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Living Anionic Polymerization of *N*-Methacryloyl-2-methylaziridine

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Summary: Anionic polymerization of *N*-methacryloyl-2-methylaziridine (**1**) proceeded with 1,1-diphenyl-3-methylpentyllithium (DMPLi) in the presence of LiCl or Et_2Zn to give the polymers possessing predicted molecular weights and narrow molecular weight distributions ($M_w/M_n < 1.1$) at $-78 \sim -40$ °C in THF. In each polymerization initiated with DMPLi/LiCl at the various temperatures ranging from −40 to −60 °C, the linear relationship between polymerization time and conversion of monomer was obtained from the GLC analysis. The 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. Poly(**1**) showed the glass transition temperature at 98 °C, and gave the insoluble product at higher temperature around 150 °C through the thermal cross-linking of highly strained *N*-acyl-aziridine moiety.

Keywords: activation energy; kinetic study; living anionic polymerization; *N,N*-dialkylmethacrylamide; *N*-methacryloyl-2-methylaziridine

Introduction

It is well known that acrylates and methacrylates can be readily polymerized under the radical or anionic conditions. Similar to the α,β-unsaturated esters, acrylamide, methacrylamide, and their *N*-monoalkyl-substituted counterparts undergo the radical polymerizations,[1,2] while the hydrogen transfer polymerizations simultaneously occur during the course of the anionic polymerizations due to the acidic amide protons.[3,4] On the other hand, the vinyl polymerizations of *N,N*-dialkylacrylamides exclusively proceed by the initiation with the radical or anionic initiators. In particular, the living polymerizations of *N,N*-dialkylacrylamides have been demonstrated by the various nucleophilic initiators.[5–10]

By contrast, the polymerizations of *N,N*-disubstituted-methacrylamides such as *N,N*-dimethylmethacrylamide (**DMMA**) and *N,N*-diphenylmethacrylamide are extremely limited due to their inherent low polymerizability under the radical and basic conditions.[11–15] There are no successful examples to produce the polymers of *N,N*-disubstituted-methacrylamides under the various conditions. Only one exception is a vinyl polymerization of *N*-methacryloylaziridine (**MAz**) possessing a highly strained and small three-membered aziridine ring.[15] Yuki and Okamoto have reported that **MAz** is polymerized with either AIBN or *n*-BuLi, while the detailed polymerization results have not been shown. This indicates that the small substituents on amide moiety will provide the positive polymerizability of *N,N*-disubstituted-methacrylamides. However, the plausible side reactions such as ring-opening reaction of aziridine ring are also suggested in the anionic polymerization, since the insoluble products are occasionally obtained. In the organic synthesis, ring-opening and isomerization reactions of *N*-acyl- and *N*-sulfonylaziridines with nucleophiles are reported,[16–18] because the *N*-substituted electron-withdrawing groups certainly decrease the electron

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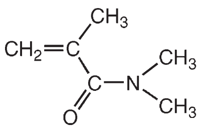
density of aziridine rings and enhance the reactivity toward the nucleophilic attack. Therefore, a suitable selection of the polymerization condition is essential for the anionic polymerizations of **MAz** to prevent the serious side reactions and to regulate the primary chain structures.

Very recently, we have reported a first example of living anionic polymerization of *N,N*-dialkylmethacrylamide, *N*-methacryloyl-2-methylaziridine (**1**), as a substitute of **MAz** (Chart 1).[19–20] We used propyleneimine (2-methylaziridine) for the synthesis of **1**, since aziridine (ethyleneimine) is recently hardly available due to the high toxicity. The well-defined poly(**1**)s possessing predicted molecular weights and narrow molecular weight distributions (MWDs) were quantitatively obtained by selecting the suitable initiator system. In this report, we will demonstrate the results of kinetic study to further discuss the anionic polymerizability of **1** and compare the polymerizability with **DMMA**. In addition, the thermal cross-linking of pendant strained *N*-acylaziridine rings of the resulting polymer is examined to show the potentials as thermosetting resins on heat curing.

Results and Discussion

Anionic Polymerization of 1

Anionic polymerization of **1** was performed with 1,1-diphenyl-3-methylpentyllithium (DMPLi), an adduct of *sec*-BuLi and 1,1-diphenylethylene, and diphenylmethylpotassium (Ph_2CHK) in THF at various temperatures (−78, −40, and 0 °C). In most case, LiCl[21,22] or $ZnEt_2$[23–25] was added to the polymerization system, since they have been proved as the effective additives for the controlled anionic polymerization of (meth)acrylates and *N,N*-dialkylacrylamides. The polymerization was terminated



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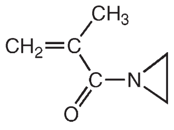
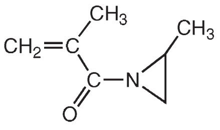


MAz



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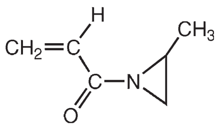

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Table 1.
Anionic Polymerization of 1 and DMMA in THF.

Monomer	Initiator	temp.	time	conv.	$10^{-3}M_n$		M_w/M_n[c]
		°C	h	%	calcd[a]	obsd[b]	
1	Ph_2CHK	−78	15	100	12	16	1.20
1	Ph_2CHK/Et_2Zn	−78	72	82	13	6.2	1.29
1	DMPLi[d]	−78	15	90	6.1	7.0	1.14
1	DMPLi/LiCl	−78	2	52	3.1	2.6	1.09
1	DMPLi/LiCl	−78	72	100	6.1	7.2	1.05
1	$DMPLi/Et_2Zn$	−78	72	100	12	15	1.08
1	DMPLi/LiCl	−40	2.5	100	14	15	1.03
1	DMPLi/LiCl	−40	24	100	47	50	1.09
1	DMPLi/LiCl	0	15 min	100	15	16	1.05
DMMA	Ph_2CHK	−78	72	0	–	–	–
DMMA	Ph_2CHK/Et_2Zn	−78	72	0	–	–	–
DMMA	DMPLi	−78	72	0	–	–	–
DMMA	DMPLi/LiCl	−78	72	0	–	–	–
DMMA	$DMPLi/Et_2Zn$	−78	72	0	–	–	–

[a] $M_n$calcd = [monomer]/[initiator] × MW of monomer × conversion (%)/100 + MW of initiator residue;
[b] $M_n$obsd was estimated by ^1H NMR using end group analysis;
[c] M_w/M_n was estimate by SEC in DMF containing 0.01 M LiBr;
[d] 1,1-Diphenyl-3-methylpentyllithium.

with degassed isopropanol. Polymeric product was precipitated by pouring a polymerization mixture into hexane. The polymer was isolated by filtration, and characterized by ^{1}H and ^{13}C NMR spectroscopies and elemental analysis. The spectroscopic observations strongly indicate that the vinyl polymerization of **1** exclusively proceeds to give a soluble poly(**1**) on the contrary to the previous report for **MAz**.[15]

The polymerization results of **1** are summarized in Table 1. The polymerization of **1** occurred with Ph_2CHK at −78 °C to provide a polymer in 100% yield. The size exclusion chromatography (SEC) curve of the resulting poly(**1**) was unimodal, and the polydispersity index, M_w/M_n, was 1.20, indicating the relatively narrow MWD. We then added Et_2Zn to the reaction system to control the polymerization. However, in the presence of Et_2Zn, the MWD became rather broad, and the conversion of **1** was not quantitative even after 72 h. We then changed the counterion of the initiator from K^+ to Li^+. 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 with the calculated value based on the molar ratio between monomer to initiator and the conversion of **1**. The M_w/M_n was 1.14, indicating the fairly narrow MWD. In the presence of 3.8-10-fold LiCl to DMPLi, 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, and M_w/M_n values were regulated in the range of 1.05–1.09. We next added Et_2Zn to DMPLi to tune the polymerization at −78 °C. The resulting poly(**1**) had a controlled molecular weight with the narrow MWD. We then elevated the polymerization temperature to −40 or 0 °C in order to increase the rate of polymerization. Poly(**1**)s of controlled M_ns and narrow MWDs yielded with DMPLi/LiCl at −40 °C. Moreover, the polymerization of **1** completed within 15 min at 0 °C, and the poly(**1**) possessed controlled and narrow MWD.

We then attempted to polymerize **DMMA** under the similar reaction conditions as shown in Table 1. We changed counterions of the initiator and the additives to check the polymerizability of **DMMA**. However, no polymeric product was obtained from each polymerization system of **DMMA** in THF at −78 °C, although the polymerization was always performed even for 72 h. Although we also carried out the polymerization at 0 °C, no polymerization occurred similar to the results at −78 °C. We thus conclude that **DMMA** is difficult to polymerize even under the ideal conditions for the controlled polymerization of **1**.

On the basis of ^{1}H and ^{13}C NMR chemical shifts and MNDO calculations, Kodaira[13,14] and Hogen-Esch[5] have suggested that the low polymerizability of **DMMA** is derived from the twisted conformation between C=C and C=O groups due to the steric repulsion between α-methyl group and two methyl substituents on nitrogen. On the basis of ^{1}H and ^{13}C NMR, the different polymerizability between **1** and **DMMA** can be attributed to the lack of amide conjugation in **1**, arisen from the strained small aziridine moiety.[26–28] This leads to the effective resonance between carbonyl and vinyl groups to result in the positive polymerizability of **1**. The ^{13}C NMR chemical shifts of vinyl β-carbons of **1** and **DMMA** were observed at 125 and 115 ppm, respectively. These values clearly indicate the lower π-electron densities of vinyl groups and the higher anionic polymerizability in **1**, compared to **DMMA**. The evaluations of the stable conformation and the electron density of the monomers are now in progress by using the ab initio calculation.

Kinetic Studies

In the preceding section, we realized that the polymerization of **1** quantitatively

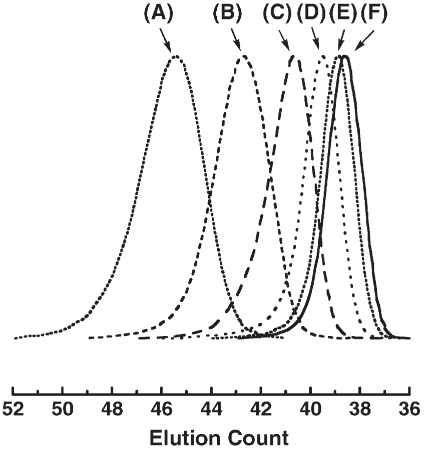

Figure 1.
SEC curves of a series of poly(**1**)s obtained with DMPLi and 4.9-fold LiCl in THF at −50 °C: (A) after 6.0 min, 21% conversion, $M_n = 5300$, $M_w/M_n = 1.10$; (B) after 29 min, 41% conversion, $M_n = 7500$, $M_w/M_n = 1.07$; (C) after 62 min, 62% conversion, $M_n = 10{,}000$, $M_w/M_n = 1.06$; (D) after 125 min, 80% conversion, $M_n = 12{,}000$, $M_w/M_n = 1.05$; (E) after 210 min, 91% conversion, $M_n = 14{,}000$, $M_w/M_n = 1.03$; (F) after 300 min, 96% conversion, $M_n = 15{,}000$, $M_w/M_n = 1.03$.

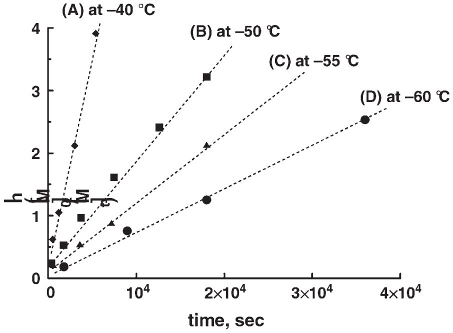

Figure 2.
First-order plots for the polymerization of **1** at $[M]_0 = 0.47–0.49$ M and $[I]_0 = 3.8–4.2 \times 10^{-3}$ M: (A) at −40 °C; (B) at −50 °C; (C) at −55 °C; (D) at −60 °C.

proceeded but the polymerization rate was very low. The polymerization rate of **1** can be easily traced by monitoring of the residual monomer and the resultant polymer, while such kinetic studies of alkyl (meth)acrylates and *N,N*-dialkylacrylamides are usually very difficult because of the rapid propagations of these monomers. Figure 1 shows a series of SEC curves of poly(**1**) produced with DMPLi/LiCl (4.9 equiv.) at −50 °C. The SEC curves clearly shift from the low molecular weight region to the higher molecular weight side with keeping the unimodal 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.

Four kinetic studies of **1** were attempted in THF at −40, −50, −55, and −60 °C by the initiation with DMPLi, $[I]_0$ $3.8–4.2 \times 10^{-3}$ M, in the presense of LiCl (4.4–4.9 equiv) in order to estimate the polymerization rate. The conversion of **1** could be 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 2. This also demonstrates that the concentration of the propagating species is constant and the propagating carbanions derived from **1** are stable during the course of the polymerization at least below −40 °C. From the slopes observed in Figure 2, the k_p^{ap} value at each temperature was estimated 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. From the viewpoint of polymer synthesis, 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 methyl methacrylate (MMA) in THF at −65 °C initiated with methyl α-lithioisobutyrate in the presence of 5-fold LiCl.[29] This k_p^{ap} value for MMA at −65 °C is almost 770 times larger than the

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

Temperature, °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.

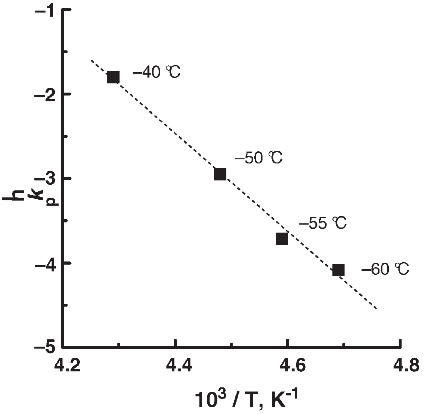

Figure 3.
Arrhenius plots of k_p for the polymerization of **1** with DMPLi and 4.4–4.9-fold LiCl in THF.

k_p^{ap} of **1** at −60 °C (0.0169 L mol^{-1} s^{-1}) under the similar polymerization conditions. The typical Arrhenius plots of k_p^{ap} for the anionic polymerization of **1** are shown in Figure 3. The relationship between k_p^{ap} and polymerization temperature is expressed as follows:

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

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 polymerization conditions.[30] This also supports the lower polymerizability of **1** compared with the ester counterpart such as MMA, although both monomers possess the same methacryloyl moieties, $CH_2{=}C(CH_3)CO$, as the polymerizing groups.

Thermal Properties of Polymers

The glass transition temperature (T_g) of poly(**1**) was analyzed by differential scanning calorimetry (DSC) and was observed at 98 °C. For the discussion of thermal property, we also analyzed the T_g of polymer of *N*-acryloyl-2-methylaziridine, **2**.[20] The T_g value of poly(**2**) obtained by the anionic polymerization was 54 °C. Thus, the poly(**1**) showed higher T_g value compared with the acryloyl counterpart of poly(**2**), as expected.

Thermal stability of poly(**1**) and poly(**2**) was then measured by thermogravimetric analysis (TG/DTA) under nitrogen. The TG/DTA thermograms of poly(**1**) and poly(**2**) are shown in Figure 4. Strong exotherms were observed between 100

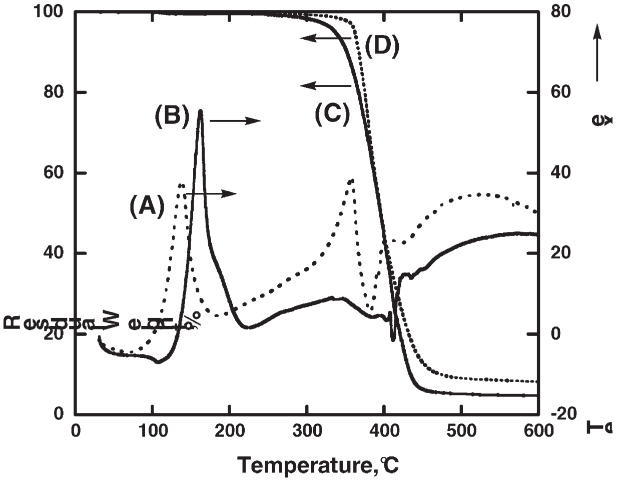

Figure 4.
TG/DTA curves of poly(**1**) and poly(**2**) at heating rate of 10 °C min^{-1}: (A) DTA curve of poly(**2**); (B) DTA curve of poly(**1**); (C) TG curve of poly(**1**); (D) TG curve of poly(**2**).

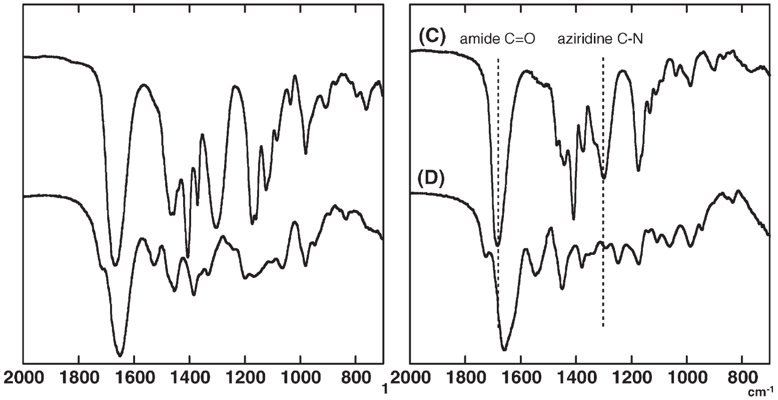

Figure 5.
IR spectra of poly(**1**) before (A) and after thermal treatment at 150 °C for 10 min (B). IR spectra of poly(**2**) before (C) and after thermal treatment at 150 °C for 10 min (D).

and 200 °C without weight losses of polymer in the DTA curves of poly(**1**) and poly(**2**). 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 of poly(**1**) and poly(**2**) were observed at 352 and 367 °C. Figure 5 shows the IR spectra of poly(**1**) and poly(**2**) before and after the thermal treatment at 150 °C for 10 min. The IR spectra after thermal treatments largely changed from the spectra of the parent polymers. In particular, the intensity of typical absorption attributed to aziridine rings around 1300 cm^{-1} drastically decreased after the thermal treatment, and the carbonyl absorptions around 1670 cm^{-1} shifted to 1650 cm^{-1}. It is very important that poly(**1**) and poly(**2**) after heating at 150 °C for 10 min became insoluble in any organic solvent. These observations strongly indicate that the intermolecular and/or intramolecular cross-linking occurs via the thermally induced ring-opening reaction of highly strained *N*-acylaziridine moieties.[31,32] This means that poly(**1**) and poly(**2**) possess potentials as thermosetting resins on heat curing. Figure 4 also indicates that the thermal stability of poly(**1**) was slightly higher than that of poly(**2**). The acryloyl poly(**2**) undergoes the cross-linking from 100 °C, while exothermic cross-linking of methacryloyl counterpart of poly(**1**) starts around 120 °C. It is noteworthy that poly(**1**) shows no change on the solubility and the IR spectrum is unchanged after the thermal treatment at 100 °C at least for 10 min. After the identical thermal treatment, poly(**2**) only swells in various solvents due to the cross-linking.

Conclusions

We have succeeded in the living anionic polymerizations of newly-synthesized *N,N*-dialkylmethacrylamide, **1**, possessing small strained aziridine ring. The polymerizations of **1** quantitatively gave the polymers having predicted M_ns and narrow MWD ($M_w/M_n = 1.1$), in contrast to the negative polymerizability of various *N,N*-dialkylmethacrylamides. We now believe that the polymerization of **MAz** possessing a non-substituted aziridine ring will be also controllable under the suitable polymerization conditions, although the occurrence of serious side reactions has been previously suggested.[15] The difference in the polymerizability of *N,N*-dialkylmethacrylamides can be well explained by the electron density of vinyl groups observed in the ^{13}C NMR chemical shifts.

Experimental Part

Materials

Monomer **1** was synthesized by the reaction of 2-methylaziridine and methacryloyl chloride in ether in 60% yield and was purified by the fractional vacuum distillation.[20] Tetrahydrofuran (THF) was refluxed over sodium wire, distilled from $LiAlH_4$, and then distilled from the sodium naphthalenenide solution on a vacuum line. 1,1-Diphenylethylene (DPE) was distilled from CaH_2 in vacuo, and diluted with dry THF. LiCl was dried under high vacuum conditions (10^{-6} mmHg) for 48 h. $ZnEt_2$ (TOSOH Akuzo Co.) was used as a THF solution. *s*-BuLi (KANTO Chemicals, 1 M, cyclohexane solution) was used without purification, and diluted with *n*-heptane. Ph_2CHK were prepared by the reactions of diphenylmethane and potassium naphthalenide in THF under argon at room temperature for 2 days. The concentration of initiator solutions were determined by colorimetric titration with 1-octanol in a sealed glass apparatus in vacuo.[33]

Anionic Polymerization

All anionic polymerizations were carried out in THF at −78 to 0 °C in an all-grass apparatus equipped with break-seals with vigorous shaking under high vacuum conditions (10^{-6} mmHg).[33] A small molar excess of DPE in THF was added to *s*-BuLi in *n*-heptane at −78 °C, and the characteristic red color of the initiator, DMPLi, appeared instantaneously. After 4–6 fold of LiCl was added to the initiator solution at −78 °C, the THF solution of monomer was added to the initiator system with vigorous stirring at −78 °C. On the addition of monomer, the characteristic red color of the initiator immediately disappeared. The, the polymerization was performed at various temperatures (−78, −40, and 0 °C). Polymerization was terminated with degassed isopropanol at −78 °C. The polymerization mixture was poured into hexane to precipitate a polymer. The resulting poly(**1**) was further purified by freeze-drying from benzene and characterized by NMR and IR spectroscopies and elemental analysis.

Kinetic Study of Polymerization of 1

Anionic polymerization of **1** was performed at −78 °C with DMPLi/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 at −78 °C. 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.

Thermal Treatment of Polymers

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.

Measurements

^1H and ^{13}C NMR spectra were recorded on a Bruker DPX300 spectrometer (300 MHz for ^1H 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 ^1H 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 was measured using a TOSOH HLC-8020 instrument equipped with two polystyrene gel columns (TOSOH TSK-GEL $\mathrm{GMH_{XL}} \times 2$) in DMF containing 0.01 M LiBr as an eluent at a flow rate of 1.0 mL min^{-1} at 40 °C with 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 250 °C, cooled to 20 °C, and then scanned at a rate of 10 °C min^{-1}.

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