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Articles

Design of Helical Poly(*N*-propargylamides) that Switch the Helix Sense with Thermal Stimuli

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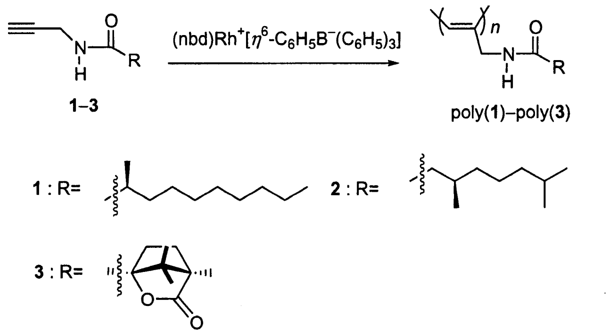
ABSTRACT: Copolymerization of chiral *N*-propargylamides, (*S*)-*N*-propargyl-2-methyldecanamide (**1**), and either (*R*)-*N*-propargyl-3,7-dimethyloctanamide (**2**) or (1*S*)-*N*-propargyl-3-oxo-2-oxa-4,7,7-trimethyl-2-bicyclo[2.2.1]heptan-1-acetamide (**3**) were conducted with (nbd)Rh$^+$[η^6-$C_6H_5B^-(C_6H_5)_3$] catalyst to obtain the corresponding copolymers with moderate molecular weights (M_n = 19 000−56 000) in good yields. The CD spectroscopic study showed that these two types of copolymers with various compositions formed helical structure and underwent a helix−helix transition driven by temperature change. In all cases, the optical activity became zero at certain temperatures, which depended on copolymer composition. The temperature dependence of helix sense of the copolymers allowed the determination of thermodynamic parameters. The helical structure of poly(**1**-*co*-**2**), which has long alkyl pendants, was affected by external stimuli more than poly(**1**-*co*-**3**) was. The thermodynamic parameters of helix inversion were also influenced by solvent polarity.

Introduction

Helical structures in biomacromolecules such as DNA and proteins are known to play important roles in nature.[1] Advances in polymer synthesis have enabled the synthesis of well-ordered synthetic helical polymers [e.g., polyacetylenes,[2] poly(alkyl methacrylates),[3] polychloral,[4] polyisocyanate,[5] polyisocyanides,[6] polysilanes,[7] and so forth[8]]. There are a number of helical polymers that are capable of undergoing transitions from one conformation to another induced by external stimuli. Although the control of helix sense of helical polymers by external stimuli, especially thermal stimuli, has been widely studied, the examples of helix inversion are restricted to the following cases: poly(L-aspartate β-esters),[9] poly(aryl isocyantes),[10] poly(silanes),[11] polyacetylenes,[12] and most recently polyisocyanate copolymers consisting of competing chiral monomers.[13] These organic and polymeric materials with two-state "on−off" function can be potentially applied to the devices of switches or data storage, and they are attracting much attention because of their relatively low cost, easiness of processing, and chemical controllability of their properties by changing substituents.

Appropriately substituted polyacetylenes can be helical polymers.[2] Substituted polyacetylenes ideally take four geometrical structures (trans−transoidal, trans−cisoidal, cis−transoidal, and cis−cisoidal), and stereoregular *cis*-polyacetylenes can take a well-ordered helical conformation. We have previously reported that *N*-propargylamides polymerize in the presence of a Rh catalyst to provide polymers having cis stereostructure. We have also found that the polymers take a helical conformation stabilized by the intramolecular hydrogen bonds between the amide groups in the side chains.[14] In this article, we report synthesis of copolymers of *N*-propargylamides, poly(**1**-*co*-**2**) and poly(**1**-*co*-**3**), composed of the chiral monomer pairs inducing opposite helix senses (Scheme 1). We demonstrate that these copolymers undergo helix inversion driven by temperature change. On the basis of CD data, we determine the thermodynamic parameters governing the stability of the helical conformation and discuss the profile of the helical conformation of poly(*N*-propargylamides).

Scheme 1



Experimental Section

Measurements. Melting points (mp) were measured with a Yanaco micromelting point apparatus. Elemental analyses were conducted at the Kyoto University Elemental Analysis Center. NMR (^{1}H: 400 MHz; ^{13}C: 100 MHz) spectra were recorded on a JEOL EX-400 spectrometer. IR spectra were obtained with a Shimadzu FTIR-8100 spectrophotometer. Number-average-molecular weights (M_n) and molecular weight

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distributions (M_w/M_n) of polymers were estimated by GPC (Shodex KF-850L columns) eluted with chloroform by use of a polystyrene calibration. Specific rotations ($[\alpha]_D$) were measured on a JASCO DIP-1000 digital polarimeter with a sodium lamp as a light source. UV−vis spectra were recorded on a JASCO V-500 spectrophotometer. CD spectra were recorded on a JASCO V-820 spectropolarimeter.

Materials. The solvents were distilled by usual methods prior to use. Propargylamine (Aldrich), (S)-(+)-2-methyldecanoic acid (Azmax), thionyl chloride (Wako), and pyridine (Wako) were used without further purification. (nbd)Rh$^+$[η^6-$C_6H_5B^-(C_6H_5)_3$] was prepared as reported.[15] Monomers **2** and **3** were prepared according to the literature.[14b,c]

Synthesis of Monomer 1. Thionyl chloride (15.9 mL, 0.134 mol) was added to (S)-(+)-2-methyldecanoic acid (5 g, 26.9 mmol), and the reaction mixture was heated with refluxing for 3 h. The excessive thionyl chloride was distilled off, and the resulting acyl chloride was add to an Et_2O solution of propargylamine (5.54 mL, 80.5 mmol) and pyridine (6.76 mL, 80.5 mmol) at 0 °C. The solution was stirred at room temperature for 24 h. After the formed white precipitate was filtered off, the solution was washed with aqueous HCl and saturated aqueous $NaHCO_3$, dried over $MgSO_4$, and concentrated by rotary evaporation. Monomer **1** was purified by recrystallization from hexane. Mp 67−68 °C; $[\alpha]_D = +7.98°$ (c = 0.0446 g/dL in $CHCl_3$). IR (KBr): 3290 ($\nu_{H-C\equiv}$), 2921, 2162 ($\nu_{C\equiv C}$), 1636 ($\nu_{C=O}$), 1541 (δ_{N-H}), 1240, 675 cm^{-1}. ^1H NMR ($CDCl_3$): δ 0.85 ($CH_2\mathit{CH_3}$, t, 3H, J = 7.32 Hz), 1.13 ($CH\mathit{CH_3}$, d, 3H, J = 6.84 Hz), 1.16−1.38 ($(\mathit{CH_2})_7CH_3$, m, 13H), 1.60−1.72 ($\mathit{CH}H(CH_2)_6CH_3$, m, 1H), 2.15−2.18 ($\mathit{CH}CH_3$, m, 1H), 2.22 ($C\equiv C\mathit{H}$, d, 1H, J = 2.44 Hz), 4.05 ($C\equiv C\mathit{CH_2}$, d, 2H, J = 2.44 Hz), 5.70 (NH, s, 1H). ^{13}C NMR ($CDCl_3$): δ 14.07, 17.64, 22.61, 27.39, 29.01, 29.21, 29.43, 29.56, 31.79, 34.26, 41.34, 71.47, 79.67, 176.23. Anal. Calcd for $C_{14}H_{25}NO$: C, 75.28; H, 11.28; N, 6.27. Found: C, 74.98; H, 11.56; N, 6.28.

(Co)polymerization Procedures. A $CHCl_3$ solution of the monomers was added to a $CHCl_3$ solution of (nbd)Rh$^+$[η^6-$C_6H_5B-(C_6H_5)_3$] under dry nitrogen, and the solution ($[M]_{total}$ = 1.0 M, $[M]_{total}/[cat] = 100$) was kept at 30 °C for 24 h. The reaction solution was poured into a large amount of methanol to precipitate polymers. The resulting polymers were dried under reduced pressure.

Poly(**1**): IR (KBr): 3290, 2926, 1647 ($\nu_{C=O}$), 1543 (δ_{N-H}), 1253 cm^{-1}. ^1H NMR ($CDCl_3$): δ 0.78−0.99 ($CH_2\mathit{CH_3}$), 0.99−1.18 ($CH\mathit{CH_3}$), 1.18−1.43 ($CHCH_2(\mathit{CH_2})_6CH_3$), 1.43−1.77 ($CH\mathit{CH_2}$), 1.98−2.37 ($\mathit{CH}CH_3$), 3.61−4.49 ($CH{=}C\mathit{CH_2}$), 5.88−6.31 ($\mathit{CH}{=}C$), 8.22−8.64 (N$H$).

Results and Discussion

Synthesis and Secondary Structure of Homopolymer. The polymerization of N-propargylamides with Rh catalyst gives polymers with highly cis stereoregularity.[14] Thus, polymerization of **1**−**3** was conducted with (nbd)Rh$^+$[η^6-$C_6H_5B^-(C_6H_5)_3$] in $CHCl_3$. The results of the polymerization are listed in runs 1, 6, and 11 in Table 1. Polymers with moderate molecular weights (M_n = 8100−32 000) were obtained. The ^1H NMR spectra of the resulting polymers, poly(**1**)−poly(**3**), showed the cis-olefinic proton in the main chain around 6 ppm. By comparison of the integrated intensities of its and other protons, the content of the cis structure was estimated to be 100%. These chiral homopolymers, poly(**1**)−poly(**3**), took predominantly one-handed helical conformation, which was supported by intense CD effects in $CHCl_3$ (Figure 1). The differences in the sign of the Cotton effects suggest that the helix sense of poly(**1**) and those of poly(**2**) and poly(**3**) are opposite to each other. The thermal stability of helical conformation was next studied. When the measuring temperature was raised from 0 to 55 °C, the intensity of the CD effects of poly(**1**)−poly(**3**) only slightly decreased, as shown in Figure 1. We can conclude that the helical structures of these polymers are stable against heating and do not show helix inversion.

Table 1. Homo- and Copolymerizations of *N*-Propargylamides[a]

run	monomer M$_1$	monomer M$_2$	monomer feed ratio (M$_1$/M$_2$)	yield[b] (%)	compostion[c] (M$_1$/M$_2$)	M_n[d]	M_w/M_n[d]
1	**1**	**2**	100/0	53	100/0	26 000	1.45
2			80/20	40	77/23	55 000	3.15
3			75/25	51	75/25	48 000	2.38
4			70/30	48	68/32	56 000	1.95
5			65/35	53	66/34	30 000	4.05
6			0/100	62	0/100	8 100	1.68
7	**1**	**3**	75/25	70	74/26	24 000	1.59
8			73/27	68	72/28	22 000	1.49
9			70/30	74	69/31	19 000	1.71
10			67/33	73	67/33	22 000	1.65
11			0/100	68	0/100	32 000	1.77

[a] Polymerized with (nbd)Rh$^+$[η^6-$C_6H_5B^-(C_6H_5)_3$] in $CHCl_3$ at 30 °C for 24 h. [b] Methanol-insoluble part. [c] Determined by ^1H NMR. [d] Estimated by GPC ($CHCl_3$, PSt standards).

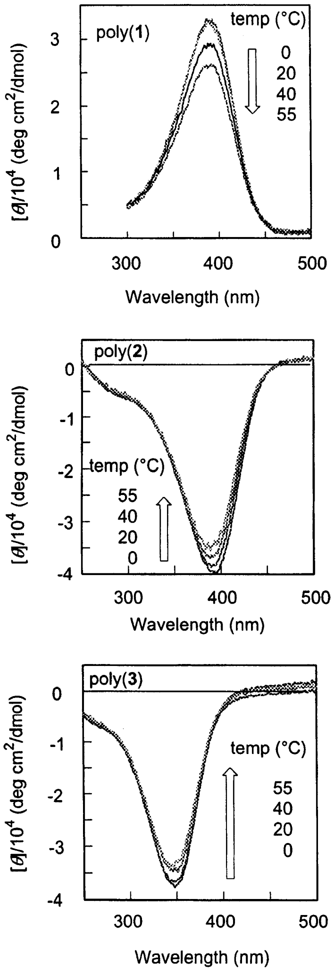

Figure 1. Temperature-variable CD spectra of poly(**1**), poly(**2**), and poly(**3**) measured in $CHCl_3$ (c = 0.0936−0.108 mM).

Helix Inversion of Copolymers. Recently, Choen and co-workers have reported that the helix sense can be controlled through the synthesis of copolymers with various compositions of the chiral monomer pairs, wherein the homopolymers prefer the opposite helix senses to each other.[13] We therefore conducted the copolymerizations of **1** and either **2** or **3** at various compositions. The results of the copolymerization are

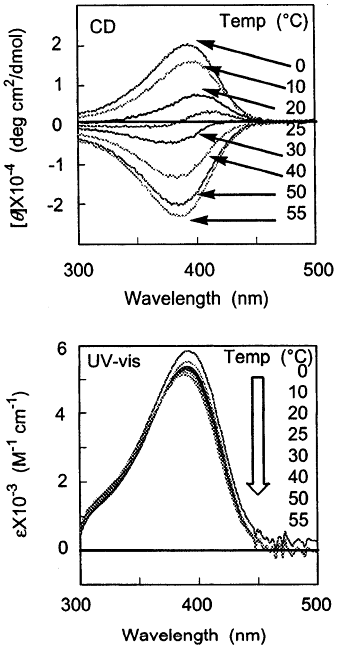

Figure 2. Temperature-variable CD and UV−vis spectra of poly(**1**-*co*-**2**) (**1**/**2** = 68/32) measured in $CHCl_3$ (c = 0.124 mM).

summarized in Table 1. We chose these feed compositions in order that the helix−helix transition of the formed copolymers occurs at around room temperature. Copolymers with moderate molecular weights (M_n = 19 000−56 000) were obtained.[16] Figure 2 shows the temperature-variable CD and UV−vis spectra of poly(**1**-*co*-**2**) (**1**/**2** = 68/32). The copolymer displayed a positive CD signal at the same wavelength (390 nm) as for the UV−vis absorption at 0 °C in $CHCl_3$, which is assignable to the polymer main chain. When the temperature was raised, the magnitude of the CD signal decreased, and the sign was inverted around 25 °C. During this CD inversion phenomenon, only a slight change was observed in the UV−vis absorption of polymer main chain. We have previously demonstrated that poly(*N*-propargylamides) exhibit a UV−vis absorption centered at ca. 390 nm when they take a helical conformation.[14b] Meanwhile, randomly coiled poly(*N*-propargylamides) show an absorption maximum (λ_{max}) at 320 nm. Consequently, this result indicates that poly(**1**-*co*-**2**) transformed from one helical motif to another directly without taking random coil conformation or accompanying the change of conformation such as helix pitch. Figure 3 shows the optical activity ($[\theta]_{390\ nm}$) as a function of temperature for two sets of copolymers with various compositions. In both of these cases, the copolymers took a helical conformation of the same preferential helix sense as that of poly(**1**) at lower temperature, and $[\theta]_{390\ nm}$ became zero at a temperature T_c (compensation temperature), which depended on the composition of copolymer. This is consistent with the reversal of helical sense. The transition (compensation) temperature rose with increasing ratio of monomer **1**. It is apparent that the transition (compensation) temperature can be varied by changing the ratio of the competing chiral units in each copolymer.

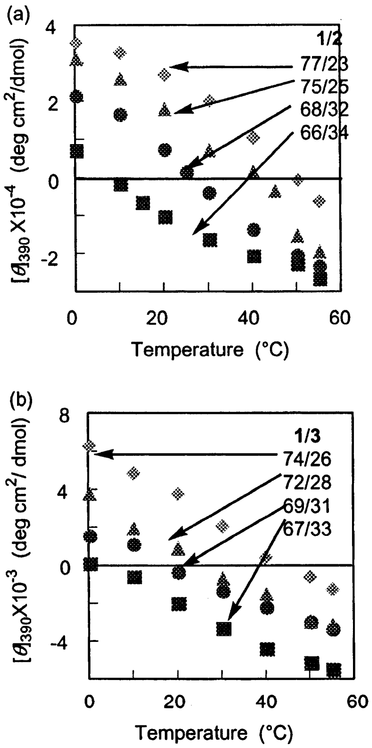

Figure 3. Temperature profile of $[\theta]_{390}$ of (a) poly(**1**-*co*-**2**)s and (b) poly(**1**-*co*-**3**)s measured in $CHCl_3$ (c = 0.110−0.137 mM).

Thermodynamics of the Helical Conformation. The temperature dependence of the ratio of one helical structure to the opposite-sense helix was estimated from the temperature-variable CD spectra, which enabled the determination of thermodynamic parameters. The free energy difference of helix−helix transition, ΔG,[17] can be defined as

$$\Delta G = -RT \ln K$$

where K is the equilibrium constant for the helix−helix transition process. The proportion of one helix to the other determines the constant K. Thus, the constant is given by

$$K = N_P/N_M$$

where N_P and N_M are the mol % of monomer units which exist in helical structures that show positive- and negative-signed CD effects, respectively. Here we assume that poly(**2**) is in a purely one-handed helical conformation at 0 °C and use its $[\theta]_{max}$ (−40 000 deg cm²/dmol) value to normalize the $[\theta]_{390}$ values observed for the copolymers at each temperature such that[11a,c]

$$N_P = 100[1 + [\theta]_{390}/[\theta]_{max}]/2$$

$$N_M = 100 - N_P$$

The thermodynamic theory predicts

$$-R \ln K = \Delta H/T - \Delta S$$

where ΔH and ΔS are the enthalpy and entropy changes upon helix−helix transition. The plot of $-R \ln K$ against $1/T$ and the equation $T_c = \Delta H/\Delta S$ gave ΔH and ΔS at T_c (Figure 4 and Table 2). Here, the entropy difference, ΔS, relates to the flexibility of polymer main chain, and the enthalpy difference, ΔH, relates to the energy difference between P- and M-motifs.[11c,13] The ΔS values of poly(**1**-*co*-**2**) were larger in negative sign than those of poly(**1**-*co*-**3**), and they tended to take negative larger values with increasing ratio of monomer **1** in both types

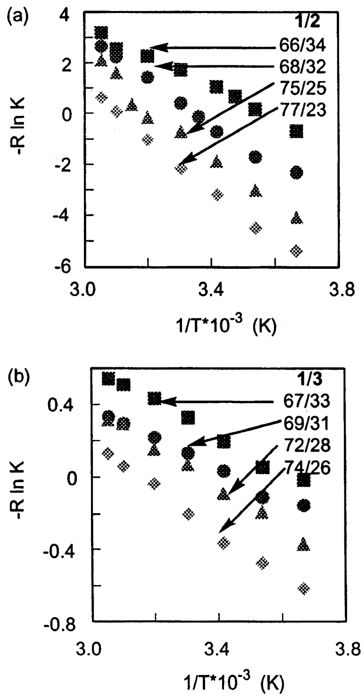

Figure 4. Temperature dependence of the equilibrium constant (*K*) for a helix−helix transition determined by the CD spectra of (a) poly(**1**-*co*-**2**)s and (b) poly(**1**-*co*-**3**)s measured in $CHCl_3$ ($c = 0.110{-}0.137$ mM).

Table 2. Thermodynamic Parameters of Poly(1-*co*-2) and Poly(1-*co*-3) in $CHCl_3$ at T_c

polymer	composition (M_1/M_2)	T_c (°C)	ΔH (kcal/mol)	ΔS (cal/(mol K))
poly(**1**-*co*-**2**)	66/34	9	−5.97	−21.3
	68/32	28	−8.47	−28.4
	75/25	40	−9.73	−31.4
	77/23	50	−9.93	−30.8
poly(**1**-*co*-**3**)	67/33	2	−0.96	−3.5
	69/31	18	−0.84	−2.9
	72/28	26	−1.12	−3.7
	74/26	48	−1.24	−3. 9

of copolymer. This result means that long alkyl pendant groups make the polymer main chain flexible and that the order of the flexibility is **1** > **2** > **3**. Fujiki et al. calculated the enthalpy difference of [(*S*)-3,7-dimethyloctyl-3-methylbutyl]silylene ($T_c = -20$ °C, the viscosity index, $\alpha = 1.11$ in $CHCl_3$ at 30 °C) from the energy difference between *P*- and *M*-motifs of a model compound (31-mer) of the corresponding poly(dialkylsilane) and the entropy difference from $T_c = -20$ °C and the equation $T_c = \Delta H/\Delta S$ to be −0.67 kcal/Si repeating unit and −2.9 cal/Si repeating unit K, respectively.[11a] Hence, it can be said that monosubstituted acetylene polymers such as poly(*N*-propargylamides) in $CHCl_3$ at around room temperature possess main chains more flexible than poly(silanes) in isooctane at around −20 °C, which have a rodlike backbone.[7]

Solvent Effect on Helix Inversion. Because the intramolecular hydrogen bonding between the amide groups in the side chain significantly contribute to the stabilization of helical conformation of poly(*N*-propargylamides), solvent polarity is expected to affect the stability of helical conformation. Therefore, we examined the effect of solvent on the helical structure. Poly(**1**-*co*-**2**), the copolymer of monomers **1** and **2**, which have a methyl branch at the α- and β-positions of the amide group, respectively, can take helical structure in $CHCl_3$ and CH_2Cl_2. We have previously demonstrated that poly(*N*-propargylamides) having a branch at the β-position of the amide group transform from helix to random state by the addition of methanol, presumably because the β-branch cannot prevent the solvent from approaching the amide group, which disturbs hydrogen bonding between the amide groups.[14b,c] Even the copolymer of **1** and **2** containing 70% of **1** could not keep helical structure when methanol was added. Poly(**1**-*co*-**3**)s took helical conformation in various solvents such as toluene and THF, but they kept positive signed CD signals, and no helix−helix transition could be observed up to the boiling points of the solvents. We thus measured CD spectra of poly(**1**-*co*-**3**) (**1**/**3** = 67/33) which showed the lowest transition temperature in the series of poly(**1**-*co*-**3**) in $CHCl_3$ containing a small amount of toluene or methanol in order to reduce or raise the solvent polarity (Figure 5). The T_c rose on the addition of toluene or methanol to a $CHCl_3$ solution of the copolymer, especially methanol effectively changed the T_c. We can determine the thermodynamic parameters of helix transition from the temperature-variable CD spectra. Figure 6 shows the temperature dependence of *K* for helix−helix transition of poly(**1**-*co*-**3**) (**1**/**3** = 67/33) in toluene/$CHCl_3$ and methanol/$CHCl_3$. From this figure, we can calculate the ΔH and ΔS values (Table 3). The ΔS became small upon the addition of toluene, while it increased with the addition of methanol. This result indicates that the polymer backbone becomes stiff by the addition of nonpolar toluene, presumably because hydrogen bonding strengthens. On the other hand, it is likely that methanol softens the polymer main chain because it should weaken hydrogen bonding.

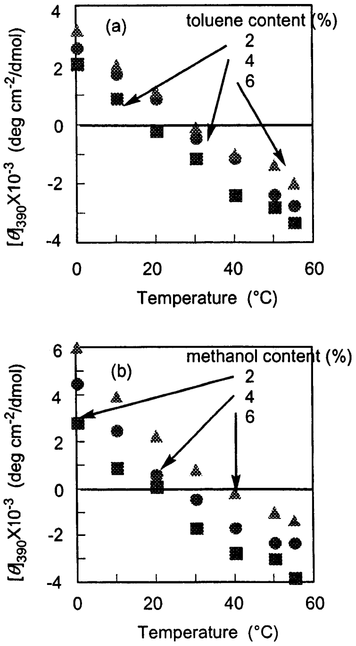

Figure 5. Temperature profile of $[\theta]_{390}$ of poly(**1**-*co*-**3**) (**1**/**3** = 67/33) (a) measured in toluene/$CHCl_3$ and (b) methanol/$CHCl_3$ ($c = 0.108$ mM).

Summary

Chiral poly(*N*-propargylamides), poly(**1**)−poly(**3**), formed predominantly the one-handed helical structure. The CD sign of these homopolymers demonstrated that the helix senses of poly(**1**) and either poly(**2**) or poly(**3**) are opposite to each other. Variable composition of copolymers of two structurally different chiral mono-

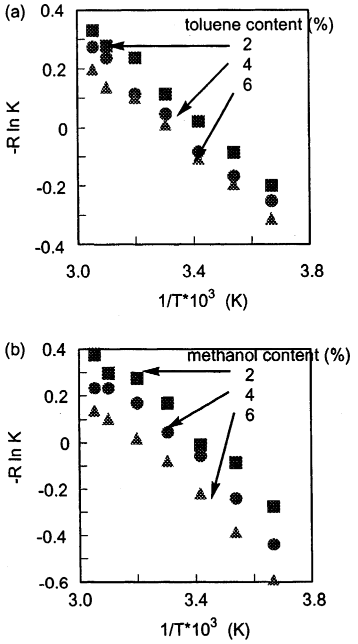

Figure 6. Temperature dependence of the equilibrium constant (K) for a helix–helix transition obtained from poly(**1**-*co*-**3**) (**1**/**3** = 67/33) (a) measured in toluene/$CHCl_3$ and (b) in methanol/$CHCl_3$ (c = 0.108 mM).

Table 3. Thermodynamic Parameters of Poly(1-*co*-3) (1/3 = 67.2/32.8) at T_c

solvent composition (CHCl$_3$/MeOH/toluene)	T_c (°C)	ΔH (kcal/mol)	ΔS (cal/(mol K))
98/0/2	19	−0.86	−3.0
96/0/4	28	−0.87	−2.9
94/0/6	30	−0.82	−2.7
98/2/0	21	−1.03	−3.5
96/4/0	27	−1.11	−3. 7
94/6/0	38	−1.17	−3.8

mers, **1** and either **2** or **3**, constructed helical structure and underwent a helix–helix transition driven by temperature change. In both cases, the helix–helix transition temperature rose with increasing ratio of monomer **1** in the copolymers. We determined the thermodynamic parameters ΔH and ΔS from the temperature dependence of helix sense of the copolymers. It was concluded that the main chain of poly(**1**-*co*-**2**) having longer alkyl side chains was more flexible than that of poly(**1**-*co*-**3**) because the absolute value of ΔS of the former copolymer was larger than that of the latter. The solvent polarity also affected the thermodynamic parameters of helix inversion.

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