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Anionic Living Polymerization of an α-Methylstyrene Derivative Containing the Bis(diethylamino)phosphino Group

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ABSTRACT: The anionic polymerization of *N,N,N′,N′*-tetraethyl-4-isopropenylphenylphosphonous diamide (PA) was studied. From the kinetic analyses, the thermodynamic parameters, ΔH_{ss} and ΔS_{ss}, and the ceiling temperature, T_c, of the polymerization reaction of the PA monomer were found to be -6.5_1 kcal mol^{-1}, $-2.3_0 \times 10$ cal mol^{-1} K^{-1}, and 283 K, respectively. It is concluded that if the polymerization of the monomer is initiated with *n*-butyllithium in tetrahydrofuran above its T_c and then propagated below T_c, the polymerization proceeds at a first-order reaction rate without side reactions. The resulting poly(PA)s have predictable molecular weights and narrow molecular weight distributions.

Introduction

We have fabricated various types of charge-mosaic membranes.[1-9] A charge-mosaic membrane consists of cation- and anion-permeable microdomains across the membrane. Strong acid–strong base type charge-mosaic membranes are effective for the mutual separation of electrolyte and nonelectrolyte of low molecular weights.[1-6,8] Weak acid–strong base type charge-mosaic membranes, for example, a carboxylic acid–quaternary amine system, have not only a high mutual separability but also a high ionic selectivity.[9] Such ionic selectivity is due to a specific interaction between a functional group having a low degree of dissociation and various ionized substances. Acids of phosphorus are interesting because of their unique interactions with heavy-metal ions, and this has prompted us to fabricate a charge-mosaic membrane having acids of phosphorus.

There are five requirements for fabricating a practical charge-mosaic membrane. The first is to use a pentablock copolymer of an ABACA type composed of three incompatible polymers A, B, and C.[10,11] The second is that each block has a narrow molecular weight distribution.[10-13] The third is $P(\mathrm{B}) \simeq P(\mathrm{C})$, $P(\mathrm{A}_1) \simeq P(\mathrm{A}_2) \simeq P(\mathrm{A}_3)$, and the total content of component A must be in the range 30–50%, where $P(\mathrm{X})$ and A_i (i = 1–3) denote the degree of polymerization of the X component and each of the three A blocks, respectively.[3] The fourth is that the cation- or anion-exchange groups must be introduced into the B and C blocks after the microphase-separated structure is formed.[11] The fifth is high charge densities in both the anion- and cation-exchange domains.[5,14,15]

Therefore, the present objective is to prepare polymers containing appropriate groups convertible into acids of phosphorus in all the monomer units and having predictable molecular weights and sharp molecular weight distributions. We think the best way is to carry out an anionic polymerization of a monomer having a suitable phosphorus group. There are only a few reports for anionic polymerizations of vinyl monomers containing phosphorus in the side chains. The monomers used were styrene[16] and butadiene[17,18] derivatives containing a bis(alkyloxy)phosphinoyl [P(O)(OR)$_2$] or bis(alkyloxy)phosphinothioyl [P(S)(OR)$_2$] group. However, no information was provided regarding the living nature of the polymerizations and the preparation conditions of the polymers having narrow molecular weight distributions.

Bis(dialkylamino)phosphino groups [P(NR$_2$)$_2$] are interesting. The P–N bond shows a low reactivity against initiators of anionic polymerization such as an alkyllithium.[19] These groups can be converted into hydroxyphosphinoyl [HP(O)(OH)][20] or dihydroxyphosphinoyl [P(O)(OH)$_2$][21] groups. Hence, if a vinyl monomer containing a bis(dialkylamino)phosphino group in the side chain could be anionically polymerized, the resulting polymer might be converted into a well-defined polymer containing hydroxyphosphinoyl or dihydroxyphosphinoyl groups in all the monomer units. It is relatively easy to purify monomers of the α-methylstyrene type because of their low ability to undergo thermal polymerization.[22] Therefore, we try to polymerize a new monomer, *N,N,N′,N′*-tetraethyl-4-isopropenylphenylphosphonous diamide [$\mathrm{CH_2{=}C(CH_3)C_6H_4P(NEt_2)_2}$] (abbreviated PA). The aim of this work is to study the anionic polymerization of PA kinetically and also thermodynamically.

In subsequent papers, we will study block copolymerizations of the monomer with other monomers, polymer reactions of the phosphorus groups into acids of phosphorus, and a fabrication of a charge-mosaic membrane having acids of phosphorus as cation-exchange groups.

Experimental Section

Monomer. *N,N,N′,N′*-Tetraethyl-4-isopropenylphenylphosphonous diamide (PA) was prepared in the following way.

Methyl iodide (156 g, 1.10 mol) in diethyl ether (400 mL) was added dropwise to magnesium turnings (29.2 g, 1.20 mol) with cooling in an ice bath under nitrogen gas and then stirred at 40 °C for 1 h to give the Grignard reagent. *p*-Bromoacetophenone (200 g, 1.00 mol) dissolved in diethyl ether (500 mL) was added dropwise to the Grignard reagent with cooling in an ice bath and then stirred at 40 °C for 30 min. Hydrolysis of the product with 1 N HCl gave *p*-bromocumyl alcohol, which was then dehydrated at 150 °C under vacuum (4×10^2 Pa) in the presence of potassium hydrogen sulfate (4 g). Fractional distillation of the product gave 182 g (0.920 mol, 92%) of *p*-bromo-α-methylstyrene at 73–77 °C (4×10^2 Pa).

p-Bromo-α-methylstyrene (42.0 g, 0.213 mol) dissolved in tetrahydrofuran (THF) (300 mL) was added dropwise to magnesium turnings (5.3 g, 0.22 mol) at 65 °C and then refluxed for 1 h to give the Grignard reagent. Diethylamine (92.7 g, 1.27 mol) was added dropwise to a mixture of phosphorus trichloride (43.5 g, 0.317 mol) and diethyl ether (400 mL) at 0 °C and then stirred for 2 h at 25 °C. After the precipitated salt was filtered off, *N,N,N′,N′*-tetraethylphosphorodiamidous chloride was obtained.[23,24] To this filtrate, the Grignard reagent of *p*-bromo-α-methylstyrene was added dropwise at 0 °C and then stirred at

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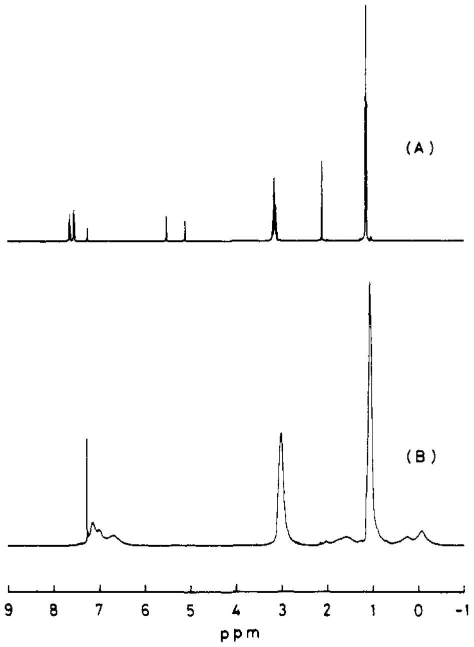

Figure 1. ^{1}H NMR spectra: (A) PA monomer; (B) poly(PA).

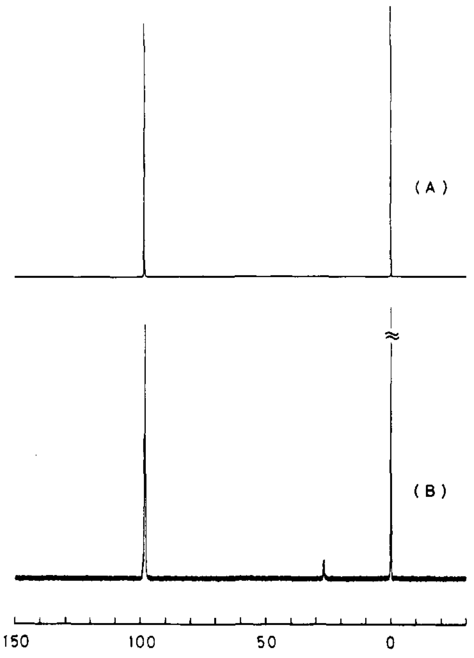

Figure 2. ^{31}P NMR spectra: (A) PA monomer; (B) poly(PA).

25 °C for 30 min.[23-25] The product was washed with NaCl-saturated aqueous solution and then dried with anhydrous magnesium sulfate. After evaporation of the solvents, distillation of the residue gave 49.8 g (0.170 mol, 80%) of PA as a pale yellow liquid at 138–141 °C (1×10^2 Pa). The overall yield was 74%.

The purification of the monomer was carried out in an all-glass apparatus equipped with breakseals under a pressure of 1×10^{-3} Pa or lower. After PA was dried with calcium hydride, PA was transferred into a vacuum apparatus and purified with octylbenzophenone sodium.[7,26] Distillation was repeated until the color of the anion remained unchanged. Further purification was performed in the presence of *sec*-butylmagnesium bromide. Finally, the purified PA was diluted to about 10% w/v with purified toluene or THF just before polymerization.

Figures 1A and 2A show the ^{1}H NMR and ^{31}P NMR spectra of the monomer. From these and the mass spectra, the monomer was confirmed to be PA: 270-MHz ^{1}H NMR (C_6D_6) δ 1.17 (12 H, t, $C\mathit{H}_3CH_2$), 2.13 (3 H, s, $C\mathit{H}_3C{=}$), 3.18 (8 H, m, $C\mathit{H}_2CH_3$), 5.14, 5.55 (2 H, ss, $C\mathit{H}_2{=}C{<}$), 7.54–7.70 (4 H, m, $C_6\mathit{H}_4$); 202-MHz ^{31}P NMR (C_6D_6) δ 98.3; DI/MS *m/z* 292 (M^+). The density of PA was determined to be 0.95_5 at 20 °C with a pycnometer.

Initiators. *n*-Butyllithium (*n*-BuLi) was purchased from Nakarai Chemicals, Ltd. and diluted with purified *n*-heptane. *sec*-Butyllithium (*sec*-BuLi) and cumylpotassium (cumyl-K) were prepared by the methods of Smith et al.[27] and Ziegler et al.,[28] respectively. The concentrations of the initiators were determined by titration with a standard HCl solution.

Solvents. THF used for the polymerization and the dilution of the initiator was purified by distillation in vacuo (1×10^{-3} Pa) in the presence of the dipotassium salt of α-methylstyrene tetramer after the usual purification.[29] Toluene used for the polymerization and *n*-heptane used for the dilution of the initiators were purified by distillation in vacuo (1×10^{-3} Pa) with the addition of *n*-BuLi after the usual purifications.[30] Deuterated THF (THF-d_8) used for ^{1}H NMR measurements was purified by a procedure similar to that for THF.

Polymerization. Anionic polymerizations were carried out in a sealed glass apparatus under 1×10^{-3} Pa or lower, using essentially the same procedures as reported previously.[29-31] After quenching with methanol, the polymers were thoroughly purified by repeating precipitations from benzene solutions into an excess of methanol. The purified polymer was freeze-dried from the benzene solution for 24 h.

Molecular Characterization. Number-average molecular weights, $\bar{M}_n$, were determined by osmometry in toluene at 303 K with a Hewlett-Packard Type 502 high-speed membrane osmometer. Molecular heterogeneities were tested by gel permeation chromatography (GPC) at 298 K using an HLC Type 803 instrument (Tosoh Ltd.) with a refractive index detector and high-resolution columns (GMH6 + G4000H8). *N*-Methylpyrrolidine (2% v/v) was added to THF as an eluent in order to depress adsorption of the polymer onto the GPC gels.[10,26] ^{1}H NMR spectra were obtained at room temperature in C_6D_6 with a JEOL GX-270 FT NMR spectrometer (270.05 MHz). Chemical shifts were referred to benzene (7.27 ppm) in C_6D_6. ^{31}P NMR spectra were obtained at room temperature in C_6D_6 with a JEOL GX-500 FT NMR spectrometer (202.35 MHz). Chemical shifts were referred to phosphoric acid employed as an external standard. The DI/MS spectrum of the PA monomer was obtained at an ionization energy of 70 eV with a JEOL JMS-DX 303 HF mass spectrometer.

Dilatometric Measurements for the Kinetic Study. The dilatometer and techniques employed were almost the same as reported previously.[32] The volume of the main vessel was 61 mL. The inner diameter and the length of the capillary connected with the main vessel were 0.15 and 100 cm, respectively. The monomer (3.1 mL), initiator (0.038 N, 1.9 mL), and solvent (THF) (62.5 mL) were introduced into the dilatometer under vacuum (1×10^{-3} Pa). The amounts of them were determined volumetrically at 20 °C. The dilatometer was equipped with a reservoir (ca. 10 mL) at the top. The meniscus height of the solution was adjusted by transferring an excess of solution into the reservoir. The solution was stirred sufficiently by a magnetic stirrer. First, the solution was kept at −10 °C for at least 12 h to depolymerize the polymer. Then the dilatometer was moved quickly into a methanol bath thermostated at a given temperature. The rates of polymerization were measured by reading the position of the meniscus as a function of time. After the meniscus reached an quilibrium level, the dilatometer was again kept at −10 °C. Such a procedure was repeated. The measurement temperatures ranged from −40 to −59 °C. After the final measurement, the dilatometer was immersed in a dry ice–methanol bath for 24 h, and methanol was added to the solution after opening the dilatometer. The resulting polymer was used to determine the number-average molecular weight, $\bar{M}_n$.

The concentrations of living ends, [LE], were calculated from the value of $\bar{M}_n$ and the yield of the polymer. The volume of the solution was estimated by assuming the additivity of the specific volumes of the solvent, the monomer, and the polymer. The density of the solvent, THF, between +25 and −70 °C was reported by Carvajal et al.[33] The density of THF at −78 °C was estimated by extrapolation. Because of the low concentration of the monomer and the polymer, however, we assumed the density of the polymer was equal to that of the monomer and their temperature coefficients could be neglected.

^{1}H NMR Measurements for the Kinetic and Thermodynamic Studies. The sample solution was prepared with the apparatus shown in Figure 3. After the all-glass apparatus was

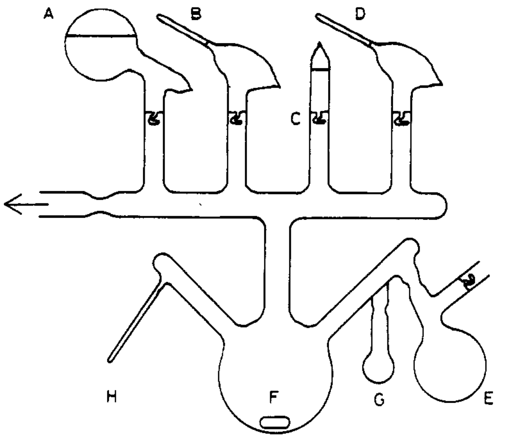

Figure 3. Apparatus for preparing the sample solution used for the kinetic and thermodynamic measurements by the ^{1}H NMR method.

evacuated to 1 × 10^{-3} Pa and sealed off, it was washed with a THF solution of the dipotassium salt of α-methylstyrene tetramer in flask A, which was afterward taken back into flask E and sealed off. Then an *n*-heptane solution of *n*-BuLi (0.036 N, 0.80 mL) in capillary B was introduced into reactor F. *n*-Heptane was collected in flask G by distillation and sealed off. After cooling with dry ice–methanol, the polymerization solvent THF-d_8 (9.5 mL) in C was introduced. Finally, the PA monomer (0.50 mL) in capillary D was introduced, and the reaction mixture was sufficiently stirred at −10 °C. Part of the reaction mixture was transferred into NMR sample tube H and sealed off. The remaining reaction mixture was polymerized at −78 °C for 24 h. The resulting polymer was used to determine the number-average molecular weight, $\bar{M}_n$.

The procedure for measurements was similar to that in dilatometry. Initially, the solution was kept at −10 °C and the depolymerization was checked by ^{1}H NMR signals. Then the temperature was decreased to a given temperature. It took scores of seconds or a minute to reach a constant temperature. The polymerization rates were determined by measuring the conversion as a function of time. After the conversion reached an equilibrium level, the temperature was raised to −10 °C again. Such a procedure was repeated. The measurement temperatures ranged from −50 to −78 °C. In the ^{1}H NMR method, the equilibrium monomer concentrations, $[M]_e$, can be directly measured. We do not need to take out the polymer after each polymerization. This is the advantage of the ^{1}H NMR method. $[M]_e$ was measured between −30 and −78 °C. The spectra were obtained with a JEOL GX-270 FT NMR spectrometer: pulse repetition time, 13 s; accumulated scans, 1 time (for the kinetic studies) or 16–100 times (for the estimation of $[M]_e$). Chemical shifts were referred to THF (3.60 ppm) in THF-d_8.

The concentrations of living ends, [LE], were calculated from the conversion at −78 °C, which was estimated from the ^{1}H NMR spectrum, and the value of $\bar{M}_n$ of the polymer obtained at −78 °C. The density of THF-d_8 was 0.99 at 20 °C. The densities of THF-d_8 at other temperatures were estimated by assuming the same temperature coefficient as that of THF. Other assumptions used in calculating [LE] and the initial concentrations of the monomer, $[M]_0$, were the same as in the dilatometric measurements.

Results and Discussion

Anionic Polymerization of PA. The results of the polymerization of PA are shown in Table I. When PA was added to a mixture of *sec*-BuLi and toluene at 35 °C, the solution immediately became light red. The polymerizations were carried out at 35 °C for 15 h (no. 1) and at −78 °C for 23 h (no. 2). The color gradually disappeared in no. 1 but remained unchanged in no. 2. However, neither solution gave polymer.

When cumylpotassium and THF were used as an initiator and a solvent, respectively, the polymer solution showed a reddish purple color at −78 °C, which remained unchanged and disappeared instantly upon addition of methanol (no. 3). This gave only a small amount of oligomer whose molecular weight was estimated to be 2 × 10^3 by GPC. It is considered that the polymerization of PA can proceed with a very low rate of propagation in this system.

When *n*-BuLi and THF were used as an initiator and a solvent, respectively, the solution showed a bluish purple color at −78 °C, which remained unchanged and disappeared instantly upon addition of methanol (no. 4). The polymer yield was 93%. The GPC chromatogram of the obtained polymer showed a unimodal but relatively broad peak (curve A in Figure 4). The molecular heterogeneity index, $\bar{M}_w/\bar{M}_n$, was estimated to be 1.3_4 on the basis of a calibration curve of standard polystyrenes. When the polymerization was carried out at −20 °C for 23 h in the same system, no polymer was obtained, though the polymerization solution showed the same color (no. 5). These results may indicate an equilibrium polymerization of PA monomer. A number of studies have been reported on the equilibrium polymerizations of α-methylstyrene[34,35] or α-methylstyrene type monomers,[36-38] where no propagation reaction occurred at a temperature above the ceiling temperature, T_c.[39]

Taking into account the nature of equilibrium polymerization, Fujimoto et al. prepared poly(α-methylstyrenes) having very narrow molecular weight distributions.[29] They carried out the initiation and the propagation reactions above T_c and at −78 °C, respectively. PA is an α-methylstyrene type of monomer. Therefore we applied their technique to PA monomer. The polymerization of PA was initiated with *n*-BuLi in THF at −20 °C and then propagated at −78 °C (no. 6). The polymer yield was 93%. As shown by curve B in Figure 4, the GPC chromatogram showed a sharp peak. The $\bar{M}_w/\bar{M}_n$ value was 1.0_9. The number-average molecular weight, $\bar{M}_n$, was 6.2 × 10^4. This value is fairly close to the value of the kinetic molecular weight, M_k (5.5 × 10^4), which is calculated from the ratio of the amounts of monomer to initiator and the polymer yield. This result may reveal that no side reactions occur during the polymerization reaction under such conditions. In addition, from curve A in Figure 4, it can be said that the rate of initiation of PA with *n*-BuLi at −78 °C is not so high compared to that of propagation.

The chemical structure of the obtained polymer (no. 6) was checked by the ^{1}H and ^{31}P NMR spectra, shown in Figures 1B and 2B, respectively. The ^{1}H NMR spectrum showed no signal in the olefinic proton region. Signals at 1.2 and at 3.2 ppm are assigned to the methyl and methylene protons in the ethyl groups, respectively. The intensity ratios of these signals to the phenyl proton signals are 3:1 and 2:1, respectively. Thus, it is certain that the diethylamino groups remain in the polymer. The ^{31}P NMR spectrum showed a main signal at 98.3 ppm. The signal can be assigned to $P(NEt_2)_2$, because the low molecular weight model compound, *N,N,N′,N′*-tetraethylphenylphosphonous diamide, has a signal at the position of the same chemical shift.[40]

From the foregoing results, it is clear that a well-defined polymer is obtained. The polymer (no. 6) was soluble in heptane, hexane, pentane, benzene, toluene, THF, 1,4-dioxane, diethyl ether, chloroform, carbon tetrachloride, and diethylamine but insoluble in water, methanol, ethanol, acetone, and *N,N*-dimethylformamide.

As shown in Table I, the polymer yields in the *n*-BuLi/THF system were 84% for 5 h (no. 7) and 93% for 23 h (no. 6). This result may indicate that the rates of the polymerization are relatively low and that the thermodynamic parameters for the polymerization are somewhat different from those for the polymerization of α-methyl-

Table I
Anionic Polymerizations of PA Monomer under Various Conditions

no.	monomer,[a] mol L^{-1}	initiator	initiator, 10^3 mol L^{-1}	solvent	temp, °C	time, h	yield, %	$10^{-4}M_k$[b]	$10^{-4}\bar{M}_n$[c]	$\bar{M}_w/\bar{M}_n$[d]
1	0.12	*sec*-BuLi	2.7	toluene	35	15	0			
2	0.12	*sec*-BuLi	2.7	toluene	−78[e]	23	0			
3	0.10	cumyl-K	1.3	THF	−78	17			oligomer	
4	0.17	*n*-BuLi	2.1	THF	−78	23	93	2.2		1.3_4
5	0.20	*n*-BuLi	2.9	THF	−20	23	0			
6	0.20	*n*-BuLi	0.9_8	THF	−78[f]	23	93	5.5	6.2	1.0_9
7	0.19	*n*-BuLi	2.5	THF	−78[f]	5	84	1.9		1.1_0

[a] The amounts of monomer used were 2.6–3.1 g in each run. [b] M_k was calculated from the polymer yield and the ratio of the amounts of monomer and initiator. [c] $\bar{M}_n$ was determined by membrane osmometry. [d] $\bar{M}_w/\bar{M}_n$ was estimated from the GPC peak on the basis of a standard polystyrene calibration curve. [e] Initiation was carried out at 35 °C for 1 h. [f] Initiation was carried out at −20 °C for 1 h.

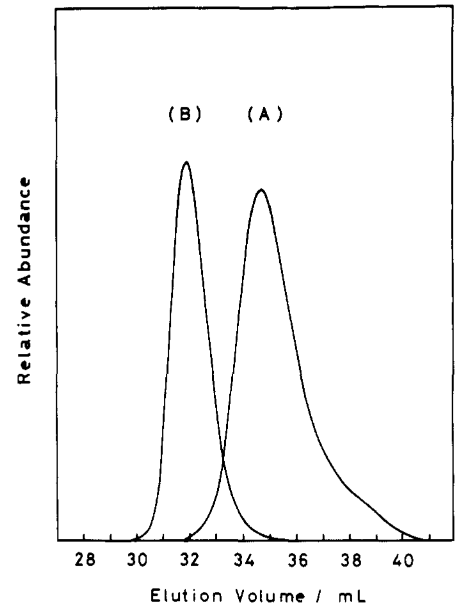

Figure 4. GPC chromatograms of poly(PA)s: (A) sample 4; (B) sample 6. Carrier solvent, THF containing *N*-methylpyrrolidine (2% v/v); flow rate, 1.0 mL min^{-1}; concentration, about 0.05% w/v; detector, RI detector.

styrene, which proceeds quantitatively under the same conditions. Therefore the kinetics and thermodynamics for the polymerization of PA in the system were studied in detail.

Kinetic Studies. During the dilatometric measurements with repetition of the polymerizations and the depolymerizations, the color of the living polymer solution remained unchanged. After the polymerization at −78 °C, the polymer was obtained in 94% yield. The GPC chromatogram showed a unimodal, sharp peak, from which the $\bar{M}_w/\bar{M}_n$ was estimated to be 1.0_7. The number-average molecular weight was 4.0 × 10^4, which was close to the value of the kinetic molecular weight, 3.9 × 10^4. These results reveal that deactivation reactions of the living ends do not occur during the dilatometric measurements.

If the rate of initiation is much faster than that of propagation, the polymerization rate can be expressed by

$$-\mathrm{d}[\mathrm{M}]_t/\mathrm{d}t = k_\mathrm{p}[\mathrm{LE}]([\mathrm{M}]_t - [\mathrm{M}]_\mathrm{e}) \tag{1}$$

where k_p is the propagation rate constant, [LE] the concentration of the living ends, $[\mathrm{M}]_t$ the monomer concentration at time t, and $[\mathrm{M}]_\mathrm{e}$ the equilibrium monomer concentration. If [LE] is constant during the polymerization, eq 1 can be integrated as

$$\ln\,([\mathrm{M}]_0 - [\mathrm{M}]_\mathrm{e})/([\mathrm{M}]_t - [\mathrm{M}]_\mathrm{e}) = k_\mathrm{p}[\mathrm{LE}]t \tag{2}$$

where $[\mathrm{M}]_0$ is the initial concentration of the monomer. In a dilatometric measurement, the meniscus height of the solution is proportional to the monomer concentration.

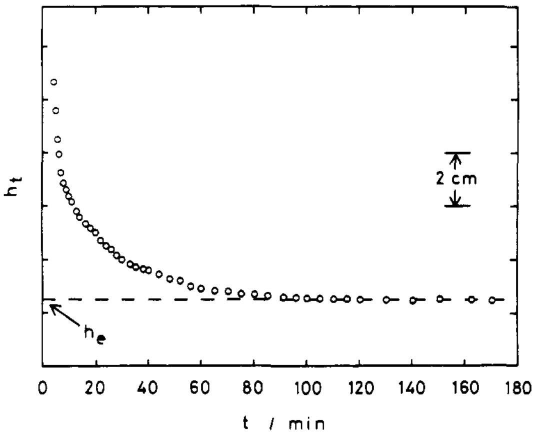

Figure 5. Example of the variation of the meniscus height h_t with time t in the dilatometric measurement at −50 °C.

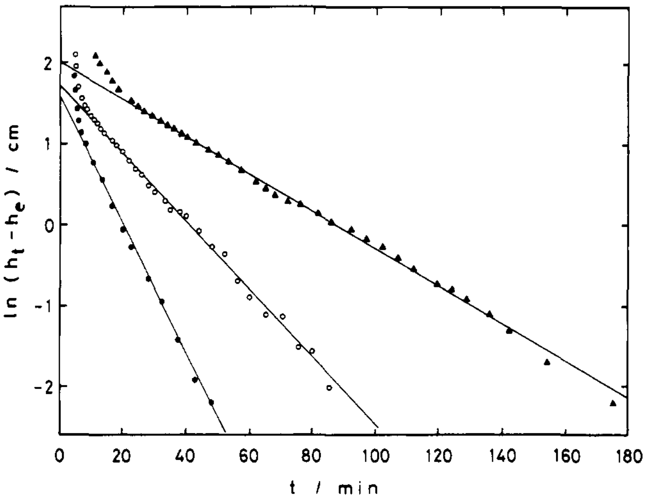

Figure 6. First-order plots for the polymerization of PA measured by dilatometry. Temperature: −40 °C (●); −50 °C (○); −59 °C (▲).

Therefore, eq 2 can be expressed as

$$\ln\,(h_t - h_\mathrm{e}) = -k_\mathrm{p}[\mathrm{LE}]t + \ln\,(h_0 - h_\mathrm{e}) \tag{3}$$

where h_t, h_0, and h_e are the meniscus heights at time t, t = 0, and the equilibrium state, respectively. Thus, k_p can be determined from the value of [LE] and the slope of the plots of ln (h_t − h_e) vs time.

Figure 5 shows an example of the variation of the meniscus height with time t. Other dilatometric measurements gave similar curves. Thus, the values of h_e can be determined experimentally. Figure 6 shows first-order plots according to eq 3. As stated in the Experimental Section, the dilatometer was moved from a bath at −10 °C to one at a given different temperature. Thus, it took a time for the solution to reach the given temperature. This is why some initial data points decrease rapidly. After

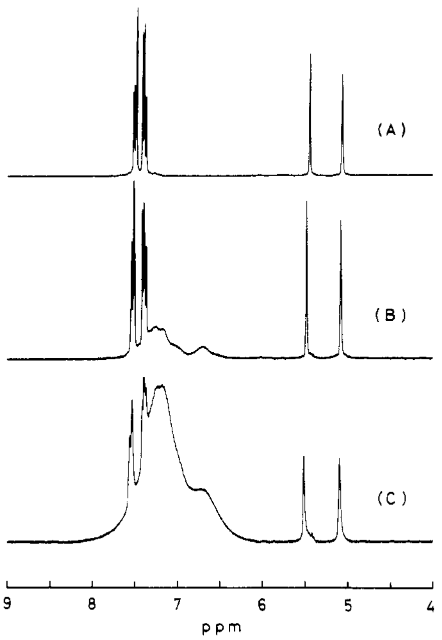

Figure 7. Examples of ^{1}H NMR spectra of the living poly(PA) in THF-d_8 at the equilibrium states: (A) -10 °C; (B) -40 °C; (C) -60 °C.

Table II
Conversions and Equilibrium Monomer Concentrations for the Polymerization of PA with *n*-BuLi in THF-d_8

temp, °C	conv, %	$[M]_e$, 10^2 mol L^{-1}
-30	19 ± 2	14
-40	52 ± 2	8.3 ± 0.3
-50	77 ± 1	4.0 ± 0.2
-60	88 ± 1	2.1 ± 0.2
-78	96 ± 1	0.7 ± 0.2

the initial periods, however, fairly good linear relationships are obtained for all polymerizations.

Figure 7 shows examples of the ^{1}H NMR spectra of the living polymer solutions at the equilibrium states. Signals at 5.1 and 5.5 ppm are assigned to olefinic protons in the monomer, split ones at 7.3–7.6 ppm to phenyl protons in the monomer, and broad ones at 6.2–8.0 ppm to phenyl protons in the polymer. The conversion x is given by

$$x = 1 - 2I_0/I_p \tag{4}$$

where I_0 and I_p are the relative intensities of the olefinic and phenyl proton signals, respectively. From Figure 7, it is apparent that the conversion at an equilibrium state increases with decreasing temperature. The conversions estimated with eq 4 at various temperatures are listed in Table II. The conversion at -78 °C was 0.96. On the other hand, the remaining solution after taking part of the solution into the NMR tube gave 94% yield of polymer at -78 °C. Thus the reliability of the present estimation of the conversion according to eq 4 seems to be fairly high. In Figure 7A, the broad signal at 6.2–8.0 ppm is not observed. The value of I_0/I_p is not 0.50 but 0.47, from which the conversion is calculated to be 0.06. This observation may indicate that living oligomers are formed at -10 °C. When the sample solution was kept at the equilibrium state at -60 °C followed by the elevation of the temperature to -10 °C, the same spectrum as shown in Figure 7A was observed within a few minutes. Thus, it is clear that the depolymerization proceeds rapidly at -10 °C. The depolymerizations at -10 °C were considered to be sufficient for our purpose in both dilatometric and ^{1}H NMR measurements.

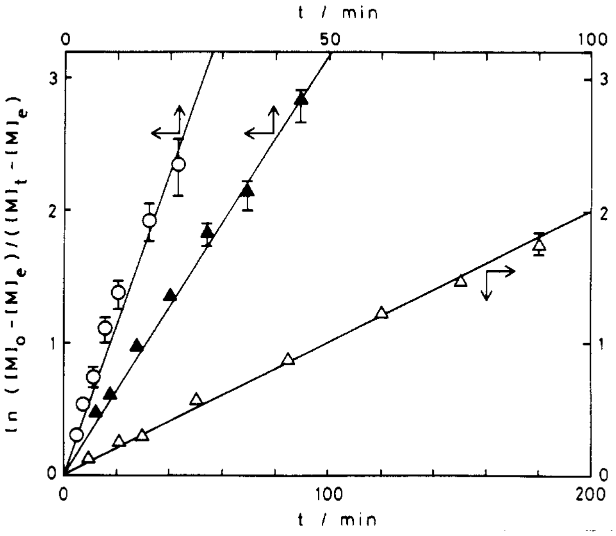

Figure 8. First-order plots for the polymerization of PA measured by the ^{1}H NMR method. Temperature: -50 °C (○); -60 °C (▲); -78 °C (△).

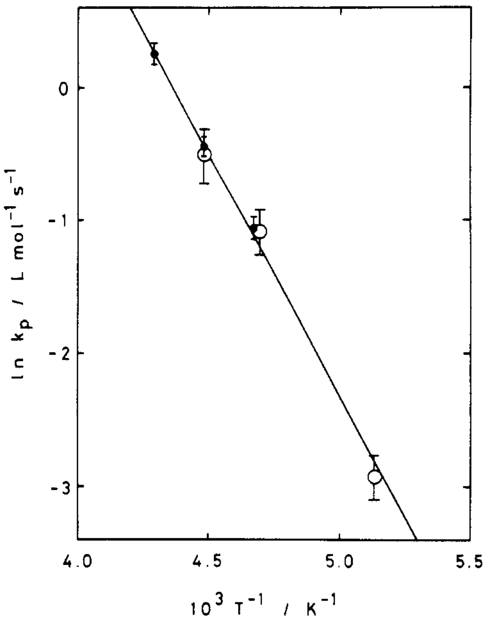

Figure 9. Arrhenius plots of k_p for the polymerization of PA with *n*-BuLi in THF or THF-d_8. Open and filled symbols show the data by ^{1}H NMR and dilatometry, respectively.

Table III
First-Order Reaction Rate Constants for the Polymerization of PA with *n*-BuLi in THF or THF-d_8

	k_p, L mol^{-1} s^{-1}	
temp, °C	dilatometry	^{1}H NMR
-40	1.3 ± 0.1	
-50	0.65 ± 0.05	0.61 ± 0.13
-59	0.35 ± 0.03	
-60		0.34 ± 0.06
-78		0.054 ± 0.009

Figure 8 shows first-order plots according to eq 2, where the monomer concentration at 6% conversion is used as $[M]_0$. Linear relationships are obtained within the experimental errors for all polymerizations between -50 and -78 °C. From both first-order plots (Figures 6 and 8), we may conclude that the polymerization of PA in the *n*-BuLi/THF system proceeds by a first-order mechanism.

The values of k_p estimated from the slopes in Figures 6 and 8 are summarized in Table III and plotted in Figure 9. The two different measurements give consistent values of k_p. This confirms the reliability of the present ^{1}H NMR measurements. In Figure 9, a linear relationship is

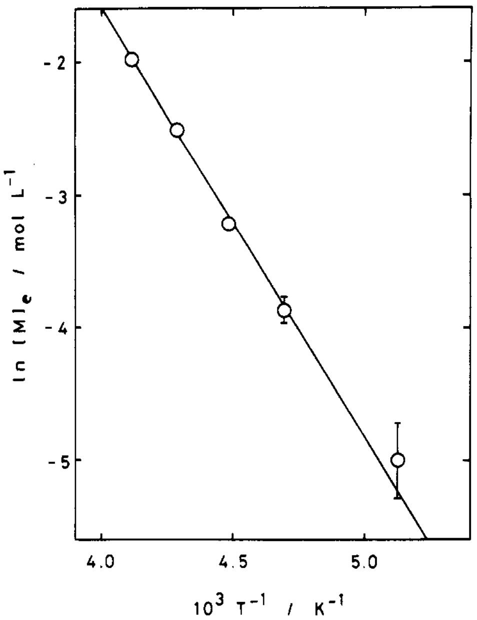

Figure 10. Semilogarithmic plots of the equilibrium monomer concentration $[M]_e$ against T^{-1} for the polymerization of PA with *n*-BuLi in THF-d_8.

obtained within experimental errors. The apparent activation enthalpy is 7.3 ± 0.5 kcal mol^{-1}.

Thermodynamic Studies. Table II gives $[M]_e$ estimated in the ^1H NMR measurements at several temperatures. Plots of ln $[Me]_e$ vs reciprocal temperature are shown in Figure 10, where a good linear relationship is observed. The relationship between $[M]_e$ and thermodynamic parameters can be expressed by

$$\ln [M]_e = \Delta H_{ss}/RT - \Delta S_{ss}/R \qquad (5)$$

where ΔH_{ss} is the heat of polymerization, ΔS_{ss} the corresponding entropy for a 1 mol L^{-1} solution, and R the gas constant. Hence, ΔH_{ss} and ΔS_{ss} in THF-d_8 are estimated to be -6.5_1 kcal mol^{-1} and $-2.3_0 \times 10$ cal mol^{-1} K^{-1}, respectively. The ceiling temperature, T_c ($\equiv \Delta H_{ss}/\Delta S_{ss}$), for a 1 mol L^{-1} solution in monomer is calculated to be 283 K.

Typical values of ΔH_{ss} and ΔS_{ss} for the polymerization of α-methylstyrene in THF were reported to be −8.02 kcal mol^{-1} and −28.8 cal mol^{-1} K^{-1}, respectively,[35] while those for monomers having a bulky side group were lower than the above values (for example, $\Delta H_{ss} = -6.80$ kcal mol^{-1} and $\Delta S_{ss} = -25.2$ cal mol^{-1} K^{-1} for *p*-isopropyl-α-methylstyrene,[37] $\Delta H_{ss} = -7.10$ kcal mol^{-1} and $\Delta S_{ss} = -25.5$ cal mol^{-1} K^{-1} for *p-tert*-butyl-α-methylstyrene[38]). These lower values of ΔH_{ss} and ΔS_{ss} for the latter monomers may be due to steric effects of the bulky side groups. A similar steric effect of the bis(diethylamino)phosphino group on ΔH_{ss} and ΔS_{ss} may be expected for the PA monomer, too, though a quantitative comparison cannot be made since the present data have been obtained not in THF but in THF-d_8.

When poly(PA) (no. 6) was prepared, the initial concentration of the monomer was 0.20 mol L^{-1}. The corresponding T_c for the solution is estimated to be −23 °C. Thus the initiation in experiment no. 6 was certainly carried out above the corresponding T_c. Therefore, we can conclude that if the polymerization of the PA monomer is initiated with *n*-BuLi in THF above its T_c and then propagated below T_c, we can obtain polymers having predictable molecular weights and narrow molecular weight distributions.

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References and Notes

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Registry No. PA, 132260-78-7; PA (homopolymer), 132260-79-8; *sec*-BuLi, 598-30-1; *n*-BuLi, 109-72-8; MeI, 74-88-4; $(Et)_2NH$, 109-89-7; *p*-bromoacetophenone, 99-90-1; *p*-bromocumyl alcohol, 2077-19-2; *p*-bromo-α-methylstyrene, 6888-79-5; phosphorus trichloride, 7719-12-2; *N,N,N′,N′*-tetraethylphosphorodiamidous chloride, 685-83-6; cumylpotassium, 3003-91-6.