Stereospecific Anionic Polymerization of *N,N*-Dialkylacrylamides

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ABSTRACT: *N,N*-Dimethylacrylamide (DMA), *N,N*-diethylacrylamide (DEA), *N,N*-dipropylacrylamide (DPA), *N*-ethylmethylacrylamide (EMA), *N*-acryloylpyrrolidine (APY), *N*-acryloylpiperidine (API), and *N*-acryloylmorpholine (AMO) were polymerized with 1,1-bis[(4′-trimethylsilyl)phenyl]-3-methylpentyllithium (**1**) and with 1,1-bis[(4′-trimethylsilyl)phenyl]-3,3-diphenylpropylpotassium (**2**) in THF in the presence of additives. Although the polymers produced directly with **1** or **2** have broad molecular weight distributions, the addition of Et_2Zn to the polymerization systems leads to slow propagation reaction and narrow molecular weight distributions of the polymers. The poly(*N,N*-dialkylacrylamides) produced with **1** are rich in isotactic configuration, while the addition of Et_2Zn reduces isotacticity and increases the degree of syndio- and heterotacticity. In particular, the poly(DEA)s generated with **1**/Et_2Zn and **1**/LiCl are highly syndiotactic and isotactic, respectively. Although the broad distributions of triad sequence are observed for the polymers produced with **2**, the highly heterotactic poly(DEA) is formed with **2**/Et_2Zn at 0 °C. The additive effects of Et_2Zn on the molecular weight and tacticity are supposed to be caused by the coordination of Et_2Zn with the propagating enolate anion.

Introduction

The early work on the anionic polymerizations of *N,N*-dimethyacrylamide (DMA), *N,N*-dipropylacrylamide (DPA), *N,N*-dibutylacrylamide, *N,N*-diphenylacrylamide, and *N*-acryloylmorpholine (AMO) initiated with alkyllithium in toluene was reported by Butler et al. to give highly crystalline polymers.[1] They described that poly(DMA) exhibited a sharp X-ray scattering pattern and a high softening point around 300 °C, suggesting stereospecific polymerization of DMA. Two decades later, a ^1H and ^{13}C NMR study on the tacticity of poly(DMA) produced with *sec*-butyllithium (*s*-BuLi) was performed by McGrath.[2] Although ambiguousness remained in the assignment of the triad sequence, the poly(DMA) produced with *s*-BuLi was regarded as a highly isotactic polymer (*mm* = 81%). Webster et al.[3] obtained poly(DMA) in quantitative yield by group transfer polymerization (GTP) using dimethylketene methyl trimethylsilyl acetal in THF. Although PMMA with the well-defined chain structure was produced by GTP,[4] the poly(DMA) had lower number-average molecular weight (M_n) than the theoretical one and broad molecular weight distribution (MWD). Freitag et al. compared and discussed the lower critical solution temperatures (LCST) in water of the poly(*N,N*-diethylacrylamide)s (poly(DEA)s) produced by GTP and those obtained with *n*-butyllithium.[5] Recently, Hogen-Esch et al. found that the poly(DMA) produced with triphenylmethyllithium was insoluble in THF and highly isotactic, whereas the one formed with (1,1,4,4-tetraphenylbutyl)dicesium possessed low content of *mm* configuration (6%), narrow MWD, and good solubility in THF at −78 °C.[6] Although several investigations have been thus attempted to control the primary structure of poly(DMA), a successful example is still limited to a few cases. Accordingly, it would be very important to develop a synthetic route for the poly(*N,N*-dialkylacrylamides) having predictable M_n and narrow MWD together with highly regulated stereostructures.

In the anionic polymerizations of methacrylates or acrylates, a variety of additives, in the so-called "ligated" approach, have so far been investigated in order to control the activity of the propagating ester enolate anion. Teyssié et al. found the additive effect of LiCl[7] and lithium 2-(2-methoxyethoxy) ethoxide[8] on the anionic polymerizations of MMA and *tert*-butyl acrylate to give narrow MWDs. A similar additive effect of *tert*-BuOLi was observed by Lochmann.[9] Much attention is also given to Lewis acids as another type of additive. Hatada et al. reported that the anionic polymerization of MMA initiated by *tert*-butyllithium (*t*-BuLi) modified with trialkylaluminum[10] and with bis(2,6-di-*tert*-butylphenoxy)methylaluminum[11] afforded highly syndiotactic and heterotactic PMMA, respectively. They suggested that the aluminum compounds coordinated with the carbonyl group of the monomer and with the propagating enolate anion to regulate the stereostructure of the polymer. Smets et al. studied the polymerization of MMA initiated with *n*-butyllithium (BuLi)/diethylzinc (Et_2Zn) in toluene−THF mixtures in various proportions.[12] They discussed dependence of the polymerization rate on ratio of THF and toluene in the medium, but they did not mention the role of Et_2Zn in the polymerization mechanism. Hsieh also investigated the additive effect of Et_2Zn on the anionic polymerizations of butadiene, isoprene, and styrene initiated with BuLi in cyclohexane.[13] Hsieh explained that Et_2Zn dissociated the aggregate of alkyllithium initiator in the hydrocarbon solvent to increase the initiation rate and efficiency. The interactions between (oligo-MMA)$^-Li^+$ and a Lewis acid, such as Et_2Zn, triethylaluminum, or triethylborane, were studied by Tsvetanov et al. from the IR band shifts due to the ester enolate anion.[14] Recently, we have reported anionic polymerization of alkyl methacrylates[15] and acrylates[16] with diphenylmethylpotassium in THF in the presence of Et_2Zn. A remarkable decrease of the propagating rate was observed by the addition of Et_2Zn to the organopotassium initiator system, and living polymers with narrow

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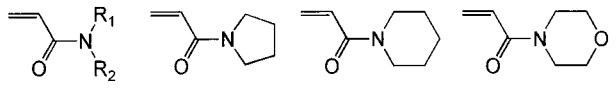
Chart 1



DMA : R_1, R_2 = Me
DEA : R_1, R_2 = Et
DPA : R_1, R_2 = *n*-Pr
EMA : R_1 = Me, R_2 = Et

APY API AMO

MWDs were obtained in quantitative yields. It is suggested that Et_2Zn coordinates with the enolate anion of propagating end to lower its activity and to suppress the side reactions. Furthermore, it has been found that the addition of Et_2Zn to the anionic polymerization system of DEA with an organolithium initiator in THF afforded a syndiotactic polymer with narrow MWD.[17]

In this study, the additive effects of Et_2Zn to the anionic polymerization systems of various *N*,*N*-dialkylacrylamides with lithium and potassium initiators are investigated with respect to precise control of M_n, MWD, and tacticity.

Experimental Section

Materials. Tetrahydrofuran (THF) was refluxed over sodium wire, distilled over $LiAlH_4$, and then distilled from sodium naphthalene solution on a vacuum line. Et_2Zn was purchased from TOSOH Akuzo Co. and was used as a THF solution. To remove impurities, LiCl was dried under high vacuum (10^{-6} mmHg) for 48 h with baking every 1 h.

1,1-Bis[(4′-trimethylsilyl)phenyl]ethylene (TMS_2DPE)[18] was dried and distilled over CaH_2. Commercially available *s*-BuLi was used without further purification. Diphenylmethylpotassium was prepared by the reaction of diphenylmethane and potassium naphthalene in THF at room temperature. The concentration was determined by colorimetric titration with 1-octanol in a sealed tube in vacuo.[19]

***N*,*N*-Dimethylacrylamide (DMA), *N*,*N*-Diethylacrylamide (DEA), and Acryloylmorpholine (AMO).** Commercially available DMA, DEA, and AMO monomers were purified by fractional distillation under reduced pressure from CaH_2. The distilled monomers were diluted with THF and were further distilled over CaH_2 on a vacuum line, and then sealed into evacuated ampules before use. For the postpolymerization experiment, DEA was prepared by the reaction of acryloyl chloride (30.4 g, 336 mmol) and diethylamine (49.5 g, 677 mmol) in dry Et_2O. The crude product was purified by silica gel column chromatography using hexane/ethyl acetate (10/1, v/v) as an eluent, and the purified fraction was distilled from CaH_2 five times to afford 9.70 g (23%) of DEA. DMA: bp 48−49 °C (5 mmHg). DEA: bp 83−85 °C (15 mmHg). AMO: bp 105−107 °C (1 mmHg). Structures for DMA, DEA, DPA, and EMA are shown in Chart 1.

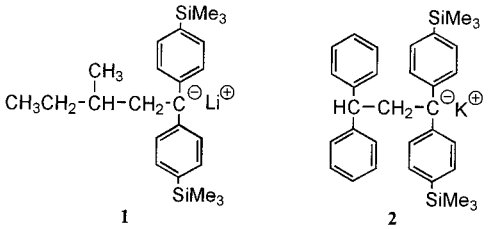
***N*,*N*-Dipropylacrylamide (DPA) and *N*-Acryloylpyrrolidine (APY).** DPA or APY was respectively prepared by the reaction of acryloyl chloride and a 2-fold molar of dipropylamine or pyrrolidine in dry Et_2O. The monomer was purified by flash silica gel column chromatography using hexane/ethyl acetate (10/1, v/v) as an eluent, and by repeated distillation from CaH_2.

DPA: yield 65%; bp 46−47 °C (2 mmHg). APY: yield 24%; bp 50−53 °C (0.9 mmHg).

***N*-Ethylmethylacrylamide (EMA) and *N*-Acryloylpiperidine (API).** EMA or API was prepared by the reaction of acryloyl chloride and *N*-ethylmethylamine or piperidine in the presence of triethylamine in dry Et_2O. After the precipitated ammonium salt was filtered off, EMA was purified by repeating distillation from CaH_2. API was purified by flash silica gel column chromatography using hexane/ethyl acetate (8/1, v/v) and by distillation.

EMA: yield 69%; bp 53.0−53.5 °C (3.5 mmHg). 300 MHz ^{1}H NMR ($CDCl_3$): δ 1.17 (m, 3H, CH_3), 2.99 and 3.06 (s, 3H, NCH_3), 3.46 (m, 2H, NCH_2), 5.67 (dd, 1H, cis β-CH_2, J = 10.4 and 1.9 Hz), 6.31 (dd, 1H, trans β-CH_2, J = 16.8 and 1.9 Hz), 6.58 (dd, 1H, α-CH, J = 16.8 and 10.4 Hz). 75 MHz ^{13}C NMR ($CDCl_3$): δ 12.7 and 13.9 (CH_3), 33.2 and 34.8 (NCH_3), 42.6 and 44.6 (NCH_2), 127.4 (vinyl, CH_2=), 127.6 and 128.0 (vinyl, =CH), 165.9 and 166.2 (C=O). API : yield 51%; bp 53−54 °C (0.4 mmHg).

Chart 2



1 **2**

Initiators. To a heptane solution of *s*-BuLi or a THF solution of diphenylmethylpotassium was added a small molar excess of TMS_2DPE in THF, and the mixture was kept at −78 °C for 20 min to give1,1-bis[(4′-trimethylsilyl)phenyl]-3-methylpentyllithium (**1**) or 1,1-bis[(4′-trimethylsilyl)phenyl]-3,3-diphenylpropylpotassium (**2**). The M_n of the resulting polymer was evaluated based on the relative intensities of the proton NMR signals of the main and side chain of the polymer and trimethylsilyl proton signal (0.1−0.2 ppm) of the initiator fragment attached to the polymer chain end. The structures of **1** and **2** are shown in Chart 2.

Polymerization. The polymerization was typically performed under vacuum conditions in a glass apparatus equipped with break-seals as follows; 2−15 equiv mol of Et_2Zn vs initiator was introduced into the initiator solution and maintained at −78 °C for 10 min, and then the monomer in THF was added to the initiator system with vigorous stirring at 0 °C for 60 min. On addition of the monomer, the characteristic red color of the initiator rapidly disappeared and turned pale yellow or purple. The reaction was terminated with methanol. After the reaction mixture was concentrated by evaporation and poured into a large excess of hexane to precipitate the polymer, the isolated polymer was again dissolved in THF (or methanol) and filtered to remove the precipitated zinc compound. The polymer was further purified by freeze-drying from benzene.

Measurements. Gel-permeation chromatogram (GPC) of the polymer with low level *mm* configuration was measured by a TOSOH HLC-8020 instrument equipped with three polystyrene gel columns (TOSOH $G5000H_{XL}$, $G4000H_{XL}$, and $G3000H_{XL}$) with ultraviolet (254 nm) and refractive index detection using THF as an eluent at a flow rate 1.0 mL min^{-1} at 40 °C. As eluents, chloroform and *N*,*N*-dimethylformamide (DMF) containing 0.01 M LiBr were employed for the isotactic polymers and for poly(APY), poly(AMO), and the syndiotactic poly(DMA), respectively, using the polystyrene gel columns (TOSOH TSK-GEL GMH_{XL} ×2).

The NMR spectra were recorded in $CDCl_3$ or 1,4-dioxane-d_8 solution at 50 °C with a JEOL GSX-500 (^{1}H 500.16 MHz) and a BRUKER DPX-300 (^{1}H 300.13 MHz). The chemical shifts in ppm were referenced to tetramethylsilane (δ 0) internal standard for ^{1}H NMR and $CDCl_3$ (δ 77.1) or 1,4-dioxane-d_8 (δ 66.5) for ^{13}C NMR.

Matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI−TOF−MS) was performed on REFLEX II (BRUKER DALTONICS) in positive linear and reflector mode at 27.5 kV ion acceleration, 30 kV reflector and −1.5 kV multiplier voltages with a 337 nm nitrogen laser, and a gridless pulsed ion extraction ion source. A SCOUT computerized XY-motion target control and 2 GHz digitizer were used. *trans*-3-Indoleacrylic acid (IAA) was used as the matrix. Polymer, IAA, and sodium trifluoroacetate (NaTFA) were dissolved in THF at a concentration of 1.5, 10, and 10 mg/mL, respectively. The MALDI sample was prepared by mixing 10 μL of the polymer solution, 90 μL of the IAA solution, and 10 μL of the NaTFA solution, and a 5 μL aliquot of the mixed solution was applied to a target and air-dried.

Table 1. Anionic Polymerization of *N,N*-Dialkylacrylamides with 1 in THF at −78 °C

run	initiator/additive (ratio)	monomer	time, min	yield, %	$M_n \times 10^{-3}$ calcd[a]	$M_n \times 10^{-3}$ obsd[b]	M_w/M_n[c]	polymerization state	remarks[f]
1	**1**	DMA	60	100	9.4	11	2.58[d]	heterogeneous	ref 17
2	**1**	DEA	60	100	9.9	11	2.83[d]	heterogeneous	ref 17
3	**1**	DEA	0.25	93	59	46[c]	3.07[d]	heterogeneous	this work
4	**1**	DPA	60	97	11	14	1.52	homogeneous	ref 17
5	**1**	EMA	30	99	11	16	4.75[d]	heterogeneous	this work
6	**1**	APY	30	100	8.2	14	2.26[e]	homogeneous	this work
7	**1**	API	30	100	9.3	11	2.42[d]	heterogeneous	this work
8	**1**	AMO	60	100	14	13	2.73[d]	heterogeneous	this work
9	**1**/LiCl (1/4.4)	DMA	60	100	11	13	6.17[d]	heterogeneous	ref 17
10	**1**/LiCl (1/2.8)	DEA	60	99	10	11	3.00[d]	heterogeneous	ref 17
11	**1**/LiCl (1/5.4)	DPA	60	99	8.2	8.1	2.32	homogeneous	ref 17
12	**1**/LiCl (1/6.2)	EMA	30	100	11	16	8.18[d]	heterogeneous	this work
13	**1**/LiCl (1/6.0)	API	30	100	10	11	10.3[d]	heterogeneous	this work
14	**1**/Et_2Zn (1/12.0)	DMA	60	96	9.2	9.3	1.14[e]	homogeneous	ref 17
15	**1**/Et_2Zn (1/18.2)	DEA	60	100	9.6	11	1.12	homogeneous	ref 17
16	**1**/Et_2Zn (1/19.2)	DEA	0.25	48	8.3	2.7[c]	1.09	homogeneous	this work
17	**1**/Et_2Zn (1/17.5)	DPA	60	100	7.5	6.7	1.41	homogeneous	ref 17
18	**1**/Et_2Zn (1/12.0)	EMA	15	86	8.3	8.2	1.35[e]	homogeneous	this work
19	**1**/Et_2Zn (1/16.7)	APY	15	100	9.5	10	1.11[e]	homogeneous	this work
20	**1**/Et_2Zn (1/18.5)	API	60	52	5.1	6.7	1.08	homogeneous	this work
21	**1**/Et_2Zn (1/14.1)	AMO	60	100	10	10	1.23[e]	heterogeneous	this work
22	Et_2Zn[g]	DEA	60	40		1.8[c]	1.57	homogeneous	this work
23	Et_2Zn[g,h]	DEA	60	44		2.4[c]	1.71	homogeneous	this work
24	Et_2Zn[g,h]	DEA	540	78		53[c]	1.18	homogeneous	this work
25	AIBN[i]	DEA	120	100		73[c]	1.92	homogeneous	this work

[a] M_n(calcd) = (MW of monomer) × yield/100 × [monomer]/[**1**] + (MW of **1**). [b] Determined by ^{1}H NMR based on the relative intensities of the main chain and initiator fragment. [c] Measured by GPC using PMMA standards in THF. [d] GPC in chloroform. [e] GPC in DMF. [f] These data were obtained in this work and in our previous one. [g] [DEA]/[Et_2Zn] = 3. [h] At 0 °C. [i] Radical polymerization was carried out with AIBN in benzene at 60 °C for 2 h under N_2 ([DEA]/[AIBN] = 100).

LCST of poly(DEA) in water was determined as an onset of the transmittance decrease with the increasing temperature using JASCO UVIDEC-660 spectrometer. Transmittance of 0.2 wt % polymer solution at 500 nm was continuously monitored in a flow-through PMMA cell (path length of 1.0 cm) at the rate of temperature increase 0.05 °C/min under controlled temperature (±0.1 °C).

Results and Discussion

Anionic Polymerization with Organolithium Initiator (1). It is well-known that the radical polymerization of DMA gives a polymer soluble in water and most of organic solvents. However, the poly(DMA) anionically produced with an organolithium initiator exhibits poor solubilities in organic solvents, probably due to the high stereoregularity and crystallinity of the polymer.[1] From the ^{1}H and ^{13}C NMR spectroscopic analysis, McGrath et al. first suggested that the poly(DMA) produced with *s*-BuLi was highly isotactic as described in detail later.[2] Hogen-Esch et al.[6] also reported that the anionic polymerization of DMA initiated with organolithium initiators resulted in the polymer being insoluble in toluene, 1,4-dioxane, THF, and DMF. Accordingly, the M_n and MWD of the polymer have not been determined so far by GPC measurements because of the poor solubility in the solvents. By a MALDI−TOF−MS measurement, Freitag et al. estimated M_n and MWD of poly(DEA) produced with BuLi in THF at −70 °C; M_n^{calc} = 2800, M_n^{obs} = 3505, and M_w/M_n = 1.99.[5] However, the M_n evaluated by MALDI−TOF−MS should be calibrated by the other method, since the relative signal intensity in the wide range of the spectrum may not be completely independent of M_n. Recently, we have investigated the anionic polymerization of DMA with **1** in THF at −78 °C.[17] The polymers generated with both **1** and **1**/LiCl were insoluble in THF, but soluble in chloroform, as Hogen-Esch reported.[6] The GPC measurements of the poly(DMA)s using chloroform as an eluent revealed that the polymer yielded with **1**/LiCl possessed a much broader MWD than that obtained with **1**.[17] Although many researchers investigated the anionic polymerization of *N,N*-dialkylacrylamides with organolithium initiators, the chain structures of resulting polymers have not been well controlled yet.

In this study, a series of *N,N*-dialkylacrylamides were polymerized with **1** in THF at −78 °C to discuss their polymerization behaviors. During the polymerizations with **1** in the absence and presence of LiCl, the reaction systems became soft gels to afford polymers insoluble in THF except for the cases of DPA and APY. The results of the anionic polymerizations of *N,N*-dialkylacrylamides are summarized in Table 1. The polymers were obtained in quantitative yields within 1 h at −78 °C for most of the cases. The M_n's of the polymers were estimated from the ^{1}H NMR relative signal intensities of silylmethyl protons (0.1−0.2 ppm) of the initiator residue and those of the protons on the main and side chain. The observed M_n's agree with the calculated ones based on the molar ratios of monomer to initiator in the feed as shown in Table 1. These results indicate that the polymerizations are initiated with **1** in quantitative efficiency and proceed without chain transfer reactions. The M_w/M_n values of the polymers generated with **1** or **1**/LiCl were estimated by the GPC calibrated with PMMA standards using chloroform as an eluent. As the case of poly(DMA), the polymers produced in the absence of additive (runs 1−8) exhibit broad MWDs. Although the addition of LiCl to the anionic polymerization system of *tert*-butyl acrylate inhibits backbiting termination resulting in a narrow MWD,[7b] the **1**/LiCl initiator system affords poly(*N,N*-dialkylacrylamide)s with very broad MWDs (runs 9−13).

Table 2. Anionic Polymerization of *N,N*-Dialkylacrylamides with 2 in THF

run	initiator/additive (ratio)	monomer	temp, °C	time, min	yield, %	$M_n \times 10^{-3}$ calcd[a]	$M_n \times 10^{-3}$ obsd[b]	M_w/M_n[c]
26	**2**	DMA	−78	60	98	11	14	2.85
27	**2**	DEA	−78	60	100	10	15	2.37
28	**2**	DEA	−78	0.25	97	21	23	1.63
29	**2**	DPA	−78	60	100	8.6	13	1.86
30	**2**	EMA	−78	30	100	9.6	8.1	2.18
31	**2**	APY	−78	15	100	7.9	8.0	3.03
32	**2**	API	−78	30	100	9.9	11	1.60
33	**2**	AMO	−78	60	100	9.4	9.0	1.67[d]
34	**2**/Et_2Zn (1/14.8)	DMA	−78	60	60	8.5	5.6	1.07
35	**2**/Et_2Zn (1/18.1)	DMA	0	30	100	11	9.8	1.07[d]
36	**2**/Et_2Zn (1/14.6)	DEA	−78	60	57	10	7.8	1.12
37	**2**/Et_2Zn (1/18.2)	DEA	−78	360	93	6.6	6.8	1.16
38	**2**/Et_2Zn (1/ 1.0)	DEA	−78	1	100	15	21	1.31
39	**2**/Et_2Zn (1/15.1)	DEA	−40	60	100	10	8.6	1.09
40	**2**/Et_2Zn (1/16.8)	DEA	0	60	100	9.3	8.6	1.08
41	**2**/Et_2Zn (1/15.8)	DEA	0	20	100	41	45	1.05
42	**2**/Et_2Zn (1/14.1)	DEA	18	60	100	9.1	8.7	1.10
43	**2**/Et_2Zn (1/15.8)	DEA	40	60	100	9.2	8.7	1.15
44	**2**/Et_2Zn (1/16.8)	DPA	−78	60	33	8.9	7.8	1.16
45	**2**/Et_2Zn (1/19.6)	DPA	0	60	100	11	15	1.17
46	**2**/Et_2Zn (1/15.2)	DPA	25	30	100	7.4	6.5[c]	1.16
47	**2**/Et_2Zn (1/17.2)	EMA	0	30	100	10	8.0	1.12
48	**2**/Et_2Zn (1/16.4)	APY	0	15	100	9.6	8.2	1.10
49	**2**/Et_2Zn (1/19.1)	API	0	30	100	10	10	1.07
50	**2**/Et_2Zn (1/15.5)	AMO	0	60	100	10	10	1.09[d]

[a] M_n(calcd) = (MW of monomer) × yield/100 × [monomer]/[**2**] + (MW of **2**). [b] Determined by ^1H NMR based on relative intensities of the main chain and initiator fragment. [c] Measured by GPC using PMMA standards in THF as an eluent. [d] Measured by GPC using PMMA standards in DMF as an eluent.

We have been so far investigating the additive effect of Et_2Zn on the anionic polymerization of alkyl methacrylates[15] and *tert*-butyl acrylate[16] to stabilize the propagating enolate anion generating the polymers with predictable M_n's and very narrow MWDs. A similar effect is expected for the cases of *N,N*-dialkylacrylamides. The polymerization of the acrylamide derivatives with **1**/Et_2Zn system proceeded almost homogeneously to give the THF-soluble polymers in quantitative yields at −78 °C within 1 h (runs 14−21), except for EMA (run 18) and API (run 20). The resulting polymers had predicted M_n's and narrower MWDs than the ones produced with **1** or **1**/LiCl. When the polymerization of DEA was carried out with **1**/Et_2Zn for 15 s (run 16), 52% of unreacted monomer remained. In contrast, 93% conversion was achieved within 15 s in the absence of Et_2Zn (run 3). Although the detailed kinetic investigation had not been performed yet, it is apparent that the polymerizations with **1** proceed much faster than those with **1**/Et_2Zn. Et_2Zn may function as a weak Lewis acid to coordinate with the enolate anion to stabilize the carbanionic species resulting in slow propagation reaction and narrow MWD. In the absence of Et_2Zn, the propagating rate might be too fast to stir the reaction mixture enough resulting in broad MWD.

It is already known that Et_2Zn itself is capable of catalytic activity for the polymerization of some polar vinyl monomers. Tsuruta and co-workers reported that methyl vinyl ketone was directly polymerized with Et_2Zn.[20] We also examined the activity of Et_2Zn for the polymerization of DEA as an initiator (runs 22−24). Quantitative yield of the polymer was not obtained even after 9 h at 0 °C. In addition, the observed molecular weights could not be correlated to the polymer yields and the amount of Et_2Zn added, whereas the polymer bearing a well-defined chain structure was generated with **1**/Et_2Zn. Considering these results, the polymerization of DEA initiated with Et_2Zn seems not to proceed concurrently during the polymerization with **1**/Et_2Zn system. This is also substantiated in terms of the tacticity of the poly(DEA)s produced with Et_2Zn and **1**/Et_2Zn as described later.

Anionic Polymerization with Organopotassium Initiator (2). Hogen-Esch et al. first reported that the polymerization of DMA initiated with an organopotassium proceeded in homogeneous state in THF to give the polymers bearing moderate polydispersity indices of 1.31−1.24.[6] In this study, the polymerizations of *N,N*-dialkylacrylamides were performed with **2** at −78 °C in the homogeneous THF solution, which showed the characteristic red color. When the reaction was quenched with methanol, the red color disappeared. All the polymers were obtained quantitatively within 1 h. The results are summarized in Table 2 (runs 26−33). The observed M_n's agree with the calculated values, indicating the quantitative initiation efficiency of **2** and the absence of chain transfer reaction. The MWDs of the polymers produced were rather broad (M_w/M_n > 1.6) (runs 26−33), as well as the cases of alkyllithium initiator. Hogen-Esch et al. suggested that initiator or active chain end attacked the carbonyl carbon of monomer or polymer to leave the dialkylamide anion.[6c] However, these Claisen type deactivations are unlikely because of high pK_a value of dialkylamine and the results of MALDI−TOF−MS.[21] We are considering that the propagating carbanions do not abstract the methine proton of the polymer backbone during the polymerization of *N,N*-dialkylacrylamides, in contrast to the case of acrylates.[21] Since the polymerization proceeded very rapidly, the initiator and the monomer could not be well mixed during the polymerization to lead to broad MWD. Actually, DEA was completely converted into the polymer within 15 s at −78 °C (run 28).

To lower the propagation rate and to obtain a polymer with narrow MWD, Et_2Zn was added to the polymerization system at the molar ratio of Et_2Zn/**2** = 15−20.

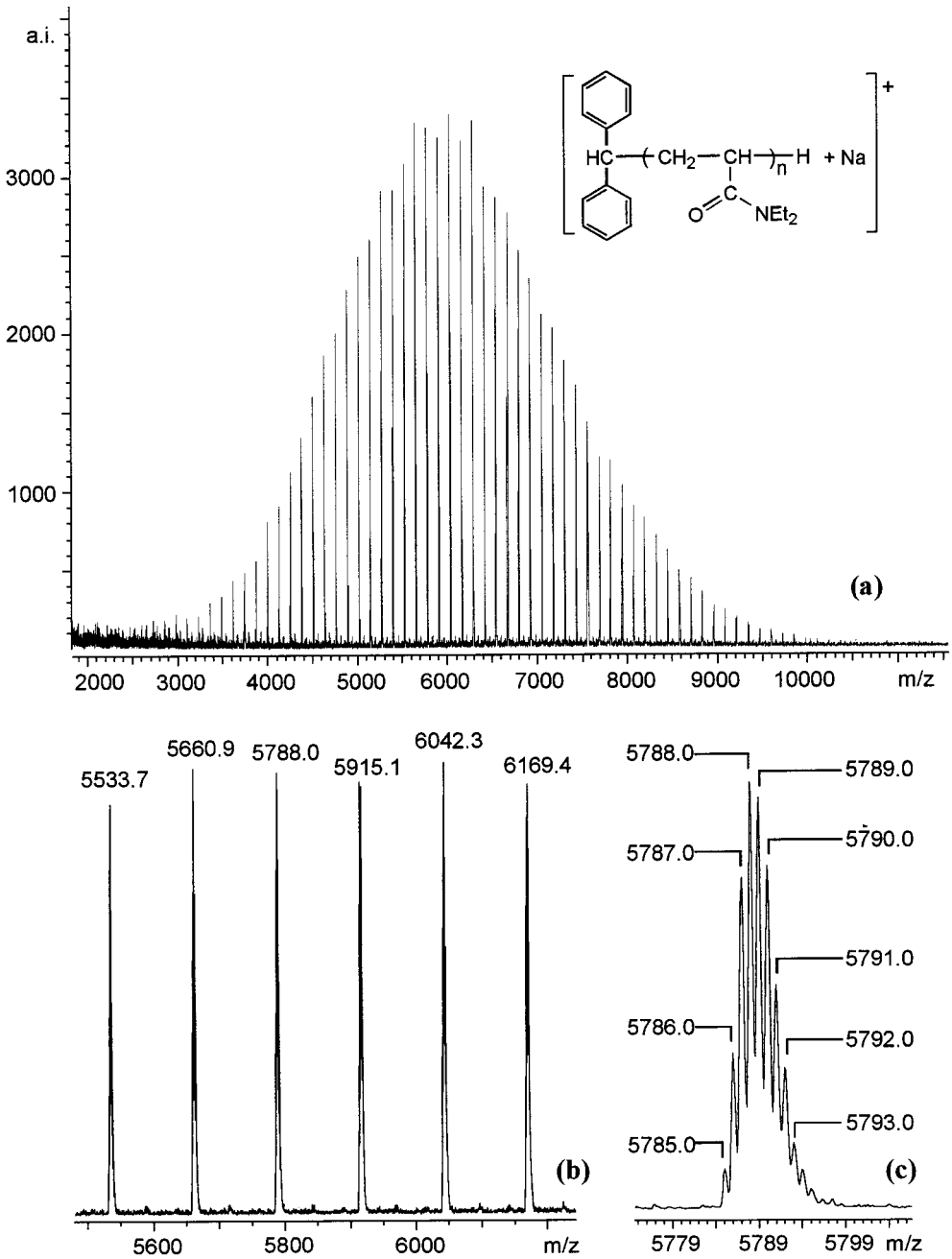


Figure 1. MALDI−TOF−MS of poly(DEA) produced with diphenylmethylpotassium in the presence of Et_2Zn at 0 °C: (a) broad band spectrum in reflector mode; (b) expanded spectrum; (c) peak distribution due to isotopic abundance.

The polymerizations of *N*,*N*-dialkylacrylamides with **2**/Et_2Zn proceeded in the colorless homogeneous solution to result in narrow MWDs in most of the cases (runs 34−50) except for the case of a small amount of Et_2Zn (run 38). Since the polymerizations were not virtually completed in 1 h at −78 °C (runs 34, 36, and 44), the reaction time was prolonged to 6 h, generating the polymer in 93% yields (run 37). It is supposed that the slow propagation reaction is caused by coordination of Et_2Zn with the propagating enolate anion. Therefore, an anionic polymerization of DMA was carried out at an elevated temperature (0 °C) to accelerate the propagation (run 35). As a result, polymerization at 0 °C was finished within 30 min to yield a poly(DMA) having an expected M_n and narrow MWD ($M_w/M_n = 1.11$). Hogen-Esch et al. reported that the poly(DMA)s obtained with triphenylmethylcesium in THF at −78 °C had narrow MWDs ($M_w/M_n = 1.07$), while the polymer generated at 0 °C showed broad MWD ($M_w/M_n = 1.87$).[6] Interestingly, the **2**/Et_2Zn system afforded also the poly(DEA) having a narrow MWD in quantitative yield even at 0−40 °C (runs 40−43). As well as the cases of DMA and DEA, the other polymers with narrow MWDs were obtained from DPA, EMA, APY, API, and AMO in 100% yield at 0 °C within 1 h.

Figure 1 illustrates the MALDI−TOF−MS of poly(DEA) produced with diphenylmethylpotassium/Et_2Zn (1/17, mol/mol) at 0 °C. The broad band spectrum (Figure 1a), covers a molecular weight distribution beginning with the sodiated polymer of *m*/*z* 3000 up to 10000. The expanded spectrum from 5500 to 6200 Da was shown in Figure 1b. The series of observed masses (*m*/*z* = 5533.7, 5660.9, 5788.0, etc.) are in good agreement with the exact values of the DEA monomer unit

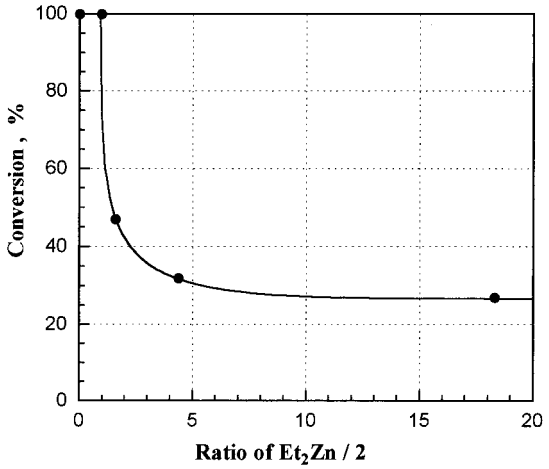


Figure 2. Relationship between conversion (%) of DEA and feed ratio of Et_2Zn/**2**. Reaction conditions: in THF at −78 °C for 15 s.

(127.186 Da) multiplied by *n* (*n* = 42, 43, 44, etc.) plus initiator fragment (Ph_2CH, 167.23 Da) plus Na^+ (22.99 Da). Each peak splits further into multiplet at intervals of 1 mass due to the isotope distribution in Figure 1c. These results mean that the initiation reaction certainly occurs with the diphenylmethyl anion and not with ethylide derived from Et_2Zn and that polymerization proceeds without any side reactions even at 0 °C.

To elucidate the effect of Et_2Zn on the polymerization, the rate of polymerization of DEA was briefly investigated by changing the molar ratio between Et_2Zn and **2**, as shown in Figure 2. The conversion was measured by detection of the residual monomer using gas chromatography after the polymerization at −78 °C for 15 s. The polymerization was finished completely within 15 s in the absence of Et_2Zn. When an only 1.6-fold molar amount Et_2Zn was added to polymerization system, the conversion was remarkably reduced to 47%. The reduction seemed to be leveled off at the ratio Zn/**2** = 4. Although large excess amount of Et_2Zn (18-fold molar amount) was added to the reaction mixture, the propagating enolate anion still kept the activity to attain 27% conversion of DEA in 15 s. These results suggest that a small definite number of Et_2Zn molecules coordinate with the amide enolate anion leading to the low activity of the propagating end and the slow propagation reaction.

Persistency of the propagating enolate anion of DEA was evaluated by the postpolymerization with **2** in the presence of Et_2Zn in THF at 0 °C. The GPC profiles of the products are shown in Figure 3. After the first stage polymerization of DEA with **2** for 1 min at 0 °C, the postpolymerization was subsequently carried out for 3 min by addition of a second feed of DEA. It was confirmed in advance that DEA was consumed completely with **2**/Et_2Zn (1/20) at 0 °C within 1 min. As can be seen, a small peak appears in the lower molecular weight region of the GPC (Figure 3a). This peak is attributed to the polymer of the first stage, the propagating end of which is partly deactivated before the second-stage polymerization. A shoulder in the higher molecular weight region was also observed, probably due to the coupling reaction. From the relative peak areas of the GPC, the amount of the deactivated propagating end at 0 °C for 1 min was estimated to be 12 mol % (Figure 3a). The first-stage polymerization time was elongated to 20 min, resulting in similar level

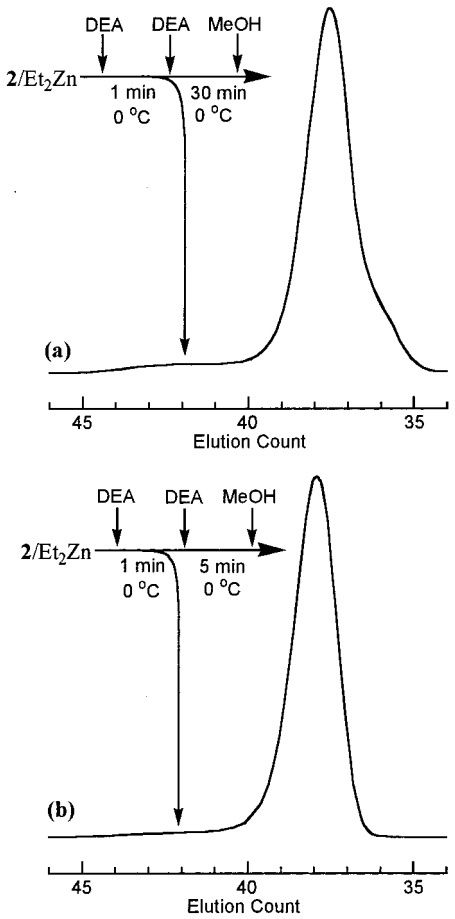


Figure 3. GPC curves of second-stage poly(DEA) generated with **2**/Et_2Zn in THF at 0 °C, after the first stage polymerization for 1 min: (a) purchased DEA and (b) DEA prepared from acryloyl chloride and diethylamine.

deactivation (19 mol %). These suggest that the deactivation takes place with impurities in the monomer solution. In this polymerization, commercial DEA (KOJIN Co.) produced from methyl acrylate and diethylamine was employed. The purified monomer still included a very small amount of methyl acrylate, its Michael adduct with diethylamine, and *p*-methoxyphenol, which were detected by gas chromatography. It was very difficult to remove these impurities from the DEA monomer. Once the methyl acrylate unit is incorporated in the polymer chain, several termination reactions would occur to result in broad MWD. Then, postpolymerization was carried out again (Figure 3b) with DEA synthesized from acryloyl chloride and diethylamine (see Experimental Section). As can be seen in Figure 3b, the peak of the base polymer is not observed in the GPC curve of the postpolymer. This indicates that the coordination of Et_2Zn with amide enolate anion completely suppresses the α-proton abstraction and the backbiting reaction, even at 0 °C, and that the polymerization has a living nature at least for 1 min at 0 °C in THF.

Tacticity and Solubility of Poly(*N,N*-dialkylacrylamides). As described before, DMA was polymerized with a lithium initiator to give the highly crystalline polymer, which is insoluble in benzene, THF, and DMF and partially soluble in water,[22] while the poly(DMA) prepared with a radical initiator was amorphous and soluble in most organic solvents and water. From these results, Butler and co-workers suggested

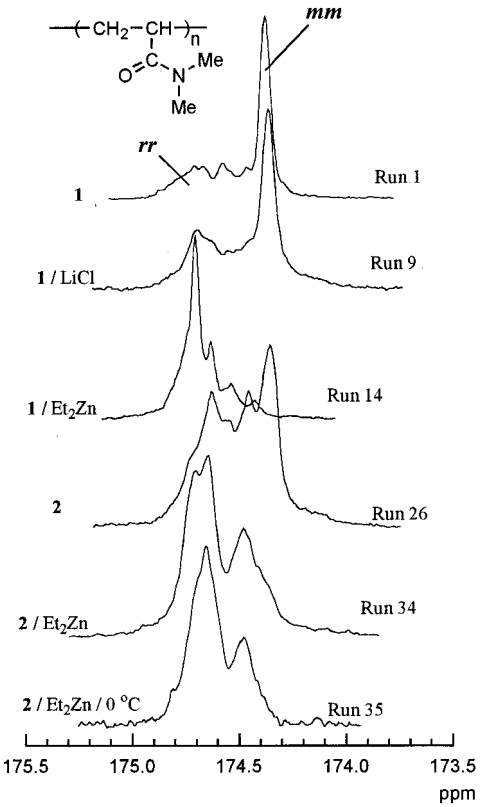


Figure 4. ^{13}C NMR spectra of the carbonyl carbons of the poly(DMA)s measured in $CDCl_3$ at 50 °C. For the conditions of polymerization, see Tables 1 and 2.

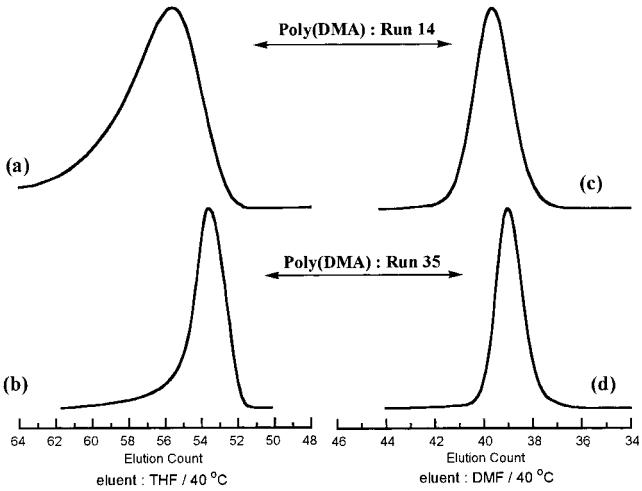


Figure 5. THF−GPC (left) and DMF−GPC (right) profiles of poly(DMA): M_n(^{1}H NMR) = 9300, M_n(THF−GPC) = 2900 (M_w/M_n = 1.30) (a), M_n(DMF−GPC) = 10 400 (M_w/M_n = 1.14) (c) for run 14; M_n(^{1}H NMR) = 9800, M_n(THF−GPC) = 6700 (M_w/M_n = 1.11) (b), M_n(DMF−GPC) = 14000 (M_w/M_n = 1.07) (d) for run 35. M_n(GPC) was estimated using PMMA standards.

that the poly(DMA) obtained with a lithium initiator was rich in the isotactic configuration and also pointed out that acid hydrolysis of the isotactic polymer proceeded faster than that of the atactic polymer, presumably due to the neighboring group effect on the polymer chain.[1,23] McGrath et al. reported an NMR study on the tacticity of poly(DMA).[2a,b] However, the stereostructure could not be appropriately characterized by *N*-methyl proton resonances, which showed complex patterns owing to the combination of the tacticity and the partially hindered rotation around the amide bond.

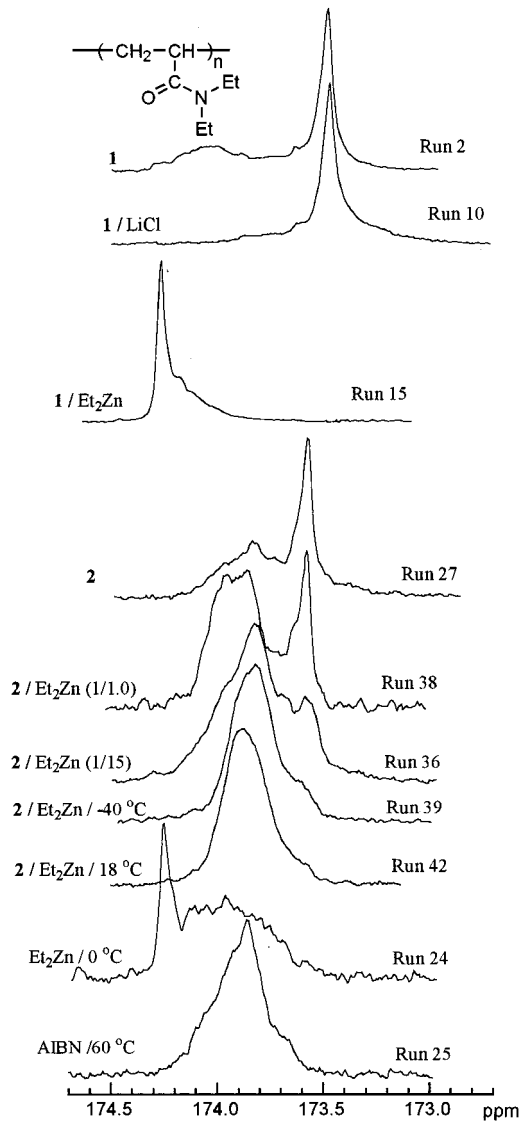


Figure 6. ^{13}C NMR spectra of the carbonyl carbons of the poly(DEA)s measured in $CDCl_3$ at 50 °C. For the conditions of polymerization, see Tables 1 and 2.

Thus, they analyzed ^{13}C NMR signals of carbonyl carbon of the poly(DMA) produced with *s*-BuLi, assigning the isolated sharp peak at 174.4 ppm to the *mm* configuration (*mm* = 81%),[2d] although the other signals at the lower magnetic field around at 174.7 ppm due to *rr* and *mr* sequence were not well resolved. Hogen-Esch et al. investigated the ^{13}C NMR analysis of the poly(DMA) prepared with initiators associated with lithium, potassium, and cesium counterions.[6] They described that the isotactic triad content of poly(DMA) decreased with increasing counterion size of the anionic initiator, although the contents of *mr* and *rr* triads could not be measured separately.

A series of ^{13}C NMR spectra of the poly(DMA)s produced are shown in Figure 4. According to McGrath's results, the poly(DMA) produced with **1** exhibits a sharp isolated signal at 174.3 ppm with large intensity, indicating that the polymer is rich in isotactic configuration (run 1). Although the additive effect of LiCl is negligible on the tacticity (run 9), the addition of Et_2Zn to **1** causes an explicit change of the spectrum in the carbonyl carbon region: complete disappearance of *mm* signal and emergence of the sharp peak at 174.7 ppm

Table 3. Solubilities[a] of the Resulting Polymers

			solvent					
run	polymer	initiator	H_2O	MeOH	DMF	$CHCl_3$	THF	benzene
1	poly(DMA)	**1**	S	S	I	S	I	I
9	poly(DMA)	**1**/LiCl	S	S	I	S	I	I
14	poly(DMA)	**1**/Et_2Zn	S	S	S	S	S	S
35	poly(DMA)	**2**/Et_2Zn	S	S	S	S	S	S
10	poly(DEA)	**1**/LiCl	S	S	I	S	I	Sw
15	poly(DEA)	**1**/Et_2Zn	I	S	S	S	S	S
40	poly(DEA)	**2**/Et_2Zn	S	S	S	S	S	S
4	poly(DPA)	**1**	I	S	I	Sw	S	S
45	poly(DPA)	**2**/Et_2Zn	I	S	S	I	S	S
12	poly(EMA)	**1**/LiCl	S	S	S	S	I	I
18	poly(EMA)	**1**/Et_2Zn	S	S	S	S	S	S
30	poly(EMA)	**2**	S	S	S	S	S	S
47	poly(EMA)	**2**/Et_2Zn	S	S	S	S	S	S
6	poly(APY)	**1**	S	S	S	S	S	S
19	poly(APY)	**1**/Et_2Zn	S	S	S	S	S	S
48	poly(APY)	**2**/Et_2Zn	S	S	S	S	S	S
7	poly(API)	**1**	I	S	I	S	I	S
13	poly(API)	**1**/LiCl	I	I	I	S	I	I
20	poly(API)	**1**/Et_2Zn	I	S	S	S	S	S
32	poly(API)	**2**	I	S	S	S	S	S
8	poly(AMO)	**1**	S	I	I	S	I	I
21	poly(AMO)	**1**/Et_2Zn	S	I	S	S	I	I
33	poly(AMO)	**2**	S	I	S	S	I	I
50	poly(AMO)	**2**/Et_2Zn	S	I	S	S	S	I

[a] Key: S, soluble; I, insoluble; Sw, swelling; DMF, *N*,*N*-dimethylformamide.

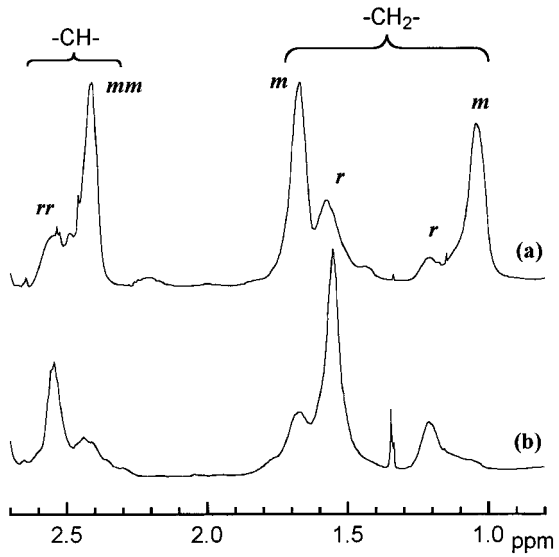


Figure 7. ^1H NMR spectra of poly(DMA)s: (a) run 1; (b) run 14. ^1H NMR spectra were measured in $CDCl_3$ at 50 °C using 500 MHz NMR.

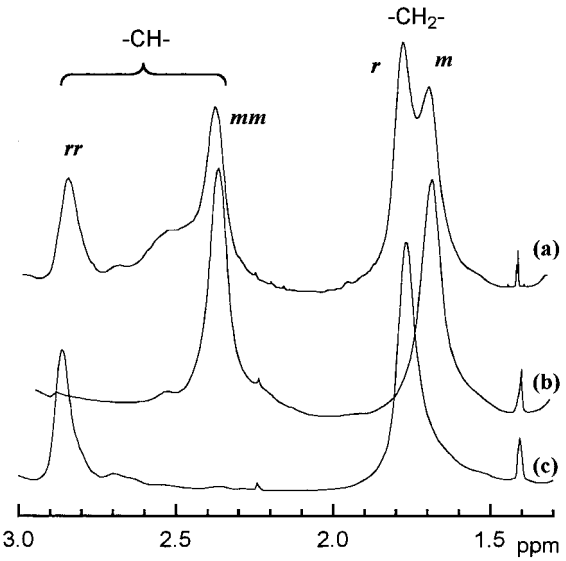


Figure 8. ^1H NMR spectra of poly(DEA)s: (a) poly(DEA) produced with the **1**/Et_2Zn (1/2, mol/mol) system;[17] (b) run 10; (c) run 15. ^1H NMR spectra were measured in $CDCl_3$ at 50 °C using 500 MHz NMR.

(run 14). The signal is clearly separated from the other ones and may be assigned to the *rr* configuration. Several small peaks observed between the *mm* and *rr* signals (174.3 and 174.7 ppm) might be attributable to *mr*, *mmr*, and *mrr* configurations, although the exact assignment could not be determined yet. Anyhow, the syndiotactic poly(DMA) produced with **1**/Et_2Zn is soluble in water and most organic solvents in contrast to the isotactic one, as shown in Table 3. With a potassium initiator, **2**, poly(DMA) bearing a broad triad distribution was formed (Figure 4, run 26), as was described by Hogen-Esch.[6] The addition of Et_2Zn to **2** decreases isotacticity markedly remaining mostly hetero- and syndiotactic sequences (run 34). The poly(DMA) obtained at a higher temperature (0 °C) also shows a similar spectrum (run 35). Now, it is clear that the coordination of Et_2Zn with the anionic propagating species causes the change of the stereostructure of the resulting polymer along with the retardation of the polymerization as described before.

It is obvious from the NMR spectra that the poly(DMA) produced with **1**/Et_2Zn (run 14) has higher degree of syndiotacticity than the one with **2**/Et_2Zn (run 35). Such a difference in the tacticity is interestingly reflected in the elution behavior of GPC using DMF and THF eluent, as shown in Figure 5. In the DMF−GPC's, sharp and symmetric curves are observed for both of the polymers, and the higher molecular weights are estimated by using PMMA standard calibration rather than the exact M_n values measured by ^1H NMR. On the other hand, the much lower molecular weights are evaluated from the THF−GPC, especially for the highly syndiotactic polymer (run 14), although both polymers

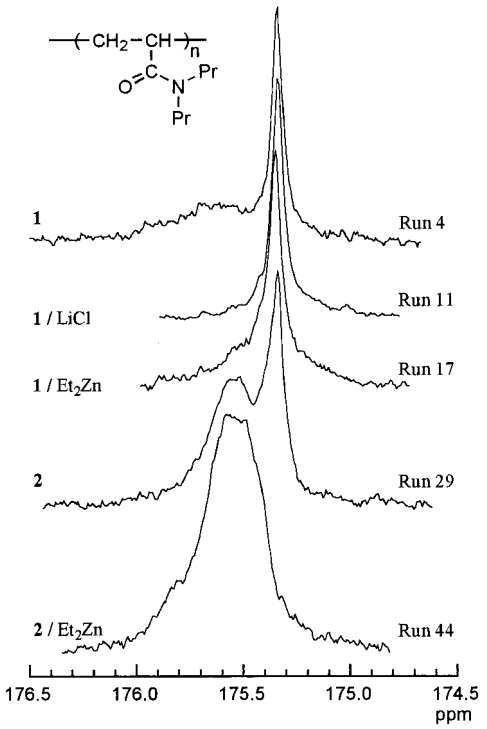


Figure 9. ^{13}C NMR spectra of the carbonyl carbons of the poly(DPA)s measured in 1,4-dioxane-d_8 at 50 °C. For the conditions of polymerization, see Tables 1 and 2.

possess approximately the same molecular weights. These results suggest that the poly(DMA)s have an expanded chain structure in DMF and contracted ones in THF. The poor solubility of the syndiotactic polymer in THF may cause significant tailing in the lower molecular weight region of the GPC curve. A similar trend is observed for poly(DEA) and poly(EMA) having different tacticities.

The poly(DEA)s produced with **1** in the absence and presence of Et_2Zn exhibit well-resolved carbonyl carbon signals in the wide region of 173.3−174.5 ppm (Figure 6). In analogy with the case of poly(DMA), the resonances at 173.3−173.6 and 174.1−174.5 ppm can be attributable to *mm* and *rr* triads, respectively. The signal in the middle region, 173.6−174.1 ppm, may be assigned to heterotactic triad. Although these assignments should be proved by the analysis of triad model compound,[24] the contents of *mm*, *mr*, and *rr* configurations are tentatively estimated for the poly(DEA) in this study. DEA was polymerized with **1** to afford a polymer having 60% *mm* triad (run 2). The addition of LiCl to the polymerization system increased remarkably the degree of isotacticity of the resulting polymer to 91% (run 10), although little effect of LiCl was observed in the case of DMA. When **1**/Et_2Zn (1/18.2) was used as an initiator system, the tacticity of resulting polymer was almost completely changed from isotactic to syndiotactic (*rr* = 88%, run 15).

The well-resolved 500 MHz ^1H NMR signals of the methine and methylene protons were observed for poly(DMA) and poly(DEA) (Figure 7).[25] The two resonances of methylene proton of isotactic poly(DMA) appeared at 1.05 and 1.68 ppm (Figure 7a), while the signals were observed at 1.20 and 1.55 ppm for the syndiotactic polymer (Figure 7b). The *mm* and *rr* methine proton signals of poly(DMA) appeared at 2.41 and 2.54 ppm, respectively. Similarly, the *mm* and *rr* methine resonances of poly(DEA) appeared at 2.37 and 2.86 ppm,

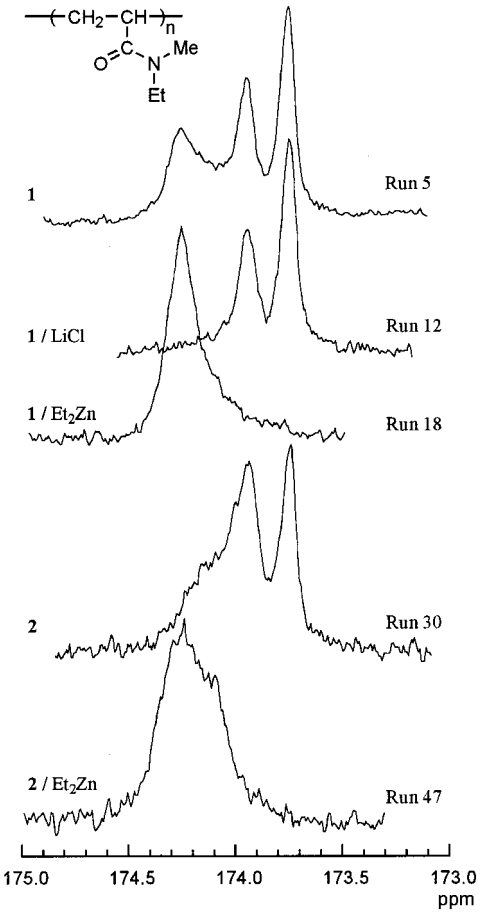


Figure 10. ^{13}C NMR spectra of the carbonyl carbons of the poly(EMA)s measured in $CDCl_3$ at 50 °C. For the conditions of polymerization, see Tables 1 and 2.

respectively. Resonances of the *m* and *r* methylene proton signals of poly(DEA) were observed at 1.69 and 1.77 ppm, respectively, and the others overlapped with methyl proton signals (NCH_2CH_3) (Figure 8a−c). The triad contents estimated by the relative intensities of methine proton signals agree well with those of carbonyl carbon signals, which suggests the consistency of the assignment of each signal.

With a potassium initiator, **2**, the poly(DEA) having rich in isotactic configuration was generated, as can be seen in Figure 6 (run 27). The addition of an equivalent molar amount of Et_2Zn to **2** increased the heterotactic content and decreased the isotactic one (run 38), and an increase in the amount of Et_2Zn added enhanced this trend (run 36). Furthermore, the heterotacticity increases significantly up to 90% by raising the polymerization temperature to 0−40 °C (runs 40−43). Since the observed signal is broad compared with those of *mm* and *rr* triad, it may include a few different heterotactic sequences on the pentad level, for example *rmrr*, *mmrr*, and so on.[26] The highly heterotactic polymers have been only obtained so far by the anionic polymerization of ethyl, propyl, allyl, and propargyl methacrylate with *t*-BuLi/bis(2,6-di-*tert*-butylphenoxy)methylaluminum in toluene at −78 or −95 °C.[11] It is interesting that the highly heterotactic poly(DEA) can be obtained in the current work with an organopotassium initiator in conjunction with Et_2Zn at a rather high temperature.

As we mentioned before, the polymerization of DEA took place only by Et_2Zn without any anionic initiators. The resulting polymer exhibits the broad signal ac-

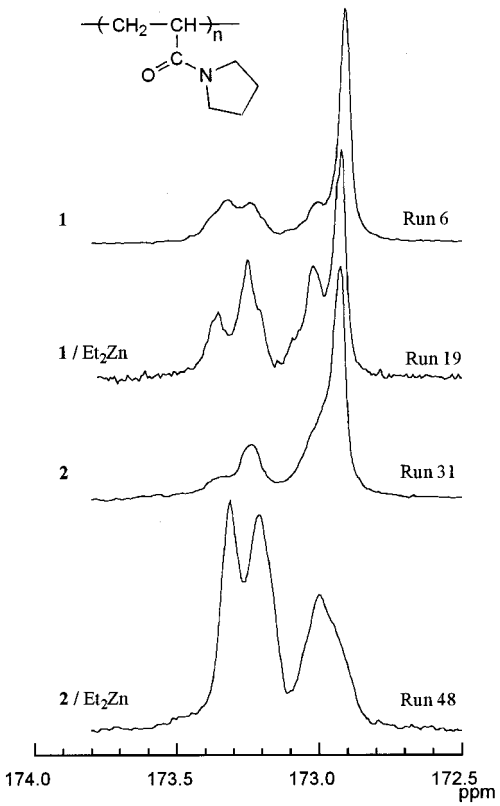


Figure 11. ^{13}C NMR spectra of the carbonyl carbons of the poly(APY)s measured in $CDCl_3$ at 50 °C. For the conditions of polymerization, see Tables 1 and 2.

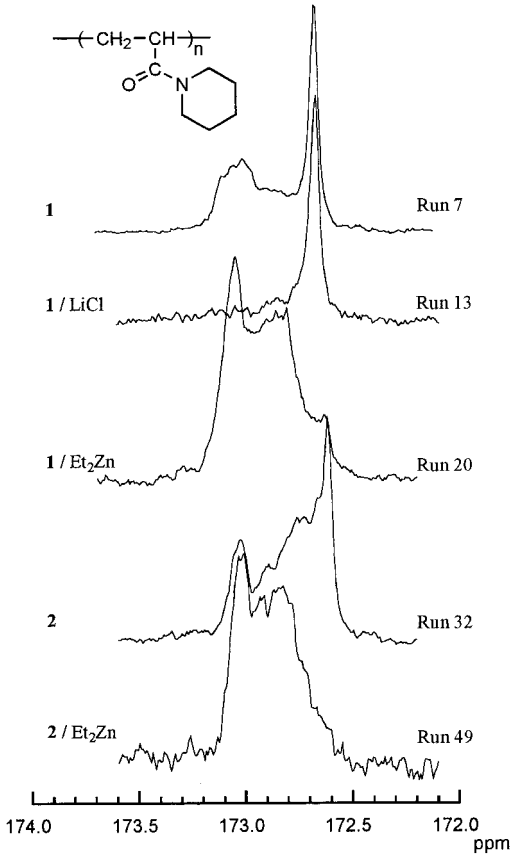


Figure 12. ^{13}C NMR spectra of the carbonyl carbons of the poly(API)s measured in $CDCl_3$ at 50 °C. For the conditions of polymerization, see Tables 1 and 2.

companying sharp peak due to *rr* configuration (run 24), which is quite different from those of the poly(DEA) produced with **1**/Et_2Zn or **2**/Et_2Zn. As a reference, the very broad carbonyl carbon signal of the poly(DEA) prepared with a radical initiator is also shown in Figure 6.

Solubilities of poly(DEA)s are summarized in Table 3. The isotactic poly(DEA) (run 10) is soluble in water, methanol, and chloroform and insoluble in DMF and THF, whereas the highly heterotactic poly(DEA) (run 40) is soluble in water and in most organic solvents. However, the syndiotactic poly(DEA) (run 15) is insoluble in water, while the syndiotactic poly(DMA) is dissolved in water. Although poly(DMA) does not show a coil−globule transition in the aqueous solution,[27] the isotactic and heterotactic poly(DEA)s possess LCST in water, at 31 (run 2) and 27 °C (run 42), respectively. These differences of LCST, depending on the tacticity, were also observed in the cases of poly(EMA) and poly(APY). Similar results were previously mentioned by Freitag.[5b]

The ^{13}C NMR spectra of the carbonyl carbon region of the poly(DPA)s obtained at −78 °C are shown in Figure 9. The poly(DPA)s obtained with **1** and **1**/LiCl seem to be isotactic (runs 4 and 11), although the assignments of the signals have not yet been confirmed. The addition of Et_2Zn to **1** shows little effect on the stereostructure of the resulting poly(DPA), in contrast to the cases of poly(DMA) and poly(DEA). A broad distribution of triad sequence is observed for the poly(DPA) obtained with **2** as well as poly(DEA). The addition of Et_2Zn to **2** decreases the isotacticity and increases the heterotacticity of the polymer (run 44). A similar spectrum was observed for the poly(DPA) produced with **2**/Et_2Zn at 25 °C (run 46). The solubilities of the isotactic and heterotactic poly(DPA)s in DMF and chloroform were different (Table 3, runs 4 and 45).

In the cases of poly(EMA)s, well-resolved methine proton signals were observed, although the ^1H NMR spectra are not shown here. The poly(EMA)s produced with **1**/LiCl and with **1**/Et_2Zn showed single methine peaks at 2.40 and 2.55 ppm, respectively, which were attributable to the *mm* and *rr* triads by analogy with the cases of poly(DMA) and poly(DEA). The ^{13}C NMR spectra of the poly(EMA)s are shown in Figure 10. Two carbonyl carbon signals were observed at 173.65 and 173.95 ppm for the polymer generated with **1**/LiCl (run 12), while just the one peak appeared at 174.25 ppm for the poly(EMA) (run 18) obtained with **1**/Et_2Zn. It is supposed that the two signals of the isotactic polymer (run 12) are both attributable to inequivalent carbonyl carbons of the *mm* triad due to the unsymmetrical *N*-alkyl substituents with restricted amide bond rotation.[28] For some reason, the rotation around the amide bond of the isotactic sequence might be hindered more strongly than that of the syndiotactic sequence. The polymerization with **2** leads to the poly(EMA) (run 30) having a relatively high content of isotacticity. The addition of Et_2Zn to the polymerization system increases hetero- and syndiotacticity (run 47), as observed for poly(DMA), poly(DEA), and poly(DPA). The poly(EMA)s have good solubilities in various solvents, but the isotactic one is exceptionally insoluble in THF (Table 3, run 12).

The ^{13}C NMR spectra of carbonyl region of poly(APY), poly(API), and poly(AMO) are shown in Figures 11−13, respectively. Although accurate assignments have not yet been determined for each signal in the spectra,

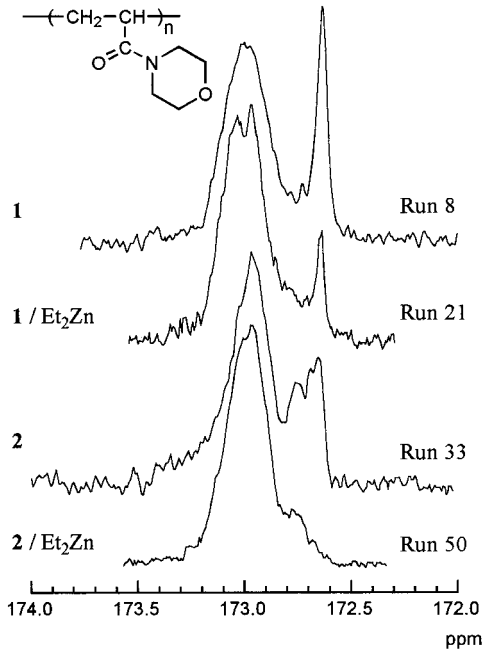


Figure 13. ^{13}C NMR spectra of the carbonyl carbons of the poly(AMO)s measured in $CDCl_3$ at 50 °C. For the conditions of polymerization, see Tables 1 and 2.

the signals at the highest and lowest magnetic field in the carbonyl carbon region may be attributable to isotactic and syndiotactic configurations, respectively, by analogy to the cases of poly(DMA) and poly(DEA). As can be seen in Figures 11−13, each polymer obtained with **1** or **2** in the absence of Et_2Zn is rich in isotactic sequence (runs 6, 7, 8, 31, 32, and 33). In particular, the isotacticity of poly(API) is increased by the addition of LiCl to **1** (run 13). On the other hand, the isotacticity was decreased and the syndiotactic and heterotactic sequences are alternatively increased by the addition of Et_2Zn to **1** or **2** (runs 19, 20, 21, 48, 49, and 50). The isotactic poly(API) is insoluble in DMF and THF like poly(DMA) and poly(DEA) (Table 3). The solubility of poly(APY) and poly(AMO) seems to be predominantly affected by the *N*-alkyl substituent regardless of the tacticity.

In this study, notable results are that highly stereospecific poly(*N*,*N*-dialkylacrylamide)s were obtained by anionic polymerization in the presence of LiCl and Et_2Zn—isotactic poly(DEA), poly(DPA), poly(EMA), and poly(API), syndiotactic poly(DMA) and poly(DEA) with narrow MWDs, and heterotactic poly(DEA) having narrow MWD—and that these stereoregular polymers showed characteristic solubilities in water, DMF, and THF depending upon their tacticities. These drastic effects on the tacticities by addition of Et_2Zn were not observed in the case of methacrylates[15] and acrylates.[16] It is suggested that coordination of Et_2Zn with amide enolate anion may be more effective than ester enolate in changing the steric environment around the active center, leading to the stereospecific propagating reaction.

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Supporting Information Available: Text giving the experimental procedures for the synthesis, purification, and NMR analyses of all monomers. This material is available free of charge via the Internet at http://pubs.acs.org.

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(21) Although the initiator **2** was added to *N*, *N*-diethylpropionamide which is model compound of the polymer, the α-proton of this *N*,*N*-diethylpropionamide was not abstracted in THF at 40 °C even after 24 h in our experiment. The abstraction of α-proton by the propagating end would not occur, because the amide enolate anion is less basic than initiator **2**. We also measured MALDI−TOF−MS of the polymer produced with **2** in the absence of Et_2Zn; the signal due to the polymer terminated by the Claisen type reaction leaving NEt_2^- was not detected, although the spectrum was not shown in this article.
(22) Butler and Hogen-Esch described that the poly(DMA) generated with alkyllithium was insoluble[1] or partially soluble[6c]

in water. However, the poly(DMA)s obtained in our experiment were soluble in water regardless of the tacticity.

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(25) Although McGrath et al. did not determine the tacticity of poly(DMA) by methylene proton, they estimated the degree of dyad sequence by use of the methylene carbon spectra in D_2O. Since the methine and methylene carbon signals overlapped with each other in $CDCl_3$ at 50 °C, tacticity could not be determined from those signals in this study.

(26) The carbonyl carbon signal (run 42) was split into three peaks in CD_3OD at 50 °C, whereas those of isotactic (run 10) and syndiotactic (run 15) polymers in CD_3OD showed just one peak, as well as in $CDCl_3$.

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(28) The carbonyl carbon of EMA monomer also exhibits two signals (see Experimental Section), probably due to the restricted rotation around the amide bond.

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