Case
NGR-36-003-054

MORPHOLOGY of CRYSTALLINE POLYETHYLENE TEREPHTHALATE (PET)

13330

Various forms of crystallization of PET, both from supercooling and from orientation, have been studied. The purpose of this work is to characterize in detail the morphology and structure of the various types of crystalline units in PET. These results are being utilized in other studies being carried out presently at Case; including IR studies of the chain conformation and folding of PET, mechanical behavior of PET under well-controlled conditions, etc..

This report summaries the preliminary investigation of PET. Much work is needed in the clarification of the various observations reported here.

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I. CRYSTALLIZATION of PET from SOLUTION & on SOLVENT EVAPORATION

Figure 1 shows a typical example of the type of crystallites obtained by crystallization in solution, both by cooling and under isothermal conditions. They are spherulitic in nature, consisting of fibrillar ribbons, each about 100Å thick, few hundred Å wide and several thousand Å in length. Depending on the crystallization conditions, the size of these spherulites varies from about .5μ to 10μ. Attempts to establish the chain conformation within the fibrillar ribbons by means of selected area electron diffraction were unsuccessful. This is due to a number of unfavorable experimental conditions; among these are the size and randomness of the aggregates as well as the low diffracting power of these fibrillar ribbons. These difficulties were circumvented by growing fibrillar ribbons epitaxilly on a NaCl substrate. By this method the fibrillar ribbons were aligned in an orderly fashion making possible detailed diffraction studies. The discussion of their chain conformation will be considered later.

By means of solvent evaporation it was possible to obtain some lamellar-type crystals of PET. (Figure 2) They are quite irregular, with little or no recognizable crystallographic growth faces. Each crystal consists of a lamellar base layer. Fibrillar overgrowths can be seen, but they do not seem to have any particular orientation with each other or the base layer. At times regular lamellae with the presence of several dislocations in the center were observed as shown in Figure 3. They were generally found with the fibrillar ribbons. These mixed structures should be of interest for studies of the nucleation and growth mechanism of polymer crystallites because of their fundamental relationship to each other. However attempts to reproduce them under similar, controlled conditions were unsuccessful. In general, crystallization during solvent evaporation has not been found to be reproducible to the extent that systematic studies can be made on the products.

II. EPITAXIAL CRYSTALLIZATION of PET & EVIDENCE for CHAIN-FOLDED CONFORMATION

Under suitable conditions fibrillar ribbons can be obtained epitaxially on NaCl both in solution and on solvent evaporation. Figure 4 shows an example of these fibrils oriented along the <110> direction of the NaCl substrate. They are seen with their thin edges layed down parallel to the (001) face of NaCl. The edges, i.e., the thicknesses, of these fibrillar ribbons measured about 100Å, the same as that obtained previously for solution grown fibrils (Figure 1). From shadow lengths, the height of these ribbons was estimated to be between a few hundred Å and several thousand Å.

Electron diffraction studies on these well-aligned structures, with the help of a cooling stage in the specimen chamber of the electron microscope, were generally successful. The chain molecules are nearly parallel to the NaCl substrate surface, but inclined at a large angle (about 70°) to the fibril long axis. An electron diffraction pattern and its corresponding selected area are shown in the lower right-hand corner of Figure 4. The strong reflections are from $\bar{1}10$ and $1\bar{1}1$ planes. A weak reflection that barely showed up along the meridian or fiber axis is due to the $\bar{1}05$ planes. These studies give evidence that the molecules, which are about a thousand Å long, must assume a folded type conformation within these 100Å thick fibrillar ribbon as in the case of polymer single crystals.

III. CRYSTALLIZATION of PET from BULK MATERIAL

Spherulitic structures, consisting of lamellar ribbons, can be obtained from the melt and from the annealing of glassy materials. (Figures 5 & 6) The major difference between the two cases is the rate of spherulitic growth. The spherulitic growth rate is much faster in the case of crystallization from melt than from glass, (spherulitic diameter 8 to 1) but this effect may be masked by the higher nucleation density present in the latter. They were grown at the same temperature (~154°C) for equal lengths of time. The original polymer prior to crystallization showed no gross, recognizable features (Figure 7) except for some minute, ball-like structures of the order of 50Å in diameter. The amorphous, glassy material was prepared by quenching quickly the molten material into ice water. The material appeared transparent and showed no order either from wide angle or small angle X-rays.

IV. STRAIN-INDUCED CRYSTALLIZATION of PET

X-ray studies of cold drawn PET give evidence for molecular order along the fiber axis, even at temperatures well below the glass transition temperature (ca. 70°C). This order may be related to some form of crystallization induced during drawing. The morphology and the chain conformation of these strain-induced crystallites are presently unknown. We are interested in looking into the possibilities of studying these crystallites directly by means of electron microscopy together with small-angle and wide-angle X-ray techniques.

Preliminary results showed some type of morphological structure present in cast drawn thin films of PET (Figure 8). No fiber morphology was observed in any of the samples studied so far. Instead, some structures, similar to those shown in Figure 7 of the glassy material, are seen arranged in rows at a substantial angle to draw direction. Other preparations, for example, using a staining agent of phorstungstic acid, seem to indicate presence of some kind of periodicities of the order of 100Å, which are also at a large angle of about 60° with respect to the draw direction (Figure 9). The periodicities are quite noticeable in the highly drawn portion. Investigations are being carried out to establish the nature of these observed phenomena in drawn PET.

V. INFRARED STUDIES of FOLDING in POLY-(ETHYLENE TEREPHTHALATE)

A. In conjunction with the intensive work being done in the area of polymer crystallization and morphology, it is surprising that no means is yet available to detect (except in single crystal studies where the deductions are obvious) the presence or absence of a folded conformation in a typical crystalline polymer material.

Long before the theory of polymer chain folding had been proposed the infrared spectrum of poly-(ethylene terephthalate) had been analyzed quite extensively. And because of the commerical importance and unique properities of the material under various severe chemical and physical tests, the spectrum and its correlative changes with properties has continued to be studied to the point where now its infrared band assignments are fairly complete.

With these thoughts in mind, it was our purpose to achieve the following ends:

1) Assignment of "fold" bands -- those which arise because of a conformation which is concentrated in the folded regions, which may or may not occur in the normal polymer.
2) Measurement of the relative fold content in polymer samples prepared under different conditions.

That it might be possible to obtain a band in the spectrum which is due solely to the requirements of the folded chain seems reasonable if one analyzes models to determine the possible ways in which a molecule of poly-(ethylene terephthalate) might fold. The stiffness of the benzene-carbonyl conjugated system along with the bulkiness of the glycol linkage imposes stringent steric requirements and highly energetic conformations upon the molecule. If the poly-(ethylene terephthalate) molecule folds (and it has been proven that it does), it must of necessity exist in a highly strained conformation which may produce shifts of the usual vibrations in PET.

B. The poly-(ethylene terephthalate) samples studied were analvzed using a Perkin-Elmer 521 double beam infrared spectrometer.

Samples of various preparations have been analyzed. The solution crystallized poly-(ethylene terephthalate) was obtained by crystallizing from two different solvents--both giving spectroscopically nearly identical crystalline samples. The first set of crystals were grown overnight from both 0.1% to 1% solutions in dimethyl phthalate at approximately 130°C. The second set of crystals were grown from a 0.1% solution of PET in 2 (2 butoxyethoxy) ethanol by very slowly cooling the solution from the boiling point of the solvent.

Because of the impossibility of obtaining mats of the solution grown crystals, they were analyzed by preparing KBr pellets of them and running them with the beam condenser.

Melt samples were prepared by simply heating "Mylar" sheets in a ram press with electric heating plattens. The polymer was held at the at the melt temperature for about ten minutes, then the press was turned off and the polymer was allowed to crystallize very slowly from the melt. Again, because it was not possible to obtain samples which were thin enough to give satisfactory spectra, the films prepared were ground up and un in KBr pellets, using the beam condenser.

Melt spectra were obtained using a heating cell and compensation was made for the radiation from the cell at these high temperatures.

Completely amorphous poly-(ethylene terephthalate) was obtained by two means. A strict "glass" was obtained by heating the polymer to melting then withdrawing and quenching in an ice water bath.

Another source of amorphous films was graciously provided by C. Heffelfinger of the E. I. DuPont Company at Circleville, Ohio. These films were cast at room temperature from a solution of the polymer in 70% tetrachloroethane and 30% phenol. They were initially analyzed to be amorphous by infrared and by differential thermal analysis.

Oligomers were obtained from several sources. C. Heffelfinger sent a sample of PET which had an average degree of polymerization of 15 to 20.

Samples of PET pentamer and prepolymer were obtained from M. Ishibashi, of Nippon Rayon in Japan and a sample of pentamer was obtained from Y. Yamashita of Okayama University, Japan.

Types of experiments upon the aforementioned samples:

1) Chemical treatment --- a highly crytalline sample (solution grown crystals) of PET was chemically

degraded with aqueous methylamine at room temperature. The base hydrolysis of PET by methylamine is well known; the method used here is basically the one used by Farrow(2) et. al. in their studies of the chemical degradation of PET. A 20% aqueous methylamine solution was allowed to come in contact, with continuous agitation, with the polymer for times up to 48 hours.

2) Crystallization from the glass. A 0.8 mils amorphous film, which had been obtained from C. Heffelfinger was placed between salt plates into a heat-cell and was crystallized in the infrared machine and the spectrum recorded as a function of time.

3) Successive infrared scans were obtained after two consecutive treatments upon the same amorphous film. One of the amorphous films was stretched 4½ times its original length in a hand stretcher. While still in tension it was placed in the oven to be further crystallized by heat setting at 200°C for 11 hours.

4) Annealing studies were also performed on the solution crystallized material as well as upon the pre-polymer obtained from C. Heffelfinger. In order to minimize degradation of the polymer (which is known

to be normally quite extensive at the temperatures in question) the samples were placed in the vacuum oven which was highly evacuated before any heat was applied and the vacuum held while the sample cooled to below 70°C after the annealing. The samples were annealed in the oven at temperaures between 230-245°C, for times up to 144 hours. Even though the above precautions were taken it was obvious that extensive degradation took place in the samples used under these conditions.

C. The first results were qualitative but extremely important. Figure 10 shows how the 988 cm^{-1} band behaves in the melt, glass, melt crystallized and solution crystallized materials.

Figure 11 shows the same results for the 1380 cm^{-1} band. These figures clearly show that the 988 cm^{-1} band and the 1380 cm^{-1} band are bands associated with polymer samples in a crystalline state.

The effects of the base hydrolysis of the crystalline PET by methylamine upon the infrared spectrum are shown in Table 1. It can been seen that the 988 cm^{-1} band (which we shall call a "fold" band) irreversibly decreases with time of degradation. (The 1380 cm^{-1} band shows somewhat similar results but seems to have a disordered contribution.) At the same time that the "fold" band is decreasing, the disordered band decreases abruptly then starts increasing, indicating crystalline areas are now being attacked causing disordered regions to and so the results are obviously inconclusive. It was felt that perhaps besides oxidative degradation, water entrapped in the KBr pellet was causing hydrolysis.

D. The studies of this investigation have led to the assignment of the 988 cm^{-1} band to a conformation which is prevalent in the folded portion of the molecule. It has been demonstrated that the major contribution of the 1380 cm^{-1} band is from the folded conformation.

Further, it has been found that for drawing of the glassy polymer below T_g, crystallization does not occur by a folding mechanism.

In addition, future work is planned in further elucidating the network of these bands and for obtaining the complete structure of the fold. Along thse lines pleochroism studies are envisioned, studies upon high pressure crystallized PET and studies upon epitaxially grown PET.

VI. STRUCTURE - PROPERTY RELATIONSHIPS

Structure - property relationships at cryogenic temperatures will be studied in a torsion pendulum apparatus for measuring internal be friction and modulus changes at low frequencies. The apparatus which is currently being built is similar to instruments previously designed by Weinig(3) and Gwartz(4). An inverted pendulum will be enclosed in a vacuum system designed for "low temperatures" in the range 4.2 to 300°K. In addition, a "high temperature" chamber, 300°-600°K is being constructed. Both optical and electronic recording techniques for measuring the internal friction will be used. A detailed description of the pendulum will be given in the annual report. The apparatus should be completed and running by January 1, 1966.

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1. Y. Yamashita, J. Polymer Sci., Prt. A, <u>81</u>, 92 (1965).
2. G. Farrow, D.A.S. Ravens, and [illegible], J. Polymer Sci., 3, 17 (1965).
3. S. Weinig, Rev. Sci. Instr., <u>26</u>, 91 (1955).
4. J.C. Swartz, Rev. Sci. Instr., <u>32</u>, 335 (1961).

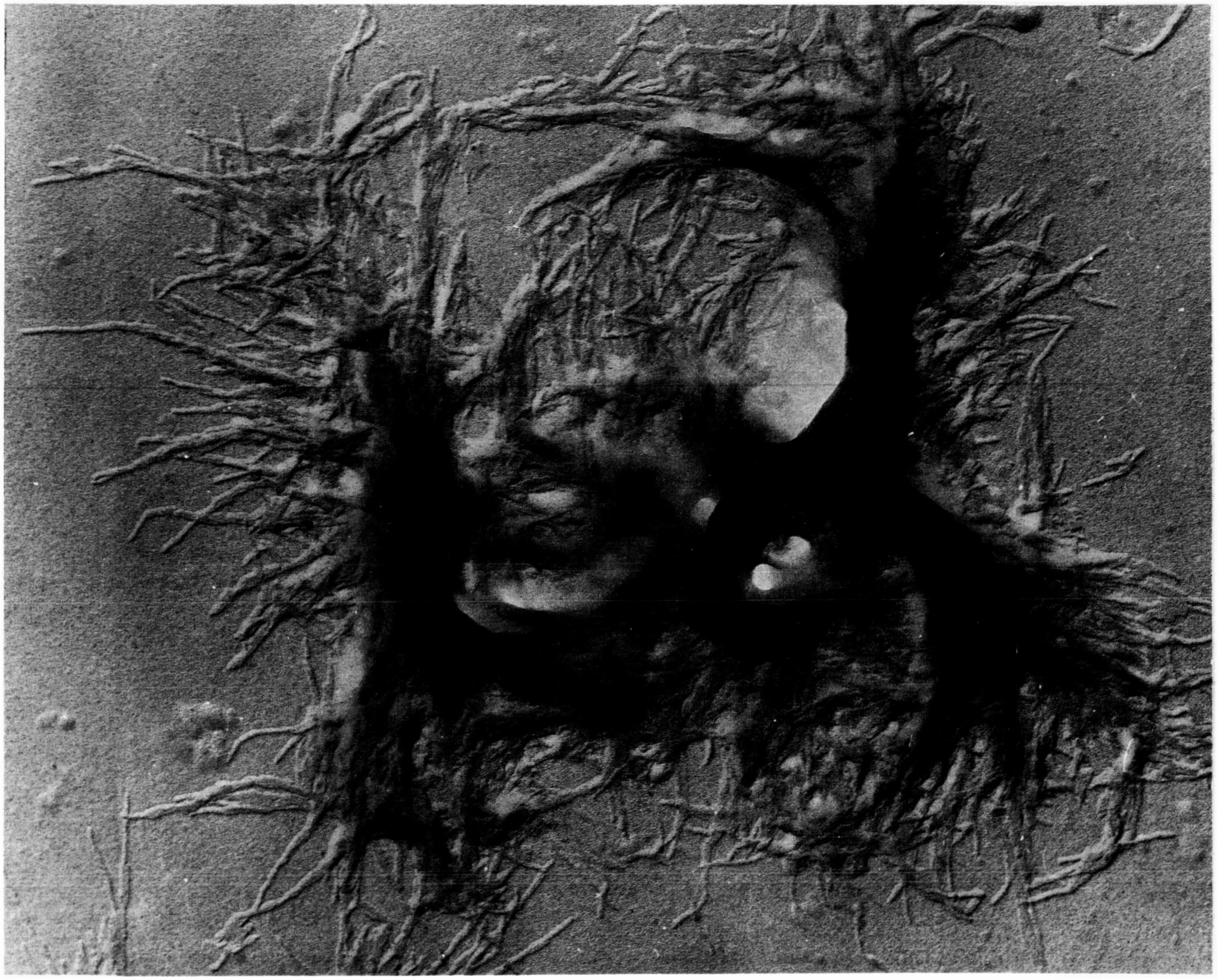


Fig. 1. Fibrillar spherulitic structures of PET crystallized isothermally from a .05% dimethyl phthalate solution at 125°C. (Pt-C shadowed at $\tan^{-1} 5/7$) Magnification: 33,000X

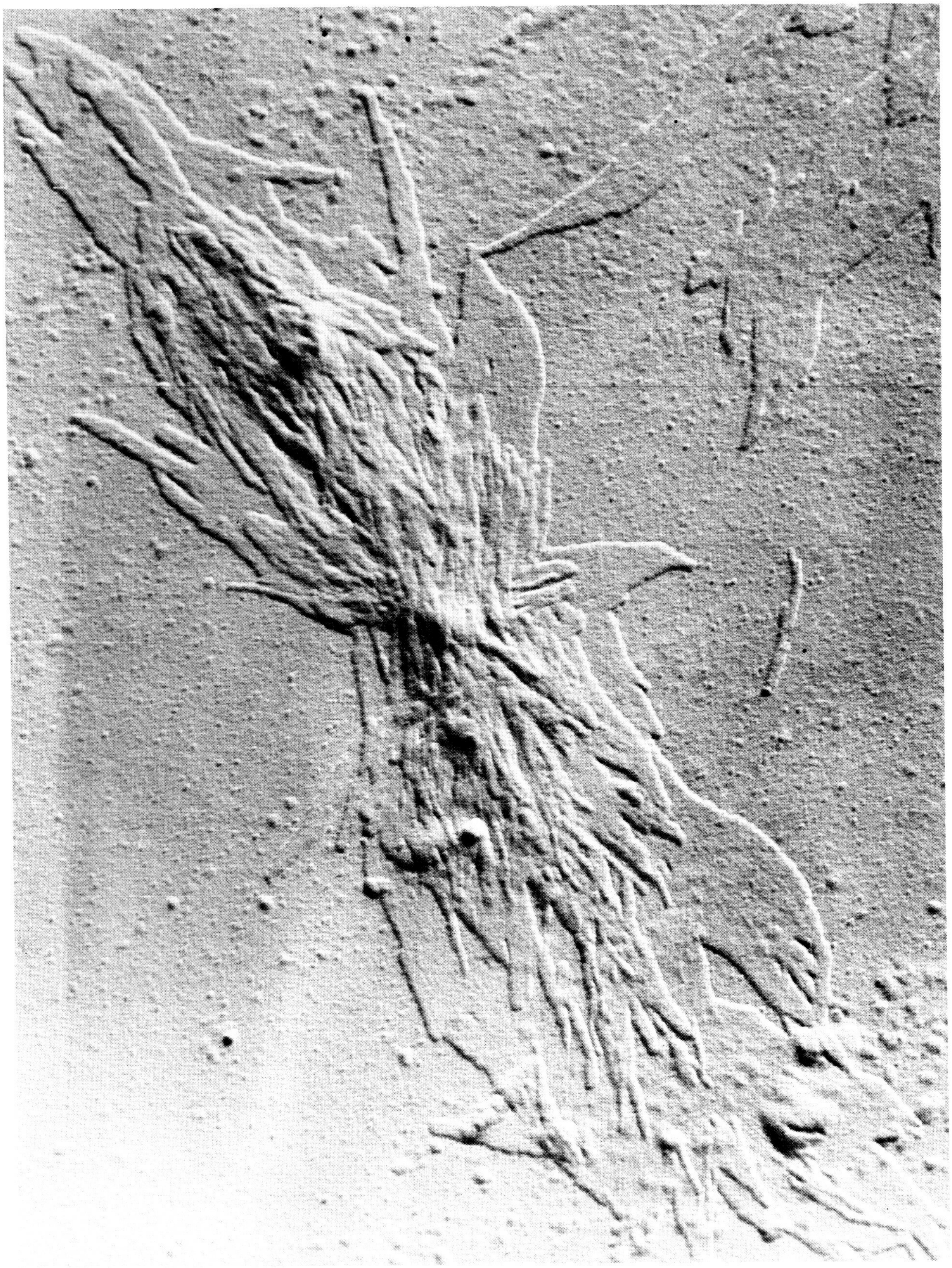


Fig. 2. Lamellar platelets with fibrillar overgrowths of PET obtained during solvent evaporation from a .005% dimethyl phthalate solution in an air oven controlled at 145°C. (Pt-C shadowed at $\tan^{-1} 4/8$) Magnification: 35,000X

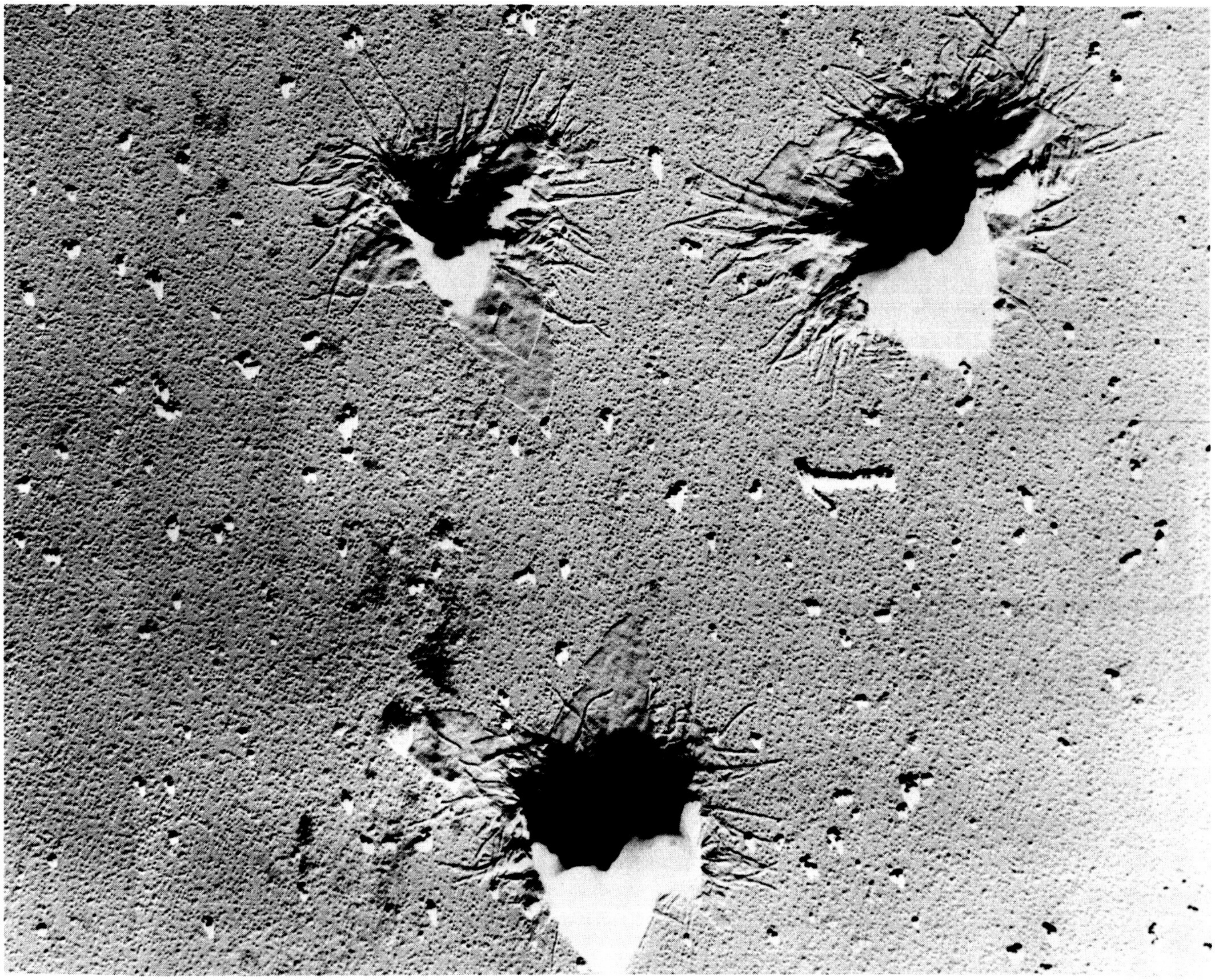


Fig. 3. "Spherulites" of PET obtained during solvent evaporation from a .005% dimethyl phthalate solution in an air oven controlled at 125°C. Single lamellae are seen in the same structure together with the fibrils. (Pt-C shadowed at $\tan^{-1} 4/8$) Magnification: 15,000X

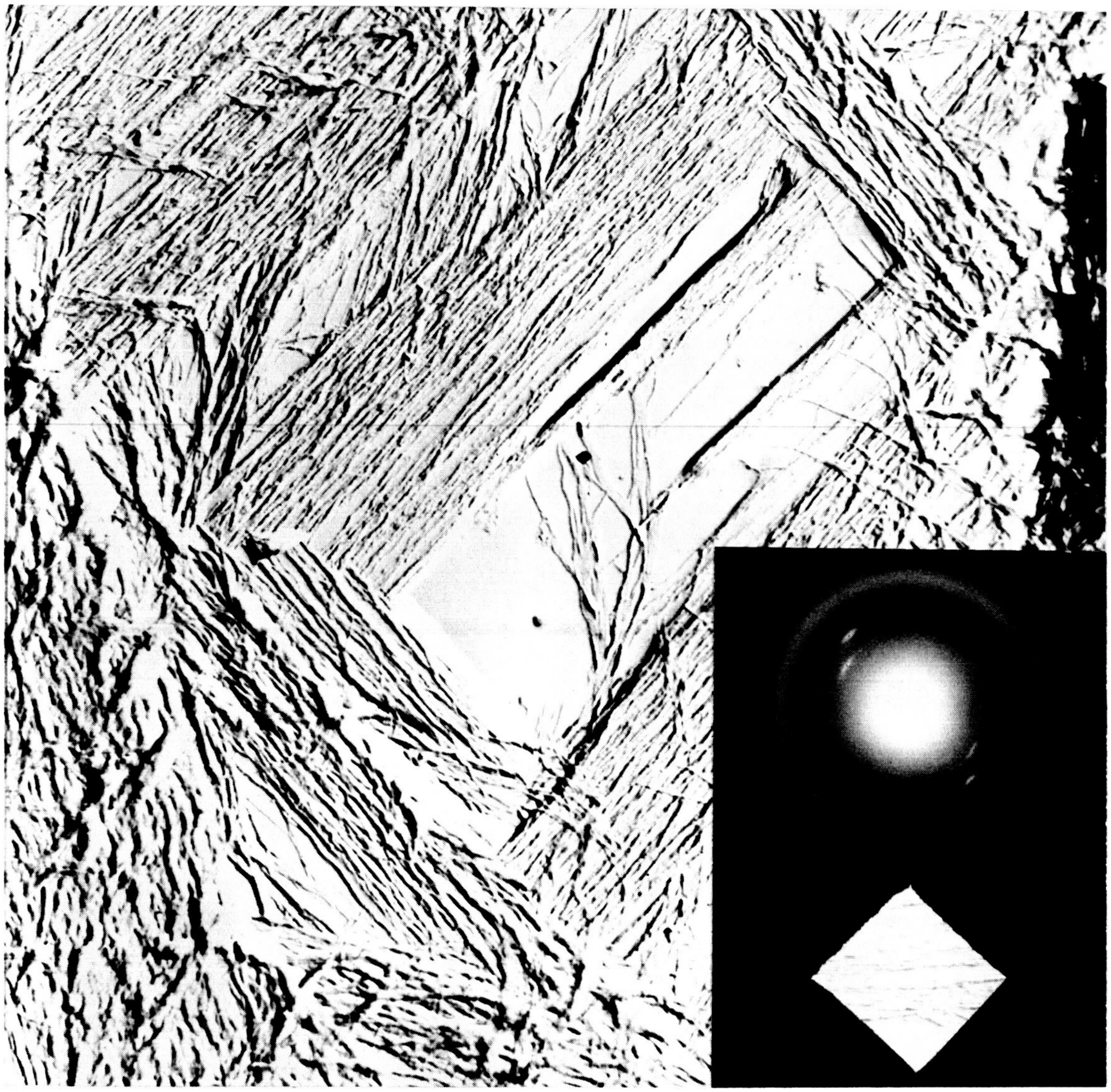
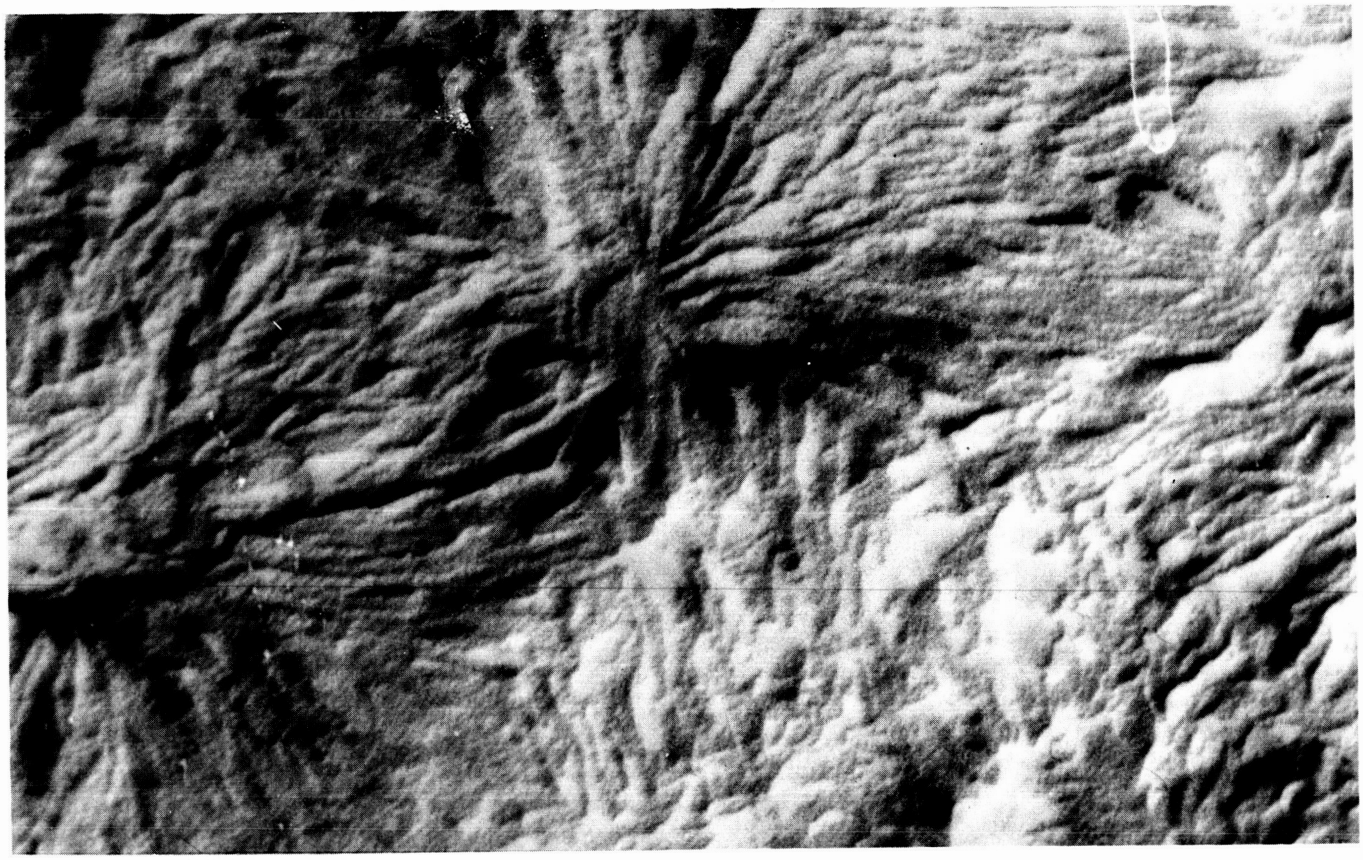


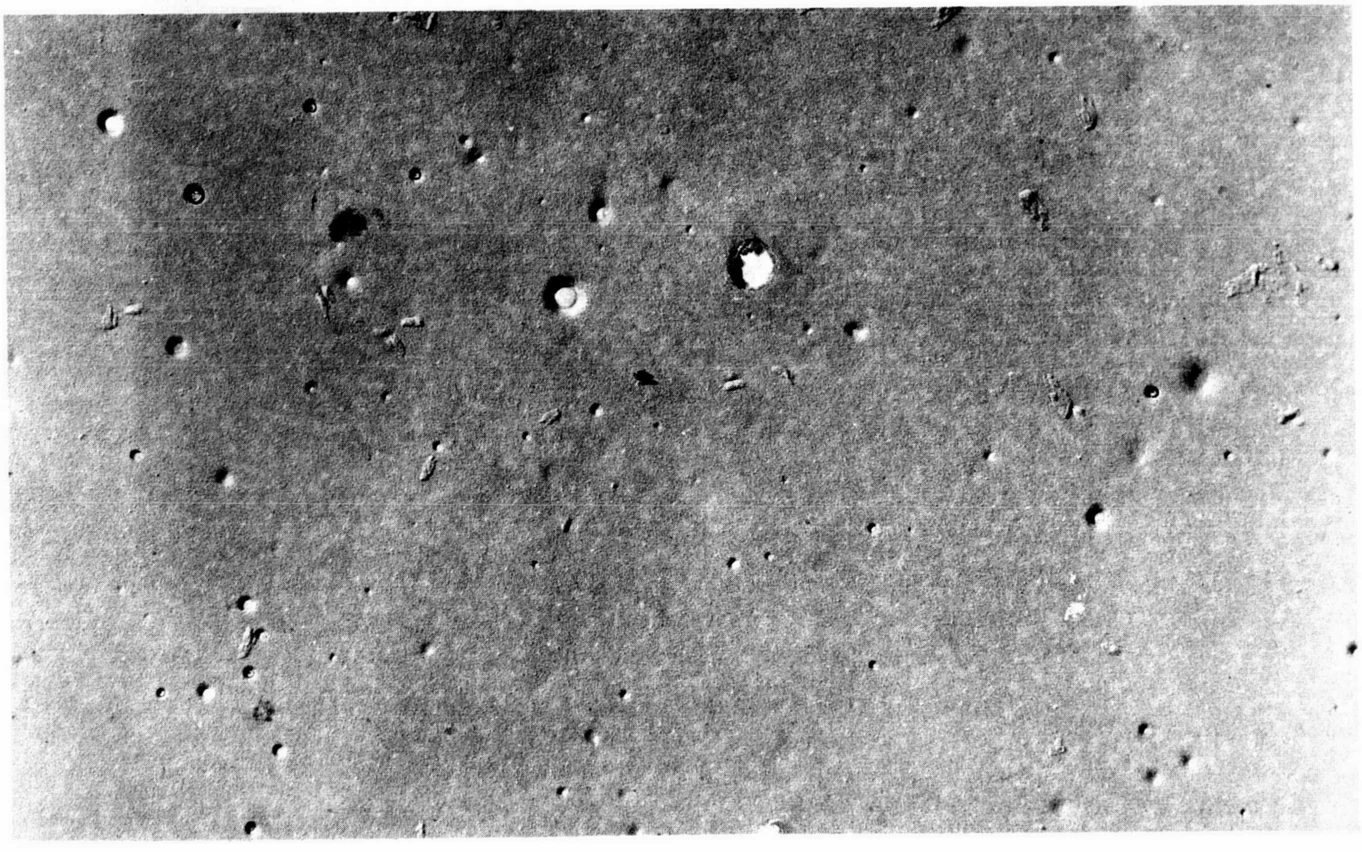
Fig. 4. Oriented overgrowth of PET on (001) NaCl. Fibrils are seen oriented along <110>. (Pt-C shadowed at tan^{-1} 4/8) Magnification: 18,000X

Lower right:

Selected area diffraction pattern of oriented fibrils and its corresponding selected area. The two strong reflections are 1$\bar{1}$0 and 1$\bar{1}$1. The third reflection, a very weak one, is $\bar{1}$05. The ring is due to the Pt-C shadowing material.

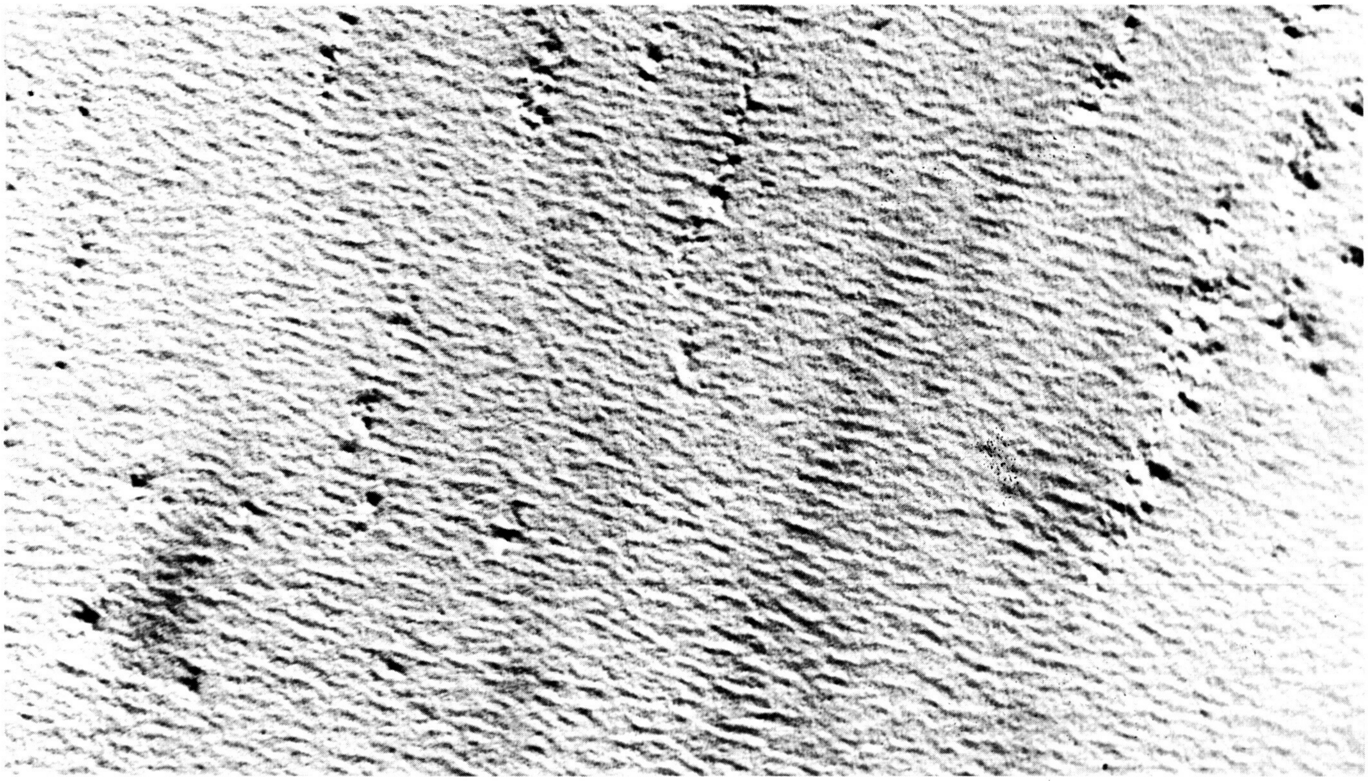
Fig. 5. Spherulite of PET crystallized from a molten film with an unrestrained surface. Lamellar ribbons are seen extending outward from center. Crystallization temperature is about 154°C. Magnification: 30,000X





Top Fig. 6. Spherulites of PET crystallized by annealing from a glassy film at about 154°C. Lamellar ribbons are present. Magnification: 86,000X

Bottom Fig. 7. Surface replica of a glassy film before annealing. (pt-C shadowed at $\tan^{-1} 5/7$) Magnification: 19,200X



Top Fig. 8. Surface structure of PET thin film, cast on water surface using a 1% m-cresol solution and stretched to 3x at 50°C. (Pt-C shadowed parallel to stretch direction at $\tan^{-1} 4/8$) Magnification: 22,000X

Bottom Fig. 9. Stretched thin film of PET stretched as in Fig. 8, but stained with 3% PTA for 1 day. Magnification: 42,800X

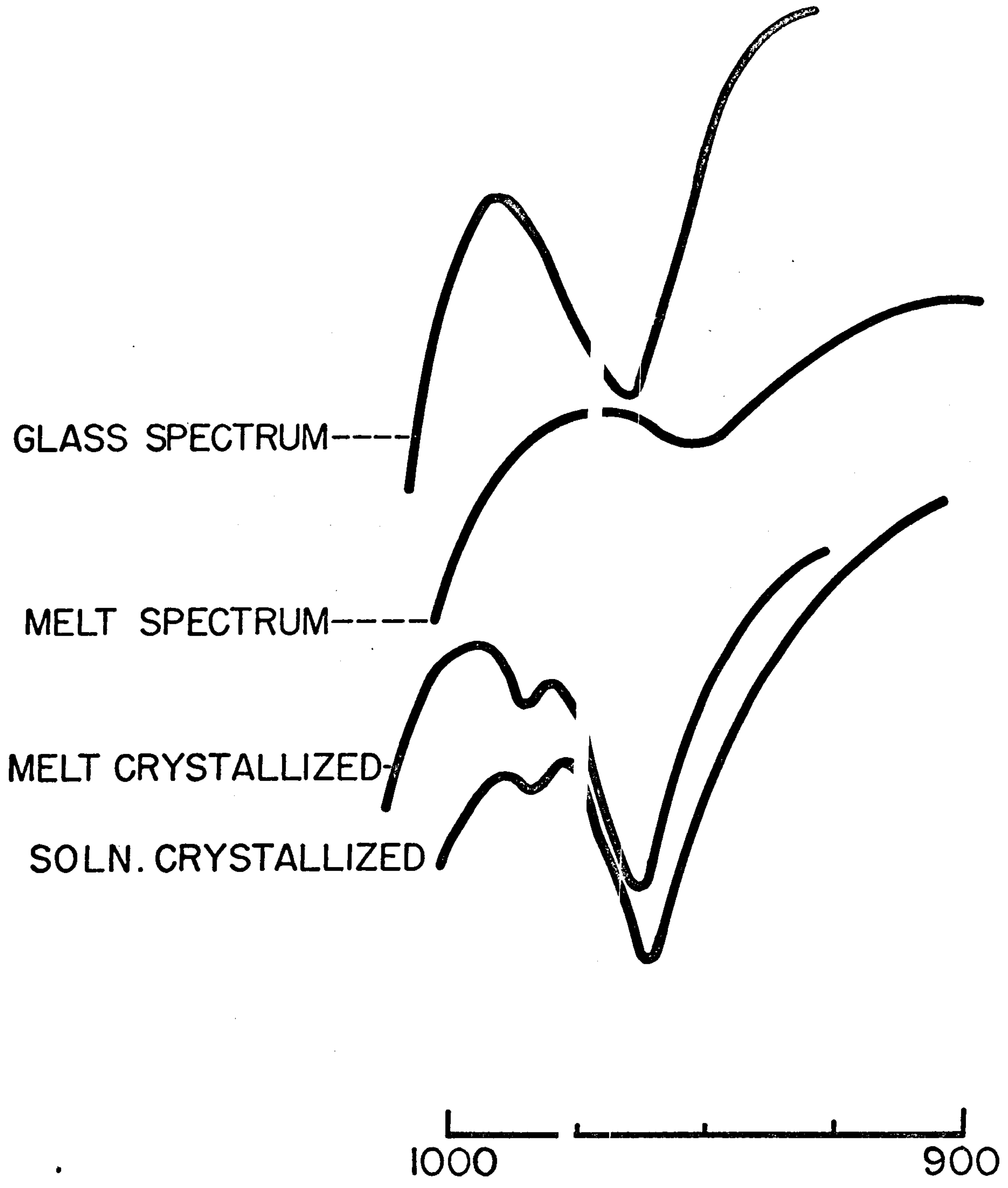


Fig. 10 988CM^{-1} REGION IN VARIOUS PET SAMPLES

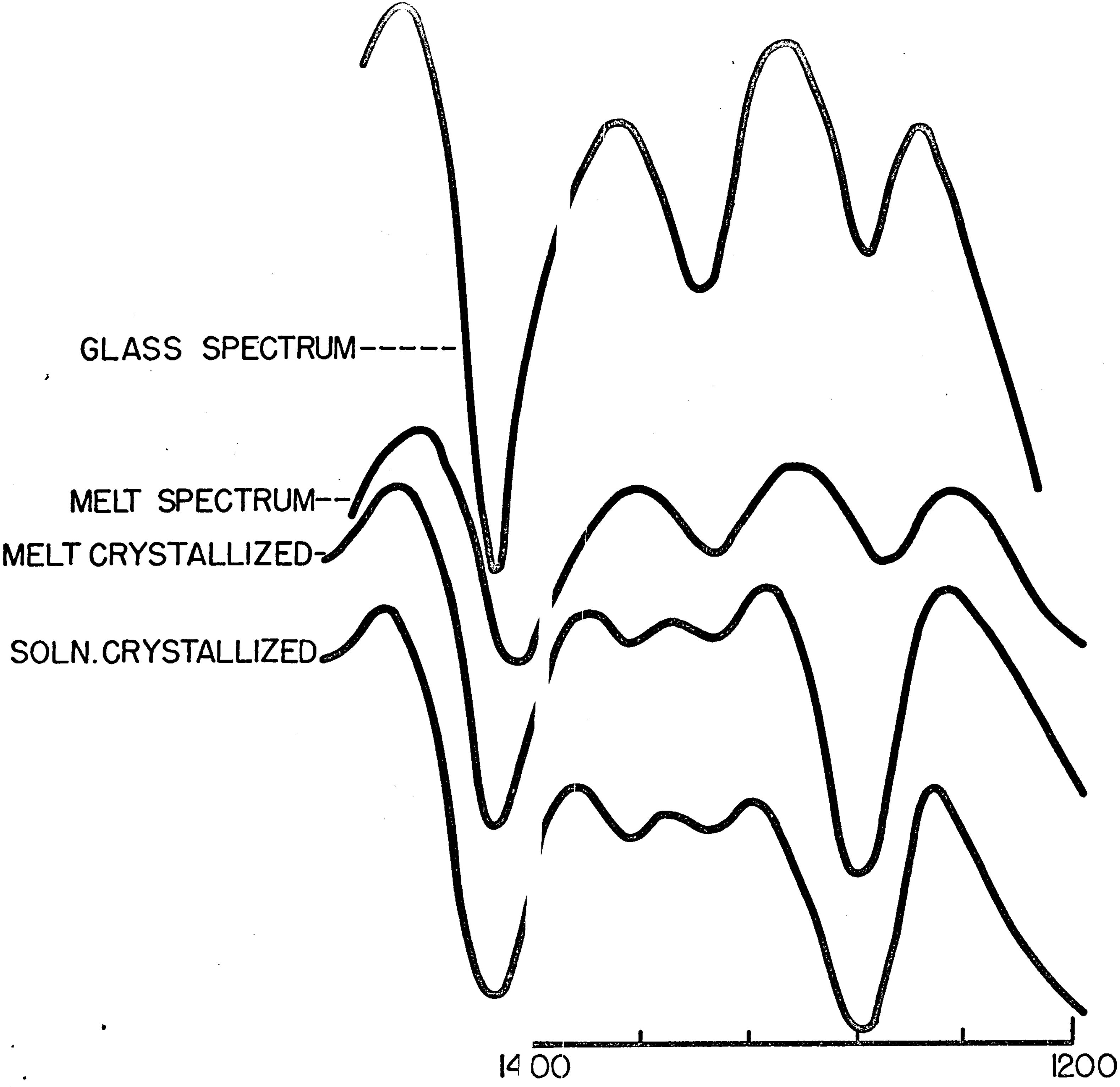


Fig.11 1380 CM^{-1} REGION IN VARIOUS PET SAMPLES

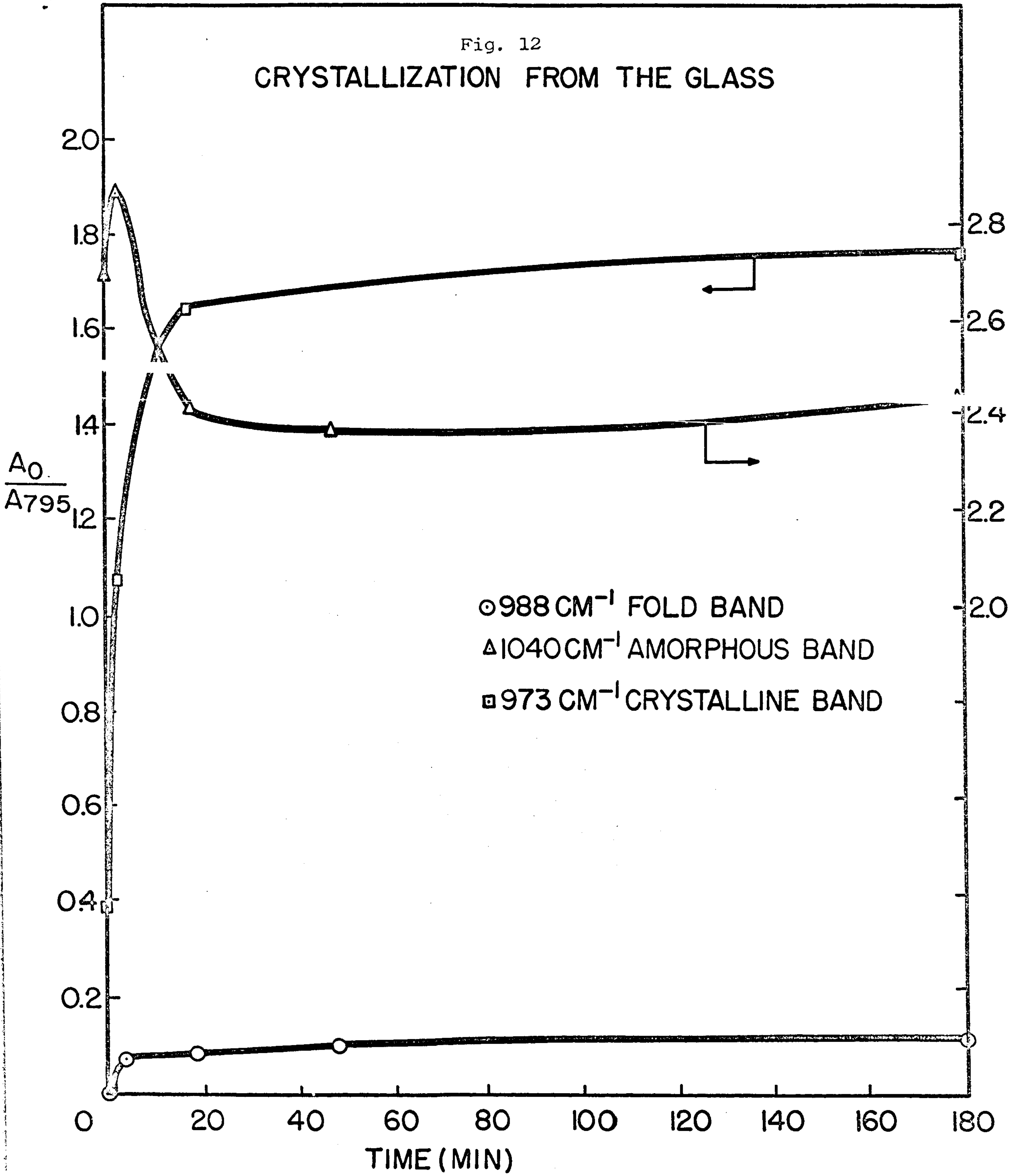


Fig. 12

CRYSTALLIZATION FROM THE GLASS

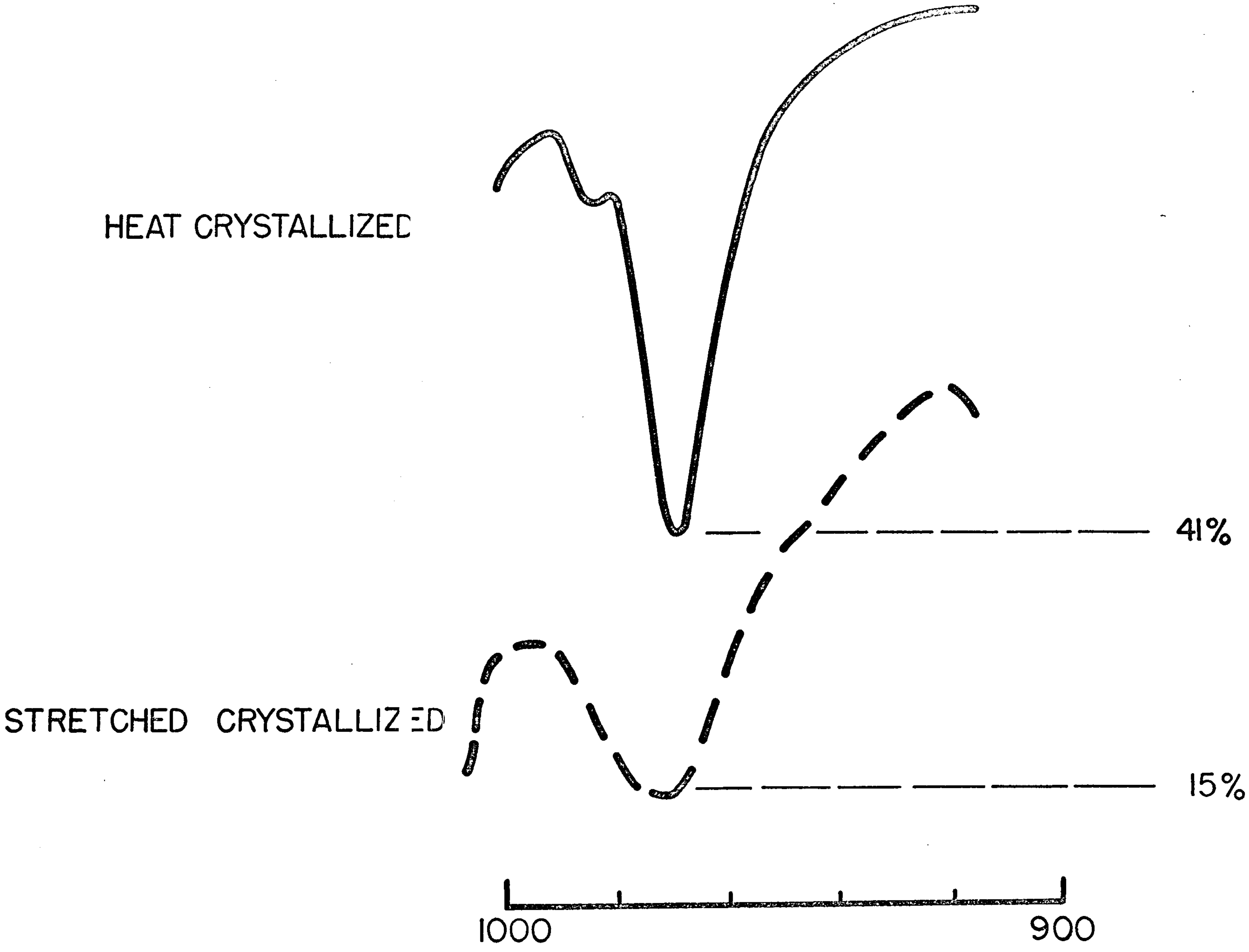


Fig. 13 BEHAVIOR OF THE 988 CM^{-1} BAND IN CRYSTALLINE PET

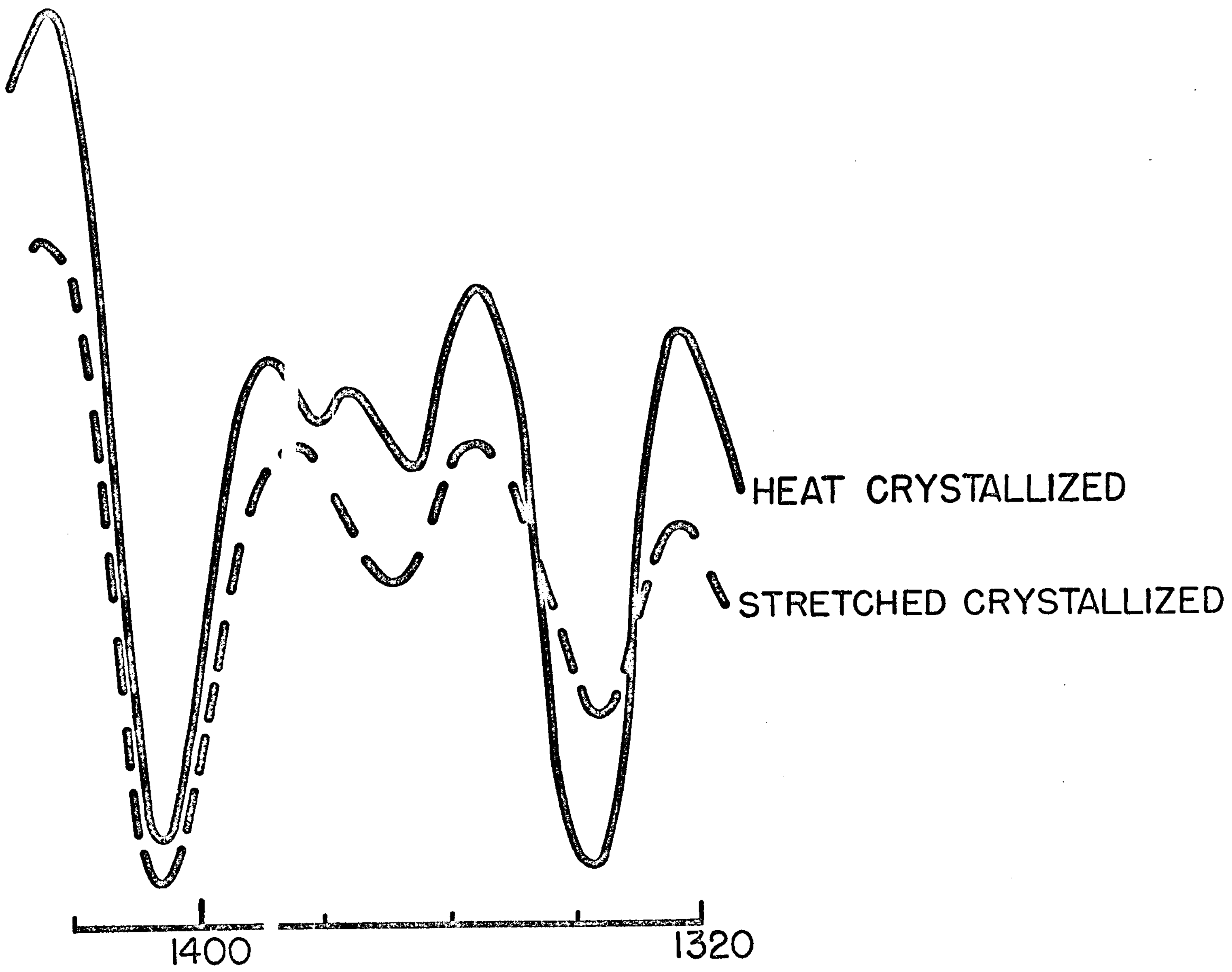


Fig. 14 BEHAVIOR OF THE 1380 CM^{-1} BAND IN CRYSTALLINE PET

DEGRADATION STUDIES

	$\frac{A_{988}}{A_{795}}$ (fold)	$\frac{A_{9[illegible]3}}{A_{7[illegible]5}}$ (crystalline)	$\frac{A_{848}}{A_{795}}$ (crystalline)	$\frac{A_{896}}{A_{795}}$ (amorphous)
Orig.	0.236	1.[illegible]8	2.04	0.600
2 Hrs.	0.080	0.793	0.887	0.178
8 Hrs.	0.071	1.01	1.17	0.198
48 Hrs.	0.039	1.37	1.61	0.453

TABLE I

CRYSTALLIZATION AS FUNCTION OF TIME

	$\frac{A_{988}}{A_{795}}$(fold)	$\frac{A_{1040}}{A_{795}}$(morp.)	$\frac{A_{973}}{A_{795}}$(cryst.)	$\frac{A_{896}}{A_{795}}$(amorp.)	$\frac{A_{848}}{A_{795}}$(cryst.)
Original	(.055)	2.73	0.392	1.63	0.613
3 Mins.	0.078	2.89	1.08	1.80	1.45
18 Mins.	0.086	2.43	1.65	1.56	1.59
48 Mins.	0.102	2.38	1.67	1.54	1.57
183 Mins.	0.102	2.44	1.75	1.58	1.71
1053 Mins.	0.154	2.40	1.83	1.50	1.70

TABLE 2

ANNEALING STUDIES

	A_{988} [illegible] / A_{795}	$A_{[illegible]}$ (crystalline) / A_{795}	A_{848} (amorphous) / A_{795}
Orig.	0.144	1.77	1.98
26 Hrs.	0.349	2.38	2.45
52 Hrs.	0.374	2.35	2.39
96 Hrs.	0.504	2.75	2.71
144 Hrs.	0.482	2.40	2.44

TABLE 3