

X-Ray Diffraction Studies of the Crystallinity in Polyethylene Terephthalate

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INTRODUCTION

The physical properties of crystalline polymers depend not only on their molecular properties, but also on their structural features associated with the ordered (crystalline) regions. In the fabrication of articles, films, and fibers, the thermal and mechanical treatments to which the polymer is subjected result in considerable variations in the extent of crystallization. A precise method for determining the per cent crystallinity is desirable, therefore, in order to characterize these materials.

For such studies, polyethylene terephthalate is a convenient crystallizable material to use. Its so-called second-order transition temperature of about 70°C. allows the obtaining of a completely amorphous polymer at room temperature. Furthermore, this amorphous material can be crystallized to various extents by heating to appropriate temperatures above the second-order transition temperature. Since the crystal structure of polyethylene terephthalate is known,¹ an estimate for specific volume of completely crystalline material is available.

Density,² infrared absorption,³ and x-ray diffraction⁴ methods have been used to estimate the crystalline-amorphous ratio in polyethylene terephthalate.

The per cent crystallinity obtained by x-ray diffraction methods is the fraction of the total polymer which is sufficiently ordered to give an x-ray diffraction pattern characteristic of crystalline material. Whether results thus obtained agree with results from other methods is a matter for investigation.

Quantitative methods for the determination of the degree of crystallinity by x-ray diffraction techniques are, in principle, a comparison of the relative amounts of energy diffracted by the crystalline and by the amorphous regions in the polymer. The success of such methods rests on the

assumption of equivalence in the scattering power of the two regions for equal masses. In the most commonly used procedure, a photometer trace of the x-ray diffraction pattern of a partially crystalline sample is taken. After correction for background, the diffraction curve is graphically resolved into peaks representing the scattering from the amorphous material and the reflections from the crystal planes in the crystalline regions. In so doing, it is necessary to estimate the course of the amorphous scattering which is usually to a greater or lesser extent buried beneath the crystalline reflections. The present method, which is similar to the one used by Falkai and Bodor,⁴ differs from the above graphical method in that the resolution of the crystalline and amorphous diffraction effects is made in a manner which eliminates the necessity of estimating the amorphous scattering curve and depends, instead, on the assumption that the shape of this curve is independent of the degree of crystallinity. Also, instead of using the photographic method for measuring the diffracted intensities, a continuous counting technique similar to the one developed by Aggarwal and Tilley for polyethylene⁵ was employed. A rotating sample assembly permitted randomization of orientation effects prominent in drawn fibers. The use of the x-ray diffractometer with a rotating sample assembly and a continuous counting technique has a number of advantages. It eliminates the difficulties involved in reproducing the film processing conditions and in obtaining reliable photometer curves of the diffracted intensities. In addition, the use of a rotating sample assembly for averaging out the crystallite orientation effects makes the method applicable to oriented films and fibers of polyethylene terephthalate. The use of a scaler counter for continuously registering and totalizing the diffracted intensities permits direct integration of scattering intensities over selected angular intervals and is less subject to errors than either the photographic method or the use of the counter and re-

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order which is subject to linearity difficulties, particularly at low intensity levels.

EXPERIMENTAL

Method Development

In Figures 1 and 2 are the x-ray diffraction traces of amorphous and partially crystalline polyethylene terephthalate obtained with an x-ray diffractometer used in association with a recording potentiometer. There is a considerable overlapping of the several diffraction peaks which bury a large portion of the amorphous scattering curve. The background scattering is assumed to be represented by the level parts of the scattering curve at the low and high diffraction angles. It is judged that the amorphous scattering curve intersects the background scattering at the lower and upper diffraction limits of diffraction angle (2θ) of 6.0 and 36.0°, and that between these diffraction limits the background scattering changes linearly. Its maxi-

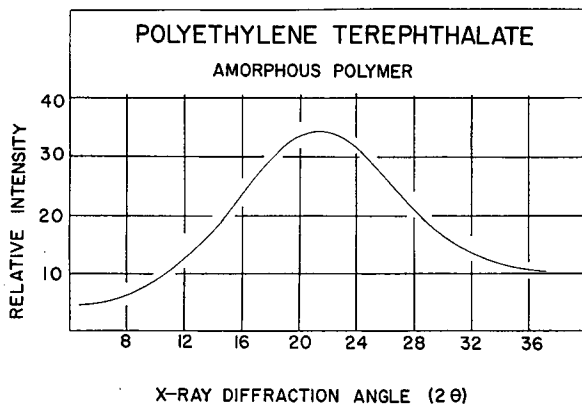


Fig. 1. X-ray diffractometer scan of amorphous polyethylene terephthalate.

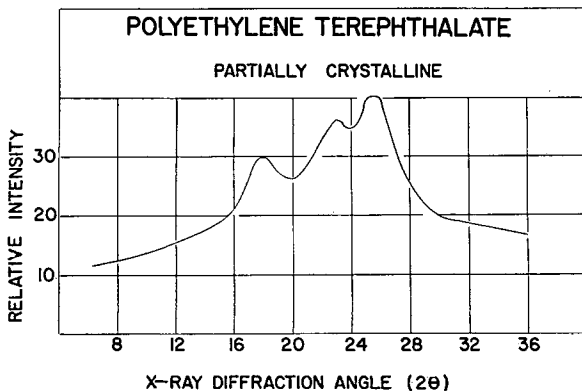


Fig. 2. X-ray diffractometer scan of partially crystalline polyethylene terephthalate.

mum intensity occurs at $2\theta = 21.3^\circ$ which corresponds to a spacing of 4.17 Å. The diffraction trace of the partly crystalline polymer has three crystalline peaks superimposed on the scattering curve due to the amorphous regions. These peaks occur at $2\theta = 17.0, 22.5,$ and 25.5° . They correspond to side spacings in the crystal structure of 5.21, 3.95, and 3.49 Å., respectively. These are the reflections from the (100), (010), and ($1\bar{1}0$) crystal planes.¹ It is assumed that (1) the background intensity changes linearly between the lower and upper diffraction limits; (2) the scattering curves of the amorphous material, and the diffraction curves of the three crystalline reflections, (100), (010), and ($1\bar{1}0$), are symmetrical about their centers; and (3) the shape of the amorphous scattering curve is independent of the degree of crystallinity. In Figure 3, lines extending from the peak

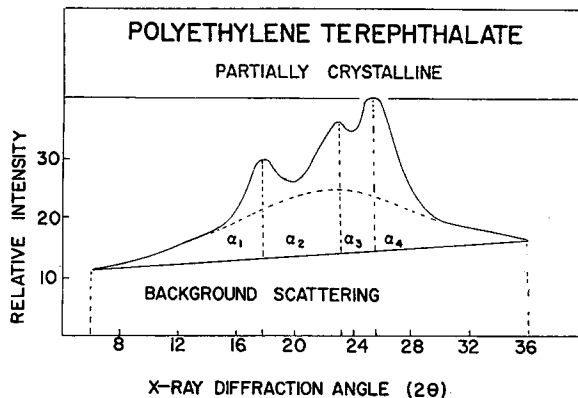


Fig. 3. X-ray diffraction curve of partially crystalline polyethylene terephthalate showing the manner of resolving the crystalline and amorphous scattering effects.

diffraction angles of the (100), (010), and ($1\bar{1}0$) crystalline reflections to the background line and parallel to the intensity axis divide the total area of the x-ray diffraction curve, after background correction, into four smaller areas. These areas are designated by $\alpha_1, \alpha_2, \alpha_3,$ and α_4 , and cover the respective diffraction angle intervals from $2\theta = 6.0$ to 17.0° , from $2\theta = 17.0$ to 22.5° , from $2\theta = 22.5$ to 25.5° , and from $2\theta = 25.5$ to 36.0° . Let $B_1, B_2, B_3,$ and B_4 be the fractions of the total amorphous scattering area, A (Fig. 1), included in the above angular intervals, and let the areas of the diffraction curves due to the three crystalline reflections (100), (010), and ($1\bar{1}0$) be designated by $s_{(100)}, s_{(0\bar{1}0)},$ and $s_{(1\bar{1}0)}$, respectively. The four areas of the diffraction curve are, then

$$\begin{aligned}\alpha_1 &= \frac{1}{2}s_{(100)} + B_1A \\ \alpha_2 &= \frac{1}{2}(s_{(100)} + s_{(010)}) + B_2A \\ \alpha_3 &= \frac{1}{2}(s_{(010)} + s_{(1\bar{1}0)}) + B_3A \\ \alpha_4 &= \frac{1}{2}s_{(1\bar{1}0)} + B_4A\end{aligned}$$

The simultaneous solution of these equations for A , s_{100} , s_{010} , and $s_{1\bar{1}0}$ gives

$$\begin{aligned}A &= (\alpha_1 + \alpha_3) - (\alpha_2 + \alpha_4)/(B_1 + B_3) - \\ &\quad (B_2 + B_4) \\ s_{(100)} &= 2(\alpha_1 - B_1A) \\ s_{(010)} &= 2[\alpha_2 - \alpha_1 + (B_1 - B_2)A] \\ s_{(1\bar{1}0)} &= 2(\alpha_4 - B_4A)\end{aligned}$$

The multiplication of the areas by a correction factor which accounts for absorption, diffraction angle, and temperature variations converts them to relative integrated intensity values. These correction factors are proportional to the reciprocal of the expression $f_c^2 (1 + \cos^2 2\theta) \csc^2 \theta \sec \theta e^{-2T}$, where f_c is the atomic structure factor for carbon, $(1 + \cos^2 2\theta) \csc^2 \theta \sec \theta$ is the diffraction angle correction (θ is the Bragg angle of diffraction), and e^{-2T} is the temperature correction ($T = 5 \sin^2 \theta/\lambda^2$ as calculated by Bunn⁶ where λ is the wavelength of x-rays employed). The correction factors were computed by using the diffraction angles corresponding to the maximum intensities of the amorphous bands and the diffraction curves of the (100), (010), and (1 $\bar{1}$ 0) crystalline reflections, and it is assumed that this is sufficiently representative of the proper correction for the area associated with the peak. The atomic structure values, f_c , of Cochran⁷ were used. The correction factors for the amorphous band and the (100), (010), and (1 $\bar{1}$ 0) crystalline reflections for polyethylene terephthalate are 1.01, 0.54, 1.29, and 2.89, respectively. A completely amorphous sample of polyethylene terephthalate was continuously counted to determine the values of B_1 , B_2 , B_3 , and B_4 , and these are 0.26, 0.40, 0.20, and 0.14, respectively. The substitution of the appropriate correction factors and the fractions of the total area of the scattering curve due to the amorphous material gives the intensity equations applicable to polyethylene terephthalate

$$\begin{aligned}I_A &= 12.62[(\alpha_2 + \alpha_4) - (\alpha_1 + \alpha_3)] \\ I_{(100)} &= 1.08\{\alpha_1 + 3.25[(\alpha_1 + \alpha_3) - (\alpha_2 + \alpha_4)]\} \\ I_{(010)} &= 2.58\{\alpha_2 - \alpha_1 + 1.75[(\alpha_1 + \alpha_3) - \\ &\quad (\alpha_2 + \alpha_4)]\} \\ I_{(1\bar{1}0)} &= 5.78\{\alpha_4 + 1.75[(\alpha_1 + \alpha_3) - (\alpha_2 + \alpha_4)]\}\end{aligned}$$

I designates the integrated intensity, the subscripts A, (100), (010), and (110) refer to the amorphous band and the particular crystalline re-

flections, and α_1 , α_2 , α_3 , and α_4 have the meanings previously defined.

These equations make it possible to obtain the integrated intensity values from the values of α_1 , α_2 , α_3 , and α_4 . These are obtained by continuously counting the intensity diffracted in the specified angular intervals, for a sample of any degree of crystallinity.

The weight per cent crystallinity is calculated by way of the equation

$$\text{Per cent crystallinity} = 100I_c/(I_c + KI_A)$$

K involves the relative scattering efficiencies of unit weight of crystalline and amorphous polymer. In this study, it is taken as unity. $I_c = I_{(100)} + I_{(010)} + I_{(1\bar{1}0)}$.

Experimental Measurement of X-Ray Crystallinity

a. Apparatus

The Norelco x-ray diffractometer with auxiliary equipment, consisting of a rotating sample assembly, Geiger tube, and scaler counter, was used. Nickel-filtered radiation from a copper anticathode was employed. A divergence slit, 0.5°, before the x-ray beam and a nickel foil, 0.0006" thick, insured operation at intensities where the Geiger tube response to the diffracted intensities was linear.

b. Sample Description

The polyethylene terephthalate samples were cast films and spun fibers. Films, prepared by quenching the molten polymer so as to obtain essentially amorphous material, were crystallized various amounts by heating them in silicone oil at temperatures ranging from 100 to 200°C. The spun, amorphous, and unoriented fibers were oriented and crystallized various amounts by drawing them under appropriate conditions to 150, 200, 300, 400, and 425% of their original lengths.

c. Method

In the continuous counting technique, the sample is rotated at 77 r.p.m. The scaler counter is used and operated below counting rates of 150 counts/sec. The operating conditions are such as to give a linear response from the Geiger tube. A scanning rate of $1/3^\circ (2\theta)$ per minute is also used. The total counts between the following scanning limits are obtained: from $2\theta = 6.0$ to 17.0° , from $2\theta = 17.0$ to 22.5° , from $2\theta = 22.5$ to 25.5° , and from $2\theta = 25.5$ to 36.0° . The background at the lower diffraction limit, $2\theta = 6.0^\circ$, and at the upper diffrac-

tion limit, $2\theta = 36.0^\circ$, is measured by recording the time in seconds necessary to totalize 3200 counts at each of these 2θ angles. The background counting rates at $2\theta = 17.0, 22.5,$ and 25.5° are computed from the counting rate at $2\theta = 6.0^\circ$ and the rate of change of counting rate with angle. It is assumed in this calculation that the background intensity varies linearly between the lower and upper diffraction limits. The total background counts are then calculated for the angular interval from $2\theta = 6.0$ to 17.0° by multiplying the average counting rate by the time in seconds required to scan the angular interval. The background counts for the angular intervals from $2\theta = 17.0$ to 22.5° , from $2\theta = 22.5$ to 25.5° , and from $2\theta = 25.5$ to 36.0° are computed in a similar manner. These background corrections are applied to the total counts obtained for each of the angular intervals to give the net total counts (total uncorrected counts minus background counts) $\alpha_1, \alpha_2, \alpha_3,$ and α_4 for the given angular intervals. Integrated intensity values for the crystalline reflections and the amorphous scattering are calculated by substituting $\alpha_1, \alpha_2, \alpha_3,$ and α_4 into the equations previously developed. These intensity values are then substituted into the equation for obtaining the weight per cent crystallinity.

It is important, in this study, to show that the crystallite orientation of the oriented fibers is being adequately averaged out by rotation of the sample. A comparison of the results on fibers chopped up to average the orientation effects and fibers which were rotated to average these effects follows.

RESULTS AND DISCUSSION

In Table I the crystallinities obtained for fiber samples in which the orientation effects were averaged out by cutting the fiber into very small pieces are compared with those obtained for the fibers in which these effects are averaged out by rotating the sample 77 r.p.m. during exposure. The two randomization processes do not produce significantly different average crystallinities. It is concluded, therefore, that satisfactory elimination of the effects of orientation is achieved by the sample rotation.

In Table II the x-ray crystallinities, densities, and the specific volumes for the films and fibers of polyethylene terephthalate are given. The specific volumes were computed from the densities which were measured at $25 \pm 0.1^\circ\text{C}.$ in sodium iodide-water solutions by a flotation technique. These data show that the specific volume decreases with increasing x-ray crystallinity.

TABLE I

Comparison of the X-Ray Crystallinities of Chopped and Rotated Oriented Fibers of Polyethylene Terephthalate

Sample	Chopped	Rotated
1	37	39
2	39	39
3	38	38
4	39	39
5	39	39
6	38	40
7	38	39
8	38	39
9	38	39
10	37	39

TABLE II

Densities and X-Ray Crystallinities of Films and Fibers of Polyethylene Terephthalate

Sample	Treatment	X-ray crystallinity	Density, 25°C.	Specific volume
Film #1	1 hour, 100°C.	9	1.346	.743
Film #2	1 hour, 120°C.	19	1.355	.738
Film #3	1 hour, 150°C.	36	1.376	.727
Film #4	1 hour, 200°C.	60	1.405	.712
Film #5	1 hour, 100°C.	27	1.365	.733
Film #6	1 hour, 120°C.	33	1.370	.730
Film #7	1 hour, 150°C.	36	1.378	.726
Film #8	1 hour, 200°C.	45	1.390	.719
Fiber #1	0% extension	0	1.331	.751
Fiber #2	150% extension	20	1.353	.739
Fiber #3	200% extension	17	1.350	.741
Fiber #4	300% extension	18	1.350	.741
Fiber #5	400% extension	36	1.373	.728
Fiber #6	425% extension	39	1.375	.727

Figure 4 is a plot of the specific volume vs. the x-ray crystallinity for the films and fibers of polyethylene terephthalate.

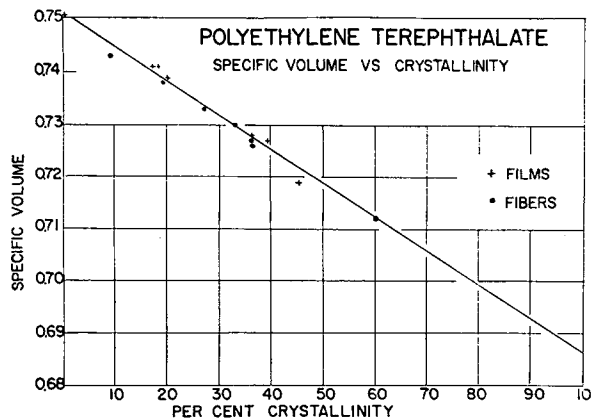


Fig. 4. Plot of the specific volume versus the weight per cent crystallinity in films and fibers of polyethylene terephthalate.

Evidently there is a linear relationship between the specific volume and the x-ray crystallinity within the limits of the data. The solid line in Figure 4 is the least squares line for the data. The reliability, at the 95% confidence level, of estimating the specific volume from a single x-ray crystallinity measurement is ± 0.003 units.

The measured specific volume of amorphous polyethylene terephthalate was found to range from 0.752 to 0.749 cc./g. The specific volume calculated from the x-ray crystal structure analysis made by Bunn¹ for crystalline polyethylene terephthalate is 0.687 cc./g. By assuming a linear relationship between specific volume and x-ray crystallinity for polyethylene terephthalate and extrapolating the density vs. crystallinity line to zero and 100% crystallinities, values of 0.751 and 0.689 cc./g. are obtained for the specific volumes of amorphous and crystalline polyethylene terephthalate. It appears, therefore, that within the experimental error of the crystallinity measurement, the specific volumes estimated from the x-ray crystallinity measurements presented in this work are consistent with those which have been measured for amorphous polymer and that which has been computed from the known crystal structure for crystalline polyethylene terephthalate.

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Synopsis

An x-ray diffraction method is described for the determination of per cent crystallinity in oriented films and fibers of polyethylene terephthalate by using an x-ray diffractometer in association with a scaler counter. Results are presented to show that sample rotation approximately averages out the crystallite orientation effects. Results are presented on

per cent crystallinity and specific volume of a number of films and fibers of polyethylene terephthalate possessing different degrees of crystallinity. A linear specific volume-x-ray crystallinity correlation is found. Extrapolation to zero and 100% crystallinity gives values of specific volume for amorphous and crystalline polyethylene terephthalate in good agreement with the measured specific volume of amorphous polymer and the specific volume calculated from the x-ray crystal structure analysis made by Bunn² for crystalline polyethylene terephthalate.

Résumé

Une méthode de diffraction aux rayons-X est décrite pour la détermination du pourcentage de cristallinité dans des films orientés et des fibres de téréphthalate de polyéthylène, en utilisant un diffractomètre aux rayons-X en association avec un compteur. Les résultats montrent que la rotation de l'échantillon, et les effets de l'orientation du cristallite, reviennent en moyenne approximativement au même. Les résultats expriment le pourcent de cristallinité et le volume spécifique d'un nombre de films et de fibres de téréphthalate de polyéthylène de différents degrés de cristallinité. On a trouvé une relation linéaire entre le volume spécifique et la cristallinité aux rayons-X. L'extrapolation à zéro et à 100% de cristallinité donne des valeurs du volume spécifique pour le téréphthalate de polyéthylène amorphe et cristallin en bon accord avec le volume spécifique mesuré du polymère amorphe et le volume spécifique calculé par Bunn à partir de l'analyse aux rayons-X de la structure cristalline, pour le téréphthalate de polyéthylène cristallin.

Zusammenfassung

Eine Röntgenbeugungsmethode zur Bestimmung des prozentuellen kristallinen Anteils von orientierten Filmen und Fasern aus Polyäthylenterephthalat, unter Verwendung eines Röntgendiffractometers in Verbindung mit einem Proportionalzähler wird beschrieben. Es werden Ergebnisse mitgeteilt, die zeigen, dass durch Rotation der Probe über die Kristallitorientierungseffekte in geeigneter Weise gemittelt werden kann. Ergebnisse für den prozentuellen kristallinen Anteil sowie das spezifische Volumen einer Reihe von Filmen und Fasern von Polyäthylenterephthalat mit verschiedenem Grad von Kristallinität werden mitgeteilt. Es wird eine lineare Beziehung zwischen spezifischem Volumen und Röntgenkristallinität gefunden. Eine Extrapolation auf null und 100% Kristallinität liefert Werte für das spezifische Volumen des amorphen und kristallinen Polyäthylenterephthalats, die in guter Übereinstimmung mit dem am amorphen Polymeren gemessenen spezifischen Volumen und dem aus der von Bunn durchgeführten Röntgenkristallstrukturanalyse für kristallines Polyäthylenterephthalat berechneten spezifischen Volumen stehen.

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