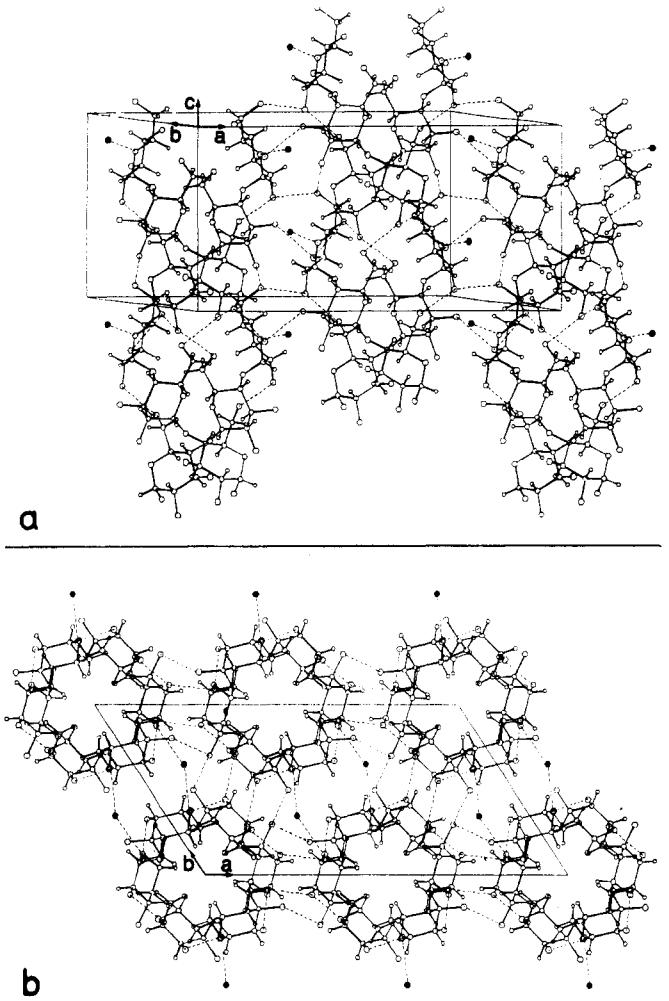


Figure 3. Two projection views of the double helices of A-amylose and of the four water molecules (as black spots) in one unit cell. (a) Meridional projection of the face (a,c) with the center chain translated by $c/2$ and $a/2$ from the corner chains. (b) Equatorial projection on the face (a,b). The polysaccharide structure, without water, refined with the LALS program[13] yields good R factors (0.26 and 0.29 for fiber and powder data, respectively) and no serious short contact was found between the chains. Further contact energy and X-ray refinement gave the localization of the four water molecules. The final R factor in three dimensions is 0.25 for fiber diffraction intensities and 0.27 for powder diffraction intensities. The final structure is characterized by numerous hydrogen bonds (represented as dashed lines) between the chains and the water molecules and between the molecules of different chains also. The drawing was created with the PITMOS program.[17]

In the last step of this study, the model was checked against both packing constraints and experimental data. The refinement of the three $\alpha(1\rightarrow4)$ linkage conformations and of the rotation of the double helices was performed with the help of the LALS program[13] (linked-atom least-squares reciprocal space refinement system) which combines X-ray and contact refinements. Calculations were performed in three independent runs (1) with contact energy values, (2) with diffraction intensity data from the fiber, and (3) with data from the powder. These three refinements converged to the same structure with good reliability factors (R factors) and no serious short contacts between the chains. Comparison between calculated and measured density suggested the presence of four water molecules per unit cell. Further refinement indicated that these molecules are located between the amylosic chains, where there is sufficient space to accommodate them (see Figure 3).

All crystalline samples of amylose studied here, i.e., synthetic crystals, polycrystalline powders, and artificial fibers, exhibit the same scattering features and therefore the same crystal and molecular organization as the crystalline components of native starch. The formation of double-helical structures involving short amylose chains appears to be a ubiquitous phenomenon governed either by biosynthesis (in the starch granule) or by simple thermodynamic rules (in solution). The single-strand conformation can be predicted from the conformational energy map of the $\alpha(1\rightarrow4)$ linkage.[11] The formation of such double helices in solution has been postulated to explain two majors properties of starch: gelatinization and retrogradation.[14]

The size of short branches of amylopectin (12–20 glucose residues for wheat starch) is ideal for the formation of double helices; these chains are densely packed in crystallites arranged radially in the granule. Therefore, the three-dimensional structure of amylose A, or more precisely of the linear branches of amylopectin in A-type starch, is consistent with the "cluster" model of amylopectin[5] as well as with the overall architecture of the starch granule.[1]

Registry No. Starch, 9005-25-8; amylose, 9005-82-7.

References and Notes

(1) Lineback, D. R. *J. Jpn. Soc. Starch Sci.* **1986**, *33*, 80–88.
(2) Robin, J. P.; Mercier, C.; Charbonnière, R.; Guilbot, A. *Cereal Chem.* **1974**, *51*, 389–406.
(3) Wu, H. C. H.; Sarko, A. *Carbohydr. Res.* **1978**, *61*, 27–40.
(4) Duprat, F.; Gallant, D.; Guilbot, A.; Mercier, C.; Robin, J. P. In *Les Polymères Végétaux*; Monties, B., Ed.; Gauthier-Villars: Paris, 1980; pp 176–229.
(5) Manners, D. J.; Matheson, N. K. *Carbohydr. Res.* **1981**, *90*, 99–110.
(6) Buléon, A.; Duprat, F.; Booy, F. P.; Chanzy, H. *Carbohydr. Polym.* **1984**, *4*, 161–173.
(7) Tran, V.; Buléon, A. *J. Appl. Crystallogr.*, in press.
(8) Natta, G.; Corradini, P. *J. Polym. Sci.* **1959**, *39*, 29–46.
(9) Pérez, S.; Vergelati, C. *Biopolymer* **1985**, *24*, 1809–1822.
(10) French, A. D.; Murphy, V. G. *Cereal Food World* **1977**, *22*, 61–70.
(11) Pérez, S.; Vergelati, C. *Polym. Bull.* **1987**, *17*, 141–148.
(12) Pangborn, W.; Langs, D.; Pérez, S. *Int. J. Biol. Macromol.* **1985**, *7*, 363–369.
(13) Smith, P. J. C.; Arnott, S. *Acta Crystallogr., Sect. A* **1978**, *A34*, 3–11.
(14) Matsukura, U.; Matsunaga, A.; Kainuma, K. J. *J. Jpn. Soc. Starch Sci.* **1983**, *30*, 106–113.
(15) Robin, J. P. Ph.D. Thesis, Paris, 1976.
(16) Chanzy, H.; Guizard, C.; Vuong, R. J. *Microscopy* **1977**, *111*, 143–150.
(17) Pérez, S.; Scaringe, R. P. *J. Appl. Crystallogr.* **1986**, *19*, 65–66.

† Affiliated to the Université Scientifique, Technologique et Médicale de Grenoble, France.

Anne Imberty,* Henri Chanzy, and Serge Pérez
Centre de Recherches sur les Macromolécules Végétales,† C.N.R.S., B.P. 68 F-38402 Saint-Martin d'Hères, France

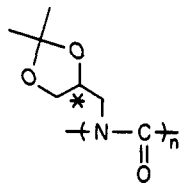
Alain Buléon and Vinh Tran
Laboratoire de Physico-Chimie des Macromolécules I.N.R.A., F-44072 Nantes, France

Received March 5, 1987; Revised Manuscript Received June 8, 1987

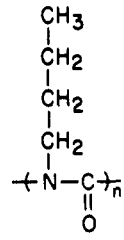
Broken Worm and Wormlike Models for Polyisocyanates

In a recent publication[1] we discussed the effect of pendant group structure on the axial dimension of polyisocyanates. It was established that poly[(*S*)-(2,2-di-

0024-9297/87/2220-2636$01.50/0



1[S], 1[RS]



2

methyl-1,3-dioxolan-4-yl)methyl isocyanate](1(*S*)) has a more extended chain than the stereoirregular isomer 1(*RS*) or poly(*n*-butyl isocyanate) (**2**). These polymers assume wormlike conformations in solution.

The question of the contribution of a wormlike structure and specific breaks[2] to the overall chain dimension of polyisocyanates has been of interest for some time. Although Tonelli,[3] on the basis of theoretical potential energy calculations, has suggested helix reversals as an important contribution to chain flexibility, earlier workers[4] had reasoned that small random torsional fluctuations within one helical sense could explain the chain characteristics of poly(*n*-alkyl isocyanates). More recently, conformational flexibility calculations by one of us[5] have shown that torsional motions attended by small energy changes are capable of predicting the known dimensions of poly(*n*-alkyl isocyanates) without the necessity of helix reversals.

It has been suggested[6] and recently reemphasized[7] that it is extremely difficult to distinguish experimentally between wormlike polymers with equal persistence lengths which do or do not have specific breaks. This conclusion, based on experiments sensitive to the overall chain dimension, may not be applicable to experiments directed to the microscopic structure. In the work below we discuss the differences in spectroscopic properties of two polyisocyanates of comparable persistence lengths and show that each can be best described by one or the other of these models.

The polyisocyanates 1(*RS*) and **2** have been shown to have persistence lengths of 250 Å[1] and between 200 and 350 Å,[8] respectively, in chlorinated hydrocarbons. These macromolecules have also been studied by high-field ^{13}C NMR in chloroform at 50–55 °C. The polymers share two common nuclei, the backbone carbonyl and the methylene adjacent to nitrogen. At 125.7 MHz the line widths for the resonances of these nuclei are observed to be 18.3 and 31.3 Hz, respectively, in **2** and ~200 and ~500 Hz in 1(*RS*).[1] Such data are well understood to be related to local segmental motion with **2** therefore exhibiting by this criterion far more local motion than 1(*RS*).[9,10]

This fundamental difference between these polymers is reinforced by their UV spectra. The backbone chromophore[11] in **2** appears at λ_{max} = 254 nm with an extinction coefficient, ϵ, of 3.7×10^3 L mol^{-1} cm^{-1} while the equivalent band in 1(*RS*)[1] has λ_{max} = 242 nm with $\epsilon = 2.5 \times 10^3$. Bathochromic shifts and increases in ϵ have long been known to be associated with increased conjugation.[12] This conjugation is at a maximum in the planar conformation. However, the steric repulsion between neighboring side chain groups is also at a maximum in this conformation. The helical conformation in polyisocyanates results in a loss of conjugation but a minimizing of steric interactions.[3,11,13] Therefore, the observed increased conjugation in **2** can be logically ascribed to a more loosely wound helix. Such a helix would allow more motion, an identical conclusion with that drawn on the basis of the NMR line widths.

One can proceed to assign the predominant mode of flexibility to 1(*RS*) and **2** by noting that 1(*S*), the optically active stereoisomer of 1(*RS*), prepared from the enantiomerically pure *S* monomer shows by optical rotation and circular dichroism[1,14] a preference for one of the helical senses. Therefore, the stereoirregular polymer derived from racemic monomer, i.e., 1(*RS*), could contain a helix reversal at each location in the chain where the pendant group changes from an *R* to an *S* unit or vice versa. Since the NMR and UV characteristics of 1(*S*) and 1(*RS*) are almost the same,[1] suggesting, for the reasons discussed above, similar microscopic motional properties, the increased persistence length found for 1(*S*), 600 Å as compared to 250 Å for 1(*RS*), must be caused by the increased number of specific breaks, i.e., helix reversals, in 1(*RS*) over 1(*S*).

Since the NMR and UV characteristics discussed above show **2** to be far more flexible in local motions than 1(*RS*), the similar persistence lengths of 1(*RS*) and **2** must arise from the specific breaks in 1(*RS*) compensating for the increased torsional flexibility in **2**. This is also consistent with the compared steric sizes of the 2,2-dimethyldioxolane and *n*-butyl pendant groups. These results do not imply the absence of helix reversals in **2**.[3]

Thus, there is a fundamental difference between the polyisocyanates 1(*RS*) and **2** even though their chain dimensions as evaluated by the persistence length are similar. Microscopic probes, i.e., NMR and UV, allow us to distinguish between wormlike chains with similar extension but different frequency of specific breaks, a distinction which is difficult to make on the basis of light scattering or hydrodynamic data.

This comparison of wormlike polymers illustrates that spectroscopic methods can be useful in characterizing the relative contributions of minor conformational fluctuations and specific breaks to the extension of relatively stiff chains.

Acknowledgment. Work done at the Polytechnic University was reported by the National Science Foundation (DMR-8416323). We are grateful for this support and as well to Professor Herbert Morawetz for his encouraging comments. Part of this work was performed under the auspices of the U.S. Department of Energy by the Lawrence Livermore National Laboratories under Contract W-7405-ENG-48.

Registry No. (±)-1, 96743-47-4; (*S*)-1, 107797-37-5; **2**, 25067-04-3.

References and Notes

(1) Green, M. M.; Gross, R. A.; Crosby, C. C., III; Schilling, F. C. *Macromolecules* **1987**, *20*, 992.
(2) Bailey, R. T.; North, A. M.; Pethrick, R. A. *Molecular Motion in High Polymers*; Oxford: New York, **1981**; p 68. Yamakawa, H. *Modern Theory of Polymer Solutions*; Harper and Row: New York, 1971; p 324.
(3) Tonelli, A. E. *Macromolecules* **1974**, *7*, 628.
(4) Bur, A. J.; Roberts, D. E. *J. Chem. Phys.* **1969**, *51*, 406.
(5) Cook, R. *Macromolecules* **1987**, *20*, 1961.
(6) This work was specifically directed to sedimentation equilibria. Hearst, J. E.; Stockmayer, W. H. *J. Chem. Phys.* **1962**, *37*, 1425.
(7) Mansfield, M. L. *Macromolecules* **1986**, *19*, 854.
(8) Conio, G.; Bianchi, E.; Ciferri, A.; Krigbaum, W. R. *Macromolecules* **1984**, *17*, 856. Kuwata, M.; Murakami, H.; Norisuye, T.; Fujita, H. *Ibid.* **1984**, *17*, 2731. Rubingh, D. H.; Yu, H. *Ibid.* **1976**, *9*, 681. Murakami, H.; Norisuye, T.; Fujita, H. *Ibid.* **1980**, *13*, 345.
(9) Bovey, F. A. *Chain Structure and Conformation of Macromolecules*; Academic: New York, 1982. Levy, G. C.; Lichter, R. L.; Nelson, G. L. *Carbon-13 Nuclear Magnetic Resonance Spectroscopy*, 2nd ed.; Wiley-Interscience: New York, 1980. See: Bailey, R. T.; North, A. M.; Pethrick, R. A., ref 2, Chapter 9, p 243 ff.

(10) Evaluation of the symmetry characteristics of the lines shows that the majority of the line broadening arises from the stiff characteristics of the chains with some contribution from chemical shift dispersion, the latter reasonably expected from the (R)(S) copolymerization. See ref 1.
(11) Milstien, J. B.; Charney, E. *Macromolecules* **1969**, *2*, 678. Troxell, T. C.; Scheraga, H. *Ibid.* **1971**, *4*, 528.
(12) Jaffe, H. H., Orchin, M. *Theory and Applications of Ultraviolet Spectroscopy*; Wiley: New York, 1962; p 273 ff in particular and other examples throughout the text.
(13) Bur, A. J.; Fetters, L. J. *Chem. Rev.* **1976**, *76*, 727.
(14) Analogous results were found for two other asymmetric pendant polyisocyanates. See: Goodman, M.; Chen, S. *Macromolecules* **1970**, *3*, 398; **1971**, *4*, 625.

Mark M. Green* and Richard A. Gross
Department of Chemistry and Polymer Research Institute Polytechnic University, Brooklyn, New York 11201

Robert Cook
Lawrence Livermore Laboratory Livermore, California 94550

Frederic C. Schilling
AT&T Bell Laboratories Murray Hill, New Jersey 07974

Received April 13, 1987; Revised Manuscript Received July 29, 1987

Direct Evidence for Cocrystallization in Binary Mixtures of Ferroelectric Copolymers

Recently, increasing attention has been devoted to polymer mixtures from both the theoretical and the experimental points of view. Most polymer blends are incompatible because the contribution from the mixing entropy is very small as a result of the large degree of freedom of polymer chains. Miscibility between two *amorphous* polymers has been demonstrated by many researchers and studied intensely, especially in relation to phase-separation dynamics. Miscibility between *crystalline* and *amorphous* polymers has also been examined, and a number of compatible blends are known (e.g., poly(vinylidene fluoride)/poly(methyl methacrylate)[2] or poly(ε-caprolactone)/polystyrene[3]). These two categories of polymer blend have been reviewed extensively.[4,5]

However, only a few studies have been reported on the miscibility between two *crystalline* polymers, and cocrystallization within a single lattice is extremely rare and in many cases questionable. Commonly, the necessary conditions for cocrystallization are thought to be (a) miscibility in the melt and (b) similarity in crystalline structures of the individual constituents. Polymers that might satisfy such conditions have been sought among those having similar chemical compositions. For example, poly(vinyl fluoride) (PVF) and poly(vinylidene fluoride) (PVF_2) had been considered for over 20 years to cocrystallize within a single lattice.[6,7] However, recent evidence[8] indicates that these two polymers are in fact immiscible in both the amorphous and the crystalline states. Ethylene–propylene–diene rubbers of very low crystallinity were reported[9] to undergo only partial cocrystallization with branched (but not with linear) polyethylene. Poly(butylene terephthalate) showed a single melting endotherm with one composition of its segmented block copolymer with tetramethylene oxide, although cocrystallization could not be demonstrated by X-ray diffraction because of the similarity in the diffraction patterns of the two components of the blend.[10] Very recently,[11] blends of poly(ether ketone) and poly(ether ether ketone) have been reported to be miscible in the crystalline phase on the basis of their melting behavior, although the glass-transition temperatures of the two constituents are too close to allow definitive confirmation of compatibility.

Other crystalline polymers that might at first be thought of as forming compatible crystalline blends actually do not. For example, poly(vinylidene chloride) copolymers are compatible with a variety of polyesters only in the amorphous phase; the crystalline morphology shows separate populations of the two constituents.[12] The same is true for blends of isotactic polystyrene with poly(2,6-dimethylphenylene oxide).[13] In blends of PVF_2 with stereoregular poly(methyl methacrylates) (PMMA), only the former crystallizes.[14] And isotactic and syndiotactic PMMA do not form a true blend, but rather a bimolecular complex consisting of a double-stranded helix with the syndiotactic chain wrapped around the isotactic one.[15]

On the other hand, if a blend of two crystalline polymers is studied in which *both* crystalline phases undergo solid-state transformations (such as Curie transitions) and if the temperatures of such transitions depend strongly on the crystalline structure, there exists the possibility for a clear and unequivocal determination of cocrystallization within the same lattice.

In most materials that are miscible in the melt the system undergoes microscopic phase separation below the melting point; as a result, two types of crystal, having lattice dimensions characteristic of the individual components, coexist independently. In some cases (e.g., Cu and Ni) the two components can form *solid solutions*, in which they remain miscible even below the melting point, thus cocrystallizing within a *single* lattice. Such coexistence within the same lattice is very rare, especially in polymeric crystals because they are stabilized by van der Waals forces, which are of very short range. Therefore, small lattice mismatches result in high energetic states. In polymeric blends, isomorphic crystallization should thus be favored when the crystal structures of the two components are very similar but especially when they already contain some disorder which should render them more tolerant of slight additional mismatch.

In this sense, ferroelectric copolymers of vinylidene fluoride and trifluoroethylene (VF_2/F_3E) differing in composition represent some of the best candidates for unambiguous determination of cocrystallization, for the following reasons: (1) their crystalline structures are very similar; (2) they already contain a degree of intramolecular disorder stemming from the random sequencing of VF_2 and F_3E units; and (3) they undergo Curie transitions whose temperatures are *very sensitive* to composition.[16,17] Because of the solid-state nature of these transitions, it is possible to probe molecular mixing *unequivocally*: In the case of phase separation upon crystallization, *two* Curie transitions should appear, whereas true cocrystallization should yield only *one* transition.

The samples investigated here were three random copolymers of vinylidene fluoride/trifluoroethylene (VF_2/F_3E), blended in equal weights by casting from solution in methyl ethyl ketone, followed by vacuum drying. Three VF_2/F_3E mixtures were examined: 52/48 mol % + 65/35 mol % (termed M1); 65/35 mol % + 73/27 mol % (M2); and 52/48 mol % + 73/27 mol % (M3). Thermal studies were performed by differential scanning calorimetry at a rate of 10 °C/min. Structural studies were made by wide-angle X-ray diffractometry by using Ni-filtered Cu Kα radiation at a scanning speed of 0.25° 2θ/min. The miscibility of these copolymers in the melt was examined by direct observation under a phase-contrast microscope. No phase separation was found in any of our mixtures at

0024-9297/87/2220-2638$01.50/0