Conformational Study of α- and γ-Polypivalolactone Based on Intra- and Intermolecular Interactions

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ABSTRACT: Conformational and packing energy of crystalline α- and γ-polypivalolactone has been analyzed with a computational procedure where both intra- and intermolecular interactions are simultaneously taken into account within each energy minimization cycle. This methodological improvement yields results in good agreement with the models directly refined by the powder X-ray diffraction profile and by electron diffraction data. In particular intermolecular interactions prove to have a determinant influence on the detailed conformations of the polymer chain in the two crystalline forms.

1. Introduction

Molecular mechanics is an empirical approach that, using different techniques (energy minimization, molecular dynamics, Monte Carlo methods, statistical mechanics), may simultaneously provide the structure (i.e., molecular models) and the energy of a molecular system. The empirical nature of this approach always requires that the model obtained be tested against experiment. On the other hand, when the observed structure or structural changes are reproduced with good accuracy, this method, by providing also the corresponding energy or energy changes, has the benefit of giving an insight into the underlying forces that determine such a structure or structural changes. In this respect, as an example of the usefulness of molecular mechanics in connection with X-ray crystal structure determinations, we present here the results of the application of a novel method for evaluating the packing energy of a crystalline polymer chain.[1]

The traditional approach to the evaluation of packing energy in crystals[2,3] rests on the separation of intramolecular interactions from intermolecular ones. This factorization of the problem allows for a two-step procedure where the conformation of the molecule is first refined to minimize all intramolecular (bonded and nonbonded) energy contributions and subsequently a rigid-body adjustment in the crystal lattice is carried out to minimize intermolecular interactions.

The basic underlying assumption is that the depth of intramolecular potential energy minima is much more pronounced than that pertaining to minima of packing energy. This approximation is certainly true in general, but it can be only the basis for a preliminary approach devoted to an overall definition of the fundamental features of the system under investigation. When high accuracy is required in the refined model or several structures of comparable energy are to be discriminated, the two-step procedure may bias the final results in a significant way.

A more realistic single-step approach, where both intra- and intermolecular interactions are simultaneously taken into account during the final minimization procedure, does not involve, however, any prohibitive requirements of computer memory nor exceedingly time-consuming calculations, provided that a sufficiently small portion of the crystal is taken into account. Since we are interested in the total (conformational + packing) energy of a single monomer within a crystal lattice, the dimensions of the microcrystal are determined by the operating range of all nonbonded interactions of the monomer. This usually involves a number of neighboring monomers, on the order of 15–20, and represents a system that, though complex, is still tractable from a computational point of view provided monomeric units are not too big (less than ca. 30 atoms). Moreover, due to symmetry, the number of independent variables is only slightly increased with respect to the case of the isolated chain. A computer program performing such a single-step minimization has been already successfully employed in the case of crystalline isotactic polypentadiene[1] and is here applied to the study of the α- and γ-crystal forms of polypivalolactone (PPVL). A similar methodology has also been proposed by Boyd et al.[4,5]

There are several reasons for studying the crystal structures of PPVL; first of all, recent crystallographic analyses provided reliable structural parameters for both crystal forms;[6,7] secondly, relevant discrepancies are detected between the conformation of the polymer chain in the α form and the conformation corresponding to the minimum energy for the isolated chain;[6,8,9] and finally, the two different packing environments have a relevant effect on the chain conformation.[7]

A quantitative explanation of these facts can only be sought in calculations involving both intra- and intermolecular adjustments and represents a stimulating test for our computational procedure.

2. Method of Calculation

The same method already adopted for isotactic *trans*-1,4-poly(1,3-pentadiene)[1] was applied to α- and γ-PPVL, i.e., the energy minimization with respect to all degrees of freedom for a microcrystal comprising a number of polymer fragments, therefore considering simultaneously intra- and intermolecular interactions for a given space group symmetry and given unit cell dimensions. The program adopted is REFINE/HP;[10] the force-field parameters were taken from Allinger's MM2 set[11] with minor differences involving the torsional and dipole energy. The former is computed at each bond by means of a single-term function, best-fitted to Allinger's combination of several terms, while the dipole energy is treated in the monopole approximation. The dipole moment of the ester group was decomposed into the atomic partial charges

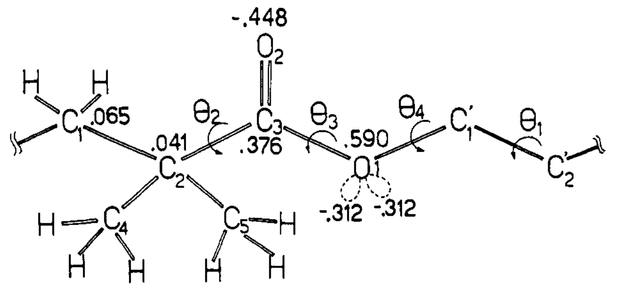

Figure 1. Fragment of the PPVL chain with the numbering scheme of atoms and torsion angles and with the atomic partial charges adopted in the evaluation of Coulombic energy term.

reported in Figure 1 and the Coulombic terms were calculated with ϵ (the effective dielectric constant) taken as 3. This initial choice was not reexamined in successive runs since the Coulomb contribution turned out to be of scarce relevance in determining the phenomena we were interested in. A cutoff limit of 6 Å was chosen, meaning that all atoms of one unit interact with all atoms of another unit if at least one pair of atoms is within the limit. This means that, in practice, many interactions beyond the cutoff limit are taken into account as well. No geometrical constraints were imposed on the atomic coordinates, except for keeping the unit cell dimensions equal to the observed values. For practical reasons the same nonbonded parameters were utilized for both intra- and interchain interactions, although according to our experience two distinct potential sets would be required for a proper simulation of thermal expansion. As stated in the previous article,[1] we feel that while the use of more appropriate intermolecular nonbonded potentials is necessary when energy is minimized *also with respect to the unit cell dimensions*, the effects of our choice are much less relevant in the present study.

3. Results and Discussion

(a) The Isolated Chain. A first conformational energy minimization was carried out on the isolated PPVL chain (see Figure 1 for torsion angle labeling). Only the GGTT region of the conformational space (referred to the dihedral angles θ_1, θ_2, θ_3, and θ_4, respectively) was explored and a 2_1 helix symmetry was imposed since these features are shown by both crystal forms of PPVL under investigation. The monomer was taken as the asymmetric unit. The axial advancement per monomer unit, h, was assumed as a variable parameter and an energy minimization, with respect to the Cartesian coordinates of the asymmetric unit, was performed in correspondence of each selected value of h in the range $2.7 \leq h \leq 3.25$ Å. Results are summarized in Figure 2, where it may be seen that the minimum occurs at $h = 3.005$ Å, in close agreement with the observed chain repeat in the crystal ($c = 6.02$ Å). The same figure also shows a plot of the values assumed by the four main-chain torsion angles in correspondence to each h value. The energy curve in Figure 2 is rather shallow, as a Δh of 0.1 Å around the minimum corresponds to a raise in energy ΔE of only 0.1 kcal/mol. There is a small discontinuity at $h = 3.07$ Å. The chain torsion angles at the minimum are 51°, 50°, 178°, and −167° for θ_1, θ_2, θ_3, and θ_4, respectively, with a marked deviation from planarity at θ_4 rather than at θ_3, as observed in α-PPVL.[6] This feature is in agreement with previous calculations,[8] although the deviation in θ_4 is not that large. However, the minimum energy conformation found by us differs significantly with respect to θ_2, for which, as shown in Figure 2, a value of 34°, as proposed by Cornibert et al., is reached only in correspondence to $h = 2.75$ Å ($\Delta E = 0.72$ kcal/mol).

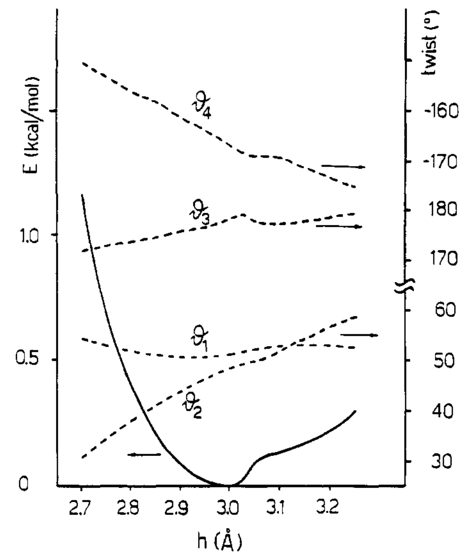

Figure 2. Plot of the conformational energy of the isolated chain as a function of the axial advancement per monomer unit h (full line) and of the corresponding values of the four torsion angles (dotted lines).

(b) The α-PPVL Crystal Structure. The conformation corresponding to the minimum in Figure 2 was assumed as the starting point for building up the α-PPVL microcrystal with space group symmetry and cell dimensions taken from published data.[6] The initial location of the chain in the unit cell was rather arbitrarily obtained by superimposing, through proper rototraslation along c, the C(2) atom on the coordinates published by Perego et al.[9] for the same atom (Brükner's coordinates[6] were deliberately ignored). In the following we shall refer to this model as model A. The subsequent energy minimization gave rather interesting results since the conformation changed to 51°, 51°, −170°, and 178° for θ_1, θ_2, θ_3, and θ_4, respectively, with the deviation from trans planarity migrating from θ_4 to θ_3 in complete agreement with the model refined on experimental X-ray diffraction data.[6] Refined fractional coordinates for this model (labeled as model B) are reported in Table I together with the most relevant geometrical data. An accurate inspection reveals that both conformation and position in the unit cell of the present model are very close to those resulting from the previous crystallographic analysis, the positional root mean square deviation (rmsd) between the two models being only 0.096 Å. This close resemblance is also confirmed in Figure 3 where the powder X-ray diffraction profile computed with the present model is compared with the observed profile. The disagreement factor of 0.165 is only slightly higher than the value of 0.135 obtained after a complete crystallographic refinement and represents a very satisfactory agreement considering that the theoretical model has been refined without reference to the observed X-ray diffraction profile.

A number of exploring calculations were performed in the neighborhood of this minimum to verify its uniqueness. The starting point was changed by rototraslations of moderate amounts (about 10° and 0.2 Å) along c and the energy minimized again. These runs lead to structures differing by no more than 0.01 kcal/mol in the total energy and less than 2° in the torsion angles; the rmsd's of atomic coordinates were also quite small (less than 0.03 Å) so that no doubt exists about the uniqueness of

Table I
Fractional Coordinates and Geometrical Features of Refined α-PPVL (Model B)[a]

O(1)	0.0209 (0.0198)	0.6271 (0.6136)	0.2727 (0.2704)
O(2)	0.2340 (0.2285)	0.5040 (0.4956)	0.4805 (0.4814)
C(1)	0.0591 (0.0691)	0.2635 (0.2196)	0.1656 (0.1711)
C(2)	0.2189 (0.2211)	0.3616 (0.3566)	0.2786 (0.2792)
C(3)	0.1619 (0.1607)	0.5033 (0.4937)	0.3585 (0.3581)
C(4)	0.3559 (0.3686)	0.1912 (0.1993)	0.3740 (0.3764)
C(5)	0.2982 (0.2881)	0.5151 (0.5136)	0.2188 (0.2116)
Bond Lengths, Å			
C(1)′-O(1)	1.417 (1.44)		
C(2)-C(3)	1.533 (1.53)		
C(2)-C(5)	1.538 (1.54)		
O(1)-C(3)	1.358 (1.35)		
C(2)-C(1)	1.546 (1.53)		
O(2)-C(3)	1.212 (1.23)		
C(2)-C(4)	1.542 (1.54)		
Bond Angles, deg			
C(1)′-O(1)-C(3)	114.4 (114.6)		
O(1)-C(3)-C(2)	110.0 (109.0)		
O(2)-C(3)-C(2)	124.4 (125.9)		
O(1-)-C(3)-O(2)	125.6 (125.0)		
C(1)-C(2)-C(3)	108.9 (109.5)		
C(1)-C(2)-C(5)	110.9 (109.5)		
C(3)-C(2)-C(4)	109.3 (109.5)		
C(3)-C(2)-C(5)	108.8 (109.5)		
C(1)-C(2)-C(4)	109.3 (109.5)		
C(4)-C(2)-C(5)	109.6 (109.3)		
O(1)-C(1)′-C(2)′	107.0 (109.4)		
Torsion Angles, deg			
C(3)′-C(2)′-C(1)′-O(1)	51.4 (46.2)		
O(1)-C(3)-C(2)-C(1)	50.2 (53.5)		
C(1)′-O(1)-C(3)-C(2)	-170.3 (-169.4)		
C(2)′-C(1)′-O(1)-C(3)	178.2 (182.2)		
Unit Cell Constants			
$a = 9.03$ Å, $b = 11.62$ Å, $c = 6.01$ Å, $\gamma = 121.5°$			
space group $P2_1/b$			

[a] We report, in parentheses, also the values of the model refined by X-ray diffraction data.

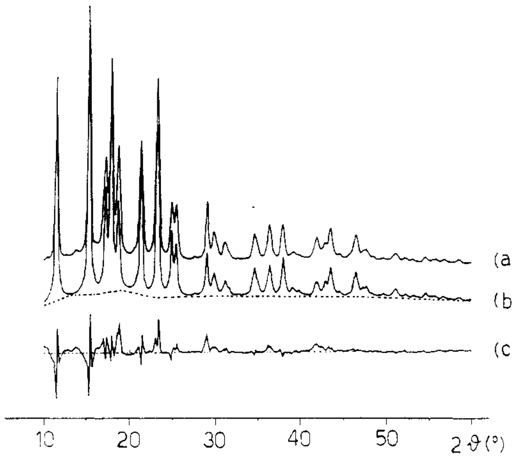

Figure 3. Comparison of the observed powder profile of α-PPVL (curve a) with the profile calculated with model B (curve b). Curve c is the difference profile, while the dotted line is the background contribution.

the minimum found in this region of the conformational space. Another important result of these calculations concerns the Coulombic contribution to the total energy. It turned out quite surprisingly that the torsion angle changes taking place in the minimization procedure do not involve any significant variation in the Coulomb energy; in fact an increase of 0.03 kcal/mol for this contribution is to be compared with an overall decrease of 0.44 kcal/mol for the total energy. The hypothesis of Perego et al.[9] about the dominant role played by dipole interactions in determining the deviations from the conformation computed for the isolated chain is not supported by our calculations. The Coulomb term certainly represents a relevant amount of the total energy, but its *change* with the conformation of the polymer chain is of scarce importance. For this reason we did not investigate any further on the value of ϵ. We want to stress, however, that our conclusion does not exclude at all a role of the electrostatic energy in favoring the GGTT conformer over other possible helical arrangements.

(c) The γ-PPVL Crystal Structure. As for the α form, the microcrystal of γ-PPVL was built up starting from the conformation of minimum energy of the isolated chain and using the space group symmetry and the cell dimensions recently published by Meille et al.[7] A preliminary rototraslation of the molecule along c was performed to place C(2) at the same position in the unit cell as that occupied in the model refined from electron diffraction data.[7] This was the starting point for the simultaneous minimization of conformational and packing energy. A very similar result was later obtained by optimizing the packing energy by means of rigid rototranslations along c prior to the full energy minimization.

The conformation proposed by Meille et al.[7] is quite close to the one we find for the isolated chain and this was confirmed by the results of the present calculations; in fact the polymer chain underwent only modest changes upon completion of the minimization run (model C). An overall energy lowering of only 0.13 kcal/mol was found with conformational changes of less than 2° and the rmsd between the starting and the final models is 0.05 Å (it is 0.23 Å when the isolated chain model and the α-PPVL model are compared).

Fractional coordinates and the most relevant geometrical features of γ-PPVL are reported in Table II.

We consider this an important result since, first of all, it gives additional support to the crystallographic analysis carried out on γ-PPVL; second, it clearly explains the origin of the conformational differences between the two crystal forms in terms of different packing effects. This was further confirmed by the results of the following two runs: (i) a starting model corresponding to the conformation found in α-PPVL was introduced into the γ crystal and then refined as usual; (ii) a starting model corresponding to the conformation found in γ-PPVL was introduced into the α crystal and refined. A complete conversion of the two conformations is observed, thus proving that the differences observed between the α and γ forms, although small, are real and well reproduced by molecular mechanics.

(d) Intermolecular Interactions in α- and γ-PPVL. We have already pointed out the scarce role played by the Coulombic contributions upon conformational changes leading from the isolated chain model to the model optimized in the α crystal. These are substantially the two conformations available to the PPVL chain in this region of the conformational space; the γ crystal stabilizes in fact a conformation that is quite close to that of the isolated chain with an increase in intramolecular energy of only 0.05 kcal/mol. The corresponding energy increase in the case of the α model of 0.30 kcal/mol is *entirely due to the torsional term*, the intramolecular nonbonded term being substantially unchanged. Therefore it appears worthwhile to compare the packing interactions in the two crystal forms. This comparison was done by grouping the atoms of the monomer moiety into five different fragments and evaluating, for each one, the cor-

Table II
Fractional Coordinates and Geometrical Features of Refined γ-PPVL (Model C)[a]

atom	*x*	*y*	*z*
O(1)	0.0132 (0.0100)	0.1173 (0.1175)	0.0226 (0.0250)
O(2)	0.2501 (0.2499)	0.0190 (0.0186)	−0.0532 (−0.0472)
C(1)	0.1994 (0.1941)	−0.1184 (−0.1177)	0.3199 (0.3226)
C(2)	0.0553 (0.0510)	−0.0797 (−0.0779)	0.1738 (0.1778)
C(3)	0.1007 (0.1028)	0.0313 (0.0329)	0.0405 (0.0492)
C(4)	−0.0932 (−0.0980)	−0.0528 (−0.0532)	0.3218 (0.3262)
C(5)	−0.0108 (0.0032)	−0.1778 (−0.1789)	0.0065 (0.0183)

Bond Lengths, Å

C(1)′–O(1)	1.419 (1.44)
C(2)–C(3)	1.534 (1.53)
C(2)–C(5)	1.540 (1.54)
O(1)–C(3)	1.360 (1.35)
C(2)–C(1)	1.545 (1.53)
O(2)–C(3)	1.212 (1.23)
C(2)–C(4)	1.543 (1.54)

Bond Angles, deg

C(1)′–O(1)–C(3)	114.1 (115.3)
O(1)–C(3)–C(2)	110.7 (111.7)
O(2)–C(3)–C(2)	123.7 (121.4)
O(1)–C(3)–O(2)	125.6 (126.7)
C(1)–C(2)–C(3)	110.2 (108.3)
C(1)–C(2)–C(5)	110.9 (109.5)
C(3)–C(2)–C(4)	109.4 (111.5)
C(3)–C(2)–C(5)	107.5 (111.1)
C(1)–C(2)–C(4)	109.4 (109.5)
C(4)–C(2)–C(5)	109.4 (107.0)
O(1)–C(1)′–C(2)′	108.1 (109.1)

Torsion Angles, deg

C(3)′–C(2)′–C(1)′–O(1)	52.6 (52.2)
O(1)–C(3)–C(2)–C(1)	45.8 (47.7)
C(1)′–O(1)–C(3)–C(2)	179.7 (178.3)
C(2)′–C(1)′–O(1)–C(3)	−163.6 (−165.5)

Unit Cell Constants, Å
$a = 8.23$, $b = 11.28$, $c = 6.02$
space group $P2_12_12_1$

[a] We also report, in parentheses, the values of the model refined by X-ray and electron diffraction data.

Table III
Analysis of the Intermolecular van der Waals Interactions in the α- and γ-Crystal Forms of Polypivalolactone[a]

	α-PPVL		
fragment	model A	model B	γ-PPVL model C
$C(1)H_2$	−0.81	−1.19	−1.00
C(2)	−0.43	−0.44	−0.46
$C(4)H_3$	−2.08	−2.22	−2.03
$C(5)H_3$	−1.42	−1.58	−2.00
$C(3)O_2$	−1.78	−1.90	−1.56
	−6.52	−7.33	−7.05

[a] Energies are in kcal/mol.

responding intermolecular van der Waals energy term in the α and γ crystals; corresponding data for model A were computed for comparison. Results are given in Table III, while a comparison of packing in the α- and γ- forms is shown in Figure 4. The packing energies of the two minima differ by only 0.3 kcal/mol, the α form being favored with regard to the ester, the CH_2, and the $CH_3(4)$ groups, while the other methyl is significantly more stable in the γ crystal. In both structures there is only one repulsive intermolecular interaction (greater than 0.1 kcal/mol) between one H atom belonging to $CH_2(1)$ and O(2). In contrast, when the isolated helical conformation (or the substantially equivalent γ conformation) is forced into the α crystal (model A) four short contacts occur (see Figure 4), raising the energy by about 0.5 kcal/mol. It is just the release of these repulsive interactions that drives the conformational change toward model B.

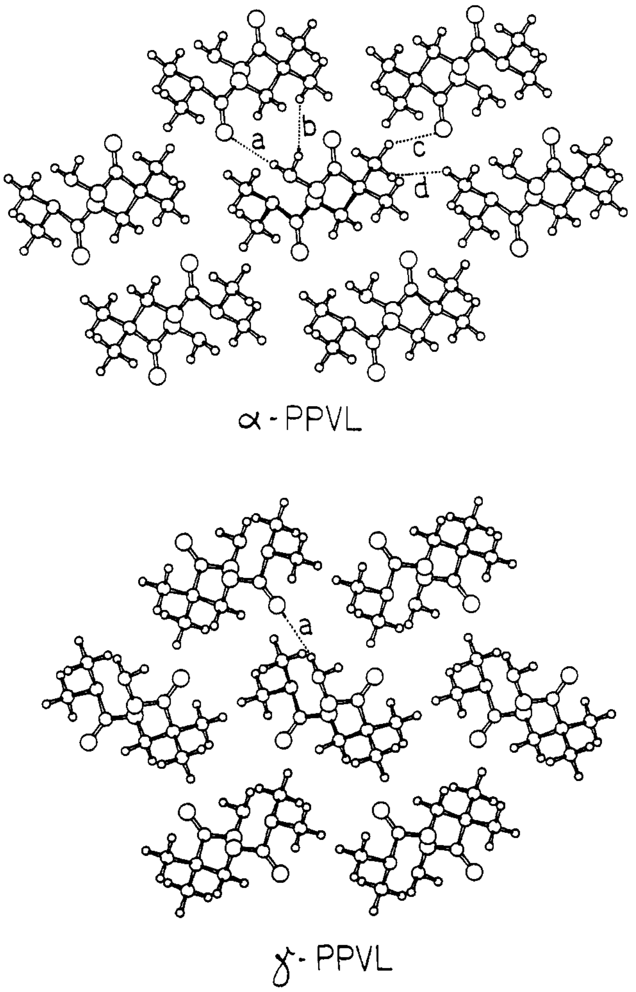

Figure 4. Packing in the α and γ crystals viewed along the chain axes. The shortest intermolecular contacts in the α form are labeled a, b, c, and d and correspond to H(1,1)···O(2), H(1,2)···H(5,2), H(4,3)···O(2), and H(4,2)···H(5,1), respectively. They undergo the most relevant adjustments upon transition from model A to model B (see text) changing from 2.38, 2.23, 2.60, and 2.30 Å respectively to 2.56, 2.37, 2.68, and 2.47 Å. The interaction labeled with a is also present in the γ form.

Such a factorization of the total energy must be considered with caution, since the various terms of the potential are interconnected and the force field as a whole was empirically fitted to observed data; nevertheless it gives an insight into the forces that control the conformational change. It is worthwhile mentioning that the difference between the *total* energies computed for the two crystal forms is very small (the α form being more stable by only 0.07 kcal/mol), in qualitative agreement with the corresponding melting temperatures (235 °C for α-PPVL and 219 °C for γ-PPVL),[12] with the reasonable assumption of identical $\Delta S_{\text{melting}}$ for the two crystalline phases.

4. Conclusion

The present conformational analysis completely confirms previous structural results obtained by X-ray (α-PPVL) and electron diffraction (γ-PPVL) analyses. The conformational differences displayed by the polymer chain in the α and γ crystals are reproduced and can be explained in terms of different packing interactions. From this point of view Coulombic interactions appear unexpectedly to be by far less important than nonbonded (van der Waals) interactions; this is also the reason for not having investigated any further the role of the effective dielectric constant. We want also to stress that the close resemblance of computed models with models best-fitted to experimental data is obtained without any ad hoc parameter adjustment in the force field adopted. In our view the success of the present approach in tackling the rather severe task of discriminating between the two conformational states (α and γ) of PPVL relies on two factors, both essential: (i) the avoidance of unnecessary restrictions and artifacts, by means of simultaneous optimization of intra- and intermolecular interactions in Cartesian coordinates; (ii) the use of Allinger's force field, of which only the electrostatic part has not been fully tested in the present study due to the specific features of the PPVL system.

The results of the present work are very promising in view of the possible application of our computational procedure for generation of reliable starting models, in dealing with unknown crystal structures, to be further refined by experimental diffraction data.

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References and Notes

(1) Ferro, D. R.; Brückner, S. *Macromolecules*, in press.
(2) Corradini, P.; Petraccone, V.; Pirozzi, B. *Eur. Polym. J.* **1986**, *19*, 235.
(3) Tripathy, S. K.; Hopfinger, A. J.; Taylor, P. L. *J. Phys. Chem.* **1981**, *85*, 1371.
(4) Sorensen, R. A.; Liau, W. B.; Boyd, R. H. *Macromolecules* **1988**, *21*, 194.
(5) Sorensen, R. A.; Liau, W. B.; Kesner, L.; Boyd, R. H. *Macromolecules* **1988**, *21*, 200.
(6) Brückner, S.; Meille, S. V.; Porzio, W. *Polymer* **1988**, *29*, 1586.
(7) Meille, S. V.; Brückner, S.; Lando, J. B. *Polymer* **1989**, *30*, 786.
(8) Cornibert, J.; Hien, N. V.; Brisse, F.; Marchessault, R. H. *Can. J. Chem.* **1974**, *52*, 3742.
(9) Perego, G.; Melis, A.; Cesari, M. *Makromol. Chem.* **1972**, *157*, 269.
(10) Ragazzi, M.; Ferro, D. R. A version of REFINE/HP for HP/9000 computers is available on request.
(11) Allinger, N. L.; Yuh, Y. H. *Q.C.P.E.* **1980**, *12*, No. 395.
(12) Prud'homme, R. E.; Marchessault, R. H. *Makromol. Chem.* **1974**, *175*, 2705.

Registry No. PPVL (homopolymer), 24969-13-9; PPVL (SRU), 24937-51-7.

Studies on Spin-Labeled Poly(*n*-butyl isocyanate)

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ABSTRACT: The stiff-chain polymer poly(*n*-butyl isocyanate) was labeled with the nitroxide 3-carbamoyl-PROXYL covalently positioned at the main-chain terminus. ESR spectra were measured as function of solvent composition and temperature using carbon tetrachloride, a good solvent, and benzene, a poor solvent. In the dry solid the nitroxide exhibits little motion up to 25 °C but rapidly gains motion and by 60 °C is motionally narrowed. Addition of small amounts of either solvent at any temperature gives rise to bimodal nitroxide relaxation times, one characteristic of the dry polymer at that temperature and the other characterizing a fast motion of 0.02–0.2-ns relaxation time. These results are correlated with side-chain motion as observed by ^{1}H NMR and known mechanical, thermal, and morphological properties of the polymer. The effect of diluent or temperature on side-chain motion has a corresponding effect on the motion of the nitroxide positioned at the end of the main chain.

Introduction

Nitroxide spin labeling of synthetic polymers has been shown to be a useful tool in the study of the motion of polymers under different conditions.[1] Most of the work on labeled rigid rodlike polymers has been done with poly(amino acids),[2–6] where the labels were attached either to the side chain or to the end terminus of the main chain. Information concerning the motion of the rod can be limited by the internal rotation about the bonds between the nitroxide and the main chain; therefore, in the case of the side-chain-labeled polymer, the quantitative interpretation of the EPR spectra describes the nitroxide movement and only limited conclusions can be obtained with respect to the polymer. End-labeled rods have lead to a more specific understanding of the rotational motion about the long axis of the rod.[6] Properties of polyisocyanates such as viscosity,[7,8] dynamics,[9–11] and phase behavior[12,13] have been determined. We have spin-labeled molecules of poly(*n*-butyl isocyanate) (PBIC) with a nitroxide label and present here the study of the polymer as a function of temperature and concentration in different solvents.

Experimental Section

Preparation of Spin-Labeled Polymer. The polymer was prepared by a procedure similar to Shashoua et al.[14] using *n*-butyl isocyanate (Eastman) as monomer in DMF (Merck). Both