Molecular Weight Dependence of the Optical Rotation of Poly((*R*)-1-deuterio-*n*-hexyl isocyanate) in Dilute Solution

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ABSTRACT: Poly((*R*)-1-deuterio-*n*-hexyl isocyanate) (αPdHIC) in dilute solution is characterized by an extraordinarily large specific optical rotation [α]. Detailed [α] data were obtained for a number of nearly monodisperse αPdHIC samples in different solvents over a wide range of temperature. The results were similar to those for poly((*R*)-2-deuterio-*n*-hexyl isocyanate) (βPdHIC) reported in a previous publication (Gu, H., et al. *Macromolecules* **1995**, *28*, 1016). The molecular weight dependence of [α] was remarkable over a wide range and consistently analyzed by the statistical mechanical theory of Lifson et al. (Lifson, S., et al. *J. Am. Chem. Soc.* **1989**, *111*, 8850) for a polyisocyanate chain consisting of an alternating sequence of right-handed and left-handed helices intervened by helix reversals. It was shown that the large [α] arises from the helical conformation, where the left-handed helix exists in some excess over the right-handed one due to a small free energy favoring the former helix ($2\Delta G_h$). This energy accumulates to a significant amount on a given chain assisted by a very small helix reversal probability (ν). This confirmed a similar conclusion on βPdHIC reported in the previous paper. It was found that ν is almost the same for the two polyisocyanates but the magnitude of $2\Delta G_h$ for αPdHIC, though smaller than a few calories per mole, is about twice as large as that for βPdHIC, exhibiting a remarkable hydrogen−deuterium isotope effect *on chain conformation*.

Introduction

Polyisocyanates are known to be stiff because of their backbone amide groups, which tend to be coplanar.[1−9] However, steric reasons prohibit them from remaining coplanar and force them to adopt helical conformations.[3,10−17] For a polyisocyanate built of achiral units, there is no preference of one particular sense of the helix over the other, in contrast to a polyisocyanate synthesized from nonracemic chiral units. Goodman and Chen[18,19] were the first to synthesize optically active polyisocyanates and suggested that their large optical activities might be due to a helical conformation. Recently, there has been much attention on chiral interactions in the polyisocyanates and many polyisocyanates showing large optical activities have been synthesized.[20−26] Among the materials synthesized are the chiral deuterated polyisocyanates poly((*R*)-1-deuterio-*n*-hexyl isocyanate) (**1**, αPdHIC) and poly((*R*)-2-deuterio-*n*-hexyl isocyanate) (**2**, βPdHIC). They have been the targets of our previous[27] and present studies. These polymers are chiral only due to one deuterium atom replaced stereospecifically for one hydrogen atom at the α-carbon and β-carbon atom on the side chain, respectively. They both show extraordinarily large optical rotations (OR) depending remarkably on the molecular weight of the polymer as well as on temperature and solvent.[21,23−27] It is considered that their large OR is not due to the intrinsic chirality of their monomeric units, but to the excess of a particular helix sense. The OR of the monomers are negligibly small compared with those of the polymers. This is the first finding of a hydrogen−deuterium isotope effect on *chain conformation*, which is very small on a monomer unit basis but is greatly amplified on the polymer chain.

A statistical mechanical theory was proposed[23] to account for this OR behavior. In this theory, a polymer chain is assumed to consist of an alternating sequence of left-handed and right-handed helices with helix reversal points joining them. The extraordinarily large OR is ascribed to the symmetry break in helix sense, which is predicted to arise from a slight imbalance in energy between the two helices due to chiral perturbation. In our previous study,[27] this extraordinary optical rotation was investigated for polymer **2** in detail with respect to temperature, solvent, and molecular weight dependence. Under every solvent condition examined, the molecular weight dependence of the OR is fully consistent with the theoretical prediction, thus substantiating its validity. Theoretical analyses of the data have revealed that the free energy difference is as small as about 1 cal per monomeric unit but it is accumulated on a long chain to a few hundred calories, favoring one helix sense over the other. On the other hand, the helix reversal costs more than 3000 cal mol^{-1} and occurs only once on a few hundred units.

According to an empirical force field calculation,[28] the symmetry break in helix sense is induced by nonbonded interactions between the chiral side chain of a given monomeric unit and the main chain atoms of the preceding units. Thus it is reasonable to consider that these interactions may be stronger and have a more profound influence on the OR behavior for polymer **1** than for polymer **2**, because the chiral center is located closer to the main chain for polymer **1** compared with polymer **2**. Therefore in the present study we have

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investigated the OR behavior of polymer **1** using well-fractionated samples covering a wide range of molecular weight. This paper presents detailed experimental data and their analysis by Lifson et al.'s theory.[23] It is shown that the molecular mechanism for the extraordinary OR is the same for polymers **1** and **2**, but the hydrogen–deuterium isotope effect is more pronounced in polymer **1** than in polymer **2**; i.e., the free energy difference for polymer **1** is about twice as large as that for polymer **2**. No such difference is seen in the helix reversal energy.

Experimental Section

Polyisocyanate Samples. An original sample α-170 of poly((*R*)-1-deuterio-*n*-hexyl isocyanate) (**1**, αPdHIC) of about 1.7×10^6 molecular weight synthesized as described elsewhere[23,24] was degraded and fractionated as follows.

First about 30 mg of α-170 dissolved in chloroform was degraded by adding dropwise a 10% chloroform solution of trifluoroacetic acid. The reaction was performed in a Ubbelohde viscometer at 25 °C. The degree of degradation was monitored by measuring viscosity. When it reached an appropriate value, the reaction was stopped by adding triethylamine, and the resulting polymer was recovered by pouring the solution into a large excess of methanol. In this way, two samples, α-104 of about 10^6 molecular weight and A-40 of about 400 000 molecular weight, were obtained. Since sample A-40 was broad in molecular weight distribution, it was further separated into three fractions by fractional precipitation with benzene as the solvent and methanol as the precipitant to obtain the middle fraction, α-40. In a similar way, sample α-104 was degraded to an αPdHIC sample of about 40 000 molecular weight. About 16 mg of this polymer was dissolved in 8 cm^3 of chloroform. The resulting solution was divided into 8 parts, and each part was subjected to gel permeation chromatography (GPC) to separate 17 nearly monodisperse fractions. Use was made of a TOSOH HLC-8070 gel permeation chromatograph equipped with a TOSOH TSK-GEL G4000H8 column. Combining the same fractions from 8 runs, we obtained 12 fractions, A4 to A15, for use in OR measurements. Series C samples of higher molecular weights were obtained by fractionating about 20 mg of α-40 first on the TSK G4000H8 column, combining fractions of similar molecular weights, refractionating them with a series connection of TSK G4000HXL and G5000HXL, and collecting central fractions C5–C8. Another unfractionated sample, αHM, was used after purification.

Molecular Weight Determination. Molecular weights of fractionated samples were determined by GPC on a TOSOH HLC8020 gel permeation chromatograph at 40 °C using TSK-G5000HXL and G4000HXL columns connected in series, with the concentrations of eluted solutions being detected by the peak UV absorption at 254 nm. As will be shown in a forthcoming publication, the deuterated polymers and hydrogenated polymer PHIC have essentially the same global conformation in dilute solution. Therefore the molecular weight calibration curve for this machine was determined using 18 narrow molecular weight distribution reference PHIC samples of known weight-average molecular weights M_w taken from our stock,[4,5,7] and the curve was shown to be valid for fractionated αPdHIC and βPdHIC[27] samples.

Concentration and Optical Rotation Measurements. Commercial *n*-hexane, toluene, 1-chlorobutane, and dichloromethane were purified according to the usual procedure. Mass concentrations c (g cm^{-3}) of solutions for optical rotation measurements were determined from optical density $[\mathrm{OD}]_{250}$ at 250 nm assuming that $[\mathrm{OD}]_{250} = 10^4 \gamma c$, where γ is a numerical coefficient depending on the molecular weight. It was found that γ is essentially unaffected by deuterium substitution and solvent, but decreases inversely with molecular weight as $\gamma = 0.3077 + 755/M_w$ (g^{-1} cm^3). Optical rotation measurements were made on a JASCO ORD/UV-5 spectropolarimeter using quartz cells of 10 cm optical pass length for solutions at c of about 10^{-4} g cm^{-3}. Data were taken at wavelengths between 290 and 600 nm, but those at 300 nm were used for quantitative analysis because of high sensitivity. For either sample, solutions in *n*-hexane, 1-chlorobutane, and dichloromethane (DCM) were prepared successively after measurements on the respective solutions by evaporating the solvent and dissolving in the next new solvent. The unfractionated sample αHM was dissolved directly in the respective solvents, and their mass concentrations were determined by weight.

Table 1. Average Molecular Weights of αPdHIC Samples

sample code	$M_w/1000$	N_w	M_w/M_n
A4	98.3	767	1.03
A5	71.2	555	1.02
A6	58.5	456	1.01
A7	48.1	375	1.01
A8	40.1	313	1.01
A9	33.3	260	1.01
A10	27.2	212	1.01
A11	21.6	168	1.02
A12	16.3	127	1.03
A13	11.8	92	1.03
A14	8.06	62.9	1.05
A15	5.03	39.2	1.08
C5	425	3315	
C6	335	2613	
C7	168	1318	
C8	118	920	
αHM	1950	15210	
βHM[a]	2500	19500	

[a] Poly((*R*)-2-deuterio-*n*-hexyl isocyanate).

Experimental Results

Fractionation and Average Molecular Weights. The molecular weight M–elution time t calibration curve was constructed using 18 narrow molecular weight distribution PHIC samples of known weight-average molecular weights[4,5,7] so that it would reproduce most closely the M_w of all the samples.[27] Use of this calibration for αPdHIC is based on the assumption that PHIC and αPdHIC have the same global conformation in chloroform, which will be justified later experimentally.[29] Indeed the M_w of sample B-7 so determined agreed with that obtained by low-angle light scattering within 6%. Thus the average molecular weights and molecular weight distribution curves were determined by GPC using this calibration curve. Table 1 summarizes the results for series A and C samples, which were mainly used for OR measurements. It can be seen that these samples cover a wide range in M_w from 5030 to 425000 and the polydispersity index M_w/M_n is smaller than 1.08 except for two high molecular weight samples C5 and C6. In the following presentation, the molecular weight is identified with M_w unless otherwise stated and the weight-average degree of polymerization N_w is calculated from $N_w = M_w/128.2$.

Solvent Dependence of Optical Rotation. Figure 1a compares the temperature dependence of specific rotation at 300 nm, $[\alpha]_{300}$, of an unfractionated sample αHM in various solvents; $[\alpha]_{300}$ is expressed in units of 10^{-1} deg cm^2 g^{-1}. In either solvent, $-[\alpha]_{300}$ increases steadily with decreasing temperature and at any temperature, $-[\alpha]_{300}$ increases with the solvent order DCM, 1-chlorobutane, toluene, and hexane. It is interesting to note that this solvent order coincides with that for the stiffness expressed in terms of persistence length. This is the same order as that found with βPdHIC as shown in panel b of the same figure.[27] When compared in the same solvent, the magnitude of $[\alpha]_{300}$ is larger for αPdHIC than for βPdHIC. However, the sign of $[\alpha]_{300}$ is opposite for the two polymers. This is due to the opposite preference of helix sense for the two PdHICs.

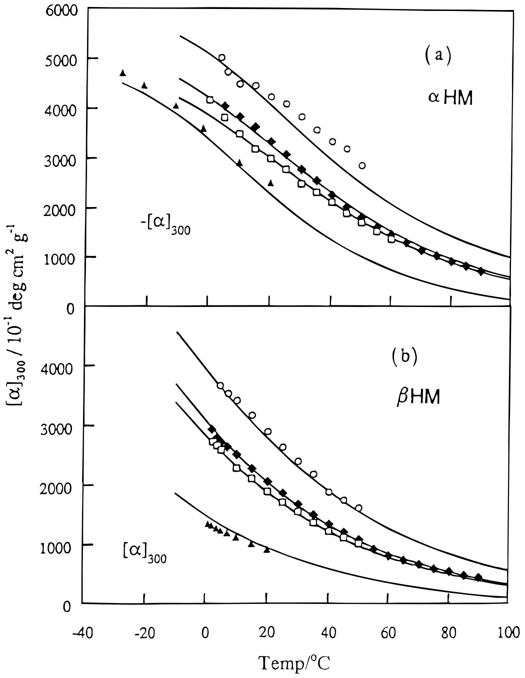

Figure 1. Plots of $[\alpha]_{300}$ vs temperature for unfractionated samples αHM and βHM. Symbols, experimental data for hexane (○), 1-chlorobutane (□), toluene (◆), and DCM (▲); solid curves, theoretical values calculated with the parameter values given in Table 2 and the $[\alpha]_m$ values assumed, assuming βHM to be monodisperse with N of 2000 and αHM to be a mixture of polymers with N of 3000 (60 wt %) and 200 (40 wt %) (see text).

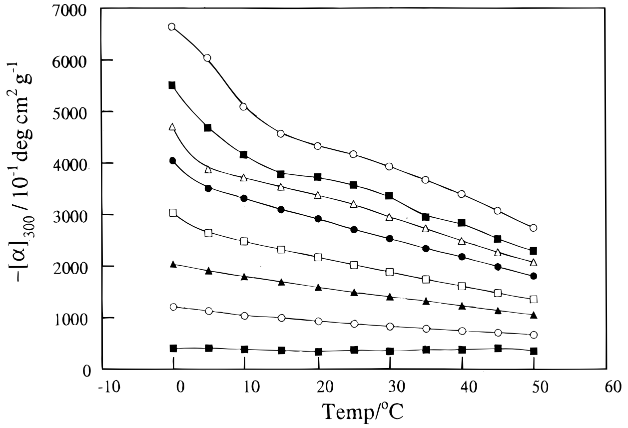

Figure 2. Temperature dependence of $[\alpha]_{300}$ for fractionated αPdHIC in hexane. $N_w = 3315$, 1318, 767, 456, 313, 212, 127, and 39.2 from top to bottom.

For αPdHIC the hexane curve shows an upswing below 10 °C, which is characteristic of the hexane solution and may be related to aggregation.[30] In toluene, the measurements were made between 0 and 90 °C. For both polymers, the magnitude of $[\alpha]_{300}$ is rather large at low temperatures but decreases steadily with increasing temperature. Within the temperature range examined, the polymer was stable and gave reproducible temperature variation of OR. The stability of the polymer was also supported by viscosity measurement on a PHIC sample.

Molecular Weight Dependence of Optical Rotation. Figure 2 shows the temperature dependence of $[\alpha]_{300}$ for fractionated samples of indicated N_w in hexane. For either sample, $-[\alpha]_{300}$ is larger for higher molecular weight samples and increases monotonously with decreasing temperature down to 10 °C, but shows an upswing below this temperature just as shown above with the unfractionated sample. At a fixed temperature, $-[\alpha]_{300}$ shows a remarkable molecular weight dependence. Figure 3 illustrates this molecular weight dependence in 1-chlorobutane at fixed temperatures more clearly by plotting $-[\alpha]_{300}$ against $1/N_w$. It can be seen that $-[\alpha]_{300}$ increases rapidly with N_w at low N_w and approaches an asymptotic limit at high N_w. Figure 4 presents similar optical rotation data for αPdHIC in dichloromethane, which resembles closely Figure 2. Essentially the same feature noted in Figure 3 is seen for either system,and indeed this is the characteristic behavior common to αPdHIC and βPdHIC[27] at all the solvent conditions examined.

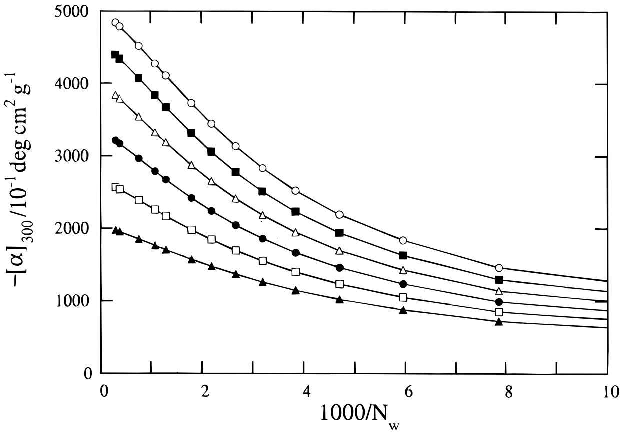

Figure 3. Plots of $[\alpha]_{300}$ vs $1/N_w$ for fractionated αPdHIC in 1-chlorobutane at 0, 10, 20, 30, 40, and 50 °C from top to bottom.

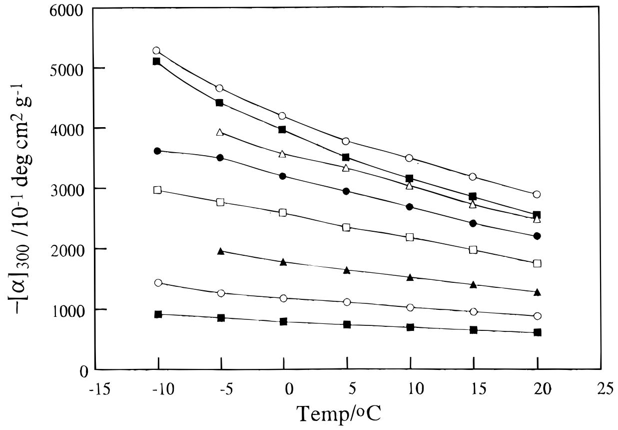

Figure 4. Temperature dependence of $[\alpha]_{300}$ for fractionated αPdHIC in dichloromethane. $N_w = 3315$, 1318, 555, 375, 260, 168, 92, and 62.9 from top to bottom.

Discussion

Theoretical Background. It has been shown in the previous paper[27] that such molecular weight dependence of $[\alpha]_{300}$ for βPdHIC as that shown in Figure 2 can be described quantitatively by the statistical mechanical theory,[23] and it is naturally expected to hold for the experimental data of αPdHIC presented in Figures 2−4. In this theory, it is assumed that a polyisocyanate chain consists of alternating sequences of left-handed and right-handed helical conformations and the optical activity arises from the presence of the helical conformation of a particular sense in excess of the other. The expression for $[\alpha]$ reads

$$[\alpha]/[\alpha]_m = (\delta u/w)\frac{1 - a\exp(-2wN) - b[1 - \exp(-2wN)]/wN}{1 + a\exp(-2wN)} \qquad (1)$$

with

$$\delta u = (1/2)(u_P - u_M), \qquad w = (\delta u^2 + \nu^2)^{1/2}$$

$$a = (w - \nu)/(w + \nu), \qquad b = \nu/(w + \nu) \qquad (2)$$

where $[\alpha]_m$ is the maximum value obtained by $[\alpha]$ when all helices have only one sense. Here δu, w, and a and b are functions of T only in a given solvent, which may be obtained from the two independent free energy functions $\Delta G_h(T)$ and $\Delta G_r(T)$ through the statistical weights of eq 3 as follows:

$$u_M = \exp[-\Delta G_h(T)/RT], \qquad u_P = 1/u_M$$

$$\nu(T) = \exp[-\Delta G_r(T)/RT] \qquad (3)$$

where T and R are the absolute temperature and gas constant, respectively. As in the previous study,[27] M and P refer to the left-handed and right-handed helices, respectively, and $2\Delta G_h(T)$ is defined by $2\Delta G_h(T) = G_M(T) - G_P(T)$, where $G_M(T)$ and $G_P(T)$ are the free energies of the monomer units in the left-handed and right-handed helices, respectively. To be consistent with this convention, $[\alpha]_m$ represents the $[\alpha]$ for the perfect right-handed helix and hence is positive.

On the other hand, $\Delta G_r(T)$ is the free energy of the reversal unit measured from $(1/2)(G_M(T) + G_P(T))$. Since $2\Delta G_h(T)$ was found to be less than 1 cal/mol for βPdHIC, the excess presence of a particular sense would be a rare event on the monomer level, while the helix reversal would seldom occur because of large $\Delta G_r(T)$.[27]

Comparison between Experiment and Theory. According to eq 1, $[\alpha]$ is a known function of N with the three parameters, $[\alpha]_m$, $\Delta G_h(T)$, and $\Delta G_r(T)$, which are numerical constants under a given solvent condition. In principle, it would be possible to verify the validity of the theory by comparing eq 1 with experimental $[\alpha]_{300}$ vs N relationships under fixed solvent conditions and to determine the values of the parameters involved under the specified condition. This is true only when the theoretical curve is sensitive enough to the variations of the parameter values and the data are sufficiently accurate. This was not the case with βPdHIC studied before. We could not find this possibility with the data for αPdHIC under all the solvent conditions examined; the data were not accurate enough to permit such an analysis.

Therefore we follow the same process as that in the previous study, that is, to assume $[\alpha]_m$ as a numerical constant and regard $\Delta G_h(T)/RT$ and $\Delta G_r(T)/RT$ as adjustable parameters for a given solvent condition. We assume that $[\alpha]_m$ would be inherent to the amide backbone irrespective of alkyl side chains but depend on solvent and try to determine $[\alpha]_m$ using some reference helical polyisocyanates with no helix reversal. We choose again poly((*R*)-2,6-dimethylheptyl isocyanate) (PNIC) for this purpose, which was suggested to have no helix reversal in ordinary organic solvents, i.e., to be in a purely left-handed helical conformation,[28,31] taking $[\alpha]_m$ to be 7420, 6240, and 5590 10^{-1} deg cm^2 g^{-1}, respectively, for hexane, 1-chlorobutane, and dichloromethane. With this assumption, we are left with only two theoretical parameters, u_M and ν, at a given temperature T. Trial-and-error procedures were repeated with the data at each temperature in Figure 5 until the standard percent deviation σ was minimized, and the resulting values of u_M and ν were taken as optimal. Figure 5 compares the experimental data (symbols) with the theoretical values (curves) calculated by eq 1 for the optimal parameter values so determined. It is seen that the experimental and theoretical $[\alpha]_{300}$ agree satisfactorily, thus validating the theory[23] for this system; the standard deviation σ is 4.3 ± 1.0%. Analyses were performed on the data given in Figures 2 and 4 as well with a similar agreement, with σ being 3.4–6.8% for the data in Figures 2 and 4, respectively. Fragmentary data in DCM at −10 °C have not been used for the analysis. However, it should be noted in Figure 4 that the data points for higher molecular weights tend to deviate upward just as seen in Figure 2 for hexane solutions. At present, it is not clear whether this is also related to gelation or not.

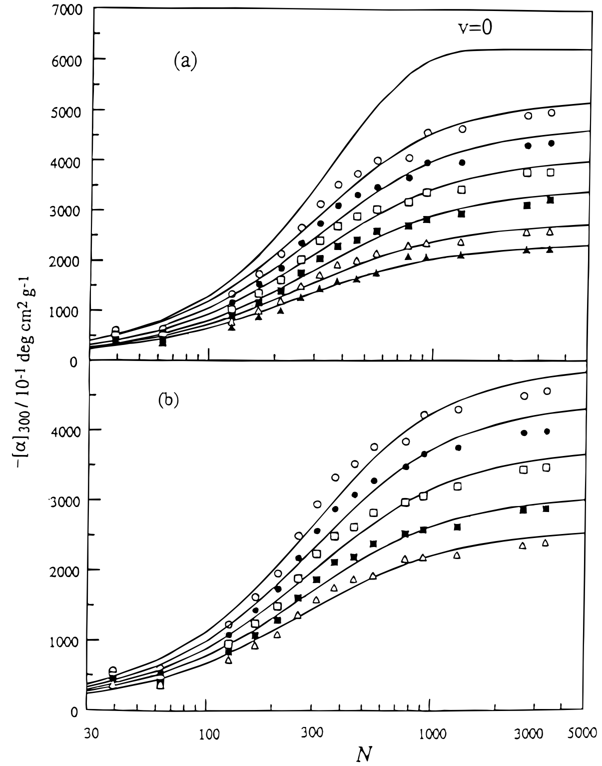

Figure 5. Comparison of theory and experiment for $[\alpha]_{300}$: (a) at 0, 10, 20, 30, 40, and 50 °C from top to bottom; (b) at 5, 15, 25, 35, and 45 °C from top to bottom. Symbols, experimental data for αPdHIC in 1-chlorobutane; solid curves, theoretical values calculated with the optimal parameter values derived (cf. Figure 6) and $[\alpha]_m = 6240 \times 10^{-1}$ deg cm^2 g^{-1}. The curve with $\nu = 0$ represents the theoretical values for $\nu = 0$ with the same values for the other parameters.

Temperature Dependence of $\Delta G_h(T)$ and $\Delta G_r(T)$. Figure 6 shows plots of $2\Delta G_h(T)/RT$ and $\Delta G_r(T)/RT$ against $1/T$ for αPdHIC in hexane, 1-chlorobutane, and DCM solutions (filled marks). It is seen that the values of $2\Delta G_h(T)/RT$ and $\Delta G_r(T)/RT$ change significantly with $1/T$ within the range of T investigated for either solvent and are represented reasonably well by linear equations of $1/T$, which read

$$2\Delta G_h(T)/RT = a_h + b_h/T, \qquad \Delta G_r(T)/RT = a_r + b_r/T \qquad (4)$$

where a_i and b_i (i = h and r) are numerical parameters.

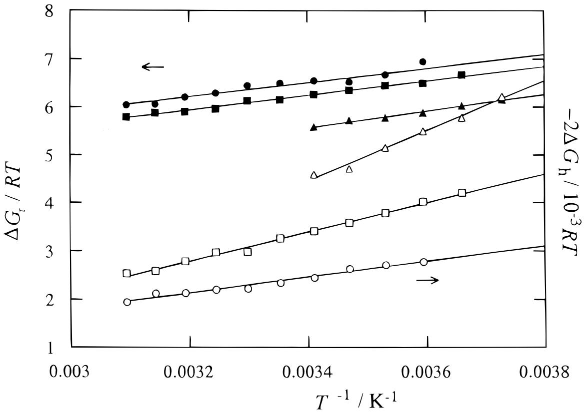

Figure 6. Temperature dependence of $2\Delta G_h(T)/RT$ and $\Delta G_r(T)/RT$ for αPdHIC. Open and filled symbols, experimental data for $2\Delta G_h(T)/RT$ and $\Delta G_r(T)/RT$, respectively, in hexane (○,●), 1-chlorobutane (□,■), and DCM (△,▲); curves, values calculated by eq 4 with the values for a_i and b_i given in Table 2.

For the hexane solutions, the values of $2\Delta T_h(T)/RT$ at 0 and 5 °C have not been used in this analysis, because they deviate significantly above the straight lines. This may be related to the gelation found by Green et al.[30] The data of $\Delta G_r(T)/RT$ for βPdHIC are reproduced from our previous paper.[27] Table 2 summarizes the best-fit values for these parameters in the three solvents investigated in comparison with those for βPdHIC calculated similarly. It is seen in Figure 6 that $2\Delta G_h(T)/RT$ depends significantly on solvent with a smaller dependence in $\Delta G_r(T)/RT$.

Figures 7 and 8 show comparison of experiment and theory with the $[\alpha]_{300}$ data for fractionated αPdHIC in hexane and DCM. Here the experimental data (symbols) are seen to be fitted reasonably well by theoretical curves calculated from eq 1 with the parameters given by eq 4 (Table 2) along with the $[\alpha]_m$ values given above; the agreement between experimental and calculated values is accurate to 3−7%. The agreement was better for the 1-chlorobutane data.

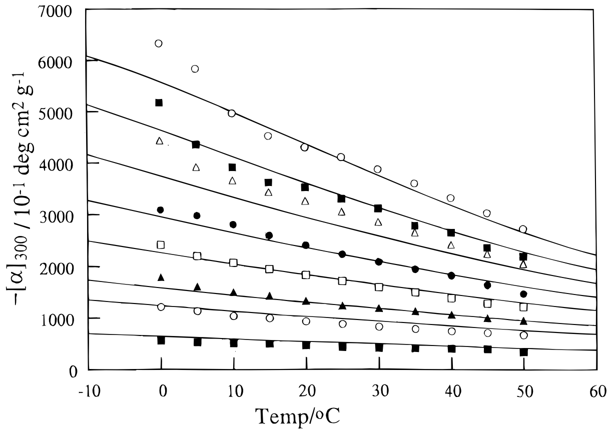

Figure 7. Temperature dependence of $[\alpha]_{300}$ for αPdHIC fractions in hexane. Symbols, experimental data for $N = 2613$, 920, 555, 375, 260, 168, 127, and 62.9 from top to bottom; solid curves, theoretical values calculated with the parameter values given in Table 2 and $[\alpha]_m = 7420 \times 10^{-1}$ deg cm^2 g^{-1}.

Figure 1 presents the data for high molecular weight unfractionated samples αHM (polymer **1**) and βHM (polymer **2**). It was impossible to fit these data to eq 1 for monodisperse samples using their N_w values given in Table 1 (15 200 for αHM and 19 500 for βHM). This is obviously due to the polydispersities of these HM samples. Since no detailed information was available about the polydispersities, we have assumed βHM to be monodisperse with N of 2000 and αHM a mixture of polymers with N of 3000 (60 wt %) and with N of 200 (40 wt %). Since no parameter values are available for toluene, they have been replaced by the 1-chlorobutane values with an appropriate value of 6800 10^{-1} deg cm^2 g^{-1} assumed for the magnitude of $[\alpha]_m$. The solid curves in Figure 1 represent the values of $[\alpha]_{300}$ calculated in this way, which fit the data points (symbols) nicely for both polymers in every solvent tested. However, the fitting is poor for αHM in hexane for some unknown reason.

Table 2. Free Energy Parameters for Poly((*R*)-1-deuterio-*n*-hexyl isocyanate) and Poly((*R*)-2-deuterio-*n*-hexyl isocyanate) in the Indicated Solvents

free energy functions	poly((*R*)-1-deuterio-*n*-hexyl isocyanate)			poly(*R*)-2-deuterio-*n*-hexyl isocyanate)[a]		
	hexane	1-chlorobutane	dichloromethane	hexane	1-chlorobutane	dichloromethane
$2\Delta G_h/RT$						
$a_h/(\mathrm{K}^{-1})$	0.0031	0.0069	0.0134	−0.0020	−0.0032	−0.0040
$b_h/(\mathrm{K}^{-2})$	−1.64	−3.02	−5.25	0.98	1.42	1.62
$\Delta G_r/RT$						
$a_r/(\mathrm{K}^{-1})$	1.49	1.07	−0.34	1.85	1.57	1.97
$b_r/(\mathrm{K}^{-2})$	148	1520	1740	1410	1320	1040

[a] Reanalysis of the data reported in ref 27.

Table 3. Free Energy Parameters and Statistical Averages for Poly((*R*)-2-deuterio-*n*-hexyl isocyanate) and Poly((*R*)-1-deuterio-*n*-hexyl isocyanate) in Solution

	poly((*R*)-1-deuterio-*n*-hexyl isocyanate)			poly((*R*)-2-deuterio-*n*-hexyl isocyanate)		
	hexane	1-chlorobutane	dichloromethane	hexane	1-chlorobutane	dichloromethane
$2\Delta H_h/(\mathrm{cal\ mol}^{-1})$	−3.25	−6.01	−10.4	1.94	2.82	3.22
$2\Delta S_h/(\mathrm{cal\ K}^{-1}\ \mathrm{mol}^{-1})$	−0.0062	−0.014	−0.027	0.0040	0.0063	0.0080
T_h/K	530	440	390	480	450	400
			20 °C			
$2\Delta G_h/(\mathrm{cal\ mol}^{-1})$	−1.40	−2.0	−2.60	0.76	0.97	0.91
$\Delta G_r/(\mathrm{cal\ mol}^{-1})$	3800	3640	3250	3870	3530	3210
u_M/u_P	1.0025	1.00340	1.00450	0.99870	0.99830	0.99840
ν	0.0015	0.00190	0.0038	0.0013	0.0024	0.0040
			20 °C, $N = 2000$			
n_M/n_P	3.7	4.1	2.9	0.45	0.54	0.70
$[\alpha]/[\alpha]_m$	−0.573	−0.610	−0.488	0.375	0.315	0.196
n_ν	2.40	3.1	6.6	2.4	4.5	8.0

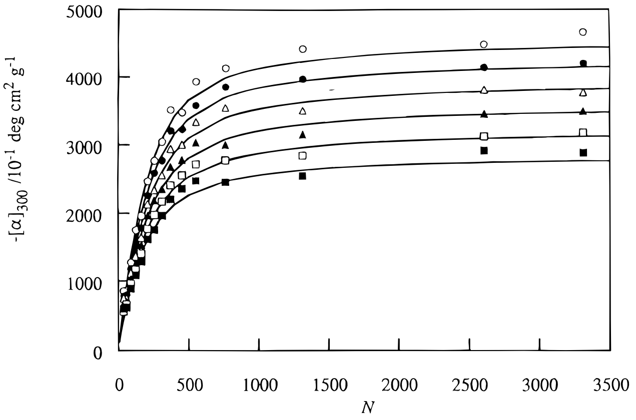

Figure 8. Chain length dependence of $[\alpha]_{300}$ for αPdHIC fractions in dichloromethan at −5, 0, 5, 10, 15, and 20 °C from top to bottom. Symbols, experimental data; solid curves, theoretical values calculated with the parameter values given in Table 2 and $[\alpha]_m = 5590 \times 10^{-1}$ deg cm^2 g^{-1}.

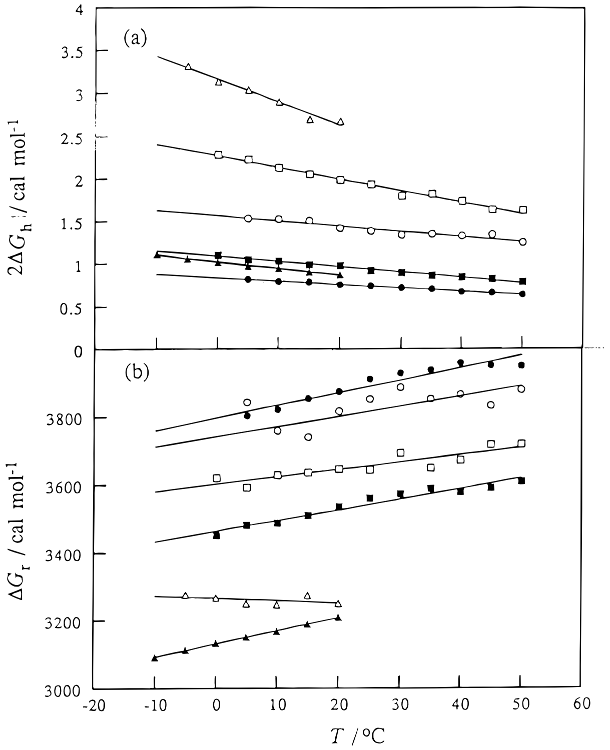

Figure 9. Comparison of $2\Delta G_h(T)$ and $\Delta G_r(T)$ between αPdHIC and βPdHIC. Open and filled symbols for αPdHIC and βPdHIC, respectively, in hexane (○,●), 1-chlorobutane (□,■), and DCM (△,▲); curves, values calculated by eq 4 (Table 2).

Equation 4 is represented alternatively by

$$\Delta G_h(T) = \Delta H_h - T\Delta S_h \tag{5}$$

where ΔH_h and ΔS_h are the corresponding enthalpy and entropy, respectively. Thus if follows that $\Delta G_h(T)$ should vanish at the temperature T_h defined by $T_h = \Delta H_h/\Delta S_h = -b_h/a_h$ if these parameters are temperature independent.

Comparison between αPdHIC and βPdHIC. Figure 9 compares the free energy differences $\Delta G_h(T)$ and $\Delta G_r(T)$ between polymers **1** and **2**. It is seen that $\Delta G_h(T)$ is of the order of less than a few cal/mol, whereas $\Delta G_r(T)$ is 3000 cal/mol or larger. It is also noticed that the former differs more than twice between the two polymers, but there is no such large difference in the latter. Table 3 compares statistical mechanical parameters and conformational averages (at 20 °C) for polymers **1** and **2**. It is seen that T_h is located around 470 K for the two polymers studied. This implies that αPdHIC would prefer the right-handed helical conformation for entropy reasons, whereas βPdHIC would prefer the left-handed helix, and the helix sense reversal would occur at T_h. The data for toluene solutions in Figure 1 appear to conform to this implication; $[\alpha]_{300}$ for βPdHIC at 90 °C is as small as 7% of that of the perfect helix, although no helix sense reversal is seen in the temperature range examined. In this regard, it is noted that the helix sense reversal is not inherent to polyisocyanates but well-known for polyaspartate derivatives[32,33] with a molecular theoretical interpretation.[34]

Concluding Remarks. The large optical rotation in polymers **1** and **2** arises from a hydrogen−deuterium isotope effect resulting from the stereospecific substitution of hydrogen with deuterium on the hexyl side chain; this is unique because here only 1 hydrogen atom among 13 atoms is replaced by a deuterium atom. The effect is larger for polymer **1** than for polymer **2**, as seen from the magnitude of [α] (see, e.g., Figure 1), that of ΔG_h (see Table 3 and Figure 9), etc. On the other hand, ΔG_r is almost the same for the two polymers under a given solvent condition but depends largely on solvent and temperature (see Figure 9). Thus we conclude that the helix reversal is common to polyisocyanates with hexyl side chains but the hydrogen−deuterium isotope effect on optical rotation appears only through ΔG_h. In terms of ΔG_h, the effect is diminished as the location of the deuterium atom is removed from the main chain. This is compatible with the empirical force field calculation of Lifson et al.,[28] who showed that the main chain has significant interactions determining its helical conformation only up to the γ-carbon atom and carbon atoms attached to it. Since the magnitude of $2\Delta G_h$ is at most a few calories per mole, it has only a marginal contribution to the imbalance in helix sense on the monomer level (see the values of u_M/u_P very close to unity). Thus the extraordinarily large optical rotation, resulting from the large imbalance in number between the monomer units in the M and P helices, n_M/n_P, which amounts to as much as 4.1 for αPdHIC in 1-chlorobutane, is due to accumulation of such a small energy over a great number of monomer units assisted by the helix reversal. With respect to u_M/u_P, the deuterated poly(hexyl isocyanate)s make a sharp contrast with poly((*R*)-2,6-dimethylheptyl isocyanates), which is suggested to be almost perfectly left-handed[28,31] and may be characterized by a much larger $2\Delta G_h$ of about 100 cal/mol.[35]

It may be added that since deuterium substitution for the higher rather than the lower frequency diastereotopic hydrogen at either C-1 or C-2 yields the lower energy state,[36] we could assign relative frequencies to these C−H groups. Considering though the magnitude of the energies (ΔG_h) an a priori prediction of such a difference would be very difficult.[26]

It has been shown that the persistence length of poly(hexyl isocyanate) in the solvents considered increases in the order of DCM, 1-chlorobutane, toluene, and hexane.[37] We have some evidence indicating that in terms of persistence length the chain stiffness is unaffected by deuteration.[29] Therefore one may be tempted to consider that the chain stiffness is in parallel with ΔG_h or ΔG_r or both. However, we defer to discuss this correlation until more detailed data of chain dimensions become available.

Supplemental material compiling the original data is available from A.T. upon request (e-mail: teramoto@chem.sci.osaka-u.ac.jp).

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(37) The persistence length of poly(hexyl isocyanate) is 21 nm in DCM at 20 °C,[7] 35 nm in 1-chlorobutane,[5] 37 nm in toluene,[7] and 42 nm in hexane at 25 °C.[4]

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