DOI: 10.1002/masy.200750412

Anionic Polymerization of *N*-Methacryloyl-2-methylaziridine and *N*-Methacryloylazetidine

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Summary: Anionic polymerizations of *N*-methacryloyl-2-methylaziridine (**1**) and *N*-methacryloylazetidine (**2**) were carried out in THF with 1,1-diphenyl-3-methylpentyllithium (DMPLi) and with diphenylmethylpotassium (Ph_2CHK) in the presence of LiCl or Et_2Zn. Poly(**1**) and poly(**2**) possessing predicted M_ns based on the molar ratios between monomer to initiators and narrow molecular weight distributions (MWD, $M_w/M_n < 1.1$) were quantitatively obtained at −40 °C within 24 h. The stability of the propagating chain end of poly(**1**) was confirmed by the quantitative initiation efficiency in the postpolymerization. The radical polymerizations of **1** and **2** with AIBN gave the polymers in 77 and 40% yields, respectively. These are first examples demonstrating the positive polymerizability of *N*,*N*-dialkylmethacrylamide derivatives, while *N*,*N*-dimethylmethacrylamide showed the negative polymerizability under the radical and anionic polymerization conditions.

Keywords: living anionic polymerization; *N*,*N*-dialkylmethacrylamide; *N*-methacryloyl-2-methylaziridine; *N*-methacryloylazetidine

Introduction

It has been reported that *N*,*N*-dialkylacrylamides readily undergo the radical and anionic polymerizations to give the vinyl polymers. In particular, the stable living polymers are obtained by the anionic polymerization [1–6] and group transfer polymerization.[7] In contrast to a number of reports on the synthesis of poly(*N*,*N*-dialkylacrylamides), little attention has been paid to the polymerization of the methacrylamide counterparts because of their very low polymerizability under the radical and basic conditions. On the basis of ^1H and ^{13}C NMR chemical shifts and MNDO calculations, Kodaira [8] and Hogen-Esch[1] have suggested that the low polymerizability of *N*,*N*-dialkylmethacrylamides is derived from the twisted conformation between C=C and C=O groups due to the steric repulsion between α- methyl group and two bulky alkyl substituents on nitrogen. Interestingly, Yuki and Okamoto[9] have reported that *N*- methacryloylaziridine (MAz), a *N*,*N*-dialkylmethacrylamide derivative, can be polymerized with anionic or radical initiators, while the detailed results of polymerization have not been shown. This result strongly prompts us to investigate the polymerizability of *N*,*N*-dialkylmethacrylamides in detail by comparing the polymerization behavior of acrylamide counterparts.[1–6] In this study, we report the anionic polymerizations of newly-designed monomers, *N*-methacryloyl-2-methylaziridine (**1**) and *N*-methacryloylazetidine (**2**). These monomers possess strained 3- and 4-membered rings containing nitrogen similar to MAz.

Results and Discussion

Monomers **1** and **2** were synthesized by the reaction of methacryloyl chloride and

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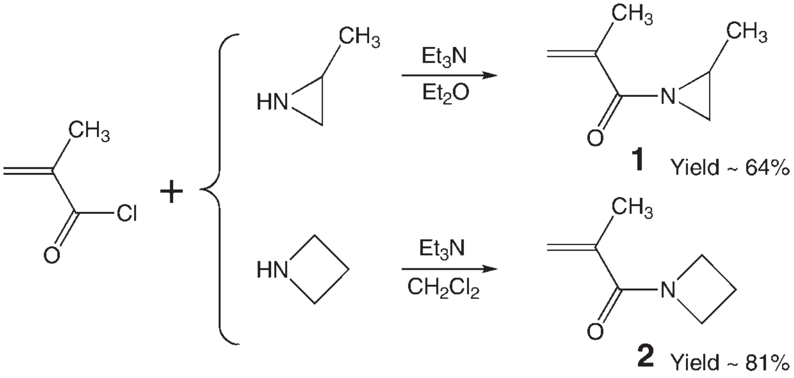

Scheme 1.

2-methylaziridine or azetidine in the presence of triethylamine in dry Et_2O or dry CH_2Cl_2, respectively, as shown in Scheme 1. Both monomers were purified by the repeating vacuum distillations from CaH_2 prior to the anionic polymerization. Anionic polymerizations of **1** and **2** were carried out with 1,1-diphenyl-3-methylpentyllithium (DMPLi), an adduct of *s*-BuLi and 1,1-diphenylethylene, diphenylmethyllithium (Ph_2CHLi), and diphenylmethylpotassium (Ph_2CHK) in THF at various temperatures (−78, −40, and 0 °C) in the presence of LiCl or $ZnEt_2$. It is demonstrated from the NMR analysis that the vinyl polymerizations of **1** and **2** exclusively occurred to give poly(**1**) and poly(**2**) quantitatively, and the highly strained aziridine and azetidine rings were intact during the course of the polymerizations. It is noteworthy that the *N*-acylaziridine moiety in **1** is stable under the strongly basic conditions, while several ring-opening reactions of *N*-acylaziridine derivatives with various nucleophiles have been reported.[10,11]

The results of polymerizations are summaried in Table 1. The polymerization of **1** with organopotassium initiators such as Ph_2CHK and $Ph_2CHK/ZnEt_2$[2,5,6] at −78 °C gave the poly(**1**) of relatively broad MWD ($M_w/M_n = 1.2–1.3$) in 82–100% yields. On the other hand, an organolithium initiator, DMPLi, gave a poly(**1**) of narrow

Table 1.
Anionic Polymerization of 1 and 2 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	72	100	6.1	7.2	1.05
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
2	Ph_2CHK/Et_2Zn	−78	72	0	–	–	–
2	Ph_2CHK/Et_2Zn	0	24	100	17	19	1.07
2	$Ph_2CHLi/LiCl$	−78	72	84	5.0	4.6	1.08
2	$Ph_2CHLi/LiCl$	−40	24	100	19	22	1.10

[a] M_n calcd = [monomer]/[initiator] X MW of monomer X conversion (%)/100 + MW of initiator residue.
[b] $M_n$obsd was estimated by ^{1}H 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.

MWD ($M_w/M_n = 1.14$) in 90% yield at $-78\,°C$ after 15 h. The MWDs of the resulting polymers effectively narrowed ($M_w/M_n < 1.1$), when 5–8 fold LiCl was added to the polymerization system as previously reported in the polymerizations of (meth)acrylates.[15,16] At elevated temperature of $-40\,°C$, the polymerization was completed within 2.5 h. The polymers obtained with DMPLi/LiCl at $-40\,°C$ also possessed the predicted molecular weights based on the molar ratios between monomer to initiator and the narrow MWDs. Even at $0\,°C$, a well-defined poly(**1**) was quantitatively obtained within 15 min. The stability of the propagating enolate anion derived from **1** was confirmed by a quantitative initiation efficiency in the postpolymerization at $-40\,°C$. Figure 1 shows a GPC curve of postpolymer shifts to the higher molecular weight region with keeping the narrow MWD, indicating the living character of polymerization system. Thus, the anionic polymerization of **1** smoothly gave the polymer similar to the case of MAz,[9] although **1** was categorized into a *N,N*-dialkylmethacrylamide derivative.

The anionic polymerization of **2** with either $Ph_2CHK/ZnEt_2$ or $Ph_2CHLi/LiCl$ initiator system proceeds very slowly compared to the polymerization of **1** under the similar conditions. No polymerization of **2** occurred with $K^+/ZnEt_2$ at $-78\,°C$ even after 72 h, while poly(**2**) was obtained with $Li^+/LiCl$ in 84% yield at $-78\,°C$ after 72 h. Complete consumption of **2** was attained with $K^+/ZnEt_2$ and $Li^+/LiCl$ initiator systems within 24 h at 0 or $-40\,°C$, respectively. Interestingly, the resulting poly(**2**)s always possessed narrow MWDs ($M_w/M_n < 1.1$). The M_ns of poly(**2**) estimated by ^1H NMR agreed with the calculated values.

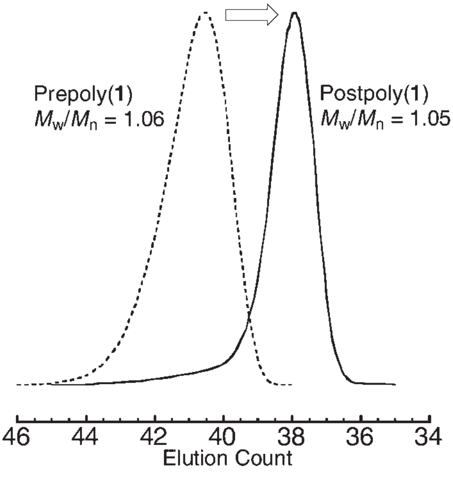

Figure 1.
GPC curves of poly(1) obtained in the postpolymerization. Polymerization of 1 was carried out with DMPLi/LiCl in THF at $-40\,°C$.

These results clearly demonstrate the anionic polymerizability of **1** and **2** in sharp contrast to the negligible one of *N,N*-dimethylmethacrylamide (DMMA) under the identical reaction conditions. Furthermore, the free-radical polymerizations of **1** and **2** with AIBN gave the polymers in 77 and 40% yields, respectively, while no polymeric product was obtained from DMMA. This suggests the possibility of controls on the molecular structures of poly(**1**) and poly(**2**) via the controlled/living radical polymerization. On the basis of ^1H and ^{13}C NMR, this different polymerizability can be attributed to the lack of amide conjugation in **1** and **2**, arisen from the strained aziridine and azetidine moieties.[8,12–14] This leads to the effective resonance between carbonyl and vinyl groups to result in the positive polymerizability of **1** and **2**. In fact, the ^{13}C NMR chemical shifts of vinyl β-carbons of **1**, **2**, and DMMA were observed at 125, 119, and 115 ppm, respectively. These values clearly indicate the lower π-electron densities of vinyl groups and the higher anionic polymerizabilities in **1** and **2**, compared to DMMA.

Poly(**1**) and poly(**2**) were soluble in $CHCl_3$, THF, DMF, and methanol but insoluble in hexane. It is noteworthy that poly(**2**) is readily soluble in water, indicating the high polarity of azetidine functionality. The glass transition temperatures (T_g) of poly(**1**) and poly(**2**) were observed at 185 and 170 °C, respectively by the DSC measurement.

In conclusion, we have succeeded in the anionic polymerizations of newly-synthesized

N,*N*-dialkylmethacrylamides, **1** and **2**, possessing small strained aziridine and azetidine rings. The polymerizations of **1** and **2** quantitatively gave the polymers having predicted M_ns and narrow MWD ($M_w/M_n = 1.1$), although they are *N*,*N*-dialkylmethacrylamides showing poor polymerizability. This is a first successful example of living polymerization of *N*,*N*-dialkylmethacrylamide. 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

Commercially available 2-methylaziridine and azetidine hydrochloride were used without purification. Methacryloyl chloride was purified by the fractional vacuum distillation. Triethylamine was distilled from CaH_2 under nitrogen. 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) and diphenylmethane were distilled from CaH_2 in vacuo, and diluted with dry THF. Isopropanol was distilled from Mg, and then 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_2CHLi and Ph_2CHK were prepared by the reactions of diphenylmethane and the corresponding metal naphthalenides 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.[17]

Synthesis of 1

Methacryloyl chloride (13.4 g, 129 mmol) in diethyl ether (45 mL) was added dropwise to a mixture of 2-methylaziridine (8.01 g, 140 mmol) and triethylamine (14.4 g, 143 mmol) in diethyl ether (140 mL) at 0 °C under nitrogen. The reaction mixture was stirred at room temperature for 3 h. After filteration to remove the precipitated ammonium salt, the filtrate was distilled under the reduced pressure repeatedly to give a colorless liquid of **1** (bp 61–62 °C/14 mmHg, 10.3 g, 82.6 mmol, 64%).

1:^{1}H NMR ($CDCl_3$, 300 MHz): $\delta = 1.34$ (d, 3H, $J = 5.4$ Hz, CH_3 (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 ($CDCl_3$, 75 MHz): $\delta = 17.7$ (CH_3 (aziridine ring), 18.6 (CH_3), 31.8 (CH_2), 34.3 (CH), 124.5 (CH_2=), 139.8 (=C–), 180.6 (C=O).

Synthesis of 2

Methacryloyl chloride (10.28 g, 98.3 mmol) in 20 mL of dichloromethane was added dropwise to a mixture of azetidine hydrochloride (9.06 g, 96.8 mmol) and triethylamine (20.17 g, 199 mmol) in dichloromethane (80 mL) at 0 °C under nitrogen. After the addition, stirring was continued at room temperature for 12 h. After filteration to remove the precipitated ammonium salt, the filtrate was washed with saturated $NaHCO_3$ solution and with saturated NaCl solution. The aqueous layer was extracted with dichloromethane, and the combined organic layer was dried over $MgSO_4$. After filteration and evaporation, the crude product was distilled twice under reduced pressure to yield a colorless liquid of **2** (bp 80–81 °C/4 mmHg, 9.82 g, 78.6 mmol, 81%).

2:^{1}H NMR ($CDCl_3$, 300 MHz): $\delta = 1.92$ (s, 3H, CH_3), 2.28 (m, 2H, CH_2), 4.08 (br, 2H, NCH_2 (cis to carbonyl)), 4.23 (br, 2H, NCH_2 (trans to carbonyl)), 5.29 and 5.36 (2s, 2H, CH_2=). ^{13}C NMR ($CDCl_3$, 75 MHz): $\delta = 15.8$ (CH_2), 19.4 (CH_3), 48.3 (CH_2 (cis to carbonyl)), 52.7 (CH_2 (trans to carbonyl)), 119.0 (CH_2=), 138.3 (=C–), 170.9 (C=O).

The monomers **1** and **2** were further purified by the repeating vacuum distillations over CaH_2. The purified monomer and CaH_2 were sealed off in an all-glass apparatus equipped with a break-seal under the vacuum conditions. After dilution with dry THF, the monomers were stirred over CaH_2 overnight and distilled on a vacuum line. The monomers were diluted with dry THF (0.5–0.8 M) and stored prior to the polymerization in the ampule equipped with a break-seal at –30 °C.

Polymerization

All the polymerizations were carried out in THF under high vacuum conditions (10^{-6} mmHg) in a sealed all-glass apparatus equipped with break-seals.[17] 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). The reaction was terminated with a degassed isopropanol at −78 °C. The reaction mixture was concentrated by evaporation, and was poured into hexane at 0 °C to precipitate the polymer. The isolated polymer was purified by freeze-drying from the benzene solution.

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. GPC was measured using a TOSOH HLC-8020 instrument equipped with two polystyrene gel columns (TOSOH TSK-GEL $GMH_{XL} \times 2$) in DMF containing 0.01 M LiBr as an eluent at a flow rate of $1.0\,mL \cdot min^{-1}$ 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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