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Conformational variability of helix sense reversals in poly(methyl isocyanate)☆

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Abstract

The conformations and energies of several helix sense reversal geometries in poly(methyl isocyanate) (PMIC) have been determined using the PCFF forcefield. In an extension of previous studies, a larger conformational variability for a helix sense reversal has been investigated. In addition to the reversal geometry previously detailed by several authors that results in a relatively small angle deviation from the rod-like polyisocyanate structure, we report the discovery of reversals of similar energy with much larger angle deviations from linearity. The effect of electrostatic interactions as controlled by the value of the dielectric constant, ε, on the conformation and energy of a reversal is also shown to be important. At $\varepsilon = 1.0$ (vacuum) the conformations of the reversals with large and small angle 'kinks' have similar energies. However, at $\varepsilon = 2.0$ (non-polar organic solvent) and $\varepsilon = 3.5$ (bulk state) the reversals corresponding to the large angle kinks have lower energies.

Keywords: Polyisocyanates; Helix reversals; PCFF forcefield

1. Introduction

Polyisocyanates (PICs) with *n*-alkyl pendant groups are 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 PICs with non-chiral side groups, the L and R helices have equal energies. For PICs with a chirotropic carbon in the side group, one helical conformation is more preferable energetically, leading to interesting optical properties [7–11]. X-ray data [1] for poly(butyl isocyanate) (PBIC) indicate a helix with eight monomers per three full rotations and it has been shown that this helical structure is consistent with experimental results in solution [12,13]. Because of the interesting helical backbone structure, numerous molecular mechanics forcefield studies of PICs have been performed [12,14–19]. The conformational properties have also been examined recently using quantum mechanical methods [20]. These studies have been confined primarily to poly(methyl isocyanate) (PMIC) and poly(ethyl isocyanate) (PEIC), both for computational efficiency and because of the expectation that the steric forces leading to the helical twist are primarily due to the α-carbon of the side group. Although early forcefield calculations yielded a number of different helix conformations [12,14,15], more recent work [16–20] has predicted conformations that are in agreement with X-ray and solution data.

For PICs in solution, the experimental data [2–4] show a gradual transition from a rod-like conformation at very low molecular weights to a coiled conformation at high molecular weights, consistent with worm-like chain persistence lengths of 20–60 nm, depending on the solvent. An early explanation of this worm-like behavior was based on the possibility of helix reversal kinks in an otherwise rod-like chain [12], however more recent work has demonstrated that these persistence lengths can be completely explained by the expected torsional angle flexibility of PICs [6,21].

However, the existence of helix reversals in PICs has been demonstrated in a series of brilliant experiments and concurrent theoretical analysis.[2] If the side group is chiral,

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[2] See Refs. [9–11] and references therein.

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the degeneracy between the right and left helical senses is broken and one sense of the helix will be in excess, giving rise to a significant optical rotation for solutions of these PICs with chiral side groups. Further, if the chiral substitution is small, for example a chiral substitution of D for H, the degree of optical rotation has large temperature dependence. From this dependence, both the energy excess per monomer of one helical sense over the other, as well as the energy cost of a helix reversal can be determined using an Ising-like statistical mechanical model. These studies show that the energy excess per monomer for D/H chiral substitutions is generally about 1 cal/mol, while the reversal energy is about 4 kcal/mol.

There have been several forcefield examinations of the helix reversal geometry and energy. In a very early work, Tonelli [12] examined a very short PIC residue with a central reversal and determined that the reversal caused a change in chain direction, which we will call the kink angle, θ, of about a 35° (i.e. the angle between the two segments of opposite helical sense was 145°). More detailed calculations with modern forcefields have also been completed [16–19]. In these studies, chain fragments of PMIC and PEIC consisting of 20 residues were considered. As a first step, the energy of the fragment without reversal was minimized to determine its energy and helical conformation, the latter being in general agreement with experimental results as noted earlier. The handedness of the fragment was then reversed following the 10th residue and the entire chain reminimized to create a 20-mer with a helix reversal in the center. An alternative approach of directly joining right and left-handed sequences followed by reminimization was also employed with the same results. In the first of these studies by Lifson [16], it is not clear how broad a conformation space was examined, in the latter two [17–19] no effort was made to explore conformation space significantly different from that described by Lifson. The major rotational angle distortions associated with the reversal were found to be confined to about three monomer residues, with only slight distortions beyond this. Values of $\theta = 49$ and 47° for PMIC [16,19] and $\theta = 57$ and 24° for PEIC [16–18] were obtained. For both PMIC and PEIC, Lifson [16] found the value of the reversal energy, E_r, to be about 7 kcal/mol using his standard forcefield, about twice the experimentally determined value. A similar value was found for PEIC by Overturf [17,18] with a different forcefield. This value is about twice the experimental one. Lifson ascribed this disagreement to the use of a torsion barrier for the amide linkage of 20 kcal/mol, which is typical for isolated amides, but probably too high for conjugated systems. To reproduce the experimental value of E_r of 4 kcal/mol, Lifson reduced the barrier to rotation about the amide linkages from 20 to 12.5 kcal/mol. Some justification for this ad hoc reassignment has recently been provided by spin-coupled quantum calculations [22]. However, the effectiveness of a forcefield is based on a relatively delicate balance of a large number of parameters, of which the rotational barrier is only one. For example, recent calculations [19] of a helix reversal in PMIC using the Merck Molecular forcefield [23], which has a 17 kcal rotational barrier, gave a geometry very similar to that reported by Lifson, but with a reversal energy of 2.9 kcal/mol.

In the work presented here, we expand upon the previous studies in two ways. First, we have performed a more extensive search of helix reversal geometries, and find two new, distinctly different reversal geometries with similar energies to those previously described. Secondly, we have performed our forcefield calculations not only with a background dielectric value of $\varepsilon = 1$, appropriate for vacuum, but have also examined the effect of using values of ε equal to 2 and 3.5, in an attempt to mimic the effect of non-polar solvent [24] or bulk, respectively. We find that the relative energy of the three reversal geometries is sensitive to this choice.

2. Forcefield and minimization procedure

In this work, we have used the PCFF forcefield [25]. An earlier version of the PCFF forcefield (PCFF91) was used by Overturf [17] in his work on PEIC. In the tables that follow we use the following terminologies for the contributions to total energy: 'bond' for bond stretching, 'angle' for bond angle bending, and 'torsion' for torsion terms. The total non-bonded steric interactions ('non-bond') are represented in the PCFF forcefield as 6–9 Lennard–Jones interactions consisting of a repulsive part ('repulsion') and an attractive part ('dispersion'). Coulombic ('coulomb') interactions are represented as interactions of partial charges assigned to each atom. In the calculations of the electrostatic interactions, we have used three values of the dielectric constant: $\varepsilon = 1.0$, 2.0, and 3.5 as noted earlier. The conjugate gradients and Newton–Raphson methods of energy minimization were used [25]. The gradient tolerances of the calculations were typically 10^{-5}–10^{-6}.

3. Helix conformation and energies

The backbone chain conformation of PMIC is described by two torsion angles φ and ψ as shown in Fig. 1. In this work, we are using the convention adopted in recent work

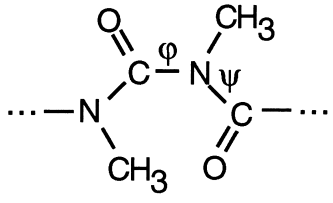

Fig. 1. Shown is the structure of PMIC and the designation of the two rotational angles. We adopt the convention that a *cis* conformation has a value of 0° while a *trans* conformation is 180°.

where the *cis* conformation has a torsional angle value of 0° while the *trans* conformation is ±180°.[3] To get preliminary guidance for the construction of helix conformations, we first calculated a conformational energy map, $E(\varphi, \psi)$. This was done for a PMIC dimer residue and calculations were performed at $\varepsilon = 1.0$ and at $\varepsilon = 3.5$. There were three sets of local minima which had different energies at $\varepsilon = 1.0$: the two deepest minima are at (±30°, ±30°); four minima with an energy 6 kcal/mol higher are at (±160°, ∓30°) and (±30°, ∓160°) and two minima an additional 10 kcal/mol higher are at (±160°, ±160°). The conformational energy map at $\varepsilon = 3.5$ has minima at about the same positions, but all these minima have nearly the same energies in contradistinction to the $\varepsilon = 1$ case.

These three sets of rotational angle conformations were then used as initial conformations for a PMIC 20-mer and the energy of the entire chain fragment was minimized. Only the (±160°, ∓30°) and (±30°, ∓160°) initial conformations relaxed to low energy regular helices. The relaxed backbone (φ, ψ) values are given in Table 1 for $\varepsilon =$ 1.0, 2.0, and 3.5 for the left-handed helix; for the right-handed helix the torsion angles have opposite signs. The obtained helix geometries are similar to those previously reported [16–20]. The various energy contributions to the total energy at the values of ε equal to 1.0, 2.0, and 3.5 are also presented in Table 1. The effect of varying ε on the coulombic energy can be clearly seen. Note that increase of ε, which effectively decreases the coulombic energy contribution, results in only a small change in the minimum energy values of the torsional angles. These angles correspond closely to a 8/3 helix (eight monomers per three full rotations) with the helix-twisting angle equal to 138° per monomer, and a monomer projection length of 2.00 Å, in close agreement with the X-ray data [1].

When we started from the conformations (±30°, ±30°) (deepest for dimer) we obtained helical structures with the torsion angles (±33.9, ±30.7) but with an energy about 50 kcal/mol higher than the low energy 20-mer helix described above. Aleman [20] reported a similar helical structure with an energy 7.7 kcal/mol higher than their low energy 8-mer helix. When we started from the conformations (±160°, ±160°) we obtained non-helical high-energy structures.

4. Helix reversals: conformations and energies

We prepared the initial conformations of the helix reversals by a procedure similar to that used by previous authors [16–19], i.e. by cutting the right and left handed helical 20-mers in the middle and by connecting halves of opposite handed helices at their middle points. The search for the minimum energy conformation was then performed in the space of all variables as for the helical 20-mer fragment.

[3] In the earlier work of Refs. [12,14,15], these definitions are reversed.

Table 1
Conformation and energy contributions for a regular PMIC helix 20-mer as a function of the background dielectric constant, ε. The total energy includes various minor energy terms not individually listed. Energies are in kcal/mol

	$\varepsilon = 1.0$	$\varepsilon = 2.0$	$\varepsilon = 3.5$
ϕ (°)	32.0	29.3	28.2
ψ (°)	−159.8	−158.2	−157.5
Bond	14.9	22.6	26.5
Angle	40.7	39.2	39.0
Torsion	184.4	179.4	178.0
Non-bond	149.9	138.0	133.4
Repulsion	651.1	624.3	613.6
Dispersion	−501.2	−486.3	−480.2
Coulomb	−1102.2	−543.8	−309.0
Total energy	−709.6	−162.2	70.2

To extend the region of the search for minima, we considered not only the initial conformation described above, which we denote as 0, but also conformations in which one or more of the torsional angles associated with monomers 10 and 11 (on either side of the reversal point) were markedly changed from the values used in the 0 reversal conformation. We considered three additional groups of the initial conformations that are detailed in Table 2. The groups are distinguished by the nature of the (φ, ψ) sign changes and interchanges, as well as the resultant initial kink angle, θ, at the reversal. The chains with conformations belonging to groups 0 and I have initially extended conformations, i.e. θ the complement to the angle between helical fragments is small. For the initial conformations from groups II and III, the chain is bent significantly at the reversal, initial values of θ exceed 90°.

The minimizations which were started from the initial conformations 0 and I all lead to the same final conformation denoted as A, which is qualitatively similar to what has previously been reported [16–19]. The relaxed conformation

Table 2
Backbone torsional angles for monomers 9–12 of the conformations of the PMIC 20-mer with reversal before minimization

Type	φ_9	ψ_9	φ_{10}	ψ_{10}	φ_{11}	ψ_{11}	φ_{12}	ψ_{12}
0	32	−160	32	−160	−32	160	−32	160
I.1	32	−160	32	160	−32	160	−32	160
I.2	32	−160	−32	−160	−32	160	−32	160
I.3	32	−160	32	160	32	160	−32	160
II.1	32	−160	32	160	160	−32	32	160
II.2	32	−160	32	160	160	32	−32	160
II.3	32	−160	32	−160	160	32	−32	160
II.4	32	−160	32	−160	−160	−32	−32	160
II.5	32	−160	32	−160	160	−32	−32	160
II.6	32	−160	32	−160	−160	32	−32	160
III.1	32	−160	−32	160	160	−32	−32	160
III.2	32	−160	−32	160	160	32	−32	160
III.3	32	−160	−160	32	32	−160	−32	160
III.4	32	−160	160	32	32	−160	−32	160
III.5	32	−160	160	32	32	160	−32	160

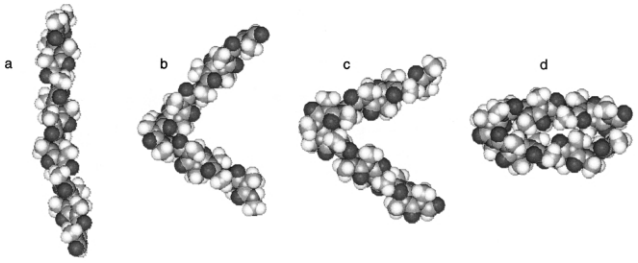

Fig. 2. Shown are four conformations of relaxed 20-mer chains corresponding to reversal types A–D as described in the text.

is shown in Fig. 2a. For $\varepsilon = 1$, the value of the helical kink angle, θ is about 17°, somewhat less than the 49° reported by Lifson [16]. The angular characteristics around the reversal of the A conformation are given in Table 3 for different values of ε. Note that there are only very minor variations as a function of ε. The changes in each of the energy contributions relative to the chain without a reversal for conformation A are presented in Table 4 for the values of ε equal to 1.0, 2.0, and 3.5. The sum of these changes gives the total reversal energy, E_r, given in the last row. Note that the primary contributions to the reversal energy arise from the torsional and non-bonded interactions as expected, and that there is also a significant bond angle contribution. Note also that the total reversal energy decreases from 6.2 to 5.3 kcal/mol as ε is increased from 1.0 to 3.5. These values are smaller than the 7.0 kcal/mol value initially obtained by Lifson by using the non-modified forcefield [16], but larger than both the experimental value [8] of about 4.0 kcal/mol or the results of Merck forcefield results of Young and Cook [19].

The minimization procedure for the initially bent conformations belonging to groups II and III give final reversal conformations with $\theta \geq 90°$. In particular, initial conformations 1 and 2 from group II (see Table 2) give a bent reversal conformation (reversal type B) that has $\theta = 100°$ for $\varepsilon = 1$. This conformation is shown in Fig. 2b. The dihedral angles and energies of this conformation are presented in Tables 5 and 6 for the three values of ε used. It can be seen that the reversal site includes nearly three monomers as for the reversal A, but the angles are more distorted from the helical values. The total energy excess, E_r, for this reversal depends on ε more strongly than for reversal A and changes from 7.1 kcal/mol at $\varepsilon = 1.0$ to 3.2 kcal/mol at $\varepsilon = 3.5$. Thus reversal B is less favorable than reversal A in vacuum but may be more favorable in non-polar solvents and in the bulk. For this reversal, the electrostatic interactions give the maximum contribution to the energy excess at $\varepsilon = 1.0$ in contrast to the reversal A, and become comparable with the torsion and non-bond contributions at larger ε.

Table 4
Energy changes by source type due to a type A reversal, as a function of the background dielectric constant, ε. Energies are in kcal/mol

ΔE_r	$\varepsilon = 1.0$	$\varepsilon = 2.0$	$\varepsilon = 3.5$
Bond	+0.3	+0.2	+0.2
Angle	+1.1	+1.1	+1.1
Torsion	+2.8	+3.2	+3.4
Non-bond	+0.7	+0.6	+0.5
Repulsion	0.0	−0.1	−0.2
Dispersion	+0.7	+0.7	+0.7
Coulomb	+1.3	+0.6	+0.3
Total energy	+6.2	+5.6	+5.3

Initial conformations 3–6 from group II give another strongly bent conformation of the reversal (C), as shown in Fig. 2c. The torsion angles around the reversal and related energies are given in Tables 7 and 8, respectively. For this reversal conformation, the kink angle θ at the reversal is 124° for $\varepsilon = 1$. The total energy, E_r, for this reversal changes from 6.0 kcal/mol at $\varepsilon = 1.0$ to 2.3 kcal/mol at $\varepsilon = 3.5$. It can be seen that the energy excess of the reversal C is approximately the same as for the reversal A at $\varepsilon = 1.0$ and more favorable at higher values of ε. For reversal C (as for B) the electrostatic interactions give the maximum contribution to E_r at $\varepsilon = 1.0$ but at higher ε the torsional and non-bonded contributions dominate.

All conformations from group III give reversal conformations of type D where the helical parts of the chain are nearly anti-parallel to each other (θ close to 180°). An example is shown in Fig. 2d. The total energy differences, E_r, for these reversal conformations were negative. The source of this apparent instability is the non-bonded attraction of monomers that are far from each other along the chain but have favorable intermolecular contacts due to the anti-parallel arrangement of the helical fragments. Such conformations might be probable in poor solvents or in the solid

Table 3
φ_n, ψ_n values for the eight adjacent monomers of the type A reversal

n	$\varepsilon = 1.0$	$\varepsilon = 2.0$	$\varepsilon = 3.5$
7	31.9, −159.6	29.2, −158.0	28.1, −157.3
8	32.2, −161.2	29.3, −159.4	28.1, −158.6
9	33.4, −154.1	30.6, −153.4	29.4, −153.0
10	30.7, 170.8	30.6, 171.6	30.5, 171.9
11	−45.1, 161.1	−42.5, 158.5	−41.6, 157.5
12	−30.6, 159.8	−27.4, 158.3	−26.2, 157.6
13	−32.4, 159.7	−29.7, 158.1	−28.6, 157.4
14	−31.7, 159.9	−29.1, 158.2	−28.0, 157.5

Table 5
φ_n, ψ_n values for the eight adjacent monomers of the type B reversal

n	$\varepsilon = 1.0$	$\varepsilon = 2.0$	$\varepsilon = 3.5$
7	31.9, −158.3	29.3, −157.1	28.2, −156.7
8	32.1, −162.0	29.2, −159.7	28.1, −158.7
9	32.5, −157.4	29.4, −155.9	28.2, −155.3
10	34.7, −159.2	30.9, −157.1	29.4, −156.1
11	−172.1, −36.7	−171.0, −35.7	−170.7, −35.3
12	−32.5, 163.3	−33.5, 161.1	−34.0, 160.1
13	−29.2, 162.2	−28.0, 160.5	−27.6, 159.7
14	−33.5, 159.1	−30.4, 157.4	−29.1, 156.6

Table 6
Energy changes by source type due to a type B reversal, as a function of the background dielectric constant, ε. Energies are in kcal/mol

ΔE_r	$\varepsilon = 1.0$	$\varepsilon = 2.0$	$\varepsilon = 3.5$
Bond	+0.6	+0.6	+0.5
Angle	+2.6	+1.8	+1.4
Torsion	+0.6	+1.9	+1.6
Non-bond	−0.9	−1.5	−1.7
Repulsion	+7.2	+6.3	+5.7
Dispersion	−8.1	−7.7	−7.5
Coulomb	+5.6	+2.7	+1.5
Total energy	+7.1	+4.3	+3.2

Table 8
Energy changes by source type due to a type C reversal, as a function of the background dielectric constant, ε. Energies are in kcal/mol

ΔE_r	$\varepsilon = 1.0$	$\varepsilon = 2.0$	$\varepsilon = 3.5$
Bond	+0.5	+0.4	+0.3
Angle	+1.9	+1.3	+1.0
Torsion	+0.6	+1.6	+2.2
Non-bond	−1.9	−2.3	−2.6
Repulsion	+5.7	+5.7	+5.6
Dispersion	−7.6	−8.0	−8.2
Coulomb	+5.1	+2.6	+1.5
Total energy	+6.0	+3.4	+2.3

(crystalline) state, but not in good solvents where there is a competition with the solvent for intermolecular contacts with the monomers of the chain. For this reason, we will exclude these conformations from further consideration of the solution conformations.

5. Discussion

It is clear from these studies that there exist reversal conformations other than the one first reported by Lifson that have comparable energies. Further, it is clear that finding these reversals computationally depends upon the initial conformation that one relaxes from. We have looked at a few initial conformations but have by no means exhausted the possibilities, and there likely exist other reversal conformations of similar energies to those reported here.

In Table 9, we summarize the total reversal energies, E_r, and kink angles, θ, for conformations A–C at values of ε equal to 1.0, 2.0, and 3.5. At $\varepsilon = 1.0$, the small kink angle structure, reversal A, and the large kink angle structure, reversal C, have similar energies. But at higher values of ε, reversal C is lower energy. One ramification of the possibility of much larger kink angles at the reversal is that the interpretation of the experimentally measured persistence length depending only upon the torsional libration needs to be reexamined [6,21]. Mansfield [26] showed for a freely rotating chain model that

$$\frac{1}{a} = \frac{1}{a_w} + \frac{1 - \cos\theta}{b} \quad (1)$$

Table 7
φ_n, ψ_n values for the eight adjacent monomers of the type C reversal

n	$\varepsilon = 1.0$	$\varepsilon = 2.0$	$\varepsilon = 3.5$
7	31.9, −159.0	29.6, −157.6	28.2, −157.0
8	31.6, −160.9	29.1, −159.2	28.0, −158.5
9	33.2, −157.5	29.5, −154.6	29.1, −153.3
10	35.7, 170.9	32.8, 170.8	31.6, 170.8
11	161.6, −32.8	152.0, −30.9	152.0, −30.2
12	−28.8, 165.6	−28.5, 163.6	−28.1, 158.6
13	−32.6, 160.7	−29.9, 159.8	−28.9, 159.4
14	−31.9, 159.3	−29.7, 157.6	−28.7, 156.8

where a and a_w are the experimentally measured persistence length and the contribution to this value from torsional oscillations, respectively, and b is the distance between freely rotating but fixed angle reversals.[4] If the distance between reversals is of the order of 100 nm as estimated by Lifson [8], then a small kink angle as in conformation A contributes negligibly to the experimentally determined persistence length. However, for the same value of b a kink angle θ in excess of 90° can contribute significantly to the experimentally measured persistence length [27].[5]

Lastly let us note that in the recent work of Young and Cook [19] on the geometric pathway for helix reversal *motion*, it was determined that the translation of a type A reversal down the chain one repeat unit involved the passage over three barriers, thus there were two metastable intermediates along the path. The energies of these intermediates relative to the initial (or final) state were about 3 and 6 kcal/mol, while the barriers were in excess of 10 kcal/mol. Although the conformations at the reversal of these intermediate states were different from conformations B and C reported here, the kink angle θ at the reversal was about 70° for the first intermediate and 90° for the second. Thus the existence of at least metastable reversal conformations with large kink angles has been previously discussed within the framework of a different forcefield, and the details of the reversal geometries we report here with large kink angles may be dependent upon the forcefield we have used.

6. Conclusion

Molecular mechanics calculations of the helical and the

[4] Although the reversal kink is certainly not freely rotating, the variation in the number of monomers between sequential reversals randomizes the new direction sufficiently that the freely rotating model is a reasonable approximation.

[5] We also note that careful experimental studies of the molecular weight dependence of the chain dimensions of stereo-specifically deuterated and normal poly(hexyl isocyanate) show identical chain dimensions. In these systems the distribution of helix reversals is different, however the average number, which depends upon the reversal energy, is the same. These authors also discuss the difficulty in distinguishing experimentally between a pure worm and broken worm models.

Table 9
The kink angle, θ, and values of the reversal energy, E_r, in kcal/mol as a function of the background dielectric constant, ε, for reversal types A–C. Values of θ vary by less than 2° over the range of ε

Type	θ	$\varepsilon = 1.0$	$\varepsilon = 2.0$	$\varepsilon = 3.5$
A	17	6.2	5.5	5.3
B	100	7.2	4.4	3.2
C	124	6.0	3.4	2.3

reversal structure of the PMIC chain were performed using a modern forcefield. In contrast to previous studies, three different reversal conformations (A, B and C) with comparable energies for helix sense reversals have been obtained. One of them (A) corresponds to the small kink angle discussed in earlier literature and two others (B and C) correspond to new, large kink angle structures. The minimum energy conformation depends on the value of the dielectric constant, ε, which is used. For $\varepsilon \geq 2.0$, the large kink angle structures become more preferable, however even at $\varepsilon = 1.0$ the type B and C structures are seen to be of comparable energy to the previously reported type A structure. As noted above, the contribution of such large kink angle structures to the experimentally measured chain flexibility (i.e. persistence length) would be comparable with that of torsional librations in the chain backbone.

In using values of ε differing from the typically used $\varepsilon = 1.0$, which is appropriate for vacuum, we attempted to mimic the effect of solvent or bulk material. We recognize that this is valid only if the distances between interacting centers are large enough, and that the use of a distant dependent dielectric constant may be more accurate. However, our initial goal was to both explore alternative geometries and to determine whether modification of ε would give rise to interesting effects. We do not expect the use of a more realistic distant dependent ε to significantly change our results, and it is hoped that the predictions made in the present study may stimulate both experimental and theoretical research.

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