

## Stereospecific Anionic Polymerization of $\alpha$ -(*N*-*tert*-Butyl aminomethyl)acrylate Having Unprotected Amino Group

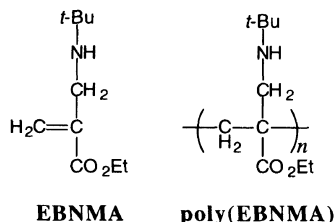
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We recently found that the anionic polymerization of  $\alpha$ -(alkoxymethyl)acrylates<sup>1</sup> and  $\alpha$ -(*N,N*-dialkylamino-methyl)acrylates,<sup>2</sup> which have a polar substituent on the  $\alpha$ -position of an acrylate, with lithium reagents gave highly isotactic polymers regardless of the polarity of solvents. Stereospecific synthesis of the polymers possessing a variety of polar and reactive functional groups<sup>3</sup> may be particularly important for generating novel highly functional polymers. In the course of our research on the stereospecific polymerization of  $\alpha$ -substituted acrylates, attention was directed to  $\alpha$ -(aminomethyl)acrylates having an unprotected amino group. Reported herein is the stereospecific anionic polymerization of a new monomer, ethyl  $\alpha$ -(*N*-*tert*-butylamino-methyl)acrylate (EBNMA).



### EXPERIMENTAL

<sup>1</sup>H and <sup>13</sup>C NMR spectra were measured on a Varian Gemini-2000 (400 MHz for <sup>1</sup>H) spectrometer in CDCl<sub>3</sub> at 60°C. Infrared (IR) spectra were recorded on a JASCO FT/IR-550 spectrometer. Number-average molecular weights (*M<sub>n</sub>*) of the polymers obtained were estimated from the relative intensities of the phenyl proton signal (initiator fragment) and the signal of ester proton in <sup>1</sup>H NMR spectra.

Solvents, toluene and tetrahydrofuran (THF), used in the polymerization were distilled from Na wire, and distilled again from butyllithium (*n*-BuLi) for toluene and LiAlH<sub>4</sub> for THF under high vacuum just before use. *n*-BuLi was prepared from 1-chlorobutane and lithium powder in heptane. A radical initiator diisopropyl peroxycarbonate [(*i*-PrOCO<sub>2</sub>)<sub>2</sub>] was generously donated by NOF Co. and used as toluene solution. Lithium amide compounds as initiators were prepared from the corresponding secondary amine in toluene by adding an

equimolar amount of *n*-BuLi at room temperature. A lithium amide complex with diamine was prepared by mixing lithium reagent with 1.2 equiv. of diamine in toluene at room temperature under dry nitrogen.

EBNMA was prepared from ethyl  $\alpha$ -(bromomethyl)acrylate<sup>4</sup> and *tert*-butylamine according to the procedure<sup>2</sup> previously reported: yield 50%; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  1.14 (s, 9H, CH<sub>3</sub>), 1.31 (t, 3H, *J* = 7.2 Hz, CH<sub>3</sub>), 1.75 (br, 1H, NH), 3.40 (s, 2H, NCH<sub>2</sub>), 4.22 (q, 2H, *J* = 7.2 Hz, OCH<sub>2</sub>), 5.78 (s, 1H, vinyl), 6.23 (s, 1H, vinyl); IR (neat, cm<sup>-1</sup>) 3323, 2966, 1716, 1635, 1473, 1458, 1363, 1294, 1217, 1151, 1099, 1028. Anal. Calcd for C<sub>10</sub>H<sub>19</sub>NO<sub>2</sub>: N, 7.56%; C, 64.83%; H, 10.34%. Found: N, 7.48%; C, 64.79%; H, 10.41%.

Similar procedures reported previously<sup>1,2</sup> were used for the anionic polymerization of EBNMA.

### RESULTS AND DISCUSSION

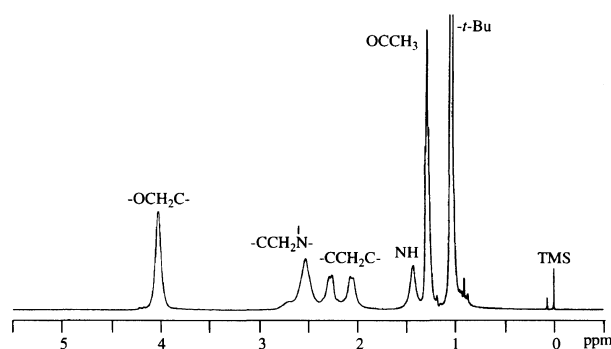
The results of the radical and anionic polymerizations of EBNMA in toluene and THF are listed in Table I. Anionic polymerization with *n*-BuLi in toluene at -78°C afforded a polymer in a poor yield (entry 1), and unreacted EBNMA was recovered as a methanol-soluble part in >90% yield. The previous paper reported that the polymerization of  $\alpha$ -(*N,N*-dialkylaminomethyl)acrylates with *n*-BuLi, a side reaction, 1,2-addition (carbonyl attack), prevents the initiation of the polymerization.<sup>2</sup>

Table I. Radical and anionic polymerization of EBNMA<sup>a</sup>

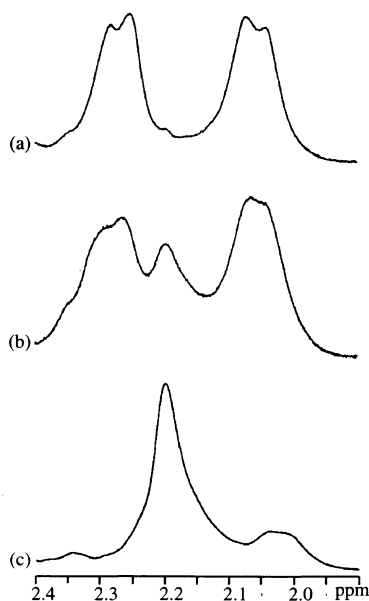
Entry	Initiator	Solvent	Time	Yield <sup>b</sup>	$\bar{M}_n^c$
			h	%	$\times 10^{-4}$
1	<i>n</i> -BuLi	Toluene	24	3	—
2	DPALi <sup>d</sup> -TMEDA <sup>e</sup>	Toluene	24	89	1.3
3	DPEDALi <sup>f</sup> -TMEDA	Toluene	24	86	1.6
4	DPEDALi(-)-Sp <sup>g</sup>	Toluene	24	76 <sup>h</sup>	1.3
5	DPALi-TMEDA	THF	42	53	1.3
6	DPALi	THF	42	42	1.1
7 <sup>i</sup>	( <i>i</i> -PrOCO <sub>2</sub> ) <sub>2</sub>	—	42	0 <sup>j</sup>	—

<sup>a</sup> [EBNMA]/[initiator] = 20, temp. = -78°C. <sup>b</sup> Methanol insoluble part. <sup>c</sup> Determined by <sup>1</sup>H NMR analysis. <sup>d</sup> Lithium diphenylamide. <sup>e</sup> *N,N,N',N'*-Tetramethylethylenediamine. <sup>f</sup> *N,N'*-Diphenylethylenediamine monolithiumamide. <sup>g</sup> (-)-Sparteine. <sup>h</sup>  $[\alpha]_D^{25} -2.5^\circ$  (in CHCl<sub>3</sub>, *c* 1.1). <sup>i</sup> Polymerization was carried out at 30°C, [EBNMA]/[initiator] = 30. <sup>j</sup> Hexane insoluble part.

<sup>†</sup> To whom all correspondence should be addressed.



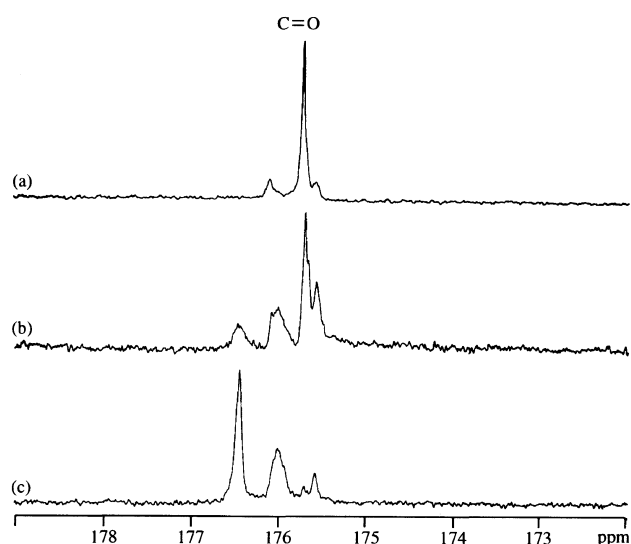
**Figure 1.** 400 MHz  $^1\text{H}$  NMR spectrum of poly(EBNMA) obtained with DPALi-TMEDA complex in toluene at  $-78^\circ\text{C}$  (entry 2) ( $\text{CDCl}_3$ ,  $60^\circ\text{C}$ ).



**Figure 2.** Expanded  $^1\text{H}$  NMR spectra of the main chain methylene protons in poly(EBNMA)s obtained with DPALi-TMEDA complex in toluene (entry 2) (a), with DPEDALi-(–)-Sp complex in toluene (entry 4) (b), and with DPALi-TMEDA complex in THF (entry 5) (c) ( $\text{CDCl}_3$ ,  $60^\circ\text{C}$ ).

However, in the present polymerization, the side reaction of unprotected amino proton with  $n\text{-BuLi}$  to yield lithium amide appeared to inhibit the initiation of the polymerization, because no by-products due to carbonyl attack were found in the methanol-soluble part. This means that the generated lithium amide from EBNMA can't initiate the polymerization of EBNMA. To avoid this side reaction, we used mild nucleophiles, lithium diphenylamide (DPALi) and  $N,N'$ -diphenylethylenediamine monolithiumamide (DPEDALi) as initiators. The polymerization of EBNMA using their complexes with  $N,N,N',N'$ -tetramethylethylenediamine (TMEDA) and (–)-sparteine ((–)-Sp) in toluene at  $-78^\circ\text{C}$  resulted in good yields (entries 2–4). Polymerizations in THF using DPALi and its complex with TMEDA also proceeded in moderate yields. The polymers are soluble in  $\text{CHCl}_3$  and THF. Radical polymerization with ( $i\text{-PrOCO}_2$ ) $_2$  at  $30^\circ\text{C}$  did not proceed (entry 7). The difficulty of radical polymerization of  $\alpha$ -( $N,N$ -dialkylaminomethyl)acrylates has been reported.<sup>2,5</sup>

The  $^1\text{H}$  NMR spectrum of the polymer obtained with the DPALi-TMEDA complex in toluene (entry 2) is demonstrated in Figure 1. The spectral pattern is simple



**Figure 3.** 100 MHz  $^{13}\text{C}$  NMR spectra of the carbonyl carbon in poly(EBNMA) obtained with DPALi-TMEDA complex in toluene (entry 2) (a), with DPEDALi-(–)-Sp complex in toluene (entry 4) (b), and with DPALi-TMEDA complex in THF (entry 5) (c) ( $\text{CDCl}_3$ ,  $60^\circ\text{C}$ ).

and each peak is assigned to a vinyl polymer corresponding to poly(EBNMA). The spectral pattern of main chain methylene protons around 2.2 ppm shows a typical AB quartet with small shoulder peaks (Figure 2(a)). These observations indicate that a polymer rich in isotacticity was produced in the anionic polymerization of EBNMA in toluene similarly to the anionic polymerization of  $\alpha$ -(alkoxymethyl)acrylates and  $\alpha$ -( $N,N$ -dialkylaminomethyl)acrylates with lithium reagents.<sup>1,2</sup> The chain-transfer reaction from the growing polymer anion to the reactive unprotected amino group is negligible.

In the anionic polymerization of  $\alpha$ -(alkoxymethyl)acrylates<sup>1</sup> and  $\alpha$ -( $N,N$ -dialkylaminomethyl)acrylates<sup>2</sup> with lithium reagents, highly isotactic polymers were obtained regardless of the polarity of solvents. The  $^1\text{H}$  NMR spectra of the main chain methylene protons in the poly(EBNMA)s obtained with the DPEDALi-(–)-Sp complex in toluene and the DPALi-TMEDA complex in THF (entries 4 and 5) are demonstrated in Figures 2(b) and (c). The spectral patterns are quite different from that of the polymer obtained with the DPALi-TMEDA complex in toluene. The polymer generated in THF shows a broad main peak probably ascribed to syndiotactic sequences. The reason for the different behavior of EBNMA from  $\alpha$ -( $N,N$ -dialkylaminomethyl)acrylate in the polymerization in THF is not clear at present, but could be ascribed to the bulky *tert*-butyl group of EBNMA which may prevent the coordination of the amino group of EBNMA to a lithium cation.

The small optical activity of the polymer (entry 4) obtained with the chiral initiator, DPEDALi-(–)-Sp, may be due to the chirality induced around the polymer ends, because the bulkiness of the side groups of EBNMA seems to be not enough to maintain the helical polymer chain which might be produced by stereospecific polymerization.

The  $^{13}\text{C}$  NMR spectra of the carbonyl carbon of the above polymers clearly exhibit splitting due to triad sequences (Figure 3), and the peaks may be assigned to *mm*, *mr*, and *rr* from high-magnetic-field. The triad

tacticities (*mm*:*mr*:*rr*) were estimated as 83:17:0 (entry 2), 62:26:12 (entry 4), and 15:37:48 (entry 5) and the diad tacticities derived from these values approximately correspond to the values obtained from the <sup>1</sup>H NMR spectra shown in Figure 2. The results are rather analogous to those reported for the anionic polymerization of  $\alpha$ -(alkyl)acrylates which afford the polymers rich in syndiotacticity in THF.<sup>6</sup>

A novel monomer, EBNMA having a reactive unprotected amino proton was anionically polymerized to provide a normal vinyl polymer. The polymer obtained with the DPALi-TMEDA complex in toluene was rich in isotacticity (*mm*=83%), while that obtained in THF was rich in syndiotacticity in contrast to the polymerizations of  $\alpha$ -(alkoxymethyl)acrylates<sup>1</sup> and  $\alpha$ -(*N,N*-dialkylaminomethyl)acrylates<sup>2</sup> in THF. The main point of the present work is that we can prepare both isotactic and syndiotactic polymers with a reactive hydrogen. With this polymer, we can readily prepare new functional polymers with different tacticities and different activity. Further work is now in progress on stereospecific anionic polymerization of  $\alpha$ -(aminomethyl)acrylates and the properties of the obtained polymers.

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