Resolution Enhancement of Polymer X-ray Diffraction Scans Using Maximum Entropy Methods: Poly(ethylene terephthalate)

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ABSTRACT: The maximum entropy method was used for deconvolving the effect of size broadening in X-ray diffraction (XRD) scans. This technique is used to determine the number of components present in the diffuse halo from amorphous polymers and to sharpen the peaks in poorly crystallized polymers. The results of deconvolution are subsequently used in profile-fitting the data. The method is illustrated using data from poly(ethylene terephthalate) (PET) samples with crystallinities ranging from ca. 0% to 50%. Our analysis showed that while one peak is sufficient to describe the amorphous scattering in some polymers (e.g., nylon 6), two or more components are necessary for others (e.g., PET) in the angular range of 5-35°. Our analysis suggests that the amorphous halo in this angular range is, in general, determined by the average interchain distances in the corresponding crystal lattices. The amorphous phase in crystallizable polymers can have a significant amount of medium-range order derived from the local order in the crystalline phase.

Introduction

X-ray diffraction (XRD) scans from commercially produced semicrystalline polymers are almost always poorly resolved. Analysis of such scans often leads to ambiguous results. A proper description of the amorphous halo and the separation of the poorly resolved peaks are the two problems frequently encountered in calculating some of the commonly used parameters such as crystalline index and phase composition. These two issues are usually addressed using various types of curve-fitting procedures.[1-4] More appropriately, the number and the positions of the overlapping peaks can be determined from a second or even a fourth derivative of the raw data prior to curve fitting.[5] This can be done using Fourier techniques since obtaining a derivative in the reciprocal space is equivalent to a multiplication operation in the real space. This approach is, however, of limited practical value since peak intensities on the order of 10^5 counts may be required to obtain reliable results (Murthy, N. S., unpublished results, 1984).

We here illustrate the application of maximum entropy methods[6-10] to these problems by analyzing the diffuse scattering from amorphous poly(ethylene terephthalate) (PET) as well as a diffraction pattern from poorly crystallized PET. We will deconvolve the XRD scan using an empirically chosen response function to represent the broadening due to size and disorder. The resulting sharpened diffractogram is used to identify the peaks in a subsequent least-squares curve-fitting procedure. Such an exercise enables us to obtain a physically meaningful and optimum analytical description of the amorphous halo and also enhances our understanding of the nature of the medium-range order in the amorphous phase.

Materials, Methods, and Results

Several amorphous PET samples (50-1650-μm-thick compression-molded films and 3-mm-thick injection-molded bars) obtained by rapid cooling were analyzed. Some of these specimens were subsequently annealed so as to increase their crystallinity. A low molecular weight PET (IV = 0.08 dL/g) powder was analyzed for use as a high crystallinity standard. Most of these data were obtained over a period of 10 years from resins with IV's of 0.53, 0.7, and 0.95 dL/g and hence can be regarded as a random selection of data, particularly in regards to the several amorphous scans used for illustrating the analysis of the diffuse scattering from the amorphous phase.

XRD scans were obtained on a Philips powder diffractometer in the parafocus geometry using copper radiation and a diffracted beam monochromator. The data were in steps of 0.1° with a counting time of 5-50 s/step. The data were analyzed using the program RAZOR in GRAMS/386 software (version 1.05A, Galactic Industries Corp.) for deconvolution and a modified version of SHADOW for profile analysis.[11] A modified Lorentzian [$I(x) = I(0)/(1 + kx^2)^m$; $k = (2^{1/m} - 1)/(\text{fwhm}/2)^2$; $m = 2$; fwhm is the full-width at half-maximum] was used to describe the peak shapes.

A typical scan from an amorphous PET sample is shown in Figure 1a. We will consider the data $2\theta < 35°$ because the contribution to the intensity in this angular range is primarily from interchain scattering.[12,13] Since the coherence length of the amorphous chain segments is not known *a priori*, this scan was deconvolved using size-broadening functions of widths ranging from 1° to 10° (Figure 1b). Also, scans from different amorphous PET samples were deconvolved using peak widths of 3° and 6° (Figure 2). On the basis of these results, we chose to describe the amorphous scattering in the angular range of 5-35° by three components (see the Discussion). Figure 3a shows the analysis of the amorphous PET (Figure 1a) using the three-peak description of the amorphous scattering. In some semicrystalline PET specimens, however, a two-peak model appears to be satisfactory; in fact the least-squares procedure eliminates the third peak at 20-21° or reduces its intensity to a very low value (Figure 3b,d).

Figure 4a shows the use of the maximum entropy method to sharpen the crystalline peaks in the scans from semicrystalline polymers. As in the case of amorphous scans, the scans with crystalline peaks were deconvolved using a single response function. Highly crystalline samples (PFLPET curve) require a narrow (1°) broadening function, and poorly crystallized samples (D91262B and -C) require a broader (2°) function. In amorphous specimens (D93173B), the "crystalline" peaks can be obtained only with a broad (3°) function, but these peaks do not correlate with the real crystalline peaks. When the broadening function is too wide (6°), then the semicrystalline samples show only three peaks (Figure 4b). Although these peaks bear some resemblance to those observed with amorphous scans (D93173B), it will be shown later that these "amorphous" peaks are artifacts of the analysis.

Discussion

The maximum entropy method is a powerful tool widely used in signal processing in such diverse applications as image reconstruction, noise reduction, and crystal structure

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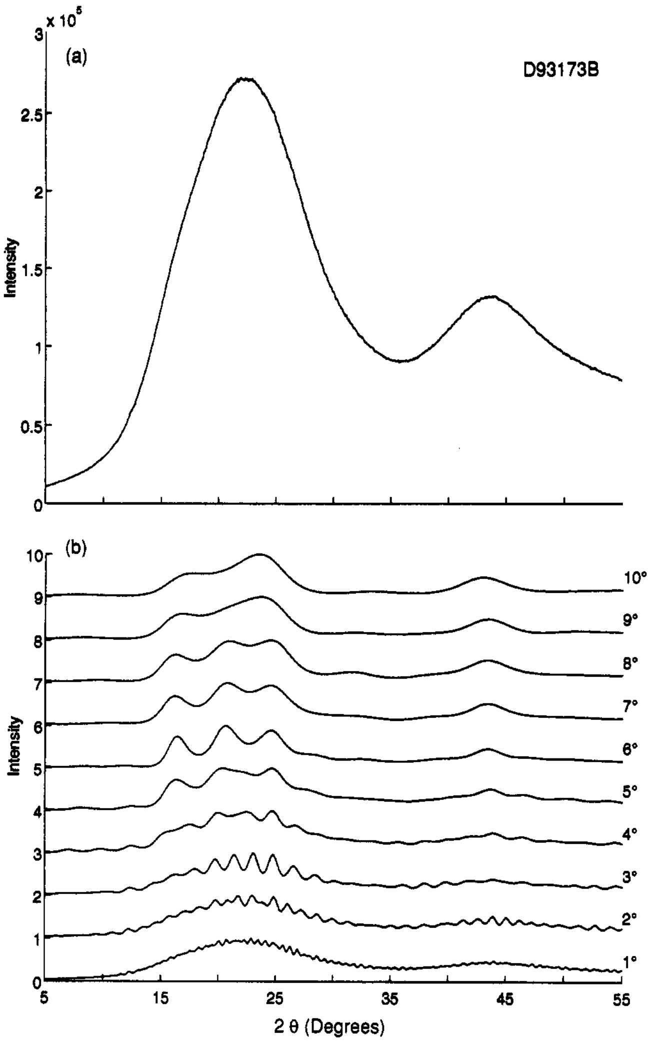

Figure 1. (a) XRD scan of a typical quick-quenched PET. (b) Effect of the width of the peak used in the deconvolution of the XRD scan of amorphous PET.

determination.[6-10] We here use the method to sharpen the peaks. Peaks are usually sharpened by deconvolving the instrumental response function from the observed spectrum. In this paper we ask the question, how will the XRD scan appear if we artificially remove the effect of broadening due to size or limited coherence length? For this purpose, we deconvolve the broadening due to small crystallites or microcrystallites (coherence length ~ 30 Å) or amorphous domains (coherence length ~ 15 Å) by using the Scherrer broadening as our system response function. The resulting sharpened diffractogram enables us to identify the various peaks which can then be used in the profile-fitting procedure to determine the relative areas.

The results of deconvolution are determined by the response function used in the analysis. We use a modified Lorentzian both for the size-broadening peak for deconvolution and for the peak shapes in profile analysis. This choice is based on the analysis of scans of highly crystalline samples which indicate that a modified Lorentzian provides the best description with the least number of parameters in the angular range under consideration. The width of the response function should be less than the width of the features being sharpened. A larger width is meaningless, and too small a width will enhance the noise in the data. In deconvolving scans from amorphous samples, a 6° wide size-broadening function gave consistent results (Figures 1 and 2) and this width corresponds to a reasonable coherence length of ca. 15 Å. The results of

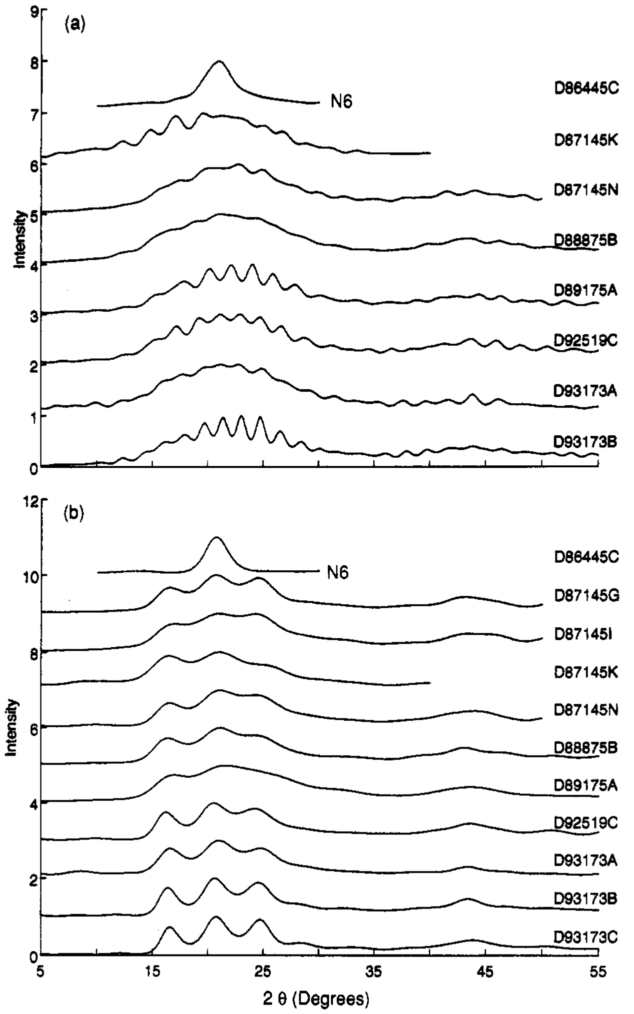

Figure 2. Deconvolved XRD scans from several different PET samples using peak widths of (a) 3° and (b) 6°. A deconvolved curve from an amorphous nylon 6 film is also shown in the figure for comparison.

deconvolution remain unchanged at widths from 5° to 8° (Figure 1b). A narrower size-broadening function would reveal any long-range order present in the specimen. However, even a 3° wide response function yields too many peaks (Figure 2a), many of which are due to noise in the data and thus are not indicative of crystalline order in our specimens (see the next paragraph). A broader response function yields an oversmoothed curve in which many of the meaningful details are lost. In deconvolving a scan in which crystalline peaks are expected to be present (Figure 3b–d), it would be necessary to use a size-broadening function of ca. 1–2°, corresponding to a crystallite size of 30–80 Å (Figure 4a). A smaller width enhances noise in the data, and the results obtained using a larger width are not meaningful (see the next paragraph).

The data from all the samples deconvolved with a 6° wide peak show the same three peaks at essentially the same angles (Figure 2b and Table 1). The three-peak description is valid over a range of widths (5–8°) of the size-broadening function (Figure 1b). Although more than three peaks are seen in the curves deconvolved using a narrower (3°) size-broadening function, these peaks do not occur at the same angles (Figure 2a). Furthermore, these sharp peaks do not correspond to the crystalline peaks as would be expected by the similarities of these deconvolved data to those from highly crystalline samples (Figure 4a). In fact, the peaks due to small glitches in the data cannot be distinguished from those due to real peaks. The three peaks in the data obtained by deconvolving

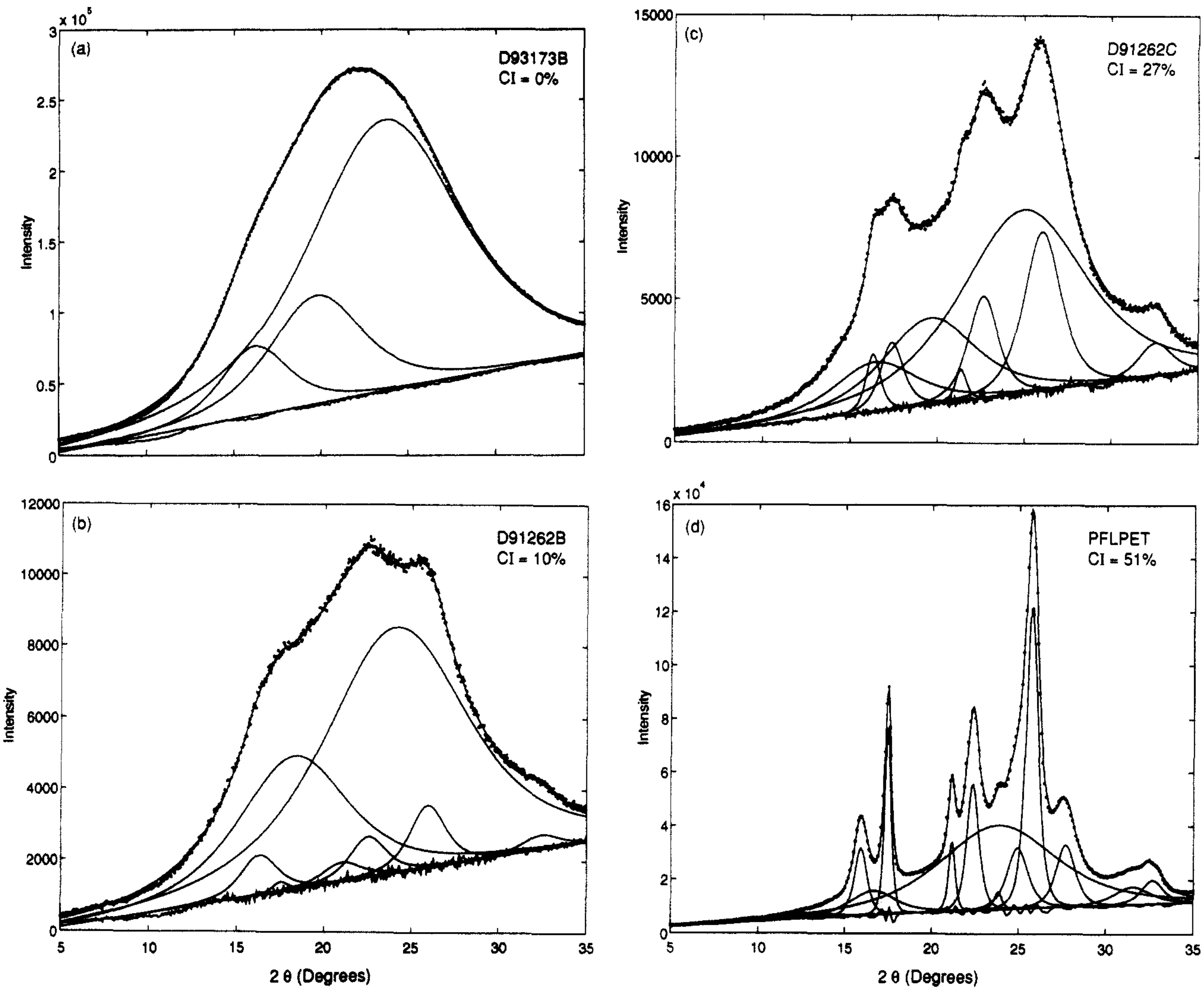

Figure 3. Profile-fitted results of four PET scans of varying crystallinity as indicated in the figure. The fitted curve is shown by the full line through the observed data points (filled circles). The resolved components are also shown by the full lines. The difference between the observed data and the fitted curve is shown by the curve oscillating above and below the base line.

the scans with crystalline peaks using a 6° width (Figure 4b) do not correspond to the amorphous peaks. The positions of these peaks vary from sample to sample, and these peaks are actually composites of closely spaced crystalline peaks. In fact, the three peaks in Figure 4b may not be meaningful, since the response function is wider than the most intense features in the raw data (Figure 3). In contrast, the peaks in Figure 2b are the real components present in the amorphous scattering. We should note that the amorphous halo in nylon 6 can be described by a single amorphous peak (Figure 2). Such a single peak description should be valid for all nylons and many other polymers like polyethylene and fluoropolymers in which the interchain interactions in the lateral directions are essentially isotropic.

In our earlier publication, on the basis of the asymmetry in the amorphous halo of PET and changes in this asymmetry with processing conditions and temperature, we came to the conclusion that at least two peaks are required to describe the amorphous scattering.[13] In many instances, especially when PET is semicrystalline, a two-peak model indeed provides a reliable curve fit. In the three semicrystalline scans shown in Figure 3, the least-squares fitting program eliminates the 21° peak in two of the scans (Figure 3b,d), and both the two-peak and the three-peak description are equally acceptable in one (Figure 3c; only the three-peak fit is shown in the figure). In general, especially with amorphous scans, a significantly better fit is obtained using a three-peak model (Figure 3a). The two-peak description of the amorphous scattering is probably appropriate when the amorphous domains are highly disordered (scan D89175A, Figure 2b).

The three-component description of the amorphous scattering in PET suggests that the characteristics of the local order in the amorphous phase and that in the crystalline phase are similar (Figure 5 and Table 1). The highest-angle peak (24–26°) represents the 4.0-Å distance between the chains normal to the plane of the aromatic groups along the *a*-axis. The two low-angle peaks represent the distance between the chains roughly in the plane of the aromatic groups: the 20–21° peak represents the 5.1-Å distance along the diagonal in the *a*–*b* plane, and the 17° peak represents the 5.9-Å distance along the *b*-axis. Table 1 shows that, with the exception of the 21° peak, there is a good agreement between the interchain distances in the crystalline and the amorphous regions (Table 1). The 5-Å distance (along the diagonal; Figure 5) corresponding to this 21° peak may not be distinguishable from the 17° and 25° peaks when the amorphous domains are highly disordered. In such instances it is necessary to describe the amorphous peak by two components as we did in our earlier studies.[13]

We have thus far discussed the use of the maximum entropy method in deconvolving the diffraction scans from amorphous specimens. The analysis of the amorphous scattering in a semicrystalline polymer using this

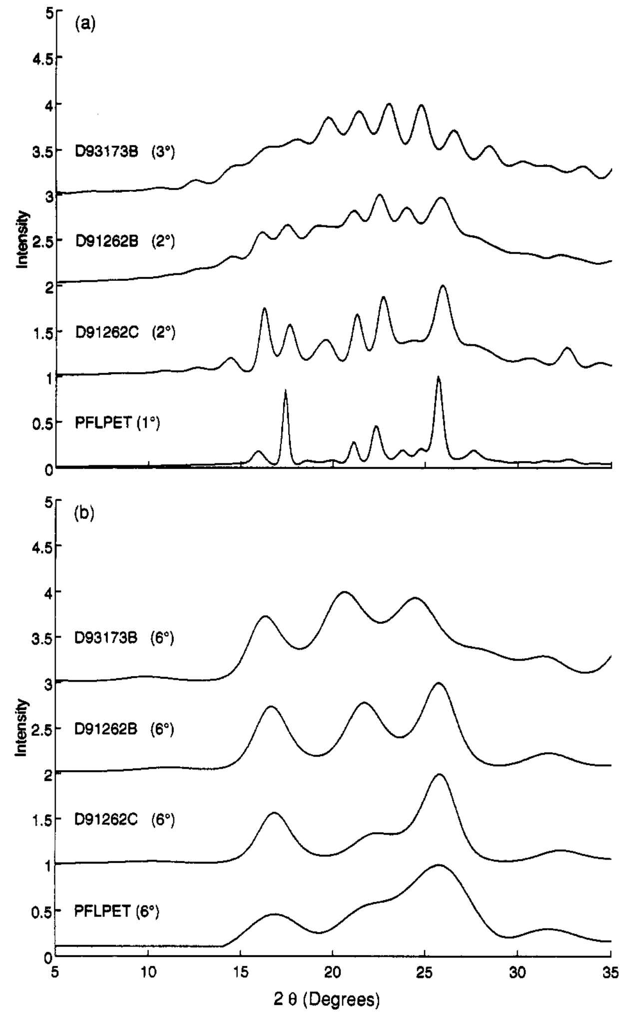

Figure 4. Deconvolved XRD scans of four PET samples with crystallinities of 0%, 10%, 27%, and 51% (from Figure 3): (a) 1–3° broadening function; (b) 6° broadening function.

Table 1. Peak Parameters Obtained from Profile Analysis of XRD Data from PET[a]

	peak number		
	1	2	3
2θ (deg)	16.9 (0.8)	20.6 (0.7)	24.7 (0.7)
fwhm (deg)	5.7 (1.1)	6.5 (1.1)	9.5 (1.9)
integrated intensity (area, %)	15 (6)	23 (6)	63 (5)
interchain distances in projection (Å):			
obsd[b]	5.82	4.78	4.00
calcd	5.87	5.11	4.03

[a] The numbers in parentheses are standard deviations from 15 different (11 amorphous and 4 semicrystalline) samples. [b] The observed amorphous interchain distances (R) are obtained from the Bragg d spacings of the amorphous halo (d_{amo}) from the relation[14] $R = 1.11d_{\mathrm{amo}}$.

method may not be feasible. Although some of the scans (e.g., D91262C in Figure 4a) show a peak at 20° due to the amorphous scattering (Figure 3c), it is, in general, not easy to distinguish the amorphous and the crystalline peaks in the deconvolved data. Nevertheless, deconvolution of the scans from semicrystalline specimens is still useful. Diffraction scans from semicrystalline polymers of the type shown in Figure 3b–d, especially the one in Figure 3d, are typically analyzed using any one of the large number of nonlinear least-squares peak-fitting programs. But the deconvolved or resolution-enhanced diffractograms (Figure 4a) can be helpful in identifying closely spaced or overlapping crystalline peaks in a polymer for which there is no prior knowledge of the number and the position of the crystalline peaks. At present we typically use a highly crystalline scan of the type shown in Figure 3d from an oligomer of the same polymer, but the resolution enhancement of the type described here makes this unnecessary.

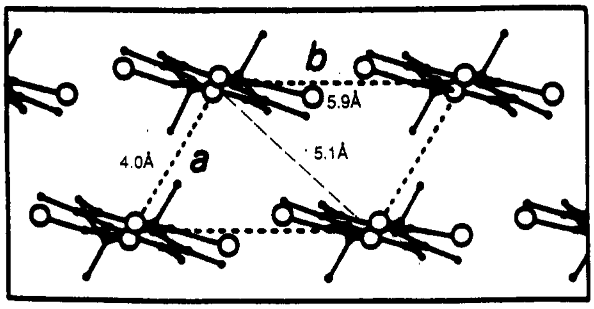

Figure 5. PET unit cell in a chain-axis projection to illustrate the relation between the three amorphous d-spacings to the structure. Reprinted with permission from ref 15. Copyright 1954 Royal Society of London.

Implications. Although the amorphous phase in many polymers could be ordered, the degree of this order is probably determined by the extent to which the conformation of a single-chain constrains the amorphous chain segments to be ordered. The high degree of ordering of the amorphous chain segments in PET which permits the various interchain distances to be distinguished is obviously due to the orientational correlations of the aromatic groups on neighboring chains.[13] Similarly, the H-bonds in nylon 6 impose constraints so that the amorphous chain segments are not totally disordered. In oriented polymers, in which it is possible to have oriented and unoriented amorphous components, the oriented amorphous component can have a substantial degree of medium-range order, somewhat similar to the paracrystalline lattice of Hosemann.[12,16] Our findings reported here suggest that there is residual crystalline-like order in the amorphous phase even in unoriented polymers. These amorphous domains could be microcrystallites perhaps between crystalline domains. We will designate all the domains which have a coherence length extending over 3–5 chains (typically 15–25 Å) as amorphous.

Implicit in our analysis is the description of semicrystalline polymers as two-phase systems consisting of amorphous and semicrystalline components. In the alternate crystal-defect model, the amorphous regions are simply defects dispersed in the crystalline phase, and the frequency of these defects could vary from one region to another.[17] In such a model the amorphous scattering is essentially a disorder or thermal diffuse scattering which contributes to the intensity near the tails of the crystalline peaks. Our attempts to fit the data in Figure 4c,d using Lorentzian and Pearson VII peaks to describe crystalline peaks with very long tails were unsuccessful. More importantly, as the crystallinity of the material increases, the peaks do not simply become sharper or change in shape, but new peaks corresponding to the crystalline domain appear at crystallinities as low as 10% (Figure 3b). These data, as well as our experience with other polymers,[2] suggest that the most useful description of a semicrystalline polymer is provided by a two-phase model in which the crystalline phase has the same characteristics of a highly crystalline material and an amorphous phase whose halo extends in many instances over two or more crystalline reflections. Our results suggest that the amorphous halo in all polymers could be drawn on the basis of interchain distances.

Conclusions

Maximum entropy methods can be used as a tool for the quantitative evaluation of the poorly crystallized, semicrystalline polymers. In particular, it helps in the identification of the crystalline peaks even when the crystallites are highly disordered. More importantly, the deconvolution of the amorphous scattering shows that medium-range order in the amorphous phase in crystallizable polymers such as PET resembles the local order of the crystalline phase.

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