for some 2-(x,y,z-trimethoxyphenyl)-4-MDO derivatives. Specially, cationic polymerization behaviors catalyzed with boron trifluoride were investigated.

Experimental Section

2,4,5-Trimethoxybenzaldehyde, 2,4,6-trimethoxybenzaldehyde, and 3,4,5-trimethoxybenzaldehyde (Aldrich Chemical Co.) were used without further purification. *tert*-Butanol was purified by distillation after drying over calcium hydride and sodium metal. Dowex-50W (H^+, strong cation exchange resin) was used as an acetalization catalyst. Boron trifluoride diethyl etherate (Aldrich Chemical 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 were reported in cm^{-1}. ^1H NMR and ^{13}C NMR spectra were obtained with a Varian Gemini 2000 spectrometer. The chemical shifts were recorded in ppm from tetramethyl silane as an internal standard. The elimination content was calculated from the NMR integration of the corresponding benzaldehyde derivative and the gas chromatography. 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 10^2, 10^3 and 10^4 Å), calibrated with polystyrene standards, in tetrahydrofuran as eluent at 254 nm.

Preparation of 4-chloromethyl-2-(2,4,5-trimethoxy-phenyl)-1,3-dioxolane (1a). In a round bottom flask (250 mL) equipped with a Dean-Stark separator, a mixture of 2,4,5-trimethoxybenzaldehyde (11.77 g, 60.0 mmol) and 3-chloro-1,2-propanediol (7.96 g, 72.0 mmol) in toluene (150 mL) were placed, followed by refluxing with 0.5 g of Dowex-50W (H^+). After the calculated amount of water was removed by azeotropic distillation, the ion exchange resin was removed by filtration. The reaction mixture was washed with an excess water to remove the excess 3-chloro-1,2-propanediol. After the evaporation of solvent, the crude product was purified by successive distillation using a Kugelrohr distillation apparatus to give a colorless viscous liquid. 4-Chloromethyl-2-(2,4,6-trimethoxyphenyl)-1,3-dioxolane (**2a**) and 4-chloromethyl-2-(3,4,5-trimethoxyphenyl)-1,3-dioxolane (**3a**) were prepared by the similar procedures to those described above.

1a: Yield 80%, bp 125 °C/0.1 mmHg. FT-IR 2940 (aromatic C-H), 2850-2882 (aliphatic C-H), 1335-1127 (C-O) cm^{-1}. ^1H NMR ($CDCl_3$) δ 7.31 and 6.54 (2s; 2 H, aromatic protons), 6.00 (d; 1H, acetal proton), 4.32-3.67 (m; 3H, -OC<u>H</u>$_2$C<u>H</u>(C<u>H</u>$_2$Cl)O-), 3.82-3.64 (3s; 9H, C<u>H</u>$_3$O-), 3.62 (m; 2H, -C<u>H</u>$_2$Cl).

2a: Yield 42%, bp 128 °C/0.1 mmHg. FT-IR 2936 (aro-

matic C-H), 2860-2880 (aliphatic C-H), 1335-1125 (C-O) cm^{-1}. ^1H NMR ($CDCl_3$) δ 6.22 (s; 2H, aromatic protons), 6.02 (d; 1H, acetal proton), 4.31-3.63 (m; 3H, -OC<u>H</u>$_2$C<u>H</u>(CH_2Cl)O-), 3.85 (s, 9H, C<u>H</u>$_3$O-), 3.68 (m; 2H, -C<u>H</u>$_2$Cl).

3a: Yield 86%, bp 127 °C/0.1 mmHg, FT-IR 2940 (aromatic C-H), 2860-2880 (aliphatic C-H), 1335-1125 (C-O) cm^{-1}, ^1H NMR ($CDCl_3$) δ 7.22 (s; 2H, aromatic protons), 6.01 (d; 1H, acetal proton), 4.32-3.63 (m; 3H, -OC<u>H</u>$_2$C<u>H</u>(CH_2Cl)O-), 3.92 (s, 9H, C<u>H</u>$_3$O-), 3.68 (m; 2H, -C<u>H</u>$_2$Cl).

Preparation of 2-(2,4,5-trimethoxyphenyl)-4-methylene-1,3-dioxolane (1b). In a three necked round-bottomed flask (250 mL) equipped with a nitrogen inlet, a condenser and a dropping funnel was placed a solution of potassium (3.30 g, 60.0 mmol) dissolved in *tert*-butanol (60 mL). A solution of 4-chloromethyl-2-(2,4,5-trimethoxyphenyl)-1,3-dioxolane (**1a**, 14.43 g, 50.0 mmol) in *tert*-butanol (10 mL) was added slowly at 25 °C under nitrogen atmosphere for 30 min. After the addition was completed, the temperature was raised to 80 °C and maintained for 12 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 the solvent was evaporated, the resulting residue was vacuum distilled through a Vigreux column to give **1b** as a colorless liquid. 2-(2,4,6-Trimethoxyphenyl)-4-MDO (**2b**) and 2-(3,4,5-trimethoxyphenyl)-4-MDO (**3b**) were also prepared by the similar methods described above.

1b: Yield 66%, bp 120 °C/0.1 mmHg, FT-IR 2986-2936 (aromatic C-H), 2900-2836 (aliphatic C-H), 1686 (C=C), 1315-1140 (C-O) cm^{-1}, ^1H NMR ($CDCl_3$) δ 7.32 and 6.42 (2 s; 2H, aromatic protons), 6.12 (s; 1H, acetal proton), 4.82-4.43 (m; 2H, =C<u>H</u>$_2$), 4.01-3.72 (m; 2H, -OC<u>H</u>$_2$C(=CH_2) -O-), 3.76 (3s, 9H, C<u>H</u>$_3$O-). Anal. Calcd for $C_{13}H_{16}O_5$: C, 61.85; H, 6.34. Found: C, 62.10; H, 6.23.

2b: Yield 43%, bp 123 °C/0.1 mmHg, FT-IR 2980-2932 (aromatic C-H), 2886-2832 (aliphatic C-H), 1688 (C=C), 1321-1140 (C-O) cm^{-1}, ^1H NMR ($CDCl_3$) δ 6.32 (s; 1H, acetal proton), 6.24 (s; 2H, aromatic protons), 4.72-4.43 (m; 2H, =C<u>H</u>$_2$), 4.01-3.85 (m; 2H, -OC<u>H</u>$_2$C(=CH_2) -O-), 3.92 (s, 9H, C<u>H</u>$_3$O-). Anal. Calcd for $C_{13}H_{16}O_5$: C, 61.85; H, 6.34. Found: C, 62.62; H, 6.27.

3b: Yield 80%, bp 121 °C/0.1 mmHg, FT-IR 2977-2926 (aromatic C-H), 2882-2852 (aliphatic C-H), 1686 (C=C), 1321-1140 (C-O) cm^{-1}, ^1H NMR ($CDCl_3$) δ 7.20 (s; 2H, aromatic protons), 6.21 (s; 1H, acetal proton), 4.71-4.44 (m; 2H, =C<u>H</u>$_2$), 4.01-3.83 (m; 2H, -OC<u>H</u>$_2$C(=CH_2)-O-), 3.92 (s, 9H, C<u>H</u>$_3$O-). Anal. Calcd for $C_{13}H_{16}O_5$: C, 61.85; H, 6.34. Found: C, 61.87; H, 6.24.

Representative polymerization 2-(trimethoxyphenyl)-4-methylene-1,3-dioxolane derivatives. A solution of **1b** (0.5 g, 2.0 mmol) in purified methylene chloride (4 mL) was placed in a septum rubber-capped glass test tube under dry nitrogen atmosphere. The tube was then cooled at -30 and boron trifluoride etherate (5 mol%, 14.25 μL) was injected. After 4 h, the mixture was quenched with excess triethylamine diluted with methylene chloride (5 mL). The solution was washed with distilled water in several times. The crude mixture was poured into a large amount of cold *n*-hexane. The white precipitate was filtered and dried at 50 for 12 h under vacuum. Other monomer **2b** and **3b** were polymerized by the similar methods as described above.

Poly1b: yield 68%, FT-IR 2970-2936 (aromatic C-H), 2832 (aliphatic C-H), 1715 (C=O), 1208, 1125, 1032 (C-O) cm^{-1}, ^1H NMR ($CDCl_3$) δ 6.81-6.21 (br; 2H, aromatic protons), 5.02 (br; 1H, -O-C<u>H</u>(Ph-)CH_2-), 3.91-3.72 (br, m; 2 H, -CO-C<u>H</u>$_2$O-), 3.84-3.62 (br, m; 9H, C<u>H</u>$_3$O-), 2.01-1.62 (br; 2 H, -CO-C<u>H</u>$_2$-), ^{13}C NMR ($CDCl_3$) 204.2 (-<u>C</u>O-), 156.4, 151.6, 137.8, 113.4 (aromatic C's), 78.6 (-O-<u>C</u>H(Ph)-), 67.9 (-O-<u>C</u>H_2-CO-), 58.2, 58.2, 57.9 (-O<u>C</u>H_3), 44.1 (-CO-<u>C</u>H_2-).

2-(2,4,5-trimethoxyphenyl)-3(2*H*)dihydrofuranone, FT-IR 2980-2940 (aromatic C-H), 2840 (aliphatic C-H), 1758 (C=O), 1262, 1140, 1025 (C-O) cm^{-1}, ^1H NMR ($CDCl_3$) δ 7.14 and 6.54 (2s; 2H, aromatic protons), 5.22-5.43 (t; 1H, -O-C<u>H</u>(Ph-)CH_2), 4.21-3.66 (s; 2H, -O-C<u>H</u>$_2$-CO-), 3.91 (s, 9 H, C<u>H</u>$_3$O-), 2.83-2.40 (m; 2H, -CO-C<u>H</u>$_2$-).

Poly2b: yield 84%, FT-IR 2965-2940 (aromatic C-H), 2836 (aliphatic C-H), 1718 (C=O), 1202, 1120, 1032 (C-O) cm^{-1}, ^1H NMR ($CDCl_3$) δ 6.82-6.21 (br, s; 2H, aromatic protons), 5.01 (br; 1H, -O-C<u>H</u>(Ph-)CH_2-), 3.82-3.56 (br, m; 2 H, -CO-C<u>H</u>$_2$O-), 3.74 (br, s; 9H, C<u>H</u>$_3$O-), 2.01-1.67 (br; 2H, -CO-C<u>H</u>$_2$-).

2-(2,4,6-trimethoxyphenyl)-3(2*H*)dihydrofuranone, 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 6.45 (s; 2H, aromatic protons), 5.24-5.42 (t; 1H, -O-C<u>H</u>(Ph-)CH_2), 4.22-3.64 (s; 2H, -O-C<u>H</u>$_2$-CO-), 3.92 (s, 9H, C<u>H</u>$_3$O-), 2.84-2.42 (m; 2H, -CO-C<u>H</u>$_2$-).

Poly3b: yield 50%, FT-IR 2960-2940 (aromatic C-H), 2840 (aliphatic C-H), 1718 (C=O), 1220, 1120, 1020 (C-O) cm^{-1}, ^1H NMR ($CDCl_3$) δ 7.22 (br s; 2H, aromatic protons), 5.01 (m; 1H, -O-C<u>H</u>(Ph-)CH_2-), 3.82-3.63 (br, m; 2H, -CO-C<u>H</u>$_2$O-), 3.92 (br, s, 9H, C<u>H</u>$_3$O-), 2.34 (br; 2H, -CO-C<u>H</u>$_2$-).

2-(3,4,5-trimethoxyphenyl)-3(2*H*)dihydrofuranone, 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 7.22 (s; 2H, aromatic protons), 5.22-5.43 (t; 1 H, -O-C<u>H</u>(Ph-)CH_2), 4.21-3.66 (s; 2H, -O-C<u>H</u>$_2$-CO-), 3.92 (s, 9H, C<u>H</u>$_3$O-), 2.84-2.42 (m; 2H, -CO-C<u>H</u>$_2$-), ^{13}C NMR ($CDCl_3$) 214.0 (-<u>C</u>O-), 157.8, 152.4, 138.2, 114.4 (aromatic C's), 78.8 (-O-<u>C</u>H(Ph)-), 68.4 (-O-<u>C</u>H_2-CO-), 58.8, 58.1, 57.7 (-O<u>C</u>H_3), 44.2 (-CO-<u>C</u>H_2-).

Results and Discussion

Preparation of 4-MDO derivatives. 2-(2,4,5-Trimethoxyphenyl)-4-MDO (**1b**), 2-(2,4,6-trimethoxyphenyl)-4-MDO (**2b**), and 2-(3,4,5-trimethoxyphenyl)-4-MDO (**3b**) were chosen to examine the effect of the methoxy substituents on the phenyl group in the polymerization of 2-phenyl-4-MDO derivatives. The monomers were prepared by treating 4-chloromethyl-2-(trimethoxyphenyl)-1,3-dioxolane obtained from the reaction of trimethoxybenzaldehyde derivative with 3-chloro-1,2-propanediol, followed by dehydrochlorination with potassium *tert*-butoxide (*t*-BuOK) in *tert*-

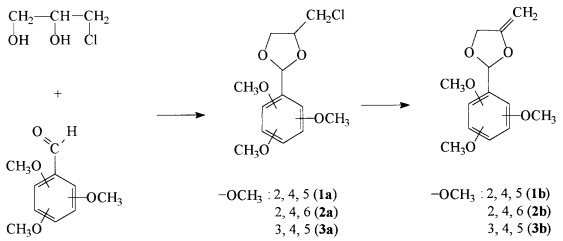
butanol as shown in Scheme 1.

2-Trimethoxyphenyl-4-MDO derivatives were stable at room temperature but rapidly changed to sticky polymer at higher temperature than 125 °C. And also the monomers were very sensitive toward acid moiety, upon contamination, they have a great tendency to polymerize. 2-(2,4,6-Trimethoxyphenyl)-4-MDO was the most reactive so it was polymerized easily during the vacuum distillation.

Characterization. The chemical structure of 2-(trimethoxyphenyl)-4-MDO derivatives were confirmed by ^{1}H NMR and IR spectroscopy. In the NMR spectra, the acetal proton of MDO ring appeared as a doublet peak at 6.0-5.8 ppm, which was attributed to the *cis* and trans isomers, but changed to a singlet peak centered at 6.1 ppm after dehydrochlorination. The characteristic methylene protons are shown between 4.7 and 4.4 ppm as a multiplet. In the IR spectrum, the absorption band of C=C is appeared around 1685 cm^{-1}. The C-O absorption bands of acetal group were shown at 1330-1125 cm^{-1}. Notably, the aromatic peaks are two singlets for **1a** and a singlet for **2a** and **3a.**

Cationic polymerization. 2-(Trimethoxyphenyl)-4-MDO derivatives were polymerized at -30 °C over a period of 4 h in the presence of 5 mol% of $BF_3 \cdot Et_2O$ as an initiator. The solid polymer was separated during the precipitation from the methylene chloride solution to a cold *n*-hexane. Fortunately, the cyclization product was soluble in large excess of *n*-hexane, so it can be obtainable as a viscous liquid after evaporation of n-hexane and further purified by vacuum distillation. The results of cationic polymerization were summarized in Table 1.

In the polymerization of **1b-3b**, the ring-opening polymerization and cyclization reaction were observed. But it is notable that the smells of trimethoxybenzaldehyde derivative were detected from the polymerization mixtures. This fact indicates that polymerization was accompanying by elimination reaction, which was observed during the polymerizations in this experiments. By using a gas chromatography, the retention time of the elimination product matched well with that of trimethoxybenzaldehyde and their contents were in the range of 2-5% in all case.



Scheme 1

All the IR spectra of the polymerization mixtures showed two kinds of absorption bands at 1720 and 1760 cm^{-1} assigned to C=O linkage. The precipitated polymer sample showed a strong absorption band at 1720 cm^{-1} in the IR spectrum, which indicates the presence of ring-opened C=O linkage. On the other hand, acetal proton in the MDO ring at 6.0 ppm in the ^{1}H NMR spectra and acetal carbon at 103 ppm in the ^{13}C NMR spectrum completely disappeared. However, viscous liquid sample obtained from the soluble portion in *n*-hexane was identified to be 3(2*H*)-dihydrofuranone derivative, which could be prepared through an intramolecular cyclization reaction.

It is interest to compare the amount of ring-opening polymerization and cyclization reaction, since the position of methoxy substituents have an effect on the reactivity of monomers to cationic species. There is a proviso that substituents be located at *meta* or *para* position in the benzene ring.[25] Rates and equilibrium constants for *ortho* substituted compounds do not fall on the equation line. However, the strong interaction of methoxy group occurred when substituents are located at *para* as well as *ortho* position. The plot of $\log k_{rel}$ against σ shows that *p*-MeO and *m*-MeO have -0.12 and 0.1, respectively. These facts mean that substitient of methoxy group at *para* position acts as an electron donating substituent. Notable that *meta* substitient acts as an electron withdrawing substituent.

When the monomer **1b** containing 2,4,5-trimethoxyphenyl group at 2-position of 4-MDO ring was polymerized at -30 °C with $BF_3 \cdot Et_2O$, a white powdery polymer was obtained after precipitation. The IR spectrum shows a strong absorption band at 1718 cm^{-1} corresponding to the C=O linkage. In the ^{13}C NMR spectrum, a peak around 204 ppm assignable to carbonyl carbon appeared but acetal carbon peak in MDO ring at 103 ppm completely disappeared. These facts demonstrated that 72% of **1b** underwent ring-opening polymerization to produce poly(keto ether). On the other hand, a

Table 1. Conditions and Results of the Polymerization of 2-(Tri-methoxyphenyl)-4-methylene-1,3-dioxolane Derivatives

Monomer	Initiator (mol%)	Solvent	Temp (°C)	Yield[a] (%)	MW[b]	Cyclization	Polymer
						Content (%)[c]	
1b (2,4,5)	BF_3 (5)	CH_2Cl_2	-30 °C	68	7200	28	72
	BF_3 (5)	〃	-70 °C	74	8700	20	80
2b (2,4,6)	BF_3 (5)	CH_2Cl_2	-30 °C	84	7420	12	88
	BF_3 (5)	CH_2Cl_2	-70 °C	90	8200	8	92
3b (3,4,5)	BF_3 (5)	CH_2Cl_2	-30 °C	50	5900	48	52
	BF_3 (5)	〃	-70 °C	42	6300	43	57

[a]Yields of a powdery polymer were measured gravimetrically. [b]Weight average molecular weight were taken with a Waters HPLC using three columns (μ-Styragel 10^2, 10^3 and 10^4 Å), calibrated with polystyrene standards in chloroform at 254 nm. [c]Ring-opened polymer and cyclization contents were determined by NMR integration or gravimetrically.

viscous liquid residue obtained from the non-solvent shows a strong absorption band at 1759 cm^{-1} indicating that 2-(2,4,5-trimethoxyphenyl)-3(2*H*)-dihydrofuranone was formed *via* an intramolecular cyclization reaction.

In the case of polymerization of **2b** carried out at -30 °C using $BF_3 \cdot Et_2O$, high yield without crosslinking was observed. 2-(2,4,6-Trimethoxy)phenyl-4-MDO (**2b**) underwent mainly ring-opening polymerization to give the poly (keto ether) in 88-92% yields. In contrast, polymer obtained from 2-(2,4-dimethoxy)phenyl-4-MDO showed no solubility in common organic solvents in the previous work.[22] The conversion of ring-opened polymer increased as the polymerization temperature was lowered to -70 °C. This fact indicates that the cationic initiator was more selectively attacked by the electron rich double bond of 4-MDO ring at low temperature.

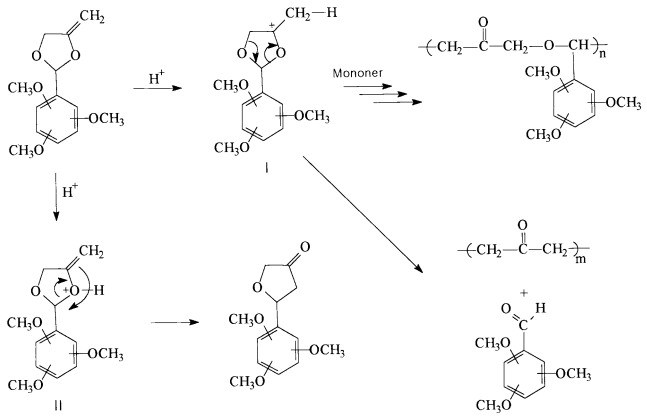
Monomer **3b** underwent a 52% of ring-opening polymerization and a 48% of intramolecular cyclization reaction to form poly(keto ether) and 2-(3,4,5-trimethoxyphenyl)-3(2*H*)-dihydrofuranone, respectively. The possible modes of reaction of **3b** also were characterized by spectroscopies. The viscous liquid residue obtained from the non-solvent can be distilled by Kugelrhor distillation apparatus to give a pure 2-(3,4,5-trimethoxyphenyl)-3(2*H*)-dihydrofuranone. In its IR spectrum, a strong absorption band at 1757 cm^{-1} corresponds to the presence of the cyclic carbonyl group.

According to the effect of the position of substituents mentioned previously, the tendency of the polymerization with $BF_3 \cdot Et_2O$ decreased as the number of *meta*-methoxy groups increased in the benzene ring. In the previous paper, 2-(dimethoxyphenyl)-4-MDO derivatives underwent both ring-opening polymerization and cyclization reaction. In the case of 2-(trimethoxyphenyl)-4-MDO derivatives, the tendencies were similar to those of 2-(dimethoxyphenyl)-4-MDO derivatives.[22]

In our experiment, the polymerizabilities of 2-(x,y,z-trimethoxyphenyl)-4-MDO derivatives are higher than those of 2-(x,y-dimethoxyphenyl)-4-MDO. As expected in the positions of methoxy group, 2-(2,4,6-trimethoxyphenyl)-4-MDO was the most reactive, hence autopolymerization proceeded slowly even at room temperature.

Further cationic reaction of 4-MDO would take place although the exact structure of such polymers and the mechanism are unclear at the present time.

On the basis of the products, the proposed polymerization mechanism is suggested as shown in Scheme 2. Polymerization is initiated by the addition of electrophile to the 4-methylene group of **1b-3b** to form carbocation intermediate **I**, which undergoes ring-opening accompanying by isomerization to keto group to afford more stable benzyl cation. The 2-5% of the benzyl cation formed was splitted to CH_2COCH_2 and trimethoxy benzaldehyde. Thus propagation proceeds by electrophilic attack of monomers and continues in a chain reaction manner to form the polymer consisting of two units poly(keto ether) and small amount of polyketone. Another competitive reaction is an electrophilic addition to oxygen atom of the 1,3-dioxolane ring to form an oxonium ion **II**,



Scheme 2

followed by intramolecularly cyclization leading to the formation of 3(2*H*)-dihydrofuranone derivative.

In conclusion, the cationic polymerization of 2-(trimethoxyphenyl)-4-MDO derivatives with $BF_3 \cdot Et_2O$ proceeded via ring-opening polymerization and cyclization reaction. The yields of poly(keto ether) and 3(2*H*)-dihydrofuranone exhibited a dependency on the position of the methoxy substituents in the benzene ring of 2-phenyl-4-MDO derivatives. Electrophilic attack of methylene and oxygen atom on 4-MDO occurred for the polymerization and cyclization, respectively. When comparing the yields of polymer with cyclization product, the polymerizavilities of monomers including 2-dimethoxyphenyl-4-MDO are in the order of 2,4,6 > 2,4 > 2,4,5 > 3,4 > 2,3 > 2,5 > 3,4,5.

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