Helical Conformations, Internal Motion and Helix Sense Reversal in Polyisocyanates, and the Preferred Helix Sense of an Optically Active Polyisocyanate

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ABSTRACT: Empirical force field studies of poly(alkyl isocyanates) are presented. A barrier of 12.5 kcal/mol for cis–trans isomerization of the polymer-backbone's conjugated partial double bonds makes the calculated energy of helix sense reversal agree best with corresponding experimental results. The alternating cis and trans torsion angles are found to be distorted, to about 170° and −55° for right-handed helices, by strong repulsions between the α-carbon of each alkyl side chain and the neighboring backbone atoms of four consecutive monomer units. Polyisocyanates are predicted to possess a soft collective internal motion, in which rotation per monomer around the polymer's helix axis varies widely, accompanied by large variations of the backbone's torsional angles, at low energy cost. When the β carbon of a normal alkyl side chain acquires an absolute configuration (R) by methyl substitution, the left-handed helical conformation is predicted to be more stable than the right-handed one by about 0.5 kcal/mol per monomer unit. Reversal of the helical sense involves conformational change of several consecutive monomers, and the angle between the helices of opposite senses is about 130°.

Introduction

Polyisocyanates (PICs) have the general formula $(-\mathrm{CONR}-)_N$ where N is the degree of polymerization and R is an alkyl side chain. PICs have been the subject of extensive research for many years. They are stiff polymers[1] due to the partial double-bond character of the backbone amide bonds. The backbone is helical,[2,3] due to steric hindrances which prevent the amide bonds from staying planar, whether trans or cis. The helices tend to be very long, because reversal of the helical sense requires that at least one monomer unit obtain a reversal conformation, and such conformations are rare because their energy is much higher than that of the helical conformations of the monomer units. The helices may be either left-handed (M) or right-handed (P), and if a polyisocyanate has no chirotopic carbon on its side groups, the M and P helices are mirror images of each other and are equally distributed in solution. In a solution of such a polymer no optical rotation (OR) is observed.

When the side group contains a chirotopic carbon, the mirror symmetry is broken, one helical conformation becomes energetically more stable and consequently contributes to the optical activity of the polymer.[4] When long M and P helices differ in energy by an amount commensurable with the thermal energy RT, they are unevenly distributed. Therefore even a very small energy difference between the monomer units in their M and P conformations produces an extraordinarily large OR, because it is greatly amplified by the length of the helical sequences. This is the source of the observed OR in poly((*R*)-1-deuterio-*n*-hexyl isocyanate) (α-PdHIC) and explains qualitatively the amplification of the minute isotope effect of replacing H by D, as well as its dependence on temperature and degree of polymerization.[5] A quantitative theory of the specific optical rotation $[\alpha]$ as a function of the absolute temperature T and degree of polymerization N was derived by a simple statistical mechanical model.[6]

Some quantitative conformational details of poly(*n*-butyl isocyanate) (PBIC) were obtained by X-ray analysis[2] that showed the polymer to be helical, with a translation along the helix axis of 1.94 Å per monomer, and 8/3 monomers per full rotation, or 135° per monomer. The backbone angles were estimated by several authors using conformational energy minimization[3a–c] with diverse results. The free energy difference between the reversal and the helical conformations has been determined to be about 4 kcal/mol, by least squares fitting the calculated to the observed $[\alpha]$ of high molecular weight αPdHIC over a wide temperature range.[6] This value may be somewhat revised by a more detailed study of the OR of this polymer over a wide range of molecular weights (Okamoto, Sato, Teramoto, Peterson, Green, and Lifson, in preparation). The published free energy difference[6] was used in the present study. Its revision is not expected to affect significantly any of the relevant results.

The present study extends the conformational analysis of PIC, trying to obtain answers to the following questions. Can we offer a better estimate of the backbone torsion angles? What are the main intramolecular contacts that determine the strain and stability of the helical conformation? It has been assumed[3b,d] that reversal of the helical sense introduces a kink, namely a change in direction of the backbone. What is the conformation of the reversal units that participate in this kink? It has been reported[5a] that both poly((*R*)-1-deuterio-*n*-hexyl isocyanate) mentioned above (αPdHIC) and poly((*R*)-2,6-dimethylheptyl isocyanate) (denoted here in short as PNIC, for its branched nonyl side group $-\mathrm{CH_2C^*H(CH_3)(CH_2)_3CH(CH_3)_2}$) exhibit the same sign and shape of their circular dichroism spectra and therefore must have the same preferred helicity. Is it left-handed (M) or right-handed (P)?

Theory

Empirical Force Field (EFF). Answers to the above questions are obtained here by the EFF method, also called molecular mechanics. Admittedly, empirical force field calculations are no more than approximations of the precise solution of the corresponding quantum mechanical equations which can never be attained for large molecules.

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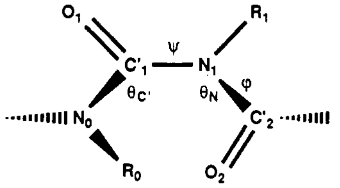
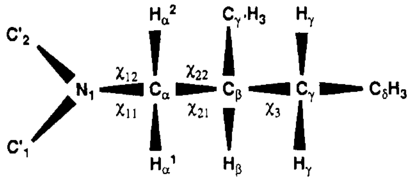
Table I
Calculated Infinite Helices of Poly(alkyl isocyanates)

		rel energy (kcal/mol)				hel parms		backbone angles (deg)				side group angles (deg)				
polymer	R	tot.[a]	str[b]	coul	L-J	ρ[c]	τ[d]	φ[e]	ψ[e]	θ_{C}[f]	θ_{N}[f]	χ_{11}	χ_{12}	χ_{21}	χ_{22}	χ_{3}
						I. Helices with Nonchiral Side Groups										
PMIC	methyl	0.00	0.00	0.00	0.00	117	1.96	172	−60	13	−13					
PEIC	ethyl	0.00	0.00	0.00	0.00	123	1.98	169	−52	13	−16	95	−69			
		0.17	1.82	−0.51	−1.14	111	1.97	173	−66	14	−18	−82	116			
PBIC	*n*-butyl	0.00	0.00	0.00	0.00	121	1.98	170	−54	13	−16	94	−69	−177		−179
		0.08	1.35	−0.63	−0.64	113	1.98	174	−64	15	−18	−81	116	178		179
						II. Helices with a Chiral Pentyl Side Group[g]										
(*S*)-PPIC	*sec*-pentyl	0.00	0.00	0.00	0.00	145	1.88	136	−13	10	−10	73	−98	−174	67	66
(*R*)-PPIC		0.41	0.05	0.61	−0.25	145	1.88	135	−12	10	−11	72	−99	70	−170	−173
		0.67	1.28	−0.75	0.14	108	2.02	−177	−73	11	−23	−59	143	165	−77	−71

[a] Total minimized energy relative to the most stable conformation. [b] The strain energy comprises all relative energy components besides the coulombic and Lennard-Lones (L-J) terms. [c] Angular twist about the helical axis from one monomer unit of the helix to the next (degrees). [d] Linear displacement along the helical axis from one monomer unit of the helix to the next (angstroms). [e] Torsional angles in degrees, according to the scheme below. [f] Out-of plane angles in degrees, according to the scheme below. [g] $-CH_2C^*H(CH_3)CH_2CH_3$.



$\varphi = (C'_1\text{-}N_1\text{-}C'_2\text{-}N_2)$
$\psi = (N_0\text{-}C'_1\text{-}N_1\text{-}C'_2)$
$\theta_{C'} = (N_0\text{-}C'_1\text{-}N_1\text{-}O_1)$
$\theta_N = (C'_2\text{-}N_1\text{-}C'_1\text{-}R_1)$
$\chi_{11} = (C'_1\text{-}N_1\text{-}C_\alpha\text{-}C_\beta)$
$\chi_{12} = (C'_2\text{-}N_1\text{-}C_\alpha\text{-}C_\beta)$
$\chi_{21} = (N_1\text{-}C_\alpha\text{-}C_\beta\text{-}C\gamma)$
$\chi_{22} = (N_1\text{-}C_\alpha\text{-}C_\beta\text{-}C_{\gamma'})$
$\chi_3 = (C_\alpha\text{-}C_\beta\text{-}C_\gamma\text{-}C_\delta)$



However, when properly applied to appropriate problems, they may yield valuable information, part of which is impossible or extremely difficult to obtain by other methods. The energy functions of the EFF used here and their associated constant parameters had been optimized by fitting calculated to observed data over a wealth of experimental studies of conformational, vibrational, and thermodynamic properties of single molecules[7] and of crystals.[8] They had been used through many years for analysis and prediction of experiments[9] with a cumulative record of success, and may therefore be applied with some confidence.

The major factor that determines the equilibrium conformations of PICs is the balance between the interatomic repulsions due to close contacts between nonbonded atoms, on the one hand, and the resistance of the polymer-backbone amides to be distorted out of planarity, on the other hand. Our EFF contains optimized energy functions for nonbonded interactions as well as for torsions of amide bonds. However, the latter may not be suitable for PIC, since its backbone's amides have a conjugated partial double-bond character. Conjugated amides are expected to have a lower barrier for cis–trans isomerization than isolated amides, however we don't know how much lower it is. Applying the nonconjugated amide bond torsion potential, with a barrier of 20 kcal/mol, we obtained an energy excess for the reversal over the helical conformation on the order of 7 kcal/mol. This is almost double the value of about 4 kcal/mol obtained from the statistical–mechanical analysis[6] of the temperature dependence of the specific optical rotation [α] of α-PdHIC. We therefore chose to reduce the potential barrier. The value of 12.5 kcal/mol reproduced the experimental value of about 4 kcal/mol for the above-mentioned energy difference and was consequently adopted.

Unfortunately, changing just one parameter in a force field to obtain the best fit to just one observable is perhaps the simplest but not the optimal adaptation of the EFF to conjugated amide bonds. Consequently, in discussing the results we shall recognize the limits set by this procedure on the reliability of the results, by stressing major trends rather than minor details.

Infinitely Long Helices. The equilibrium conformations of infinitely long polyisocyanate helices were obtained by minimizing their energy per monomer, assuming all monomers to have the same conformation, namely, to have identical internal coordinates. The energy per monomer was obtained as the sum of contributions of (a) all energy functions of the EFF that belong to the central monomer itself, namely that are defined by the atoms of that monomer only, and (b) all interactions of the central monomer with its consecutive neighbors, namely all energy functions defined by atoms from both the central monomer and its consecutive neighbors. The energy was minimized with respect to all degrees of freedom of the repeat unit and all other units related to it by the helical symmetry. Intermonomer interactions were calculated up to the tenth neighbor of the central monomer, thus ensuring excellent convergence. The minimization was executed in a canonical Cartesian coordinate system, related to a helical coordinate system in that the helix axis coincides in both with the z-axis. The transformation from internal to canonical coordinates resembles that derived by Sugeta and Myazawa[10] and is presented briefly in the Appendix.

Helix Reversal. The equilibrium conformation of the helix reversal was obtained by devising a long but finite chain, half of which is a left-handed (M) helix and the other half right-handed (P). Each of the helices starts from the midpoint with either a distorted-cis or a distorted-trans torsional angle, taking as initial conformations the equilibrium values from the calculation of the infinite helix and then minimizing the total energy of the whole chain.

Results and Discussion

(1) Infinite Helices with Nonchiral Side Chains. The first part of Table I presents conformational and energetic data for a number of infinite poly(alkyl isocyanate) helices. All data in Table I pertain to right-handed (P) helices. The corresponding data for left-handed (M) helices are obtained by mirror reflection, i.e. by changing the signs of all angles in Table I.

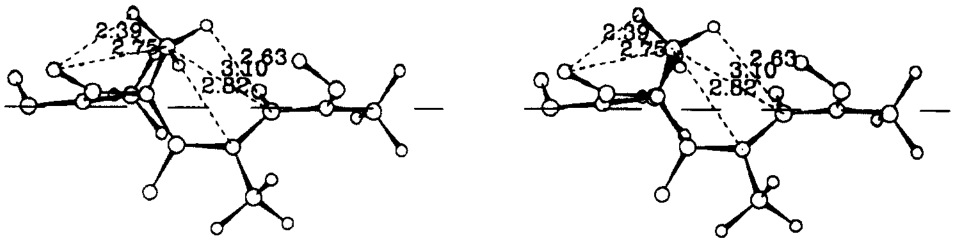


Figure 1. Stereoview of PMIC, with "short distances" (see text and Table II).

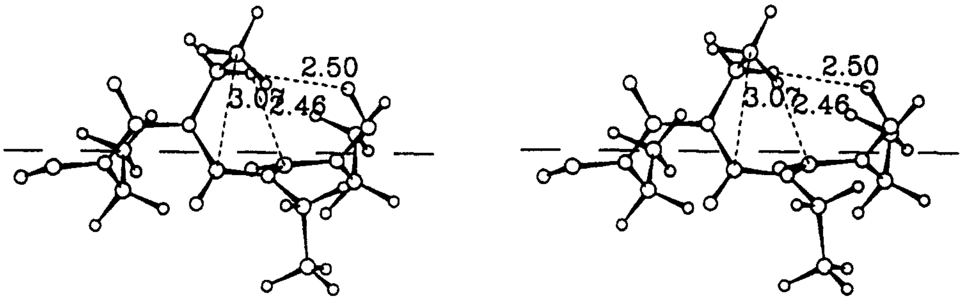


Figure 2. Stereoview of PEIC, coformation 1, with additional "short distances" (compare with Table II).

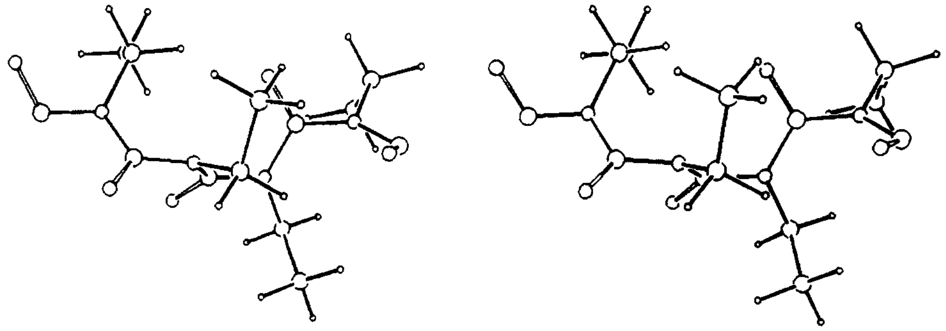


Figure 3. Stereoview of PEIC, conformation 2.

Calculations were confined to the commonly accepted backbone pattern of alternating distorted-cis distorted-trans torsional angles with opposite signs, after preliminary tests of other patterns were confirmed to be less stable. Methyl, ethyl, and *n*-butyl were chosen as side chains in order to follow the effect of the length of the alkyl chain on the conformation of the infinite helix. The corresponding PIC polymers are denoted as PMIC, PEIC, and PBIC, respectively. PMIC has a single conformation of minimum energy. It is presented as a stereoview in Figure 1. The deviations of the torsional angles of the backbone from trans (180°) and cis (0°) are not symmetric. The trans deviates by only 8°, while the cis deviates by 60° in the opposite direction. PEIC has two equilibrium conformations that differ in the direction of the ethyl side chain vis a vis the backbone. These directions are given by χ_{11} and χ_{12} in Table I and may be observed in Figures 2 and 3. The backbone angles ϕ and ψ in the two conformations of PEIC are shifted in opposite directions by a few degrees from those of PMIC. There is a small energy difference between the two conformations. The decomposition of the total energy difference into three components indicates that the second conformation has more strained internal coordinates (bond lengths, bond angles, and torsional angles), but part of this strain is offset by the nonbonded interactions (Coulomb interactions between atomic partial charges and Lennard-Jones or van der Waals interactions). PBIC is very similar to PEIC in both its conformations, thus implying that further extension of the side chains beyond C_δ has hardly any effect on the conformation of the infinite helix. The reason is that the longer side chains extend away from the backbone and are too far apart to interact, as is clearly visualized in Figure 4, a stereoview of the most stable conformation of PBIC.

The helicity of PICs is caused by intramolecular steric hindrances, as atoms that are forced by the stiff backbone to form close contacts repel each other strongly. Table II presents the *interatomic short distances*. These are defined as distances that are shorter than a *minimal contact distance*, below which atoms repel each other strongly. Only short distances between *nonbonded* atoms are presented. A pair of heavy atoms (C, C′, N, O) are considered as nonbonded if they are at least 1–4 neighbors, namely if they are linked by the chain of three or more consecutive covalent bonds. A hydrogen and a heavy atom are considered nonbonded if they are at least 1–5 neighbors. The minimal contact distances were obtained for each pair of atoms as the sum of their *minimal contact radii*. The minimal contact radii of C(sp^3) (1.65 Å) and of H (1 Å) were taken from a recent scan of the Cambridge Crystallographic Data Base[11] for distances between these atoms in molecular crystals (Lifson, Felder, and Kennard, unpublished work). The minimal contact radii of C′(sp^2) (1.6 Å), of N (1.55 Å) and of O (1.5 Å) are our estimates, being shorter than the contact radii given by Kitaigorodsky,[12] to make sure that they are in the repulsive range.

It is seen from Table II that no repulsions occur between nonbonded atoms of either the backbone only or the side chains only. All the short distances are between the alkyl side chain and backbone atoms. There is a clear distinction between the two sides of the backbone relative to the side chains. On one side, where the backbone torsional angle of the bond C′N is ψ, namely distorted cis, the short distances are only with the adjacent carbonyl across ψ. On the other side, where the backbone torsion angle of the next bond NC′ is ϕ, the side chain interacts with the

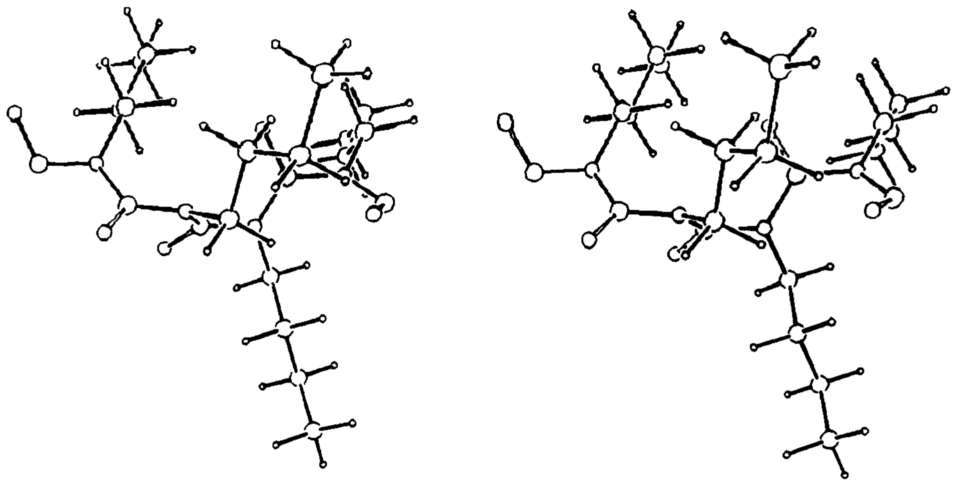


Figure 4. Stereoview of PBIC, conformation 1.

Table II
Short Distances in Polyisocyanates[a]

polymer	conf	$O'_1 \cdots C_{\alpha 1}$	$O'_1 \cdots H_{\alpha 1}{}^1$	$O'_1 \cdots H_{\alpha 1}{}^2$	$C_{\alpha 1} \cdots N_2$	$C_{\alpha 1} \cdots C'_3$	$H_{\alpha 1}{}^1 \cdots N_2$	$H_{\alpha 1}{}^2 \cdots C'_3$	$H_{\alpha 1}{}^2 \cdots O_4$	$H_{\alpha 1}{}^1 \cdots O_4$	$C_{\beta 1} \cdots C'_2$
PMIC	1	2.75	2.39		2.82	3.10					
PEIC	1	2.69	2.41		2.87	3.11		2.46	2.50		3.07
	2	2.73		2.37	2.85		2.47			2.44	
PBIC	1	2.69	2.43		2.86	3.12		2.48	2.50		3.08
	2	2.71		2.36	2.86		2.47			2.40	
(*S*)-PPIC	1	2.68	2.48		3.00	3.00		2.45	2.46		
(*R*)-PPIC	1	2.68	2.50		3.00	3.00		2.47	2.45		
	2	2.73			2.84		2.43			2.41	

[a] Distances in angstroms. Short distances are defined as distances shorter than the sum of the minimal contact radii (see text). For atom nomenclature see the scheme in footnote g of Table I. Greek subscripts identify the ordinal number of the alkyl carbons and their hydrogens; numerical subscripts identify the ordinal number of the monomer units. Superscripts distinguish between the two hydrogens bonded to the same carbon.

backbone over a long stretch. Furthermore, most repulsions involve the first carbon atom of the alkyl chain, C_α, or its hydrogens $H_\alpha{}^1$ and $H_\alpha{}^2$ (see the stereoview of Figure 1). The sole short distance involving C_β is the 1–4 distance to the next monomer backbone carbon C′, and only in the less stable conformations of both PEIC and BPIC (see the stereoview of Figure 3). No repulsive contacts were made with C_γ and beyond. The minor differences between the conformations of PEIC and PBIC are presumably due mainly to Coulombic interactions and to the attractive part of the Lennard-Jones potential that is a longer-range ($\sim r^{-6}$) function.

(2) Soft Collective Motion of Monomer Units around the Helix Axis. The calculated translation τ per monomer along the helix axis varies among the *n*-alkyls of Table I within a narrow range (1.96–1.98 Å) that is close to, though somewhat higher than, the value obtained from X-rays (1.94 Å)[2]. The calculated rotation ρ per monomer around the helix axis varies in a wide range (111–123°) and is quite far away from the experimental value[2] of 8 monomers per 3 full rotations, namely ρ = 135°. The disagreement between theory and experiment may lead at first sight to the conclusion that the theory is not good enough to fit experiment. However, upon further thought one realizes that the simple periodicity of 8/3 is not necessarily an intrinsic property of the helix and may have been imposed on the helix by close packing of neighbors in the lattice. This argument may contradict apparently our notion of the PIC backbone as a rigid, highly strained structure. However, even within highly strained molecules there may be some normal modes of collective motion of atoms that involve small changes in the total molecular energy. We have therefore asked: how much energy would it cost to twist the helix into the 8/3 observed periodicity? To obtain the answer, we introduced an artificial, external twisting potential, $E_\rho = K_\rho(\rho - \rho_0)^2$, which forced ρ to get very close to ρ_0 when we minimized the total energy, including E_ρ. We then subtracted E_ρ from the total energy, and obtained the excess internal energy per monomer of the infinite helix as a function of an externally imposed rotation, ρ. This internal excess energy was, by its definition, independent of the parameters K_ρ and ρ_0. As we varied ρ_0 over a wide range, from 100 to 150° we obtained the amazing result that it costs very little energy to twist the helix from its calculated equilibrium to the crystallographic observed 8/3 periodicity. The excess internal energy per monomer, incurred by twisting ρ up to the experimental value 135°, was 0.30 kcal/mol for the most stable conformation of PBIC. This is only a small fraction of the crystal packing energy. The translation τ shifted to 1.94 Å, fitting exactly the observed translation, and the backbone angles shifted to ϕ = 153° and ψ = −32°. The corresponding values for the second PBIC conformation were excess internal energy per monomer = 0.05 kcal/mol, ρ = 1.91 Å, ϕ = 171°, and ψ = −32°. Thus, the motion of the second conformation is even softer than that of the first one. Similar trends were obtained for the other polymers PMIC and PEIC.

These results shed a new light on PICs in general. The concept of a stiff, rigid helix needs to be replaced by that of a helix that possesses a degree of freedom of soft collective internal motion, though still rigid with respect to most or all other degrees of freedom. The main details of this collective soft motion are presented in Figure 5. In such motion, the torsional strain is shifted between the angles ϕ and ψ, so that when the twist of ψ decreases, that of ϕ increases, and vice versa, while the total energy change, including the contribution of changes in short interatomic distances, is small. For fluctuations of the excess energy within the limits of kT, namely about 0.6 kcal/mol at room

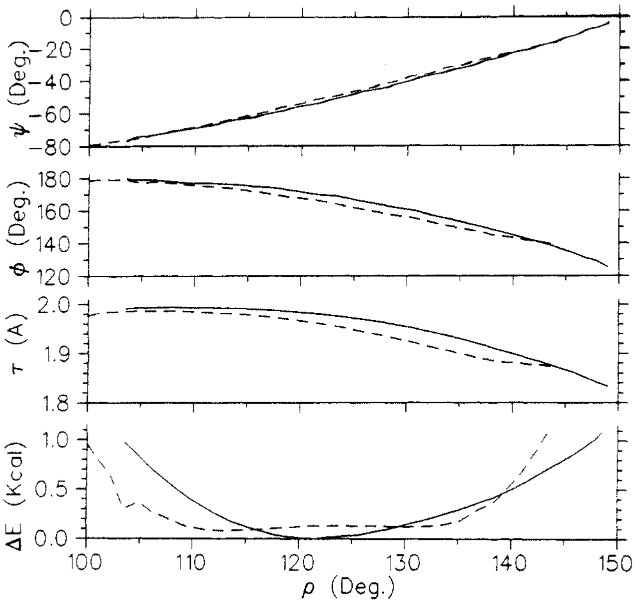


Figure 5. Excess energy ΔE, helical displacement τ, and backbone torsional angles ϕ and ψ, all as functions of the helical rotation ρ in PBIC, for conformations 1 (continuous lines) and 2 (dashed lines)..

temperature, the variables ρ, τ, ϕ, and ψ of the two conformations vary within about 103–140°, 1.99–1.89 Å, 178–142° and −72 to −20°, respectively. Note the different dependence of ΔE on ρ in the two conformations, that makes the second conformation more stable than the first one toward the edges of the range of variation of ρ.

It is consequently conceivable that the rotation, as well as the backbone torsional angles, may be free to move collectively by thermal agitation within quite a wide amplitude, while the translation τ along the helix axis may be approximately conserved. Tables I and II should therefore be viewed not as a presentation of a static, rigid helical structure, but rather as an instantaneous photograph of one position among many that maintain dynamic equilibrium, changing continuously under thermal agitation. It has been chosen by the computer because the computer is calculating the minimum energy within a very small fraction of the thermal energy kT.

In summary, our calculations predict that the helical sequences of PIC molecules in dilute solutions do not possess the rigid helicity observed crystallographically, but are rather dynamically variable within a restricted path of collective motion. Experimental examination of this prediction by spectroscopic methods, as well as further theoretical examination of the molecular motions by molecular dynamics or vibrational normal mode analysis, might be the subject of further research. The correlation of NMR line width and polymer dimension as well as variations of UV frequencies in different solvents and in the solid phase[3f] may be related to this motion.

(3) Effect of a Chirotopic Side Chain on the Balance between Right-Handed and Left-Handed Helices. The last three rows of Table I present the calculated conformational and energetic data of an infinite right-handed helix of poly(2-methylbutyl isocyanate), denoted by PPIC for its branched pentyl side chain $-CH_2C^*H(CH_3)CH_2CH_3$, in both absolute configurations (*S*) and (*R*). (*R*)-PPIC is a shortened version of the polymer that was mentioned in the Introduction. The calculated results for PPIC are also valid for PNIC, since we have seen already that the extension of alkyl chains away from the backbone has little effect. Indeed, (*S*)-PPIC was found[4b] to exhibit a positive circular dichroism band near 250 nm, and (*R*)-PNIC was found[5a] to exhibit a comparable negative band near the same wavelength.

The calculated right-handed helix with the (*S*) configuration has a single equilibrium conformation. With the (*R*) configuration it has two conformations that are less stable than (*S*) by 0.41 and 0.67 kcal/mol, respectively. While (*S*) and (*R*) configurations cannot be interconverted without breaking a bond, there is a dynamic equilibrium between the left- and right-handed helices of the polymer of a given configuration. From Table I we conclude that (*R*)-PPIC is more stable in the left-handed helix. This conclusion holds therefore also for the (*R*) configuration of PNIC, the optically active poly((*R*)-2,6-dimethylheptyl isocyanate) mentioned in the Introduction, whose optical rotation $[\alpha]$ has been determined to be negative at the sodium D line.[5a] We thus may predict that the (*R*)-PNIC helix is entirely left-handed (M). This prediction has a good change to correspond to reality, and is consistent with the cholesteric liquid crystal properties of (*R*)-PNIC (Sato, Teramoto, and Green, to be published).

The two conformations of the right-handed helix of (*R*)-PPIC differ very much in their ρ values, as well as in their ϕ and ψ values, but much less in their energies (Table I). This is another example of the internal flexibility of the PICs discussed above.

(4) Conformation and Energy Associated with Reversal of the Helical Sense. When one minimizes the energy of a long but finite helical chain, without imposing conformational identity of the monomer units, the result is very close to that of an infinite helix, with minor fluctuations of the torsional angles, except for the monomers near the two ends. Finite chains were used to study the conformation and energy of a reversal of the helical sense of PMIC and of the first conformation of PEIC. They were made as long as could be accommodated by our present computer program (30 monomers for PMIC and 20 monomers for PEIC). First, we calculated the minimum energy conformation of a single helix. Then we took one half of that helix and the mirror image of the second half, and fused them together in different ways. We then used the coordinates of this fused polymer as initial coordinates for energy minimization. The result was an equilibrium conformation of a PIC chain with a helix reversal about its center.

Table III presents the backbone torsional angles of PMIC and PEIC in the vicinity of the reversal region. The reversal itself occurs where the backbone angles change sign (−150, 52, 140, −62 in PMIC and 57, −126, −71, 150 in PEIC), but the helix is distorted in the vicinity of the reversal, particularly on the left-hand side of the chain. (The distinction between the two sides has been discussed above, see Table II and Figures 1 and 2.) Figures 6 and 7 present stereoviews of the reversals of PMIC and PEIC, respectively. It is seen that the chain is kinked by the reversal. The angle between the helices of opposite sense has been calculated as 131° for PMIC and 123° for PEIC. Examination of the stereoviews suggests that the extension of the side chain to PBIC and beyond would not greatly affect the conformation and energy of the kink. The excess energy of the helix with and without the reversal was calculated as 4.2 kcal/mol for PMIC and 3.9 kcal/mol for PEIC. These values were obtained after we had adjusted the barrier of the C′–N torsion potential to 12.5 kcal/mol to fit the results of the statistical mechanical analysis of the optical rotation of αPdHIC, as explained in the Theory.[6]

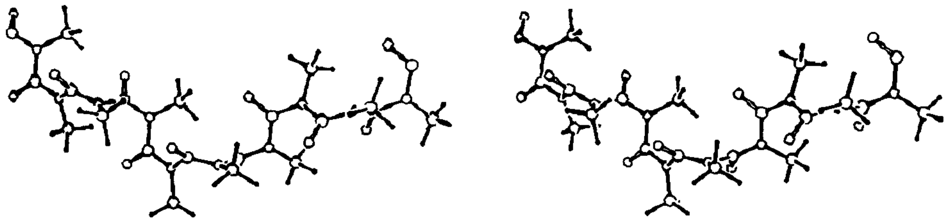


Figure 6. .Stereoview of PMIC helix reversal

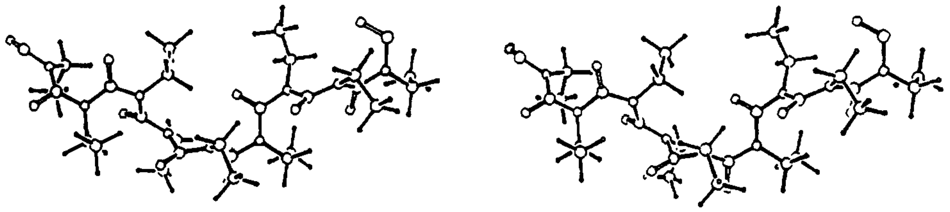


Figure 7. Stereoview of PEIC helix reversal

Table III
List of Backbone Torsional Angles (deg) around the Reversal of Helical Sense and Its Vicinity

PMIC	φ	−172		−172		−171		−169		−161		−150		140		173		172		172	
	ψ		60		60		57		52		39		52		−62		−59		−60		−59
PEIC	φ	−169		−168		−166		−159		−159		−126		150		165		167		168	
	ψ		52		50		48		31		57		−71		−48		−48		−50		−51

Concluding Remarks

The EFF theoretical study of polyisocyanates yielded conformational and energetic data that give a detailed and comprehensive microscopic picture of these molecules. Many of these data are in agreement with experimental results. Others are too detailed to be examined against the available experimental data but may be trusted to be more or less a faithful description of the main features of the PICs. It is hoped that the predictions made in the present study such as the soft intramolecular collective mode of conformational change, or the size of the kink along the chain at points of helical sense reversal, may stimulate further research.

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Appendix

Coordinate Systems for Helical Polymers. We present here the various mathematical representations of an infinitely long helical polymer.[10] Let its monomer units be enumerated by $n = ..., -2, -1, 0, 1, 2, ...$ and the m atoms of each monomer by $i = 1, 2, ..., m$. Two kinds of natural representations are available for such polymers, internal coordinates and helical coordinates.

Internal coordinates are closest to our intuitive concepts about geometric structures: they are the same for all monomeric units in the equilibrium state of the helical polymer, and they are best suited to the representation of the observed or calculated conformations. However, they are least suited for mathematical manipulations.

Helical coordinates are another natural representation, provided they are presented in a so-called canonical form, that is, that the helix axis coincides with the z-axis of a Cartesian coordinate system. In such a system the ith atom of the nth monomer unit is represented by r_i^n, ϕ_i^n, and z_i^n where r is the distance from the helix axis, ϕ is the angle between r and the x-axis, and z is the projection onto the helix axis. The advantage of this representation is the simple relations between the coordinates of the atoms of the nth monomer unit and those of the zeroth unit: $r_i^n = r_i^0$, $\phi_i^n = \phi_i^0 + n\rho$, $z_i^n = z_i^0 + n\tau$, where ρ is the rotation per monomer unit around the helix axis, and τ is the translation per monomer unit along the axis.

Transformation from Internal to Helical Coordinates. The transformations from internal coordinates to an arbitrary Cartesian coordinate system and back are standard for computational studies of molecules in general. The transformation from an arbitrary Cartesian coordinate system, in which the helix axis has an arbitrary direction and does not pass through the origin, to a canonical Cartesian coordinate system in which the helix axis coincides with the z-axis is obtained as follows.

Let $\mathbf{P}_1$, $\mathbf{P}_2$, $\mathbf{P}_3$, and $\mathbf{P}_4$ be four points that specify the location of one and the same atom in four consecutive monomer units in an arbitrary three-dimensional Cartesian coordinate system. Any atom can do, provided it is not too close to the helix axis. The three vectors $\mathbf{t}_i$, $i = 1-3$, where $\mathbf{t}_i = \mathbf{P}_{i+1} - \mathbf{P}_i$, represent the separation between the corresponding atoms in adjacent monomers. They all have the same component in the direction of the helix axis, since it is the translation τ per monomer unit. Consider now the difference vector $\mathbf{d}_1 = \mathbf{t}_2 - \mathbf{t}_1$. The components of $\mathbf{t}_2$ and $-\mathbf{t}_1$ along the helix axis are τ and $-\tau$ respectively, therefore $\mathbf{d}_1$ has a zero component along the axis. The same is true for $\mathbf{d}_2 = \mathbf{t}_3 - \mathbf{t}_2$. Consequently, $\mathbf{d}_1$ and $\mathbf{d}_2$ are perpendicular to the helix axis. The angle between them is the rotation ρ, given by

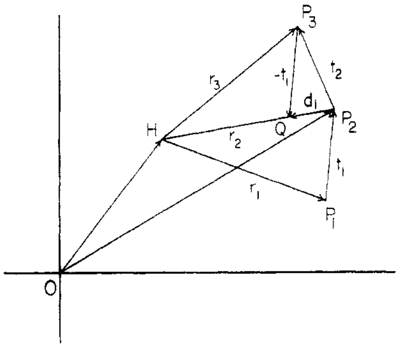
$$\cos \rho = (\mathbf{d}_1 \cdot \mathbf{d}_2)/(d^2) \qquad (1)$$

where $\mathbf{d}_1 \cdot \mathbf{d}_2$ is the scalar product of the vectors and d is their common length. The normalized vector product $\mathbf{h} = [\mathbf{d}_1 \times \mathbf{d}_2]/d^2 \sin \rho$ is a unit vector in the direction of the helix axis. The translation τ is obtained by

$$\tau = \mathbf{h} \cdot \mathbf{t}_i \qquad (2)$$

The components of $\mathbf{h}$ in the Cartesian coordinate system are $\sin \theta \cos \phi$, $\sin \theta \sin \phi$, and $\cos \theta$, where θ is the angle between the z-coordinate and $\mathbf{h}$ and ϕ is the angle between the x-coordinate and the projection of $\mathbf{h}$ onto the x, y plane. A rotation of the coordinate system by an angle $-\phi$ around the z-axis followed by a rotation by an angle $-\theta$ around the y-axis transforms the arbitrary Cartesian coordinate system into a coordinate system in which the vector **h** points in the z-direction and therefore the axis of the infinite helix is parallel to the z-axis.

A translation **s** of the new coordinate system is finally required to make its z-axis coincide with the helix axis. This translation is derived as follows, with the help of the drawing shown. The drawing shows the projections of the points $\mathbf{P}_1$, $\mathbf{P}_2$, and $\mathbf{P}_3$ and of the vectors $\mathbf{t}_1$ and $\mathbf{t}_2$ onto the x,y plane of the new coordinate system. They are denoted by P_1, P_2, P_3, t_1, and t_2, respectively. The helix axis, that is now perpendicular to the x,y plane, intersects the plane at the point H. The three two-dimensional vectors r_i that connect H to P_i have all the same length r. The vector $\mathbf{d}_1$, being perpendicular to the helix axis, is identical with its projection d_1 and is seen from symmetry considerations to lie along the line $\overline{P_2H}$. The plane vectors d_1, t_1, and t_2 are related by $d_1 = t_2 - t_1$, as is obvious from the drawing. Because of the similarity of the two isosceles triangles HP_3P_2 and P_3P_2Q we have $r/t = t/d$ where t is the length of both vectors t_1 and t_2. Consequently we obtain the vector connecting the origin O with H as



$$\mathbf{s} = \overline{OH} = \overline{OP_2} + \overline{P_2H} = \overline{OP_2} + (t/d)^2 d_1 \qquad (3)$$

In the canonical coordinate system there is a simple relation between the helical coordinates (r_i^n, ϕ_i^n, z_i^n) and the Cartesian coordinates x_i^n, y_i^n, z_i^n of the zeroth unit ($n = 0$) as well as all other units ($n \neq 0$).

$$x_i^n = r_i^\circ \cos(\phi_i^\circ + n\rho) \qquad y_i^n = r_i^\circ \sin(\phi_i^\circ + n\rho)$$
$$z_i^n = z_i^\circ + n\tau \qquad (4)$$

References and Notes

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