Table III
Elemental Analyses (%) of Polyamide 7

Polymer 7		C	H	N
a	Calcd	68.31	3.94	4.97
	Found	67.88	4.16	5.01
b	Calcd	68.31	3.94	4.97
	Found	66.81	3.98	4.99
c	Calcd	71.46	4.10	4.38
	Found	69.30	3.99	4.65
d	Calcd	69.71	4.00	4.27
	Found	69.87	4.53	4.14
e	Calcd	71.76	4.32	4.29
	Found	70.08	4.57	3.80
f	Calcd	64.94	3.72	3.98
	Found	63.42	3.86	4.17
g	Calcd	71.14	3.87	4.48
	Found	69.05	3.84	4.42

4,4′-[Sulfonylbis(*p*-phenyleneoxy)]dibenzoic Acid (4). To 30 mL of dry methanol was added under nitrogen 2.15 g (0.05 mol + 10% excess) of potassium metal and with stirring 8.4 g (0.05 mol + 10% excess) of methyl *p*-hydroxybenzoate.[8] The methanol was removed under reduced pressure with heating at 30–40 °C. To the resulting potassium salt was added 7.15 g (0.025 mol) of 4,4′-dichlorodiphenyl sulfone, 1 g of potassium fluoride, and 20 mL of dry NMP.

The mixture was heated at 175–185 °C under nitrogen with stirring for 6 h. After cooling, 50 mL of 10% aqueous sodium hydroxide was added and the mixture was then heated at 100 °C with stirring, 2–3 h. After cooling, the volume of the mixture was diluted to 1 L with water and 10% sulfuric acid was slowly added, with stirring, to pH 2. The white precipitate of crude acid was filtered, washed with distilled water 3–4 times, and dried. Recrystallization from glacial acetic acid afforded 4.3 g (36%) of pure acid 4, mp 306–308 °C.

Anal. Calcd for $C_{26}H_{18}SO_8$: C, 63.66; H, 3.69. Found: C, 63.31; H, 3.74.

4,4′-[Sulfonylbis(*p*-phenyleneoxy)]dibenzoyl Chloride (5). A mixture of 40 mL of thionyl chloride and 4.9 g (0.01 mol) of diacid (4) was heated to the reflux temperature for 2 h, after which time 3–4 drops of DMF was added. The heating was continued another 2 h and then was left overnight at room temperature. The thionyl chloride was removed under reduced pressure at 40–50 °C. The dry crude product (5) was recrystallized from dry benzene to yield 4.7 g (89%) of monomer, mp 183–185 °C.

Polymerization Reactions. Polymer 7e from 4,4′-[Sulfonylbis(*p*-phenyleneoxy)]dibenzoyl Chloride (5) and 4,4′-Diaminodiphenyl Ether (6d). The polymerization flask was charged under nitrogen with 0.666 g (0.0033 mol) of **6d** and 20 mL of dry NMP. After cooling the solution to 0 °C, 1.5 mL of propylene oxide was added. The mixture was then cooled to −25 to −30 °C and with vigorous stirring 1.757 g (0.0033 mol) of dichloride (5) was added; 5 mL of dry NMP was used to wash the dichloride addition funnel. The solution was stirred at this temperature for 1 h and then for 4 h at room temperature. The solution obtained was slowly poured into a large volume of methanol (300 mL) with vigorous stirring. The white polymer was collected by filtration, washed well with methanol (3–4 times), and dried.

The polycondensation reactions of dichloride (5) with other aromatic diamines (6) were carried out in NMP/propylene oxide, under the same conditions. The elemental analyses are given in Table III.

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References and Notes

(1) Senior Fulbright-Hays Scholar, U.S.–Romania.
(2) G. L. Brode, G. T. Kwiatkovski, and A. W. Bedwin, *J. Polym. Sci., Polym. Chem. Ed.*, **12,** 575 (1974).
(3) I. J. Goldfarb and A. C. Meeks, AFML-TR-66-375; W. L. S. Laukhuf and I. J. Goldfarb, AFML-TR-73-253.
(4) Japanese Patent 72.26,475 (1973); *Chem. Abstr.*, **78,** 59,250v (1973).
(5) Japanese Patent 72.26,877 (1972); *Chem. Abstr.*, **78,** 170,023t (1973).
(6) Caution: Hexamethylphosphortriamide is an experimental carcinogen. J. A. Zapp, Jr., *Science*, **190,** 422 (1975).
(7) L. Carmagnola, *Chim. Ind. (Milan)*, **26,** 7 (1944).
(8) G. W. K. Cavill and J. M. Vincent, *J. Soc. Chem. Ind., London*, **66,** 175 (1947).

Temperature Dependence of Positron Lifetimes in Linear Polyethylene

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When positrons enter a condensed molecular medium, they rapidly lose almost all of their energy by collisions with molecules. After a further, somewhat longer, period annihilation may take place directly between the "free" positrons and electrons bound to molecules or through a bound state of positron–electron pair, called positronium (Ps). The characteristics of the annihilation process, such as energies, momenta, and time of emission, depend almost entirely on the initial state of the positron and molecule medium. Thus, observation of positron decay in a medium provides useful information concerning electronic, atomic, molecular, and crystal properties of the medium.

The measurement of positron annihilation lifetime has been used to study many properties of polymers.[2–15] The lifetime spectrum of positrons annihilating in a polymer normally consists of at least two lifetime components, a short lifetime component with a meanlife τ_1 of about 0.3–0.4 ns and a long-lifetime component with a meanlife τ_2 of about 1–3 ns. The τ_1 component has a complex origin, such as due to self-annihilation of *p*-Ps, direct annihilation of free positrons, and conversion and chemical qenching of *o*-Ps. The τ_2 component is attributed to the pick-off annihilation of *o*-Ps in amorphous regions, including defects in the crystalline lattice, of the polymer.

The pick-off annihilation rate of *o*-Ps in a molecular substance not only depends on the "free volume" of the samples but also on the interaction between *o*-Ps and the surrounding molecules.[10,11,22]

Therefore, a plot of the annihilation rate of the long-lifetime component ($\lambda_2 = 1/\tau_2$) against temperature should generally resemble that of density against temperature. Indeed, this kind of general trend has been found for several polymers including polyethylene.[10] However, only a few data appeared for polyethylene in the temperature range below 300 K. It has also been found that the positron annihilation rate λ_2, in polystyrene,[2] polyisobutylene,[3] and Nylon 6,[4] all show a marked change at or near the glass transition temperature T_g reported by other conventional methods.

The glass transition temperature of polyethylene is still a subject of widespread and growing controversy as indicated in a recent review by Boyer[16] and by the work of Davis and Eby.[17] This situation exists, as stated by Davis and Eby,[17] because the experimental techniques which can be used to identify glass transitions in wholly amorphous polymers yield less clear results in highly crystalline polymers. In parallel with our measurements on positronium, annihilation of free positrons is sensitive to the presence of defects in crystalline solids.[18]

In this note, we report briefly the changes of positron lifetimes in linear polyethylene in a temperature range from 80 to 300 K and show that this technique is useful for detecting transitions in amorphous regions dispersed relatively sparse

Table I
Some of the Properties of the Polyethylene Samples

Samples	Mol wt (M_n)	M_w/M_n	Density, g/cm^3	Deg of crystallinity
(I) PE Grex 60-002E	11 600	13.6[a]	0.950	0.68[c]
(II) PE Grex 60-002E (pretreated)	11 600	13.6[a]	0.964	0.77[c]
(III) Polywax 1000	1 000	1.17[b]	0.961[b]	0.97[d]
(IV) Polywax 2000	2 000	1.3[b]	0.960[b]	0.96[d]

[a] Data based on ref 17. [b] Data supplied by the manufacturer. [c] Calculated from an additive rule, using a density of 1.001 g/cm^3 for the crystalline phase and 0.855 g/cm^3 for the amorphous phase. [d] Measured by NMR[32] using the method of Crist and Peterlin.[33]

within crystalline polymer such as polyethylene. For general aspects of positron annihilation, the reader is referred to several review articles.[18-22]

Experimental Section

The linear polyethylene, Grex 60-002E, was manufactured by W. R. Grace and Co., and is available through the Allied Chemical Co. It has 1.4 methyl groups per 1000 carbon atoms.[17]

The highly linear, narrow molecular weight distribution polyethylenes, Polywax 1000 and Polywax 2000, were made by Bareco Division of Petrolite Corp. Some properties of these various polymers are listed in Table I.

One sample of Grex 60-002E was precipitated from xylene under nitrogen to remove the antioxidant, washed with ethanol, and dried under vacuum. It was then melted under vacuum to remove air, kept at a constant temperature of 400 K for 1 day, and slowly cooled to room temperature. Another sample of Grex 60-002E and the Polywax 1000 and 2000 samples were measured as they were supplied without pretreatment.

Positron annihilation lifetime spectra were measured using apparatus similar to the ones described previously.[4] Samples were sealed in glass tubes and evacuated at 90 C under vacuum ($<10^{-5}$ Torr) for about 24 h before measurements. Both procedures of ascending and descending temperature were tried, but no appreciable difference in the results could be found. Because of the long time duration, 24 h, taken for each measurement, the samples should be well relaxed with the temperature of the environment.

Results and Discussion

Positron lifetime spectra were separated into two lifetime components. Values of the annihilation rate λ_2 for the four polyethylene samples at various temperatures are shown in Figure 1. The error bars indicate ranges of uncertainties in the measurements.

The patterns of the λ_2 vs. temperature curves, as shown in Figure 1, are similar for all polyethylene samples under investigation. Except for a transition region between 160 and 230 K, all of them show a nearly parallel linear temperature dependence on both high- and low-temperature sides. If the discontinuity of λ_2 in the transition region is disregarded, the change of λ_2 with temperature resembles the change of density with temperature.[23]

All λ_2–T curves show a change in slope near 150–160 K which may be attributed to the γ relaxation[16] observed by thermal expansion[23] and other methods.[24-27]

The major difference between the λ_2–T curves and the thermal expansion curves[23] is that the slopes of λ_2–T curves outside the transition region are not affected by the crystallinity of the samples, while the thermal expansion coefficient obtained is dependent on the degree of cyrstallinity. This might be due to the fact that the slopes of λ_2–T curves indicate the structural changes in the disordered region where the positronium is expected to be found. In other words, the free volume change probed by o-Ps is a microscopic property near the place where o-Ps annihilates instead of a macroscopic volumetric property.

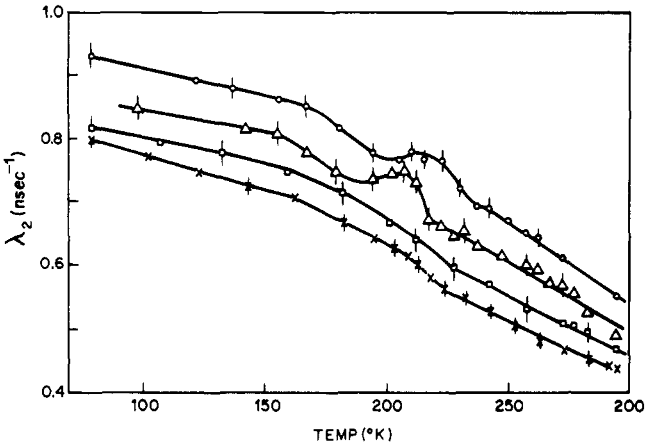

Figure 1. The annihilation rate λ_2 of the long-lifetime component as a function of temperature in polyethylene samples: (×) Grex 60-002E; (□) Grex 60-002E (pretreated); (△) Polywax 1000; (○) Polywax 2000.

The irregular change of λ_2 for the Polywax in the transition region 200–300 K might be brought about by molecular motions in amorphous regions. A plausible explanation is offered here. On the scale of the lifetime of o-Ps in polymers (a few nanoseconds), polymer molecule motions with a correlation frequency (ν_c) less than 10^7 Hz may be treated as stationary. On the other hand, if the molecular motions reach a correlation frequency comparable to λ_2, the annihilation pattern of o-Ps may be altered.[28]

Evidence of such molecular motions has in fact been reported by McCall and Douglass[29] in their NMR studies on linear polyethylene. They found that the liquid-like motions of the amorphous chains attain an average frequency of 3 × 10^7 Hz at about 240 K. This is near the temperature range at which the abnormal changes of λ_2 are observed. The onset of such molecular motion might affect positron annihilation in the following manner: First it causes the diffusion of electron density into the free volume (which o-Ps occupies); hence a slower reduction of the pick-off annihilation rate is to be expected. As temperature increased further, a point may be reached at which the Ps pressure may cause a sudden increase in the free volume if the surrounding chain segments become flexible enough. This would induce a drop in the pick-off rate.

Above this temperature, the pick-off rate would again follow the pattern of free volume change against temperature. The data of Figure 1 also contain some possible evidence for small irregularity of λ_2 in the Grex samples.

It is interesting to note that the irregularity of λ_2 for the Polywax samples investigated disappears approximately at 230 K. It might be a coincidence that this temperature, 230 K, is just the T_g reported by Davis and Eby,[17] Chang,[30] and Illers.[31] Obviously, further work is needed to clarify this point.

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References and Notes

(1) (a) National Taiwan University; (b) The New England Institute; (c) Bell Laboratories.
(2) (a) J. R. Stevens and A. Mao, *J. Appl. Phys.*, **41**, 4273 (1970); (b) B. G. Groseclose and G. D. Loper, *Phys. Rev.*, **137**, 939 (1965).
(3) J. R. Stevens and R. M. Rowe, *J. Appl. Phys.*, **44**, 4328 (1973).

(4) S. Y. Chuang, S. J. Tao, and J. Wilkenfeld, *J. Appl. Phys.*, **43**, 737 (1972).
(5) S. Y. Chuang and S. J. Tao, *J. Appl. Phys.*, **44**, 5171 (1973).
(6) A. Ogata and S. J. Tao, *J. Appl. Phys.*, 41, 4261 (1970).
(7) Y. Ito, S. Katsura, and Y. Tabata, *J. Polym. Si., Part A-2*, **9**, 1515 (1971).
(8) M. N. G. A. Khan, *J. Phys. D:*, **3**, 663 (1970).
(9) P. C. Jain, S. Bhatnagar, and A. Gupta, *J. Phys. C:*, **5**, 2156 (1972).
(10) W. Brandt and I. Spirn, *Phys. Rev.*, **142**, 231 (1966).
(11) W. Brandt, S. Berko, and W. W. Walker, *Phys. Rev.*, **120**, 1289 (1960).
(12) R. K. Wilson, P. O. Johnson, and R. Stump, *Phys. Rev.*, **129**, 2091 (1963).
(13) S. J. Tao and J. H. Green, *Proc. Phys. Soc., London*, **85**, 463 (1965).
(14) J. R. Stevens and M. J. Edwards, *J. Polym. Sci., Part C*, **30**, 297 (1970).
(15) A. E. Hamielec, M. Eldrup, O. Mogensen, and P. Jansen, *J. Macromol. Sci., Rev. Macromol. Chem.*, **9 (2)**, 305 (1973).
(16) R. F. Boyer, *Macromolecules*, **6**, 288 (1973).
(17) G. T. Davis and R. K. Eby, *J. Appl. Phys.*, **44**, 4274 (1973).
(18) R. N. West, *Adv. Phys.*, **22**, 263 (1973).
(19) A. T. Stewart and L. Roellig, Ed., "Positron Annihilation", Academic Press, New York, N.Y., 1967.
(20) V. I. Goldanskii, *At. Energy Rev.*, **6**, 1 (1968).
(21) J. A. Merrigan, J. H. Green, and S. J. Tao, "Physical Methods of Chemistry", A. Weissberger and B. W. Rossieter, Ed., Wiley, New York, N.Y., 1972, Vol. 1, Part IIID, pp 501–586.
(22) S. J. Tao, *Appl. Phys.*, **3**, 1 (1974).
(23) F. C. Stehling and L. Mandelkern, *Macromolecules*, **3**, 242 (1970).
(24) R. F. Boyer, *Plast. Polym.*, 41 (1973).
(25) M. L. Dannis, *J. Appl. Polym. Sci.*, **1**, 121 (1959).
(26) E. W. Fischer and F. Kloos, *Polym. Lett.*, **8**, 685 (1970).
(27) A. H. Willbourn, *Trans. Faraday Soc.*, **54**, 717 (1958).
(28) D. H. D. West, V. J. McBrierty, and C. F. G. Delaney, *Applied Phys.* **7**, 171 (1975).
(29) D. W. McCall and D. C. Douglass, *Polymer*, **4**, 433 (1963).
(30) S. S. Chang, *Polym. Prepr., Am. Chem. Soc., Div. Polym. Chem.*, **13**, 322 (1972).
(31) K. H. Illers, *Kolloid Z. Z. Polym.*, **250**, 426 (1970).
(32) T. Nishi, private communication.
(33) B. Crist and A. Peterlin, *J. Polym. Sci., Part A-2*, **7**, 1165 (1969).

Solid State Conformation of Poly-N^5-(3-hydroxypropyl)-L-glutamine by X Rays

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The helix–coil transition of poly-N^5-(3-hydroxypropyl)-L-glutamine, (PHPG), in water–methanol mixtures has been studied by nuclear magnetic resonance and circular dichroism spectroscopy but the actual conformation of the polymer was not clearly defined.[1] This work deals with the conformational properties of PHPG in the solid state obtained by an x-ray investigation.

Methods and Materials

Poly-N^5-(3-hydroxypropyl)-L-glutamine samples, with molecular weight about 200 000, were synthesized as described before.[1] PHPG films were prepared by stroking out a drying film until it was solid. Fibers were also drawn by means of a claw from a viscous solution of the sample. The solvents used were water and water–methanol mixtures. Both the films and the fibers were then heated to over 100 °C in vacuo for several hours to remove the solvent and to promote crystallinity. Their density was determined by flotation using benzene–carbon tetrachloride mixture allowing the sample to reach the equilibrium position. After 1 day the measured density was 1.23 g cm^{-3}. The films and the fibers were examined in a flat camera with the sample-to-photographic film distance, d, variable from 4 to 10 cm, with Ni filtered Cu Kα radiation from a fine and normal focus x-ray tube and a 0.6 mm pinhole. Tilted specimens and equiinclination techniques were also used.

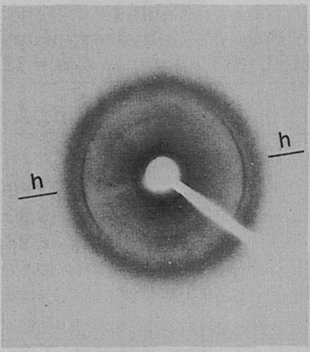

Figure 1. Normal beam x-ray diffraction pattern of PHPG oriented film; flat camera $d = 6$ cm, Cu Kα radiation; PHPG film and stroking direction horizontal (h line).

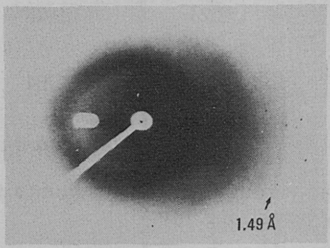

Figure 2. Equiinclination x-ray diffraction pattern of PHPG oriented film; flat camera $d = 4$ cm, Cu Kα radiation; PHPG film and stroking direction horizontal; x-ray beam at 31° to normal of the stroking direction (fiber axis) to record 1.49 Å reflection.

Results and Discussion

The diffraction pictures showed that, besides amorphous regions, some crystallinity is present in the examined samples, which also proved to be sufficiently oriented for analysis (Figure 1). Two main features of x-ray diffraction pattern are prominent: a sharp meridional reflection at 1.49 Å (Figure 2) and a layer line at 5.4 Å with a strong near meridional reflection. These data are typical of the Fourier transform of an α-helix, the helices being oriented parallel to the stroking direction.[2–5]

A detailed inspection of x-ray pictures, taken under different diffraction geometry, shows several reflections whose observed spacings, d_0, and estimated intensities, I_0, are reported in Table I. With the above data, we tried to define the unit cell dimensions. The ratio between the helical pitch (5.4 Å) and the axial translation per residue (1.49 Å) gives the number of units per turn of helix, namely 3.62 which closely corresponds to a 29/8 α-helix.[5] In addition, the relative intensities of the observed layer lines agree, well enough with the diffraction pattern of this type of helix[2] although the absence of recorded intensities for the 13th and, particularly, the 21st layer lines may appear instances of disagreement.[6] Nevertheless this behavior can be explained by remembering that the treatment of Cochran, Crick, and Vand[2] is valid in detail only when the conformational equivalence of the monomeric units (backbone and side-chain atoms) along the helix is strictly fulfilled. As the side-chain length is large the structure becomes less ordered and the previous theory may sometimes break down.

We constructed a molecular model according to the 29/8 α-helical conformation by means of a mathematical method, developed in our laboratory.[7] The results do not indicate any steric interference between the side chain and the polypeptide backbone. We may therefore assume for the true helix repeat