

Stereospecific Anionic Polymerization and Novel Hydrogen-Transfer Polymerization of α -(Aminomethyl)acrylates Having Unprotected Amino Group

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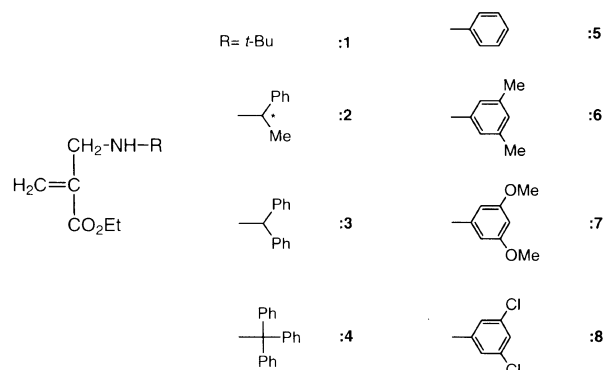
ABSTRACT: Anionic polymerization of α -(aminomethyl)acrylates (**2**–**8**) having an unprotected amino proton was carried out using lithium reagents at -78°C . Acrylates except for **4** and **8** afforded the polymers in good yields. The polymerization of ethyl α -[*N*-(diphenylmethyl)aminomethyl]acrylate (**3**) with *n*-BuLi or the $\text{Ph}_2\text{NLi}\cdot N,N,N',N'$ -tetramethylethylenediamine (TMEDA) complex in toluene afforded a polymer with a normal vinyl polymer structure and high isotacticity. Hydrogen-transfer of the amino proton hardly occurred in the polymerization process. The anionic polymerizations of ethyl α -[*N*-(1-phenylethyl)aminomethyl]acrylate (**2**) using lithium reagents in toluene and tetrahydrofuran (THF) proceeded with hydrogen-transfer reaction. CH carbon generated by hydrogen-transfer in the main chain was detected by DEPT NMR measurement of poly(**2**). The CH-containing unit in the polymer increased up to nearly 40% when THF was used as a solvent. Monomers **4** and **8** showed low polymerizability.

KEY WORDS Anionic Polymerization / Hydrogen-Transfer Polymerization / Stereospecific Polymerization / α -(Aminomethyl)acrylate / Lithium Amide / Isotactic Polymer / Optically Active Polymer /

Control of stereochemistry in the polymerization of vinyl monomers is an important area in synthetic polymer chemistry. In anionic polymerization, tacticity of polymers is often greatly affected by polymerization conditions such as polarity of solvents and initiators. Therefore, the introduction of a polar functional group to a vinyl monomer that interacts with a counteranion may greatly influence the stereoregulation of polymerization. A large number of α -substituted acrylates usually yields atactic or syndiotactic polymers through radical polymerization.¹ Recently, we found that the anionic polymerization of α -(alkoxymethyl)acrylates and α -(*N,N*-dialkylaminomethyl)acrylates with lithium reagents gave highly isotactic polymers regardless of the polarity of solvents.^{2,3} The main factor in controlling the stereochemistry of the polymerization should be the strong intra- and intermolecular coordination power of the polar groups of a growing polymer chain end and monomers to the counteranion (Li^+). Stereospecific synthesis of the polymers possessing a variety of polar groups is particularly important for generating novel functional polymers. We reported that the anionic polymerization of ethyl α -(*N*-*t*-butylaminomethyl)acrylate (**1**) having a reactive unprotected amino group with the lithium amide complexes such as the lithium diphenylamide complex with *N,N,N',N'*-tetramethylethylenediamine ($\text{Ph}_2\text{NLi}\cdot\text{TMEDA}$) in toluene afforded an isotactic polymer, while the polymerization in tetrahydrofuran (THF) gave a syndiotactic polymer.⁴ The tacticity of the obtained polymer was fairly affected by the polarity of solvents and initiators. These results are quite different from those of the previously reported monomers, which have a polar substituent on the α -position of an acrylate.^{2,3} The hydrogen-transfer polymerization^{5–10} (H-transfer polymerization) on the active amino proton did not occur in this system. The stereoregular polymer having a reactive amino proton in the side chain is attractive as a reactive

polymer, polymeric base, or ligand.

Reported herein is the anionic polymerization of novel α -(aminomethyl)acrylates having various aminomethyl groups at the α -position, ethyl α -[*N*-(1-phenylethyl)aminomethyl]acrylate (**2**), ethyl α -[*N*-(diphenylmethyl)aminomethyl]acrylate (**3**), ethyl α -[*N*-(triphenylmethyl)aminomethyl]acrylate (**4**), ethyl α -(anilinomethyl)acrylate (**5**), ethyl α -[(3,5-dimethylanilino)methyl]acrylate (**6**), ethyl α -[(3,5-dimethoxyanilino)methyl]acrylate (**7**), and ethyl α -[(3,5-dichloroanilino)methyl]acrylate (**8**). The generality of the stereospecific polymerization of acrylates bearing a reactive amino group at the α -position and effects of various amino groups on the reactivity in the anionic polymerization are examined.



EXPERIMENTAL

Measurements

¹H and ¹³C NMR spectra were measured on a Varian Unity-Inova (500 MHz for ¹H) and a Gemini-2000 (400 MHz for ¹H) spectrometers in CDCl_3 . Chemical shifts are reported in part per million (ppm) with tetramethylsilane (TMS, 0 ppm) and CDCl_3 (77.0 ppm) as an internal standard for ¹H and ¹³C NMR, respectively. Infrared (IR) spectra were recorded on a JACSO FT/IR-620 spectrometer. Circular dichroism

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(CD) spectra were taken on a JASCO J-720L. UV spectra were measured on a JASCO Ubest-55 spectrophotometer. Optical rotation was measured with a JASCO DIP-181 polarimeter. Size exclusion chromatography (SEC) analysis of obtained polymers was unsuccessful probably because of strong interactions between a polystyrene-based gel and amine containing polymers. The number-average molecular weight (M_n) of the obtained polymers was determined with a vapor pressure osmometer (VPO, Gonotec Osmomat 070) using CHCl_3 as solvent. The chromatographic resolution of racemic **2** was performed on a JASCO PU980 chromatograph equipped with a UV detector (JASCO UV970) and polarimetric detector (JASCO ORD-990) using a chiral column, CHIRALCEL OD (Daicel).

Materials

Toluene and THF used in polymerization were distilled from Na wire and distilled again from *n*-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 under an atmosphere of argon. Lithium amides, Ph_2NLi and *N,N'*-diphenylethylenediamine monolithium amide (DPEDALi), as initiators were prepared from the corresponding secondary amine by adding an equimolar amount of *n*-BuLi at room temperature. Lithium amide complexes with diamines [TMEDA and (–)-sparteine ((–)Sp)] were prepared by mixing lithium reagent with 1.2 equiv. of diamine at room temperature under dry nitrogen.

Synthesis of α -(Aminomethyl)acrylates

Ethyl α -[N-(1-Phenylethyl)aminomethyl]acrylate (2). To a mixture of racemic 1-phenylethylamine (2.8 g, 23.2 mmol) and triethylamine (2.4 g, 23.7 mmol) in dichloromethane (30 mL) was added dropwise a solution of ethyl α -(bromomethyl)acrylate¹¹ (4.4 g, 22.8 mmol) in dichloromethane (10 mL) with stirring at 0°C. After the reaction was continued for 1 h at 0°C, water (50 mL) was added to the reaction mixture, and the aqueous layer was extracted with dichloromethane. 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/ethyl acetate = 3/1, v/v) to afford pure **2** (3.5 g, 67% yield): $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 1.30 (t, 3H, $J=7.2$ Hz, CH_3), 1.34 (d, 3H, $J=6.4$ Hz, CH_3), 1.68 (br, 1H, NH), 3.20–3.40 (m, 2H, CH_2N), 3.78 (q, 1H, $J=6.4$ Hz, NCH), 4.20 (q, 2H, $J=7.2$ Hz, OCH_2), 5.65 (s, 1H, vinyl), 6.23 (s, 1H, vinyl), 7.22–7.35 (m, 5H, aromatic); IR (neat, cm^{-1}) 3336, 1713, 1631, 1492, 1450, 1369, 1304, 1264, 1176, 1158, 1116, 1027; *Elemental anal.* Found: C 72.07%, H 8.34%, N 5.98%. Calcd for $\text{C}_{14}\text{H}_{19}\text{NO}_2$: C 72.07%, H 8.21%, N 6.00%.

Resolution of racemic **2** was carried out by high-performance liquid chromatography (HPLC) on CHIRALCEL OD (25 \times 0.46 (id) cm \times 2) using hexane/ethanol = 100/1 (v/v) as an eluent.

(R)-2 (2R): $[\alpha]_{\text{D}}^{25} = +26^\circ$, $[\alpha]_{365}^{25} = +52^\circ$ ($c=1.1$, CHCl_3); *Elemental anal.* Found: C 72.05%, H 8.36%, N 6.04%. Calcd for $\text{C}_{14}\text{H}_{19}\text{NO}_2$: C 72.07%, H 8.21%, N 6.00%.

(S)-2 (2S): $[\alpha]_{\text{D}}^{25} = -25^\circ$, $[\alpha]_{365}^{25} = -51^\circ$ ($c=2.0$, CHCl_3); *Elemental anal.* Found: C 72.07%, H 8.08%, N 6.12%. Calcd for $\text{C}_{14}\text{H}_{19}\text{NO}_2$: C 72.07%, H 8.21%, N 6.00%.

Other Acrylates. Monomers **3–8** were synthesized by a similar procedure using the corresponding amines; yields were over 90%.

Ethyl α -[N-(Diphenylmethyl)aminomethyl]acrylate (3): $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 1.28 (t, 3H, $J=7.2$ Hz, CH_3), 1.96 (br, 1H, NH), 3.44 (s, 2H, CH_2N), 4.20 (q, 2H, $J=7.2$ Hz, OCH_2), 4.84 (s, 1H, NCH), 5.68 (s, 1H, vinyl), 6.27 (s, 1H, vinyl), 7.17–7.41 (m, 10H, aromatic); IR (neat, cm^{-1}) 3336, 1712, 1630, 1492, 1452, 1369, 1322, 1301, 1218, 1153, 1107, 1028; *Elemental anal.* Found: C 77.46%, H 7.17%, N 4.74%. Calcd for $\text{C}_{19}\text{H}_{21}\text{NO}_2$: C 77.26%, H 7.17%, N 4.74%.

Ethyl α -[N-(Triphenylmethyl)aminomethyl]acrylate (4): mp 67.5–68.1°C; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 1.26 (t, 3H, $J=7.2$ Hz, CH_3), 1.95 (br, 1H, NH), 2.96 (s, 2H, CH_2N), 4.17 (q, 2H, $J=7.2$ Hz, OCH_2), 5.95 (s, 1H, vinyl), 6.27 (s, 1H, vinyl), 7.16–7.51 (m, 15H, aromatic); IR (neat, cm^{-1}) 3398, 1714, 1631, 1490, 1476, 1447, 1401, 1377, 1295, 1207, 1153, 1111, 1088, 1024; *Elemental anal.* Found: C 80.76%, H 6.87%, N 3.64%. Calcd for $\text{C}_{25}\text{H}_{25}\text{NO}_2$: C 80.83%, H 6.78%, N 3.77%.

Ethyl α -(Anilinomethyl)acrylate (5): bp 144–146°C/3 mmHg; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 1.31 (s, 3H, $J=7.2$ Hz, CH_3), 4.03 (m, 2H, CH_2N), 4.07 (br, 1H, NH), 4.24 (q, 2H, $J=7.2$ Hz, OCH_2), 5.78 (s, 1H, vinyl), 6.27 (s, 1H, vinyl), 6.60 (d, 2H, $J=7.2$ Hz, aromatic), 6.61 (t, 1H, $J=7.2$ Hz, aromatic), 7.17 (t, 2H, $J=7.2$ Hz, aromatic); IR (neat, cm^{-1}) 3416, 1710, 1598, 1579, 1509, 1371, 1296, 1267, 1152, 1099, 1072, 1026, 949; *Elemental anal.* Found: C 70.12%, H 7.57%, N 6.58%. Calcd for $\text{C}_{12}\text{H}_{15}\text{NO}_2$: C 70.22%, H 7.37%, N 6.82%.

Ethyl α -[(3,5-Dimethylanilino)methyl]acrylate (6): $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 1.32 (s, 3H, $J=7.2$ Hz, CH_3), 2.22 (s, 6H, CH_3), 3.96 (br, 1H, NH), 4.00 (m, 2H, CH_2N), 4.24 (q, 2H, $J=7.2$ Hz, OCH_2), 5.77 (s, 1H, vinyl), 6.25 (s, 2H, aromatic), 6.26 (s, 1H, vinyl), 6.37 (s, 1H, aromatic); IR (neat, cm^{-1}) 3410, 1713, 1602, 1516, 1476, 1370, 1337, 1295, 1231, 1149, 1105, 1026; *Elemental anal.* Found: C 71.92%, H 8.58%, N 6.02%. Calcd for $\text{C}_{14}\text{H}_{19}\text{NO}_2$: C 72.07%, H 8.21%, N 6.00%.

Ethyl α -[(3,5-Dimethoxyanilino)methyl]acrylate (7): $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 1.31 (t, 3H, $J=7.2$ Hz, CH_3), 3.74 (s, 6H, CH_3), 4.00 (m, 2H, CH_2N), 4.09 (br, 1H, NH), 4.23 (q, 2H, $J=7.2$ Hz, OCH_2), 5.77 (s, 1H, vinyl), 5.77 (s, 1H, aromatic), 5.78 (s, 1H, aromatic), 5.88 (s, 1H, aromatic), 6.26 (s, 1H, vinyl); IR (neat, cm^{-1}) 3410, 1716, 1615, 1520, 1456, 1372, 1296, 1264, 1145, 1101, 1070, 1026; *Elemental anal.* Found: C 63.23%, H 7.58%, N 5.31%. Calcd for $\text{C}_{14}\text{H}_{19}\text{NO}_4$: C 63.38%, H 7.22%, N 5.28%.

Ethyl α -[(3,5-Dichloroanilino)methyl]acrylate (8): mp 39.0–40.0°C; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 1.32 (t, 3H, $J=7.2$ Hz, CH_3), 3.99 (m, 2H, CH_2N), 4.25 (br, 1H, NH), 4.25 (q, 2H, $J=7.2$ Hz, OCH_2), 5.74 (s, 1H, vinyl), 6.29 (s, 1H, vinyl), 6.44 (s, 2H, aromatic), 6.75 (s, 1H, aromatic); IR (neat, cm^{-1}) 3402, 1709, 1592, 1505, 1457, 1405, 1371, 1322, 1302, 1264, 1175, 1113, 1088; *Elemental anal.* Found: C 52.53%, H 4.99%, N 5.17%. Calcd for $\text{C}_{12}\text{H}_{13}\text{NO}_2\text{Cl}_2$: C 52.57%, H 4.78%, N 5.11%.

Table I. Anionic polymerization of α -(*N*-alkylaminomethyl)acrylates at -78°C^a

Entry	Monomer	Initiator	Conditions	Yield/% ^b	$M_n \times 10^{-4}$ (DP) ^c	f^d
1	2	<i>n</i> -BuLi	Toluene, 24 h	2		
2	2	Ph ₂ NLi-TMEDA ^e	Toluene, 24 h	90	0.9 (36)	0.47
3	2	DPEDALi ^f -(-)Sp ^g	Toluene, 4 h	87 ^h		
4	2	DPEDALi-(+)PMP ⁱ	Toluene, 4 h	93 ^j		
5	2	DPEDALi-(+)DDB ^k	Toluene, 4 h	24 ^l		
6	2	Ph ₂ NLi	THF, 24 h	89	1.2 (51)	0.35
7 ^m	3	<i>n</i> -BuLi	Toluene, 30 h	63	1.2 (41)	0.31
8 ^m	3	Ph ₂ NLi-TMEDA	Toluene, 30 h	96	1.2 (41)	0.47
9 ^m	3	Ph ₂ NLi	THF, 30 h	94	1.2 (41)	0.46
10 ⁿ	4	<i>n</i> -BuLi	Toluene, 24 h	0		
11 ⁿ	4	Ph ₂ NLi-TMEDA	Toluene, 24 h	0		

^a[Monomer]=1.0 M, [Monomer]/[Initiator]=20. ^bMeOH insoluble part. ^cDetermined by VPO (solvent CHCl₃, benzil standard). ^dEfficiency of initiator. ^e*N,N,N',N'*-Tetramethylethylenediamine. ^f*N,N'*-Diphenylethylenediamine monolithium amide. ^g(-)-Sparteine. ^h $[\alpha]_{365} -4^\circ$ (*c* 1.0, in CHCl₃, 25°C). ⁱ(*S*)-(+)-1-(2-Pyrrolidinylmethyl)pyrrolidine. ^j $[\alpha]_{365} -6^\circ$ (*c* 1.0, in CHCl₃, 25°C). ^k(*S,S*)-(+)-2,3-Dimethoxy-1,4-bis(dimethylamino)butane. ^l $[\alpha]_{365} -6^\circ$ (*c* 1.0, in CHCl₃, 25°C). ^m[Monomer]=0.2 M. ⁿ[Monomer]=0.1 M.

Polymerization Procedure

Polymerization was carried out in a glass ampule equipped with a three-way stopcock. Purified reagents were transferred to the ampule by syringe under dry nitrogen. The polymerization was initiated by adding an initiator solution to a monomer solution, typically using 2.0 mL of a monomer solution ([M]=1.0, 2.0 mmol) and initiator (0.1 mmol). Termination of the polymerization was done by adding a small amount of methanol and polymers were precipitated in excess methanol. The polymers were separated by centrifugation and dried *in vacuo*.

RESULTS AND DISCUSSION

Polymerization of α -(*N*-Alkylaminomethyl)acrylates

The results of the anionic polymerization of ethyl α -(*N*-alkylaminomethyl)acrylates (**2**–**4**) in toluene or THF are summarized in Table I. The polymerization of **2** with *n*-BuLi at -78°C (Table I, entry 1) as well as that of **1** reported previously,⁴ proceeded in poor yields (< 3%). Abstraction of an NH proton by a strong base *n*-BuLi may occur and the resulting lithium amide may not initiate the polymerization. In contrast, the polymerization of **3** with *n*-BuLi at -78°C provided a polymer in a moderate yield (63%) (Table I, entry 7), probably because the side reaction of unprotected amino proton with *n*-BuLi was prevented to a certain extent by the steric hindrance of bulky diphenylmethyl group. Polymerization of **2** and **3** using Ph₂NLi and its complex with diamine (TMEDA) at -78°C in toluene and THF resulted in good yields (Table I, entries 2, 6, 8, and 9). The lower basicity of Ph₂NLi appears to efficiently initiate the polymerization without abstraction of an NH proton.

The obtained polymers are soluble in CHCl₃ and THF. The ¹H NMR spectrum of the polymer obtained from **3** with the Ph₂NLi-TMEDA complex in toluene (Table I, entry 8) is demonstrated in Figure 1. Although the peak of the main chain methylene protons overlaps with that of the amino proton around 2.2 ppm, the spectral pattern is simple. Figure 2 shows the ¹³C NMR spectrum of the same polymer. All peaks are sharp and assigned to a vinyl polymer corresponding to poly(**3**) as shown in the figures. Chain-transfer reaction (hydrogen-transfer

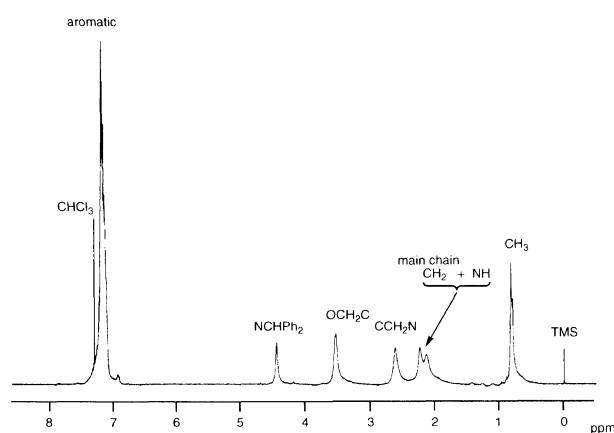


Figure 1. 400 MHz ¹H NMR spectrum of poly(**3**) obtained with Ph₂NLi-TMEDA in toluene at -78°C (Table I, Entry 8) (measured in CDCl₃ at 60°C).

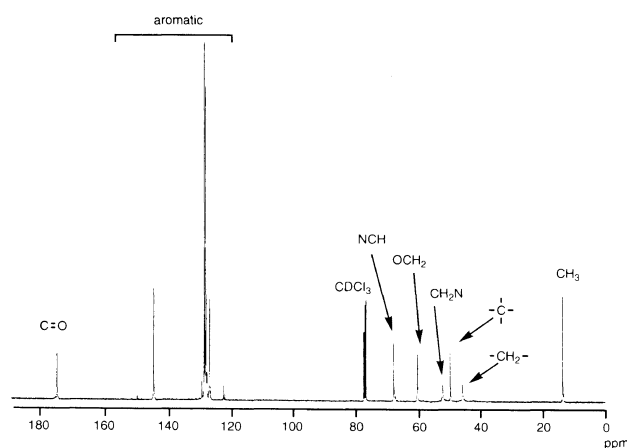
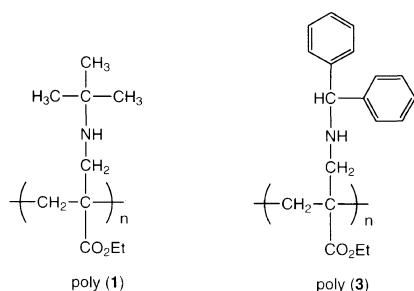


Figure 2. 100 MHz ¹³C NMR spectrum of poly(**3**) obtained with Ph₂NLi-TMEDA in toluene at -78°C (Table I, Entry 8) (measured in CDCl₃ at 60°C).

reaction) from the growing polymer chain end to the reactive unprotected amino group thus hardly occurs. The ¹³C NMR spectra of the carbonyl carbon in the poly(**3**) obtained with *n*-BuLi (Table I, entry 7) and the Ph₂NLi-TMEDA complex in toluene (Table I, entry 8) are demonstrated in Figures 3(a) and 3(b), respectively. A sharp singlet at the same chemical shift is observed in Figure 3(a) and 3(b), indicating that the polymers

obtained from **3** in toluene are highly stereoregular vinyl polymers. The polymer obtained from **1** with the $\text{Ph}_2\text{NLi-TMEDA}$ complex in toluene was isotactic ($mm=83\%$), while that in THF, rich in syndiotacticity.⁴ Therefore, the poly(**3**)s obtained in toluene must be highly isotactic. Although the ^{13}C NMR spectrum of carbonyl carbon in the polymer obtained with Ph_2NLi in THF showed multi peaks with mostly different chemical shifts from that for highly isotactic poly(**3**) (Figure 3(c)), the ^1H NMR spectrum of the same polymer was assigned to a normal vinyl polymer structure corresponding to poly(**3**). Therefore, the polymer generated in THF must have a quite different tacticity from those prepared in toluene, probably high syndiotacticity judging from the results of the polymerization of **1**.⁴



The polymerization of racemic **2** using various chiral initiators with optically active ligands afforded the polymers possessing a small optical rotation (Table I, entries 3–5). HPLC analysis of unreacted monomer indicated that enantiomer-selective polymerization^{12–14} hardly took place under these conditions. ^1H and ^{13}C

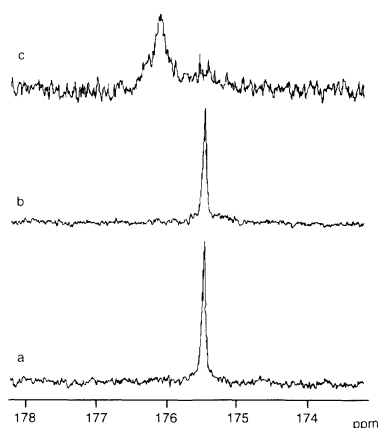


Figure 3. 100 MHz ^{13}C NMR spectra of the carbonyl carbon in poly(**3**) obtained with (a) $n\text{-BuLi}$ in toluene (Table I, Entry 7), (b) $\text{Ph}_2\text{NLi-TMEDA}$ in toluene (Table I, Entry 8), and (c) Ph_2NLi in THF (Table I, Entry 9) (measured in CDCl_3 at 60°C).

NMR spectra of the obtained polymers were very broad (Figure 4), because **2** is a mixture of enantiomeric monomers with a chiral center on the amino group¹⁵ in addition to the H-transfer from the amino proton occurred in polymerization process.

The anionic polymerization of **4** bearing the most bulky amino group in toluene at -78°C did not proceed (Table I, entries 10 and 11), probably due to the bulkiness of α -substituent which may prevent polymerization as reported previously for the anionic polymerization of α -(trityloxymethyl)acrylate having a bulky alkoxy group.¹⁶

Polymerization of Optically Active **2R** and **2S**

The results of the anionic polymerization of optically active **2R** and **2S** are listed in Table II. Polymerizations in toluene and THF resulted in good yields. The obtained polymers are soluble in CHCl_3 and THF. The ^{13}C NMR spectrum of the carbonyl carbon in the polymer obtained from **2R** with $\text{Ph}_2\text{NLi-TMEDA}$ in toluene (Table II, entry 1) is shown in Figure 5(a). A sharp singlet with a small shoulder suggests a stereoregular polymer. Figures 5(b) and 5(c) show the spectra of the polymers obtained from **2R** with DPEDALi-(-)Sp (Table II, entry 3) in toluene and Ph_2NLi in THF (Table II, entry 4), respectively. A broad peak appeared at lower-magnetic field around 176 ppm in both Figures 5(b) and 5(c). The peak at 175.3 ppm in Figure 5(c) is much broader than those in Figures 5(a) and 5(b).

^1H and ^{13}C NMR spectra of the polymers obtained from **2R** with $\text{Ph}_2\text{NLi-TMEDA}$ in toluene (a) and Ph_2NLi in THF (b) are shown in Figures 6 and 7, respectively. In Figure 7, spectral patterns of the main

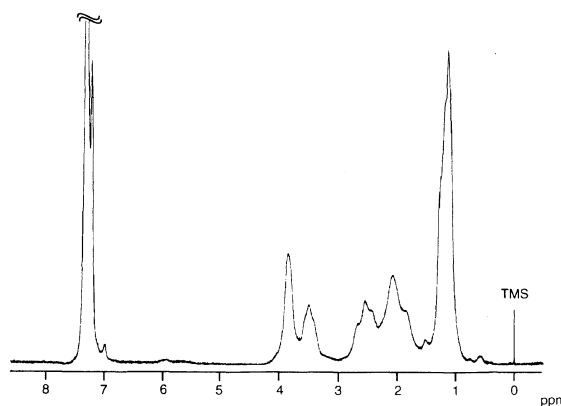


Figure 4. 400 MHz ^1H NMR spectrum of the polymer obtained from **2** with $\text{Ph}_2\text{NLi-TMEDA}$ in toluene at -78°C (Table I, Entry 2) (measured in CDCl_3 at 60°C).

Table II. Anionic polymerization of optically active **2R** and **2S** at -78°C ^a

Entry	Monomer	Initiator	Conditions	Yield/% ^b	$M_n \times 10^{-4}$ (DP) ^c	f ^d	$[\alpha]_{365}^e$
1	2R	$\text{Ph}_2\text{NLi-TMEDA}$	Toluene, 5 h	80	0.8 (34)	0.47	+238°
2	2R	$\text{Ph}_2\text{NLi-(-)Sp}$	Toluene, 24 h	73	0.6 (26)	0.57	+219°
3	2R	DPEDALi-(-)Sp	Toluene, 5 h	79	0.8 (34)	0.46	+263°
4	2R	Ph_2NLi	THF, 24 h	74	0.6 (26)	0.58	+274°
5	2S	$\text{Ph}_2\text{NLi-TMEDA}$	Toluene, 5 h	83	0.8 (34)	0.48	-227°
6	2S	Ph_2NLi	THF, 24 h	74	0.6 (26)	0.58	-238°

^a $[\text{Monomer}] = 1.0 \text{ M}$, $[\text{Monomer}]/[\text{Initiator}] = 20$. ^b MeOH insoluble part. ^c Determined by VPO (solvent CHCl_3 , benzil standard). ^d Efficiency of initiator. ^e Measured in CHCl_3 , c 1.0, temp 25°C .

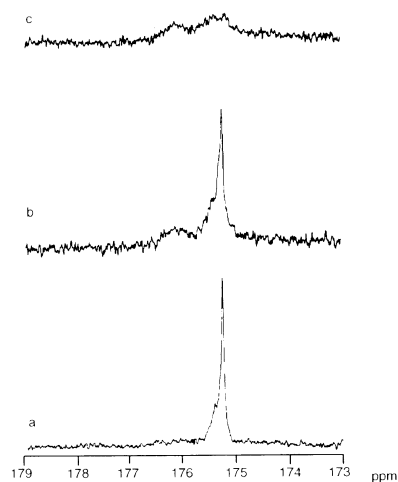


Figure 5. 100 MHz ^{13}C NMR spectra of the carbonyl carbon of polymers obtained from **2R** with (a) $\text{Ph}_2\text{NLi-TMEDA}$ in toluene (Table II, Entry 1), (b) DPEDALi(-)Sp in toluene (Table II, Entry 3), and (c) Ph_2NLi in THF (Table II, Entry 4) (measured in CDCl_3 at 60°C).

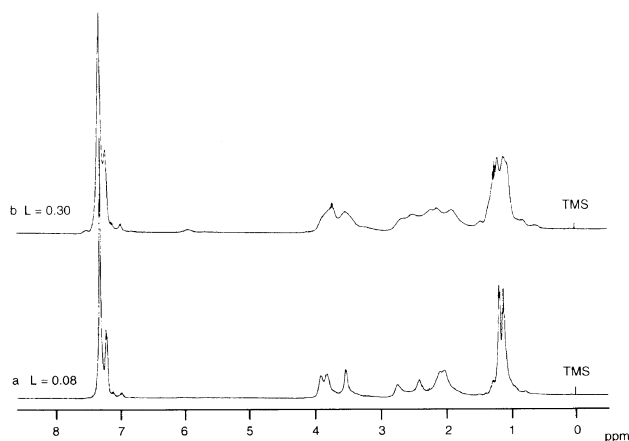


Figure 6. 400 MHz ^1H NMR spectra of polymers obtained from **2R** with (a) $\text{Ph}_2\text{NLi-TMEDA}$ in toluene (Table II, Entry 1, $L=0.08$) and (b) Ph_2NLi in THF (Table II, Entry 4, $L=0.30$) (measured in CDCl_3 at 60°C).

chain carbons around 40–50 ppm and carbonyl carbon at 175 ppm in the polymers are quite different. The methyl carbon of the ester group (marked with an arrow in Figure 7) showed two peaks at 13.8 ppm and 15.4 ppm, although the tacticity hardly affects the spectral pattern in ^{13}C NMR measurement of poly(**1**) and poly(**3**), which show a single peak regardless of the tacticity. To obtain further information on the structure, distortionless enhancement by polarization transfer (DEPT) NMR measurement was performed for the polymer obtained from **2R** with $\text{Ph}_2\text{NLi(-)Sp}$ in toluene (Table II, entry 2). A broad peak around 52 ppm in Figure 8(b) can be assigned to the main chain CH that would be generated by transfer of the amino proton to the propagation chain end during polymerization. The poly(**2**)s thus likely contain the H-transfer unit in addition to the vinyl polymerization unit. The H-transfer polymerization was reported previously for the anionic polymerization of α - and β -substituted acrylamide, N -substituted acrylamide, and p -vinylbenzamide,^{5–10} which gave polyamides through the H-transfer of the amide proton. The two peaks due to methyl carbons of the ester group in

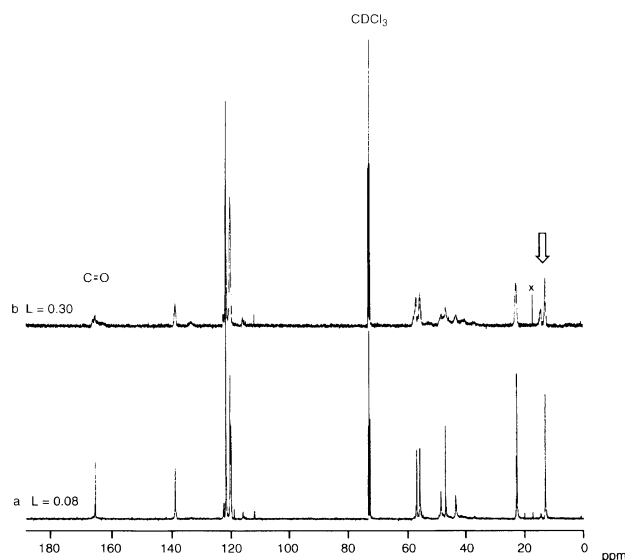


Figure 7. 100 MHz ^{13}C NMR spectra of polymers obtained from **2R** with (a) $\text{Ph}_2\text{NLi-TMEDA}$ in toluene (Table II, Entry 1, $L=0.08$) and (b) Ph_2NLi in THF (Table II, Entry 4, $L=0.30$) (measured in CDCl_3 at 60°C).

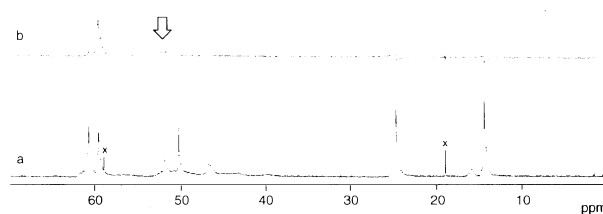


Figure 8. (a) 125 MHz ^{13}C NMR and (b) distortionless enhancement by polarization transfer (DEPT) NMR, where carbons with only one proton yield active signals; spectra of the polymer obtained from **2R** with $\text{Ph}_2\text{NLi(-)Sp}$ in toluene at -78°C (Table II, Entry 2, $L=0.19$) (measured in CDCl_3 at 55°C).

Table III. Relative intensity ratio in ^{13}C NMR spectra of methyl carbon of ester group in poly(**2R**) and poly(**2**)

Entry	Monomer	Initiator	Solvent	Lower-magnetic field (L): Higher-magnetic field (H) ^a (L + H = 1)
1	2R	$\text{Ph}_2\text{NLi-TMEDA}$	Toluene	0.08 : 0.92
2	2R	$\text{Ph}_2\text{NLi(-)Sp}$	Toluene	0.19 : 0.81
3	2R	DPEDALi(-)Sp	Toluene	0.20 : 0.80
4	2R	Ph_2NLi	THF	0.30 : 0.70
5	2	$\text{Ph}_2\text{NLi-TMEDA}$	Toluene	0.17 : 0.83
6	2	DPEDALi(+)PMP	Toluene	0.18 : 0.82
7	2	DPEDALi(-)Sp	Toluene	0.29 : 0.71
8	2	DPEDALi(+)DDB	Toluene	0.30 : 0.70
9	2	Ph_2NLi	THF	0.43 : 0.57

^a Determined by ^{13}C NMR analysis, L at 13.8 ppm and H at 15.4 ppm.

poly(**2**) may be assigned to those for the H-transfer unit at the lower-magnetic field and vinyl unit at the higher-magnetic field, respectively. This assignment is reasonably supported by the ^1H and ^{13}C NMR analyses of poly(**2**)s. On comparing Figure 6(b) with 6(a), the spectral patterns were complicated owing to the H-transfer unit and tacticity. The absorption of methylene protons of main chain in vinyl polymerization unit around 2 ppm

spectra to estimate the tacticity of the polymer was fruitless. However, H-transfer trace was hardly observed in DEPT measurement of the polymer obtained from **7** with Ph₂NLi-TMEDA in toluene at -78°C (Table IV, entry 8). The aniline groups do not seem effective for stereocontrol of the anionic polymerization.

CONCLUSIONS

The anionic polymerization of α -(*N*-substituted aminomethyl)acrylate **3** bearing a bulky amino group with lithium compounds at a low temperature afforded polymers having a normal vinyl polymer structure. A highly isotactic polymer was obtained with *n*-BuLi or the Ph₂NLi-TMEDA complex in toluene at -78°C. The obtained polymer is of interest from the viewpoint of stereoregular arrangement of reactive amino groups along the polymer backbone. However, H-transfer from the reactive amino proton to the propagating chain end occurred in the anionic polymerization of the monomer **2** bearing a less bulky amino group, (1-phenylethyl)amino group. Generation of the H-transfer units in the polymer main chain increased in the polymerization in THF and a polymer containing 43% H-transfer unit was obtained in the polymerization with Ph₂NLi in THF at -78°C.

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