Polymer Chemistry

Paper

Thermally induced cationic polymerization of isobutyl vinyl ether in toluene in the presence of solvate ionic liquid

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Radical polymerization of isobutyl vinyl ether (IBVE) was attempted with the aid of the interaction between the corresponding propagating radical and lithium cation (Li$^+$). LiN(SO$_2$CF$_3$)$_2$ (LiNTf$_2$) and ester compounds, such as methyl methacrylate (MMA) and vinyl acetate (VAc), were added as a Li$^+$ source and dissolving agent for LiNTf$_2$, respectively. Homopolymers of cationically polymerizable IBVE were obtained despite the presence of radically polymerizable monomers such as MMA and VAc. Contrary to our expectation, the polymerization proceeded *via* not a radical mechanism but a cationic mechanism. However, this cationic polymerization was found to be unusual. In particular, the polymer yield increased with the polymerization temperature; successful polymerization was observed at 100 °C, whereas no polymerization occurred at lower temperatures such as at 0 °C. The behavior of the present system was therefore defined as "thermally induced cationic polymerization". The mechanism of thermally induced cationic polymerization is still not clear, but it is assumed that the propagating cation is markedly stabilized through its interaction with the solvate ionic liquid formed between LiNTf$_2$ and the Lewis base.

Introduction

Vinyl ethers typically undergo homopolymerization *via* a cationic mechanism because of their electron-donating alkoxy groups. The propagating carbocations are highly reactive and unstable. Therefore, termination and side reactions such as *β*-proton elimination and alkoxy abstraction easily occur, resulting in the formation of oligomers. Since the living cationic polymerization of vinyl ethers was established in 1984,[1] remarkable technological innovation to control the cationic polymerization of vinyl ethers has been achieved.[2] However, precise control of the polymerization reactions requires dry and low-temperature conditions to avoid the occurrence of termination and side reactions.

In contrast, vinyl ethers are difficult to homopolymerize *via* a radical mechanism. The lack of resonance stabilization in the propagating radical species causes frequent chain-transfer reactions.[3-6] The chain-transfer reactions that occur during radical polymerization of vinyl ethers bearing labile hydrogen and electron-accepting groups at suitable positions can provide polymers with relatively high molecular weight. For example, 3-cyano-3-ethoxycarbonylpropyl vinyl ether and 3,3-

bis(ethoxycarbonyl)propyl vinyl ether can be polymerized by a radical mechanism involving intramolecular hydrogen abstraction (addition–abstraction mechanism).[7-9] Radical polymerization of 2-thiocyanatoethyl vinyl ether proceeds *via* a group transfer mechanism.[10] Note that the polymers produced by these polymerizations contain ether and thioether linkages in the main chain.

Recently, Sugihara *et al.*[11, 12] reported direct radical polymerization of 2-hydroxyethyl vinyl ether. They claimed that intermolecular hydrogen bonds affected the radical polymerization process; the formation of hydrogen bonds lowered the reactivity of the growing radicals, suppressing unfavorable side reactions such as *β*-scission and hydrogen abstraction. Moreover, block copolymers were successfully prepared by combination with the reversible addition–fragmentation chain transfer polymerization technique.

We reported that addition of lithium bis(trifluoromethanesulfonyl)imide (LiNTf$_2$) to radical polymerization of (meth)acrylamides, such as *N,N*-dimethylacrylamide and *N-n*-propylmethacrylamide, leads to notable increases in the yield and molecular weight of the resulting polymers.[13, 14] Nuclear magnetic resonance (NMR) spectroscopic analysis of a mixture of monomer and LiNTf$_2$ suggested that the monomer was activated by the coordination of its carbonyl (C=O) group to Li$^+$. Furthermore, electron spin resonance (ESR) spectroscopic analysis of the polymerization in the presence of LiNTf$_2$ suggested that the propagating radical was stabilized by Li$^+$, probably through a single-electron lithium bond, which is a recently proposed theory.[15-17]

In the single-electron bond theory, a lithium bond is stronger than a hydrogen bond.[17] In addition, Li$^+$ has been reported to

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†Electronic supplementary information (ESI) available: polymerization results in the presence or absence of TEMPO, polymerization results in the presence of VAc and LiNTf$_2$ for different reaction times, and the relationship between the polymerization time and concentration of TEMPO during IBVE polymerization.

form complexes with alkenes and thereby activate the alkenes in radical addition reactions.[18-21] It is therefore expected that Li⁺ enhances the radical polymerizability of vinyl ethers. Thus, we decided to investigate the effect of LiNTf$_2$ on the polymerization behavior of isobutyl vinyl ether (IBVE) in anticipation of achieving radical polymerization of simple vinyl ethers.

Contrary to our expectations, we find that high-molecular-weight polymers are obtained *via* not a radical mechanism but a cationic mechanism. However, the present cationic polymerization is unusual compared to conventional cationic polymerizations. The polymerization requires elevated temperatures over 40 °C despite involving a cationic mechanism. In addition, some chemical reagents including the IBVE monomer are able to be used as received without special pretreatment. Thus, we report here the facile, robust, and unique cationic polymerization of IBVE at high temperatures.

Experimental

Materials

Dimethyl 2,2'-azobisisobutyrate (MAIB) (supplied by Otsuka Chemical Co., Ltd, Osaka, Japan) was recrystallized from methanol. Toluene (Kanto Chemical Co., Inc., Tokyo, Japan) and ethyl acetate (Wako Pure Chemical Industries, Osaka, Japan) were purified by fractional distillation. Methyl methacrylate (MMA) (supplied by Mitsubishi Chemical Co., Ltd, Tokyo, Japan), *N*-vinylpyrrolidone (VP), vinyl acetate (VAc) (Wako Pure Chemical Industries), and *N*-vinylimidazole (VIm) (Tokyo Chemical Industry, Tokyo, Japan) were purified by distillation under reduced pressure. IBVE, LiNTf$_2$, boron trifluoride-diethyl ether complex (BF$_3$•Et$_2$O), allyl acetate, vinyl pivalate, vinyl benzoate, vinyl decanoate, vinyl hexanoate, 4-pentenyl acetate, 4-hydroxy-2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO), sodium trifluoroacetate, PEG 600 and 4000, and ethyl trifluoroacetate from Tokyo Chemical Industry; 2-butanone, tetrahydrofuran (THF; high-performance liquid chromatography grade), dithranol, and diethyl carbonate from Kanto Chemical Co.; and 1,4-dioxane, PEG 1500, and methanol from Wako Pure Chemical Industries were used as received.

Polymerization

In a typical polymerization procedure, IBVE (2.22 g, 22.5 mmol) was diluted to 5 mL with toluene. LiNTf$_2$ (0.256 g, 0.9 mmol) and MMA (0.451 g, 4.5 mmol) were dissolved in toluene to prepare 1 mL of solution. The former solution (4 mL) and latter solution (0.5 mL) were added to a glass ampoule to give the following final concentrations: $[IBVE]_0 = 4.0$ mol L^{-1}, $[LiNTf_2]_0 = 0.1$ mol L^{-1}, and $[MMA]_0 = 0.5$ mol L^{-1}. The glass ampoule was degassed under vacuum and filled with nitrogen six times at −50 °C before being set at the required polymerization temperature. Polymerization was initiated by immersing the glass ampoule in an oil bath at the polymerization temperature. After 4 h, the reaction was terminated by rapid cooling of the glass ampoule to −50 °C. The polymerization mixture was poured into a large amount of methanol (100 mL). The

precipitated polymer was collected by centrifugation and then dried *in vacuo*. The polymer yield was determined gravimetrically.

Measurements

^{1}H and ^{13}C NMR spectra of the polymers were measured in CDCl$_3$ at 55 °C using ECX-400 and ECA-500 spectrometers (JEOL Ltd., Tokyo, Japan), respectively. The sample concentration was set to 10 wt% to detect the signals of end group and irregular structures. The content of internal olefin groups was determined using equation (1):

$$\text{Olefin (\%)} = \frac{I_6 + I_7}{I_d + I_e} \times 150 \quad (1)$$

where I_6, I_7, I_d, and I_e are the integral intensities of the internal olefin (**6**, **7**), side-chain methylene (**d**) and main-chain methine (**e**) groups in ^{1}H NMR spectra (*cf*. Fig. 5). Olefin (%) indicates the relative composition of internal olefin groups against the normal repeating monomeric unit.

The molecular weights and molecular weight distributions of the polymers were determined by size-exclusion chromatography (SEC). SEC was performed on an HLC 8220 chromatograph (Tosoh, Tokyo, Japan) or with a PU-4185 pump (JASCO, Tokyo, Japan) connected to refractive index detector (RefractoMAX521, ERC GmbH, München, Germany) and column oven (380-B, Chemco Plus Scientific Co., Ltd., Osaka, Japan) equipped with TSKgel columns [SuperHM-M (6.5-mm inner diameter × 150-mm long) and SuperHM-H (6.5-mm inner diameter × 150-mm long)] (Tosoh). THF was used as an eluent at 40 °C and a flow rate of 0.35 mL·min^{-1}. The initial polymer concentration was 1.0 mg·mL^{-1}. The chromatographs were calibrated with standard poly(methyl methacrylate) (PMMA) or polystyrene samples.

ESR spectra were recorded on an X-band (*ca*. 9 GHz) FA100 spectrometer (JEOL Ltd.) at 60 °C with 100-kHz field modulation. ESR samples were placed in quartz tubes with an outer diameter of 1 mm and degassed by several freeze–pump–thaw cycles before being sealed under nitrogen atmosphere. The temperature was controlled within ±0.1 °C. The magnetic field and *g* tensor were calibrated with an Mn^{2+} standard. Most spectra were collected with the following parameters: sweep width 10 mT, time constant 0.3 s, scan period 4 min, and 2048 points. To monitor the TEMPO concentration during the polymerization, only one ESR signal observed at the lowest magnetic field ($m_I = +1$) of the triplet signals of TEMPO was rapidly recorded. In this case, the sweep width, time constant, and scan period were 1 mT, 0.01 s, and 5 s, respectively.

Matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectrometry was performed using an Autoflex Speed-TK spectrometer (Bruker Daltonik GmbH, Bremen, Germany). Dithranol and sodium trifluoroacetate were used as the matrix and ionizing agent, respectively.[22] Each spectrum was externally calibrated using a mixture of PEGs with different number-average molecular masses.

Results and discussion

Attempted radical polymerization of IBVE in the presence of LiNTf$_2$

Polymerization of IBVE (4.0 mol L^{-1}) was carried out in toluene at 60 °C in the presence of LiNTf$_2$ (0.1 mol L^{-1}) for 4 h (Table 1). The monomer contained a small amount of KOH to inhibit cationic polymerization. However, IBVE was used without any purification because the purpose of this experiment was to attempt radical polymerization of IBVE. MAIB (2.0 × 10^{-2} mol L^{-1}) was added as a radical initiator. LiNTf$_2$ was insoluble in the polymerization mixture at room temperature, but gradually dissolved when the system was heated to 60 °C. A polymer was obtained in 82% yield as a methanol-insoluble material. This result implies successful radical polymerization of IBVE with the aid of Li$^+$ as expected, because no polymer was obtained in the absence of LiNTf$_2$. To confirm this, polymerization of IBVE in the presence of LiNTf$_2$ was conducted without the radical initiator MAIB. However, polymer was obtained in 84% yield, suggesting that the polymerization proceeds *via* not a radical mechanism but a cationic one.

MMA was added to the polymerization system instead of MAIB. Five times the amount of MMA (0.5 mol L^{-1}) relative to that of LiNTf$_2$ was used to dissolve LiNTf$_2$ at room temperature (Table 2). Polymerization was conducted using the same method as that in the presence of MAIB. The yield was much lower, but polymer was obtained in 35% yield as a methanol-insoluble material. Vinyl ethers exhibit very little tendency to undergo radical copolymerization with MMA; if the polymerization proceeded *via* a radical mechanism, polymer mainly composed of MMA units should be obtained.[23] No signals assignable to MMA units were observed in the ^{1}H NMR spectrum of the

Table 1. Polymerization of IBVE in toluene at 60 °C in the presence or absence of MAIB[a]

[MAIB]$_0$ × 10^{-2} mol L^{-1}	[LiNTf$_2$]$_0$ mol L^{-1}	Yield %	M_n[b] × 10^{-4}	M_w/M_n[b]
2.0	0.1	82	0.8	1.4
2.0	0.0	trace	-	-
0.0	0.1	84	4.0	1.3

[a] [IBVE]$_0$ = 4.0 mol L^{-1}, 4 h.
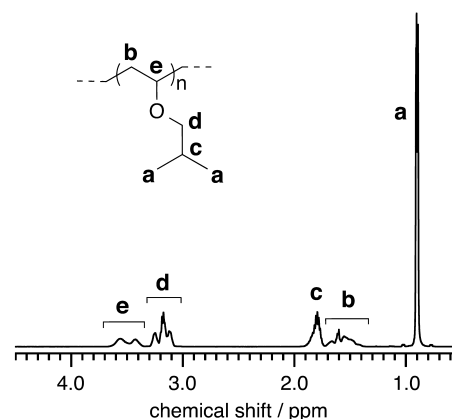[b] Determined by SEC (PMMA standards).

Fig. 1 ^{1}H NMR spectrum (500 MHz, CDCl$_3$, 55 °C) of the methanol-insoluble fraction obtained from the polymerization of IBVE in the presence of MMA at 60 °C.

obtained polymer (Fig. 1). Instead, the spectral pattern was assignable to a homopolymer of IBVE.

TEMPO is a well-known inhibitor of radical polymerization, whereas cationic polymerization of vinyl ether proceeds even in

Table 2. Polymerization of IBVE in toluene in the presence of MMA and LiNTf$_2$[a]

Temp. °C	Time h	[LiNTf$_2$]$_0$ mol L^{-1}	[MMA]$_0$ mol L^{-1}	Yield %	M_n[b] × 10^{-4}	M_w/M_n[b]	Olefin[c] %
100	4	0.1	0.5	71	2.6	1.6	0.5$_1$
80	4	0.1	0.5	54	3.0	1.7	0.1$_6$
60	4	0.1	1.0	0	-	-	-
60	4	0.1	0.5	35	4.3	1.9	0.0$_5$
60[d]	4	0.1	0.5	33	2.2	2.7	0.0$_5$
60	4	0.1	0.1[e]	60	2.4	1.6	0.5$_0$
40	24	0.1	0.5	17	1.6	1.4	
40	4	0.1	0.5	0	-	-	-
20	24	0.1	0.5	0	-	-	-
0	24	0.1	0.5	0	-	-	-
0[f]	4	0.0	0.5	77	0.7	3.8	3.1$_1$
0[f]	4	0.1	0.5	43	1.7	1.4	0.0$_5$

[a] [IBVE]$_0$ = 4.0 mol L^{-1}.
[b] Determined by SEC (PMMA standards).
[c] Determined by ^{1}H NMR spectroscopy.
[d] The polymerization was conducted in air.
[e] LiNTf$_2$ gradually dissolved during the polymerization.
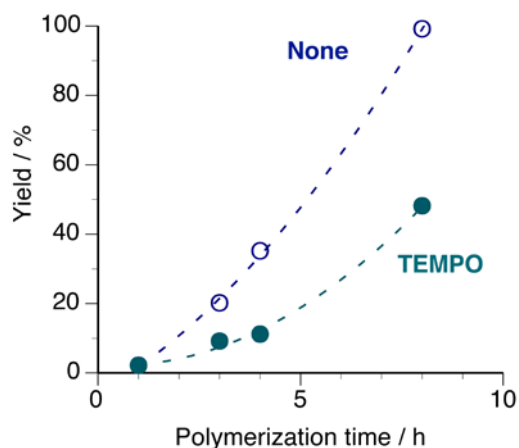[f] Initiated by BF$_3$•OEt$_2$, [BF$_3$•OEt$_2$]$_0$ = 0.02 mol L^{-1}.

Fig. 2 Relationship between the polymerization time and yield of methanol-insoluble fraction in the polymerization of IBVE in the presence or absence of TEMPO.

Fig. 3 Effect of the polymerization temperature on the yield and number-average molecular weight (M_n) of the obtained polymers.

the presence of TEMPO.[24] Therefore, TEMPO (0.01 mol L^{-1}) was added to the polymerization system (Table S1) (ESI†). Polymerization was slightly suppressed, but polymers were obtained (Fig. 2). No apparent induction period was observed. Furthermore, the TEMPO concentration monitored by ESR did not change during the polymerization (Fig. S1) (ESI†). This means that no radical species are involved in the present polymerization. Thus, it can be concluded that the IBVE monomer was polymerized *via* a cationic mechanism at elevated temperature (such as 60 °C). The decreases in polymer yield and polymerization rate in the presence of TEMPO are probably caused by its basicity.[25] In addition, the slight deviation from a linear relationship is caused by the fraction with lower molecular weight, which formed during the early stage of polymerization, being soluble in methanol. Further details about this fraction will be described below.

Temperature dependence of the cationic polymerization of IBVE in the presence of LiNTf$_2$

In general, cationic polymerization favors low temperatures at which termination and side reactions are suppressed. Polymerization of IBVE was therefore carried out in toluene at lower temperatures for 24 h (Fig. 3). Polymer that was insoluble in methanol was obtained in just 17% yield at 40 °C, even though the polymerization time was extended to 24 h. Furthermore, no polymers were obtained at 0 and 20 °C. This behavior is similar to that of thermal radical polymerization with initiators such as azo compounds and peroxides. Therefore, the behavior of the present system can be defined as "thermally induced cationic polymerization".

To investigate the upper temperature limit at which the cationic polymerization proceeded, IBVE polymerization was conducted in toluene at higher temperatures for 4 h (Fig. 3). The polymer yield increased with polymerization temperature; polymer was obtained in 71% yield even at 100 °C. It should be noted that this temperature is higher than the boiling point of IBVE (83 °C), which resulted in bubbling of the polymerization system. Therefore, no upper temperature limit was observed for
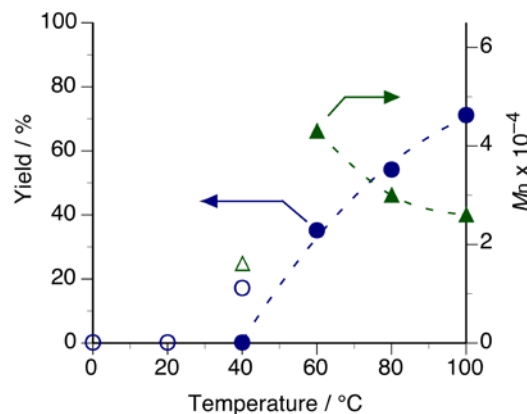
this polymerization under the conditions examined. Such high temperatures are usually used for thermal curing with divinyl ethers.[26-28] In fact, cationic polymerization of monovinyl ethers at high temperatures has seldom been reported, except for that with CrO$_3$ at 80 °C[29] and living polymerization with CH$_3$CH(O*i*-Bu)OCOCH$_3$/EtA1C1$_2$ in the presence of excess amount of ester compounds[30].

^{13}C NMR signals of the main-chain methylene carbons show splitting caused by diad stereoregularity.[31-33] Fig. 4 shows the ^{13}C NMR spectra of the methylene carbons of the poly(IBVE)s prepared at 60 to 100 °C. Regardless of the polymerization temperature, polymers with high *meso* (*m*) diad content (57%–59%) were obtained. Cationic polymerization of vinyl ethers provides *m*-rich polymers, whereas radical polymerization gives atactic polymers.[11] The *m*-rich diad tacticity also supports the
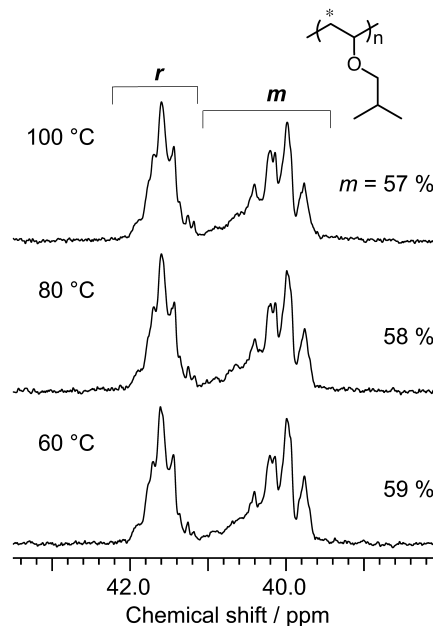

Fig. 4 ^{13}C NMR spectra (125 MHz, CDCl$_3$, 55 °C) of the main-chain methylene carbons of poly(IBVE)s prepared at 60, 80 and 100 °C.
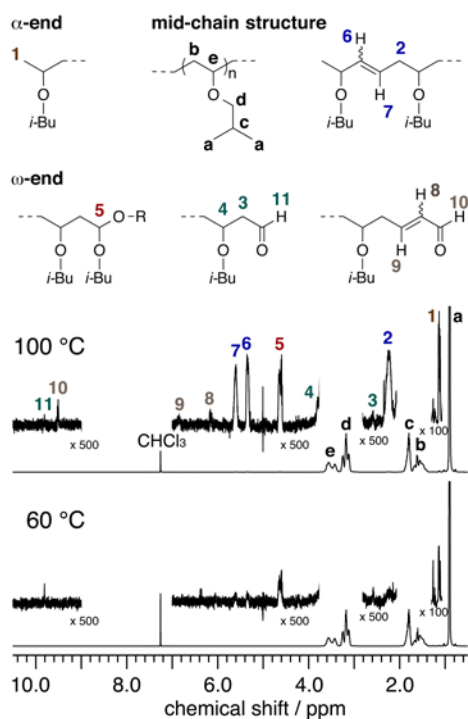
Fig. 5 ^{1}H NMR spectra (500 MHz, CDCl$_3$, 55 °C) of poly(IBVE)s prepared at 60 and 100 °C.

above-mentioned conclusion that the present polymerization proceeds *via* a cationic mechanism.

Structural analysis of the poly(IBVE)s by ^{1}H NMR spectroscopy

Fig. 5 depicts ^{1}H NMR spectra of poly(IBVE)s prepared at 60 and 100 °C. The terminal groups and structural defects were assigned according to the literature.[34] Signals assigned to internal olefin groups (labeled 2, 6, and 7) were observed in the spectrum of the poly(IBVE) prepared at 100 °C. This suggests that termination by abstraction of an isobutoxy group from the polymer chain by the propagating chain end occurs at 100 °C, leading to the formation of internal olefin and acetal (labeled 5) groups (Scheme 1).[35]

The number-average molecular weight (M_n) gradually decreased with rising polymerization temperature (Fig. 3). The abstraction reaction is a chain-transfer reaction; the generated H$^+$ can reinitiate the cationic polymerization (Scheme 1). In fact, a signal assigned to the terminal methyl group (labeled 1) was observed. The decrease of M_n with elevating temperature was therefore attributed to the abstraction reaction. A signal from the terminal methyl groups was also observed in the spectrum of the poly(IBVE) prepared at 60 °C. This indicates that the polymerization was initiated by H$^+$, which was probably derived from water present in the polymerization system, regardless of the polymerization temperature.

A signal assigned to acetal groups was observed in the spectrum of the poly(IBVE) prepared at 60 °C, even though
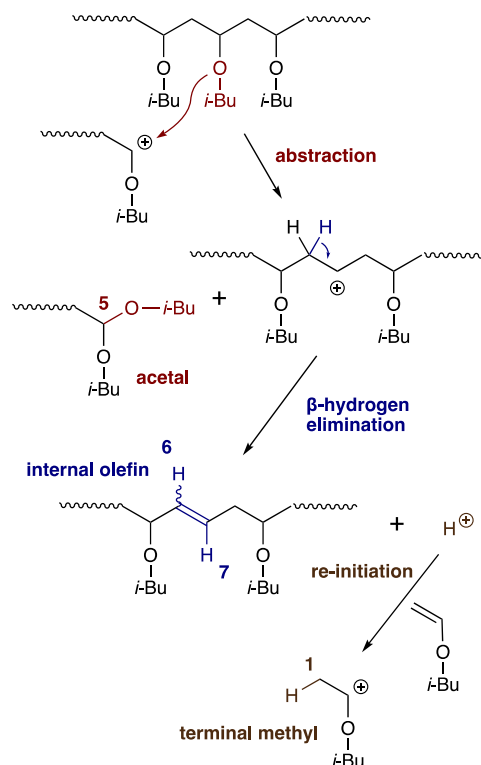
Scheme 1 Possible mechanism of isobutoxy abstraction accompanied with internal olefin formation followed by reinitiation with H$^+$.

signals from the internal olefin groups were scarcely observed. Acetal groups can form with methanol, which was used as the precipitation solvent. Furthermore, it should be noted that signals from irregular structures such as aldehydes, alkenals, and terminal double bonds, which can form through termination and side reactions, were scarcely observed (Scheme 2). These results suggest that the propagating cations were sufficiently stabilized to be long-lived even at 60 °C.
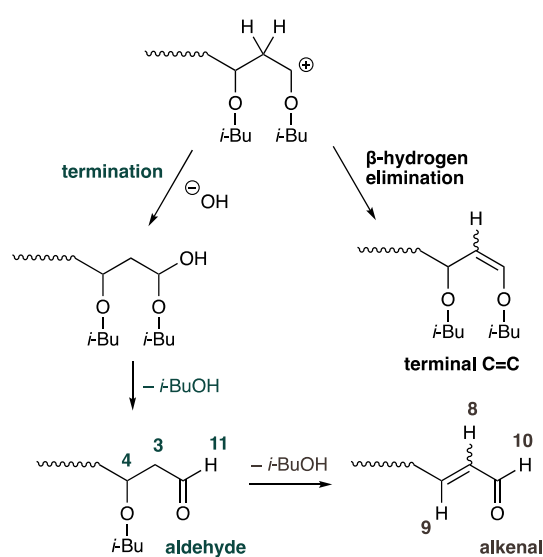

Scheme 2 Possible structures formed through termination and side reactions.

Structural effect of the added Lewis bases

The lack of MMA in the resulting polymer indicates that MMA behaved as a simple base to dissolve LiNTf$_2$. Other bases were therefore added instead of MMA to examine effect of the Lewis base on the polymerization behavior. The addition of VIm and VP resulted in immiscible liquid–liquid two-phase systems. LiNTf$_2$ is well known to form solvate ionic liquids with strong Lewis bases such as imidazoles, ureas, acetamides, and 2-oxazolidinone.[36-42] The phase separation is likely caused by the high polarity of the solvate ionic liquids formed with VIm and VP compared with that of IBVE and toluene. Conversely, the addition of weaker Lewis bases, such as 1,4-dioxane and ethyl trifluoroacetate, resulted in immiscible solid–liquid two-phase systems. Thus, the addition of Lewis bases with moderate basicity is essential to obtain miscible solutions.

The addition of 2-butanone, diethyl carbonate, and ethyl acetate gave miscible solutions (Table 3). However, no polymers were obtained even though the addition of MMA afforded polymer in 35% yield under the same conditions. The non-conjugated ester methyl propionate was reported to be more basic than the conjugated ester methyl acrylate.[43] It is therefore suggested that the slight increase in the basicity of ethyl acetate compared with that of MMA strongly suppressed the high-temperature cationic polymerization.

Despite being non-conjugated esters, the addition of VAc and allyl acetate promoted IBVE polymerization. Furthermore, vinyl
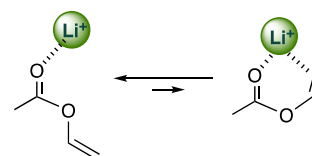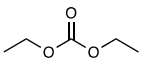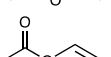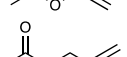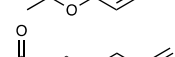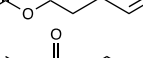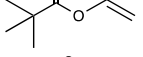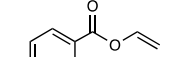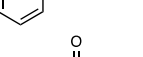

Scheme 3 Possible interaction between Li$^+$ and an olefin group.

esters afforded polymers regardless of the structure of the acyl groups. Li$^+$ and olefin groups form π-complexes, in which Li$^+$ is attached only weakly and is easily removed by stronger Lewis bases.[18-21] These results suggest that the weak interaction between the Li$^+$ and olefin group affected the coordination of C=O to Li$^+$ (Scheme 3). Of the non-conjugated esters with olefin groups examined, 4-pentenyl acetate failed to induce the cationic polymerization. This is probably because the olefin group was too far away to form an intramolecular interaction, as depicted in Scheme 3.

Mechanism of thermally induced cationic polymerization

There are two possible causes for the lack of polymerization at low temperatures such as 0 °C. One is that the initiation reaction did not occur, and the other is that the propagating cation was stabilized so that it did not react with another monomer. The cationic polymerization was therefore conducted using the

Table 3. Polymerization of IBVE in toluene at 60 °C for 4 h in the presence of LiNTf$_2$ and various Lewis bases[a]

Lewis base	Yield %	M_n[b] × 10^{-4}	M_w/M_n[b]	Olefin[c] %
(2-butanone)	0	-	-	-
(diethyl carbonate)	0	-	-	-
(ethyl acetate)	0			
(vinyl acetate)	53	2.0	2.0	0.1$_0$
(allyl acetate)	70	2.0	1.6	0.1$_3$
(4-pentenyl acetate)	0	-	-	-
(vinyl pivalate)	17	2.3	2.8	0.0$_4$
(vinyl benzoate)	73	1.6	1.8	0.1$_7$
(vinyl valerate)	21	1.7	2.5	0.1$_0$
(vinyl ester, long chain)	30	2.2	2.3	0.0$_9$

[a] [IBVE]$_0$ = 4.0 mol L^{-1}, [LiNTf$_2$]$_0$ = 0.1 mol L^{-1}, [Lewis base]$_0$ = 0.5 mol L^{-1}.
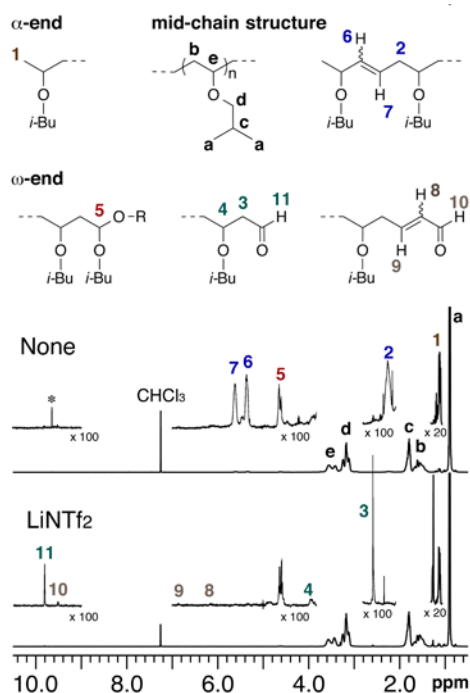[b] Determined by SEC (polystyrene standards).
[c] Determined by ^{1}H NMR spectroscopy.

Fig. 6 ^{1}H NMR spectra (500 MHz, CDCl$_3$, 55 °C) of the poly(IBVE)s prepared at 0 °C with BF$_3$•OEt$_2$ in the presence or absence of LiNTf$_2$.

typical cationic initiator BF$_3$•OEt$_2$ in the presence of MMA and LiNTf$_2$ (Table 2). Polymer was obtained in 43% yield even at 0 °C, indicating that the initiation reaction did not occur at low temperatures, which is likely because the acidity of water was not high enough to initiate the polymerization. The yield was lower than that in the absence of LiNTf$_2$. Furthermore, the formation of internal olefin groups was scarcely observed in the presence of MMA and LiNTf$_2$ (Fig. 6). It is therefore suggested that once the polymerization started, the stabilized propagating cation reacted with another monomer to grow the polymer chain.
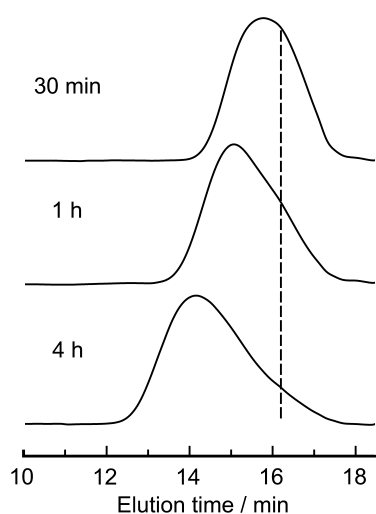
In the thermal polymerization at 60 °C, the amount of MMA added also affected the polymerization behavior. No polymer was obtained when the concentration of MMA was increased from 0.5 to 1.0 mol L^{-1}, whereas the yield increased when the MMA concentration was decreased to 0.1 mol L^{-1} (Table 2). It has been reported that MMA forms a solvate ionic liquid with LiNTf$_2$.[44, 45] It is therefore suggested that the propagating cation was stabilized through its interaction with the solvate ionic liquid formed between LiNTf$_2$ and the Lewis base.

Fig. 7 shows SEC curves of poly(IBVE)s prepared in toluene at 60 °C for 0.5, 1, and 4 h in the presence of VAc and LiNTf$_2$. The poly(IBVE)s were purified by extraction with CHCl$_3$, followed by concentration *in vacuo* to recover the polymerization product including the fraction with lower molecular weight (Table S2) (ESI†). With lengthening polymerization time, the main peak shifted to the higher molecular weight, but a small peak remained at lower molecular weight. This suggests that multiple species with different reactivities existed in the present polymerization system, and thus less-stabilized propagating cations were deactivated in the early stage of the polymerization.

A MALDI-TOF mass spectrum was measured for the poly(IBVE) prepared in toluene at 60 °C for 4 h in the presence of VAc and LiNTf$_2$ (Fig. 8). The monomer concentration was decreased to 1.5 mol L^{-1} to obtain poly(IBVE) with lower molecular weight. The oligomer peaks were selectively observed because of a mass discrimination effect.[46, 47] The spectrum showed two series of peaks, both with an interval of 100.10 m/Z, corresponding to the repeating unit mass. The m/Z values for the series with higher intensities (series A) agreed well with the monoisotopic masses of the Na$^+$ adducts of oligo(IBVE) with a methyl group at the α-end and an acetal group at the ω-end; for example, $n = 8$, $M_{theor} = 897.77$, $M_{obs} = 897.85$. The m/Z values for the series with lower intensities (series B) agreed well with the monoisotopic masses of the Na$^+$ adducts of oligo(IBVE) with a methyl group at the α-end and an aldehyde group at the ω-end; for example, $n = 8$, $M_{theor} = 867.73$, $M_{obs} = 867.81$.

Fig. 7 Size-exclusion chromatograms of poly(IBVE)s prepared in toluene at 60 °C in the presence of VAc and LiNTf$_2$.
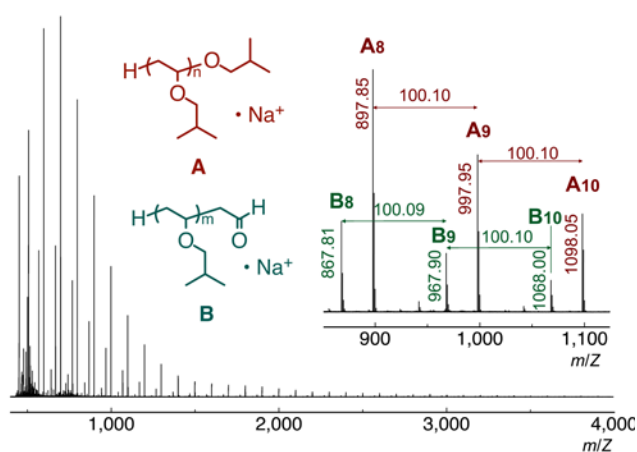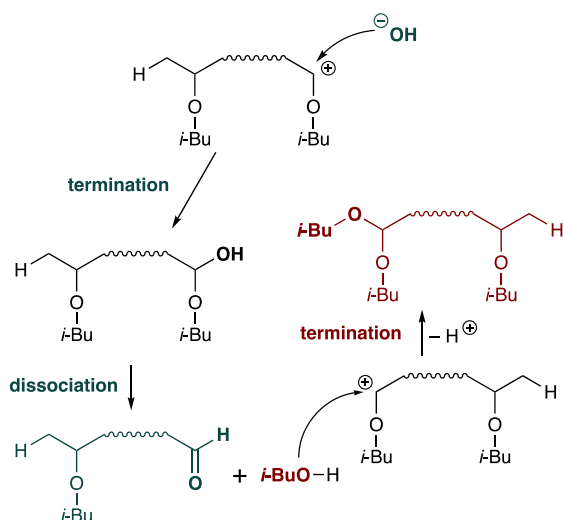

Fig. 8 MALDI-TOF mass spectrum of the poly(IBVE) prepared in toluene at 60 °C for 4 h in the presence of VAc and LiNTf$_2$.

Scheme 4 Possible route for oligomer formation during the early stage of polymerization.

The methyl groups in both series suggest that polymerization was initiated with H$^+$, which was probably derived from water present in the polymerization system. This corresponds to the ^{1}H NMR analysis of the poly(IBVE)s (Fig. 5). The aldehyde group observed for series B suggests that the less-stabilized propagating cation was terminated with a hydroxy anion, which is a counteranion, to form hemiacetal. This was followed by dissociation of the hemiacetal into aldehyde and isobutanol (Scheme 4). The by-product isobutanol quenched another less-stabilized cation to form the acetal group observed for series A. The reason why the intensities of series A look stronger than those of series B is probably because the ionization efficiency of oligomers depends on the chemical nature of their end groups.[47,][48] Note that peaks from oligomers with internal olefins were scarcely observed. In addition, no peaks assignable to oligomers containing VAc monomeric units were observed, confirming again that radical polymerization did not proceed and only cationic polymerization proceeds in this polymerization system.

Conventional cationic polymerization is usually carried out under dry nitrogen or argon, because water is a typical inhibitor of cationic polymerization. However, in the present system, the propagating cation is sufficiently stabilized to be able to eliminate the need for purification processes of chemical reagents like the IBVE monomer. The polymerization in the presence of LiNTf$_2$ and MMA was therefore conducted in air at 60 °C for 4 h (Table 2). The polymer was successfully obtained in 33% yield, which is comparable to that of 35% achieved under nitrogen. The decrease of molecular weight and broadening of the molecular weight distribution are likely caused by the increased humidity when the reaction was conducted in air rather than under nitrogen.

Conclusions

Polymerization of IBVE in the presence of LiNTf$_2$ was investigated with the aim of polymerizing simple vinyl ethers *via*

a radical mechanism. However, it was found that IBVE polymerized by a cationic mechanism. This serendipitously discovered cationic polymerization was unusual, particularly with regard to the polymerization temperature. Polymers were obtained at high temperatures like 60 °C, but not at low temperatures such as 0 °C. Furthermore, the polymer yield increased with the polymerization temperature, resulting in successful polymerization *via* a cationic mechanism at 100 °C, which is higher than the boiling point of IBVE. Thus, we defined this polymerization behavior as thermally induced cationic polymerization.

The polymerization behavior was affected by the Lewis bases that were added as dissolving agents for LiNTf$_2$. It is therefore assumed that this unique cationic polymerization was achieved because of the unusual stabilization of the propagating cations by their interaction with the solvate ionic liquids formed between LiNTf$_2$ and the Lewis bases. The facile and robust nature of the present polymerization system allowed us to use some chemical reagents as received without special pretreatment, even though conventional cationic polymerization requires dry and low-temperature conditions to avoid the occurrence of termination and side reactions. Polymerization at high temperature is advantageous to increase reaction rate. Therefore, further work exploring the extent to which the present polymerization system is applicable to less-reactive monomers that do not provide polymers with high molecular weights by conventional cationic polymerization is now in progress.

Acknowledgements

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