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Anionic Polymerization Behavior of α-Methylene-*N*-methylpyrrolidone

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Summary: Anionic polymerization of α-methylene-*N*-methylpyrrolidone (**MMP**) was carried out in THF at $-78 \sim 0\ ^\circ C$ with diphenylmethylpotassium (Ph_2CHK) and with diphenylmethyllithium (Ph_2CHLi) in the presence of Lewis acidic diethylzinc (Et_2Zn). Poly(**MMP**)s possessing predicted molecular weights based on the molar ratios between monomer and initiators and narrow molecular weight distributions ($M_w/M_n < 1.1$) were obtained in quantitative yields. It was demonstrated that the propagating chain end of poly(**MMP**) was stable at $-30\ ^\circ C$ to form the polymers with well-defined chain structures. From the polymerizations at the various temperatures ranging from -50 to $-30\ ^\circ C$, the apparent rate constant and the activation energy of the polymerization were estimated as follows: $\ln k_p^{ap} = -6.93 \times 10^3/T + 25.7$ and 57 ± 5 kJ mol^{-1}, respectively.

Keywords: anionic polymerization; *exo*-methylene monomer; molecular weight distribution; molecular weight; *N,N*-dialkylmethacrylamides; α-methylene-*N*-methylpyrrolidone

Introduction

The anionic polymerizations of polar monomers such as acrylates and methacrylates, α,β-unsaturated esters, have been intensely studied from the synthetic viewpoints and the industrial interest. The controls on molecular architectures such as molecular weight, molecular weight distribution (MWD), and stereoregularity of their (co)polymers are realized in several polymerization systems. The formation of stable living polymers is also achieved in the anionic polymerization of various *N,N*-dialkylacrylamides.[1–4] On the other hand, among the polar monomers carrying the electron-withdrawing substituents, *N,N*-dialkylmethacrylamides such as *N,N*-dimethylmethacrylamide (**DMMA**) show very strange negative polymerizability under the various reaction conditions. In fact, a number of research groups have reported that *N,N*-dialkylmethacrylamides are difficult to polymerize with the radical or anionic initiators.[5–9] 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 ^1H and ^{13}C NMR study and Modified Neglect of Differential Overlap (MNDO) calculations, it is 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.[1,10] 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**), possessing small and highly strained three-membered aziridine ring, can be polymerized with either radical or anionic initiators to give vinyl polymers.[9] We recently reported that *N*-methacryloyl-2-methylaziridine (**M3**) and *N*-methacryloylazetidine (**M4**) readily underwent the vinyl polymerizations under the basic

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conditions to form the stable anionic living polymers with predicted molecular weights and very narrow MWDs (M_w/M_n <1.1).[11,12] On the other hand, the polymerizations of *N*-methacryloylpyrrolidine (**M5**) gave the polymers in 30-77% yields, but did not complete even after 1 week at 0 °C. Furthermore, no polymer was obtained from the anionic polymerization system of *N*-methacryloylpiperidine (**M6**) similar to the case of **DMMA**. Thus, 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** = **DMMA**), as shown in Chart 1. 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, may play a very important role for the effective resonance between carbonyl and vinyl groups in **M3** and **M4**, which induces their positive polymerizability.

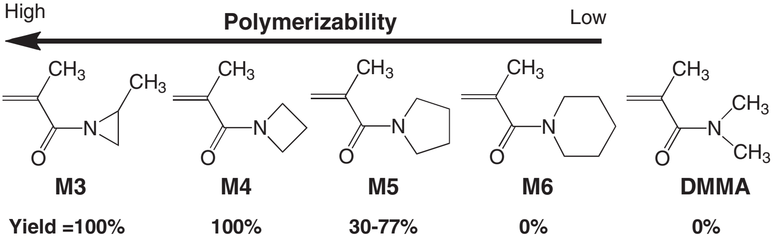


Chart 1 Anionic Polymerizability of *N,N*-Dialkylmethacrylamides.

We here focus on the anionic polymerizability of α-methylene-*N*-methylpyrrolidone (**MMP**), a cyclic analogue of **DMMA**. In this particular case, the C=C bond and C=O bond are almost flat and may effectively conjugate because of the restricted conformation of monomer. In fact, **MMP** is a typical *exo*-methylene monomer showing radical polymerizability,[13] which gives a unique polymer possessing ring structure perpendicular to the main chain via the vinyl polymerization.

Experimental Part

Materials

Tetrahydrofuran (THF) was refluxed over sodium wire, distilled from $LiAlH_4$, and then distilled from the sodium naphthalenide solution on a vacuum line. Diphenylmethylpotassium (Ph_2CHK) and diphenylmethyllithium (Ph_2CHLi) 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. Et_2Zn (TOSOH Akuzo Co.) was used as a THF solution.

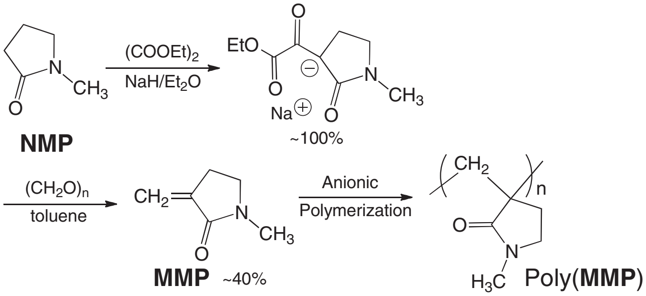
Monomer Synthesis

MMP was synthesized from *N*-methylpyrrolidone (NMP) in 40% yield as shown in Scheme 1.[13] At first, NMP was reacted with diethyl oxalate to form an intermediate enolate in the presence of sodium hydride in diethyl ether. The reaction of the resultant enolate with paraformaldehyde (a carbon source of *exo*-methylene group) and the subsequent elimination gave **MMP** monomer possessing *exo*-methylene group.

^1H NMR ($CDCl_3$, 300 MHz): $\delta = 2.78$ (m, 2H, $CH_2C{=}CH_2$), 2.94 (s, 3H, NCH_3), 3.38 (t, 2H, NCH_2), 5.30 and 5.96 (2s, 2H, $=CH_2$).

^{13}C NMR ($CDCl_3$, 75 MHz): $\delta = 24.0$ ($CH_2C{=}CH_2$), 30.2 (NCH_3), 46.3 (NCH_2), 115.0 ($CH_2{=}$), 139.5 ($CH_2{=}C$), 168.1 (C=O).

MMP was purified by the repeating vacuum distillations over CaH_2. The purified **MMP** and CaH_2 were sealed off in an all-glass apparatus equipped with a break-



Scheme 1.
Synthesis and Polymerization of **MMP**.

seal under the vacuum conditions. After dilution with dry THF, the monomer solution was stirred over CaH_2 overnight and distilled on a vacuum line. The monomer was further 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 anionic polymerization was carried out in THF under high vacuum conditions (10^{-6} mmHg) in a sealed all-glass apparatus equipped with break-seals. To the THF solution of Ph_2CHK or Ph_2CHLi, 10–15 fold of Et_2Zn in THF was added at −78 °C. After 10 min, the THF solution of **MMP** was added to the initiator system with vigorous stirring at −78 °C. On the addition of monomer, the characteristic orange color of the initiator immediately disappeared. The polymerization was performed at various temperatures (−78, −40, and 0 °C) and terminated with degassed methanol at −78 °C. The reaction mixture was concentrated by evaporation, and was poured into diethyl ether at room temperature 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. SEC chromatogram for determination of MWD was 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 $GMH_{XL} \times 2 + G\ 2000H_{XL}$) with refractive index detection. The glass transition temperature (T_g) of poly(**MMP**) was 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}.

Results and Discussion

We first carried out the anionic polymerization of **MMP** with Ph_2CHK in THF (Table 1). At −78 °C, the polymerization was completed within 2 h to afford a poly(**MMP**) of a relatively broad MWD ($M_w/M_n = 1.24$). When Lewis acidic Et_2Zn was added to the reaction system, the polymerization was apparently retarded. Even after 72 h, the yield of polymer was not quantitative and was 81% at −78 °C. Interestingly, the MWD of polymer was effectively narrowed in the presence of Et_2Zn and the polydispersity index, M_w/M_n, was 1.04. Even at 0 °C, the binary initiator system of Ph_2CHK and

Table 1.
Anionic Polymerization of **MMP** in THF

MMP	initiator	Et_2Zn	temp.	time	yield	M_n X 10^{-3}		M_w/M_n [b)]
mmol	mmol	mmol	°C	h	%	calcd.	obsd.[a)]	
7.09	Ph_2CHK, 0.0766	–	−78	2	100	10	14	1.24
6.75	Ph_2CHK, 0.0732	–	0	10 min	100	10	8.7	1.13
6.49	Ph_2CHK, 0.0531	0.705	−78	72	81	11	13	1.04
5.90	Ph_2CHK, 0.0967	1.36	−40	4	100	6.5	9.0	1.06
6.28	Ph_2CHK, 0.0637	0.734	0	1	100	11	12	1.06
6.08	Ph_2CHK, 0.0298	0.419	0	1	100	23	26	1.07
6.61	Ph_2CHLi, 0.0642	–	−78	2	85	9.7	24	1.51
6.65	Ph_2CHLi, 0.0804	–	0	2	100	9.2	12	1.13
6.76	Ph_2CHLi, 0.0586	0.888	0	1	100	13	14	1.05

[a)] By end-group analysis using ^1H NMR. [b)] By SEC calibration using polystyrene standards in DMF.

Et_2Zn similarly gave the poly(**MMP**)s with predicted molecular weights based on the molar ratios between monomer and initiator and narrow MWDs in quantitative yields. The well-defined polymer was also produced with Ph_2CHLi in the presence of Et_2Zn at 0 °C, although the MWD was rather broad in the absence of Et_2Zn.

We next examine the polymerization rate of **MMP** from the kinetic viewpoint. The monomer conversion was analyzed by the GLC measurement of the residual monomer and the ^1H NMR measurement of polymerization system. Figure 1 shows a series of SEC traces of poly(**MMP**)s obtained with Ph_2CHK/Et_2Zn (11.9 equivalent) in THF at −30 °C. The SEC traces clearly shift from the lower molecular weight region to the higher side, as the conversion of **MMP** increases with the polymerization time. In each case, the resulting polymer maintains the unimodal and narrow MWD. It is demonstrated from the SEC trace shift that no chain transfer and termination reaction occur during the slow polymerization reaction of **MMP** at −30 °C.

We then attempted to polymerize **MMP** at −40 and −50 °C in order to estimate the polymerization rate at each temperature. The initial concentration of Ph_2CHK, $[I]_0$, was regulated between 3.8×10^{-3} and 4.2×10^{-3} M, and the content of Et_2Zn was controlled in range of 11–16 equivalent against Ph_2CHK. At all temperatures, the first-order plots showed good linearity within the experimental error, as shown in Figure 2. This clearly indicates that the concentration of the propagating anion derived from **MMP** is almost constant during the polymerization.

Next, the k_p^{ap} value at each temperature was calculated from the slope of first-order plot shown in Figure 2. The k_p^{ap} values strongly depended on the poly-

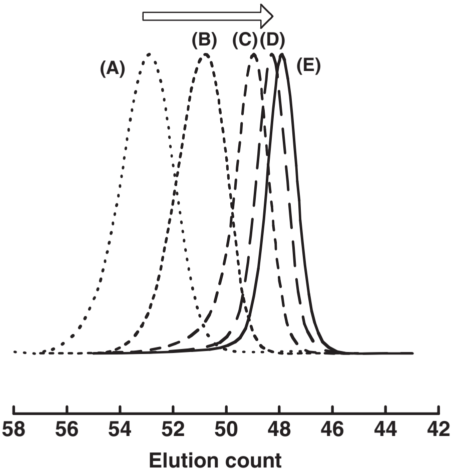


Figure 1.
SEC Traces of Poly(**MMP**) obtained with Ph_2CHK/Et_2Zn(11.9 equivalent) at −30 °C. (A) 5 min, 25%, $M_n = 4{,}900$, $M_w/M_n = 1.09$; (B) 20 min, 40%, $M_n = 8{,}300$, $M_w/M_n = 1.07$; (C) 1 h, 66%, $M_n = 13{,}300$, $M_w/M_n = 1.06$; (D) 2 h, 86%, $M_n = 16{,}600$, $M_w/M_n = 1.05$; (E) 4 h, 97%, $M_n = 18{,}400$, $M_w/M_n = 1.05$.

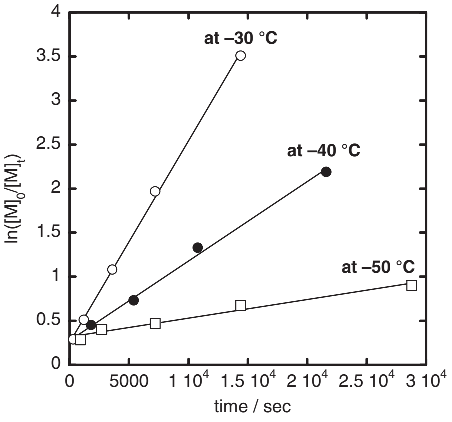


Figure 2.
First-order plots of polymerization of **MMP** at $[M]_0 = 0.49–0.58$ M and $[I]_0 = 3.6–4.1 \times 10^{-3}$ M in the presence of Et_2Zn (11–16 equivalent) in THF.

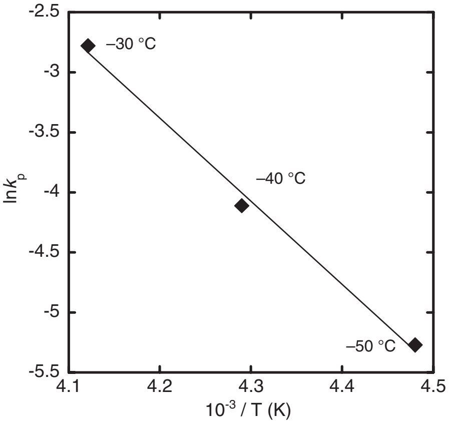


Figure 3.
Arrhenius Plots of k_p for Polymerization of **MMP** ($[M]_0 = 0.49–0.58$ M) with Ph_2CHK ($[I]_0 = 3.6–4.1 \times 10^{-3}$ M) in the presence of Et_2Zn (11–16 equivalent) in THF.

merization temperature, and varied from $0.0624\,L\,mol^{-1}\,s^{-1}$ at −30 °C to $0.00517\,L\,mol^{-1}\,s^{-1}$ at −50 °C. It has been reported that the k_p^{ap} values of the polymerization for **M3** and **M4** (with $Ph_2CHLi/LiCl$ in THF) are $0.165\,L\,mol^{-1}\,s^{-1}$ and $0.0157\,L\,mol^{-1}\,s^{-1}$ at −40 °C.[11,12] Thus, the observed k_p^{ap} value of **MMP** at −40 °C ($0.0164\,L\,mol^{-1}\,s^{-1}$) is approximately ten times smaller than that of **M3** and comparable to that of **M4**, whereas the initiator system was different. On the other hand, it was reported that the anionic polymerizations of methyl methacrylate (MMA) and *tert*-butyl acrylate (tBA) proceeded rapidly and were completed within 5 min even at −78 °C in THF by the same binary initiator system of Ph_2CHK/Et_2Zn.[14,15] By contrast, several hours were necessary for the completion of polymerization of **MMP** at −30 ~ −50 °C under the similar polymerization system. This clearly indicated that the polymerization rate of **MMP** was significantly slower than those of MMA and tBA.

The Arrhenius plots of k_p^{ap} for the anionic polymerization of **MMP** are drawn in Figure 3, and the relationship between k_p^{ap} and the polymerization temperature is expressed in the equation shown below:

$$\ln k_p^{ap} = -6.93 \times 10^3/T + 25.7$$

The activation energy of the polymerization, ΔE_a^{ap}, of **MMP** was calculated to be $57 \pm 5\,kJ\,mol^{-1}$. The significantly low anionic polymerizability of **MMP** is thus realized by the kinetic data such as small rate constant and large activation energy of polymerization. The ΔE_a^{ap} values of **M3** and **M4** (with $Ph_2CHLi/LiCl$ in THF) have been reported to be 49 and $51\,kJ\,mol^{-1}$, respectively.[11,12] The observed ΔE_a^{ap} value for **MMP** was close to those for **M3** and **M4** and was even slightly larger. The lower polymerizability of **MMP** compared to **M3** and **M4** was thus suggested, although the initiator system was different. It should be noted that the ΔE_a^{ap} of **MMP** was significantly larger than the reported value of anionic polymerization of (MMA) (20–25 $kJ\,mol^{-1}$, with organolithiums in THF).[16,17] The ΔE_a^{ap} of MMA for the present initiator system of Ph_2CHK/Et_2Zn is unknown but might be not very large, since the anionic polymerization of MMA readily and rapidly proceeds with Ph_2CHK/Et_2Zn even at low temperature as $-78\,^{\circ}$C in THF.[14] We now consider that the relative anionic polymerizability among **M3**, **M4**, and MMA can be estimated as follows: **MMP** $<$ **M4** $<$ **M3** $<<$ MMA. **MMP** also underwent the radical polymerization with AIBN to give a polymer as previously reported.[13]

The resulting poly(**MMP**) was white powder showing T_g at $169\,^{\circ}$C. The poly(**MMP**) was soluble in $CHCl_3$, THF, DMF, DMSO, methanol, and water but insoluble in hexane, benzene, and Et_2O, indicating its high polarity derived from the NMP ring.

Conclusion

Anionic polymerization of α-methylene-*N*-methylpyrrolidone (**MMP**) possessing *exo*-methylene group certainly proceeds to afford the polymer with predicted molecular weight and narrow MWD in quantitative yield, while the polymerization rate of **MMP** is significantly low. It should be emphasized that this polymerizable monomer, **MMP**, is a cyclic analogue of *N,N*-dimethylmethacrylamide (**DMMA**) showing non-polymerizability. In fact, **MMP** showed the large activation energy of the polymerization, indicating the low anionic polymerizability. This positive anionic polymerizability of **MMP** might derive from the flat conformation between the C=C bond and C=O bond to result in the effective π-conjugation.

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