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New Aspects Concerning the Structure and Degree of Crystallinity in High-Pressure-Crystallized Poly(ethylene terephthalate)

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ABSTRACT: The crystallinity (x_c) of high-pressure-crystallized poly(ethylene terephthalate) (PET), which shows values of $x_c \cong 0.90$ when measured by differential scanning calorimetry (DSC), was examined by means of wide-angle X-ray scattering (WAXS). PET samples crystallized under normal conditions were also investigated by WAXS, DSC, and density for comparison. It is shown that the degree of crystallinity derived from WAXS for the high-pressure-crystallized samples is smaller than the values obtained by calorimetry and density. However, the crystallinity values from WAXS are still larger than the values found in the material crystallized under normal pressure. Furthermore, it is shown that the unit cell dimensions of the PET samples are not affected by the pressure during crystallization. The lower value of the degree of crystallinity as measured by WAXS is discussed in terms of an interface of finite thickness between the crystals and the amorphous regions.

A. Introduction

It is well known that PET crystallized at atmospheric pressure shows crystallinity values which typically vary between 20 and 50%.[1] In a recent study, it was shown that PET crystallized from the melt under high pressure (400 MPa) in the temperature range 295−320 °C results in a material with a melting enthalpy of about 121 J g^{-1} and a density of about 1.462 g cm^{-3}.[2] By assuming the usual values for the melting enthalpy and the density of ideal crystals of PET (135 J g^{-1} and 1.490 g cm^{-3}, respectively), it follows that the degree of crystallinity of this high-pressure-crystallized material is about 90%. Such a high value has never been obtained in PET before. An analysis of the small-angle X-ray scattering (SAXS) of these samples has shown that the material is composed of lamellar stacks of $l_c \cong 10$ nm thick crystals alternated by amorphous regions having a thickness of about $l_a \cong 1.3$ nm.[3] The unusual low values of l_a obtained are characteristic for nanostructural materials.[4,5] Measurements of the microhardness have also been performed with this material.[2] A value of 393 MPa has been recently obtained, which is close to the microhardness for a material with a 100% degree of crystallinity, as derived by extrapolation of values measured on semicrystalline samples with various degrees of crystallinities. The above studies emphasized the substantial reduction in molecular weight after anabaric crystallization (from $M_w = 30000$ g mol^{-1} to $M_w = 8000$ g mol^{-1}).

There arises the question as whether the high degree of crystallinity and the high value of the microhardness obtained in these materials are just a consequence of the low molecular weight or whether they are caused by some specific structure arising during the crystallization at high pressure. Therefore, in this study we wish to present some new results concerning the wide-angle X-ray scattering (WAXS) of high-pressure-crystallized PET. Especially, we wish to report about the measurement of the degree of crystallinity x_c and the lattice distortion factor k by using Ruland's method.[6] We have also determined the position of the crystal reflections accurately in order to verify whether the dimensions of the crystallographic unit cell are the same as those in PET crystallized under atmospheric pressure. For this reason, we have also performed unit cell measurements on a PET sample crystallized at atmospheric pressure.

B. Experimental Section

Materials. The high-pressure-crystallized samples (P1, P2, and P3) (see Table 1) were prepared by Dr. R. K. Bayer, University of Kassel, by melting the PET pellets in a mold at 275 °C, pressing the molten material at 50 MPa followed by cooling to 45 °C at 50 MPa, and finally crystallizing by increasing the temperature to 320 °C and the pressure to 400 MPa. In these experiments, we used industrial PET from Hoechst.

The reference PET samples crystallized at atmospheric pressure obtained were synthesized in our laboratory as described in a previous publication.[7] The molecular weight was varied by changing the polycondensation time. Two samples with a molecular weight $M_w = 30000$ g mol^{-1} were melt pressed at 280 °C under a pressure of 4 MPa and quenched in ice water (see Table 1). The first sample (N1) was crystallized in vacuo by increasing the temperature from 20 to 260 °C within 2 h and, then, by annealing for 24 h at this temperature followed by cooling to room temperature within 12 h. The second sample (N2) was crystallized by annealing at 250 °C for 12 h followed by cooling to room temperature during a further 12 h. Finally, a third sample (N3) with the molecular weight $M_w = 6500$ g mol^{-1} was melt pressed at 270 °C and then cooled to 245 °C for 1 h under a pressure of 4 MPa. The pressure was then stopped and the sample was crystallized for 20 h at 245 °C followed by holding the temperature at 230 °C for 4 h and at 220 °C for 2 h and finally by cooling to room temperature. The values of the molecular weight of the samples after crystallization are collected in Table 1.

Techniques. The molecular weight was determined by viscosity using hexafluoro-2-propanol as a solvent by means of the equation $[\eta] = 5.2 \times 10^{-2} M_w^{0.695}$.[8]

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Table 1[a]

sample	crystallization	M_w (g mol^{-1})	T_m (°C)	ΔH_m (J g^{-1})	$x_{c,DSC}$ (%)	ρ (g cm^{-3})	$x_{c,\rho}$ (%)	$x_{c,WAXS}$ (%)	k (nm^2)
P1	320 °C/3 h, 400 MPa	8000	275	121	90	1.459	80	70	0.0060
P2	320 °C/3 h, 400 MPa	8000	281	121	90	1.462	82	70	0.0058
P3	320 °C/3 h, 400 MPa	8000	277	119	88	1.456	78	68	0.0043
N1	260 °C/24 h	30000	262	76	54	1.417	52	48	0.0026
N2	250 °C/12 h	30000	269	71	53	1.424	57	51	0.0033
N3	245 °C/20 h	6500	269	87	64	1.437	65	58	0.0026

[a] The samples N1, N2, and N3 were crystallized under atmospheric pressure.

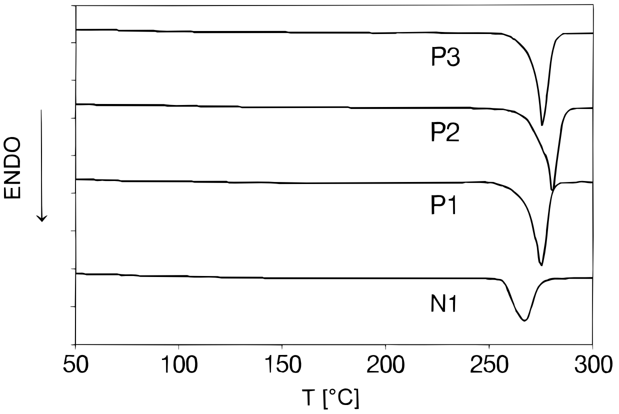

Figure 1. DSC scans of samples crystallized from the melt at 400 MPa (P1, P2, and P3) and at 0.1 MPa (N1) (see Table 1).

Calorimetric measurements were performed by using a DSC910 differential scanning calorimeter. The degree of crystallinity x_c was obtained from the melting enthalpy ΔH_m by means of the equation

$$x_c = \Delta H_m / \Delta H_m^{\circ} \tag{1}$$

where ΔH_m° is the melting enthalpy of the ideal crystal, which was assumed to be 135 J g^{-1} according to Blundell and Osborn.[9]

The density was measured in a density gradient using a mixture of hexane and tetrachloromethane. From the density ρ, we have calculated the volume degree of crystallinity x_c by using the equation

$$x_c = \frac{\rho - \rho_a}{\rho_c - \rho_a} \tag{2}$$

where the density of the amorphous regions ρ_a was assumed to be 1.338 g cm^{-3} and the density of the crystals ρ_c was assumed to be 1.490 g cm^{-3}.[10]

Wide-angle X-ray scattering (WAXS) measurements were performed at room temperature with a Siemens D500 diffractometer in transmission mode in order to determine the degree of crystallinity and Ruland's lattice distortion factor.[6] For the analysis of crystallinity, a method described earlier by Gehrke and Zachmann[10] was applied. In this method, we used a smoothing curve which is the sum of the amorphous halo and of an underground $I_u = [1 - \exp(-ks^2)]$, caused by the lattice defects within the crystalline regions. The lattice distortion factor k was varied in such a way that the degree of crystallinity is in two different regions of integration the same (from 1 to 19° and from 19 to 38° (ϑ)). To determine the angular position of the peak maxima, hkl, a Philips PW1078/50 diffractometer in the reflection mode was used. For calibration purposes, a silicon standard was employed. In both series of measurements, we used Ni-filtered Cu Kα radiation.

C. Results

Calorimetry. Figure 1 shows the DSC curves for the three high-pressure-crystallized samples and for the sample N1 crystallized 24 h at 260 °C under atmospheric pressure. It can be seen that the influence of high-pressure crystallization gives rise to unusual sharp melting peaks which are shifted to higher temperature. This suggests the occurrence of thicker crystals in the high-pressure-crystallized samples showing a narrower distribution of crystal thickness than in the normally crystallized materials. Table 1 shows the values of the melting point (T_m), the melting enthalpy (ΔH_m), the density, and the corresponding degrees of crystallinity determined by calorimetry and density, respectively.

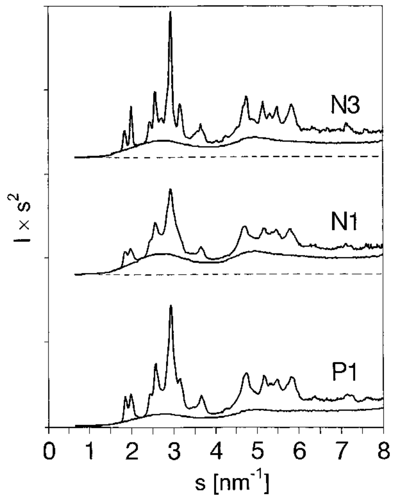

Figure 2. X-ray diffractograms of a high-pressure-crystallized (400 MPa) sample P1 (M_w = 8000 g mol^{-1}) and of two samples crystallized at atmospheric pressure, N1 (M_w = 30000 g mol^{-1}) and N3 (M_w = 6500 g mol^{-1}).

Degree of Crystallinity. Figure 2 shows the X-ray scattering curves obtained for the high-pressure-crystallized sample P1 and for the samples N1 and N3 (crystallized under normal conditions). It is to be noted that the scattering patterns of the samples P2 and P3 are nearly identical to that of P1. The Lorentz-corrected scattered intensity Is^2 is here plotted against $s = (2/\lambda) \sin \vartheta$, ϑ being half the scattering angle, after subtraction of the air and of the Compton scattering and after performing the usual polarization and absorption corrections.

Figure 2 also shows the smoothing curves obtained using the method of Gehrke and Zachmann.[10] It is noteworthy that the noncrystalline scattering is comparatively small for the high-pressure-crystallized sample in comparison with that of the X-ray scattering curves of PET crystallized under atmospheric pressure.

Table 1 also shows the values of the degree of crystallinity of the investigated samples determined by WAXS and the values of the determined lattice distortion factor.

One observes immediately that the low molecular weight sample crystallized under normal pressure (N3) shows a degree of crystallinity which is much lower than the one of the high-pressure-crystallized materials. Thus the low molecular weight alone is not sufficient

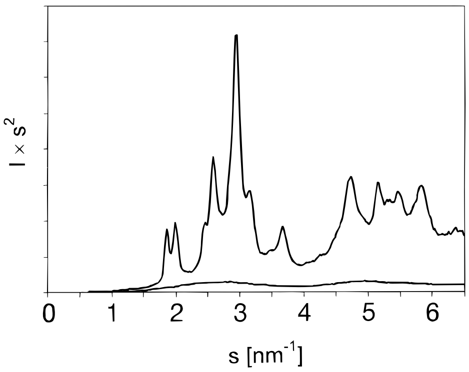

Figure 3. X-ray diffractogram of the sample P1 together with a hypothetical amorphous halo corresponding to $x_c = 0.9$.

Table 2

	$2\vartheta_{theo}$[15]	high pressure crystallized			atm pressure
		P1	P2	P3	N1
$0\bar{1}1$	16.2	16.20 ± 0.04	16.15 ± 0.05	16.22 ± 0.04	16.23 ± 0.02
010	17.4	17.43 ± 0.05	17.35 ± 0.05	17.42 ± 0.02	17.47 ± 0.02
$\bar{1}11$	21.8	21.84 ± 0.01	21.81 ± 0.01	21.84 ± 0.01	21.71 ± 0.04
$\bar{1}10$	22.9	22.88 ± 0.01	22.81 ± 0.01	22.8 ± 0.01	22.69 ± 0.02
100	26.0	25.89 ± 0.01	25.80 ± 0.01	25.82 ± 0.01	26.01 ± 0.04
$1\bar{1}1$	32.7	32.4 ± 0.1	32.4 ± 0.1	32.4 ± 0.1	32.43 ± 0.04
$\bar{1}05$	43.0	42.36 ± 0.04	42.28 ± 0.04	42.38 ± 0.04	42.39 ± 0.04

to obtain a high value of degree of crystallinity. Furthermore, the degree of crystallinity values of the high-pressure-crystallized samples obtained by WAXS are smaller than the ones obtained by DSC and by density. The disparity is so large that it is outside of the experimental error, although the evaluation of the WAXS curves involves some procedures which are not beyond any ambiguity. In order to demonstrate that the disparity is outside of the experimental error, in Figure 3 we have plotted once more the WAXS curve of the high-pressure-crystallized sample P1 together with an amorphous halo corresponding to a degree of crystallinity of 90%. One can clearly recognize that the intensity of this halo is too small to explain the experimentally obtained WAXS crystallinity of 70%. Thus, the results obtained by WAXS are smaller than those for the other two methods. This is, to our knowledge, the first example where such a contrast is found in the crystallinity of PET obtained by different methods.

Unit Cell Dimensions. To explain this discrepancy, one might first think of the possibility that the dimensions of the crystallographic unit cell in the high-pressure-crystallized material are smaller than in the material crystallized under normal conditions. Smaller unit cell dimensions would result in a higher value of ρ_c in eq 2 and thus in a smaller value of the degree of crystallinity. It is also reasonable to assume that a higher value of ρ_c should increase the value of ΔH_m° in eq 1, which also would lead to a decrease of crystallinity measured by DSC. In order to investigate the influence of the crystallization conditions on the unit cell dimensions, we have carefully measured the position of the X-ray reflections in the reflection mode. Table 2 shows the angular position of the reflections for the different samples. It is seen that within the experimental error no difference in the lattice spacings is found between the high-pressure-crystallized material and the samples crystallized under normal pressure. In order to obtain by density measurements the same degree of crystallinity as by WAXS, the value of ρ_c should be increased from 1.490 to 1.515 g cm^{-3}. If we assume that this is caused by a decrease of the a and b lattice cell dimensions, then these axes would have to assume the values 4.61 and 6.00 Å, respectively (if the angles between the axes were kept constant). This would shift the position of the 100 reflection to $2\vartheta = 26.2°$ and of the 010 reflection to $2\vartheta = 17.6°$, at variance with the results of Table 2.

D. Discussion

The lower value of the degree of crystallinity found from WAXS in the high-pressure-crystallized samples as compared with other techniques can be explained if we consider that there exists an interface of finite thickness between the crystals and the amorphous regions. This interface will not be seen as crystalline by the X-ray scattering experiment, because this region may have a higher density and thereby a higher enthalpy, as compared to the amorphous regions, although no long-range order. On the other hand, such an interface would increase the density and also the enthalpy melting values.

In order to estimate the possible influence of such an interface, it is convenient to recall the microstructure of high-pressure-crystallized PET, found in a previous study by SAXS.[3] The analysis of the interface distribution function (IDF) showed the occurrence of three positive peaks before the long period peak, appearing with negative sign. This indicates that, at least, two different kinds of lamellar stacks with different layer thicknesses are present. In addition, the large damping obtained for the IDF implies that the long-range order of the stacks of crystalline lamellae is very poor. Hence, the choice of one-dimensional model of lamellar stacks must be discarded, as it does not explain the experimental results. The best fit of the calculated IDF with experiment is obtained by two different lamellar stacks, both corresponding to paracrystalline type of structures.

Furthermore, from the decomposition of the IDF into various distance distributions, according to the above double-component fit, the following results were obtained: 90% of the material in the high-pressure-crystallized samples consists of lamellar stacks with a crystalline thickness l_c of 10 nm and an amorphous thickness l_a of 1.3 nm. However, the remaining 10% of the material forms lamellar stacks with a crystal thickness $l_c = 4$ nm and an amorphous thickness of $l_a = 5$ nm. In the major component of the two-phase structure, the crystallinity is 90% and in the minor component, the crystallinity is only 40%, which results in an average crystallinity of 85% for the whole sample. The structural parameters l_c and x_c are determined from the two-component fits on the IDF with an accuracy of about 2−3%. If we assume that there exists a boundary region which is seen as crystalline by means of DSC and density measurements and as amorphous by means of WAXS measurements, we would obtain smaller values of x_c by the latter technique. Supposing an interface thickness l_d of 0.75 nm for the major component and of 0.3 nm for the minor component (see Figure 4), we would, then, have an average crystallinity of 72%, in accordance with the crystallinity values obtained from WAXS (see Table 1). This would mean that 14% of the crystalline regions belong to the interface. One may expect that such an interface should influence most specially the crystallinity values of highly crystalline samples. Indeed, in the example of Figure 4 such an interface represents nearly 14% of the total crystallinity of the highly crystalline component and only 6% crystal-

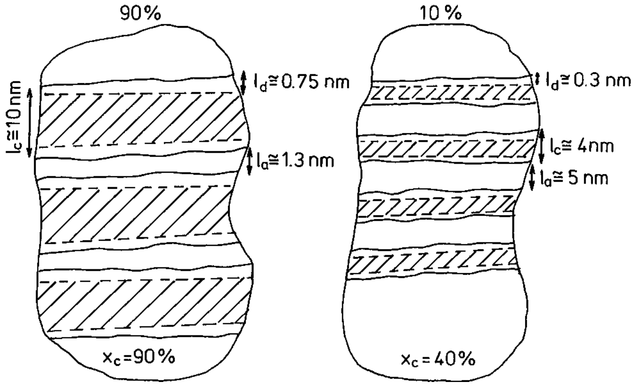

Figure 4. Schematic representation of the bimodal microstructure of high-pressure-crystallized PET consisting of 90% of highly crystalline material ($x_c = 0.9$) and 10% of low crystallinity material ($x_c = 0.4$) according to a preceding analysis of the IDF.[3] The thickness (l_c) of the laminar crystals comprises an ordered core plus a defective boundary l_d.

linity for the less crystalline component. This explains why in the atmospheric-pressure-crystallized systems such a large discrepancy has not been found between the crystallinity results from WAXS and from the other two methods.

The importance of such an interface has been demonstrated also by other authors.[11–13] Unfortunately, it was not possible to determine the interface thickness by SAXS in the high-pressure-crystallized samples because the Porod region was not sufficiently well defined.[3] In PET samples crystallized at atmospheric pressure, one finds a thickness of the interface of up to 10 Å.[14] Therefore our assumption of a thickness of 15 Å for samples crystallized under other conditions with a different morphology seems to be feasible. Another important result, which would favor the existence of a thicker interface, is the larger lattice distortion factor k in the high-pressure-crystallized material in comparison with the material crystallized under normal conditions (see Table 1).

E. Conclusions

The high value of the degree of crystallinity found in the high-pressure-crystallized samples is a consequence of the high-pressure-induced crystallization rather than of the low molecular weight.

The crystallographic unit cell in the high-pressure-crystallized material turns out to be the same as that in the material crystallized under normal conditions.

The result that the degree of crystallinity as determined by WAXS is smaller than the one determined by DSC and by density can be explained by assuming the occurrence of an interface between the lamellar crystals and the amorphous layers. Such an interface affects the value obtained by WAXS more markedly in a material with a high degree of crystallinity than in the case of a degree of crystallinity of, for example, 50%.

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