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NOTE

Neutron Scattering from PEEK

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INTRODUCTION

The high-performance thermoplastic poly(aryl-ether-ether-ketone), referred to as PEEK, has been the subject of various recent investigations [1-12]. Its degree of crystallinity and crystalline structure have been studied using electron microscopy [2], electron and x-ray diffraction [1, 2], Raman spectroscopy [3], and solid-state NMR [4], among other techniques. Due to its low solubility, large single crystals cannot be grown. Small-size single crystals have been prepared [5], though, by dissolving PEEK in α-chloronaphthalene (at 205°C) or in benzophenone (at 220°C). Moreover, thermodynamic and mechanical properties have also been investigated [6-12].

Neutron scattering is a useful probe to characterize polymers in the bulk state. When used on partially deuterated samples, small-angle neutron scattering (SANS) is ideal to extract single-chain conformations and therefore relate morphological features to physical properties and sample treatments. In that sense, SANS is a unique technique. Wide-angle neutron scattering (WANS), on the other hand, has not been the subject of much consideration in the field of

polymer science. High incoherent backgrounds (mainly due to hydrogen scattering) and competition from wide-angle x-ray scattering (WAXS) have been the main reasons for this. It should be noted, though, that since no deuterated PEEK was available to us for these experiments, our neutron scattering measurements are equivalent to x-ray scattering except for the fundamental differences between the two scattering techniques.

SMALL- AND WIDE-ANGLE NEUTRON SCATTERING

SANS is useful to extract characteristic single-chain properties such as the radius of gyration from partially deuterated polymer solutions or bulk polymer mixtures. Unfortunately, perdeuterated PEEK is not readily available. Also PEEK could not be dissolved to acceptable concentrations to form dilute solutions (of PEEK in deuterated solvents). With these restrictions, SANS can only be used interchangeably with SAXS, that is, to probe naturally occurring inhomogeneities between amorphous and crystalline regions.

PEEK samples in the form of injection-molded 2-mm- and 6-mm-thick plaques were obtained from RTP Co. of Winona, Minnesota. The injection nozzle temperature was between 360°C and 410°C, and the mold temperature was between 160°C and 180°C. SANS data from PEEK samples cut out of the 2-mm-thick plaque were taken on the University of Missouri spectrometer in the following configuration: 4.5-m matched flight paths, 4.75-Å wavelength, 2-cm and 1-cm source and sample apertures, respectively. For SANS, the two samples were melted (400°C) and then either quenched in ice water or slowly cooled to ambient temperature. The SANS spectrum (Fig. 1) shows a broad hump (centered around 0.04 $Å^{-1}$) characteristic of two-phase systems. This broad hump is due to interference (Bragg-like) scattering between inhomogeneities of one phase in a continuum of the other phase. It is more prominent for the melted and slowly cooled sample than for the quenched one because the crystalline fibriles are better developed in the slowly cooled sample. Electron microscopy shows [5] that these fibrils are highly anisotropic (feather-like) but their orientations are random. Because of this fact (random orientation of highly anisotropic inhomogeneities), no quantitative data analysis scheme (such as obtaining a pair correlation function by Fourier transforming the radially averaged data) was attempted.

WANS data were also taken from the same as-molded PEEK 2-mm-thick sample plaque (two pieces 2 mm × 4 mm × 5 cm stacked together). These measurements were taken on the University of Missouri powder diffractometer (wavelength of 1.29 Å). Two scans

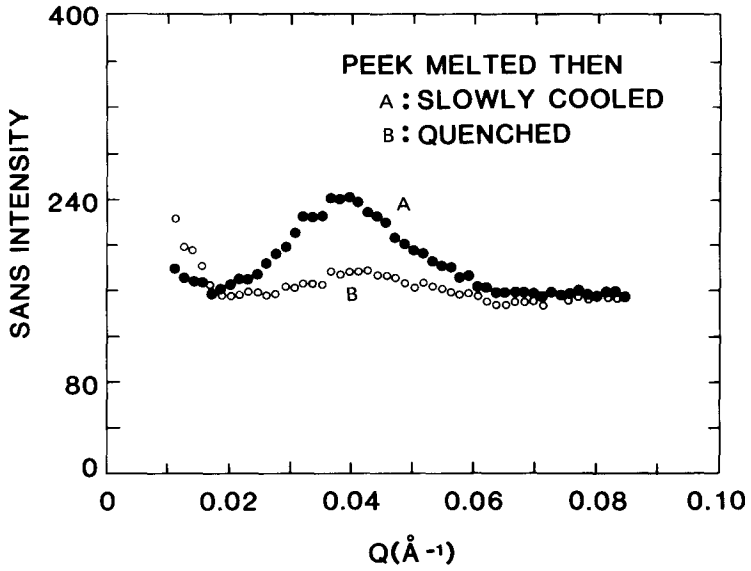


FIG. 1. SANS from PEEK samples that have been melted (400°C) and then either (A) slowly cooled to room temperature or (B) quenched in ice water.

(both shown in Fig. 2) were taken, in which the incident neutron beam was chosen parallel or perpendicular to the sample surface. A 25° angular range was chosen to cover the main spectral features (the (110) reflection, the (200) reflection, and a mixture of the (111) and the (102) reflections in-between). The crystalline structure of PEEK had been solved previously [1] showing an orthorhombic unit cell. Figure 2 shows that the (200) reflection is less intense in the perpendicular sample orientation, that is, when the incident beam is perpendicular to the plane of the plaque. This observation motivated texture studies on molded PEEK samples.

TEXTURE STUDIES

Three PEEK sample pieces (2 mm × 6 mm × 3 cm) were cut out of the as-molded 2-mm-thick plaque, glued together (using a small amount of epoxy), and machined to make a cylindrical sample 6 mm in diameter appropriate to mount on a four-circle single-crystal neutron diffractometer. Theta, 2θ scans were taken at 13 sample orientations. A Soller collimator was affixed to the detector to permit good 2θ resolution for this large sample. The sample was oriented so that the

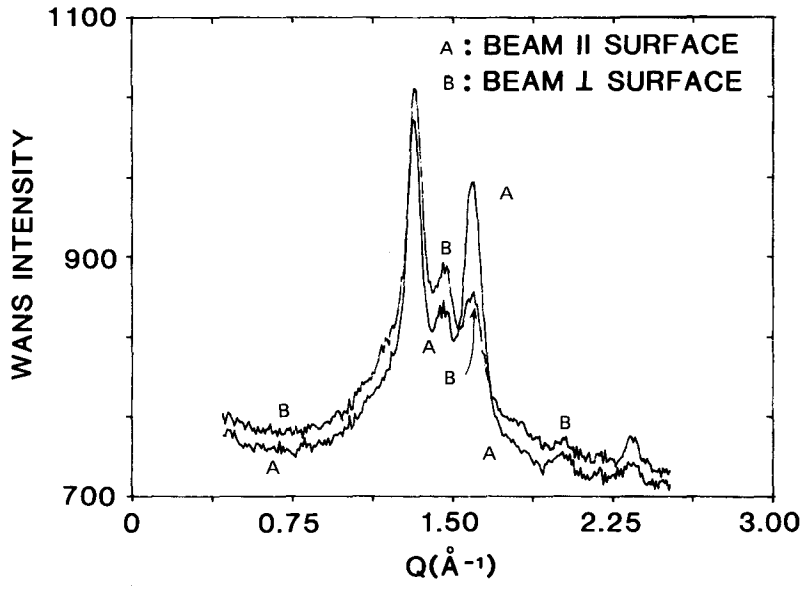


FIG. 2. WANS from PEEK samples (from a 2-mm-thick injection molded plaque) oriented (A) parallel or (B) perpendicular to the incident neutron beam. These data were taken on a powder diffractometer. The (110) and the (200) reflections are prominent.

scattering vector, $\underline{Q}$, was normal to the plane of the PEEK sheet when $\chi = 0°$, $\phi = 90°$ or 270° (see Fig. 3). Data from these scans were smoothed (using a standard IMSL subroutine package) and are plotted in Fig. 4(a). The scattering (Bragg) angle was then set either at 15.7° for the (110) reflection or at 19° for the (200) reflection, and both ϕ and χ angles (shown in Fig. 3) were varied to generate pole figures [Figs. 5(a) and 5(b)], that is, standard stereographic projections, representing the orientational texture of the crystallites. To be more specific, for each of the χ, ϕ sample orientations, intensity measurements were made at the 2θ corresponding to the crystalline Bragg peak and approximately 1° above and below. This permitted subtraction of the large background due to hydrogen incoherent scattering and to coherent scattering from the amorphous component. It can be seen that the (200) direction in the crystalline component of PEEK is predominantly oriented perpendicular to the plane of the sample—that is, perpendicular to the surface, which is shown as enhanced intensity close to the $\phi = 90°$ and $\phi = 270°$ directions. The (110) reflection shows less orientation than the (200), as would be expected because of its higher multi-

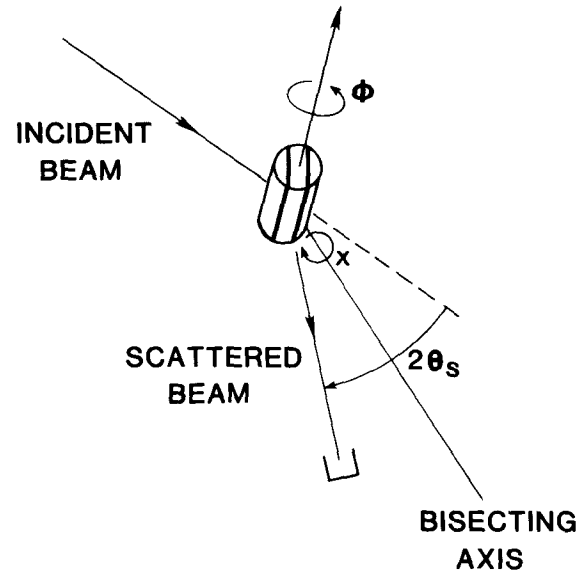
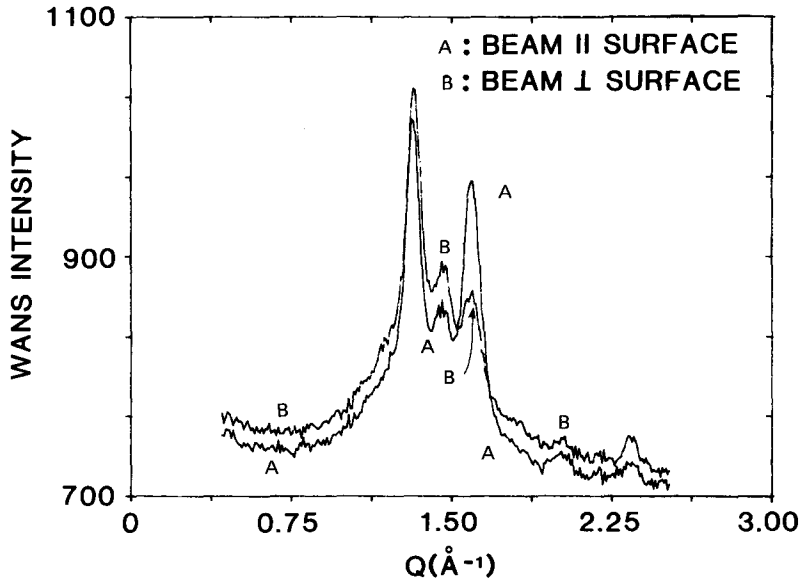


FIG. 3. Angular orientation of the sample. 2θ is the Bragg angle, ϕ is the rocking angle when $\chi = 0$, and χ is the angle of rotation around the bisecting axis.

plicity. Because each data point of the pole figure required the subtraction of a large background (85% of the observed signal), the statistical quality of the data only permits the pole figure to show qualitative features of the PEEK texture. Figure 4(a) gives more quantitative results.

Similar measurements were taken on a set of two PEEK samples that were cut from a 6-mm-thick injection-molded plaque. The first sample was used as a control whereas the second one was annealed at 200°C for 4 hr and then cooled at 6°C/hr until T_g was crossed. These samples showed much lower levels of texture [Fig. 4(b)] compared to the 2-mm-thick plaque. The annealing studies of both 2-mm- and 6-mm-thick plaque samples showed that annealing does not appreciably change the texture. Finally, for the sake of comparison, a rolled sample was examined. It consisted of 16 very thin (thickness of 0.25 mm each) pieces stacked together to form a sample (4 mm × 4 mm × 5 cm) appropriate for use on the powder diffractometer. The thin pieces were cut from an amorphous rolled plaque (less than 1% crystallinity), then annealed for 1 hr at 230°C to introduce crystallinity. For annealing, the 16 thin pieces were



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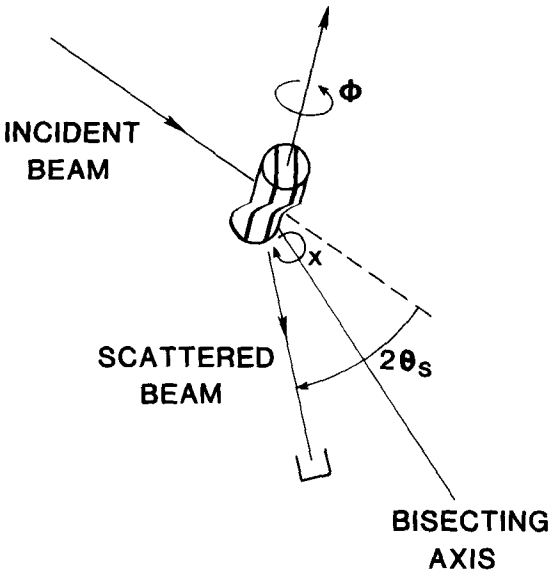

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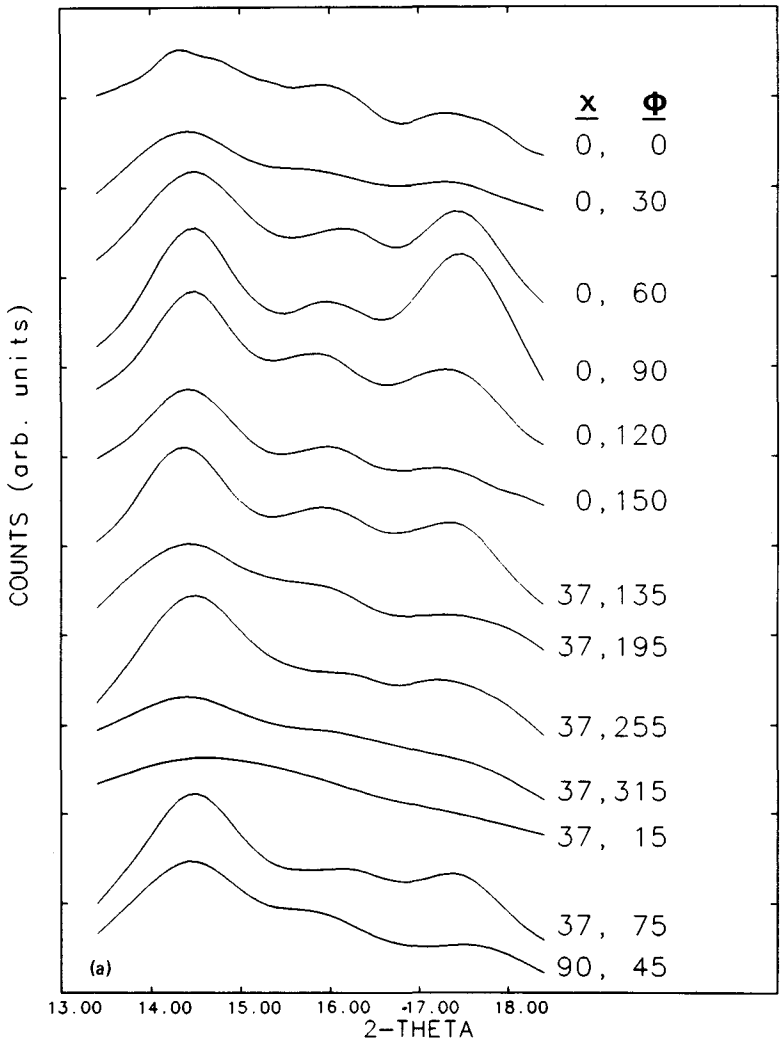
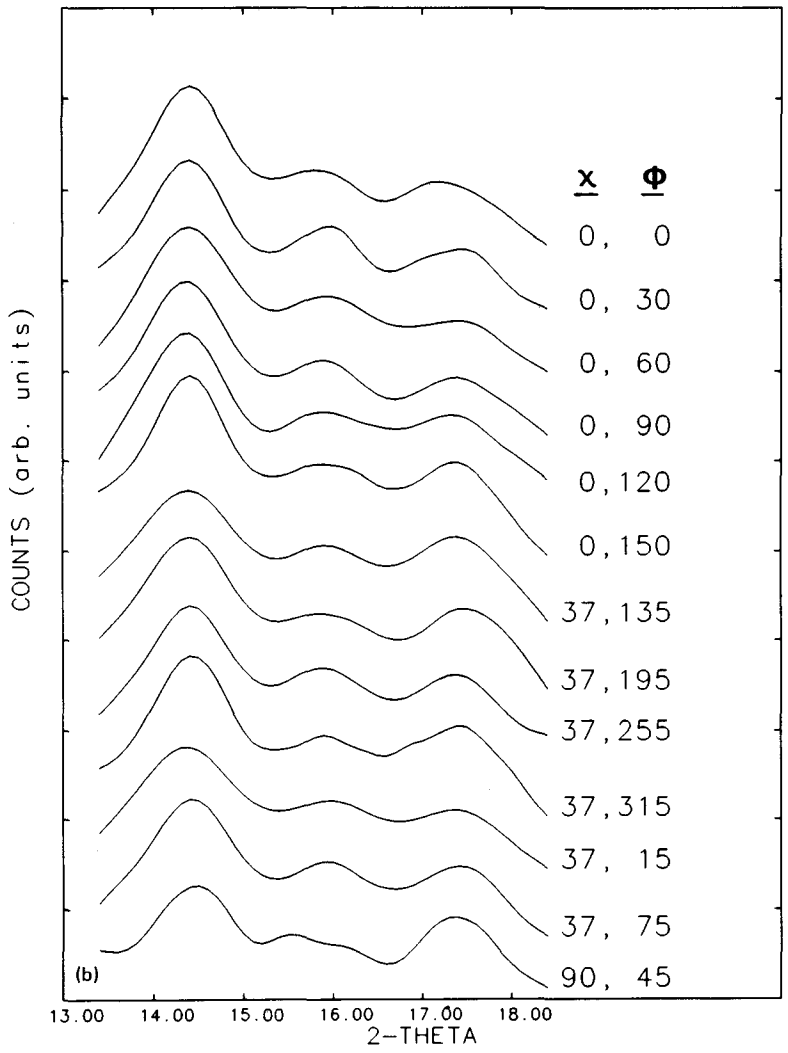


FIG. 4. (a) Theta, 2θ scans from a PEEK sample cut from the 2-mm-thick injection-molded plaque. The orientation angles ϕ and χ are fixed for each scan. (b) Theta, 2θ scans from a PEEK sample cut from the 6-mm-thick injection-molded plaque. The orientation angles ϕ and χ are fixed for each scan.



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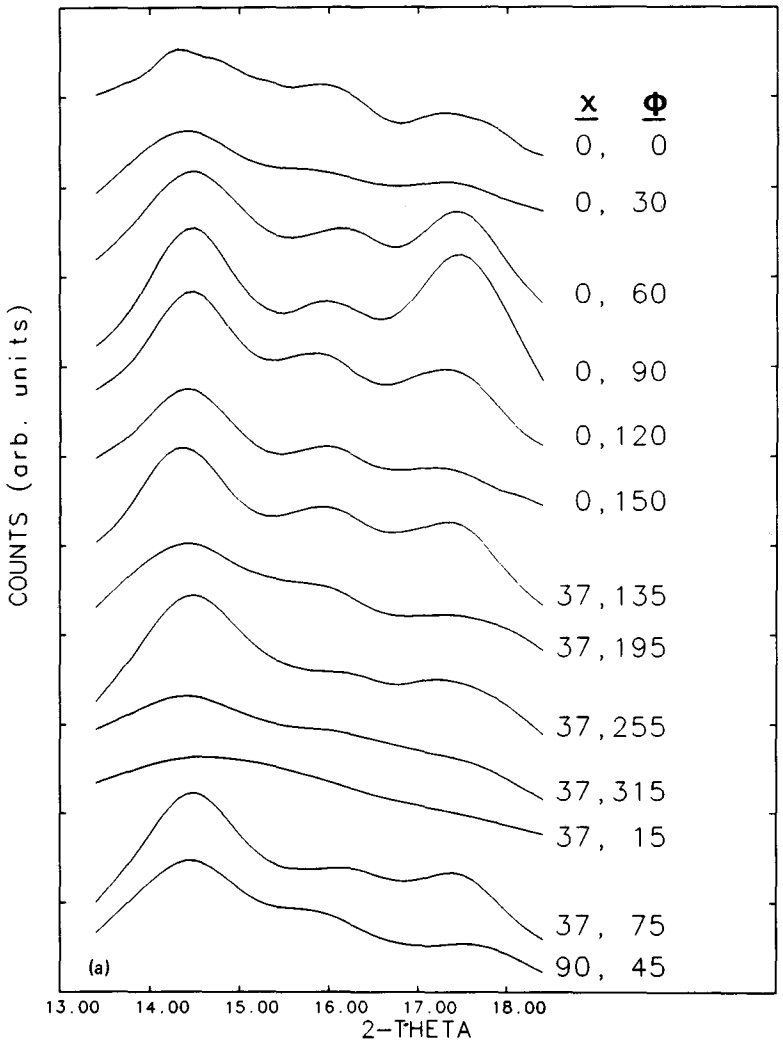

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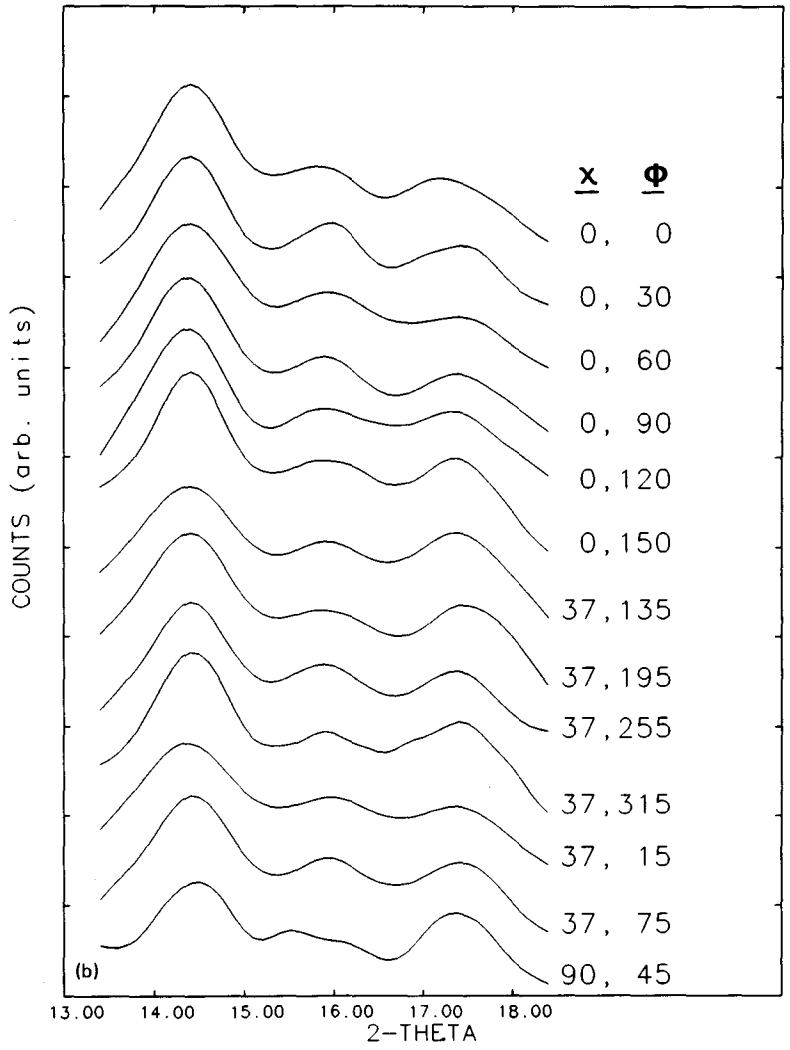

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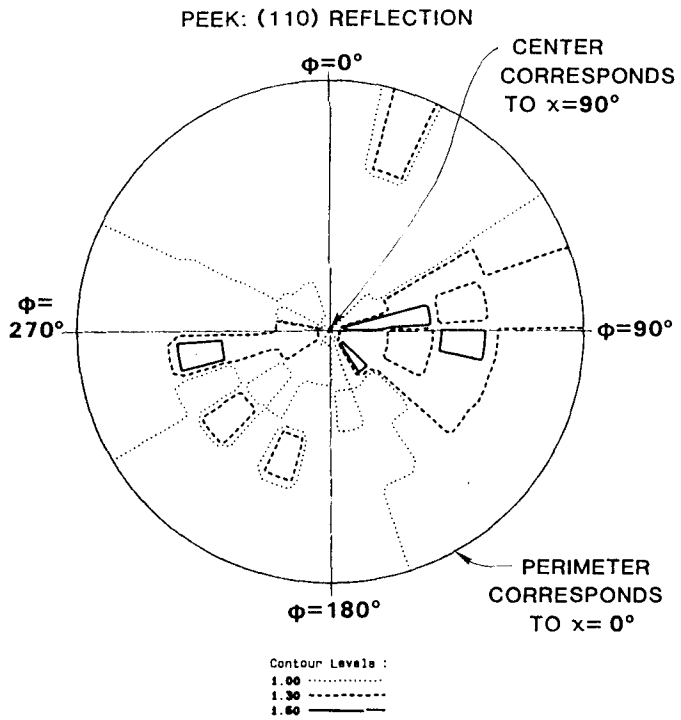

FIG. 5. (a) Pole figure for the (110) reflection from PEEK. The ϕ = 90° direction corresponds to the (110) reflection perpendicular to the plane of the sheet. (b) Pole figure for the (200) reflection from PEEK. The ϕ = 90° direction corresponds to the (200) reflection perpendicular to the plane of the sheet.

tightly stacked in a cylindrical vanadium cell that is used for WANS. After annealing these samples did not show a substantial increase in their thickness, nor did they show appreciable orientational texture.

DISCUSSION

A common application of wide-angle scattering from semicrystalline polymers is to estimate areas underneath $Q \cdot I(Q)$ versus Q

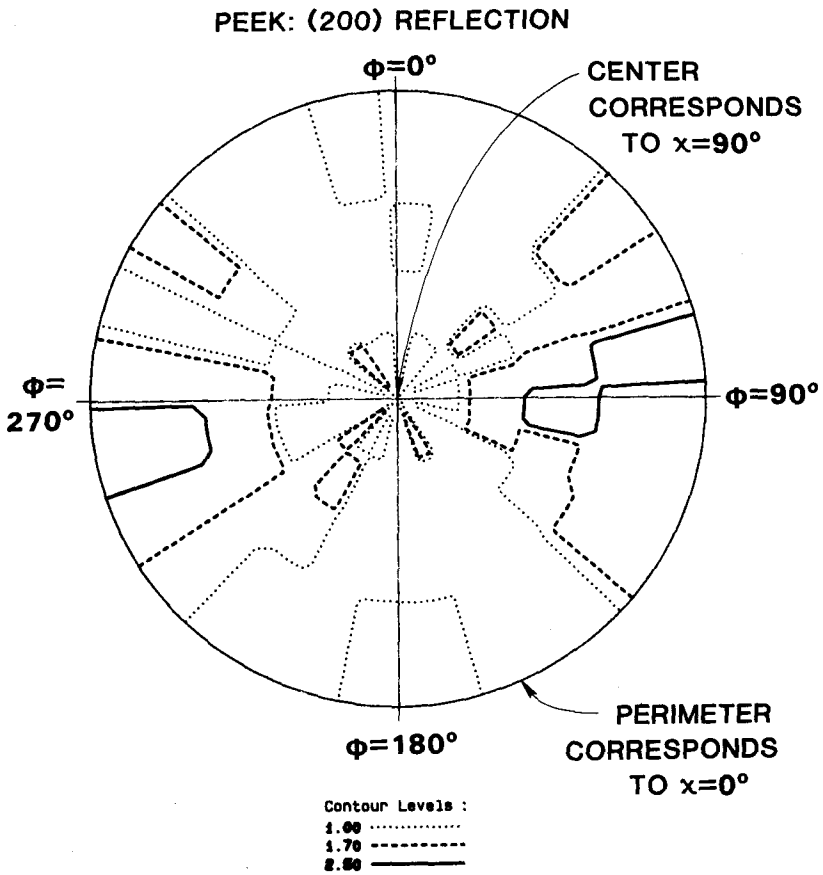

FIG. 5. Continued.

curves to obtain the degree of crystallinity and disorder parameters (Ruland's method [13]). This method requires data from both a semicrystalline and an amorphous sample, and has been done for PEEK using WAXS [2]. In previous estimates of crystallinity and orientation parameter, orientational texture of the crystallites, such as that presented here, has been neglected. The 2-mm-thick injection-molded plaque showed an appreciable amount of texture—which could change the degree of crystallinity as estimated by Ruland's method—while the 6-mm-thick injection molded plaque showed less. An amorphous rolled film which was annealed to induce crystallinity also showed little if any texture. We did not attempt using Ruland's method with our data due to the fact that only two peaks are well resolved in the WANS measurements, namely the (110) and (200); the

other observed peaks are not resolved and appear as mixtures: (111) and (102) at Q = 1.45 $Å^{-1}$; (211), (103), and (202) at Q = 2.0 $Å^{-1}$; and (121) and (300) at Q = 2.3 $Å^{-1}$.

Acknowledgments

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