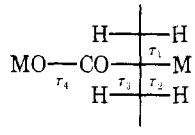
Communications to the Editor

Double Strand Helix of Isotactic Poly(methyl methacrylate)

In a previous paper[1] the possibility of the (5/2) (proposed by Stroupe and Hughes[2]) and the (5/1) helix (proposed by Liquori et al.[3-5]) models of isotactic poly(methyl methacrylate) was examined by x-ray and infrared studies, especially by the interpretation of the cylindrical Patterson function, and a (5/1) helix was reported to be the most reasonable at that stage (1970). Thereafter, trial-and-error efforts were made assuming a crystal structure model which should consist of four (5/1) helices in an orthogonal unit cell of a = 20.98 Å, b = 12.06 Å, and c(fiber axis) = 10.40 Å, but no reasonable packing was found under this assumption. On the other hand, the calculation of the intramolecular interaction energy was made under the assumption of helical symmetry without fixing the fiber period, and the result suggested that helices with larger radii such as a (12/1) helix should be more stable than the (5/1) helix.[6] By taking into account these facts, the authors reexamined the molecular models with larger radii, and found that the x-ray data can be explained reasonably by a double strand helix, the first known case for synthetic polymers.

As shown in Figure 1, the double strand helix consists of two chains with the same helix sense and direction (denoted by solid and broken lines) shifted 10.40 Å along the helix axis with respect to each other, each chain having ten chemical units and one turn in the period of 20.80 Å; a (10/1) helix. Consequently the double strand helix has a translational identity period of 10.40 Å (the observed fiber identity period). This helix has a twofold rotation axis coinciding with the helix axis.

In the double helix model, the molecular parameters were assumed as follows: (1) the bond lengths and bond angles are the same as for the previous (5/1) helix model except for



$\angle$C-CH_2-C = 124°,[7-10] (2) the α-CH_3 group points outward, and (3) $\tau_1 = -179°$, $\tau_2 = -148°$, τ_3[MCC(O)O] = −24°, and τ_4[CC(O)OM] = 174° (cf. Fischer projection), for a right-handed helix with the ester group pointing upward as shown in Figure 1.

In Figure 2 the square roots of the molecular structure factors (cylindrically averaged in intensity) calculated for the double helix (solid lines) and for the (5/1) helix (broken lines)[1] are compared with the square roots of the observed reflection intensities (vertical rods). Far better agreement is found for the double helix.

The result of energy calculations indicated that the double strand helix is more stable by 4.4 kcal/mol of monomer unit than two isolated (10/1) helices, suggesting appreciable stabilization owing to good fitting of the intertwined two chains, although there is no hydrogen bonding between them as in the case of DNA.[11]

If two double strand helices are contained in the aforementioned orthogonal unit cell, the density requirement is fulfilled: ρ(calcd) = 1.26 g/cm^3 and ρ(obsd) = 1.21 g/cm^3. Apparent systematic absences of the reflections $h + k$ = odd for $hk0$ suggest that two double helices pass through the center and corner of the unit cell. Furthermore good packing in the lattice was found using the relationship that the helix at the center of the unit cell is displaced from the helix at the corner by about $c/2$ along the c axis. However, the crystal structure seems to have a kind of statistical disorder with respect to the helix sense and direction of the helix. The crystal structure is shown in Figure 3, in which only right-handed upward helices are shown for simplicity. The lowest discrepancy factor R at present is 32% by taking the statistical disorder into account. Detailed refinement of the molecular and crystal structure is being currently carried out using the constrained least-squares method and the packing energy minimization method.[12]

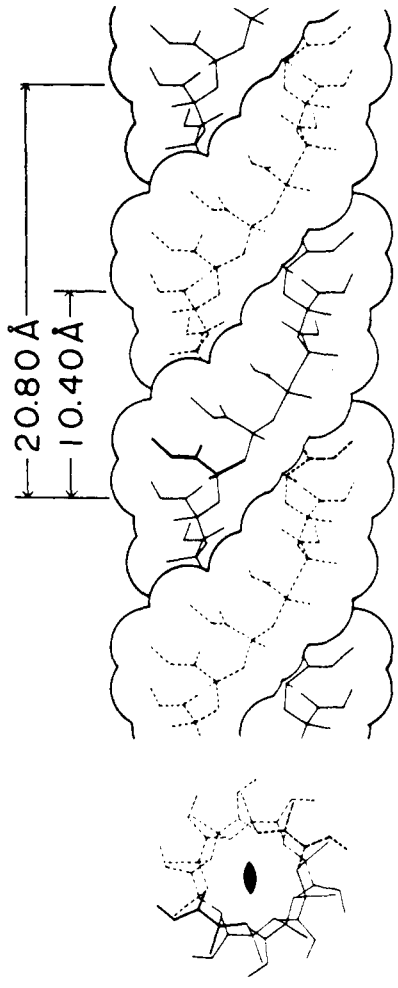


Figure 1. Double strand helix of isotactic poly(methyl methacrylate).

The present double helix structure is considered to be closely related to the formation of the stereocomplex of isotactic and syndiotactic poly(methyl methacrylate).[4]

Note Added in Proof. The aforementioned intermolecular potential energy difference 4.4 kcal/mol of monomer unit is mainly attributed to the carbonyl oxygen atom (1.40 kcal), the ester methyl group (0.66 kcal), one of the methylene hydrogen atoms (0.63 kcal), and the carbonyl carbon atom (0.61 kcal). The potential functions and parameters are the same as in ref 6.

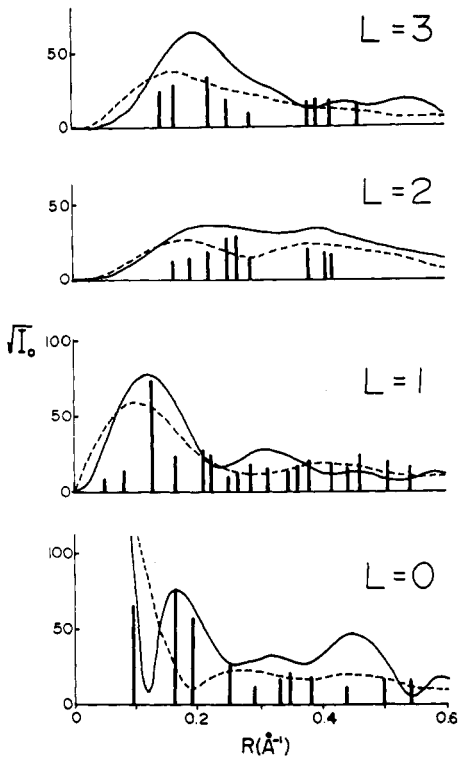


Figure 2. Comparison between the square roots of the observed reflection intensities (vertical rods) and the calculated molecular structure factors for the double helix (solid lines) and for the (5/1) helix (broken lines).

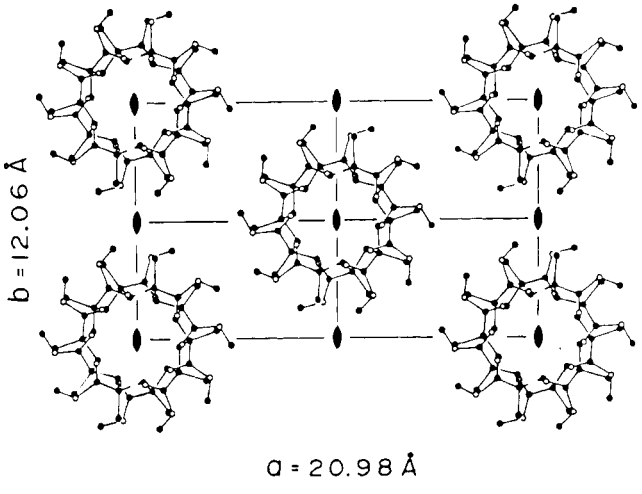


Figure 3. Crystal structure of isotactic poly(methyl methacrylate).

References and Notes

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(6) H. Tadokoro, K. Tai, M. Yokoyama, and M. Kobayashi, *J. Polym. Sci., Polym. Phys. Ed.*, **11**, 825 (1973).
(7) Examples of large values for the C–CH_2–C bond angle are as follows: 122.6° for 2,2,4,4-tetramethyladipic acid;[8] 124 or 128° for polyisobutylene.[9,10]
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Hiroshi Kusanagi,* Hiroyuki Tadokoro, and Yozo Chatani
Department of Polymer Science, Faculty of Science, Osaka University, Toyonaka, Osaka, Japan
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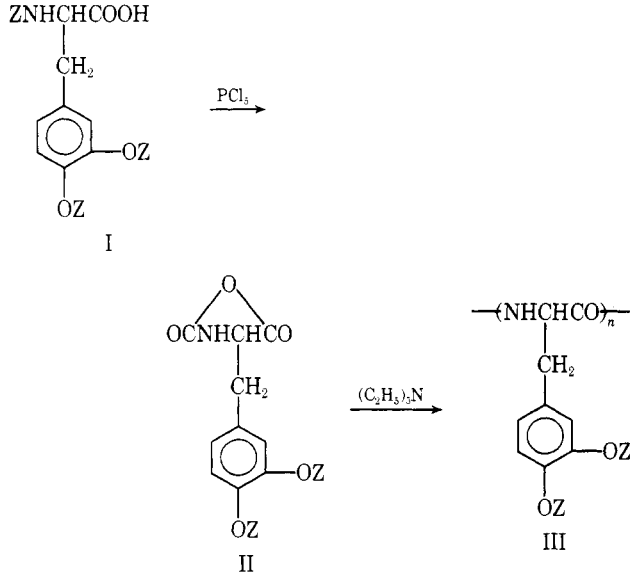
Sense of Helix of Poly-*O,O'*-dicarbobenzoxy-L-DOPA in Solution

We wish to report the helical sense of poly-*O,O'*-dicarbobenzoxy-L-DOPA in helicogenic solvents.[1] The polypeptide was synthesized according to the following scheme:



where Z denotes carbobenzoxy.

Carbobenzoxylation of L-DOPA gave *N,O,O'*-tricarbobenzoxy-L-DOPA (I). Pure crystalline *O,O'*-dicarbobenzoxy-L-DOPA-NCA (II) was prepared from *N,O,O'*-tricarbobenzoxy-L-DOPA and phosphorus pentachloride at 0 to ca. −5 °C in anhydrous ether:[2] yield, 88%; mp 71 °C; ir bands, 1852 and 1788 cm^{-1} (cyclic anhydride). Anal. Calcd for $C_{26}H_{21}O_9N$: C, 63.54; H, 4.31; N, 2.85. Found: C, 63.62; H, 4.59; N, 2.50. The acetone solution of the NCA was passed through a dry charcoal–silver oxide column. After removal of the solvent, poly-*O,O'*-dicarbobenzoxy-L-DOPA (III) was prepared by polymerizing the NCA in 10% dioxane solution using triethylamine as an initiator (A/I = 100): yield, 48%; ir bands (see below). Anal. Calcd for $(C_{25}H_{21}O_7N)_n$: C, 67.11; H, 4.73; N, 3.13. Found: C, 67.50; H, 4.84; N, 3.01. The polypeptide had an intrinsic viscosity $[\eta]$ of 0.26 dl/g in DCA at 25 °C. The molecular weight was estimated to be 28 000 (DP = 60) from an empirical equation for poly-*O*-carbobenzoxy-L-tyrosine in DCA[3] and from the *N*-terminal titration with perchloric acid in chloroform using crystal violet as an indicator.[4]

The CD curves of poly-*O,O'*-dicarbobenzoxy-L-DOPA are shown in Figure 1A. The CD values are $[\theta]_{225}$ = −13 600 in chloroform, $[\theta]_{225}$ = −18 900 in methylene dichloride, $[\theta]_{228}$ = 24 800 in THF, and $[\theta]_{228}$ = 24 000 in dioxane. A model compound, *N,O,O'*-tricarbobenzoxy-L-DOPA-glycine ethyl ester, exhibits the same positive CD band in dioxane or chloroform (see Figure 1A). Thus, the CD behavior of the polypeptide is anomalous.

The solution ir spectra of poly-*O,O'*-dicarbobenzoxy-L-