New Conformations and New Types of Helix Sense Reversals and Defects in the Chains of Nonchiral Poly(alkyl isocyanates).

Natalia V. Lukasheva*, Satu Niemela**, Igor M. Neelov*,Anatolii A. Darinskii*, Franciska Sundholm**, Robert Cook***

*Institute of Macromolecular Compounds of Russian Academy of Sciences
199004 Saint Petersburg, Bolshoy pr., 31 , Russia, e-mail luk@imc.macro.ru
**Polymer Chemistry Department, Helsinki University, PB55,
A.I. Virtasen Aukio 1, FIN-00014, Helsinki, Finland
***Lawrence Livermore National Laboratory, Livermore, California, USA

SUMMARY: Molecular mechanics studies of helix sense reversals and defects of the regularity in the helices of the same sense in the chains of poly(alkyl isocyanates) were performed. The effect of medium was studied by using different values of the dielectric constant. Additionally to the reversals between the helix mirror images (MI) considered in the literature new types of reversals have been investigated. These reversals connect the helices having backbone torsion angles not only with opposite signs but also with inverse angle values (MII). For the MI reversals we report in addition to the small angle break conformations known from literature the discovery of new conformations of similar energy but with large angle breaks. Large angle reversals can be responsible for up to 50% of the chain persistence length in non-polar solvents. In vacuum MII reversals and defects have energies higher than MI reversals because of the strong electrostatic repulsion. At ε =3.5 some defects have energy even lower that that of MI reversals.

Introduction

Polyisocyanates (PIC) with n-alkyl pendant groups known to have a relatively stiff, helical backbone structure due to a competition between electronic and steric factors $^{1-6)}$. The helices may be either left-handed (L) or right-handed (R). For nonchiral PICs (with symmetrical side groups) L and R helices have equal probabilities. For chiral PICs with a chirotropic carbon in side groups helices of one sign are more preferable energetically, leading to interesting optical property $^{7-9)}$. PICs in solution $^{2-4)}$ show a significant flexibility at high molecular weights, consistent with worm-like persistence lengths of from 20 to 60 nm, depending upon solvent. Two possible causes for the flexibility of the PIC's chains have been discussed $^{10-13)}$: (1) cumulative effect of torsion and angular librations and (2) the existence of helix reversal "breaks" along the chain backbone which might be considered as defining a freely rotating chain. Every break changes the helix direction on a definite angle (θ).

The contributions of the both mechanisms to the experimental value of the persistence length a can be evaluated by the equation $^{13)}$:

CCC 1022-1360/99/$ 17.50+.50/0

$$\frac{1}{a}=\frac{1}{a_0}+\frac{1-\cos\theta}{b} \qquad (1)$$

where a_0 is the persistence length due only to librations and b is the average lengths of helical sections between reversals.. b depends on the energy excess E_r due to the reversal [8]:

$$b = l_m \times \exp(E_r / RT) \qquad (2)$$

where l_m is a projection of the monomer unit on the helix axis ($l_m \cong 0.2$ nm).

There are several force-field calculations of the conformations and energies PIC helix sense reversals [10,14,15]. Only reversals connecting the helices which are the mirror images of each other (MI reversals) were considered. The most careful calculations were done in [14,15] for fragments consisting of 20 residues. One possible conformation of the MI reversal corresponding to the breaks with small θ was obtained. For PMIC θ = 49 [14] and for PEIC θ=57 [14] and θ=24 [15]. In spite of the difference of the used force-fields in the both studies the value of E_r = 7 kcal/mol was obtained higher than the experimental value [8] $E_r \cong$ 4 kcal/mol . This disagreement the authors [14,15] prescribed to the use of the torsion barrier of the amid linkage 20 kcal/mol which is correct for isolated amides. For the conjugated amides this barrier should be lower but its value is not known. To reproduce the experimental value of E_r authors [14,15] reduced this barrier to 12.5 kcal/mol.

For a=40 nm (in non-polar solvents) and b =100 nm (corresponding to the experimental E_r) eq 1 gives the contribution of the small angle breaks to the chain flexibility lower than 10%.

There are some limitations in the above mentioned calculations. First of all only MI reversals have been considered. But another type of the reversals is also possible. These reversals connect helices where backbone torsion angles not only change their signs but also inverse their values (MII reversals). Defects of the regularity in the helices of the same sense are possible as well.

Authors of [10,14,15] by calculations of the electrostatic interactions did not vary the value of the dielectric constant ε and used ε =1.0 [14,15] or ε =3.5 [10]. But the contribution of Coulombic interactions could be very important and depend on the value of ε which reflects the effect of the medium (solvent, bulk).

The main goals of present work were:

(1) to check the conformational unitness of MI reversals;

(2) to consider other possible types of the reversals (MII) and defects;

(3) to study the effect of medium by using different values of ε.

Poly(methyl isocyanate) (PMIC) and poly(ethyl isocyanate) PEIC were considered. We used the PCFF force-field of MSI program of the class II. By the calculations of the electrostatic interactions we used different values of the dielectric constant: ε =1.0 (vacuum), ε =2.0 (non-polar organic solvent) and ε =3.5 (bulk state). The Conjugate gradients method and DISCOVER procedure of minimization were used. The accuracy of the calculations was usually $10^{-5} - 10^{-6}$.

Helical Conformations

PMIC contains CH3 side groups and PEIC has -CH2-CH3 side groups. For the description of the backbone conformations of one residue of both polymers torsion angles φ and Ψ were used. For PEIC the side group torsion angle κ was also used. Similar to [14,15] the chain fragment consisting of 20 residues was considered. The search of the minima was performed in the space of all variables. Four global minima with the same energies corresponding to two right-handed and two left-handed helical conformations were found. For ε =1.0 these conformations are characterized by the following angles:

for PMIC

(φ = 159.8° and Ψ = 32.0°) (R1 and L1) and ((φ = 32.0° and Ψ = 159.8°) (R2 and L2),

and for PEIC:

(φ =-163.8°, Ψ=40.0°, (κ =-93.7°) (L1) ; (φ =163.8°, Ψ=-40.0°, (κ =-93.7°) (R1)

(φ =40.0°, Ψ =-163.8°, (κ =-66.5°) (l2); (φ =-40.0°, Ψ=163.8°, (κ =-66.5°) (R2).

These angles correspond to the 8/3 helix (8 monomers per 3 full rotations) with the helix twisting angle about 138° (PMIC) and 135° (PEIC) per monomer. These values are in a good agreement with X-ray data[1]. Increase of ε leads to some decrease of the equilibrium values of the torsion angles on 1-3°.

Helix Reversals: Conformations and Energies

Initial conformations

MI reversals. The reversals between L1 and R1 helices and between L2 and R2 helices are the MI reversals. The initial conformations for the calculation of these reversals were prepared by the procedure similar to that used in . The right and left handed helical 20-mers were cut in the middle and the half of the right-handed helix and the half of the left-handed helix were connected by their middle points. We considered a number of the initial conformations differing by the values or signs of the torsion angles in one or two monomers near the connection point. These conformations corresponded as to extended chain configurations (was close to 0°)as well as configurations benched significantly (in the interval 100° -140°).

MII reversals and defects. The reversals L1R2 and R2L1 are MII helix sense reversals. The defects L1L2(L2L1) and R1R2(R2R1) are the defects in the helices of one sense. The calculations of these reversals and defects were executed for PEIC only. Two initial conformations for each reversal and defect were considered: (A) conformation with direct connection of the helices and (B) conformation with changed torsion angles in one monomer near the connection point. For example for L1R2 reversal these conformations were the following ones: A ...-163.0°,40.0°)(-163.0°,40.0°)(-40.0°,163.0°)(-40.0°,163.0°.

B ...-163.0°,40.0°)(-163.0°,163.0°)(-40.0°,163.0°)(-40.0°,163.0°

All other reversals and defects have the initial conformations constructed by the same way.

Results and Discussion

MI Reversals. Three groups of the final conformations for MI reversals were obtained:

(I) with small angle breaks (< 90°); (II) with large angle breaks (>90° }; (III) with the anti parallel arrangement of the helical parts. The characteristics of MI reversals for PMIC and PEIC corresponding to first two groups are presented in Tables 1 and 2.

Table 1. Energies of the MI helix sense reversals in PMIC.

Small angle reversals					
ε =1.0		ε =2.0		ε =3.5	
θ	E_r	θ	E_r	θ	E_r
17.0	6.2	16.5	5.5	16.5	5.3
Large angle breaks					
ε =1.0		ε =2.0		ε = 3.5	
θ	E_r	θ	E_r	θ	E_r
99.0	7.2	100.0	4.4	100.0	3.2
126.0	6.0	125.0	3.4	125.0	2.3

Table 2. Energies of the MI helix sense reversals in PEIC.

Small angle reversals					
ε =1.0		ε =2.0		ε =3.5	
θ	E_r	θ	E_r	θ	E_r
100.0	10.0	10.0	8.2	9.0	7.6
16.0	7.9	19.0	6.5	18.0	6.1
20.0	7.4				
45.0	9.2	38.0	8.4		
Large angle reversals					
ε =1.0		ε =2.0		ε =3.5	
θ	E_r	θ	E_r	θ	E_r
90.0	9.1	90.0	6.5	90.0	4.9
128.0	8.1	90.0	5.2	90.0	5.2
130.0	8.6	110.0	6.8	112.0	5.7
132.0	8.7	129.0	7.4	126.0	3.0
134.0	8.4	129.0	7.2	129.0	6.2
135.0	9.1	130.0	8.2	130.0	6.3
		131.0	8.1	130.0	6.9
		133.0	9.1	131.0	7.2
				134.0	7.6

Due to the possibility of the different orientations of the side group (angle κ) relative to the main chain the greater conformational variability of the final reversal structures in PEIC was obtained. E_r is the excess of the reversal energy over the helix energy.

The torsion energy gives the main contribution to E_r of the conformations of group I. This is the origin of a weak dependency of E_r on ε. The values of E_r for the reversals of group II depend on ε stronger because the electrostatic interactions contribute significantly to the energies of these reversals. For PMIC in vacuum (ε =1.0) the reversals of both groups have comparable energies but for PEIC only small angle breaks are favorable. At larger ε (2.0 and 3,5) MI reversals with large angle breaks become even more favorable than those with the small angle breaks. These values of ε correspond to non-polar solvents. The discovery of the reversals with large angle breaks bring the conclusion about minor contribution of the reversals into the PIC flexibility in question. The estimation (by eq 1, given b =100 nm} shows that the contribution of large angle breaks to the experimental value of the chain persistence length can be about 50 %.

Values of E_r for the conformations of the reversals with the anti parallel arrangement of the helical fragments of the chain occurred to be negative. Origin of the energetical preferability of such structures is the non-bonded attraction of the monomers which are distanced along the chain but occur to be sufficiently close to each other. We think that such conformations could be possible in poor solvents. In good solvents due to a competition of the solvent molecules for the intermolecular contacts with the monomers of the chain the energy of the reversals with the anti parallel arrangement may be much higher.

MII Reversals and Defects. The calculated values of the reversals and defects in PEIC are presented in Table 3 for =1.0 and 3.5.

Table 3. Energies of the MII reversals and defects in PEIC.

MII reversal or defect	Conformation	ε =1.0 E_r	ε =3.5 E_r
R1L2(L1R2)	A	24.3	11.6
	B	21.2	11.5
L2R1(R2L1)	A	19.1	7.6
	B	13.9	8.0
R1R2(L1L2)	A	26.9	11.6
	B	15.1	5.7
R2R1(L2L1)	A	16.0	7.6
	B	10.5	1.8

At ε = 1.0 the energies of all reversals and defects are much higher than the energies of the most favorable MI reversals due to the large electrostatic repulsion between monomers of neighboring helical parts. MII reversals and defects connect the helical fragments with the alternating dipole moments in contrast to the case of MI reversals where the dipole moments of the neighboring helices are of the same sign. For this reason E_r of MII reversals and defects strongly decreases with increase of ε . At ε =3.5 the energy of one of the defects (R2R1 or L2L1) is equal to 1.8 kcal/mol . This value is lower than E_r =3.0 kcal/mol for the most favorable MI reversal. In spite of the small value of θ = 60° for such defects their contribution to the chain flexibility could be significant due to the exponential dependency of the average length of the helical fragments between the defects on the value of E_r (eq 2).

Conclusion

In contrast to previous studies large angle breaks of MI reversals in PMIC and PEIC have been obtained. Their contribution to the PIC chain flexibility could be comparable with the contribution of the angular librations. At large ε there are some defects in the helices of the same sense with energies lower than those of MI reversals.

Using the values of ε differing from $\varepsilon = 1.0$ we supposed to mimic the effect of solvent or bulk material. But we supposed $\varepsilon = const$. It is only valid if the distances between interacting centers is large enough. The use of the distance dependent dielectric constant would be more correct. The calculations with the distant dependent values of ε are in the processing now. New values of E_r and θ could differ from those obtained in the present study but our main conclusions will remain.

Acknowledgment.

N.V.Lukasheva, I.M.Neelov and A.A.Darinskii acknowledge financial support from the Russian Foundation for Fundamental Research (grants 99-03-33314 and 961597901).

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