

# Chiral Solvation as a Means to Quantitatively Characterize Preferential Solvation of a Helical Polymer in Mixed Solvents

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**Abstract:** Poly(*n*-hexyl isocyanate) adopts a helical structure in solution and the preference of one helical sense induced by a nonracemic chiral solvent can be detected by the circular dichroism (CD) of the backbone chromophore of the polymer. Addition of an achiral or racemic cosolvent leads to a reduction of the CD intensity, which can be interpreted quantitatively as reflecting the composition of the solvent mixture in contact with the helical backbone of the polymer. Equilibrium constants characterizing the relation between the solvent composition in contact with the polymer and the bulk of the system are given for mixtures of (*S*)-1-chloro-2-methylbutane and a number of achiral or racemic cosolvents. The relationship between the structure of the cosolvent and the extent of the preferential solvation was surprising in several instances. The polymer was preferentially solvated by a highly branched hydrocarbon although it was a precipitant and the preferential solvation by alcohols extended up to the point of polymer precipitation. This unusual method for characterizing preferential solvation of this rod-like polymer is compared with other methods used previously on flexible chain macromolecules.

## Introduction

Poly(*n*-hexyl isocyanate) ( $-\text{N}(\text{C}_6\text{H}_{13})\text{CO}-$ ) prepared by polymerization of *n*-hexyl isocyanate is known to adopt a helical conformation in solution.<sup>1</sup> Although left- and right-handed helices are equally probable when the polymer is constructed of achiral monomer units, it has been found that a bias toward one helical sense introduced by hardly chiral chain substituents such as (*R*)-1-deuteriohexyl groups leads to a surprisingly large preference for one helical sense.<sup>2</sup> This unusual effect is due to the high energetic cost of helical reversals in the polymer chain, so that a very small energetic preference per monomer residue for one helical sense is magnified by the large number of these residues between helical reversals. Statistical thermodynamic analysis has shown how the excess of one helical sense depends on the small free energy difference per monomer residue between the left- and right-handed helical senses,  $G_h$ , the much larger free energy difference between the helical and the helical reversal states,  $G_r$ , and the chain length of the polymer.<sup>3</sup>

In line with these properties it was found that the solution of poly(*n*-hexyl isocyanate) in nonracemic chiral solvents also causes an excess of one helical sense.<sup>4</sup> We have now found that the circular dichroism arising from this chiral solvation in (*S*)-1-chloro-2-methylbutane solution decreases on addition of achiral or racemic cosolvents in a manner that can be interpreted in terms of the composition of the solvent mixture in contact with the helical backbone of the polymer. This constitutes a highly sensitive method for the study of preferential solvation of a polymer in mixed solvents. We shall compare our data, obtained with a rod-like polymer, with data on preferential solvation obtained by various methods on flexible chain macromolecules stressing, particularly, the different response

to precipitating cosolvents. A good deal of information is available on preferential solvation of small molecular species in mixed solvents,<sup>5–8</sup> and our results may possibly aid in the understanding of these phenomena and stimulate theoretical approaches to the interpretation of our results.

## Results

In a previous communication<sup>4</sup> it was shown that the optical activity of poly(*n*-hexyl isocyanate) in solutions of (*S*)-1-chloro-2-methylbutane decreases to different extents on addition of different achiral cosolvents. The data suggested that this decrease becomes more pronounced with an increasing affinity of the cosolvent for the polymer. In this report we shall propose to use this effect for the quantitative characterization of preferential solvation of the polymer in the mixed solvent medium.

For polyisocyanates sufficiently long to contain many reversals of the helical sense, the optical activity  $[\alpha]$  of their solution was shown to be given<sup>3</sup> as

$$[\alpha]/[\alpha]_{\infty} = (LG_h/RT)/(LG_h/RT)^2 + 1)^{1/2} \quad (1)$$

where  $[\alpha]_{\infty}$  is the optical activity of a polymer having a single helical sense and  $L = \exp(G_r/RT)$  is the average number of monomer residues between helix reversals. For poly(*n*-hexyl isocyanate) in (*S*)-1-chloro-2-methylbutane  $[\alpha]/[\alpha]_{\infty}$  is 0.03,<sup>9</sup> i.e., sufficiently small that it may be taken as  $LG_h/RT$ . This must also be the case for mixtures of this solvent with various

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**Table 1.** Preferential Solvation of Poly(*n*-hexyl isocyanate) by 1-Chloro-2-methylbutane in Solutions of This Solvent Mixed with an Achiral or Racemic Cosolvent

cosolvent	<i>K</i>		vol % cosolvent at polymer precipitation
	<i>a</i>	<i>b</i>	
2,2-dimethylbutane		2.90	
octane	2.45	2.37	
hexane	2.08	2.14	
2,2-dimethylhexane	1.40	1.40	
2-chlorobutane	0.99	0.99	
2-butanol	0.86		55
tetrahydrofuran	0.84	1.04	
1-bromobutane	0.75		
1-butanol	0.75		40
chloroform	0.63	0.53	
2-octanol	0.57		50
1-octanol	0.36		25
2,2,4,4,6,8,8-heptamethylnonane	0.27		60

<sup>a</sup> Present study. <sup>b</sup> Reference 9.

cosolvents. Although studies on the solvent dependence of the properties of poly(*(R)*-2-deuteriohexylisocyanate)<sup>10</sup> show some effect of the solvent on  $LG_n$ , different chiral groups may exhibit a sensitivity of this parameter to the solvent medium that is unknown. We shall therefore assume that the optical activity of the polyisocyanate in mixtures of an optically active and an achiral solvent reflects only the fraction of the optically active cosolvent in contact with the polymer backbone, where it can affect the excess of one helical sense. Thus, if  $[\alpha]$  and  $[\alpha]_0$  are the intensities of the CD spectra in the solvent mixture and in the pure optically active solvent, respectively,

$$[\alpha]/[\alpha]_0 = [PA]/([PA] + [PI]) \quad (2)$$

where  $[PA]$  and  $[PI]$  are the concentrations of the optically active and inactive solvents in contact with the polyisocyanate backbone.

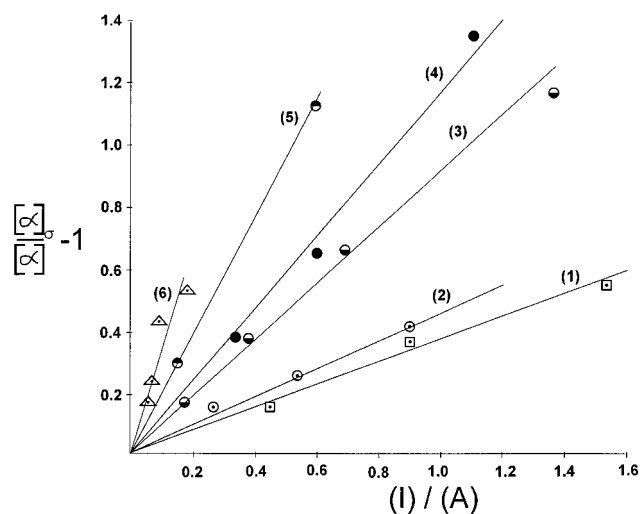
Expressing then the relation between the concentrations of the solvent species in the bulk of the system,  $[A]$  and  $[I]$ , and their concentrations in the polymer microdomain by the equilibrium

$$([PA][I])/([PI][A]) = K \quad (3)$$

we obtain

$$\{[\alpha]/[\alpha]_0\} - 1 = (1/K)\{[I]/[A]\} \quad (4)$$

(A similar equilibrium between the composition of a solvent mixture in the bulk of the system and in the solvation shell of a dye has been shown to account<sup>6,7</sup> for the dependence of the spectroscopic properties of dyes on the composition of mixed solvents.) We found that in mixtures of (*S*)-1-chloro-2-methylbutane with a number of achiral cosolvents, plots of  $[\alpha]/[\alpha]_0$  against  $[I]/[A]$  are linear as predicted by this simple model. This does not necessarily exclude the possibility that the change in the polarity of the medium might make a contribution to the dependence of the optical activity of the polymer on the composition of the binary solvent, but we believe that such an effect would be minor and that  $K$  as defined by eq 4 gives at least a close approximation to the composition of the solvent mixture in contact with the helical backbone of the polymer. Table 1 lists  $K$  values obtained for 13 cosolvents, where  $K > 1$  indicates preferential solvation by the (*S*)-1-chloro-2-methylbutane, whereas  $K < 1$  indicates that the achiral cosolvent is



**Figure 1.** Ratio of the CD intensity  $[\alpha]$  of poly(*n*-hexyl isocyanate) in mixtures of (*S*)-1-chloro-2-methylbutane (*A*) with an optically inactive cosolvent (*I*), and in the absence of the cosolvent  $[\alpha]_0$  as a function of the molar ratio  $[I]/[A]$ : (1) 2,2-dimethylbutane; (2) hexane; (3) 2,2-dimethylhexane; (4) racemic 2-chlorobutane; (5) chloroform; and (6) 1-octanol.

concentrated in the polymer domain. Representative plots in Figure 1 show that the difficulty of displacing the achiral cosolvent increases in the order hexane < racemic 2-chlorobutane < chloroform, as might be expected. Chloroform may be hydrogen bonded to the CO group of the polymer, chlorobutane may be attracted to the CO group by dipole-dipole interaction, whereas the nonpolar hexane should have the weakest interactions with the polymer.

Surprising results were obtained with cosolvents which precipitated the polymer at sufficiently high concentration, i.e., two isomeric alcohols, and the highly branched 2,2,4,4,6,8,8-heptamethylnonane, which all exhibited strong preferential solvation of the polymer. In the case of the alcohols, the attraction to the polymer was more pronounced with the isomer which was the stronger precipitant. While hydrogen bonding of the alcohols to the polymer would account for this behavior at low alcohol concentrations, it is striking that the preferential solvation continues up to the point of polymer precipitation, in sharp contrast, as we shall see, with the behavior of alcohol cosolvents of hydrogen bonding flexible chain macromolecules. As for the high solvating power of the highly branched nonane, we might conjecture that it acts by bridging two alkyl side chains of the polymer, impeding access of the polar cosolvent to the polymer backbone. Another anomaly is that while hexane and octane have similar  $K$  values, their isomers 2,2-dimethylbutane and 2,2-dimethylhexane have  $K$  values differing by a factor of 2 (Table 1).

### Comparison with Previous Studies of Preferential Solvation of Polymers in Mixed Solvents

Past studies of preferential solvation of polymers in mixed solvents by light scattering, dialysis equilibrium, and centrifuge sedimentation equilibrium were all carried out on flexible chain macromolecules. Any difference in the results obtained previously and in the present study may be due both to the rigidity of the polyisocyanate and to our method for evaluating the preferential solvation. Our method reflects the cosolvent composition in contact with the helical polymer backbone, where it may affect the sense of the helix, rather than this composition in the entire polymer domain.

(10) Okamoto, N.; Mukaida, F.; Gu, H.; Nakamura, Y.; Sato, T.; Teramoto, A.; Green, M. M.; Andreola, C.; Peterson, N. C. *Macromolecules* **1996**, *29*, 2878.

In 1946 Debye and his co-workers<sup>11</sup> pointed out that it would be advantageous to determine the molecular weight  $M$  of a polymer by light scattering in solutions in which the expansion of the chain molecule would be reduced by addition of a precipitant so as to minimize the destructive interference of the scattered light. However, in that case one has to take account of the difference in the composition of the solvent mixture in the polymer microenvironment and in the bulk of the system if the components of the solvent mixture have different refractive indices. This was done by using in place of the factor  $\delta n/\delta c_p$ , where  $n$  is the refractive index and  $c_p$  is the polymer concentration, employed when deriving the molecular weight of a polymer from light scattering in a single solvent,  $\delta n/\delta c_p - (\delta\Psi_1/\delta c_p)(\delta n/\delta\Psi)$ , where  $\Psi_1$  and  $\Psi$  are volume fractions of cosolvent 1 in the polymer environment and the bulk of the system, respectively.

Stockmayer<sup>12</sup> showed how the ratio of the apparent light scattering molecular weight of a polymer in a mixed solvent to its true value,  $M_{app}/M$ , depends on the thermodynamic parameters and binary refractive index increments of the system, and Read<sup>13</sup> used his formalism with the two Flory–Huggins polymer–solvent and solvent–solvent interaction parameters from the literature to estimate a “preferential solvation coefficient”  $\lambda_1$  specifying the volume of cosolvent 1 bound per unit weight of polymer (mL/g). He also showed that  $\lambda_1$  can be obtained from the ratio of the apparent molecular weight  $M_{app}$  obtained by light scattering from a mixed solvent without regard to the preferential solvation to its true value  $M$  from

$$\lambda_1 = [(M_{app}/M)^{1/2} - 1] (dn/dc_p)/(dn/d\phi_1) \quad (5)$$

where  $\phi_1$  is the volume fraction of component 1 in the mixed solvent. The calculated and experimental values of  $\lambda_1$  for the sorption of benzene by polystyrene in a benzene/cyclohexane mixture were in reasonably close agreement. Later, this system was studied by Strazielle and Benoit,<sup>14</sup> who used a similar approach to estimate  $\lambda_1$  from light scattering, and their results are compared with Read’s in Figure 2.

For solvent mixtures whose components differ appreciably in their refractive index, dialysis equilibrium was also found to be convenient for the study of preferential solvation.<sup>15–17</sup> If the refractive index increment is  $(\delta n/\delta c_p)_c$  for a constant solvent composition and  $(\delta n/\delta c_p)_\mu$  for a constant composition of the solvent mixture in dialysis equilibrium with the polymer solution, then,

$$\lambda_1 = [(\delta n/\delta c_p)_\mu - (\delta n/\delta c_p)_c]/(dn/d\phi_1) \quad (6)$$

A third approach to the characterization of preferential solvation was pioneered by Cowie et al.,<sup>18</sup> who derived  $\lambda_1$  from the distribution of the high density cosolvent bromoform in a benzene solution of polystyrene at ultracentrifuge sedimentation equilibrium. A detailed analysis of this technique was presented by Chu and Munk,<sup>19</sup> who applied it to a number of systems. Their result for polystyrene in benzene/cyclohexane is similar to those obtained by light scattering. An excellent bibliography of preferential solvation is a valuable part of their paper. Note

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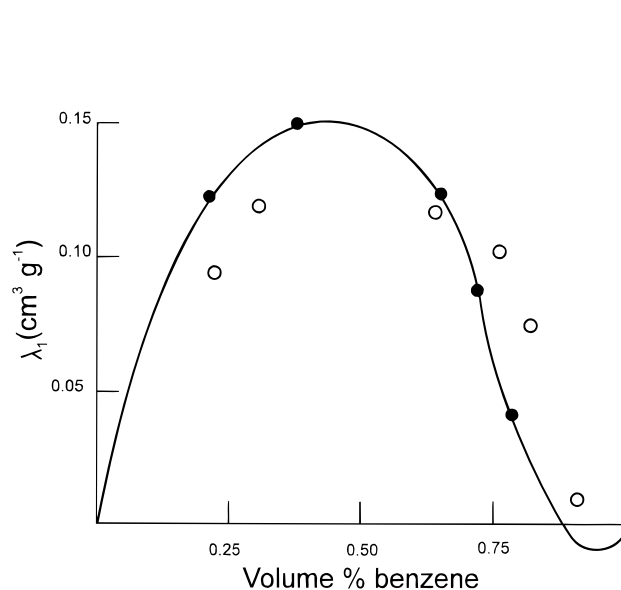
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**Figure 2.** Preferential solvation coefficient of benzene in a polystyrene solution of benzene/cyclohexane. The solid line is calculated from binary interaction coefficients. Experimental Points: (●) ref 14; (○) ref 13.

that all three investigators estimated the maximum of  $\lambda_1$  for polystyrene in benzene/cyclohexane to be about 0.15 mL/g, and as Strazielle and Benoit pointed out,<sup>14</sup> this corresponds to one benzene molecule preferentially sorbed to five monomer residues of polystyrene.

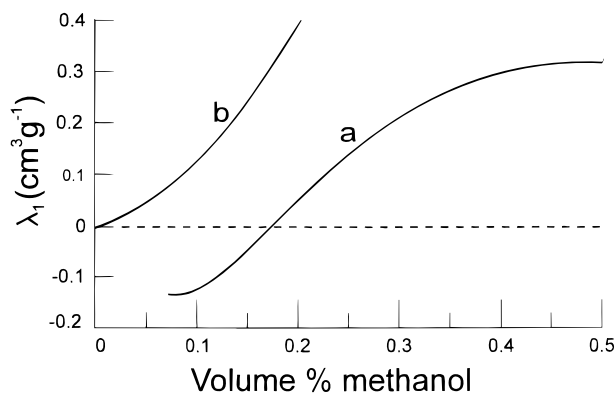
We may then inquire how the equilibrium constant  $K$  used in our work to characterize preferential solvation is related to the parameter  $\lambda_1$ . If  $x$  is the mole fraction of the preferentially sorbed component and  $y$  is its mole fraction in contact with the monomer residues of the polyisocyanate helical backbone, then  $y/(1-y) = Kx/(1-x) = Z$  and  $y = Z/(1+Z)$ . The preferential solvation coefficient is then given by  $\lambda_1 = (y-x)V/m$ , where  $V$  is the molar volume of the preferentially sorbed solvent and  $m$  is the molecular weight of a monomer residue of the polymer. For instance, for poly(*n*-hexyl isocyanate) in an equimolar mixture of hexane and 1-chloro-2-methylbutane,  $K = 2.1$ ,  $x = 0.5$ ,  $V = 122$  mL,  $m = 125$  g, and  $\lambda_1 = 0.17$  mL/g. Note that in our case we define preferential solvation in terms of the chiral cosolvent in contact with the helical backbone of the polymer (where it can exert an effect on the sense of the helix) whereas results obtained by light scattering, dialysis equilibrium, or ultracentrifuge sedimentation equilibrium do not distinguish between the manner in which the cosolvent is sorbed by the polymer.

When Strazielle and Benoit proposed eq 5 for the estimation of preferential solvation,<sup>14</sup> they assumed that this effect is independent of the chain length of the polymer. This assumption was later shown to be at fault with  $\lambda_1$  declining to a limiting value  $\lambda_\infty$  for long chain molecules, particularly when the cosolvent was a precipitant for the polymer. Dondos and Benoit found that the data fitted the relation  $\lambda_1 = \lambda_\infty + A/(M)^{1/2}$ ,<sup>20</sup> where  $A$  was a constant, and this was substantiated by later work. Since the probability of contact between a given chain segment with any other segment of the chain is linear in  $M^{-1/2}$ ,<sup>21,22</sup> the decrease of  $\lambda_1$  to a limiting value as the chain length is increased may be understood as reflecting the competition between segment–segment and segment–solvent contacts.

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(21) Goodman, N.; Morawetz, H. *J. Polym. Sci.* **1971**, *A-2,9*, 1657.

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**Figure 3.** Preferential solvation coefficients of benzene for poly(methyl methacrylate) solutions in benzene/methanol<sup>23a</sup> (a) and for polystyrene in benzene/methanol<sup>23b</sup> (b).

In view of our observation that the polyisocyanate dissolved in (*S*)-1-chloro-2-methylbutane is preferentially solvated by alcohols up to the point of polymer precipitation, it was of particular interest to compare these results with those obtained by light scattering in analogous systems. Živný et al.<sup>15</sup> and Katime and Strazielle<sup>23a</sup> studied poly(methyl methacrylate) in good solvents with methanol as a cosolvent and found that  $\lambda_1$  changes sign as the composition of the solvent medium is varied, with methanol adsorbed preferentially only at low alcohol concentrations. (Casassa<sup>22</sup> tried to interpret the dependence of preferential solvation on the composition of the binary solvent by a simple equilibrium such as proposed in eq 3, but pointed out that this could obviously not account for a sign reversal of  $\lambda_1$ ). On the other hand, with polystyrene in benzene/methanol mixtures,<sup>23b</sup> benzene is preferentially sorbed at all solvent compositions up to the polymer precipitation (Figure 3). This different behavior is clearly due to the fact that poly(methyl methacrylate) is a hydrogen-bond acceptor, so that a small addition of methanol to a benzene solution of the polymer improves the solvent power of the medium. In fact, Gavara et al.<sup>24</sup> and Maillols et al.<sup>25</sup> found that in a number of systems the solvent composition at which the preferential solvation coefficient changes sign corresponds to the optimization of the solvent medium. A theoretical treatment of such reversals in terms of the three binary interaction parameters in the ternary system was presented by Živný and Pouchlý<sup>26</sup> and by Gavara et al.,<sup>24</sup> and a compilation of numerous data illustrating the reasonable agreement between the composition dependence of  $\lambda_1$  as predicted by theory and as found experimentally was published by Horta and Criado-Sancho.<sup>27</sup> Yet, one may wonder whether the power of available theory would be adequate to explain such consequences of small changes of molecular structure as found by Katime et al.,<sup>28</sup> who reported that for poly(methyl methacrylate) in benzyl alcohol/butanol mixtures an inversion of preferential solvation is observed with the secondary, but not the primary, butanol. Unfortunately, no studies exist on the trend of the preferential solvation parameter in systems of a flexible polymer, such as polystyrene or poly(methyl methacrylate), in a mixture of a good solvent and a nonpolar paraffin precipitant. Would such a system exhibit

preferential solvation by the paraffin? Would it involve a reversal of the sign of  $\lambda_1$ ?

### Concluding Comments

Our data show that a simple equilibrium can relate the composition of a mixture of a chiral nonracemic solvent and an achiral or racemic solvent in contact with the backbone of a polyisocyanate with the composition of the solvent mixture in the bulk of the system. This is accomplished by observation of the circular dichroism of the helical chromophore of the polyisocyanate, which reflects the ratio of the right and left handed helical senses controlled by the solvent in contact with the backbone. The use of the stiff polyisocyanate reduces complicating effects due to changes in the extension of the polymer chain, since the polyisocyanate backbone is known to be independent of the population of the helical reversals along the chain<sup>1</sup> and only weakly dependent on solvent composition compared to flexible polymers.<sup>1,29</sup> With flexible polymers, transitions in the local chain conformation have also been assumed to affect preferential solvation.<sup>30,31</sup> On the other hand, the interpretation of the data is made more difficult since the components of the solvent mixture interact with both the polar backbone of the polymer and its long paraffinic substituents.

It is surprising that alcohols are preferentially adsorbed by the polyisocyanate up to the point of precipitation. This is in contrast with the behavior of the flexible hydrogen-bond acceptor poly(methyl methacrylate) in mixtures of a good solvent and methanol. Here the polymer is preferentially solvated by the alcohol only when its concentration in the mixed solvent is low and the preferential solvation coefficient changes sign well before the polymer precipitation. A possibly related unexpected result was the strong sorption of the heptamethylnonane, a precipitant for the polyisocyanate.

It should also be noted that the formulation of the equilibrium between the cosolvents in the bulk of the system and in contact with the helical backbone of the polymer in terms of their molarity (eq 3) assumes implicitly ideal solution behavior, whereas solvent mixtures containing 2-chlorobutane with isomeric butanols were shown<sup>32</sup> to exhibit large positive deviations from solution ideality. In spite of this, the plots in Figure 1 were linear, which implies that activity coefficients of the cosolvents in contact with the polymer backbone are similar to those in a polymer-free cosolvent mixture.

It would be desirable to obtain data on the preferential solvation of polyisocyanate by one of the techniques which have been employed for flexible polymers, so as to compare them to our results. Also, it would be interesting to apply such methods to the determination of preferential solvation of flexible polymers in mixtures of a good solvent and a paraffinic precipitant.

Whereas there have been many studies on preferential polymer solvation in mixed solvents, this is the first attempt to explore the dependence of this effect with a single polymer on the nature of a large number of cosolvents. The results found here will require further exploration. Why is it, for instance, that we found little difference between the behavior of hexane and octane while branched paraffins and alcohols exhibited a substantial dependence of their behavior on the chain length?

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(32) Artigas, H. et al. *J. Chem. Eng. Data* **1994**, *39*, 729. Cea, P. et al. *J. Chem. Eng. Data* **1995**, *40*, 692.

Such questions may stimulate interesting interactions between this work and theoretical methods designed to understand the nature of solvation.<sup>33</sup> It is remarkable that although the excess of one helical sense of the polyisocyanates, leading to the circular dichroism signal, is brought about by a minute energetic interaction of the chiral solvent with the polymer backbone (with  $G_h$  of the order of 0.04 cal/mol),<sup>1,4</sup> this effect can be potentially used to estimate the much larger solvation energies involved in the preferential solvation studied here.

### Experimental Section<sup>34</sup>

Circular dichroism spectroscopy was carried out by using a JASCO 710 spectrophotometer with cylindrical quartz cells with 0.01–0.05 cm path lengths. Temperature controlled scans were performed with use of a thermostated cell holder attached to a Neslab constant temperature thermostat.

Poly(*n*-hexyl isocyanate) was prepared according to the literature with a viscosity average molecular weight of 66 000.<sup>35</sup> (*S*)-1-Chloro-2-methylbutane was used as purchased from TCI America and had a specific rotation at the D-line compared to the literature<sup>36</sup> corresponding

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to a 96% enantiomeric excess. All the cosolvents (Table 1) for the (*S*)-1-chloro-2-methylbutane were purchased from Aldrich Chemical Co. in the highest purity available and used without further purification except for the *n*-alkanes, which were washed with water and acid and distilled, and chloroform, which was shaken with calcium carbonate and distilled.<sup>9</sup> In the cases of 2,2-dimethylbutane and 2,2-dimethylhexane, carbon-13 NMR data were consistent with the structures.

From a stock solution of 16 mg of poly(*n*-hexyl isocyanate) in 2 mL of (*S*)-1-chloro-2-methylbutane 0.25 mL was transferred to a volumetric flask which was made up to 1 mL with a mixture of the cosolvent and the (*S*)-1-chloro-2-methylbutane. The consistency of the polymer concentration was checked in all the final solutions by the absorbance at 257 nm. Circular dichroism intensities were measured at 257 nm from scans made over a wavelength range allowing observation of the helical chromophore with repeated scans to attain a necessary signal-to-noise ratio. The circular dichroism spectra were all identical in form with that shown for poly(*n*-hexyl isocyanate) dissolved in the (*S*)-1-chloro-2-methylbutane.<sup>4</sup> As in earlier work,<sup>4</sup> the circular dichroism intensity was about 2.2 mdeg in a 0.01 cm cell in the absence of the cosolvent.

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