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POLYMERIZATION OF *N,N*-DIALKYLACRYLAMIDES WITH ANIONIC INITIATORS MODIFIED BY DIETHYLZINC

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ABSTRACT

N,N-Dimethyl-, diethyl-, and dipropylacrylamides were polymerized with 1,1-bis(4'-trimethylsilylphenyl)-3-methylpentyllithium (**I**) in the presence and absence of diethylzinc in THF. Although the polymers produced with **I** in the absence of diethylzinc have rather broad molecular weight distributions, the addition of diethylzinc to the polymerization systems causes narrow molecular weight distributions of the polymers. The addition of diethylzinc also affect the stereospecificities of the polymers obtained. The poly(*N,N*-diethylacrylamide) produced with **I**/diethylzinc (molar ratio of 1/3-15) is highly syndiotactic, while the one obtained with **I** is isotactic. The configuration of the poly(*N,N*-dimethylacrylamide) is changed from isotactic to syndio and heterotactic rich by the addition of diethylzinc to the polymerization mixture. Little effect of diethylzinc is observed on the stereospecificity of the polymerization of *N,N*-dipropylacrylamide. The stoichiometric additive effect of Et_2Zn toward the initiator in the polymerization of DEAA suggests that the coordination of Et_2Zn aggregates with the propagating carbanionic species narrows the molecular weight distribution and controls the tacticity of the polymer.

INTRODUCTION

Poly(*N,N*-dialkylacrylamides) produced with radical initiators have been applied as functional specialty polymers for coatings, paper and textile treatment agents, although scale of the production is very small compared with that of polyacrylamide [1]. The properties and functionalities of the polymers generally depend upon the primary and high ordered structures, but the poly(*N,N*-dialkylacrylamides) used commercially are amorphous and do not have well-defined chain structures. Butler *et al*. reported that the anionic polymerization of *N,N*-dimethylacrylamide (DMAA) was initiated with ethyl lithium in toluene to give the highly crystalline polymer. They also described that the poly(DMAA) exhibited the sharp X-ray scattering pattern and high softening point around 300°C, suggesting the stereospecific polymerization of DMAA [2]. McGrath *et al.* reported the NMR study on the tacticity of poly(DMAA) [3]. The ^{13}C NMR signals due to the carbonyl carbon in the range of 174.2-174.6 ppm were not well resolved; the peak at 174.2 ppm may be attributable to *mm* configuration, while the ones at downfield region overlapped each other not to be appropriately assigned to *rr* and *mr* triads. Although ambiguousness remained in the assignment of the triad sequence, the poly(DMAA) produced with *sec*-butyl lithium in benzene, THF, or hexane was found to be highly isotactic, *mm*= 81% [3d]. Recently, Hogen-Esch *et al.* found that poly(DMAA)s having different tacticities were generated by the anionic initiators with Li^+, and Cs^+ countercations [4]. The poly(DMAA) produced with triphenylmethyllithium was insoluble in THF and highly isotactic, whereas the one formed with 1,1,4,4-tetraphenylbutyldicesium was soluble in THF, had low content of *m m* configuration (6%), and possessed narrow molecular weight distribution [4a].

In this study, the anionic initiators modified with diethylzinc are applied to the polymerization of *N,N*-dialkylacrylamide for the precise control of molecular weight, molecular weight distribution, and tacticity.

EXPERIMENTAL

Anionic Initiators

1,1-Bis(4'-trimethylsilylphenyl)ethylene (TMS_2DPE) prepared according to the procedure reported previously was dried and distilled over CaH_2 [5]. *sec*-Butyllithium was allowed to react with TMS_2DPE in THF at -78°C for 20 minutes to afford 1,1-bis(4'-trimethylsilylphenyl)-3-methylpentyllithium(**I**). The concentration of **I** in THF was determined by titration with 1-octanol in a sealed tube *in vacuo*. For the experiments in the presence of diethylzinc, 2-15 fold molar excess of Et_2Zn was added to the initiator solution in THF, and the resulting solution was maintained at -78°C for 10 minutes prior to the polymerization.

N,*N*-Dimethylacrylamide (DMAA) and *N*,*N*-Diethylacryl Amide (DEAA)

Commercially available DMAA and DEAA were purified twice by fractional distillation under reduced pressure from CaH_2. The purified monomer were diluted with THF and introduced into ampoules equipped with breakseals though a vacuum line. **DMAA**: bp 48-49°C/5 Torr. 500MHz ^1H NMR ($CDCl_3$): d 3.06(s, 6H, CH_3), 5.65-5.69(dd, 1H, trans CH_2=), 6.27-6.31(dd, cis CH_2=), 6.57-6.63(dd, 1H, -CH=). 125MHz ^{13}C NMR ($CDCl_3$): d 35.5, 37.0(NCH_3), 127.1(vinyl, CH_2=), 127.5(vinyl, -CH=), 166.3(C=O). **DEAA**: bp 40-43°C/3 Torr. 500MHz ^1H NMR ($CDCl_3$)(ppm): d 1.18(s, 6H, CH_3), 3.44(br, 4H, NCH_2), 5.65-5.68(dd, 1H, trans CH_2=), 6.33-6.36(dd, 1H, cis CH_2=), 6.53-6.58(dd, 1H, -CH=). 125MHz ^{13}C NMR ($CDCl_3$): d 12.9, 14.6(CH_3), 40.6, 42.0(NCH_2), 127.2(vinyl, CH_2=), 127.8(vinyl, -CH=), 165.4(C=O).

N,*N*-Dipropylacrylamide (DPAA)

Acryloyl chloride (5.43 g, 60.0 mmol) in 50 ml of dry Et_2O was added dropwise into a rapidly stirred solution of dipropylamine (12.6 g, 125 mmol) in dry Et_2O (40 ml) with cooling in an ice bath. After the addition, the reaction mixture was stirred at room temperature overnight. The precipitated dipropylamine HCl salt was filtered off and resulting solution was washed with water. The product was extracted with Et_2O and dried over $MgSO_4$. The crude product was purified by column chromatography using hexane/AcOEt(10/1,v/v) and distilled under reduced pressure from CaH_2; yield 6.01 g (65%), bp 46-47°C/2 Torr. 500MHz ^1H NMR ($CDCl_3$): d 0.90-0.93(t, 6H, CH_3), 1.60-1.61(br, 4H, CH_2), 3.28, 3.34(br, 4H, NCH_2), 5.64-5.68(dd, 1H, trans CH_2=), 6.32-6.36(dd, 1H, cis CH_2=), 6.53-6.58(dd, 1H, -CH=). 125MHz ^{13}C NMR ($CDCl_3$): d 11.2, 11.4(CH_3), 21.0, 22.8(CH_2), 48.3, 49.8(NCH_2), 127.5(vinyl, CH_2=), 127.9(vinyl, -CH=), 166.0 (C=O).

Polymerizations

Anionic polymerization was carried out under a high vacuum condition in a glass apparatus equipped with breakseals. The monomer was added to the initiator system with vigorous stirring and the reaction mixture was kept at the required temperature for 60 minutes. On addition of the monomer, the characteristic red color of the initiator rapidly changed to pale yellow or purple. After completion of the polymerization, the reaction was terminated with methanol. The concentrated reaction mixture was dissolved in a small mount of THF (or THF/methanol mixture) and poured to a large excess of hexane to precipitate the polymer. The crude polymer was again dissolved in a mixture of THF and methanol and filtered to remove the zinc compound. The purified polymer was freeze-dried from benzene.

Measurements

The ^1H and ^{13}C NMR spectra of the polymers in 3wt% $CDCl_3$(for poly(DMAA) and poly(DEAA)) or 1,4-dioxane d_6 (for poly(DPAA)) at 50°C were recorded on a JEOL GSX-500 with tetramethylsilane and $CHCl_3$ as internal standards, operating at 500 and 250 MHz, respectively. The gel-permeation chromatograms (GPC) of the polymers with low level of *m m* configuration were measured by a TOSOH HLC-8020 instrument with G3000H_{XL}, G4000H_{XL}, G5000H_{XL} column using THF as a carrier solvent at a flow rate 1.0 mL/min at 40°C. The GPC's of the polymers rich in isotactic configuration were measured by a Shimadzu LC-6A with TSK-GEL GMH_{XL} using $CHCl_3$ at a flow rate 1.0 mL/min at 40°C.

RESULTS AND DISCUSSION

Anionic Polymerization of DMAA and DPAA

The results of the anionic polymerizations of DMAA and DPAA with **I** in the absence and presence of LiCl or Et_2Zn in THF for 1 hour at -78°C are summarized in Table 1. Poly(DMAA) and poly(DPAA) were obtained in quanitative yields in all cases. The number-average molecular weights (*M*n) of the polymers were determined by ^1H NMR spectroscopy. The degree of polymerization was estimated from the relative signal intensities of silylmethyl protons (0.1-0.2 ppm) of the initiator fragment attached to the chain head and those of the protons on the main and side chain. The observed Mn's agree with the calculated ones from the molar ratios of monomer to initiator in the feed as shown in Table 1. These results indicate that the polymerizations are initiated with **I** in quantitative efficiency and proceed without transfer reactions. Hogen-Esch *et al.* also reported the similar results that the anionic polymerizations of DMAA initiated with triphenylmethyllithium (TPM-Li), -cesium(TPM-Cs), and 1,1,4,4-tetraphenylbutyl-dilithium (TPB-Li) -dipotassium(TPB-K) -dicesium(TPB-Cs) were essentially quantitative

TABLE 1. Anionic Polymerization of DMAA and DPAA with I in THF for 1 hour at -78°C

Run	Monomer	Initiator/Additive [a]	MnX10^{-3} Calcd.	MnX10^{-3} Obsd.[b]	Mw/Mn[c]
1	DMAA	I	9.4	11	2.58
2	DMAA	I / LiCl (1 / 3)	11	13	6.17
3	DMAA	I / Et_2Zn (1 / 15)	9.2	9.3	1.28
4	DPAA	I	11	14	1.52
5	DPAA	I / LiCl (1 / 3)	8.2	8.1	2.32
6	DPAA	I / Et_2Zn (1 / 15)	7.5	6.7	1.41

[a] molar ratio. [b]determined by ^1H NMR. [c]measured by GPC using PMMA standard.

[4]. The values of Mw/Mn's of the polymers obtained in this study were estimated by the GPC calibrated with PMMA standards. The broad molecular weight distributions were observed for the poly(DMAA) and poly(DPAA) produced in the absence of Et_2Zn, especially the former is much broader than latter (Runs 1 and 4). Similarly, Hogen-Esch *et al.* reported that the poly(DMAA)s obtained with TPM-Li and TPB-K in THF at -78°C had broad molecular weight distributions while that of the polymer generated with TPM-Cs was narrow [4c]. These results suggest that the termination reaction occurs during the polymerization; the propagating carbanion may eliminate the methine proton on the main chain to terminate the polymerization. To suppress the termination reaction for the synthesis of the polymer with narrow molecular weight distribution, the additive effects of LiCl and Et_2Zn were investigated. Although the addition of LiCl to the anionic polymerization system of *tert*-butyl acrylate inhibits back-biting termination leading to the living polymer [6], broadening of the molecular weight distribution was observed for the poly(DMAA) and poly(DPAA) produced in the presence of LiCl (Run 2 and 5). On the other hand, poly(DMAA) of narrow molecular weight distribution was obtained in the presence of Et_2Zn (Run 3). We have found the similar effect of Et_2Zn on the anionic polymerization of methacrylates [7]. Since Et_2Zn is a weak Lewis acid, it may coordinate with the propagating end to stabilize the carbanionic species resulting in narrow molecular weight distribution.

McGrath [3d] and Hogen-Esch [4c] investigated the stereo structure of poly(DMAA)s generated with anionic initiators by ^{13}C NMR spectroscopy. They observed three peaks due to the carbonyl carbon in the region of 174.2-174.6 ppm. A peak at 174.2 ppm is clearly resolved and may be assigned to isotactic triad. On the other hand, the signals at the lower field are poorly resolved and cannot be

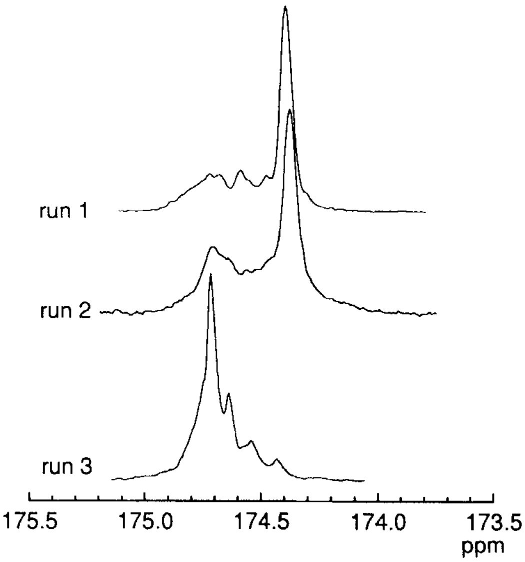

Figure 1. ^{13}C NMR spectra of the carbonyl carbons of the poly(DMAA) measured in $CDCl_3$: the conditions of the polymerization, see Table 1.

separately attributable to hetero and syndiotactic triads. Thus, the contents of the hetero and syndiotactic triad could not be estimated accurately. Hogen-Esch and co-workers described that the poly(DMAA)s produced with TPB-Li and with TPB-Cs were soluble and insoluble in THF, respectively. The difference of the tacticities of these polymers appeared in the ^{13}C NMR spectra of the carbonyl carbon and was reflected in the solubility in THF [4]. The ^{13}C NMR of the poly(DMAA) and poly(DPAA) produced in this study are measured in $CDCl_3$ and 1,4-dioxane-d_6, and are shown in Figures 1 and 2, respectively. Although the higher resolution spectra including more than five peaks are obtained, the accurate assignments of the peaks are not determined yet. Similarly to Hogen-Esch's result, the poly(DMAA) produced with **I** shows a sharp peak at 174.3 ppm, indicating the isotactic rich configuration (Run 1 in Figure 1). LiCl gives little additive effect on the triad configuration (Run 2). However, the polymer produced with **I** in the presence of Et_2Zn affords a sharp peak at 174.7 ppm (Run 3 in Figure 1). This spectrum is quite different from those of the poly(DMAA)s generated with **I** in the absence of Et_2Zn and with TPB-Cs. The isotactic rich structure is clearly changed to syndiotacitic one, if the peak at 174.7 ppm is assigned to the *rr* configuration. These results suggest that Et_2Zn coordinates with the anionic propagating species to control the

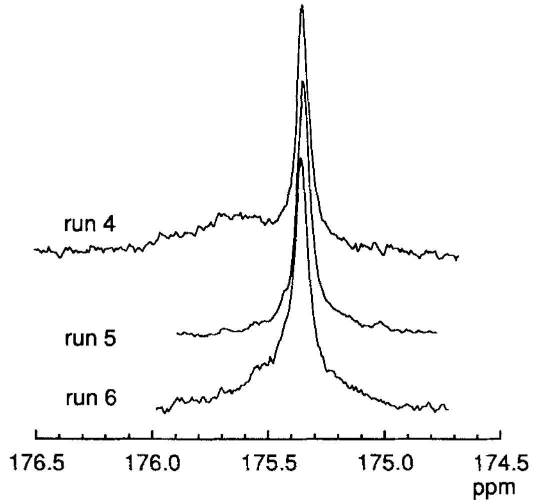

Figure 2. ^{13}C NMR spectra of the carbonyl carbons of the poly(DPAA) measured in 1,4-dioxane d_6: the conditions of the polymerization, see Table 1.

tacticity. In contrast to the cases of poly(DMAA), Et_2Zn shows little effect on the stereo structure of poly(DPAA) as shown in Figure 2. The poly(DPAA)s obtained with **I** in the absence and in the presence of LiCl and Et_2Zn are insoluble in THF and seem to be isotactic.

Anionic Polymerizaton of DEAA

The results of the anionic polymerizatoins of DEAA with **I** in the absence and presence of LiCl or Et_2Zn in THF for 1 hour at -78°C are summarized in Table 2. Poly(DEAA)s were obtained in quantitative yields in all cases. The observed Mn's agree with those calculated from the molar ratios of monomer to initiator in the feed (Table 2), indicating that the polymerizations are initiated with **I** in quantitative efficiency and proceed without transfer reactions. The polymer produced in the absence of Et_2Zn has rather broad molecular weight distribution (Runs 7 and 8), which is also observed in the case of *N,N*-dimethylacrylamide. The broader molecular weight distributions are probably due to elimination of the methine proton by the propagating carbanion. In expectation of the additive effect of LiCl on narrowing the molecular weight distribution as observed in the case of alkyl acrylates, [6] LiCl was added to the polymerization system of DEAA with **I**, but in vain (Run 8). Et_2Zn was added to the polymerization system of DEAA at the molar ratio of

TABLE 2. Anionic Polymerization of DEAA with I in THF for 1 hour at -78°C

Run	Initiator / Additive[a]	Mn X10^{-3}		Mw/Mn[c]	Tacticity, %		
		Calcd.	Obsd.[b]		*mm*	*mr*	*rr*
7	**I**	9.9	11	2.83	**61**	12	28
8	**I** / LiCl (1 / 3)	10	11	3.00	**78**	17	5
9	**I** / Et_2Zn (1 / 2)	8.6	10	5.44	**44**	13	43
10	**I** / Et_2Zn (1 / 3)	11	13	1.74	9	15	**76**
11	**I** / Et_2Zn (1 / 15)	12	11	1.57	0	12	**88**

[a]molar ratio. [b]determined by ^{1}H NMR. [c] measured by GPC using PMMA standard.

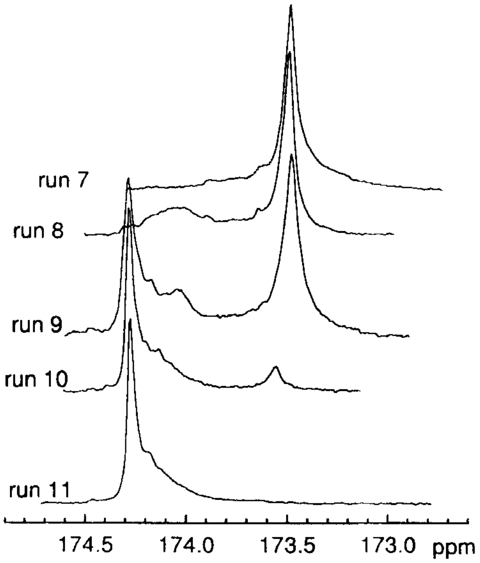

Figure 3. ^{13}C NMR Spectra of the carbonyl carbons of the poly(DEAA) measured in $CDCl_3$: the conditions of the polymerization, see Table 1.

Et_2Zn/**I** = 3-15 to result in narrow molecular weight distribution (Runs 10 and 11), while the lower molar ratio of Et_2Zn/**I** = 2 caused broader distribution (Run 9). The reason for this is explained later. The ^{13}C NMR signals of carbonyl carbon of the poly(DEAA)s are shown in Figure 3. The well resolved signals are observed in the region of 173.3- 174.5 ppm for the poly(DEAA)s produced with **I** in the absence and presence of Et_2Zn (Runs 7-11 in Figure 3). The resonances at 173.3-173.6 and 174.1-174.5 ppm may be attributable to *mm* and *rr* triad, respectively.

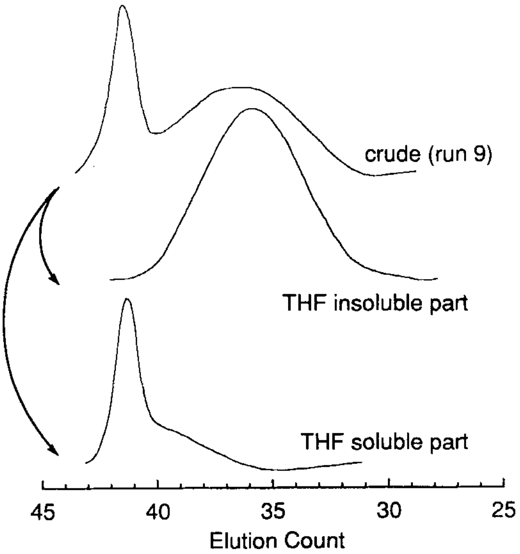

Figure 4. The GPC curves of poly(DEAA) (Run 9): eluent is chloroform.

The middle region, 173.6-174.1 ppm, is tentatively assigned to heterotactic triad, although these assignments should be proved by the analysis of the model compound. According to the assignment, the contents of *mm*, *mr*, and *rr* configuration are estimated and listed in Table 2. The poly(DEAA)s produced with **I** and **I**/LiCl is highly isotactic (Runs 7 and 8). However, the tacticity is unambiguously changed from isotactic to syndiotactic, when large excess amount of Et_2Zn is added to the reaction mixture (Run 11). Almost a similar result is obtained at the molar ratio of **I**/Et_2Zn =1/3. In the case of **I**/Et_2Zn =1/2, both of *mm* and *rr* contents are high and *mr* one is rather low, suggesting that two types of polymerizations proceed concurrently to lead isotactic and syndiotactic polymers (Run 9). The GPC curve of the crude polymer obtained in Run 9 is shown in Figure 4, where bimodal molecular weight distribution is observed. The polymer can be separated into THF soluble and insoluble parts, the GPC and NMR spectra of which are shown in Figures 4 and 5, respectively. It is obvious that the THF insoluble part is isotactic and has higher molecular weight and broad molecular weight distribution, and that the THF soluble one is syndiotactic and has lower molecular weight and narrow molecular weight distribution. Since the product is a mixture of two types of polymers, very large value of Mw/Mn is observed. These results suggest that the aggregate of Et_2Zn may coordinate with the propagating carbanion to control the tacticity and to lower the propagating activity leading to narrow molecular weight distribution.

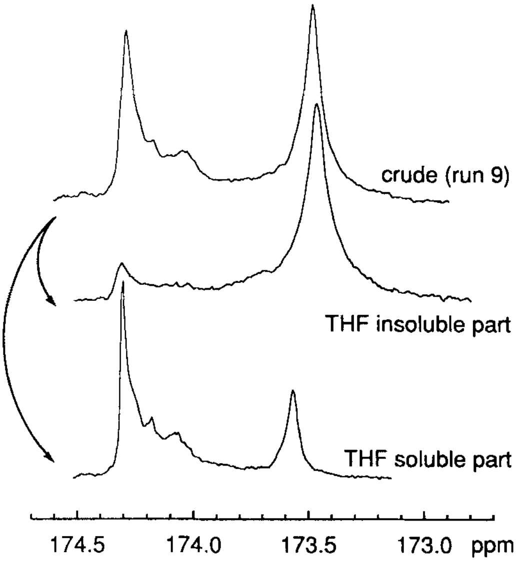

Figure 5. ^{13}C NMR spectra of the carbonyl carbons of the poly(DEAA) (Run 9) measured in $CDCl_3$: the conditions of the polymerization, see Table 1.

CONCLUSION

The anionic polymerizations of DMAA, DEAA, and DPAA with **I** are quantitative in THF at -78°C. The addition of Et_2Zn to the polymerization systems of DMAA and DEAA results in narrow molecular weight distribution and highly syndiotactic configuration, while the isotactic polymers with broad molecular weight distributions are produced in the absence of Et_2Zn. Little additive effect of Et_2Zn is observed for the anionic polymerization of DPAA. The almost stoichiometric additive effect of Et_2Zn toward the initiator in the polymerization of DEAA suggests the coordination of Et_2Zn aggregates with the propagating carbanionic species.

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