Superstructural ordering in oriented nylon 66 film *

In this note we report the results of an electron microscopic examination of the surfaces of oriented nylon 66 (polyhexamethylene adipamide) films combined with a small-angle light scattering (SALS) examination of their supermolecular structure.

The commercial nylon 66 film (Du Pont of Canada Ltd) was already slightly oriented in the machine direction and so samples to be deformed were always cut parallel to this direction. The film was briefly washed with acetone to remove surface contaminants before microscopic examination. A Cambridge Mk IIa scanning electron microscope (SEM) was used for most of the microscopy work, although some surface replicas (using Formvar, then shadowing at $30°$ with platinum–carbon) were prepared for transmission electron microscopy (TEM). SALS patterns were obtained using a He–Ne laser essentially as described by Rhodes and Stein [1]. Film samples were further characterized by optical microscopy, wide-angle X-ray diffraction (WAXS) and density measurements [2] (hexane/carbon tetrachloride column). Room temperature drawing took place on an Instron Tensile tester, at $23°$ C, 65% r.h. and 10% min^{-1}, or in the light scattering apparatus on a small mechanical stretcher. Draw ratios were calculated from calibration marks on the film. Film samples were also hot drawn at 1500% min^{-1} in a silicone oil bath.

The results of the characterization of the undrawn film are shown in Fig. 1. SALS (Fig. 1a) showed that the average spherulite diameter [3] was about 4 μm while optical and electron microscopy (Figs. 1b to d) showed that the range of spherulite diameters was from 10 μm to <1 μm. WAXS analysis (not shown) indicated that the crystalline component was unoriented, although the film was slightly bi-refringent ($\Delta n \sim 5 \times 10^{-3}$) indicating that some amorphous orientation was present. The density of the undrawn film was 1.1315 $g\,cm^{-3}$.

The SALS characteristics of the deformed film were examined in some detail. During room temperature drawing the original four-lobe pattern (Fig. 1a) decreased appreciably in intensity with the scattering maxima moving to a slightly higher azimuthal angle. At about 2 × elongation a new four-lobe pattern at low ($\sim 30°$) azimuthal angle became visible (Fig. 2a). Also present (barely visible in Fig. 2a) were faint equatorial streaks. On continued drawing the azimuthal angle of the maxima of the new four-lobe pattern increased and the equatorial streaks increased in intensity. At elongations approaching break, another four-point pattern was introduced at very low azimuthal angle ($\sim 10°$). This corresponded to the onset of void formation. On hot drawing, similar SALS patterns were produced although their corresponding elongations were, of course, different from the cold-drawn samples. A typical pattern (drawn 3 × at $230°$ C) is shown in Fig. 2b, where a four-lobe pattern (azimuth of maximum intensity $\sim 35°$) together with equatorial streaking, is apparent. The V_v SALS patterns (not shown) consisted of an equatorial streak and this pattern did not vary greatly with the draw conditions used. The SALS patterns were little changed by annealing the drawn film with fixed ends in boiling water, or by swelling with aqueous phenol implying that the patterns were not the result of frozen-in strain in the film, but corresponded to discrete superstructural entities.

During room temperature drawing the film density varied very little (at 2 × draw $\rho = 1.130$ g cm^{-3}). WAXS analysis indicated that progressive crystalline orientation occurred with increasing draw. For example, for the 2 × room temperature drawn film, the azimuthal width at half height of the two major equatorial WAXS reflections was about $20°$.

SEM examination of the 2 × drawn film (Figs. 3a and b) demonstrated that shallow ellipsoidal features were present, typically with major axis (corresponding to the transverse direction) dimensions of about 8 μm and minor axis (corresponding to the draw direction) dimensions of about 5 μm. Note that the sample shown in Fig. 3 was appreciably tilted with respect to the electron beam to produce adequate contrast for the shallow surface features and this was allowed for in the calculation of dimensions. It should also be noted that the transverse direction of the film was aligned perpendicular to the sample-to-detector direction, with
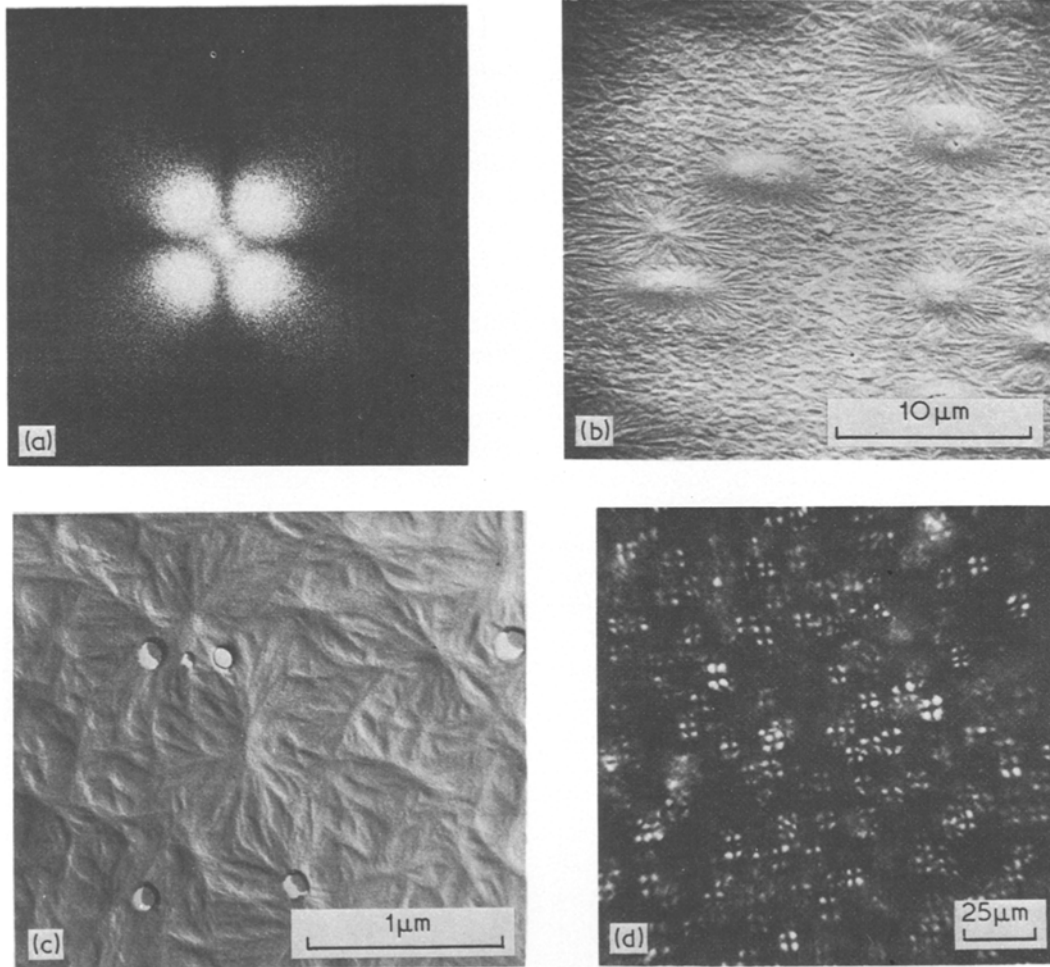
Figure 1 Characterization of undrawn film. (a) SALS; (b) SEM, tilt angle 45° (i.e. foreshortened); (c) TEM; (d) optical microscopy with crossed polars.

the result that contrast (and hence visibility) of features oriented in the transverse direction was enhanced. Rotation in the plane of the film enhanced contrast in other directions, so that fibrillar elements oriented parallel to the draw direction could be clearly seen when the film was rotated (photographs not shown). The samples were examined over a wide range of tilt and rotation angles to confirm the validity of the observed features. At higher magnifications (SEM and TEM) no fine structure was visible, possibly because the features being examined were obscured by a featureless surface layer.

The theoretically predicted H_v SALS pattern of an anisotropic prolate spheroid, with dimensions $8 \mu m \times 5 \mu m$ (as shown in Figs. 3a and b), in an isotropic medium, calculated by the method of Samuels [3], is shown in Fig. 3c. Agreement with the observed SALS pattern in Fig. 2a is quite good, implying that the ellipsoidal features shown by microscopy might correspond to the super-structure responsible for the meridional lobes of the SALS pattern. The observation of equatorial streaks in the SALS patterns (Fig. 2) is consistent [3] with the microscopic observation that fibrillar elements are also present in the film.

Thus, a commerical film of nylon 66 has been shown to exhibit complex SALS patterns when deformed. Similar observations of eight-, or even twelve-lobe patterns have been made with poly-ethylene terephthalate (PET) [4, 5], poly(ϵ-caprolactam) [5, 6], polyvinylidene fluoride [7]
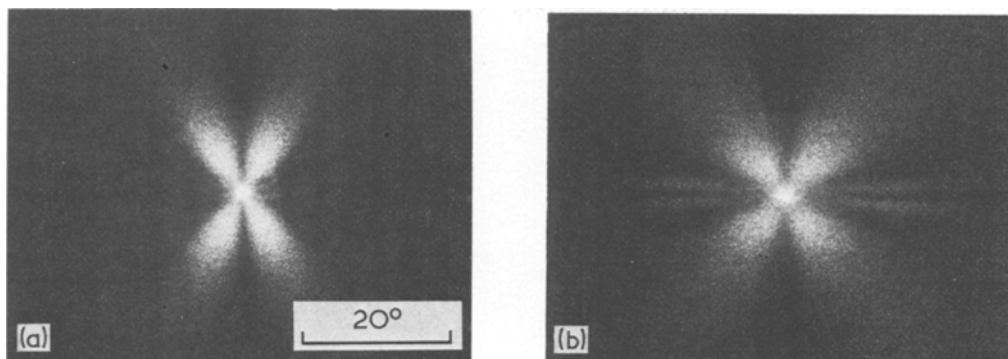
Figure 2 H_v patterns from deformed nylon 66 films, draw direction vertical. (a) 2 × at 23° C; (b) 3 × at 230° C.
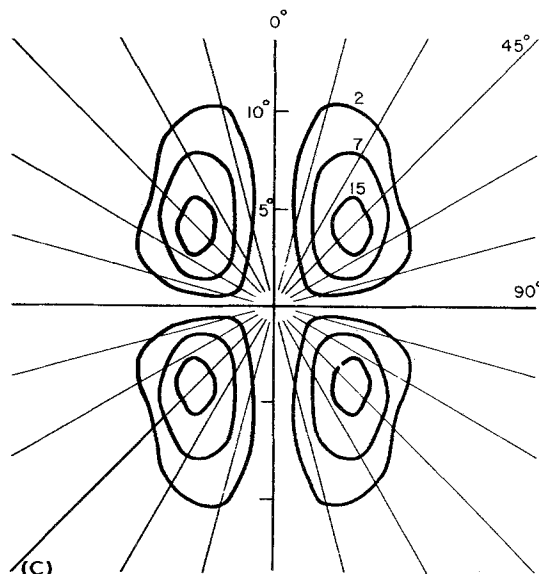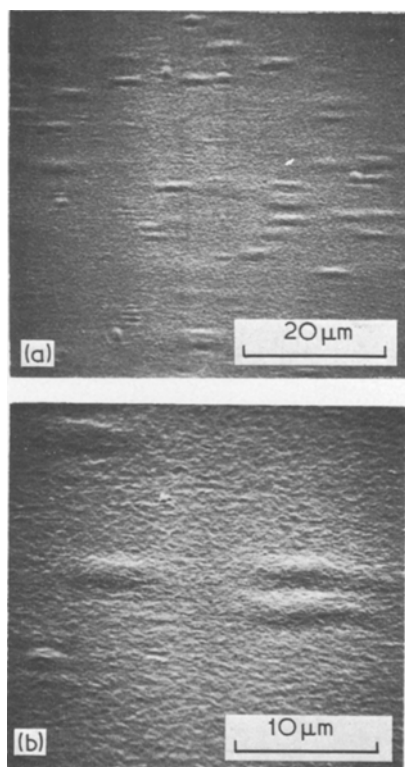

Figure 3 2 × drawn (23° C) film, draw direction vertical. (a) and (b) SEM, sample tilted at 65°; (c) predicted H_v pattern by Samuels method [3], for 5 μm × 8 μm spherulites. Figures on contour lines represent relative intensities.

and some polyethylene samples [8]. This behaviour is, however, quite different from that generally found for spherulitic polyethylene and polypropylene samples where the initially symmetrical four-lobe pattern elongates perpendicular to the deformation direction consistent with the spherulites becoming elongated parallel to the draw direction [3, 9].

The structural significance of the complex SALS patterns displayed by the drawn samples, particularly the four lobes at low azimuthal angles, is unclear. For PET, a model has been proposed in-volving the production of spherulites elongated perpendicular to the draw direction [10]. These spherulites were suggested to result from crystallization on fibrillar nuclei. For nylon 6, low density polyethylene and polyvinylidene fluoride, where the polymer is spherulitic even in the un-deformed state, it has been proposed [6–8] that internal reorganization of the lamellae within the spherulites is responsible for the multi-lobed H_v pattern, with elongation of the spherulites taking place parallel to the deformation direction. The microscopic evidence produced here favours the interpretation that for nylon 66 discrete super-

structural units, elongated perpendicular to the draw direction, are the features responsible for the four-lobed pattern at low aximuthal angle.

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Comments on "New compound in the system La—Si—O—N"

In a recent note [1], the "discovery" of the apatite phase $La_5(SiO_4)_3N$ was disclosed. Not, unfortunately, for the first time, as a variety of rare earth nitrogen apatites have been announced before [2]. It is considered that the authors are mistaken in suggesting that the formula $La_5(SiO_4)_3N$ should be thus written to show the similarity to the isotypic $Ca_5(PO_4)_3F$. It can readily be shown that the site occupied by F in fluorapatite is a low bonded site (with a valence sum of 1 by Pauling's second crystal rule) which is why the crystal is stable with F (or (OH) or Cl) in this position. The equivalent site in $La_5(SiO_4)_3N$ has a valence bond sum of 1.29 to 1.50, depending on the exact method of calculation [3]. Sites in the silicon tetrahedra have values or 2.33 to 2.60, again depending slightly on method of calculation. Recent work [4, 5] has shown that bond sum calculation in oxides (and by extension oxynitrides) can be made rather exact, for example, they work precisely in apatites [3] but lacking accurate bond-length/bond-strength values for M—N bonds we can only use approximate Pauling type values. Nevertheless, it is clear that the N

atoms in these apatites *all* go to the silicon tetrahedra sites. Oxygen* or vacancies are to found at the F sites and vacancies at the low bonded sites can, of course, readily explain the excess of nitrogen atoms at the silicon tetrahedra sites and, indeed, stabilize the structure. Limiting cases would be represented by the formulae:

$$La_5(SiO_{3.67}N_{0.33})_3\,O - La_5(SiO_3N)_3\,\square$$
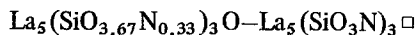
The formula type given by the authors is not based upon normal crystallographic rules as understood to apply in the multitude of substituted mineral structures that have been studied.

The citation of Morgan [6] implies that the compound had been overlooked in that work; in fact we knew of reference [2]. Our study was concerned with the crystallography of $CeSiO_2N$ using, not results obtained by us, but taking the data of Wills *et al.* [7]. We suggested [6] that $LaSiO_2N$ existed and was present in the X-ray data of [8]; in addition an examination of the X-ray patterns in [8], those of "$Si_3N_4\cdot La_2O_3$" and "$La_4Si_2O_7N_2$", suggests that, not only was $LaSiO_2N$ present in the seeming mixtures [6], but also many of the *d*-values of the apatite "$La_5(SiO_4)_3N$" as published in [1] appear, so that the compound under discussion was also present.

*Several rare earth mineral apatites with O at the low bonded sites are well known.