

Cationic homopolymerization of *trans*-anethole in the presence of solvate ionic liquid comprising LiN(SO₂CF₃)₂ and Lewis bases

Tomohiro Hirano,^a Takumi Yuki,^a Ryotaro Kizu,^a Ryota Kamiike,^{a,b} Miyuki Oshimura,^a and Koichi Ute^a

^aDepartment of Applied Chemistry, Tokushima University, 2-1 Minamijosanjima, Tokushima 770-8506, Japan

^bR&D center, Nippon A&L Inc., 2-10-2 Kikumoto, Niihama, Ehime 792-0801, Japan

*Corresponding author. Tel.: +81-88-656-7403; fax: +81-88-656-7404

E-mail address: hirano@tokushima-u.ac.jp (T. Hirano)

Abstract

Cationic homopolymerization of a biomass-derived monomer, *trans*-4-methoxy- β -methylstyrene (*trans*-anethole: Ane), was achieved with a combination of bis(trifluoromethylsulfonyl)imide and solvate ionic liquid comprising lithium bis(trifluoromethylsulfonyl)imide and a Lewis base, such as ethyl acetate and diisopropyl ether (*i*Pr₂O). The number-average molecular weight (M_n) of the obtained poly(Ane) reached 15.6×10^3 by adding *i*Pr₂O in toluene at -10 °C. The solubility of poly(Ane) varied drastically with a change of solvent: the polymers obtained in CH₂Cl₂ were not completely soluble in common organic solvents such as toluene, chloroform, and tetrahydrofuran, except for 1,1,2,2-tetrachloroethane (C₂H₂Cl₄) at 140 °C, whereas the polymers obtained in toluene were soluble in these solvents. The ¹H NMR spectrum measured in C₂D₂Cl₄ at 140 °C revealed that the stereostructure of poly(Ane) depended significantly on the solvent and the temperature: a polymer with a more regulated stereostructure was obtained from polymerization in CH₂Cl₂ at -40 °C than those obtained by polymerization in toluene at -10 °C.

Keywords: *trans*-4-methoxy- β -methylstyrene (*trans*-anethole); Cationic polymerization; Solvate ionic liquid

1. Introduction

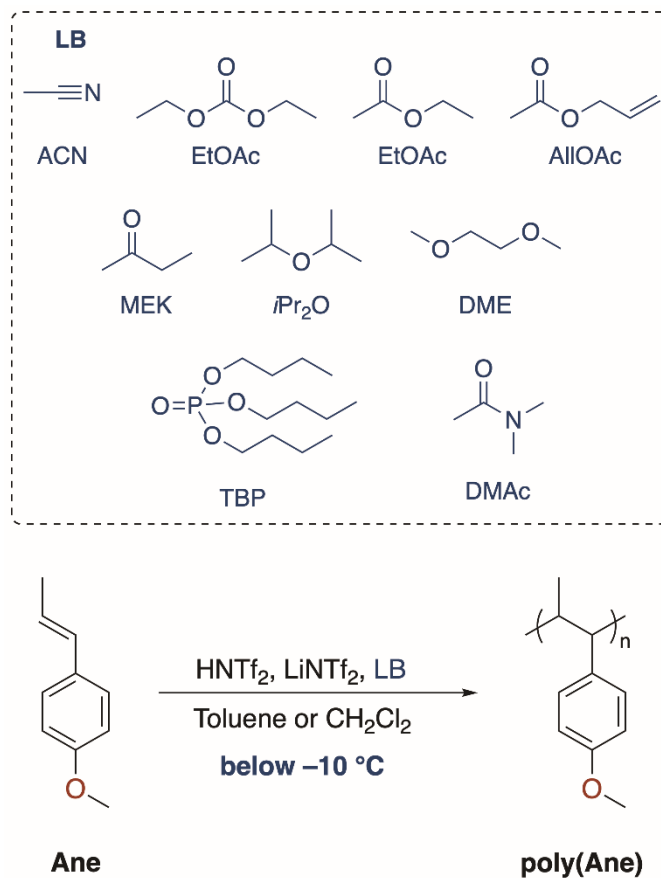
A biomass-derived monomer, *trans*-4-methoxy- β -methylstyrene (*trans*-anethole: Ane), is present abundantly in anise or fennel oil. Although Ane is a *p*-methoxystyrene (pMOST) derivative, a limited number of studies of cationic polymerizations of Ane has been reported, likely because steric repulsion of the β -methyl group significantly reduces its polymerizability [1-6]. For example, conventional cationic polymerization of Ane with

$\text{BF}_3 \cdot \text{OEt}_2$ in $\text{CH}_3\text{CN}/\text{CH}_2\text{Cl}_2$ at $0\text{ }^\circ\text{C}$ gives a polymer with number-average molecular weight (M_n) of 3.9×10^3 and broad molecular weight distribution ($M_w/M_n = 9.22$) [7], where M_w is the weight-average molecular weight. Furthermore, Ane polymerization with $\text{EtAlCl}_2/\text{SnCl}_4$ in CH_2Cl_2 at $0\text{ }^\circ\text{C}$, in conjunction with the adduct of isobutyl vinyl ether (IBVE) with acetic acid, provides a polymer with M_n of 5.4×10^3 and M_w/M_n of 4.91 [8], even though the $\text{EtAlCl}_2/\text{SnCl}_4$ system is effective for living cationic polymerizations of various styrene derivatives [9]. As a result, Ane has been generally considered as a non-homopolymerizable monomer and has been widely used as a comonomer in radical [10-15] and cationic [1-4, 7, 8] copolymerizations, until the recent successful cationic polymerization by cumyl chloride combined with SnCl_4 and 2,6-lutidine [16].

Lithium bis(trifluoromethylsulfonyl)imide (LiNTf_2) is known to form solvate ionic liquids with Lewis bases (LBs), in which LiNTf_2 is changed into molten salt composed of complexed Li^+ cations and counteranions [17-24]. Recently, we have reported that the addition of LiNTf_2 to radical polymerization of (meth)acrylamides leads to notable increases in the yield and molecular weight of the resulting polymers [25, 26]. In the course of investigating the extent to which LiNTf_2 enhances radical polymerization of other vinyl monomers, it was found that cationic polymerization of IBVE was thermally induced in toluene at high temperatures in the presence of LiNTf_2 and LBs such as methyl methacrylate (MMA) and vinyl acetate [27]. The polymerization was initiated by H_2O , which existed in the system because all reagents, including the monomer, were used without any purification. For example, a polymer with M_n of 2.6×10^4 was obtained in 71% yield in toluene at $100\text{ }^\circ\text{C}$ for 4 h in the presence of LiNTf_2 and MMA, whereas no polymerization occurred at $0\text{ }^\circ\text{C}$ even if the polymerization time was prolonged to 24 h. IBVE homopolymer was obtained even though radically-polymerizable MMA existed

in the system. These results indicate that cationic polymerization of IBVE proceeds at 100 °C, which is higher than the boiling point of the IBVE monomer. Therefore, we concluded that the propagating cations were specially stabilized by the solvate ionic liquid. One possible explanation is that the propagating cations are incorporated into coulombic networks of the solvate ionic liquids [28-33].

In this study, we conducted the Ane polymerization in the presence of LiNTf₂ and one of several LBs to examine the ability of solvate ionic liquids to stabilize the propagating cations for the cationic homopolymerization of Ane. Thermally induced cationic polymerization failed, although pMOST gave a polymer with high molecular weight under the same conditions. However, cationic homopolymerization of Ane proceeded successfully at low temperatures using bis(trifluoromethylsulfonyl)imide (HNTf₂) as an initiator (Scheme 1). Consequently, poly(Ane) with M_n of 15.6×10^3 was successfully prepared.



Scheme 1 Cationic homopolymerization of Ane in the presence of LiNTf₂ and LB

2. Experimental

2.1. Materials

Ethyl acetate (EtOAc) and toluene (FUJIFILM Wako Pure Chemical Corporation, Osaka, Japan) were purified by fractional distillation, followed by drying over 4Å molecular sieves (MS). Acetonitrile (ACN) and chloroform (FUJIFILM Wako Pure Chemical Corporation) were dried over 4Å MS. IBVE (Tokyo Chemical Industry, Tokyo, Japan) was fractionally distilled. Methyl ethyl ketone (MEK), diisopropyl ether (*i*Pr₂O), 1,1,2,2-tetrachloroethane (C₂H₂Cl₄), HNTf₂, LiNTf₂, methanol (FUJIFILM Wako Pure Chemical Corporation), diethyl carbonate (DEC), tetrahydrofuran (THF; high-performance liquid chromatography grade) (Kanto Chemical Co., Inc., Tokyo, Japan), pMOST, *p*-

methylstyrene (pMSt), Ane, allyl acetate (AlIOAc), sodium methoxide (CH₃ONa), 1,2-dimethoxyethane (DME), tri-*n*-butyl phosphate (TBP), and *N,N*-dimethylacetamide (DMAc) (Tokyo Chemical Industry) were used as received.

2.2 Thermally induced polymerization

In a typical polymerization procedure, Ane (3.33 g, 22.5 mmol) was diluted to 5 mL with toluene. LiNTf₂ (0.258 g, 0.9 mmol) and EtOAc (0.396 g, 4.5 mmol) were dissolved in toluene to prepare 1 mL of a second solution. The former solution (4 mL) was added to a glass ampoule. The glass ampoule was degassed under vacuum and filled with nitrogen six times at -50 °C before being set in an oil bath at 60 °C. Polymerization was initiated by adding the latter solution (0.5 mL) to the glass ampoule. The initial concentrations were [Ane]₀ = 4.0 mol L⁻¹, [LiNTf₂]₀ = 0.1 mol L⁻¹, and [EtOAc]₀ = 0.5 mol L⁻¹, respectively. After 4 h, the reaction was terminated by adding a methanol solution of CH₃ONa (0.1 wt%, 5.0 mL). The polymerization mixture was diluted with chloroform and then washed with brine three times. After the solvent was evaporated, the polymer was dried under vacuum. The polymer yield was determined gravimetrically.

2.3 Polymerization at low temperatures

In a typical polymerization procedure, Ane (1.667 g, 11.25 mmol) was diluted to 5 mL with toluene (solution A). Another portion of Ane (0.0167 g, 0.113 mmol) was diluted to 5 mL with toluene (solution B). HNTf₂ (50 mg, 0.045 mmol), LiNTf₂ (0.256 g, 0.9 mmol), and EtOAc (0.396 g, 4.5 mmol) were dissolved in toluene to prepare 1 mL of solution (solution C), of which 0.5 mL was added to a glass ampoule that was degassed under vacuum and filled with nitrogen six times at -50 °C, then set at -10 °C. After 15 min,

solution B (2.0 mL) was added to solution C dropwise using a syringe. After 30 min, polymerization was initiated by adding solution A (2.0 mL) using a syringe. The initial concentrations of all reagents in the ampoule at this point were $[Ane]_0 = 1.0 \text{ mol L}^{-1}$, $[LiNTf_2]_0 = 0.1 \text{ mol L}^{-1}$, $[EtOAc]_0 = 0.5 \text{ mol L}^{-1}$ and $[HNTf_2]_0 = 5.0 \text{ mmol L}^{-1}$. After 4 h, the reaction was terminated by adding a methanol solution of CH_3ONa (0.1 wt%, 5.0 mL). The polymerization mixture was diluted with chloroform and then washed with water three times. After the solvent was evaporated, the polymer was dried at $100 \text{ }^\circ\text{C}$ under vacuum. The polymer yield was determined gravimetrically.

2.4 Measurements

^1H nuclear magnetic resonance (NMR) spectra of the polymers were measured in $CDCl_3$ at $55 \text{ }^\circ\text{C}$ using an ECA-500 spectrometer (JEOL Ltd., Tokyo, Japan) or in $C_2D_2Cl_4$ at $140 \text{ }^\circ\text{C}$ using an ECZ-400 spectrometer (JEOL Ltd.). Diffusion-ordered two-dimensional NMR spectroscopy (DOSY) [34-39] was conducted in $C_2D_2Cl_4$ at $140 \text{ }^\circ\text{C}$ using an AVANCE NEO 400 spectrometer (Bruker BioSpin GmbH, Rheinstetten, Germany) equipped with a 5 mm cryogenically cooled probehead. Inversion of the Laplace transform of the raw data was performed by the maximum-entropy method [40]. The M_n and M_w/M_n of the polymers were determined by size-exclusion chromatography (SEC) on an HLC 8220 chromatograph (Tosoh, Tokyo, Japan) equipped with TSKgel columns [SuperHM-M (6.5 mm inner diameter \times 150 mm long) and SuperHM-H (6.5 mm inner diameter \times 150 mm long)] (Tosoh). THF was used as an eluent at $40 \text{ }^\circ\text{C}$ 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 polystyrene samples.

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 NaI were used as the matrix and the ionizing agent, respectively. Mass calibration was performed using monoisotopic mass peaks of sodium adducts of 7mer and 20mer having hydrogen at the initiating chain end and an olefinic group at the terminating chain end as 1059.62 and 2984.77 m/Z , respectively.

Differential scanning calorimetry (DSC) was performed on a DSC7020 calorimeter (Hitachi High-Tech Corp., Tokyo, Japan) at a heating rate of 10 °C min⁻¹ in nitrogen flow. Several heating/cooling cycles from 30 to 300 °C were carried out to remove thermal histories of the samples. The glass transition temperature (T_g) was evaluated from the intersection of pre- and post-transition lines on the enthalpy plot of the fourth heating. Thermogravimetric analysis (TGA) was conducted with NEXTA STA200RV (Hitachi High-Tech Corp.) by heating polymer samples from 30 to 100 °C at the rate of 20 °C min⁻¹, holding at 100 °C for 5 min, then heating from 100 to 500 °C at the rate of 10 °C min⁻¹ in nitrogen flow.

3. Results and Discussion

3.1 Thermal polymerizations of cationically polymerizable vinyl monomers at 60 °C in the presence of solvate ionic liquid

To examine the monomer generality of the stabilization effect by solvate ionic liquid, polymerizations of several cationically polymerizable vinyl monomers were conducted in toluene at 60 °C in the presence of solvate ionic liquid comprising LiNTf₂ and one of several LBs (Table 1). First, IBVE was polymerized in the presence of EtOAc or AlLOAc to examine the effect of Lewis basicity on the polymerization behavior in more detail. The recovery process was changed from methanol precipitation to chloroform extraction,

because it was suspected that oligomers were lost as a methanol-soluble fraction [27]. The addition of AlLOAc gave a polymer quantitatively, whereas the addition of EtOAc provided scarcely any polymer product (Table 1, Runs 1 and 3). This tendency is consistent with the results described in the previous paper [27]. Next, the IBVE monomer was purified by fractional distillation prior to the polymerization. However, the purification of the monomer scarcely affected the polymerization behaviors (Table 1, Runs 2 and 4). These results suggest that the present cationic polymerization is particularly robust against impurities.

Table 1. Polymerization of several cationically polymerizable vinyl monomers in toluene at 60 °C in the presence of solvate ionic liquid comprising LiNTf₂ and LBs^a

Run	Monomer	LB	Yield / %	M_n^b $\times 10^{-3}$	M_w/M_n^b
1	IBVE	EtOAc	0.5	n.d. ^d	n.d. ^d
2	IBVE ^c	EtOAc	2.3	0.9	1.4
3	IBVE	AlLOAc	>99	6.1	2.3
4	IBVE ^c	AlLOAc	>99	6.2	2.2
5	pMSt	EtOAc	trace	n.d. ^d	n.d. ^d
6	pMSt	AlLOAc	2.5	4.7	1.6
7	pMOST	EtOAc	trace	n.d. ^d	n.d. ^d
8	pMOST	AlLOAc	>99	83.4	2.0
9	Ane	EtOAc	-	-	-
10	Ane	AlLOAc	-	-	-

^a $[M]_0 = 4.0 \text{ mol L}^{-1}$, $[\text{LiNTf}_2]_0 = 0.1 \text{ mol L}^{-1}$, $[\text{LB}]_0 = 0.5 \text{ mol L}^{-1}$, 4h.

^b Determined by SEC.

^c The monomer was purified by fractional distillation.

^d Not determined.

In another set of experiments, pMSt or pMOST was used as a monomer instead of IBVE. The addition of EtOAc afforded scarcely any polymer products in both polymerizations (Table 1, Runs 5 and 7), as well as in the IBVE polymerizations. By adding AlLOAc, however, a polymer was quantitatively obtained by the polymerization of the more-reactive pMOST, whereas a small amount of polymer was obtained by the polymerization of the less-reactive pMSt (Table 1, Runs 6 and 8). The M_n of the poly(pMOST) is significantly higher than those of poly(IBVE)s prepared under the same conditions. The formation of a vinyl polymer was confirmed by the ¹H NMR spectrum, in which signals derived from side reactions such as β -proton elimination and intra- or intermolecular Friedel-Crafts reactions were not clearly observed (Figure 1) [41]. These

results indicate that the stabilization effect by solvate ionic liquid is effective at least for pMOST, although the cationic polymerizability of pMOST is much lower than that of IBVE [42]. Therefore, polymerizations of Ane were conducted under the same conditions. However, no polymers were obtained, regardless of the identity of the added LB (Table 1, Runs 9 and 10). These results once again prove the poor polymerizability of Ane.

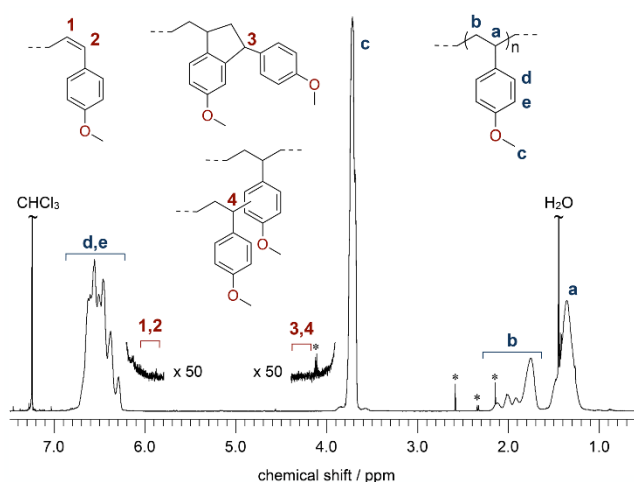


Figure 1 500 MHz ^1H NMR spectrum of poly(pMOST) prepared by thermal cationic polymerization in the presence of LiNTf_2 and $\text{Al}(\text{OAc})_3$ (CDCl_3 , 55°C). * denotes impurities.

3.2 Cationic polymerization of Ane at low temperatures

HNTf_2 , a strong Brønsted acid, has been widely used as a catalyst in organic syntheses [43, 44]. Recently, HNTf_2 was shown to play multiple roles of initiator, activator, and stabilizer in IBVE polymerization, resulting in living polymerization at temperatures lower than -40°C [45]. Therefore, cationic polymerizations of Ane with HNTf_2 were examined in toluene at 25°C in the presence of LiNTf_2 and EtOAc . In the previous paper, less-stabilized propagating cations were found to be deactivated in the early stage of the IBVE polymerization [27]. Therefore, a two-fold amount of Ane monomer to HNTf_2 was

added to generate stabilized species at first. After 30 min, polymerization was initiated by adding Ane monomer ($[M]_0 / [I]_0 = 200$). However, just a trace amount of oligomer with M_n of 1.1×10^3 was obtained (Table 2, Run 3). Therefore, the polymerization temperature was decreased from 25 °C to 0 °C (Table 2, Run 4). The system turned into a red-colored gel after 4 h. The red color suggests the formation of a long-lived propagating species [46]. Both the yield and the M_n significantly increased by lowering the temperature: a polymer with M_n of 7.3×10^3 was obtained in 85 % yield. This M_n is higher than the M_n (5.4×10^3) of the polymer prepared with the $\text{EtAlCl}_2/\text{SnCl}_4$ system [8]. This result suggests that lowering the temperature is effective to conduct the Ane polymerization. Therefore, the polymerization temperature was further reduced to –10 °C; the Ane monomer was precipitated from toluene at temperatures below –10 °C. As a result of lowering the temperature, both the yield and the M_n further increased: a polymer was quantitatively obtained, and the M_n reached 9.2×10^3 (Table 2, Run 5).

Table 2. Cationic polymerization of Ane with HNTf₂ in toluene in the presence of solvate ionic liquid comprising LiNTf₂ and one of several Lewis bases^a

Run	LB	DN ^b	Temp. / °C	Yield / %	M_n^c $\times 10^{-3}$	M_w/M_n^c
1	ACN	14.1	-10	>99	10.2	2.7
2	DEC	16.1	-10	97	10.1	3.3
3	EtOAc	17.1	25	trace	1.1	4.6
4	EtOAc	17.1	0	85	7.3	3.0
5	EtOAc	17.1	-10	>99	9.2	4.1
6	EtOAc ^d	17.1	-10	63	7.6	1.8
7 ^e	EtOAc	17.1	-10	>99	7.4	3.6
8	MEK	17.4	-10	>99	12.1	2.9
9	<i>i</i> Pr ₂ O	19.0	-10	88	15.6	3.1
10	DME	20.0	-10	5	0.4	2.5
11	TBP	23.7	-10	-	-	-
12	DMAc	27.8	-10	-	-	-
13 ^f	EtOAc	17.1	-10	92	-	-
14 ^f	EtOAc	17.1	-40	32	-	-

^a [Ane]₀ = 1.0 mol L⁻¹, [LB]₀ = 0.5 mol L⁻¹, [LiNTf₂]₀ = 0.1 mol L⁻¹, [HNTf₂]₀ = 5.0 × 10⁻³ mol L⁻¹, 4h. ^b Donor Number [47]. ^c Determined by SEC. ^d Without LiNTf₂. ^e [Ane]₀ = 0.5 mol L⁻¹. ^f CH₂Cl₂ was used as a solvent.

Figure 2 shows the ¹H NMR spectrum of the polymer prepared by cationic homopolymerization of Ane at -10 °C in the presence of LiNTf₂ and EtOAc. Many signals were observed for oligomers and the toluene used as a solvent, because not only the polymer but also low-molecular-weight compounds were recovered by extraction with chloroform. However, the integral intensities of the signals **a-f** were in good agreement with the theoretical values calculated from the structure depicted in Figure 2. This agreement indicates that vinyl polymerization of Ane proceeded successfully via a cationic mechanism under the given conditions.

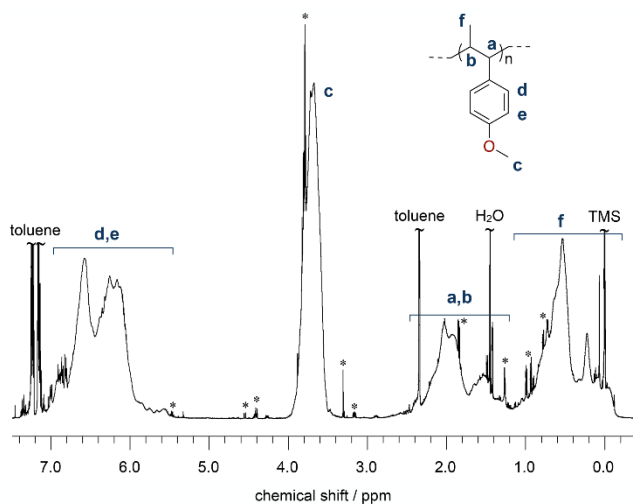


Figure 2 500 MHz ¹H NMR spectrum of poly(Ane) prepared by cationic homopolymerization in the presence of LiNTf₂ and EtOAc (CDCl₃, 55 °C). * denotes impurities.

To examine the effect of LiNTf₂ on the polymerization behavior, the Ane polymerization was conducted in toluene at −10 °C without adding LiNTf₂ (Table 2, Run 6). A polymer with M_n of 7.6×10^3 was obtained in 63% yield, probably because EtOAc stabilized the propagating cations. A similar stabilizing effect by LBs is known in the polymerization of vinyl ethers, for which LBs are combined with Lewis acids [48, 49]. However, adding both LiNTf₂ and EtOAc significantly enhanced the yield and the M_n , indicating that solvate ionic liquids exhibit a stabilizing effect greater than that observed from the presence of a LB alone.

To examine the effect of Lewis basicity on the polymerization behavior, the Ane polymerization was conducted in toluene at −10 °C in the presence of solvate ionic liquid comprising LiNTf₂ and one of several LBs. Lewis basicity can be quantified empirically by Guttmann's Donor Number, DN: the stronger the Lewis basicity, the higher the DN value [47, 50]. The addition of weaker LBs such as CH₃CN (DN = 14.1) and DEC (DN = 16.1) afforded polymers with comparable M_n s to that obtained with the addition of

EtOAc (DN = 17.1) (Table 2, Runs 1, 2, and 5). The M_n increased significantly when stronger LBs, such as MEK (DN = 17.4) and $i\text{Pr}_2\text{O}$ (DN = 19.0), were used (Table 2, Runs 8 and 9). In particular, the M_n reached 15.6×10^3 when $i\text{Pr}_2\text{O}$ was used. However, both the polymer yield and the M_n drastically decreased when DME (DN = 20.0) was used (Table 2, Run 10). Furthermore, no polymerizations were observed in the presence of much stronger LBs, such as TBP (DN = 23.7) and DMAc (DN = 27.8) (Table 2, Runs 11 and 12). These results suggest that moderate Lewis basicity is essential for conducting cationic homopolymerization of Ane.

Figure 3a shows time-conversion curves for the Ane polymerization in toluene at $-10\text{ }^\circ\text{C}$ in the presence of solvate ionic liquids. As shown in the figure, cationic polymerization proceeded more slowly when using the more basic $i\text{Pr}_2\text{O}$, suggesting that the solvate ionic liquid containing $i\text{Pr}_2\text{O}$ stabilized the propagating species more efficiently than that containing EtOAc. Furthermore, the M_n scarcely varied with the conversion, regardless of the solvate ionic liquid used (Figure 3b and c), suggesting that a chain-transfer reaction occurred during the polymerization. Slower polymerizations with $i\text{Pr}_2\text{O}$ gave polymers with a higher M_n , implying that the solvate ionic liquid containing $i\text{Pr}_2\text{O}$ suppressed the chain-transfer reaction more efficiently than that containing EtOAc, probably because of the greater stabilization of the propagating species. Shoulder peaks indicated by arrows were observed in the chromatograms. Similar tendencies were observed in the quasi-living polymerization of Ane by cumyl chloride combined with SnCl_4 and 2,6-lutidine, in which the high-molecular-weight fractions formed at up to 30 wt%, depending on solvent and temperature [16]. This matter will be discussed at the last part of the section 3.3.

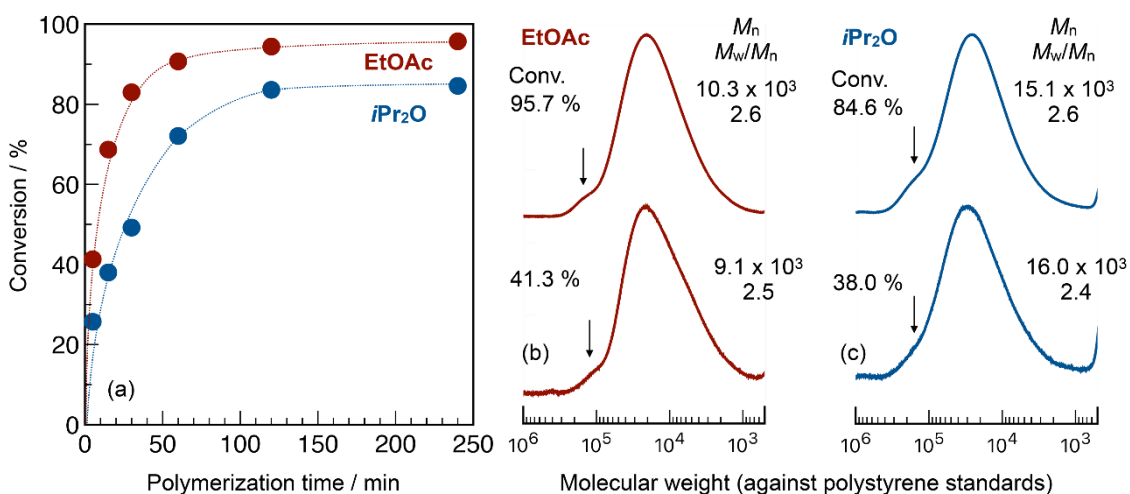


Figure 3 (a) Time-conversion curves for the Ane polymerization in toluene at $-10\text{ }^{\circ}\text{C}$ in the presence of solvate ionic liquids. SEC chromatograms of poly(Ane)s obtained in the presence of LiNTf₂ and (b) EtOAc or (c) *i*Pr₂O.

To examine the chain-end structures of the polymers, MALDI-TOF mass spectrometric analysis was performed for the poly(Ane) prepared at $-10\text{ }^{\circ}\text{C}$ in the presence of LiNTf₂ and EtOAc (Figure 4). Because the M_n of the polymer obtained in the presence of LiNTf₂ and EtOAc was slightly high for conducting a MALDI-TOF mass measurement, the monomer concentration was decreased to 0.5 mol/L to reduce the M_n (Table 2, Run 7). A polymer with a slightly decreased M_n and a wide molecular weight distribution was observed. Peaks arising from species with lower molecular masses were observed, likely because of a mass discrimination effect [51-53]. The spectrum showed a series of peaks with intervals of 148.09 m/Z , corresponding to the repeating unit mass. The m/Z values for the series agreed well with the monoisotopic masses of the Na⁺ adducts of poly(Ane)s with a hydrogen at the α -end and an olefinic group at the ω -end; for example, at $n = 12$, $M_{\text{theor}} = 1800.06$ and $M_{\text{obs}} = 1800.06$. The structure can be formed via a β -proton elimination from the propagating chain end (Scheme 2). This result confirms that a chain-transfer reaction occurs during the polymerization, as mentioned

above.

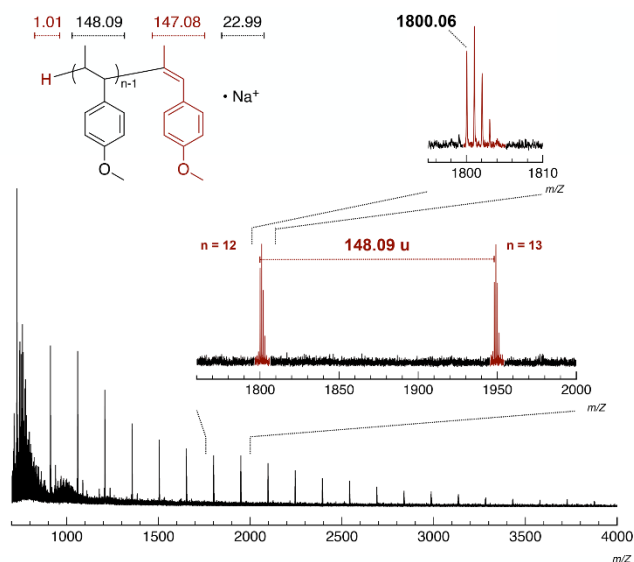
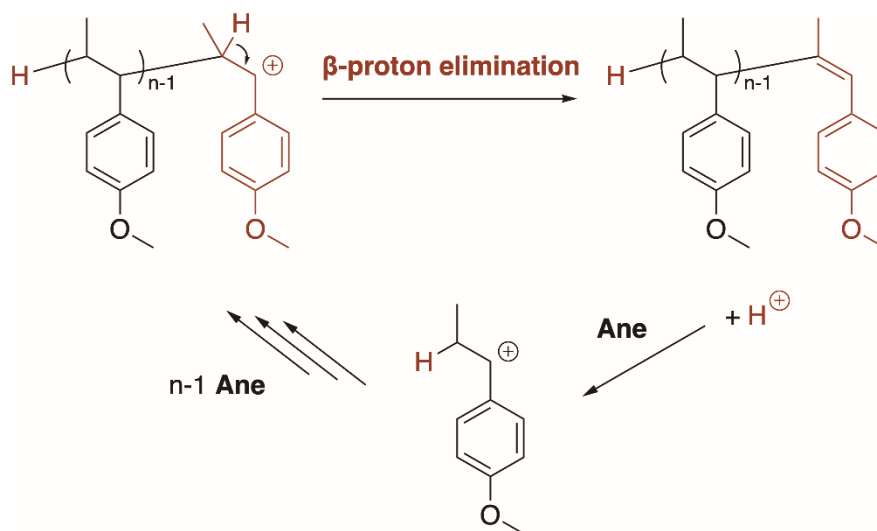


Figure 4 MALDI-TOF mass spectrum of the poly(Ane) prepared at $-10\text{ }^{\circ}\text{C}$ in the presence of LiNTf₂ and EtOAc.



Scheme 2 Chain transfer reaction in the cationic homopolymerization of Ane.

3.3 Cationic polymerization of Ane in CH₂Cl₂

Polymerization at lower temperatures could not be investigated, because the Ane monomer was precipitated from toluene at temperatures below $-10\text{ }^{\circ}\text{C}$. However, the Ane

monomer was soluble in CH_2Cl_2 even at $-40\text{ }^\circ\text{C}$. Therefore, the Ane polymerizations in CH_2Cl_2 in the presence of LiNTf_2 and EtOAc were conducted at -10 and $-40\text{ }^\circ\text{C}$ (Table 2, Runs 13 and 14). The system turned into a red-colored gel at $-10\text{ }^\circ\text{C}$, as did the polymerizations in toluene. Furthermore, white solids were precipitated during the polymerization at $-40\text{ }^\circ\text{C}$. The polymers obtained in CH_2Cl_2 were insoluble in common solvents such as toluene, chloroform, and THF, except for $\text{C}_2\text{H}_2\text{Cl}_4$ at $140\text{ }^\circ\text{C}$. Therefore, the polymers were purified by dissolving them in $\text{C}_2\text{H}_2\text{Cl}_4$ at $140\text{ }^\circ\text{C}$, followed by dropping the solution into methanol at room temperature. The polymer yields were determined to be 92% ($-10\text{ }^\circ\text{C}$) and 32% ($-40\text{ }^\circ\text{C}$), respectively.

The formation of insoluble materials by the Ane polymerization in CH_2Cl_2 at lower temperatures, such as $-45\text{ }^\circ\text{C}$ [5] or $-78\text{ }^\circ\text{C}$ [8], has been reported. A crosslinked or branched structure has been considered to be the cause of the heterogeneity. Therefore, the ^1H NMR spectra of poly(Ane)s prepared at lower temperatures were measured in $\text{C}_2\text{D}_2\text{Cl}_4$ at $140\text{ }^\circ\text{C}$ (Figure 5). The poly(Ane) obtained in CH_2Cl_2 at $-10\text{ }^\circ\text{C}$ dissolved in a few minutes after being warmed at $140\text{ }^\circ\text{C}$, whereas the poly(Ane) obtained in CH_2Cl_2 at $-40\text{ }^\circ\text{C}$ took several minutes longer to dissolve than did the poly(Ane) obtained at $-10\text{ }^\circ\text{C}$. Regardless of the polymerization solvent and temperature, the integral intensities agreed well with those expected for the poly(Ane) as illustrated in the figure. In addition, no signals derived from intermolecular Friedel-Crafts reactions were observed in the spectra, meaning that no cross-linking and branching reactions occurred, at least in the present polymerization system. However, the spectral pattern of the poly(Ane)s prepared in CH_2Cl_2 is obviously different from that of the poly(Ane) prepared in toluene. For example, the relative intensity of the signal at 6.2 ppm to that at 6.6 ppm (indicated by arrows) increased upon changing the solvent from toluene to CH_2Cl_2 . The tendency was

enhanced by lowering the temperature to $-40\text{ }^{\circ}\text{C}$. α,β -Disubstituted monomers afford ditactic polymers, such as diisotactic, diheterotactic, and disyndiotactic polymers [54-56]. Different stereostructures were obtained for poly(Ane)s formed by changing the solvent from toluene to CH_2Cl_2 , although the relationship of the change to the consequent stereostructure is still unclear. Consequently, one possible explanation for the change in the solubility of the poly(Ane) is that the stereoregularity of the poly(Ane) varied depending on the solvent and temperature.

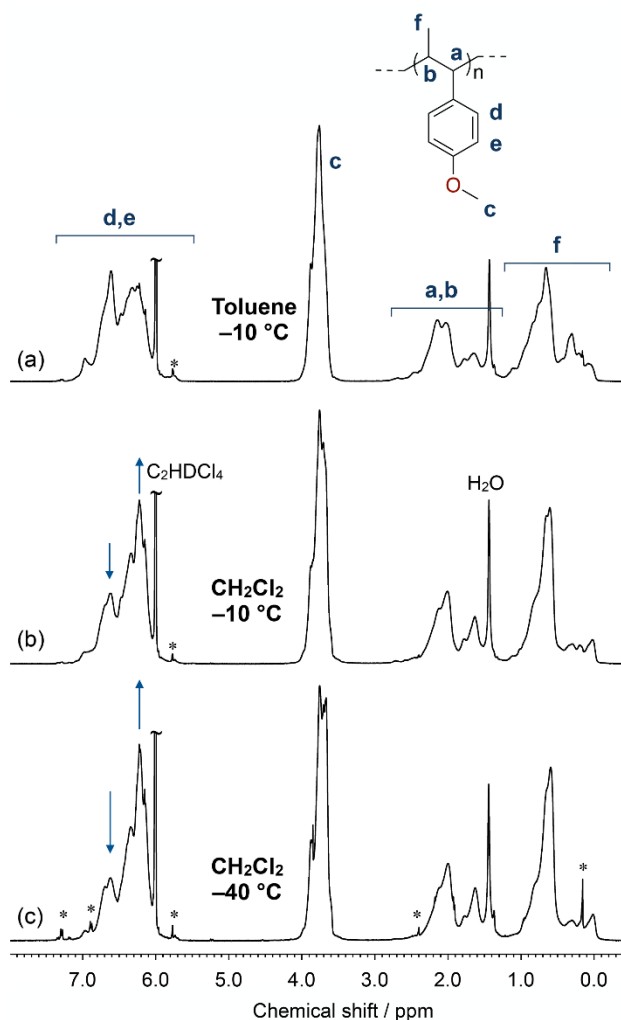


Figure 5 The 400-MHz ^1H NMR spectra of poly(Ane)s prepared by cationic homopolymerization in the presence of LiNTf_2 and EtOAc (a) in toluene at $-10\text{ }^{\circ}\text{C}$, (b) in CH_2Cl_2 at $-10\text{ }^{\circ}\text{C}$ and (c) in CH_2Cl_2 at $-40\text{ }^{\circ}\text{C}$ ($\text{C}_2\text{D}_2\text{Cl}_4$, $140\text{ }^{\circ}\text{C}$). * denotes impurities.

Another possible explanation is that poly(Ane)s with higher molecular weights were prepared in CH₂Cl₂. However, the poly(Ane)s are insoluble in common solvents, so that the molecular weights are unable to be determined by conventional SEC. Therefore, DOSY was used to estimate the range of molecular weights of the poly(Ane) obtained in CH₂Cl₂, because the self-diffusion coefficient (*D*) of the molecular species allows the separation of the complex NMR spectrum of a mixture in the DOSY experiment. A double-stimulated echo sequence was used to suppress artifacts caused by thermal convection.[57] Figure 6 shows the DOSY plots of the poly(Ane) obtained from polymerization in CH₂Cl₂ at -10 °C, measured in C₂D₂Cl₄ at 140 °C. The contour peaks of methoxy and β-methyl groups derived from poly(Ane) were observed in the *D* range between the two standard polystyrene samples. This result suggests that at least the poly(Ane) prepared in CH₂Cl₂ at -10 °C has a molecular weight comparable to that of poly(Ane) prepared in toluene at -10 °C (*cf.* Figure 3b and c). Furthermore, the DOSY measurement failed without the two standard polystyrene samples, likely because thermal convection occurred due to the low viscosity of the solution of poly(Ane) alone. Consequently, the more-regulated stereostructure of poly(Ane) obtained in CH₂Cl₂ is assumed to be responsible for the poor solubility. In addition, a gel was formed when the C₂H₂Cl₄ solution of the poly(Ane) obtained in CH₂Cl₂ at -40 °C (2.5 wt%) was cooled from 140 °C to room temperature, suggesting that poorly soluble segments can associate intra- and/or intermolecularly to form the gel. Therefore, the shoulder peaks observed in the SEC chromatograms of poly(Ane)s are considered to be caused by association of the polymers, which have segments with poor solubility.

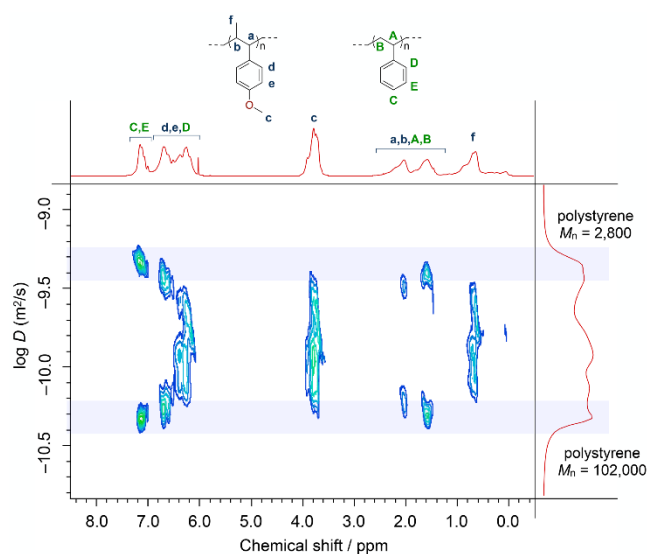


Figure 6 DOSY contour plots of the poly(Ane) (3.0 wt%) obtained in CH_2Cl_2 at $-10\text{ }^\circ\text{C}$. Two polystyrene samples ($M_n = 2,800$, $M_w/M_n = 1.01$, 1.0 wt% and $M_n = 102,000$, $M_w/M_n = 1.02$, 1.0 wt%) were mixed as internal standard. Measurement was conducted in $\text{C}_2\text{D}_2\text{Cl}_4$ at $140\text{ }^\circ\text{C}$.

DSC can be used to determine the T_g of poly(Ane)s [16], whereas dynamic mechanical analysis is required to determine the T_g of polymers derived from α,β -disubstituted vinyl monomers such as alkyl crotonates [58] and methyl cinnamate [59]. Therefore, DSC measurements were conducted for poly(Ane)s prepared in toluene at $-10\text{ }^\circ\text{C}$ and in CH_2Cl_2 at $-10\text{ }^\circ\text{C}$ or $-40\text{ }^\circ\text{C}$ (Figure S1). The T_g of poly(Ane) prepared in toluene at $-10\text{ }^\circ\text{C}$ (Table 2, Run 5) was determined to be $181.2\text{ }^\circ\text{C}$. The value is lower than the T_g of the poly(Ane) with a similar molecular weight ($M_n = 10.2 \times 10^3$, $M_w/M_n = 1.26$, $218.2\text{ }^\circ\text{C}$), although the reported T_g was determined by a different method (inflection point) [16]. The decrease in T_g is probably because of a wider molecular weight distribution: poly(Ane)s with lower molecular weights behave as softener agents [60]. The T_g of poly(Ane) prepared in CH_2Cl_2 at $-10\text{ }^\circ\text{C}$ was determined to be $229.2\text{ }^\circ\text{C}$. The increase in the T_g value is assumed to be caused by a change in the stereostructure, although the exact M_n and M_w/M_n values of the poly(Ane) are unknown. In addition, the

DSC curve for the poly(Ane) prepared in CH₂Cl₂ at -40 °C did not exhibit any change due to T_g , likely because the stereostructure was more regulated.

The degradation behavior of poly(Ane)s was monitored by TGA (Figure S2). Weight losses by small molecules, including solvents, were observed in the range of 100 to 250 °C. Therefore, a 5% weight-loss temperature (T_{d5}) was determined based on the weight at 300 °C. The poly(Ane)s prepared at -10 °C showed almost the same T_{d5} regardless of the solvent (Toluene: 375.0 °C; CH₂Cl₂: 374.0 C). The values are similar to the reported values [16, 61, 62]. However, a slight increase in T_{d5} was observed for the poly(Ane) prepared in CH₂Cl₂ at -40 °C (379.3 °C). This result also suggests a better-controlled stereostructure of poly(Ane) prepared in CH₂Cl₂ at -40 °C, because the degradation behavior of PMMA depended on both stereostructure and molecular weight [63].

4. Conclusions

The cationic polymerization of Ane in the presence of solvate ionic liquid comprising LiNTf₂ and a LB was investigated. No polymerization of Ane occurred in toluene at 60 °C in the presence of LiNTf₂ and Al(OAc)₃, whereas cationic polymerization of pMOST proceeded under the same conditions. However, cationic homopolymerization of Ane was successfully achieved by adding HNTf₂ as an initiator at -10 °C. The polymerization behavior depended on the identity of the added LB. Moderate Lewis basicity was essential for conducting cationic homopolymerization of Ane. The M_n reached 15.6×10^3 by adding *i*Pr₂O. The polymerization solvent was another important factor in the present polymerization system. Polymers insoluble in common organic solvents were obtained from the Ane polymerization in CH₂Cl₂, whereas soluble polymers were obtained from

polymerization in toluene. ^1H and DOSY NMR spectra suggested that the change in stereoregularity was responsible for the change in the solubility of poly(Ane). Further work is underway to determine the stereoregularity induced by various factors when obtaining highly stereoregulated polymers.

Acknowledgements

This work was supported in part by JSPS KAKENHI Grant Number JP19K05585. The authors thank Ms. Hinano Tamura of Nippon A&L Inc. for the DSC measurements. We thank Alicia Glatfelter, PhD, from Edanz (<https://jp.edanz.com/ac>) for editing a draft of this manuscript.

References

- [1] Alfrey Jr. T, Arond L, and Overberger CG. *J Polym Sci* 1949;4(4):539-41.
- [2] Overberger CG, Tanner D, and Pearce EM. *J Am Chem Soc* 1958;80(17):4566-8.
- [3] Mizote A, Tanaka T, Higashimura T, and Okamura S. *J Polym Sci, Part A: Gen Pap* 1965;3(7):2567-78.
- [4] Higashimura T, Kawamura K, and Masuda T. *J Polym Sci, Part A-1: Polym Chem* 1972;10(1):85-93.
- [5] Alexander R, Jefferson A, and Lester PD. *J Polym Sci, Polym Chem Ed* 1981;19(3):695-706.
- [6] Trumbo DL. *Polym Bull* 1994;33(6):643-9.
- [7] Satoh K, Saitoh S, and Kamigaito M. *J Am Chem Soc* 2007;129(31):9586-7.
- [8] Yasuoka K, Kanaoka S, and Aoshima S. *Kobunshi Ronbunshu* 2011;68(7):517-9.
- [9] Aoshima S and Kanaoka S. *Chem Rev* 2009;109(11):5245-87.
- [10] Murahashi S, Nozakura Si, Emura K, and Yasufuku K. *Bull Chem Soc Jpn* 1965;38(9):1560-2.
- [11] Kokubo T, Iwatsuki S, and Yamashita Y. *Macromolecules* 1970;3(5):518-23.
- [12] Fujimori K, Schiller WS, and Craven IE. *Polym Bull* 1988;20(4):355-8.
- [13] Fujimori K, Schiller WS, and Craven IE. *Makromol Chem* 1991;192(4):959-66.
- [14] Braun D and Hu F. *Prog Polym Sci* 2006;31(3):239-76.
- [15] Nonoyama Y, Satoh K, and Kamigaito M. *Polym Chem* 2014;5(9):3182-9.

- [16] Hulnik MI, Kuharenko OV, Vasilenko IV, Timashev P, and Kostjuk SV. *ACS Sustainable Chemistry & Engineering* 2021;9(19):6841-54.
- [17] Hu Y, Wang Z, Li H, Huang X, and Chen L. *J Electrochem Soc* 2004;151(9):A1424-A8.
- [18] Chen R, Wu F, Liang H, Li L, and Xu B. *J Electrochem Soc* 2005;152(10):A1979-A84.
- [19] Chen R, Wu F, Li, Xu B, Qiu X, and Chen S. *J Phys Chem C* 2007;111(13):5184-94.
- [20] Chen R, Wu F, Li L, Qiu X, Chen L, and Chen S. *Vib Spectrosc* 2007;44(2):297-307.
- [21] Whitley JW, Jeffrey Horne W, Danielsen SPO, Shannon MS, Marshall JE, Hayward SH, Gaddis CJ, and Bara JE. *Eur Polym J* 2014;60:92-7.
- [22] Mandai T, Yoshida K, Ueno K, Dokko K, and Watanabe M. *Phys Chem Chem Phys* 2014;16(19):8761-72.
- [23] Yamada Y and Yamada A. *J Electrochem Soc* 2015;162(14):A2406-A23.
- [24] Hamilton JR, Abedini A, Zhang Z, Whitley JW, Bara JE, and Turner CH. *Chem Eng Sci* 2015;138:646-54.
- [25] Hirano T, Saito T, Kurano Y, Miwa Y, Oshimura M, and Ute K. *Polym Chem* 2015;6(11):2054-64.
- [26] Hirano T, Segata T, Hashimoto J, Miwa Y, Oshimura M, and Ute K. *Polym Chem* 2015;6(27):4927-39.
- [27] Hirano T, Kizu R, Hashimoto J, Munekane N, Miwa Y, Oshimura M, and Ute K. *Polym Chem* 2018;9(12):1421-9.
- [28] Marcus Y and Hefter G. *Chem Rev* 2006;106(11):4585-621.
- [29] Buchner R and Hefter G. *Phys Chem Chem Phys* 2009;11(40):8984-99.
- [30] Yamada Y, Furukawa K, Sodeyama K, Kikuchi K, Yaegashi M, Tateyama Y, and Yamada A. *J Am Chem Soc* 2014;136(13):5039-46.
- [31] Seo DM, Reininger S, Kutcher M, Redmond K, Euler WB, and Lucht BL. *J Phys Chem C* 2015;119(25):14038-46.
- [32] Self J, Wood BM, Rajput NN, and Persson KA. *J Phys Chem C* 2018;122(4):1990-4.
- [33] Hwang S, Kim D-H, Shin JH, Jang JE, Ahn KH, Lee C, and Lee H. *J Phys Chem C* 2018;122(34):19438-46.
- [34] Morris KF and Johnson CS. *J Am Chem Soc* 1992;114(8):3139-41.
- [35] Johnson CS. *Prog Nucl Magn Reson Spectrosc* 1999;34(3):203-56.
- [36] Barrère C, Mazarin M, Giordanengo R, Phan TNT, Thévand A, Viel S, and

- Charles L. *Anal Chem* 2009;81(19):8054-60.
- [37] Li W, Chung H, Daeffler C, Johnson JA, and Grubbs RH. *Macromolecules* 2012;45(24):9595-603.
- [38] Guo X, Laryea E, Wilhelm M, Luy B, Nirschl H, and Guthausen G. *Macromol Chem Phys* 2017;218(1):1600440.
- [39] Ute K, Nagao R, and Watanabe K. *New Dev NMR* 2019;20:80-100.
- [40] Delsuc MA and Malliavin TE. *Anal Chem* 1998;70(10):2146-8.
- [41] Kanazawa A, Shibutani S, Yoshinari N, Konno T, Kanaoka S, and Aoshima S. *Macromolecules* 2012;45(19):7749-57.
- [42] Sawamoto M, Ohtoyo T, Higashimura T, Gührs K-H, and Heublein G. *Polym J* 1985;17(8):929-33.
- [43] Rendina VL. *Synlett* 2011;2011(20):3055-6.
- [44] Zhao W and Sun J. *Chem Rev* 2018;118(20):10349-92.
- [45] Song J, Xu J, and Tang D. *J Polym Sci, Part A: Polym Chem* 2016;54(10):1373-7.
- [46] Higashimura T, Mitsuhashi M, and Sawamoto M. *Macromolecules* 1979;12(2):178-82.
- [47] Cataldo F. *Eur Chem Bull* 2015;4(1-3):92-7.
- [48] Aoshima S and Higashimura T. *Polym Bull* 1986;15(5):417-23.
- [49] Aoshima S and Higashimura T. *Macromolecules* 1989;22(3):1009-13.
- [50] Gutmann V. *The Donor-Acceptor Approach to Molecular Interactions*: Plenum, 1978.
- [51] Montaudo G, Samperi F, and Montaudo MS. *Prog Polym Sci* 2006;31(3):277-357.
- [52] Puglisi C, Samperi F, Alicata R, and Montaudo G. *Macromolecules* 2002;35(8):3000-7.
- [53] Hirano T, Ogasa Y, Oshimura M, and Ute K. *Polymer* 2020;201:122664.
- [54] Ute K, Tarao T, and Hatada K. *Polym J* 1997;29(11):957-8.
- [55] Ute K, Tarao T, Hongo S-y, Ohnuma H, Hatada K, and Kitayama T. *Polym J* 1999;31:177.
- [56] Ute K, Tarao T, and Kitayama T. *Polym J* 2005;37:578.
- [57] Jerschow A and Müller N. *Journal of Magnetic Resonance* 1997;125(2):372-5.
- [58] Ute K, Tarao T, Nakao S, and Kitayama T. *Polymer* 2003;44(26):7869-74.
- [59] Imada M, Takenaka Y, Tsuge T, and Abe H. *Polym J* 2021;53(9):989-99.
- [60] Ute K, Miyatake N, and Hatada K. *Polymer* 1995;36(7):1415-9.
- [61] Appiah-Ntiamoah R, Kim H, Gadisa BT, Baye AF, Abebe MW, and Kostjuk SV. *Mater Chem Phys* 2018;219:468-77.

- [62] Hulnik MI, Kuharenko OV, Timashev P, Vasilenko IV, and Kostjuk SV. *Eur Polym J* 2022;165:110983.
- [63] Hatada K, Kitayama T, Fujimoto N, and Nishiura T. *J Macromol Sci, A* 1993;30(9-10):645-67.