

## General procedure for evaluating amorphous scattering and crystallinity from X-ray diffraction scans of semicrystalline polymers

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The separation of amorphous and crystalline contributions in diffraction and spectroscopic data is a necessary step in the study of the structure of the less-ordered regions and in the calculation of crystallinity of a semicrystalline polymer. We suggest here that the diffraction pattern of a polymer with a high degree of crystalline order be fitted with easily resolvable crystalline peaks, and the intensity not attributable to the crystalline peaks be regarded as amorphous scattering. This amorphous halo can be used as a template in analysing the diffraction patterns of less-crystalline samples, and to follow changes in the amorphous regions. This method is most useful for polymers for which a completely amorphous sample cannot be easily prepared, and in the analysis of poorly crystallized polymers. The method is illustrated with examples from several polymers.

(Keywords: amorphous scattering; crystallinity; X-ray diffraction; semicrystalline polymers)

### INTRODUCTION

X-ray diffraction (XRD) is a definitive technique for estimating the degree of crystallinity in polymers. Many methods have been devised to calculate the crystallinity of XRD<sup>1</sup>. All methods require that the intensity due to amorphous scattering be separated before one begins to evaluate the crystallinity. While this is not a problem in some polymers, for example poly(ethylene terephthalate) (PET), which can be quick-quenched to produce amorphous specimens, the unavailability of an amorphous template is a serious problem in analysing polymers such as nylon-6 and certain fluoropolymers. The scattering from the molten polymer does not provide an appropriate template because the interchain distances might increase due to thermal expansion, and the shapes of the amorphous halo in the melt and in the solid may be different. Thus, a reliable description of the amorphous scattering, i.e. the shape, position and half-width of the amorphous halo, is difficult to establish. Similar problems exist in spectroscopic (e.g. infra-red and magnetic resonance) methods as well. In this report we discuss how such parameters in X-ray diffraction can be obtained by profile fitting a highly crystalline sample available for that particular polymer, and illustrate this idea by using the data from several polymers.

### METHODS

Wide-angle X-ray diffraction data were collected on a Philips goniometer in parafocus geometry using Cu K $\alpha$  radiation with a graphite monochromator in the diffracted beam. Data were collected by counting typically for 4 s at each 0.1° step in 2 $\theta$ . In analysing the data we made no corrections for incoherent scattering and for Lorentz and polarization factors. These corrections, if made, should be done consistently both for the curve from which the template was extracted as well as for the data that

are being evaluated. Such corrections, which may not be important in the evaluation of relative crystallinity, are necessary in the evaluation of absolute crystallinity, and in any detailed evaluation of amorphous scattering such as by radial distribution function (RDF) analysis.

The program SHADOW written by Howard<sup>2</sup> was used for profile fitting after modifying the program to fit several amorphous peaks of different shapes. Since the data were obtained in the parafocus mode, the profiles could be described by a modified Lorentzian:

$$I(x) = I(0)/(1 + kx^2)$$

where  $k = 0.4142/(FWHM/2)^2$ ,  $FWHM$  is the full-width at half-maximum and  $I(0)$  is the intensity at peak maximum. An upper limit of 2.5° (corresponding to a crystallite size of ~32 Å at 2 $\theta$  ~25° with Cu K $\alpha$  radiation) was set for the  $FWHM$  of the crystalline peaks. The number of amorphous peaks was kept to a minimum, and additional amorphous peaks were added only when the fit could not be improved by changing any of the parameters. Starting values for the positions of the crystalline peaks could be easily estimated for the diffraction patterns of highly crystalline samples, and these refined peak positions were used as starting parameters in profile fitting the less-crystalline samples. Relative crystallinity (crystalline index,  $CI$ ) was evaluated from the ratio of the areas of the crystalline peaks to the total area under the scattering curve.

Ideally, all the parameters of the amorphous template, i.e. the positions, half-widths and asymmetry factors if any, should be fixed while varying only the height of the amorphous halo; if there is more than one amorphous halo, then the heights of the various peaks need to be varied while keeping the ratio constant. We will call this model A. In practice, however, it is necessary to vary other amorphous parameters in addition to the height of the amorphous halo. For example, to allow for small

**Table 1** Description of various profile fitting models

Model	Parameter varied	
	Overall amorphous scattering	Individual amorphous peaks
A	Height	None
B	Height and position	None
C	Height and position	Height
D	Height and position	Height and position
E	Height, position and <i>FWHM</i>	Height, position and <i>FWHM</i>

variations in data collection, such as the position of the sample, the position of the amorphous template may have to be shifted by a small value. If there is more than one amorphous peak, then all the peaks will be shifted by the same amount. This is model B, and is most useful. When the amorphous halo in the region of interest, typically  $2\theta = 10^\circ$  to  $30^\circ$ , needs to be described by more than one amorphous peak, as in PET, poly(*p*-phenylene sulphide) and poly(ether ether ketone), the parameters of each of the peaks describing the amorphous scattering might vary independently depending, for example, on crystallinity. To allow for such changes in relative heights, positions and half-widths, we include models C, D and E, as described in Table 1. In using model E, the template only serves to provide good initial estimates of the amorphous scattering. Such a model may still provide useful results for reasonably crystalline samples, but the results may be difficult to interpret for poorly crystallized samples. In all of these models, one cannot overemphasize the necessity of choosing a proper baseline. A linear baseline was found to be sufficient for our data. To determine the appropriate slope and intercept, it was necessary in some instances to collect data up to reasonably high angles, typically to more than  $2\theta = 90^\circ$  with Cu K $\alpha$  radiation.

## RESULTS

Most of the semicrystalline polymers can be arbitrarily divided into two categories: those which readily crystallize into highly ordered structures, and those which do not. Diffractometer scans from the first class of polymers (e.g. polyethylene, Figure 1) have well resolved crystalline peaks, and therefore the scan can be fitted with an amorphous halo and crystalline peaks reliably and reproducibly over a wide range of crystallinities without imposing any special constraints in the least-squares procedure (Figure 1 and Table 2). The only potential problem is the possibility that there may be weak reflections from other ill-defined crystalline phases (monoclinic or triclinic in polyethylene). The problem that concerns us here, however, is the analysis of scans from the second class of polymers, such as nylon-6 and certain fluoropolymers, which do not always form highly ordered structures. In such instances it is difficult to draw an amorphous halo unambiguously. Therefore, we had to seek new methods for determining and describing the amorphous halo. In doing so, we sought a general procedure that can be applied to all semicrystalline polymers.

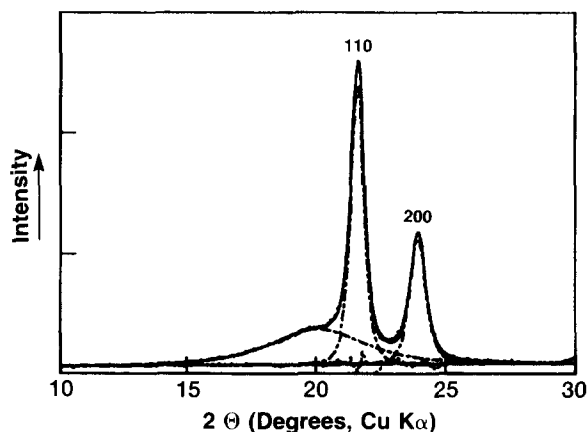
### Nylon-6

An indirect determination of the amorphous template is especially important in nylon-6. A quick-quenched amorphous film is difficult to prepare, and when prepared

such a film rapidly crystallizes upon exposure to ambient atmosphere. Therefore, an amorphous template was obtained by resolving the diffraction pattern of a highly crystalline nylon-6 powder (obtained by hydrolysing a nylon-6 film in water at  $150^\circ\text{C}$  for 2 h) into crystalline peaks and an amorphous halo (Figure 2a). The crystalline peaks due to the  $\alpha$  crystalline form of nylon-6 are indexed in the figure. The amorphous halo derived from the profile analysis of this well resolved pattern was then used as a template in analysing diffractometer scans from nylon-6 with less well resolved peaks (Figures 2b and 2c).

In nylon-6, as well as with other polymers, the positions of the crystalline peaks are sensitive to processing. Therefore, in profile fitting the data from an arbitrary sample, the positions of the crystalline peaks cannot be fixed at the values determined from the template. Further, although the sample used for the template may have only one crystalline modification, an arbitrary sample of the same polymer is likely to have more than one crystalline modification. Thus, while the crystalline peaks in the diffractometer scan shown in Figure 2a are due to the  $\alpha$  form, Figure 2b shows a sample with only  $\gamma$  crystalline fraction, and a scan from a sample with mixtures of  $\alpha$  and  $\gamma$  is shown in Figure 2c. In analysing these nylon-6 data, the half-width of the amorphous peak was allowed to vary over a small range ( $0.5^\circ$ ). The results of profile analysis of the three scans in Figure 2 are given in Table 3. Such analysis is now being used routinely in our laboratory, and has produced reliable and reproducible results for *CI* and crystallite size.

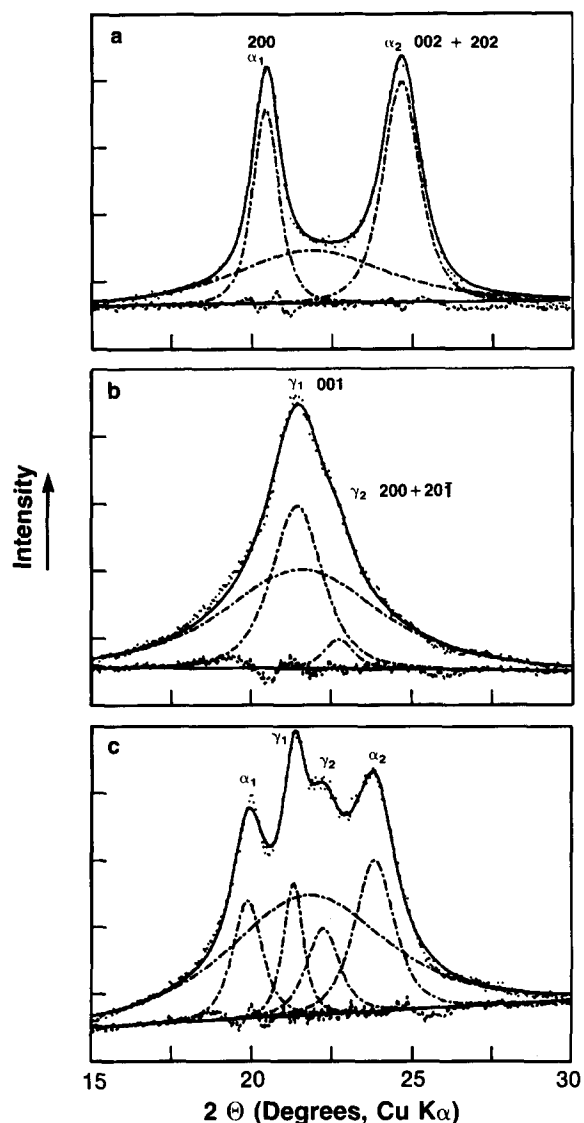
In our analysis, we have consistently found that the amorphous halo is at  $2\theta \approx 21^\circ$ . In contrast, Heuvel and Huisman<sup>3</sup>, who have done extensive profile fitting work on nylon-6 fibres, suggest that the amorphous halo is at



**Figure 1** Profile analysis of a diffractometer scan from polyethylene. In this and the following figures, the dots are the observed data points, peaks in broken curves are the resolved components, the full curves are the sum of the components (this should overlap the observed data points) and the broken lines over the baseline (shown by full line) represent the difference between the observed intensities and the calculated values. The numbers identifying the peaks are Miller indices

**Table 2** Profile parameters for polyethylene

	Am.	110	200
Template			
<i>CI</i> = 63%			
$2\theta$	20.06	21.62	23.94
$I(0)$	1456	11 624	5218
<i>FWHM</i>	4.28	0.59	0.72



**Figure 2** Profile analysis of diffractometer scans from nylon-6: (a) template from a highly crystalline film of nylon-6; (b) analysis of a diffractometer scan in which the peaks are not well resolved; (c) analysis of a typical scan with a mixture of  $\alpha$  and  $\gamma$  phases

**Table 3** Profile parameters for nylon-6

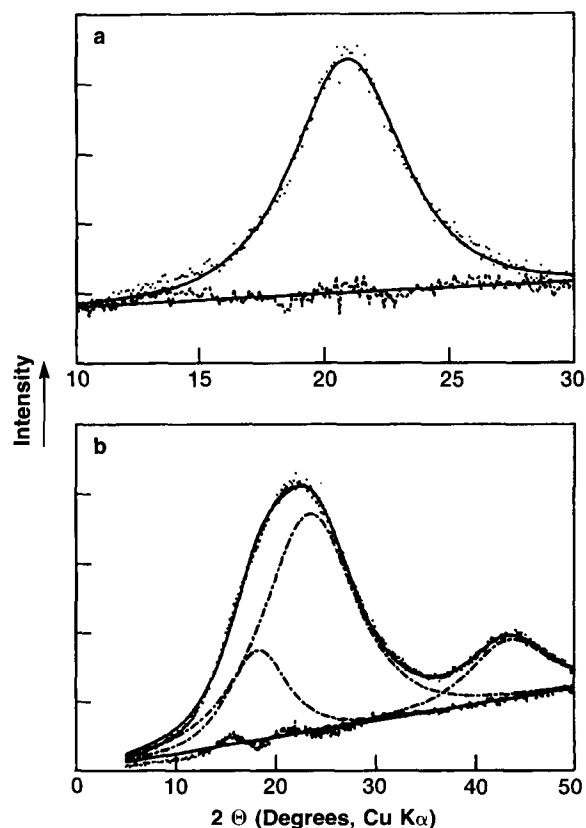
	Am.	$\alpha$		$\gamma$	
		200	002+202	001	200+20I
Template					
CI=64%					
$2\theta$	21.83	20.43	24.67	—	—
$I(0)$	783	2922	3338	—	—
FWHM	5.49	0.98	1.39	—	—
Test 1					
CI=36%					
$2\theta$	21.59	—	—	21.46	22.73
$I(0)$	1471	—	—	2399	450
FWHM	5.67	—	—	1.75	1.03
Test 2					
CI=45%					
$2\theta$	21.73	19.87	23.82	21.30	22.22
$I(0)$	1796	1748	2284	2002	1275
FWHM	5.67	1.07	1.47	0.73	1.17

$2\theta = 19.8^\circ$ . Our value of  $2\theta \approx 21^\circ$  agrees well with the data from carefully prepared films of amorphous nylon-6 either by quick-quenching (Figure 3a, FWHM fixed at  $5.5^\circ$ , and the fitted  $2\theta$  value of  $20.93^\circ$ ) or by gelation<sup>4</sup>. The small differences between the observed diffractometer

scan of the quick-quenched film (points) and the amorphous template derived from the analysis of the highly crystalline sample (full curve overlapping the points) can be attributed to a small amount of crystallinity (about 5%) even in this carefully prepared 'amorphous' film. The value chosen by Huevel and Huisman is closer to that of the amorphous halo in the melt and in the meridional scan of a nylon-6 fibre. The lower value in the melt is partly due to thermal expansion, and hence cannot be used as a template in analysing the data from samples at room temperature. The lower  $2\theta$  value of the amorphous halo along the meridian in a fibre corresponds to the fraction of the amorphous chain segments oriented perpendicular to the fibre axis, and hence may not be representative of the whole amorphous component in the sample. Therefore, our value of  $21^\circ$  is likely to be the most reasonable average  $2\theta$  position for the amorphous halo in most nylon-6 samples.

#### Poly(ethylene terephthalate)

The parameters for the amorphous halo were obtained by analysing the diffractometer scan of a highly crystalline sample obtained from a PET powder with  $M_w \approx 3000$  (intrinsic viscosity,  $IV \approx 0.08 \text{ dl g}^{-1}$ ) (provided to us by S. M. Aharoni). This pattern was resolved into easily identifiable crystalline peaks (Figure 4a). The intensity that could not be attributed to the crystalline peaks was used to determine the amorphous template, and the parameters of the template were then used to determine the crystallinity of poorly crystallized samples, such as the one shown in Figure 4b. Because of the low degree of crystalline order in the test sample, which is typical of the PET samples, we were not able to resolve the three



**Figure 3** Comparison of the amorphous halo obtained as a template from analysing highly crystalline polymer with the scan from an 'amorphous' polymer: (a) nylon-6; (b) poly(ethylene terephthalate)

peaks at  $2\theta = 23.89^\circ$ ,  $24.82^\circ$  and  $25.73^\circ$ . The results of profile analysis for PET are given in Table 4. As in the case of nylon-6, the half-width of the amorphous peak was allowed to vary over a small range ( $0.5^\circ$ ). PET amorphous scattering determined here is different from that published earlier by us<sup>5</sup> and by Johnson<sup>6</sup>, both of which are for equatorial scans, and by Wakelyn<sup>7</sup> from both an unoriented film and an equatorial scan of a fibre. But the amorphous scattering derived here (Figure 3b, full curves overlapping the observed data points) is in agreement with that obtained from quick-quenched PET (points). In fitting this quick-quenched amorphous sample we used model E, i.e. the parameters obtained from the template were used only as starting values in fitting the observed scattering from the quick-quenched film. The *FWHM* calculated for the three components are  $6.88^\circ$ ,  $10.71^\circ$  and  $9.31^\circ$  at values of  $2\theta = 18.16^\circ$ ,  $23.36^\circ$  and  $43.45^\circ$ , respectively; the corresponding values in the template are  $4.55^\circ$ ,  $7.15^\circ$  and  $8.79^\circ$  at  $2\theta = 16.62^\circ$ ,  $24.04^\circ$

and  $41.87^\circ$ . The differences between the values of the template and that of the quick-quenched film, especially the *FWHM*, can be attributed to the differences in the structure of the amorphous phase in samples of differing crystallinities. The implications of such changes in amorphous scattering of PET will be discussed elsewhere.

#### Fluoropolymers

Amorphous standards of certain fluoropolymers are even more difficult to obtain than that of nylon-6. Therefore, the method that we illustrate here with two different fluoropolymers was found to be extremely useful in the routine analysis of these polymers.

A highly crystalline sample of a copolymer of ethylene and chlorotrifluoroethylene (poly(E/CTFE), sold as Halar 300 by Ausimont Inc.) was obtained by annealing a film of this polymer at  $200^\circ\text{C}$  for 100 h<sup>8</sup>. The scan from this sample was resolved into crystalline and amorphous components (Figure 5a) to obtain the amorphous template. The amorphous scattering at  $\sim 18^\circ$  is due to lateral packing of the polymer chains, while the halo at  $2\theta = 22^\circ$  is due to the layer line corresponding to the ordering of the chemical groups along the chain axis. To obtain values consistent with those calculated for other polymers we have analysed thus far, the *CI* reported in Table 5 are obtained by comparing the area of the crystalline peaks to that of the equatorial amorphous halo. Figure 5b shows the use of this template in evaluating the crystallinity of a less-crystalline sample of poly(E/CTFE). The results of profile fitting are tabulated in Table 5. Note that we had to use two almost overlapping crystalline peaks in fitting data from these highly crystalline samples. The two peaks may be due to an asymmetric peak shape arising from the geometry of the data collection. However, it is more likely that poly(E/CTFE) may not be pseudohexagonal, and this may cause the split in the most intense peak. The split peaks may also be due to the presence of two slightly different crystalline lattices. Further work is necessary to understand the changes in the shape of the crystalline peaks in this polymer.

As a last example we present in Figure 6 analysis of a copolymer of chlorotrifluoroethylene and vinylidene fluoride (poly(CTFE/VF<sub>2</sub>)). Depending on the processing conditions, this polymer can have unusually large ( $\sim 500 \text{ \AA}$ ) crystallites. In such instances, an accurate determination of crystallite sizes over a wide range of values ( $50\text{--}500 \text{ \AA}$ ), as well as crystallinity, required the use of a template derived from an analysis of highly crystalline polymer (Figure 6a). This diffraction pattern was obtained by slow-cooling (16 h) of a film ( $\sim 50 \mu\text{m}$  thick) while still in the moulding press. Using this

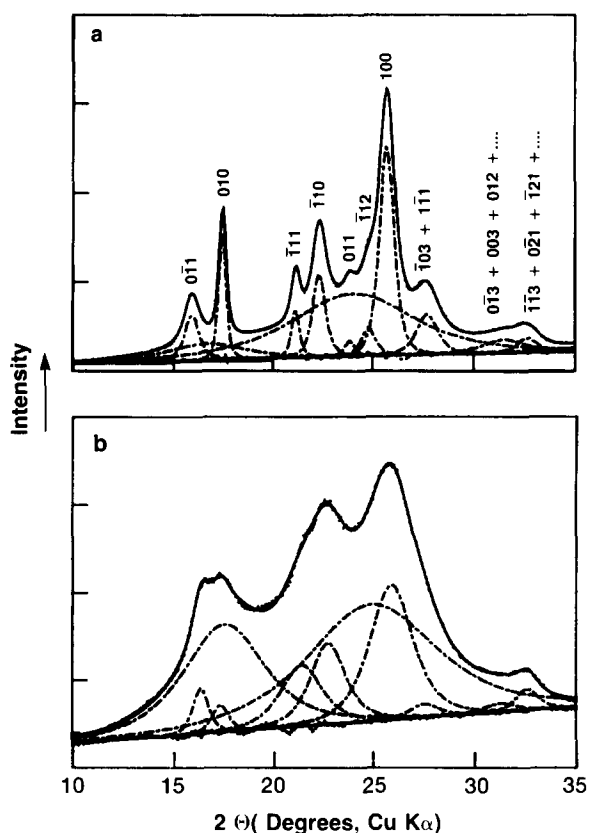
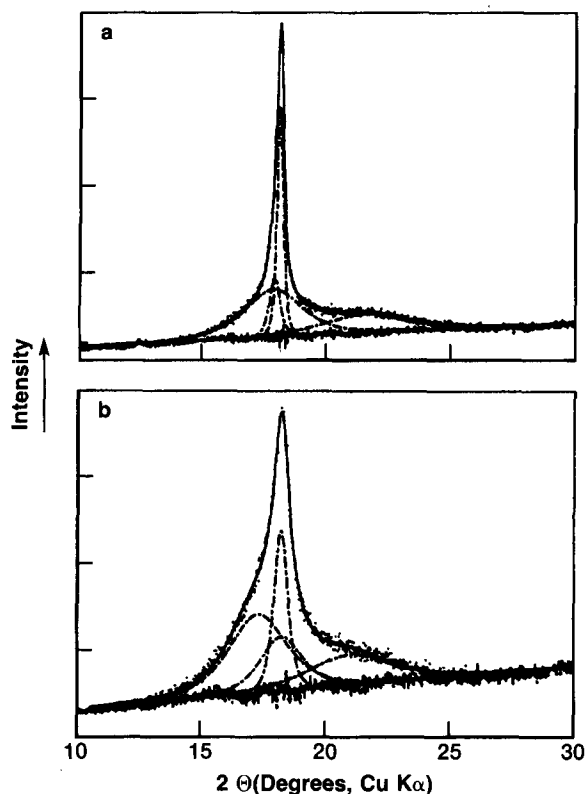


Figure 4 Profile analysis of diffractometer scans from PET: (a) template from a highly crystalline sample of PET; (b) fitting of a scan from a typical sample of PET with poorly resolved peaks

Table 4 Profile parameters for PET

	Am.-1	Am.-2	011	010	111	110	011	112	100	103+111	Mix.	Mix.
Template												
<i>CI</i> = 49%												
$2\theta$	16.62	24.04	15.92	17.46	21.16	22.36	23.89	24.82	25.73	27.72	31.54	32.67
<i>I</i> (0)	91	350	254	716	267	466	88	157	1170	234	75	82
<i>FWHM</i>	4.55	7.15	0.86	0.43	0.48	0.78	0.57	0.82	0.85	1.24	2.50	1.18
Test												
<i>CI</i> = 38%												
$2\theta$	17.49	24.92	16.32	17.30	21.40	22.76	—	25.92	—	27.54	31.29	32.60
<i>I</i> (0)	122	133	51	30	69	92	—	153	—	15	10	24
<i>FWHM</i>	4.79	7.53	0.93	1.00	2.50	2.11	—	2.50	—	1.67	1.86	1.26



**Figure 5** Profile analysis of diffractometer scans from poly(E/CTFE): (a) template from a highly crystalline polymer; (b) fitting of data from poorly crystallized polymer

**Table 5** Profile parameters for poly(E/CTFE)

	Am.-1	Am.-2	C.-1	C.-2
<b>Template</b>				
CI=43%				
$2\theta$	17.88	21.57	17.93	18.16
$I(0)$	541	209	649	2673
FWHM	2.71	3.85	0.50	0.30
<b>Test</b>				
CI=49%				
$2\theta$	17.31	21.0	18.23	18.23
$I(0)$	455	176	861	375
FWHM	2.71	3.85	0.62	1.80

**Table 6** Profile parameters of copolymers of CTFE and VF<sub>2</sub>

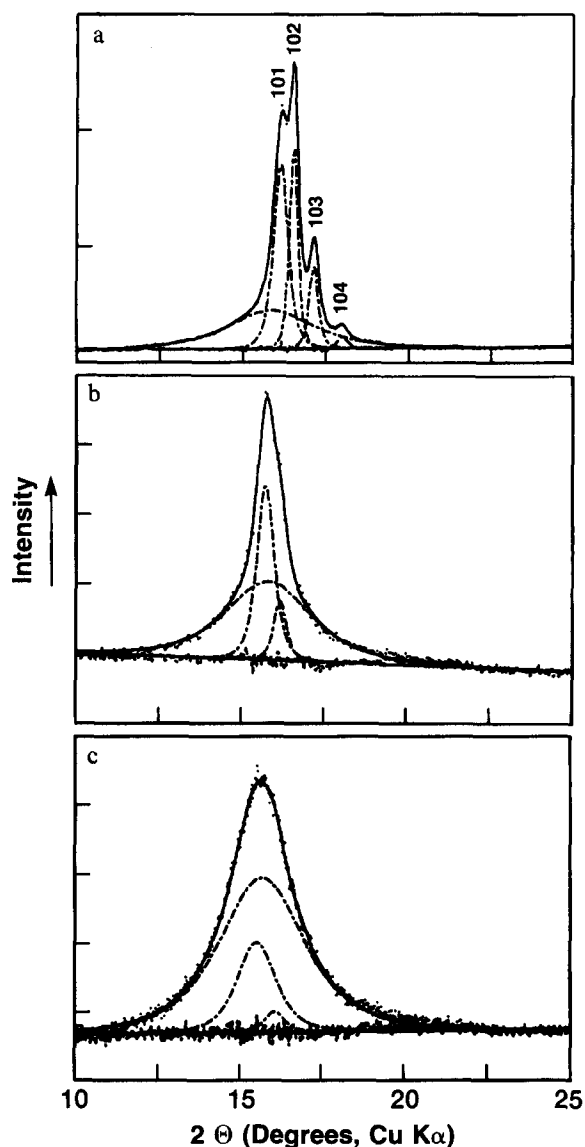
	Am.	101	102	103	104
<b>Template (~3% VF<sub>2</sub>)</b>					
CI=61%					
$2\theta$	15.86	16.15	16.53	17.15	18.01
$I(0)$	3331	15838	17267	7012	1024
FWHM	3.08	0.52	0.30	0.35	0.34
<b>Test 1 (&lt;1% VF<sub>2</sub>)</b>					
CI=36%					
$2\theta$	15.82	15.73	16.17	—	—
$I(0)$	1130	2516	855	—	—
FWHM	3.08	0.61	0.46	—	—
<b>Test 2 (~3% VF<sub>2</sub>)</b>					
CI=23%					
$2\theta$	15.69	15.53	16.08	—	—
$I(0)$	1125	657	146	—	—
FWHM	3.08	1.39	0.72	—	—

template we could reproducibly obtain the crystallite sizes and the crystallinity of the poorly ordered material (Figure 6b). Figure 6c shows a similar analysis on an even more poorly crystallized sample prepared from the

same resin as that used in preparing the template. The results are summarized in Table 6. It can be seen in the table that the apparent crystallite size, which is also a measure of crystalline perfection, can be a more sensitive parameter than crystallinity in relating the morphology to the properties of the polymer.

## DISCUSSION

The objective of this study was to calculate reliably the amorphous scattering in semicrystalline polymers, and to obtain an amorphous template that can be used in estimating the crystallinity. The methods described here are useful in analysing data from polymers collected under similar conditions. The parameters are not transferable from one set of instrumental settings to another, since the shape of the template depends on collimation and, more importantly, on the mode of data collection (e.g. transmission vs. parafocus geometry). The method described here is not limited to diffraction measurements, and is equally applicable to spectroscopic (i.r. and n.m.r.) measurements as well.



**Figure 6** Profile analysis of diffractometer scans from poly(CTFE/VF<sub>2</sub>): (a) template from a highly crystalline polymer; (b) analysis of a test sample; (c) analysis of another test sample prepared from the same resin as the template

In our analysis, we have implicitly assumed the crystalline component of the polymer to be that fraction of the polymer whose scattering (and therefore the structure) deviates from that of the amorphous template. In this sense, the crystallinity calculated by our method is the non-amorphous component, with the template defining the term 'amorphous'. In many instances, this might correspond to the true crystallinity, but there might be occasions in which the crystallinity as calculated by this method is simply an ordered phase that is different from the template. This idea is not very different from the more common technique of density measurement, in which the crystallinity is calculated with reference to an amorphous and a crystalline standard. In fact, there is a good correlation between such X-ray crystallinity values and the crystallites obtained from density measurements (see ref. 9 for data on PET). But, unlike in density and other methods, no amorphous or crystalline standard is necessary in the method we have described here. Ideally, an amorphous phase possesses only a short-range order, and a perfect crystalline phase has long-range order extending over a large number (thousands) of unit cells. For our purpose, however, a crystalline fraction is defined as one in which 'long-range' order persists over at least about three unit cells, and the amorphous phase is regarded as one in which the coherence length is less than the length of about two unit cells ( $\sim 25 \text{ \AA}$ ). Finally, we do not imply that the structure of the amorphous regions, and hence the scattering, is independent of the processing conditions. On the contrary, the models C, D and E are introduced to account explicitly for such structural changes.

Model A is ideal in quality-control environments in which the measurements are carried out on presumably identical samples under identical conditions. In such instances, model A can readily detect samples that fall outside the acceptable range of crystallinity and crystallite size. Model B is appropriate when samples of different shapes and sizes, and whose crystallinity is expected to vary over a small range (30 to 50%), are analysed. If the crystallinity varies over a wider range (0 to 80%), and if there are other significant changes in processing parameters, then models C and D are necessary to take into account changes in the structure of the amorphous regions. We have rarely used model D, which is included for the sake of completeness. Model E is applicable when the objective is to obtain a good set of starting parameters, such as for the analysis of new copolymers whose scattering patterns resemble that of homopolymers. Model E is also useful in analysing polymers in which the structure of the amorphous phase changes significantly during crystallization, and hence the template obtained from highly crystalline polymers may not be suitable in analysing polymers with low crystallinity.

The technique described here is applicable to all polymers, and is especially useful in estimating the crystallinity of individual polymers in blends and laminates. Most importantly, there is no need for an amorphous standard, or of the least and the most crystalline samples, as required by other methods<sup>1</sup>. The only requirement in our method is that a reasonably crystalline sample of the polymer be obtained, for example by annealing a small piece of the sample being analysed. Samples with extremely high crystallinity (>85%) are not desirable since the amorphous halo in such samples is only a small fraction of the total intensity,

and hence the parameters of the amorphous scattering may not be reliably estimated. The essential requirement is that the crystallite size be as large as possible, because this allows accurate subtraction of the crystalline components in determining the amorphous halo. Samples with crystallinities of about 50% and with crystallite sizes  $\sim 100 \text{ \AA}$  or higher serve as good templates. In some instances, it is possible to generate powder diffraction patterns from established crystal structures of the polymer, or to determine the crystalline peaks from scans of polycrystalline powder samples of oligomers.

The availability of a template permits one to follow small changes in crystallinity within a given set of samples, to characterize samples with low levels of crystallinity (<10%) and to follow small differences (<10  $\text{\AA}$ ) in crystallite sizes. Our emphasis throughout this work had been to seek a method that would provide a reliable estimation of relative crystallinity in an industrial environment. The method can, however, be easily extended to calculate absolute crystallinity by the method of Ruland<sup>10</sup>. Further, the method of stripping the crystalline peaks will permit us to follow small changes in the amorphous segments in polymers.

In our analyses, we have chosen the shape of the amorphous peaks to be the same as that of the crystalline peaks, and the number of amorphous peaks we have chosen is of only practical convenience in evaluating the crystallinity. In the angular range commonly used for routine analysis ( $2\theta = 10^\circ$  to  $30^\circ$ ), the amorphous halo can be described by one peak along the equator, as in nylon-6, polyethylene and copolymers of CTFE, or by two peaks, as in PET. The relative heights of these peaks in polymers with more than one peak (e.g. PET) can vary depending on the sample history. The interpretation of these peaks is ambiguous, and we have refrained from discussing the significance of these amorphous peaks. Miller and Boyer<sup>11</sup> have attempted to correlate these peaks to chain dimensions such as cross-sectional area. On the other hand, it has been shown that both inter- and intramolecular scattering contribute to the intensity at distances up to  $8 \text{ \AA}$ <sup>12</sup>. One can in fact carry out *RDF* analysis on the amorphous scattering, obtained after stripping the crystalline peaks from the observed diffraction pattern, for a detailed study of the structure in the amorphous segments of the polymer. Such analysis will be useful in following small changes in the structure of the amorphous regions induced by heat, stress and moisture, which might be otherwise masked by similar change in the crystalline regions of the polymer.

## CONCLUSIONS

The amorphous scattering obtained by profile analysis of a highly crystalline sample of a semicrystalline polymer can be used to characterize the amorphous regions, and as a template in analysing poorly crystallized polymers. This method is quite general, and is valuable in instances when a reliable amorphous specimen of the polymer cannot be obtained.

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