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Part I

INFRARED STUDIES OF CHAIN FOLDING IN POLYETHYLENE TEREPHTHALATE

Work Performed By

Martin J. Hannon

Report Prepared By

J. L. Koenig and Martin J. Hannon

ABSTRACT

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INTRODUCTION

Currently, crystallization for most polymer processes is postulated to occur by a folded chain mechanism. A great deal of controversy exists concerning the structure of the fold and changes in the fold during annealing, deformation, and crystallization. The "switchboard" model of Flory (1) pictures the chains leaving the crystal, forming loops of random length and returning at some random point in the crystal. The resulting crystal is sandwiched between two amorphous areas. The irregular fold model differs from the "switchboard" model in that the molecules do not randomly traverse an amorphous area, but re-enter the crystal in an adjacent position. In this model, the fold loop is variable in size and structure. A regular fold model, proposed by Keller (2), pictures the fold as being regular in structure and length and formed by adjacent re-entry into the crystal.

Much work has been done on the crystallization of polyethylene single crystals to establish the exact nature of the fold. The results of Niegisch and Swan (3), Geil (4), Kawai (5), and Bassett (6) have been interpreted by a regular fold model, while the work of Flory (1) and Mandelkern (7) has made use of the "switchboard" model. The irregular type of folding (8) seems to exist in polyethylene single crystals when first grown - later rearranging to a more perfect crystal.

Bulk crystallization is considerably more complex and has been the subject of intensive study in recent years. Single crystals have been grown from the melt (9) providing evidence that polymers also crystallize from the melt by a chain folding mechanism. Brown (10) has studied single crystals and bulk polyethylene. He reports the two are morphologically similar. Subsequently, Koenig and Witenhafer (11) have provided evidence for the similarity of fold structure in bulk and solution crystallized polyethylene.

The nature of the crystals in oriented polymer samples has also been studied. Geil has studied polyethylene single crystal deformation (12) and subsequent annealing (13) in order to further elucidate the nature of the morphology and its folding mechanisms. Studies on Nylon 6 and polyoxymethylene (14) show the manner of folding in these polymers. Mechanisms for the deformation process in bulk crystalline polymers have been proposed by Peterlin (15) as a result of intensive studies upon polyethylene. The studies indicate twinning and phase transformation in the early stages of deformation. As the chains are further oriented, one observes tilting of the lamellae and slipping of the molecules past one another. In the final stage of orientation, Peterlin postulates the "breaking off of larger blocks of folded chains which are then incorporated into the fibril."

A recent study of crystallization in oriented 66-Nylon fibers has been done by Dismore and Statton (16). Highly oriented fibers were annealed at high temperatures, causing an enormous increase in the discrete small angle x-ray diffraction. There were concomitant increases in the long period, crystallinity, and defect mobility, while the sonic modulus decreased. The authors (17) concluded that molecules were "converted by heating to the folded form, similar to, but not necessarily identical with, those found in single crystals."

The physical and chemical properties of polymers are controlled to a large extent by the morphology induced by the crystallization process and the folded molecule plays an important role in determining these properties. Diffusion studies (18) in linear polyethylene show the diffusion constant is not proportional to density (as a measure of crystallinity) since upon annealing the amorphous content decreases by a factor of two while the diffusion constant remains almost constant.

Chemical properties of polyethylene are sensitive to the nature of the morphology. Recent halogenation studies upon polyethylene single crystals by Keller and coworkers (19) show the halogen molecule selectively attaches itself to the fold. In addition, the uptake of halogen is the same for bulk polyethylene as for single crystal mats. Nitric acid treatment (20) of bulk polyethylene indicates attack at the fold, amorphous material, and molecular links. Studies on single crystals show that oxidation occurs selectively at the fold in the chain.

Dynamic mechanical testing of polyethylene and other polymers has been interpreted in terms of present folding concepts. Takayanagi (21) has done extensive dynamic mechanical work on many crystalline polymers and discusses the peaks in terms of the morphology of the polymers involved. Sinnott (22) has studied polyethylene single crystals using dynamic mechanical and NMR measurements and discusses the changes in the peaks in terms of the fold theories. For example, he associates the γ peak with defects in the lamellae and the α peak to the motion of the folds at the surface of the lamellae.

A great deal of conjecture still exists as to the structure of the fold in crystalline polymers with regard to the mechanisms of crystallization and deformation. It is our purpose to provide a method for isolating a band in the infrared spectra (if one exists) which is due solely to the folded molecule. Such a band will allow us to probe into the morphology and mechanisms of crystallization and deformation in semicrystalline polymers.

SPECTROSCOPY OF THE FOLDED CHAIN

Infrared spectroscopy is a useful tool for measuring differences in the configuration, conformation, and environment of polymers (23), as well as low molecular weight materials. Bands attributable to the trans and gauche rotational isomers in polymers are well known. Stereoregularity in polymers has been characterized by infrared spectroscopy. Hydrogen bonding and crystallinity are environmental effects in polymers which have been shown to produce differences in the infrared spectra. Therefore, infrared spectroscopy would appear to be an effective tool for studying folding in polymers if a method of assigning and interpreting the bands can be developed.

When a polymer folds, one of two factors may cause changes in the infrared spectra. The regularity of the fold may induce spectral coupling of the repeat units due to the unique environment of the atoms in the fold. This coupling effect, if it is large enough, may cause a change in the vibrational frequency, absorption coefficient or both. Koenig and Witenhafer (11) have shown that the consecutive gauche ethylene units in the polyethylene fold produce a difference in the extinction coefficient for the 1304 cm^{-1} and 1350 cm^{-1} bands. With proper calibration, they were then able to measure the relative amounts of folded and amorphous material in various polyethylene samples from their respective contributions to the 1304 cm^{-1} and 1350 cm^{-1} bands. The second possibility is that the fold may exist in a unique conformation. A new conformation would obviously cause a perturbation of frequency in the spectra.

In order to facilitate the systematic study of polymer spectra for the existence of a band due to the folded molecule, the bands will be divided into four different types based upon their spectral properties during melting, crystallization, annealing, and chemical treatment of the semicrystalline polymer. Figure 1 shows a model of a growing spherulite with the various morphological forms. We expect that the molecules existing in the highly ordered region (C), in the amorphous regions (A), and in the folded regions at the surface will have different environments and perhaps different conformations. This will produce frequency shifts in the infrared spectra. The structures producing the four types of bands will be termed crystalline, non-crystallizable, crystallizable and folded. The spectral behavior of these bands are shown in Table 1.

Those infrared bands associated with the crystalline phase will: 1) appear in intensity proportional to the crystallinity, but disappear above the melting point, 2) be absent in the amorphous polymer but appear and increase in intensity with time during crystallization, 3) increase in intensity when annealing occurs, 4) be unaffected by a chemical treatment which

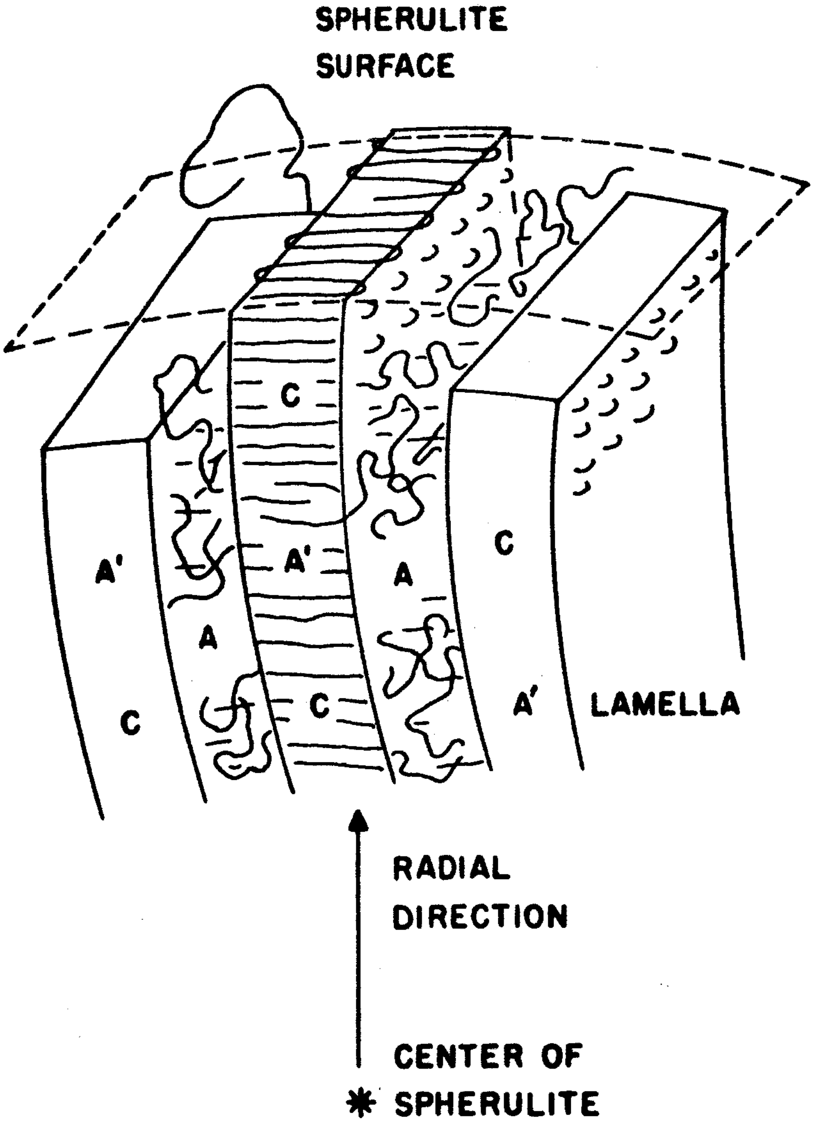

Figure 1 - Model of a Growing Spherulite

TABLE 1

BEHAVIOR OF POLYMER INFRARED BANDS

Structure	Crystalline → Melt	Amorphous → Crystalline	Chemical Treatment	Annealing
Crystalline	(-)	(+)	(0)	(+)
Noncrystallizable	(0)	(0)	(0) or (-)	(0)
Crystallizable	(+)	(-)	(-)	(-)
Fold	(-)	(+)	(-)	(-)

(-) Intensity decreases
(0) No change in intensity
(+) Intensity increases

is not able to penetrate into the crystalline regions. There are many bands in the spectra of polyethylene terephthalate (PET) which exhibit predominantly crystalline behavior. The most significant of these is the band at 973 cm^{-1}.

Non-crystallizable structure will exhibit bands whose intensity will be little affected by melting, crystallization, annealing or chemical treatment. These bands may arise from end groups, branches and other forms of heterogeneities due to side reactions during the polymerization.

Crystallizable bands arise from components of the polymer chain in the non-crystalline phase which can be made to crystallize by heat, strain or pressure. These bands will: 1) exhibit intensity inversely proportional to the degree of crystallinity and may increase in intensity on melting, 2) appear in the glass and melt, but decrease as crystallization occurs, 3) decrease in intensity as annealing transforms the structure to the crystalline phase, 4) decrease in intensity proportional to the degree of attack of a chemical reagent on the disordered or amorphous portion of the polymer. These crystallizable bands will arise from rotational isomeric conformations of the polymer chain (as the gauche form) which can be converted by heat, pressure or strain to the stable isomeric form found in the crystalline phase. In PET the 896 cm^{-1} and 1042 cm^{-1} bands are examples of crystallizable bands. These bands are believed to arise from vibrations of the molecule in the gauche conformation of the ethylene oxide unit.

Bands attributable to the fold conformation in the semicrystalline polymer will: 1) have an intensity in the solid state proportional to the amount of folding and will disappear on melting, 2) appear if crystallization from the glass occurs by the folded chain mechanism, 3) decrease during the annealing process when the annealing increases the fold period at the expense of the folds, 4) disappear rapidly and irreversibly during the chemical treatment. This final behavior results since the folds constitute the accessible lamellar surfaces and due to the energetic nature of the conformation are chemically more reactive. Unique fold bands will occur only when the fold introduces a characteristic conformation having resolvable energy differences from conformations in the disordered regions. When the fold conformation arises from a combination of ordinary rotational isomers as it apparently does in polyethylene, no unique fold band would be expected. For this case, no spectral differentiation between a fold band and a crystallizable type can be made and the fold contribution is reflected as part of the intensities of the crystallizable bands. We propose to show that the 988 cm^{-1} band in the PET spectrum is a band arising from a unique fold conformation.

Theoretically, all four types of bands have different energy levels but, due to small energy differences and the inherent band width, an observed spectral band may be a combination of one, two or all four types. If a band is attributable to a single structural type, however, it can be assigned by the analysis scheme shown in Figure 2.

When one crystallizes from the glass, one expects an increase in the fold and crystalline bands according to their behavior explained above. The crystallizable bands will decrease and the non-crystallizable bands will be unaffected. If one now takes the semicrystalline polymer and treats it with a reagent which will attack the "amorphous" areas, but will not penetrate the crystalline areas, one can assign the four types of bands. The fold band will decrease, the crystalline band will be unaffected, the crystallizable band will decrease and, again, the non-crystallizable band will remain unaffected. Thus, the fold band can be isolated and assigned as a result of these two treatments.

It is also possible to assign these four types of bands by starting with a semicrystalline polymer. Melting will cause a decrease in the fold and crystalline bands and an increase in the crystallizable band. The non-crystallizable band will be unaffected. Annealing the semicrystalline polymer, the crystalline regions should elongate causing an increase in crystallinity at the expense of the fold.

The method outlined above will be used to analyze the spectra of polyethylene terephthalate for a band arising from

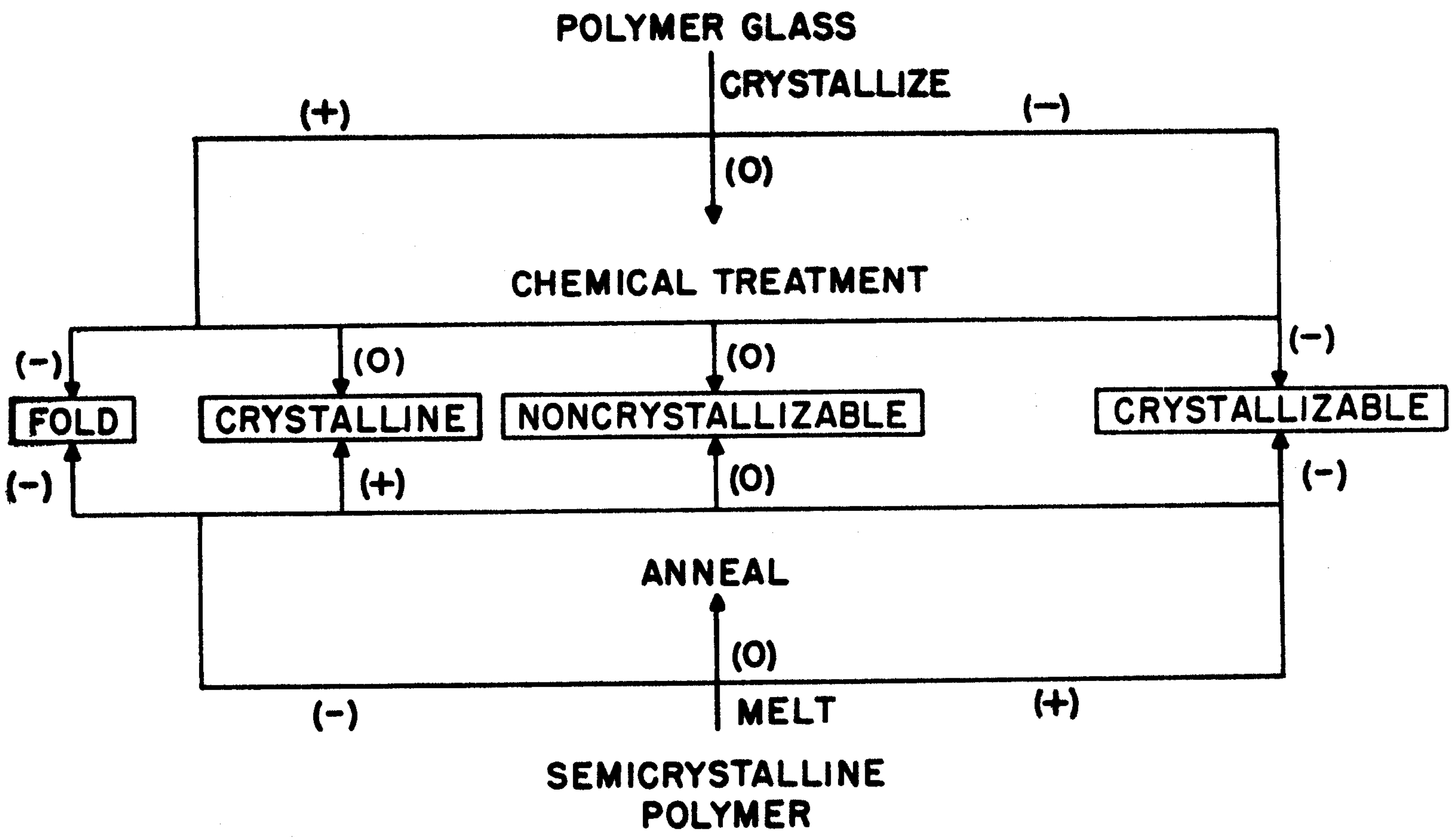

Figure 2 - Analysis Scheme
Infrared Band Assignments to Structures in Semicrystalline Polymers

the folded molecule. Evidence will show the 988 cm^{-1} band is such a fold band. Then, having found such a band, we propose to study crystallization and deformation in PET with regard to the effect upon the folds. From these results, we hope to infer mechanisms for these processes in PET.

EXPERIMENTAL

Instrumental

The Perkin-Elmer 521 infrared spectrometer was used to analyze all the polymer samples. The solid to molten transition was studied using a heating cell, attached to a temperature controller, in the sample compartment of the instrument.

The stretching experiments were carried out by means of an Instron tester. The very thin samples, which were used, required a set of rubber jaws to prevent tear in the sample.

The DuPont 900 Differential Thermal Analyzer was used to characterize all samples. The D.T.A. was useful in ascertaining the crystalline or amorphous character of some of the samples. It was also useful in checking the purity of the samples under study - in particular, the samples of oligomers, which were not prepared in our own laboratory.

Small angle x-ray results were obtained on the Rigaku-Denki unit, which is equipped with a rotating anode allowing a much more intense beam on the sample. The unit is attached to a recorder which allows one to scan the region of interest.

The annealing experiments were carried out using a specially designed cell. The cell was made of thin aluminum tubing and was fitted with valves to allow quick heat transfer and a dry nitrogen purge.

Sample Preparation

Solution crystallized PET was obtained from two different solvents, under several conditions of crystallization. One set of crystals was grown isothermally from a 0.1% solution of dimethyl phthalate at 130°C. The second set of crystals was grown from a 0.1% solution of PET in 2-(2-Butoxy ethoxy) ethanol by slowly cooling from the boiling point of the solvent. A final set was grown isothermally from a 1% solution of 2-(2-Butoxy ethoxy) ethanol at 190°C. This was close to the temperature that the maximum rate of crystallization occurs. It is necessary to grow the crystals just prior to use since hydrolysis occurs if they are stored for any length of time.

The study of oligomers of PET was very important in the analysis of the spectra. Our oligomer samples were obtained from several different sources:

1) linear trimers were obtained from the Mobil Chemical Company, the Goodyear Company and by A. Miyake.

2) a linear oligomer with a DP of 5 was provided by Y. Yamashita and by M. Ishibashi.

3) a linear oligomer with an average DP of 10-20 was also provided by M. Ishibashi.

4) finally, a prepolymer of commercial PET with an average DP equal to 15-20 was provided by C. Heffelfinger of the E. I. duPont Company.

All of the solution crystallized samples and oligomers were analyzed by preparing KBr pellets and running them using a beam condenser made of KBr lenses.

Melt crystallized samples were prepared by sandwiching very thin films between rolled silver chloride. This unit was then pressed causing flow of the AgCl, which completely encompassed the polymer film. The film was melted while embedded in this AgCl matrix which prevented flow and kept the sample at the same thickness as the original film sample. The polymer was then allowed to slowly cool - forming a coherent, very thin film of melt crystallized PET.

The annealing experiments were performed on solution cast amorphous films which were obtained from C. Heffelfinger of the E. I. duPont Company. These films were cast from a tetrachloroethylene-phenol solution and had a number average molecular weight of about 15,000 gms/mole. They were initially analyzed by DTA and x-ray to verify their completely amorphous character. An exotherm around 115°C in the DTA indicates crystallization from the glass.

Base Line Study

Before performing any quantitative study on the spectra, it was first necessary to determine which baselines gave the most accurate and reproducible results. The following criterion was used to select the baselines. A band was found at 1955 cm^{-1} which is isolated from all other bands in the spectrum. Only one reasonable baseline could be drawn for this band. Samples of various thicknesses, having the identical preparation (annealed at 200°C for a half hour) were analyzed. The various baselines to be tested were drawn and the ratio of the absorbance of the band to the 1955 cm^{-1} band was calculated. Those baselines which gave the most reproducible results are shown in Figure 3. These baselines were used for all subsequent calculations.

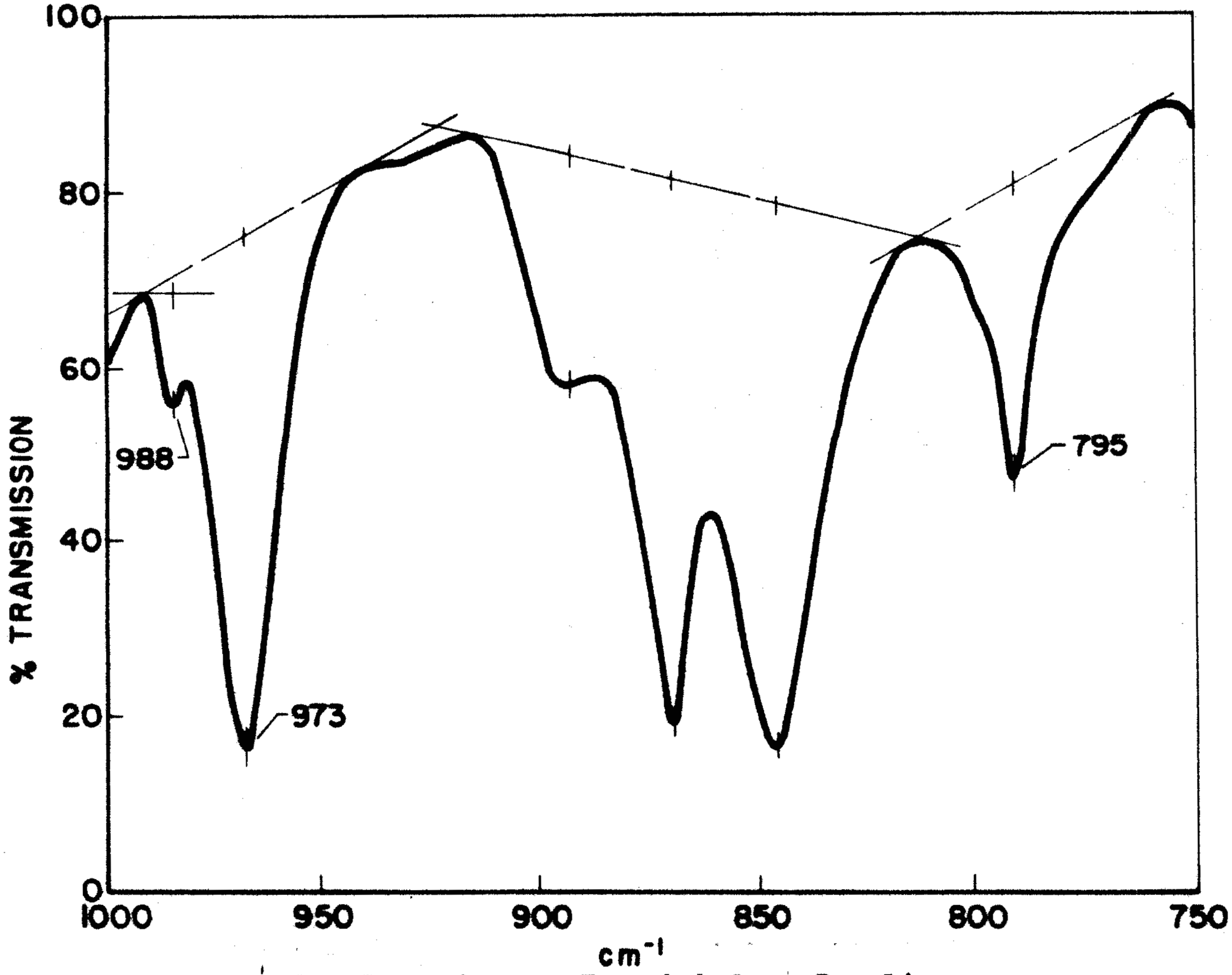

Figure 3 - Polyethylene Terephthalate Baselines

RESULTS

Non-Crystalline Samples

Analysis of the glass and melt spectra showed strong amorphous bands at 896 cm^{-1} and at 1042 cm^{-1}. Most of the bands which have been assigned as crystalline conformation bands were very weak. No new bands appeared in these spectra.

Melt and Solution Crystallized Samples

Melt and solution crystallized samples of polyethylene terephthalate, as had previously been shown (24), are highly crystalline and contain a high degree of folding. The sharp wide angle x-ray pattern shown in Figure 4 indicates the high degree of crystallinity in these samples. The crystalline bands at 973 cm^{-1} and 848 cm^{-1} were quite intense. In addition, two bands appeared in the spectra at 988 cm^{-1} and 1380 cm^{-1} which had been reported previously only by Miyake (25). Figures 5 and 6 show these two bands in the solution and melt crystallized samples, as well as their absence in the non-crystalline samples. Table 2 gives a quantitative measure of the relative 973 cm^{-1} and 988 cm^{-1} absorbances in melt and solution crystallized samples.

Annealing Studies

We annealed the amorphous films of PET at temperatures

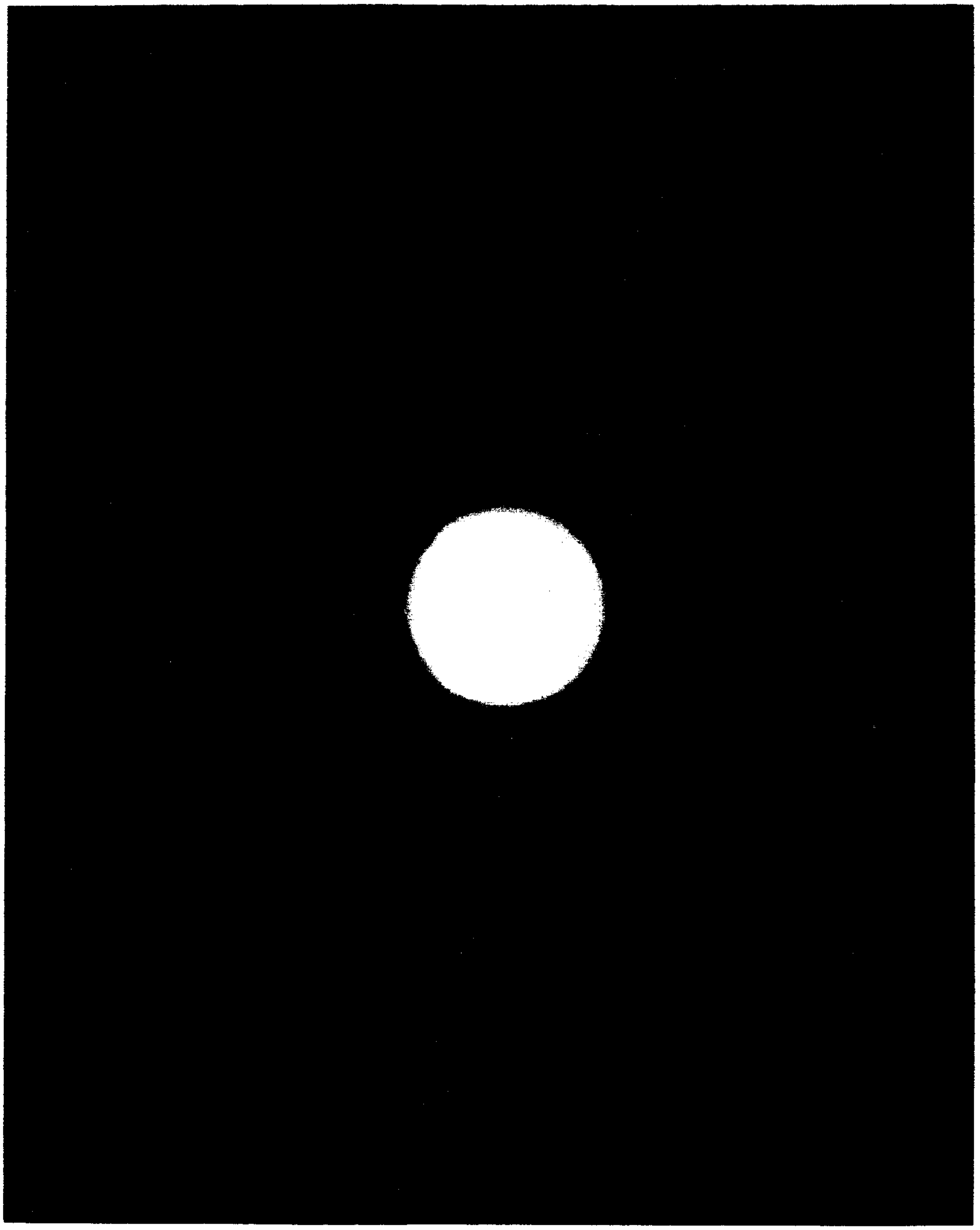

Figure 4 Wide Angle X-ray Pattern of Crystalline PET

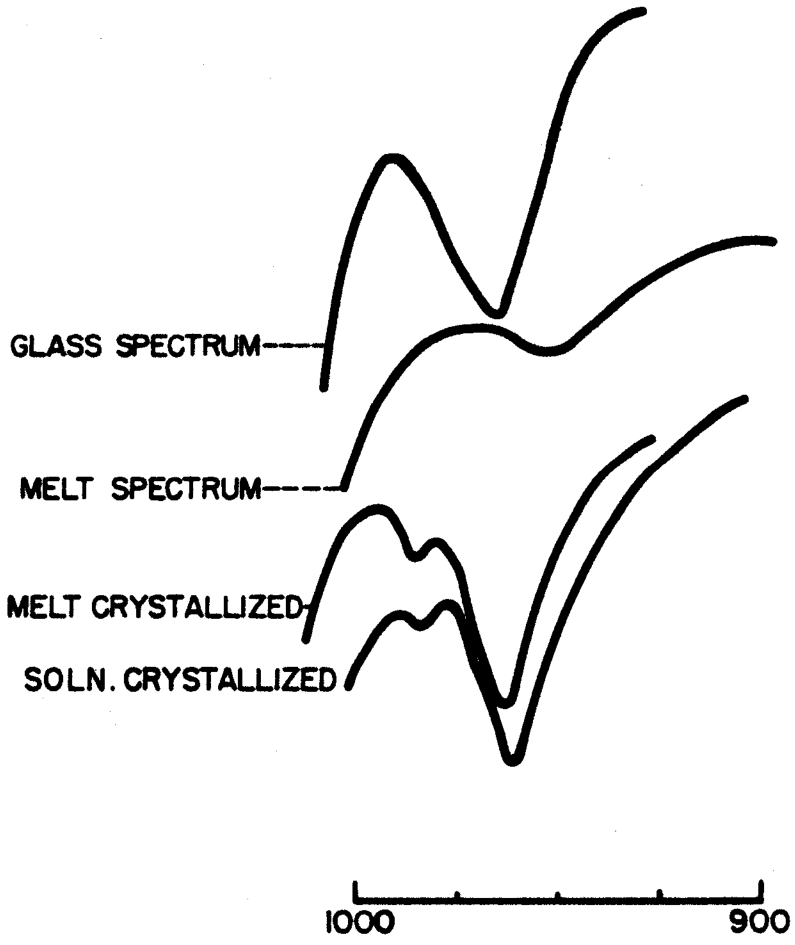

Figure 5 - 988CM^{-1} REGION IN VARIOUS PET SAMPLES

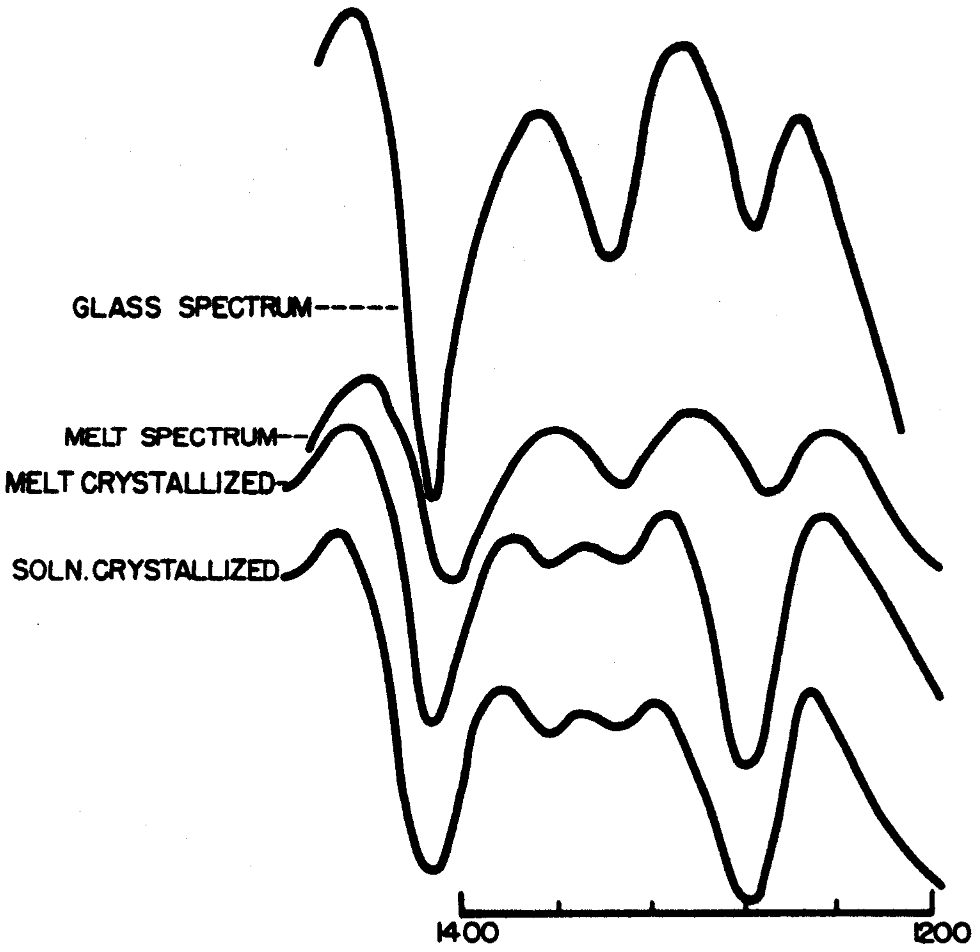

Figure 6 - 1380 CM^{-1} REGION IN VARIOUS PET SAMPLES

TABLE 2

COMPARISON of CRYSTALLINE and FOLD BANDS in POLYETHYLENE TEREPHTHALATE

Sample	$\frac{A_{973}}{A_{795}}$ (cryst.)	$\frac{A_{988}}{A_{795}}$ (fold)	$\frac{A_{988}}{A_{973}}$
Melt Crystallized	2.94	0.44	0.15
PET High I.V. (0.89) Melt Crystallized	2.85	0.52	0.18
Crystallized from 2-(2-Butoxy ethoxy) ethanol (slow cool)	2.75	0.17	0.06
PET High I.V. (1.60) Melt Crystallized	2.65	0.41	0.16
Crystallized from 2-(2-Butoxy ethoxy) ethanol (190°C)	2.42	0.25	0.10
Crystallized from Dimethyl Phthalate	2.04	0.24	0.12
PET High I.V. (0.89) as Polymerized	1.66	0.11	0.07
PET High I.V. (1.60) as Polymerized	1.64	0.16	0.10

of 115°C, 140°C, 200°C and 240°C. The behavior of the band at 973 cm^{-1} with annealing time is shown in Figure 7. (We divide by the internal thickness band at 795 cm^{-1} in order to compare samples of various thickness on the same basis.) The observed behavior is typical of a crystalline band in crystallization from the glass. Figure 8a shows the same ratio for the 988 cm^{-1} band, while Figure 8b compares the 973 cm^{-1} and 988 cm^{-1} bands. Likewise, Figure 9a shows the absorbance values for the 1380 cm^{-1} band as a function of annealing time, while Figure 9b gives the ratio of the 973 cm^{-1} and 1380 cm^{-1} bands. One expects two crystalline bands to vary in the same manner, and the ratio should be relatively constant as a function of annealing time. Notice the difference in behavior of the 988 cm^{-1} and 1380 cm^{-1} bands as shown by Figures 8b and 9b. The 1380 cm^{-1} band seems to vary in the same manner as the 973 cm^{-1} crystalline band while the 988 cm^{-1} band obviously does not.

Small angle x-ray results were obtained for all the annealed samples. The results of the x-ray long period plotted against the reciprocal of the absorbance of the 988 cm^{-1} band at the various temperatures are shown in Figures 10, 11, and 12. A clearly defined peak could not be obtained for the samples annealed at 115°C, so no correlation could be obtained at this temperature. At temperatures above 200°C the data showed quite a bit of scattering. Further study of the small angle

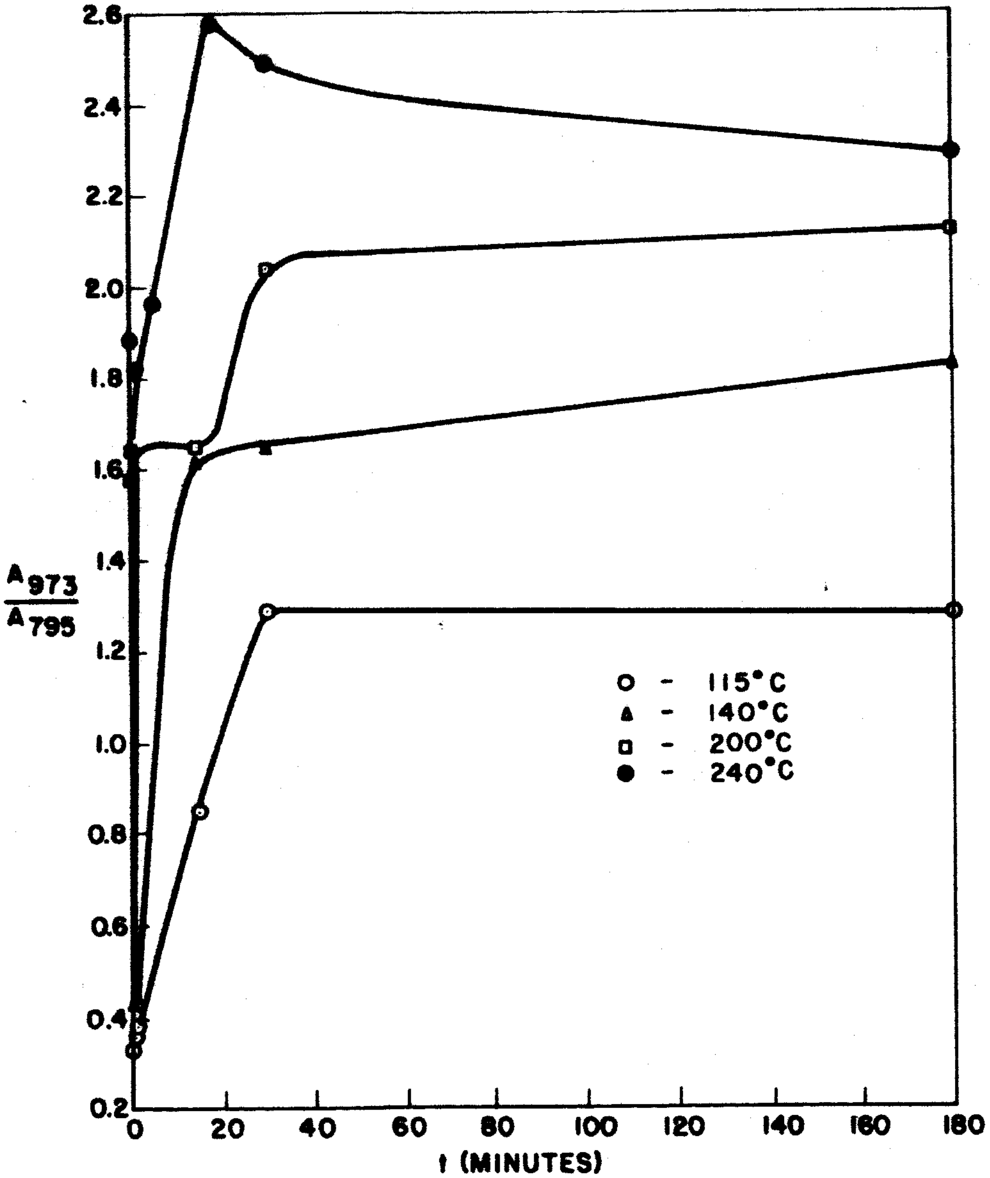

Figure 7 - Behavior of the 973 cm^{-1} Crystalline Band During Annealing

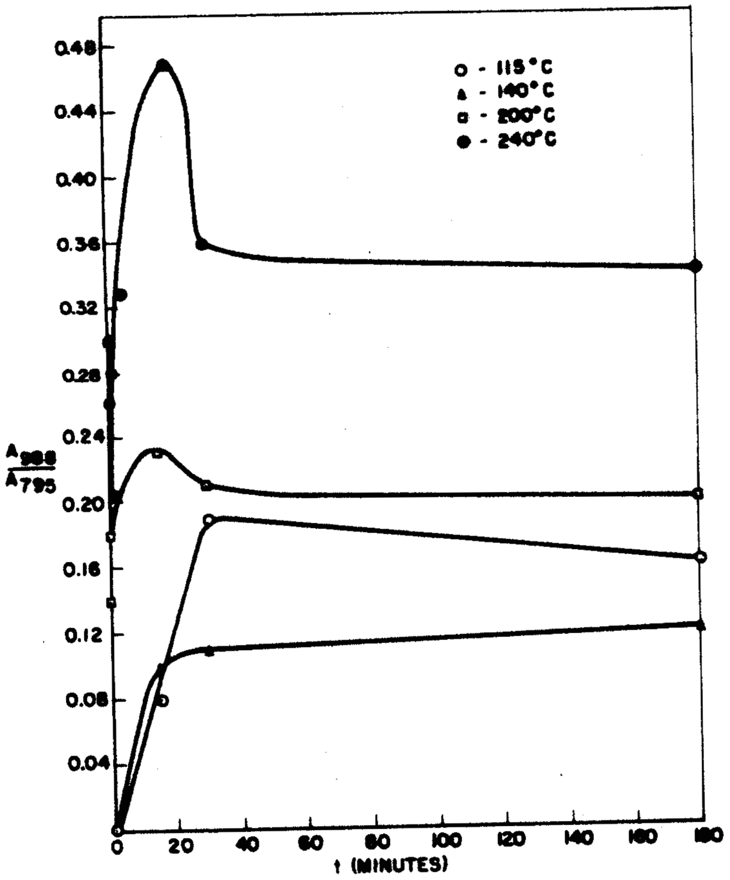

Figure 8a - Behavior of the 988 cm^{-1} Band During Annealing

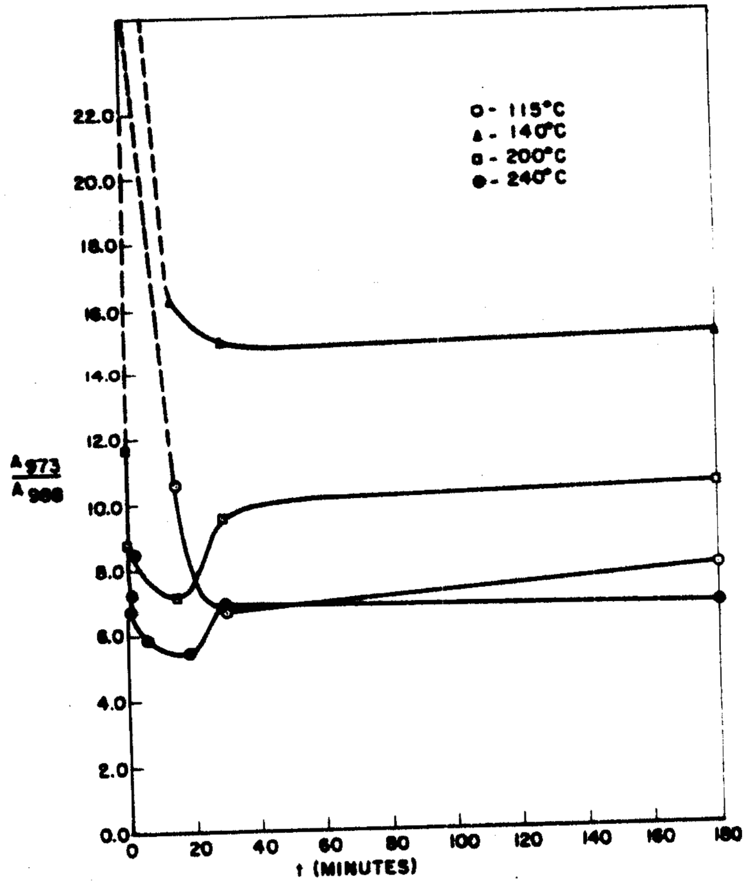

Figure 8b - Behavior of the A_{973} cm^{-1}/A_{988} cm^{-1} Ratio During Annealing

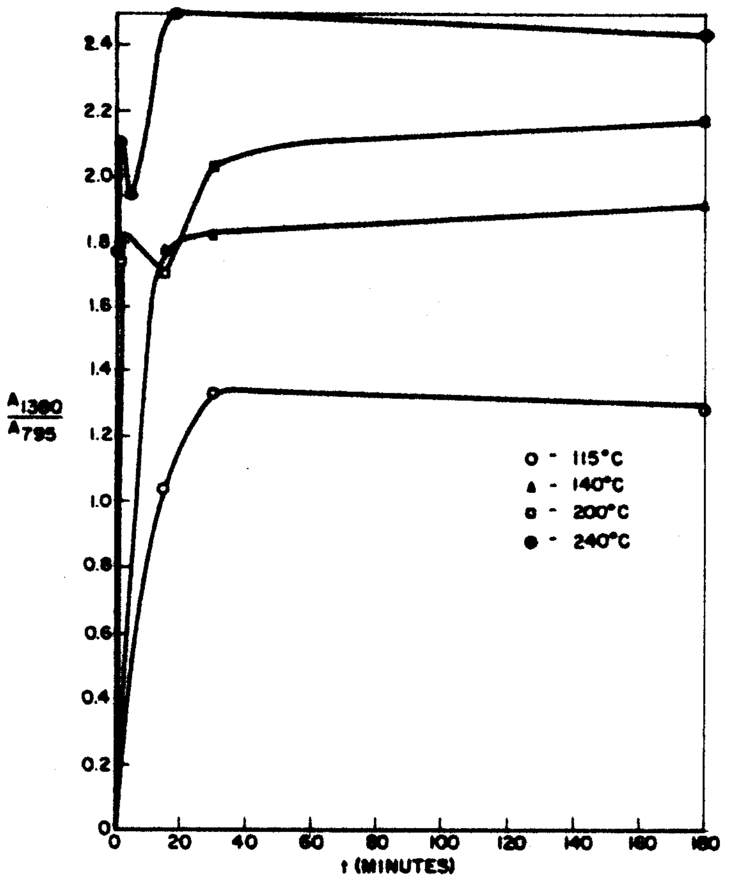

Figure 9a - Behavior of the 1380 cm^{-1} Band During Annealing

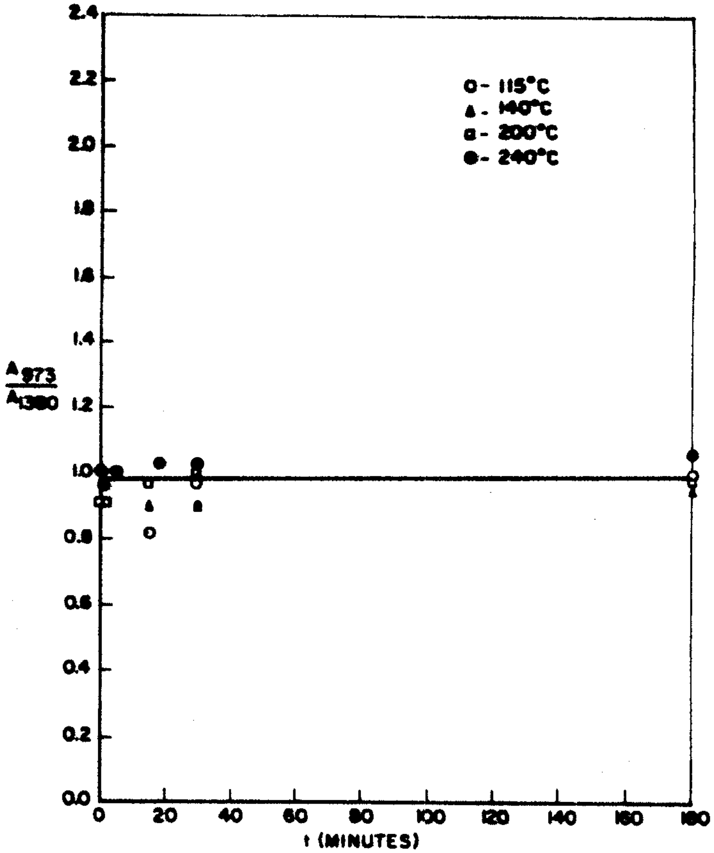

Figure 9b - Behavior of the A_{973} cm^{-1}/A_{1380} cm^{-1} Ratio During Annealing

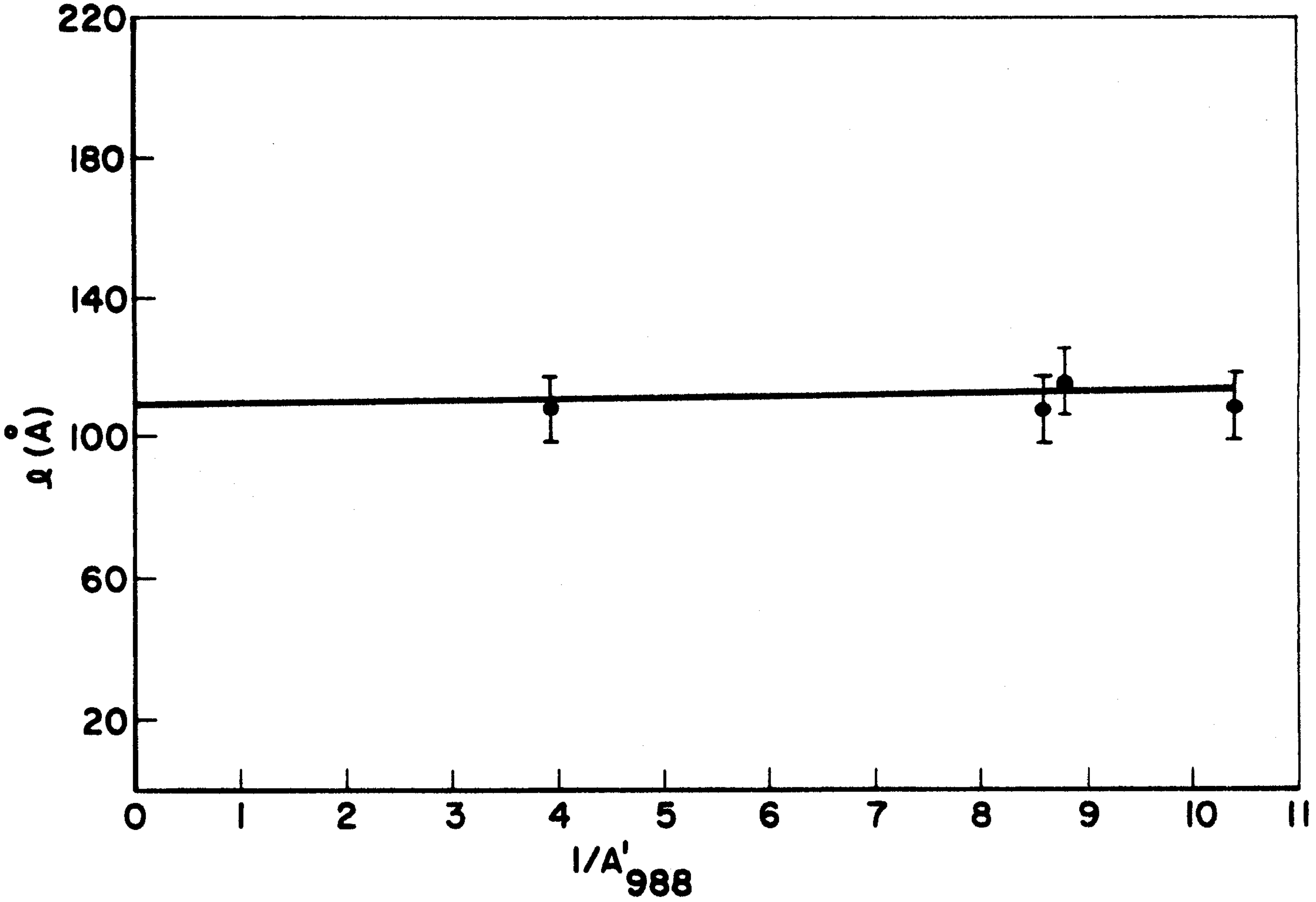

Figure 10 - Small Angle Long Period versus Reciprocal Fold Absorbance at 140°C

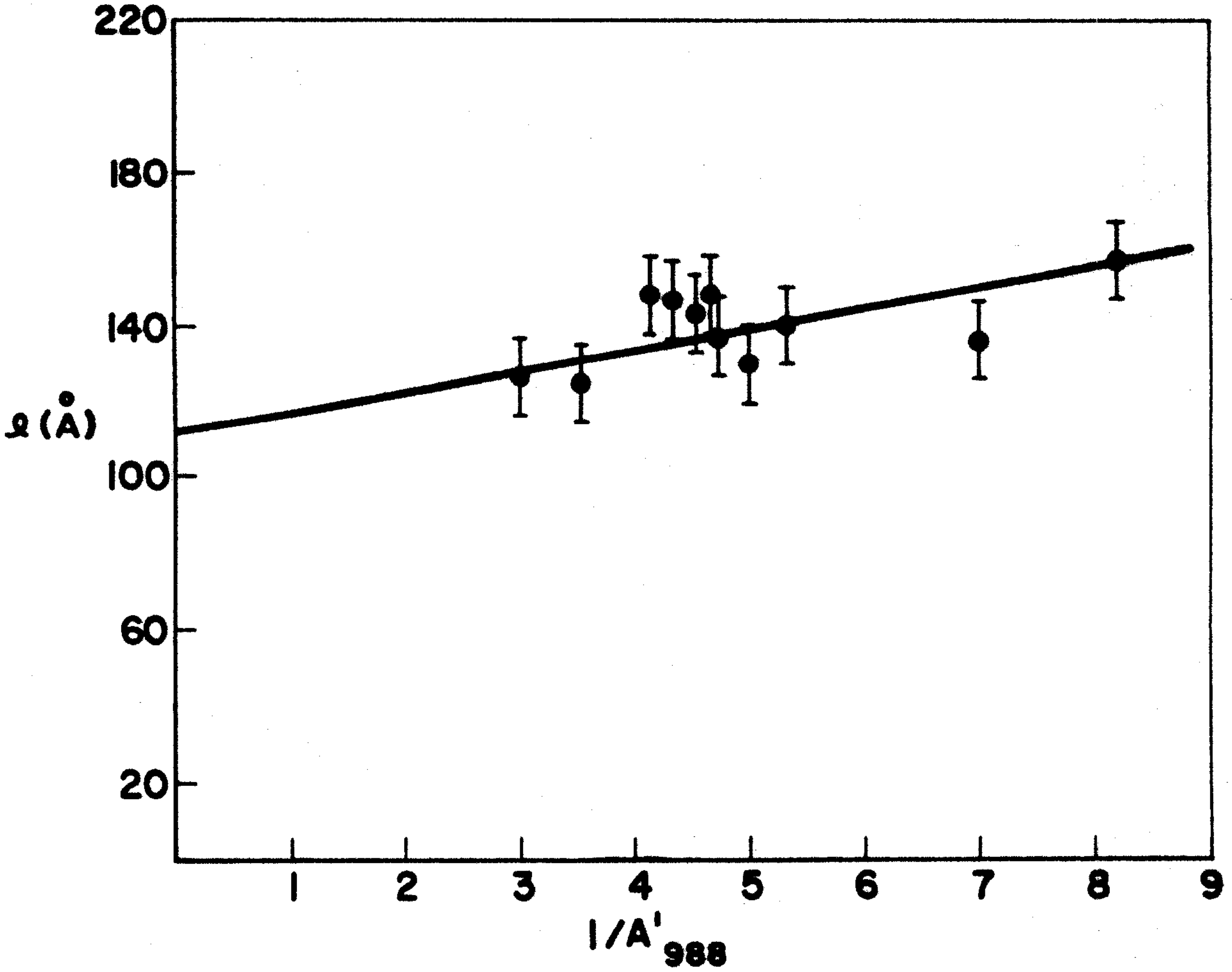

Figure 11 - Small Angle Long Period versus Reciprocal Fold Absorbance at 200°C

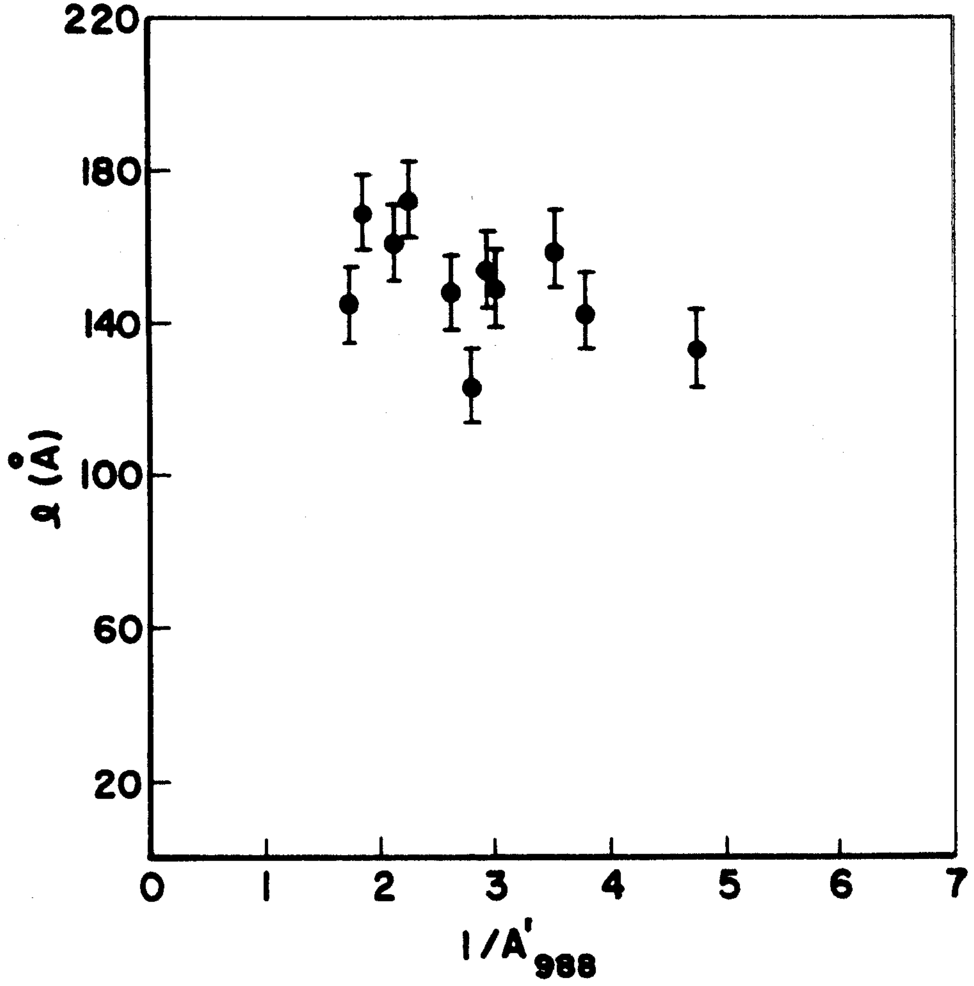

Figure 12 - Small Angle Long Period versus Reciprocal Fold Absorbance at 240°C

results shows the appearance of a second peak above 200°C. In order to verify that this second peak was real, a step scan was run on one of the samples. The x-ray was placed at a certain angle reading, counts were recorded for 1000 seconds and a new angle set. This step scan essentially eliminated the noise in the data since so many counts were recorded. The results of the scan showing two peaks are shown in Figure 13. The effect of annealing for different times and temperatures are shown in Table 3, as compared to other film samples.

Degradation

We carried out degradation experiments on solution crystallized PET, which initially exhibited a very intense 988 cm^{-1} band. Farrow (26) previously did an extensive study on PET but interpreted the results only in terms of the "amorphous" and crystalline content of the polymer. A 20% solution of methylamine in water was prepared and allowed to come in contact with the polymer for times up to 48 hours with continuous agitation. The results in Table 4 show the 988 cm^{-1} band decreases with time while the 973 cm^{-1} band is not appreciably affected. The crystalline and amorphous band ratios are sensitive to the fact that the 795 cm^{-1} band is no longer a valid internal thickness band. This conclusion is quite obvious if one looks at the spectra before and after degradation (Fig. 14). One of the degradation products is obviously interfering with the 795 cm^{-1}

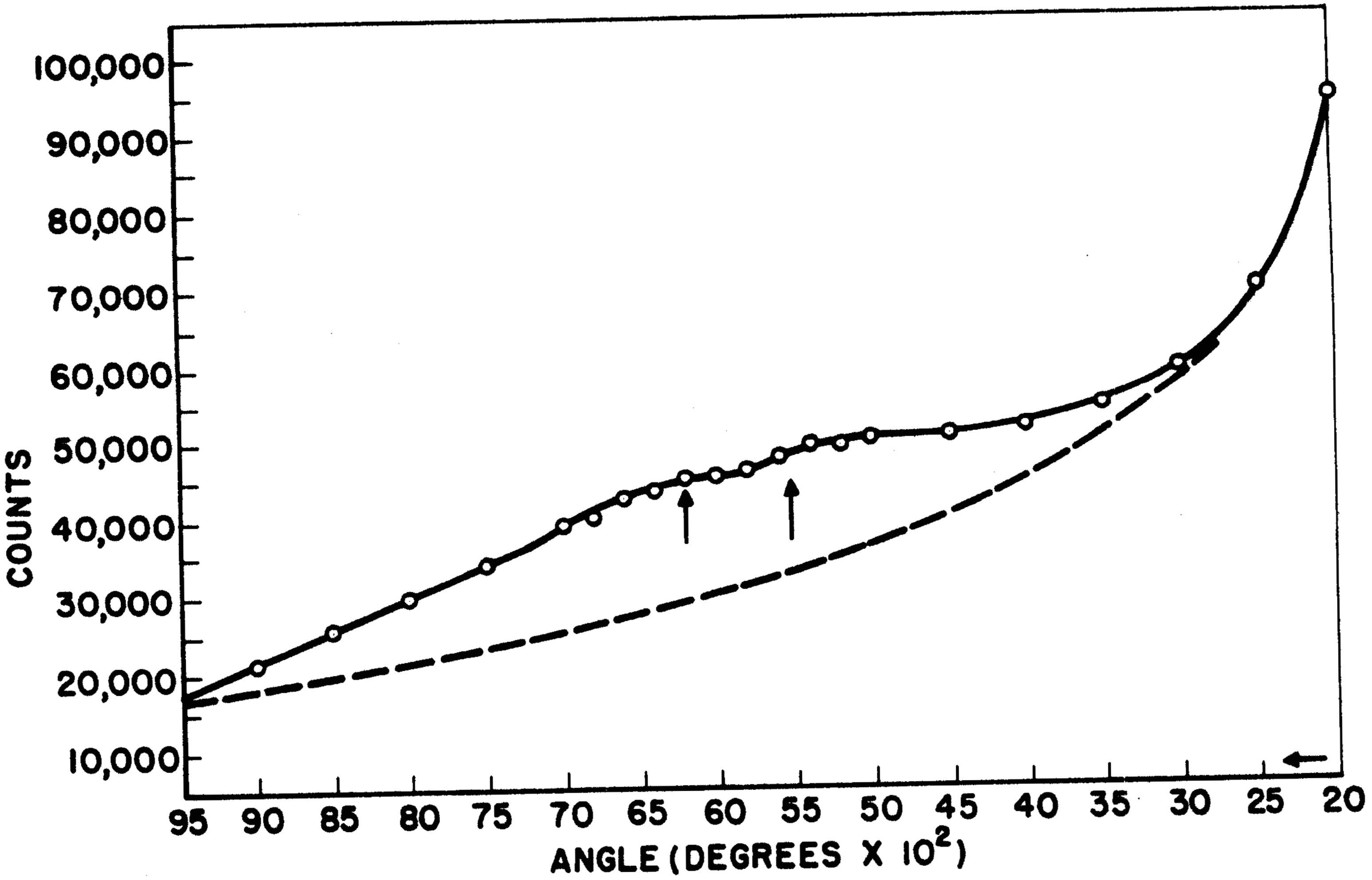

Figure 13 - Small Angle Scan of Annealed Amorphous PET

TABLE 3

COMPARISON of CRYSTALLINE and FOLD BANDS in POLYETHYLENE TEREPHTHALATE

Sample	$\frac{A_{973}}{A_{795}}$ (cryst.)	$\frac{A_{988}}{A_{795}}$ (fold)	$\frac{A_{988}}{A_{973}}$
Heat Set Amorphous Film (51 hrs. at 240°C)	3.84	0.65	0.17
Commercial "Mylar"	2.74	0.38	0.14
Biaxially Stretched Amorphous Film	1.85	0	0
Heat Set Amorphous Film (3 hrs. at 140°C)	1.82	0.12	0.07
Uniaxially Stretched Amorphous Film	1.60	0	0
Heat Set Amorphous Film (3 hrs. at 115°C)	1.28	0.16	0.13
Amorphous Cast Film	0.33	0	0

TABLE 4

DEGRADATION STUDIES

	$\frac{A_{988}}{A_{795}}$ (fold)	$\frac{A_{973}}{A_{795}}$ (cryst.)	$\frac{A_{896}}{A_{795}}$ (amor.)
Orig.	0.24	1.88	0.60
2 Hrs.	0.08	0.79	0.18
8 Hrs.	0.07	1.01	0.20
48 Hrs.	0.04	1.37	0.45

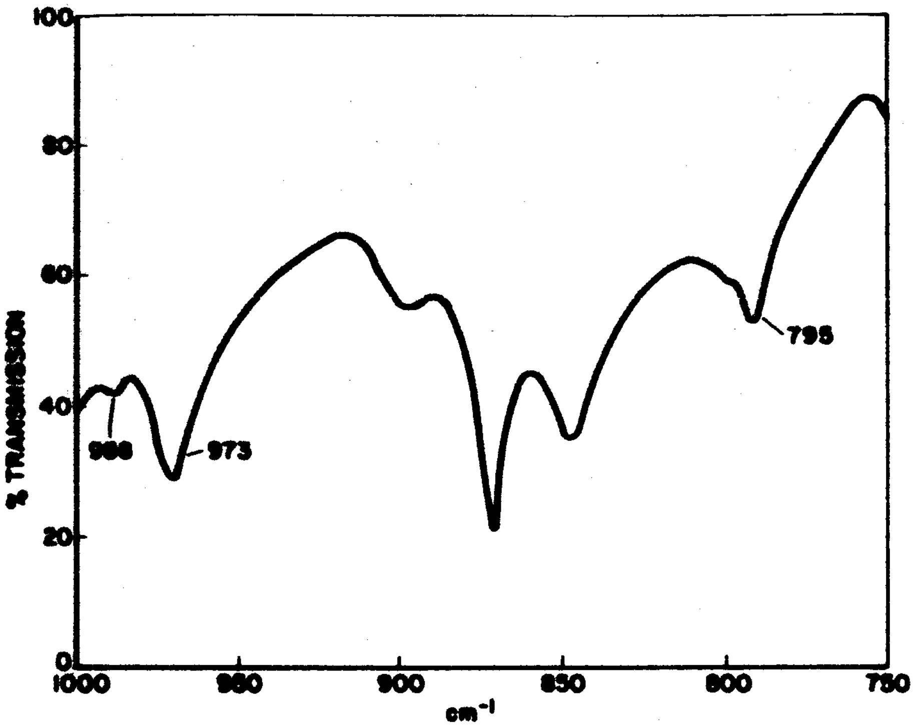

Figure 14a - Crystalline PET before Degradation

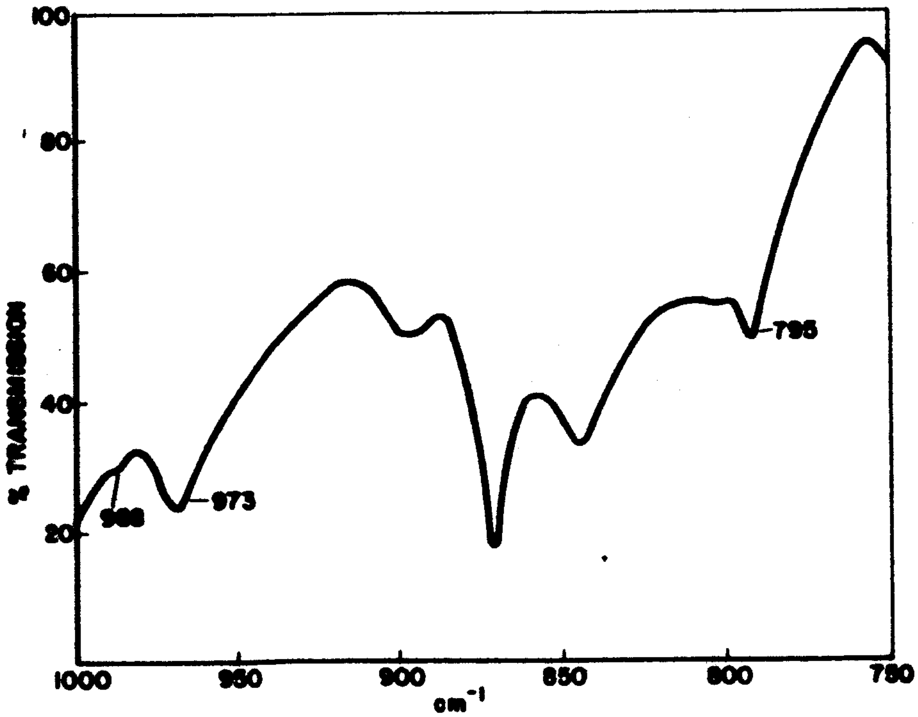

Figure 14b - Crystalline PET after Degradation band. This difficulty is minimized by dividing the 988 cm^{-1} band by the 973 cm^{-1} band. The ratio is plotted in Figure 15. The x-ray results of Farrow have shown that the crystalline areas are not attacked initially. Therefore, the decrease in this ratio as shown in the plot reflects the decrease in the 988 cm^{-1} band as a function of time. The ratio of the 1380 cm^{-1} band to the 973 cm^{-1} band, on the other hand, does not show such a decrease (Fig. 16). This ratio is relatively constant and indicates that the 1380 cm^{-1} band is constant during the degradation process.

Oligomers

The 988 cm^{-1} and 1380 cm^{-1} bands are also observed in the crystalline low molecular weight oligomers. The 988 cm^{-1} band did not show the same decrease upon degradation in the oligomers that it did in the polymer. Relative values for the 973 cm^{-1} band in the oligomers are shown in Table 5 for PET having a wide range of molecular weights.

Strain Induced Crystallization

An experiment was run in which PET was crystallized similar to the commercial "Mylar" process. An amorphous film was stretched to 450% elongation. The crystalline band at 973 cm^{-1} was quite intense while the bands at 988 cm^{-1} and 1380 cm^{-1} were absent. The film was subsequently annealed while still in tension at 200°C in the vacuum oven. As a

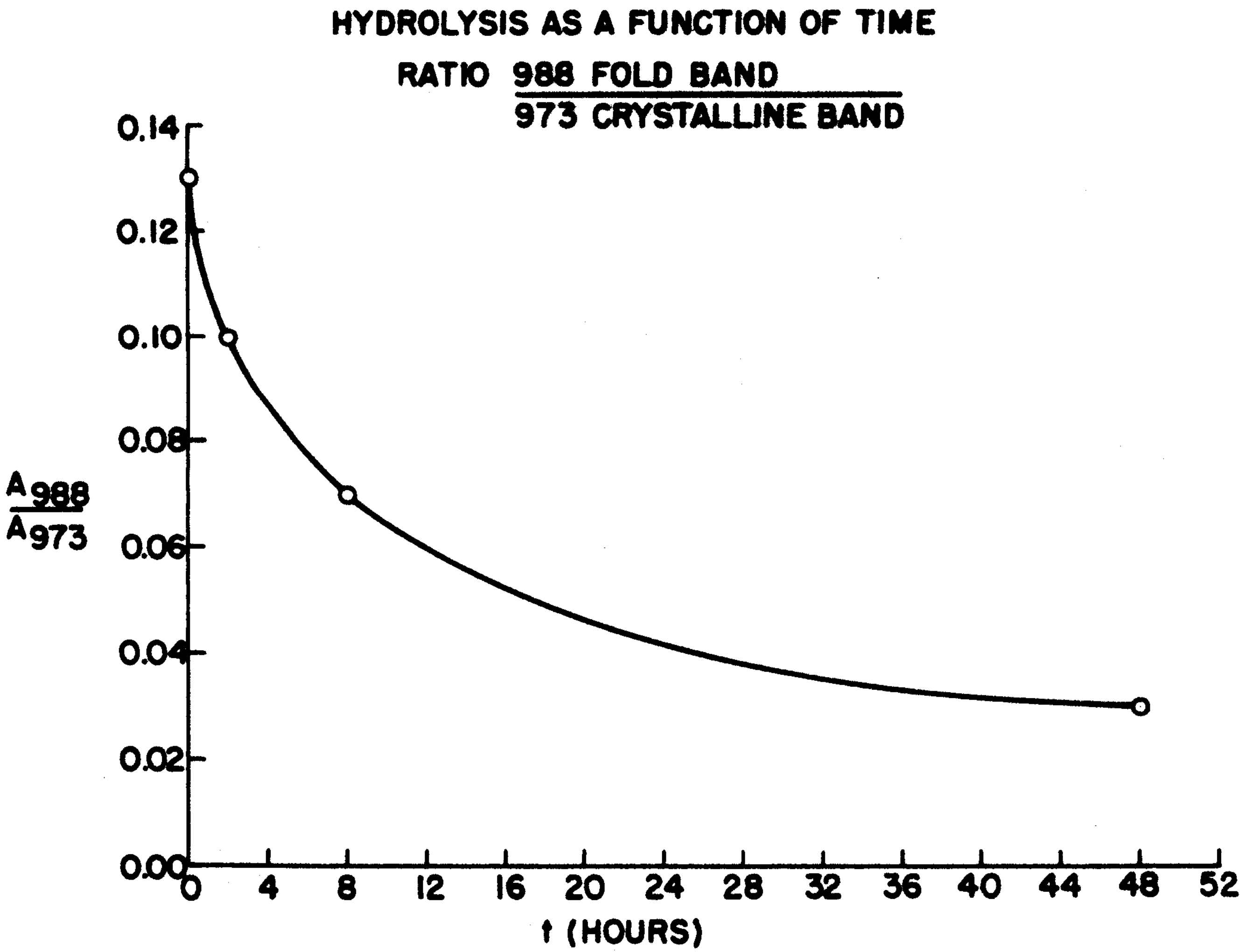

Figure 15 - Hydrolysis as a Function of Time Ratio A_{988}/A_{973}

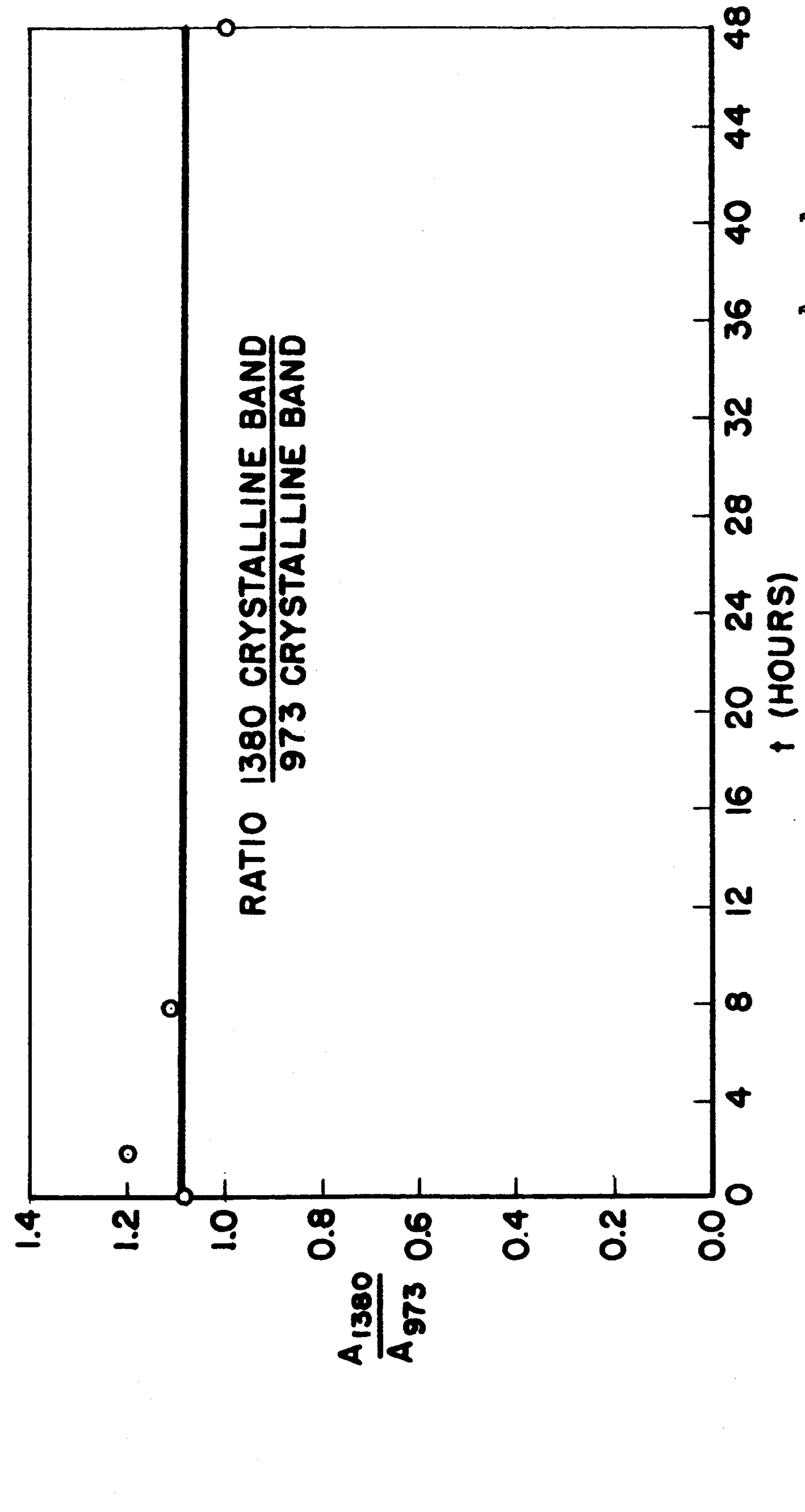

Figure 16 - Hydrolysis as a Function of Time Ratio A_{1380}/A_{973}

TABLE 5

MOLECULAR WEIGHT DEPENDENCE of 973 cm^{-1} and 988 cm^{-1} BANDS

Sample	$\frac{A_{973}}{A_{795}}$ (cryst.)	$\frac{A_{988}}{A_{795}}$	$\frac{A_{988}}{A_{973}}$
Mobil Chem. Trimer DP = 3	1.85	0.24	0.13
Goodyear Trimer DP = 3	1.97	0.24	0.12
Yamashita Pentamer DP = 5	2.05	0.26	0.13
Ishibashi Pentamer DP = 5	1.72	0.18	0.11
Ishibashi DP = 10-20	1.85	0.22	0.12
Heffelfinger DP = 15-20	1.48	0.15	0.10
Solution Crystallized (DMP)	2.04	0.24	0.12
Goodyear (I.V. = 0.89) DP = 133 (as received)	1.66	0.11	0.07
Goodyear (I.V. = 1.60) DP = 264 (as received)	1.64	0.16	0.10
Goodyear (I.V. = 0.89) DP = 133 (melt crystallized - slow cool)	2.85	0.52	0.18
Goodyear (I.V. = 1.60) DP = 264 (melt crystallized - slow cool)	2.65	0.41	0.16

result of this treatment, the 973 cm^{-1} band increased slightly and the bands at 988 cm^{-1} and 1380 cm^{-1} appeared. The region of the 988 cm^{-1} band before and after the annealing process is shown in Figure 17.

Deformation

In order to study deformation mechanisms in crystalline polymers, we performed a sequence of treatments on the same polymer sample and measured the changes which occurred. A film was first stretched to 430% elongation. The spectrum of the 973 cm^{-1} region is shown in Figure 18a. The sample was then annealed while still in tension. Figure 18b shows that the 988 cm^{-1} band appears. This very crystalline sample was restretched another 50% giving now a total elongation of 645%. Analysis of the spectrum (Fig. 18c) shows that the 988 cm^{-1} band has disappeared and the band width of the 973 cm^{-1} band has increased significantly. Reannealing of the strained sample, at 140°C for a half hour, again produces the 988 cm^{-1} band and a sharpening of the band at 973 cm^{-1} (Fig. 18d). The quantitative absorbance values of the 973 cm^{-1} and 988 cm^{-1} bands as well as their ratio were calculated. These values are shown in Table 6. The relative amount of crystallinity as measured by the 973 cm^{-1} band steadily increases during the experiment.

Absorbance values were calculated for all the poly-

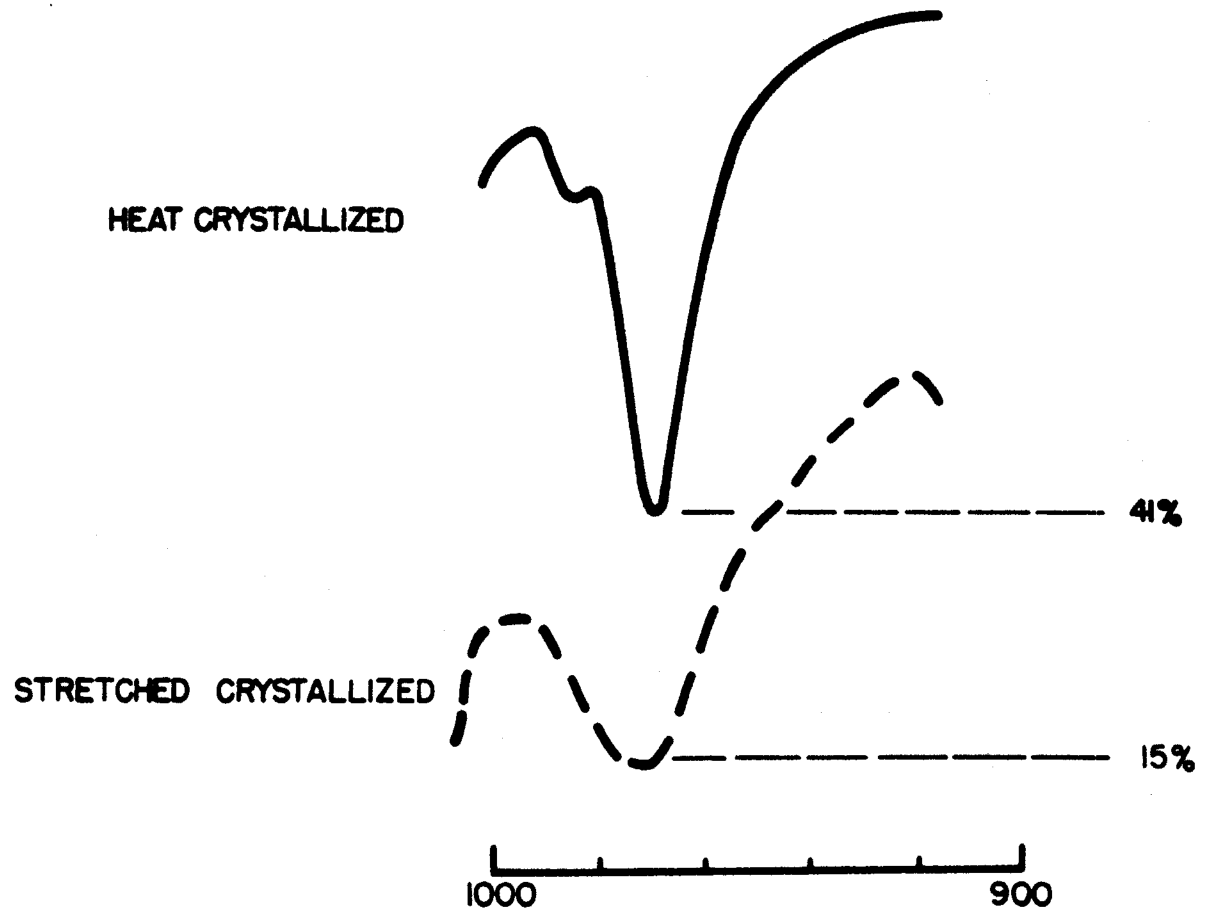

Figure 17 - BEHAVIOR OF THE 988 CM^{-1} BAND IN CRYSTALLINE PET

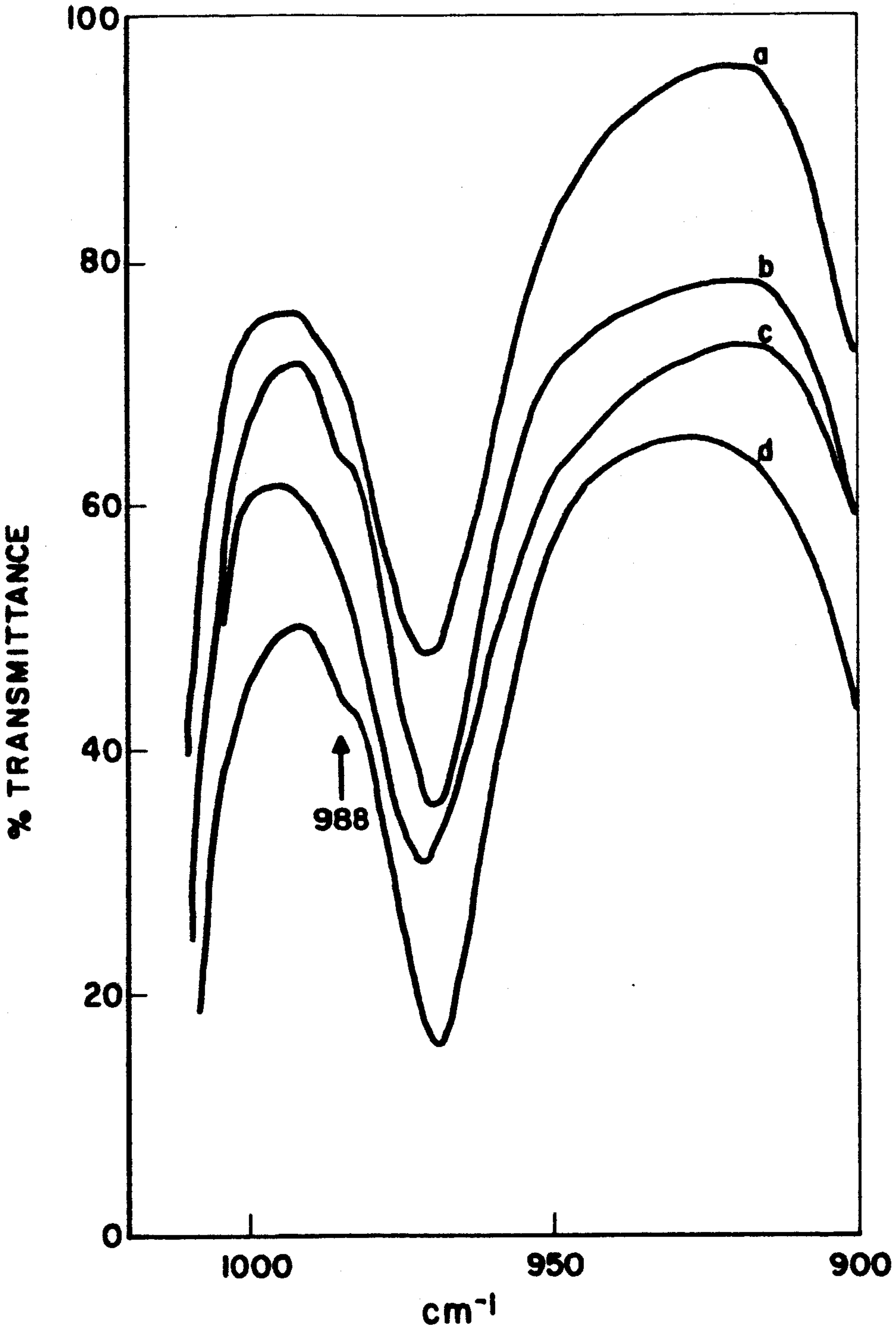

Figure 18 - Deformation Studies Upon PET Film

TABLE 6

DEFORMATION STUDY

Sample	$\frac{A_{973}}{A_{795}}$ (cryst.)	$\frac{A_{988}}{A_{795}}$ (fold)	$\frac{A_{988}}{A_{973}}$
a) Amorphous Film	0.33	0	0
b) Sample (a) Stretched 430%	1.28	0	0
c) Sample (b) Annealed at 140°C - ½ hour	1.49	0.25	0.17
d) Sample (c) Stretched 50%	1.76	0	0
e) Sample (d) Annealed at 140°C - ½ hour	1.89	0.25	0.13

ethylene terephthalate samples which had been analyzed. Table 2 shows the data for the solution and melt crystallized samples, while the results for the films under different thermal and mechanical conditions are shown in Table 3.

DISCUSSION

Band Assignment

The analysis scheme proposed to assign a band to a fold structure is shown in Figure 2. The annealing and degradation experiments have been performed and the results presented. Figures 8a and 8b show the behavior of the 988 cm^{-1} band as a function of time during the annealing process, while Figures 9a and 9b show the behavior of the 1380 cm^{-1} band. Both bands show an increase with time indicating a crystalline or fold assignment, although their respective ratios with the 973 cm^{-1} crystalline band show a difference. One of the distinguishing factors between crystalline and fold bands is their behavior upon degradation. Farrow (26) has already shown by x-ray crystallinity that initially the crystalline areas are not attacked during the degradation process. The ratio of 988 cm^{-1} absorbance to the 973 cm^{-1} absorbance (Fig. 15) decreases rather abruptly indicating that the 988 cm^{-1} band can be assigned to a fold conformation. The leveling off of the ratio in the later stages of degradation indicates there is very little folding left and the crystalline areas are slowly being attacked. The ratio of the 1380 cm^{-1} band to the 973 cm^{-1} band is relatively constant over the time of the experiment, as shown in Figure 16. This indicates the structure giving rise to the 1380 cm^{-1} band is changing in the same manner as the 973 cm^{-1} band, so a crystalline band assignment for the 1380 cm^{-1} band can be made. We were not able to further verify these assignments by the second independent means,i.e., melting and annealing of the semicrystalline polymer, since thermal degradation took place at the high temperatures. However, sufficient evidence has accumulated to justify both the assignment of the 988 cm^{-1} band to the fold and examination of crystalline systems with the band assignment.

Structure of the Fold in PET

Having assigned the band at 988 cm^{-1} to the fold, we would like to relate it to a particular conformation. Because of the length of the repeat unit, the effect of coupling should be minimal. Therefore, a unique conformation of the fold not easily accessible to the disordered chain is demanded. Figure 19 shows one possible conformation which is not easily accessible to the chain, but satisfies the requirement of a regular, adjacent re-entry fold model. Strained conformations would also arise from the loose-loop and "switchboard" fold models. However, these conformations would appear to be accesible to the disordered chain and would absorb as crystallizable bands in the spectra. To date, insufficient work has been done to preclude these additional folding mechanisms in PET.

The 988 cm^{-1} Band in the Linear Trimer

A band at 988 cm^{-1} also appears in the linear trimer.

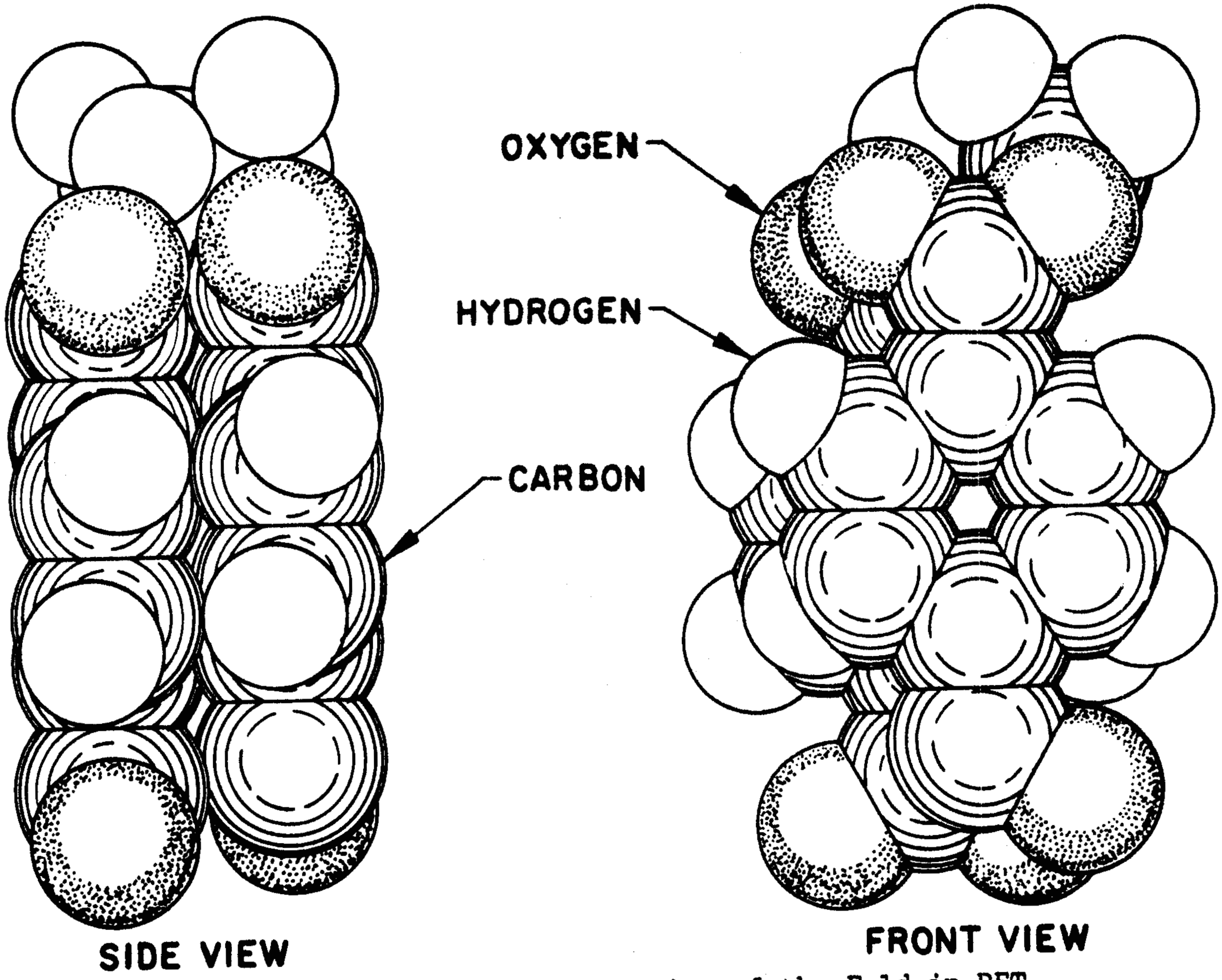

Figure 19 - Possible Conformation of the Fold in PET

We must, therefore, show the absorption arising from the trimer is not sufficient to be of concern in our systems during the process of annealing, degradation, and crystallization. There are several facts worth considering:

1) Strong absorption bands in the spectra of the linear trimer are not present in the polymer spectra.

2) The deformation studies show that the formation of trimer is not a factor. The fold band appeared upon annealing, disappeared upon stretching and reappeared once again upon annealing. One cannot simply create and destroy a chemical species such as the linear trimer by such treatments.

3) Breaking bonds simply by heating the polymer to a temperature of 110^{o}C to form trimer is remote. This is the temperature at which the fold band first appears upon crystallization.

4) It is a known fact that polyethylene terephthalate normally contains low molecular weight materials comprising about 1.3 - 1.7% of the polymer sample. This low molecular weight material is the result of an equilibrium established in the melt. Goodman and Nesbitt (27) have extracted all the low molecular weight material, remelted the polymer, crystallized and obtained once again precisely the same percentage of low molecular weight material that they had previously extracted. This small amount of material could not possibly produce a detectable amount of the very weak band at

988 cm^{-1}.

The trimer is not long enough to fold. The structure giving rise to the 988 cm^{-1} band in the trimer did not suffer any significant change during the degradation. Therefore, we conclude that the conformation in the linear trimer gives rise to a different mode than the vibration giving rise to the 988 cm^{-1} band in the folded polymer chain.

Melt and Solution Crystallized Samples

The PET grown from solution and from the melt have a large degree of folding, as evidenced by the very intense band at 988 cm^{-1}, shown in Figure 5. The absorbance values, shown in Table 2 give a quantitative measure of the absorbance. While one cannot obtain an absolute value for the amount of folding, the relative values are useful. Samples of PET crystallized by very slowly cooling from the melt contain a large degree of folding as measured by the 988 cm^{-1} band, in agreement with current concepts of crystallization. Solution grown crystals were observed to be spherulitic in nature. These samples also had large degrees of folding as measured by the 988 cm^{-1} band. Crystals were grown from 2-(2-Butoxy ethoxy) ethanol under two sets of conditions. Those grown isothermally at 190°C contained a larger amount of folding (0.25) than those grown by slowly cooling from the boiling point of the solvent (0.17). These latter crystals probably all crystallized above 190°C with a larger fold period than the isothermally grown crystals. The as-polymerized high I.V. PET which had been received from the Goodyear Tire and Rubber Company had a relatively small amount of folding, probably due to the solid state polymerization process. Upon melting the sample and slowly crystallizing it from the melt, the molecules recrystallize to a state containing a large degree of folding. The behavior of the 988 cm^{-1} band in both melt and solution crystallized samples is consistent with current theories of fold formation.

Annealing Studies

The annealing results for the 973 cm^{-1} crystalline band as a function of time are shown in Figure 7. The intensity initially increases sharply and then more slowly with time. The amount of crystallinity is higher at higher annealing temperatures. We assume subsequent to the initial crystallization annealing occurs only in the crystalline regions already formed, but no further crystallization occurs. The annealing would produce an increase in the long period at the expense of the folds. A linear correlation of the small angle long period with the reciprocal of the fold concentration is expected. Figure 10 shows that while a linear relationship is obtained at 140°C, we do not obtain a large enough change in the long period to note any trends. Above 200°C we do not find the linear relationship anticipated (Figs. 11 and 12). These results are complicated by secondary crystallization. An additional small angle long period peak appears in these samples (Fig. 13). Mayhan (28) postulated secondary crystallization above 200°C from his density measurements. His results (Fig. 20) show a slight increase in the limiting density between 110°C and 200°C with a rather sharp increase above this temperature. These density results are completely consistent with the limiting values of the 973 cm^{-1} band as a measure of crystallinity.

The ratio of the crystallinity to the folding as shown by Figure 8b exhibits some reverses. A priori,we would expect that crystallization at a higher temperature should produce a larger fold period, and therefore a larger ratio of crystallinity to folding. This is observed for crystallization at 115°C and 140°C. At 200°C and 240°C, however, one obtains a much larger amount of folding than is warranted by this assumption. We postulate the following behavior. Crystallization from the glass occurs by a collapse of adjacent polymer chains into a crystalline cell. The degree of crystallinity is a function of the order in the glass and the thermal mobility of the chains. At lower temperatures, where the thermal mobility is low, perfection of the crystallinity is restricted by the inability of the chains to diffuse together; large loops of uncrystallized chains can result. Only a portion of them will have sufficient energy to collapse to the regular fold struc-

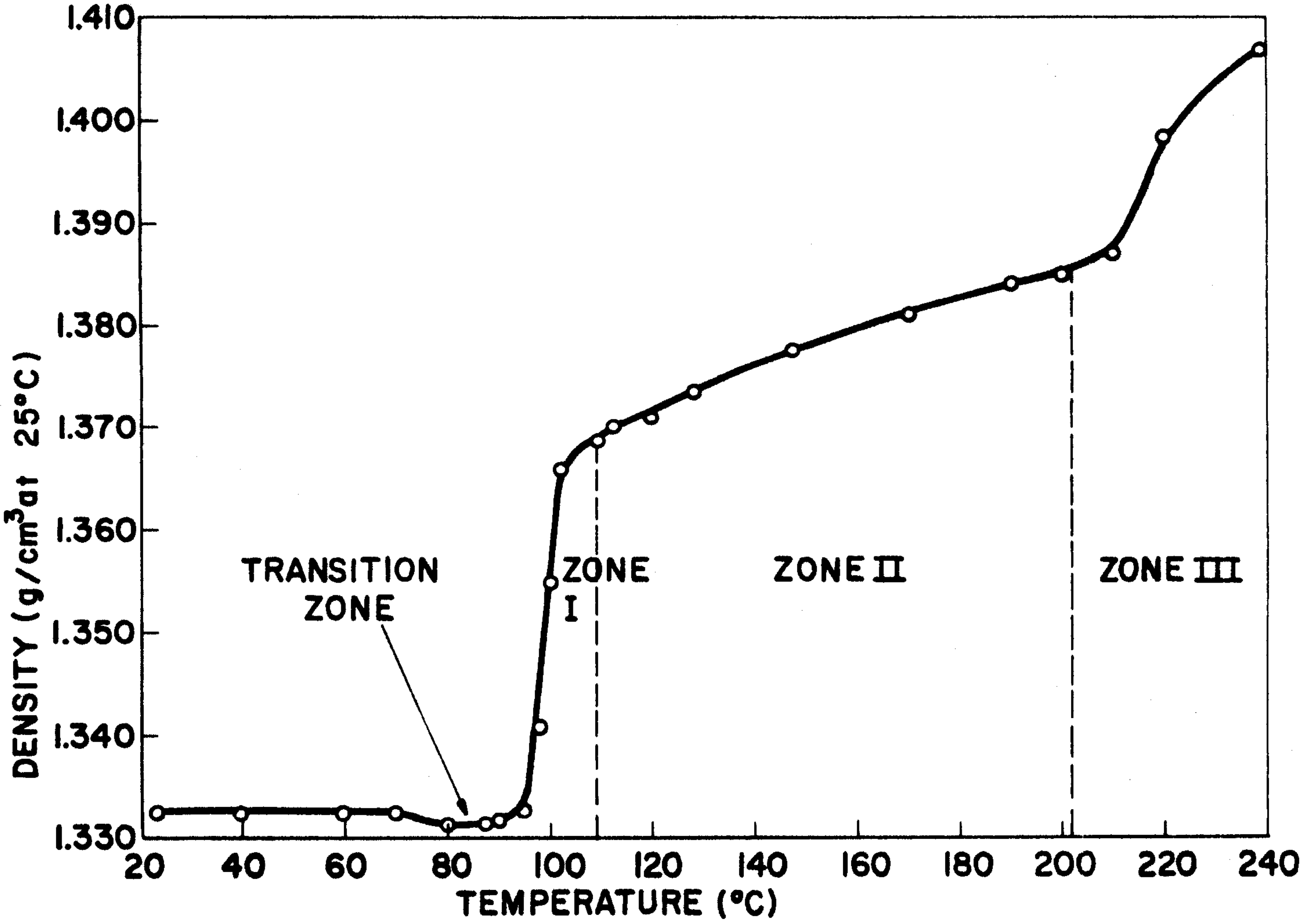

Figure 20 - Limiting Density as a Function of Temperature in PET

ture demanded by 988 cm^{-1} band. At higher temperatures, where the mobility of the chain is greater, the large loops perfect themselves until the restricted conformation measured by the 988 cm^{-1} band is formed. Therefore, at 200°C and 240°C, one obtains a more intense 988 cm^{-1} band in relation to the crystallinity.

Oligomers

The values of the 988 cm^{-1} band absorbances for the DP = 3 and DP = 5 samples, as shown in Table 5, do not represent the fold structure and can be used only in comparison to the other samples. The folding in the remaining samples varies depending upon the manner of crystallization. The melt and solution crystallized samples show the greatest amounts of folding, in agreement with the current theories of crystallization.

Strain Induced Crystallization

Crystallization studies of drawn films, shown in Figure 17, indicate that, before annealing, crystallization occurs by a folding type which is not measured by the 988 cm^{-1} band. The molecules are simply drawn tightly enough for large segments to come into lattice register but the loop portions do not crystallize sufficiently to produce regular folds. When this sample, while still in tension is heated above 110°C, crystallization continues wherever thermal motion is large enough in those loop portions to form a regular fold. If one follows up the drawing process by heating above 200°C, many more of the molecules now have sufficient energy to form a regular fold, and an increase in the amount of folding is observed as in the annealing studies. Hence, we are proposing a model for the crystallization process in oriented systems - when crystalline regions are formed by stretching, a long-loop type of fold occurs. Heating the oriented film generates additional mobility to allow these random length long-loop type folds to become regular; the degree of regularity depends upon the temperature. This mechanism is similar to, but not precisely the same as, the mechanism presented by Dismore and Statton (16) in oriented 66-Nylon.

Deformation

The deformation results give an indication of the types of changes occuring in crystalline PET. Upon deformation of the previously stretched and annealed polymer, we observed a disappearance of the 988 cm^{-1} fold band and a broadening of the 973 cm^{-1} band (Fig. 18c), indicating both a loss of the precise conformation formed in the fold and wider range of interaction on the molecules which give rise to this 973 cm^{-1} band. While it is unlikely that the folds are being destroyed completely when one stretches the previously stretched and heat set polymer, the fold no longer exists in the same conformation. Peterlin (15) has speculated that one obtains molecular slip, chain tilt, or both in the deformation of crystalline polyethylene. Upon annealing the PET, the amount of folding was precisely the same as before the second stretching, as shown quantitatively in Table 6. This is consistent with the above interpretation. The molecules are not being pulled out completely, causing the folds to be destroyed, but are merely being distorted. During subsequent annealing, sufficient energy is introduced to re-perfect the folding.

Future Work

The assignment of the exact conformation producing the 988 cm^{-1} fold band is desirable. This is accomplished by:

1) Normal Coordinate Analysis - it is hoped that a computer program, which will allow one to predict wave lengths of vibrations in simple molecules, in simple polymers, and finally in more complicated polymer molecules, such as PET, will be written. Having such a program, one can vary the molecular conformation, as well as the force constants, due to changes in environment, and then predict an exact model for the molecule under study.

2) Model compound studies will be useful in determining the band assignment in two ways: first of all, it may be possible to obtain a model compound which will simulate the conformation in the fold. For example, one can obtain a cyclic trimer which has all three ethylene oxide units in a gauche

conformation, or a cyclic tetramer which has two trans units and two gauche units. Secondly, the model compounds will be useful in setting up and testing band assignments in the normal coordinate analysis.

3) Deuteration studies on PET have been done in the past but the results have been inconsistent (29,30). Also, these results have not been used in assigning the 988 cm^{-1} band. There is a possibility that this band arises from a vibration involving the oxygen in the chain backbone. If one were to saturate the PET chain with O^{18} in the glycol linkage, one would observe shifts in those bands arising from vibrations involving this atom. Therefore, synthesis of O^{18} saturated PET may be useful in the band assignment.

A quantitative measure of the long-loop irregular type folding is possible. A detailed study will be performed to measure this type folding.

Further studies will be done in verifying the modes of crystallization and deformation in oriented films. The effects of percentage elongation, annealing conditions and prior treatment will be studied.

CONCLUSIONS

The results of this study are consistent with the following conclusions:

1) The band at 988 cm^{-1} arises due to the requirements of the folded PET molecule. The results are consistent with a unique highly regular conformation.

2) High degrees of folding, as measured by the 988 cm^{-1} band, are obtained by crystallizing PET from solution or from the melt. To effect high degrees of folding in glassy samples, one must anneal the sample for long periods of time at relatively high temperatures.

3) The annealing of amorphous PET indicates the possibility of two types of folding. Irregular folds formed at the lower temperatures seem to become regular when annealed at higher temperatures.

4) Strain induced crystallization does not produce the regular fold as measured by the 988 cm^{-1} band. Subsequent annealing of these samples will induce this regular type folding.

5) Deformation of a film containing regular folds, as measured by the 988 cm^{-1} band, causes this regularity to be disrupted and the band disappears. Subsequent annealing reperfects the folds.

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