

Crystallinity of Pure and Nucleated PET

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Synopsis

Pure and $\text{Al}(\text{OH})_3$ -containing PET films were prepared, quenched, and subsequently annealed under identical conditions. The level of crystallinity of the films was determined by three methods: density measurements, X-ray crystallinity determination, and measurements by IR of the relative concentration of trans $-\text{O}-\text{C}-\text{C}-\text{O}-$ conformation in the polymer. For pure PET it was found that the percentage crystallinity measured in annealed samples by X-ray and IR is about the same. The density measurements agree with these techniques only when the amorphous density is taken as 1.348 g/cm^3 . In the case of quenched pure PET, a 7% correction to the concentration of trans conformation must be introduced (in agreement with recent literature) to fit the IR results to the X-ray and density data. Annealed PET containing $\text{Al}(\text{OH})_3$ crystallizes to about the same level as annealed pure PET. The agreement between X-ray and IR data is reasonably good. In the quenched PET/ $\text{Al}(\text{OH})_3$ there exists a higher level of trans conformation (enhanced order), probably resulting from adsorption of relatively extended PET chain segments on the surface of the hydroxide particles. These extended units may possibly serve as nucleation sites for PET crystallization upon cooling from the melt.

INTRODUCTION

In a study on the crystallization of poly(ethylene terephthalate) (PET) in the presence or absence of inorganic nucleating agents, it was found that when measured by three different techniques the same specimens did not give the same percent crystallinity. As the discrepancies between these initial results were systematic, it was felt that the observed differences fall out of the range of experiment scatter and are inherent to the characterization techniques. In the following the observed differences between various techniques will be explained and the results reconciled.

EXPERIMENTAL

The three characterization techniques used were wide angle X-ray diffraction (WAXD), infrared (IR) spectroscopy, and density measurement by means of density gradient columns. PET having intrinsic viscosity of 0.53 dL/g was dried for 16 h under high vacuum at 160°C . Then a part was mixed with $\text{Al}(\text{OH})_3$ predried at 150°C , and coextruded at a melt temperature of about 270°C to yield a uniform extrudate containing 1% by weight of $\text{Al}(\text{OH})_3$. Films of less than 5 mils in thickness were molded from the pure PET and from the PET/ $\text{Al}(\text{OH})_3$ formulation. The films were molded under pressure at about 275°C between Teflon®-coated thin aluminum sheets for about 15 s. Then they were quick-quenched by immersion in water/ice bath. Each quenched film was tested by the three techniques above to determine its level of crystallinity. Several small

specimens were cut from each film for the density measurements. After the data were obtained from the quenched films, they were annealed at progressively longer times (from 1 min up to 45 min) to obtain a reasonably broad range of crystallinity. Almost all films were annealed at 165°C with a few annealed at 200°C for 2.5 h to obtain the highest crystallinity level. Films of pure PET and of Al(OH)₃-nucleated PET were always annealed together for the same duration, in order to compare the percentage crystallinity obtainable under otherwise identical conditions. From each series of films, a few were randomly selected and their percentage crystallinity determined by WAXD and IR as a function of the position of the films in the sample holders. It was found that for each technique the percentage crystallinity was within 1% for films positioned at 0°C, 45°C, and 90°C. This indicates that no preferential orientation was induced in the films during their molding. After the annealing procedures, each of the films was again evaluated by the three techniques, with four specimens being cut from each of the density measurements.

The percent crystallinity was initially determined as follows: densities of specimens were measured in CCl₄/*n*-heptane columns equipped with calibrated floats. No change in densities took place even after 24-h immersion in the nonsolvent mixture. The volume percent crystallinity V_c was determined using the formula

$$V_c = 100 \left(\frac{d - d_a}{d_c - d_a} \right) \quad (1)$$

where d_a is the density of the amorphous phase, d_c the density of the crystalline phase, and d the density of the specimen. The values initially used for d_a and d_c were the conventional ones. As will be shown later, the experimental results compelled us to change the density of the amorphous phase to be used in eq. (1).

WAXD patterns were obtained with a Norelco diffractometer operating in parafocus geometry and using monochromatized copper K_α radiation. The determination of crystalline fraction was performed following the procedure of Hermans and Weidinger as summarized by Alexander.¹

The data for the determination of crystalline fraction by IR were collected with a Nicolet FTIR instrument. After initial scans of each film, the regions around the bands at 973 cm⁻¹ and 1578 cm⁻¹ were expanded to allow as accurate as possible measurements of the absorption of these bands. The 1578 cm⁻¹ band is associated with an in-plane ring C—C stretch.² In agreement with Miyake³ (his assignment: 1580 cm⁻¹), we have found this band to be insensitive to the development of crystallinity in PET samples. The band at 973 cm⁻¹ was assigned to an asymmetric C—O stretch and is associated with the trans conformation of the —O—C—C—O— group^{2,4,5} along the PET chain. Its intensity is very sensitive to the development of order in the polymer^{3,5} and, thus, lends itself extremely well to the measurement of crystallinity in PET. With our experimental capabilities, we could not separate the band at 973 cm⁻¹ into two components, at 973 cm⁻¹ and at 975 cm⁻¹, the latter claimed⁶ to be associated with the amorphous component of PET. The consistency of our results to be shown below, and the analysis of Stokr et al.⁵ lead us to believe that the assignment of the 975 cm⁻¹ band as an "amorphous band" is a mere reflection of the

TABLE I
Crystallinity of Annealed PET by X-Ray, IR, and Density Methods

| Sample code | % Crystallinity by X-ray | IR A_{973}/A_{1578} | % Crystallinity by IR ^a | Density (g/cm ³) | Vol % crystallinity by density ^b | Vol % crystallinity by density ^c |
|-------------|-----------------------------|-----------------------|---------------------------------------|---------------------------------|--|--|
| -11A-1 | 37 | 1.227 | 32.5 | 1.3781 | 35.9 | 31.1 |
| -2 | 19 | 0.724 | 19.2 | 1.3649 | 24.9 | 17.3 |
| -3 | 28 | 1.170 | 31.0 | 1.3779 | 35.8 | 31.0 |
| -4 | 32 | 1.252 | 33.1 | 1.3795 | 37.1 | 33.1 |
| -5 | 32 | 1.279 | 33.8 | 1.3804 | 37.8 | 34.0 |
| -6 | 34 | 1.251 | 33.1 | 1.3786 | 36.3 | 32.3 |
| -7 | 39 | 1.472 | 38.9 | 1.3870 | 43.3 | 39.8 |
| -8 | 41 | 1.513 | 40.0 | 1.3848 | 41.5 | 38.0 |
| -9 | 38 | 1.501 | 39.7 | 1.3855 | 42.1 | 39.9 |
| -10 | 37 | 1.548 | 41.0 | 1.3874 | 43.7 | 40.4 |
| -11 | 51 | 1.764 | 46.7 | 1.3937 | 48.9 | 46.4 |
| -12 | 51 | 1.787 | 47.3 | 1.3935 | 48.8 | 46.2 |
| -13 | 55 | 2.166 | 57.3 | 1.3966 | 51.3 | 49.0 |
| -14 | 60 | 2.256 | 59.7 | 1.3990 | 52.0 | 51.1 |

^a IR crystallinity was obtained from $A_{973}/A_{1578} = 0.0378/1\%$ crystallinity; see text.

^b % crystallinity based on amorphous density of 1.335 g/cm³.

^c % crystallinity based on amorphous density of 1.348 g/cm³.

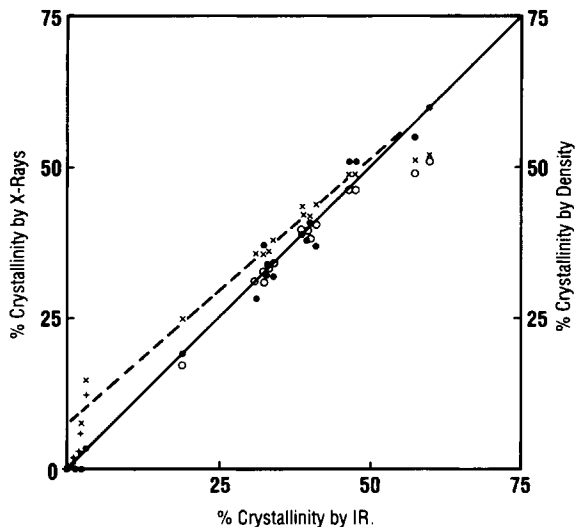


Fig. 1. Correlations between % crystallinity of pure PET obtained by three methods: (●) IR/X-ray correlation; (○) IR/density correlation $d_a = 1.348 \text{ g/cm}^3$; (+) IR/density correlation for quenched samples, $d_a = 1.337 \text{ g/cm}^3 \times$ IR/density correlation assuming $d_a = 1.335 \text{ g/cm}^3$ (+ × data at <3% crystallinity deleted to avoid clutter). IR crystallinity of quenched samples corrected by 7%.

fact that a small but nonnegligible fraction of the —O—C—C—O— groups are present in the amorphous state in the trans conformation.

RESULTS AND DISCUSSION

In Table I are shown the data obtained from the annealed PET films. Samples coded by numbers 1–12 were annealed at 165°C and samples 13 and 14 at 200°C . The normalizing factor for the calculation of crystallinity from IR data was obtained from the observation that the IR ratios for samples -2 and -14 scale relative to each other at practically the same ratio as the percentage crystallinity of these samples obtained from WAXD patterns. Dividing all the IR ratios by the normalizing factor of 0.0378 gave percentage crystallinity in remarkably good agreement with the X-ray percentage crystallinity. The correlation of the IR and X-ray crystallinities is shown in Figure 1. It is important to recognize that, for the range of crystallinity in Table I, no correction factor was required to fit all the IR results to the X-ray results. As will be shown below, a factor is required, correcting the absorbance of the IR band at 973 cm^{-1} for quenched samples containing very low crystallinity levels.

Initially, the volume percent crystallinity was calculated from the measured densities using the conventional values of 1.455 g/cm^3 and 1.335 g/cm^3 for the crystalline and amorphous phase, respectively. The percentage crystallinity thus obtained was consistently higher than that obtained from IR or X-ray data. When plotted against crystallinity obtained from IR (similar plot against X-ray data is not reproduced here), the density data points all fell on a dashed line above the diagonal indicating a 1:1 correlation. The slope of the dashed line indicated that the deviation decreases with increased crystallinity and, hence, is associated with the amorphous component of the system. Recalling that it was demon-

TABLE II
Crystallinity in Quenched PET by X-Ray, IR, and Density Methods

| Sample code | % Crystallinity by X-ray | IR A_{973}/A_{1578} | % Crystallinity by IR ^a | Correct % crystallinity by IR ^b | Density (g/cm ³) | Vol % crystallinity by density ^c |
|-------------|-----------------------------|-----------------------|------------------------------------|---|---------------------------------|--|
| -11A-1 | 0 | 0.3019 | 8.0 | 1 | 1.3388 | 1.5 |
| -2 | 0 | 0.2771 | 7.3 | 0 | 1.3372 | 0 |
| -3 | 0 | 0.3476 | 9.2 | 2 | 1.3437 | 5.7 |
| -4 | 0 | 0.2975 | 7.9 | 0 | 1.3365 | 0 |
| -5 | 0 | 0.2998 | 7.9 | 0 | 1.3367 | 0 |
| -6 | 0 | 0.2802 | 7.4 | 0 | 1.3381 | 0 |
| -7 | 3 | 0.4010 | 10.6 | 3 | 1.3516 | 12.4 |
| -8 | 0 | 0.3141 | 8.3 | 1 | 1.3385 | 1.3 |
| -9 | 0 | 0.3278 | 8.7 | 1.5 | 1.3402 | 2.9 |
| -10 | 0 | 0.2901 | 7.7 | 0 | 1.3372 | 0 |

^a IR crystallinity obtained from $A_{973}/A_{1578} = 0.0378/1\%$ crystallinity.

^b IR crystallinity corrected as discussed in the text.

^c % crystallinity based on amorphous density of 1.337 g/cm³.

strated in the literature^{3,7} that annealing of PET above its glass transition temperature densifies the amorphous phase, the density data were used to recalculate the percentage crystallinity abandoning the conventional densities. The best fit to the diagonal in Figure 1 was obtained with the crystalline density unaltered at 1.455 g/cm³ and the amorphous density of 1.348 g/cm³. The two points with the highest densities clearly deviate from the diagonal in Figure 1. Recalling that these samples were annealed for a prolonged time at a temperature higher than the rest of the samples, this deviation is not surprising. Due to paucity of data we cannot assess at present whether the deviation is due to changes in amorphous density or crystalline density or both.⁷ As can be seen from Table I and Figure 1, the agreement between density data calculated on the basis of amorphous density of 1.348 g/cm³, and the IR and X-ray data is good for most entries in the table. Calculations based on crystalline densities other than 1.455 g/cm³ failed to improve the observed fit.

The density of 10 quenched PET samples showing zero crystallinity by X-ray was measured and found to be 1.3370 ± 0.0013 g/cm³. Therefore, for the calculation of percentage crystallinity of other quenched specimens, this density was used as the amorphous density instead of the conventional 1.335 g/cm³. Percent crystallinity based on IR data was initially calculated from the A_{973}/A_{1578} ratio, using the value of 0.0378 as the normalizing factor. All quenched samples, which showed zero crystallinity by X-ray and density, showed a crystallinity of 7% by IR. The 7% value is exactly the same value obtained recently by Stokr et al.⁵ for PET in solution and slightly less than the value obtained from amorphous bulk PET. The analysis of Stokr et al.⁵ makes it abundantly clear that in solution or amorphous bulk the —O—C—C—O— group exists in the trans conformation at a level of about 7% of the possible conformations, with the rest divided unevenly between the two possible gauche conformations. Therefore the value of 7% trans —O—C—C—O— conformation measured from the ratio of A_{973}/A_{1578} does not reflect crystallinity, but the level of trans conformations present in the fully amorphous polymer. Subtracting a constant value of 7% from the quenched PET specimens, resulted in IR crystallinity values recorded in Table II. The data were plotted in Figure 1 in a fashion similar to the data of Table I. It should be noted that the amorphous density of the quenched specimens is lower than the amorphous density of the annealed specimens. This is in agreement with the literature.^{3,7} It makes it, however, impossible to apply the same correction factor to the calculated crystallinities of the quenched and annealed samples, even though the plotted data seem to "invite" such a correction. The use of an amorphous density of 1.348 g/cm³ will reduce the crystallinity, for instance, of sample -11A-7 in Table II from 12.4% to 6.4%.

The reason for the applicability of the 7% correction to IR data obtained from quenched specimens only is not known at present. It may be that crystallization preferentially incorporates the trans conformation, or is nucleated by aggregates of such conformations. Thus, during the initial stages of crystallization, the amorphous phase is being depleted of trans conformation faster than this phase is being converted to the crystalline one.

The PET/Al(OH)₃ films were subjected to the same quenching and subsequent annealing as the pure PET films. Because of the limited range of the density gradient columns, the PET/Al(OH)₃ specimens were not studied by the density method. The results of the X-ray and IR measurements for the quenched and

TABLE III
Crystallinity of Quenched and Annealed Al(OH)₃-Nucleated PET

| Sample code | Quenched "amorphous" | | Corrected % | | Annealed "crystalline" | | |
|-------------|----------------------|--------------------------|---------------------------------------|----------------------------------|-----------------------------|--------------------------|---------------------------------------|
| | % Cryst. by X-ray | IR A_{973}/A_{1578} | % crystallinity by IR ^a | crystallinity by IR ^b | % crystallinity by X-ray | IR A_{973}/A_{1578} | % crystallinity by IR ^a |
| -11B-1 | 0 | 0.4046 | 10.7 | 3.5 | 50 | 1.443 | 38.2 |
| -2 | 0 | 0.3264 | 8.6 | 1.5 | 24 | 0.839 | 22.2 |
| -3 | 0 | 0.3387 | 9.0 | 2 | 30 | 1.072 | 28.4 |
| -4 | 0 | 0.3618 | 9.6 | 2.5 | 36 | 1.179 | 31.2 |
| -5 | 0 | 0.3163 | 8.4 | 1 | 37 | 1.179 | 31.2 |
| -6 | 12 | 0.7544 | 20.0 | 13 | 38 | 1.212 | 32.1 |
| -7 | 0 | 0.3480 | 9.2 | 2 | 39 | 1.335 | 35.3 |
| -8 | 0 | 0.3170 | 8.4 | 1 | 36 | 1.397 | 37.0 |
| -9 | 0 | 0.3341 | 8.8 | 1.5 | 35 | 1.327 | 35.1 |
| -10 | 0 | 0.3071 | 8.1 | 1 | 40 | 1.541 | 40.8 |
| -11 | — | — | — | — | 40 | 1.620 | 42.9 |
| -12 | — | — | — | — | 43 | 1.693 | 44.8 |
| -13 | — | — | — | — | 44 | 2.068 | 54.7 |

^a Using $A_{973}/A_{1578} = 0.0378/1\%$ crystallinity.

^b IR crystallinity corrected as discussed in the text.

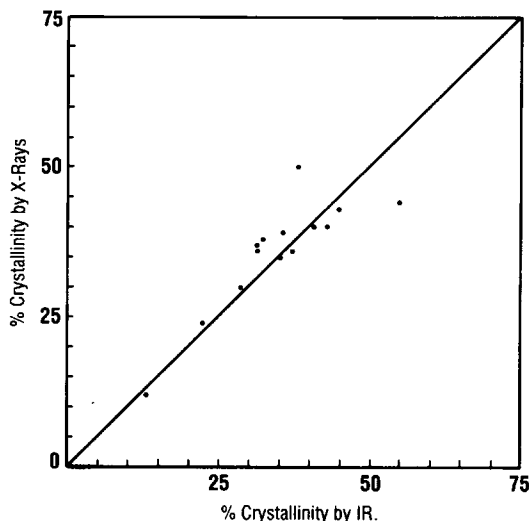


Fig. 2. Correlations between % crystallinity of PET containing 1% $\text{Al}(\text{OH})_3$, obtained by IR and X-ray. IR crystallinity of quenched samples corrected by 7%.

annealed $\text{PET}/\text{Al}(\text{OH})_3$ films are tabulated in Table III. The goodness of the fit of IR and X-ray crystallinity is not as good as for the pure PET, as can be judged from Figure 2. The elimination of annealed samples -11B-1 and -13, however, makes the fit acceptable. As in the case of annealed pure PET, the application of the 7% correction arising from the trans conformation in the amorphous state will cause a large discrepancy between the results obtained by IR and X-ray methods. It is of interest to note that samples -11B-1 through -11B-10, annealed identically as the corresponding samples -11A-1 through -11A-10, show remarkably similar levels of crystallinity. This indicates that at the annealing temperature of 165°C the aluminum hydroxide is not an effective crystallization nucleating agent. There is an order of magnitude agreement among the samples annealed at 200°C , -11A-13 and -14 and -11B-11 through 13. Here again the $\text{Al}(\text{OH})_3$ did not contribute measurably to the development of crystallinity upon annealing. The inability of $\text{Al}(\text{OH})_3$ to nucleate the crystallization of PET upon heating from the glassy state is in agreement with the fact that $\text{Al}(\text{OH})_3$ nucleates PET only in the temperature interval of $250\text{--}310^\circ\text{C}$ due to the release of water by the hydroxide over this interval.⁸

The more important observation on the $\text{PET}/\text{Al}(\text{OH})_3$ films is that in their quenched state, where they show zero crystallinity by X-ray, a consistently measurable amount of order is observed by IR. This level of order is above and beyond the 7% of trans —O—C—C—O— conformation indicated by Stokr et al.⁵ Levels of crystallinity of the order of 2–3% are usually observed as minor peaks superimposed above the major amorphous halo in WAXD patterns. For the quenched samples -11B-1 through -10, with the obvious exception of -11B-6, no such perturbations were observed. Hence, the “crystallinity” observed by IR from these samples cannot legitimately be called crystallinity and may, preferably, be called “enhanced order.” From Tables II and III it is obvious that this enhanced order is due to the presence of $\text{Al}(\text{OH})_3$ in the quenched samples. We do not know at present the mechanism causing the enhanced order, but the

fact that it is present in specimens rapidly cooled from the melt, and not in specimens heated from the glass to 200°C or less, seems to indicate that the enhanced order is somehow associated with the particular manner in which $\text{Al}(\text{OH})_3$ nucleates PET crystallization and not with the mere presence of some finely dispersed foreign particles in the polymer. Since $\text{Al}(\text{OH})_3$ is an effective nucleator for PET cooled from the melt, it is apparent from Tables II and III that, at the quenching rate employed in the present study, the $\text{Al}(\text{OH})_3$ containing films developed a degree of order higher than pure PET before being arrested by the solidifying polymer. It is of interest to note that the degree of order of quenched PET films seems not to affect the level of crystallinity of the subsequently annealed films.

At present, one can only speculate on the nature of the enhanced order in the quenched PET specimens containing $\text{Al}(\text{OH})_3$. The measured enhanced order is in fact the measure of trans $-\text{O}-\text{C}-\text{C}-\text{O}-$ conformations in the system indicating a higher degree of trans conformation and chain extension in the presence of the $\text{Al}(\text{OH})_3$ particles. It stands to reason that the effect of these particles will be felt in their close proximity and not in the bulk of the polymer far removed from them. Thus it is conceivable that a measurable amount of PET chain segments are interacting with the $\text{Al}(\text{OH})_3$ particles to be more extended than in their absence. The nature of this interaction is not known to us but we believe it is most likely that the interacting chain segments are adsorbed on the hydroxide particles surfaces in a rather extended conformation. These chains most likely serve as the nucleation sites for the crystallization of PET upon cooling from the melt. To crystallize upon cooling from the melt, the chain mobility must be arrested, and upon heating from the glass it must be enhanced. We believe that this difference may be the reason why $\text{Al}(\text{OH})_3$ is not an effective nucleator for PET crystallization upon heating from the glass. Hence the lack of significant difference in level of crystallinity among annealed specimens of pure PET and PET/ $\text{Al}(\text{OH})_3$.

Finally, the temperature of 165°C, to which most annealed specimens were subjected, is about the point where the rate of cooling from the annealing temperature to room temperature does not affect the difference in densities between the crystalline and amorphous phases.⁹ It is also in the temperature range where the effects of annealing below the glass transition become negligibly small.¹⁰ The difference between d_c and d_a observed by us was 0.107 for samples annealed at 165°C and 0.118 for the quenched specimens. These differences are in agreement with literature values.^{7,9} In fact, the amorphous and crystalline densities best describing our data are in very good agreement with the "effective densities" obtained by Fischer and Fakirov⁷ from unoriented PET samples annealed at similar temperatures.

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