Living Anionic Polymerization of *N*-Methacryloyl-2-methylaziridine: Polymerizable *N*,*N*-Dialkylmethacrylamide

Takashi Suzuki, Jun-ichi Kusakabe, and Takashi Ishizone*

Department of Organic and Polymeric Materials, Tokyo Institute of Technology, 2-12-1-H-119, Ohokayama, Meguro-ku, Tokyo 152-8552, Japan

Received November 25, 2007; Revised Manuscript Received January 11, 2008

ABSTRACT: Anionic polymerization of *N*-methacryloyl-2-methylaziridine (**1**) was carried out with 1,1-diphenyl-3-methylpentyllithium (DMPLi) in the presence of LiCl or Et_2Zn in THF. Poly(**1**)s possessing predicted molecular weights and narrow molecular weight distributions (MWD, $M_w/M_n < 1.1$) were quantitatively obtained at −78 to −40 °C within 72 h. The stability of the propagating chain end of poly(**1**) was confirmed by the quantitative initiation efficiency in the postpolymerization. In the polymerizations initiated with DMPLi/LiCl at the various temperature ranging from −40 to −60 °C, the relationship of time−conversion was obtained from the GLC analysis of the residual monomer. The apparent rate constant and the activation energy of the anionic polymerization for **1** were determined as follows: $\ln k_p^{ap} = -5.85 \times 10^3/T + 23.3$ L mol^{-1} s^{-1} and 49 ± 4 kJ mol^{-1}, respectively. *N*-Acryloyl-2-methylaziridine (**2**) also underwent the anionic polymerization initiated with DMPLi/LiCl at −78 °C to give the well-defined polymer. The radical polymerizations of **1** and **2** with AIBN proceeded in 77 and 100% conversions, respectively. Poly(**1**) and poly(**2**) showed the glass transition temperatures at 98 and 54 °C but gave the insoluble products at higher temperatures around 150 °C through the thermal cross-linking of highly strained *N*-acylaziridines. The ring-opening and/or the substitution reactions of aziridine moieties of poly(**1**) and poly(**2**) also occurred with nucleophiles such as lithium methoxide and sodium salts of di(ethylene glycol).

Introduction

It is well-known that acrylates and methacrylates, α,β-unsaturated esters, are readily polymerized under the various reaction conditions.[1] The π-conjugated electron-withdrawing ester substituents certainly enhanced the polymerizability of acrylates and methacrylates toward the radical and anionic species. Similar to the cases of esters, α,β-unsaturated amides, acrylamide, methacrylamide, and their *N*-monoalkyl-substituted counterparts can be converted into the vinyl polymers under the radical polymerization conditions,[2] while the hydrogen transfer polymerizations simultaneously occur during the course of the anionic polymerizations.[3] On the other hand, the vinyl polymerizations of *N*,*N*-dialkylacrylamides exclusively proceed by the initiation with the radical or anionic initiators because of the absence of the acidic amide hydrogens. Even the living polymers are often formed in the anionic polymerization[4,5] and the group transfer polymerization of *N*,*N*-dialkylacrylamides.[6]

By contrast, the reports on the polymerization of *N*,*N*-dialkylmethacrylamides are extremely limited probably due to their inherent low polymerizability under the radical and basic conditions.[2a,4,7−11] On the basis of ^{1}H and ^{13}C NMR chemical shifts and MNDO calculations, Kodaira[10] and Hogen-Esch[4] have suggested that the observed low polymerizability of *N*,*N*-dialkylmethacrylamides is presumably derived from the twisted conformation between C═C and C═O groups due to the steric repulsion between α-methyl group and two alkyl substituents on nitrogen. To our best knowledge, only one exception is a vinyl polymerization of *N*-methacryloylaziridine (MAz), a *N*,*N*-dialkylmethacrylamide derivative possessing a highly strained and small three-membered aziridine ring.[12] Yuki and Okamoto have reported that MAz can be polymerized with either AIBN or *n*-BuLi, while the detailed results of polymerization have not been shown. It is noteworthy that the plausible side reactions such as ring-opening reaction of aziridine ring are also suggested in the anionic polymerization systems which afforded the insoluble products. In fact, ring-opening and isomerization reactions of *N*-acylaziridines and *N*-sulfonylaziridines with nucleophiles are reported in the organic synthesis,[13] since the *N*-substituted electron-withdrawing groups certainly decrease the electron density of aziridine rings and enhance the reactivity toward the nucleophilic attack. Furthermore, the resulting anion on the nitrogen is stabilized by the *N*-acyl or *N*-sulfonyl substituents, when the nucleophilic ring-opening takes place. Therefore, a great care and a precise selection of the polymerization condition will be necessary for the anionic polymerizations of *N*-(meth)acryloylaziridines to prevent the serious side reactions and regulate the primary chain structures.[12]

In this study, we have newly synthesized *N*-methacryloyl-2-methylaziridine (**1**)[14] as a substitute of MAz, since aziridine (ethylenimine) is recently hardly available due to the high toxicity. We herein demonstrate a first successful example of living anionic polymerization of *N*,*N*-dialkylmethacrylamide, **1**, as well as the positive polymerizability under the anionic and radical polymerization conditions. The polymerization of an acryloyl counterpart, *N*-acryloyl-2-methylaziridine (**2**), is also attempted to compare the polymerization behavior. Furthermore, the polymer reactions of the resulting polymers are examined to show the reactivity of pendant strained aziridine rings.

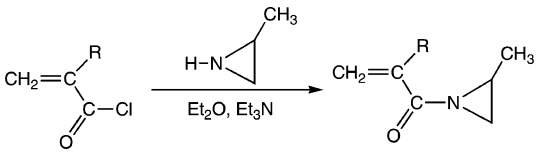
Results and Discussion

Synthesis of Monomers. Monomers **1** and **2** were synthesized in 60 and 46% yields by the reaction of methacryloyl or acryloyl chloride and 2-methylaziridine in the presence of triethylamine in diethyl ether, as shown in Scheme 1. Both liquid monomers were thoroughly purified by the repeating vacuum distillations from CaH_2 prior to the polymerization.

* Corresponding author. E-mail: tishizon@polymer.titech.ac.jp.

10.1021/ma702615u CCC: $40.75
Published on Web 02/23/2008

Scheme 1



Anionic Polymerization of 1. Anionic polymerization of **1** was carried out with 1,1-diphenyl-3-methylpentyllithium (DMPLi), an adduct of *sec*-BuLi and 1,1-diphenylethylene, diphenylmethylsodium (Ph_2CHNa), and diphenylmethylpotassium (Ph_2CHK) in THF at various temperatures (−78, −40, and 0 °C). In most case, LiCl[15] or Et_2Zn[5,16] was added to the polymerization system since they are well-known as the effective additives for the controlled polymerization of (meth)acrylates[15,16] and *N*,*N*-dialkylacrylamides.[5] The polymerization was terminated with degassed isopropanol.[17] Polymeric product was precipitated by pouring a polymerization mixture into hexane. The precipitated polymer was isolated by filtration and characterized by ^{1}H and ^{13}C NMR spectroscopies and elemental analysis. Figure 1 shows the typical ^{1}H NMR spectra of **1** and a polymer obtained with DMPLi/LiCl.[18] After the polymerization, two signals derived from the CH_2= group at 5.63 and 6.09 ppm completely disappear, and new broad signal of methylene group in the main chain alternatively appears at 1.8−2.3 ppm. The signals corresponding to the aziridine ring in the polymer were observed in the same region of **1**, suggesting that the aziridine moiety was intact. In the case of ^{13}C NMR, two signals of olefinic carbon at 124.5 and 139.8 ppm were no longer present after the polymerization, and new signals of methylene and quaternary carbons in main chain were observed at 53.3 and 47−50 ppm, respectively. These spectroscopic observations indicate that the vinyl polymerization of **1** unequivocally proceeds to give a poly(**1**) similar to the previous report of MAz.[12] Contrary to the polymerization results of MAz, the resulting poly(**1**) was always soluble and contained no insoluble fraction. The bulky and electron-donating 2-methyl group on the aziridine ring on **1** and poly(**1**) might play a role to prevent the side reactions to form the insoluble product.

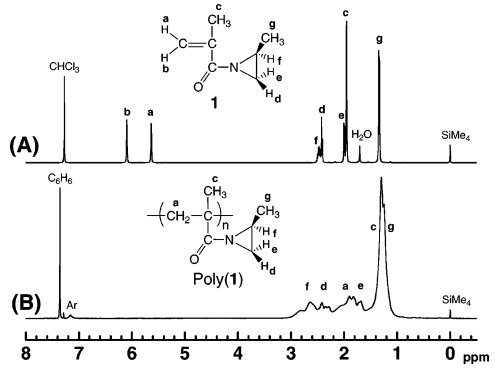


Figure 1. ^{1}H NMR spectra of **1** (A) and poly(**1**) obtained with DMPLi/LiCl (B) measured in $CDCl_3$.

The polymerization results of **1** are summarized in Table 1. At first, the polymerization of **1** was performed with DMPLi at −78 °C for 15 h. After termination, poly(**1**) was isolated in 90% yield. The molecular weight of poly(**1**) was estimated from the ^{1}H NMR by using end-group analysis of the initiator residue. The observed M_n agreed well with the calculated value based on the molar ratio between monomer to initiator and the conversion. The size exclusion chromatography (SEC) curve of the resulting poly(**1**) was unimodal, and the polydispersity index, M_w/M_n, was 1.14, indicating the fairly narrow molecular weight distribution (MWD). Then, we added LiCl to the polymerization system. In the presence of 3.8−10-fold LiCl to DMPLi (runs 2−4), the quantitative conversion of **1** was attained within 72 h at −78 °C, whereas 52% of **1** was consumed after 2 h. The polymer obtained with DMPLi/LiCl possessed the predicted M_n, as expected. More interestingly, the MWD of poly(**1**)s became narrower, and M_w/M_n values were regulated in the range of 1.04−1.09. We next employed Et_2Zn as an additive to DMPLi (run 5). The polymerization of **1** quantitatively proceeded with DMPLi/Et_2Zn at −78 °C within 72 h. The resultant poly(**1**) had a controlled molecular weight with the narrow MWD. Thus, **1** underwent the controlled anionic polymerizations at −78 °C by the initiations with DMPLi in the presence of either LiCl or Et_2Zn similar to the polymerization behaviors of (meth)acrylates[15,16] and *N*,*N*-dialkylacrylamides.[5] We then elevated the polymerization temperature to −40 or 0 °C in order to increase the rate of polymerization (runs 6−11). Poly(**1**)s of controlled M_ns and narrow MWDs yielded with DMPLi/LiCl at −40 °C within 2.5 h. Moreover, the polymerization of **1** completed within 15 min at 0 °C, and the poly(**1**) possessed controlled and narrow MWD. However, the SEC curve of poly(**1**) obtained at 0 °C became slightly broader after 24 h, and a small shoulder at higher molecular weight region was observed. This suggests that the intermolecular side reaction slowly occurred at 0 °C between the propagating chain end and

Table 1. Anionic Polymerization of 1 in THF

run	**1** (mmol)	initiator, (mmol)	additive, (mmol)	temp (°C)	time h	conv (%)	$M_n \times 10^{-3}$ calcd[a]	$M_n \times 10^{-3}$ obsd[b]	M_w/M_n[c]
1	7.91	DMPLi,[d] 0.152		−78	15	90	6.1	7.0	1.14
2	6.50	DMPLi, 0.138	LiCl, 0.588	−78	2	52	3.1	2.6	1.09
3	6.52	DMPLi, 0.138	LiCl, 0.531	−78	72	100	6.1	7.2	1.05
4	6.70	DMPLi, 0.0529	LiCl, 0.539	−78	72	90	14	12	1.04
5	7.39	DMPLi, 0.0789	Et_2Zn, 0.907	−78	72	100	12	15	1.08
6	14.0	DMPLi, 0.126	LiCl, 0.558	−40	2.5	100	14	15	1.03
7	7.73	DMPLi, 0.112	LiCl, 0.480	−40	4.5	100	8.9	10	1.05
8	8.46	DMPLi, 0.0519	LiCl, 0.241	−40	17	100	21	25	1.03
9	9.48	DMPLi, 0.0253	LiCl, 0.132	−40	24	100	47	50	1.09
10	7.96	DMPLi, 0.0689	LiCl, 0.297	0	15 min	100	15	16	1.05
11	7.68	DMPLi, 0.0605	LiCl, 0.326	0	2	100	16	17	1.10
12	5.69	Ph_2CHNa, 0.0933		−78	72	100	7.8	9.9	1.06
13	7.21	Ph_2CHK, 0.0618		−78	15	100	15	16	1.20
14	6.09	Ph_2CHK, 0.0468	Et_2Zn, 0.573	−78	72	82	13	6.2	1.29

[a] M_n(calcd) = (MW of monomer) × conversion/100 × [monomer]/[initiator] + (MW of initiator fragment). [b] M_n(obsd) was obtained by end-group analysis using ^{1}H NMR. [c] M_w/M_n was obtained by SEC calibration using polystyrene standards in THF. [d] 2−3-fold 1,1-diphenylethylene was added to *sec*-BuLi.

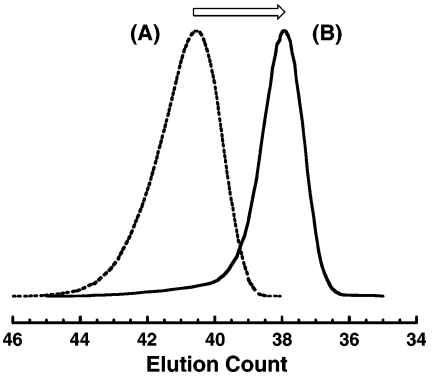


Figure 2. SEC curves of poly(**1**)s: prepolymer (A); M_n(calcd) = 7300, M_n(obsd) = 8600, M_w/M_n = 1.06; peak, postpolymer (B); M_n(calcd) = 14 000, M_n(obsd) = 15 000, M_w/M_n = 1.06.

the aziridine ring and/or the amide carbonyl group after the complete consumption of monomer. We finally changed the counterion of the initiators from Li^+ to Na^+ and K^+ (runs 12−14). The polymerizations of **1** similarly occurred with Ph_2CHNa and Ph_2CHK at −78 °C to provide the polymers of well-defined chain structures in 100% yields, while the MWD was relatively broad in the polymer obtained with Ph_2CHK. Thus, we have successfully demonstrated that **1** undergoes the anionic polymerization quantitatively to afford the polymers of well-defined chain structures. We now believe that the polymerization of MAz possessing a nonsubstituted aziridine ring will be also controllable under the suitable polymerization conditions, although the occurrence of serious side reactions has been previously suggested to result in the formation of insoluble polymer during the anionic polymerization of MAz with *n*-BuLi in THF or toluene at 0 °C.[12,13]

Postpolymerization of 1. We then performed the postpolymerization of **1** to prove the living nature of the polymerization system. The first-stage polymerization of **1** was carried out with DMPLi in the presence of 4.5-fold LiCl in THF at −40 °C for 3.5 h. The resulting polymerization system was then divided into two portions. One portion was terminated with isopropanol, while second feed of **1** was added to the other one. The second-stage polymerization of **1** was further continued for 3.5 h for the completion. Prepolymer and postpolymer of **1** were quantitatively obtained after the termination. As can be seen in Figure 2, the SEC curve of postpolymer is still narrow and shifts toward the higher molecular weight region from the elution count of prepolymer. The observed molecular weights of the pre- and postpolymers agreed well with the predicted M_ns. These results substantiate that the propagating chain end of poly(**1**) is satisfactorily stable at −40 °C.

Kinetic Studies. The polymerization of **1** certainly proceeded, but the polymerization rate seemed very low in contrast to the rapid propagations of alkyl (meth)acrylates and *N*,*N*-dialkylacrylamides even at low temperatures. We can easily trace the polymerization behavior of **1** by monitoring of the residual monomer and the resultant polymer. Figure 3 shows a series of SEC curves of poly(**1**) produced with DMPLi/LiCl (4.4 equiv) at −40 °C. The SEC curves clearly shift from the low molecular weight region to the higher molecular weight side with keeping the narrow MWDs, as the conversion of **1** increases with polymerization time. This is a strong evidence of the absence of chain termination and transfer reactions under the polymerization conditions, as well as the postpolymerization study shown above.

Four polymerizations of **1** were attempted in THF by the initiation with DMPLi/LiCl (4.4−4.9 equiv) at −40, −50, −55, and −60 °C in order to estimate the polymerization rate. The concentration of DMPLi, $[I]_0$, was regulated between 3.8×10^{-3} and 4.2×10^{-3} M. The conversion of **1** could be independently estimated from the GLC measurement of the polymerization systems and the yield of the polymeric products. At each temperature, the first-order plots show good linear relationships, as shown in Figure 4. This also demonstrates that the propagating carbanions formed from **1** are fairly stable, and the concentration of the propagating species is constant during the course of the polymerization at least below −40 °C. From the slopes observed in Figure 4, we have estimated the k_p^{ap} value at each temperature as shown in Table 2. The k_p^{ap}s largely varied from 0.165 L mol^{-1} s^{-1} at −40 °C to 0.0169 L mol^{-1} s^{-1} at −60 °C and were strongly dependent on the polymerization temperature. These k_p^{ap} values are very small and indicate the inherent low polymerizability of **1**. In fact, the k_p^{ap} has been reported to be 13 L mol^{-1} s^{-1} for the anionic polymerization of MMA in THF at −65 °C initiated with methyl α-lithioisobu-

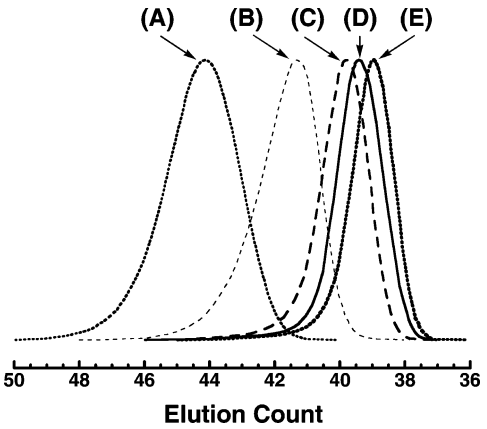


Figure 3. SEC curves of a series of poly(**1**)s obtained with DMPLi and 4.4-fold LiCl in THF at −40 °C: (A) after 6.5 min, 47% conversion, M_n = 3800, M_w/M_n = 1.07; (B) after 20 min, 65% conversion, M_n = 6700, M_w/M_n = 1.06; (C) after 50 min, 88% conversion, M_n = 10 000, M_w/M_n = 1.03; (D) after 90 min, 98% conversion, M_n = 11 000, M_w/M_n = 1.03; (E) after 210 min, 100% conversion, M_n = 13 000, M_w/M_n = 1.03.

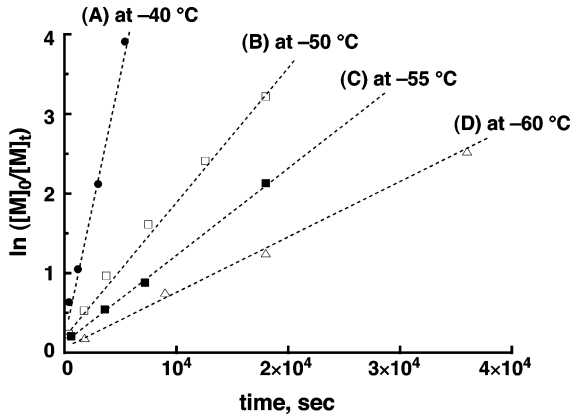


Figure 4. First-order plots for the polymerization of **1** at $[M]_0$ = 0.47−0.49 M and $[I]_0 = 3.8-4.2 \times 10^{-3}$ M: (A) at −40 °C; (B) at −50 °C; (C) at −55 °C; (D) at −60 °C.

Table 2. Apparent Rate Constants of Anionic Polymerization of 1[a]

temp, °C	k_p^{ap}, L mol^{-1} s^{-1}
−40	0.165 ± 0.01
−50	0.0522 ± 0.005
−55	0.0246 ± 0.003
−60	0.0169 ± 0.002

[a] In THF in the presence of 4.4−4.9-fold of LiCl.

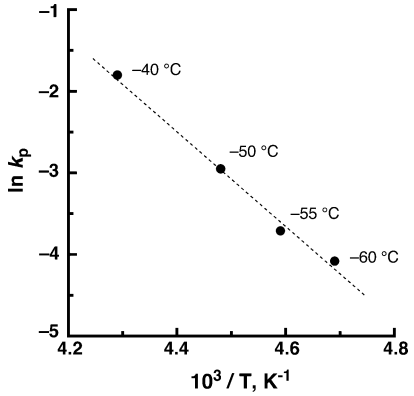


Figure 5. Arrhenius plots of k_p for the polymerization of **1** with DMPLi and 4.4−4.9-fold LiCl in THF.

tyrate in the presence of 5-fold LiCl.[19] Thus, the k_p^{ap} value for MMA is almost 770 times larger than that of **1** (0.0169 L mol^{-1} s^{-1}) under similar polymerization conditions. Figure 5 shows the Arrhenius plots of k_p^{ap} for the anionic polymerization of **1** in the presence of 4.4−4.9-fold of LiCl. The relationship between k_p^{ap} and polymerization temperature can be expressed as follows:

$$\ln k_p^{ap} = -5.85 \times 10^3/T + 23.3 \text{ L mol}^{-1} \text{ s}^{-1}$$

Then, the apparent activation energy of the polymerization, ΔE_p^{ap}, of **1** is estimated to be 49 ± 4 kJ mol^{-1}. This ΔE_p^{ap} is significantly larger than the reported values of anionic polymerization of MMA (ΔE_p^{ap} = 20−25 kJ mol^{-1}) under the similar conditions.[20] This also supports the lower polymerizability of **1** compared with the ester counterpart such as MMA, although both monomers are α,α′-disubstituted alkenes and possess the same methacryloyl moieties, CH_2═$C(CH_3)CO$, as the polymerizing groups.

Anionic Polymerization of 2. We next polymerized **2**, acryloyl counterpart of **1**, under the similar polymerization conditions, as shown in Table 3. The polymerization of **2** with DMPLi completed in THF at −78 °C within 5 min and gave a polymer with a very broad and bimodal MWD (run 15). By contrast, the MWDs of the resulting poly(**2**)s became unimodal and significantly narrowed, when we added 4.3−22-fold LiCl to the polymerization system (runs 16−18). The M_w/M_n values were reduced below 1.2, along with the controls on M_n values of poly(**2**) produced with DMPLi/LiCl. By contrast, the MWDs were very broad, when the polymerizations of **2** were carried out with DMPLi in the presence of 11−19-fold Et_2Zn. These polymerization behaviors of **2** largely differed from the result of *N*,*N*-diethylacrylamide (DEA).[5a,b] In the case of DEA, the polymerizations initiated with DMPLi and DMPLi/LiCl induced the broad MWDs of poly(DEA)s, whereas the addition of Lewis acidic Et_2Zn drastically reduced the polydispersity index within 1.1. The Ph_2CHK-induced polymerization of **2** at −78 °C afforded a polymer having relatively narrow MWD (M_w/M_n = 1.40). On the addition of Et_2Zn, the MWD further narrowed, and the M_w/M_n values were around 1.2, while the polymerization rate became slower. On the other hand, the broadening of MWD occurred, when the polymerization of **2** was performed with Ph_2CHK/Et_2Zn at 0 °C. In summary, the poly(**2**) of well-defined chain structures could be obtained quantitatively by the polymerization systems of DMPLi/LiCl and Ph_2CHK/Et_2Zn at −78 °C.

Radical Polymerization of 1 and 2. The radical polymerization of **1** was attempted with AIBN in toluene at 70 °C. The conversion of **1** reached 77% after 9 h, and the resulting poly(**1**) possessed very low molecular weight and broad MWD (M_n = 2800, M_w/M_n = 3.98). On the other hand, the radical polymerization of **2** quantitatively proceeded at 70 °C within 6.5 h. After precipitation in hexane, a polymer (M_n = 11 000, M_w/M_n = 1.51) was obtained in 89% yield. NMR and IR measurements of the resulting polymers substantiate that *N*-(meth)acryloyol-2-methylaziridines, **1** and **2**, undergo the free-radical polymerizations in vinyl addition modes, similar to the anionic polymerizations.

Solubility of Polymers. Poly(**1**) and poly(**2**) were white powders and cast into the brittle transparent films from their THF solutions. They were insoluble in *n*-hexane but soluble in various organic solvents such as benzene, chloroform, ethyl acetate, acetone, 1,4-dioxane, THF, DMSO, DMF, and methanol, as shown in Table 4. Higher polarity of poly(**2**) was indicative compared to poly(**1**), since poly(**2**) was soluble in cold water and insoluble in diethyl ether. Interestingly, an aqueous solution of poly(**2**) exhibits a phase transition with a lower critical solution temperature (LCST) around 14 °C. This thermosensitive behavior of poly(**2**) resembles with the properties of other poly(*N*,*N*-dialkylacrylamide)s such as poly(*N*-methyl-*N*-ethylacrylamide) (LSCT = 59−67 °C) and poly(*N*,*N*-diethylacrylamide) (LCST = 27−31 °C).[5a,b] On the other hand, poly(**1**), polymethacrylamide derivative, was insoluble in water and soluble in diethyl ether probably due to the effect of hydrophobic α-methyl substituents on the main chain.

Thermal Properties of Polymers. The glass transition temperatures (T_g) of poly(**1**) and poly(**2**) were analyzed by differential scanning calorimetry (DSC) and were observed at 98 and 54 °C, respectively. The methacryloyl type poly(**1**) showed higher T_g value compared with the acryloyl counterpart of poly(**2**), as expected.

Table 3. Anionic Polymerization of 2 in THF

run	**2** (mmol)	initiator, (mmol)	additive, (mmol)	temp (°C)	time (h)	conv (%)	$M_n \times 10^{-3}$ calcd[a]	$M_n \times 10^{-3}$ obsd[b]	M_w/M_n[c]
15	8.38	DMPLi,[d] 0.0662		−78	5 min	100	14	21	2.30
16	7.19	DMPLi, 0.132	LiCl, 0.574	−78	1	100	6.1	7.3	1.19
17	7.56	DMPLi, 0.0690	LiCl, 0.467	−78	2	100	12	15	1.12
18	8.37	DMPLi, 0.0589	LiCl, 1.29	−78	2	100	16	19	1.14
19	7.82	DMPLi, 0.129	Et_2Zn, 1.47	−78	1	100	7.0	9.3	2.03
20	7.24	DMPLi, 0.128	Et_2Zn, 2.37	−78	2	100	6.5	8.2	2.06
21	7.84	Ph_2CHK, 0.134		−78	1	100	6.7	8.2	1.40
22	7.62	Ph_2CHK, 0.113	Et_2Zn, 1.22	−78	1	85	6.0	6.9	1.18
23	7.90	Ph_2CHK, 0.0463	Et_2Zn, 0.698	−78	2	93	18	10	1.21
24	7.63	Ph_2CHK, 0.118	Et_2Zn, 2.49	−78	3	77	5.7	5.0	1.17
25	7.71	Ph_2CHK, 0.0992	Et_2Zn, 1.60	0	2	100	8.8	8.8	1.64

[a] M_n(calcd) = (MW of monomer) × conversion/100 × [monomer]/[initiator] + (MW of initiator fragment). [b] M_n(obsd) was obtained by end-group analysis using ^{1}H NMR. [c] M_w/M_n was obtained by SEC calibration using polystyrene standards in THF. [d] 2−3-fold 1,1-diphenylethylene was added to *sec*-BuLi.

Table 4. Solubility of Polymers[a]

solvent	poly(**1**)	poly(**2**)
hexane	I	I
benzene	S	S
$CHCl_3$	S	S
ethyl acetate	S	S
diethyl ether	S	Sw
1,4-dioxane	S	S
THF	S	S
DMSO	S	S
DMF	S	S
methanol	S	S
water	I	S[b]

[a] I = insoluble, S = soluble, and Sw = swelling. [b] Cloud point at 14 °C.

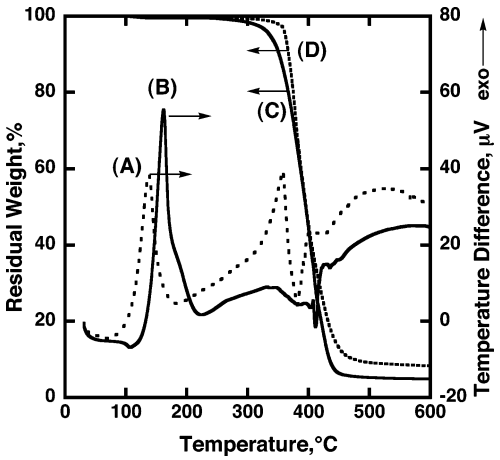


Figure 6. TG/DTA curves of poly(**1**) and poly(**2**) at heating rate of 10 °C min^{-1}: (A) DTA curve of poly(**2**); (B) DTA curve of poly(**1**); (C) TG curve of poly(**1**); (D) TG curve of poly(**2**).

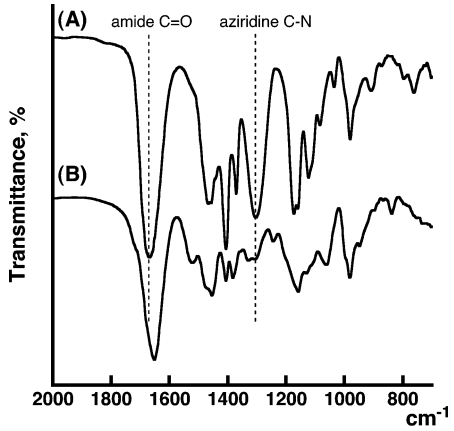


Figure 7. IR spectra of poly(**1**) before (A) and after thermal treatment at 150 °C for 10 min (B).

Thermal stability of poly(**1**) and poly(**2**) was then measured by thermogravimetric analysis (TG/DTA) under nitrogen. Figure 6 shows the TG/DTA thermograms of poly(**1**) and poly(**2**). In the DTA curves of poly(**1**) and poly(**2**), strong exotherms were observed between 100 and 200 °C without weight losses of polymers. When we heated samples to higher temperature, the thermal degradations of poly(**1**) and poly(**2**) occurred from 270 °C with decreasing the weight of polymer sample. The 10% weight loss temperatures, T_{10}, of poly(**1**) and poly(**2**) were observed at 352 and 367 °C. Figure 7 shows the IR spectra of poly(**1**) before and after the thermal treatment at 150 °C for 10 min. The IR spectrum after thermal treatment dramatically changed from the spectrum of the parent poly(**1**). In particular, the intensity of typical absorption attributed to aziridine rings at 1304 cm^{-1} drastically decreased after the thermal treatment, and the strong carbonyl absorption at 1668 cm^{-1} shifted to 1652 cm^{-1}. Moreover, poly(**1**) and poly(**2**) after heating at 150 °C for 10 min became insoluble in any organic solvent. These observations in the TG/DTA and IR measurements and the solubility change strongly indicate that the intermolecular and/or intramolecular cross-linking occurs via the thermally induced ring-opening reaction of highly strained *N*-acylaziridine moieties, as previously reported for the similar derivatives.[21] A plausible reaction mechanism is presented in Scheme 2. This means that poly(**1**) and poly(**2**) possess potentials as thermosetting resins on heat curing. Figure 6 clearly indicates that the exothermic cross-linking of methacryloyl poly(**1**) starts around 120 °C, while the acryloyl counterpart of poly(**2**) undergoes the cross-linking from 100 °C. It is also noteworthy that poly(**1**) is stable at 100 °C at least 10 min, since the polymer is soluble and no change in the IR spectrum is detected after the thermal treatment. On the other hand, poly(**2**) only swells in various solvents due to the partial cross-linking after the identical thermal treatment.

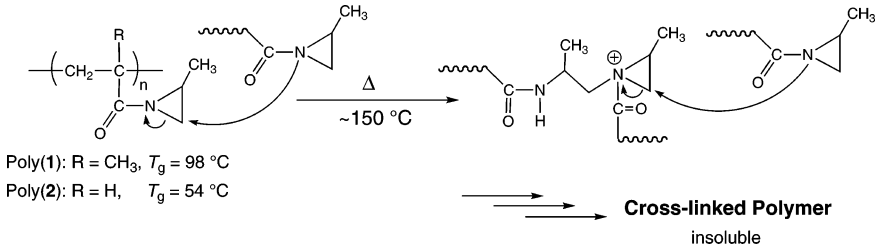
Reaction of Polymers. Besides the thermally induced cross-linking, poly(**1**) and poly(**2**) are expected to react with nucleophiles as well as the electrophiles, since they possess the highly strained aziridine moieties activated by the electron-withdrawing *N*-acyl groups.[13] At first, we attempted to react poly(**2**) with lithium methoxide in methanol at 40 °C for 24 h (Scheme 3). A soluble polymer was quantitatively obtained after the reaction. ^1H and ^{13}C NMR spectra of the product showed simple signals and were in good accordance with those of authentic poly(methyl acrylate), although a trace amount of nitrogen was detected in the elemental analysis of the product (Experimental Section). From the IR spectrum, the absorptions derived from the amide and aziridine rings at 1684 and 1299 cm^{-1} completely disappeared, but the absorption of carbonyl group due to the ester linkage newly appeared at 1731 cm^{-1}. These spectroscopic observations indicate that nucleophilic acyl substitution of lithium methoxide predominantly takes place on the pendant carbonyl group of poly(**2**), as shown in a route A of Scheme 3. The SEC trace of the resulting poly(methyl acrylate), however, showed a peak with a small shoulder at higher molecular side, suggesting the presence of intermolecular side reaction along with the broadening of MWD.

We also carried out the similar polymer reaction of poly(**1**), the methacryloyl counterpart, with lithium methoxide under the identical conditions. On the contrary to the simple product from poly(**2**), the reaction of poly(**1**) gave a complicated product. The solubility of the product from poly(**1**) slightly changed, and it became insoluble in diethyl ether after the reaction. NMR and IR measurements and elemental analysis revealed that the product possessed no aziridine moieties and involved both poly(methyl methacrylate) units (45%, route A) and ring-opening units (55%, route B),[22] as shown in Scheme 3. The nucleophilic acyl substitution and the ring-opening reaction of electrophilic *N*-acylaziridine occurred simultaneously in the case of poly(**1**). The observed difference on the reactivity between poly(**1**) and poly(**2**) might derive from the steric effect of the polymer main chain. We have thus realized the reactivity of *N*-acylaziridine moieties in poly(**1**) and poly(**2**) toward the nucleophiles. In fact, the insoluble gels were quantitatively obtained from poly(**1**) and poly(**2**) after the reaction with sodium salts of di(ethylene glycol) due to the intermolecular cross-linking.

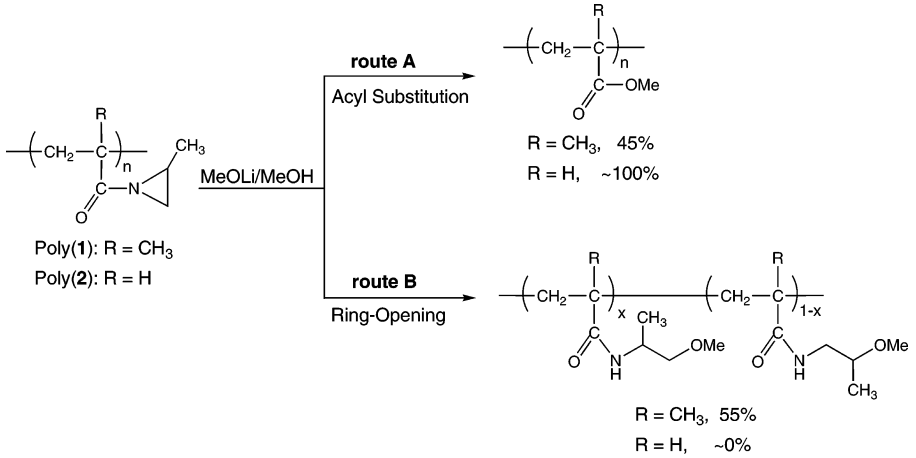
Conclusions

We have succeeded in the anionic polymerization of **1** to afford the novel functional polymer having the predicted

Scheme 2



Scheme 3



molecular weight and the narrow MWD (M_w/M_n < 1.1). To our best knowledge, this is a first example of the living polymerization of *N*,*N*-dialkylmethacrylamide derivative. The anionic polymerization of **2**, acrylamide counterpart, also gives the well-defined polymers under the suitable conditions. The ring-opening reactivity of pendant *N*-acylaziridine moieties in poly(**1**) and poly(**2**) is successfully demonstrated under the thermal treatment and the basic conditions. We now consider that the highly strained three-membered aziridine ring of **1** plays very important role to realize the anionic and radical polymerizations on the contrary to the negative polymerizability of *N*,*N*-dialkylmethacrylamides.[2a,4,7−11] The present results strongly prompt us to further investigate the polymerization behaviors of a series of *N*,*N*-dialkylmethacrylamides structurally analogous to monomer **1**. The polymerizations of *N*-methacryloylazetidine (four-membered ring), *N*-methacryloylpyrrolidine (five-membered ring), and *N*-methacryloyolpiperidine (six-membered ring) are now in progress to clarify the relationship between the polymerizability and the monomer structure and the conformation.

Experimental Section

Materials. 2-Methylaziridine and triethylamine were distilled from CaH_2. Acryloyl chloride and methacryloyl chloride were used without purification. Diethyl ether was dried over sodium wire. THF used as a polymerization solvent was refluxed over sodium wire for 3 h, distilled over $LiAlH_4$, and further distilled from sodium naphthalenide solution on a vacuum line. *n*-Heptane was washed with concentrated H_2SO_4 and dried over $MgSO_4$ and then dried over P_2O_5 for 1 day under reflux. It was then distilled in the presence of *n*-BuLi under nitrogen. 1,1-Diphenylethylene (DPE) was distilled from CaH_2 in vacuo and then distilled in the presence of 1,1-diphenylhexyllitihum on a vacuum line. The purified DPE was diluted with dry THF. LiCl was dried in vacuo for 2 days and used as a THF solution. Et_2Zn (TOSOH-Akzo) was distilled under reduced pressure and was diluted with dry THF.

Initiators. Commercially available *sec*-BuLi (1.0 M in cyclohexane, Kanto Chemical Co., Inc.) was used without purification and diluted with dry *n*-heptane. DMPLi was prepared prior to the polymerization from *sec*-BuLi and 2−3-fold DPE in THF at −78 °C for 10 min. Ph_2CHNa and Ph_2CHK were synthesized by the reaction of the corresponding metal naphthalenide and 1.5-fold of diphenylmethane in dry THF under argon at room temperature for 48 h. These initiators were sealed off under high-vacuum conditions in ampules equipped with break-seals and stored at −30 °C. The concentration of initiator was determined by colorimetric titration using standardized 1-octanol in THF in a sealed reactor under vacuum, as previously reported.[23] AIBN for radical polymerization was purified by recrystallization from methanol.

Synthesis of 1. A solution of methacryloyl chloride (14.8 g, 142 mmol) in dry ether (120 mL) was added dropwise to a mixture of 2-methylaziridine (8.19 g, 143 mmol), triethylamine (14.7 g, 145 mmol), and dry ether (120 mL) at 0 °C under nitrogen. The reaction mixture was stirred at room temperature for 3 h. Then, the precipitated triethylammonium chloride was removed by the filtration, and the filtrate was concentrated in vacuo. The residue was purified by the repeating vacuum distillations to give colorless liquid of **1** (10.71 g, 85.7 mmol, 60%, bp 51−52 °C/9 mmHg). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.34 (d, 3H, J = 5.4 Hz, CH_3 on aziridine ring), 1.95 (s, 3H, CH_3), 2.00 (d, 1H, J = 3.6 Hz, CH_2 trans to CH_3), 2.42 (d, 1H, J = 5.7 Hz, CH_2 cis to CH_3), 2.47 (m, 1H, CH), 5.63 and 6.09 (2s, 2H, CH_2=). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 17.7 (CH_3 on aziridine ring), 18.6 (CH_3), 31.8 (CH_2), 34.3 (CH), 124.5 (CH_2=), 139.8 (CH_2=*C*), 180.6 (C=O). IR (ATR): 2963, 2929, 1673 (C=O), 1628 (C=C), 1454, 1406, 1370, 1334, 1257, 1173, 1124, 932 cm^{-1}. Anal. Calcd for $C_7H_{11}NO$ (125.168): C, 67.17; H, 8.86; N, 11.19. Found: C, 66.90; H, 8.85; N, 11.04.

Synthesis of 2. 2 was prepared according to the similar procedure for **1** by using acryloyl chloride (14.3 g, 158 mmol), 2-methylaziridine (9.37 g, 164 mmol), and triethylamine (16.2 g, 160 mmol). Repeating vacuum distillations of the crude product gave colorless liquid of **2** (8.12 g, 73.2 mmol, 46%, bp 43−44 °C/5 mmHg). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.35 (d, 3H, J = 5.5 Hz, CH_3), 2.03 (d, 1H, J = 3.5 Hz, CH_2 trans to CH_3), 2.41 (d, 1H, J = 5.8 Hz, CH_2 cis to CH_3), 2.54 (m, 1H, CH on aziridine ring), 5.80 (d, 1H, J = 9.4 Hz, trans CH_2=), 6.29 (dd, 1H, J = 9.4 and 17 Hz, −CH=), 6.38 (d, 1H, J = 17 Hz, cis CH_2=). ^{13}C NMR (75 MHz,

$CDCl_3$): δ = 17.8 (CH_3 on aziridine ring), 31.7 (CH_2), 33.5 (CH), 129.0 (CH_2=), 131.6 (=CH−), 177.9 (C=O). IR (ATR): 2996, 2970, 1677 (C=O), 1615 (C=C), 1469, 1406, 1371, 1310, 1272, 1184, 986, 963 cm^{-1}. Anal. Calcd for $C_6H_9NO\cdot0.15H_2O$ (hygroscopic): C, 63.30; H, 8.23; N, 12.31. Found: C, 63.00; H, 8.05; N, 12.25.

Purification of 1 and 2. After careful fractional distillations, **1** or **2** was degassed and sealed off in an apparatus equipped with a break-seal in the presence of CaH_2 and diluted with dry THF. The monomer solution in THF was distilled from CaH_2 on a vacuum line into an ampule fitted with a break-seal and further diluted with dry THF. The resulting monomer solutions (0.76−0.87 M) in THF were stored at −30 °C until ready to use for the anionic polymerization.

Anionic Polymerization. All anionic polymerizations were carried out in THF at −78 to 0 °C in an all-glass apparatus equipped with break-seals with vigorous shaking under high-vacuum conditions (10^{-6} mmHg).[23] Polymerization was terminated with degassed isopropanol at −78 °C.[17] When Et_2Zn was used as an additive, the reaction mixture was immediately concentrated to remove THF and excess amount of isopropanol and again diluted with THF to precipitate the zinc compounds. After filtration of the system to remove the precipitated zinc compounds, the filtrate was concentrated by evaporation. The residue was precipitated in hexane either at room temperature for poly(**1**) or at 0 °C for poly(**2**). The resulting poly(**1**) and poly(**2**) were further purified by freeze-drying from benzene and characterized by NMR and IR spectroscopies and elemental analysis. The following is the complete list.

Poly(1). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.0−1.5 (6H, CH_3 on aziridine ring and α-CH_3), 1.6−2.3 (3H, CH_2 trans to CH_3 and main chain CH_2), 2.3−2.6 (1H, CH_2 cis to CH_3), 2.6−3.0 (br, 1H, CH on aziridine ring). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 17.7 (CH_3 on aziridine ring), 19−24 (CH_3), 29−32 (CH_2 on aziridine ring), 32−36 (CH), 47−50 (main chain quaternary), 53.3 (main chain CH_2), 189.3 (C=O). IR (KBr): 2989, 2930, 1668 (C=O), 1467, 1406, 1371, 1304, 1173, 1123 cm^{-1}. Anal. Calcd for $C_7H_{11}NO$ (125.168): C, 67.17; H, 8.86; N, 11.19. Found: C, 66.72; H, 8.51; N, 10.41.

Poly(2). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.27 (d, 3H, CH_3 on aziridine ring), 1.5−1.9 (br, 2H, main chain CH_2), 1.7−2.0 (br, 1H, CH_2 trans to CH_3), 2.2−2.5 (2H, main chain CH and CH_2 cis to CH_3), 2.5−2.7 (br, 1H, CH on aziridine ring). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 17.9 (CH_3 on aziridine ring), 31.5 (CH_2 on aziridine ring), 32−33 (CH on aziridine ring), 36.0 (main chain CH_2), 43.0 (main chain CH), 186.9 (C=O). IR (KBr): 2966, 2930, 1684 (C=O), 1442, 1409, 1376, 1299, 1175 cm^{-1}. Anal. Calcd for $C_6H_9NO\cdot0.25H_2O$ (hygroscopic): C, 62.31; H, 8.28; N, 12.11. Found: C, 62.13; H, 8.07; N, 11.76.

Kinetic Study of Polymerization of 1. Anionic polymerization of **1** was performed at −78 °C with DMPLi in the presence of LiCl in THF in an all-glass apparatus equipped with break-seals and several ampules under high-vacuum conditions. After a THF solution of **1** was added to the initiator solution at −78 °C, the mixture was immediately divided into several ampules and sealed off. Then, the sealed ampules were placed in an acetone bath thermostated at a desirable temperature between −40 and −60 °C. After the given time, the polymerization was terminated with isopropanol at −78 °C. The total content of each ampule was diluted to an appropriate volume, and the concentration of the residual monomer $[M]_t$ was measured by GLC with undecane as an external standard. The observed experimental error of $[M]_t$ was 5% in the range 0.04−0.45 M.

Radical Polymerization. Radical polymerization of **1** (0.60 g, 4.80 mmol) was performed with AIBN (0.079 g, 0.48 mmol) in toluene (11 mL) at 70 °C for 9 h under nitrogen. The reaction mixture was poured into hexane to precipitate a polymer (0.46 g, conversion ∼77%). The resulting polymer collected by filtration was purified by freeze-drying from the benzene solution.

Thermal Treatment of Polymers. White powder of poly(**1**) or poly(**2**) was heated in the air at 150 or 250 °C for 10 min in an aluminum pan for the DSC measurement. The resulting insoluble polymer was analyzed by IR spectroscopy and elemental analysis.

Poly(1) Treated at 150 °C for 10 min. IR (KBr): 3423, 2975, 1652 (C=O), 1521, 1455, 1406, 1383, 1329, 1158, 1064, 981 cm^{-1}. Anal. Calcd for $C_7H_{11}NO$ (125.168): C, 67.17; H, 8.86; N, 11.19. Found: C, 57.15; H, 7.58; N, 9.16.

Poly(2) Treated at 150 °C for 10 min. IR (KBr): 3406, 2970, 1661 (C=O), 1542, 1450, 1379, 1248, 1173, 986 cm^{-1}. Anal. Calcd for C_6H_9NO (111.142): C, 64.84; H, 8.16; N, 12.60. Found: C, 57.53; H, 7.41; N, 10.75.

Reaction of Polymers. A mixture of poly(**2**) (0.25 g, 2.3 mmol) and lithium methoxide (0.12 g, 3.2 mmol) was reacted in methanol (5 mL) at 40 °C for 24 h. After evaporation of methanol, the reaction mixture was poured into hexane to precipitate the polymeric products. The resulting polymer was further purified by the freeze-drying from benzene and characterized by NMR and IR spectroscopies and elemental analysis. The reaction of poly(**1**) and lithium methoxide was similarly performed.

Poly(2) Reacted with MeOLi. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.3−2.1 (br, 2H, CH_2), 2.29 (1H, CH), 3.64 (3H, OCH_3). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 34−36 (CH_2), 41−42 (CH), 51.8 (OCH_3), 175 (C=O). IR (ATR): 2951, 1731 (C=O), 1434, 1256, 1161 cm^{-1}. Anal. Calcd for $C_4H_6O_2$ (86.088, methyl acrylate): C, 55.80; H, 7.03; N, 0.00. Found: C, 40.37; H, 5.05; N, 0.38.

Poly(1) Reacted with MeOLi. IR (ATR): 2934, 1719 (C=O, ester), 1666 (C=O, amide), 1511, 1452, 1389, 1326, 1195, 1106 cm^{-1}. Anal. Calcd for $C_7H_{11}NO$ (125.168): C, 67.17; H, 8.86; N, 11.19. Found: C, 58.14; H, 8.25; N, 5.83.

Measurements. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker DPX300 spectrometer (300 MHz for ^{1}H and 75 MHz for ^{13}C) in $CDCl_3$. The chemical shifts were reported in ppm downfield relative to $CHCl_3$ (δ 7.26) for ^{1}H NMR and $CDCl_3$ (δ 77.1) for ^{13}C NMR as standard. IR spectra were recorded on a JASCO FT/IR-4100 instrument using either an attenuated total reflectance (ATR) attachment or KBr disk method. SEC chromatograms for determination of MWD were obtained in DMF containing 0.01 M LiBr at 40 °C at a flow rate of 1.0 mL min^{-1} with a TOSOH HLC8120 instrument equipped with three polystyrene gel columns (TSK-GEL GMH_{XL} × 2 + $G2000H_{XL}$) with either ultraviolet (254 nm) absorption or refractive index detection. The T_gs of the polymers were measured by DSC using a Seiko instrument DSC6220 apparatus under nitrogen flow. The polymer sample was first heated to 80 °C, cooled to 30 °C, and then scanned at a rate of 10 °C min^{-1}. A Seiko Instrument TG/DTA6200 was used for TGA analysis at 30−600 °C under nitrogen flow with heating rate of 10 °C min^{-1}. The cloud point of poly(**2**) in water was determined by monitoring the transmittance using a JASCO UVITEC-660 spectrometer. Transmittance of 0.2 wt % aqueous solution of polymer at 500 nm was monitored in a PMMA cell (path length = 1.0 cm) with stirring at a heating rate of 0.5 °C min^{-1}.

Acknowledgment. This work was partially supported by a Grant-in Aid (No. 14550833) from the Ministry of Education, Science, Sports, and Culture, Japan.

References and Notes

(1) (a) Davis, T. P.; Haddleton, D. M.; Richards, S. N. *J. Macromol. Sci., Rev. Macromol. Chem.* **1994**, *C34*, 243. (b) Collins, S.; Ward, D. G.; Suddaby, K. H. *Macromolecules* **1994**, *27*, 7222. (c) Baskaran, D.; Müller, A. H. E.; Kolshorn, H.; Zagala, A. P.; Hogen-Esch, T. E. *Macromolecules* **1997**, *30*, 6695. (d) Kato, M.; Kamigaito, M.; Sawamoto, M.; Higashimura, T. *Macromolecules* **1995**, *28*, 1721. (e) Hatada, K.; Kitayama, T. *Polym. Int.* **2000**, *49*, 11. (f) Webster, O. W. *J. Polym. Sci., Part A: Polym. Chem.* **2000**, *38*, 2855.

(2) (a) Otsu, T.; Inoue, M.; Yamada, B.; Mori, T. *J. Polym. Sci., Polym. Lett. Ed.* **1975**, *13*, 505. (b) Sato, T.; Miyamoto, J.; Otsu, T. *J. Polym. Sci., Polym. Chem. Ed.* **1984**, *22*, 3921. (c) Guo, Y.; Feng, F.; Miyashita, T. *Macromolecules* **1999**, *32*, 1115. (d) Zhang, J.; Liu, W.; Nakano, T.; Okamoto, Y. *Polym. J.* **2000**, *32*, 694.

(3) (a) Breslow, D. S.; Hulse, G. E.; Matlack, A. S. *J. Am. Chem. Soc.* **1957**, *79*, 3760. (b) Kennedy, J. P.; Otsu, T. *J. Macromol. Sci., Rev.*

Macromol. Chem. **1972**, *C6*, 237. (c) Otsu, T.; Yamada, B.; Itahashi, M.; Mori, T. *J. Polym. Sci., Polym. Chem. Ed.* **1976**, *14*, 1347.
(4) Xie, X.; Hogen-Esch, T, E. *Macromolecules* **1996**, *29*, 1746.
(5) (a) Kobayashi, M.; Okuyama, S.; Ishizone, T.; Nakahama, S. *Macromolecules* **1999**, *32*, 6466. (b) Kobayashi, M.; Ishizone, T.; Nakahama, S. *Macromolecules* **2000**, *33*, 4411. (c) Ito, M.; Ishizone, T. *J. Polym. Sci., Part A: Polym. Chem.* **2006**, *44*, 4832. (d) Ishizone, T.; Yashiki, D.; Kobayashi, M.; Suzuki, T.; Ito, M.; Nakahama, S. *J. Polym. Sci., Part A: Polym. Chem.* **2007**, *45*, 1260.
(6) (a) Sogah, D. Y.; Hertler, W. R.; Webster, O. W.; Cohen, G. M. *Macromolecules* **1987**, *20*, 1473. (b) Freitag, R.; Baltes, T.; Eggert, M. *J. Polym. Sci., Part A: Polym. Chem.* **1994**, *32*, 803.
(7) Yokota, K.; Oda, J. *Kogyo Kagaku Zasshi* **1970**, *73*, 224.
(8) Butler, G. B.; Myers, G. R. *J. Macromol. Sci., Chem.* **1971**, *A5*, 135.
(9) Kodaira, T.; Aoyama, F. *J. Polym. Sci., Polym. Chem. Ed.* **1974**, *12*, 897.
(10) Kodaira, T.; Tanahashi, H.; Hara, K. *Polym. J.* **1990**, *22*, 649.
(11) Although we have also carried out the anionic polymerizations of *N*,*N*-dimethylmethacrylamide and *N*,*N*-dibutylmethacrylamide under the various conditions, no polymeric products have been virtually obtained.
(12) Okamoto, O.; Yuki, H. *J. Polym. Sci., Polym. Chem. Ed.* **1981**, *19*, 2647.
(13) (a) Stamm, H. *J. Prakt. Chem.* **1999**, *341*, 319. (b) Lin, P. Y.; Bentz, G.; Stamm, H. *J. Prakt. Chem.* **1993**, *335*, 23. (c) Ham, G. E. *J. Org. Chem.* **1964**, *29*, 3052. (d) Iwakura, Y.; Nabeya, A. *J. Org. Chem.* **1960**, *25*, 1118. (e) Sweeney, J. B. *Chem. Soc. Rev.* **2002**, *31*, 247.
(14) Preliminary results of polymerization of **1** have been reported in the IUPAC-PSK30 conference in Busan, Korea in 2006. Suzuki, T.; Kusakabe, J.; Ishizone, T. *Macromol. Symp.* **2007**, *249*−*250*, 412.
(15) (a) Fayt, R.; Forte, R.; Jacobs, C.; Jérôme, R.; Ouhadi, T.; Teyssié, Ph.; Varshney, S. K. *Macromolecules* **1987**, *20*, 1442. (b) Varshney, S. K.; Hautekeer, J. P.; Fayt, R.; Jérôme, R.; Teyssié, Ph. *Macromolecules* **1990**, *23*, 2618.
(16) (a) Ozaki, H.; Hirao, A.; Nakahama, S. *Macromol. Chem. Phys.* **1995**, *196*, 2099. (b) Ishizone, T.; Yoshimura, K.; Hirao, A.; Nakahama, S. *Macromolecules* **1998**, *31*, 8706.
(17) Acyl substitution toward the pendant moieties of the resulting polymer might partially occur, when the polymerization was quenched with methanol instead of isopropanol. After the termination, the resulting methoxide found to attack toward the carbonyl groups on the polymers but not the hindered isopropoxide.
(18) It was difficult to determine the stereoregularities of poly(**1**) and poly(**2**), since the signals in the ^{1}H and ^{13}C NMR spectra were overlapped and complicated.
(19) Kunkel, D.; Müller, A. H. E.; Janata, M.; Lochmann, L. *Makromol. Chem. Macromol. Symp.* **1992**, *60*, 315.
(20) Baskaran, D.; Müller, A. H. E.; Sivaram, S. *Macromolecules* **1999**, *32*, 1356.
(21) (a) Iwakura, Y.; Nabeya, A.; Nishiguchi, T. *Yuki Gosei Kagaku Kyokaishi* **1968**, *26*, 101. (b) Fanta, P. E.; Deutsch, A. S. *J. Org. Chem.* **1958**, *23*, 72.
(22) In the organic chemistry, it has been reported that the ring-opening reactions between *N*-acyl-2-methylaziridines and several nucleophiles proceed not regioselectively (ref 13). We could not estimate the ratio of x and $(1 - x)$ for the product in Scheme 3.
(23) Hirao, A.; Takenaka, K.; Packrisamy, S.; Yamaguchi, K.; Nakahama, S.; *Makromol. Chem.* **1985**, *186*, 1157.

MA702615U