

## Crystallization of Poly(chlorotrifluoroethylene)

Yasuhiko MIYAMOTO

*Department of Applied Physics, Faculty of Science,  
Fukuoka University, Fukuoka, Japan.*

Chitoshi NAKAFUKU and Tetuo TAKEMURA

*Department of Applied Science, Faculty of Engineering,  
Kyushu University, Fukuoka, Japan.*

(Received April 30, 1971)

**ABSTRACT:** Crystallizations of poly(chlorotrifluoroethylene)(PCTFE) from dilute solution and from the melt of dispersion powder at atmospheric pressure and from the melt of the bulk material under high pressure have been carried out and examined by electron microscope. A folded-type single crystal of hexagonal shape has been obtained from dilute solution of *p*-xylene and that of irregular shape has been obtained from the melt of dispersion powder.

To determine the optimum crystallization temperature under high pressure, DTA measurements have been carried out and the melting and recrystallization curves have been obtained. Remarkable increase of  $T_m$  with respect to pressure ( $dT_m/dP=60^\circ\text{C}/1000\text{ kg/cm}^2$ ) has been observed. Experiments on the crystallization have been performed on the basis of these data. The fracture surface of the bulk sample crystallized under high pressure shows a completely developed band structure. In this polymer this structure has been obtained easily by the application of pressure of only a few hundred  $\text{kg/cm}^2$ . From the examination of X-ray fibre pattern of stretched film crystallized under high pressure, a 17 monomer 1 turn helix configuration has been determined.

**KEY WORDS** Poly(chlorotrifluoroethylene) / Crystallization / Solution / Melt / High Pressure / Electron Microscopy / DTA / X-ray Diffraction /

It is by now well established that crystalline polymers possess different types of microstructure in morphology, generally distinguished into two classes, folded-chain crystal and extended-chain crystal. Typical forms of folded-chain crystal are single crystals from dilute solution and spherulites from the molten state. Solution-grown single crystals have been reported for a number of polymers, but the single crystal from the molten state has been reported only for poly(tetrafluoroethylene)(PTFE).<sup>1</sup> Extended-chain crystals were observed by Wunderlich and Arakawa<sup>2</sup> on crystallization of bulk linear polyethylene from the melt at elevated pressure in 1964. However this is not a remarkable fact, because bands identical to those of extended-chain crystal have been observed in 1957 by Bunn and coworkers<sup>3</sup> on the fracture surface

of PTFE crystallized at atmospheric pressure. In the case of PTFE, crystallization has not been performed under high pressure, so that it seems that the formation of the band is due to the residual stress existing in the interior region of the bulk after the moulding of powdered materials. As this residual stress is assumed to be as much as several hundred  $\text{kg/cm}^2$ , extended-chain crystals of PTFE can be formed under relatively low pressure as compared with polyethylene.

Poly(chlorotrifluoroethylene)(PCTFE) is one of polymers expected to form both types of crystals. Spherulites of PCTFE have been described sufficiently<sup>4</sup> but there have been no reports on the formation of individual single crystals from the melt and the growth of extended-chain crystals under high pressure. Single crystals from solution have been reported by

Kargin, *et al.*,<sup>5</sup> but not fully investigated. Although the crystallization of molten PCTFE normally results in the formation of spherulites, the growth of single crystals is expected from the powdered material after the same methods as Symons,<sup>1</sup> since PCTFE has a somewhat similar character to PTFE. It is considered that extended-chain crystals are not formed at atmospheric pressure in this polymer, because the residual stress after the moulding will be relaxed easily because of the low melt viscosity of this polymer. Consequently, the formation of the band structure in PCTFE is expected only by the application of hydrostatic high pressure.

In this paper, on the basis of the considerations described above, the growth of a single crystal from dilute solution and from the melt, the formation and the distribution of the size of the extended-chain crystal under high pressure and the structure of this material using the fiber crystallized under high pressure are reported.

#### THE GROWTH OF SINGLE CRYSTALS FROM THE MELT

The growth of single crystals from the melt of PTFE was investigated by Symons. He obtained individual single crystals from dispersion based PTFE. In the case of PCTFE, however, reports on the growth of single crystals from the melt have not been previously presented. The crystallization of PCTFE from the melt was carried out after the Symons method. Experimental details are as follows: a fine powder of PCTFE was put on glass slides and these slides were then enclosed in an air bath and the bath heated to well above the melting point. After the sample had been held in this temperature, it was cooled below the melting point. The optimum crystallization temperature has been known to be 190°C, and the specimen was annealed at this temperature for 36 hr. Isolated crystals were pulled out from the glass slides with cellulose acetate film. After chromium shadowing the specimen was evaporated with carbon and examined by direct transmission in the electron microscope. Single crystals, such as those shown in Figure 1, were observed.

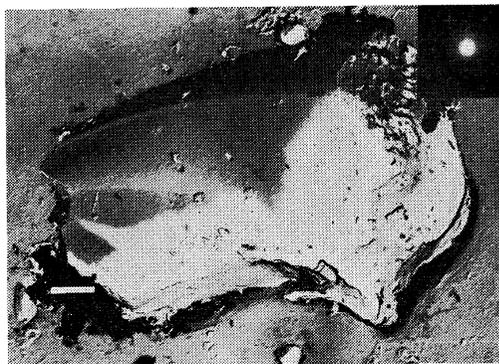


Figure 1. Electron micrograph of single crystal from the melt. Inset: electron diffraction pattern. Scale bar represents 1  $\mu$ .

In the case of PTFE, single crystals were grown from dispersion particles of high crystallinity; on the other hand, in the case of PCTFE, single crystals were formed from powdered material of relatively low crystallinity.

#### THE GROWTH OF SINGLE CRYSTALS FROM SOLUTION

Since the growth of single crystals of linear polyethylene was reported in 1957,<sup>6-8</sup> solution grown single crystals for a number of other polymers have been found and examined by electron diffraction and microscopy. With respect to PCTFE, two types of lamellar crystals have been grown from 0.005-% to 0.02-% solution of mesitylene.<sup>5</sup> These were lamellar aggregates or rectangular lamellae.

In our experiment *p*-xylene was used as a

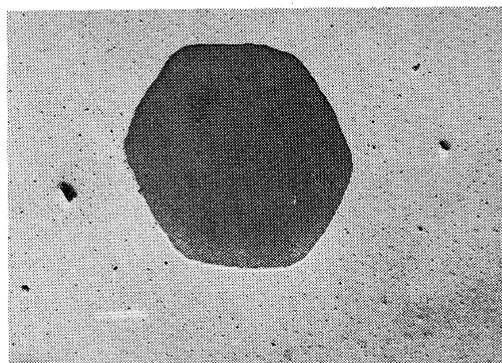


Figure 2. Electron micrograph of single crystal from *p*-xylene solution. Scale bar represents 1  $\mu$ .

solvent. 5 mg of powdered PCTFE plus 50 cc of *p*-xylene were placed in a flask and then heated to 140°C, and the white powder was found to dissolve in the solvent completely. The solution was cooled slowly, kept at 130°C for 6 hr, and single crystals were then observed to precipitate. The electron micrograph shows the formation of hexagonal-shaped single crystal of this material (Figure 2). Spiral growth or circular shaped crystals were also observed on the same grid.

#### CRYSTALLIZATION FROM THE MELT AT ELEVATED PRESSURE

Since the melting temperature increases with increasing pressure for most polymers, the melting temperature vs. pressure curve must be obtained in order to determine the optimum crystallization temperature under elevated pressure. However in the case of PCTFE there is no report on the measurement of the melting temperature under high pressure. Therefore, the melting data on bulk PCTFE under high pressure have been examined in the present experiment. Differential thermal analysis(DTA) has been used to study the melting and recrystallization of the bulk specimen under high pressure. The DTA cell used in this experiment is shown in Figure 3. The cell is a

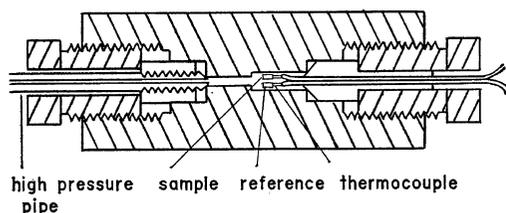


Figure 3. High pressure DTA cell.

cylinder of 12 cm in length, 5 cm in outside diameter, with a 0.6-cm bore. One end of the bore is closed by a plug, the other end is connected to the high pressure generator. The plug was drilled axially and two sheathed Chromel-Alumel thermocouples were inserted. Figures 4 and 5 show DTA traces of the melting and recrystallization under elevated pressure, respectively. The normal heating rate chosen was 5°C/min. Above 1000 kg/cm<sup>2</sup> DTA traces

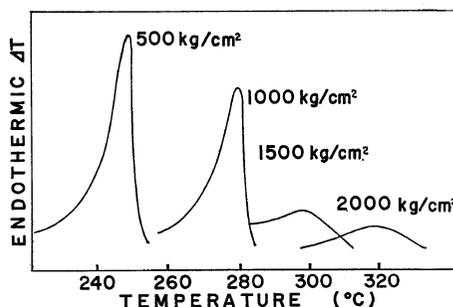


Figure 4. DTA traces of melting under high pressure.

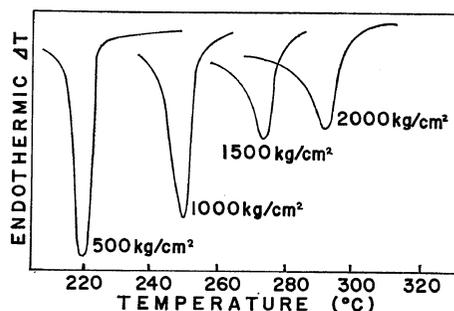


Figure 5. DTA traces of recrystallization under high pressure.

become broad and difficult to distinguish from the baseline. On the other hand, the traces of recrystallization remain still sharp up to 2000 kg/cm<sup>2</sup>. The melting and recrystallization curves were obtained from each DTA peak as shown in Figure 6, respectively. In this figure, the melting point increases with increasing

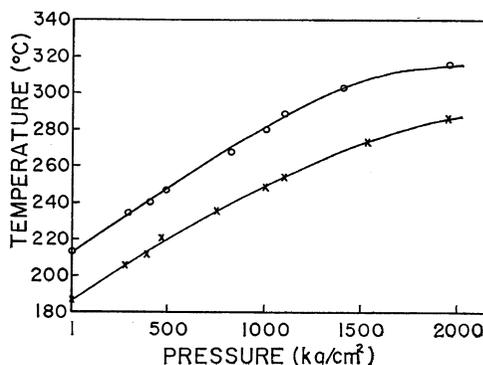


Figure 6. Melting curve, and recrystallization curve of PCTFE: ○, melting peak; ×, recrystallization peak.

pressure up to  $1000 \text{ kg/cm}^2$  and the curve decreases in slope above  $1000 \text{ kg/cm}^2$ . The pressure dependence of the melting temperature ( $dT_m/dP$ ) obtained from this curve is about  $65^\circ\text{C}/1000 \text{ kg/cm}^2$  below  $1000 \text{ kg/cm}^2$ . This value is extremely large in comparison with that of polyethylene<sup>10</sup> (about  $20^\circ\text{C}/1000 \text{ kg/cm}^2$ ), but small in comparison with that of PTEE (about  $140^\circ\text{C}/1000 \text{ kg/cm}^2$ ).

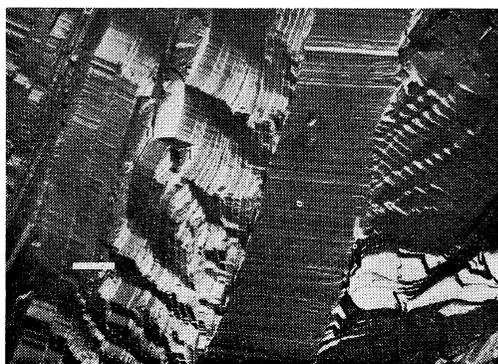
It seems that this is one of the remarkable physical properties of fluorine polymers as well as the effect of pressure on the morphological structure. On the basis of the experiments described above the crystallization was carried out under high pressure. Compression moulded samples were used as the starting material (sample A). Column-like samples ( $3 \text{ mm}\phi \times 10 \text{ mm}$ ) machined from the starting material were crystallized under various conditions as listed in Table I. All

**Table I.** Crystallization condition under high pressure

Sample	Melting temp, $^\circ\text{C}$	Crystallization pressure, $\text{kg/cm}^2$	Crystallization temp, $^\circ\text{C}$	Crystallization time, hr	Melting temp, at $1 \text{ atm. } ^\circ\text{C}$
A	230	Compression moulded			214
B	295	1000	250	16	219
C	248	500	225	16	219
D	230	1	190	18	214

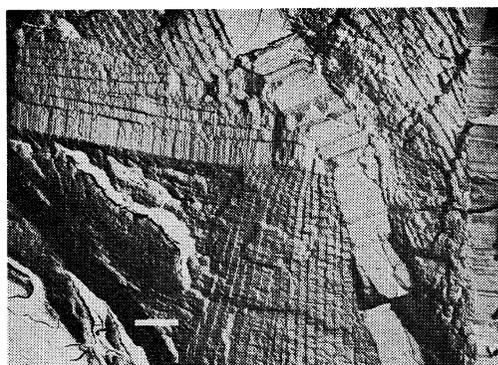
samples were heated about  $10^\circ\text{C}$  above melting temperature and then crystallized at the proper temperature several degrees above recrystallization temperature under each hydrostatic pressure in a high pressure vessel of 30 mm inside diameter. The sample, wrapped in aluminum foil, was placed in a internal heating assembly of the pressure vessel. The temperature was controlled within  $\pm 1^\circ\text{C}$  automatically by an electric controller. After holding the sample at each pressure and temperature for a proper time, the samples were cooled rapidly to room temperature and the pressure then released. The sample pieces were fractured at liquid nitrogen temperature, then replicated and observed by electron microscope.

Figure 7 shows the fracture surface of sample B crystallized under the pressure of  $1000 \text{ kg/cm}^2$



**Figure 7.** Fracture surface of sample B. Scale bar represents  $1 \mu$ .

at  $250^\circ\text{C}$ . The outstanding feature of this sample is the orientation of long bands,  $0.5\text{--}2 \mu$  in width,  $10\text{--}50 \mu$  in length. Such features have not been observed on the fracture surface of PTFE or pressure crystallized polyethylene;<sup>11</sup> this fact seems to illustrate a remarkable characteristic of PCTFE. The figure suggests that this sample is crystallized practically completely. The high crystallinity of sample B is also suggested by the character of brittle fracture. Figure 8 shows the fracture surface of sample



**Figure 8.** Fracture surface of sample C. Scale bar represents  $1 \mu$ .

C crystallized at the pressure of  $500 \text{ kg/cm}^2$ . Band width varies from  $0.5$  to  $1 \mu$ . The orientation of this sample is irregular compared with sample B and these structures are similar to the bands of PTFE or type III lamellae observed on the fracture surface of polyethylene crystallized under high pressure. From these observations it is concluded that the order of

orientation and the width of the band increases with crystallization pressure. It seems that under lower-pressure chain molecules of lower molecular weight extend to form a narrow band and under higher pressure the chain molecules of higher molecular weight also begin to extend to form a broad band. Therefore, the determination of the molecular weight distribution should be possible by statistical treatment of the measurement of the band width distribution in the electron micrograph of these samples crystallized under high pressure. A comparison of the band width distribution with the molecular weight distribution is discussed by Prime and Wunderlich<sup>12</sup> in polyethylene. According to them, up to molecular weight 10000, eutectic separation of completely extended-chain crystals occurred and beyond molecular weight 10000 mixed crystals were formed, *i.e.*, crystals composed of components of different molecular weight, some of which must fold in crystallizing. In our investigation on PCTFE crystallized at 1000 kg/cm<sup>2</sup>, a comparison of molecular weight distribution and crystal size distribution shows a partial match but the latter shift to the low molecular weight side, in comparison with the former. This may be due to the degradation of this polymer during crystallization, and this is also supported by the fact that the color of this sample changed to dark brown after crystallization.

The growth of extended-chain crystals under comparatively lower pressure has not been reported previously, but in the case of PCTFE, it seems that extended-chain crystals are formed

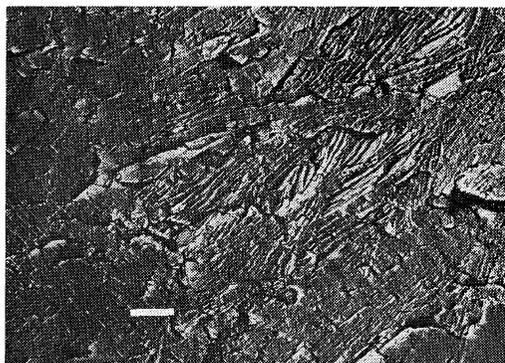


Figure 9. Fracture surface of sample A. Scale bar represents 1  $\mu$ .

at only 100 kg/cm<sup>2</sup>. In fact, the electron micrograph of the fracture surface of sample A which is melted under the pressure of 50–100 kg/cm<sup>2</sup> in order to remove cavities, presents partially developed bands of width about 2000 Å (Figure 9). It seems that these bands are formed by the application of this pressure. In order to confirm this, it is necessary to examine the fracture surface of PCTFE crystallized from the melt at atmospheric pressure on sample A.



Figure 10. Fracture surface of sample D. Scale bar represents 2  $\mu$ .

This is shown in Figure 10 (designated as sample D). Spherulites are formed and observed in this figure. From the experiments performed here, it is concluded that PCTFE crystallizes into extended-chain conformation under relatively low pressure and the width of the band as well as the order of orientation increases with increasing pressure. These facts indicate that the crystal structure will be given by the investigation of the sample crystallized under high pressure.

#### MOLECULAR CONFIGURATION OF STRETCHED PCTFE

Reports on X-ray fiber diagrams of the stretched PCTFE film had been given by Kondrashev<sup>13</sup> and Gal'perin,<sup>14</sup> *et al.*, but the molecular configuration of PCTFE was not fully revealed in their investigations. From the electron microscopy of the high-pressure crystallized PCTFE, it is expected that the annealing under high pressure gives rise to high crystallinity.

## Crystallization of Poly(chlorotrifluoroethylene)

On the basis of this consideration, PCTFE films were drawn at the temperature near the melting point, annealed under the pressure of  $600 \text{ kg/cm}^2$  at  $240^\circ\text{C}$  for 8 hr, and examined by X-ray measurement. Figure 11 shows X-ray fiber pattern of the specimen using  $\text{CuK}\alpha$  radiation. The photograph was taken on a cylindrical camera with film diameter 70 mm. The characteristic feature of this photograph is the presence of the sharp and well resolved spots on both the equatorial and the low-order layer lines. The sharpness of the equatorial reflec-

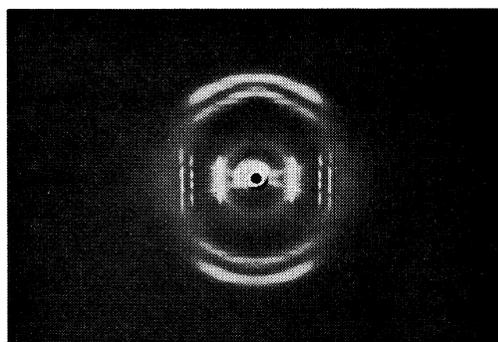


Figure 11. X-ray fiber pattern of stretched PCTFE annealed under  $600 \text{ kg/cm}^2$  at  $240^\circ\text{C}$  for 8 hr.

Table II. X-ray diagram of stretched PCTFE annealed under high pressure<sup>a</sup>

Index, <i>l</i> , of the layer	<i>d</i> (obsd), Å	<i>d</i> (calcd), Å	Index ( <i>hkl</i> )	Intensity <i>I</i> (obsd)	Order, <i>n</i> , of the Bessel function
0	5.64	5.53	100	V.S	0
	2.80	2.76	200	M	
	2.12	2.09	210	V.W	
	1.86	1.84	300	V.W	
1	5.53	5.50	101	V.S	1
	3.20	3.19	111	M	
	2.12	2.09	211	V.W	
	1.87	1.85	301	V.W	
2	5.39	5.36	102	V.V.S	2
	2.79	2.75	202	M	
	2.11	2.09	212	V.W	
	1.86	1.85	302	V.W	
3	5.18	5.16	103	V.V.S	3
	3.12	3.12	113	V.W	
	2.10	2.07	213	V.W	
	1.86	1.84	303	V.W	
4	4.94	4.91	104	M	4
	3.07	3.06	114	M	
	2.73	2.68	204	V.W	
	1.86	1.82	304	V.W	
5	4.64	4.64	105	V.W	5
	2.99	2.99	115	W	
	2.68	2.63	205	W	
	2.07	2.09	215	V.V.W	
6	2.63	2.58	206	V.V.W	6
	2.05	2.01	216	V.V.W	
7	2.02	1.98	217	V.V.W	7
	1.80	1.77	307	V.V.W	
8	1.78	1.74	308	V.V.W	8
9					
10	None				
11					
12					
13				W	-4
14	Diffuse streak			W	-3
15				W	-2
16	Near meridional streak			S	-1
17	2.50	2.50	0017	M	0
18	Near meridional streak			S	1
19	Diffuse streak			V.V.W	2

<sup>a</sup>  $a=b=6.4 \text{ \AA}$ ,  $c=42.5 \text{ \AA}$ ,  $\gamma=120^\circ$ .

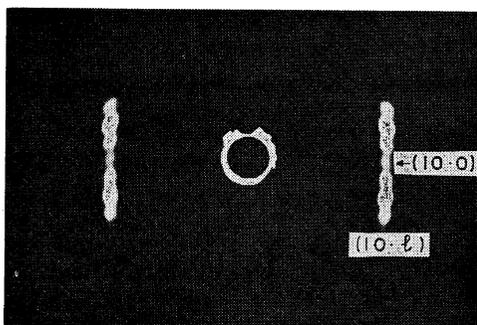


Figure 12. Portion of Figure 11 near (10.0) reflection.

tions shows that the side-by-side packing is highly regular. The equatorial reflections fit a hexagonal projected cell base with  $a=b=6.4 \text{ \AA}$  and the chain repeat distance calculated from layer line spacings is  $42.5 \text{ \AA}$ , these values being in close agreement with the data of Gal'perin, *et al.* Figure 12 shows the portion of Figure 11 near the (100) reflection. The equatorial (100) reflection is weak but clearly observed on this figure. This fact shows that the first reflection should be indexed as (100) and not as (101) as has been done by Gal'perin, *et al.* The observed and calculated spacings are listed in Table II. The presence of meridional reflection of  $2.50 \text{ \AA}$  on the 17th layer line, especially strong near the meridional streak on the 16th and 18th layer lines, and the strong intensities of the near equatorial layer lines suggest that the configuration of PCTFE film is 17 monomer 1 turn helix. This is also suggested by the absence of reflections on the 9 to 12-layer lines. Consequently, the following selection rule for the X-ray diffraction may be applied to this configuration.<sup>15</sup>

$$l = n + 17m$$

where  $l$  is the layer line number,  $n$  is the order of the Bessel function,  $m$  is an integer, +, -, or 0. In Table II, the lowest order of the Bessel function determined by the selection rule cited above and the observed intensity are list-

ed. Low-order Bessel functions correspond to both near-equatorial layer lines and near 17th layer lines and high orders correspond to intermediate layer lines.

From these considerations, it is concluded that the PCTFE molecule has a configuration of 17 monomers in 1 turn helix.

*Acknowledgment.* The authors wish to thank Mr. M. Yasuniwa of this laboratory (Kyushu University) for supplying the fibered sample crystallized under high pressure. The authors also wish to thank Lecturer K. Imada, of the Applied Chemistry Department of this University, for many valuable discussions and for a critical reading of the manuscript.

#### REFERENCES

1. N. K. J. Symons, *J. Polym. Sci., Part A*, **1**, 2843 (1963); *J. Polym. Sci., Part C*, **3**, No. 3, 109 (1963).
2. B. Wunderlich and T. Arakawa, *J. Polym. Sci., Part A*, **2**, 3697 (1964).
3. C. W. Bunn, A. J. Cobbold, and R. P. Palmer, *J. Polym. Sci.*, **28**, 365 (1958).
4. P. H. Geil, "Polymer Single Crystals," Interscience, New York, N. Y., 1963.
5. V. A. Kargin, N. F. Bakeev, and L. Li-shen, *Vysokomol. Soedin.*, **3**, 1100 (1961) (in Russian).
6. P. H. Till, *J. Polym. Sci.*, **24**, 301 (1957).
7. A. Keller, *Phil. Mag.*, **2**, 1171 (1957).
8. E. W. Fisher, *Z. Naturforsch.*, **12a**, 753 (1957).
9. H. T. Hall, *J. Amer. Chem. Soc.*, **74**, 68 (1951).
10. T. Davidson and B. Wunderlich, *J. Polym. Sci., Part A*, **2**, **7**, 377 (1969).
11. T. Davidson and B. Wunderlich, *J. Polym. Sci., Part A*, **2**, **7**, 2051 (1969).
12. R. B. Prime and B. Wunderlich, *J. Polym. Sci. Part A*, **2**, **7**, 2061 (1969).
13. Yu. D. Kondrashev, *Tr. Gos. In-Ta Prikl. Khimii*, **46**, 158 (1960).
14. E. L. Gal'perin, S. S. Dubov, E. V. Volkova, and M. P. Mlenik, *Kristallografiya*, **9**, No. 1, 102 (1964).
15. W. Cochran, F. H. Crick and V. Vand, *Acta Cryst.*, **5**, 581 (1952).