SHORT COMMUNICATIONS

**Solution-Grown Single Crystal of Polyacrylonitrile Polymerized
by γ -Ray Irradiation on Urea–Acrylonitrile Canal Complex:
Preparation and Preliminary Structure Analysis**

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(Received March 27, 1987)

KEY WORDS Polyacrylonitrile / Stereoregularity / Single Crystal /
Solution Grown Crystal / Crystal System / Crystal Lattice Constant /
Isotactic Polymer /

Up to now, many attempts to analyze comprehensively the crystal structure of polyacrylonitrile (PAN)¹⁻⁹ have unfortunately ended unsuccessfully, due to lack in off-equatorial sharp reflections in X-ray diffraction photographs of PAN fibers and an insufficient number of sharp reflections of multi-layered solution grown crystals in the electron diffraction patterns. The experimental difficulties encountered in the above studies are (1) preparation of fibers with highly-oriented and well-developed crystals and (2) preparation of solution-grown single crystals.

Table I summarizes the polymerization method of the polymer sample employed and the crystal form and its lattice constants proposed so far. For all polymer samples in literature,¹⁻⁹ stereoregularity was not evaluated. Considering that these polymer were, without exception, synthesized by free-radical or anionic polymerization and also considering the recent advance in NMR characterization of PAN, these polymers could be classified as atactic PAN (*i.e.*, completely random in stereoregularity, shortly random polymers). Therefore, it is concluded that the

fragmental crystallographic knowledge in literature was obtained only from atactic, or at most less stereoregular PAN samples, and this fact could explain why unsatisfactory crystallographic data have accumulated.

Kast² was probably the first to study the X-ray diffraction of atactic PAN fibers, prepared by radical polymerization, concluding that the PAN crystals are hexagonal lattices. Two years later, Natta *et al.*³ reached to a similar conclusion (hexagonal form) for atactic PAN fibers, prepared by anionic polymerization. Urbanczyk⁴ reported the PAN crystal form to be pseudo hexagonal. Stefani *et al.*⁵ proposed an orthorhombic cell (space group Cmc2) for PAN, although the density calculated from the proposed crystal structure (1.13 g cm^{-3}) was significantly lower than the experimental value (1.20 g cm^{-3}). The validity of the orthorhombic form was hence repeatedly confirmed for PAN crystals by Mencik⁶ and Colvin and Storr⁷, who showed the calculated density to agree with the experimental density. Holland and his coworkers⁸ insisted on the orthorhombic cell by analyzing the electron diffraction photographs of crystal mats with

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Table I. Crystal system and lattice constants of polyacrylonitrile in the literature

Author(s)		Crystal system	Point group	Space group	Lattice constant			Polymn. method	Sample	Method	Ref
					Å						
					<i>a</i>	<i>b</i>	<i>c</i>				
Kast	(1957)	Hexa ^a	—	—	6.17	6.17	5.1	Radical	F ^d	XD ^g	2
Natta <i>et al.</i>	(1958)	Hexa	—	—	5.99	5.99	—	Anionic	F	XD	3
Stefani <i>et al.</i>	(1960)	Ortho ^b	mm2	Cmc2	10.22	6.10	5.10	Radical	F	XD	5
Mencik	(1960)	Ortho	—	—	18.1	6.12	5.00	Radical	F	XD	6
Holland <i>et al.</i>	(1962)	Ortho	—	—	10.55	5.82	—	Radical	CM ^e	ED ^h	8
Urbanczyk	(1962)	PHexa ^c	—	—	6.1	6.11	(5.1)	Radical	F	XD	4
Klement and Geil	(1968)	Ortho	—	—	21.18	11.60	(5.1)	Radical	CM	XD, ED	9
Colvin and Storr	(1974)	Ortho	—	—	21.48	11.55	7.096	Radical	F	XD	7
This work	(1987)	Ortho	(mm2)	(Pna ₂ 1)	10.7	12.1	—	Urea canal (γ-ray)	SC ^f	ED	—

^a Hexa, hexagonal. ^b Ortho, orthorhombic. ^c PHexa, pseudo hexagonal. ^d F, fiber.^e CM, crystal mat. ^f SC, single crystal. ^g XD, X-ray diffraction. ^h ED, electron diffraction.

about 100 Å thickness (they claimed platelet for the mats), grown from 0.1–1.0% PAN solution in propylenecarbonate at 90–100°C. Similarly, Klement and Geil⁴ performed a study on solution grown radical PAN mat from a propylenecarbonate solution, concluding the orthorhombic cell. The lattice constants *a* and *b* by Klement and Geil are in good agreement with those by Colvin and Storr, but are just twice those by Holland *et al.* (see Table I). Solution grown crystal mats, reported by Holland *et al.*⁸ and Klement and Geil⁹, were of ellipse shape and no distinct growing plane was observed. Therefore, these mats, in a strict sense, cannot be regarded as single crystals. Moreover, the electron micrographic investigation showed that these mats were very occasionally heavily multilayered. As the results, their reflection spots were not sharp, but very diffuse (see for example, Figure 11 of ref 9).

In this article, an attempt was made to prepare single crystals from dilute solution of highly isotactic PAN, polymerized by γ -ray irradiation, and to determine the crystallographic features such as the crystal form, its growth plane and the lattice constants.

EXPERIMENTAL

Preparation and Characterization of Polymer Samples

Recently, Yamazaki¹⁰ succeeded in establishing a method for controlling the molecular weight of highly isotactic PAN in the polymerization process of γ -ray irradiation on acrylonitrile–urea canal complex (γ -PAN) with the addition of *n*-alkyl mercaptan. We used a γ -PAN sample, synthesized according to the procedure by Yamazaki.¹⁰

The stereoregularity of the sample was evaluated from the ¹³C NMR spectrum in DMSO-*d*₆ to be 70% isotactic triad, 22% heterotactic triad and 8% syndiotactic triad.^{11,12} The viscosity-average molecular weight $\bar{M}_v$, determined from the limiting viscosity number $[\eta]$ in DMSO at 25°C using the Mark–Howink–Sakurada equation proposed by Kamide *et al.*,¹³ was 1.49×10^5 .

Preparation of Single Crystals

The γ -PAN sample was dissolved in ethylenecarbonate at $155 \pm 5^\circ\text{C}$ to give a 0.5 wt% solution. The solution settled in glycerin bath maintained at $95 \pm 0.2^\circ\text{C}$ for 7 days to com-

plete isothermal crystallization.

Electron Diffraction and Electron Micrographs

A small amount of the solution, isothermally well crystallized, was dropped onto the grid of an electron micrograph (EM), washed with ethylenecarbonate and methanol several times. The specimen was shadowed with platinum at an angle of 30°C toward the grid surface in a vacuum evaporator HUS-4 type manufactured by Hitachi (Tokyo, Japan) at 10^{-6} mmHg . The specimen, prepared thus, was transferred to an EM JEM-1200EX, manufactured by JEOL (Tokyo) and the morphology of the specimen was observed under the following conditions: bright field image, magnification $\times 5000$. The selected area electron diffraction was also obtained for the specimen. In order to minimize possible damage to the crystals due to electron irradiation, the photographs were taken at an electron dose as small as possible.

RESULTS AND DISCUSSION

Figure 1 shows a typical micrograph of γ -PAN crystals grown from the solution in ethylenecarbonate at 95°C for 7 days. Although the crystal mats reported in literature for atactic PAN were heavily multilayered or agglomerated, Figure 1 indicates that highly isotactic PAN gives a single lamella if the polymer is isothermally crystallized under adequate conditions. Holland *et al.*⁸ and Klement and Geil⁹ obtained elongated ellipse crystal mats for atactic PAN and the latter noted that it was no longer possible to detect the main original lamella. A solution-grown γ -PAN crystal is a lozenge, with well-defined sides, closely associated with crystal growth faces. Judging from the electron diffraction patterns (see Figure 2), the directions of the *a*- and *b*-axes are determined as indicated by arrows and one of four sides is assigned to the (110) plane. The solution-grown crystals each has a side of about $3\mu\text{m}$ in length and ap-

Figure 1. Electron micrograph of a single γ -PAN crystal, grown for 7 days from a 0.5 wt% ethylenecarbonate solution at 95°C .

Figure 2. Electron diffraction patterns of a single γ -PAN crystal, grown for 7 days from a 0.5 wt% ethylenecarbonate solution at 95°C .

proximately $100\text{ \AA}$ in thickness. The solution-grown crystals of γ -PAN have a shape similar to that of polyethylene single crystals (but not hollow pyramids) and these γ -PAN crystals can be regarded as single planar lamella crystals.

Figure 2 shows an electron diffraction pat-

tern of a solution-grown γ -PAN crystal. All reflection spots are sharp and higher ordered reflections can be observed. The reflections, corresponding to the crystallographic planes, 200 and 040, are designated.

From Figure 2, the following lattice constants were determined: $a = 10.7 \text{ \AA}$ and $b = 12.1 \text{ \AA}$. The electron diffraction pattern corresponds to the symmetry of the diffraction group¹⁴ $2mm$ and accordingly, we can conclude that the c -axis is perpendicular to the surface plane of the lamellae, on which PAN molecules are folded. The crystal system of the solution-grown γ -PAN crystal is orthorhombic.

The 200 and 120 reflections have relatively large intensities and in general, $hk0$ reflections are observable under any condition (indicating that the crystal is not C-centered) and $h00$ and $0k0$ reflections are observed only in the case of $h = 2n$ and $k = 2n$, respectively. For an orthorhombic system, the space groups satisfying these rules are evidently limited to $P2_12_12_1$, $Pba2$, $Pna2_1$, $Pnn2$, $Pnnm$, and $Pnam$. Unfortunately, the information about extinction rules in relation to the c -axis direction cannot be obtained from the electron diffraction pattern of lamella crystals and hence, judging from the X-ray diffraction patterns of Colvin and Storr (Figure 2 of ref 7) 001 reflections should be possible only in the case of $l = 2n$. The space groups among the above six types of symmetry, satisfying this additional condition, are $P2_12_12_1$, $Pna2_1$, $Pnn2$, $Pnnm$, and $Pnam$. If we assume a two-fold

screw axis in the c -direction, the probable space groups are $P2_12_12_1$, $Pna2_1$, and $Pnam$ (full symbol, $P 2_1/n 2_1/a 2_1/m$). These space groups do not coincide with $Cmc2$ proposed by Stefani *et al.*⁵ More detailed work on solution grown PAN crystals is in progress.

REFERENCES

1. C. R. Bohn, J. R. Schaefgen, and W. O. Statton, *J. Polym. Sci.*, **55**, 531 (1961).
2. W. Kast, in "Londolt-Börnstein Tabellen," Vol. 4, 6th ed, Part 3, Springer-Verlag, Berlin, 1957.
3. G. Natta and G. Dall'Asta, Italian Patent, 570,434 (1959); G. Natta, G. Mazzanti, and P. Corradini, *Atti. Accad. Nazl. Lincei. Rend. Classe Sci. Fis. Mat. Nat.*, **25**, 3 (1958).
4. G. W. Urbunczyk, *Zeszyty Nauk, Politech. Lodz, Wlokiennictwo*, **9**, 79 (1962); *Chem. Abstr.*, **61**, 5836B (1964).
5. R. Stefani, M. Chevereton, M. Garnier, and C. Eyraud, *Compt. Rend.*, **251**, 2174 (1960).
6. Z. Mencik, *Vysokomolekul. Soedin, Ser. A*, **2**, 1635 (1960).
7. B. G. Colvin and P. Storr, *Eur. Polym. J.*, **10**, 337 (1974).
8. V. H. Holland, S. B. Mitchell, W. L. Hunter, and P. H. Lindenmeyer, *J. Polym. Sci.*, **62**, 145 (1962).
9. J. J. Klement and P. H. Geil, *J. Polym. Sci., A-2*, **6**, 1381 (1968).
10. H. Yamazaki, unpublished results.
11. K. Kamide, H. Yamazaki, K. Okajima, and K. Hikichi, *Polym. J.*, **17**, 1233 (1985).
12. K. Kamide, H. Yamazaki, K. Okajima, and K. Hikichi, *Polym. J.*, **17**, 1291 (1985).
13. K. Kamide, H. Yamazaki, and Y. Miyazaki, *Polym. J.*, **18**, 819 (1986).
14. see, for example, B. F. Buxton, J. A. Eades, J. W. Steeds, and G. M. Rackham, *Phil. Trans. R. Soc. London, Ser. A*, **281**, 171 (1976).