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X-Ray Study of an All-Para Wholly Aromatic Polyamide-Hydrazide*†

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ABSTRACT

Preliminary x-ray studies were carried out on the wholly para-oriented aromatic polyamide-hydrazide fiber based on p-aminobenzhydrazide and terephthaloyl chloride. Clearly evident from a quantitative study of the meridional scattering are many orders of a large repeat length (29.69 Å, or a multiple thereof) giving the diffraction pattern a "collagen-like" appearance. An orthorhombic unit cell with a = 8.5 Å, b = 4.9 Å, and c = 29.69 Å (chain axis repeat) fits the available x-ray data. With two molecules per unit cell, the calculated density is 1.51 g/cm^3.

Preliminary x-ray studies were carried out on the all-para, wholly aromatic polyamide-hydrazide which formed the basis of this Symposium. First impressions, gained from inspection of a flat-plate x-ray photograph of an oriented film, were of the

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"collagen-like" nature of the fiber pattern, i.e., many sharp peaks on the meridian and only rather diffuse scattering along the equator. A quantitative study of the meridional scattering was obtained by means of a point-counting technique [1] with the sample maintained in the symmetrical transmission arrangement. The results of this study are shown in Fig. 1. Clearly evident are many orders of a

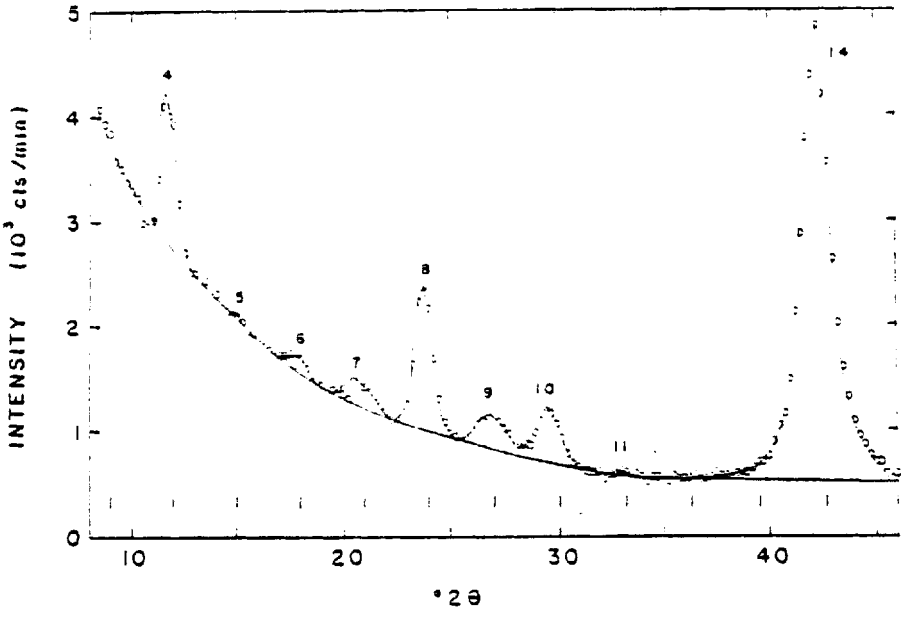

FIG. 1. X-ray diffractiometric scan along the meridian (fiber direction). The ℓ index of each peak is shown.

large repeat length (29.69 Å, or a multiple thereof). These orders appeared as short streaks across the meridian on flat plate x-ray photographs. Upon heat-treatment, six equatorial peaks were developed which fit a rectangular cross-section of a = 8.5 Å and b = 4.9 Å. The heat treatment to bring out the (hk0) peaks also caused vertical streaks to appear through the equatorial peaks. These appeared to be incipient "row-lines" but discreet (hkℓ) spots, with $\ell \neq 0$, could not be detected. The x-ray data obtained in this study are collected in Table 1.

TABLE 1. Observed X-ray Spacings and Intensities and Assignment of the Observed Peaks

d_{obs} (Å)	I	hkℓ[a]
7.44	s	004
5.82	w	005
4.97	w	006
4.21	w	007
3.72	s	008
3.31	m	009
2.97	m	00.10
	vw	00.11
2.11	vs	00.14
8.49	w	100
4.31	vs	200,110
3.23	s	210
2.46	w	310,020
1.9	vw	410
1.60	vw	130,420

[a]Based upon an orthorhombic cell with a = 8.5 Å, b = 4.9 Å, and c = 29.69 Å.

An orthorhombic unit cell with a = 8.5 Å, b = 4.9 Å, and c = 29.69 Å (chain axis repeat) fits the available x-ray data (Table 1). With two molecules per unit cell, the calculated crystal density is 1.51 g/cm^3. These values are in excellent agreement with those deduced from electron diffraction studies by Holland [2]. Absence of an (010) reflection and weakness of the (100) reflection relative to (200) indicates a unit cell which essentially is centered (in projection).

The magnitude of c (29.69 Å) agrees well with the length calculated for a completely extended chain (29.5-29.6 Å) from acceptable

bond-length, bond-angle values [3]. The magnitude of the b axis (4.9 Å) is reasonable for hydrogen-bonded polyamide chains [4]. From geometrical considerations the planar conformation with all possible positions trans- is a satisfactory model. For this conformation a monoclinic cell is predicted with $\alpha = 38°$—hence, pseudoorthogonal. If the p-phenylene rings are rotated out of the plane of the backbone (probably randomly), the pseudohexagonal nature mentioned by Holland [2] and the streaked-nature of the "row-lines" would also be accounted for.

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[3] For example, see L. Pauling, The Nature of the Chemical Bond, 3rd ed., Freeman, San Francisco, 1960.
[4] Compare values in the Crystallographic Data Tables of R. L. Miller in Polymer Handbook, J. Brandrup and E. H. Immergut, eds., Wiley (Interscience), New York, 1966, p. III-16.