Polymerization of Vinylketene Cyclic Acetals

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ABSTRACT: A convenient synthetic method for vinylketene cyclic acetals, 2-propenylidene- (**Ia**) and 4-phenyl-2-propenylidene-1,3-dioxolane (**Ib**), was developed by the reaction of 2-bromoethyl or 2-bromo-2-phenylethyl 3-butenoate with potassium *tert*-butoxide. The radical and cationic polymerizations of vinylketene cyclic acetals were investigated. In the radical polymerization, **Ia** gave copolymers consisting of the 1,2-, 1,4-, and 1,7-polymerization structures whereas **Ib** afforded homopolymer with the complete 1,7-polymerization structure. In the cationic polymerization, the structure of the polymers was dependent on the employed initiator. Although **Ia** gave copolymers composed of the 3,4- and 3,7-polymerization structures when boron trifluoride, trifluoromethanesulfonic acid, or tin(IV) chloride was used, copolymers with the 1,4- and 1,7-polymerization structures were obtained with iodine or aluminum chloride. On the other hand, homopolymers of **Ib** with the 3,4-polymerization structure and the 1,7-polymerization structure were obtained with boron trifluoride, trifluoromethanesulfonic acid, or tin(IV) chloride, and iodine or aluminum chloride, respectively.

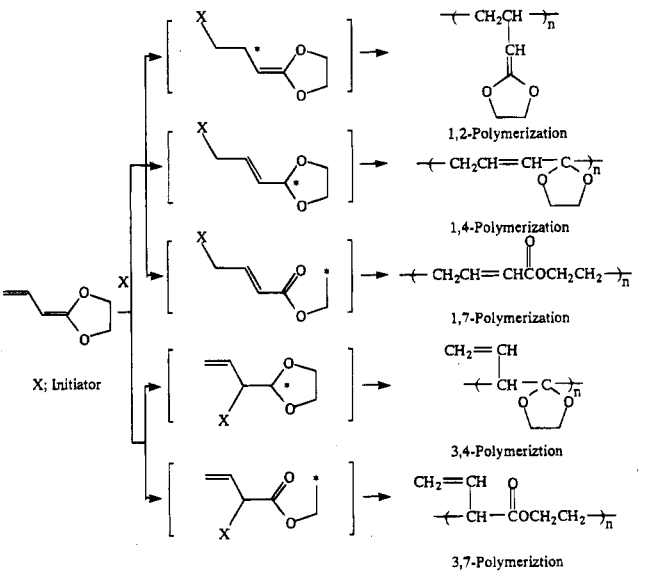
Introduction

It is known that the carbon–carbon double bond of ketene acetals is highly polarized and that the β-carbon atom has a strong anionic character which arises from the electron-donating property of the two conjugated oxygen atoms. Therefore, most of the ketene acetals are subjected to reaction with protic substrates and easily undergo cationic polymerization.[1] It is anticipated that this unique character of the β-carbon atom can be used to develop new reaction processes. We have reported cationic polymerization of cyclic ketene acetals,[2] reaction of cyclic ketene acetals with methanol,[3] isocyanate,[4] and isothiocyanate,[5] and copolymerization of cyclic ketene acetals with carbon disulfide.[6] From a different viewpoint, radical polymerization of cyclic ketene acetals has been reported.[7]

In the course of our study of ketene acetal chemistry, we have designed vinylketene cyclic acetals, which are 1,3-diene monomers having one more conjugated carbon–carbon double bond at the β-carbon atom of the carbon–carbon double bond of ketene acetals. Taking into account the facts that (1) vinylketene acetals are 1,3-diene monomers, (2) the β-carbon atom of the carbon–carbon double bond of cyclic ketene acetals has a strong anionic character,[1–6] and (3) radical polymerization of ketene cyclic acetal gives rise predominantly to polyester by ring-opening isomerization polymerization,[7] several polymerization modes can be expected as shown in Scheme 1. Therefore, we have great interest in their polymerizability by means of radical and cationic initiators. In our previous paper[8] it has been demonstrated that the regioselective polymerization of vinylketene cyclic acetal is attained by cationic initiators. Recently, Cho and his co-worker also studied the radical polymerization of vinylketene cyclic acetals independently.[9]

In this paper we wish to describe the novel synthesis and the polymerization of vinylketene cyclic acetals together with the polymer structure on the basis of the model compounds.

Scheme 1



Experimental Section

General Methods. Unless stated otherwise, all chemicals and reagents were obtained commercially and used without further purification. All solvents such as tetrahydrofuran (THF), *N*,*N*-dimethylformamide (DMF), benzene, carbon tetrachloride, and so on were dried and purified according to the accepted methods. 2-Propenyl-1,3-dioxolane was prepared from crotonaldehyde and ethylene glycol.[10] ^{1}H and ^{13}C NMR spectra were recorded on a Hitachi R-90H spectrometer. IR spectra were recorded on a Hitachi 295 infrared spectrophotometer. The average molecular weight and the molecular weight distribution of polymers were measured by a modular system for gel permeation chromatography (GPC) consisting of a Shodex Degas, a Jasco Model 880-PU solvent delivery system, a Shodex Model AO-50 injector and column oven system, and a Shodex RI SE-61 differential refractometer, which was interfaced with a System Instruments Chromatocorder 12. The columns (AC-803 and AC-80M) and polystyrene standards that were used were purchased from Showa Denkko K.K.

Synthesis of 2-Propenylidene-1,3-dioxolane (Ia). To a suspension of 6.73 g (60 mmol) of potassium *tert*-butoxide in

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50 mL of DMF was added a solution of 9.65 g (50 mmol) of 2-bromoethyl 3-butenoate (prepared from vinylacetic acid and 2-bromoethanol) in 25 mL of DMF dropwise with stirring at −15 °C for 1 h. After the addition was completed, the reaction mixture was stirred at the same temperature overnight. The product mixture was diluted with 200 mL of ether and then washed with 100 mL of water three times. After the organic layer was dried over anhydrous magnesium sulfate, the solvent was removed under reduced pressure. The residue was fractionally distilled over metallic sodium *in vacuo*, and the distillate was further purified by redistillation over metallic sodium to give 3.39 g (60%) of **Ia**; bp 84−86 °C/35 torr [lit.[11] bp 38−40 °C/0.5 torr]; IR (neat) 1680, 1050 cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.40 (s, 4H), 4.52−4.88 (m, 3H), 6.42 (ddd, J = 10.7, 10.7, 17.4 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 65.7, 66.2, 75.3, 131.0, 160.6.

Synthesis of 4-Phenyl-2-propenylidene-1,3-dioxolane (Ib). To a solution of 5.05 g (45 mmol) of potassium *tert*-butoxide in 25 mL of DMF was added a solution of 8.07 g (30 mmol) of 2-bromo-2-phenylethyl 3-butenoate, prepared from vinylacetic acid and 2-bromo-2-phenylethanol, in 25 mL of DMF dropwise with stirring at −15 °C for 1 h. After the reaction mixture was stirred at the same temperature overnight, the DMF was removed under reduced pressure. The residue was dissolved in 50 mL of ether, and the precipitated solid was filtered off. After evaporation of the ether, the residue was fractionally distilled over metallic sodium *in vacuo*. The purification of the product was carried out by further distillation over metallic sodium to give 2.64 g (50%) of **Ib**; bp 95−96 °C/0.12 torr [lit[9] bp 96 °C/0.05 torr]; IR (neat) 1680, 1040 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.94−4.16 (dt, J = 8.2 Hz, 1H), 4.42−4.96 (m, 4H), 5.27−5.50 (dt, J = 8.2 Hz, 1H), 6.51 (ddd, 10.7, 10.7, 17.6 Hz, 1H), 7.39 (s, 5H); ^{13}C NMR ($CDCl_3$) δ 69.6, 70.1, 73.4, 76.0, 76.4, 104.8, 104.9, 123.5, 125.7, 126.0, 126.3, 128.4, 128.5, 158.1.

Addition Reaction of Methanol to Ia. To a solution of 0.92 g (8 mmol) of **Ia** in 4 mL of chloroform was added 4 mL of methanol at 0 °C. The reaction mixture was allowed to stand overnight at room temperature. After the solvent and excess methanol were removed under reduced pressure, the residue was fractionally distilled *in vacuo* to give 1.04 g (90%) of 2-allyl-2-methoxy-1,3-dioxolane (**IIa**); bp 46−47 °C/2 torr; IR (neat) 1650, 1080 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.56 (d, 2H), 3.27 (s, 3H), 3.90−4.28 (m, 4H), 4.97−5.26 (m, 2H), 5.56−6.09 (m, 1H); ^{13}C NMR ($CDCl_3$) δ 40.0, 49.0, 65.0, 117.8, 121.5, 131.8.

Addition Reaction of Methanol to Ib. The procedure is similar to the foregoing, starting from 1.5 g (8.5 mmol) of **Ib** and 4 mL of methanol. The crude product was fractionally distilled *in vacuo* to afford 1.78 g (95%) of 2-allyl-2-methoxy-4-phenyl-1,3-dioxolane (**IIb**); bp 105−106 °C/0.2 torr; IR (neat) 1640, 1070 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.50−2.83 (m, 2H), 3.39 (s, 3H), 3.52−3.96 (m, 1H), 4.14−4.56 (m, 1H), 4.90−5.38 (m, 3H), 5.65−6.21 (m, 1H), 7.34 (s, 5H); ^{13}C NMR ($CDCl_3$) δ 40.2, 40.6, 49.5, 71.7, 72.3, 78.1, 78.4, 118.1, 122.3, 125.9, 126.0, 128.1, 128.4, 131.9, 138.4.

Radical Polymerization. Radical polymerization was carried out by the sealed-tube method. A typical polymerization (Table 2, entry no. 6) was performed as follows. A solution of 0.28 g (1.5 mmol) of **Ib** and 7.2 mg (3 mol %) of 2,2′-azobis(isobutyronitrile) in 2 mL of benzene was heated at 50 °C for 24 h. After the polymerization was completed, the mixture was poured into *n*-hexane to precipitate the polymer as a white powder. The precipitated polymer was collected, washed thoroughly, and dried under reduced pressure to yield 0.18 g (64%) of poly-**Ib**: IR (film) 1715, 1635, 1260, 1160 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.23−2.80 (br m, 2H), 2.80−3.37 (br m, 1H), 3.90−4.45 (br d, 2H), 5.50−5.88 (br d, 1H), 6.40−6.92 (br m, 1H), 6.92−7.50 (br s, 1H); ^{13}C NMR ($CDCl_3$) δ 35.1, 44.1, 67.2, 122.7, 127.0, 127.6, 128.5, 140.1, 146.2, 165.6.

Cationic Polymerization. Cationic polymerization was performed under an argon atmosphere. Typically (Table 3, entry no. 4), a solution of 0.5 g (2.7 mmol) of **Ib** in 4 mL of dichloromethane was placed in a polymerization tube equipped with a No-Air stopper. After the solution was purged with a stream of argon at −30 °C for 30 min, 1 mL of dichloromethane solution containing 5.75 mg (1.5 mol %) of boron trifluoride etherate was added by a syringe. The reaction mixture was maintained at the same temperature for 10 min and then allowed to stand at room temperature for 72 h. The reaction mixture was poured into *n*-hexane to precipitate a white solid. The precipitated polymer was collected and purified by reprecipitation from chloroform solution into *n*-hexane to obtain 0.48 g (96%) of poly-**Ib**: IR (film) 1745, 1510, 1460, 1165 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.07−3.10 (br m, 1H), 3.20−3.85 (br m, 1H), 3.92−4.47 (br m, 1H), 4.60−5.40 (br m, 2H), 5.57−6.15 (br m, 1H), 6.42−7.68 (br s, 5H); ^{13}C NMR ($CDCl_3$) δ 35.3, 43.0, 53.8, 65.5, 67.8, 71.3, 78.8, 112.5, 120.0, 126.0, 128.0, 136.5, 138.0, 171.3.

Table 1. Synthesis of Vinylketene Acetals (I)

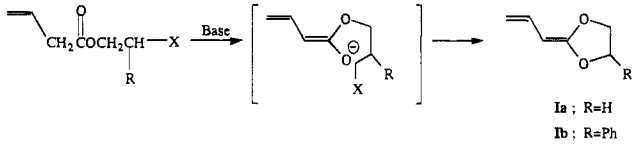
			reaction conditions			product	
no.	R	X	base	temp (°C)	solvent	type	yield (%)
1	H	Cl	*t*-BuOK	0	THF	**Ia**	2-chloroethyl crotonate[b]
2	H	Cl	*t*-BuOK	−15	THF	**Ia**	trace
3	H	Cl	*t*-BuOK	−15	DMF	**Ia**	43
4	H	Cl	NaH	0	THF		2-chloroethyl crotonate
5	H	Cl	KH	0	DME[a]		2-chloroethyl crotonate
6	H	Cl	$(i\text{-Pr})_2NH$/BuLi	−78	THF	**Ia**	trace
7	H	Br	*t*-BuOK	0	THF	**Ia**	23
8	H	Br	*t*-BuOK	−15	DMF	**Ia**	60
9	Ph	Cl	*t*-BuOK	0	THF		styrene oxide
10	Ph	Cl	*t*-BuOK	−15	DMF	**Ib**	trace
11	Ph	Br	*t*-BuOK	0	THF	**Ib**	10
12	Ph	Br	*t*-BuOK	−15	DMF	**Ib**	50

[a] DME = 1,2-dimethoxyethane. [b] Trace amount of **Ia** was detected.

Results and Discussion

Synthesis of Monomers. It was reported that vinylketene cyclic acetal, 2-propenylidene-1,3-dioxolane (**Ia**), was prepared by the reaction of 2-(1,2-dibromopropyl)-1,3-dioxolane with potassium amide or potassium *tert*-butoxide.[11] We traced these reactions carefully to find that the isolation yield of the pure monomer is too low to apply these reactions as the synthetic method because of the contamination of byproducts such as allene and acetylene derivatives.

A new synthetic route was designed by using 2-chloroethyl, 2-bromoethyl, and 2-bromo-2-phenylethyl 3-butenoate as the starting material. It can be expected that the enolization of 3-butenoate by means of a suitable base should bring about the cyclization by the reaction of enolate anion and the haloethyl moiety to give vinylketene cyclic acetal (**I**).



In order to determine the optimum conditions, the reaction of butenoate with several kinds of bases was carried out under various conditions. The results are summarized in Table 1. When sodium hydride or potassium hydride was used, cyclization did not take place but the complete isomerization reaction of 2-chloroethyl 3-butenoate to 2-chloroethyl crotonate occurred. It is clear that the most suitable reaction conditions are (i) haloester, bromoester; (ii) base, potassium *tert*-butoxide; (iii) solvent, DMF, and (iv) temperature, −15 °C.

Radical Polymerization. Radical polymerization of vinylketene cyclic acetals was carried out under various

Table 2. Radical Polymerization of Vinylketene Acetals (I)

		reaction conditions				polymer		
no.	monomer	initiator[a]	temp (°C)	time (h)	solvent	yield (%)[b]	M_n[c]	M_w/M_n[c]
1	**Ia**	AIBN	50	48	benzene	8	*d*	
2	**Ia**	AIBN	50	48	neat	14	*d*	
3	**Ia**	AIBN	80	48	benzene	36	*d*	
4	**Ia**	BPO	50	96	benzene	8	*d*	
5	**Ia**	BPO	50	96	neat	6	*d*	
6	**Ib**	AIBN	50	24	benzene	64	45 000	8.2

[a] Initiator, 3 mol %. [b] Insoluble in *n*-hexane. [c] Estimated by GPC calibrated with polystyrene standards. [d] Gelation occurred during the purification.

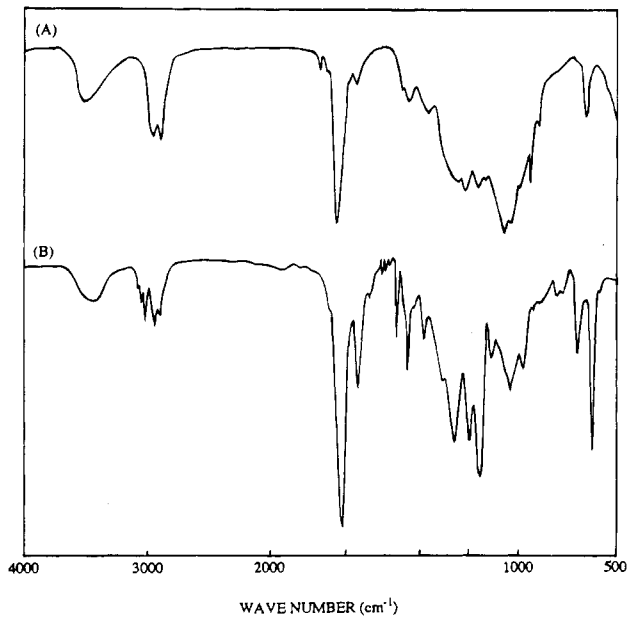


Figure 1. IR spectra of polymers obtained by the radical polymerization: (A) poly-**Ia**; (B) poly-**Ib**.

conditions. Polymers were isolated by pouring polymer solution diluted with chloroform into *n*-hexane. As can be seen in Table 2, **Ia** has a very low radical homopolymerizability and affords oligomers with low molecular weight whereas **Ib** has a fairly high homopolymerizability and hence gives rise to relatively high molecular weight polymers. The structures of the resulting polymers were determined by means of IR, ^{1}H NMR, and ^{13}C NMR spectroscopies. The IR spectra of poly-**Ia** and poly-**Ib** clearly show (Figure 1) strong characteristic ester carbonyl absorption bands at 1735 and 1715 cm^{-1} together with the absorptions of the carbon–carbon double bond at 1660 and 1645 cm^{-1}. These facts strongly suggest that radical polymerization of vinylketene cyclic acetals predominantly proceeds through the 1,7-propagation mechanism. The ^{1}H NMR spectra of the polymers, in fact, revealed the characteristic multiplet signal at around 6.5–7.2 ppm, assignable to the olefinic β-methine proton adjacent to the carbonyl group (–C**H**=CHCO–). The ^{1}H and ^{13}C NMR spectra of poly-**Ia** are very complicated but clearly showed the existence of the ketal ring structure produced from the 1,4-propagation mechanism. However, poly-**Ia** was moderately unstable and gradually became insoluble in any organic solvents during the purification process, which indicates that poly-**Ia** contained the ketene cyclic acetal structure derived from the 1,2-propagation mechanism.[1,10] Therefore, it can be assumed that radical polymerization of **Ia** gives rise to the copolymers consisting of the 1,2-, 1,4-, and 1,7-structures.

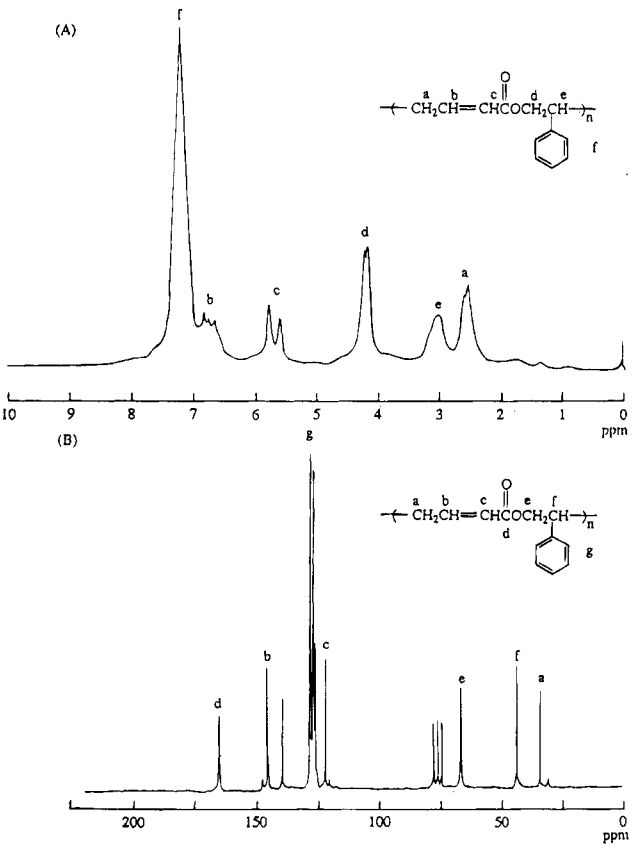
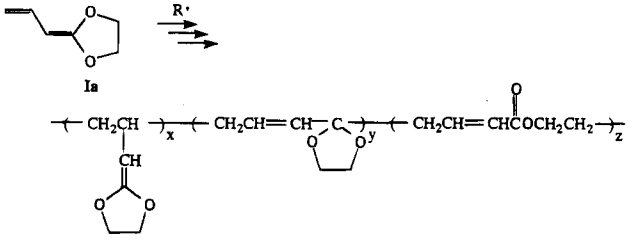
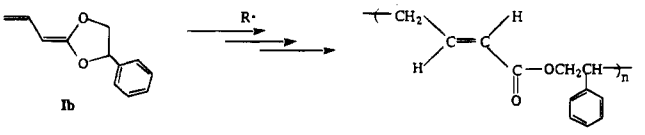


Figure 2. ^{1}H and ^{13}C NMR spectra of poly-**Ib** obtained by the radical polymerization in $CDCl_3$.



On the other hand, it is noteworthy that any signals ascribed to the remaining ketal ring structure were not detected in the ^{1}H and ^{13}C NMR spectra of poly-**Ib** as shown in Figure 2. Consequently, it might be assumed that the increased radical homopolymerizability of **Ib** arises from the formation of a stable benzylic radical as the reactive species by the ring-opening isomerization of the ketal ring, similar to the radical polymerization of 2-methylene-4-phenyl-1,3-dioxolane.[7,8] The coupling constant (15.2 Hz) of the olefinic β-methylene proton signal at 5.7 ppm revealed that the resulting polymer consists completely of the trans structure.



Cationic Polymerization. Before the cationic polymerization of the vinyl ketene cyclic acetals, the calculation (PM3) of the atomic charges of **Ia** and **Ib** was performed by using MOPAC 6.00. The results are summarized in Scheme 2. It is of particular interest that the β-carbon atom of cyclic ketene acetals has the

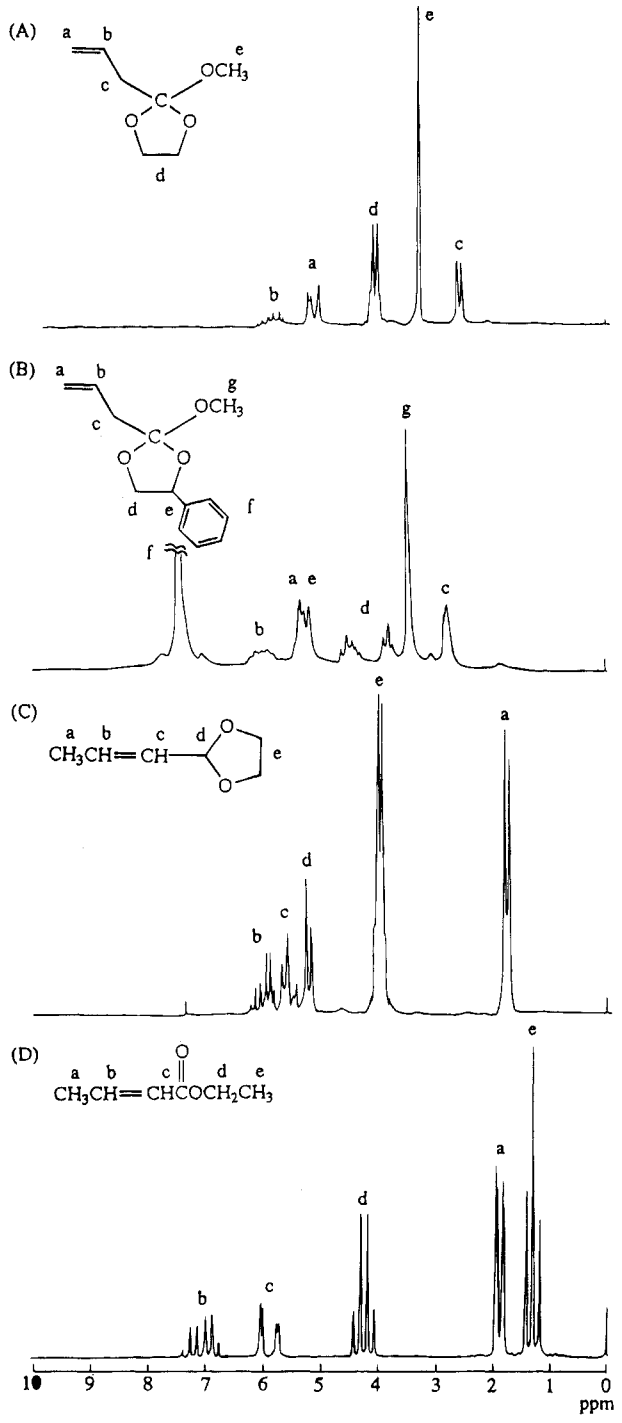
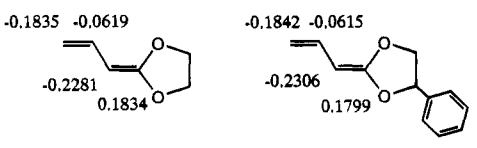


Figure 3. ^{1}H NMR spectra of the model compounds in $CDCl_3$: (A) **IIa**; (B) **IIb**; (C) 2-propenyl-1,3-dioxolane; (D) ethyl 2-butenoate.

Scheme 2



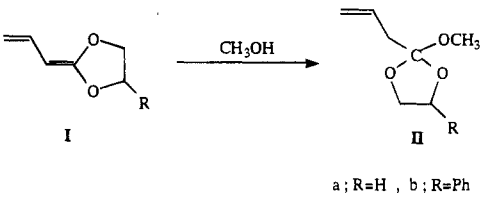
most negative charge. This result indicates that the most probable position attacked by the cationic species is not the terminal δ-carbon atom but the β-carbon atom of cyclic ketene acetals. In order to confirm this prediction, the reaction of **Ia** or **Ib** with methanol was carried out. Upon the mixing of **Ia** with a large excess of methanol, a rapid exothermic reaction took place. The

Table 3. Cationic Polymerization of Vinylketene Acetals (I)

		reaction conditions				polymer		
no.	monomer	initiator (mol %)	temp (°C)	time (h)	solvent	yield (%)[a]	M_n[b]	M_w/M_n[b]
1	**Ia**	BF_3·OEt_2 (2.4)	25	*c*	CCl_4	60	4400	3.8
2	**Ia**	CF_3SO_3H (2.0)	25	72	CH_2Cl_2	98	2100	2.3
3	**Ia**	I_2 (4.5)	25	72	CH_2Cl_2	50	1200	2.3
4	**Ib**	BF_3·OEt_2 (1.5)	25	72	CH_2Cl_2	96	6800	3.1
5	**Ib**	BF_3·OEt_2 (3.0)	25	48	$CHCl_3$	52	1100	1.8
6	**Ib**	BF_3·OEt_2 (3.0)	−15	72	$CHCl_3$	66	1900	2.1
7	**Ib**	$SnCl_4$ (4.5)	25	72	$CHCl_3$	28[d]	4200	2.0
8	**Ib**	CF_3SO_3H (2.0)	25	72	CH_2Cl_2	91	2800	2.2
9	**Ib**	I_2 (2.5)	25	72	CCl_4	55	2300	2.5
10	**Ib**	I_2 (4.5)	25	72	ether	68	2200	1.4
11	**Ib**	$AlCl_3$ (4.5)	25	72	$CHCl_3$	64	19000	1.8

[a] Insoluble in *n*-hexane. [b] Estimated by GPC calibrated with polystyrene standards. [c] Instantaneous. [d] Insoluble in ether.

^{1}H NMR spectra of model compounds are shown in Figure 3. The ^{13}C NMR spectrum of the product showed signals ascribed to $\mathbf{C}H_2$=CH, CH_2=$\mathbf{C}$H, and −$\mathbf{C}$− at 117.8, 131.8, and 121.5 ppm, respectively. These spectra demonstrate that the complete 3,4-addition reaction occurs to produce 2-allyl-2-methoxy-1,3-dioxolane (**IIa**).



Ib also reacted with methanol to afford 2-allyl-2-methoxy-4-phenyl-1,3-dioxolane (**IIb**) quantitatively. Further, it is reported that the cationic polymerization of cyclic ketene acetals proceeds through vinyl polymerization without the ring-opening reaction.[1,8] Therefore, it is reasonable to assume that the cationic polymerization of **Ia** and **Ib** should proceed through the 3,4-propagation mechanism.

Based on the above consideration, cationic polymerization of **Ia** and **Ib** was carried out by using iodine, trifluoromethanesulfonic acid, and Lewis acids such as boron trifluoride, tin(IV) chloride, and aluminum chloride. The polymers were isolated by poring the polymer solutions into *n*-hexane. The results are summarized in Table 3. All initiators were effective for cationic polymerization of vinylketene cyclic acetals. The resulting polymers were stable and soluble in chloroform, THF, acetone, etc., indicating the absence of the 1,2-polymerization structure in contrast with the radical polymerization of **Ia**. Polymer structures were examined by IR, ^{1}H NMR, and ^{13}C NMR spectroscopy. Typical IR spectra of poly-**Ia** (entry nos. 1 and 3) and poly-**Ib** (entry nos. 4, 9, and 11) are shown in Figure 4.

Contrary to our expectation, these spectra showed the ester carbonyl absorption around 1745−1715 cm^{-1}, suggesting the existence of the ring-opened structure derived from the 1,7-polymerization and/or 3,7-polymerization modes.[7] The IR spectra of the polymers obtained from iodine or aluminum chloride as an initiator showed especially strong carbonyl absorption bands. The spectrum of poly-**Ib** was identical to that obtained from the radical polymerization.

Figure 5 displays the ^{1}H NMR spectra of poly-**Ia** produced by boron trifluoride (entry no. 1) and iodine (entry no. 3). It is obvious that the ^{1}H NMR spectrum of poly-**Ia** obtained from boron trifluoride shows only a trace signal at around 7 ppm, which is assignable to

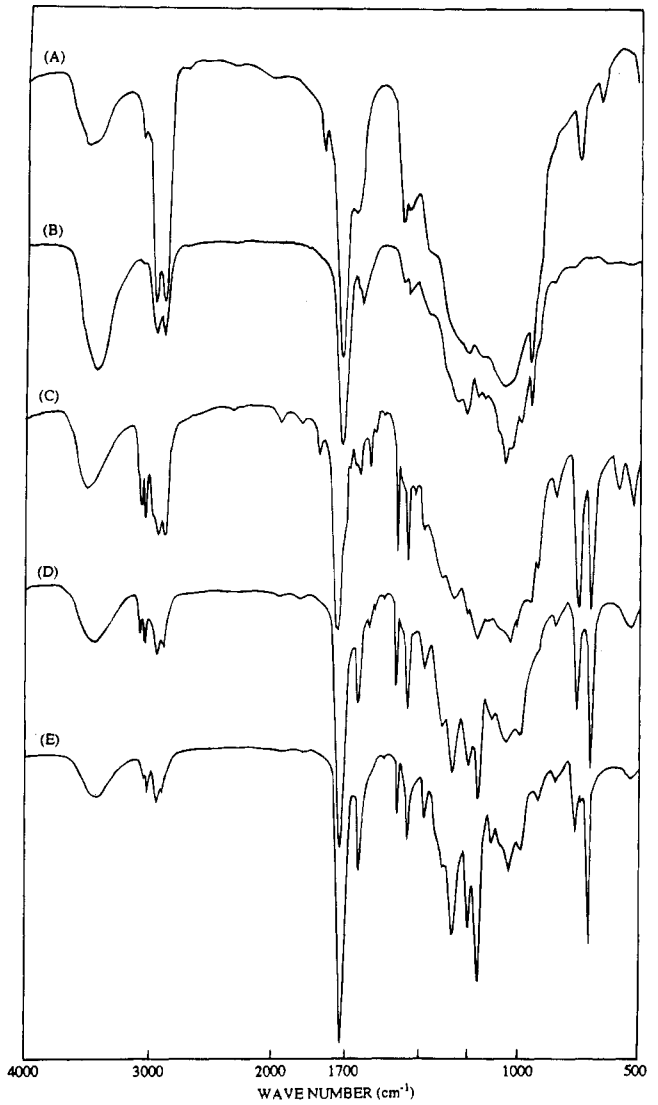
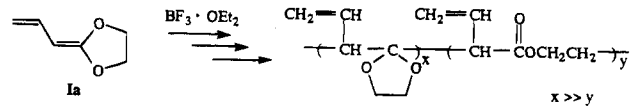


Figure 4. IR spectra of polymers obtained by the cationic polymerization: (A) poly-**Ia** obtained with BF_3·OEt; (B) poly-**Ia** obtained with I_2; (C) poly-**Ib** obtained with BF_3·OEt; (D) poly-**Ib** obtained with I_2; (E) poly-**Ib** obtained with $AlCl_3$.

the unsaturated β-methine proton adjacent to the carbonyl group (−C**H**=CH−CO). The peaks in the range 4.8−6.2 ppm can be assigned to the typical vinyl protons (CH_2=C**H**−) on the basis of the ^{1}H NMR spectrum of the model compound (**IIa**) as shown in Figure 3. Further, the signal centered at 3.9 ppm and the small shoulder at 4.2 ppm may be due to methylene protons of the ethylene ketal structure (−OCH_2CH_2O−) and the ring-opened structure (−$COOCH_2$−), respectively. Although the determination of the polymer composition is impossible because of the overlapping of these two signals, it is reasonable to assume that poly-**Ia** obtained from boron trifluoride is a copolymer which consists mainly of the 3,4-polymerization structure and only slightly of the 3,7-polymerization structure. The ^{13}C NMR spectrum of the polymer also supports this assumption.



However, the ^{1}H NMR spectrum of poly-**Ia** initiated by iodine or aluminum chloride clearly shows the broad

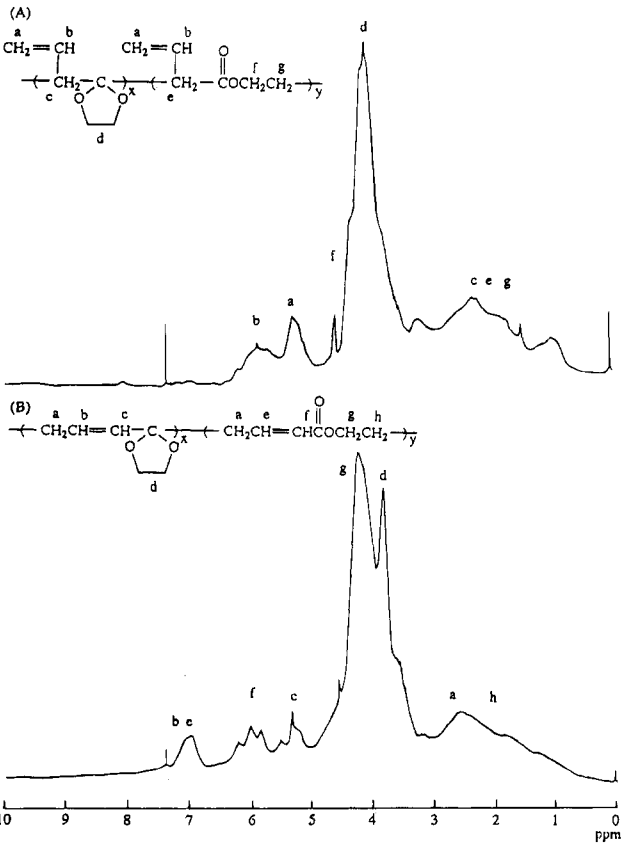
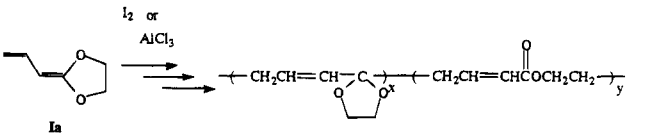


Figure 5. ^{1}H NMR spectra of polymers obtained by the cationic polymerization in $CDCl_3$: (A) poly-**Ia** obtained with BF_3·OEt; (B) poly-**Ia** obtained with I_2.

signal at about 7 ppm ascribed to the β-methine proton adjacent to the carbonyl group (−C**H**=CH−CO) and two signals at around 5.3 and 6.0 ppm due to inner olefinic methine protons (−C**H**=C**H**−). These signals are well coincident with those of the model compounds, ethyl crotonate (**III**) and 2-(1-propenyl)-1,3-dioxolane (**IV**), as shown in Figure 3. From the ratio of the signal at 4.2 ppm ascribed to the methylene proton of the ester structure (−$COOCH_2$−) to that at 2.8 ppm assignable to the methylene protons of the ethylene ketal structure (−OCH_2CH_2O−), the composition of poly-**Ia** obtained from iodine or aluminum chloride was estimated to be 6:1 for the 1,7-polymerization structure to the 1,4-polymerization structure.



Cationic polymerization of **Ib** more remarkably showed the difference of polymerization mode by means of the kind of initiator. The IR spectra of the polymers obtained from boron trifluoride, trifluoromethanesulfonic acid, and tin(IV) chloride showed the strong broad absorption band ascribed to the ketal linkage at about 1100 cm^{-1} together with the ester band as shown in Figure 4. A typical ^{1}H NMR spectrum of poly-**Ib** obtained from boron trifluoride (entry no. 4) is depicted in Figure 6. Five broad signals centered at 5.7 (CH_2=C**H**−), 5.0 (CH_2=CH− and −C**H**Ph−), 4.2 and 3.6 (−OCH_2C**H**Ph), and 2.4 ppm (−C**H**− of the polymer backbone) were observed, and these signals are in good agreement with those observed for the model compound

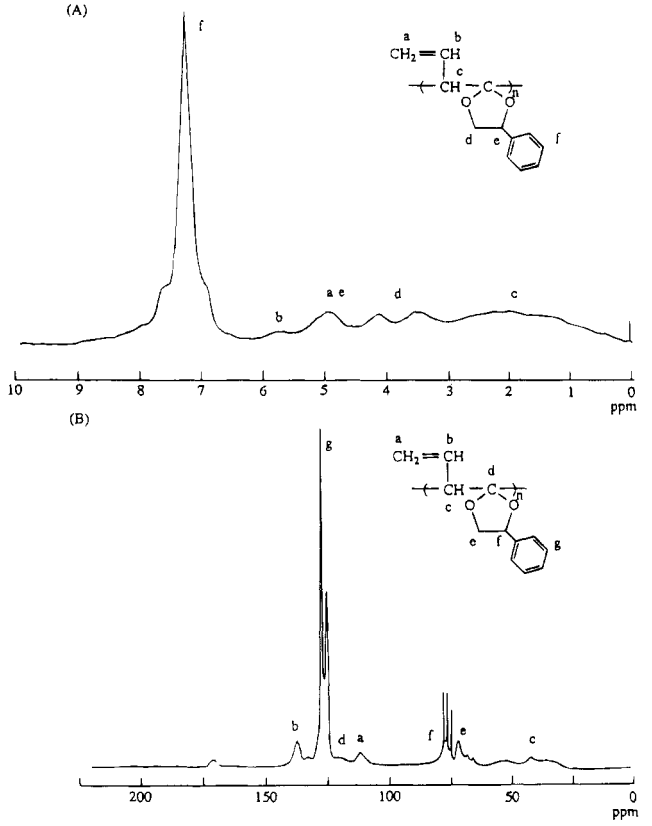
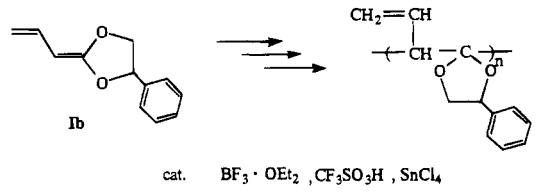
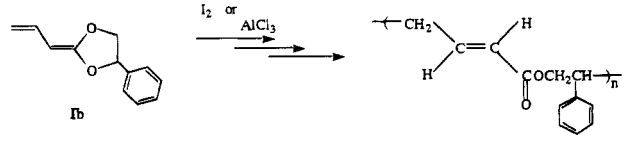


Figure 6. ^1H and ^{13}C NMR spectra of poly-**Ib** obtained by the cationic polymerization with BF_3·OEt in $CDCl_3$.

of the 3,4-polymerization structure, **IIb**, in Figure 3. Although the intensity ratio of these signals (1:3:1:1:1) indicates the almost complete 3,4-polymerization structure, the IR (Figure 4c) and ^{13}C NMR (Figure 6) spectra clearly show the presence of the ester structure from the ring opening through the 3,7-polymerization mode. Therefore, it can be assumed that polymerization of **Ib** using boron trifluoride, trifluoromethanesulfonic acid, or tin(IV) chloride gives rise almost completely to the 3,4-polymerization structure with some 3,7-polymerization structure included in the copolymer.



On the other hand, it was found that the IR spectra (Figure 4d,c) as well as the ^1H and ^{13}C NMR spectra (Figure 7) of poly-**Ib** initiated by aluminum chloride (entry no. 11) or iodine are exactly the same as that obtained by radical polymerization. These results demonstrate the complete 1,7-polymerization mechanism for **Ib** by means of aluminum chloride or iodine as an initiator.



It has been reported that quaternary ammonium salts depress the ring-opening isomerization of the zwitterion

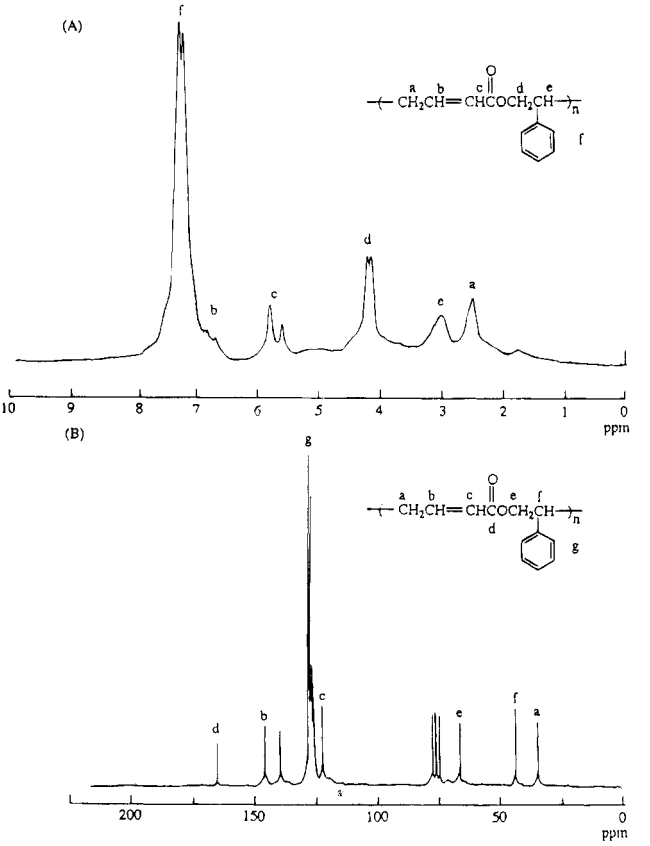


Figure 7. ^1H and ^{13}C NMR spectra of poly-**Ib** obtained by the cationic polymerization with $AlCl_3$ in $CDCl_3$.

Table 4. Cationic Polymerization of Ib in the Presence of Ammonium Halide[a]

	reaction conditions			polymer		
no.	ammonium halide	time (h)	solvent	yield (%)[b]	M_n[c]	M_w/M_n[c]
1	TBAC[d]	96	CH_2Cl_2	36	1100	7.2
2	TBAB[e]	96	CH_2Cl_2	70	2000	3.9
3	TBAI[f]	96	CH_2Cl_2	68	900	3.6
4	TBAB	72	ether	56	1100	3.0
5	TBAB	72	neat	72	1700	4.8

[a] Cationic polymerization of **Ib** was carried out by using I_2 (4.5 mmol %) in the presence of ammonium halide (5.4 mmol %) at 25 °C. [b] Insoluble in *n*-hexane. [c] Estimated by GPC calibrated with polystyrene standards. [d] Tetrabutylammonium chloride. [e] Tetrabutylammonium bromide. [f] Tetrabutylammonium iodide.

formed from 4-phenyl-2-methylene-1,3-dioxolane and methyl α-cyanoacrylate.[12] Therefore, it can be assumed that cationic polymerization of **Ib** by means of iodine as an initiator should bring about the complete 1,4-polymerization if a quaternary ammonium salt, such as tetrabutylammonium bromide, chloride, or iodide, is employed as an additive. Hence, polymerization of **Ib** with iodine in the presence of a quaternary ammonium salt was carried out under various conditions. The results are summarized in Table 4. The number-average molecular weight of the obtained polymers was somewhat smaller than that of the polymer produced without quaternary ammonium salt. The molecular weight distribution of the polymers was fairly large, which indicates that the chain transfer reaction might easily take place by the addition of a quaternary ammonium salt. Contrary to our expectation, the structure of the resulting polymers was found to be the 1,7-structure as confirmed by the IR, ^1H NMR, and ^{13}C NMR spectra.

Conclusion

A convenient method for the synthesis of vinylketene cyclic acetals was developed by the reaction of 2-bromoethyl or 2-bromo-2-phenylethyl 3-butenoate and potassium *tert*-butoxide in DMF at −15 °C. Radical polymerization of vinylketene cyclic acetals gave polymers consisting predominantly of the 1,7-polymerization structure together with minor structures from the 1,2- and 1,4-polymerization mechanism. Especially, polymerization of vinylketene acetal having a phenyl group proceeded through the complete 1,7-propagation mechanisms.

As for cationic polymerization of vinylketene cyclic acetals, the structure of the polymers was dependent on the initiator employed. If boron trifluoride, trifluoromethanesulfonic acid, or tin(IV) chloride was used as an initiator, copolymers composed of the 3,4-polymerization and the 3,7-polymerization structures were obtained. On the other hand, cationic polymerization of vinylketene cyclic acetal with iodine or aluminum chloride gave copolymers with the 1,7-polymerization and 1,4-polymerization structures. In this case, vinylketene acetal with a phenyl substituent afforded the complete homopolymer with the 1,7-polymerization structure. The reason why the structure of the polymers is influenced by the kind of initiator is not clear at present.

References and Notes

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