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Small angle X-ray scattering in nylon 6 using exponential distribution of phase lengths

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Abstract

The experimental variation of scattered intensity of angles from 0.3 to 2.5° from modified nylon 6 samples has been compared with that obtained by the linear paracrystalline model when the distribution of phase lengths was given by the exponential function and the quantitative parameters describing the changes in morphology have been reported.

Keywords: Nylon 6; Linear paracrystalline model; Quasi-periodic alternation of electron density

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1. Introduction

Quasi-periodic alternation of electron density in polymer fibres has been investigated by using small angle X-ray scattering studies [1,2]. It is also now well established that the structure contains stacks in which crystalline lamellae are separated by less dense regions. Hosemann and Bagchi [3] have obtained the following relations:

$$I_B(s) = \frac{\Delta\rho^2 N}{(2\pi s)^2}\left\{\frac{|1-H_y|^2(1-|J_z|^2)+|1-J_z|^2(1-|H_y|^2)}{|1-H_yJ_z|^2}\right\} \tag{1a}$$

$$I_c(s) = \frac{\Delta\rho^2}{2(\pi s)^2}\,\mathrm{Re}\left\{\frac{J_z(1-H_y)^2(1-(H_yJ_z)^N)}{(1-H_yJ_z)^2}\right\} \tag{1b}$$

$$I(s) = I_B(s) + I_c(s) \tag{1c}$$

where $I(s)$ is the intensity of scattering by such a paracrystal entity described above as a function of s ($s = 2\sin\theta/\lambda$), where 2θ is the scattering angle and λ the wavelength of the radiation. (H_y, J_z) is the Fourier transforms of the normalized distribution function of the lengths of the units of the two phases. N is the number of repeating units in the paracrystal and $\Delta\rho$ the difference between the electron densities of the phases.

In the present work, Eq. (1) is developed into a form, which is easier to compute in terms of exponential distribution function for the two phase lengths in polymer fibres.

2. Theory

It has been shown by Hall et al. [4,5], that Eq. (1) can be reduced to

$$\frac{2I(\pi s)^2}{\Delta\rho^2} = \frac{C}{F} + \frac{D+E}{F^2} \tag{2a}$$

where

$$F = 1 + A^2B^2 - 2AB\cos X \tag{2b}$$

$$C = N\{1 - A^2B^2 - A(1-B^2)\cos\phi - B(1-A^2)\cos\chi\} \tag{2c}$$

$$D = B[(1-A^2)(1-A^2B^2)\sin X\sin\phi + \{(1+A^2B^2)\cos X - 2AB\}\{(1+A^2)\cos\phi - 2A\}]/G \tag{2d}$$

$$G = 1 - A^NB^N\cos NX \tag{2e}$$

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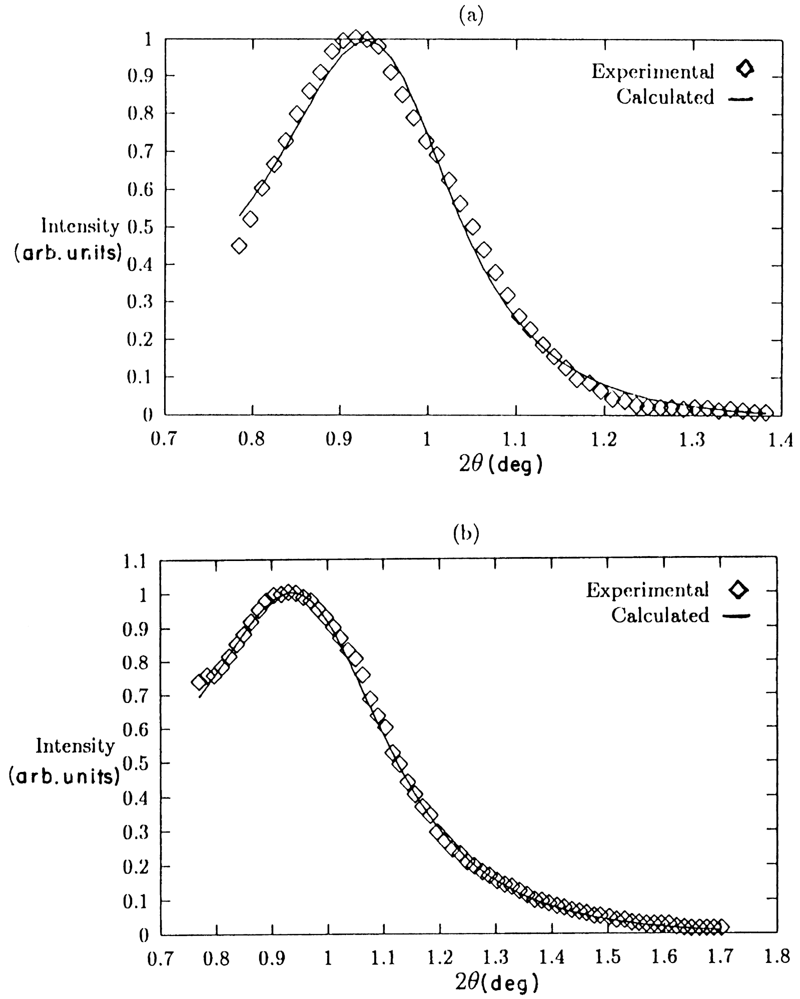

Fig. 1. (a)–(d) The goodness of fit between experimental and calculated small angle X-ray scattering curve for iodinated nylon 6 film at various stages of iodine desorption.

$$E = A^N B^{N+1} \sin NX[(1 - A^2B^2)\{(1 + A^2)\cos\phi - 2A\}\sin X - (1 - A^2)\{(1 + A^2B^2)\cos X - 2AB\}\sin\phi] \tag{2f}$$

By taking

$$H_y = A\exp(-\mathrm{i}\chi) \tag{3a}$$

$$J_z = B\exp(-\mathrm{i}\phi) \tag{3b}$$

and

$$X = \chi + \phi \tag{3c}$$

and simplifying Eq. (1). We have used an exponential distribution function, for the phase lengths, because it gave fairly reliable results in WAXS study of polymer fibres [6]. The normalized exponential distribution function is given by

$$h(x) = \alpha\exp(-\alpha(x - \epsilon)) \tag{4}$$

where $\alpha = 1/2\gamma\langle Y\rangle$; $\epsilon = \langle Y\rangle(1 - 2\gamma)$. γ is a parameter controlling both the skew and the dispersion of the distribution and $\epsilon = \langle Y\rangle(1 - 2\gamma)$. Provided $0 < \gamma < 0.5$, lengths less than ϵ are not possible, since this would cause $h(x)$ to be negative. By taking the Fourier transform of this function (4), we get

$$A = \frac{1}{(1 + 4s^2\gamma_y^2Y^2)^{1/2}} \tag{5}$$

$$\chi = s\epsilon_y + \cos^{-1}\left[\frac{1}{(1 + 4s^2\gamma_y^2Y^2)^{1/2}}\right] \tag{6}$$

similar equations for B and ϕ are given by

$$B = \frac{1}{(1 + 4s^2\gamma_z^2Z^2)^{1/2}} \tag{7}$$

$$\phi = s\epsilon_z + \cos^{-1}\left[\frac{1}{(1 + 4s^2\gamma_z^2Z^2)^{1/2}}\right] \tag{8}$$

Thus with the exponential distribution for each phase, we

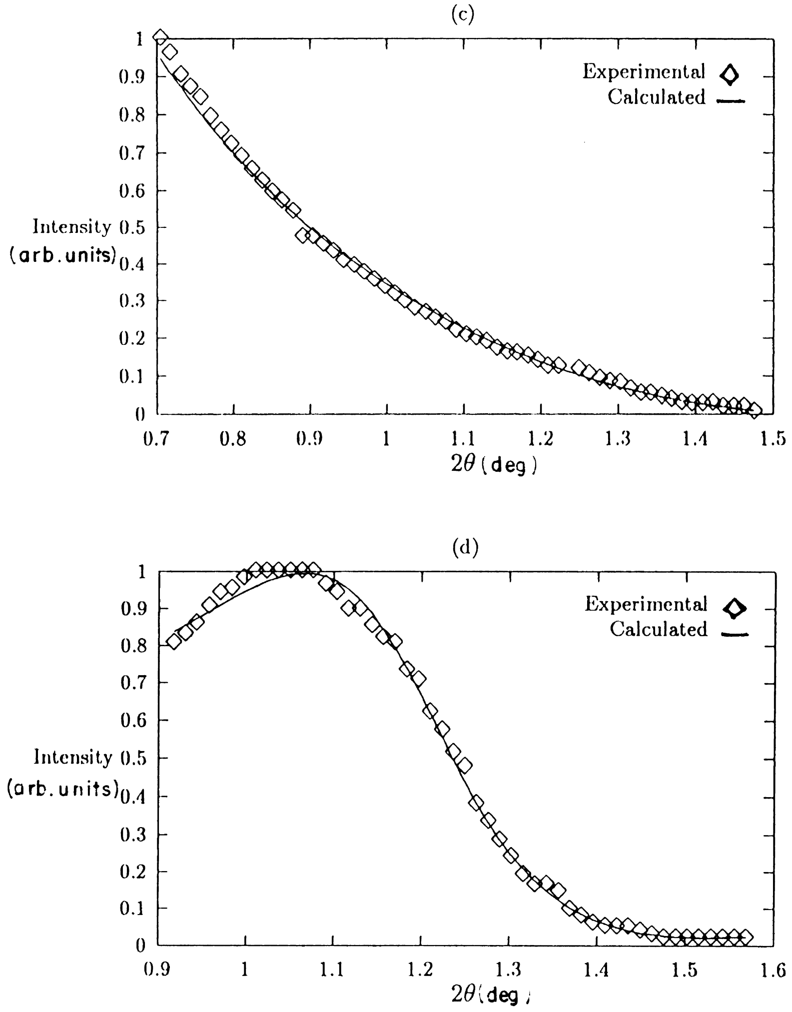

Fig. 1. (*continued*)

have A, B, χ, and ϕ which can be used in Eq. (2) and the intensity can be calculated as a function of s using the parameters describing the distribution. Here, suffices y and z refer to two phases present in the polymers.

3. Analysis

To test the above model, we have used small angle X-ray scattering curves of uniaxially oriented iodinated nylon 6 film at various stages of iodine desorption [7].

From Eqs. (2), (5) and (6) the intensity distribution of a function of five variables, the periodicity $(\langle Y\rangle + \langle Z\rangle)$ where $\langle Y\rangle$ and $\langle Z\rangle$ are the mean lengths of the two phases, the phase ratio $(\langle Y\rangle/\langle Y\rangle + \langle Z\rangle)$, the two parameters defining the widths of the distribution functions of the lengths of the phases can be obtained; and N is the number of units in the paracrystal. To find the combinations of these which, for an exponential distribution function, will give the best fit to the experimental data, a stepping refinement procedure minimising the sum of χ^2 over all data points was used.

4. Results and discussion

Best fit was obtained with an exponential distribution function for all the samples and is shown in Fig. 1(a)–(d). There is a good fit to the experimental data for scattering angles (2θ) between 0.5 and 1.5°. Fig. 2 shows the exponential probability distribution functions of the lengths of the phases (crystalline and amorphous) for this model. These plots (Fig. 2) are obtained by using the model parameters given in Table 1 using Eq. (4) for the two phases Y and Z. These figures bring out the corresponding changes in the distribution of phase lengths in the three samples with meridional reflection for various amount of iodine desorption. It is observed that there are changes in width and shape of these functions for various stages of iodine desorption. The best computed model parameters for the nylon 6 treated samples are given in Table 1. The widths of these distribution increases with increase in iodine desorption. Nylon 6 washed with aqueous sodium thiosulfate for the duration of 27 min and an 8 h exposure to air does not show a discrete meridional reflection, but the intensity decreases with the

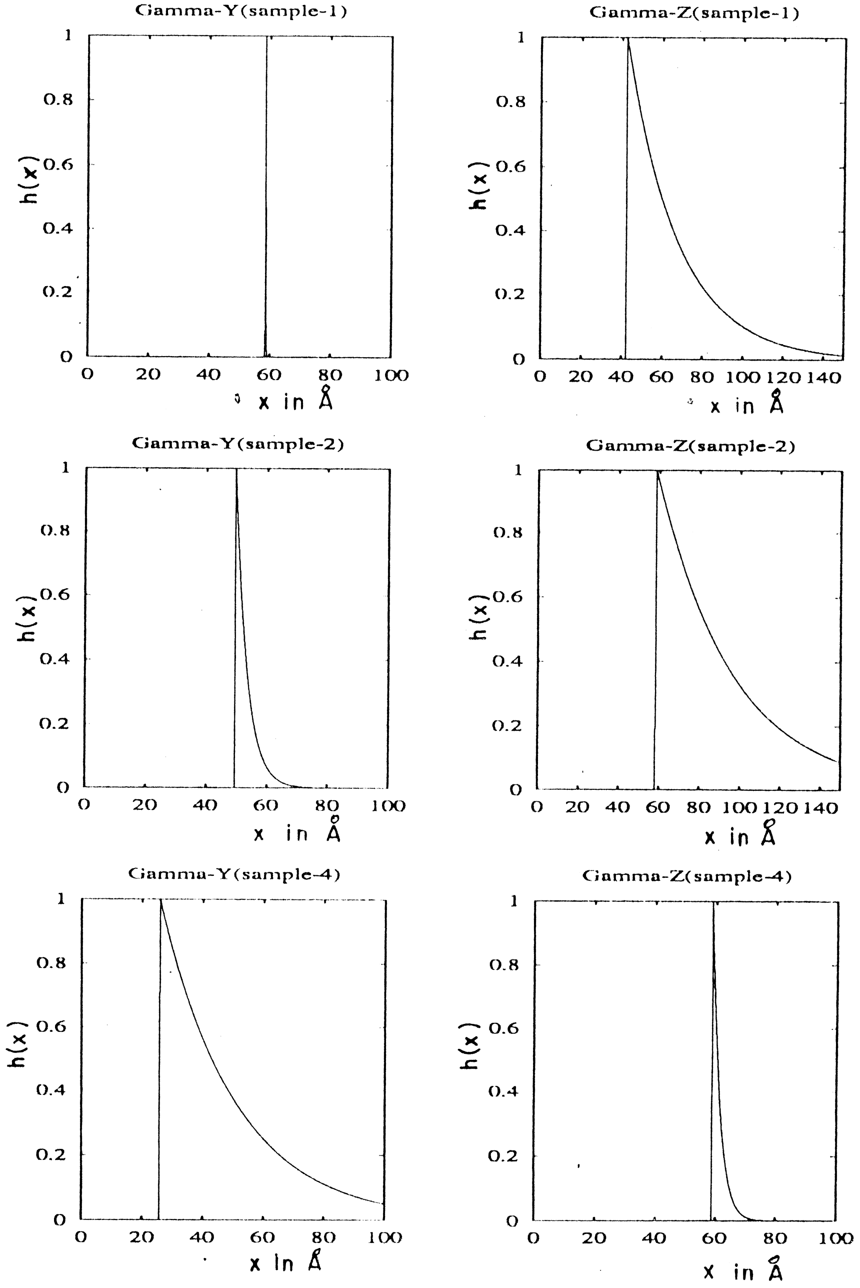

Fig. 2. The exponential probability distribution functions of lengths of the phases *Y* and *Z* for iodine desorption.

scattering angle (see Fig. 1(c)). The linear paracrystalline model used here gives a good fit with modelling parameters $\langle Y \rangle$ and $\langle Z \rangle$ of the two phase lengths. The reason for not obtaining the γ parameters for phases *Y* and *Z* is due to the absence of a discrete meridional reflection, which indicates irregular distribution of these phases and hence the parameter which controls the dispersion of the distribution of these phases becomes greater than 0.5 leading to the negative behaviour of $h(x)$. In such cases the refinement is carried out only with respect to the phase lengths $\langle Y \rangle$ and $\langle Z \rangle$ and not the parameter which controls the dispersion of the distribution.

Physically the abrupt change in distribution function indicates that the smallest crystallite/amorphous region is given by the peak position value. In the absence of proper identification of the distribution functions associated with crystalline/amorphous phase length, we can at best here mention that the observed variation in width of the distribution function of phase lengths is due to change in shape of the electron density profile across the lamellae along the chain axis.

5. Conclusion

A good fit to the distribution of intensity along the

Table 1
Values of morphological parameters for uniaxially oriented iodinated Nylon 6 film at various stages of iodine desorption

Sample	Periodicity (Å)	Phase ratio	γ_y	γ_z	$\langle Y \rangle$ (Å)	$\langle Z \rangle$ (Å)
Nylon 6 5 min in KI/I_2	101	0.58	0.001	0.299	58.58	42.25
Nylon 6 wash 2 min	107.82	0.46	0.039	0.322	49.57	58.25
Nylon 6 wash 27 min dry 8 h	90.12	0.61	–	–	55.17	34.95
Nylon 6 wash 60 min dry 20 h	84.54	0.31	0.480	0.022	25.75	58.79

meridian of the SAXS pattern of nylon 6 samples at various stages of iodine desorption has been obtained with a linear paracrystalline model whose phase lengths have an exponential distribution function. The various stages of iodine desorption is well indicated at the microscopic level in terms of the changes in the width of the distribution functions as well as in terms of mean periodicity.

It is well known that I_5^- ion columns play a significant role in twisting the amide groups out of the CH_3 plane leading to the formation of the γ form upon removal of iodine. During the course of these changes, the lamellar crystalline regions in nylon 6 gets modulated due to the presence of $K^+I_3^-$ and these changes are quantified in terms of the phase length and phase distribution.

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