of carbon. At present, we have no data on the thermal decomposition of the Li-mont–NA complex at higher temperatures. Considering the phenomenum reported in this letter, it seems that it would be possible to prepare a layer-type complex of clay and carbon.

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Small-angle X-ray scattering from polybutene-1 films crystallized from a highly extended melt

In an experimental analogue to many industrial processes, Petermann and Gohil [1] have produced very thin (0.1–0.2 micron) polymer films under elongational strain rates of more than 10^4sec^{-1}. The microstructure of these films is thus of considerable technological importance. As is the case in most materials science research, it is essential to characterize such films with a variety of physical techniques. These films are sufficiently thin to permit transmission electron microscopy (TEM), and the results of such an investigation have been reported previously [1]. In this companion paper, we present results of a small-angle X-ray scattering (SAXS) investigation of the same films.

Phase contrast TEM micrographs of polybutene-1 (PB-1) show a fibrous microstructure with the fibrils oriented along the draw direction [1]. (See [2] for a description of the method). The chain and fibril axes coincide. The fibril spacing is approximately 200 Å, while the fibril diameter is approximately 100 Å. No lamellar overgrowths on the fibrils were observed for any annealing conditions.

Dark-field ($h\,k\,0$) TEM micrographs, also shown in [1], reveal an alternating dark–light contrast along the fibrils. The mean periodicity of this contrast is ~ 300 Å. Whether this dark–light contrast reflects an orientation or a density variation cannot be determined from TEM alone. In the present work, SAXS was used to study the same films. SAXS is sensitive only to electron density fluctuations, and hence should be useful in identifying the nature of the dark-field contrast alternation along the fibrils. The method also provides a quantitative evaluation of fibril dimensions.

PB-1 materials were supplied by Chemische Werke Marl. Four materials, of viscosity average molecular weights 5.54×10^5, 8.02×10^5, 10.32×10^5 and 30.0×10^5, were used. Films, approximately 1000 Å thick and 5 cm wide, were prepared by drawing from a molten film on a microscope slide held at 132° C as described in [1]. Adhesion of the film to the slide causes the drawing region to be highly localized.

The experiments were performed using the ORNL 10-m SAXS camera [3]. This instrument includes a 6 kW rotating anode X-ray source (CuKα radiation), a graphite monochromator, pinhole collimation and a two-dimensional position sensitive proportional counter. Data were collected using the instrument in its highest resolution geometry, with a specimen-to-detector distance of 5.15 m and an angular resolution of approximately 0.5 mrad.

The most useful information available from SAXS from these specimens relates to (1) density modulation along the fibre direction and (2) the diameters of the fibrillar units. As we already know the approximate diameters of the fibrils from the TEM investigation, the principal atten-

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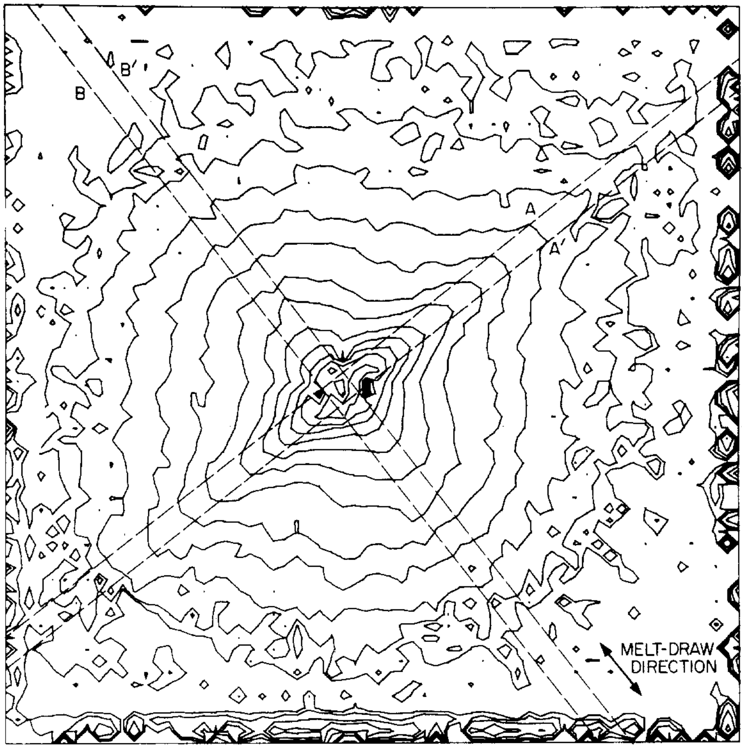

Figure 1 SAXS contour plot for PB-1 film of molecular weight 802 000. Contour levels are stepped by factors of 2^n with an initial contour level of 16. The direction of melt-draw is indicated by an arrow. Double dashed lines AA′ and BB′ indicate the paths used in the one-dimensional traces shown in Figs. 2 and 3.

tion of this note focuses on the SAXS intensity profiles in the fibre direction.

Fig. 1 is a typical SAXS contour plot. Appropriate corrections for instrumental background and detector sensitivity have been made. The melt-draw direction is indicated by an arrow. The pattern is characterized by a narrow streak normal to the draw direction and a broader streak parallel to the draw direction. Materials of all four molecular weights exhibited qualitatively similar patterns. The absence of microvoids, as determined by TEM, rules out that source of scattering. Hence, the streak normal to the draw direction arises from the density variation between the fibrils and the regions separating them. The scattering component parallel to the draw direction evidences electron density variations in that direction.

Fig. 2 shows intensity traces along paths BB′ (see Fig. 1), parallel to the melt-draw direction. The data are plotted as log(intensity) versus ϵ^2 (Guinier plot), where ϵ is the scattering angle. In this format independent scattering units must produce curves which are monotonically decreasing with angle and can exhibit no humps or plateaus. The two low molecular weight materials both show humps in the Guinier plots, manifesting a dense or somewhat ordered packing of regions of similar density. To a first approximation, Bragg's law can be used to obtain the periodicity of packing along the fibre direction for those materials. This simple analysis yields spacings of 330 and 210 Å for the 5.54×10^5 and 8.02×10^5 molecular weight materials, respectively.

There is a molecular weight dependence in the intensity levels of the curves in Fig. 2; the intensity is controlled primarily by the mean square deviation of local density along the fibril.

A Guinier analysis of the streak normal to the axis was used to test the quantitative correspondence between the TEM and SAXS results. For independent circular rods the initial slope S_1 of the Guinier plot can be used to compute the diameter D of the fibril (rod). Here D is $(2000\,\lambda/\pi)(2.303\,S_1/2)^{1/2}$, where λ is the X-ray wavelength [4]. Fig. 3 is a trace along AA′ of Fig. 1. The scattering shows an initial region (I) of very large slope, followed by a region (II) of considerably smaller slope. The curve finally tails off into a region (III) of constant intensity. This last scattering is taken to represent thermal diffuse scattering (TDS); the

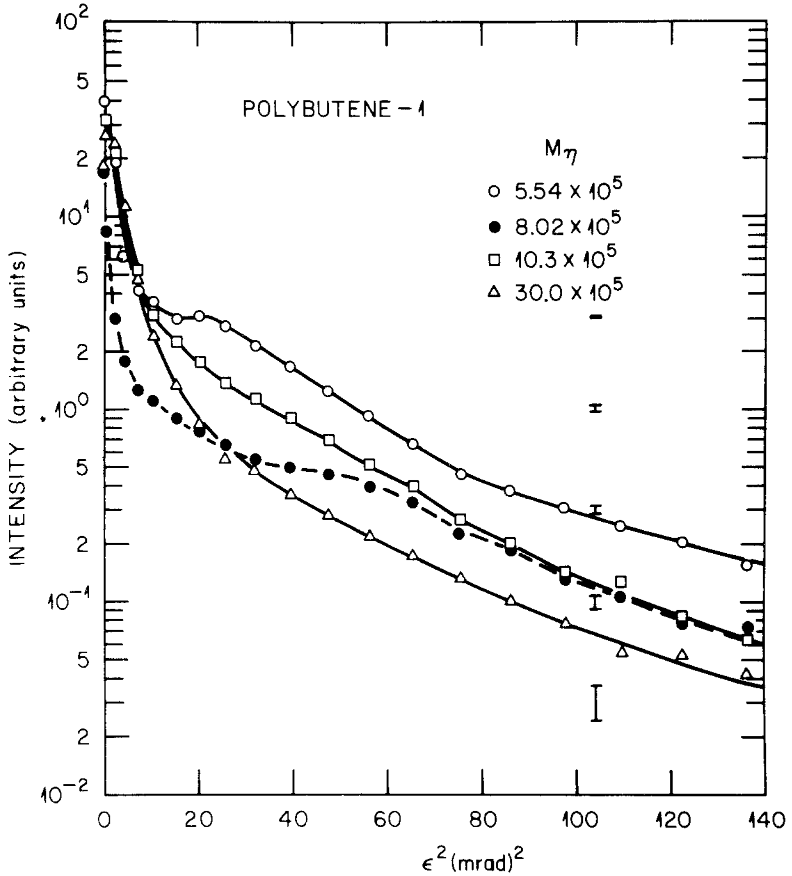

Figure 2 SAXS scans along strips such as BB′, parallel to the melt-draw direction. Estimates of the stochastic error are shown at several intensity levels.

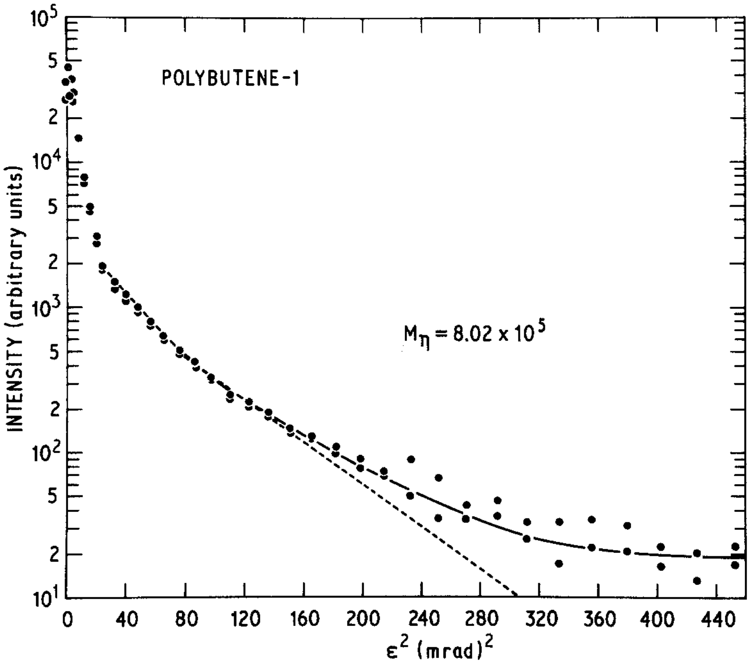

Figure 3 SAXS scan along the strip AA′, perpendicular to the melt-draw direction. The dashed line is a fit through the data corrected for thermal diffuse scattering.

TDS intensity must be subtracted from each point in regions I and II before quantitative analysis can be done.

The TEM and SAXS results are interpreted in terms of a microstructural model. TEM discloses very clearly a fibrillar microstructure in which the fibrils exhibit random lateral packing. The diameter of the fibrils, as observed directly by TEM is approximately 100 Å and is independent of molecular weight. Guinier analysis of SAXS streaks normal to the draw direction yield an apparent fibril diameter consistent with this number. This is seen with reference to Fig. 3. Guinier slopes taken from regions I and II, after TDS correction, give effective diameters of greater than 400 Å and of approximately 90 Å, respectively. The first is totally inconsistent with the TEM observations. The origin of this scattering is presently unknown. The smaller diameter, reduced from region II scattering, is identical for all four preparations (within experimental error) and is in agreement with the microscopic result for the diameter of the fibrils.

Along the fibrils, there is an alteration of relatively more and less dense regions. A contrast variation along the fibril axis is seen in $(h\,k\,0)$ dark-field micrographs. Such a contrast variation could be due to either orientation or density changes. SAXS streaks demonstrate that a density modulation along that axis exists. The density periodicity obtained by Bragg analysis of the lower molecular weight SAXS data agree reasonably well with the periodicities observed by TEM. Further, Guinier analysis of the SAXS streaks from the higher moelecular weight films yield density domain sizes of approximately 150 Å. Based on the identity between TEM- and SAXS-derived dimensions it is reasonable to conclude that both effects arise from a density modulation along the fibril length. The appearance of a Bragg periodicity for the lower molecular weight materials requires a dense packing of regions of similar density, whereas the packing in the higher molecular weight materials must be less regular. Relative intensity results show, further, that the amplitude of axial density modulation increases with decreasing molecular weight.

A possible morphogenesis is as follows: Basically crystalline fibrillar entities are formed during the cooling of the highly extended melt. The very rapid rate of growth of these fibrils (some 4 cm sec^{-1})[1] produces a high concentration of volume-dilating effects in the fibrils. Some rearrangement of the defects is possible before the segmental mobility becomes too low, due to either chain entanglements or to relatively low temperatures. It has been suggested [5] that in such cases the defects will aggregate by a spinodal-like process. In the present case, it appears that the degree and order of aggregation is hindered by high molecular weight, perhaps because of a high degree of chain entanglement and the associated low segmental mobility.

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