Effect of swelling on the structure of oriented polyamide 6

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The effect of swelling on the structure of polyamide 6 fibres was studied by means of small-angle and wide-angle X-ray scattering. The wide-angle data show that only the amorphous phase undergoes swelling. Changes in the scattering contrast caused by such preferential sorption are in agreement with the increased 'apparent density' of liquids in the amorphous phase. Due to the fact that the increase in the long period corresponds to the amount of the liquid sorbed, swelling is virtually one-dimensional. If there is an interfibrillar non-crystalling phase, its content is very low, or its structure is not accessible to molecules of the swelling agent. The elongation of intrafibrillar amorphous interlayers due to swelling is reflected in changes in the small-angle four-point diagram. The changes suggest that swelling causes narrowing of the distribution of distances between crystallites in fibrils, increases the angle between crystalline layers and the fibre axis and reduce waviness of crystalline–amorphous interfaces.

(Keywords: polyamide 6 fibres; swelling; wide-angle X-ray scattering; small-angle X-ray scattering)

INTRODUCTION

Swelling of polyamide 6, which is accompanied by great changes in its physical and mechanical properties, stimulated an interest in the structural elucidation of this phenomenon. It is assumed that the swelling agent predominantly penetrates into the amorphous phase. Accordingly, two types of swelling have been suggested[1]. The crystalline phase of the polymer is partly affected by swelling of interlamellar amorphous layers, or directly by swelling of the crystalline phase[2–5]. Changes in interlamellar spacings during swelling depend on the preceding annealing[1,2], on molecular orientation[6] and on the type of the swelling agent[7]. Oriented polyamide 6 swells anisotropically[6,7]. The main attention was concentrated on structural changes in the swelling of polyamide 6 in water[1–6,8–11].

To contribute to the knowledge of structural changes occurring in the swelling of polyamide 6, we used wide-angle X-ray scattering (WAXS), small-angle X-ray scattering (SAXS) and density and swelling measurements in an investigation of the effect of five different swelling agents on the crystalline and amorphous phase of the polymer. A one-dimensionally oriented string was used as the specimen, because owing to its anisotropy more structural information can be obtained than with an unoriented system.

EXPERIMENTAL

Samples

A commercial string made from polyamide 6, 1 mm in diameter, was the starting material. The polymer was extracted in water at 50°C for 24 h. After that, the fibres were annealed in an autoclave in water vapour at 100°C and 130°C for 2 h, then dried at 50°C *in vacuo* for 24 h. Three samples having different structure were obtained: the starting sample (ORIG) and the samples annealed at 100° and 130°C.

Swelling and density

The samples were swollen immersed in methyl (MTA), ethyl (ETA), and benzyl (BZA) alcohol, water, and ethyleneglycol (EGL). The starting samples were swollen to equilibrium within three weeks. Annealed samples reached the swelling equilibrium after another four weeks of swelling at 50°C. The degree of swelling was determined by weighing. Annealing and swelling were carried out without stress. The densities of both the dry sample and swollen samples were measured by the flotation method in a gradient column (in a mixture of tetrachloromethane and toluene). Because polyamide 6 absorbed CCl_4 to some degree and flotated samples sank during flotation, the densities were extrapolated to zero immersion time.

X-ray measurements

The fibres were measured dry, swollen, and after repeated drying. Swollen samples were measured in sealed capillaries in the presence of a swelling agent.

Wide-angle data, equatorial and azimuthal scans were obtained on a four-circle Syntex $P2_1$ diffractometer, using Cu radiation monochromatized with a graphite monochromator. The scans were evaluated by profile analysis[12,13].

SAXS photographs were obtained with a Kiessig camera at the sample–film distance 20 cm. Ni-filtered Cu radiation was used. Small-angle four-point diagrams were analysed by means of a Syntex AD 1 autodensitometer and profile analysis[12,13]. SAXS curves of the fibres in the equatorial direction were measured with a Kratky camera. Ni-filtered Cu radiation was used.

Table 1 Swelling of polyamide 6

	T_a (°C)	Swelling agent					
		DRY	MTA	ETA	Water	EGL	BZA
Swelling wt%		100	113	113	110	115	120
Density of fibres (g cm^{-3})	Original	1.137	1.095	1.097	1.141	1.147	1.133
	100	1.148	1.113	1.111	1.148	1.155	1.141
	130	1.153	1.117	1.112	1.152	1.155	1.146
Density of liquid in fibres (d_f)			0.886	0.869	1.116	1.198	1.110
Density of free liquid (d_l)			0.792	0.789	1.000	1.113	1.046
d_f/d_l			1.12	1.10	1.11	1.08	1.06
$\langle(\Delta\rho)^2\rangle$ (mol electrons em^{-3})$^2 10^3$	Original	1.25	2.68	2.44	0.67	0.51	1.04

RESULTS AND DISCUSSION

Swelling and density

The results obtained by swelling and density measurements are summarized in *Table 1*. The degree of swelling depends on the type of liquid and varies in the range 10–20 wt%. The sample densities grow with increasing annealing temperature. The equilibrium degree of swelling does not vary with annealing, unlike swelling in water vapours[1,2]. The reason may consist in a direct contact between liquid and polymer and in an elevated temperature during swelling, in our case. Using the density values of dry and swollen samples and the degree of swelling, and assuming a simple mixing rule, it is shown that the 'apparent density' of the swelling agent in the amorphous phase of fibres is by 6–12 wt% higher, compared with the density of the free liquid. A similar effect has been reported for the swelling of polyamide 6 and polyamide 66 with water[2,8–11].

WAXS

To assess the smallest changes in the crystalline structure of our samples during swelling, the experimental diffracted intensity distributions $I(x)$ were fitted to the sum of baseline and a number of bell-shaped Pearson VII curves $f_i(x)$ which represent crystalline reflections, i.e.

$$I(x) = a + bx + \sum f_i(x)$$

where

$$f(x) = I(x_0)[1 + 2((x - x_0)^2/H_0^2)(2^{1/m} - 1)]^{-m}$$

x is the diffraction angle 2θ, x_0 is the position of the maximum of reflection with the half width H, m is the shape factor.

The profile analysis of an equatorial and azimuthal scan of a starting fibre swollen in ETA are shown in *Figure 1*. Results of the profile analysis allow three groups of structural parameters of the crystalline phase of fibres to be obtained; parameters of the unit cell a and c; apparent crystallite sizes (corrected for instrumental broadening) D_{200}, $D_{002+202}$; and the degree of orientation H_{200} and $H_{002+202}$ characterized by the azimuthal half-breadth of reflections 200 and 202+002. The results are summarized in *Table 2*. The crystal structure of all samples was a pure α modification of polyamide 6 (ref. 14). Structural parameters obtained for a dry sample, samples swollen in five liquids, and samples dried after swelling had the same values in the limits of accuracy of measurement (estimated standard deviations in *Table 2*).
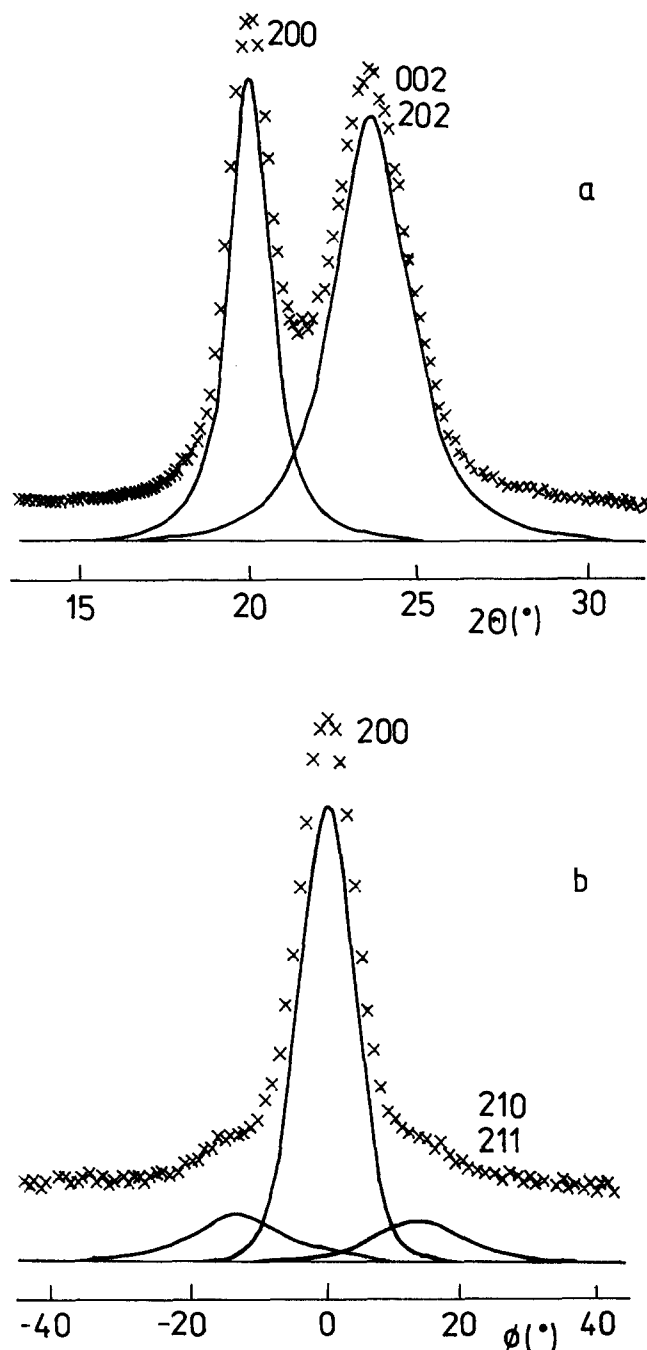

Figure 1 Analysis of WAXS patterns of ORIG polyamide 6 fibres swollen in ETA; (a) equatorial and (b) azimuthal scans. ×, Measured values; ———, profile analysis

Table 2 Structure parameters obtained from wide-angle data. (Estimated standard deviations are given in parentheses and refer to the last decimal positions at respective values)

	T_a (°C)		
	ORIG	100	130
Unit cell, nm			
a	0.957 (3)	0.957 (3)	0.958 (3)
c	0.811 (3)	0.807 (2)	0.804 (1)
Crystal size, nm			
D_{200}	6.3 (3)	7.2 (3)	7.8 (3)
$D_{002+202}$	3.7 (1)	4.5 (1)	4.8 (1)
Orientation (deg)			
H_{200}	9.9 (4)	9.2 (2)	9.1 (4)
$H_{002+202}$	13.0 (5)	12.5 (3)	12.7 (6)
Density (g cm^{-3})			
d_{cr}	1.218	1.225	1.229
Crystallinity (wt%)			
Cr	34	41	44

This fact indicates that the swelling process has a negligible effect on the crystalline phase. Liquids penetrate into the amorphous phase only. Water was reported to have only a weak effect on the crystalline phase of polyamide 6, both with and without diffusion into the crystalline phase[1,3].

Table 2 shows that the density of the crystalline phase is slightly increased by annealing. The parameter c of the unit cell, i.e. the distance between hydrogen-bonded sheets, diminishes, while the parameter a representing the distance between chains linked by hydrogen bonds remains virtually unchanged. The estimated density of the crystalline phase (assuming that the parameters b and β of the unit cell remain unchanged during annealing) increases in the process. Lateral dimensions of the crystallites also increase, and the degree of orientation is slightly higher.

SAXS

Integral intensities. Because density of liquids used in swelling varies in the range 0.8–1.11 g cm^{-3} and differs from that of the amorphous phase of polyamide 6 (1.08 g cm^{-3}) (refs. 15, 16; *Table 1*), diffusion of these liquids into the amorphous phase of the polymer should cause scattering contrast variation in the system. The mean square electron density fluctuation for the two-phase structure of polyamide 6 is given by

$$\langle(\Delta\rho)^2\rangle = v_c v_a (\rho_c - \rho_a)^2$$

where v_c, $v_a = (1 - v_c)$ are the volume fractions and ρ_c, ρ_a are the electron densities of crystalline and amorphous phases respectively. After swelling is the mean electron density of swelled amorphous phase given by

$$\bar{\rho}_a = v'_a \rho_a + v_s \rho_s$$

where v_s ($= 1 - v'_a$) and ρ_s are the volume fraction and the electron density of swelling agent. This change of electron density $\bar{\rho}_a$ should be reflected in the values of $\langle(\Delta\rho)^2\rangle$ for swollen samples.

To reveal this effect, SAXS intensities $\bar{I}_\parallel(h)$ were measured. For fibres with a cylindrical symmetry around the fibre axis, the mean square electron density fluctuation is given by[17,18]

$$\langle(\Delta\rho)^2\rangle = \frac{k}{P_0} \int_0^\infty \bar{I}_\parallel(h) h \, dh$$

where $I_\parallel(h)$ is the intensity measured in a direction perpendicular to the fibre axis in a camera with slit collimation. P_0 is the intensity of the primary beam, $h = (4\pi/\lambda)\sin\theta$ is the magnitude of the scattering vector, λ is the wavelength of radiation, 2θ is the scattering angle. *Figure 2* gives the scattering curves $\bar{I}_\parallel(h)$ of unannealed fibres. In the figure we can clearly see maxima of the four-point diagram, particularly in the case of fibres swollen in alcohols. After subtraction of the constant background caused by statistical fluctuations of electron densities in the phases and WAXS contribution from the scattering curves[19] and using a Lupolene calibration sample the $\langle(\Delta\rho)^2\rangle$ values in absolute units were obtained (*Table 1*).

If swelling of the amorphous phase was determined by the simple mixing rule, the scattering contrast and SAXS intensities should be higher than those of a dry sample for all swollen samples, with the exception of swelling in EGL. The scattering curves on the same scale (*Figure 2*) and the $\langle(\Delta\rho)^2\rangle$ values do not meet this assumption. However, the values obtained indicate a lower scattering contrast, in agreement with the increased 'apparent densities' of swelling agents in the amorphous phase of polyamide 6 (*Table 1*).

Small molecules of swelling agents penetrate into the amorphous phase due to its lower density. Molecules occupy places between polymer chains of polyamide 6, and as a mixture of two components of different shape form a denser system than monodisperse systems consisting of free liquids and the dry amorphous phase, it is assumed that due to their polarity water molecules are coordinated to amide groups[20,21]. A similar situation arises in the case of other swelling agents, because they possess OH groups. The coordination may also contribute to the higher 'apparent density' of swelling agents in the amorphous phase.

Four-point diagrams. SAXS photographs of dry fibres consist of meridional reflections which are very broad in the direction perpendicular to the fibre axis. The position and shape of these reflections, in the meridional direction, gave long period values (Bragg spacing) and integral breadths of reflections β_M. On swelling in MTA, ETA and BZA, meridional reflections changed to a more or less pronounced four-point diagram. We assumed that broad reflections observed with other fibres are degenerated four-point diagrams. By means of profile analysis[12,13] the reflections were resolved into the sum of two
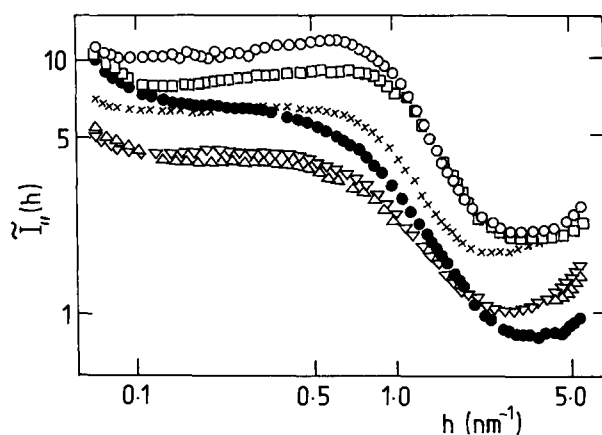

Figure 2 Equatorial SAXS curves of ORIG polyamide 6 fibres (●, Dry; ○, MTA; □, ETA; ▽, water; △, EGL; ×, BZA)

profiles, symmetrically related with respect to the meridian (*Figure 3*). The analysis yielded the transverse integral breadth of the SAXS reflection β_E and the angle ϕ of the four-point diagram (*Figure 4*). Long periods which correspond to the intercrystalline spacing in fibrils, grow with increasing degree of swelling. For all five swelling agents the increase in the long period very closely corresponds to the volume fraction of sorbed liquid (*Table 3*). Hence, swelling is virtually only one-dimensional in the direction of the fibre axis. The anisotropic behaviour was observed with oriented samples of polyamide 6 and polyamide 11 (refs. 6, 7). The predominant part of the liquid is consumed by swelling of the intrafibrillar amorphous phase. If the interfibrillar non-crystalline phase does exist, its content is very low or it has a non-swelling structure. On the basis of SANS and i.r. measurements of hydrated polyamide 6 films, Murthy et al.[1] suggested the existence of two types of amorphous phase, both of which are accessible to the swelling agent.

One-dimensional swelling has as a consequence a considerable expansion of the intrafibrillar amorphous phase in the direction of the fibre axis. A comparison between the degree of swelling and crystallinity determined by means of densities (*Table 1*) gives the maximum value of expansion, about 25%, for fibres swollen in BZA. For a two-dimensionally oriented polyamide 11 swollen in m-cresol the expansion value is 100%[7]. If some intrafibrillar tie molecules are stretched in such oriented systems[22,23] expansion must either cause their scission or pull out the chains from the crystallites. The former possibility is not very likely, because swelling is completely reversible from the structural viewpoint.

Other parameters of the four-point diagrams, i.e. the angle ϕ, the integral breadths β_M and β_E (*Figure 4*) also vary in the one-dimensional swelling. This behaviour reflects changes in the supramolecular fibre structure during swelling, which are largest in the starting
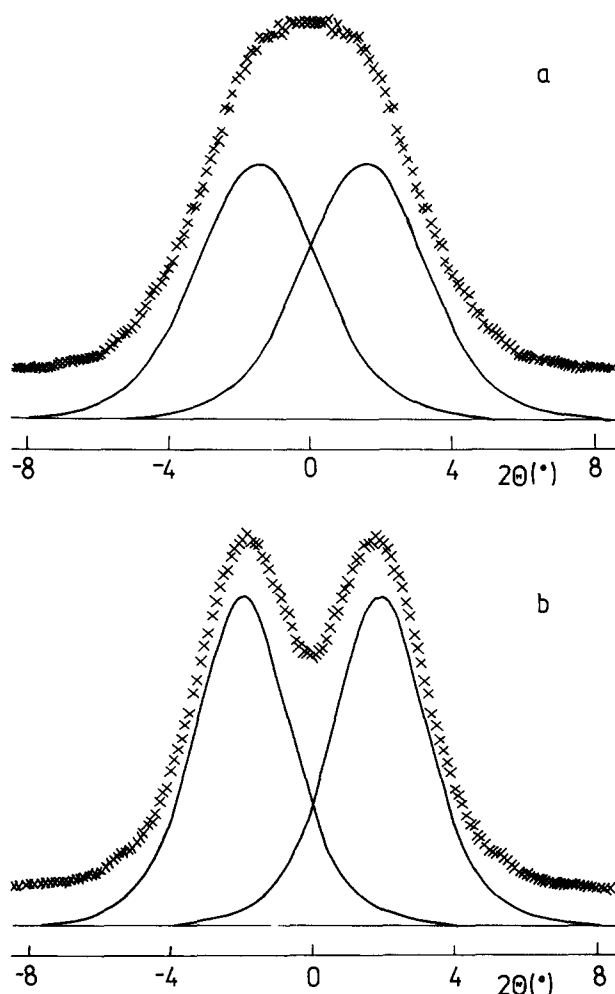
Figure 3 Analysis of SAXS four-point diagrams of (a) ORIG polyamide 6 fibres DRY and (b) fibres swollen in MTA. ×, Measured values; ———, profile analysis
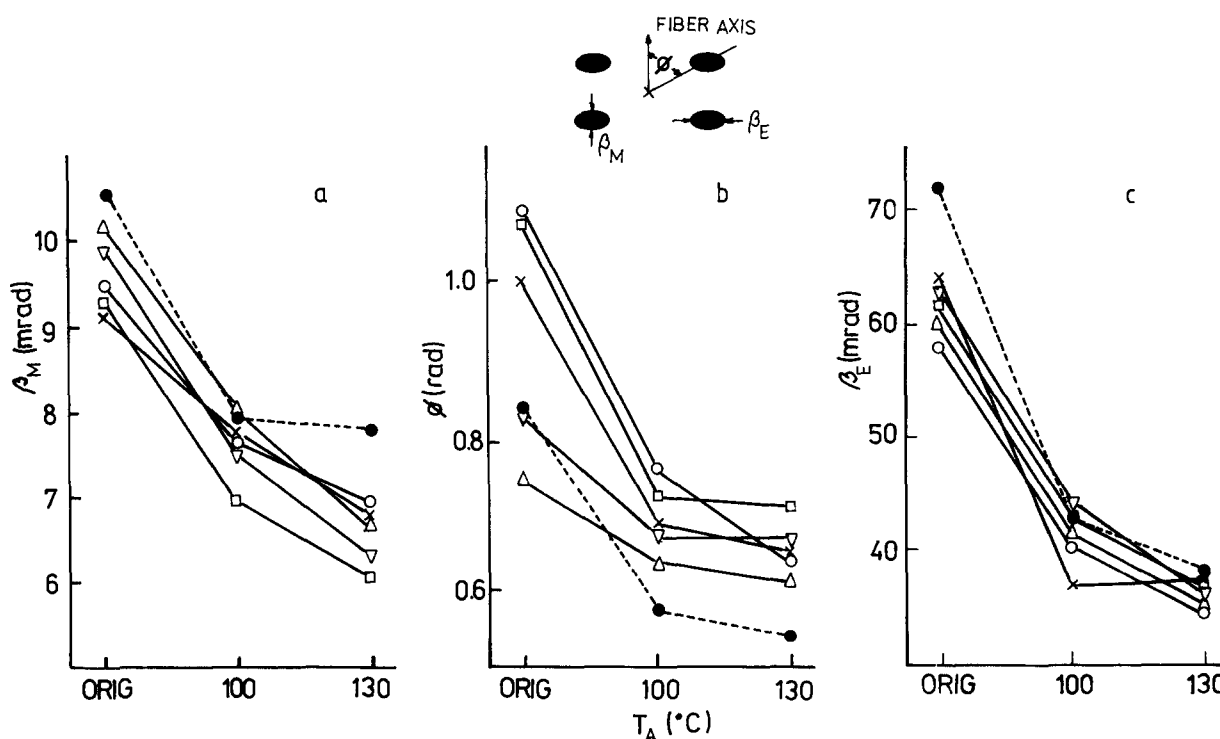
Figure 4 Changes of four-point diagram parameters (a) β_M; (b), ϕ; and (c) β_E with annealing and swelling (●, DRY; ○, MTA; □, ETA; ▽, Water; △, EGL; ×, BZA)

Table 3 Changes of long periods with annealing and swelling

Swelling agent	T_a (°C)	Degree of swelling (vol%)	Long period L (nm)	$L_{Swollen}/L_{Dry}$
Dry	ORIG		7.4	1.00
	100	100	8.3	1.00
	130		9.1	1.00
MTA	ORIG		8.7	1.18
	100	117	9.6	1.15
	130		10.5	1.15
ETA	ORIG		8.8	1.20
	100	117	9.9	1.19
	130		10.5	1.17
Water	ORIG		8.1	1.10
	100	110	9.2	1.10
	130		9.9	1.10
EGL	ORIG		7.9	1.08
	100	114	9.2	1.10
	130		9.9	1.10
BZA	ORIG		8.8	1.20
	100	120	9.9	1.19
	130		10.5	1.16

unannealed samples and decrease with increasing temperature of annealing. The magnitude of the changes depends on the degree of swelling.

For a well oriented supramolecular structure the integral breadth of the SAXS reflection in the direction of the fibre axis (meridian) can be expressed through[16,24]

$$\beta_M = (\lambda/L)[N^{-2} + (n\,\delta L/L)^2 + n\pi g_M]^{1/2}$$

where N is the weight average number of scattering particles in the macrolattice, $\delta L/L$ is the interlattice fluctuation of L, g_M is the paracrystalline factor of the macrolattice in the direction of the fibre axis, and n is the order of reflection. Hence, β_M depends on the density and on the distance distribution of scattering centres (crystallites) in the direction of the fibre axis. With all swollen fibres this value is lower than with dry samples (*Figure 4a*). Due to the fact that the number of crystallites remains unchanged during swelling, the latter improves the distribution of intercrystallite distances in the fibrils.

The transverse breadth of the SAXS reflexion is given by[16,24]

$$\beta_E = \lambda[D^{-2} + (nkg_E)^4]^{1/2} + (n\lambda \sin \phi)/L$$

where D is the mean diameter of the fibrils, g_E is the paracrystalline coefficient proportional to the curvature or waviness of crystalline amorphous interfaces in the direction perpendicular to the fibre axis and k is a constant. The latter term is related to the angle ϕ of the four-point diagram (*Figure 4*).

The transversal width of the SAXS reflexion β_E in swollen samples is smaller than in dry ones (*Figure 4c*). Due to the fact that during swelling the cross-section of fibrils D_{200}, $D_{002+202}$ (*Table 2*) remains unchanged, the decrease in β_E is due to a smaller waviness in paracrystalline layers of the crystallites.

The angle ϕ of the four-point diagram which is given by the mean tilt of supramolecular layers consisting of crystallites in neighbouring fibrils has high values in the case of fibres swollen in alcohols (*Figure 4b*). This behaviour is given by the higher degree of swelling in alcohols compared with water and EGL. The one-dimensional elongation of amorphous interlayers is not homogeneous along the fibrils. It should be caused by

local intra- and interfibrillar stresses. Amorphous interlayers of various thicknesses could have a partially different structure, which is not equally accessible to molecules of swelling agents. This is demonstrated not only in the narrowing of the distribution of intercrystallite distances in the fibrils and reduction of waviness of crystalline amorphous interfaces, but also by growing in the tilt of crystallite layers with increasing degree of swelling.

Changes in the four-point diagrams of dry samples during annealing suggest a behaviour of the supramolecular structure similar to that observed in swelling (*Figure 4*). The effect of swelling on the supramolecular structure of fibres of annealed samples is similar to that found with the unannealed samples, only the range of changes of the structure parameters is smaller. The structure of annealed samples is better developed, and thus much more resistant to swelling.

CONCLUSIONS

It was shown that in the structure of oriented polyamide 6 fibres the swelling agents diffuse only into the intrafibrillar amorphous phase. The crystallites remain unchanged during swelling. Expansion of the amorphous phase only in the direction of the fibre axis increases the mean intercrystallite spacing in fibrils and causes mutual sliding of the latter. This behaviour is reflected in the changed tilt of crystalline layers, in the decreased waviness of crystal–amorphous interfaces and in a narrower distribution of intercrystallite distances in fibrils.

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