

Dynamic NMR Determination of the Barrier for Interconversion of the Left- and Right-Handed Helical Conformations in a Polyisocyanate

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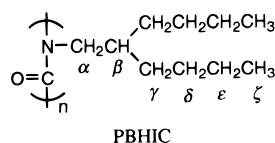
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Abundant evidence demonstrates that poly(alkyl isocyanate)s adopt a chain conformation with long blocks of left- and right-handed helices separated by kinked and mobile helical reversals.^{1,2} The low population of these reversals in poly(*n*-hexyl isocyanate) leads to such an extreme sensitivity of these polymers to chiral information that even minute chiral forces give rise to large excesses of one helical sense and therefore to large optical activities.¹ This cooperative phenomenon has been described by the one-dimensional Ising model which, together with fitting to the experimental observations, allowed determination of the thermodynamic helical reversal energy in poly(*n*-hexyl isocyanate). This is nearly 4 kcal/mol in hydrocarbon solvents, which translates to about one reversal every thousand chain units at nearly ambient temperatures.^{3,4} The cooperative characteristics of the chain are the result of many units necessarily taking the same helical sense.

A key unanswered question, though, is the speed of the interconversion of the helical senses, which depends on the barrier energy for movement of the reversal along the chain backbone. NMR offers an interesting approach because movement of the reversal will interconvert a left- and right-handed helical segment, causing all constitutionally identical groups in the side chain to exchange their diastereotopic positions.⁵ If such diastereotopic groups have distinguishable chemical shift properties in the NMR, the barrier could be determined by the temperature at which the differing signals collapsed because at this point the frequency of the motion interconverting the signals can be related to the frequency difference of the signals in the spectrum.⁶ Although the difference we searched for in the diastereotopic hydrogen pairs on each methylene group in poly(*n*-hexyl isocyanate) could not be observed,⁷ we have found this effect in poly(2-butylhexyl isocyanate) (PBHIC) in both the proton and carbon NMR spectra so that



the temperature dependence of these spectra then revealed the barrier to movement of the helical reversal

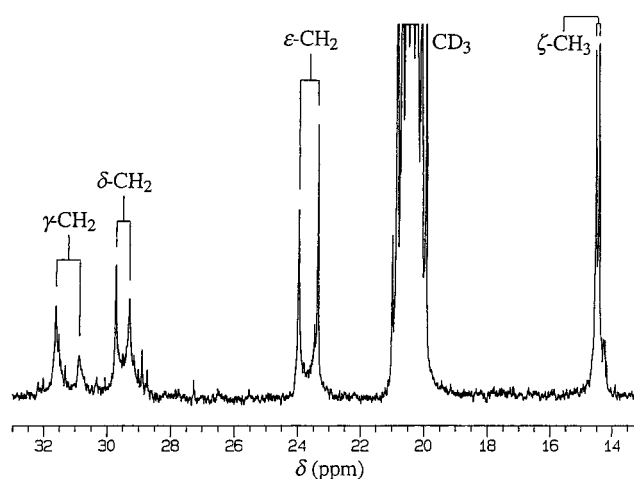


Figure 1. Butyl carbon resonances in the 125 MHz ¹³C NMR spectrum of poly(2-butylhexyl isocyanate) in toluene-*d*₈ at 30 °C. The strong multiplet at 21 ppm is due to the CD₃ group of toluene-*d*₈.

along the chain backbone. This energy, about 19 kcal/mol, could be compared to a lower limit for the thermodynamic excess energy of the helical reversal over the helical state in this polymer, 5 kcal/mol, determined by the correlation of the optical activity properties of a copolymer of 2-butylhexyl isocyanate and (*R*)-2,6-dimethylheptyl isocyanate with a random-field Ising model.⁸ Knowledge of both energies is necessary to correlate the chiral amplification characteristics and the dynamic response of the polymer with respect to side chain structure.⁹

Although the moderate sensitivity of NMR is not usually adequate for studying the properties of a small population of conformational defects along a polymer chain, there is a special stereochemical situation here in which the reversal movement interconverts large numbers of left- and right-handed units along the chain which amplifies the presence of the defect.¹⁰

Figure 1 shows the constitutionally identical butyl carbon resonances in the ¹³C NMR spectrum of PBHIC¹¹ measured in toluene-*d*₈ at 30 °C. The resonances due to each CH₃ and all of the CH₂ groups of the two butyl groups in each side chain appear as doublets. The source of this splitting reasonably arises from a chiral influence on these groups, which here must reside in the backbone (see further discussion below). In this way, Figure 1 is the first NMR observation of the helical structure of the polyisocyanates and demonstrates that the interconversion of the left- and right-handed helices is slow on the NMR time scale of this experiment at ambient temperature. The line widths of the ζ-CH₃, ε-CH₂, δ-CH₂, and γ-CH₂ resonances increased in this order, indicating also the increasingly restricted segmental mobility in the vicinity of the backbone (Figure 1).⁷ The β-CH, N-(α)-CH₂ and C=O resonances, not shown, were observed as broad singlets at 38.09, 53.61, and 157.50 ppm, respectively.

In the 500 MHz ¹H NMR spectrum of PBHIC in *o*-xylene-*d*₁₀ at 30 °C, the two N-(α)-CH₂ protons, which are also diastereotopic, give two broad and beautifully separated peaks with an equal intensity at 3.70 and 4.02 ppm (Figure 2a). When the spectrum was measured at

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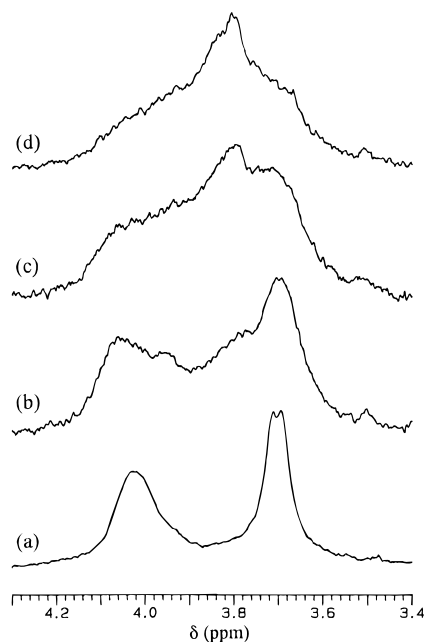


Figure 2. N-CH₂ resonances in the 500 MHz ¹H NMR spectra of poly(2-butylhexyl isocyanate) in *o*-xylene-*d*₁₀ at (a) 30, (b) 110, (c) 130, and (d) 140 °C.

a higher temperature, the doublets became broader (parts b and c of Figure 2) and almost coalesced at 140 °C, which is slightly below the boiling point of the solvent (Figure 2d). Cooling the sample solution to 30 °C again reproduced the spectrum in Figure 2a. These changes show that the rate of the process interconverting these signals becomes too fast at 140 °C for the time scale of 500 MHz NMR to distinguish between the two diastereotopic hydrogens. From the temperature dependence of the resonance, ΔG^\ddagger was determined to be 19.6 kcal/mol (at 140 °C).⁶ Because the coalescence temperature necessary here is dangerously close to the decomposition point of the polymer,¹² we studied the NMR properties of the ζ -CH₃ proton diastereotopic resonances (Figure 3a), which because of a reduced chemical shift difference coalesced at only ca. 100 °C (Figure 3e). Here again, fitting the data yielded⁶ a ΔG^\ddagger of 19.0 kcal/mol for the barrier for the process which interconverts these methyl hydrogen signals. The fine splittings in the methyl resonance are attributable to the *J* coupling from the adjacent methylene protons.

The interconversion of the two diastereotopic butyl groups in a repeating unit of PBHIC was evidenced further by ¹³C two-dimensional exchange spectroscopy (2D EXSY)¹³ experiments in toluene-*d*₈ at 30 °C. As shown in Figure 4, positive correlation peaks were observed between the ¹³C NMR signals at 30.9 and 31.6 ppm due to the γ -CH₂ group. Each of the doubled ¹³C NMR signals due to the δ -CH₂ and ϵ -CH₂ groups also showed positive correlation peaks arising from the interconversion.

In principle, the doubled NMR signals observed in Figures 1–3 could arise from some restriction in conformational properties of the side chain independent of the helical sense characteristics of the backbone. Although the equal intensities of the split signals argues against this interpretation, firm evidence that this is not the case and that supports the hypothesis of the helical backbone casting the constitutionally identical groups into magnetic nonequivalence is the result of the experiment shown in Figure 5. Here we have measured

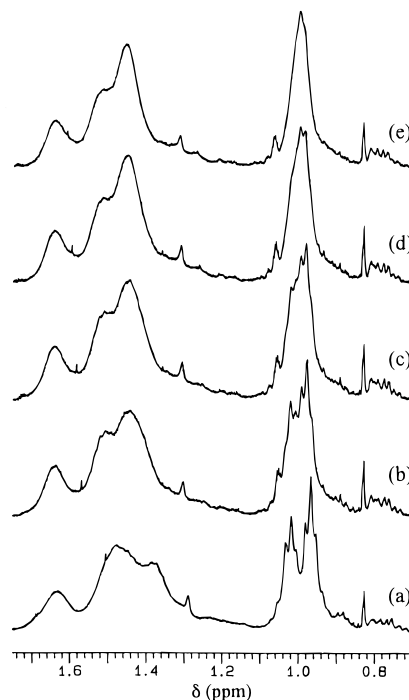


Figure 3. CH₃ and CH₂ resonances in the 500 MHz ¹H NMR spectra of poly(2-butylhexyl isocyanate) in *o*-xylene-*d*₁₀ at (a) 30, (b) 70, (c) 80, (d) 90, and (e) 100 °C.

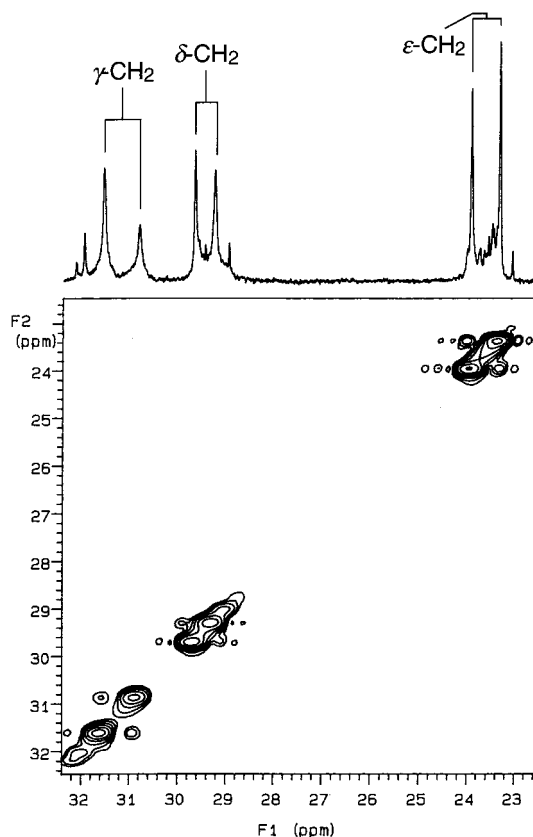


Figure 4. ¹³C 2D EXSY of poly(2-butylhexyl isocyanate) in toluene-*d*₈ at 30 °C. The spectra were recorded with a mixing (exchange) time of 100 ms. The original 8192 × 256 matrix covering a spectral width of 16 598 Hz in both dimensions was zero-filled to 8192 × 4096.

the temperature dependence of a copolymer of (*R*)-2,6-dimethylheptyl isocyanate and 2-butylhexyl isocyanate where the proportions of the chiral and achiral comonomers, 2/98, are such as to cast the backbone entirely

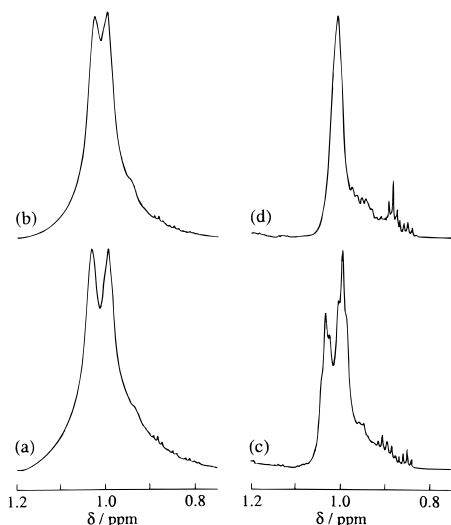


Figure 5. CH_3 signals in the 750 MHz ^1H NMR spectra for the 2/98 copolymer of (*R*)-2,6-dimethylheptyl isocyanate and 2-butylhexyl isocyanate in *p*-xylene- d_{10} at (a) 70 and (b) 110 $^\circ\text{C}$. The 750 MHz ^1H NMR spectra for poly(2-butylhexyl isocyanate) in *p*-xylene- d_{10} at (c) 70 and (d) 110 $^\circ\text{C}$ are also shown.

into a single helical sense.¹⁴ The strong preference for one helical sense in this copolymer evidenced by the chiral optical properties¹⁴ precludes the interconversion of the left- and right-handed helices, and as seen in Figure 5, heating through the temperature-causing coalescence of the identical signal in Figure 5d causes no coalescence of the methyl doublet in Figure 5b. The broadened signals for the optically active polymer are associated with both the higher molecular weight of this material and the presence of the randomly dispersed chiral comonomer units.

The absence of split signals for the diastereotopic hydrogen atoms on the methylene groups of poly(*n*-hexyl isocyanate) is negative evidence from which we cannot conclude that the helical reversal movement is faster than that for PBHIC, which is subject to a barrier determined above as ca. 19 kcal/mol. Nevertheless, it is reasonable that the barrier in PBHIC should be substantially higher based on the steric bulk of the side group which causes an increase in the thermodynamic excess energy of the reversal over that in poly(*n*-hexyl isocyanate).^{8b} How the energy barrier for movement of the reversal is related to the thermodynamic excess energy of the helical reversal is an open question.¹⁵ This kind of question is of concern in other helical polymers studied by NMR such as isotactic chloral oligomers where the barrier has been determined at 19.6 kcal/mol for the hexamer,¹⁰ threodiisotactic poly(triphenylmethyl crotonate) with a barrier of 28.4 kcal/mol,¹⁶ and isotactic poly(diphenyl-2-pyridylmethyl methacrylate) with a barrier of 23 kcal/mol.¹⁷ Recent work on poly-(guanidines)¹⁸ shows that certain side chains in this polymer class allow laboratory time scale interconversion of the helical sense such as is known for the threodiisotactic poly(triphenylmethyl crotonate) and the isotactic poly(diphenyl-2-pyridylmethyl methacrylate) noted above. The barrier reported for the polyisocyanate studied here by NMR¹⁹ suggests that such atropisomeric characteristics may be encountered here, as well at appropriate temperatures in dilute solution. On the basis of other studies, the characteristics of the reversal are strongly altered when these polymers are encoun-

tered in gels,²⁰ liquid crystals,²¹ and the solid glassy state,²² allowing the reversal to act as a probe of these states.

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