

Comparative Crystal Morphology Study Using WAXS and CDT Techniques

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SYNOPSIS

Changes brought about in the crystal morphology of drawn (oriented) PET fibers following both heat and liquid treatments were studied using wide angle X-rays and critical dissolution time techniques. The results obtained showed that the two techniques were sensitive to different but closely related morphological properties of the polymer, the former being sensitive to the apparent degree of the crystalline content, and the latter, a measure of the size of such crystallites that were produced.

INTRODUCTION

For the purpose of crystal study, a polymer such as PET has often been considered as a two-phase model of semicrystalline material consisting of impermeable, well-ordered arrangements of crystallites embedded in an amorphous matrix. Interphase materials having properties intermediate between amorphous and crystalline regions are ignored.^{1,2} Wide angle X-ray photographs of drawn (oriented) semicrystalline polymer do show sharp diffraction arcs for the crystalline phase and a diffuse halo for the amorphous. The extent or degree of crystalline content is proportional to the intensities of the diffraction spots.

For PET, heat and treatment in certain liquids lead to appreciable crystallization of the amorphous polymer and the three equatorial arcs obtained following crystallization, i.e., (100), (1 $\bar{1}$ 0), and (010) are used to follow up changes in crystallinity as the polymer is subjected to treatments that bring about modification of its crystal morphology. Various workers have obtained useful results based on this method.^{3,4} Others have used changes in IR absorption peaks to follow the development of crystallinity

in amorphous polymers, and in most of these studies, PET has been used as model for investigation.⁵⁻⁷

Changes in a fiber's crystal morphology can also be investigated by the critical dissolution time (CDT) technique. Essentially, the CDT measures the rate of dissolution of crystallites that developed in a polymer following treatment in a suitable liquid, and it is assumed that since the rate at which the crystallites dissolve in such liquid is dependent on the concentration of such crystallites produced the results obtained should corroborate with the extent of the crystallization and, therefore, the overall density of the fiber. Several workers have shown that an appreciable degree of correlation was obtained between the density of the fibers investigated and the intensity of the diffraction spots. Increase in the CDT values of the crystallized PET has also been correlated with an increase in the crystal size in the fiber.

In the present investigation, drawn PET fibers were exposed to both dry heat and liquid treatments to effect crystal growth. Using simple mathematical relations, apparent crystallinity values were obtained for WAXS and CDT data. Although the results obtained from these two techniques showed a good correlation with the density and, hence, with the degree of crystallinity of the fiber, the abnormally high dissolution times obtained for fibers annealed at the working temperature for a period longer than 1 h seem to cast some doubt on the use of the CDT technique to measure the degree of crystallinity induced in the fiber.

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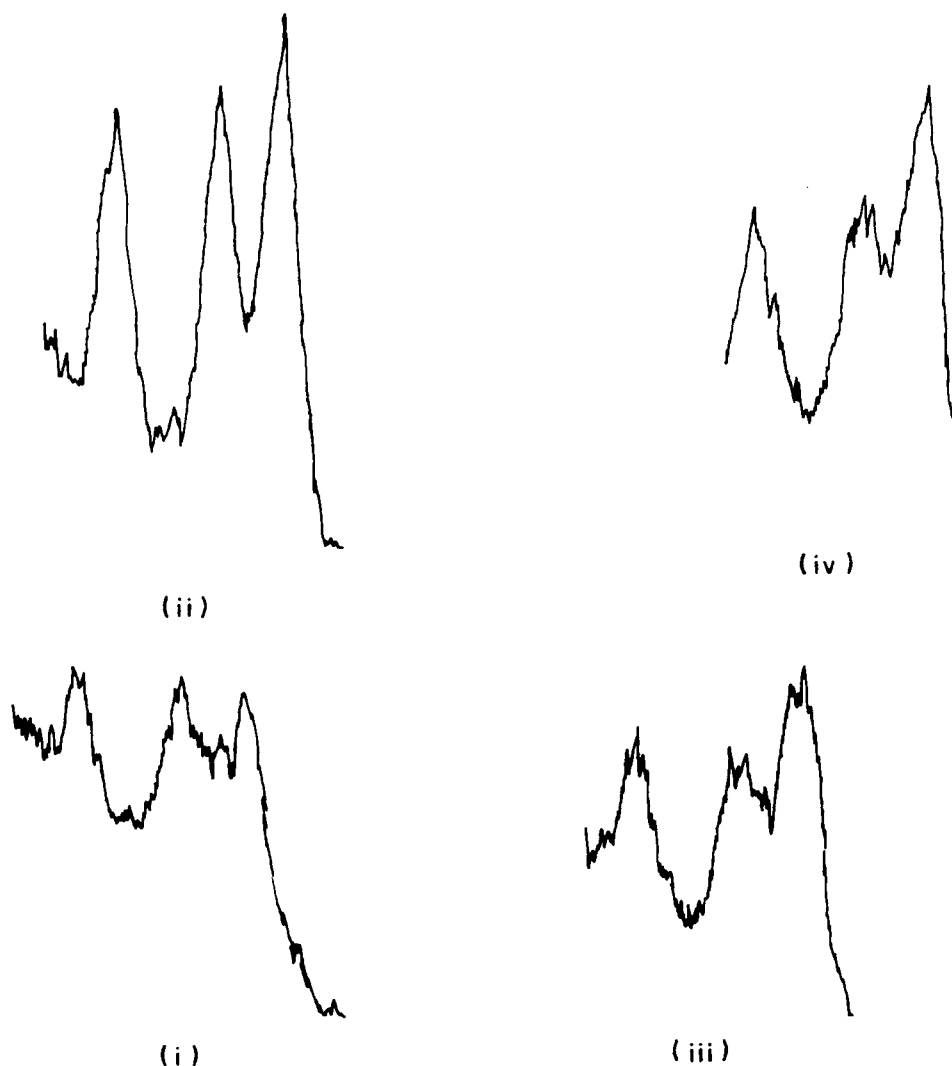


Figure 1a WAXS diffractograms for PET fiber showing the three equatorial peaks after annealing at 200°C for (i) 1 min, (ii) 3 hours, and treatment in Benzaldehyde at 95°C for (iii) 1 min and (iv) 3 hours.

EXPERIMENTAL

Materials

PET fibers obtained from bright polymer chips (Courtauld U.K. Ltd.) were used. The fibers were drawn (D.R. 5 : 1) and purified from spin finish by extraction with petroleum ether at 60°C for 1 h followed by scouring at 60°C in an aqueous solution of Lissapol (nonionic surfactant), washing, and then drying under vacuum at 60°C for a further period of 24 h prior to use. Distilled benzaldehyde and dimethylformamide of general purpose grade were used as the liquid crystallizing media.

Crystallization

The oriented fibers were annealed in a dry state without tension in a vapor-bathed jacket at 200°C for varying times to induce the necessary crystallinity. Samples were also treated in both DMF and benzaldehyde at 95°C for varying times for liquid-induced crystallinity. Residual liquids were removed from the fibers by pressing between filter papers under weight and thereafter dried under vacuum to constant weight at 60°C for 24 h.

Density Measurement

The densities of the fibers were measured using a density gradient column established with CCl₄ and

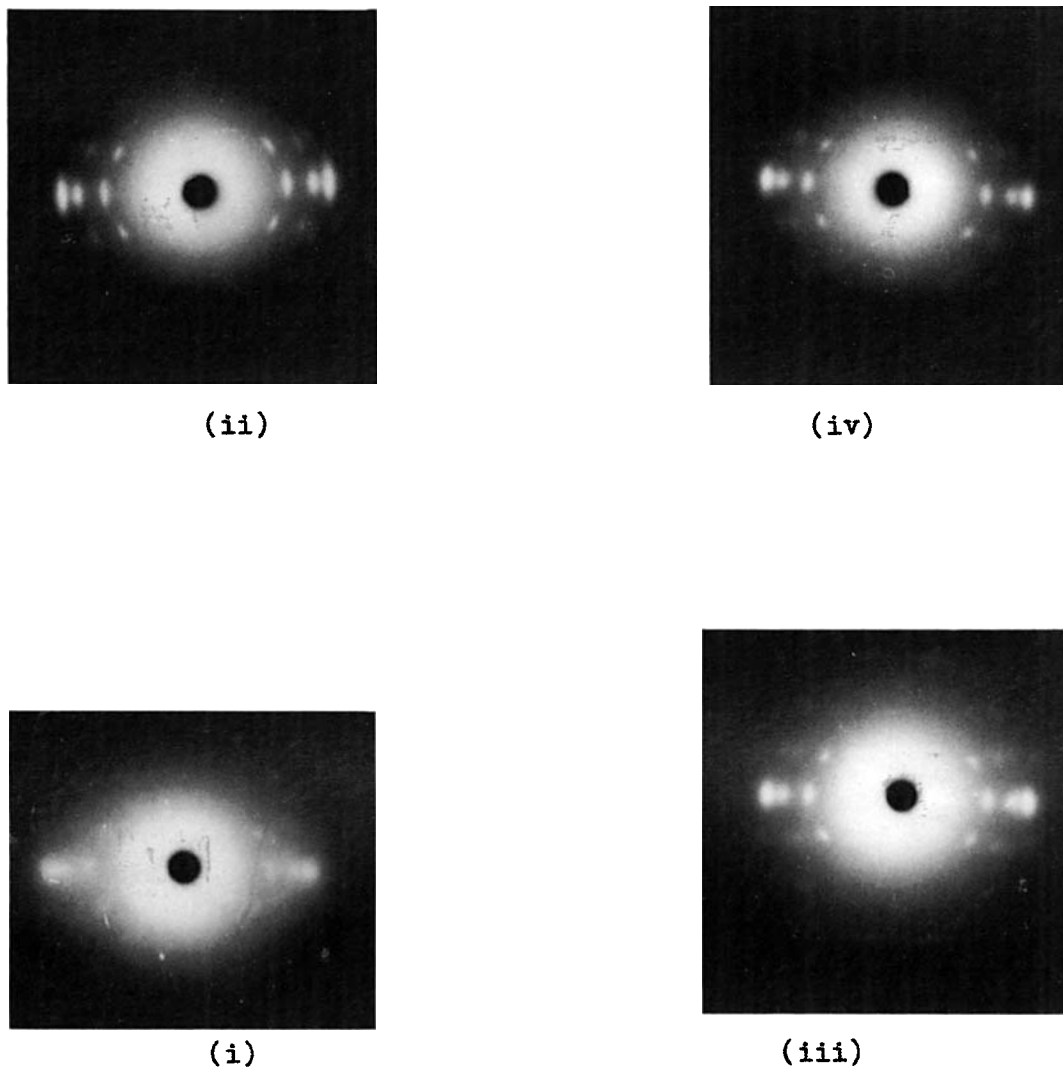


Figure 1b WAXS photographs for PET fiber showing the diffraction arcs following annealing at 200°C for (i) 1 min, (ii) 3 h, and treatment in benzaldehyde at 95°C for (iii) 1 min and (iv) 3 h.

n-heptane. Appropriate ratios of the two liquids were chosen to give a working range of 1.30–1.45 g cm⁻³, within which the densities of both the treated and untreated fibers were expected to fall. The column was calibrated using standard floats and the tube maintained at 23°C by means of a thermostat water bath.⁸ Crystallinity values were obtained from density data by means of the appropriate conversion equation reported elsewhere.⁹

WAXS Diffractograms

These were recorded on a Philips X-ray diffractometer consisting of a generator type PW 1010/80 with

nickel filter radiation from a copper anode tube. The source of radiation was CuK_α operated at 40 kV and 19 mA. Photographs were taken at positions normal to the fiber axis. Pictures obtained on negatives were printed on Kodak photopaper and were, in addition, scanned using a Joyce-Loebl densitometer. Apparent crystallinity values were calculated from the intensities of the diffraction arcs obtained at 2θ degrees between 10 and 30° using Kasai and Kaku-do's eq. (1) shown below.

CDT Data

The time of immersion-to-dissolution (CDT) of the fibers was determined in phenol at 60°C. Yarns were

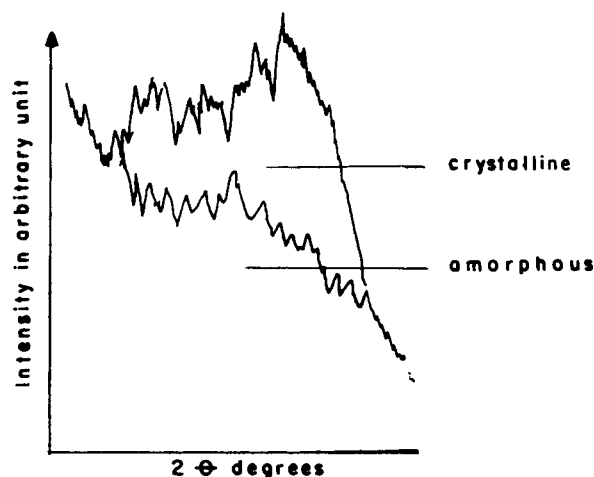


Figure 1c WAXS diffractogram for PET fiber (D.R. 5 : 1) with amorphous diffraction superimposed.

hung one at a time from a stainless-steel spring attached to a wood cork stopper and suspended freely in phenol contained in a Pyrex tube by means of a constant load of 6.6×10^{-2} g, just sufficient to remove crimps. The tube was immersed in a water bath preset at 60°C .

RESULTS AND DISCUSSION

The results obtained for crystallinity values using WAXS and CDT data were correlated with that of

density measurement. In the case of WAXS, the peak intensities of the three equatorial diffraction spots at 2θ degrees between 10 and 30°C , i.e., (100), $(1\bar{1}0)$, and (010), were used to follow the relative changes in the crystallinity. These intensities are shown in form of densitometer tracings in Figure 1(a) together with the corresponding X-ray photographs producing them in Figure 1(b). The areas under these peaks, calculated using the "Albrit" planimeter, with allowance made for amorphous and background scatterings by superimposing amorphous diffractograms on crystalline ones as illustrated in Figure 1(c), represent diffractions from the crystalline domains. These relate to the diffraction intensities of the spots, which, in turn, depend on the relative amount of crystallinity induced in the fibers by either dry heat or liquid treatment. Crystallinity values were calculated from diffraction areas with the aid of eq. (1)¹⁰:

$$\% \text{ crystallinity} = \frac{100 I_c}{I_c + I_a} \quad (1)$$

I_a and I_c are diffraction intensities from amorphous/background and crystalline centers.

The areas obtained from the X-ray diffractometer as well as the crystallinity values calculated from them is shown in Table I. Also shown are the crystallinity values obtained from density data.

The correlation between the result obtained for both density and diffraction intensities is shown in Figure 2, where it is observed that an increase in the

Table I Diffraction Peak Areas (cm^2), Density, and Crystallinity Values (%) for PET D.R. 5 : 1, Annealed at 200°C and Liquid Treated at 95°C

Sample Detail	Diffraction Area (cm^2)	% Crystallinity (WAXS)	Density	% Crystallinity
Amorphous fiber	10.0	0	1.335	0
Drawn fiber	15.5	35	1.340	4.5
Annealed for				
1 min	16.0	38	1.380	44.0
1 h	18.0	44	1.402	58.0
3 h	19.5	49	1.404	59.0
6 h	20.0	50	1.404	59.0
DMF treated				
1 min	16.5	39	1.390	48.0
1 h	18.0	44	1.390	48.0
6 h	18.5	47	1.390	48.0
Benzaldehyde treated				
1 min	16.0	38	1.390	48.0
1 h	18.0	44	1.390	48.0
6 h	19.0	48	1.390	48.0

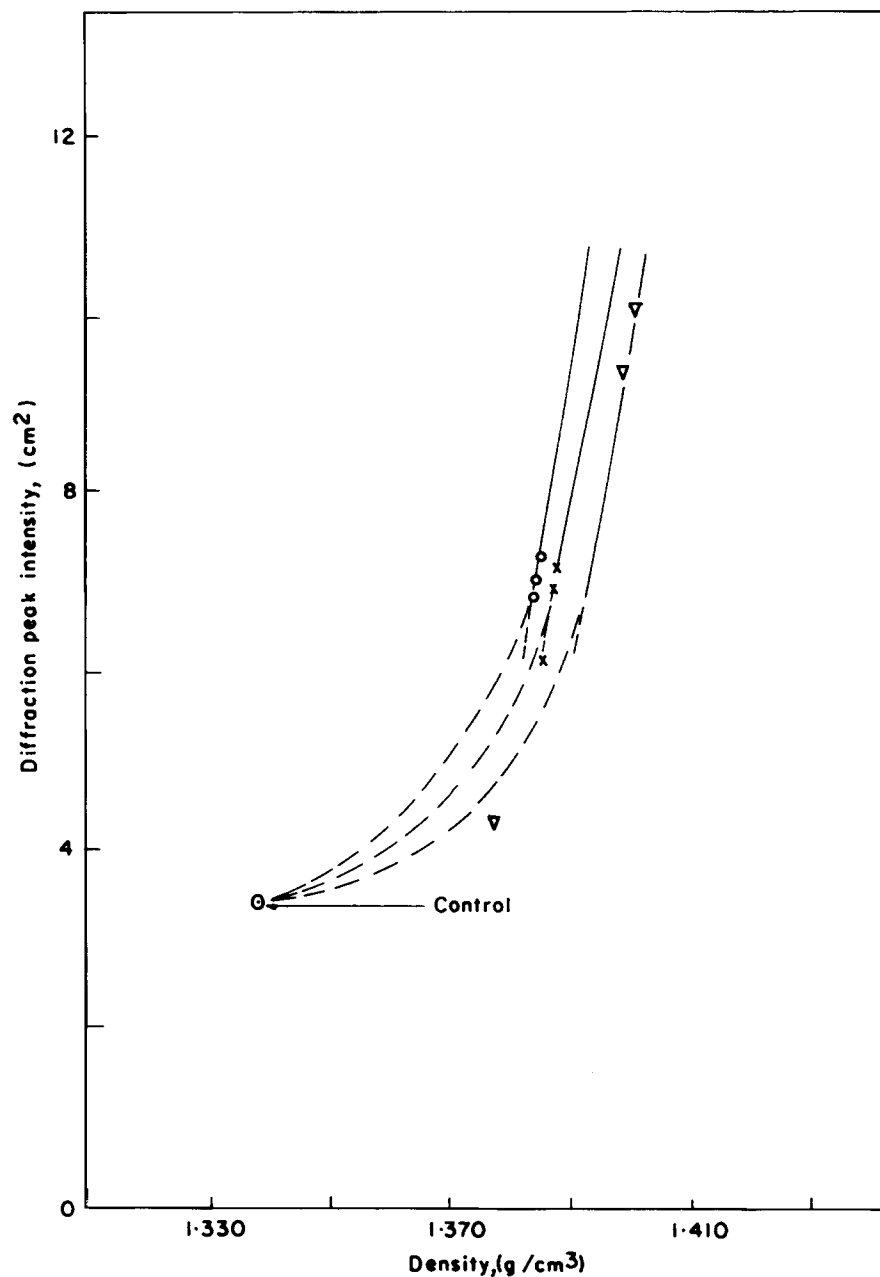


Figure 2 Diffraction peak intensity (cm^2) vs. density for PET fiber (D.R. 5 : 1) (\odot), annealed at 200°C (∇), DMF treated at 95°C (\circ), and Benzaldehyde treated, (\times).

diffraction peak intensity with increase in the density (crystallinity) of the fibers occurred. The different crystallinity values observed using these two approaches have also been noted by other workers.^{11,12}

CDT Results

The immersion-to-dissolution times (CDT) obtained for the fibers are shown in Table II and the

plot of \log_{10} CDT as a function of treatment times in Figure 3. Annealing treatment at 200°C for a period longer than 1 h led to an appreciable increase in the dissolution time, and since it did not show the same time-dependent relationship observed in Figure 3, it is not incorporated into it. However, this behavior has been explained in terms of onset of major structural change in the polymer crystal morphology that presumably corresponds to the increase in crystal size.¹³

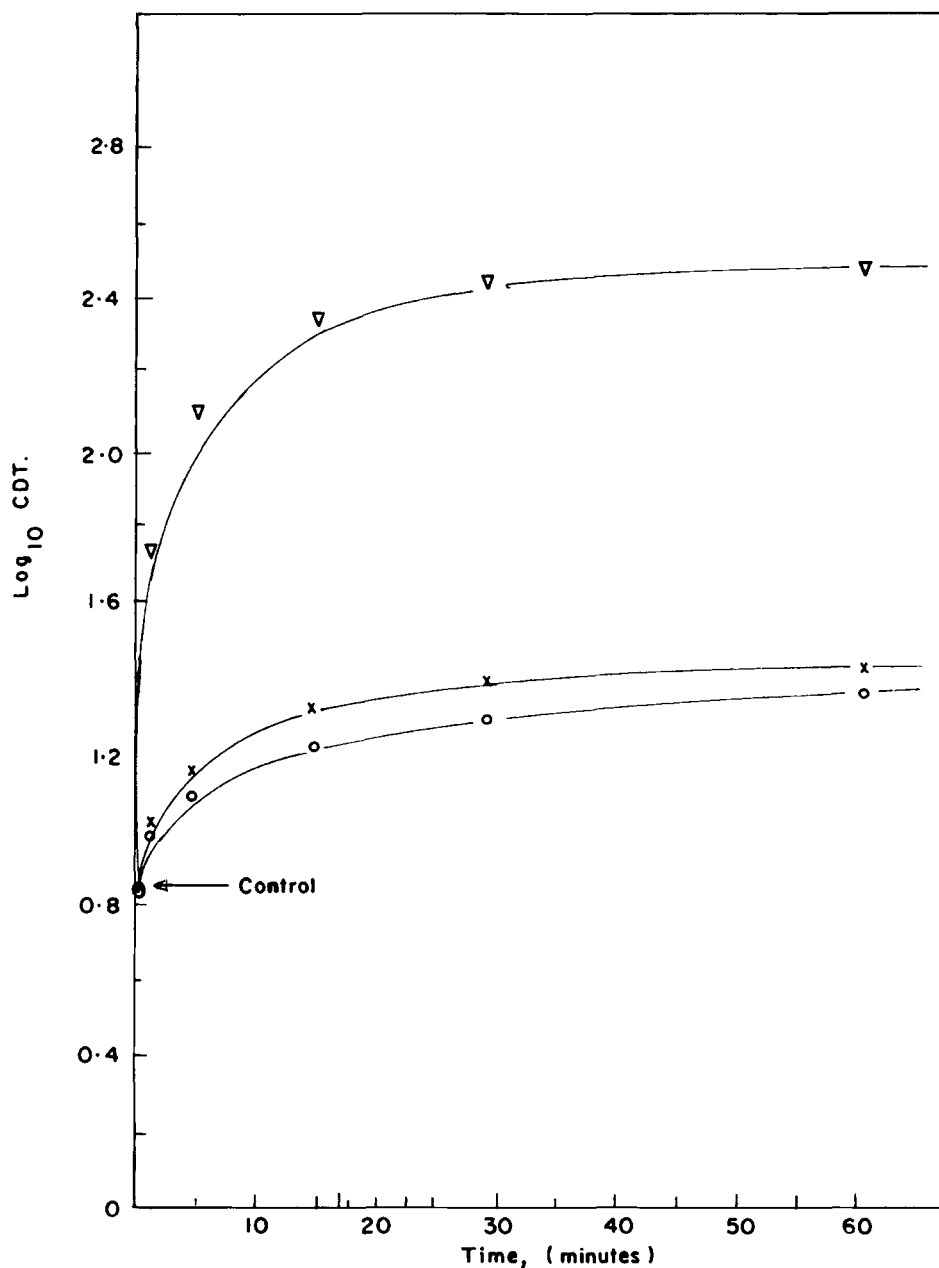


Figure 3 Log_{10} CDT vs. time of treatment for PET fiber, control (○), annealed at 200°C, (▽), DMF treated at 95°C (○), and Benzaldehyde treated (×).

Using a simple mathematical relation similar to eq. (1), an attempt has been made to estimate corresponding crystallinity values from the CDT data:

% crystallinity

$$= \frac{\text{CDT}_{\text{treated}} - \text{CDT}_{\text{control}}}{\text{CDT}_{\text{treated}}} \times 100 \quad (2)$$

The following assumptions are made in the use of this equation:

1. That the annealed fibers consist essentially of two phases, i.e., impermeable crystallites embedded within the amorphous matrix.
2. On immersion of the fibers in the solvent, there is complete penetration of the solvent

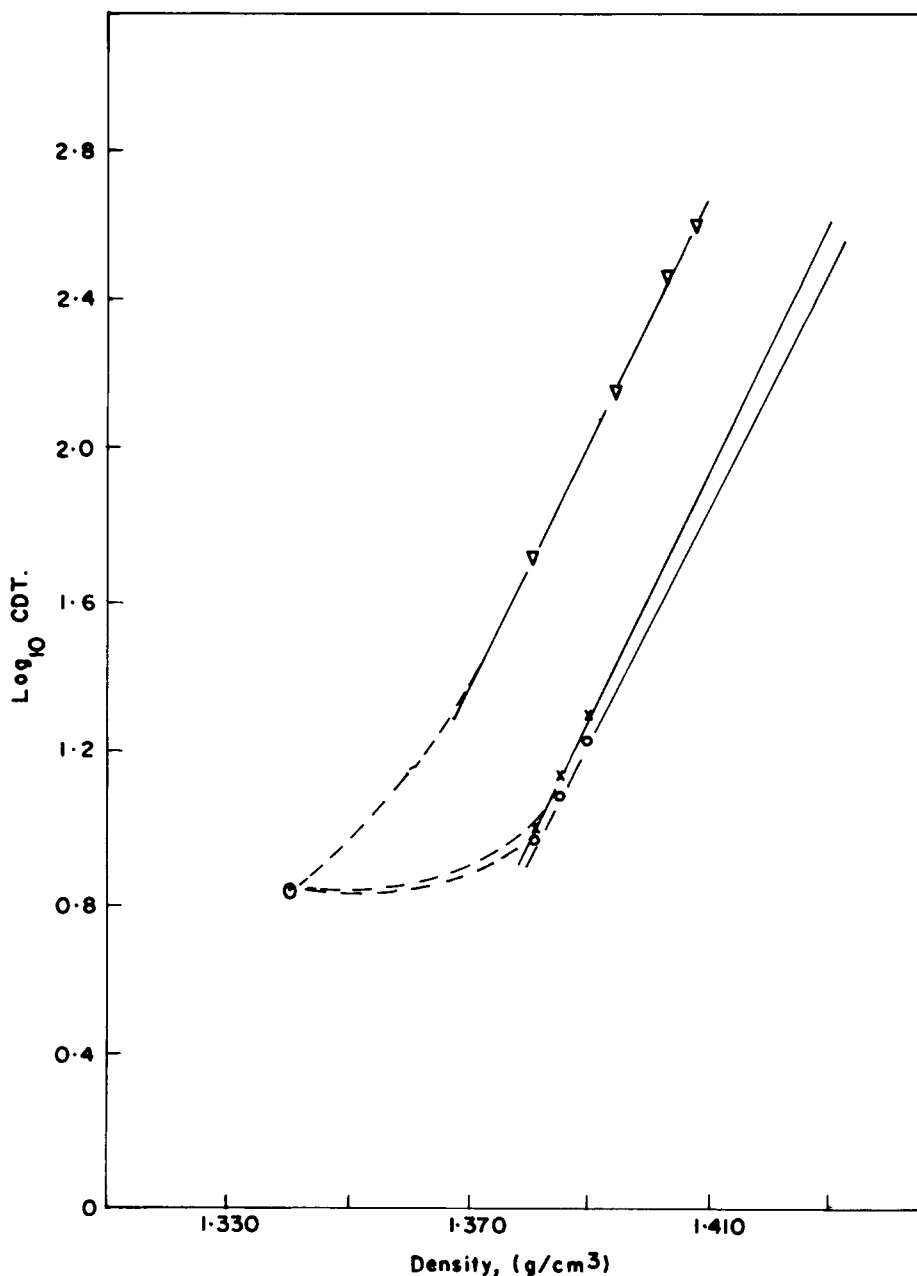


Figure 4 Log_{10} CDT vs. PET fiber, control, (\odot) annealed at 200°C (∇), DMF treated at 95°C (\circ), and Benzaldehyde treated (\times).

molecules through the amorphous regions and that each crystal plane of the embedded crystallites experiences the same concentration of the solvent.

3. Finally, that the amorphous matrix is dissolved prior to the crystalline region.

Thus, in adopting these simplified assumptions, apparent crystallinity values were calculated, and

these are shown in parentheses in Table II. It is observed that extremely high estimates for the degrees of crystallinity were obtained, especially for the annealed fibers.

The relationship between the log_{10} CDT and density of the fiber is shown in Figure 4, where it is seen again that a direct correlation occurs as with diffraction intensity (areas) and density (see Fig. 2). This indicates that an increase of crystallinity leads

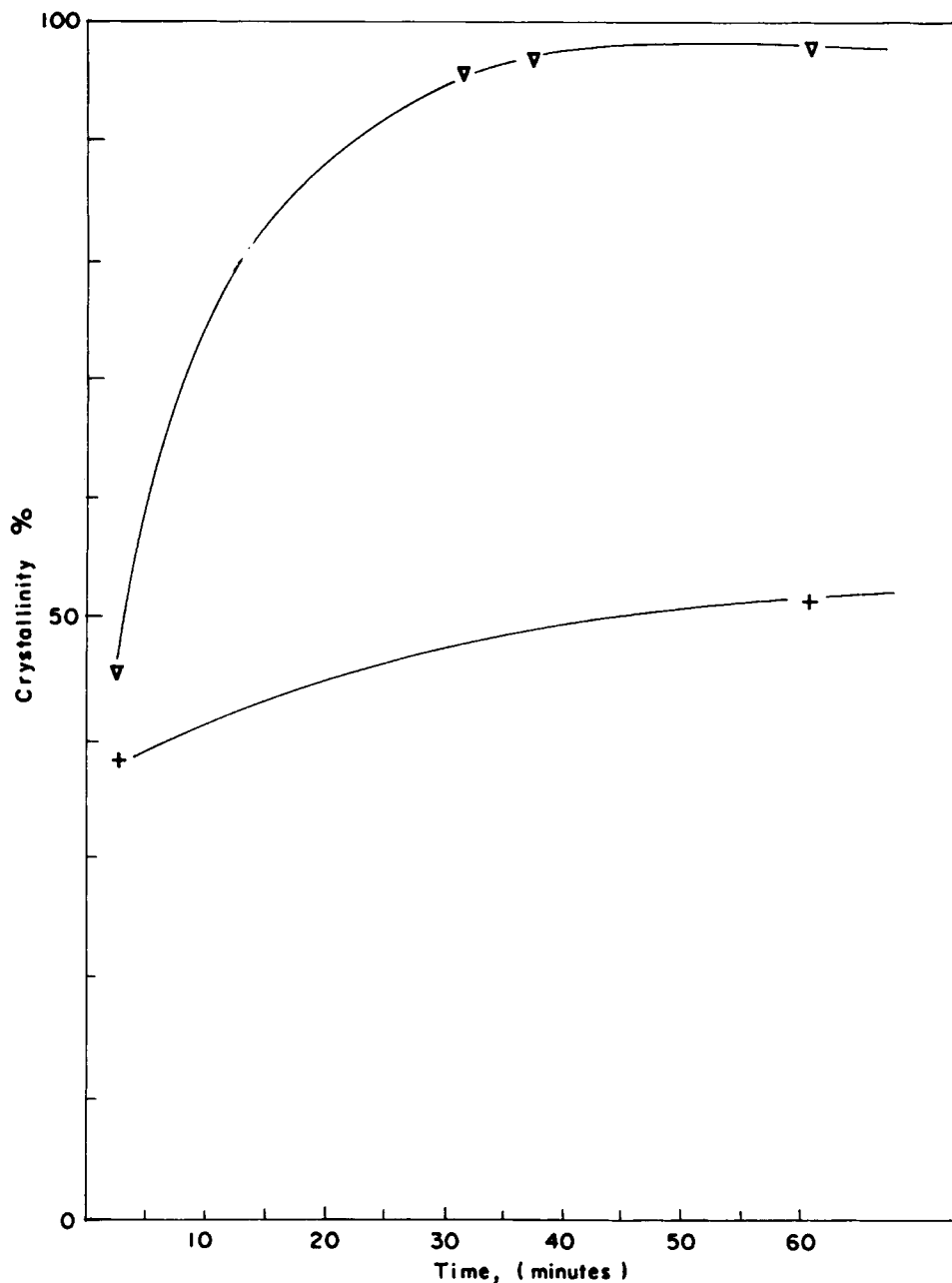


Figure 5 Crystallinity values, (%) vs. time of treatment for PET fiber, annealed at 200°C. From WAXS data (+) and from CDT data (▽).

to an increase in both density and dissolution time. An observation of considerable significance is that the annealing treatment produced crystallites that required much longer time to dissolve than they did in the liquid treatment as evident from Figure 3, thus supporting the claim by Desai Ajit et al.¹² that different crystal morphologies were induced by these treatments: the heat treatment, on the one hand, leading to the development of few large crystals that

require longer time to dissolve and the liquid treatment, on the other hand, producing relatively higher concentration of small crystallites. Much as the interpretation of the result shown in Figure 3 is indicative of the size of crystals produced from both heat and liquid treatments, the abnormally high degree of crystallinity obtained from CDT data in the plot of crystallinity values obtained from WAXS and CDT calculations following thermal treatment,

Table II Critical Dissolution Time (s) and Crystallinity Values for PET Fiber Annealed at 200°C and Liquid Treated at 95°C

Treatment		Annealed (% Crystallinity)	DMF Treated		Benzaldehyde Treated	
Min	CDT _s		CDT _s	(% Crystallinity)	CDT _s	(% Crystallinity)
	1.0	50 (86)	13	(46)	10	(30)
	5.0	125 (94)	12	(41)	13	(46)
	15.0	229 (96)	15	(53)	20	(65)
	30.0	288 (97)	19	(63)	23	(69)
	60.0	347 (98)	25	(72)	28	(75)

Control fiber, amorphous; CDT = 7.0 s; % crystallinity = 0.0

shown in Figure 5, seems to suggest that although the WAXS technique is sensitive to the degree of crystallinity induced by heat and liquid treatments the CDT can also be used as a measure of the size of such crystallites rather than as the overall degree of crystallinity induced in the polymer.

CONCLUSION

Both wide angle X-rays and critical dissolution time techniques were used on a comparative basis to study the crystal morphology of thermally annealed and liquid crystallized PET fibers. The results obtained from the study on the crystallinity induced in the fiber showed a time-dependent relationship in the plot of crystallinity as a function of time until equilibrium was achieved in the degree of crystallinity measured by these two methods. The abnormally high degrees of crystallinity obtained in respect of CDT data seem to cast some doubt on the use of this technique in determining the overall degree of crystallinity induced in PET by both heat and liquid treatments.

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