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Optical Rotation of Random Copolyisocyanates of Chiral and Achiral Monomers: Sergeant and Soldier Copolymers[†]

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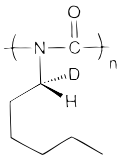
ABSTRACT: Optical rotation (OR) of random copolymers of chiral 2,6-dimethylheptyl isocyanate (NIC) and achiral hexyl isocyanate (HIC) was measured as a function of mole fraction *x* of the chiral monomer, temperature, and molecular weight, with hexane, 1-chlorobutane, and dichloromethane as the solvents. The data as a function of molecular weight were analyzed by the statistical mechanical theory of copolymers developed (Gu, H.; et al. *Polym. J.* **1997**, *29*, 77−84), in which a polyisocyanate chain is modeled by an alternating sequence of left-handed and right-handed helices occasionally interrupted by helical reversals. The theory involves two parameters, the left-handed−right-handed free energy bias, $2\Delta G_h$, and the helical reversal free energy, ΔG_r. With appropriate values for these parameters, the experimental OR values were well described by the theory. When compared with poly((*R*)-*i*-deuterio-*n*-hexyl isocyanate ($i = 1, 2$), the values of ΔG_r were nearly the same but those of $|2\Delta G_h|$ were much larger: 71 ± 14 cal/mol for the terpene derived chiral unit vs 1~2 cal/mol for the deuterated chiral monomer units. These free energy values are reasonable considering the chemical structures of the respective chiral monomer units.

Introduction

Incorporation of chiral monomer units into achiral polyisocyanates induces remarkable optical activity in the copolymers, which changes disproportionately with the mole fraction of the chiral monomer.[1−4] This is due to the chiral perturbation of the chiral units forcing the achiral units to adopt the helical conformation with the same sense as itself. The chiral unit is referred to as a sergeant because it forces the achiral unit, a soldier, to adopt a particular helical conformation, thus the resulting polymer is referred to as a sergeant and soldier copolymer.[1] It has been argued[3−5] that the optical activity of polyisocyanates arises from an excess presence of the helical conformation of one particular sense over that of the other and the sense of the helix depends on the side chain. In the present case, the two monomer units share the same backbone with different side chains for each monomer type. The chain consists of an alternating sequence of left-handed and right-handed helices separated by helical reversals with one helical sense in excess. Selinger and Selinger[6,7] and Gu *et al.*[8] have shown that these polymers can be treated as typical linear Ising systems just as for the poly((*R*)-*i*-deuterio-*n*-hexyl isocyanates) ($i = 1$ or 2, α,*β*PdHIC) (**1** or **2**) discussed recently.[9−11] The optical activities arise from their helical conformations, and the system can be described by standard procedures in statistical mechanics.[12−14] Indeed, these studies have elucidated the molecular mechanism that the disproportionate optical activity change is due to the perturbation by the chiral units to favor one helical sense, and this is amplified on the polymer chain by the difficulty of the occurrence of a helical reversal. However, in the previous discussions[1,6−8] a detailed numerical analysis was hampered by the lack of information about the molecular weight dependence of the optical activity, and as shown previously,[9−11] such data are crucial in characterizing polymer systems that behave as linear Ising systems. This situation motivated us to carry out a series of systematic studies of the sergeant and soldier copolymers with particular emphasis on the molecular weight dependence of the optical rotation (OR). The present study is concerned with the random copolymers of (*R*)-2,6-dimethylheptyl isocyanate (NIC) and *n*-hexyl isocyanate (HIC) (**3**) and those of (*R*)-1-deuterio-*n*-hexyl isocyanate (αdHIC) and HIC (**4**), both of which were synthesized as described elsewhere.[1,2] The copolymers of NIC and HIC are referred to as a NH*x*/*y*, and those of αdHIC and HIC to as αdHIC/HIC*x*/*y*, where *x* and *y* stand for the mole percent of chiral and achiral monomer units, respectively. Detailed OR data for the sergeants and soldiers random copolymers are presented and analyzed in terms of the theory for polymers of type 1 developed in the preceding study,[8] which is an extension of Lifson *et al.*'s theory[9] of homopolymers.



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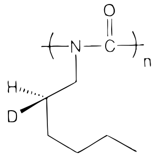

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[†] Taken in part from the doctoral thesis of Hong Gu, Osaka University, 1997.

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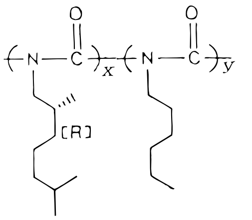

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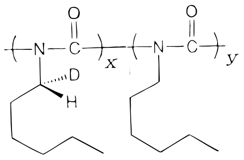

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In passing, we note that similar disproportionate OR changes have been reported for chiral−achiral polysilanes,[15−17] and D,L-copolypeptides.[18−20]

Experimental Section

Polymer Samples. One PNIC sample of 600 000 molecular weight, six random copolymers of HIC and NIC, NH*x*/*y*, and two random copolymers of HIC and αdHIC, αdHIC/HIC*x*/*y* (x = the mole percent of NIC or αdHIC), were synthesized as described.[1,2] The samples NH37/63, NH15/85, NH4/96, NH2.3/97.7, NH1/99, αdHIC/HIC74/26, and αdHIC/HIC25/75 were separated into three parts by fractional precipitation with benzene as the solvent and methanol as the precipitant. Each middle part designated below as NH*x*/*y*(MF) (middle fraction) was used for the optical rotation measurements. An unfractionated sample NH0.5/99.5(UF) was used as prepared.[1,2] Finely fractionated samples were obtained as follows. About 20 mg of a PNIC sample of 600 000 molecular weight was degraded by trifluoroacetic acid in chloroform and separated into fifteen fractions on a preparative gel permeation chromatograph (GPC) following the procedure employed for βPdHIC[10] and αPdHIC.[11] The polymer samples PNIC(F*i*) (i = 1−15) were recovered from the solutions eluted from GPC by evaporating the solvent, washing with methanol, and drying in vacuo. Samples NH37/63 and NH4/96 were treated in the same way to obtain 15 and 14 fractionated samples, respectively, NH*x*/*y*(F*i*) (i = 1−15 and 1−14).

Preparation of Polymer Solutions and Concentration Determination. Solutions of the middle fractions were prepared by mixing weighed amounts of the polymer and the solvent in a stoppered flask with their mass concentrations c determined gravimetrically. Solutions of the fractionated samples were prepared by adding appropriate amounts of the solvent to the dried sample. Their mass concentrations were determined from the optical density at 252 nm $[\mathrm{OD}]_{252}$ using the relation

$$[\mathrm{OD}]_{252} = g\gamma_0(1 - B/M)c \qquad (1)$$

where M is the molecular weight of the sample, $\gamma_o = 3.08 \times 10^4$ cm^3 g^{-1} and $B = 2.50 \times 10^3$. This relation with $g = 1$ was established for PHIC using a series of samples with different molecular weights.[10,11] It was found, however, that the UV spectrum of NH*x*/*y* shows a blue shift with increasing NIC content and $[\mathrm{OD}]_{252}$ for the copolymer is smaller than that for PHIC. Since the amounts of the fractionated samples were too small to determine this calibration curve directly for each copolymer, we assume that eq 1 is valid for every copolymer but with different g values. The values of g have been determined from $[\mathrm{OD}]_{252}$ of middle fractions of sufficiently high molecular weights: $g = 0.78$ for PNIC, $g = 0.9$ for NH37/63, and $g = 1$ for NH4/96.

Molecular Weight and Molecular Weight Distribution. For the middle fractions the weight-average molecular weights M_w were determined by light scattering and the viscosity-average molecular weights M_v were estimated from the intrinsic viscosities in hexane at 25 °C using the intrinsic viscosity−M_w relationships established for each copolymer elsewhere.[21,22] These data were converted to degree of polymerization N (N_w or N_v) by $N = M/M_0$, where M_0 is the molecular weight of the monomer unit (for copolymers, $M_0 = (xM_{\mathrm{chiral}} + yM_{\mathrm{HIC}})/100$, with M_{chiral} or M_{HIC} being the monomer molecular weights of the chiral and achiral units, respectively). The intrinsic viscosities $[\eta]$ and N_w of the middle fractions thus obtained are summarized in Table 1. Fractionated samples on the other hand were analyzed by GPC to obtain their M_w and molecular weight distributions following the procedure established elsewhere.[21,22] However the $N_w < 100$ evaluated in this way were not reliable and will not be used for quantitative discussions to follow.

Table 1. Polymer Samples Used for Optical Rotation Measurements[a]

polymer	$[\eta]/10^{-2}$ cm^3 g^{-1} (hexane at 25 °C)	$10^{-3}N_w$
Unfractionated Samples or Middle Fractions		
PNIC(MF)	4.03	8.6[a]
NH37/63(MF)	53.8	9.96[a]
NH15/85(MF)	66.6	14.3[a]
NH4/96(MF)	29.5	5.18[a]
NH2.3/97.7(MF)	35.5	6.25[b]
NH1.0/99.0(MF)	59.8	11.4[b]
NH0.5/99.5(UF)		8.65[c]
αdHIC/HIC76/24(UF)	66.6	13.3[b]
αdHIC/HIC25/75(UF)	59.8	11.6[b]
α104(MF)	46.5	8.13[a]
β250(MF)	86.8	19.5[a]
Fractionated Samples		
PNIC(F*i*)		0.029−2.03[d]
NH37/63(F*i*)		0.018−2.05[d]
NH4/96(F*i*)		0.038−4.15[d]

[a] The data obtained by (a) light scattering, (b) intrisic viscosities in hexane at 25 °C,[21] (c) Michael P. Reidy, Ph.D. Thesis, Polytechnic University, 1991,[2] and (d) by GPC (the N_w below 80 are less reliable).

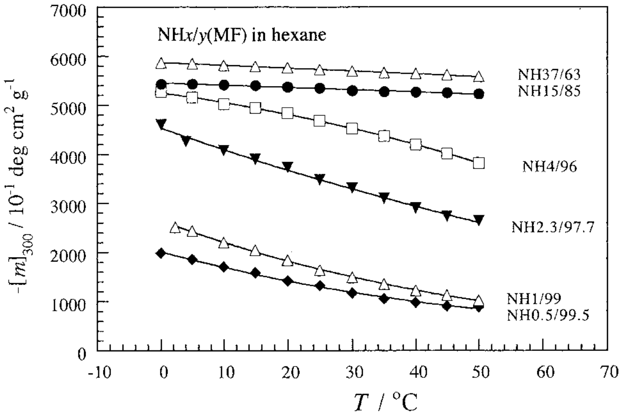

Figure 1. Plots of $-[m]_{300}$ vs temperature for NH*x*/*y*(MF&UF) in hexane.

Optical Rotation Measurement. Optical rotation measurements were made on an ORD/UV-5 spectropolarimeter to obtain specific rotations at 300 nm $[\alpha]_{300}$ expressed in units of 10^{-1} deg cm^2 g^{-1}. However, it is more appropriate to express it on a *monomer mole base*, since the optical activity of the polyisocyanate is due to the excess of one helical sense, that is, the *relative number of monomer units* in the right-handed and left-handed helical conformations.[8−11] Therefore, we use the quantity $[m]_{300}$ defined by $[m]_{300} = (M_0/128)\,[\alpha]_{300}$, with αPdHIC taken as the reference. This is also expressed in units of 10^{-1} deg cm^2 g^{-1}.

Experimental Results

Middle Fractions and Unfractionated Polymers.

Optical rotation measurements were made on solutions of unfractionated or roughly fractionated polymers (middle fractions) in hexane, 1-chlorobutane, dichloromethane, and toluene in the range of temperature between 0 and 50 °C. Figure 1 shows the plots of $-[m]_{300}$ vs temperature for NH*x*/*y*(MF&UF) in hexane. As is shown by the negative sign of $[m]_{300}$, these

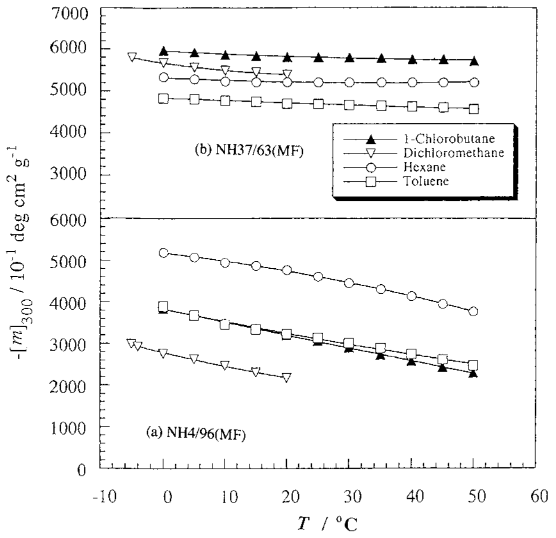

Figure 2. Plots of $-[m]_{300}$ vs temperature for NH*x*/*y*(MF) in different solvents.

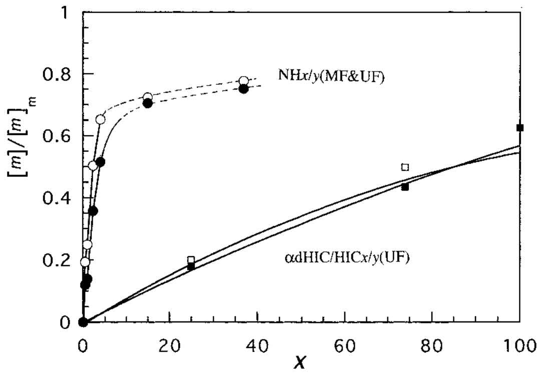

Figure 3. Plots of $[m]/[m]_m$ vs x: (○ and ●) NH*x*/*y*(MF&UF) in hexane at 20 and 50 °C; (□ and ■) αdHIC/HIC(UF) in hexane and 1-chlorobutane at 20 °C. Curves for NH*x*/*y*(W) are eye-guides; curves for αdHIC/HIC(UF) are theoretical values (cf. Figure 11).

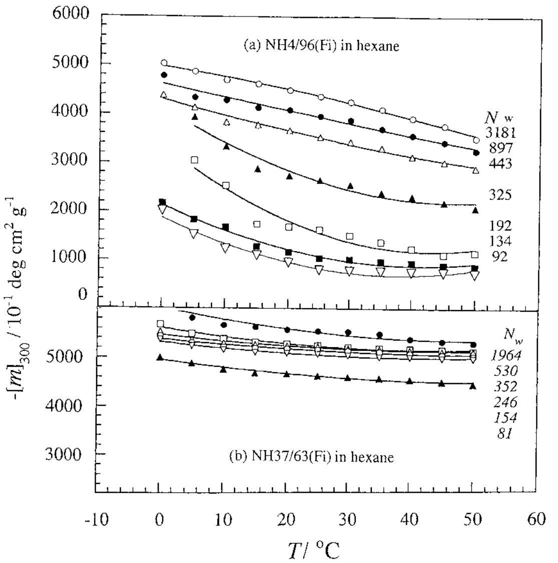

Figure 4. Plots of $-[m]_{300}$ vs temperature for fractionated NH*x*/*y*(F*i*) in hexane: (a) NH4/96(F*i*); (b) NH37/63(F*i*). Curves are eye-guides.

polymers prefer the left-handed helix, as does PNIC.[21,23,24] It is see that $-[m]_{300}$ is larger for larger NIC content (x), and those for NH37/63(MF) and NH15/85(MF) are largest and change little with temperature. The temperature dependence is most remarkable for NH2.3/97.7(MF) and tends to become gradual with the decrease in x. However, it is noted that the copolymer containing only 0.5% NIC, NH0.5/99.5(UF), shows a significant optical activity change with temperature. Figure 2 shows the temperature dependence of $-[m]_{300}$ for NH37/63(MF) and NH4/96(MF) in the four solvents indicated. Although $-[m]_{300}$ is different for the different solvents, it is larger for NH37/63(MF) than for NH4/96(MF) and there is almost no temperature dependence for NH37/63(MF) in each solvent. This is the same trend as noted for the hexane solutions in Figure 1. Furthermore, the solvent dependence is more conspicuous for NH4/96(MF) than for NH37/63(MF).

As previously found,[1] $[m]$ changes disproportionately with the mole percent x of the chiral monomer. This has been confirmed by the data shown in Figures 1 and 2. Indeed, it is more explicitly illustrated in Figure 3, where $[m]/[m]_m$ is plotted against x; $[m]_m$ is the value of $[m]$ for the perfect left-handed helix. For NH*x*/*y*(MF&UF), $[m]/[m]_m$ initially increases very rapidly with x but tends to level off for $x > 10\%$. OR measurements were also made on high-molecular-weight αdHIC/HIC*x*/*y*(UF) and αPdHIC(UF). A portion of such data at 20 °C in hexane and 1-chlorobutane are presented in Figure 3. This system shows a nearly proportionate change of $[m]/[m]_m$ with x. Unlikely NH*x*/*y* with $x \geq 37\%$, all the other samples of NH*x*/*y*(MF) showed a significant temperature dependence of $[m]/[m]_m$. The above data for NH*x*/*y*(MF) confirm the previous finding[1] for the same system on the change in the $[\alpha]_D$ values.

Fractionated Samples—Molecular Weight Dependence of Optical Rotation. In order to examine the chain length dependence of $[m]_{300}$, optical rotation measurements were made on a number of well-fractionated samples of PNIC(F1−15), NH37/63(F1−15), and NH4/96(F1−14) covering a wide range of N_w between 18 and 4150; N_w is the weight-average degree of polymerization $N_w = M_w/M_0$. Figure 4 shows the temperature dependence of $-[m]_{300}$ for NH4/96(F*i*) and NH37/63(F*i*) in hexane. For NH37/63(F*i*), $-[m]_{300}$ decreases slightly with temperature for either sample but the decrease from 10 to 50 °C is smaller than 8%. Except for the lowest and highest molecular weight samples, $-[m]_{300}$ changes little with molecular weight either. Considering this fact, we see $-[m]_{300}$ is almost constant for NH37/63(F*i*) under the solvent conditions examined. On the other hand, for NH4/96(F*i*) $-[m]_{300}$ decreases steadily with increasing temperature in the whole range; this change amounts to about 30% between 0 and 50 °C. It is clearly seen that $-[m]_{300}$ is larger for NH37/63(F*i*) than for NH4/96(F*i*). This is, of course, due to the larger amount of NIC units contained in the former, which induces a greater excess of one helical sense.

Similar data in 1-chlorobutane are presented in Figure 5, where $-[m]_{300}$ is plotted against N_w. As in hexane, $[m]_{300}$ in NH37/63(F*i*) changes only slightly with N_w for N_w larger than 100 nor with temperature. On the other hand the optical activity for NH4/96(F*i*) varys significantly with N_w and temperature. In Figure 6 the N_w dependence of $|[m]_{300}|$ in hexane at 25 °C is compared among PNIC(F*i*), NH*x*/*y*(F*i*), αPdHIC,[11] and βPdHIC.[10] It is seen that for every polymer $|[m]_{300}|$ increases first rapidly with N_w but tends to level off at some asymptotic value at larger N_w. However, the trend is very conspicuous for PNIC(F*i*) and NH37/63(F*i*), and in fact,

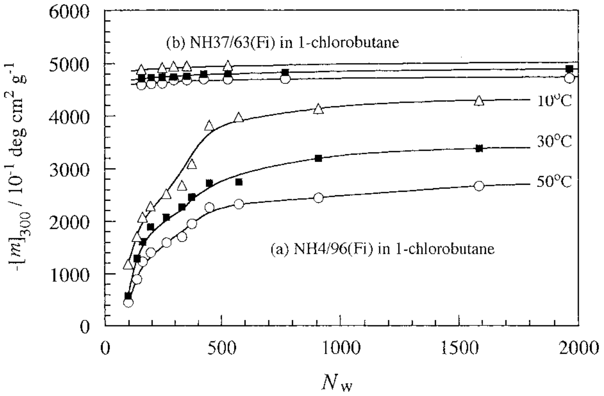

Figure 5. Plots of $-[m]_{300}$ vs N_w for fractionated NH*x*/*y*(F*i*) in 1-chlorobutane: (a) NH4/96(F*i*); (b) NH37/63(F*i*). Symbols: (△) 10 °C; (■) 30 °C; (○) 50 °C.

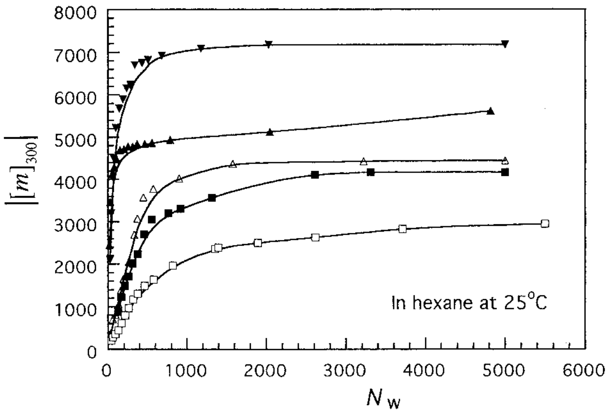

Figure 6. Comparison of N_w dependence of $|[m]_{300}|$ among NH*x*/*y*(F*i*), αdHIC/HIC*x*/*y*(F*i*), αPdHIC(F*i*), and *β*PdHIC(F*i*) in hexane at 25 °C. Symbols: (▼) PNIC(F*i*); (▲) NH37/63(F*i*); (△) NH4/96(F*i*); (■) αPdHIC(F*i*);[11] (□) *β*PdHIC(F*i*).[10]

$|[m]_{300}|$ increases first rapidly with N_w but ceases to change completely above $N_w = 200$. On the other hand, the rest of the samples show more gradual N_w dependence at larger N_w. It was found that $[m]_{300}$ for PNIC(MF) showed no detectable change in the range of temperature examined between 0 and 50 °C.[10,21,24] This resembles the behavior of NH37/63(MF) shown in Figures 1, 2, and 4. In passing, we have some reason to consider that the data for N_w below 80 for PNIC(F*i*), NH37/63(F*i*), and NH4/96(F*i*) are of questionable accuracy with respect to both N_w and $[m]_{300}$, and such data are omitted in Figures 4 and 5 and the quantitative discussion to follow.

Discussion

Analysis on the Basis of the Helical Reversal Model. We are here concerned with polyisocyanates of the same backbone structure −(NR−CO)− containing monomer units with chiral side chains. The polymer chains tend to be helical of either left-handed or right-handed sense, but the energetic equivalence of the helical sense is broken due to the perturbation from the chiral side chain. The copolymers, NH*x*/*y* and αdHIC/HIC*x*/*y* are random copolymers of chiral and achiral monomer units. Therefore, they are classified as a polymer of type 1 discussed in the preceding study.[8] First we analyze the data for NH4/96(F*i*) according to the theory previously developed.

For NH*x*/*y*, the chiral unit is 2,6-dimethylheptyl isocyanate (NIC) and the achiral unit is hexyl isocyanate (HIC). Following Lifson *et al.*'s theory,[9] the polymer chain is assumed to consist of an alternating sequence of M-helix (left-handed) and P-helix (right-handed) interrupted by helical reversal units and the optical activity arises only from the excess presence of the M-helix over the P-helix (the two-state model). The latter assumption may be reasonable from the fact that the OR of a monomer is negligible compared with that of the corresponding polymer.[5] Therefore, the optical rotation of the polymer, substantially arising from the helical conformation, is given by

$$[\alpha] = [\alpha]_m(2f_M - 1) \tag{2}$$

where $[\alpha]_m$ is the optical rotation of a perfect M-helix and f_M is the fraction of the units in the M-helix.

In the statistical mechanical treatment of this system on the basis of the above two-state model, each unit is given a 2 × 2 statistical weight matrix **M**, which reads

$$\mathbf{M} = \begin{pmatrix} u_M & vu_P \\ vu_M & u_P \end{pmatrix} \tag{3}$$

The components of the matrix are expressed as functions of temperature T as

$$u_M(T) = \exp(-G(T)_M/RT)$$
$$u_P(T) = \exp(-G(T)_P/RT) \tag{4a}$$

$$v(T) = \exp(-\Delta G(T)_r/RT) \tag{4b}$$

where $G(T)_M$ and $G(T)_P$ are the free energies of the units on the M- (left-handed) and P-helices (right-handed), respectively, and ΔG_r is the free energy of the helical reversal unit. It is noted that $G(T)_M$ and $G(T)_P$ do not appear separately but in pairs together as $2\Delta G_h(T) = G_M(T) - G_P(T)$, the free energy bias between the units in the M- and P-helices. Actually, the free energy reference is taken such that $G_M(T) = -G_P(T)$. In the theoretical treatment to follow, we assume that these free energies are characteristic of the type of the unit concerned but do not depend on its location on the polymer chain. This assumption may be justified for the present system of NH*x*/*y* with small *x*, where most chiral units are in the same environment, i.e., being sandwiched by achiral units, and there is little chance that they would appear in pairs, triplets, etc. This assumption may be also justified for αdHIC/HIC*x*/*y*, because the difference in chemical structure is minute between the two monomer units and $\Delta G_h(T)$ is found to be very small compared with RT.[10,11] For simplicity, furthermore, we assume that $v(T)$ is independent of the type and location of the unit. At present we find no a priori reason to justify the second assumption. However, we expect there would be no greater difference in $\Delta G_r(T)$ unless the side chain is very big. On these assumptions, theoretically $[m]/[m]_m$ $(=2f_M - 1)$ is given as a known function of N, with $\Delta G_h(T)/RT$ and $\Delta G_r(T)/RT$ as adjustable parameters.

NH4/96(F*i*). First we choose NH4/96(F*i*) to test the theory developed. As in the analysis of the data for αPdHIC and *β*PdHIC in the previous studies,[10,11] $[\alpha]_m$ or $[m]_m$ is estimated from $[\alpha]_{300}$ for PNIC of high molecular weight corrected for the average residue molecular weight: $[\alpha]_m = -7420$ for hexane, −6240 for 1-chlorobutane, and −5590 for dichloromethane, because PNIC is considered to be perfectly in the left-

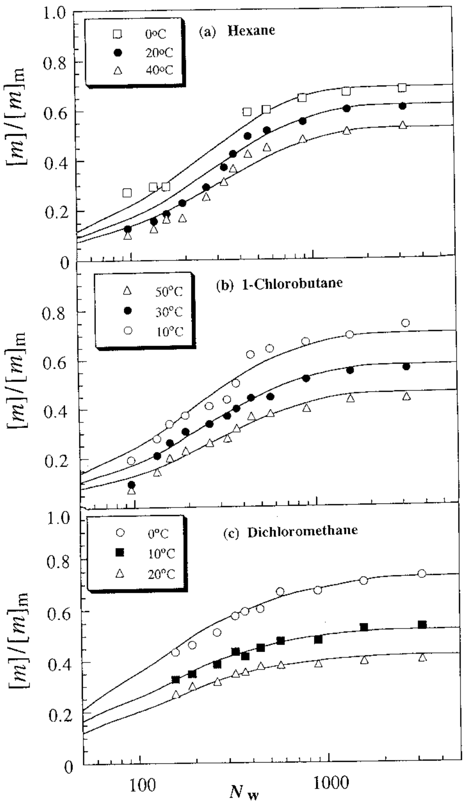

Figure 7. Test of the theory with $[m]_{300}$ data for NH4/96(F*i*): (symbols) experimental data; (curves) theoretical values with $2\Delta G_h(T)/RT$ and $\Delta G_r(T)/RT$ in the order of increasing temperature. The following pairs of figures in the parentheses represent the values of $2\Delta G_h(T)/RT$ and $\Delta G_r(T)/RT$ at the three temperatures for each solvent used for fitting the data: (a) hexane (−0.124, 6.19; −0.0976, 6.166; −0.0784, 6.119); (b) 1-chlorobutane (−0.145, 5.952; −0.103, 5.952; −0.0746, 5.992); (c) dichloromethane (−0.241, 5.522; −0.172, 5.203; −0.145, 5.150).

handed helix[23] with no helical reversal.[10,11,21,24] Thus we are left with the two adjustable parameters $\Delta G_h(T)$ and $\Delta G_r(T)$ for each solvent condition, i.e., at a given temperature for a specific solvent. For a sample with a given N and x, at least 10−20 random copolymer chains were generated and their average OR were calculated with appropriate values of $\Delta G_h(T)$ and $\Delta G_r(T)$ to fit best the series of data points for the solvent condition. Figure 7a illustrates typical results from such procedures for the data at the three temperatures in hexane; the values for $2\Delta G_h(T)/RT$ and $\Delta G_r(T)/RT$ are given in the legend with the order of increasing temperature. The agreement between experiment and theory is moderate and not very good for the lowest N_w of 96. Similar analyses were performed for the data in 1-chlorobutane and dichloromethane solutions with the results illustrated in Figure 7b,c, respectively. The agreement is satisfactory for both solvents. In this way the values of $\Delta G_h(T)$ and $\Delta G_r(T)$ were determined as functions of temperature for each solvent. The optimum values of $\Delta G_h(T)$ and $\Delta G_r(T)$ so obtained depend on temperature, as illustrated in Figure 8. The results are approximately expressed by

$$2\Delta G_h(T)/RT = a_h + b_h/T + c_h/T^2 \qquad (5)$$

where a_h, b_h, c_h, a_r, and b_r are solvent-dependent

$$\Delta G_r(T)/RT = a_r + b_r/T \qquad (6)$$

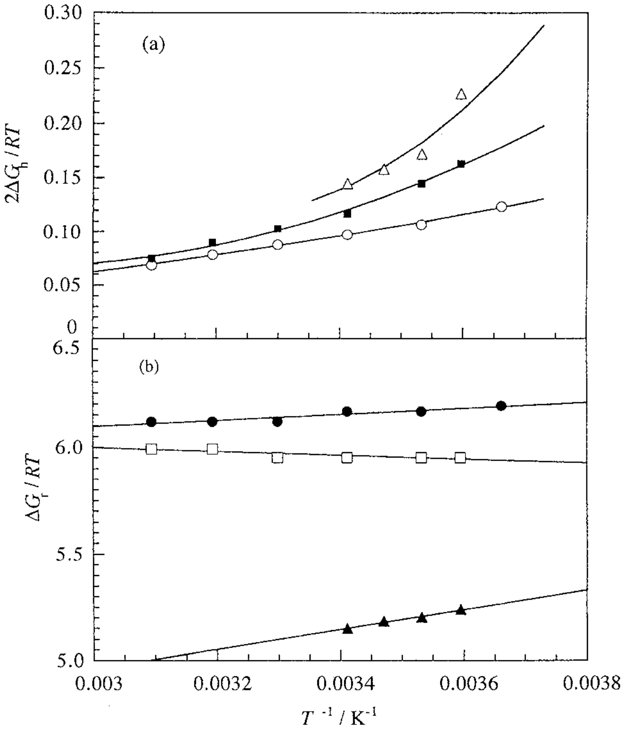

Figure 8. Plots of $2\Delta G_h(T)/RT$ and $\Delta G_r(T)/RT$ vs $1/T$ for NH4/96(F*i*) in three solvents investigated: (○, ●) hexane; (■, □) 1-chlorobutane; (△, ▲) dichloromethane.

coefficients; the data for the DCM solutions below 0 °C do not obey these equations and are omitted here. Their values are summarized in Table 2, where those for βPdHIC[10] are included for comparison. Figure 9 compares experimental data of $[m]/[m]_m$ for NH4/96(F*i*) in three solvents (symbols) with the theoretical values (curves) calculated with the smoothed parameter values given by eqs 5 and 6. The agreement is nearly quantitative, and the theory very well reproduces the data for the fractionated samples (symbols).

As seen in Table 2, the enantiomorphous bias $2\Delta G_h(T)$ for NIC at 20 °C in hexane, 1-chlorobutane, and dichloromethane is as large as −(71 ± 14) cal/mol compared with −(2.0 ± 0.6) for αPdHIC[11] and 0.88 ± 0.1 cal/mol for βPdHIC.[10] This is because of the larger pendant group $-CH_3$ on the β-carbon, which may interact strongly with the main chain, compared with deuterium on the latter. On the other hand, there is not a large difference in $\Delta G_r(T)$; it is only 5%, which corresponds only to a factor of 1.5 for the helical reversal probability $v(T)$. This conforms to the starting premise that $\Delta G_r(T)$ would be the same for the polymers studied since the overwhelming achiral unit has the same side chain structure, *n*-hexyl, for NH*x*/*y*. The present estimate of $2\Delta G_h(T)$ for the NIC unit is more reliable than the −113 cal/mol reported in the previous paper,[8] which was based on unfractionated samples.[1]

Recently, Selinger and Selinger[7] analyzed Green *et al.*'s data[1] in a different way. Actually, they determined the loci of values of $2\Delta G_h(T)$ and $\Delta G_r(T)$ to fit the experimental x dependence for the unfractionated samples[1] and chose 0.4 and 2.5 kcal/mol, respectively, for $-2\Delta G_h(T)$ and $\Delta G_r(T)$, to fit the experimental data. Indeed, their loci are consistent with the present analysis. However, compared with the previous analyses,[7,8] the present analysis is more effective for evaluating the two parameters involved separately. This is because the previous analysis had to rely only on the

Table 2. Free Energy Parameters for Poly((*R*)-2,6-dimethylheptyl isocyanate/*n*-hexyl isocyanate) Copolymer (NH4/96) and Poly((*R*)-2-deuterio-*n*-hexyl isocyanate) in the Indicated Solvents

		chiral monomer					
		(*R*)-2-deuterio-*n*-hexyl isocyanate (**2**)[a]			(*R*)-2,6-dimethylheptyl isocyanate (**3**)		
free energy	coefficient	Hexane	1-Chlorobutane	Dichloromethane	Hexane	1-Chlorobutane	Dichloromethane
$-2\Delta G_h/RT$	a_h	−0.0020	−0.0032	−0.0040	−0.0685	−1.40	−6.65
	b_h/K^{-1}	0.98	1.42	1.62	78.8	941	4076
	c_h/K^{-2}				-2.56×10^4	-16.6×10^4	-63.6×10^4
$\Delta G_r/RT$	a_r	1.85	1.57	1.97	5.682	6.258	3.547
	b_r/K^{-1}	1410	1320	1040	138	−87	470
At 20 °C							
$2\Delta G_h$, cal/mol		0.76	0.97	0.91	−56.8	−70.3	−85.4
ΔG_r, cal/mol		3870	3530	3210	3590	3470	3000

[a] Taken from ref 10.

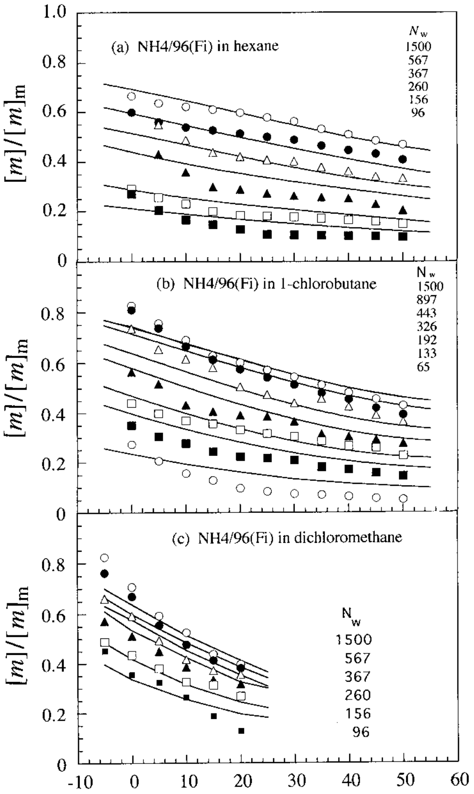

Figure 9. Comparison between experiment and theory with the data for NH4/96(F*i*) in hexane, 1-chlorobutane, and dichloromethane: (symbols) experimental data; (curves) theoretical values by eqs 5 and 6 with the parameter values given in Table 2 (see text).

composition dependence data available at that time, which were not detailed enough for a separate determination of the two parameters. Thus we see that an analysis of molecular weight dependence is essential for a quantitative discussion.

The consistency of the analysis is tested with data for NH*x*/*y*(MF&UF) of varying *x* in Figure 10, where the *x* dependence for NH*x*/*y* at 20 and 50 °C is shown. Here the solid curves represent the theoretical values with the hexane parameters of NIC (eqs 5 and 6), which have been derived from the NH4/96(F*i*) data; *N* is assumed to be 1500. The agreement between experiment and theory is seen to be moderate, implying that the parameters determined for NH4/96(F*i*) can also reproduce the data for smaller *x*. A large upward deviation for NH0.5/99.5(UF) may be ascribed to this small *x*, because in such a region of *x* the theoretical OR is very sensitive to a small variation in *x*, which may not be adequately controlled in the synthesis for the analytical requirements.

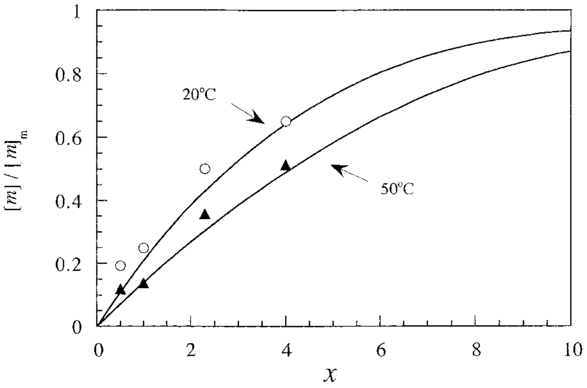

Figure 10. Test of the theory with the data for NH*x*/*y*(MF&UF) in hexane: (symbols) experimental data; (curves) theoretical values by eqs 5 and 6 with the NIC parameters given in Table 2 (see text).

αdHIC/HIC*x*/*y*. PHIC and αPdHIC have the same chemical structure except for the stereospecifically substituted deuterium at the α-carbon in the latter. Thus, random copolymers of αdHIC and HIC are analyzed as polymers of type 1 defined in the preceding paper.[8] Then it is reasonable to assume the same values for $\Delta G_r(T)$ and $[m]_m$ for the two monomer units. We further assume that $2\Delta G_h(T)$ for αdHIC in αdHIC/HIC*x*/*y* is the same as that for αPdHIC, because the chiral perturbation of αdHIC is very small due to the similarity of chemical structure between HIC and αdHIC. Thus the OR of αdHIC/HIC*x*/*y* can be calculated theoretically with these assumptions if its *N* is given; no additional parameter is needed. However, the theory indicates that $[m]$ is almost independent of *N* for $N > 1200$. Therefore, their *N* are assumed to be 1500, a sufficiently large value. In Figure 11, the theoretical values calculated on these assumptions are compared with the data in hexane and 1-chlorobutane. The agreement is almost quantitative except for a small deviation for αdHIC/HIC25/75 at lower temperatures.

PNIC(F*i*) and NH37/63(F*i*). PNIC(F*i*) and NH37/63(F*i*) show an N_w dependence of $[m]_{300}$ similar to that observed for NH4/96(F*i*) (cf. Figures 4−6). Unlike the latter, however, the dependence is limited to N_w lower than 200 and there is virtually no temperature dependence. It can be shown that the parameters for NIC, when applied to these polymers, appear to be consistent with this temperature independence. However, it was found that these parameters fail to precisely describe the N_w dependence. This failure suggests some factor is still missing in our consideration. For example, in

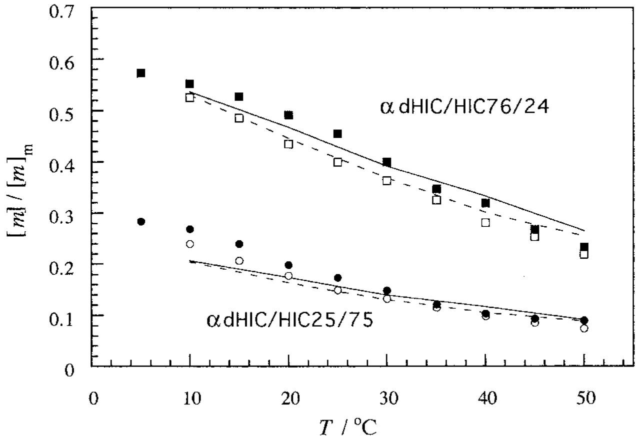

Figure 11. Test of the theory with the data for αdHIC/HICx/y(UF) in hexane and 1-chlorobutane. Symbols: experimental data, (■, ●) in hexane, (□, ○) in 1-chlorobutane. Solid and dashed curves: theoretical values with the parameters for αPdHIC in hexane and 1-chlorobutane, respectively,[11] along with N = 1500 (see text).

these polymers the chiral units do not appear as singlets but multiplets, and it is probable that u_M (and v) may be different between the singlet and multiplet configurations, leading to an inaccurate N_w prediction.

Concluding Remarks. Random copolyisocyanates of chiral and achiral monomers are polymers of type 1 and show remarkable OR, which originates from conformational perturbations from the chiral comonomers. This is due to an imbalance in the stability between left-handed and right-handed helices of the monomer, which is greatly amplified along the long chain assisted by the difficulty in the helical reversals. The experimental results for OR of NHx/y with x smaller than 5% and αdHIC/HICx/y obtained are well explained by the theory developed. The enantiomorphic bias for NIC at 20 °C is as large as −(71 ± 14) cal/mol in hexane, 1-chloromethane, and dichloromethane. Lifson *et al.*[23] gave a theoretical value of about 500 cal/mol for ΔG_h of (R)-*sec*-pentyl isocyanate by using empirical mean-field potentials. In their work, the empirical force field was directed to a system in which the chiral groups occurred all along the chain. This may cause the large difference noted, but the accuracy of the field in real solutions remains to be examined. On the other hand, the data for NH37/63(Fi) and PNIC(Fi) (NH100/0) were difficult to analyze theoretically. The reason for this is not clear at present but may be due to the high proportion of chiral units present as multiplets, which may be characterized by ΔG_h significantly different from that for the isolated unit (singlet). At any rate, it is worthwhile to quantify the correlation between the chiral bias and the chemical structure of the chiral moiety,[23] and this will be discussed in a forthcoming paper.[25] Finally, we note that the quantitative data arising from this approach and the use of this approach for other systems should be important for the use of polyisocyanates as components in chiral optical device technology.[26] In addition, the theories developed so far[6−8] may be useful to explore the detailed molecular mechanisms for the conformations and optical activities of such helical polymers as polysilanes,[15−17] poly(carbodiimide)s,[27] and others which may arise.[28]

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