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Living Anionic Polymerization of *N*-Methacryloylazetidine: Anionic Polymerizability of *N,N*-Dialkylmethacrylamides

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ABSTRACT: Anionic polymerization of a series of *N,N*-dialkylmethacrylamides such as *N*-methacryloylazetidine (**M4**), *N*-methacryloylpyrrolidine (**M5**), and *N*-methacryloylpiperidine (**M6**) was carried out with diphenylmethyllithium (Ph_2CHLi) or diphenylmethylpotassium (Ph_2CHK) in the presence of LiCl or Et_2Zn in THF to clarify the relationship between polymerizability and monomer structure. Poly(**M4**)s possessing predicted molecular weights and very narrow molecular weight distributions ($M_w/M_n < 1.1$) were obtained quantitatively with Ph_2CHLi/LiCl or Ph_2CHK/Et_2Zn at −40 to 0 °C within 24 h. From the polymerizations of **M4** at the various temperatures ranging from −40 to −20 °C, the apparent rate constant and the activation energy of the anionic polymerization were determined as follows: $\ln k_p^{ap} = -6.17 \times 10^3/T + 22.4$ L mol^{-1} s^{-1} and 51 ± 5 kJ mol^{-1}, respectively. Compared to the previous report on the anionic polymerization of *N*-methacryloyl-2-methylaziridine (**M3**), the polymerization rate of **M4** was significantly slower and the activation energy was slightly larger, indicating the lower polymerizability of **M4**. The acryloyl counterpart, *N*-acryloylazetidine (**A4**), also underwent the anionic polymerization to afford the well-defined polymer quantitatively. The polymerizations of **M5** gave the polymers in 30−77% yields but did not complete even after 1 week at 0 °C. By contrast, no polymer was obtained from the anionic polymerization system of **M6** similar to the case of *N,N*-dimethylmethacrylamide (DMMA). From the experimental results, it was demonstrated that the polymerizability of a series of *N,N*-dialkylmethacrylamides with cyclic substituents decreased drastically with increasing the ring size from three to six (**M3** > **M4** > **M5** ≫ **M6** = DMMA). The observed relative polymerizability was well correlated with the chemical shifts of vinyl β-carbons for monomers in the ^{13}C NMR spectra. The NMR data suggested that the polymerizable **M3** and **M4** attained effective conjugation between C═C and C═O double bonds, while **M5**, **M6**, and DMMA had negligible conjugation effects.

Introduction

The living/controlled polymerizations of polar monomers such as acrylates and methacrylates, α,β-unsaturated esters, have been intensely studied under the various conditions from the synthetic viewpoints and the industrial interest.[1] In fact, the controls on molecular architectures such as molecular weight, molecular weight distribution (MWD), and stereoregularity of their (co)polymers are realized in those studies to design the properties of new functional materials. Similar to the esters, α,β-unsaturated amides such as acrylamide, methacrylamide, and their *N*-monoalkyl-substituted derivatives readily undergo the vinyl polymerization under the radical conditions,[2,3] while the anionic vinyl polymerization is often accompanied by the hydrogen transfer polymerization because of the highly acidic amide hydrogen of the monomers.[4] On the other hand, it has been reported that *N,N*-dialkylacrylamides readily undergo the radical and anionic polymerizations to afford the vinyl polymers.[5−9] The formation of stable living polymers is also achieved in the anionic polymerization[5−8] and the group transfer polymerization[9] of various *N,N*-dialkylacrylamides.

Among the polar monomers carrying the electron-withdrawing substituents, the *N,N*-dialkylmethacrylamides such as *N,N*-dimethylmethacrylamide (DMMA) show the very strange negative polymerizability under the various reaction conditions.[2,10−14] In fact, a number of research groups have reported that *N,N*-dialkylmethacrylamides are difficult to polymerize with the radical or anionic initiators. The only structural difference between DMMA and the polymerizable acryloyl counterpart, *N,N*-dimethylacrylamide (DMA), is the presence of α-methyl substituent on the acryloyl framework. On the basis of ^{1}H and ^{13}C NMR study and MNDO calculations, Kodaira[15] and Hogen-Esch[5] have suggested that DMMA takes twisted conformation between vinyl and carbonyl groups probably due to the intramolecular steric repulsion between α-methyl or $CH_2=$ group and *N*-alkyl substituents. The twisted conformation should lead to the reduced π-conjugation between C═C and C═O double bonds, lowering the polymerizability of DMMA significantly.

As an exception, *N*-methacryloylaziridine (MAz), a particular *N,N*-dialkylmethacrylamide possessing small and highly strained three-membered aziridine ring, can be polymerized with either radical[16,17] or anionic[17] initiators to give vinyl polymers. In the preceding paper, we have also found that *N*-methacryloyl-2-methylaziridine (**M3**), 2-methyl-substituted derivative of MAz, readily undergoes the vinyl polymerization under the basic conditions to form the stable anionic living polymer.[18] The poly(**M3**)s possessing the predicted molecular weights and the very narrow MWDs ($M_w/M_n < 1.1$) are obtained in quantitative yields. The stability of pendant aziridine ring during the anionic polymerization is noteworthy, since the ring-opening and

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isomerization reactions of *N*-acylaziridines with various nucleophiles have been reported in the organic synthesis.[19] Very recently, Chen and co-workers also succeeded in the coordination–addition polymerization of **M3** with transition metal catalysts,[20] although **M3** possessed the strained aziridine rings activated with the electron-withdrawing *N*-acyl moiety. Thus, considering the striking findings that only **MAz** and **M3** can be polymerized, we postulate that the strained cyclic moiety as three-membered aziridine ring is essential to realize the polymerization of *N*,*N*-dialkylmethacrylamides. In contrast to the usual carboxylic amides possessing the planarity in (O=C)–NR$_2$ moiety, various aziridine amides are recognized as nonplanar amide showing characteristic features on conformation and spectroscopic properties.[21] This nonplanarity in aziridine amides is mainly derived from the pyramidal geometry of nitrogen in the highly strained three-membered ring, and it might play an important role to result in the positive polymerizability of MAz and **M3**.[16−18,20]

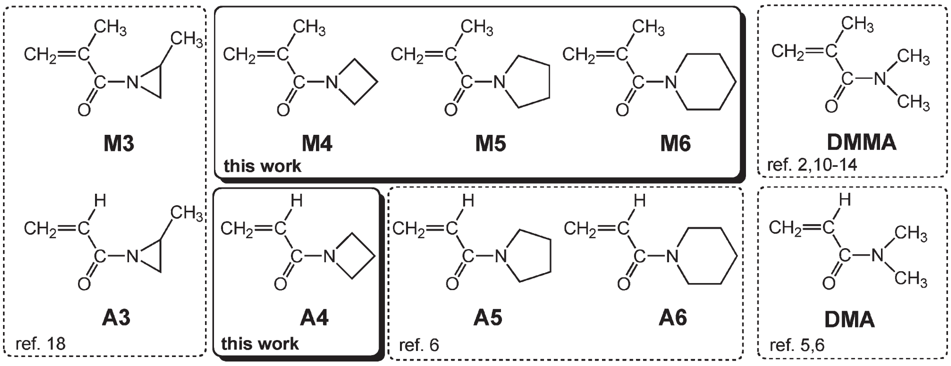
In this study, a series of monomers possessing four-, five-, and six-membered rings, *N*-methacryloylazetidine (**M4**), *N*-methacryloylpyrrolidine (**M5**), and *N*-methacryloylpiperidine (**M6**), are therefore synthesized purposefully to compare the relative polymerizability with **M3** (Chart 1). Since the ring strain continuously and drastically decreases with increasing the substituted ring size of monomers from **M3** to **M6**, the varying polymerization behaviors as a function of ring size are of great interest. We have already reported that the anionic polymerizations of the corresponding acryloyl monomers possessing aziridine, pyrrolidine, and piperidine rings, **A3**,[18] **A5**,[6] and **A6**,[6] proceed smoothly and afford the vinyl polymers quantitatively as in the case of DMA.[5,6] Herein, we also attempt to polymerize *N*-acryloylazetidine (**A4**) possessing four-membered ring as a counterpart of **M4** to verify the general positive polymerizability of acryloyl monomers.

Results and Discussion

Anionic Polymerization of M4. Anionic polymerization of **M4** was carried out with 1,1-diphenyl-3-methylpentyllithium (DMPLi), an adduct of *sec*-BuLi and 1,1-diphenylethylene, diphenylmethyllithium (Ph$_2$CHLi), diphenylmethylsodium (Ph$_2$CHNa), and diphenylmethylpotassium (Ph$_2$CHK) in THF at various temperatures (−78, −40, −20, and 0 °C). In most cases, LiCl or Et$_2$Zn was added to the polymerization system as an additive to control the polymerization of **M4**, as in the polymerization of **M3**.[18] After quenching the polymerization with degassed methanol, the polymerization solution was poured into a large excess of diethyl ether. Then, the precipitated polymer was collected by filtration and analyzed by ^{1}H and ^{13}C NMR and IR spectroscopies and elemental analysis. ^{13}C NMR spectra of **M4** and a polymer obtained with Ph$_2$CHLi/LiCl at −40 °C are shown in Figure 1. After the polymerization of **M4**, two signals corresponding to α and β vinyl carbons at 138.5 and 119.1 ppm disappeared completely, and signals of methylene carbon and quaternary carbon in main chain newly appeared at 52 and 45.5−47.0 ppm, respectively. Furthermore, after the polymerization reaction, three carbon signals assigned to azetidine ring remained at the similar region of **M4**. It is noteworthy that the two CH$_2$ groups adjacent to azetidine nitrogen (signals e and f in Figure 1) are nonequivalent in the both spectra of **M4** and poly(**M4**), indicating the restricted rotation between C=O and amide nitrogen on azetidine ring in the monomer and the resulting polymer. These spectra clearly indicate that the vinyl polymerization of **M4** successfully proceeds, and the strained azetidine moiety is intact during the course of the polymerization.

The results of anionic polymerization of **M4** are summarized in Table 1. The polymerization of **M4** with either DMPLi or Ph$_2$CHLi successfully gave a polymer in the presence of LiCl at −78 °C (runs 1 and 2). However, the resulting polymer precipitated at −78 °C during the course of the polymerization, and the polymer yields were not quantitative (72−84%) even after 96 h reaction. At elevated temperature at −40 °C, the polymerization of **M4** proceeded homogeneously and completed within 15 h (run 3). The molecular weight of poly(**M4**) was estimated from the ^{1}H NMR by using end-group analysis of the initiator residue containing aromatic protons. The M_n of poly(**M4**) agreed well with the calculated value estimated by the molar ratio between **M4** and Ph$_2$CHLi. The size exclusion chromatography (SEC) showed unimodal trace, and the MWD was narrow (M_w/M_n = 1.11).[22] Similarly, poly(**M4**)s with very narrow MWDs were produced with Ph$_2$CHLi/LiCl in quantitative yields at −40 °C within 24 h (runs 4 and 5).[23] It is noticeable that the well-defined poly(**M4**)s quantitatively yielded even at higher temperatures of −20 and 0 °C (runs 6 and 7). We next employed Lewis acidic Et$_2$Zn as the effective additive for the polymerization of various polar monomers.[6−8,24,25] The polymerization reaction with Ph$_2$CHLi/Et$_2$Zn seemed slightly slower compared with the system of Ph$_2$CHLi/LiCl, and most of monomer was consumed within 24 h at 0 °C. The poly(**M4**)s obtained with Ph$_2$CHLi/Et$_2$Zn also possessed narrow MWDs (M_w/M_n < 1.2). Interestingly, poly(**M4**) with controlled chain structures quantitatively formed at −40 °C, when the polymerization of **M4** was conducted with Ph$_2$CHLi in the absence of additives (run 10). The MWD of the polymer was slightly broadened (M_w/M_n = 1.27) in the polymerization performed with Ph$_2$CHLi at 0 °C (run 11). Ph$_2$CHNa also induced the polymerization of **M4** at −40 °C to form a polymer having predicted M_n and narrow MWD either in the presence or in the absence of Et$_2$Zn. In the presence of Lewis acidic

Chart 1



Et_2Zn, the polymerization proceeded much slower and did not complete even after 72 h at −40 °C, while the polymerization initiated with Ph_2CHNa completed within 13 h. We then attempted to polymerize **M4** with organopotassium initiator (Ph_2CHK) in the presence of Et_2Zn. No apparent polymerization of **M4** virtually occurred with Ph_2CHK/Et_2Zn at −78 °C even after 72 h (run 14). This is sharp contrast to the polymerization behavior initiating with organolithium initiator at −78 °C (runs 1 and 2). On the other hand, complete consumption of **M4** was attained at 0 °C after 24 h (runs 17−19), although monomer conversion was still 20% at −40 °C after 15 h (run 15). The binary system of Ph_2CHK/Et_2Zn always gave the poly(**M4**)s possessing very narrow MWDs ($M_w/M_n < 1.1$, runs 16−19), while the polymer obtained at higher [M]/[I] ratio (run 19) showed the apparent deviation between the observed molecular weight ($M_n = 55\,000$) and the calculated value ($M_n = 29\,000$).[23] Finally, we carried out the direct polymerization of **M4** with Ph_2CHK at 0 °C for 16 h (run 20). The polymerization reaction completely proceeded to afford the well-defined poly(**M4**), while the MWD was slightly broad ($M_w/M_n = 1.17$).

We also attempted to polymerize **M4** under the radical conditions with AIBN in toluene at 70 °C. The conversion of **M4** reached 40% after 72 h, and the resulting polymeric products were oligomers possessing very low molecular weight ($M_n < 500$). It is thus demonstrated that **M4** also undergoes the radical polymerization as well as the anionic polymerization; even **M4** is a derivative of *N*,*N*-dialkylmethacrylamide showing nonpolymerizability. From the viewpoints of polymerization rate and the yield, the relative polymerizability of **M4** under the anionic and radical conditions is apparently lower than that of **M3**.[18] In particular, compared to the anionic polymerization of **M3**, higher polymerization temperature and longer polymerization time are required for the completion of the polymerization of **M4**.

Stereoregularity of Poly(M4). In this section, we focused on the tacticity of poly(**M4**)s. In the ^{13}C NMR spectra of poly(**M4**)s measured in DMSO-d_6 at 75 °C, the split signals assigned to α-methyl carbon were observed around 18.0−21.7 ppm. We postulated that the tacticity of poly(**M4**) was observed same as that of poly(methyl methacrylate) (PMMA).[24] The α-methyl carbon signals were therefore assigned to *rr* (18.0−18.7 ppm), *mr* (19.2−19.8 ppm), and

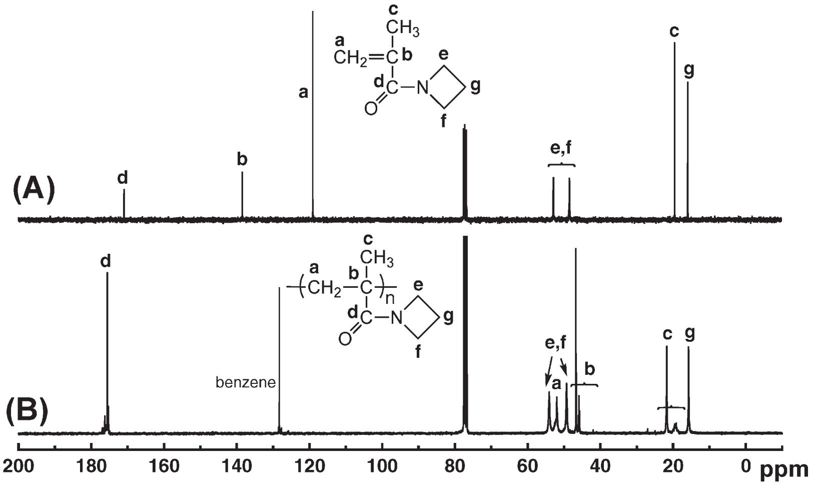


Figure 1. ^{13}C NMR spectra of **M4** (A) and poly(**M4**) obtained with $Ph_2CHLi/LiCl$ (B) measured in $CDCl_3$.

Table 1. Anionic Polymerization of M4 in THF

							$M_n \times 10^{-3}$			tacticity,[d] %		
run	**M4**, mmol	initiator, mmol	additive, mmol	temp, °C	time, h	conversion, %	calcd[a]	obsd[b]	M_w/M_n[c]	*mm*	*mr*	*rr*
1	6.69	DMPLi, 0.147	LiCl, 0.589	−78	72	84	5.0	4.6	1.09	92	8	< 1
2	5.91	Ph_2CHLi, 0.0693	LiCl, 0.317	−78	96	72	11	14	1.14	93	7	< 1
3	6.32	Ph_2CHLi, 0.115	LiCl, 0.437	−40	15	100	7.0	6.7	1.11	72	23	5
4	6.98	Ph_2CHLi, 0.0471	LiCl, 0.195	−40	24	100	18	19	1.05	70	25	5
5	10.9	Ph_2CHLi, 0.0456	LiCl, 0.286	−40	24	100	29	50	1.10	73	23	4
6	12.2	Ph_2CHLi, 0.0989	LiCl, 0.418	−20	2.5	100	16	15	1.07	72	23	5
7	7.36	Ph_2CHLi, 0.0610	LiCl, 0.396	0	2	100	15	18	1.05	68	27	5
8	6.57	Ph_2CHLi, 0.0270	Et_2Zn, 0.464	−40	36	85	26	39	1.06	27	54	19
9	6.76	Ph_2CHLi, 0.0930	Et_2Zn, 1.17	0	24	98	9.3	7.8	1.17	38	45	17
10	6.25	Ph_2CHLi, 0.0439		−40	16	100	18	23	1.08	60	33	7
11	5.79	Ph_2CHLi, 0.0906		0	16	100	8.1	9.8	1.27	55	35	10
12	7.62	Ph_2CHNa, 0.0731	Et_2Zn, 1.14	−40	72	69	9.2	6.9	1.06	11	57	32
13	8.15	Ph_2CHNa, 0.0594		−40	13	100	17	19	1.13	52	42	6
14	5.93	Ph_2CHK, 0.108	Et_2Zn, 1.25	−78	72	0	7.0					
15	6.83	Ph_2CHK, 0.100	Et_2Zn, 1.15	−40	15	20	1.7	1.5				
16	6.89	Ph_2CHK, 0.0755	Et_2Zn, 0.896	0	5	91	11	15	1.10			
17	6.83	Ph_2CHK, 0.105	Et_2Zn, 1.25	0	24	100	8.3	7.2	1.06	14	60	26
18	7.18	Ph_2CHK, 0.0521	Et_2Zn, 0.669	0	24	100	17	19	1.07	13	62	25
19	9.25	Ph_2CHK, 0.0398	Et_2Zn, 0.572	0	24	100	29	55	1.09	15	62	23
20	6.52	Ph_2CHK, 0.0692		0	16	100	12	16	1.17	12	54	34

[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 ^1H NMR. [c] M_w/M_n was obtained by SEC calibration using polystyrene standards in DMF containing 0.01 M LiBr. [d] The triad tacticity was determined by the ^{13}C NMR measurment in DMSO-d_6 at 75 °C.

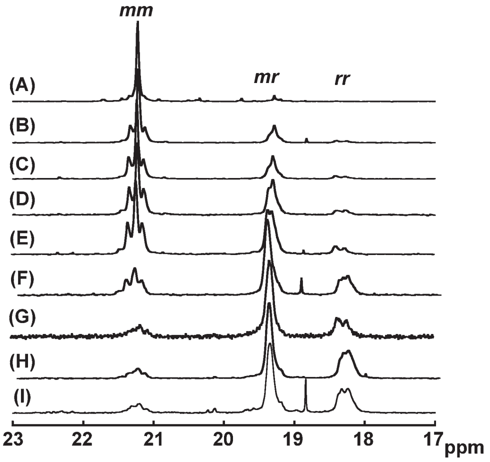


Figure 2. ^{13}C NMR spectra of α-methyl carbon of poly(**M4**)s measured in DMSO-d_6 at 75 °C: (A) DMPLi/LiCl at −78 °C, *mm*/*mr*/*rr* = 92/8/<1; (B) $Ph_2CHLi/LiCl$ at −40 °C, *mm*/*mr*/*rr* = 72/23/5; (C) $Ph_2CHLi/LiCl$ at 0 °C, *mm*/*mr*/*rr* = 68/27/5; (D) Ph_2CHLi at −40 °C, *mm*/*mr*/*rr* = 60/33/7; (E) Ph_2CHNa at −40 °C, *mm*/*mr*/*rr* = 52/42/6; (F) Ph_2CHLi/Et_2Zn at −40 °C, *mm*/*mr*/*rr* = 27/54/19; (G) Ph_2CHK/Et_2Zn at 0 °C, *mm*/*mr*/*rr* = 13/62/25; (H) Ph_2CHK at 0 °C, *mm*/*mr*/*rr* = 12/54/34; (I) Ph_2CHNa/Et_2Zn at −40 °C, *mm*/*mr*/*rr* = 11/57/32.

mm (21.1−21.7 ppm) triads in series. A series of expanded ^{13}C NMR spectra of poly(**M4**) are shown in Figure 2, and the tacticity estimated from the relative signal intensity is summarized in Table 1. The stereoregularity of the poly(**M4**) is largely changed by the polymerization conditions, as can be seen in Figure 2.

The *mm* contents of poly(**M4**)s produced with Ph_2CHLi, Ph_2CHNa, and Ph_2CHK at 0 or −40 °C were 55−60, 52, and 12%, respectively. On the other hand, *mr* contents were 33−35 (Li^+), 42 (Na^+), and 54% (K^+) and evidently increased with the radius of the counterion. These data strongly indicate the significant effect of counterion on the stereoregularity, while the effect of polymerization temperature is also observed. The smaller cation induces the isotactic configurations of poly(**M4**), but the larger one prefers the heterotactic configurations. Apparently, the stereoregularity of the poly(**M4**) changed after the addition of Lewis acidic Et_2Zn. In each case of polymer obtained with Ph_2CHM/Et_2Zn, the *mr* content was predominant. In fact, the binary initiator systems of Ph_2CHLi/Et_2Zn and Ph_2CHNa/Et_2Zn at 0 or −40 °C afforded heterotactic configurations, *mr* = 45−57%, similar to the cases of Ph_2CHK/Et_2Zn at 0 °C (*mr* = 60−62%). More interestingly, addition of LiCl to Ph_2CHLi caused a significant change of the stereoregularity of the resulting poly(**M4**)s. When 6-fold LiCl was added to the polymerization system at 0 °C, the *mm* content of the resulting poly(**M4**) increased from 55% (run 11) to 68% (run 7). A similar tendency was observed in the polymerization systems at −40 °C, and the *mm* content changed from 60 (run 10, without LiCl) to 70−73% (runs 3−5, with LiCl). In the presence of LiCl, the *mm* content tended to increase with lowering the polymerization temperature and reached 93% at −78 °C. Thus, we have found that the addition of LiCl or Et_2Zn to the organolithium initiator induces isotactic-specific or atactic polymerization of **M4**, respectively. From the synthetic viewpoint, the tacticity of poly(**M4**) can be tuned by changing the counterion of initiator, the additive, and the polymerization temperature. A similar relationship between initiator systems and stereoregularity has been observed in the anionic polymerization of *N*,*N*-diethylacrylamide[6,7] and *N*-methoxymethyl-*N*-isopropylacrylamide.[8]

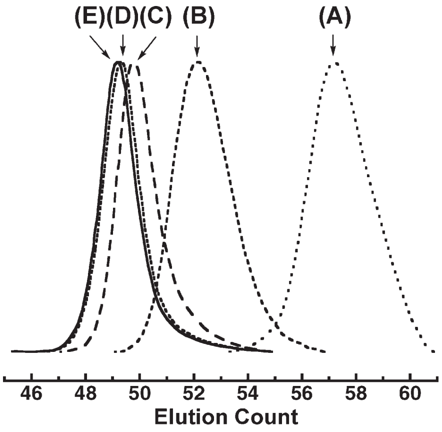


Figure 3. SEC traces of a series of poly(**M4**)s obtained with DMPLi in the presence of 4.2-fold LiCl in THF at −20 °C: (A) after 5 min, 36% conversion, M_n = 3300, M_w/M_n = 1.05; (B) after 21 min, 63% conversion, M_n = 7600, M_w/M_n = 1.08; (C) after 51 min, 84% conversion, M_n = 12 000, M_w/M_n = 1.07; (D) after 95 min, 97 conversion, M_n = 14 000, M_w/M_n = 1.07; (E) after 160 min, 100% conversion, M_n = 15 000, M_w/M_n = 1.07.

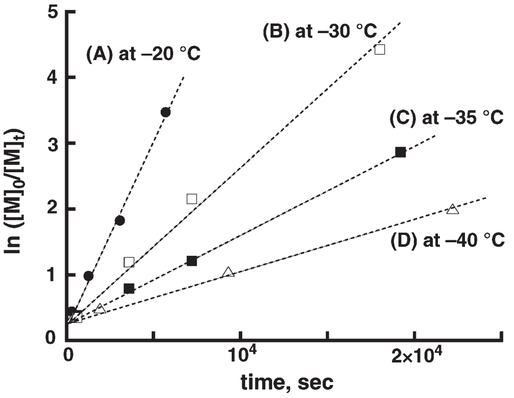


Figure 4. First-order plots for the polymerization of **M4** at $[M]_0$ = 0.48−0.50 M and $[I]_0$ = (3.8−4.2) × 10^{-3} M: (A) at −20 °C, (B) at −30 °C, (C) at −35 °C, (D) at −40 °C.

Kinetic Studies of Polymerization for M4. We herein compare the relative polymerizability of **M4** and **M3** from the kinetic viewpoint in detail. The monomer conversion was analyzed by the GLC measurement of the residual monomer. Figure 3 shows a series of SEC traces of poly(**M4**)s obtained with DMPLi/LiCl (4.2 equiv) in THF at −20 °C. The SEC traces clearly shift from the lower molecular weight region to the higher side, as the conversion of **M4** increases with the polymerization time. In each case, the resulting polymer maintains the unimodal and narrow MWD. It is proven from the SEC trace shift that no chain transfer and termination reaction occur during the polymerization reaction of **M4** at −20 °C. We then attempted to polymerize **M4** with DMPLi/LiCl at −30, −35, and −40 °C in order to estimate the polymerization rate at each temperature. The initial concentration of DMPLi, $[I]_0$, was regulated between 3.8 × 10^{-3} and 4.2 × 10^{-3} M, and the content of LiCl was controlled in range of 4.2−4.6 equiv against DMPLi. At all temperatures, the first-order plots showed good linearity within the experimental error, as shown in Figure 4. This clearly verifies that the concentration of the propagating enolate anion derived from **M4** is almost constant during the polymerization under the employed conditions. Next, the k_p^{ap} value at each temperature was calculated from the slope of first-order plot shown in Figure 4. The k_p^{ap} values strongly

Table 2. Rate Constants of Anionic Polymerization of M4[a]

temperature, °C	k_p^{ap}, L mol^{-1} s^{-1}
−20	0.129 ± 0.01
−30	0.0540 ± 0.005
−35	0.0297 ± 0.003
−40	0.0157 ± 0.002

[a] In THF in the presence of 4.2−4.6-fold LiCl.

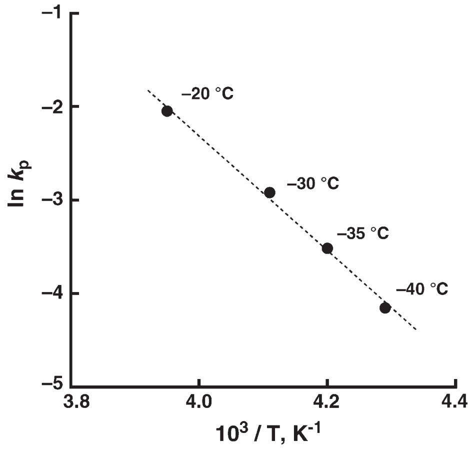


Figure 5. Arrhenius plots of k_p for the polymerization of **M4** with DMPLi and 4.2−4.6-fold LiCl in THF.

depended on the polymerization temperature, and varied from 0.129 L mol^{-1} s^{-1} at −20 °C to 0.0157 L mol^{-1} s^{-1} at −40 °C, as listed in Table 2. It has been demonstrated that the k_p^{ap} values of the polymerization for **M3** are 0.165 L mol^{-1} s^{-1} at −40 °C and 0.0169 L mol^{-1} s^{-1} at −60 °C.[18] Thus, the observed k_p^{ap} value of **M4** is ~10 times smaller than that of **M3** under the similar polymerization conditions. The Arrhenius plots of k_p^{ap} for the anionic polymerization of **M4** are drawn in Figure 5, and the relationship between k_p^{ap} and the polymerization temperature is expressed in the equation

$$\ln k_p^{ap} = -6.17 \times 10^3/T + 22.4 \text{ L mol}^{-1} \text{ s}^{-1} \qquad (1)$$

The activation energy of the polymerization, ΔE_a^{ap}, of **M4** was calculated to be 51 ± 5 kJ mol^{-1} from eq 1. This ΔE_a^{ap} was close to the reported value of **M3** (49 ± 4 kJ mol^{-1}) but was slightly larger, supporting the lower polymerizability of **M4** compared to **M3** as discussed in the preceding section. It should be emphasized that the ΔE_a^{ap}s of **M3** and **M4** were significantly larger than the reported values of anionic polymerization of methyl methacrylate (MMA, 20−25 kJ mol^{-1}) under similar conditions.[26] The low anionic polymerizability of **M4** is thus realized by the kinetic data such as small rate constant and large activation energy of polymerization for **M4**. The relative anionic polymerizability among **M3**, **M4**, and MMA is clearly determined as follows: **M4** < **M3** ≪ MMA.

Anionic Polymerization of A4. We next polymerized **A4**, acryloyl counterpart of **M4**, under similar conditions. The results of the polymerization of **A4** are summarized in Table 3. In each case, the polymerization of **A4** with either Ph_2CHLi or Ph_2CHK at 0 or −78 °C proceeded quantitatively. The direct initiation of **A4** with Ph_2CHLi gave a poly(**A4**) of broad MWD (M_w/M_n = 1.45). When LiCl was added to the polymerization solution (run 22), the MWD was further broadened (M_w/M_n = 1.65). By contrast, the poly(**A4**)s with narrow MWDs (M_w/M_n < 1.11) were obtained, when the polymerizations were performed with Ph_2CHLi in the presence of 14−35-fold Et_2Zn at −78 and 0 °C (runs 23−25). In addition, the M_ns of the resultant poly(**A4**) were in accordance with the calculated values. Poly(**A4**)s were similarly obtained with Ph_2CHK in 100% yields (run 26). Similar to the polymerization systems using organolithium initiator, the addition of Et_2Zn (13−31 equiv) to Ph_2CHK was very effective to narrow the MWD. The well-defined poly(**A4**)s were obtained when Et_2Zn was introduced to the polymerization system at −78 or 0 °C. The radical polymerization of **A4** with AIBN at 70 °C in toluene for 4 h afforded the polymer in 100% yield.

The diad tacticity of poly(**A4**) was determined from the signal intensity of main chain methylene protons in the ^{1}H NMR measurement (Table 3). Figure 6 shows a series of ^{1}H NMR spectra of poly(**A4**)s synthesized by the anionic polymerization at −78 °C. As a general trend, *m*-rich poly(**A4**)s were produced by the anionic polymerization, while the radical polymerization induced the atactic configuration (*m*:*r* = 57:43). The *m* contents of poly(**A4**)s obtained with Ph_2CHLi and Ph_2CHK were 79 and 86%, respectively. The addition of LiCl to Ph_2CHLi initiator slightly increased the *m* content to 85%. On the other hand, the addition of Lewis acidic Et_2Zn to Ph_2CHLi resulted in the lower meso-diad in addition to the narrowing the MWD of polymer. A similar additive effect of Et_2Zn was observed in the polymerization with Ph_2CHK.

Thus, we have realized that **A4** possessing the strained azetidine ring also undergoes the anionic polymerization in the controlled fashion similar to the cases of a series of *N*,*N*-dialkylacrylamides such as **A3**,[18] **A5**,[6] **A6**,[6] and DMA.[5,6] In both cases of **A4** and **M4**, well-defined polymers quantitatively yielded by tuning the reaction conditions, and the stereoregularity of polymers was affected by the counterion of initiators and by the additives.

Attempts of Anionic Polymerizations for M5, M6, and DMMA. We finally attempted to polymerize *N*,*N*-dialkylmethacrylamides carrying five-membered pyrrolidine ring (**M5**) and six-membered piperidine ring (**M6**) in order to further elucidate the relationship between the molecular structure and the polymerizability of *N*,*N*-dialkylmethacrylamides (Table 4). The controlled polymerization of the corresponding acryloyl monomers, **A5** and **A6**, has been reported.[6] We also reexamined the polymerization of DMMA under the similar polymerization conditions.

At first, we have realized the positive polymerizability of **M5** by the initiation with Ph_2CHLi at 0 °C (run 30). The resulting poly(**M5**) possessed the narrow MWD and the predicted M_n, while the monomer conversion was 69% even after 72 h. Similarly, the binary initiator system of DMPLi/LiCl induced the polymerization of **M5** at −40 °C, but only 9% of **M5** was consumed after 15 h (run 31). Even when **M5** underwent the polymerization reaction for 72 h, the monomer conversion was still 44% (run 32). At higher temperature of 0 °C after 72 h, the conversion increased to 65%. However, the conversion was almost constant (~65%), and 100% conversion could not be achieved even after longer time for 168 and 336 h (runs 33 and 34). **M5** also underwent the polymerization with Ph_2CHLi/Et_2Zn at −40 °C within 72 h in 30% conversion. In the case of Ph_2CHK, the conversions of **M5** were 74 and 77% at 0 °C after 72 and 168 h, respectively. The MWDs of polymers were very broad (M_w/M_n = 2−2.5). On the other hand, no apparent polymerization took place with Ph_2CHK in the presence of Et_2Zn at −40 °C in 72 h. Higher polymerization temperature at 0 °C was necessary to achieve the polymerization with Ph_2CHK/Et_2Zn. The additive effect of Et_2Zn to Ph_2CHK was realized at 0 °C to retard the propagation and to narrow the MWD of

Table 3. Anionic Polymerization of A4 in THF[a]

						$M_n \times 10^{-3}$			tacticity,[e] %	
run	**A4**, mmol	initiator, mmol	additive, mmol	temp, °C	time, h	calcd[b]	obsd[c]	M_w/M_n[d]	*m*	*r*
21	5.83	Ph_2CHLi, 0.108		−78	2	6.3	6.8	1.45	79	21
22	5.83	Ph_2CHLi, 0.108	LiCl, 0.513	−78	2	6.2	10	1.65	85	15
23	5.28	Ph_2CHLi, 0.107	Et_2Zn, 1.58	−78	2	5.6	7.4	1.11	72	28
24	5.93	Ph_2CHLi, 0.0494	Et_2Zn, 1.74	−78	2	14	18	1.06		
25	5.79	Ph_2CHLi, 0.120	Et_2Zn, 1.73	0	2	5.5	6.4	1.09		
26	4.92	Ph_2CHK, 0.104		−78	2	5.5	7.2	1.79	86	14
27	6.04	Ph_2CHK, 0.128	Et_2Zn, 1.81	−78	2	5.4	7.0	1.08	67	33
28	4.59	Ph_2CHK, 0.106	Et_2Zn, 1.34	0	20	5.0	6.5	1.09		
29	7.28	Ph_2CHK, 0.0680	Et_2Zn, 2.13	0	2	12	16	1.04		

[a] Conversion = 100% in all cases. [b] M_n(calcd) = (MW of monomer) × [monomer]/[initiator] + (MW of initiator fragment). [c] M_n(obsd) was obtained by end-group analysis using ^{1}H NMR. [d] M_w/M_n was obtained by SEC calibration using polystyrene standards in DMF containing 0.01 M LiBr. [e] The diad tacticity was determined by the ^{1}H NMR measurment in $CDCl_3$ at 50 °C.

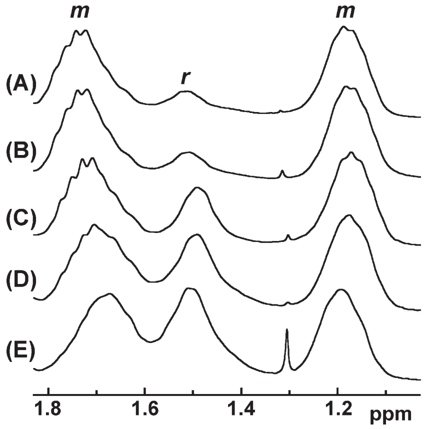


Figure 6. ^{1}H NMR spectra of main-chain methylene proton for poly(**A4**)s measured in $CDCl_3$ at 50 °C: (A) Ph_2CHK, *m*/*r* = 86/14; (B) Ph_2CHLi/LiCl, *m*/*r* = 85/15; (C) Ph_2CHLi, *m*/*r* = 79/21; (D) Ph_2CHLi/Et_2Zn, *m*/*r* = 72/28; (E) Ph_2CHK/Et_2Zn, *m*/*r* = 67/33.

poly(**M5**) (runs 40 and 41), whereas the monomer conversion was still not quantitative after the prolonged polymerization. The stereoregularity of the poly(**M5**) could not be determined, since the suitable signals in ^{1}H and ^{13}C NMR spectra were overlapped with other signals. Thus, we could manage to polymerize **M5** via the slow propagation, while the completion of polymerization had not been achieved even under the drastic reaction conditions. These clearly indicate the lower polymerizability of **M5** compared to those of **M3** and **M4**.

Next, we found that no apparent polymerization of **M6** occurred under the various reaction conditions (runs 42−48). On the addition of **M6** to DMPLi, Ph_2CHLi, or Ph_2CHK, the characteristic color of the initiator disappeared, suggesting the occurrence of initiation reaction. However, no polymer was obtained in each case after quenching the polymerization after 72 h, and the unreacted **M6** was recovered almost quantitatively. In addition, it has been reported that the radical polymerization of **M6** with AIBN also gives no polymeric product.[10] These polymerization behaviors of **M6** are in accordance with the negative polymerizability of DMMA as shown below.

Finally, the anionic polymerization of DMMA was attempted under the preferable reaction conditions with DMPLi or Ph_2CHK either in the presence or in the absence of LiCl or Et_2Zn for 72 h. When DMMA was added to DMPLi, a color change from red to colorless occurred either with or without additives such as LiCl and Et_2Zn. However, no polymeric product was formed after the termination with methanol, and the monomer was quantitatively recovered from the reaction mixture. On the addition of DMMA to Ph_2CHK, an orange color of initiator solution remained throughout the course of the polymerization, and no polymeric product of DMMA formed. We also tried to polymerize DMMA under the radical conditions with AIBN in toluene at 50 and 70 °C for 72 h. However, any trace of polymeric product was not obtained from the radical polymerization system. The nonpolymerizability of DMMA was again confirmed by our experiments similar to the previous reports from the various research groups.[2,10−14]

Relative Polymerizability of Monomers. Thus, it is demonstrated from the present study that the polymerizability of a series of *N*,*N*-dialkylmethacrylamides carrying small-membered ring decreases drastically with increasing ring size from three to six (**M3** > **M4** > **M5** ≫ **M6**). In particular, the polymerizations of **M3** and **M4** proceed quantitatively to give well-defined vinyl polymers in the living manners under the suitable basic conditions, even though they are the *N*,*N*-dialkylmethacrylamide derivatives usually showing nonpolymerizability.[2,10−14] By contrast, we have not obtained any polymeric product from the polymerization system of **M6** under the various conditions similar to the polymerization behavior of DMMA.

We have reported that the anionic polymerizability of vinyl monomers can be predicted by the β-carbon chemical shifts of vinyl groups in the ^{13}C NMR spectra,[27] which reasonably reflect the electron densities of the C=C bonds accepting the nucleophilic attack of the initiator and the propagating carbanion. In our present study, the varied polymerizability can be explained by the β-carbon chemical shifts of *N*,*N*-dialkylmethacrylamides in the ^{13}C NMR spectra. In fact, the ^{13}C NMR chemical shifts of vinyl β-carbons of **M3**, **M4**, **M5**, **M6**, and DMMA are observed at 124.5, 119.1, 116.0, 114.6, and 115.4 ppm, respectively, as can be seen in Figure 7.[28] These β-carbon chemical shifts are in good accordance with the relative polymerizability (**M3** > **M4** > **M5** ≫ **M6** = DMMA) observed in the present study. The upfield chemical shifts for **M5**, **M6**, and DMMA (115−116 ppm) are rather comparable to that of styrene (113.8 ppm) and far from the downfield values of typical polar monomers such as methyl acrylate (130.6 ppm), MMA (125.3 ppm), and DMA (125.8 ppm). We now consider that the β-carbon chemical shifts effectively reflect the π-electron densities of vinyl groups and the anionic polymerizability of a series of *N*,*N*-dialkylmethacrylamides.

Furthermore, the conformation of monomer and the dihedral angle between C=C and C=O groups are considered to be essential to determine the polymerizability of *N*,*N*-dialkylmethacrylamides, as previously Kodaira,[15] Hogen-Esch,[5] and Chen[20] suggested on the basis of the NMR chemical shifts and the theoretical calculations. The planar

Table 4. Anionic Polymerization of M5, M6, and DMMA in THF

run	monomer, mmol	initiator, mmol	additive, mmol	temp, °C	time, h	conversion, %	$M_n \times 10^{-3}$ calcd[a]	$M_n \times 10^{-3}$ obsd[b]	M_w/M_n[c]
30	**M5**, 6.84	Ph_2CHLi, 0.107		0	72	69	6.2	8.7	1.07
31	**M5**, 5.88	DMPLi, 0.107	LiCl, 0.422	−40	15	9	0.71	0.70[c]	1.07
32	**M5**, 6.25	DMPLi, 0.103	LiCl, 0.462	−40	72	44	3.8	1.6[c]	1.06
32	**M5**, 6.25	DMPLi, 0.102	LiCl, 0.592	0	72	65	5.7	6.9	1.14
34	**M5**, 6.39	DMPLi, 0.0943	LiCl, 0.478	0	168	65	6.3	8.1	1.28
35	**M5**, 5.03	Ph_2CHLi, 0.0891	LiCl, 0.322	0	336	60	4.7	2.0	1.27
36	**M5**, 5.48	Ph_2CHLi, 0.102	Et_2Zn, 1.09	−40	72	30	2.3	1.2[c]	1.07
37	**M5**, 6.77	Ph_2CHK, 0.105		0	72	74	6.6	7.0	1.98
38	**M5**, 5.97	Ph_2CHK, 0.0982		0	168	77	6.5	7.8	2.51
39	**M5**, 5.55	Ph_2CHK, 0.111	Et_2Zn, 1.17	−40	72	0			
40	**M5**, 6.09	Ph_2CHK, 0.0895	Et_2Zn, 0.986	0	72	46	4.4	4.5	1.11
41	**M5**, 6.33	Ph_2CHK, 0.0888	Et_2Zn, 0.939	0	168	68	6.7	7.7	1.14
42	**M6**, 5.18	Ph_2CHLi, 0.126		−40	72	0			
43	**M6**, 5.97	DMPLi, 0.131	LiCl, 0.688	−40	72	0			
44	**M6**, 5.89	Ph_2CHLi, 0.122		0	72	0			
45	**M6**, 5.91	DMPLi, 0.136	LiCl, 0.568	0	72	0			
46	**M6**, 5.85	Ph_2CHK, 0.129	Et_2Zn, 1.83	−40	72	0			
47	**M6**, 5.21	Ph_2CHK, 0.122		0	72	0			
48	**M6**, 6.08	Ph_2CHK, 0.156	Et_2Zn, 2.54	0	72	0			
49	**DMMA**, 6.76	DMPLi, 0.117		−78	72	0			
50	**DMMA**, 7.57	DMPLi, 0.0611		0	72	0			
51	**DMMA**, 8.60	DMPLi, 0.114	LiCl, 0.508	−78	72	0			
52	**DMMA**, 8.69	DMPLi, 0.0756	LiCl, 0.407	0	72	0			
53	**DMMA**, 8.58	DMPLi, 0.0762	Et_2Zn, 1.01	−78	72	0			
54	**DMMA**, 7.34	Ph_2CHK, 0.133		−78	72	0			
55	**DMMA**, 8.69	Ph_2CHK, 0.104		0	72	0			
56	**DMMA**, 6.51	Ph_2CHK, 0.0986	Et_2Zn, 1.15	−78	72	0			
57	**DMMA**, 8.00	Ph_2CHK, 0.0729	Et_2Zn, 0.669	0	72	0			

[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 ^1H NMR. [c] M_n and M_w/M_n were obtained by SEC calibration using polystyrene standards in THF solution.

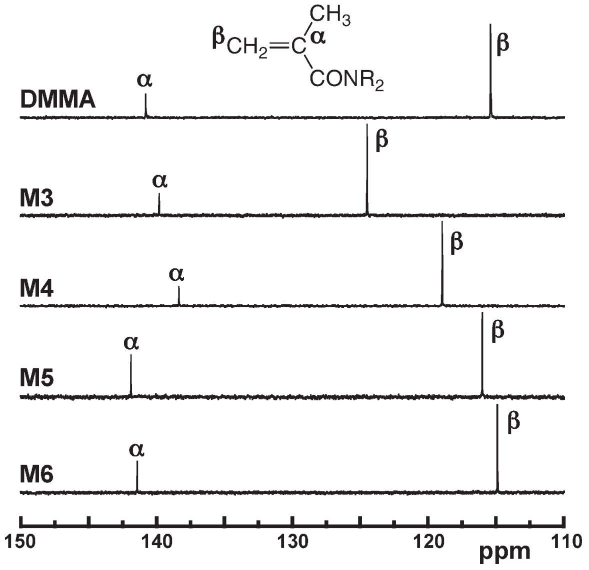


Figure 7. ^{13}C NMR spectra of vinyl group region for DMMA, **M3**, **M4**, **M5**, and **M6** measured in $CDCl_3$ at room temperature.

Table 5. Solubility of Polymers[a]

solvent	poly-(**M3**)[b]	poly-(**M4**)	poly-(**M5**)	poly-(**A3**)[b]	poly-(**A4**)	poly-(**A5**)[c]
initiator	$Li^+/LiCl$	d	d	$Li^+/LiCl$	d	e
n-hexane	I	I	I	I	I	I
benzene	S	I	S	S	S	I
$CHCl_3$	S	S	S	S	S	S
ethyl acetate	S	S	S	S	S	
diethyl ether	S	I	I	S	I	
1,4-dioxane	S	I	S	S	S	
THF	S	S	S	S	S	S
DMSO	S	S	S	S	S	S
DMF	S	S	S	S	S	S
methanol	S	S	S	S	S	S
water	I	S	S[f]	S[g]	S	S

[a] I: insoluble; S: soluble. [b] See ref 18. [c] See ref 6. [d] $Li^+/LiCl$, K^+/Et_2Zn. [e] Li^+, Li^+/Et_2Zn, K^+/Et_2Zn. [f] Cloud point at 26−28 °C. [g] Cloud point at 14 °C.

geometry of (O=C)−NR_2 moiety and the steric repulsion between α-methyl or CH_2= group and two methyl substituents on amide nitrogen in DMMA presumably induce the twisted conformation of the C=C−C=O system and the nonpolymerizability. On the other hand, aziridine and azetidine amides are considered to have characteristic features on conformation as the unusual nonplanar amides with pyramidal nitrogen.[21] The lack of amide conjugation between C=O and lone pair on amide nitrogen in **M3** and **M4**, arisen from the highly strained aziridine and azetidine moieties, is proposed as the typical nonplanar amides possessing nitrogen-pyramidal structure and may play a very important role for the effective resonance between carbonyl and vinyl groups in **M3** and **M4**. The evaluations of the stable conformation and the varied electron density of the monomers are now in progress by using the ab initio calculation. We will comprehensively discuss the relationship between the observed polymerizability and the molecular structure and/or the spectroscopic data in the forthcoming paper.

Solubility and Thermal Property of Polymers. To our best knowledge, poly(**M4**), poly(**M5**), and poly(**A4**) are newly synthesized in this study. Solubility of these polymers is listed in Table 5 in addition to those of poly(**M3**),[18] poly(**A3**),[18] and poly(**A5**)[6] as the references. Poly(**M4**), poly(**M5**), and poly(**A4**) are insoluble in *n*-hexane but soluble in polar solvents such as methanol, DMF, and DMSO. It should be noted that all three polymers had water solubility, indicating the high polarity of *N*,*N*-dialkylamide moiety. Poly(**M4**) and poly(**A4**) bearing four-membered azetidine ring presented higher polarity than their counterparts, poly(**M3**) and poly(**A3**), having three-membered 2-methylaziridine ring. For example, poly(**M4**) was completely soluble in water at any temperature, but the corresponding poly(**M3**) was insoluble in water. Furthermore, poly(**A4**) was readily soluble in water at any temperature, while the aqueous solution of poly(**A3**) showed the cloud point (T_c) around 14 °C.[18] On the other hand, the polarity of poly(**M5**) seemed lower in comparison with poly(**M4**), since the poly(**M5**) had the typical thermally dependent solubility (T_c = 26−28 °C) in water.

The glass transition temperatures (T_g) of polymers obtained with Ph_2CHK/Et_2Zn were analyzed by differential scanning calorimetry (DSC). T_gs of poly(**M4**), poly(**M5**), and poly(**A4**) were observed at 168, 178, and 114 °C, respectively. The methacryloyl type poly(**M4**) showed higher T_g value compared with the acryloyl counterpart of poly(**A4**), as expected. The strained four-membered azetidine moieties in poly(**M4**) and poly(**A4**) were stable at least below 250 °C, and the polymers were soluble even after the heating. This is sharp contrast to the facts that poly(**M3**) and poly(**A3**) possessing three-membered aziridine rings are thermosetting and become insoluble after the thermal treatment at 150 °C due to the intermolecular cross-linking.[18] Thermal stability of the resulting polymers was investigated by thermogravimetric analysis (TGA) under nitrogen. The 10% weight loss temperatures of poly(**M4**), poly(**M5**), and poly(**A4**) were observed at 327, 358, and 352 °C, respectively.

Conclusions

We have conducted the anionic polymerization of a series of *N*,*N*-dialkylmethacrylamides having 4-, 5-, and 6-membered rings in the amide moieties in order to compare the relative polymerizability with DMMA. In sharp contrast to the nonpolymerizability of DMMA, **M4** with 4-membered azetidine ring can be polymerized quantitatively to afford the stable living polymer having the predicted molecular weight and very narrow MWD ($M_w/M_n \sim 1.1$) similar to the previous report for **M3** with 3-membered aziridine ring.[18] The tacticity of poly(**M4**) is controlled from 11 to 93% in the range of *mm*-triad content by choosing the initiator system and the polymerization temperature. It is substantiated from the viewpoints of polymer yield and polymerization rate that the anionic polymerizability of *N*,*N*-dialkylmethacrylamides clearly decreases with increasing the ring size of monomers from 3 to 6 (**M3** > **M4** > **M5** ≫ **M6** = DMMA). The relative polymerizability is well correlated with the vinyl β-carbon chemical shifts of monomers in the ^{13}C NMR spectra, which reflect the electron density of C=C bonds.

Experimental Section

Materials. All reagents were purchased from Tokyo Kasei, unless otherwise stated. Azetidine hydrochloride (Aldrich) was dried under vacuum condition. Pyrrolidine, piperidine, 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, 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-diphenylhexyllithium 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. DMMA was distilled over CaH_2 under reduced pressure.

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-fold DPE in THF at −78 °C for 10 min. Ph_2CHLi, Ph_2CHNa, and Ph_2CHK were synthesized by the reaction of the corresponding metal naphthalenide and 1.5-fold 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.[29] AIBN for radical polymerization was purified by recrystallization from methanol.

Synthesis of M4. A solution of methacryloyl chloride (10.28 g, 98.3 mmol) in dichloromethane (20 mL) 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, and then the mixture was stirred at room temperature for 4 h. After the filtration of precipitated ammonium salt, the filtrate was washed with 2 N HCl, saturated $NaHCO_3$ aqueous solution, and saturated NaCl aqueous solution. The aqueous layer was extracted with dichloromethane. The combined organic layer was dried over anhydrous $MgSO_4$ and filtered. After the evaporation, the crude product was distilled twice over CaH_2 under reduced pressure to yield colorless liquid of **M4** (9.82 g, 78.6 mmol, 81%, bp 80−81 °C/4 mmHg). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.92 (s, 3H, CH_3), 2.28 (m, 2H, CH_2), 4.08 and 4.23 (br, 4H, NCH_2), 5.29 (s, 1H, cis CH_2=), 5.36 (s, 1H, trans CH_2=). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 15.8 (CH_2), 19.4 (CH_3), 48.3 and 52.7 (N−CH_2), 119.1 (CH_2=), 138.3 (=C−), 170.9 (C=O). IR (ATR): 2956, 2885, 1649 (C=C), 1612 (C=O), 1459, 1434, 925 cm^{-1}. Anal. Calcd for $C_7H_{11}NO \cdot 0.1H_2O$ (126.971, hygroscopic): C, 66.22, H, 8.73, N, 11.03. Found: C, 66.54, H, 8.95, N, 10.87.

Synthesis of A4. A solid of azetidine hydrochloride (9.75 g, 104 mmol) was added to a solution of 11.98 g (214 mmol) of KOH in water (8 mL). The reaction system was heated to 90 °C, and colorless liquid of azetidine (5.06 g, 88.6 mmol) was isolated in 85% yield by the distillation in the receiver cooled by an ice bath. A solution of azetidine (5.06 g, 88.6 mmol) and triethylamine (11.43 g, 113 mmol) in diethyl ether (100 mL) was added dropwise to a mixture of acryloyl chloride (10.67 g, 117 mmol) and diethyl ether (100 mL) at 0 °C under nitrogen. After stirring for 2 h at room temperature, the precipitated triethylammonium chloride was removed by the filtration, and filtrate was concentrated by the evaporation. The residual product was purified by the repeating vacuum distillations over CaH_2 to obtain colorless liquid of **A4** (4.72 g, 42.5 mmol, 48%, bp 47−48 °C/3 mmHg). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.31 (p, 2H, CH_2), 4.08 (t, 2H, N−CH_2), 4.23 (t, 2H, N−CH_2), 5.62 (d, 1H, J = 9.8 Hz, trans CH_2=), 6.18 (dd, 1H, J = 17 and 9.8 Hz, =CH−), 6.28 (d, 1H, J = 17 Hz, cis CH_2=). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 15.4 (CH_2), 47.9 and 50.1 (N−CH_2), 125.8 (=CH−), 127.0 (CH_2=), 165.5 (C=O). IR (ATR): 2949, 2879, 1793, 1728, 1649 (C=C), 1613 (C=O), 1434, 1287, 1049, 978, 796 cm^{-1}. Anal. Calcd for $C_6H_9NO \cdot 0.1H_2O$ (112.945, hygroscopic): C, 63.81, H, 8.03, N, 12.40. Found: C, 64.18, H, 8.17, N, 12.28.

Synthesis of M5. M5 was synthesized according to the similar procedure for **A4** by using methacryloyl chloride (15.67 g, 150 mmol), pyrrolidine (10.66 g, 150 mmol), and triethylamine (16.00 g, 158 mmol). The crude product was distilled repeatedly under reduced pressure to yield colorless liquid of **M5** (14.50 g, 104 mmol, 69%, bp 92−93 °C/4 mmHg). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.90 (m, 4H, −CH_2−CH_2−), 1.96 (s, 1H, CH_3), 3.48 (m, 4H, N−CH_2), 5.14 (s, 1H, cis CH_2=), 5.23 (s, 1H, trans CH_2=). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 20.0 (CH_3), 24.4 and 26.2 (−CH_2−CH_2−), 45.5 and 48.7 (N−CH_2), 116.0 (CH_2=), 141.9 (=C−), 170.7 (C=O). IR (ATR): 2975, 2952, 1647 (C=C), 1609 (C=O), 1451, 1428, 1368, 1340, 1224, 1186, 1168, 913 cm^{-1}. Anal. Calcd for $C_8H_{13}NO \cdot 0.1H_2O$ (140.996, hygroscopic): C, 68.15, H, 9.44, N, 9.93. Found: C, 68.18, H, 9.51, N, 9.96.

Synthesis of M6. M6 was prepared by the reaction of methacryloyl chloride (15.31 g, 146 mmol) and piperidine (13.08 g, 154 mmol) in the presence of triethylamine (15.34 g, 146 mmol) in diethyl ether. Repeating vacuum distillations of the crude product gave colorless liquid of **M6** (14.8 g, 96.7 mmol, 66%, bp 61−63 °C/0.7 mmHg). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.56 (br, 4H, N−CH_2−CH_2), 1.65 (m, 2H, N−CH_2−CH_2−CH_2), 1.95 (s, 3H, CH_3), 3.47 and 3.56 (br, 4H, N−CH_2), 5.01 (s, 1H, cis CH_2=), 5.13 (s, 1H, trans CH_2=). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 20.6 (CH_3), 24.7 (N−CH_2−CH_2−CH_2), 25.6 and 26.8 (N−CH_2−CH_2), 42.3 and 47.9 (N−CH_2), 114.6 (CH_2=), 141.1 (=C−), 171.1 (C=O). IR (ATR): 2935, 2854, 1644 (C=C), 1618 (C=O), 1469, 1432, 1371, 1294, 1245, 1204, 1134, 1016, 908, 853 cm^{-1}. Anal. for $C_9H_{15}NO \cdot 0.2H_2O$ (156.825, hygroscopic): C, 68.93, H, 9.90, N, 8.93. Found: C, 68.83, H, 10.02, N, 9.01.

Purification of Monomers. After careful fractional distillations, the liquid monomers (**M4**, **A4**, **M5**, **M6**, and DMMA) were degassed and sealed off in an apparatus equipped with a break-seal in the presence of CaH_2 under high-vacuum conditions 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 (0.75−0.82 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).[29] Polymerization was terminated with methanol. The residue was precipitated in diethyl ether at room temperature. When Et_2Zn was used as an additive, the reaction mixture was immediately concentrated in vacuo to remove THF and excess amount of methanol and again diluted with THF to precipitate the zinc compounds overnight. After filtration of the system to remove the precipitated zinc compounds, the filtrate was concentrated by evaporation and precipitated in diethyl ether. The resulting polymers 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(**M4**)*. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.0−1.6 (CH_3), 1.7−2.5 (CH_2 and main chain CH_2), 3.7−4.7 (4H, N−CH_2). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 15.8 (CH_2), 18.0−21.7 (CH_3), 45.5−47 (main chain quaternary), 49.3 (N−CH_2, cis to carbonyl), 52.0 (main chain CH_2), 54.1 (N−CH_2, trans to carbonyl), 173.0−177.5 (C=O). IR (KBr): 2946, 2882, 1594 (C=O), 1417, 1300, 1212, 1039 cm^{-1}. Anal. Calcd for $C_7H_{11}NO \cdot 0.2H_2O$ (128.783, hygroscopic): C, 65.28, H, 8.93, N, 10.88. Found: C, 65.80, H, 8.89, N, 10.10.

*Poly(**A4**)*. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.1−1.8 (2H, main chain CH_2), 1.9−2.1 (1H, main chain CH), 2.11 (2H, CH_2), 3.8−4.6 (4H, N−CH_2). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 15.2 (CH_2), 32−35 (main chain CH_2), 35−38 (main chain CH), 47.9 and 50.5 (N−CH_2), 173.5−174.5 (C=O). IR (KBr): 2956, 2886, 1623(C=O), 1476, 1448, 1364, 1153, 1016 cm^{-1}. Anal. Calcd for $C_6H_9NO \cdot H_2O$ (129.169, hygroscopic): C, 55.79, H, 8.59, N, 10.85. Found: C, 57.06, H, 6.59, N, 10.48.

*Poly(**M5**)*. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.5−1.4 (3H, CH_3), 1.4−2.4 (6H, −N−CH_2−CH_2− and main chain CH_2), 3.0−4.0 (4H, N−CH_2). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 17−22 (CH_3), 22.8 and 27.5 (CH_2), 46.9 (main chain quaternary), 48.1 and 49.2 (N−CH_2), 51−56 (main chain CH_2), 173−177 (C=O). IR (KBr): 2968, 2873, 1601 (C=O), 1456, 1409, 1342, 1182, 1161 cm^{-1}. Anal. Calcd for $C_8H_{13}NO \cdot 0.4H_2O$ (146.403, hygroscopic): C, 65.63, H, 9.50, N, 9.57. Found: C, 65.63, H, 9.50, N, 9.09.

Kinetic Study of Polymerization of M4. Anionic polymerization of **M4** 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 **M4** 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 −20 and −40 °C. After the given time, the polymerization was terminated with methanol 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 0.04−0.50 M.

Radical Polymerization. Radical polymerization of **M4** (0.74 g, 5.92 mmol) was carried out with AIBN (0.14 g, 0.80 mmol) in toluene (20 mL) at 70 °C for 72 h under nitrogen. The reaction mixture was poured into a mixture of hexane and diethyl ether to precipitate a poly(**M4**) (0.30 g, 40% yield, $M_n < 500$). The polymerization of **A4** (0.67 g, 6.08 mmol) was similarly performed with AIBN (0.11 g, 0.65 mmol) in toluene (20 mL) at 70 °C for 4 h under nitrogen. The poly(**A4**) (0.67 g, conversion ∼ 100%, M_n = 4900, M_w/M_n = 1.42) was quantitatively obtained after the precipitation in diethyl ether. The resulting polymer collected by filtration was purified by freeze-drying from benzene.

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 $CDCl_3$ or d_6-DMSO. The chemical shifts were reported in ppm downfield relative to tetramethylsilane (δ 0.00) in $CDCl_3$ for ^{1}H NMR and $CDCl_3$ (δ 77.1) or DMSO (δ 39.5) for ^{13}C NMR as standard. Tacticity of poly(**M4**) was determined by the ^{13}C NMR integral ratio of three split α-methyl carbon signals appearing at 18.0−21.7 ppm in d_6-DMSO at 75 °C. Three signals were assigned as *rr* (18.0−18.7 ppm), *mr* (19.2−19.8 ppm), and *mm* (21.1−21.7 ppm) triads. Tacticity of poly(**A4**) was determined by the ^{1}H NMR integral ratio of three split methylene proton signals appearing at 1.1−1.8 ppm in $CDCl_3$ at 50 °C. Three signals were assigned as *m* (1.1−1.3 ppm), *r* (1.3−1.6 ppm), and *m* (1.6−1.8 ppm) diads. 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 $GMH_{XL} \times 2 + G2000H_{XL}$) with either ultraviolet (254 nm) absorption or refractive index detection. The cloud point of poly(**M5**) 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}. 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 200 °C, cooled to 30 °C, and then scanned at a rate of 10 °C min^{-1}. A Seiko Instruments TG/DTA6200 was used for TGA analysis at 30−600 °C under nitrogen flow with heating rate of 10 °C min^{-1}.

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(23) In the polymerization aimed at high molecular weight (run 5), the observed M_n (50 000) was apparently higher than the calculated value (M_n = 29 000), whereas the MWD was narrow (M_w/M_n = 1.10). This is probably due to trace amount of impurities in the monomer and the lowered concentration of propagating chain end.

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