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Possibility of Carboxylic Acid Esters as Thermally Latent Initiators

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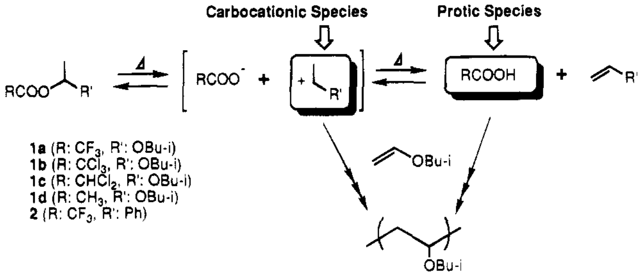
ABSTRACT: Carboxylic acid esters, or an adduct (**1**) of acetic acids with isobutyl vinyl ether (IBVE) and trifluoroacetic acid benzyl ester (**2**), were prepared and applied to cationic polymerization of IBVE at 25−100 °C for 24 h as thermally latent initiators. The GPC curves of the resulting polymers at each polymerization temperature (25−100 °C) revealed bimodal peaks, which corresponded to higher and lower molecular weight polymers, respectively. The bimodal behavior was also observed at early polymerization times (4 h, 12 h). These results may suggest the existence of two species with very slow thermal dissociation equilibria during polymerization: one is an ester moiety as an inert species, and the other is an ionic species, which would act as a propagating species. The ionic species would propagate the polymerization to obtain the higher molecular weight of polymers in M_{top} 8200−62 000.

Introduction

To construct a novel cross-linking system, we have developed some polymerizations initiated by onium salts such as sulfonium,[1] ammonium, pyridinium,[2] and phosphonium[3] salts that were employed as latent initiators. These initiators must be inert under the desired conditions such as room temperature and ambient light but should be transformed to activated species to initiate the chemical reaction or polymerization by appropriate external stimulations such as heating and photoirradiation. The previously reported onium salts were not very soluble in ordinary monomers and organic solvents. In addition, polymerizations with them often resulted in polymers containing a trace of inorganic residue from the onium salts bearing inorganic anions such as SbF_6^- and PF_6^-.

In order to improve the solubility of latent initiators in common organic compounds, it is necessary to design a novel latent initiator not in the salt form. We have already reported polymerization of aziridines with N-substituted phthalimides[4] and that of olefins and epoxides with sulfonic acid esters.[5] α-Alkoxy-substituted carboxylic acid esters are expected to be alternative latent initiators in cationic polymerization because of susceptibility to thermal heterolytic cleavage of the ester C−O bond and control of its thermal activity by varying the component substituents. By thermal stimulation, esters **1** and **2**, shown in Scheme 1, could probably be dissociated to carbocationic species and carboxylate ion followed by elimination to form a protic species and an olefin. The carbocationic and protic species are to be available for initiation species in the cationic polymerization of vinyl monomer. Cationic polymerizations of vinyl monomers with carboxylic acids and their derivatives have already been conducted.[6−9] Among them, Higashimura and co-workers[9] have succeeded in living polymerization with the adducts of vinyl ethers with carboxylic acids in the presence of a mild Lewis acid as a cocatalyst. However, there is no report dealing with cationic polymerization with only carboxylic acid ester by external thermal stimulation so far. In this paper, the possibility of carboxylic acid esters **1** and **2** as thermally latent initiators in the cationic polymerization of vinyl ether (Scheme 1) as well as the polymerization behaviors by ^1H NMR and GPC analyses are described.

Scheme 1



Experimental Section

Materials. Trifluoroacetic acid was distilled over P_2O_5. Trichloroacetic acid was recrystallized from cyclohexane. Dichloroacetic acid, acetic acid, and benzyl alcohol were distilled *in vacuo*. Isobutyl vinyl ether (IBVE) was distilled over sodium. The other chemicals were used without purification.

Measurements. ^1H NMR spectra were recorded with a JEOL JNM-EX-90 spectrometer operating in the pulsed FT modes, using tetramethylsilane (TMS) as an internal standard in $CDCl_3$, CCl_4, and toluene-d_8. FT-IR spectra were obtained with a JEOL JIR-5300. Molecular weight and its distribution (MWD: $\bar{M}_w/\bar{M}_n$) were estimated by gel permeation chromatography (GPC) on a Tosoh HPLC HLC-8020 system with a data processor, equipped with three polystyrene gel columns (TSK-

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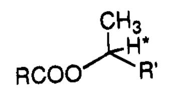
Table 1. Decomposition of the Esters 1 and 2



ester	R	R′	pK_a	chemical shift of H* (ppm)[a]	$10^5 k_1$ (s^{-1})[b]	$10^3 k_2$ ($L{\cdot}mol{\cdot}s^{-1}$)[c]
1a	CF_3	OBu-*i*	−0.23[d]	6.03	58	12
1b	CCl_3	OBu-*i*	0.66[e]	5.99	8.6	4.6
1c	$CHCl_2$	OBu-*i*	1.30[e]	5.96	1.7	1.2
1d	CH_3	OBu-*i*	4.56[e]	5.90	0.32	
2	CF_3	Ph	−0.23[d]	6.03	~0	

[a] In $CDCl_3$ + CCl_4 (1:1).[9] [b] Estimated by ^1H NMR (in toluene-d_8 at 100 °C). [c] Reference 8. [d] Evaluated from K_a = 0.588.[15] [e] Reference 16.

gel G2500H, G3000H, G4000), using tetrahydrofuran as an eluent (a flow rate of 1.0 mL/min), polystyrene calibration, and refractive index (RI) and ultraviolet (UV) detectors.

Preparation of the IBVE Adduct (Ester 1). All IBVE adducts (**1**) were prepared according to the reported method.[9] After **1a**−**1c** were isolated in the reaction vessel by sufficient evaporation of the solvent (CCl_4) and unreacted IBVE from the reaction solution, they were confirmed as acid-absent materials by ^1H NMR and IR (in CCl_4) and immediately used as initiators. **1d** was used after vacuum distillation.

Preparation of 1-Phenylethyl Trifluoroacetate (Ester 2). To a solution of benzyl alcohol (1.20 mL, 10 mmol) and pyridine (0.90 mL, 11 mmol) in 10 mL of ether was added trifluoroacetic anhydride (1.50 mL, 11 mmol) in 10 mL of ether at room temperature. After 2 h, the reaction mixture was filtrated and evaporated. The obtained residue product was distilled *in vacuo* by Kugelrohr (60 °C/1.0 mmHg) to give purified **2** in 77% isolated yield. ^1H NMR ($CDCl_3$, δ, ppm): 1.67 (d, 3H, CH_3), 6.03 (q, 1H, CH), 7.37 (s, 5H, Ph). IR (neat, cm^{-1}): 3071, 3038 (ν_{Ph}), 2992, 2940 (ν_{CH_3,CH_2}), 1784 ($\nu_{C=O}$).

Polymerization of IBVE with Esters 1 and 2. A glass tube equipped with a two-way stopcock and a stir bar was heated *in vacuo* with a heat gun and flushed with argon. Ester **1** or **2** (0.05 mmol) and IBVE (0.65 mL, 5.0 mmol) were added to the glass tube *via* syringe. The glass tube was cooled in liquid nitrogen, evacuated with a pump, and sealed off. It was kept for 24 h with stirring in an oil bath adjusted to a certain polymerization temperature (25−100 °C). To the resulting material was added 10 mL of methanol. After evaporation, the obtained polymer was dissolved in THF and analyzed by GPC.

Results and Discussion

Preparation of Carboxylic Acid Esters. Two types of carboxylic acid esters as latent initiators were prepared; one was the IBVE adduct[9] (ester **1**) obtained from isobutyl vinyl ether (IBVE) and carboxylic acids and the other was benzyl trifluoroacetate (ester **2**) derived from 1-phenylethanol and trifluoroacetic acid. The ^1H NMR spectral data of **1** are in good accordance with the reported data.[9] **2** was also confirmed by ^1H NMR and IR (see Experimental Section). The chemical shifts of the characteristic methyne protons (H*) in **1** and **2** are shown in Table 1. These chemical shifts are closely related to the electron-attracting ability of the carboxyl group as well as the pK_a (acidity) of the corresponding free acid.

Thermal Behavior of the Esters. If polymerization of IBVE is initiated either by carbocationic species or by protic species as shown in Scheme 1, the esters themselves may be finally transformed to the corresponding free acid and olefin (IBVE) by thermal stimulation. The thermal behavior of the esters was confirmed by keeping the esters at 100 °C in toluene-d_8. The k_1 rates shown in Table 1 were determined from the slopes of the first-order plots, illustrated in Figure 1, by following the conversions of **1** and **2**. The k_1 rates in **1a**−**1d** follow the order **1a** > **1b** > **1c** > **1d** (Table 1 and Figure 1). The leaving ability of the carboxyl group or the pK_a seems to affect the rate of the conversion of the ester. However, the conversion of **2** was never observed even at 100 °C for 10 h. This indicates that the conversion of **1** and **2** is affected not only by the electron-attracting ability of the carboxyl group but also by the stability of the cation from the substituent R′ (oxonium ion ≫ benzyl cation).

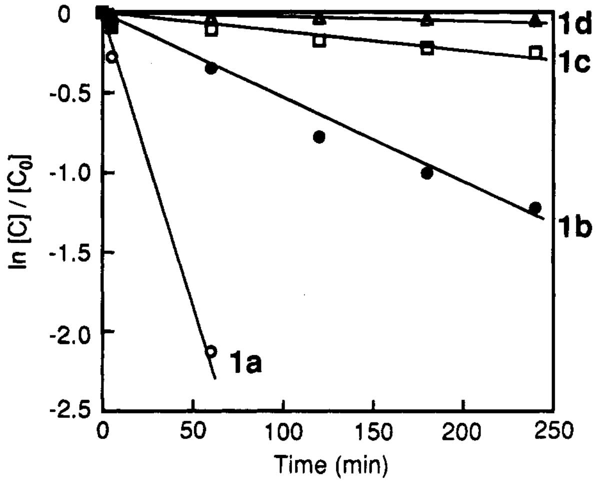


Figure 1. First-order plots of the thermal decomposition of ester **1** in toluene-d_8 at 100 °C.

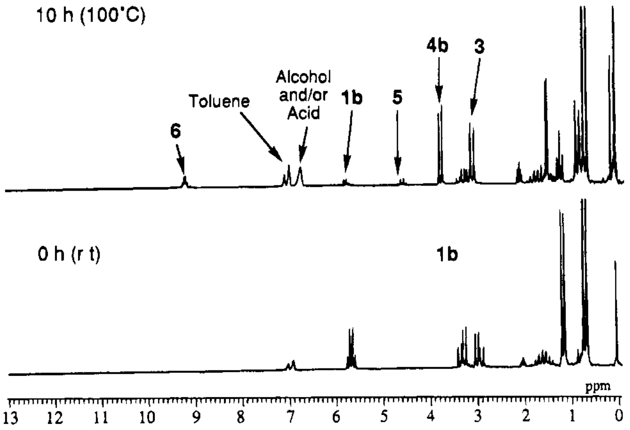
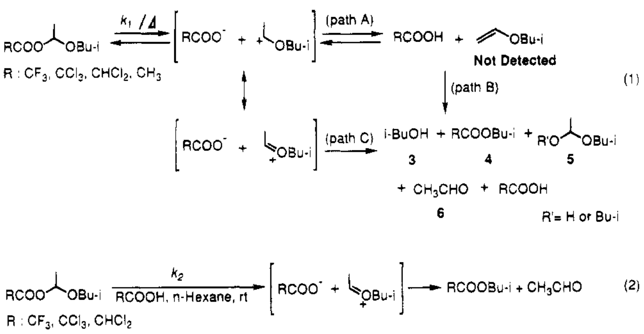


Figure 2. ^1H NMR spectra of ester **1b** (up) and decomposition compounds **3**−**6** by treatment of **1b** in toluene-d_8 at 100 °C for 10 h (down).

In the thermal reaction of ester **1**, transformation of **1** into some compounds was observed by ^1H NMR. Typically, in the case of **1b**, the products formed by thermal stimulation were confirmed as either elimination or decomposition compounds, which were assigned as isobutanol (**3**, 3.04 ppm, doublet peak, CH_2), isobutyl ester[8] (**4b**, 3.71 ppm, doublet peak, CH_2), α-alkoxyethyl isobutyl ether (**5**, 4.53 ppm, quartet peak, CH), acetaldehyde[8] (**6**, 9.17 ppm, quartet peak, CH), and carboxylic acid (CCl_3COOH, 6.85 ppm, broad) by ^1H NMR (Figure 2). However, IBVE by elimination was never observed during the thermal reaction, in which only an elimination *via* path A in eq 1 in Scheme 2 does not seem to be necessarily appropriate. The formation of the decomposition compounds **3**, **4**, and **6** may lead us to conclude the further possibilities of path B and path C. Isobutanol **3** is to be formed through path B by the reaction[10] of IBVE formed *via* path A with carboxylic acid. Isobutyl ester **4** and acetaldehyde **6** are to be formed through

Scheme 2



path C by the formation of oxonium ion followed by attack of the carboxylate ion on the isobutyl group.[8] This reaction accelerated in the presence of acid in eq 2 in Scheme 2, as reported by Kim *et al.* Further, the formation of α-alkoxyethyl ether **5** is assumed from the reaction of ester **1** with either isobutanol (R′ = Bu-i) or water (R′ = H). The water might be formed by another side reaction as follows: esterification from **3** and RCOOH or reaction[11] of **6** with RCOOH. If there is water in this system, the other process may exist in the path A, i.e. hydrolysis[12] of IBVE to give **3** and **6**. These thermal behaviors of the esters are much too complex to elucidate their mechanisms. However, the rate of decomposition of **1** apparently seems to follow the first order. This possibly supports the fact that the dissociation of **1** to carboxylate ion and carbocation is considered as a rate-determining step in the thermal decomposition. In addition, the formation of carboxylic acid could also be confirmed. These facts, therefore, support the possibility of the esters **1** as thermally latent initiators in the cationic polymerization of IBVE.

Compared with the above thermal behavior of the esters, the k_2 rates in the acid-catalyzed reaction of the esters reported by Kim *et al.*[8a] are also shown in Table 1. In this reaction,[8] ester **1** is to be transformed to an oxonium ion as an intermediate followed by formation of isobutyl ester **4** and acetaldehyde **6** (eq 2 in Scheme 2) to probably assist one of the complex thermal reactions described above. Similar to the k_1 value, the k_2 value increased with elevating acidity (pK_a) of the corresponding free acid. Consequently, k_1 and k_2 could be considered as indices of initiation and propagation activity in the cationic polymerization with ester **1**.

Thermal Latency of the Ester. Polymerization of IBVE with **1** and **2** was carried out at 25−100 °C for 24 h in the bulk. All the conversion of IBVE is shown in Table 2. The temperature−conversion curves in this polymerization are also shown in Figure 3. Because the polymerization with **1a** proceeded even at 25 °C, **1a** might not be useful as a latent initiator. In the cases of **1b**−**1d**, the polymerization never occurred below 35 °C. However, **1b**−**1d** could initiate the polymerization of IBVE at the higher temperatures in the order **1b** (50 °C) < **1c** (80 °C) < **1d** (100 °C), indicating thermal latencies. On the other hand, **2** could hardly initiate even at 100 °C (conversion <1%). The initiation activity of esters **1** and **2** was clearly found to be consistent with the k_1 and k_2 rates.

As a control experiment, the polymerization of IBVE with free acids such as CF_3COOH, CCl_3COOH, and $CHCl_2COOH$ (1 mol %) was carried out at 25 and 50 °C for 24 h in bulk. Table 3 shows the result that CF_3COOH initiates the polymerization even at 25 °C in 11% conversion. This means that ester **1a** is less active than the corresponding free acid in the cationic polymerization. Although CCl_3COOH at 25 °C and $CHCl_2COOH$ at 50 °C also showed reactivity with IBVE in <1% conversion, as shown in Table 3, the obtained products were confirmed as IBVE adducts (esters **1b** and **1c**, respectively) by ^1H NMR. The free acids showed the possibility of initiators but could initially give the corresponding adducts (esters) by the reaction with IBVE followed by polymerization.

Table 2. Polymerization of IBVE with 1 and 2 for 24 h

run	ester	temp (°C)	conv[a] (%)	high MW polymer[b]/10^4	
				M_{top}	$\bar{M}_n$ (MWD)
1	**1a**	25	3	nd[c]	nd[c]
2		35	3	4.4	3.8 (1.55)
3		50	11	6.2	4.4 (2.11)
4		65	12	4.5	2.2 (2.54)
5		80	21	1.2	0.85 (2.82)
6		90	58	1.4	0.88 (1.99)
7		100	96	0.94	nd[c]
8	**1b**	25	0		
9		35	0		
10		50	3	3.2	2.6 (1.39)
11		65	6	2.4	2.0 (1.65)
12		80	50	1.1	0.65 (3.58)
13		90	71	0.94	0.68 (3.09)
14		100	100	0.82	nd[c]
15	**1c**	25	0		
16		50	0		
17		80	2	3.2	2.5 (1.54)
18		90	12	3.3	2.0 (3.19)
19		100	24	1.8	1.0 (2.35)
20	**1d**	25	0		
21		50	0		
22		100	<1	2.9	1.4 (1.72)
23	**2**	25	0		
24		80	<1	nd[c]	nd[c]
25		100	3	nd[c]	nd[c]

[a] Conv (%) = 100[(polymer (wt) − adduct (wt)]/monomer (wt). [b] Estimated by GPC. [c] Not determined.

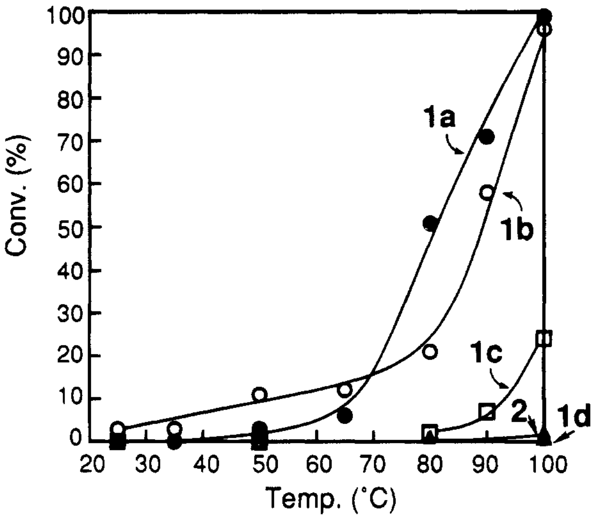


Figure 3. Thermal latency of esters **1** and **2**.

Table 3. Polymerization of IBVE with Free Acids for 24 h

run	acid	temp (°C)	conv[a] (%)	$\bar{M}_n/10^4$ (MWD)[b,c]
26	CF_3COOH	25	11	2.5 (1.38)
27		50	6	2.6 (1.42)
26	CCl_3COOH	25	<1[d]	
27		50	3	nd[e]
29	$CHCl_2COOH$	50	<1[d]	

[a] Conv (%) = 100[(polymer (wt) − acid (wt)]/monomer (wt). [b] Estimated by GPC. [c] The higher MW polymer. [d] The products were the adducts **1b** and **1c**, respectively. [e] Not determined.

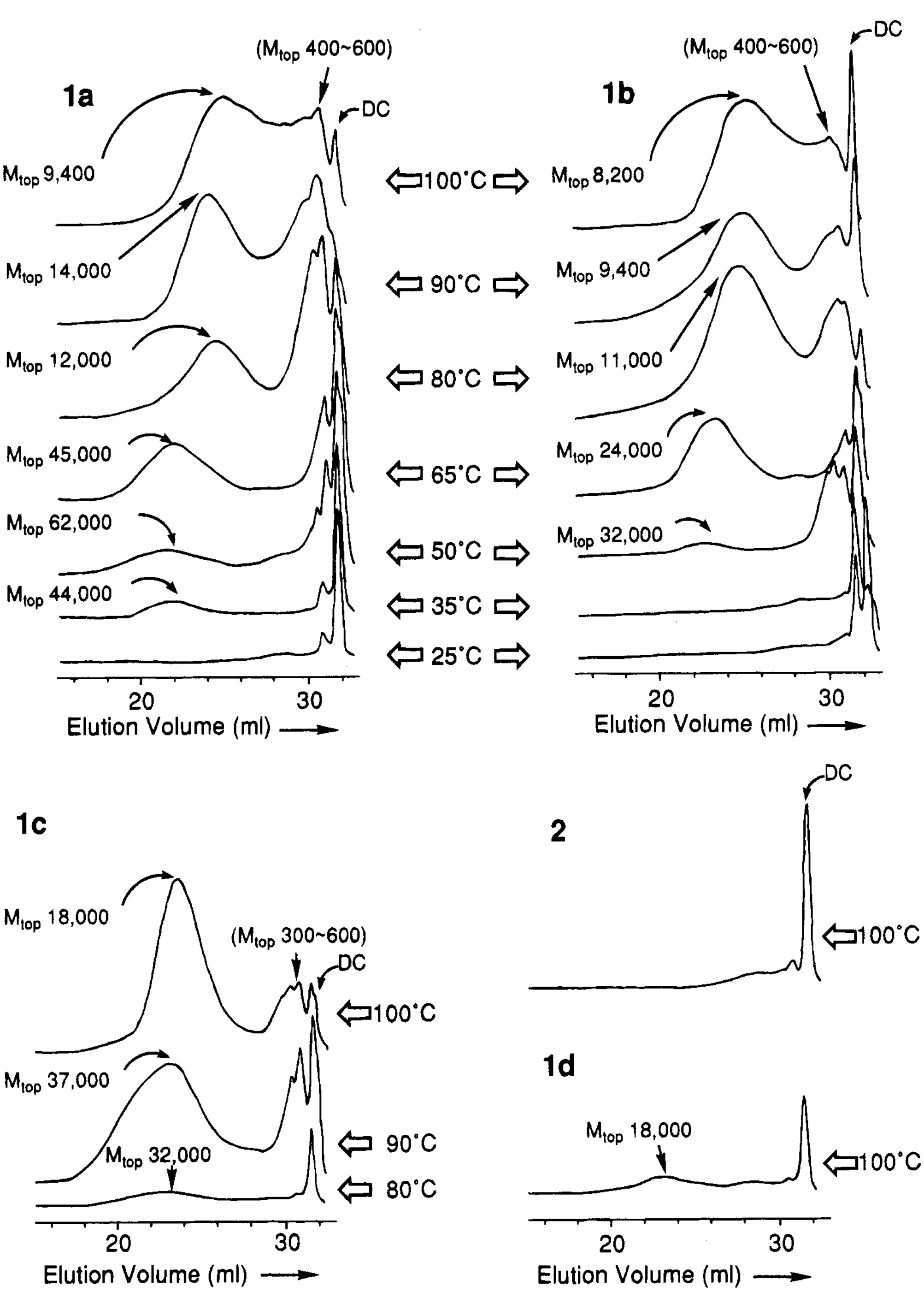


Figure 4. GPC charts of polymerization of IBVE with esters **1** and **2** for 24 h at 25–100 °C. Molecular weights (M_{top}) on the peak tops are specified beside the curves within discrimination as peaks. DC signifies undefined decomposition compound.

Polymerization Behavior of IBVE. In Figure 4, the GPC curves in the polymerizations of IBVE with **1** and **2** show multimodal curves which consist of plural peaks assigned to polymers and undefined decomposition compounds. The first detected peak and the second one corresponded to higher molecular weight (MW) and lower MW polymers, respectively. The other peaks corresponded to undefined decomposition compounds confirmed by ^{1}H NMR. In Table 2, the MW on the peak top (M_{top}) and the number average MW ($\bar{M}_n$) in the higher MW polymer are all indicated at each temperature as far as the peaks are discriminated by the GPC data processor. These MW tended to decrease with raising polymerization temperature because of chain transfer. The MW on the peak top in the low MW polymer is regularly 300–600 with no regard to the polymerization temperature, as shown in Figure 4. The polymerization must proceed cationically, and two kinds of species might exist to form higher and lower MW polymers, as shown in the bimodal behavior in the GPC chart except for formation of undefined decomposition compound.

In order to clarify the polymerization behavior, polymerization of IBVE with **1b** for 2–48 h was carried out, and the resulting GPC charts along with the conversion of IBVE at each time (2–48 h) are shown in Figure 5. The polymerization hardly proceeded at 2 h, but it occurred at 4–48 h, as shown in Figure 5. The GPC curve indicates bimodal behavior even at the lesser polymerization time (4 h). In addition, the polymer yield increased with an increase of time, but the M_{top} of the polymer decreased due to stopping the stirring at 48 h as well as spontaneous transfer independent of monomer.[13a] Thus, the possibility of two species to form

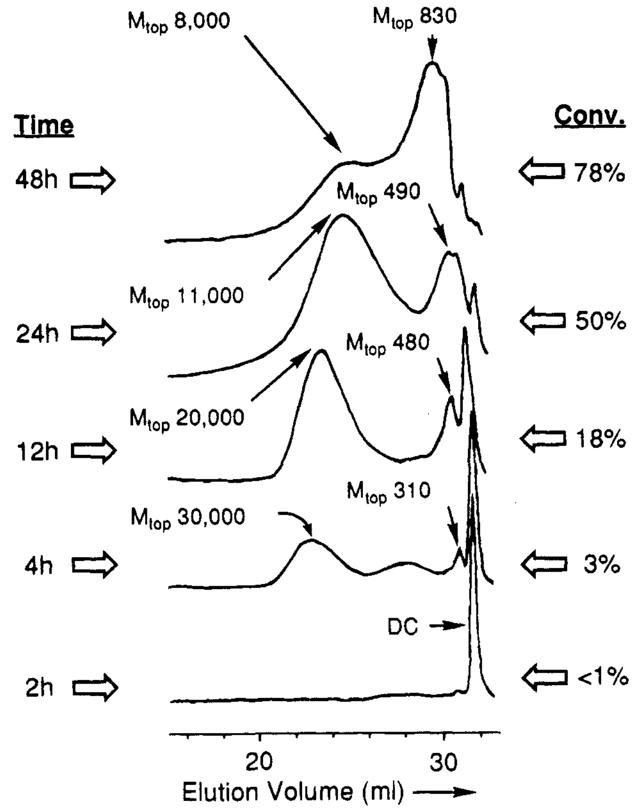
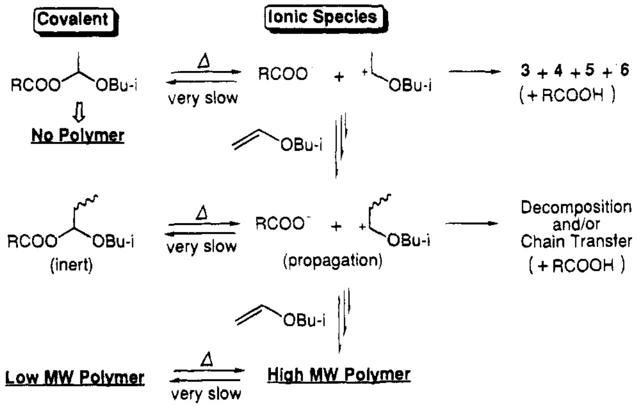


Figure 5. GPC charts of polymerization of IBVE with ester **1b** for **2**–**48** h at 80 °C. Molecular weights (M_{top}) on the peak tops and conversions on each time are specified beside the curves. DC signifies undefined decomposition compound.

higher and lower MW polymers could be confirmed practically in the initiation and propagation step.

These polymerization behaviors are similar to those in the traditional cationic polymerization of olefins with trifluoromethanesulfonic acid, perchloric acid, and trifluoroacetic acid.[13,14] Cationic polymerization of olefins with oxo acid generally seems to exhibit bimodal behavior in GPC, because of the existence of two kinds of species. These species are ionic species (free ion or ion pair) and ester (inert species or covalent) in a very slow equilibrium to form higher and lower MW polymers. This equilibrium has been extensively elucidated[13,14] in terms of solvent and ion effect as well as kinetic studies by Higashimura and Pepper. The bimodal behavior in cationic polymerization with oxo acids should be enough to be applied to the present polymerization with ester **1** by external thermal stimulation, as shown in Scheme 3, to explain the phenomena in Figures 4 and 5. At first, in the initiation step, the ester (covalent) should be activated by external thermal stimulation to generate ionic species. The ester and the ionic species are to be in very slow equilibrium (Scheme 3). Even if the initiation species is a proton from the eliminated carboxylic acid, as shown in Scheme 1, the slow equilibrium as described above might still occur. In the propagation step, the ionic species is to serve as the propagation species in equilibrium with the ester structure to eventually give two kinds (higher and lower) of MW polymers (Scheme 3). In addition, the undefined decomposition compounds correspond to the rightmost formed compounds, namely **3**–**6**, and RCOOH in Scheme 3, judging from the thermal behaviors of ester **1** alone shown in Scheme 2. In the propagation step, the decomposition as well as chain transfer may also occur as side reactions to yield undefined compounds. In the present polymerization, isobutyl viny ether, which serves as a solvent with low dielectric constant (ϵ = 3.40),[7] might hardly enhance the heterolytic cleavage of the ester C–O bond without external thermal stimulation. The adequate thermal stimulation should independently promote the heterolytic cleavage of the C–O bond with the very slow equilibrium in this polymerization. Consequently, the possible mechanism in Scheme 3 may operative in this polymerization with esters **1** by external thermal stimulation.

Scheme 3



Conclusion

The ester **1** prepared by the reaction of carboxylic acid with IBVE is found to be useful as a thermally latent initiator in the cationic polymerization of IBVE at less than 100 °C in bulk. The two species shown in Scheme 3 would probably be operative exclusively in the present ester **1** and IBVE system. Consequently, although production of oligomer by chain transfer could not be neglected, the obtained polymers were mainly divided into two kinds of polymers, namely higher and lower MW polymers, which were originated from the two species whenever the initiation species is carbocationic or protic.

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