Stereospecific Anionic Polymerization of Ethyl α-(1-Pyrrolidinylmethyl)acrylate

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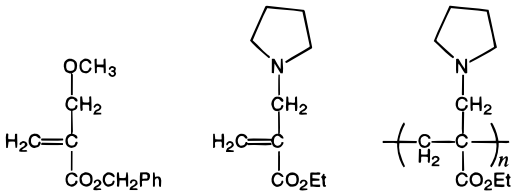
Introduction. Control of stereoregularity in the polymerization of vinyl monomers is one of the most important topics in synthetic polymer chemistry. Recently, we found that the anionic polymerization of benzyl α-(methoxymethyl)acrylate (BMMA), which has a polar substituent on the α-position of an acrylate, with alkyllithium reagents gave highly isotactic polymers regardless of the polarity of solvents.[1] The main factor in controlling the stereochemistry of the polymerization may be ascribed to the strong intra-[2] and intermolecular coordination powers of the polar groups of a growing polymer chain end and α-(alkoxymethyl)acrylate monomers to the countercation (Li^+). On the other hand, it has been reported that α-((*N*,*N*-dialkylamino)methyl)-acrylate has no radical polymerizability because of steric factor of α-substituents.[3,4] However, effects of such a polar functional group on the α-position of acrylates on the reactivity and stereoregulation in anionic polymerization are of great interest from the view points of the intra- and intermolecular coordination to a countercation and the polymerization mechanism of α-substituted acrylates. The obtained polymer is also interesting as a polymeric base and ligand. Reported herein is the stereospecific anionic polymerization of a new monomer, ethyl α-(1-pyrrolidinylmethyl)acrylate (EPNMA), bearing an amino group as an α-substituent.



BMMA **EPNMA** **poly(EPNMA)**

Experimental Section. ^1H and ^{13}C NMR spectra were measured on a Varian Gemmini-2000 (400 and 100 MHz) or UNITY-INOVA (500 and 125 MHz) spectrometer in $CDCl_3$ at 60 °C. Infrared (IR) spectra were recorded on a Jasco FT/IR-7000 spectrometer. Gel permeation chromatographic (GPC) analysis was carried out on a Jasco 880-PU equipped with an RI (Jasco 830-RI) detector using dry $CHCl_3$ as an eluent. Two GPC columns, TSK G5000H and Shodex AC802.5, were connected in series. Number-average molecular weight (M_n) of the polymers obtained with lithium diphenylamide and lithium 4-benzylpiperidide was also estimated from the relative intensities of the phenyl proton signal (initiator fragment) and the signal of ester proton in the ^1H NMR spectrum.

The solvents, toluene and tetrahydrofuran (THF), used in polymerization were distilled from Na wire and then distilled again from butyllithium (*n*-BuLi) for toluene and $LiAlH_4$ for THF under high vacuum just before use. *n*-BuLi was prepared from 1-chlorobutane and lithium powder in heptane. A pentane solution of *tert*-butyllithium (*t*-BuLi) was purchased from Aldrich. The radical initiator diisopropyl peroxydicarbonate (Perloyl) was kindly supplied by NOF Co. and used as a toluene solution. Lithium amide compounds as initiators were prepared from the corresponding secondary amine in toluene by adding an equimolar amount of *t*-BuLi at room temperature.

Table 1. Radical and Anionic Polymerization of EPNMA[a]

entry	initiator	solvent	conditions	yield[b] (%)	$\bar{M}_n \times 10^{-4}$ [c]
1	$(i\text{-PrOCO}_2)_2$	toluene	30 °C, 48 h	0[d]	
2	*n*-BuLi	toluene	−78 °C, 48 h	0	
3	lithium piperidide	toluene	−78 °C, 48 h	80	
4	lithium piperidide	THF	−78 °C, 48 h	79	
5	BPNLi[e]	toluene	−78 °C, 24 h	84	2.3
6	BPNLi	THF	−78 °C, 24 h	94	4.0
7	Ph_2NLi	THF	−78 °C, 48 h	16	0.90

[a] Radical polymerization: [EPNMA]/[initiator] = 30. Anionic polymerization: [EPNMA]/[initiator] = 10. [b] MeOH insoluble part. [c] Determined from ^1H NMR analysis.[6] [d] Hexane insoluble part. [e] Lithium 4-benzylpiperidide.

Ethyl α-(1-Pyrrolidinylmethyl)acrylate (EPNMA). To a mixture of ethyl α-(bromomethyl)acrylate[5] (7.4 g, 38 mmol) and pyrrolidine (2.7 g, 38 mmol) in CH_2Cl_2 (50 mL) was added triethylamine (3.9 g, 39 mmol) under stirring at 0 °C. The reaction was continued for 1.5 h at room temperature. H_2O (50 mL) was added to the reaction mixture, and the aqueous layer was extracted with CH_2Cl_2. The combined organic extracts were dried over anhydrous $MgSO_4$ and concentrated in *vacuo* after filtration. The crude product was purified by column chromatography on silica gel (hexane/ether = 2/1) to afford EPNMA (5.4 g, 78% yield): ^1H NMR (400 MHz, $CDCl_3$) δ 1.30 (t, 3H, J = 7.2 Hz, CH_3), 1.78 (m, 4H, CH_2), 2.54 (m, 4H, NCH_2), 3.33 (s, 2H, NCH_2), 4.22 (q, 2H, J = 7.2 Hz, OCH_2), 5.77 (s, 1H, vinyl), 6.25 (s, 1H, vinyl); IR (neat, cm^{-1}) 1723, 1634, 1462, 1386, 1352, 1301, 1265, 1176, 1122, 1031. Anal. Calcd for $C_{10}H_{17}NO_2$: N, 7.64; C, 65.54; H, 9.35. Found: N, 7.56; C, 65.54; H, 9.53.

Polymerization was carried out in a glass ampule equipped with a three-way stopcock. The purified reagents were transferred into the ampule with syringes under a dry nitrogen atmosphere. The anionic polymerization was initiated by adding an initiator solution to a monomer solution. The polymerization was typically carried out using the monomer (0.27 g, 1.50 mmol), an initiator (0.15 mmol), and a solvent (1.5 mL). The termination of the polymerization was accomplished by adding a small amount of methanol, and then the polymer was precipitated in a large amount of methanol. The polymer was separated by centrifugation and dried *in vacuo*.

Results and Discussion. The results of the radical and anionic polymerizations of EPNMA in toluene or THF are summarized in Table 1. The radical polymerization with Perloyl in toluene at 30 °C did not proceed (entry 1). It has been already reported that methyl α-(*N*-methyl-*N*-propylaminomethyl)acrylate has no polymerizability in radical polymerization.[3] This has been explained by the bulkiness of the amino group as well as the difficulty of the radical polymerization of α-(alkoxymethyl)acrylates having a bulky alkoxy group.[1b,4] The anionic polymerization with *n*-BuLi in toluene at −78 °C also gave no polymer (entry 2). In marked contrast, the polymerizations using lithium amides at −78 °C resulted in good yields in both toluene

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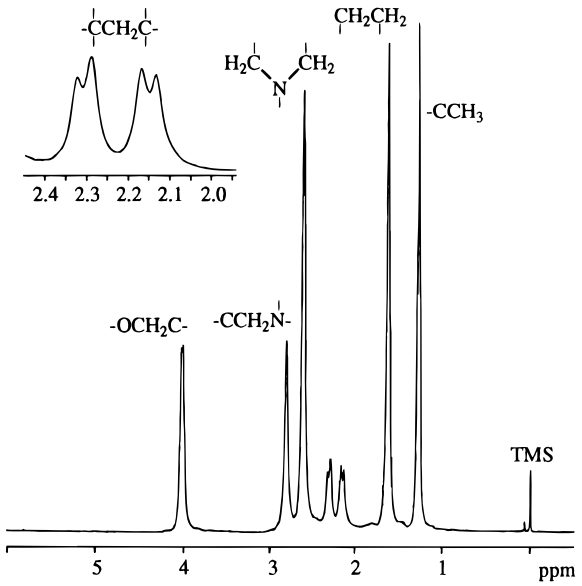
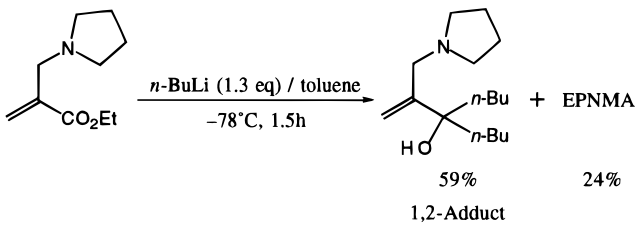


Figure 1. 400 MHz ^{1}H NMR spectrum of poly(EPNMA) (Table 1, entry 3) obtained with lithium piperidide in toluene at −78 °C ($CDCl_3$, 60 °C).

and THF (entries 3−7). In the anionic polymerization with *n*-BuLi, a side reaction, 1,2-addition (carbonyl attack), appears to prevent the initiation of the polymerization, because the 1,2-adduct (3-butyl-2-(1-pyrrolidinylmethyl)-1-hepten-3-ol) was obtained as a major product (59% yield) in the reaction of EPNMA with *n*-BuLi (1:1.3) in toluene at −78 °C. The obtained poly(EPNMA)s are soluble in $CHCl_3$, but insoluble in THF.



The ^{1}H NMR spectrum of the poly(EPNMA) obtained by the anionic polymerization with lithium piperidide in toluene (entry 3) is demonstrated in Figure 1. The spectral pattern of the main chain methylene protons around 2.2 ppm shows a typical AB quartet with a coupling constant of 13 Hz. This observation indicates that an isotactic polymer was produced in the anionic polymerization of EPNMA in toluene in the same way as in the anionic polymerization of α-(alkoxymethyl)-acrylates with lithium reagents.[1] Figure 2 shows the ^{13}C NMR spectra of the carbonyl carbon of poly(EPNMA)s obtained with lithium piperidide in toluene and THF (entries 3 and 4). A sharp singlet is observed for both the polymers indicating that the anionic polymerization is highly likely to proceed in an isotactic-specific manner regardless of the polarity of solvents. The results are analogous to those for the polymerization of benzyl α-(methoxymethyl)acrylate,[1] but in contrast to those of the anionic polymerization of α-(alkyl)-

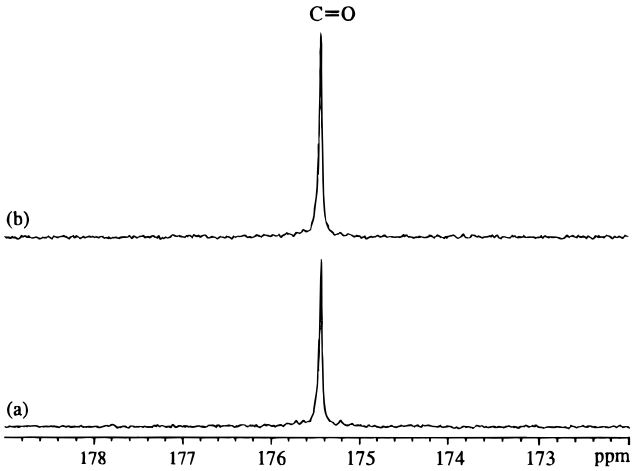


Figure 2. 125 MHz ^{13}C NMR spectra of the carbonyl carbon in poly(EPNMA) obtained with lithium piperidide in toluene (Table 1, entry 3) (a) and in THF (Table 1, entry 4) (b) ($CDCl_3$, 60 °C).

acrylates, which usually afford polymers rich in syndiotacticity under the conditions using polar solvents.[8]

Conclusion. Highly isotactic polymers were obtained in the polymerization of EPNMA, bearing an amino group on the α-position of an acrylate, using lithium amides as initiators, although radical polymerization of EPNMA did not proceed mainly because of the steric factor of α-substituent. The isotactic specific anionic polymerization takes place regardless of the polarity of solvents. The polymer may show significant features as a polymeric base or ligand caused by the stereoregular structure. A further work is now in progress on the detail investigation of the stereospecific anionic polymerization of α-(aminomethyl)acrylates and the properties of the obtained polymers.

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