Macromolecules **2000,** *33,* 4411−4416

Additive Effect of Triethylborane on Anionic Polymerization of *N*,*N*-Dimethylacrylamide and *N*,*N*-Diethylacrylamide

Motoyasu Kobayashi, Takashi Ishizone, and Seiichi Nakahama*

Department of Polymer Chemistry, Faculty of Engineering, Tokyo Institute of Technology, 2−12−1 Ohokayama Meguro-Ku, Tokyo 152-8552, Japan

Received November 22, 1999

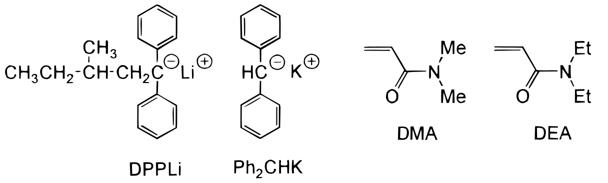
ABSTRACT: Anionic polymerizations of *N*,*N*-dimethylacrylamide (DMA) and *N*,*N*-diethylacrylamide (DEA) proceeded slowly and steadily with 1,1-diphenyl-3-methylpentyllithium (DPPLi) and with diphenylmethylpotassium (Ph_2CHK) in the presence of triethylborane (Et_3B) in THF even at 30 °C to afford the polymers having the predicted molecular weights and very narrow molecular weight distributions in quantitative yields. The result of the postpolymerization of DEA with Ph_2CHK/Et_3B confirmed the formation of a living polymer with heterotactic configuration at 30 °C. The poly(DMA) and poly(DEA) produced with DPPLi/Et_3B were highly syndiotactic, while the isotactic polymers were formed in the absence of Et_3B. The additive effects of Et_3B on retarded reaction rate and stereospecificity of the polymerization are attributed to the coordination of Et_3B with the propagating enolate anion.

Introduction

Among the various poly(*N*,*N*-dialkyl substituted acrylamides), a limited number of water-soluble polymers are obtained from *N*,*N*-dimethylacrylamide (DMA), *N*,*N*-diethylacrylamide (DEA), *N*-ethylmethylacrylamide, *N*-acryloylpyrrolidine, etc. The polymers and the gels of DMA[1−4] and DEA[5−8] have been prepared so far, and their swelling and transition behaviors in water were investigated. Poly(DMA) and its copolymers were applied in various fields, such as oil-recovery[3] and slow release medical materials.[4] Ilavský et al.[5] and Tanaka et al.[6] individually reported studies of the reentrant volume transition behavior of poly(DEA) hydrogel. Since the polymers and the gels were prepared via free-radical mechanism, their structures were not precisely regulated. Consequently, the relationship between transition behavior and the primary structures of the polymer gel has not been elucidated. On the other hand, several research groups generated highly crystalline and isotactic poly(DMA) with alkyllithium initiator,[9,10] although the molecular weight distribution (MWD) of the polymers were very broad. Living polymerizations of DMA were also studied to control the molecular weight and MWD.[11−17] The first successful quantitative synthesis of poly(DMA) with narrow MWD was achieved by Hogen-Esch and co-workers,[18] using an anionic initiator with Cs^+ counterion at −78 °C. In contrast, the corresponding polymer produced at 0 °C had much broader MWD, which they attributed to chain transfer based on the pronounced tailing in its SEC curve.

To control the polymerization of *N*,*N*-dialkylacrylamides, we have developed a new effective anionic initiator system modified with weak Lewis acid, such as diethylzinc (Et_2Zn).[19,20] The addition of Et_2Zn to the alkylpotassium initiator decreased the rate of propagation reaction remarkably, resulting in the living poly(DEA) with predictable number-average molecular weight (M_n) and narrow MWD even at 0 °C. Furthermore, the polymerization is stereospecific. We also polymerized alkyl methacrylates,[21] and acrylates[22] using diphenylmethyl potassium (Ph_2CHK) as the initiator in the presence of dialkylzinc in THF at −78 °C to give polymers having predetermined M_n values and narrow MWDs. We recently reported that Ph_2CHK combined with triethylborane (Et_3B) initiated the polymerization of *tert*-butyl acrylate at 0 °C to give a polymer with predicted M_n and extremely narrow MWD.[23] These results suggest that strong coordination of Et_3B produces a stable propagating species which affords the polymer with well-defined chain structure even at higher temperature. Similarly, Et_3B should coordinate with the propagating enolate anions of *N*,*N*-dialkylacrylamides.

Chart 1



This paper describes the anionic polymerization of DMA and DEA using lithium and potassium initiators in the presence of Et_3B, with precisely controlled M_n, MWD, and tacticity.

Experimental Section

Materials. Tetrahydrofuran (THF) was refluxed over sodium wire, distilled from $LiAlH_4$, and then distilled from sodium naphthalene solution on a vacuum line. Et_3B (Aldrich, 1.0 M, THF solution) was purified by distillation from CaH_2 and trioctylaluminum and was used as a THF solution. Commercially available *s*-BuLi (KANTO Chemicals, 1 M, cyclohexane solution) was used without further purification. 1,1-Diphenyl-3-methylpentyllithium (DPPLi) was prepared by reaction of a slight molar excess of 1,1-diphenylethylene in THF with the heptane solution of *s*-BuLi at −78 °C for 20 min. Ph_2CHK was produced by reaction of diphenylmethane with potassium naphthalene in THF at room temperature. The concentrations of the initiator solutions were determined by colorimetric titration with 1-octanol in a sealed tube in vacuo.[24] DMA and DEA monomers were prepared by reported procedures.[20] The structures of the initiators and monomers are shown in Chart 1.

Polymerization. The polymerization was typically performed in THF under vacuum conditions in a glass apparatus equipped with break-seals. This is an example for run 15. On

10.1021/ma991957t CCC: $19.00

Table 1. Anionic Polymerization of DMA in THF

	reagent, mmol							$M_n \times 10^{-3}$		
run	initiator	Lewis acid	Lewis acid/I	DMA	temp, °C	time, h	conversion, %	calcd[a]	obsd[b]	M_w/M_n[c]
1	DPPLi, 0.0817		0.0	4.19	−78	0.02	100	5.3	6.5	3.41[d]
2	DPPLi, 0.0338	Et_3B, 0.199	5.9	2.15	−78	1	<2	0.4		
3[f]	DPPLi, 0.112	Et_2Zn, 1.34	12	10.0	−78	1	96	9.2	9.3	1.14[e]
4	DPPLi, 0.0967	Et_3B, 0.202	2.1	15.8	0	4	100	16	16	1.13
5	DPPLi, 0.0649	Et_3B, 0.481	7.4	8.30	0	4	61	8.1	11	1.14[e]
6	Ph_2CHK, 0.0469		0.0	5.76	−78	0.02	100	12	11	1.51
7	Ph_2CHK, 0.0642	Et_3B, 0.157	2.4	7.92	−78	1	<1	0.3		
8[f]	Ph_2CHK, 0.0919	Et_2Zn, 1.36	15	7.41	−78	1	60	8.5	5.6	1.07
9	Ph_2CHK, 0.0909	Et_3B, 0.205	2.3	10.3	0	6	34	4.0	2.8	1.11
10	Ph_2CHK, 0.0909	Et_3B, 0.205	2.3	10.3	0	24	56	6.5	4.7	1.07
11	Ph_2CHK, 0.0909	Et_3B, 0.205	2.3	10.3	0	48	69	7.9	6.2	1.07
12	Ph_2CHK, 0.0909	Et_3B, 0.205	2.3	10.3	0	96	96	11	8.9	1.08
13	Ph_2CHK, 0.108	Et_3B, 0.135	1.3	11.1	30	1.5	100	10	11	1.11[e]
14	Ph_2CHK, 0.0884	Et_3B, 0.199	2.3	12.5	30	1.5	95	14	12	1.05
15	Ph_2CHK, 0.0435	Et_3B, 0.148	3.4	12.5	30	6	98	28	30	1.06
16	Ph_2CHK, 0.0869	Et_3B, 0.549	6.3	12.7	30	6	80	12	12	1.04[e]

[a] M_n(calcd) = (MW of DMA) × conversion/100 × [DMA]/[initiator] + (MW of initiator fragment). [b] Estimated by ^1H NMR. [c] Measured by SEC using PMMA standards in THF at 40 °C. [d] SEC in $CHCl_3$. [e] SEC in DMF containing 0.01 M of LiBr. [f] Previously reported in ref 20.

addition of 3.4 molar equiv of Et_3B (0.148 mmol, 0.0437 M) to Ph_2CHK (0.0435 mmol, 0.0197 M) at −78 °C, the characteristic red color of the initiator rapidly disappeared. However, the solution of DPPLi/Et_3B (1/2, mol/mol) maintained a red color. After the binary initiator system was kept at −78 °C for 10 min, DMA (12.49 mmol, 0.919 M) in THF was added to the initiator solution with vigorous stirring at 30 °C. The polymerization reaction proceeded in homogeneous and colorless solution for 6 h, and was terminated with methanol. The conversion estimated by gas chromatography detection of the residual monomer in the reaction mixture was 98%. The reaction mixture was concentrated by evaporation and poured into a large excess amount of hexane to precipitate the polymer. After purification by freeze-drying from benzene, the isolated polymer was obtained (1.20 g, 97%). Size exclusion chromatography (SEC) measurements were performed before and after the precipitation of the polymer. Since both SEC curves have shown the identical shape and its distribution, we believe that fractionation did not occur during the precipitation. 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 the phenyl proton signal (7.1−7.2 ppm) of the initiator fragment.

Measurements. SEC of the polymer was measured using a TOSOH HLC-8020 instrument equipped with three polystyrene gel columns (TOSOH G4000H_{XL}, G3000H_{XL}, and G2000H_{XL}) in THF, or with the polystyrene gel columns (TOSOH TSK-GEL GMH$_{XL}$ × 2) in chloroform and *N*,*N*-dimethylformamide (DMF) containing 0.01 M LiBr as eluents at a flow rate 1.0 mL min^{-1} at 40 °C with ultraviolet and refractive index detection. The NMR spectra were recorded in $CDCl_3$ at 50 °C with a JEOL GSX-500 (^1H 500.16 MHz) and a BRUKER DPX-300 (^1H 300.13 MHz). The chemical shifts in ppm were referenced to tetramethylsilane ($\delta = 0$) internal standard for ^1H NMR, and $CDCl_3$ ($\delta = 77.1$) for ^{13}C NMR.

Results and Discussion

Anionic Polymerization of DMA. The results of DMA polymerizations are summarized in Table 1. In the absence of Et_3B, DMA was quantitatively converted to polymer in 1 min with DPPLi in THF at −78 °C (run 1), which was insoluble in THF as described previously.[20] On addition of DMA to DPPLi/Et_3B (1/5.9, mol/mol) system, the characteristic red color disappeared immediately due to the initiation reaction of DPPLi with DMA, however, no polymer was obtained at −78 °C (run 2). In contrast, the initiator system of DPPLi/Et_2Zn maintained its activity at −78 °C to afford polymer quantitatively (run 3), which suggests that the propagating enolate anion is highly stabilized by stronger coordination with Et_3B than Et_2Zn. The anionic polymerization was then carried out at elevated temperatures to accelerate propagation. As a result, the polymerization of DMA with DPPLi/Et_3B (1/2, mol/mol) proceeded homogeneously to give the polymer having predicted M_n and narrow MWD in quantitative yield at 0 °C within 4 h (run 4). Increasing the molar ratio of Et_3B to DPPLi, further decreased the rate of propagation; for Et_3B/DPPLi = 7.4, 39% of unreacted monomer still remained at 0 °C after 4 h (run 5). This retardation effect was even greater in the presence of potassium counterion; only 34% of the polymer was obtained after 6 h at 0 °C with Ph_2CHK/Et_3B (run 9), whereas the polymerization was completed in 4 h under the similar conditions with lithium counterion (run 4). In the presence of Et_2Zn, a similar counterion effect was observed in the anionic polymerizations of *N*,*N*-dialkylacrylamide[20] and *tert*-butyl acrylate.[22]

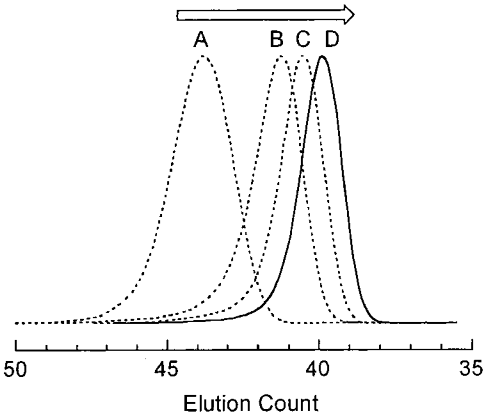


Figure 1. SEC curves of a series of poly(DMA)s obtained with $Et_3B/Ph_2CHK = 2.3$ in THF at 30 °C: peak A, after 15 min, 49% conversion, $M_n = 6100$, $M_w/M_n = 1.05$; peak B, 30 min, 72%, 9700, 1.08; peak C, 54 min, 85%, 11000, 1.06; peak D, 90 min, 95%, 12000, 1.05. This corresponds to run 14 in Table 1.

Figure 1 shows that the SEC curves of a series of poly(DMA)s shift from the lower molecular weight region to the higher one without detectable tailing with increasing the DMA conversion. Et_3B apparently coordinates effectively with the enolate anion even at 30 °C

Table 2. Anionic Polymerization of DEA in THF

run	reagent, mmol				temp, °C	time, h	conversion, %	$M_n \times 10^{-3}$		M_w/M_n[c]
	initiator	Lewis acid	Lewis acid/I	DEA				calcd[a]	obsd[b]	
17	DPPLi, 0.0309		0.0	14.3	−78	0.004	93	59	46[d]	3.07[d]
18[f]	DPPLi, 0.0839	Et_2Zn, 1.53	18	6.08	−78	1	99	9.6	11	1.12
19	DPPLi, 0.0917	Et_3B, 0.216	2.4	5.45	0	12	100	7.8	7.1	1.13
20	DPPLi, 0.0496	Et_3B, 0.428	8.6	7.01	0	12	100	18	21	1.05
21	Ph_2CHK, 0.0630		0.0	10.2	−78	0.004	97	21	23[c]	1.63
22	Ph_2CHK, 0.104	Et_2Zn, 1.27	12	4.19	0	0.02	100	5.3	4.5	1.06
23	Ph_2CHK, 0.0893	Et_3B, 0.189	2.1	7.13	0	3	44	4.6	2.4	1.15
24	Ph_2CHK, 0.0893	Et_3B, 0.189	2.1	7.13	0	72	94	9.7	9.0	1.24
25	Ph_2CHK, 0.0675	Et_3B, 0.152	2.3	7.15	30	1	97	13	14	1.07
26	Ph_2CHK, 0.0925	Et_3B, 0.954	10	5.83	30	3	88	7.2	7.2	1.19
27		Et_3B, 0.257	17[e]	4.33	25	48	44		3.9[c]	1.59

[a] M_n(calcd) = (MW of DEA) × conversion/100 × [DEA]/[initiator] + (MW of initiator fragment). [b] Estimated by ^1H NMR. [c] Measured by SEC using PMMA standards in THF at 40 °C. [d] SEC in $CHCl_3$. [e] [DEA]/[Et_3B]. [f] Previously reported in ref 20.

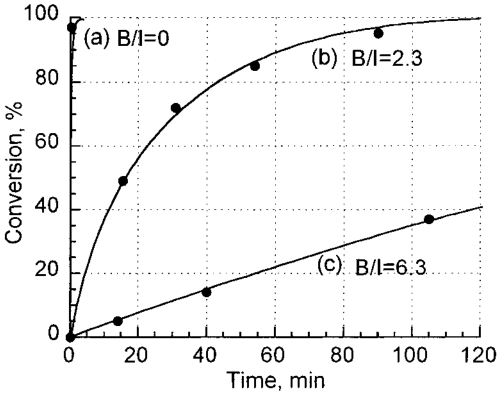


Figure 2. Time−conversion curves of the anionic polymerization of DMA with Ph_2CHK/Et_3B in THF at 30 °C. [Ph_2CHK] = 3.9 × 10^{-3} M. Curve a: control experiment in the absence of Et_3B. Curves b and c are for runs 14 and 16, respectively. The conditions of polymerization are shown in Table 1. Conversion was measured by detection of the residual monomer using GC.

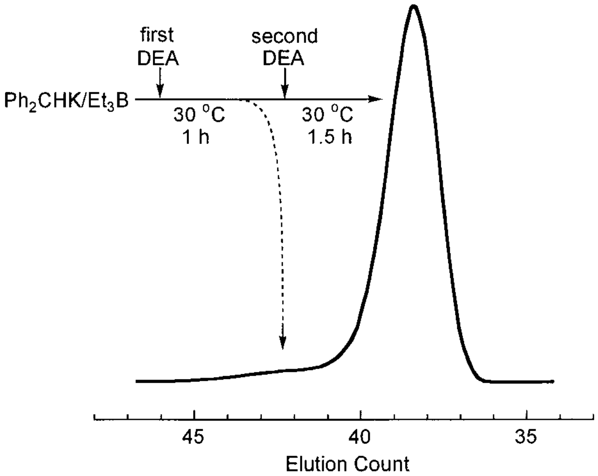


Figure 3. SEC curve of second-stage poly(DEA) produced with Ph_2CHK/Et_3B (1/2.2, mol/mol) in THF at 30 °C, M_n(calcd) = 14 500, M_n(SEC) = 11 700, M_w/M_n = 1.08. The dotted arrow shows the elution volume of the base polymer.

to slow the propagation reaction and to produce a polymer with narrow MWD ($M_w/M_n = 1.05$, run 14). The observed M_n values of the polymers agree well with the calculated values based on the molar ratios of DMA to the initiator. These results indicated that the termination and transfer reactions are absent during the polymerization. Figure 2 shows a time−conversion plot of the polymerization with Ph_2CHK in the presence and absence of Et_3B at 30 °C. The propagation rate constant (k_p) was estimated from the first-order plot. Although the polymerization of DMA was completed within a few seconds in the absence of Et_3B ($k_p > 10^2$), the addition of only 2.3-fold molar Et_3B drastically reduced the propagating rate ($k_p = 8.2 \times 10^{-2}$ L mol^{-1} s^{-1}). The rate of the polymerization was decreased further with increasing amounts of added Et_3B ($k_p = 4.5 \times 10^{-3}$ L mol^{-1} s^{-1} for $Et_3B/Ph_2CHK = 6.3$) (run 16). This suggests that plural propagating species present in the equilibrium, like as an active and a dormant species. We suppose that an enolate anion combined with Et_3B strongly, such as a borate complex, works as a dormant. The active enolate anion would be also coordinated with Et_3B, not be free ion, since the stereospecificity was changed by addition of Et_3B, as described later.

We previously reported that the Ph_2CHK/Et_2Zn system also afforded the poly(DMA) having narrow MWD in quantitative yield at 0 °C within 1 min (run 8).[20] However, a large excess of Et_2Zn (more than 15 equiv) vs initiator was required to produce well-defined poly(DMA). On the other hand, the addition of 1−2 equiv of Et_3B relative to Ph_2CHK led to satisfactory control of the polymerization (runs 13 and 14) even at 30 °C. Thus, coordination of Et_3B with the propagating anion is apparently much stronger than that with Et_2Zn. This is supported by the greater shift of IR bands of the ester enolate anion interacted with Et_3B, as described by Tsvetanov.[25]

Anionic Polymerization of DEA. As shown in Table 2, the results of the polymerization of DEA are similar to those of DMA. In the absence of Et_3B, DEA rapidly polymerizes with DPPLi or Ph_2CHK at −78 °C to give the polymer with broad MWD (runs 17 and 21). In contrast, the polymerization proceeds very slowly in the presence of Et_3B in THF. For instance, it took 12−72 h to complete the polymerization of DEA even at 0 °C (runs 19, 20, 23, and 24).[26] At 30 °C, the addition of two equiv amount of Et_3B toward Ph_2CHK was enough to control the polymerization; the resulting poly(DEA) possessed the predictable M_n and narrow MWD ($M_w/M_n = 1.07−1.19$, runs 25 and 26). This suggests that a small number of Et_3B molecules coordinate with amide enolate anion help to control the chain structure.

The livingness of the propagating enolate anion of DEA was evaluated by the postpolymerization with Ph_2CHK in the presence of Et_3B in THF at 30 °C. The SEC profile of the product is shown in Figure 3. After the first-stage polymerization of DEA with Ph_2CHK/Et_3B for 1 h, the postpolymerization of a second feed of DEA was subsequently carried out for 1.5 h. As shown

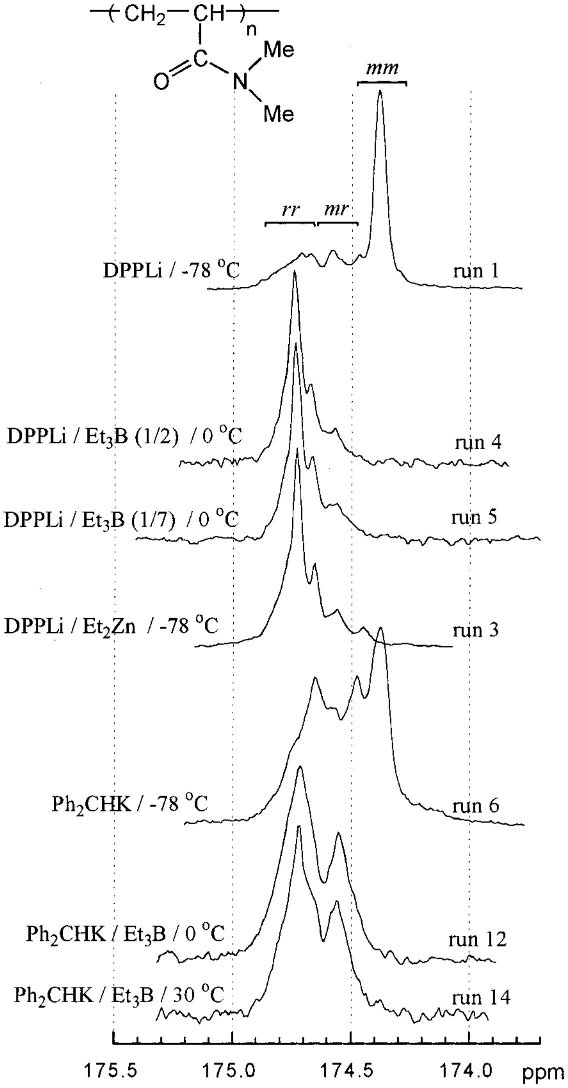


Figure 4. ^{13}C NMR spectra of carbonyl carbons of the poly(DMA)s measured in $CDCl_3$ at 50 °C. For the conditions of polymerization, see Table 1.

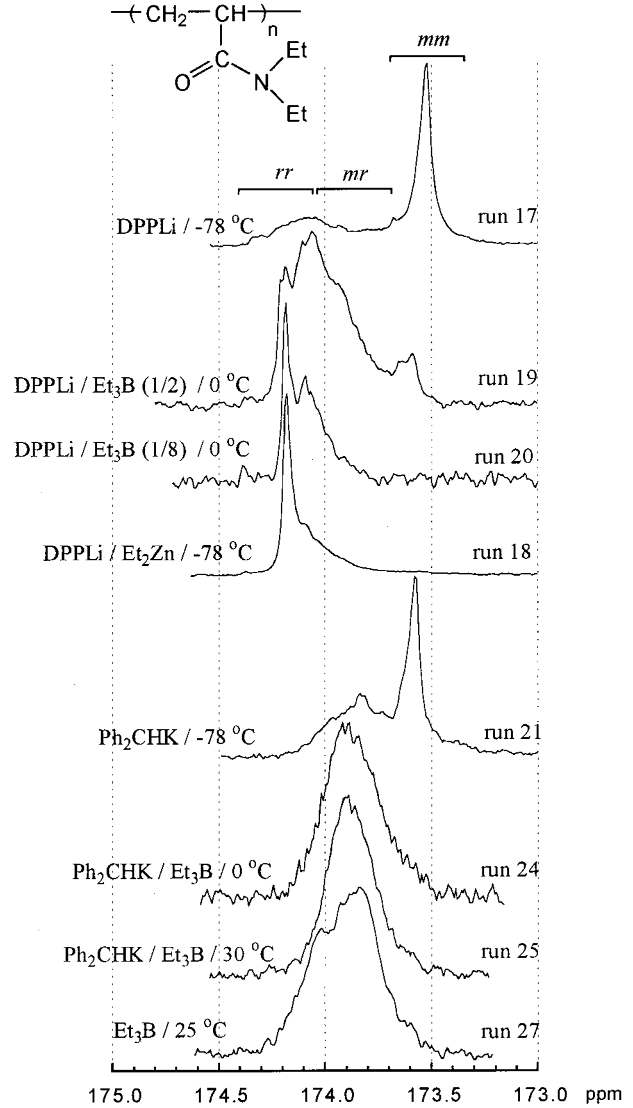


Figure 5. ^{13}C NMR spectra of carbonyl carbons of the poly(DEA)s measured in $CDCl_3$ at 50 °C. For the conditions of polymerization, see Table 2.

in Figure 3, the SEC curve of the postpolymer shifted toward the higher molecular side while maintaining a narrow MWD. This indicates that the propagating chain end of poly(DEA) is stable under these conditions. The slight detection of the base-polymer in the lower molecular weight region may be attributed to a small amount of impurities in the monomer solution of the second feed. We conclude that the propagating species of poly(DEA) maintains its activity during the polymerization without chain transfer and termination reactions.

Furukawa et al. reported that trialkylborane itself initiates redox polymerization of vinyl monomers in the presence of oxygen or oxidants.[27] However, the oxygen and oxidants were scrupulously removed from the polymerization mixture in our experiments, and hence free-radical polymerization was very unlikely. Recently, Takeishi and co-workers mentioned that acrylates were directly polymerized with 9-BBN in the absence of oxidants or anionic initiators via a group transfer mechanism.[28] In our control experiment (run 27), a mixture of DEA and Et_3B in THF produced a polymer with broader MWD in low yield after 2 days under vacuum at 25 °C. Therefore, the polymerization with Et_3B alone is essentially different from the anionic one with DPPLi/Et_3B or Ph_2CHK/Et_3B, and does not occur concurrently.

Tacticity of Poly(DMA) and Poly(DEA). We estimated the tacticity of the polymers from the ^{13}C NMR signals of carbonyl carbon according to McGrath's[10] and our protocols.[20,29] A series of ^{13}C NMR spectra of the poly(DMA)s produced are shown in Figure 4, where the signals were assigned to *mm*, *mr*, and *rr* triad in series from high magnetic field. The poly(DMA) produced with DPPLi exhibits a sharp isolated signal at 174.3 ppm, which is assigned to isotactic configuration (run 1). On the other hand, the poly(DMA) generated with DPPLi in the presence of Et_3B (run 4) shows the sharp peaks around at 174.7 ppm attributed to *rr* triad configuration, and the *mm* signal at 174.3 ppm disappears in the spectrum. Thus, a highly syndiotactic poly(DMA) was generated with DPPLi/Et_3B at 0 °C, as was also produced with DPPLi/Et_2Zn at −78 °C[20] (run 3). Several small peaks observed from 174.4 to 174.6 ppm might be attributable to *mmrm*, *mmrr*, *rmrm*, and *rmrr* configurations, although the exact assignment could not be determined yet. Both polymerizations of runs 4 and 5 (Et_3B/DPPLi = 2−7, mol/mol) afforded poly(DMA)s having high degree of syndiotacticity, which indicated

Table 3. Solubilities of the Resulting Polymers[a]

				solvent						
run	polymer	tacticity	initiator	H_2O[b]	MeOH	DMF	$CHCl_3$	THF	benzene	hexane
1	poly(DMA)	*mm*	DPPLi	S	S	I	S	I	I	I
4	poly(DMA)	*rr*	DPPLi/Et_3B	S	S	S	S	S	S	I
15	poly(DMA)	*rr*	Ph_2CHK/Et_3B	S	S	S	S	S	S	I
17	poly(DEA)	*mm*	DPPLi	S	S	I	S	I	Sw	I
19	poly(DEA)	*rr* + *mr*	DPPLi/Et_3B	I[c]	S	S	S	S	S	I
20	poly(DEA)	*rr* + *mr*	DPPLi/Et_3B	I[c]	S	S	S	S	S	I
18	poly(DEA)	*rr*	DPPLi/Et_2Zn	I	S	S	S	S	S	I
25	poly(DEA)	*mr*	Ph_2CHK/Et_3B	S	S	S	S	S	S	I

[a] Key: S, soluble; I, insoluble; Sw, swelling; DMF, *N*,*N*-dimethylformamide. [b] At 25 °C. [c] Soluble below 10 °C.

that the additive effect of Et_3B on the stereospecificity leveled off at Et_3B/DPPLi = 2 (mol/mol). In contrast to Et_3B, much larger amount of Et_2Zn is required to obtain similar degree of syndiotacticity (run 3).[20] Such difference of coordination strength of Et_3B and Et_2Zn with the propagating enolate anion was also observed in propagating rate and control of MWD as mentioned above. Poly(DMA) produced with Ph_2CHK had broad distribution of tacticity (run 6), as was described by Hogen-Esch.[18] The addition of Et_3B to Ph_2CHK decreases isotacticity markedly and mostly heterotactic and syndiotactic sequences remain (run 12). The additive ratio and polymerization temperature did not induce significant change of tacticity of the resulting poly(DMA) (runs 13−16).

The poly(DEA)s produced with DPPLi in the absence and presence of Et_3B exhibit a well-resolved carbonyl carbon signals in the wide region of 173.3−174.5 ppm (Figure 5). The signal assignments of poly(DEA) were previously determined;[20] i.e., the resonances at 173.4−173.7, 173.7−174.0, and 174.0−174.3 ppm were attributed to *mm*, *mr,* and *rr* triads, respectively. Although the assignments of carbonyl carbon signals are not confirmed by using the model compounds with absolute configuration, they correspond reasonably with those of the methine proton signals.[20] DEA was polymerized with DPPLi to afford a polymer having 60% *mm* triad (run 17). Upon addition of Et_3B to DPPLi, the isotacticity of the resulting polymer decreased markedly (run 19). However, very broad distribution of the carbonyl carbon resonance appeared at Et_3B/DPPLi = 2 (run 19), while highly syndiotactic poly(DMA) was generated under similar conditions (run 4). The degree of syndiotacticity increased by addition of large amount of Et_3B (run 20), but it did not reach high level as that with DPPLi/Et_2Zn initiator system (run 18). These differences of tacticity between runs 18 and 20 affected their solubilities in water, as described later. With a potassium initiator, the poly(DEA) rich in isotactic configuration was generated, as can be seen in Figure 5 (run 21). The addition of Et_3B to Ph_2CHK affected stereostructure of the polymer produced. In the spectra, the heterotactic signal appeared, and the isotactic and syndiotactic ones diminished (runs 24 and 25). Higher degree of stereo control seem to be achieved for poly(DEA) compared with the case of poly(DMA) containing *mr* and *rr* triads. Similar results are obtained in the polymerization with Ph_2CHK/Et_2Zn system.[20] The ^{13}C resonances of runs 24 and 25 at 173.9 ppm are broader than those observed for runs 17 and 18 and do not accompany these sharp peaks. The broad signals of runs 24 and 25 may include several pentads such as *mmrr*, *mmrm*, *rmmr*, *rrrm* and so forth. Considering these results, it is supposed that the sharp peaks at 173.5 and 174.2 ppm for runs 17 and 18 should be attributable to higher order of isotactic and syndiotactic sequence than triad level, respectively.[30]

As described above, the polymerization of DEA took place only by Et_3B without any anionic initiators. The resulting polymer (run 27) exhibits the broader signal than the one generated with Ph_2CHK/Et_3B system.

The solubilities of the stereospecific polymers obtained are summarized in Table 3. The poly(DMA) and poly(DEA) moieties rich in isotacticity have poor solubility in THF, DMF, and benzene; on the contrary, the polymers without the *mm* triad were soluble in those solvents. Although the syndiotactic poly(DEA)s produced with DPPLi/Et_3B initiator (runs 19 and 20) were not soluble in water at 25 °C, they became soluble below 10 °C showing the lower critical solution temperature at 10−12 °C. Taking into account that the highly syndiotactic poly(DEA) generated with DPPLi/Et_2Zn system (run 18) was insoluble in water even at 0 °C as described in the previous paper,[20] small amount of heterotactic sequence contained in run 20 might improve the solubility of the polymer in water.

In conclusion, we propose that Et_3B coordinates with potassium amide enolate as a Lewis acid to produce living poly(DEA) with narrow MWD even at 30 °C, and that the enolate anion coordinated with Et_3B reacts stereoselectively with monomer. As a result, syndiotactic poly(DMA), poly(DEA), and heterotactic poly(DEA) having narrow MWD were obtained, and these stereoregular polymers show characteristic solubilities in water, DMF, and THF, depending on their tacticities.

Acknowledgment. This research was supported by Grant-in-Aid for Scientific Research on Priority Areas, “New Polymers and Their Nano-Organized Systems” (08246102 and 06750906), from The Ministry of Education, Science, Sports, and Culture, Japan, and M.K. appreciates the Research Fellowships of the Japan Society for the Promotion of Science for Young Scientists.

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