ternuclear distances, the predicted line width becomes ≈ 4 Oe. We tentatively conclude, therefore, that at 20 °C we were able to observe only the ^{31}P nuclei in amorphous regions of the sample, in which a partially narrowed line would be expected. The ^{31}P line was very easily saturated, so a poor signal-to-noise ratio precluded observation of the broader, crystalline line predicted by the calculation.

The ^{31}P line narrows to 1.1 Oe when the temperature is raised to 120 °C, indicating the presence of rapid motion. One of the simplest models for such motion is rotation about the backbone axis. If γ_i is the angle between the axis of rotation and the line which links the ^{31}P nucleus under consideration and the nucleus i, the second moment in the presence of rotation, M_{Rot}, may be written[16]

$$M_{\mathrm{Rot}} = \sum_i M_{\mathrm{RL},i}[\tfrac{1}{2}(3\cos^2\gamma_i - 1)]^2 \qquad (1)$$

where $M_{\mathrm{RL},i}$ is the contribution of nucleus i to the "rigid lattice" second moment. Equation 1 presumes the axes of rotation have random orientations relative to the external magnetic field, as in a polycrystalline sample.

We assume the side groups make a negligible contribution to M_{Rot} because of their high degree of motion. The ^{31}P–^{31}P and ^{31}P–^{14}N distances used in the $M_{\mathrm{RL},i}$, and the cos γ_i, are determined from the data for $[F_2PN]_n$.[15] We let the sum in eq 1 run over the two nitrogen and two phosphorous nuclei which are nearest the ^{31}P nucleus under consideration, and which are on the same backbone. The result is $M_{\mathrm{Rot}} = 0.50$ Oe^2, which corresponds to a Gaussian line width of 1.4 Oe.

This estimate is in reasonable agreement with the experimentally determined 1.1 Oe, suggesting strongly that segments of the polymer backbone go into rapid motion at temperatures above $T(1)$. By "rapid" we mean that the correlation frequency of the motion exceeds 5 kHz. Such rotational motion in the mesomorphic state will appear as loss of static order in the chain axis direction but will not affect order in the plane perpendicular to the axis. Thus the NMR results provide a convenient interpretation for the x-ray results for the mesomorphic state. A dynamically disordered pseudohexagonal structure might be expected from the essentially cylindrical volume which molecules with rotating segments would occupy, similar to that found[4] for the meta and para isomers of poly[bis(chlorophenoxy)phosphazene].

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References and Notes

(1) R. E. Singler, N. S. Schneider, and G. L. Hagnauer, *Polym. Eng. Sci.*, **15**, 321 (1975).

(2) N. S. Schneider, C. R. Desper, and R. E. Singler, *J. Appl. Polym. Sci.*, **20**, 3087 (1976).

(3) G. Allen, C. J. Lewis, and S. M. Todd, *Polymer*, **11**, 44 (1970).

(4) C. R. Desper and N. S. Schneider, *Macromolecules*, **9**, 424 (1976).

(5) C. R. Desper, N. S. Schneider, and E. Higginbotham, *J. Polym. Sci., Polym. Lett. Ed.*, in press.

(6) D. Hyndman and G. F. Origlio, *J. Appl. Phys.*, **31**, 1849 (1960).

(7) D. W. McCall, D. C. Douglass, and D. R. Falcone, *J. Phys. Chem.*, **71**, 998 (1967).

(8) S. Iwayanagi and I. Miura, *Rep. Prog. Polym. Phys. Jpn.*, **8**, 303 (1965).

(9) H. R. Allcock, R. L. Kugel, and K. J. Valan, *Inorg. Chem.*, **5**, 1709 (1966).

(10) E. G. Stroh, Jr., Ph.D. Thesis, Pennsylvania State University, 1972.

(11) A. J. Leffler, M. N. Alexander, P. L. Sagalyn, and N. Walker, *J. Chem. Phys.*, **63**, 3971 (1975).

(12) M. Goldman, "Spin Temperature and Nuclear Magnetic Resonance in Solids", Oxford University Press, London, 1970, Chapter 5.

(13) M. N. Alexander, P. L. Sagalyn, and A. J. Leffler, *J. Magn. Reson.* **13**, 291 (1974).

(14) C. L. Beatty, J. M. Pochan, M. F. Froix, and D. D. Hinman, *Macromolecules*, **8**, 547 (1975).

(15) H. R. Allcock, R. L. Kugel, and E. G. Stroh, *Inorg. Chem.*, **11**, 1120 (1972).

(16) C. P. Slichter, "Principles of Magnetic Resonance", Harper and Row, New York, N.Y., 1963, pp 57–58.

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A Large Single Crystal of Poly(γ-benzyl L-glutamate)

The study of synthetic high polymers by x-ray methods encounters special difficulties, which arise mainly because these substances cannot be obtained in the form of well-developed single crystals large enough to be investigated by usual x-ray diffraction techniques.[1,2]

In spite of extensive efforts for preparation of large single crystals of synthetic polymers for polymer crystallography, by a number of investigators, such crystals have been reported only for poly(ethylene oxide) complexes with urea[3] and mercuric chloride.[4]

The crystal and molecular structures of synthetic polypeptides have been studied by x-ray,[5,6] electron diffraction,[7] and infrared (IR) absorption spectroscopy.[8] Poly(γ-benzyl L-glutamate) (PBLG) $\text{-}[\text{CHR–NH–CO}]_n\text{-}$ (in which R = $CH_2CH_2COOCH_2C_6H_5$) was the first synthetic polypeptide to be obtained in a highly oriented form, giving a striking x-ray diffraction pattern and polarized infrared spectrum. These results indicated that the PBLG fiber took the α-helical conformation with an identity period of 27 Å, and that the packing of the molecules was shown to be nearly, but not exactly, hexagonal with a repeat length of 15 Å.[9,10]

In most of the polypeptides examined, however, only the conformation of the backbone has been determined, the precise arrangement of the atoms in the side chain being unknown.

In this communication, we should like to report some preliminary results on a large single crystal of PBLG.

The sample, PBLG, used in this study was prepared by polymerizing highly purified γ-benzyl L-glutamate N-carboxyanhydride in dichloroethane with triethylamine as initiator.[11] The intrinsic viscosity of the resultant polymer was $[\eta] = 1.336$ dL/g in dichloroacetic acid at 25 °C, corresponding to a weight-average molecular weight $\overline{M}_{\mathrm{w}} = \text{ca. } 2.41 \times 10^5$ (degree of polymerization $\overline{\mathrm{DP}}_{\mathrm{n}} = \text{ca. } 1100$), estimated from eq 1 by Doty et al.,[12]

$$[\eta] = 2.78 \times 10^{-5}\overline{M}_{\mathrm{w}}^{0.87} \qquad (1)$$

The large single crystals of PBLG were successfully prepared from a chloroform solution of PBLG by concentrating very gradually at room temperature. These crystals were grown from the viscous residue of this polymer.

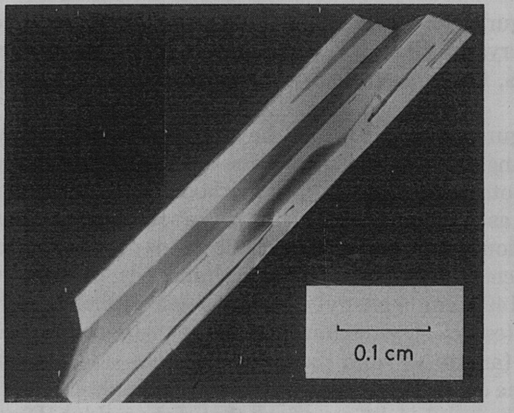

Figure 1. Polarized optical micrograph of the single crystal of poly(γ-benzyl L-glutamate).

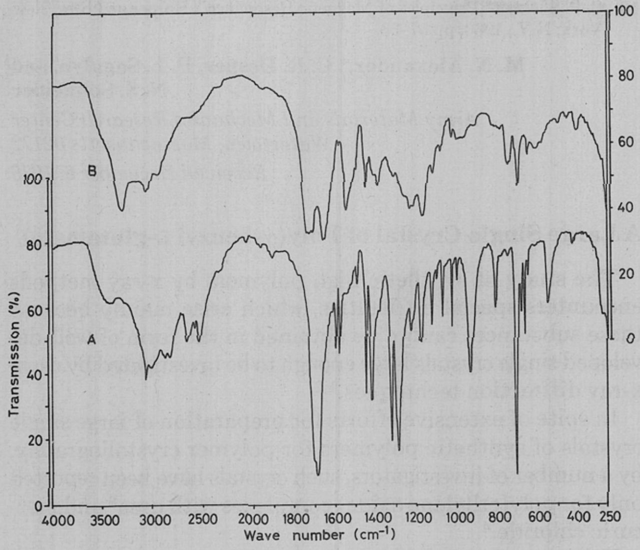

Figure 2. Infrared absorption spectra of (A) the single crystal, and (B) the residue of poly(γ-benzyl L-glutamate) prepared from a chloroform solution of this polymer, using the potassium bromide disk method.

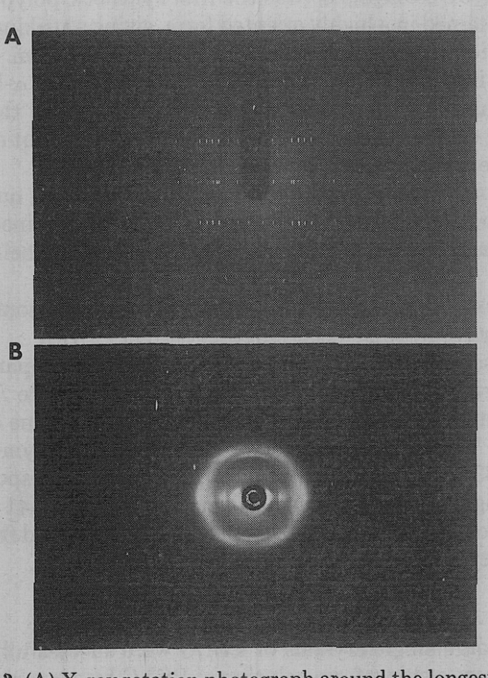

Figure 3. (A) X-ray rotation photograph around the longest axis of the single crystal, and (B) the fiber pattern of the oriented poly(γ-benzyl L-glutamate) monofilament. Cu Kα radiation (Ni filtered), cylindrical camera.

Figure 1 shows the polarized optical microphotograph of this crystal. The crystals had the form of slim rods or thin plates, the largest of which was ca. 2 cm × 0.3 cm × 0.05 cm.

Figures 2A and 2B show the infrared absorption spectra of the single crystal and the residue of PBLG respectively using the potassium bromide disk method. The latter is quite the same as that of α-helical PBLG in the solid state or chloroform solution, giving the characteristic bands of the α-helix;[13] i.e., 1736 cm^{-1}(ester C=O), 1653 cm^{-1}(amide I), 1550 cm^{-1}(amide II), 1495 cm^{-1}(phenyl A_1), 1450 cm^{-1}(phenyl B_1), 1167 cm^{-1}(ester C–O stretching), ca. 700 cm^{-1} (phenyl B_2), and 614 cm^{-1}(amide V) from the high-frequency side, respectively. On the other hand, the spectrum of the single crystal (Figure 2A) is somewhat different from that of the residue (Figure 2B). The absorption bands of the single crystal in the region below 1400 cm^{-1}, which are mostly characteristic of the individual molecules, coincide essentially in position with those of the residue in Figure 2B except for the amide V band (703 cm^{-1}) and the ester C–O stretching band (1180 cm^{-1}).

On the contrary, the amide I, II, and V bands, which depend upon the molecular conformation, split markedly from their original positions, indicating that the molecular conformation in the single crystal is different from that of the residue in Figure 2B. In addition, it seems that the ester bands of the single crystal shift to 1703 and 1180 cm^{-1}.

These results give evidence that the single crystal surely consists of PBLG molecules and that it takes an ordered structure but not an α-helical conformation.

Figures 3A and 3B show the x-ray rotation photograph around the longest axis of this single crystal and the fiber pattern of oriented PBLG, respectively. The latter was prepared from a solution in chloroform and subsequently heated in vacuum for 10 h at 170 °C and shows the characteristic features of α-helix. The diffraction spots of the single crystal, on the other hand, were indexed with monoclinic lattice of the cell dimensions a = 5.52 Å, b = 5.11 Å, c = 22.25 Å, and β = 97.8°, which was confirmed from both the Weissenberg photograph of the equatorial plane of the reciprocal lattice and the rotation photograph around the shortest axis. The x-ray results show, in agreement with the IR results, that the single crystal of PBLG has a crystal lattice different from that made up of α-helices.

It may be interesting that although the molecules are α-helical in the viscous residue from which the crystals have been grown, they have another conformation when they pack in the single crystal grown from the same solvent. The reason why the differences of molecular conformation and crystal structure occur will be solved by clarifying the mechanism of single crystal formation and by analyzing the detailed structure of the single crystal.

Detailed x-ray analysis of this crystal and attempts to obtain analogous large single crystals of other synthetic polypeptides are now in progress.

References and Notes

(1) B. K. Vainstein, "Diffraction of X-Rays by Chain Molecules", Elsevier, Amsterdam, The Netherlands, 1966.

(2) M. Kakudo and N. Kasai, "X-Ray Diffraction by Polymers", Kodansha, Tokyo, Japan, 1972.

(3) H. Tadokoro, T. Yoshihara, Y. Chatani, and S. Murahashi, *Polym Lett.*, **2**, 363 (1964).

(4) R. Iwamoto, Y. Saito, H. Ishihara, and H. Tadokoro, *J. Polym. Sci., Part A-2*, **6**, 1509 (1968).

(5) L. Pauling, R. B. Corey, and H. R. Branson, *Proc. Natl. Acad. Sci. U.S.A.*, **37**, 205 (1951); L. Pauling and R. B. Corey, *ibid.*, **37**, 235, 729 (1951).

(6) C. H. Bamford, A. Elliott, and W. E. Hanby, "Synthetic Polypeptides", Academic Press, New York, N.Y., 1956.

(7) B. K. Vainstein and L. I. Taterinova, *Sov. Phys.-Dokl. (Engl. Transl.)*, **6**, 663 (1962).

(8) T. Miyazawa, "Poly-α-amino acids", G. D. Fasman, Ed., Marcel Dekker, New York, N.Y., 1967.

(9) C. H. Bamford, W. E. Hanby, and F. Happey, *Proc. R. Soc. London, Ser. A*, **205**, 30 (1951).

(10) D. F. Persons and V. Martus, *J. Mol. Biol.*, **10**, 530 (1964).

(11) E. R. Blout and R. H. Karlson, *J. Am. Chem. Soc.*, **78**, 941 (1956).

(12) P. Doty, J. H. Bradbury, and A. M. Hdtzer, *J. Am. Chem. Soc.*, **78**, 947 (1956).

(13) M. Tsuboi, *J. Polym. Sci.*, **59**, 139 (1962).

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