Anionic Polymerization of Monomers Containing Functional Groups. 12. Anionic Equilibrium Polymerization of 4-Cyano-α-methylstyrene

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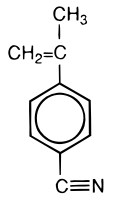
ABSTRACT: The anionic polymerization of 4-cyano-α-methylstyrene **1** was carried out in THF with (diphenylmethyl)potassium (Ph_2CHK) as an initiator. At the various temperature ranging from 0 to −78 °C, conversion and equilibrium monomer concentration, $[M]_e$, were obtained from the GLC analysis of the residual monomer. From the plot of ln $[M]_e$ against reciprocal temperature, the thermodynamic parameters, ΔH and ΔS, and the ceiling temperature, T_c, of the anionic polymerization of **1**, were determined to be -7.64 ± 0.5 kcal mol^{-1}, -25.5 ± 1.3 cal mol^{-1} K^{-1}, and 27 ± 3 °C, respectively. The apparent rate constant and the activation energy of the anionic polymerization for **1** were determined as follows: $\ln k_p^{ap} = -1.83 \times 10^3/T + 5.74$ L mol^{-1} s^{-1} and $E_a = 3.6 \pm 0.2$ kcal mol^{-1}, respectively. Depolymerization of the living poly(**1**) proceeded to give a low molecular weight oligomer and starting monomer when the temperature of the polymerization system was raised from −78 to 0 °C. The resulting poly(**1**)s produced at low temperatures (−30 to −78 °C) possessed narrow molecular weight distributions ($M_w/M_n < 1.1$) and controlled molecular weights based on the molar ratios of monomer to initiator. Over −20 °C, after the reaction mixture stood for a period of time, the broadening of the MWD of the poly(**1**) was apparently observed due to the reversible equilibrium polymerization under the thermodynamic conditions.

Introduction

There has been considerable interest over the years in the anionic polymerization of the various functional monomers to produce well-defined polymers containing useful functional groups in each repeating unit. The use of protecting groups to mask reactive functional groups is one of the prominent methods to realize the anionic living polymerization of monomers bearing functional groups,[1] which are incompatible with highly reactive anionic species. In addition, we have found that the anionic living polymerizations of a series of styrenes *para*-substituted with the electron-withdrawing groups similarly proceed without protection of the reactive functions.[2] Successful examples of electron-withdrawing substituents introduced are *N,N*-dialkylamide,[3] (trimethylsilyl)ethynyl,[4] alkylethynyl,[5] *N*-alkylimine,[6] *N*-arylimine,[7] oxazoline,[8] *tert*-butyl ester,[9] *N,N*-dialkylsulfonamide,[10] and cyano groups.[11] The *para*-substituted styrenes bearing these functional groups provide stable living polymers having controlled molecular weights and narrow molecular weight distributions (MWDs). The propagating carbanions derived from these monomers are stabilized by the electron-withdrawing character of the substituents to suppress the undesirable side reactions between the propagating carbanions and the substituents.[12] The extended π-conjugation system[13] from the terminal benzylic carbanion to the substituents also contributes to stabilizing the propagating species to eliminate the serious side reactions.

Thus, the introduction of the electron-withdrawing substituent plays a very important role in realizing the anionic living polymerization of a series of the functional styrenes.[2−12] Our recent study clearly demonstrates that this strategy is also very effective in the anionic polymerization of α-methylstyrene derivatives similar to the cases of styrenes. In fact, we have found that the anionic polymerization of 4-cyano-α-methylstyrene (**1**) proceeds quantitatively to give a stable living



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polymer in THF at −78 °C.[14] The result of incomplete crossover reaction between the living poly(**1**) and styrene monomer indeed expresses the lowered nucleophilicity of the terminal carbanion derived from **1**, compared to that of living poly(α-methylstyrene), which can readily initiate the styrene polymerization. It also elucidated that the anionic polymerizability of **1** is remarkably enhanced by the electron-withdrawing character of the cyano group, compared with that of α-methylstyrene itself.[14]

A number of studies have been so far directed to the thermodynamic and kinetic behaviors in the anionic equilibrium polymerization of α-methylstyrene,[15−22] while those of substituted α-methylstyrenes have been quite limited. Actually, although the thermodynamic constants of 4-isopropyl-,[23] 4-*tert*-butyl-,[24] and 4-phenyl-α-methylstyrenes[25] have been reported under equilibrium conditions, no information is available on the kinetic parameters, molecular weights, MWDs, and particularly the living character of the polymerization system. Recently, similar equilibrium polymerizations of α-methylstyrenes *para*-substituted with bis(diethylamino)phosphino,[26] 2-((*tert*-butyldimethylsilyl)oxy)eth-

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yl,[27] and bis(trimethylsilyl)methyl groups[28] have been individually investigated,[29] and partial deactivations of the propagating carbanions during the polymerizations suggested from the analyses of M_n's and MWDs in the latter reports.[27,28] Only one report[26] deals with the satisfactory kinetic study of polymerizations other than that of α-methylstyrene itself.[16,18−22] In addition to the thermodynamic studies, careful analyses on the kinetics and the molecular characteristics should also be needed to discuss the polymerization behavior of these α-methylstyrenes containing functional groups essentially susceptible to the side reactions.

In this report, we investigate the equilibrium behavior and the kinetics of the anionic polymerization of **1** under the various temperatures. The process to reach the equilibrium and the depolymerization of the living polymer are clarified from the analyses of the molecular weights and their distributions along with the residual monomer concentration. The effect of the electron-withdrawing cyano group on the polymerization behaviors of **1** under the thermodynamic and kinetic conditions is of considerable interest.

Experimental Section

Materials. 1,1-Bis(4-(trimethylsilyl)phenyl)ethylene (TMS_2-DPE) was synthesized by the Grignard reaction of 4-(trimethylsilyl)chlorobenzene and ethyl acetate and the subsequent dehydration of the resulting carbinol, as previously reported.[10] THF used as a polymerization solvent was refluxed over sodium wire for 5 h, distilled from lithium aluminum hydride, and finally distilled through a vacuum line from the sodium naphthalenide solution. Diphenylmethane and dodecane were distilled from CaH_2 under reduced pressure.

Initiator. (Diphenylmethyl)potassium (Ph_2CHK) was prepared by the reaction of diphenylmethane and potassium naphthalenide in THF at room temperature for 3 days. The concentration of initiator was determined by colorimetric titration with standardized 1-octanol in a sealed reactor under high vacuum conditions, as previously reported.[30] The resulting initiator solutions were stored at −30 °C prior to the polymerization.

Monomer. 4-Cyano-α-methylstyrene (**1**) was synthesized from 4-formyl-α-methylstyrene according to our preceding report.[14] After careful fractional distillations over CaH_2, the purified monomer was then sealed off in an apparatus equipped with a breakseal under high vacuum conditions (10^{-6} mmHg). To remove impurities in the monomer (35 mmol) furthermore, phenylmagnesium chloride (0.2 M, 1 mmol) in THF was added to the monomer at −78 °C and the mixture was stirred for 0.5 h at ambient temperature. It was distilled under vacuum into the apparatus equipped with breakseals and diluted with dry THF. The resulting monomer solution (0.5−0.7 M in THF) was stored at −30 °C until ready to use for the polymerization.

Polymerization Procedures. Anionic polymerizations of **1** were initiated at 0 °C with a monofunctional initiator system prepared from Ph_2CHK and TMS_2DPE in THF in an all-glass apparatus equipped with breakseals and several ampules under high vacuum conditions.[30] After a THF solution of **1** was added to the initiator solution, the resulting reaction mixture was immediately divided into several ampules and sealed off in order to trace the reaction. Then, the sealed tubes were placed in an acetone bath thermostated at a desirable temperature between −10 and −78 °C. After the given time, the polymerization was instantaneously terminated with degassed methanol at the polymerization temperature. The total content of each ampule was diluted to an appropriate volume and the concentration of the residual monomer $[M]_t$ was then measured by gas−liquid chromatography (GLC) with dodecane as an external standard. The observed experimental error of $[M]_t$ was ±3% in the range 0.02−0.5 M. After concentration with evaporator, the reaction mixture was then poured into a large excess of methanol to precipitate a polymer for the analysis of the yield and for the characterization of the molecular weight and the distribution. The yields of poly(**1**)s precipitated in methanol were shown in Tables 1, 2, 6, and 7 as reference for the conversions, but they were sometimes scattered due to the small mass scale of the resulting polymer. The M_n's and the MWDs of the resultant poly(**1**)s were estimated by the size exclusion chromatograms (SEC) calibrated with poly(4-cyanostyrene)s having very narrow MWDs,[11] although the M_n values thus obtained were underestimated (ca. 0.7 times) compared to the correct molecular weights, as previously suggested.[14] In several experiments at high $[M]_t$ values, the observed M_n values were rather higher than the calculated values, since the low molecular weight region of poly(**1**) (probably lower than 1000) might be removed via the precipitation process in methanol. The M_n values of several poly(**1**) samples were measured by the end-group analysis using ^1H NMR spectroscopies according to our previous reports.[10,11] They were close to the calculated M_n values, indicating the fine molecular weight control of poly(**1**) under the conditions.

Measurements. SEC measurements for MWD and M_n determination were performed at 40 °C with a TOSOH HLC-8020 instrument equipped with two polystyrene gel columns (TOSOH GMH_{XL} × 2) with ultraviolet (270 nm) or refractive index detection. A DMF solution of LiBr (0.01 M) was used for a carrier solvent at a flow rate of 0.8 mL min^{-1}. GLC for the determination of the residual monomer concentration $[M]_t$ was performed with a Shimadzu GC14B instrument equipped with a capillary column at 170 °C by FID detection.

Results and Discussion

Equilibrium Polymerization of 1. As mentioned in the Introduction, the anionic polymerization of α-methylstyrene is a well-established example for the equilibrium polymerization,[15−22] which produces a stable living polymer. The simple equilibrium polymerization system can be expressed by several equations as follows:

$$P^*_n + M \underset{k_d^{ap}}{\overset{k_p^{ap}}{\rightleftharpoons}} P^*_{n+1} \quad (1)$$

$$d[M]/dt = k_p^{ap}[M][P^*_n] - k_d^{ap}[P^*_{n+1}]$$

$$\text{at equilibrium, } R_p = R_d \quad (2)$$

$$k_p^{ap}[P^*_n][M]_e = k_d^{ap}[P^*_{n+1}] \quad (3)$$

$$[M]_e = k_d^{ap}/k_p^{ap} \quad (4)$$

Thus, $[M]_e$ should be calculated from the apparent rate constant of propagation k_p^{ap} and the apparent rate constant of depolymerization k_d^{ap} at equilibrium. The $[M]_e$ here observed might be dependent on the polymerization temperature and be independent of the initial monomer concentration. We will herein discuss the polymerization behavior of **1** according to the above equations.

Our previous report has clearly demonstrated that the anionic polymerization of **1** affords a stable living polymer having a predictable molecular weight and a narrow MWD in quantitative yield in THF at −78 °C.[14] The main subject of this study is to demonstrate the equilibrium behavior in the anionic polymerization of **1**. Therefore, equilibrium monomer concentrations, $[M]_e$ were measured at the various temperatures ranging from −78 to 0 °C. The initiating system of a mixture of (diphenylmethyl)potassium (Ph_2CHK) and 1,1-bis(4′-(trimethylsilyl)phenyl)ethylene (TMS_2DPE)[10] in THF enabled us to analyze the polymerization rate and polymeric products without difficulty, since the rate of

Table 1. Anionic Polymerization of 1 with Ph_2CHK/TMS_2DPE in THF at −78 °C

time, h	conversion,[a] %	yield,[b] %	$[M]_t$,[a] 10^2 M	$M_n \times 10^{-3}$ calcd[c]	$M_n \times 10^{-3}$ obsd[d]	M_w/M_n[d]
			Series 1, $[M]_0 = 0.39$ M			
15 min	57	60	16.7 ± 0.5	5.8	4.9	1.05
1	78	74	8.63 ± 0.3	8.0	5.7	1.04
4	86	79	5.35 ± 0.2	8.9	6.1	1.03
8	86	94	5.32 ± 0.2	8.9	6.0	1.03
24	98	94	0.688 ± 0.02	10.1	6.8	1.03
72	99	92	0.516 ± 0.02	10.1	6.8	1.05
			Series 2, $[M]_0 = 0.36$ M			
15 min	51	52	18.2 ± 0.5	5.3		
1	60	64	14.8 ± 0.4	6.2		
3	66	80	12.4 ± 0.3	6.9		
6	73	86	9.99 ± 0.3	7.5		
20	85	99	5.47 ± 0.2	8.8		
48	97	92	1.01 ± 0.03	10.1		
			Series 3, $[M]_0 = 0.27$ M			
15 min	50	29	19.3 ± 0.6	4.9	2.5	1.03
1	45	28	12.3 ± 0.4	4.5		
4	69	66	11.8 ± 0.3	6.9	4.3	1.04
8	78	88	8.28 ± 0.2	7.8		
20	86	100	5.33 ± 0.2	8.6		
100	100	100	∼0	9.9	6.9	1.06

[a] Conversion and $[M]_t$ were measured by GLC. The observed experimental error of $[M]_t$ was ±3% in the range 0.02−0.5 M. [b] Isolated polymer yield after precipitation in methanol. [c] M_n(calcd) = [monomer] × (MW of monomer) × conversion/[initiator] + MW of initiator residue. [d] M_n(obsd) and M_w/M_n were estimated by SEC calibration using standard poly(4-cyanostyrene)s in DMF.

polymerization for this system was moderately easy to follow at the given polymerization time at temperatures ranging from −78 to 0 °C. The polymerization of **1** was actually carried out as follows. After the instantaneous initiation of **1** with Ph_2CHK/TMS_2DPE at 0 °C, the polymerization system was rapidly cooled to an appropriate temperature and the polymerization was terminated with methanol at that temperature after standing for an appropriate time. To investigate the polymerization behavior of **1** under similar conditions, the initial concentrations of monomer and initiator were controlled in the ranges 0.3−0.4 M and 0.003−0.006 M in THF, respectively. In each polymerization, the residual monomer concentration, the polymer yield, and the molecular weight and the MWD of poly(**1**), were analyzed.

To reinvestigate the polymerization behavior at −78 °C, we first carried out three polymerizations of different initial monomer concentrations, $[M]_0$, ranging from 0.27 to 0.39 M. The polymerization results are shown in Table 1 and the time−conversion curves are shown in Figure 1. As has been observed previously,[14] the conversions obtained by the GLC quantitative within 48−100 h in each initial monomer concentration, although the rate of polymerization was quite slow at −78 °C. In these polymerization systems at −78 °C, the poly(**1**)s were actually obtained in quantitative yield after precipitation into methanol. Hence, $[M]_e$ could not be accurately determined at −78 °C, since the quantity of residual monomer was too small at the final stage of polymerization.

We next carried out the polymerization of **1** at −30 °C under conditions similar to those at −78 °C. The polymerization was similarly initiated at 0 °C, and the reaction system was allowed to propagate at −30 °C. The reaction system at −30 °C in a sealed tube always showed a characteristic red color during the course of polymerization and even after 113 days. The results at −30 °C are summarized in Table 2. The polymerization rate of **1** at −30 °C was obviously faster than that at −78 °C. The conversion of monomer reached 90% within 3 h in both polymerizations ($[M]_0 = 0.29$ and 0.35 M). No increase of conversion from 90% was observed at −30 °C, when the polymerization system was allowed to stand at the temperature even for 24 h or 113 days.[31] This strongly indicates that the polymerization reaction of **1** reaches the equilibrium state at −30 °C. The $[M]_e$ at −30 °C was thus determined to be ca. 0.029 M in each polymerization of the different $[M]_0$ values.[32]

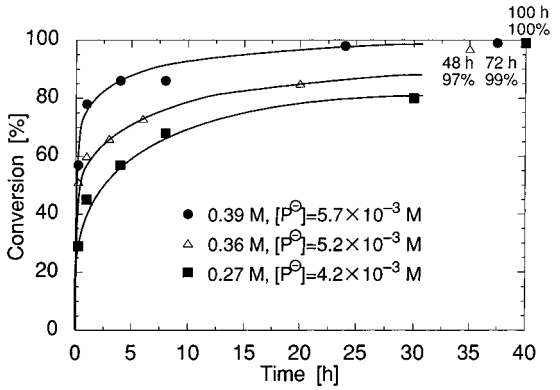

Figure 1. Time−conversion curve for the polymerization of **1** at −78 °C (Table 1).

Table 2. Anionic Polymerization of 1 with Ph_2CHK/TMS_2DPE in THF at −30 °C

time, h	conversion, %	yield, %	$[M]_t$, 10^2 M	$M_n \times 10^{-3}$ calcd	$M_n \times 10^{-3}$ obsd	M_w/M_n
			Series 4, $[M]_0 = 0.35$ M			
5 min	69	72	10.9 ± 0.3	6.1	4.6	1.04
15 min	81	77	6.48 ± 0.2	7.2		
1	85	90	5.37 ± 0.2	7.5		
6	87	100	4.49 ± 0.1	7.7	6.4	1.10
			Series 5, $[M]_0 = 0.29$ M			
5 min	51	43	14.4 ± 0.4	5.4	4.8	1.02
15 min	62	78	11.0 ± 0.3	6.6		
45 min	86	90	4.00 ± 0.1	9.1	6.2	1.04
1.5	91	93	2.63 ± 0.08	9.6	8.7	1.04
5	90	92	3.06 ± 0.1	9.4	8.6	1.06
25	90	100	2.89 ± 0.08	9.5	9.0	1.12
113 days	91	95[a]	2.83 ± 0.08	9.8	6.6	1.48[a]

[a] After precipitation in methanol. The MWD was unimodal but significantly broadened by the reversible polymerization at −30 °C.

The equilibria of anionic polymerizations of **1** were similarly observed at −40, −20, −10, and 0 °C, respectively, as well as at −30 °C. Figure 2 shows time−conversion curves at each temperature in ca. 0.3 M of initial monomer concentration $[M]_0$. At each temperature between −40 and 0 °C, the polymerizations of **1** clearly afford the equilibrium states within several hours. The rate of polymerization obviously increased with an increase of reaction temperature, as expected. Table 3 shows the final conversion of monomer and $[M]_e$ at the equilibrium state of each temperature in the range 0 to −40 °C.

Thermodynamic Parameters

A plot of ln $[M]_e$ vs reciprocal temperature in Table 3 shows a good linear relationship (Figure 3). According to the following equation, the thermodynamic parameters of anionic polymerization for **1** are determined.

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

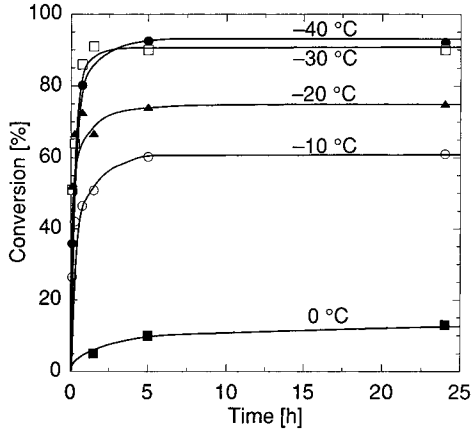

Figure 2. Time−conversion curve for the polymerization of **1** at −40, −30, −20, −10, and 0 °C, $[M]_0$ = ca. 0.3 M, $[P^*]_0$ = ca. 4×10^{-3} M.

Table 3. Equilibrium Monomer Concentration of 1 at 0 to −78 °C[a]

temp, °C	conversion, %	$[M]_e$, M
−78	100	∼0
−40	93	0.022 ± 0.002
−30	90	0.029 ± 0.003
−20	75	0.072 ± 0.004
−10	60	0.11 ± 0.01
0	13	0.25 ± 0.01

[a] $[M]_0 = 0.3 \pm 0.03$ M.

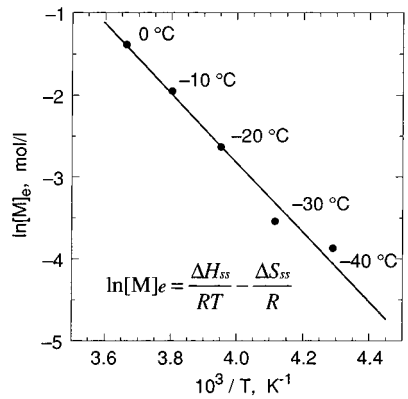

Figure 3. Plots of the equilibrium concentration $[M]_e$ against T^{-1} for the polymerization of **1** in THF.

ΔH_{ss} and ΔS_{ss} are the enthalpy at polymerization (heat of polymerization) and the entropy for a 1 M solution, respectively. By using the slope and the intercept in Figure 3, ΔH_{ss} and ΔS_{ss} of **1** in THF are estimated to be −7.64 ± 0.5 kcal mol^{-1} and −25.5 ± 0.3 cal mol^{-1} K^{-1}, respectively. It is reported that ΔH_{ss} and ΔS_{ss} for anionic polymerization of α-methylstyrene (in THF, K^+) are −8.02 kcal mol^{-1} and −28.8 cal mol^{-1} K^{-1}.[15] The reported values of ΔH_{ss} and ΔS_{ss} for α-methylstyrene derivatives are shown in Table 4. The thermodynamic parameters for **1** are comparable to those of other α-methylstyrenes but significantly deviated from those for styrene and methyl methacrylate.[33] Compared with the value of α-methylstyrene itself, **1** shows a smaller heat of polymerization ΔH_{ss} and a smaller entropy ΔS_{ss} at the polymerization, similar to the other *para*-substituted α-methylstyrenes. Although these differences might be explained by the steric effect of the substituent according to the suggestion of Isono et al.,[26,27] there is room for further investigation to discuss in detail. Electronic contribution of the substituents may also play an important role in determining these thermodynamic parameters in addition to the steric effect.

At the ceiling temperature (T_c), the rates of propagation and depropagation are defined to be equal and the change of Gibbs's free energy is zero. Therefore, T_c (= $\Delta H_{ss}/\Delta S_{ss}$) of **1** for a 1 M solution is calculated to be 27 ± 3 °C. This value is apparently higher than those of other α-methylstyrene derivatives, as shown in Table 4. One possible explanation is the electronic effect of the *para*-substituted cyano group of **1**. Either the strong electron-withdrawing nature of the cyano group (σ_p = 0.66)[34] or the extended π-conjugated system of the monomer skeleton[13,14] may possibly contribute to this high T_c value. This is consistent with the fact that the T_c values for the other monomers containing $P(NEt_2)_2$ ($\sigma p = 0.25$)[34] and C_6H_5 ($\sigma p = 0.05$)[34] are also higher than that of α-methylstyrene itself, while the extended studies on the substituent effect are necessary for the certain conclusion.

Kinetic Studies

The living character of the polymerization system of α-methylstyrene allows one to analyze the kinetic behavior easily and clearly. It has been already shown that the polymerization rate of α-methylstyrene is strongly dependent on the solvents and the countercations of the employed initiators,[16,18−22] as have been observed in the case of styrene.[18,35,36] These studies reveal that several active species such as solvent-separated ion pairs, contact ion pairs, and free ions concern the ionic propagation during the course of polymerization. In a polar solvent such as THF, it is shown that the rate constant of polymerization for free ion is much larger than the value for ion pairs, whereas the degree of dissociation of the propagating species to free ion is only less than 1%. Although a similar participation should be considered in the anionic polymerization of **1**, we here simply discuss the kinetic study for **1** only by using the apparent kinetic constant, $[M]_e$.

As shown before, the rate of monomer consumption can be expressed by 7, if the concentration of the propagating carbanion is constant during the course of the polymerization.

$$-d[M]/dt = k_p^{ap}[P^*_n][M] - k_d^{ap}[P^*_{n+1}] \quad (6)$$

$$= k_p^{ap}[P^*]([M] - k_d^{ap}/k_p^{ap}) \quad (7)$$

After substitution with eq 4, eq 7 can be integrated as follows:

$$\ln([M]_0 - [M]_e)/([M]_t - [M]_e) = k_p^{ap}[P^*]t \quad (8)$$

Two attempts of the polymerization of **1** were carried out at −30 °C in different initial monomer and initiator concentrations in THF. In each polymerization at −30 °C, the first-order plot according to eq 8 shows fairly good linear relationships, as can be seen in Figure 4, indicating the absence of chain termination reactions at this temperature. From the slope in Figure 4, the values of k_p^{ap} can be independently obtained to be 0.175 ($[I^*]_0 = 9.3 \times 10^{-3}$ M, $[M]_0 = 0.35$ M) and 0.179 L mol^{-1} s^{-1} ($[I^*]_0 = 5.4 \times 10^{-3}$ M, $[M]_0 = 0.29$ M). The agreement of the two experimental values indicates that the k_p^{ap} is only dependent on the polymerization tem-

Table 4. ΔH, ΔS, and T_c Values of 4-Substituted α-Methylstyrenes

substituent	σ_p[a]	ΔH, kcal mol^{-1}	ΔS, cal mol^{-1} K^{-1}	T_c, °C	ref
H	0.00	−8.02	−28.8	5	15
Pr^i	−0.15	−6.80	−25.2	−3	23
Bu^t	−0.20	−7.10	−25.5	5	24
C_6H_5	−0.01	−8.11	−28.3	14	25
$P(NEt_2)_2$	0.25	−6.52	−23.0	10	26
$CH_2CH_2OSiMe_2Bu^t$	na[b]	−7.88	−28.1	5	27
$CH(SiMe_3)_2$	na[b]	−7.24	−26.3	1	28
C≡N	0.66	−7.64 ± 0.5	−25.5 ± 1.3	27 ± 3	this work
styrene		−16.4	−24.8	∼390	33
MMA		−13.5	−27.9	∼200	33

[a] Reference 34. [b] Not available.

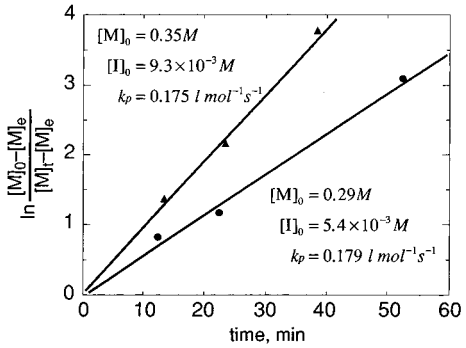

Figure 4. First-order plots for the polymerization of **1** at −30 °C (Table 2).

Table 5. Apparent Rate Constants of Anionic Polymerization for 1

temp, °C	k_p^{ap}, L mol^{-1} s^{-1}
−30	0.179 ± 0.01
−40	0.117 ± 0.01
−50	0.0776 ± 0.005
−78	0.0271 ± 0.005

perature but independent of the initial concentrations of initiators and monomer. This also supports the accuracy of the $[M]_e$ values estimated by the GLC measurement. The effect on the degree of dissociation of the propagating species seemed negligible, at least within the employed range of initiator concentration.

According to the above procedure, the k_p^{ap} values at −40, −50, and −78 °C were determined from the first-order plots at each temperature (Table 5). Figure 5 shows Arrhenius plots of k_p^{ap} for the polymerization of **1** in THF. From this plot, the relationship between k_p^{ap} and polymerization temperature can be determined as follows:

$$\ln k_p^{ap} = -1.83 \times 10^3/T + 5.74 \qquad (9)$$

The apparent activation energy of the polymerization for **1** is hence estimated to be 3.6 ± 0.2 kcal mol^{-1}. This value is considerably smaller than the reported value of α-methylstyrene (ΔE_p^{ap} = 5.5−7.2 kcal mol^{-1})[18−20] and supports the higher polymerizability of **1** under the anionic mechanism, as confirmed in our preceding report.[14] This higher polymerizability of **1** compared with α-methylstyrene would reflect the electron-withdrawing character of the cyano group introduced.

Depolymerization of Living Poly(1)

As expected from the observation that $[M]_e$ is dependent on the reaction temperature, the equilibrium may shift to the other state by changing the temperature. Theoretically, the depolymerization will be observed if

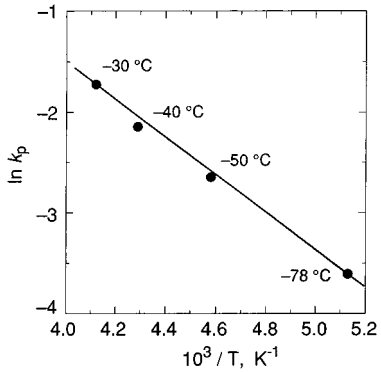

Figure 5. Arrhenius plots of k_p for the polymerization of **1** in THF.

Table 6. Depolymerization of Living Poly(1) at 0 °C in THF[a]

time, min	conversion, %	yield, %	$[M]_t$, 10^2 M	$M_n \times 10^{-3}$ calcd	$M_n \times 10^{-3}$ obsd	M_w/M_n
0	81	66	5.91 ± 0.2	8.3	9.8	1.03
5	30	25	20.0 ± 0.6	3.1	4.3	1.13
10	16	∼0	24.1 ± 0.7	1.6	3.2	1.18
20 h	13	∼0	25.0 ± 0.8	1.3	2.8	1.20

[a] The polymerization of **1** was initially carried out in THF at −78 °C for 70 h ($[M]_0$ = 0.29 M, $[P^*]_0 = 4.23 \times 10^{-3}$ M), and then the reaction mixture was allowed to depolymerize at 0 °C.

the temperature of the equilibrium polymerization system rises to a higher value.

The polymerization of **1** was initially attempted at −78 °C for 70 h, and the resultant polymerization system was then allowed to react at 0 °C to depolymerize. The depolymerization of the resulting poly(**1**) in fact proceeded, and the residual monomer concentration $[M]_t$ significantly increased again and the yield of polymer decreased with the reaction time, as shown in Table 6. The observed rate of depolymerization was quite rapid at 0 °C, since the conversions were decreased from 81% to be 30% and 16% only after 5 and 10 min, respectively. No polymeric products were obtained from the reaction systems after than 10 min by pouring the polymerization mixture into methanol to precipitate, indicating that all the propagating chain ends effectively concerned with the depolymerization. It was found that the reaction mixture contained a trace amount of low molecular weight oligomers and starting monomer. After 20 h, $[M]_t$ was observed to be 0.250 M, which agreed well with the $[M]_e$ value obtained from the normal polymerization procedure at 0 °C (Table 3), and the system appeared to reach a new equilibrium state. From this experiment, the k_d^{ap} at 0 °C was roughly estimated to be 0.11 s^{-1} and this was fairly close to the k_d^{ap} value of 0.096 s^{-1} (0 °C) calculated with eq 9. Thus,

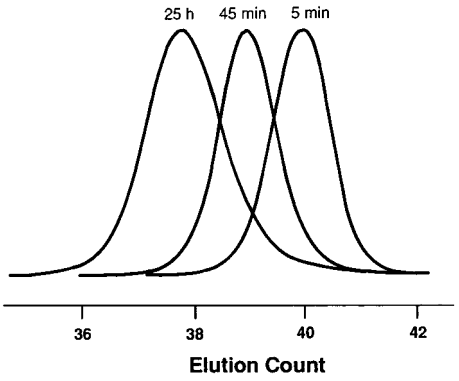

Figure 6. SEC curves of poly(**1**)s produced at −30 °C (Table 2, series 5).

the reversible depolymerization behavior of **1** was substantiated from the kinetic feature under the anionic condition along with the change of the equilibrium monomer concentration and the yield of polymeric product.

M_n's and MWDs of Poly(1)s Obtained at −78 to 0 °C

The thermodynamic and kinetic features of the anionic equilibrium polymerization of **1** have been clarified as discussed above. We here mention the molecular characteristics of the poly(**1**) obtained at the various temperatures mainly from the synthetic viewpoint.

As previously reported,[14] poly(**1**)s obtained at −78 °C possessed the predicted M_n's based on the molar ratios of monomer to initiators, although the M_n's obtained by SEC measurements tended to be underestimated (ca. 70%, Experimental Section). In addition, the SEC curves of poly(**1**)s were unimodal and sharp even after a 100 h reaction. The polydispersity index, M_w/M_n, was always within 1.1, supporting the narrow MWDs of the polymers. Similarly, the polymerization at −30 °C afforded the poly(**1**)s having narrow MWDs (M_w/M_n < 1.12) and well-controlled molecular weights. Figure 6 clearly shows the change of SEC curves of poly(**1**)s produced at −30 °C. The SEC curves of poly(**1**)s shift from the low molecular weight region to the higher region with the reaction time, the narrow MWDs are maintained.[31] The living nature of the polymerization system below −30 °C can be thus reconfirmed from this observation in accordance with the above discussions.

Over −20 °C, the MWDs were similarly narrow (M_w/M_n < 1.1) within several hours before reaching those equilibria. Interestingly, the broadening of MWD occurred after reaching the equilibrium state over −20 °C, while the SEC traces were always unimodal. The typical SEC curves of poly(**1**)s at −10 °C are shown in Figure 7. Although the molecular weights are controlled by the conversion of **1** and the initial molar ratio of **1** to initiator, as shown in Table 7, the MWDs become broader with the polymerization time. This phenomenon has been already predicted for the reversible equilibrium polymerization system in the literature.[16,37−39] At the initial stage of the polymerization over −20 °C, the MWD of the living poly(**1**) produced can be well regulated by the kinetic control. However, the recombination of the degree of polymerization in each polymer chain unequivocally takes place to afford the polymer having a broader MWD with time under the equilibrium conditions.[16,37−39] From the synthetic point of view, this information on the polymerization

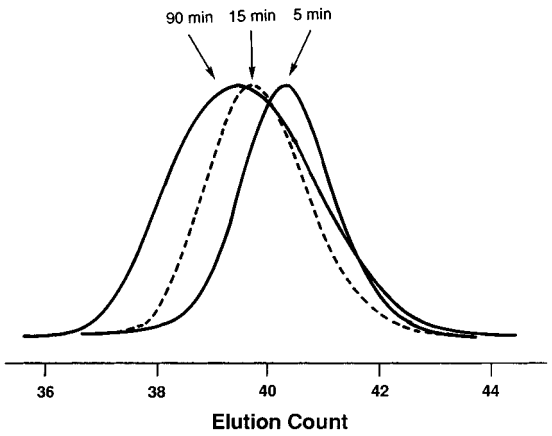

Figure 7. SEC curves of poly(**1**)s produced at −10 °C (Table 7, series 6).

Table 7. Anionic Polymerization of 1 with Ph_2CHK/TMS_2DPE in THF at −10 °C

time, min	conversion, %	yield, %	$[M]_t$, 10^2 M	$M_n \times 10^{-3}$ calcd	$M_n \times 10^{-3}$ obsd	M_w/M_n
Series 6, $[M]_0 = 0.282$ M						
5	26	54	20.8 ± 0.6	2.7	4.8	1.10
15	42	59	16.4 ± 0.5	4.3	5.7	1.08
45	46	55	15.3 ± 0.5	4.8	5.9	1.12
5 h	60	59	11.4 ± 0.3	6.2	5.8	1.21

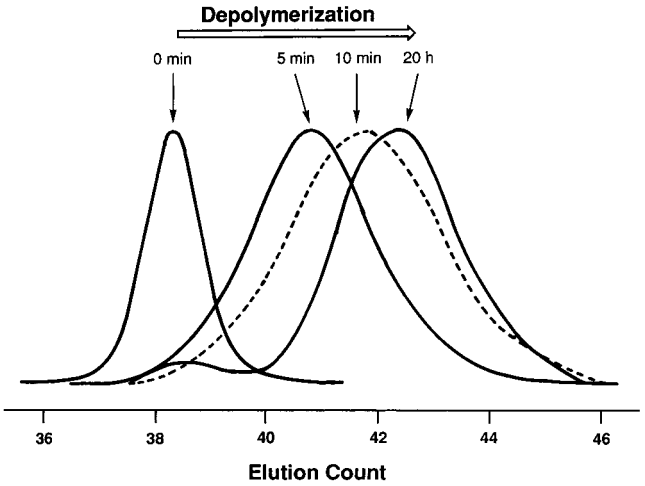

Figure 8. SEC curves of poly(**1**)s during the course of depolymerization at 0 °C (Table 6).

temperature is quite important for the fine control of the molecular characteristics of the poly(**1**). The polymerization of **1** should be carried out below −30 °C under the kinetic control conditions[31] if one wishes to obtain the polymer having a narrow MWD.

Figure 8 presents the change of SEC curves during the course of depolymerization of the resulting poly(**1**) as discussed above. As the depolymerization proceeds at 0 °C, SEC curves apparently shift from the starting poly(**1**) formed at −78 °C toward the lower molecular weight region. The MWDs were almost unimodal but became broader with the reaction time. The SEC trace after 20 h of reaction possessed a small shoulder at the higher molecular weight side in addition to the main peak of the low molecular weight oligomers, although the yield of polymeric product was negligible. This suggests that the propagating carbanion of the poly(**1**) is not completely stable at 0 °C for a long time. The intermolecular nucleophilic attack of the propagating

carbanion of poly(**1**) toward the cyano group might take place to some extent at this temperature. A similar side reaction leading to the MWD broadening was previously observed at 0 °C in the anionic polymerization of 4-cyanostyrene, the styrene counterpart of **1**, whereas the polymerization system was completely stable below −30 °C.[10] For the success of living polymerization of (α-methyl)styrenes containing reactive electrophilic cyano groups, great care is needed with the polymerization temperature to control the M_n and MWD of the resultant polymer precisely.

In conclusion, we have ascertained the anionic equilibrium polymerization of 4-cyano-α-methylstyrene (**1**) in THF at various temperatures between −40 and 0 °C. The analysis of the thermodynamic and kinetic parameters for the anionic polymerization of **1** suggests the substituent effects of the strong electron-withdrawing cyano group. It should also be mentioned that the shifts of SEC curves clearly demonstrate both the behaviors of reaching the equilibrium state and the depolymerization of the living poly(**1**).

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(32) Although a noticeable dependence of $[M]_e$ on the polymer concentration in the anionic polymerization of α-methylstyrene was reported in ref 21, the range of concentration seemed considerably higher than our experimental conditions. We have carried out the polymerization of **1** to determine the $[M]_e$ values at each temperature in 0.3 ± 0.03 M of $[M]_0$ values. We consider that the effect of $[M]_0$ values might be quite small or negligible in our experiment.
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