Chemoselective radical polymerization of *N*-allylmethacrylamide with an aid of complexation with Li+ cation

Tomohiro Hirano, Yuta Ogasa, Miyuki Oshimura, Koichi Ute

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

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

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

Abstract

Radical polymerization of *N*-allylmethacrylamide (NAlMAAm) was conducted in CH_3CN in the presence or absence of lithium bis(trifluoromethanesulfonyl)imide ($LiNTf_2$). The addition of $LiNTf_2$ accelerated the polymerization and affected the molecular weight distribution of the polymers obtained. Polymers with unimodal molecular weight distributions were obtained in the presence of $LiNTf_2$, whereas those with multimodal distributions were obtained in the absence of $LiNTf_2$. This suggested that $LiNTf_2$ suppressed side reactions such as cross-linking reaction, commonly observed in polymerization of divinyl monomers, and allylic hydrogen abstraction reaction. The ^{1}H NMR, IR and MALDI-TOF mass analyses of the polymers obtained suggested that the radical polymerization proceeded in a chemoselective manner, leading to preferential formation of linear polymers having pendant allyl groups.

Keywords: radical polymerization, *N*-allylmethacrylamide, chemoselective polymerization

1. Introduction

Divinyl compounds are commonly used as cross-linking and branching agents in polymerization reactions. Radical copolymerizations of difunctional monomers with monovinyl monomers result in formation of cross-linked material [1], unless a high concentration of radical initiator relative to divinyl monomers is employed [2-5]. The compounds having two vinyl groups with the same reactivity, such as divinylbenzene, ethylene glycol dimethacrylate and divinyl adipate, are widely used as divinyl monomers.

In radical polymerizations of the monomers with two vinyl groups of different polymerizing tendencies, more reactive vinyl group is preferentially consumed more than the other one. In particular, monomers with a combination of conjugated and unconjugated vinyl groups allow chemoselective polymerization through more reactive vinyl group under appropriate conditions [6-10]. For example, radical polymerization of allyl methacrylate in the presence of chain transfer agents gives soluble polymers having pendant allyl groups [6]. The cross-linking reactions are suppressed by diminishing the chain length, because intermolecular cross-linking processes are enhanced by the entanglement of polymer chains [11]. Insoluble material are formed at the later stage of the polymerization, because the intermolecular cross-linking reaction of polymer radical proceeds predominantly through the pendant allyl groups of the preformed poly(allyl methacrylate). Therefore, anionic and coordination polymerizations are adopted to obtain soluble poly(allyl methacrylate) with high molecular weights [12-22].

N-Allylmethacrylamide (NAlMAAm) is an amide analog of allyl methacrylate. Methacrylamides are less reactive than methacrylates [23], owing to the cross-conjugation between the C=C–C=O and O=C–N–H groups [24]. Consequently, it is more difficult to obtain linear polymers by radical polymerization of NAlMAAm, because the propagating radicals derived from methacrylamides shows higher reactivity than those from methacrylates. Intramolecular cross-propagation forms five-membered cyclic structure in the repeating monomeric unit, whereas intermolecular cross-propagation results in formation of cross-linked

materials (Scheme 1) [25-27]. In addition, possible abstraction reaction of allylic hydrogen is likely to be enhanced [28]. Therefore, linear poly(NAlMAAm) has been synthesized not by direct polymerization but by polymer reaction of functionalized polymer; modification with allylamine of poly(methacryloyl chloride) [28] and poly(pentafluorophenyl methacrylate) [29].
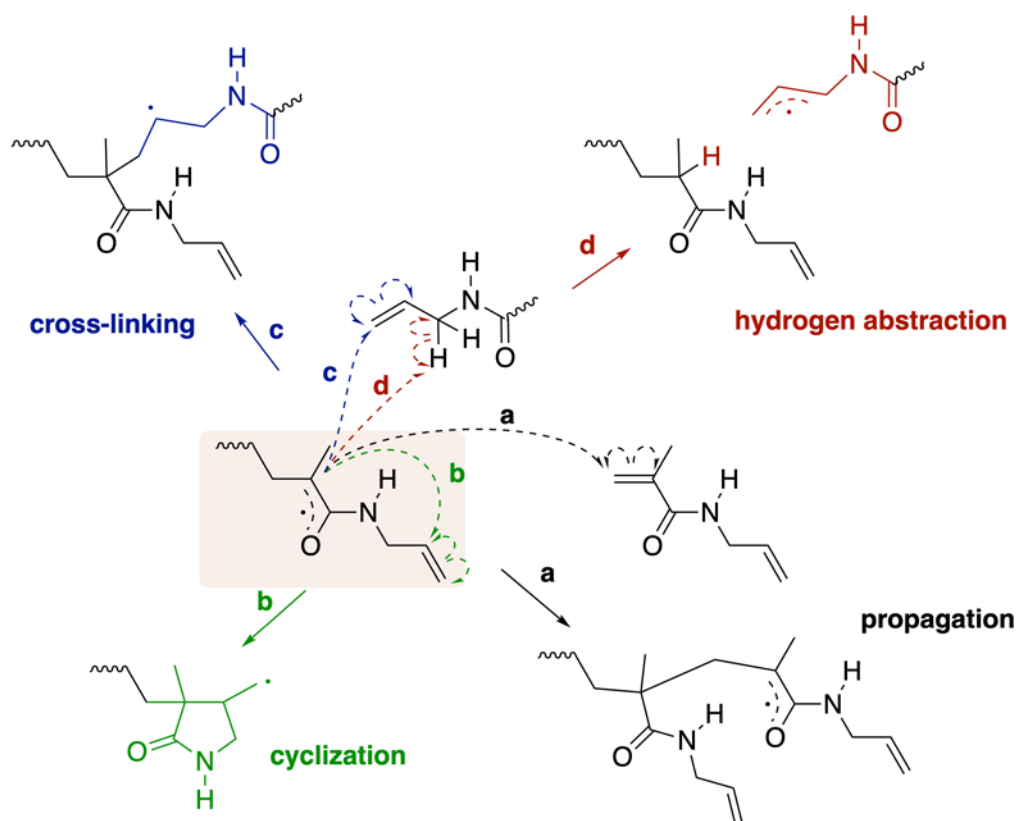

Scheme 1 Possible reactions by the propagating radicals derived from NAlMAAm

NAlMAAm can be essentially polymerized only *via* a radical mechanism owing to the acidic N-H proton, which do not allow vinyl polymerizations *via* anionic and coordination mechanisms. In the case of *N*-alkylacrylamides, the N-H protons can be protected for anionic polymerizations. Indeed, stereoregular poly(*N*-isopropylacrylamide)s [poly(NIPAAm)s] were prepared by anionic polymerization of protected monomers, followed by deprotection [30, 31]. However, this protection strategy is unsuitable for NAlMAAm, because *N,N*-disubstituted methacrylamides show nonpolymerizability *via* any reaction mechanism [24, 32-36], unless the

N-substituents are small and highly strained ring structures, such as aziridine and azetidine [37-39]. Consequently, development of chemoselective radical polymerization is required to obtain the linear poly(NAlMAAm) with pendant allyl groups.

Recently, we found that addition of alkali metal salts, such as lithium, sodium and potassium bis(trifluoromethanesulfonyl)imides (LiNTf$_2$, NaNTf$_2$ and KNTf$_2$), accelerated radical polymerization of *N,N*-dimethylacrylamide [40]. Of the alkali metal salts, LiNTf$_2$ exhibited most pronounced effect, because the enhancing effects of NaNTf$_2$ and KNTf$_2$ almost disappeared at 60 °C. In addition, enhancing effect of Li$^+$ was also observed in low-temperature radical polymerization of *N-n*-propylmethacrylamide (NNPMAAm) [41]. As a result of an acceleration effect, the polymer was obtained at 8% yield even at −80 °C, whereas reaction with NNPMAAm produced no polymers, at least it did not under the given conditions. Spectroscopic analyses suggested that the Li$^+$ cation played a dual role in the polymerization process, with Li$^+$ stabilizing the propagating radical species and also activating the incoming monomer (Scheme 2). It is therefore expected that chemoselective propagating reaction preferentially occurs between the stabilized radical species and activated methacryloyl groups even in the radical polymerization of divinyl monomers. In this paper, we report the radical polymerization of NAlMAAm in the presence of LiNTf$_2$. Addition of LiNTf$_2$ at low temperatures successfully suppressed both the addition reaction at the allyl group and allyl hydrogen abstraction reaction, leading to preferential formation of linear polymers having pendant allyl groups.
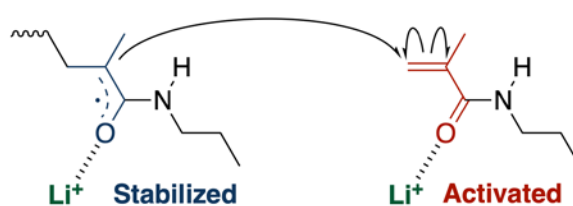
Scheme 2 Propagating reaction by the radical stabilized with Li$^+$ to the monomer activated with

Li$^+$.

2. Experimental

2.1. Materials

NAlMAAm was prepared in a way similar to the synthesis of *N-n*-propylacrylamide [42]. Dimethyl 2,2′-azobisisobutyrate (MAIB) (supplied by Otsuka Chemical Co., Ltd., Osaka, Japan) was recrystallized from CH_3OH. CH_3OH (Kanto Chemical Co., Inc.) was fractionally distilled. LiNTf$_2$ (Tokyo Chemical Industry, Tokyo, Japan), CH_3CN, *N,N*-dimethylformamide (DMF; high-performance liquid chromatography grade) (Kanto Chemical Co., Inc.), acetone, acetylacetone, deuterated dimethyl sulfoxide (DMSO-d_6), hexane, lithium bromide (LiBr, anhydride) (Kishida Chemical Co., Ltd, Osaka, Japan), chloroform were used as received.

2.2. Polymerization

In a typical polymerization procedure, NAlMAAm (1.25g, 10.0 mmol), LiNTf$_2$ (1.44 g, 5.0 mmol), and MAIB (0.023 g, 1.0×10^{-1} mmol) were dissolved in CH_3CN to prepare 5.0 mL of solution. Four milliliters of the solution was transferred to a glass ampoule, which was degassed under vacuum and filled with nitrogen twelve times at −50 °C before the temperature was raised to the required polymerization temperature. Under reduced pressure, the mixture was irradiated at a distance of *ca*. 5 cm by a UV-LED lamp (LED-41UV375N100VF, $\lambda = 375$ nm, 410 mW, Optocode Co., Tokyo, Japan) to initiate polymerization. (The glass ampoule was placed at 40 °C or 60 °C when NAlMAAm was thermally polymerized.) After 24 h, the reaction mixture was dialyzed against CH_3OH/acetone (1:1 vol/vol) containing a small amount of acetylacetone (Spectra/Por 3, molecular mass cutoff 3.5 kDa, Spectrum Laboratories Inc., Shiga, Japan) until it was free from salts. The dialysate was evaporated to dryness under reduced pressure to give a residue, which was dissolved in chloroform and poured into hexane (200 mL).

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

2.3. Measurements

The molecular weights and molecular weight distributions of the polymers were determined by size exclusion chromatography (SEC); the chromatograph was calibrated with standard PMMA samples. SEC was performed on an HLC 8220 chromatograph (Tosoh Corp., Tokyo, Japan) equipped with TSKgel columns [SuperHM-M (6.5 mm inner diameter $\times$ 150 mm) and SuperHM-H (6.5 mm inner diameter $\times$ 150 mm)] (Tosoh Corp.). DMF containing 10 mmol·L^{-1} LiBr was used as an eluent at 40 °C and a flow rate of 0.35 mL·min^{-1}. The initial polymer concentration was set at 1.0 mg·mL^{-1}.

^{1}H magnetic nuclear resonance (NMR) spectra were measured in DMSO-d_6 at 100 °C using ECX-400 and ECA-500 spectrometers (JEOL Ltd., Tokyo, Japan). Fourier-transform infrared (FT-IR) spectrometer equipped with a TGS detector (FT/IR-620, JASCO, Tokyo, Japan) was used. FT-IR attenuated total reflection (ATR) spectra were collected with single reflection ATR accessory (ATR PRO470-H, JASCO) having a diamond ATR crystal fixed at incident angle of 45°. ATR effect was corrected by software (Spectra Manager, JASCO).

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 ionizing agent, respectively. Mass calibration was made using a peak of sodium adduct of 13mer having MAIB fragment at the initiating chain-end and vinylidene group at the terminating chain-end as 1749.135 *m/Z*.

3. Results and Discussion

3.1. Radical polymerization of NAlMAAm in CH₃CN in the presence or absence of LiNTf₂

Radical polymerizations of NAlMAAm were carried out in CH_3CN at $-40\ °C$ to $80\ °C$ in the presence or absence of $LiNTf_2$ (Table 1). The amount of the added $LiNTf_2$ was set to be 0.5 mole equivalent relative to the NAlMAAm monomer, because NNPMAAm formed 2:1 complex with Li^+ in CH_3CN [41]. Polymerizations at 60 and $80\ °C$ provided insoluble materials due to cross-linking reaction within several hours. Therefore, the polymerizations were quenched by cooling to $0\ °C$ before gelation occurred. The addition of $LiNTf_2$ increased the polymer yield and number-average molecular weight (M_n), regardless of the polymerization temperature. In particular, polymer was obtained even at $-40\ °C$ in the presence of $LiNTf_2$, whereas no polymerization was observed under the corresponding conditions in the absence of $LiNTf_2$. $LiNTf_2$ played an acceleration role in the NAlMAAm polymerization as well as in the NNPMAAm polymerization [41].

Table 1. Radical polymerization of NAlMAAm in CH_3CN in the presence or absence of $LiNTf_2$.[a]

Run	Temp. / °C	$[LiNTf_2]_0$ /mol·L^{-1}	Time / h	Yield /%	$M_n \times 10^{-4}$ [b]	M_w/M_n [b]
1	80	1.0	0.17	31	4.2	6.4
2	80	0.0	0.5	20	2.7	9.7
3	60	1.0	0.5	13	6.5	3.0
4	60	0.0	2	10	2.8	3.2
5	0	1.0	24	25	2.4	2.8
6[c]	0	1.0	3.5	61	1.0	2.7
7	0	0.0	24	11	0.76	4.2
8	−40	1.0	24	11	1.7	2.6
9	−40	0.0	24	trace	-	-

[a] $[NAlMAAm]_0 = 2.0\ mol·L^{-1}$, $[MAIB]_0 = 2.0 \times 10^{-2}\ mol·L^{-1}$.
[b] Determined by SEC.
[c] $[MAIB]_0 = 1.0 \times 10^{-1}\ mol·L^{-1}$.

Unimodal SEC profiles were observed for the polymers prepared at 0 and $-40\ °C$ in the presence of $LiNTf_2$, whereas multimodal one was observed for the polymer prepared at $0\ °C$ in the absence of $LiNTf_2$ (Fig. 1). This suggests that the intermolecular cross-linking

reaction was suppressed by adding LiNTf$_2$ at low temperatures. However, the SEC profiles of the polymers prepared over 60 °C showed multimodal distribution in molecular weight, even in the presence of LiNTf$_2$. It is therefore suggested that low temperature is essential to suppress the cross-linking reaction with the aid of Li$^+$ in the radical polymerization of NAlMAAm.
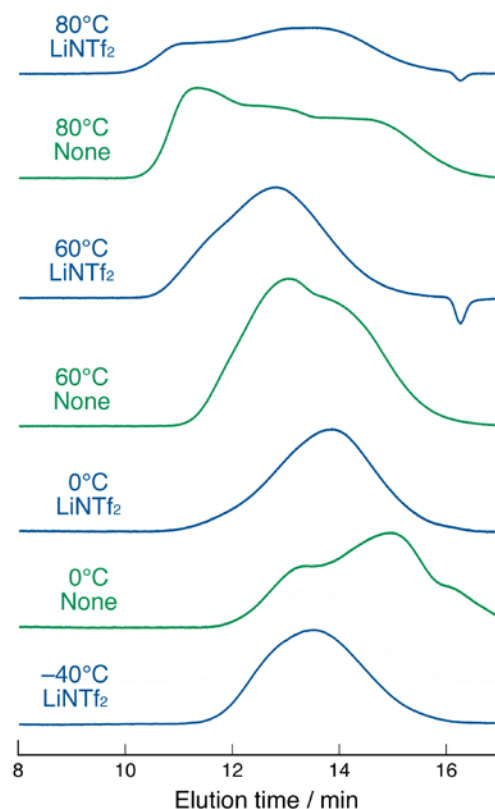

Fig. 1 SEC profiles of poly(NAlMAAm)s prepared in the presence or absence of LiNTf$_2$

3.2. Structural analysis of the polymers by IR and NMR spectroscopies

Five-membered rings are formed via intramolecular cyclopropagation in the NAlMAAm polymerization (Scheme 1). The cyclopolymerizability of NAlMAAm increases with an increase in the polymerization temperature [27]. The stretching vibration bands of the carbonyl groups in IR spectra can detect the formation of the five-membered rings; the absorption band shifts significantly to longer wavenumber with the ring-structure formation. The IR measurements were therefore conducted for the poly(NAlMAAm)s obtained at 60 and 0 °C (Fig. 2). The absorptions around 1700~1800 cm^{-1}, assigned to the five-membered rings,

were completely eliminated by adding LiNTf$_2$, regardless of the polymerization temperature. This result suggests that the addition of LiNTf$_2$ also suppressed the intramolecular cyclopropagation.
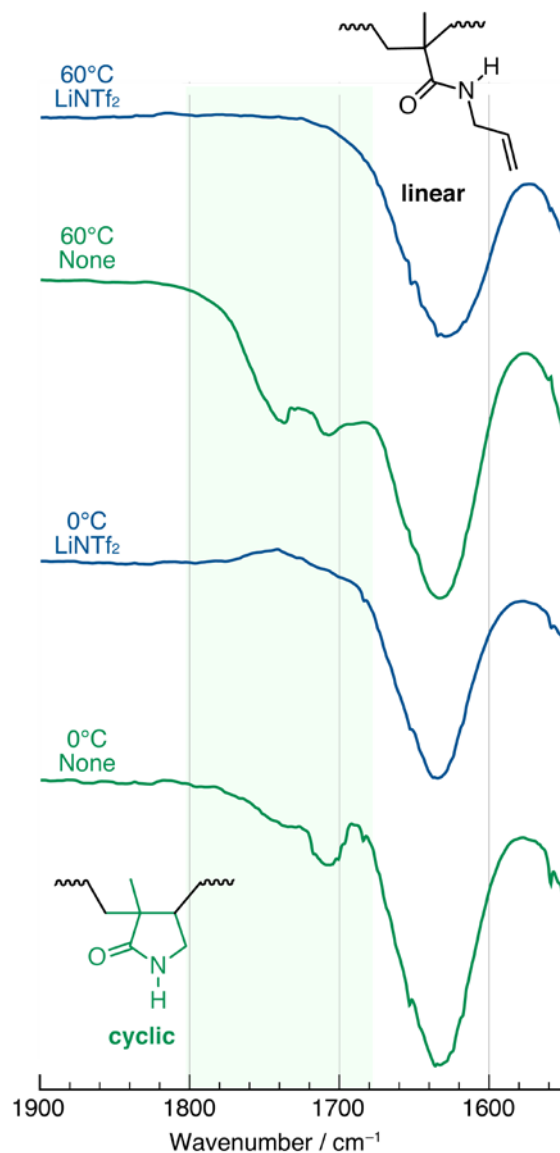
Fig. 2 Expanded IR spectra of poly(NAlMAAm)s prepared at 0 and 60 °C in the presence or absence of LiNTf$_2$

The NMR signals of the polymer prepared at 60 °C in the absence of LiNTf$_2$ were obviously broadened, likely because of slowing down of the molecular motion of branched structures (Fig. 3) [43]. However, the addition of LiNTf$_2$ sharpened the NMR signals of the

9

resulting polymer. This tendency was enhanced by lowering the polymerization temperature. In particular, the signals of the vinylidene proton (**g**) at the side-chain allyl group were well resolved in the spectra of the polymers obtained at 0 and –40 °C in the presence of LiNTf$_2$.
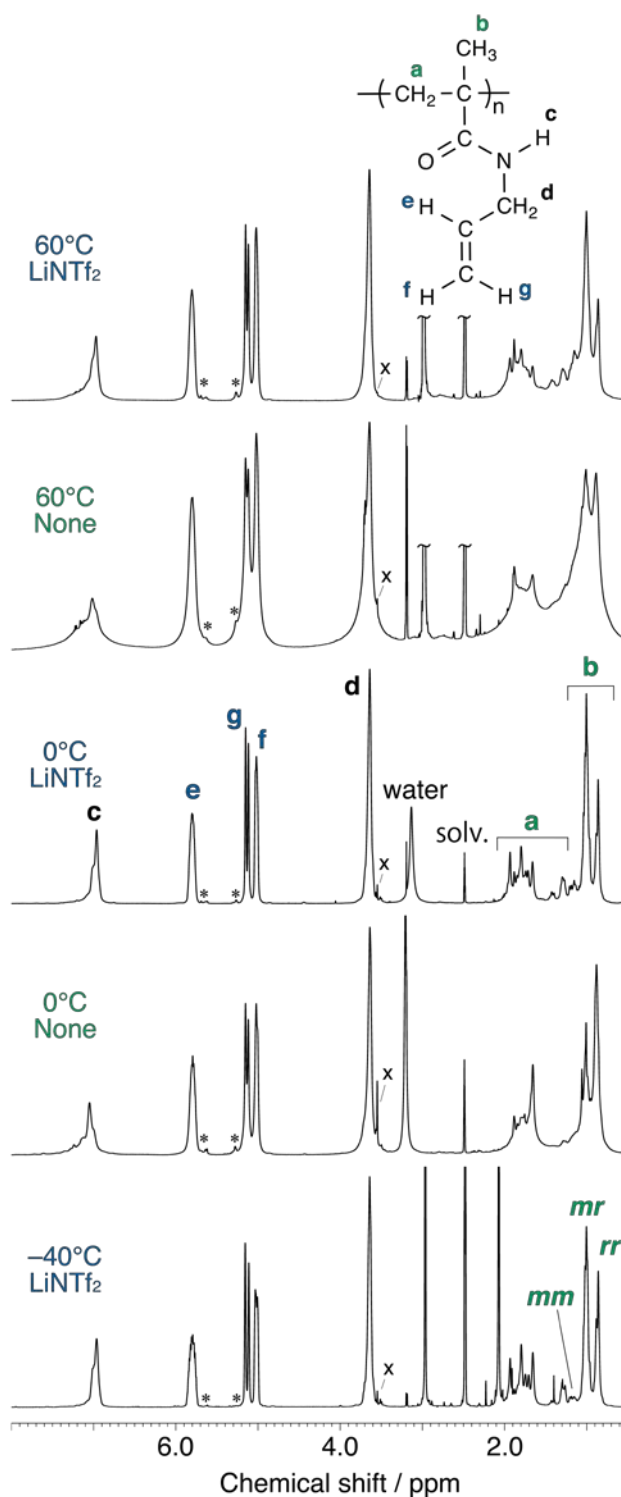
**Fig. 3** ^{1}H NMR spectra of poly(NAlMAAm)s prepared in the presence or absence of LiNTf$_2$.

The $\times$ denotes the signals of the methoxy group in the initiator fragment. The * denotes the vinylidene protons formed through the disproportionation reaction.

The integral intensities of the polymers prepared at low temperatures in the presence of $LiNTf_2$ almost agreed well with those expected for the linear poly(NAlMAAm). It is therefore concluded that the addition of $LiNTf_2$ at low temperatures is effective to suppress the side reactions such as intermolecular cross-linking reaction and intramolecular cyclopropagation. However, signals of methoxy and methyl groups derived from MAIB fragment were overlapped with those of side-chain methylene groups (**d**) and main-chain methylene groups (**a**), respectively [44]. In addition, signals of the vinylene groups formed through disproportionation reaction were overlapped with those of side-chain vinyl groups (**e** and **g**) [45]. These overlaps prevented us from conducting further quantitative analysis of the chemical structure of the resulting polymers. The details about the chain-end structures will be described below.

The signal of the α-methyl groups exhibits splitting due to triad stereoregularity. For example, the signal of syndiotactic triad (*rr*) was observed with the strongest intensity in the spectrum of the polymer prepared at 0 °C in the absence of $LiNTf_2$. On the other hand, the signal of heterotactic triad (*mr*) was observed with the strongest intensity in the spectrum of the polymer prepared in the presence of $LiNTf_2$. Similar tendency was observed in the NNPMAAm polymerizations; syndiotactic polymers were obtained in CH_3OH, whereas heterotactic polymers were obtained in CH_3CN [41]. Job's plots suggested that the stereospecificity of the NNPMAAm polymerization depended on the stoichiometry of the monomer–Li^+ complex; the 1:1 complex gave syndiotactic-rich polymers, whereas the 2:1 complex gave heterotactic-rich polymers. It is therefore suggested that NAlMAAm forms 2:1 complex with Li^+ as well as NNPMAAm, even though NAlMAAm has coodinatable allyl group.

*3.3. Chain-end analysis of the polymers by MALDI-TOF mass spectrometry*

To examine the chain-end structures of the polymers, MALDI-TOF mass spectrometric analyses were performed for the poly(NAlMAAm)s prepared at 0 °C in the presence or absence of LiNTf$_2$ (Fig. 4). Because the M_n of the polymer obtained in the presence of LiNTf$_2$ was too high for conducting MALDI-TOF mass measurement, the initiator concentration was increased to 1.0×10^{-1} mol/L to reduce the M_n (Table 1, Run 6). A polymer of comparable M_n to the polymer prepared in the absence of LiNTf$_2$ was obtained. The peaks due to lower molecular masses were observed for both polymers, likely because of a mass discrimination effect [46, 47]. The both spectra showed a series of peaks (series **A**) with intervals of ca. 125.1 m/Z, corresponding to the repeating unit mass.
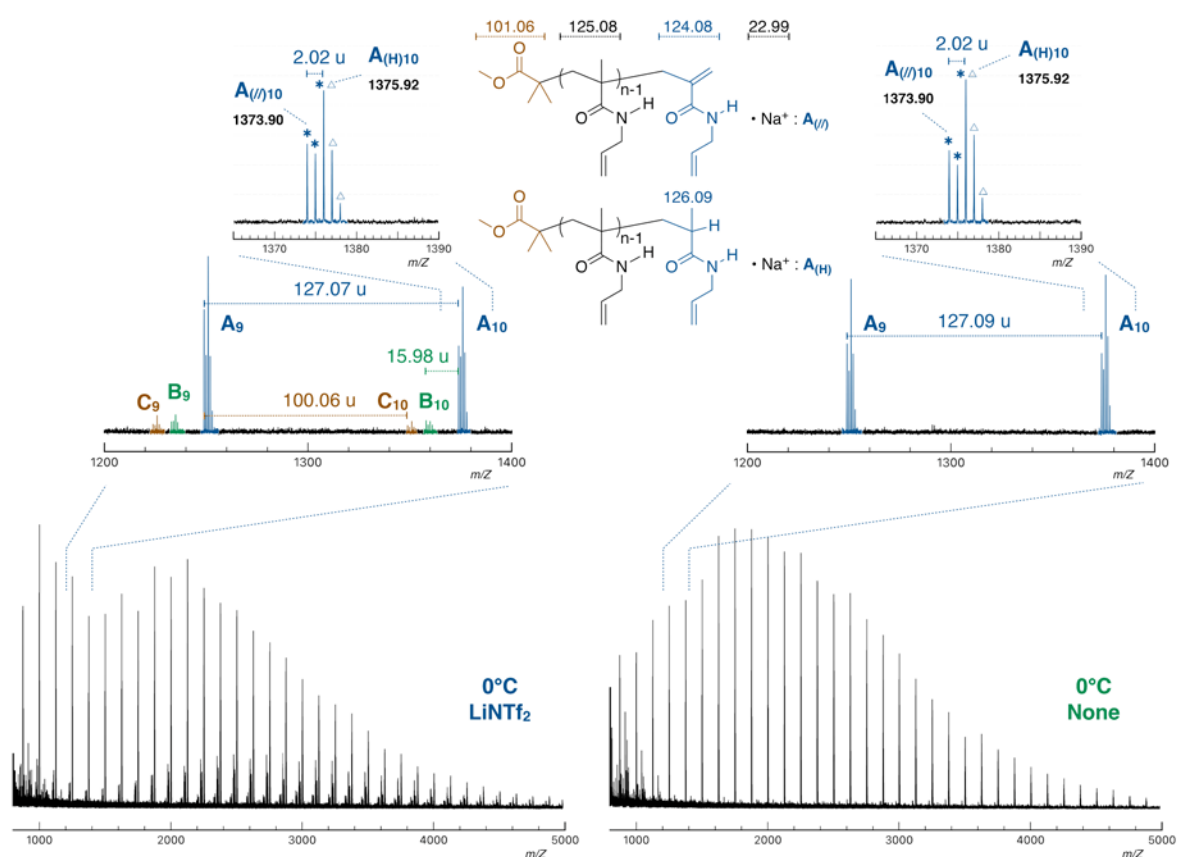
Fig. 4 MALDI-TOF mass spectra of the poly(NAlMAAm)s prepared at 0 °C in the presence or absence of LiNTf$_2$.

The series **A** of peaks were further divided into two subseries of peaks (marked with

* and ᴬ). The differences in the m/Z value between the two subseries were ca. 2.0 u. This result indicates that the polymerization was predominantly terminated *via* a disproportionation reaction (Scheme 3), because polymers with unsaturated and saturated chain-ends are formed through disproportionation reaction [48]. The m/Z values for the series **A** agreed well with the monoisotopic masses of the Na$^+$ adducts of poly(NAlMAAm)s with an MAIB fragment at the α-end and a vinylidene (**A**$_{(//)}$: *) or hydrogen (**A**$_{(H)}$: ᴬ) at the ω-end; for example, n = 10; $M_{theor, (//)}$ = 1373.88, $M_{obs, (//)}$ = 1373.90; $M_{theor, (H)}$ = 1375.90, $M_{obs, (H)}$ = 1375.92.
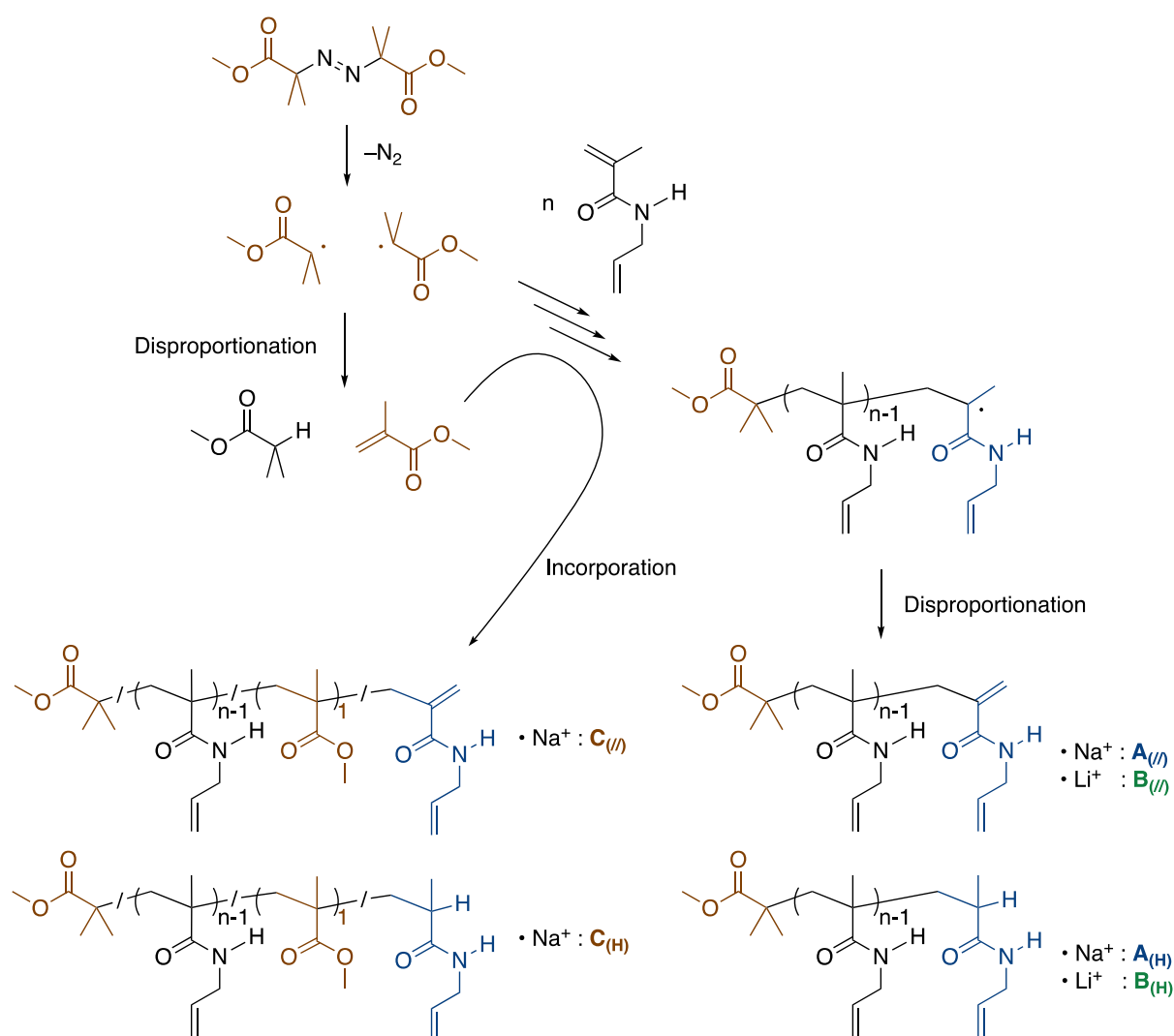
Scheme 3 Possible reactions in the radical polymerization of NAlMAAm with MAIB

The ionization efficiency of oligomers depends on the chemical nature of their end groups [46, 47]. In addition, the second isotopic peak of the Na$^+$ adducts of $\mathbf{A}_{(//)\mathbf{10}}$ containing one or two of less abundant naturally occurring isotopes, such as ^{2}H, ^{13}C, ^{15}N, ^{17}O and ^{18}O, overlapped with the monoisotopic peak of the Na$^+$ adducts of $\mathbf{A}_{(\mathbf{H})\mathbf{10}}$. However, the addition of LiNTf$_2$ decreased significantly the relative intensities of peaks of the $\mathbf{A}_{(\mathbf{H})}$-series. As a result, $\mathbf{A}_{(//)}$-series and $\mathbf{A}_{(\mathbf{H})}$-series became comparable in peak intensity. The structure for the $\mathbf{A}_{(\mathbf{H})}$-series can be also formed *via* a hydrogen abstraction from the allylic position (Scheme 1). It is therefore suggested that the addition of LiNTf$_2$ suppressed the hydrogen abstraction reaction as expected.

In the spectrum of the polymer prepared in the presence of LiNTf$_2$, other two series of peaks were observed. The *m*/*Z* values for the series $\mathbf{B}$ were smaller than those for the series $\mathbf{A}$ by ca. 16.0 u, corresponding to the monoisotopic masses of the Li$^+$ adducts (Scheme 3). The Li$^+$ would be derived from LiNTf$_2$ employed in the polymerization reaction. The *m*/*Z* values for the series $\mathbf{C}$ were larger than those for the series $\mathbf{A}$ by ca. 100.1 u. In general, initiator efficiency of azo-initiators is 50-70% because of the cage effect [49]. The disproportionation reaction by the primary radicals derived from MAIB produces MMA monomer, whose monoisotopic mass is 100.05 u. Therefore, it is assumed that increased MAIB concentration enhances the formation of MMA *in situ*, and incorporation of MMA into the resulting macromolecules is responsible for the observation of the series $\mathbf{C}$ in the MALDI-TOF mass spectrum (Scheme 3).

4. Conclusions

The effect of LiNTf$_2$ on the radical polymerization of asymmetric divinyl monomer, NAlMAAm, was investigated. The addition of LiNTf$_2$ led to a significant improvement in the yield and molecular weight of the resulting polymers. This suggests that Li$^+$ cation played a dual role even in the NAlMAAm polymerization, with Li$^+$ stabilizing the propagating radical

species and also activating the incoming monomer. The polymerizations at high temperature resulted in gellation. However, the polymers with unimodal molecular weight distributions were obtained by adding $LiNTf_2$ at low temperatures. Spectroscopic analyses revealed that addition of $LiNTf_2$ suppressed intermolecular cross-linking reaction and intramolecular cyclopropagation. Furthermore, MALDI-TOF mass analysis suggested that hydrogen abstraction reaction was also suppressed in the presence of $LiNTf_2$. As a result of chemoselective radical polymerization, soluble linear polymers were successfully prepared from radical polymerization of asymmetric divinyl monomer.

Conflict of Interest

The authors declare no conflict of interest.

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