

Energy-scanning small-angle X-ray scattering: polyethylene

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Energy-scanning small-angle X-ray scattering is demonstrated. Here, λ -, rather than θ -space is scanned. Patterns in times as low as 100 sec are observed. Good correlation between θ - and λ -scanning is shown.

1. Introduction

A general problem associated with small-angle X-ray scattering (SAXS) is the data acquisition time. Times under 1 h are seldom possible, while times up to 1 day are sometimes required. The recent French report of a very fast SAXS system based on a linear detector [1, 2] has spurred interest by materials scientists in following SAXS changes during structural transitions. We describe here an instrument made up of components available in many laboratories. The instrument provides fast data acquisition, relative to the standard angle-scanning method.

scattering angle 2θ . During a run the instrument is stationary. A Kratky small-angle camera [9] was used to provide the high resolution slit system needed for SAXS. The intrinsic germanium crystal detector provides data in the form of number of photons at each increment of incident energy (wavelength). Since the scattering parameter $s = 2(\sin \theta)/\lambda$ can be scanned via either θ or λ , the polychromatic data at constant θ from the detector is equivalent to a θ -scan at constant λ . The pulse/energy data are processed and stored in a multichannel analyser. The advantage over 2θ collection are (a) parallel collection of all s -space data and (b) no monochromatization of the primary beam. Both of these make for more rapid scanning. The parallel nature of the collection alleviates in large measure the need for stringent short- and long-term stability of anode focal spot position and X-ray generation.

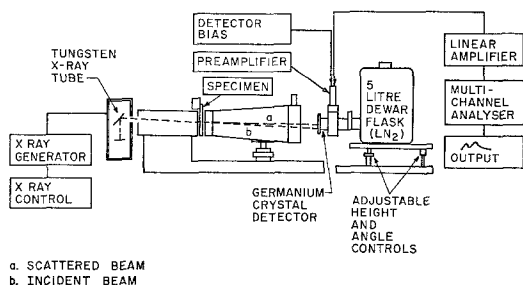


Figure 1 The energy-scanning SAXS system, consisting primarily of a tungsten X-ray tube, a Kratky camera, a Ge crystal detector, and a multichannel analyser.

The instrument described in Fig. 1 scans energy (wavelength), rather than angle. The method mimics, at small angles, the energy-scanning X-ray scattering technique previously described by several authors [3-8]. Here the white output of a tungsten X-ray tube driven at 60 kV is input at normal incidence to a polymeric specimen. An intrinsic germanium detector is set to receive scattered radiation at constant

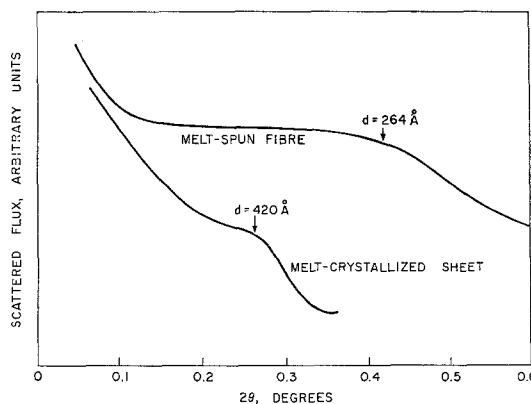


Figure 2 SAXS patterns from a melt-spun linear polyethylene fibre and a melt-crystallized polyethylene sheet, obtained by angle scanning.

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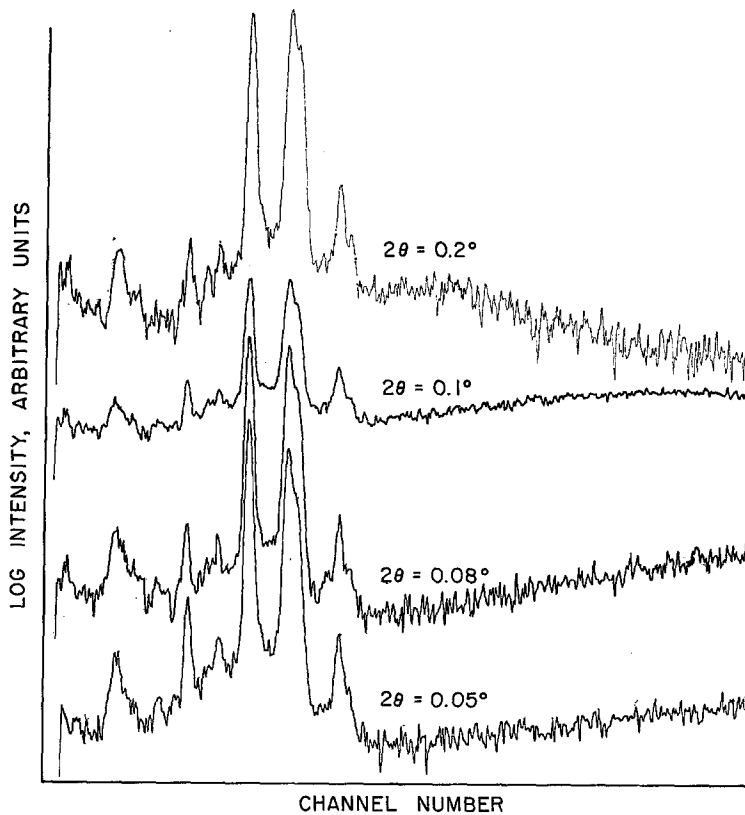


Figure 3 SAXS patterns from the melt-crystallized sheet, obtained by energy scanning. Here channel number is proportional to energy. Scans taken at four different 2θ values are shown

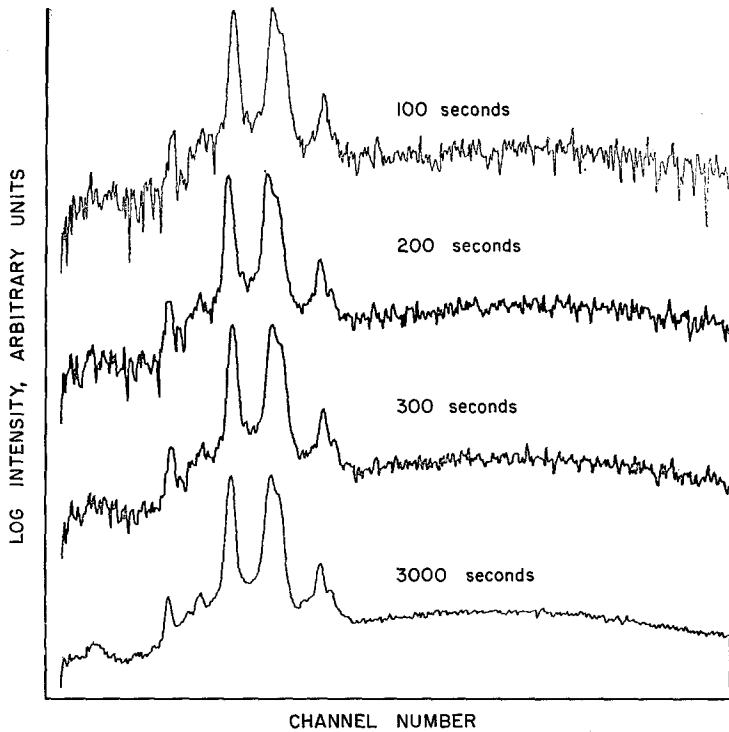


Figure 4 Energy-scanning SAXS patterns of the melt-crystallized polyethylene sheet at 81°C ; $2\theta = 0.1^\circ$. Four different counting times are shown.

Except for the Kratky camera component, the experimental system has been described elsewhere [7].

2. Results

Two specimens have been examined, one a melt-crystallized linear polyethylene sheet, the other a melt-crystallized bristle. SAXS patterns obtained by the conventional θ -scanning (using a Kratky camera) are shown in Fig. 2. The unoriented sheet shows a 420 Å small-angle periodicity, whereas the fibre exhibited a (meridional) spacing of some 260 Å. (The microstructure of the bristle is further described by Nadkarni [10].)

Fig. 3 shows a set of energy-scanning SAXS scans from the unoriented polyethylene. The scans were taken at three different values of 2θ , always using a 20 μm Kratky collimator. Each scan was taken over a period of 6000 sec. The left-hand portion of each curve is dominated by fluorescence peaks from the stainless steel of the Kratky slit system, and is of no utility here. The SAXS data are found as a broad hump in right-hand portion of each curve. The maximum of the hump is seen to move to higher channel number (energy) as the angle 2θ is increased. This is as predicted by Bragg's law in the form

$$\text{channel number} \propto \frac{1}{\sin \theta} \quad (1)$$

It should be pointed out here that careful choice of collimator materials should eliminate much of the fluorescence "noise" in the left-hand portion of the scan, thus making more channels available for the scattering data.

The effect of scanning time is demonstrated in Fig. 4 for the same material. It is clear that noise is reduced by longer exposure, but that a counting time of 100 or 200 sec is sufficient to produce a useful set of data. These times are somewhat larger than those needed for a comparable material using a position-sensitive detector (work in progress by one of the authors, J.M.S.). The principal reason for the detection time difference relates to the finer slit-size necessary for comparable resolution in the energy-scanning method. Otherwise, detection times for both methods are limited merely by coincidence times at the detector and should be essentially the same.

The SAXS peak is exaggerated because of the shape of the incident beam spectrum. That spectrum exhibits a maximum near channel

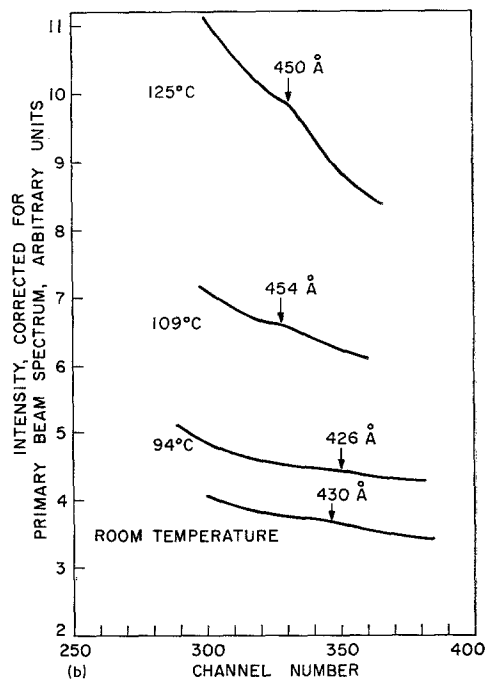
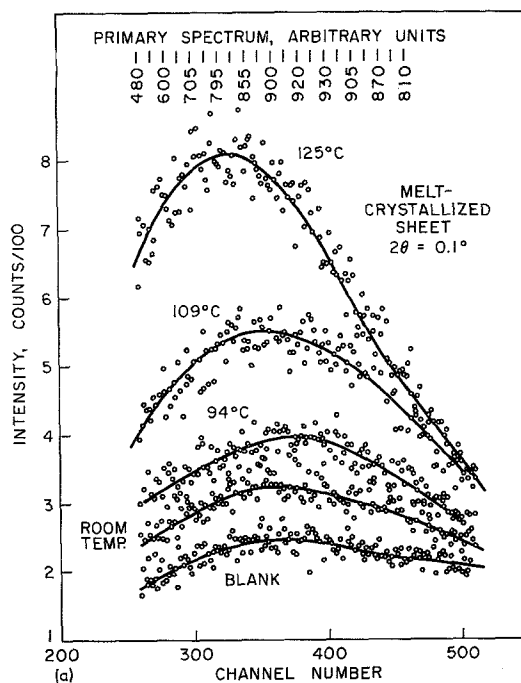


Figure 5 Energy-scanning SAXS patterns of melt-crystallized sheet at several temperatures; $2\theta = 0.1^\circ$, 3000 sec counting time. (a) Raw data. Primary spectrum values (arbitrary units) indicated at top. (b) Same data, smoothed and corrected for primary beam spectrum.

number 400. Thus the SAXS peak sits on a hump in the primary beam spectrum. To obtain the

intrinsic SAXS signal $I(\lambda)$, one must divide each point in the observed signal $i(\lambda)$ by the incident beam intensity $i_0(\lambda)$ for the same point in energy space:

$$I(\lambda) = \frac{i(\lambda)}{i_0(\lambda)}. \quad (2)$$

Fig. 5 shows uncorrected (a) and corrected (b) spectra for the melt-crystallized sheet at four temperatures. Primary spectrum values, found via the method of Prober and Schultz [7] are indicated at the top of Fig. 5a at room temperature, good agreement with the d -spacing obtained from angle-scanning is found. In accordance with previous investigations on the temperature dependence of small-angle scattering from unoriented polyethylene [11, 12], the intensity of the SAXS hump is found to increase and to move in discrete manner to higher d -spacing as the temperature is increased. Fig. 6 indicates the

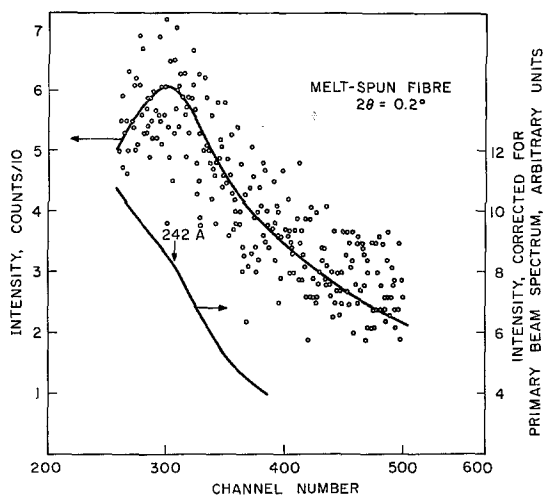


Figure 6 Uncorrected and corrected energy-scanning room temperature SAXS pattern from melt-spun bristle.

agreement in long period between θ - and λ -scanning for the melt-spun bristle.

In summary, a new, faster method for accumulating SAXS data has been presented. Identity of results between this method and traditional angle scanning has been demonstrated.

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