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Macromolecular Stereochemistry: Effect of Pendant Group Structure on the Conformational Properties of Polyisocyanides[1,2]

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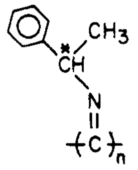
ABSTRACT: The hydroxyl function of the S enantiomer of the 1,2-acetone ketal of propylene glycol was converted, via the amine, to the isocyanide ($[\alpha]_{546}$ +32.9° ($CHCl_3$)), which was polymerized by using $NiCl_2$ hexahydrate in the neat state to the derived poly((S)-2,2-dimethyl-1,3-dioxolane-4-methyl isocyanide) ($[\alpha]_{546}$ +68.5° (p-dioxane); $M_w = 165\,000$). The ultraviolet spectrum of this brown solid in $CHCl_3$ exhibited a band, as a shoulder on lower wavelength absorptions, with $\lambda_{max} = 295$ nm and 3.2×10^2 L mol^{-1} cm^{-1}, and a long low-intensity visible region tail. The circular dichroism (CD) spectrum was similar to published spectra for α-substituted asymmetric polyisocyanides and showed three maxima (λ_{max}, nm; $\Delta\epsilon$, L mol^{-1} cm^{-1}): 328, −0.082; 290, +0.015; 275, −0.047. High-field ^{13}C NMR studies exhibited extensive chemical shift dispersion for both the backbone carbon and the pendant carbons. Similar shift dispersion was encountered in poly(n-butyl isocyanide) and in poly(benzyl isocyanide). Poly((R)-α-phenylethyl isocyanide) also exhibited chemical shift dispersion superimposed on symmetrical but broadened lines in its ^{13}C NMR spectrum. Zimm plots constructed from wide-angle 633-nm light scattering data on poly((R)-α-phenylethyl isocyanide) ($M_w = 107\,000$) and on poly((S)-2,2-dimethyl-1,3-dioxolane-4-methyl isocyanide) ($M_w = 165\,000$) showed no angular dependence. The weight average hydrodynamic radii of these polymers in tetrahydrofuran were determined by photon correlation spectroscopy to be 51 and 24 Å, respectively. If one adopts a 4/1 helix with a pitch of 4 Å proposed in the literature for poly(α-phenylethyl isocyanide), our data yield a persistence length of 32 Å, which is substantially larger than that for poly((S)-2,2-dimethyl-1,3-dioxolane-4-methyl isocyanide). The results show that some form of stereoirregularity, which could involve syn–anti isomerism about the carbon–nitrogen double bond, is seen in each of the polymers studied. In addition, the chain dimension is strongly dependent on the pendant group structure.

Introduction

Millich and co-workers in Missouri,[4] followed by independent efforts in Japan,[5,6] demonstrated that strong acid promotes the polymerization of certain alkyl and arylalkyl isocyanides. Somewhat later Drenth and co-workers in Holland developed an additional route for the polymerization of isocyanides using Ni^{II} salts.[7] These polymers prepared by either route were assigned the poly-Schiff base structure on the basis of infrared bands analogous to models and to the known mode of reactivity of the functional group.[5–7] Thus the later literature, based on the assumption that this structural characteristic would persist in all cases, designated these materials as poly(iminomethylenes).[8]

Millich's early concern[9] that the unsaturation could shift to the pendant group led him to study the polymerization of the optically active α-phenylethyl isocyanide. The resulting polymer 1 exhibited a large increase in optical rotation over the monomer, which served to discount the concern and also suggested a regular conformation for 1.[10]



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Structural regularity in 1 was shown by space-filling models to be consistent with a 4/1 helix. Although this structure was supported by X-ray studies in the solid, unoriented samples were examined, which necessitated assumptions about packing as a prerequisite to the helix assignments.[5,11–14] For 1 prepared from the racemic monomer, the proposal of a 4/1 helix with a pitch of 4 Å is consistent with the absolute intensity of X-ray scattering of toluene solutions. These solution data indicate a monomer projection length of 1.04 Å,[5,15,16] a value near to that expected for a helix with a pitch of 4 Å.

A regular helical conformation for 1 in solution would suggest a stiff polymer, and this characteristic is supported by solution properties of narrow molecular weight fractions.[15,17] The Mark–Houwink exponent for 1 from the racemic monomer is 1.3 in toluene, and the second virial coefficient is nearly invariant in toluene over the $\bar{M}_n$ range from 20 000 to 123 000. In contrast, for the same samples the radii of gyration obtained from the angular dependence of X-ray scattering in toluene solutions were not proportional to the molecular weight[13,15,16] over the range 20 000–90 000 ($\bar{M}_w$), indicating some flexibility in the polymer chains.

In a remarkable experiment, poly($tert$-butyl isocyanide) of a number average degree of polymerization of 20 was resolved into optically active fractions.[18] From an analysis of the resulting circular dichroism spectrum the authors[19,20] assigned the helical sense and concluded that the earlier proposed 4/1 helix[11–14] was applicable also to poly($tert$-butyl isocyanide).

Other data on polyisocyanides suggest that the structure of the pendant groups has a large effect on backbone conformation. The Mark–Houwink exponents for the polymers of β-phenylethyl isocyanide (tetrahydrofuran)[21] and racemic 2-octyl isocyanide (toluene)[22,23] are 0.68 and

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1.75, respectively, both measured over approximately the same molecular weight range. These values, known to be sensitively related to molecular dimensions,[24] taken with the value of 1.3 for poly(α-phenylethyl isocyanide) (see above),[15,17] suggest that pendant group structure strongly affects chain dimensions.

In recent years a large effort in synthetic chemistry has produced a wide range of polyisocyanides for general studies of the relationship of structure to optical activity and circular dichroism characteristics[22,23,25] and as models for catalysis and various biological functions.[26] Most of these systems, of quite variable structure, have been substituted on the carbon adjacent to the nitrogen (α-substitution) giving them a formal analogy to poly(α-phenylethyl isocyanide) and poly(2-octyl isocyanide). The Mark–Houwink exponent of 1.75, for the poly(2-octyl isocyanide),[22] has been generally used to yield $\bar{M}_v$ from viscosity data for these polymers, and the structures have been assigned as rigid 4/1 helical rods with a pitch of 4 Å. In more recent efforts in this field a variety of polyisocyanides without α-substituents have been assigned a 4/1 helical rodlike conformation.[27]

Circular dichroism measurements are used to support the assumption that a wide variety of optically active polyisocyanides with asymmetric pendant groups adopt a rigid 4/1 helix.[22,23,25,26] Although it has been suggested that an exciton is associated with the imino group chromophore near 300 nm and has been used to interpret the screw sense and helical preference of the 4/1 model,[22,23,25,26] it is well-known that an exciton may arise from a variety of chiral conformations that may not involve extended helical forms.[28]

The assignment of a polyimine structure to the isocyanide polymers makes possible a unique polymer stereoisomerism associated with the carbon–nitrogen double bond. This question of syn–anti isomerism was addressed early in the literature but dismissed on the basis of space-filling models, although it was suggested that chain-breaking impurities could allow such isomerism.[10] It seems important to increase our understanding of when this structural isomerism may be reasonably excluded.

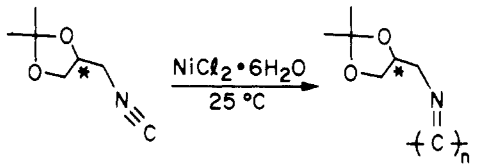
So far the only polyisocyanide studied extensively in solution is poly(α-phenylethyl isocyanide) initiated by strong acid.[10–17] The possible stereoselectivity of this polymerization could greatly affect the dimensions of the polymer in solution in a manner similar to that observed on polyisocyanates.[2] The change to Ni^{II} salt initiators and the use of enantiomerically pure monomer followed by studies of chain dimensions could therefore play a role in increasing our understanding of the conformational properties of these polymers.

In this work we have prepared, using Ni^{II} initiation, three polyisocyanides without α-substituents, one of which is optically active. We have also prepared poly(α-phenylethyl isocyanide) from both racemic and optically active monomer. We hope our studies on these materials, reported below, will help to strengthen the basis for the structural characterization of this interesting class of polymers.

Results

Synthesis. The optically active and racemic 2,2-dimethyl-1,3-dioxolane-4-methyl isocyanides were intermediates in the preparation of the analogous isocyanates and are described in detail in that work.[2] These stereoisomers were polymerized by following the Dutch procedures[7] with NiCl$_2$·6H$_2$O in the neat state to yield, after purification by two precipitations, brown solids in moderate yield.[29] These materials, (*S*)-2 and (*RS*)-2 were characterized by intrinsic viscosity η, weight average molecular weight $\bar{M}_w$, second virial coefficient A_2, and optical activity for (*S*)-2, and these data appear in Table I.

Table I
Characteristics of Monomer and the Polyisocyanides ((*S*)-2 and (*RS*)-2)



configuration at C*	monomer $[\alpha]^{25}_{546}$,[a] deg	polymer $[\alpha]^{25}_{546}$,[a] deg	polymer $\bar{M}_w$[b]	polymer 10^4A_2[b]	polymer η, dL g^{-1}
S[d]	+35.8	+68.5	165 000	6.14	1.08[c]
S[e]	+35.8	+68.0			0.08
RS[d]			110 000	3.15	0.61[c]

[a] In *p*-dioxane. [b] In tetrahydrofuran by low-angle laser-light scattering. Units for A_2 are in m cm^3 g^{-2}. [c] In CHCl$_3$ at 25 °C; intrinsic viscosities. [d] Polymerized neat. [e] Polymerized in methanol.

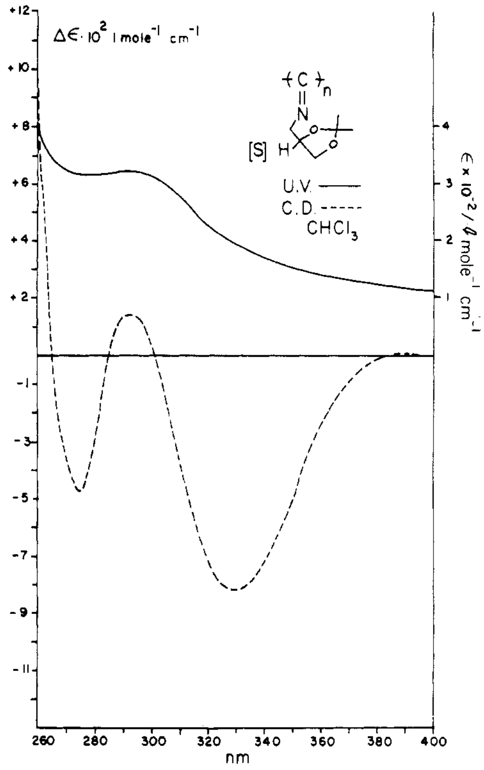
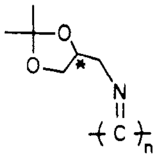


Figure 1. Circular dichroism and ultraviolet spectra of (*S*)-2.



2[S], 2[RS]

Ultraviolet and Circular Dichroism Spectra. Circular dichroism (CD) has been utilized to determine the helical preference[20,22,23,25,26] in optically active α-substituted polyisocyanides, suggesting a comparable measurement for (*S*)-2. The CD and the associated ultraviolet (UV) spectra are exhibited in Figure 1. The circular dichroism literature is based on an analysis of the spectrum of the resolved

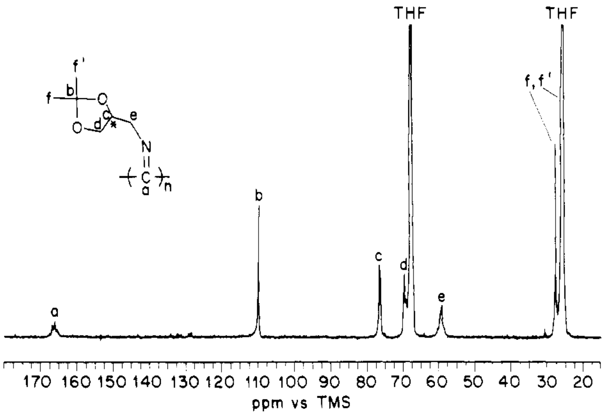


Figure 2. 125.7-MHz ^{13}C NMR spectrum of (*S*)-**2** recorded at 40 °C in THF.

poly(*tert*-butyl isocyanide),[18-20] which exhibits a UV shoulder close to 300 nm, just as is seen in Figure 1 for (*S*)-**2**.[30] This band in poly(*tert*-butyl isocyanide) is attended by a positive CD band with $\Delta\epsilon$ of about 0.2. This feature was interpreted as arising from a preference for the left-handed helix,[20] and this has been extrapolated[22,23] to indicate the helical preference in a series of asymmetric α-substituted aliphatic pendant polyisocyanides. In these cases the CD band position varies from 300 to about 320 nm, and the intensities are diminished compared to the resolved poly(*tert*-butyl isocyanide). The intensity change was interpreted as a weaker helical preference consistent with the smaller size of these groups.[22]

The change in band wavelength could also be interpreted as suggesting a change in the helix parameters, giving rise to a change in conjugation.[31] This would be significant because the interpretation of the CD spectrum of poly(*tert*-butyl isocyanide)[20] has been offered as support for the assignment of a 4/1 helix to other α-substituted pendant polyisocyanides.[8,14,25-27] The 20-nm shift pointed out above could therefore suggest unreliability in the use of poly(*tert*-butyl isocyanide) as such a model.

The characteristics of this long-wavelength CD band have, nevertheless, been suggested as adequate for the analysis of other optically active polyisocyanides,[22] and therefore one could conclude from Figure 1 that (*S*)-**2** exists in a helical conformation with approximately the same helical preference as in poly((*R*)-3-methyl-*sec*-butyl isocyanide).[22] The sign of the CD maximum, according to this analysis,[22] would point to a preference for the right-handed helix for (*S*)-**2**.

It seemed desirable to find confirmation of this analysis of (*S*)-**2**. In this regard the high-field ^{13}C nuclear magnetic resonance spectrum (NMR) of (*S*)-**2** was determined. This is presented in Figure 2.

Nuclear Magnetic Resonance Spectra. The ^{13}C NMR spectrum of (*S*)-**2** appears in Figure 2 and was recorded at 125.7 MHz and 40 °C in deuteriated tetrahydrofuran. The assignments noted on the spectrum are reasonable chemical shifts for these nuclei and were confirmed by observation of ^{13}C–^{1}H coupling. The resonances for carbons a and e were assigned from the ^{13}C NMR spectrum of the monomer, which showed a triplet, arising from nitrogen coupling for these nuclei.[32] We are unable to make a specific assignment for the diastereotopic methyl groups f and f′. Most noteworthy is the backbone carbon, appearing near 165 ppm. This nucleus, which should be the most sensitive to polymer backbone conformation, appears as a complex multiplet as seen in the expanded spectrum in Figure 3. Indeed, every carbon in the macromolecule is similarly complex as is evidenced by the other expansions in Figure 3.

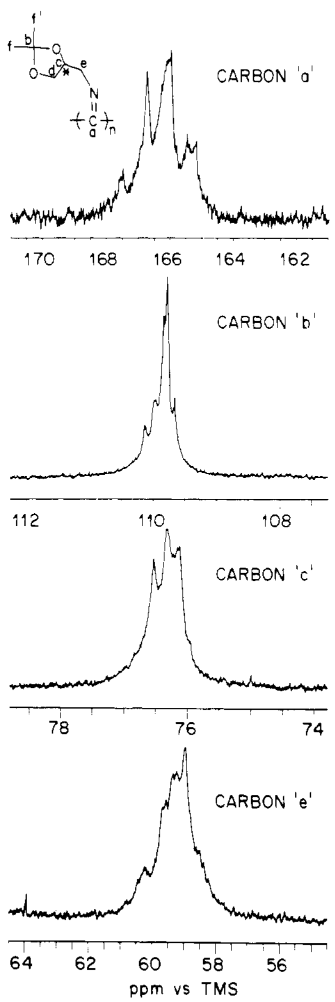
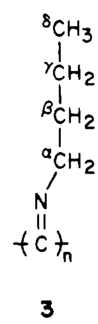


Figure 3. Expanded regions of the ^{13}C NMR spectrum of (*S*)-**2** from Figure 2.

The inherent line width of the quaternary side-chain carbon b (Figure 3) is less than 10 Hz, while that of the backbone carbon a is less than 20 Hz. These data suggest considerable local motion, a conclusion well supported by the line widths for comparable nuclei in poly((*S*)-2,2-dimethyl-1,3-dioxolane-4-methyl isocyanate).[2]

There is a potential stereochemical source of the chemical shift dispersion observed in Figure 3. Left- and right-handed helical arrangements of the polymer chain place the carbon nuclei, by virtue of the stereogenic center at carbon c, into diastereomeric states. Moreover, this would be complicated by regions where there is a reversal in helical sense if such a process were slow on the NMR time scale. To test this source of the observed chemical shift dispersion, we sought the comparable ^{13}C NMR spectrum of a polyisocyanide from an achiral isocyanide monomer.

Poly(*n*-butyl isocyanide) **3** was prepared similarly to



3

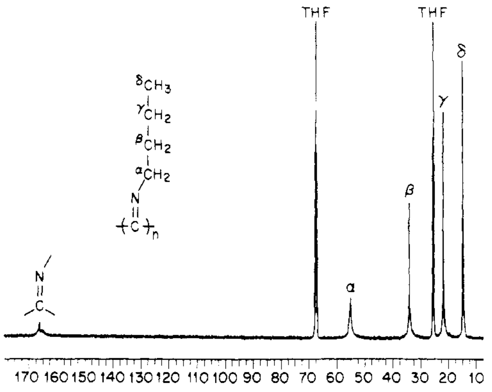


Figure 4. 125.7-MHz ^{13}C NMR spectrum of **3** recorded at 40 °C in THF.

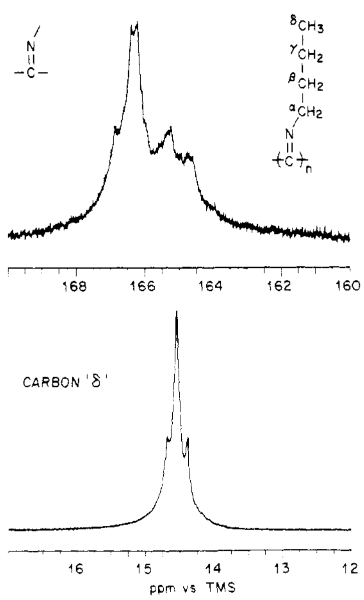


Figure 5. Expanded regions of the ^{13}C NMR spectrum from Figure 4.

(*S*)-**2**, utilizing $NiCl_2 \cdot 6H_2O$, from commercially available monomer.[29] In this polymer, left- and right-handed helical regions are related as enantiomers and must be isochronous, i.e., yield identical chemical shifts. The ^{13}C NMR spectrum of **3** was taken at 125.7 MHz in deuteriated tetrahydrofuran and is exhibited in Figure 4. The spectrum confirms the structure and indicates, because of a comparable chemical shift dispersion for the backbone carbon between 164 and 167 ppm (Figure 5), that the stereoirregularity indicated by the shift dispersion in the ^{13}C NMR of (*S*)-**2** (Figure 3) is not associated with the asymmetric pendant. Figure 5 reinforces this point in also showing chemical shift dispersion for the methyl group δ at 14.5 ppm. A similar result[33] for the backbone carbon is found in poly(benzyl isocyanide) prepared similarly to (*S*)-**2** and **3**. None of these polymers has an α-substituent. This is consistent with earlier findings[12,13] that poly(α-phenylethyl isocyanide) exhibits the characteristics of a stiff polymer while the regioisomer poly(β-phenylethyl isocyanide) is more coillike.

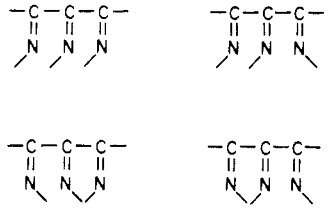


Figure 6. Stereoisomeric possibilities for a triad of a polyisocyanide.

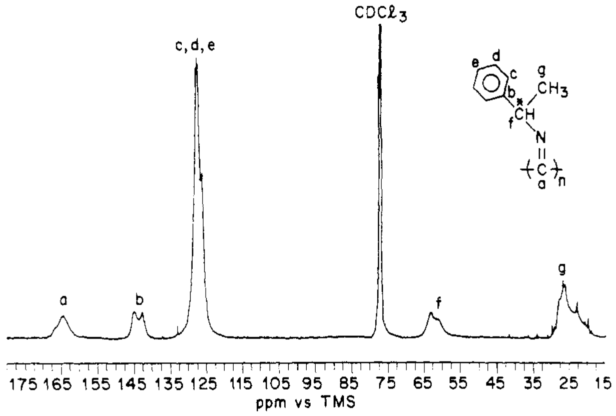


Figure 7. 125.7-MHz ^{13}C NMR spectrum of (*R*)-**1** at 23 °C in $CDCl_3$.

One potential source of the chemical shift dispersion (Figures 2–5) is stereoirregularity associated with syn–anti isomerism about the carbon–nitrogen double bond. The four possibilities for the triad are shown in Figure 6. We have not evaluated the NMR spectra in an attempt to correlate the number of resonances with the possibilities exhibited (Figure 6). The carbon nuclei may be sensitive to sequences longer than triads, and there may be other additional sources for the variety of chemical shifts observed, including the kinds of structural breaks suggested by Millich and Baker.[10]

Whatever may be the source of the stereoirregularity reflected in the chemical shift dispersion in (*S*)-**2** (Figure 3), it would be difficult to reconcile the conformational picture proposed from interpretation of the CD spectrum of (*S*)-**2**, discussed above, with the structural disorder revealed by the high-field ^{13}C NMR data. This conclusion, in turn, must cast a shadow on the use of CD spectra, as interpreted,[23] to yield information on the conformational properties of other asymmetric polyisocyanides, i.e., on polyisocyanides in which the optical activity arises from other than conformation (i.e., asymmetric side groups). In particular, in (*S*)-**2** the CD long-wavelength band may arise from local asymmetric perturbations[34] of the chromophore rather than from an extended helical conformation. This conclusion is reinforced by the dimensional properties of (*S*)-**2** determined by light scattering and discussed below.

The complex chemical shift patterns encountered for polymers without α-substituents (Figures 2–5) suggested observation of the high-field ^{13}C NMR spectrum of optically active poly(α-phenylethyl isocyanide) (*R*)-**1**. This orange polymer (*R*)-**1**, previously prepared in optically active form by using initiation by sulfuric acid adsorbed on glass,[10] was synthesized for this work from the neat monomer (*R*)-(+)-α-phenylethyl isocyanide by using $NiCl_2 \cdot 6H_2O$. The $[\alpha]^{25}{}_D$ was within experimental error[29] of the published value.[10] The light-scattering weight average molecular weight, $\bar{M}_w$, was 107 000, and the intrinsic viscosity η in chloroform was 0.57 dL g^{-1} at 25 °C. The ^{13}C NMR spectrum recorded at 125.7 MHz in $CDCl_3$ at 23 °C is presented in Figure 7.

It is clear from a comparison of Figures 2 and 7 that the resonances of (*S*)-^{2} show far narrower line widths than those of (*R*)-**1**. The chemical shifts for the latter polymer are consistent with the structure, with broadening suggesting decreased segmental motion as compared to (*S*)-**2**. Although the symmetry of the lines is consistent with the dipolar broadening associated with motional restrictions,[35]

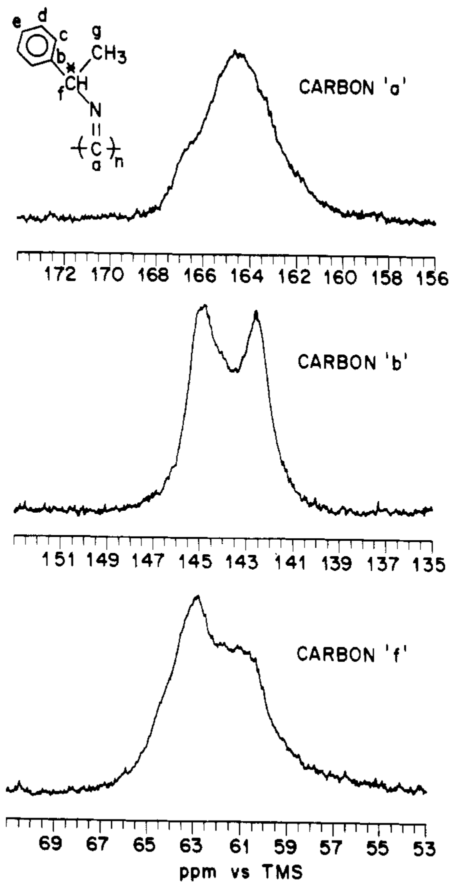


Figure 8. Expanded regions of the ^{13}C NMR spectrum of (*R*)-1 from Figure 7.

there is also significant chemical shift dispersion. Expansion of the resonances for carbons a, b, and f emphasize this point (Figure 8) and suggest, as for (*S*)-2, some stereoirregularity for (*R*)-1. This result causes concern because poly(α-phenylethyl isocyanide) is the only well-studied polyisocyanide with regard to chain dimensional characteristics, and the assignment of a 4/1 helical rod structure to many polyisocyanides[25-27] rests on analogy to the proposed properties of this polymer.[5,11-17] The NMR results above suggest that this polymer does not possess a highly regular structure.

Light Scattering. The circular dichroism and nuclear magnetic resonance probes of (*S*)-2 and (*R*)-1 are concerned only with local structure. We therefore decided to investigate the overall dimensions by light scattering to determine how this correlated with the local properties. As noted above, (*RS*)-1, prepared by acid initiation, has been studied by small-angle X-ray scattering in toluene.[13,15,16] The resulting measured radii of gyration could be smaller compared to (*R*)-1 if the polymerization were not stereoselective.[36] In addition, the ^{13}C NMR line widths suggest a large difference in flexibility for (*R*)-1 and (*S*)-2, stimulating a comparison of their dimensions.

With some difficulty, following from the visible absorption characteristics of (*S*)-2 and (*R*)-1, Zimm plots were constructed from light-scattering data by using 633-nm wavelength light.[29,37] The slopes of the angular dependence of the Rayleigh ratios extrapolated to zero concentration were zero within experimental error for both (*S*)-2 and (*R*)-1, offering no estimate for the radius of gyration.

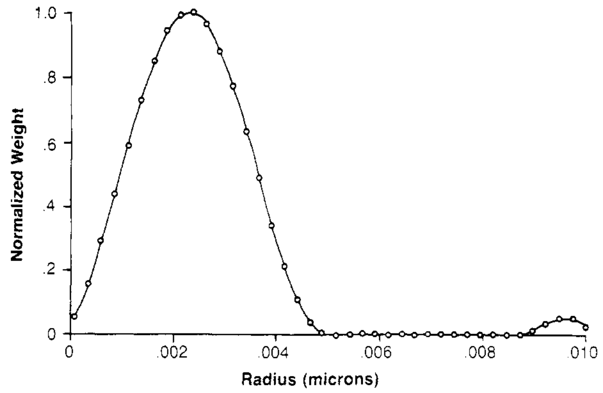


Figure 9. Size distribution of (*S*)-2 from CONTIN analysis of PCS data ($\bar{M}_w$ = 165 000 g/mol).

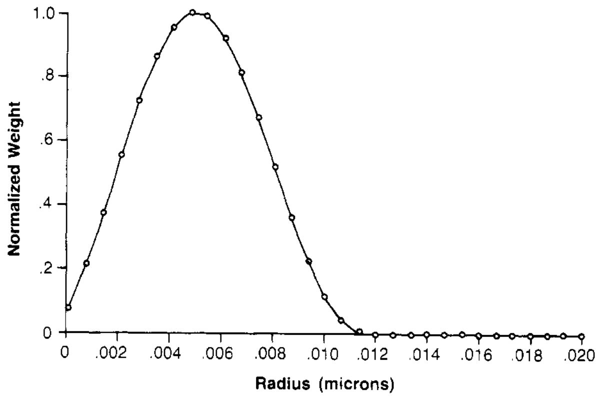


Figure 10. Size distribution of (*R*)-1 from CONTIN analysis of PCS data ($\bar{M}_w$ = 107 000 g/mol).

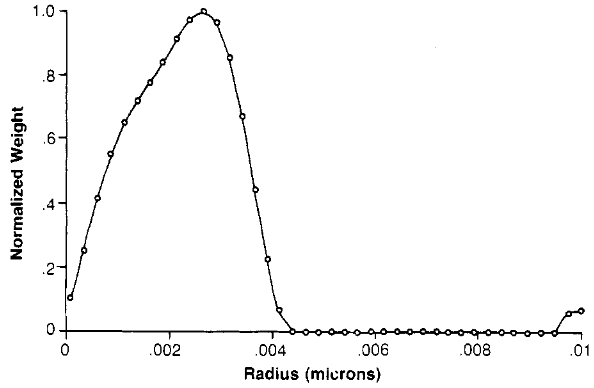


Figure 11. Size distribution of (*RS*)-1 from CONTIN analysis of PCS data ($\bar{M}_w$ = 34 000 g/mol).

Table II
Molecular Weights and Hydrodynamic Radii

polymer	$\bar{M}_w$	$\overline{DP}$	R_h, Å
(*S*)-2	165 000	1170	24
(*R*)-1	107 000	817	51
(*RS*)-1	34 000	260	23

The size of these polymers could be evaluated more precisely by photon correlation spectroscopy.[38] This technique, which measures the time fluctuations in intensity of scattered light, yields information on the diffusive properties of the system. In this manner, for a dilute solution of polydisperse particles, a distribution of diffusion coefficients is experimentally obtained that can be transformed into a size distribution of the particles.[29,39] Figures 9–11 present this information as a distribution of hydrodynamic radii for (*S*)-2, (*R*)-1, and (*RS*)-1, respectively.

The hydrodynamic radii (R_h) presented in Figures 9–11 are related to the weight average molecular weight ($\bar{M}_w$ determined by low-angle light scattering), and these data, including the weight average degree of polymerization ($\overline{DP}$), are presented in Table II.

Although the $\bar{M}_w$ and $\bar{DP}$ of (*R*)-**1** are substantially lower than those of (*S*)-**2**, the photon correlation experiment demonstrates that (*R*)-**1** is considerably larger as judged by the hydrodynamic radii (Table II). If we use the conformational characteristics derived from the work of the Missouri group[13-17] for poly(α-phenylethyl isocyanide) (*RS*)-**1A**, i.e., diameter 18 Å and monomer projection length of 1.04 Å, the persistence length (q) of (*R*)-**1** can be calculated from the relationship for a wormlike chain[40] between R_h, q, the pitch a, contour length L, and the diameter d:

$$2R_h = L/[1.843(L/2q)^{1/2} - \ln (a/2q) - 2.43 - a/d]$$

This calculation[40] yields a value of q = 32 Å for (*R*)-**1**. Since the Missouri group[13,15,16] had determined the radius of gyration and the weight average molecular weight for narrow dispersity samples of (*RS*)-**1A** by X-ray scattering, we took the opportunity to calculate the persistence length q for this material.[41] Three samples of (*RS*)-**1A** had been studied, and the values of the molecular weight and radius of gyration were 18 000 (28 Å), 45 800 (55 Å), and 91 500 (80 Å) and led to respective values of q of 27, 32, and 30 Å, in excellent agreement with the photon correlation derived persistence length of 32 Å (see above). Note also that (*R*)-**1** was measured in tetrahydrofuran and (*RS*)-**1A** in toluene both at or near to room temperature. The hydrodynamic radius for (*RS*)-**1**, prepared in this work by using Ni^{II} initiation,[29] was 23 Å for an $\bar{M}_w$ of 34 000. The low molecular weight of this material leads to a large uncertainty in the calculated value of q so that the value obtained, 21 Å, cannot be shown to differ from the values of q for (*R*)-**1** and (*RS*)-**1A**.

Discussion

Although an exact persistence length, q, cannot be calculated from the hydrodynamic radius and molecular weight of (*S*)-**2** (Table II) in the absence of information on the detailed conformation, a comparison of the characteristics of (*R*)-**1** (Table II) demonstrates that q for (*S*)-**2** must be far less than 32 Å, the value for (*R*)-**1**. This comparison of (*R*)-**1** and (*S*)-**2** is consistent with the ^{13}C NMR spectra, which show far narrower line widths for (*S*)-**2** compared to (*R*)-**1** (Figures 2 and 7). Both the small dimensions, as judged by the light-scattering data and the ^{13}C NMR line widths, suggest that (*S*)-**2** can be well described as a flexible coil. This conclusion is also consistent with the stereoirregularity demonstrated by the chemical shift dispersion observed in the ^{13}CNMR of (*S*)-**2** (Figures 2 and 3).

Both the dimension of (*R*)-**1**, as determined by light scattering (Table II), and the ^{13}C NMR line widths (Figure 7) require a stiff conformation as compared to (*S*)-**2**. Nevertheless, the light-scattering and ^{13}C NMR data are also consistent with considerable flexibility in this macromolecule. This is seen in the chemical shift dispersion (Figures 7 and 8), which requires that nuclei in both the backbone and in the pendant groups see a variety of environments. This state is inconsistent with the strong bias toward regular conformational properties suggested by the literature.[8,14] The light-scattering data reinforce this point since the chain dimension, if the 4/1 model is accepted,[8,14] is consistent with a persistence length of only 32 Å. For a monomer projection length of approximately 1 Å this corresponds to about 30 residues along the chain. It is instructive to compare this number with that derived from the persistence length, 600 Å, and monomer projection length, 2 Å, of poly((*S*)-2,2-dimethyl-1,3-dioxolane-4-methyl isocyanate), i.e., about 300 residues along the chain.[2]

The following polyisocyanides have been reported to form lyotropic solutions: poly(*n*-octyl isocyanide);[42] poly(β-phenylethyl isocyanide);[12] poly(α-phenylethyl isocyanide).[12,14] This observation seems remarkable for poly(*n*-octyl isocyanide) and poly(β-phenylethyl isocyanide) in the light of the coillike properties of polyisocyanides without α-substituents reported above.[43]

We have in addition the question of stereoselectivity in the polymerization of the racemic monomer leading to (*RS*)-**1** and (*RS*)-**1A**. In both polyalkenes and polyisocyanates[36] nonstereoselective polymerization of racemic mixtures leading to incorporation of both enantiomeric residues in a single chain gives rise to reduced dimensions compared to the polymerization of the single enantiomer monomer. This could be considered to arise from increased helix reversals between left- and right-handed helical segments in the nonstereoselective produced copolymers.[2] This question of stereoselectivity is of importance in the literature of polyisocyanides because racemic mixtures of chiral monomer isocyanides have been polymerized to yield polyisocyanides in which the pendant groups are claimed to be stacked in regular arrays.[44] This structural consequence requires that a 4/1 helix be formed and that the polymerization be stereoselective.[44]

Unfortunately the data in Table II and the derived values of the persistence lengths (see above) fall short of answering this question of stereoselectivity with the Ni^{II}-initiated system. Although (*R*)-**1** and (*RS*)-**1A** exhibit the same dimensions, the polymerization procedures vary, with the acid–glass system[10] being used for (*RS*)-**1A** and Ni^{II} initiation for (*R*)-**1**. The persistence length for (*RS*)-**1**, derived from the racemic monomer by Ni^{II} initiation, is too imprecisely known (as discussed above) to draw a comparison to (*R*)-**1**. The data therefore offer no conflict or support to an assumption of stereoselectivity in the polymerization of racemic mixtures of chiral isocyanides.[44]

In conclusion, on the basis of the ^{13}C NMR and photon correlation spectra, it appears that the long-accepted assignment of a stereoregular 4/1 helical rod structure to poly(α-phenylethyl isocyanide) is probably an oversimplification.[8,14] Caution is certainly suggested in extrapolating that assignment too far.[27,45] Such extrapolations would be unwarranted even if the conformation of poly(α-phenylethyl isocyanide) were assured. In polyisocyanides where helical characteristics are hypothesized[8,14] to arise from a steric conflict, it is reasonable that conformational characteristics would change with the steric demands of the pendent group. This expectation well-known in vinyl polymers,[46] is borne out by our results on the polyisocyanides with methylene adjacent to nitrogen. In these cases the ^{13}C NMR and photon correlation spectra point to coillike polymers.

Experimental Section

The synthesis of optically active and racemic 2,2-dimethyl-1,3-dioxolane-4-methyl isocyanides have been described in our earlier work.[2] The general, routine procedures are also described therein.[2]

The poly(α-phenylethyl isocyanides) (*R*)-**1** and (*RS*)-**1** and the precursor monomers were prepared following the literature.[23] The racemic and *R* enantiomer of α-methylbenzylamine are available from Aldrich Chemical Co. The monomer *R*-isocyanide has $[\alpha]^{25}_D$ −43° (*c* 1.5, methanol) (lit.[23] *S*) enantiomer, $[\alpha]^{25}_D$ −40.9° (*c* 5, methanol).

All the monomeric isocyanides had a sickening stench and must be handled only in a well-functioning hood. All materials including gloves used can be soaked in a solution of a soluble Ni^{II} salt to remove the odor, which is otherwise difficult to eliminate. We used, for this purpose, Ni cyclohexane butyrate (purchased from Aldrich Chemical Co.).

Poly(2,2-dimethyl-1,3-dioxolane-4-methyl isocyanide) ((*RS*)-2). Ni^{II} chloride hexahydrate (0.0068 g, 2.86×10^{-5} mol), as purchased from Fisher Scientific Co. is added to a three-neck 25-mL flask under N_2 with overhead stirring at room temperature. The racemic isocyanide above (4 g, 0.028 mol) was syringed through a septum cap while stirring rapidly. Within 1 h a glassy brown solid precluded stirring. The system was let stand overnight followed by dissolution in $CDCl_3$ (90 mL) and precipitation by dropwise addition to a vigorously stirred solution of 90% methanol–10% water (1220 mL). After being left overnight at 5 °C the orange solid was separated by centrifugation, and the precipitation procedure repeated once more. We obtained 1.8 g (40%) of a brown shiny solid: IR (film cast from $CHCl_3$) 2980 (s), 2930 (m), 2880 (m), 1685 (sh), 1640 (m), 1381 and 1371 (s), 1158 (s), 850 (s) cm^{-1}. Anal. Calcd: C, 59.56; H, 7.85; N, 9.92. Found: C, 58.48; H, 7.77; N, 9.86.[47] Intrinsic viscosity was 0.61 dL/g in $CHCl_3$ at 25.2 °C.

Poly(2,2-dimethyl-1,3-dioxolane-4-methyl isocyanide) ((*S*)-2). The procedure and IR spectrum for the derived polymer were identical with that for the (*RS*)-**2** but with use of optically active monomer.[2] The ^{13}C NMR spectrum appears in Figure 2. Yield was 32%, intrinsic viscosity 1.08 dL/g, and optical rotation $[\alpha]^{25}_{546}$ +68.5° (*c* 0.37, *p*-dioxane).

Poly(*n*-butyl isocyanide). Precisely as described above for (*RS*)-**2**, 5 g (0.060 mol) of *n*-butyl isocyanide, as purchased from Aldrich Chemical Co. (this material has a horrible stench), was polymerized with 0.007 g (2.9×10^{-5} mol) of $Ni^{II}Cl_2 \cdot 6H_2O$. After two precipitations, as described above for (*RS*)-**2**, there was obtained 3 g (60%) of a light brown solid. Anal. Calcd: C, 72.24; H, 10.91; N, 16.85. Found: C, 71.38; H, 10.96; N, 16.74.[47] The ^{13}C NMR spectrum is shown in Figure 4.

High-Field NMR Measurements. The 125.75-MHz ^{13}C NMR spectra were recorded on a JEOL GX-500 spectrometer. The experimental conditions employed were as follows: poly((*S*)-2,2-dimethyl-1,3-dioxolane-4-methyl isocyanide), (*S*)-**2**, 6.6% w/v in THF-d_8 at 40 °C; poly((*R*)-α-phenylethyl isocyanide), (*R*)-**1**, 6.7% w/v in $CDCl_3$ at 23 °C; poly(*n*-butyl isocyanide), **3**, 16.7% w/v in THF-d_8 at 25 °C. In all samples hexamethyldisiloxane (HMDS) was used as an internal reference. A total of 5–24 000 scans were accumulated with a delay between sampling pulses of 10 s. No attempt was made to acquire the data under quantitative conditions.

Light-Scattering Measurements. Weight average molecular weights were determined by low-angle laser-light-scattering photometer techniques using a Chromatix KMX-6 spectrometer. Differential refractive indices were determined with a C. N. Wood differential refractometer.

A custom made Langely/Ford LSA II photon correlation spectrometer was used to obtain the Zimm plots and the photon correlation spectra. This system uses a 50-mW He–Ne laser as the light source and a Thorn EMI RFI/B263F phototube as the detector for the scattered light. Fiber optic cables were set at seven different scattering angles, ranging from about 10° to 152°, and used to channel the scattered light to the detector; an electrically controlled rotating prism selected which cable's light would reach the detector. A pulse amplifier/discriminator converted the phototube output to TTL pulses, and a 256-channel Langely/Ford 1096 correlator was used to count the pulses and find the time correlation function. The total intensity was calculated by dividing the total number of pulses by the total measurement time. The data were transferred through an IEEE interface to an IBM Instruments 9000 microcomputer for further analysis and storage.

The dissolution and clarification process of the polymer samples was as described in our earlier work.[2]

The correlation functions of the polymer solutions of (*S*)-**2**, (*R*)-**1**, and (*RS*)-**1** were measured at two different scattering angles (63.8° and 90°) and at several concentrations, and there was no dependence on either of these parameters. Additionally, a logarithmic plot of the correlation function versus time for (*R*)-**1** (0–0.00024 s) is linear, indicating fairly low polydispersity. The size distributions in Figure 9 for (*S*)-**2**, in Figure 10 for (*R*)-**1**, and in Figure 11 for (*RS*)-**1** were obtained from numerical transformation of measured correlation functions, by using Provencher's CONTIN program.[39] Since the amplitude factors depend not only on the weight but also on the size and shape of the particles, some assumption must usually be made about the light-scattering structure factor to obtain a true weight distribution. In our calculations, we used the structure factors for a random coil; however, because of the small size and relatively narrow size distribution of the polymers investigated, using other structure factors (such as those for a sphere) had little effect on the final size averages and distributions we obtained.

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Registry No. (*S*)-**1** (homopolymer), 26714-26-1; (*S*)-**1** (SRU), 68810-68-4; (*S*)-**2** (homopolymer), 114532-43-3; (*S*)-**2** (SRU), 114506-89-7; **3** (homopolymer), 28391-59-5; **3** (SRU), 41205-63-4.

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Molecular Weight Effects in the Relaxation of Orientation of Polystyrene Chains As Revealed by Infrared Dichroism

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ABSTRACT: The relaxation of orientation of narrow distribution polystyrenes of different molecular weights is studied over 4 decades of time by infrared dichroism and compared to the predictions of the Doi–Edwards and related models. The behavior at short times appears to be independent of the molecular weight, whereas molecular weight effects at longer time are observed, as predicted by the theory. A careful comparison between theory and experiment shows that the kinetics of the relaxation at short times are slower than predicted by the model. The experimental behavior at longer times is in good agreement, especially for the highest molecular weights, with the predictions of a self-consistent treatment including a process of equilibration across slip-links.

Introduction

The viscoelastic properties of polymer melts have been widely investigated from experimental and theoretical points of view. The presence of molecular relaxation motions, especially in the case of deformed polymers, plays an important role in many processing methods such as fiber spinning, film blowing, and thermoforming. Practically, the state of orientation of the macromolecular chains allows the control of mechanical properties in the final product. It is therefore necessary to know, as precisely as possible, how the orientation is influenced by macroscopic parameters such as deformation ratio, temperature, and strain rate and by molecular quantities like length and structure of the chains. Besides an experimental approach, theoretical work has been recently developed from a molecular point of view via the reptation concept introduced by de Gennes[1] and its application to highly deformed amorphous polymers by Doi and Edwards.[2,3]

This model describes the relaxation of a deformed and highly entangled polymeric medium through three different processes which are well separated in time.

The first relaxation motion (A) is a Rouse motion of a part of chain between two entanglements, considered here as fixed points, and is characterized by a relaxation time τ_A, which is independent of the molecular weight of the

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