Notes

Helical Conformation of Poly(D,L-α-methyl-α-*n*-propyl-β-propiolactone)

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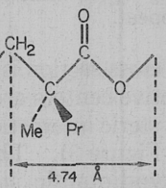
In the synthesis of biopolymers based on a backbone of poly(β-propiolactone) two cases[1,2] have been reported where polymerization of a D,L racemic mixture of monomers led to an optically inactive but crystalline polymer. Since the crystal structure of the resulting polymer was the same as that of the optically pure natural polymer it was concluded that optical neutrality was due to intercrystal compensation, i.e., crystallites of predominantly D or predominantly L segments were formed. Thus crystalline segments of optically active substituted polyesters based on the poly(β-propiolactone) backbone appear to be able to accomodate some monomers of the opposite configuration without reversing the helix chirality. It is expected however that this will lead to lowering of the degree of crystallinity and melting point.

This note presents some additional information on this subject in relation to poly(D,L-α-methyl-α-*n*-propyl-β-propiolactone) which will be refered to as PMPPL:



PMPPL is shown above in its extended chain form where the residue length is 4.74 Å. This repeat distance is found in one of the polymorphs[3] of poly(β-propiolactone) and also in poly(pivalolactone).[4]

Previous work,[5] using wide-angle X-ray diffraction analysis on PMPPL, has shown that this polymer could exist in two crystalline polymorphs. After stretching, a planar conformation having a fiber repeat distance of 4.74 Å is observed as the predominant crystalline entity; this corresponds to one extended monomer unit. The unoriented polymer film (solvent cast or hot molded) contains only a nonplanar helical crystalline form[5] with a fiber repeat of 5.9 Å corresponding to two monomer units related by a 2_1 axis. Any attempt to orient the latter crystallites brought forth the oriented pattern of the planar form which relaxed on annealing to the disoriented helical conformation.

In the course of studying the orientation behavior of the grafted elastomer poly(isobutylene)-*g*-poly(D,L-α-methyl-α-*n*-propyl-β-propiolactone) abbreviated PIB-*g*-PMPPL, a method was found that yields a good X-ray diffraction pattern of the nonplanar form of PMPPL. When solvent-case films of PIB-*g*-PMPPL are stretched to about 600% and studied using wide-angle X-ray diffraction, five well-defined reflexions are observed (Figures 1 and 2). These reflexions correspond to the nonplanar form of PMPPL.[5] The fiber direction of the PMPPL phase was determined in a straightforward manner by tilting the sample in the X-ray beam.[6] Along the fiber axis, a meridional reflexion having a *d* spacing of 6.1 Å is observed. Tilting the sample in the X-ray beam failed to reveal any other meridional reflexions. Due to the presence of reflexions on the first and third layer lines (Figure 2) the observed meridional reflexion can only be indexed as (002) and must be associated with the occurrence of a 2_1 helix along the macromolecular chain. Thus the fiber diagram indicates a repeat along the chain axis of ~12 Å corresponding to the length of four units related two by two by a 2_1 helix. The observed reflexions have been indexed according to an orthorhombic cell containing four chains with $a = 17.9$, $b = 13.5$, and $c = 12.0$ Å (fiber axis). The relevant indexing of the observed reflexions is summarized in Figure 2, while the comparison of calculated and observed spacings for the unit cell corresponding to the helical conformation of PMPPL is summarized in Table I.

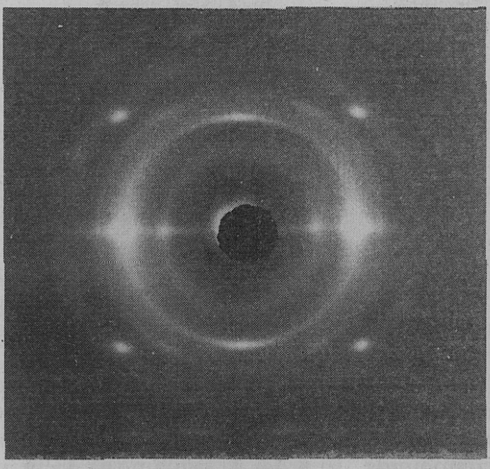


Figure 1. Wide-angle X-ray diffraction pattern of a sample of PIB-g-PMPPL strained about 600% at room temperature.

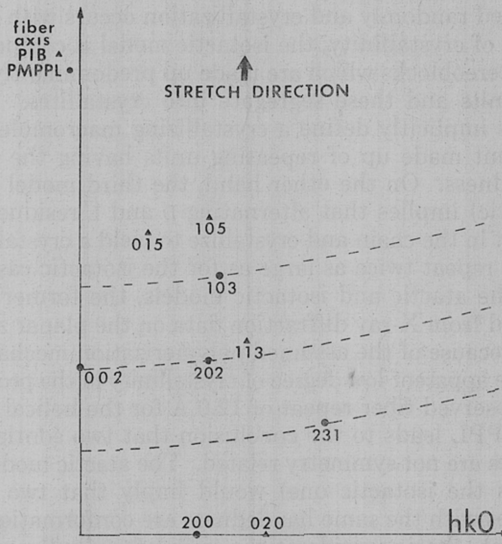


Figure 2. Schematic diagram of the superposed fiber diffraction patterns of PMPPL of PIB shown in Figure 1.

Using the flotation method, the measured density of the homopolymer (in which the helical conformation of the

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Table I
Observed and Calculated *d* Spacings, in Å, for the Proposed Unit Cell of PMPPL

hkl	*d*(obsd)	*d*(calcd)
200	9.2	9.0
002	6.1	6.0
202	5.0	5.0
103	4.0	3.9
231	3.9	3.8

chain is mainly present in the relaxed state) has been reported[3] to be 1.07 g cm^{-3}. This is in agreement with the calculated value of 1.17 g cm^{-3} obtained with an orthorhombic cell accomodating four chains made up of four units each.

These results are to be compared with those reported previously[1,2] concerning the presence of crystalline domains of a single stereoisomer in the optically neutral product from the polymerization of a D,L monomer mixture. Since PMPPL is prepared from an equimolar monomer mixture and the polymer is optically inactive, the resulting polymer must be considered as a configurational copolyester of D and L compounds. In order to explain the occurrence of crystallinity three basic models can be considered. The atactic model requires that the D and L monomers are arranged randomly and crystallization occurs with a low degree of crystallinity; the isotactic model is compatible with stereoblocks which are made up predominantly of D or L units and these segregate into crystallites. Both models implicitly define a crystallizing macromolecular fragment made up of repeating units having the same handedness. On the other hand, the third model (syndiotactic) implies that alternating D and L residues are present in the chain and crystallize to yield a crystal with a fiber repeat twice as large as for the isotactic case.

Of the atactic and isotactic models, the former[5] was selected from X-ray diffraction data on the planar zigzag form because of the assumed polymerization mechanism and the apparent low degree of crystallinity in the product. The observed fiber repeat of 12.0 Å for the helical form of PMPPL leads to the conclusion that two contiguous residues are not symmetry related. The atactic model (as well as the isotactic one) would imply that two such residues with the same handedness are conformationally different. Steric considerations arising from bulky propyl groups could explain such a difference.

On the other hand, the occurrence of a helical conformation with a fiber repeat of 12.0 Å would favor the syndiotactic structure with a regular pattern of D–L residues in the chain. Such a model is in apparent contradiction with the atactic structure proposed for the planar zigzag form.[5] However, it is probable that the planar crystalline form could be produced independently of polymer tacticity and that the polymer could presumably pack in a lattice in this conformation in such a way that the nature of the pendant groups is not of great significance. Until sufficient data are at hand it is difficult to propose a final model among the atactic, isotactic, and syndiotactic structures. The objective here is to impress that a syndiotactic model consisting of alternating D,L monomers cannot be discarded and that there is evidence for occurrence of alternating stereoisomers. The reason could be a simple enthalpic factor which counters the atactic or isotactic placements during the polymerization.

Because of the nature of the general 2_1 helix with ~6 Å fiber repeat,[7] for substituted polyesters based on the poly(β-propiolactone) backbone, a D,L alternation (syndiotactic) is sterically as favorable as the isotactic placements. Since the backbone atoms are helically arranged and the helix cross-section is ellipsoidal, contiguous opposite optically active centers are sufficiently far away from each other that steric interactions of the substituents are nonexistent (cf. Figure 3). The four-chain unit cell proposed for the syndiotactic structure suggests the presence of antiparallel chains as well as helices of opposite handedness.

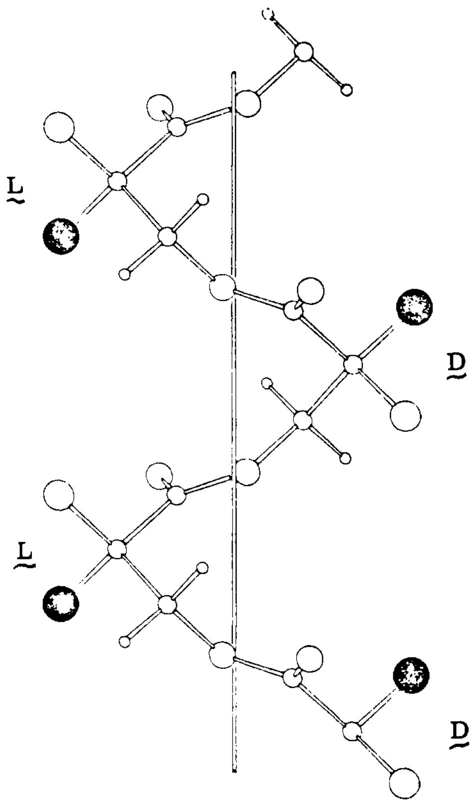

Figure 3. General twofold helix conformation with 3 Å advance per monomer for α,α-disubstituted β-propiolactones.[7] The methyl (○) and propyl (●) substituents are shown as a D,L pair making up a chemical repeating repeat while two such pairs constitute the crystallographic repeat.

The original argument which favored the proposal of an isotactic structure over a D,L sequence (syndiotactic) for crystalline polypropylene was based on X-ray data.[8] The fiber repeat and unit cell data required three monomers per helix turn. The present argument is similar but opposite in its conclusion since in this case the unit cell requires an even number of monomers per turn of the helix rather than an odd number. Using the conformationally most stable[7] helix (~3 Å/monomer) this leads to a structure with two helix turns per unit cell and a D,L monomer alternation is the logical interpretation. This is a case of intramolecular compensation of the monomer chiralities in each chain, i.e., a meso structure. It is possible that this tactic form is limited to a relatively small part of the total polymer and the remainder corresponds to some other tacticity not detected in this study.

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Absorption of Various Substituted Phenols by Nylon 6

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We have previously reported the absorption by Nylon 6 of a range of hydroxylic solvents.[1] In the course of this work, it was noted that phenol was absorbed to an unusual degree and a separate investigation of phenol absorption seemed warranted. We have therefore examined the equilibrium absorption by Nylon 6 of a range of para-substituted phenols from solutions in carbon tetrachloride and in benzene at 30 °C and have analyzed the results in terms of the Hammett linear free energy relationship.

In order to stabilize the initial crystalline structure of the polymer (1-mil extruded Capran 77C film, a Nylon 6 supplied to us by Allied Chemical Corp.), the film was first heated in an oven to 160 °C for 2 h and then cooled to room temperature in a vacuum desiccator, before carrying out swelling measurements. The solvents used were Baker Analyzed grade and were dried over anhydrous magnesium sulfate before use. The phenols were all reagent grade or better, except 4-*tert*-butylphenol which was purified by recrystallizing from cyclohexane to mp 99–100 °C. All liquid phenols displayed a single gas chromatographic peak using a polar column. Solutions of the various phenols were prepared, each 0.1 M phenol in solvent. Solutions in both carbon tetrachloride and benzene were used, except in cases where insolubility prevented this. Film samples weighing initially about 0.25 g were immersed in the solutions at a constant temperature of 30 °C until equilibrium was reached. The samples were periodically removed from the solution, dried with filter paper, and weighed on an analytical balance, to measure the gain in weight. As in the previous study, at least three duplicate samples were averaged and observations were made over a sufficient period of time to ensure that equilibrium had been attained. Control samples immersed in the pure solvents under identical conditions but without dissolved phenol showed weight changes varying from −1.0 to +2.0% which may be considered negligible within experimental error.

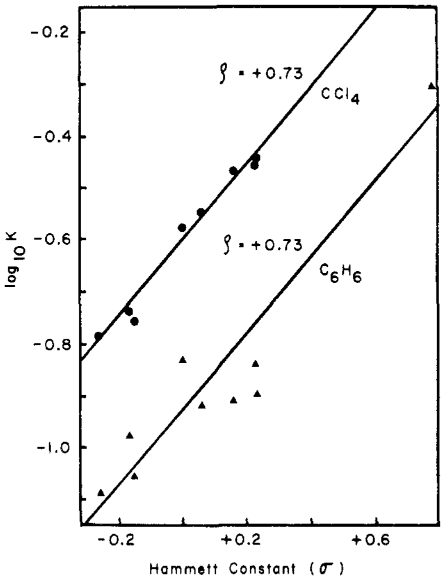

Figure 1. Hammett linear free energy plot for absorption of para-substituted phenols by Nylon 6 from carbon tetrachloride and benzene solutions.

The swelling data obtained for the phenol solutions are shown in Tables I and II. Table I gives data for solutions in CCl_4 while Table II gives data for solutions in benzene. The equilibrium swelling values are given both as weight percent increase based on weight of the dry film and as moles of phenol per mole of monomer units or amide groups. It will be noted that degrees of swelling both greater and less than that of unsubstituted phenol are obtained for the substituted phenols, and two of these (4-*tert*-butyl and 4-phenoxy) gave zero absorption. An effective equilibrium constant for the absorption, K, is defined, as in our previous publication, as:

$$K = [\text{concn absorbed (mol/mol)}] = e^{-\Delta G°/RT} = e^{-\Delta H°/RT}e^{\Delta S°/R} \quad (1)$$

The values of both K and $\log K$ are given in Tables I and II.

Values of the Hammett constant σ are also listed in the two tables for the various substituents (using literature values of McDaniel and Brown[2]). The corresponding Hammett equation can be written in the simplified form:

$$\log K = \log K_0 + \rho\sigma \quad (2)$$

where σ represents the ability of the substituent to donate electrons to the reactive site, ρ is a constant characteristic of the particular process involved, and K_0 is the equilibrium constant for the unsubstituted aromatic ring. This simplified form neglects steric considerations, but should be appropriate because the benzene ring should give an approximately constant steric effect except in the case of the very largest substituents. A plot of $\log K$ vs. σ is given in Figure 1 for both sets of solutions. This plot has several interesting features. First, a linear relation is obtained for both sets of solutions, as predicted by eq 2. The two sets of solutions do not fall on the same straight line, but the slopes of the two straight lines seem to be the same (corresponding to ρ = +0.73, as drawn). This suggests that the same process is taking place in the polymer, independent of the solvent used to make the phenol solution.

The positive slope (value of ρ) indicates an increase of absorption, or value of K, with electron-withdrawing groups (which have positive values of σ) and a corresponding decrease of absorption with electron-releasing groups (with negative σ values). Nitrophenol (with a highly positive σ value) could represent a unique case (electron withdrawal assisted by a conjugated position in the ring); however, this compound nevertheless seems to fall on the same straight line as the other phenols.

The value of ρ = +0.73 can be compared with the standard reference value of ρ = +1.00 for the substituent effect on the ionization of benzoic acids. The substituent effect observed here is therefore less strong than in the

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