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POLYETHYLENES REVISITED: WAXS AND THE PHASE STRUCTURE

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Abstract—The use of multiple Cauchy/Gauss envelopes to describe crystalline and amorphous reflections in the deconvolution of X-ray diffraction patterns is examined. Crystallinities were estimated for a number of ethylene polymers and copolymers with a variety of sample configurations and of band inputs. These are compared with crystallinities estimated from density and enthalpy of fusion data. The significance of the extra bands required to give an optimum fit with the diffraction pattern is discussed briefly.

INTRODUCTION

Polyethylene is a semicrystalline polymer, that is, it contains both crystalline and amorphous material. The crystallinity of a given sample depends upon a number of factors including branch content, thermal history and molecular weight. The percentage crystallinity can be estimated by a variety of techniques including density [1], enthalpy of fusion [2] wide angle X-ray diffraction [3], ^{13}C-NMR spectroscopy [4] and Raman spectroscopy [5, 6]. The results often are only in fair agreement with one another [7, 8] and this raises questions concerning the assumptions made in the various analyses. Two of the procedures—NMR and Raman spectroscopy—identify a third phase which might be considered as partly or wholly crystalline by the other techniques. The phase structure of polyethylene is undoubtedly complex but the techniques used in this present work all are based on the assumption of a two-phase structure.

Wide angle X-ray scattering provides a direct method for the determination of crystallinity. The diffraction pattern can be analyzed either by Ruland's method [9–11] or by the more common procedure of profile fitting by which the pattern is separated into crystalline reflections and an amorphous halo [12–14]. The crystallinity is taken to be the sum of the scattering in the profiles of the crystalline reflections divided by the total coherent scattering. A comparison of the two procedures—Ruland's and that of profile fitting—was published recently by Rabiej [15].

Most of the computer programs assume that the profiles can be represented by Gaussian or Cauchy functions or a combination of the two. Often the fit of experimental data and the sum of the profiles is not satisfactory because the reflections are not symmetrical. Wu and Wang [16] have suggested the addition of new analytical functions to the Cauchy/Gauss functions to force analytical compliance, while Murthy *et al.* [17] have used two Cauchy/Gauss envelopes to accommodate the asymmetry of the amorphous halo in poly(ethylene terephthalate).

For some time now, we have been using multiple envelope analysis to estimate degrees of crystallinity of ethylene polymers and copolymers at temperatures up to their melting points. In this paper the efficacy of the procedure as applied to the room temperature patterns of a number of ethylene polymers and copolymers is examined, and the results compared to values of crystallinity obtained for the same samples from density and DSC measurements. The implications of multiple band analysis are considered briefly.

EXPERIMENTAL PROCEDURES

The polymer samples used in this study were: **A**, an oriented high density polyethylene (Alcan); **B**, **C**, unoriented high density polyethylenes (Phillips, Dow); **D**, an ultrahigh molecular weight linear polyethylene (Dow); **E**, a medium density butene copolymer (Esso); **F**, **G**, **H**, low density homogeneous copolymers containing 4.6, 5.0 and 6.4 mol% 1-octene [18]; **I**, a homogeneous ethylene copolymer containing 6.4 mol% 1-octadecene. Films of samples **B** to **I** were formed by heating under pressure to 170°C and allowing to cool to 70°C over a period of 3 min. n-Tritriacontane (98%) was obtained from Aldrich.

Film densities were determined at 23°C using a 2-propanol–water density gradient column with standard glass floats [19]. Crystalline mass fractions were calculated using the relation:

$$X_\rho = \frac{\rho_c(\rho - \rho_a)}{\rho(\rho_c - \rho_a)}$$

where ρ is the density of the sample, ρ_c is the density of the crystalline phase (assumed constant at 1.000 g ml^{-1}) and ρ_a is the density of the amorphous phase (0.853 g ml^{-1}) [1].

Enthalpies of fusion were obtained by differential scanning calorimetry using a Mettler TC 10A processor with a DSC 30 measuring cell. The samples were heated at a rate of 20°C min^{-1}. Crystallinities were estimated assuming a value of 289 J g^{-1} for the enthalpy of fusion of perfectly crystalline polyethylene [2].

X-ray diffraction

Diffraction patterns were obtained on a STOE STADI 2/PL diffractometer using California Scientific software. The diffractometer has a graphite incident beam focussing monochromator with the usual incident and receiving slits and collimators, and a scintillation counter with pulse height discrimination. Copper K_α radiation was used,

$\lambda = 154.18$ pm. Data were obtained for unsupported polymer samples in three configurations—transmission (T), reflection (R) and Debye–Scherrer (DS) modes. All of the data were gathered in 0.050° steps between 8° and 34° 2θ. Total counts of $1\text{–}7 \cdot 10^5$ were recorded.

Density, DSC and X-ray data in transmission and reflection were obtained with film samples having identical thermal histories. The rods used in DS studies were given approximately the same thermal treatment.

Baseline and Lorentz polarization corrections

All of the programmes and procedures devised for the extraction of crystallinity values from diffraction data depend on the subtraction of intensity data below some arbitrary baseline. No other step introduces greater uncertainty into the end result. In treating data from polyethylene polymers and copolymers it is traditional to draw a straight line on the raw diffractometer trace spanning the linear low intensity regions between *ca* 8–12° 2θ and 31–35° 2θ, and to assign all of the radiation data below the line to scattering effects which cannot be readily handled analytically. Indeed there seems to be little reason to do otherwise. In our treatment of the data, the baseline was drawn from the pattern between 8–10° 2θ and 32–34° 2θ. In all instances the slope of this baseline was essentially zero. The baseline was deduced prior to applying the Lorentz correction because that correction destroys the linearity of the baseline.

The fraction of the total scattering lying below this arbitrary baseline represents *ca* 10% of the total scattering for polymers of high crystallinity (80%); the percentage increases with decreasing crystallinity and is *ca* 33% at 24% crystallinity. This may represent greater thermal diffuse scattering by the amorphous component relative to that of the crystalline phase.

The standard Lorentz polarization term, applied to powder diffraction intensities to correct for diffractometer geometry as well as polarization of the radiation by an incident monochromator and the sample,

$$\mathrm{Lp} = \frac{1 + \cos^2 2\theta_\mathrm{m} \cos^2 2\theta}{(1 + \cos^2 2\theta_\mathrm{m})(\sin^2 \theta \cos \theta)}$$

(where θ_m refers to the monochromator) has the effect of increasing the observed intensity with increasing values of θ. For polyethylenes, in which the amorphous halo lies at lower values of the scattering angle than the crystalline reflections, the relative intensities of the crystalline reflections are enhanced, as shown in Table 1. The correction is not insignificant. We mention it here because it is not always evident in the literature that the correction has been applied.

WAXS analysis

The profile fitting program used here is a modification of a program written by Jones and Pitha to deconvolute overlapping peaks in i.r. spectra [20]. Operator input to the program comprises estimates of intensity, position and weighting factors for the Cauchy and Gauss functions for each reflection in the trial. For polyethylenes in the 2θ range of this study, a minimum of four bands or envelopes is expected—one amorphous halo and three crystalline reflections. A trial can contain a greater number of envelopes if desired, and one might expect that the greater the number of envelopes the better the fit of the sum of the envelopes with the experimental pattern. In practice, this is not always so.

Table 1. Effect of Lorentz polarization correction on WAXS crystallinity values

Polymer	No Lp correction (%)	Lp correction (%)
C	66.8	70.4
D	48.4	54.5
G	25.3	27.9

Identical WAXS input parameters in each pair of analyses.

Determination of goodness of fit

The choice of the optimum analysis in a series of trials on a given set of diffraction data is best made by visual comparison of the WAXS plots. Three such plots are shown in Fig. 1. The examination is aided by the superimposed plot of $(I_\mathrm{o} - I_\mathrm{c})$ where I_o and I_c are the observed and calculated intensities at each step.

We have not found an analytical function which can express the goodness of fit in a numerical way with the same confidence as can be ascribed to visual examination. The delta function used by Wu and Wang [16],

$$\delta \simeq \left[\sum_n (I_\mathrm{c} - I_\mathrm{o})^2 / \sum_n I_\mathrm{o}^2\right]^{1/2} \tag{1}$$

where n is the step in the counting sequence, does not distinguish between differences caused by misfit and those caused by statistical fluctuations in the experimental data. If the average count per step is I'_o, the statistical uncertainty is approximately the square root of this value. If the fit were exact, then

$$\delta' \simeq (I'_\mathrm{o})^{1/2}/I'_\mathrm{o} = (I'_\mathrm{o})^{-1/2}. \tag{2}$$

For a very good fit, the value of δ could not be expected to be much smaller than δ'. In compiling our data, we have included a fit function f defined by

$$f = \delta/\delta'. \tag{3}$$

If the value of f in any trial is less than unity, the value of δ, whatever it may be, must be due primarily to statistical fluctuations in the raw data. In these calculations, I'_o is taken to be the average count in the raw data, i.e. the intensity before the background is deducted.

RESULTS AND DISCUSSION

The effects of the use of multiple bands in the WAXS computer analysis were examined using a number of ethylene polymers and copolymers. These include the oriented linear polyethylene **A**, two high density polyethylenes **B** and **C**, a medium density butene copolymer **E** and three homogeneous 1-octene copolymers **F**, **G**, **H**, with random distributions of comonomer units. The results are summarized in Table 2. In general the use of multiple profiles improves the fit of calculated and experimental patterns. If a reflection is weak, one band is usually sufficient. Trials with more than two bands assigned to a reflection normally fail with the third band squeezed out during refinement.

With the high density polymers, the fit is improved for both the (110) and (200) reflections if they are each represented by two bands. Representation of these crystalline reflections by two bands each is also required in the WAXS analysis of tritriacontane, n-$C_{33}H_{68}$. This particular paraffin was chosen because very strong (00*l*) reflections at low orders indicated relatively high purity and little or no amorphous phase. The pattern shown in Fig. 2 was taken in transmission for a sample on plantinum gauze and oriented with the *c* axis parallel to the incident beam. Although there are still areas at the base of the strong reflections which have not been accounted for, the fit

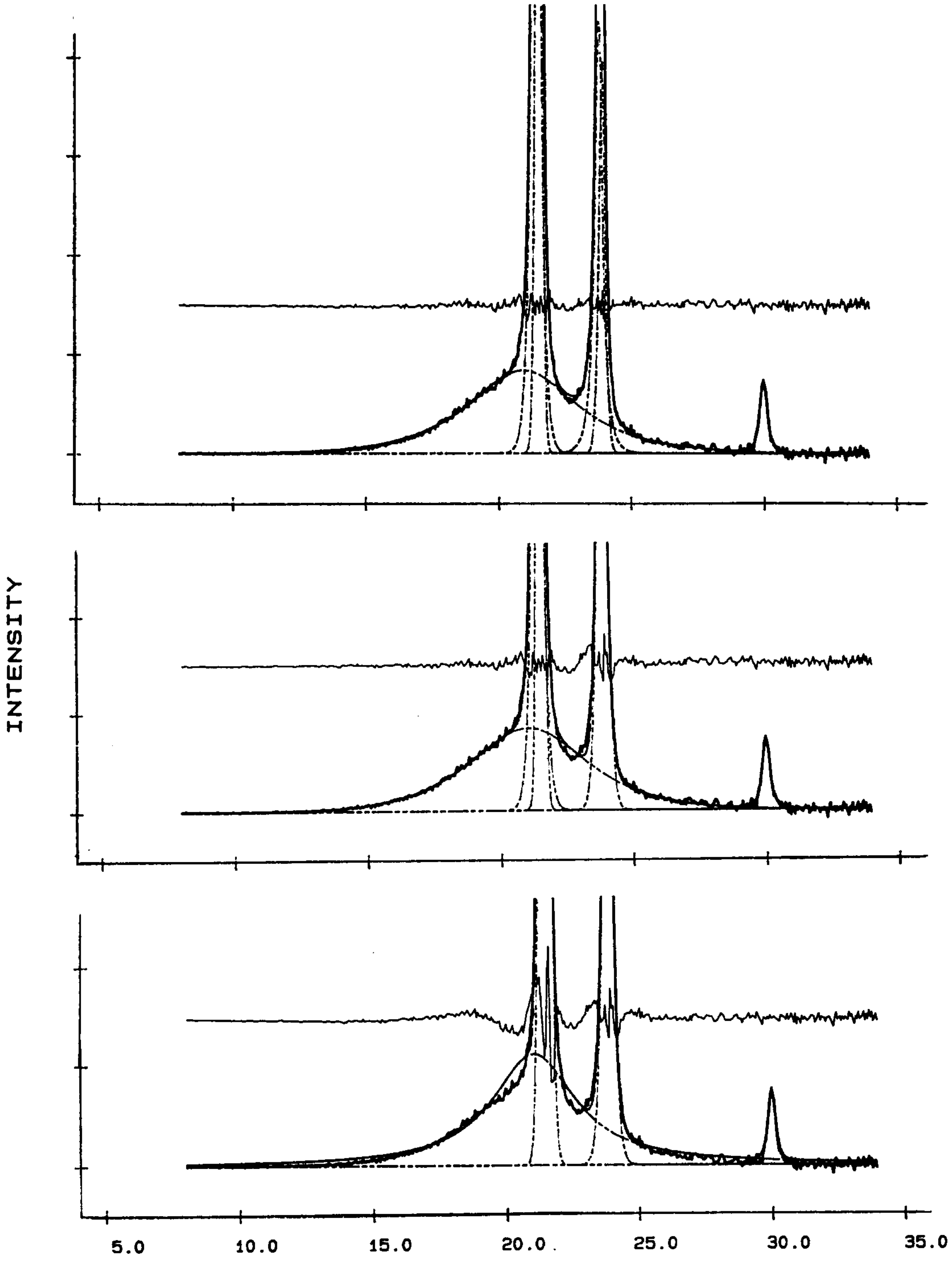

Fig. 1. Effect of band input on WAXS analysis. The sample is a high density PE (Dow). Transmission pattern. The relative peak height intensity, $(I/I_m)100$, of the (210) reflection at 30° 2θ is 2.4. Total count, $3.97 \cdot 10^5$. The horizontal trace in each of the plots is the difference between calculated and observed intensities, $I_c - I_o$, at each step. Top, Six band input, two bands each for the (110) and (200) reflections, one band each for the amorphous and (210) reflections. Fit, a; $f = 0.37$; $X_W = 70.4\%$. Middle, Five band input, two bands for the (110) reflection. Fit, a; $f = 0.50$; $X_W = 69.7\%$. Bottom, Four band input. Fit, b; $f = 1.13$; $X_W = 65.0\%$.

Table 2. The effect of band input on WAXS analysis

Polymer[1]	No. of bands in input[2] Halo	(110)	(200)	Fit[3]	f[4]	Crystallinity X_w(%)
A	1	1	1	b	0.52	76.0
	1	2	2	a	0.28	85.4
B	1	1	1	c	0.97	69.0
	1	2	2	a	0.34	75.2
C	1	1	1	b	1.13	65.0
	1	2	1	a	0.50	69.7
	1	2	2	a	0.37	70.4
E	1	1	1	d	1.00	43.8
	1	2	2	a	0.48	52.3
F	1	1	1	b	1.20	32.8
	1	2	1	a	1.10	33.4
	1	2	2	d	2.15	28.2
	2	1	1	a	1.07	33.5
	2	2	1	a	0.90	37.1
G	1	1	1	b	1.40	27.9
	1	2	2	b	1.27	27.9
	2	2	1	a	0.93	30.2
H	1	1	1	b	1.04	26.8
	2	2	1	a	0.97	30.0

[1] See footnotes to Table 3 for polymer identification.

[2] All WAXS input trials included a band for the (210) reflection except for polymer **H** for which the reflection intensity was negligible.

[3] Visual observation of WAXS plots: a, good; d, poor.

[4] Goodness of fit, equation (3).

is not improved if an amorphous band is included in the trial. It seems likely that the WAXS program will have difficulty in distinguishing between polyethylenes if the crystalline content is >90%.

The last two entries for polymer **F** in Table 2 show that with some samples the goodness of fit criteria, equation (3) and visual evaluation of overall fit, are insensitive to the form of the individual envelopes. The plots for these two analyses are shown in Fig. 3. The upper plot is the result of a six-band input and the lower, a five-band input. Each includes two broad bands to represent the non-crystalline material in the copolymer. The values of f for the five and six-band analyses are 1.07 and 0.90 respectively and visual examination of the fit leaves little ground for choice. The difference values, $I_c - I_o$, represented by the horizontal traces, do suggest that the six-band analysis is to be preferred. It is surprising that the estimates of the crystallinity differ by 4 percentage units. Although the total envelopes are almost identical, the additional (110) band in the six-band analysis alters the amorphous halos, changing their positions and decreasing their areas, and thus leads to a crystallinity estimate of 37.1% compared with the five-band value of 33.5%.

It is seen from Table 2 and Fig. 1 that the best fit is obtained with sample C if the (110) and (200)

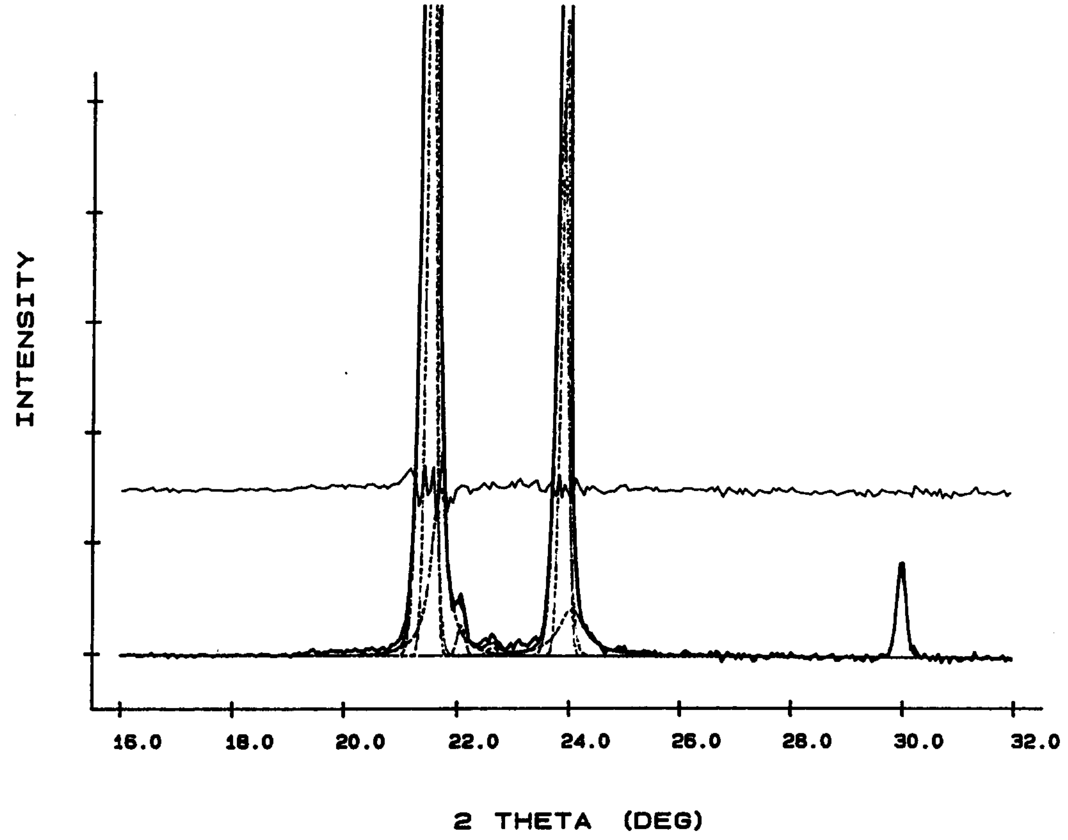

Fig. 2. WAXS analysis of diffraction pattern of n-tritriacontane, $C_{33}H_{68}$. Transmission pattern. Relative peak height intensity of (210) reflection is 2.6. Nine band WAXS analysis; with increasing 2θ, the bands represent reflections (110) (two bands); (113); (115); (117); (200) (two bands); (203); and (210). No amorphous halo. Fit, a; $f = 0.29$; $X_W = 100\%$.

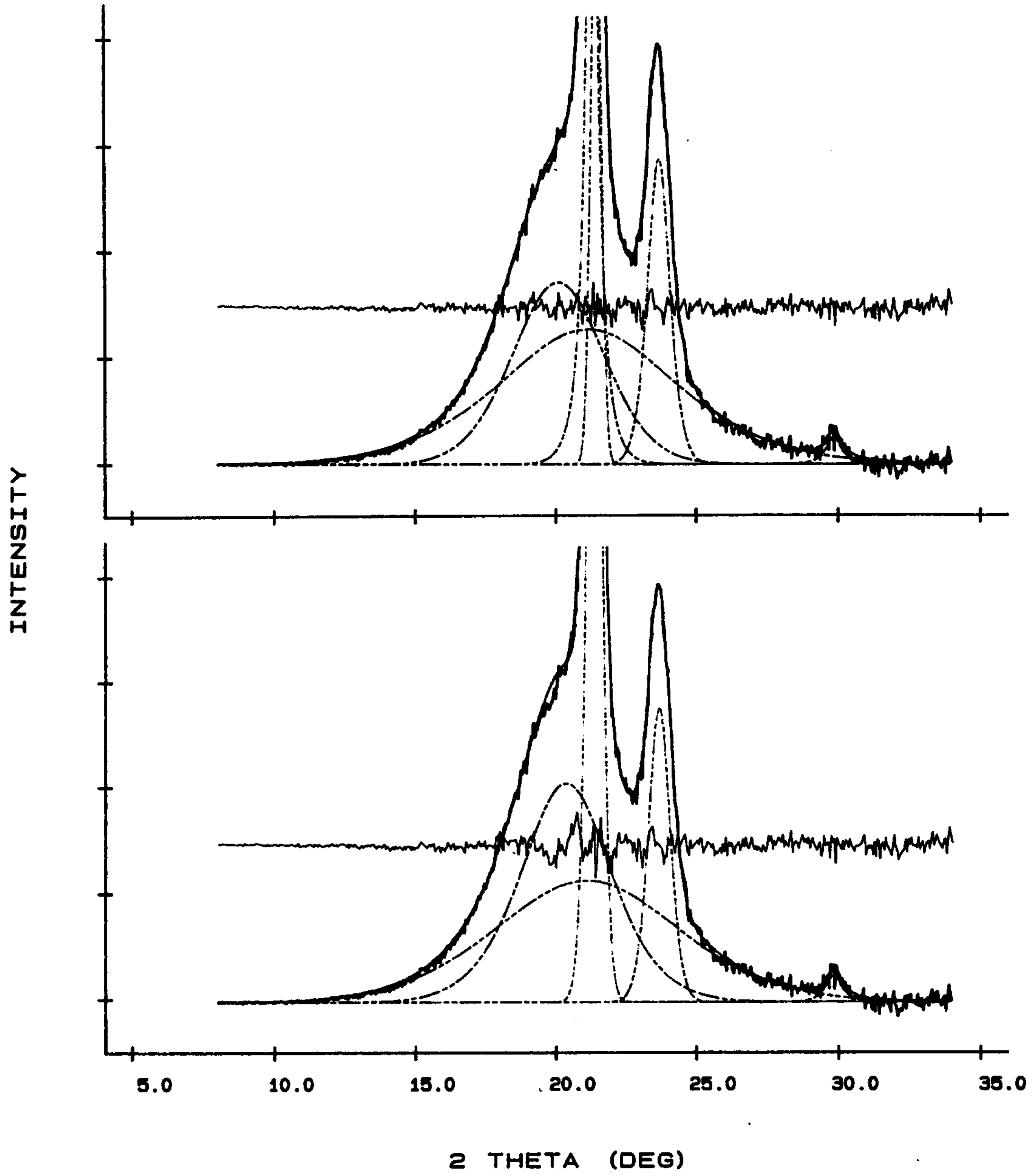

Fig. 3. WAXS analysis of polymer F, a 4.6 mol% 1-octene copolymer. Top: Six band input. Two bands each for the amorphous and (110) reflections, one each for the (200) and (210) reflections. Fit, a; $f = 0.90$; $X_W = 37.1\%$. Bottom, Five band input. Two bands for the amorphous halo. Fit, a; $f = 1.07$; $X_W = 33.5\%$.

reflections are each made up of two envelopes. The band to slightly higher θ has a smaller width at half maximum, implying that the crystallites contributing to it have larger dimensions perpendicular to the appropriate crystal plane. This suggests that a better profile fit is obtained if the crystallites are arbitrarily split into two groups—larger crystallites with slightly tighter packing and smaller crystallites with slightly looser packing. The work of Voigt-Martin and Mandelkern [21] shows that crystallite thicknesses vary with comonomer content and thermal history but that groups averaging, say, 60 and 80 Å might well be present. It is known that unit cell dimensions decrease with increasing crystallite size [22, 23] so that this explanation for the requirement of two envelopes by each crystalline reflection appears to be reasonable. Considerable care must however be exercised in interpreting patterns which require two envelopes per crystalline reflection. It is seen above that the alkane $C_{33}H_{68}$ also requires two bands per reflection. Inspection of Table 2 shows that only one envelope is required to give the best fit for the (200) reflection in low density polyethylenes. The (200) reflection is of relatively low intensity but, if the above explanation is correct, a better fit with two envelopes for this reflection might have been anticipated.

According to Table 2, a single envelope is required to represent the amorphous halo for the high density polyethlenes investigated whereas two envelopes give a better fit for the low density copolymers. The value of 2θ for the halo maximum is higher than anticipated from melt studies. This is particularly evident for the high density polyethylenes implying that their amorphous components contain chains which are more closely packed than in the melt. The extent to which this is due to trans segments at the crystalline–amorphous interface or to very small crystallites or to a different crystalline form [24] is not known. Of the two envelopes representing the amorphous material in the low density polyethylenes, one has a 2θ value only slightly greater than that of the melt and the other represents somewhat more ordered material. Murthy *et al.* [17] have noted the presence of a second amorphous peak in poly(ethylene terephthalate) and have suggested that it arises from incipient crystalline order in the amorphous phase.

Studies on the effect of sample configuration on WAXS results are summarized in Table 3. In general crystallinity values obtained for samples in transmission and Debye–Scherrer mode are in good agreement. Data for the same samples in reflection mode show greater disagreement but these mountings were less than ideal in that the sample was not the equivalent of infinitely thick.

Table 3 also shows a comparison of the crystallinities obtained by WAXS with those derived from density and enthalpy of fusion data. Agreement between the various estimates is only fair. However, when the nature of the assumptions underlying the three methods is considered, it is surprising that the agreement is as good as it is. Each of the methods assumes a two phase structure (although there is ample evidence that material intermediate in properties is present) and any real differences in crystallinity estimates beyond those derived from experimental uncertainty have their origins in the ways in which these two phases are defined.

In principle, WAXS provides the best approach to arrive at the true crystallinity of a semi-crystalline polymer such as polyethylene. The estimate may be low if very small crystallites or a small amount of another crystalline form are counted as part of the amorphous halo.

In the density method, it is assumed that the crystalline phase has a constant density of $1.000\ \mathrm{g\,ml^{-1}}$ and the amorphous phase a density of $0.853\ \mathrm{g\,ml^{-1}}$ independent of branch content. It is known from unit cell dimensions that the density of the crystalline phase decreases with increasing branch content but when the actual crystallographic densities are used in the estimation of crystallinities the discrepancies in Table 3 are increased. It is also observed that the position of the maximum in the amorphous halo is dependent on the crystallinity. Low density polyethylenes exhibit maxima at 2θ values only slightly higher than that anticipated for the melt, but high density polyethylenes give significantly higher values. This indicates the presence of more closely packed material which is contributing to the amorphous halo. If the density of the amorphous phase increases with crystallinity, the density estimate of crystallinity is too high.

The simplest enthalpy of fusion analysis compares the heat of fusion of the sample with that of a

Table 3. Multiple envelope WAXS analyses. Comparison with density and enthalpy of fusion crystallinities

		Number of profiles[3]							
Polymer[1]	Mode[2]	Halo	(110)	(200)	Fit[4]	f^5	X_w^6	X_ρ	$X_{\Delta H}$
A	DS	1	2	2	a	0.28	85.4	—	—
B	DS	1	2	2	b	0.26	78.8	77.5	75.5
	DS	1	2	2	b	0.31	77.4		
	T	1	2	2	a	0.34	75.2		
	R	1	2	2	a	0.57	72.5		
C	T	1	2	2	a	0.37	70.4	72.0	68.4
	R	1	2	2	a	0.68	70.7		
D	T	1	2	2	a	0.62	54.5	57.3	48.9
	T	1	2	2	a	0.62	56.6		
E	DS	1	2	2	a	0.48	52.3	54.2	51.0
	T	1	2	2	a	0.75	49.8		
	R	1	2	2	b	0.76	46.2		
F	T	2	2	1	a	0.90	37.1	37.9	34.5
	R	1	2	1	a	1.04	39.9		
G	T	2	2	1	a	0.93	30.2	33.7	29.0
H	T	2	2	1	a	0.97	30.0	33.0	—
I	T	2	1	1	b	1.00	24.4	36.0	—

[1] Polymer: **A**, linear PE, stressed: **B**, **C**, high density PE from Phillips, Dow; **D**, UHMW PE from Dow; **E**, medium density butene copolymer (Esso); **F**, **G**, **H**, low density random ethylene copolymers containing 4.6, 5.0 and 6.4 mol% 1-octene; **I**, low density ethylene copolymer, 6.5 mol% 1-octadecene.

[2] Sample configuration: DS, Debye–Scherrer; **T**, transmission; **R**, reflection.

[3] Number of profiles used in WAXS trial to represent the amorphous halo and the (110) and (200) crystalline reflections. All trials included a single band for the (210) reflection except for polymers H, I, for which the reflection was missing.

[4] Visual evaluation: a, good; b, acceptable.

[5] Goodness of fit: equation (3).

[6] % Crystallinity: X_W, WAXS; X_ρ, density; $X_{\Delta H}$, enthalpy of fusion.

perfectly crystalline sample at its melting point (289 J g^{-1}). Corrections can be made for the temperature variation of ΔH_{fus} for samples with lower melting points. In branched polyethylenes, however, premelting takes place over a wide temperature range mainly because of a wide range of crystallite sizes. If ΔH_{fus} is indeed a function of crystallinity and crystallite size, it again becomes difficult to arrive at a precise value of the crystallinity from a single experimental measurement.

Density and enthalpy of fusion measurements are convenient to make and the experimental data are readily converted to crystallinities. These estimates are generally close enough to the 'true' values provided by X-ray analysis for the methods to continue to be preferred in routine crystallinity determinations.

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