indicates that the ETP-rich phase is to some extent constrained by the presence of the HBA-rich mesophase. The aforementioned lowering in temperature of the α transition of the copolymers with respect to that of PETP seems anomalous in view of the low value of symmetric width parameter observed for the 0.6–0.4 copolymer. However, at this stage no explanation can be given that fully reconciles these apparently contradictory findings.

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Registry No. (Ethylene glycol)(*p*-hydroxybenzoic acid)(terephthalic acid) (copolymer), 25822-54-2.

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Macromolecular Stereochemistry: The Effect of Pendant Group Structure on the Axial Dimension of Polyisocyanates[1]

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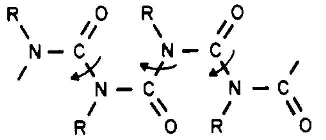
ABSTRACT: The optically active and racemic forms of the 1,2 acetone ketal of propylene glycol were converted via the hydroxyl function to the derived isocyanates. These monomers were polymerized following Shashoua, using sodium cyanide in dimethylformamide at −65 °C. Light scattering determination in chloroform of the weight-average molecular weight and the root-mean-square radius of gyration ($\bar{M}_w$, $\langle S^2 \rangle^{1/2}$) shows, by estimates of the persistence lengths, that the optically active polymer (730 000, 1600 Å) has a more extended chain than its racemic derived isomer (500 000, 850 Å) and, based on the literature, is also more extended than poly(*n*-butyl isocyanate). The optically active polymer exhibited a circular dichroism spectrum ($\Delta\epsilon = -3$, $\lambda_{max} = 244$ nm) similar to that observed by Goodman and Chen on poly(2-methylbutyl isocyanate). The ultraviolet spectra showed an unusual sensitivity to the pendant group: the optically active and racemic derived polyisocyanates were similar ($\lambda_{max} = 238$ nm, $\epsilon = 2.4 \times 10^3$) and ($\lambda_{max} = 242$ nm, $\epsilon = 2.5 \times 10^3$) and differed from poly(*n*-butyl isocyanate) ($\lambda_{max} = 254$ nm, $\epsilon = 3.7 \times 10^3$). These data require the sense of the polyisocyanate helix to be related to the pendant group configuration and also demand the formation of a *d*,*l* copolymer in the polymerization of the racemic monomer. In addition, the results are consistent with helix reversals as important contributors to wormlike behavior in polyisocyanates. The 125.7-MHz carbon-13 NMR spectra showed broadened resonances for both backbone and side-chain nuclei in the isocyanate polymers as compared to random coil polymers. Further work is needed to separate the role of pendant group asymmetry and steric bulk in the conformational properties of the polyisocyanates.

Introduction

A variety of physical chemical probes demonstrate that poly(*n*-alkyl isocyanates) adopt wormlike conformations in solution.[3] In the solid state X-ray studies[4] show these polymers to exist in a helical conformation with eight monomer units in three turns and a pitch of 5.17 Å. This can be pictured as a cis–trans array with a 45° angle between the amide units.[3–6]

Although this helical characteristic is found to be consistent with the solution properties,[3,5,6] the dipole moment



and the radius of gyration of the poly(*n*-alkyl isocyanates) are not prportional to the degree of polymerization, as expected for a rod, and the polymers are, therefore, best described as wormlike. Both the increasing number of

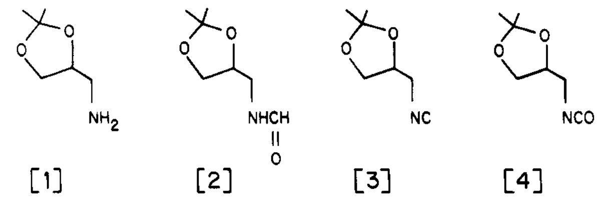


Figure 1. Synthesis of 2,2-dimethyl-1,3-dioxolane-4-methylene isocyanate, (*S*)-4 and (*RS*)-4.

helix reversals per chain as the degree of polymerization increases and the vibrational motions within one helical sense have been suggested as the cause of the rod-to-worm transition.[5,6]

In polyisocyanates derived from an achiral monomer, the left- and right-handed helical senses are mirror image related and, therefore, of equal energy and probability. In the polymerization of a nonracemic chiral isocyanate monomer, the helical senses are related as diastereomers and, therefore, may differ enough in their properties for one to be substantially preferred. Goodman and Chen[7] have shown in the polymerization of two optically active isocyanate monomers that the resulting polymers show a large increase in chiral-optical power over the monomers. This is consistent with the formation of a regular conformation,[8] i.e., in this case, a predominant helical sense.[6]

If helix reversals are important in limiting the axial extension of polyisocyanates and if an optically active polyisocyanate is characterized by a predominant helical sense, it must follow that such an optically active polyisocyanate must be more rodlike than a comparable polyisocyanate from an achiral monomer or from a racemic monomer if, in the latter case, the copolymerization of the enantiomers proceeds in a nonstereoselective manner.

We have attempted to test this idea on the polyisocyanates prepared from the optically active and racemic isocyanates derived from the 1,2 acetone ketal of propylene glycol. This chiral pendant group was chosen because it also opens the possibility, by hydrolysis of the ketal, for the conversion to a variety of functional groups, some of which could confer water solubility on these polymers.[9] In the present work, we have not yet accomplished these chemical objectives.

Results

The optically active 2,2-dimethyl-1,3-dioxolane-4-methanol was prepared by oxidative cleavage of 1,2,5,6-diacetone D-mannitol with sodium metaperiodate followed by immediate in situ reduction using sodium borohydride as reported in the literature.[10] The racemic material is commercially available in large quantities. The synthetic work proceeded almost identically on the optically active and racemic materials to produce, via the tosylate,[11] the known 2,2-dimethyl-1,3-dioxolane-4-methyleneamine (**1**)[12] (Figure 1).

The acid sensitivity of the ketal suggested finding a mild path to the isocyanate. This was accomplished via the formamide (**2**) conversion to the isonitrile (**3**)[13,14] with subsequent oxidation to the desired isocyanate **4** (Figure 1).[15] This overall procedure produced the (*S*) enantiomer of **4** in the optically active series. Attempts to produce **4** by direct displacement of the tosylate or the bromide with metal cyanate salts failed completely.[16]

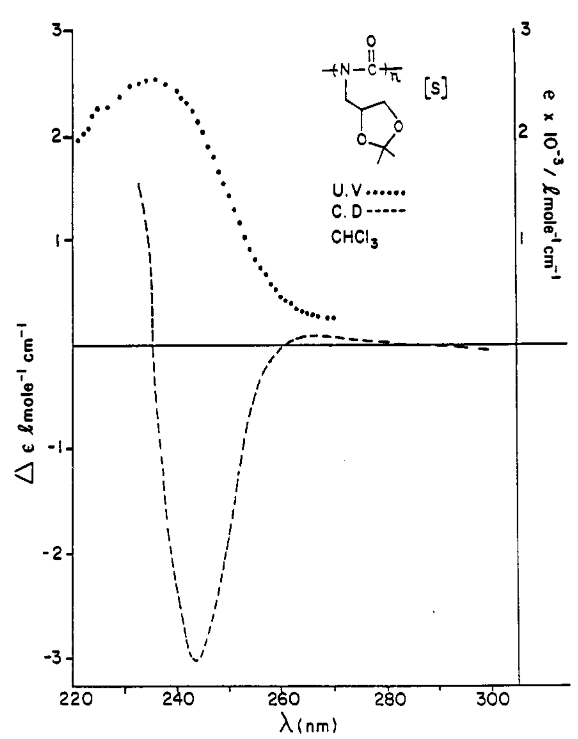
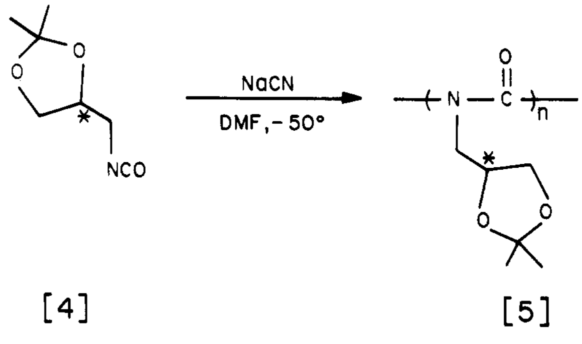


Figure 2. Circular dichroism and ultraviolet spectra of (*S*)-5 recorded in $CHCl_3$.

Table I
Characteristics of Monomer 4 and the Polyisocyanates (*S*)-5 and (*RS*)-5[a]



config at C*	monomer 4 $[\alpha]_{546}$	polymer 5 $[\alpha]_{546}$	$\bar{M}_w$	$[\eta]$, dL g^{-1}	A_2, m cm^3 g^{-2}	$\langle S^2\rangle^{1/2}$, Å
(*S*)	-21.1°[b]	-311°	730 000	17.5	8.6×10^{-4}	1600
(*RS*)			503 000	6.3	8.3×10^{-4}	860
(*RS*)			500 000[c]			

[a] All measurements in $CHCl_3$ except where noted. [b] In ethyl ether. [c] In THF.

The polymerization of the isocyanate **4** in either optically active or racemic form proceeded well with NaCN in dimethylformamide at low temperature.[17] After two precipitations from solvent–nonsolvent mixtures the polymers (*S*)-**5** and (*RS*)-**5** (see Table I) were obtained in good yield as fibrous white solids. The polymers synthesized from the optically active and racemic monomer, (*S*)-**5** and (*RS*)-**5**, respectively, readily dissolved in chloroform, but only the optically active polymer was insoluble in tetrahydrofuran. The polymer characteristics of intrinsic viscosity ($[\eta]$), optical activity ($[\alpha]$), weight-average molecular weight($\bar{M}_w$), second virial coefficient (A_2), and root-mean-square radius of gyration ($\langle S^2\rangle^{1/2}$) are presented in Table I.

The circular dichroism and ultraviolet spectra in $CHCl_3$ for (*S*)-**5** are presented on the same scale in Figure 2. The ultraviolet spectrum of (*S*)-**5** is replotted in Figure 3 on the same scale with (*RS*)-**5** and poly(*n*-butyl isocyanate) (PBIC). PBIC with intrinsic viscosity $[\eta] = 6.1$ dL g^{-1} in $CHCl_3$ was obtained from fractionally distilled commercially available *n*-butyl isocyanate, using the same procedures as for the isomers of **5**.[17] The angular dependence

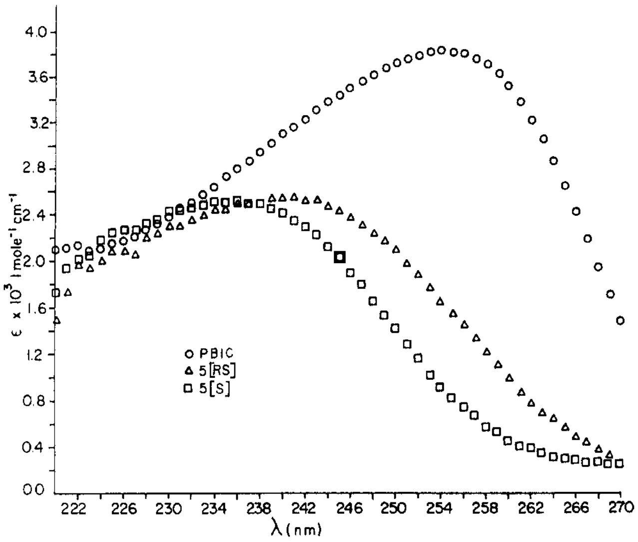


Figure 3. Ultraviolet spectra of (*S*)-**5**, (*RS*)-**5**, and PBIC recorded in $CHCl_3$.

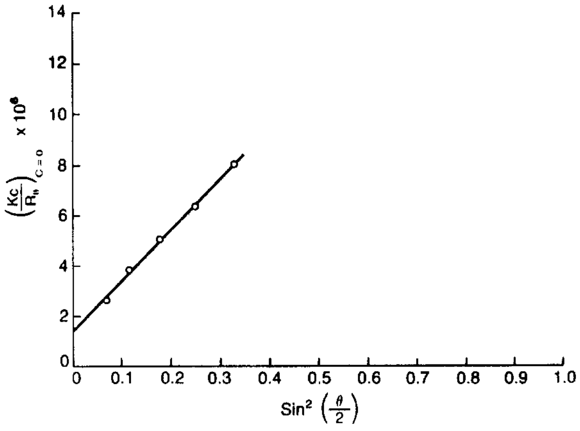


Figure 4. Light scattering angular dependence for (*S*)-**5**.

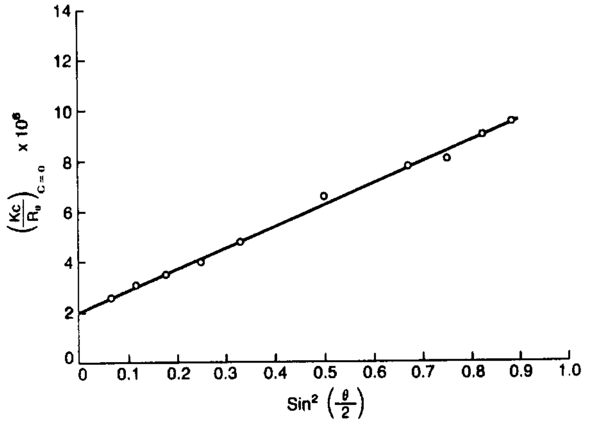


Figure 5. Light scattering angular dependence for (*RS*)-**5**.

of the light scattering[18] are shown for (*S*)-**5** and (*RS*)-**5** in Figures 4 and 5, respectively. The polymers (*S*)-**5** and (*RS*)-**5**, and PBIC for comparison, were further characterized by high-field ^{13}C nuclear magnetic resonance (NMR) spectra. These spectra are exhibited respectively in Figures 6–8.

Discussion

Circular Dichroism and Ultraviolet Measurements. The large increase in optical rotation in going from the monomer to the polymer (*S*)-**5** (Table I) parallels the observations of Goodman and Chen[7] and can be similarly interpreted as arising from a stereoregular structure[8] which is very probably a helix[7,8] with an excess of one sense. One cannot simply, from the optical rotation, assign a quantitative preference to this helical sense or assign which handedness is in excess.

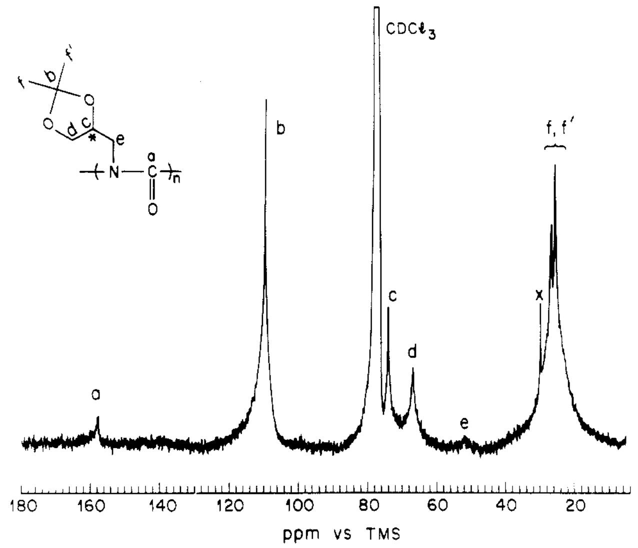


Figure 6. 125.7-MHz ^{13}C NMR spectrum of (*S*)-**5** recorded in $CDCl_3$ at 60 °C.

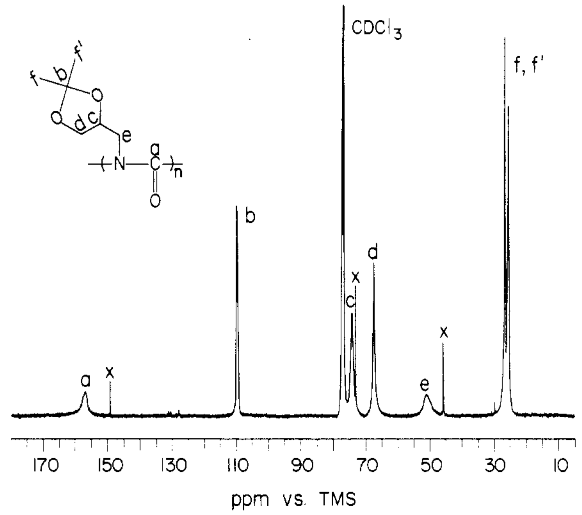


Figure 7. 125.7-MHz ^{13}C NMR spectrum of (*RS*)-**5** recorded in $CDCl_3$ at 55 °C.

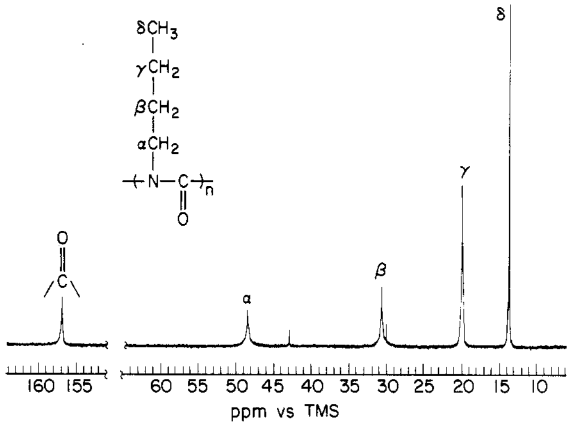


Figure 8. 125.7-MHz ^{13}C NMR spectrum of poly(*n*-butyl isocyanate) recorded in $CDCl_3$ at 55 °C.

The observed [α] in the visible region arises from the tail of a Cotton effect centered in the ultraviolet region of the spectrum at about 242 nm (Figure 2). This strong negative circular dichroism (CD) band is followed by a positive dichroism of increasing intensity up to the point where solvent absorption precludes measurement. The fact that the UV absorption maximum is displaced to lower wavelength than the CD band could suggest exciton coupling, a phenomenon associated with helical polymer conformations,[19] or that the CD band arises from a transition other than that associated with the UV maximum. The observation of a change in sign in the CD spectrum in the region of the absorption maximum was also observed for poly(*S*)-2-methylbutyl isocyanate).[7] Troxell and Scheraga,[20] however, in their study of the electric dichroism of poly(*n*-butyl isocyanate) found no evidence for exciton coupling and suggested that a lower wavelength absorption might account for the CD pattern observed for poly((*S*)-2-methylbutyl isocyanate).[7] In that work, the UV spectrum was not measured, and one cannot, therefore, determine if the CD maximum at 253 nm is displaced from the absorption maximum as is apparently the situation for (*S*)-**5** (Figures 2 and 3). The UV absorption maximum for PBIC in chloroform occurs at 254 nm,[21] but it is clear from the data in Figure 3 that the UV band position and intensity are dependent on the pendant group and, therefore, may be different for the *n*-butyl and 2-methylbutyl chain substituents.

The CD maximum in (*S*)-**5** is about 10 nm lower in wavelength than that observed by Goodman and Chen,[7] while the molar ellipticity (ϕ) in the published spectrum[7] is higher than that for (*S*)-**5**, i.e., a minimum value[22] of 13 300 vs. 9900. Although the relative values of the molar ellipticity cannot be interpreted without knowing the excess of one helical sense over the other in the compared systems, the lower wavelength CD band observed for (*S*)-**5** suggests the two polymers have different UV spectra.

Although Troxell and Scheraga[20] suggested, from their studies, no evidence for electron delocalization in PBIC, such a phenomenon offers a convenient explanation for the data in Figure 3. Steric effects are recognized to play an important role in the formation of the helix and while the existing information[3] points to an 8/3 helix with a pitch of 5.17 Å in poly(*n*-alkyl isocyanates) (at least in the solid state) there is no information available on the nature of the helix with other pendant groups.[23] With α- substituted pendant groups, isocyanates will not polymerize.[17] The lower wavelength absorption maximum in (*S*)-**5** compared to PBIC (Figure 3)[20,21] could be associated with the increased steric bulk of the 2,2-dimethyl-1,3-dioxolane ring compared to the linear alkane, thereby forcing the polymer to turn further out of conjugation.

The UV absorption spectra of (*S*)-**5** and (*RS*)-**5** are similar, especially compared to PBIC (Figure 3), suggesting that the characteristics of the chromophore are similar. Since, as discussed above, the helix parameters should strongly affect the chromophore, these data (Figure 3) point to similar helical characteristics for (*S*)-**5** and (*RS*)-**5**. That this structural similarity cannot arise from a highly stereoselective polymerization follows from the data presented below. If the racemic monomer polymerized to yield a mixture of enantiomeric polymers, the dilute solution properties of the polymers from optically active or racemic monomers would be identical. Since the molecular weights of (*S*)-**5** and (*RS*)-**5** differ by a factor of 1.5 while the $[\eta]$ values are related by a factor of nearly 3, the two materials must differ in their chain characteristics. These data suggest that (*S*)-**5** for the same degree of polymerization possesses a larger hydrodynamic size than that for (*RS*)-**5**.[24] The difference between the polymers is consistent with the tetrahydrofuran solubility of (*RS*)-**5** but not (*S*)-**5**.

Light Scattering. The difference in the $\langle S^2 \rangle^{1/2}$ values for (*S*)-**5** and (*RS*)-**5**, 1600 Å and 860 Å, respectively (Table I, Figures 4 and 5), cannot be accounted for by the molecular weight differences. Under the extreme condition that (*RS*)-**5** were a perfect rod, $\langle S^2 \rangle^{1/2}$ would be proportional to the molecular weight. This would predict a value of 1255 Å for (*RS*)-**5** at a molecular weight of 730 000, far below what is observed for (*S*)-**5**.

The quantitative relationship of the chain dimensions of (*S*)-**5** and (*RS*)-**5** could be evaluated by calculation of the persistence length. This chain characteristic has been evaluated in poly(*n*-alkyl isocyanates)[3] by using the relationship between light scattering radius of gyration and contour length developed by Benoit and Doty for a Kratky–Porod wormlike chain.[25] Calculation of the prerequisite contour length requires knowledge of the monomer projection length, *h*, and the degree of polymerization corresponding to the square root of the product of the *z*-average and ($z + 1$)-average molecular weights. Although it is likely that *h* is the same for the two polymer stereoisomers, it may differ, as suggested by the UV data, from the value of 1.94 Å determined by the X-ray study[4] on poly(*n*-butyl isocyanate).

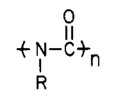
The value of the contour length (*L*) is simply *h* multiplied by the degree of polymerization, *n*. Although the prerequisite $(\bar{M}_z \bar{M}_{z+1})^{1/2}$ was not determined, gel permeation chromatography (GPC) on (*S*)-**5** and (*RS*)-**5** showed the polymers to be of similar polydispersity.[26-28] This is adequate for our purpose of comparing the stereoisomeric polymers, and with the discussion above in mind, we simply set the highest order moleclar weight average to be $1.5\bar{M}_w$ and took *h* to be 2.0 Å. Following the same model used by earlier workers on poly(*n*-alkyl isocyanates),[29] the persistence lengths, *q*, for (*S*)-**5** and (*RS*)-**5** with the above assumptions were calculated to be 627 and 245 Å in chloroform, respectively.

Although the optically active polyisocyanate is clearly of far higher axial dimension than the polymer derived from racemic monomer, it is desirable, if possible, to relate these numbers to the poly(*n*-alkyl isocyanates). The solubility characteristics of (*S*)-**5** limit this comparison to chloroform solutions, the solvent used for the light scattering work.

Fetters and Yu[29] calculated a persistence length of between 500 and 600 Å for poly(*n*-butyl isocyanate) based on a correlation of the $\bar{M}_w$ with $\langle S^2 \rangle^{1/2}$ data taken in chloroform.[30] We have isolated from their wide-ranging data base the radii of gyration based on polymers obtained in an identical manner to the polymerizations carried out in this work (see Experimental Section). Applying a polydispersity correction, i.e., $\bar{M}_w/(\bar{M}_z \bar{M}_{z+1})^{1/2} = {}^2/_3$, to their data,[29] we obtain a persistence length close to 300 Å for poly(*n*-butyl isocyanate) in $CHCl_3$. This correction brings the persistence length of poly(*n*-butyl isocyanate) closer to other later work (see below) on the chain dimensions of poly(*n*-hexyl isocyanate).

In one determination,[24] narrow molecular weight fractions of poly(*n*-hexyl isocyanate) were studied by light scattering in tetrahydrofuran to yield a persistence length of between 400 and 500 Å. In another study,[28] intrinsic viscosity–molecular weight data yielded values of 185 Å in dichloromethane and 375 Å in toluene. The large solvent effect is consistent with the known properties of these polymers.[31] We have determined that dichloromethane and chloroform have nearly identical effects on the intrinsic viscosity of poly(*n*-hexyl isocyanate) while the lit-

Table II
Persistence Lengths of Polyisocyanates



$$\left[N(R)-C(=O) \right]_n$$

R	q, Å (solvent)	method
n-C_4H_9	300 ($CHCl_3$)	light scattering[a] [29]
n-C_6H_{13}	400–500 (THF)	light scattering[24]
n-C_6H_{13}	200 (CH_2Cl_2)	viscosity[b] [28]
n-C_6H_{13}	400 (toluene)	viscosity[b] [28]
n-C_6H_{13}	350 (n-C_4H_9Cl)	viscosity[b] [31,32]
n-C_6H_{13}	420 (hexane)	viscosity[b] [32]
(*S*)-**5**	600 ($CHCl_3$)	light scattering[c]
(*RS*)-**5**	250 ($CHCl_3$)	light scattering[c]

[a] Calculated from published result assuming $(\bar{M}_w/\bar{M}_z\bar{M}_{z+1})^{1/2} = {}^2/_3$. [b] Viscosity–molecular weight relationship. [c] Present work. See text.

erature shows this also to be true of the pair toluene and tetrahydrofuran.[24] More recent work based on viscosity measurements[32] yielded a persistence length for poly(n-hexyl isocyanate) of 350 Å in n-butyl chloride and 420 Å in hexane.

The published data based on both viscosity and light scattering measurements[24,28,29,32] point to a persistence length in chloroform between 200 and 300 Å with an increase to over 400 Å in the more chain-extending solvents for poly(n-alkyl isocyanates.[33] The persistence length determinations of this work for (*S*)-**5** and (*RS*)-**5** in chloroform shows that (*S*)-**5** ($q \sim 600$ Å), even considering the approximations made in the calculation (see above), is highly axially extended compared both to (*RS*)-**5** ($q \sim 250$ Å) and to poly(n-alkyl isocyanates). This information is summarized in Table II.

Structure of (*S*)-5 and (*RS*)-5. In so far as the ultraviolet (UV) spectral characteristics are associated with the helix parameters controlling the conjugation, one must conclude that the similar chain dimensions for (*RS*)-**5** and PBIC as judged by the persistence lengths do not suggest similar polymer conformational properties. In contrast, by the criterion of the UV spectra (Figure 3) (*S*)-**5** and (*RS*)-**5** are similar in their local structure and differ substantially from PBIC. This may be associated with the formation of blocks of (*R*) and (*S*) enantiomeric units in the polymerization of the racemic monomer. If this picture were accurate and one added the fact of the high axial extension in (*S*)-**5** as discussed above, it would then follow that the points of interchange between the mirror image residues, determined by the details of the polymerization mechanism, would be kinks in the rod that could not move throughout the chain.[34] These regions of helix reversal in the polymer chain could be associated with the higher wavelength component of the UV spectrum of (*RS*)-**5** compared to (*S*)-**5** (Figure 3).

An unusual intrinsic viscosity [η] characteristic we have observed on (*RS*)-**5** may pertain to this discussion. As discussed above, there is a large solvent dependence on the values for [η] for poly(n-alkyl isocyanates) which has been shown to be associated with the chain dimensions (as evaluated by the persistence lengths)[24,28,29,32] in various solvents.[31] The fact that addition of a nonsolvent to solutions of poly(n-hexyl isocyanates) in a good solvent to the point near to precipitation does not change the intrinsic viscosity–molecular weight relationship[24] suggests that the solvent sensitivity of [η] is associated with local conformational properties rather than the excluded volume effects encountered in coil polymers.

In detail, for poly(n-hexyl isocyanate), the Mark-Houwink a values vary widely, with chloroform and tetrahydrofuran occupying, respectively, near to the low and high extremes.[24] In (*RS*)-**5**, in contrast, we find that [η] is *reduced* slightly on substituting tetrahydrofuran for chloroform as the solvent. Thus, the conformational properties of (*RS*)-**5** appear to be insensitive to the solvent, in contrast to poly(n-alkyl isocyanates). This is consistent with, but does not require the existence of, blocks of (*R*) and (*S*) residues. The ^{13}C NMR spectrum of (*RS*)-**5** discussed below is also consistent with a block structure exhibiting only limited chemical shift dispersion.

PBIC would therefore contrast to (*RS*)-**5**, and, as suggested by Tonelli,[6] the helix reversals could proceed as mobile defects throughout the chain. It is not possible at this time to separate the role of the asymmetry from that of steric size in accounting for the difference between the polyisocyanates with n-butyl and dioxolane pendant groups. Work is currently under way here on a comparison of an achiral and a chiral pendant polyisocyanate with almost identical steric dimensions.

^{13}C NMR. Further insight into the compared properties of (*S*)-**5**, (*RS*)-**5**, and PBIC were gained from the high-field ^{13}C NMR spectra (Figures 6–8). At the first level of inquiry, the signals for the pendant carbons in the three polymers exhibit nearly the same chemical shift pattern as in the respective precursor monomers and are consistent with the structures. Chemical shift assignments of the polymer spectra are based on this comparison and the use of empirical shift rules. The assignments of carbons c and d in Figures 6 and 7 are tentative and may be reversed. The backbone carbonyl signal appears in each case at close to 158 ppm from hexamethyldisiloxane. This is reasonable since the adjacent atoms are identical in the three polymers. The low-intensity sharp lines appearing in (*RS*)-**5** (Figure 7) at 46, 73, and 149 ppm and in PBIC (Figure 8) at 30, 43, and 149 (not shown) ppm are identified by their line width as low molecular weight impurities that were not removed by our purification procedures. The chemical shift assignments and the line widths of the polymer signals in the three spectra are listed in Table III.

The values of 6–31 Hz observed for PBIC are larger than line widths typically recorded for the random coil polymers in solution.[35] The carbonyl resonance with a line width of 18 Hz indicates a substantial loss of backbone motion, consistent with the large axial dimension of this polymer.[3] The reduction in line width observed for the side-chain

Table III
Line Width (lw, Hz) of ^{13}C Resonances

poly(C_4H_9NCO)[a]			poly($C_6H_{11}O_2NCO$)			
ppm[b]	carbon[c]	lw	ppm[b]	carbon[d]	lw (*S*)-**5**	lw (*RS*)-**5**
157	carbonyl	18.3	158	carbonyl	~175	~200
48	α	31.3	51	e	>300	~500
31	β	22.1	75	c	75	185
20	γ	9.2	67	d	110	88
14	δ	6.1	110	b	100	132
				f, f′	130,200	30, 50

[a] PBIC $\bar{M}_v \sim 150\,000$.[24] [b] Relative to Me_4Si. [c] See Figure 8 for carbon designations. [d] See Figure 6 for carbon designations.

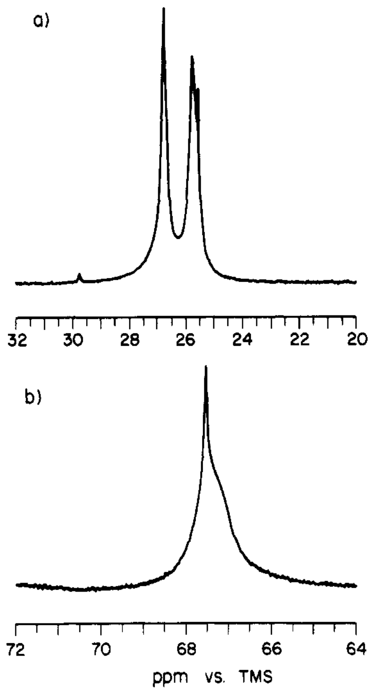


Figure 9. 125.7-MHz ^{13}C NMR spectrum of the methyl carbons (a) and ring methylene carbon (b) of (*RS*)-**5** recorded in $CDCl_3$ at 60 °C.

carbon nuclei further removed from the backbone is expected as a result of the additional degrees of freedom produced by the less restricted bond rotations.

Observation of the NMR spectra of (*S*)-**5** and (*RS*)-**5** (Figures 6 and 7) shows substantially increased line widths over PBIC (Table III). One source of the increased line widths in (*RS*)-**5** is chemical shift dispersion arising from the diastereomeric environments in the copolymerization of the (*R*) and (*S*) units. The resultant resonances if not individually resolved may be expected to appear asymmetric. Examination of Figure 7 shows the resonances to appear predominantly symmetrical, suggesting restricted segmental motion as the major contributor to the line width. Nevertheless, if we examine an expansion of several resonances (Figure 9), we observe some asymmetry. In particular, the methyl resonances show differences in line width and some resonance splitting, and the ring methylene resonance at 67 ppm is asymmetric and appears to have some structure.

Therefore, it is possible that both the combination of shift dispersion resulting from different stereosequences and the extended helical nature of the molecule produce the broad resonances of (*RS*)-**5**. In examining the NMR data we conclude that most of the observed line broadening results from an incomplete averaging of the ^{13}C–^{1}H dipole–dipole interactions in these very stiff chains.

In comparing the line widths of the carbon nuclei of (*S*)-**5** and (*RS*)-**5** (Table III), we find that the side-chain resonances are not dissimilar. This observation indicates that local side-chain motions are significant and similar in the two polymers but slow as compared to coil polymers or to PBIC. The line widths of the carbonyl and the methylene e (Table III) resonances indicate substantial loss of backbone motion. The larger line width of the methylene signal, relative to the carbonyl, is expected since the directly bonded hydrogens will produce a much larger carbon–proton dipolar interaction than that experienced by the carbonyl nuclei.

Concluding Remarks

Although the experiments described above do not yet allow a distinction between the role of the steric size and the asymmetry of the polyisocyanate pendant group, we can conclude that changes in the nature of the group have a large effect on the axial dimension of these stiff polymers. The role of the asymmetry of the pendant group follows from the fact that these polymers, prepared from achiral isocyanates, owe their chirality only to helicity and are distinguished from most other stiff-chain polymers which are either symmetric, as in the polyaramides, or asymmetric, as in polymers of biological interest. The steric role of the pendant group, in contrast, arises from the conjugated nature of the amide backbone which forces these groups to occupy sterically difficult sites. In polymers in which this conjugation force is not present, only extreme steric size is capable of enforcing a stiff conformation.[36]

It follows that we can expect the characteristic ratio of these polymers to strongly depend on pendant group character.[37] The ability to so adjust the axial dimension, combined with the wide solubility of polyisocyanates and the important properties of polymers that depend on noncentrosymmetry and chain stiffness, makes these unusual polymers a desirable area of study.

The polyisocyanates described in this work and analogous materials may also be of use for testing ideas concerned with the differences between broken rods and wormlike chains.[38]

Experimental Section

Routine Procedures. Proton and ^{13}C NMR spectra were taken respectively on a Varian EMU 390 and a JEOL FX-90Q spectrometer and infrared spectra on either a Perkin-Elmer 1320 or a Schimatzu IR435 spectrometer. Analyses were carried out by Schwartzkopf Microanalytical Laboratory, Woodside, NY. Circular dichroism and ultraviolet spectra were respectively obtained on a Jasco J-40 and a Varian-Cary 2300 spectrometer and gas chromatographic analyses on a Varian 920 instrument using a 6-ft 20% SE-30 column. Mass spectra were measured on a Hitachi RMU-6L spectrometer at 75 eV. Optical rotations were recorded on a Bendix Series 1100 polarimeter at the mercury line (546 nm) or on a Perkin-Elmer 141 polarimeter at the sodium D line (589 nm). A single-bulb Cannon–Ubbelohde type viscometer, not corrected for shear-rate dependence, was utilized for the intrinsic viscosities.

Synthetic Procedures. The optically active and racemic tosylates of 2,2-dimethyl-1,3-dioxolane-4-hydroxymethylene were prepared exactly following the literature from diacetone D-mannitol and racemic solketal, respectively. The 1,2,5,6-diacetone D-mannitol prepared in this way (see text) yielded the derived tosylate in two steps.[10–12] This material was an oil and identical in optical rotation to the reported value.[11] The proton NMR and IR spectra were consistent with the structure. The racemic tosylate derived from commercially available solketal (Aldrich Chemical Co.) was a solid of mp 45–47.5 °C (lit.[11] 46–48 °C). Although both the optically active and racemic amines are known, our synthesis, reported below, was an improvement on these procedures.[12]

(*S*)-2,2-Dimethyl-1,3-dioxolane-4-methyleneamine (1). (*R*)-2,2-Dimethyl-1,3-dioxolane-4-methylene tosylate (70 g, 0.245 mol) was placed in a 500-mL Parr autoclave and to this was transferred 300 mL of ammonia by distillation from sodium metal. All the valves were closed securely, and the bomb was kept at 50 °C for 4 days. The pressure remained nearly constant at 250 psi. After this time, the temperature was reduced to 0 °C, and the ammonia was released through a needle valve and a drying tube filled with lime. The bomb was opened and washed with ether. The ether was filtered and the brown solution was dried and evaporated. The resulting brown oil was short path distilled at bp 40 °C (2 mmHg). Colorless liquid (26 g, yield 81%) was thus received with IR and proton NMR spectra consistent with the structure of 1. GC showed the material to be in excess of 98% pure. $[\alpha]^{25}{}_{546} = +5.7°$ ($c = 5.6$, CH_2Cl_2).

(*S*)-2,2-Dimethyl-1,3-dioxolane-4-methyleneformamide (2). The amine 1 (7.4 g, 0.56 mol) was added to 100 mL of ethyl formate (Aldrich Chemical Co.) which had been distilled. This solution was refluxed for 16 h, and the volatiles were then removed at 40 °C and 10 mmHg, leaving 8.8 g of a colorless liquid. $[\alpha]^{25}_{546} = -1.4°$ (c = 11.4, $CHCl_3$): yield, 99%.

(*S*)-2,2-Dimethyl-1,3-dioxolane-4-methyleneisonitrile (3). Transferring all materials with syringes through septum caps under dry argon and working in an excellent hood, we added 7.4 mL (0.053 mol) of triethylamine, dried by distillation from BaO; 40 mL of methylene chloride, distilled from P_2O_5, and 4 g (0.025 mol) of the formamide **2** to a three-neck flask fitted with an equalizing dropping funnel and a Dewar condenser. Diphosgene (1.52 mL, 0.013 mol), from Fluka Chemical Corp., and 8 mL of dry methylene chloride were syringed into the dropping funnel. With the reaction flask at 0 °C and with dry/ice acetone in the condenser, the contents of the funnel were added dropwise with stirring over 1.5 h. The solution turned brown and a white solid appeared. After 0.5 h more, the solution was filtered and extracted with 7.5% aqueous Na_2CO_3 and H_2O (brine). After the solution was dried with Na_2SO_4, the solvent was removed to yield 3.8 g of a brown liquid. Flash chromatography on 80 g of 230–400 mesh silica gel using 8:2 pentane:ether yielded in elution volumes 275 to 675 mL a light brown liquid after solvent evaporation. Short path distillation, bp 40 °C (0.5 mmHg) yielded 2.61 g (74%) of a colorless liquid that slowly turns brown on standing and was shown to be >98% pure by GC: ^{13}C NMR ($CDCl_3$, 22.5 MHz, to Me_4Si) 160.2 (t, J = 5.2 Hz), 110.7 (s), 74.2 (s), 67.3 (s), 44.9 (t, J = 6.6 Hz), 27.0 (s), 25.6 (s) ppm. IR: 2155 (str), 1220 (str), 1083 (str) cm^{-1}. The isonitrile **3** has a penetrating odor even at extremely low levels. $[\alpha]^{25}_{546} = +32.9°$ (c = 1.2, $CHCl_3$).

(*S*)-2,2-Dimethyl-1,3-dioxolane-4-methylene Isocyanate (4).[39] Under an inert atmosphere 300 mL of dry chloroform (distilled form P_2O_5) and 42.9 g (0.198 mol) of yellow mercuric oxide (Aldrich Chemical Co.) were mixed in a flask to which 6.9 g (0.049 mol) of **3** was quickly added. This mixture was refluxed for 5 h with excellent stirring and cooled to room temperature. Most of the solid was separated by filtration through a 2-in. × 3-in. column of Celite (545) and Na_2SO_4. The column was flushed with dry ether, and the solvents were evaporated to yield a liquid with suspended solid. This was short path distilled, bp 44 °C (0.8 mmHg) to obtain 5.6 g (73%) of a colorless liquid. This material was greater than 99% pure by GC. The IR spectrum showed 2260 (str.), 1370 (m), 1260 (m), 1215 cm^{-1} (m). ^{13}C NMR ($CDCl_3$, 22.5 MHz, Me_4Si) 110.2 (s), 74.7 (s), 66.6 (s), 45.3 (s), 26.7 (s), 25.2 (s) ppm. $[\alpha]^{25}_{546} = -21.1°$ (c = 2.8, ether). The synthetic steps of (*RS*)-1-(*RS*)-4 were identical with that reported for the optically active materials.

Poly((*S*)-2,2-dimethyl-1,3-dioxolane-4-methylene isocyanate) ((*S*)-5).

The initiator solution was prepared from 0.064 g (1.31×10^{-3} mol) of finely powdered NaCN that had been dried in a vacuum oven at 100 °C (2 mmHg). This was dissolved in 10 mL of dimethylformamide (DMF) that had been distilled from P_2O_5 at 1 atm. The monomer was distilled just before use and 5.0 g (0.032 mol) was syringed under argon into a three-neck flask that had been through a flame vacuum argon cycle and that contained 27.5 mL of DMF (purified as above and injected by syringe). The vessel was overhead stirred and cooled to −65 °C. Under a positive pressure of argon, 1 drop of initiator solution added by syringe caused the onset of polymerization as evidenced by an increase in viscosity. After 3 drops were rapidly added, a thick clear gellike material stopped the stirrer. After 1 h, methanol precooled to −78 °C was added, and after another hour at this temperature, the liquid was decanted away and replaced with 150 mL of a solution of 40% methanol and 60% chloroform also precooled to −78 °C. The gellike mass was, with great difficulty, physically broken apart and stored overnight at −15 °C. This material was dissolved in $CHCl_3$ at room temperature and precipitated from the nonsolvent 80% methanol/20% H_2O. Precipitation was repeated once more. There was obtained 3.3 g of a white fibrous solid (yield 66%). IR (thin film) 1698 (v str), 1377 (str), 1368 (str), 1357 (str), 1171 (str), 1062 cm^{-1} (v str). (^{13}C NMR see Figure 6 in text.) $[\alpha]^{25}_{578} = -333°$ (c = 0.20, $CHCl_3$). $[\eta]^{25}$ = 17.50 dL g^{-1} ($CHCl_3$). Anal. Calcd for $C_7H_{11}NO_3$: C, 53.50; H, 7.05; N, 8.91. Found: C, 52.75; H, 7.11; N, 8.06.

Poly(2,2-dimethyl-1,3-dioxolane-4-methylene isocyanate) ((*RS*)-5) Made from Racemic Monomer. The polymerization apparatus and procedure were identical with the above. The amounts used were the same and yield was 56% (2.8 g). The polymer appeared granular and fibrous. The precipitation nonsolvent was methanol. In the optically active polymer, pure methanol gave gellike behavior as the drops of the chloroform solution hit the nonsolvent and, therefore, water was added (see above). IR: identical with that for (*S*)-**5**. (^{13}C NMR see Figure 7 in text.) $[\eta]^{25}$ = 6.2 dL g^{-1} ($CHCl_3$).

Light Scattering. Weight-average molecular weight ($\bar{M}_w$) and second virial coefficients (A_2) were determined by low-angle laser light scattering (LALLS) techniques using a KMX-6 spectrometer (LDC/Milton Roy). The polymers were dissolved in chloroform by gentle agitation on a wrist-action shaker for 2 h prior to measurement. For purposes of enhanced solution clarity, the optically active polyisocyanate was prefiltered through a 5.0-μm Teflon filter (Millipore Corp.), precipitated, and redissolved prior to the reported measurements. Differential refractive index (dn/dc) measurements were obtained at 436- and 633-nm wavelength using a C. N. Woods differential refractometer (C. N. Woods Manufacturing Co.) with a tungsten source. The samples were filtered with a Fluoropore 0.5-μm pore diameter filter before passing through the LALLS cell.

The root-mean-square radius of gyration $\langle S^2 \rangle^{1/2}$ was calculated from the ratio of the slope of the intercept of the angular dependence of the light scattering (Figures 4 and 5).[18] These measurements were performed with a C. N. Woods spectrometer operating at 436 nm. The spectrometer calibration was carefully checked and then verified by light scattering measurement of a polystyrene standard. We could detect no depolarization in either of the polyisocyanate samples. Thus, the results were obtained with unpolarized incident and scattered light.

The wide-angle measurements and the LALLS results gave the same values for $\bar{M}_w$.

High-Field NMR Measurements. The ^{13}C NMR spectra were recorded at 125.75 MHz on a JEOL GX-500 NMR spectrometer. The sample concentrations employed were 12% (w/v) for the poly(*n*-butyl isocyanate) (PBIC) and racemic-derived polyisocyanate (*RS*)-**5**. The optically active polyisocyanate (*S*)-**5** was examined as a 3.6% (w/v) solution. Spectra were recorded at 50–55 °C using $CDCl_3$ as solvent and hexmethyldisiloxane (HMDS) as an internal reference. A total of 15–27 000 scans was accumulated for each polymer solution. The delay time between sampling pulses was 15.0 s; however, no attempt was made to acquire data under quantitative conditions.

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Regioselectivity in Isoprene Inclusion Polymerization

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ABSTRACT: Polyisoprene obtained by radiation polymerization in perhydrotriphenylene clathrates possesses a pure 1,4-trans structure but contains a significant number of head-to-head, tail-to-tail defects. Triad and tedrad sequences are detected in the ^{13}C NMR spectrum: their distribution is interpreted as a succession of direct and inverted units. Probability parameters and their temperature coefficients are determined both in a Bernoullian approximation and as a first-order Markov chain.

In the past few years we have pointed out several times the high degree of regularity existing in polymers obtained by radiation polymerization in perhydrotriphenylene (PHTP) clathrates,[1-4] the only notable exception being polyisoprene. A 1,4-trans structure was assigned to this polymer on the basis of the IR spectrum;[5] however on

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