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X-ray diffraction study of poly(p-phenylene)

Part 1. Variation of crystallite size with annealing temperature

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A line profile analysis of the (*hk*0) reflections of sintered poly(p-phenylene) is presented. The wide angle X-ray diffraction maxima were analyzed to study the average size of the coherently diffracting domains as a function of annealing temperature T_A. The results show that the lateral size of the coherently diffracting domains increases first slightly for $T_A < 300\,°C$ and then rapidly for $T_A > 300\,°C$. This is related to a rearrangement of rigid chains from disordered into the crystalline regions. The absence of SAXS supports the view of a nematic frozen-in liquid crystalline structure contributing to about 40% of the material.

Röntgenbeugungsuntersuchungen an Poly(p-phenylen). Teil 1. Änderung der Kristallitgröße mit der Temperatur

Eine Linienprofilanalyse der (*hk*0)-Reflexe von gesintertem Poly(p-phenylen) wird vorgestellt. Die Maxima der Weitwinkelröntgenbeugung wurden analysiert, um die mittlere Größe der kohärent streuenden Bereiche in Abhängigkeit von der Temperatur T_A zu untersuchen. Die Ergebnisse zeigen, daß die Querabmessung der kohärent streuenden Bereiche bis $T_A = 300\,°C$ zuerst leicht zunimmt und dann für $T_A > 300\,°C$ stark anwächst. Dies hängt mit der Umordnung starrer Ketten aus den ungeordneten in kristalline Bereiche zusammen. Das Fehlen einer Röntgenkleinwinkelstreuung stützt die Annahme einer eingefrorenen nematischen flüssig-kristallinen Struktur, die etwa 40% des Materials umfaßt.

Исследования полифенилена рентгеновским структурным анализом. Часть 1. Зависимость размера кристаллитов от температуры отжига

Представлен анализ профилей линий *hk*0-отражений агломерированного полифенилена. Анализировались максимумы дифракции рентгеновских лучей на больших углах, чтобы исследовать зависимость средних размеров рассеивающих областей от температуры отжига T_A. Результаты показывают, что поперечный размер этих областей до температуры $T_A = 300\,°C$ слегка увеличивается, а при $T_A > 300\,°C$ резко возрастает. Это связано с перераспределением жестких цепей из неупорядоченных областей в кристаллические области. Отсутствие рассеяния рентгеновских лучей на малых углах поддерживает предположение о существовании замороженной нематической жидко-кристаллической структуры, которая занимает приблизительно 40% материала.

1. *Introduction*

Electric conductivity (σ) measurements of poly(p-phenylene) (PPP) as a function of annealing temperature (T_A) have been previously reported in relation with microstructure changes [1]. The initial conductivity rise observed up to $T_A = 250\,°C$ was correlated to an increase of crystallinity. Beyond $T_A = 250\,°C$ the observed decrease in σ was ascribed to the loss of the residual chlorine containing material [1]. Furthermore, the conductivity increase of PPP as a function of doping level with $SbCl_5$ and chlorosulphonic acid has been also studied [2]. The variation in conductivity of these materials as a function of storage time in various atmospheres was likewise examined [3]. Kawaguchi and Petermann [4] have explained the electron diffraction pattern of oriented annealed PPP on the basis of an orthorhombic unit cell suggesting that the material is paracrystalline showing a nematic structure. In a recent study carried out in this laboratory the modification of the lattice constants as a result of doping with SbF_5 and $SbCl_5$ has been discussed in terms of structural models which account for the intercalation of dopant species within the PPP crystal lattice [5]. However, the microstructure of this polymer before doping is not fully explored.

In the present study we report an structural investigation of this material using wide angle X-ray diffraction techniques. The first paper of this series (part 1) deals with the annealing behaviour of PPP and examines the variation of the coherent diffracting domains as derived from the line broadening analysis of the *hk*0 reflections. The second paper, which follows, will be concerned with the correlation between crystal size and yield behaviour (microhardness) being highlighted in terms of current thermodynamical predictions.

2. *Experimental*

2.1. *Materials*

PPP was synthesized using the KOVACIC method [6] as reported previously [2]. Sintered samples were prepared using a pressure of 0.75 GPa in the form of ≈ 0.5 mm thick platelets with a diameter of ≈ 13.0 mm. The materials were annealed by heating in a glass cell placed into an oven under diffusion pump vacuum at several temperatures between 175 and 500 °C for 15 h. For this purpose 4 sintered samples were prepared for each annealing experiment. The weight and dimensions of the samples were measured at room temperature as a function of the temperature of annealing.

2.2. *X-ray diffraction techniques*

Wide angle X-ray diffractograms (WAXD) were obtained at room temperature using Ni filtered CuKα radiation from a 40 kV, 40 mA X-ray source. 1° divergence and antiscatter and 0.15 mm receiving slits were used. Scans were analyzed in the 10 to 36°(2θ) range using a goniometer speed of 1°(2θ)/min and a time constant of $\tau = 1$. The number of counts per second for the (110) reflection (strongest) varies between 1.5 and 3×10^3. The separation of the amorphous halo from the main three reflections was carried out using a curve analyzer by adjusting gaussian profiles. The maximum of the amorphous halo was placed at ≈ 22°(2θ) being tangent to the experimental profile at 25.5°(2θ).

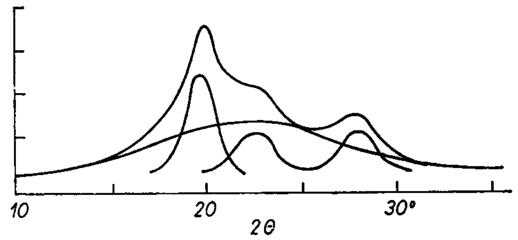

Fig. 1. Separation of the crystalline reflections for sintered PPP before annealing

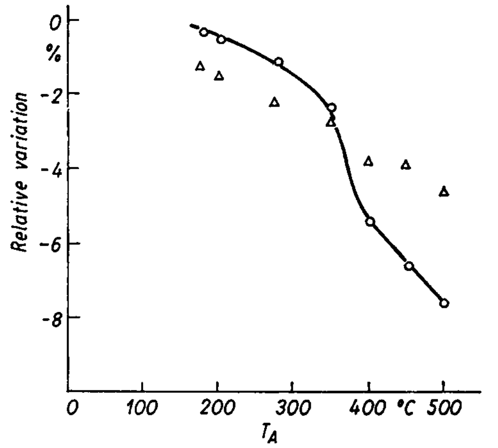

Fig. 2. Relative variation of weight (○) and width (△) of the sintered PPP platelets before and after annealing at different temperatures

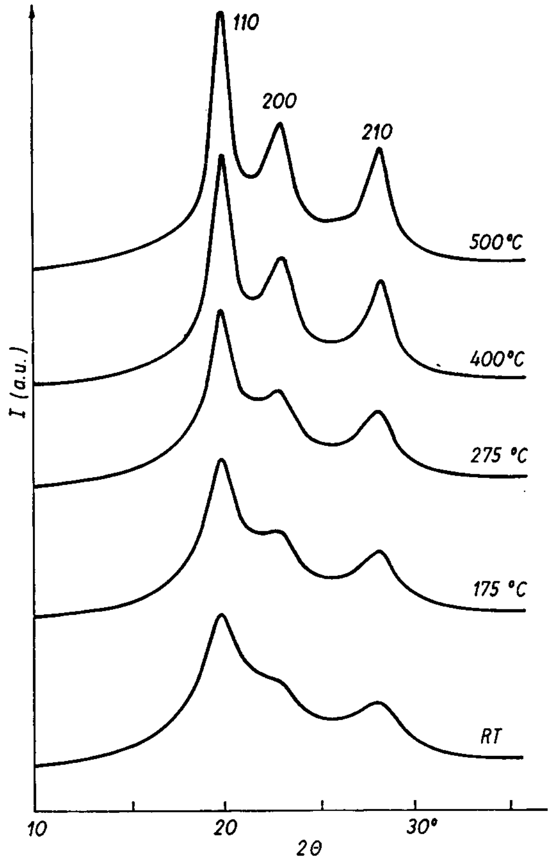

Fig. 3. Wide angle X-ray diffraction profiles of sintered PPP before and after annealing at different temperatures

Figure 1 illustrates the separation used for the crystalline reflections of the sintered PPP sample before annealing. The correction due to instrumental broadening was taken into account using a standard sample of silicon. The (111) diffraction peak of this sample exhibited an integral width of $\delta\beta_{ins} = 1.8 \times 10^{-4}$ nm^{-1}.

3. *Results and discussion*

The relative variations in weight and in the width of the sintered samples are illustrated in Figure 2 as a function of annealing temperature T_A. The thickness of the samples shows on the contrary an average increase with annealing of ≈ 4.5%. As a result, the average value for the macroscopic density shows a decrease from 1.235 (untreated) down to 1.206 gcm^{-3} (annealed).

The WAXD patterns of the PPP sintered material, annealed at various temperatures, are shown in Figure 3. With increasing T_A a better definition of the crystalline reflections is obtained. Table 1 shows the increase in volume crystallinity (X_c) with T_A. After an initial rise of X_c, from ≈ 41 up to 48% for $T_A = 175$ °C, crystallinity increases thereafter only very slightly with T_A up to $T_A = 500$ °C. Even after a long annealing treatment of PPP, during 6 days at 400 °C, the level of crystallinity did not improve any further.

Most revealing is the analysis of the X-ray wide angle diffraction lines. Since only one diffraction order for the

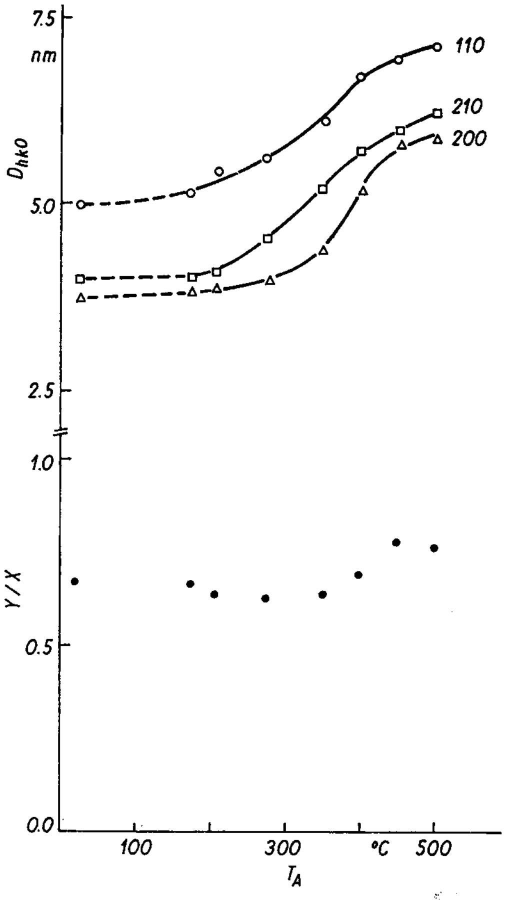

Fig. 4. Variation of the crystal size values D_{110}, D_{210}, and D_{200} (top) and the ellipsoid eccentricity (bottom) for sintered PPP as a function of annealing temperature

various WAXD reflections was obtained, an evaluation following the paracrystalline analysis [7] was not feasible. Hence, the size of the coherently diffraction domains (crystallite size) of the samples was directly calculated from the integral breadth $\delta\beta$ of the first order reflection according to $\delta\beta \sim 1/D_{hkl}$ [8]. This obviously provides a minimum value for the crystallite size. Figure 4 illustrates the initial gradual increase of D_{110}, D_{210}, and D_{200} up to $T_A \approx 300\,°C$ and a faster rate of increase of these dimensions for $T_A > 300\,°C$. The increase of the D_{hk0} values with T_A corresponds to about 44% for the [110] and to 55% for the [210] and [200] directions, respectively. The crystal size values obtained for this conjugated rigid polymer are smaller, but of the same order of magnitude than the crystallite dimensions occurring in many other flexible polymers [8].

Table 1. Volume crystallinity of PPP measured from WAXD as a function of annealing temperature

T_A °C	X_c %
RT	41.5
175	48.6
207	48.4
275	48.1
350	49.0
400	51.4
450	51.3
500	51.4
400 (6 days)	50.5

Table 2. Crystallite size values, principal axes (X, Y) and eccentricity (Y/X) of the shape ellipsoid along various [hk0] directions for poly(p-phenylene) as a function of annealing temperature T_A

T_A °C	$D_{110} \equiv X$ nm	D_{200} nm	D_{210} nm	D_{210}^{calc} nm	Y mn	Y/X
RT	4.96	3.74	4.00	4.22	3.39	0.68
175	5.15	3.84	4.00	4.35	3.47	0.67
207	5.36	3.84	4.12	4.41	3.44	0.64
275	5.59	3.95	4.49	4.56	3.53	0.63
350	6.10	4.34	5.14	5.00	3.88	0.64
400	6.71	5.18	5.61	5.80	4.72	0.70
450	6.92	5.86	5.92	6.32	5.48	0.79
500	7.07	5.86	6.20	6.38	5.45	0.77
400 (6d)	6.58	5.10	5.68	5.91	4.66	0.71

In conventional flexible polymers the presence of D values within the range of colloidal dimensions is related to the appearance of lattice distortions in the crystallites which prevent unlimited crystal growth [9]. According to the α^* relation, $g\sqrt{N} = \alpha^*$ [9], the higher is the level of lattice distortions the smaller is the average size of stable crystallites (N is the number of lattice planes within a paracrystallite and g is the relative distance fluctuation between lattice planes). From the experimental D_{hkl} value for PPP before annealing, g values of about 4 to 6% can be derived. If lattice distortions are contributing to the broadening of the reflections, then, according to the α^* relation the D values should be approximately 20% larger than the obtained data. On the other hand, it has been shown that in other polymers the g values remain constant after annealing at high temperature [10]. Consequently one may imagine that the sharpening of the reflections in Figure 3 with increasing T_A could be primarily due to the contribution of lateral crystal thickening. In previous studies it has been demonstrated that the experimental line widths can be fitted by a shape ellipsoid whose mean diameter corresponds to the crystallite size in various directions [11].

Using the data of Figure 4 (top) we have fitted the D values of PPP before and after annealing into an ellipsoid with principal semiaxes X, Y given by:

$$(2/D_{hk0})^2 = (\cos\theta/Y)^2 + (\sin\theta/X)^2 \qquad (1)$$

where θ is the angle between the Y-axis and the [hk0] direction. Table 2 collects the X and Y values calculated according to eq. (1) assuming $X = D_{110}$ and using D_{200} as radius vector. Table 2 also includes the eccentricity Y/X of the ellipsoid as a function of T_A (see Figure 4, bottom).

Figure 5 illustrates the shape ellipsoid (which represents a minimum estimate) for PPP before and after annealing at 500 °C. The observed crystallite size in the [210] direction fits reasonably well with the calculated data using eq. (1) (see Table 2). Figure 4 (bottom) shows the well defined faster increase of the Y/X-value (i.e. an eccentricity decrease) above $T_A \approx 300\,°C$ which parallels the observed increase of D_{hk0} in Figure 4 top and the rapid weight decrease shown in Figure 2.

Finally it is worth mentioning that the X-ray small angle patterns of the investigated PPP show the presence

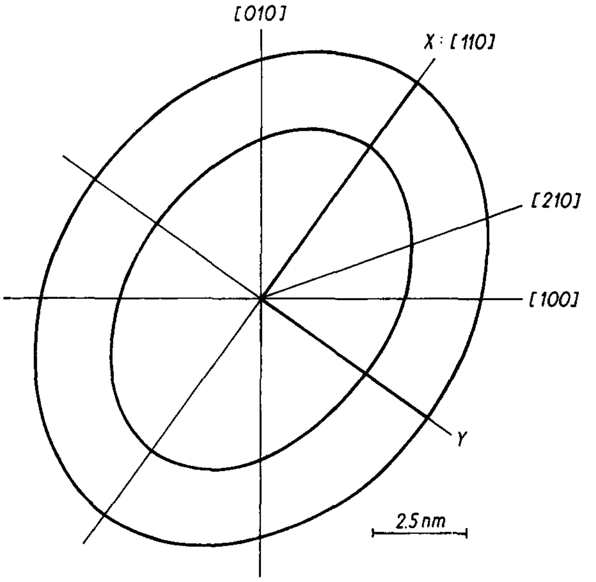

Fig. 5. Shape ellipsoid orthogonal to the $(hk0)$ planes for sintered PPP before and after annealing at $T_A = 500\,°C$

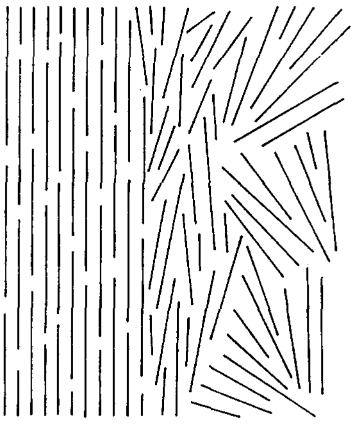

Fig. 6. Sketch of the microstructure of poly(p-phenylene) before annealing showing a segregation of nematic-like ordered regions and disordered material. The straight lines denote the short ($\approx$ 5 nm) rigid chains of PPP

of an intense isotropic diffuse scatter. A Guinier analysis of the scattering profile obtained using a point collimation camera with a resolution of 67 nm was carried out. By assuming cylindrical shaped particles, limiting values of 7 and 28 nm for the smallest and largest particle sizes (diameter), respectively, are obtained. This would imply that PPP particles could consist of aggregates containing from 1 (smallest) up to 7 (largest) crystallites.

From the foregoing the following picture emerges: it is known that the PPP synthesized using the Kovacic method exhibits average molecular lengths of about 10 phenylene units [2]. Since no discrete SAXS maxima are observed for these samples one may infer the occurrence of a predominant nematic structure, which is supported by the observations of Kawaguchi and Petermann [4], contributing to the measured crystallinity of $\approx 40\%$ (Figure 6). Owing to the inherent rigidity of the PPP chains the more or less disordered regions can be visualized as consisting of an irregular packing of bunches of disordered molecular rods.

The annealing treatment at high temperature provokes a weight loss of material, which could be related to the loss of a fraction of low molecular weight species. This substantial loss of material must create a number of microvoids within the polymer and is consistent with the overall density decrease observed. Concurrently crystallinity is slightly improved and the average crystal size values in $[hk0]$ directions are enlarged owing probably to rearrangement of the longer chains from the disordered regions. Such a substantial rearrangement of material at molecular level contributes to the observed eccentricity decrease of the shape ellipsoid leading, as a result, to a more homogeneous shape of the crystals. However, despite the molecular rearrangements undergone by the material at the applied high annealing temperatures, the nematic order prevails and the structure cannot be modified into a better ordered, smectic-like microstructure having a regular chain-end packing.

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