

# Vibrational Spectroscopic Study of Poly(ethylene Terephthalate) Crystallized by Annealing in the Oriented State

G. M. VENKATESH,\* P. J. BOSE, and A. H. KHAN, *Ahmedabad Textile Industry's Research Association (ATIRA), Ahmedabad 380 015, India*, and J. P. SIBILIA and S. L. HSU,\* *Chemical Research Centre, Allied Chemical Corporation, Morristown, New Jersey 07960*

## Synopsis

Poly(ethylene terephthalate) filament yarn has been annealed in nitrogen atmosphere, in silicone oil, or in nonreacting organic solvents. Morphological changes resulting from the annealing processes have been followed by Raman spectroscopy. Crystallinity, as evidenced by the width of the  $1730\text{ cm}^{-1}$  carbonyl stretching vibration, is shown to affect the macroscopic properties of these filaments. Furthermore, these spectroscopic results, together with shrinkage measured, suggest that the shrinkage and the crystallization processes in the polymer fiber proceed at different rates in different fluid media.

## INTRODUCTION

The structure–property relationship for oriented poly(ethylene terephthalate) (PET) fibers or films has been studied extensively. Complementary characterization techniques such as nuclear magnetic resonance spectroscopy, thermal analysis, x-ray diffraction, density, birefringence, and vibrational spectroscopy have been used to analyze structural aspects both qualitatively and quantitatively. Vibrational spectroscopy, which is sensitive to both chain conformation and molecular environment, has become an important tool in characterizing polymers. The intensities and half-widths of several bands in the vibrational spectra of PET are quite sensitive to sample treatments such as thermal annealing or drawing. Correlation between these spectral changes and the degree of crystallinity has been investigated frequently.<sup>1–14</sup> It is generally accepted that the ethylene glycol residues in amorphous PET exist mainly in the gauche conformation, with a small portion of the trans conformation. In contrast, the trans isomer exists mainly in the oriented amorphous as well as in the crystalline state. The departure of the carbonyl group from planarity of the terephthaloyl group was suggested earlier by Liang and Krimm,<sup>2</sup> and recently theoretical evidence for a considerable degree of freedom around the ring ester C—C bond has been produced by Tonnelli.<sup>15</sup> When PET fibers are drawn, the orientation of the macromolecules with respect to the fiber axis improves, and crystallinity often develops. Infrared spectroscopy has successfully followed the trans–gauche isomerization.<sup>1,3,8</sup> Similar structural changes have also been observed for thermally treated PET fibers and films.<sup>1–9</sup>

\* Present address: Polymer Science and Engineering Department, University of Massachusetts, Amherst, Massachusetts 01003.

Melveger established that the half-width of the  $1730\text{ cm}^{-1}$  band, assignable to the carbonyl stretching vibration, is linearly related to density.<sup>11</sup> Unlike some of the infrared measurements, this correlation is independent of orientation effects in the sample and has been confirmed by measurements in PET powders, unoriented heat crystallized filaments, yarns drawn and oriented above  $T_g$ , and high-pressure crystallized material. From this analysis, Purvis and Bower have concluded that the width of the line may be more related to the crystallinity than to density.<sup>14</sup> Often we found quality infrared transmission spectra are difficult to obtain for PET fibers. In contrast, with laser-Raman method, being a scattering process, one can obtain a spectrum from these same fibers quite easily. The measurement of the half-width of the carbonyl stretching vibration requires no internal intensity standard and can be used for characterization.

A number of preoriented semicrystalline PET filament yarns were heat set at different temperatures in oil, nitrogen atmosphere, and nonreacting organic solvents. The changes in dimensional stability and mechanical properties were found to be highly dependent on time and temperature, as well as tension applied to yarn during treatment.<sup>16-18</sup> Moreover, the medium of heat setting plays an important role in modifying these properties. During annealing, the molecular chain segments may crystallize into a structure with higher perfection, resulting in partial or complete removal of strains introduced during the melt spinning and the subsequent drawing process. A better understanding of the vibrational spectra obtained for these variously prepared samples contributes a fuller understanding of the structural changes occurring during annealing. Our results are reported here.

## EXPERIMENTAL

PET continuous filament yarns were annealed under various conditions. Details of preparation and the mechanical data have been published elsewhere.<sup>16-18</sup> Raman spectra were obtained on a Spex Ramalog spectrometer incorporating a Spex 1401 double monochromator with holographic gratings, a Coherent Radiation 52 G Krypton laser, and an RCA C 31034 photomultiplier operating at  $-30^\circ\text{C}$  with standard photon counting techniques. The Raman data were obtained with the 5682 and 6471 Å laser excitations. The band pass was kept at  $1.5\text{ cm}^{-1}$  at 5100 Å. In order to avoid the problem of morphological nonuniformity along one fiber, Raman spectra of a bundle of fibers were recorded. In general, all the samples showed high fluorescent background, although significant reduction in the fluorescent background can be achieved with the yellow and red laser excitations. The error involved in the width measurements is approximately  $0.5\text{ cm}^{-1}$ . No difference beyond the experimental error was observed for samples exposed to the laser beam for different times (no annealing or degradation). As shown in Figure 1, with minor differences, the Raman spectrum obtained is similar to the ones presented elsewhere.<sup>10,11</sup> The measurements of the half-width,  $\Delta\nu_{1/2}$ , of the  $1730\text{ cm}^{-1}$  carbonyl stretching vibration are shown in Table I.

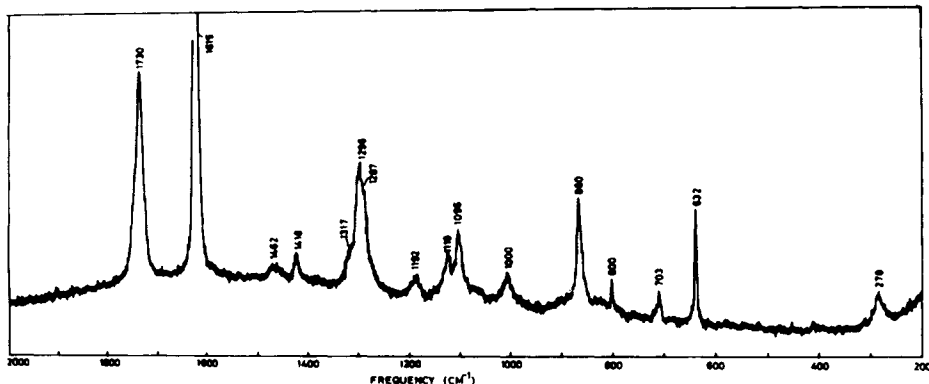


Fig. 1. Laser spectrum of PET fibers.

## RESULTS AND DISCUSSION

As can be seen in Table I, significant variations in the half-width,  $\Delta\nu_{1/2}$ , of the carbonyl stretching vibration observed in Raman were found for samples annealed under different conditions. As expected, the undrawn PET showed the broadest half-width, indicating a considerable number of chains existing in irregular conformations or low crystallinity. The thermally annealed (heat set either in nitrogen atmosphere or in silicone oil) samples showed the highest level of conformation order and crystallinity as suggested by the narrow bandwidths ( $10\text{--}14\text{ cm}^{-1}$ , except for sample 3) of the carbonyl stretching vibration. Furthermore, the PET fibers annealed under slack conditions have a narrower average carbonyl half-width, implying higher crystallinity than the samples annealed at constant length. This comparison is even more favorable when consideration of time is included. For long time periods, samples annealed at slack condition showed much narrower carbonyl half-widths than the corresponding samples treated at constant length. These results clearly show that crystallization continues to occur for extended periods even though equilibrium shrinkage would be achieved at much shorter periods under the conditions of treatment. According to Fischer and Fakirov<sup>19</sup> and Weigmann et al.,<sup>20</sup> heat setting at high temperatures leads to an increase in the size of the mosaic blocks building up the crystalline layers and their longitudinal order resulting from a recrystallization of small crystallites.

In contrast to thermal annealing, the samples treated in solvents at constant length for short durations showed little, if any, increase in order. This result suggests a lower level of crystallinity in the solvent-treated material. Weigmann et al.<sup>19</sup> have shown that during solvent-induced crystallization in the presence of a strongly plasticizing solvent such as DMF, a structure that is swollen to a considerable extent resulting in the formation of a large number of small crystallites (high nucleation rates) occurs. Preliminary results from x-ray crystallinity measurements are consistent with this picture. It can be seen that high crystallinity is developed in a short time when annealed at high temperature in silicone oil, irrespective of whether the fibers are allowed to shrink freely or not during the treatment.

On the other hand, the Raman data obtained for solvent-treated samples indicate that constant length treatments, even for long time durations, especially

TABLE I  
Laser Raman Spectral Data for Pretreated PET Fibers

Sample No.	Experimental conditions for treatment <sup>a</sup>				Tension	Bandwidth $\Delta\nu_{1/2}$ (1730 cm <sup>-1</sup> ), cm <sup>-1</sup>	Density $\rho$	Intensity ratio	
	Medium	Temp., °C	Time, min	1096 cm <sup>-1</sup> / 632 cm <sup>-1</sup>					
0	Undrawn yarn	—	—	—	24.0 <sup>b</sup>	1.34	—	—	
1	Starting control for samples 1-19	—	—	—	16.5 ± 0.5	1.37	0.58	—	
2	Nitrogen	200	5	S	12.5	1.40	0.58	—	
3	Nitrogen	200	5	CL	16.4	1.39	0.60	—	
4	Nitrogen	200	60	S	10.0	1.41	—	—	
5	Nitrogen	200	60	CL	13.0	1.40	—	—	
6	Nitrogen	230	5	S	10.0	1.41	—	—	
7	Nitrogen	230	60	CL	12.0	1.40	—	—	
8	Silicone oil	200	1	S	11.5	1.40	—	—	
9	Silicone oil	200	1	CL	14.0	1.39	—	—	
10	Silicone oil	200	30	S	10.5	1.41	—	—	
11	Silicone oil	200	30	CL	14.0	1.39	—	—	
12	Methylene chloride	5	5	S	16.4	1.38	0.53	—	
13	Methylene chloride	5	5	CL	20.9	1.36	0.63	—	
14	Methylene chloride	5	300	S	14 ± 1.0	1.39	—	—	
15	Methylene chloride	5	300	CL	17.0	1.38	—	—	
16	s-Tetrachloroethane	70	5	S	17.8	1.37	0.67	—	
17	s-Tetrachloroethane	70	5	CL	20.3	1.36	0.60	—	
18	s-Tetrachloroethane	70	300	S	12.0	1.40	—	—	
19	s-Tetrachloroethane	70	300	CL	14.0	1.39	—	—	

<sup>a</sup> S = Slack, CL = constant length.

<sup>b</sup> Band maximum appears at 1726 cm<sup>-1</sup>.

for methylene chloride, do not lead to substantial increases in crystallinity. It appears that the solvent swells the fibers and either produces a large number of tiny crystallites<sup>20</sup> or, in the absence of appreciable thermal energy as in the case when fibers are treated at 5°C in methylene chloride, produces a small increase in crystallinity. However, the increased thermal energy available at 70°C in *s*-tetrachloroethane leads to much larger increases in crystallinity, as evidenced by the narrower half-widths of the carbonyl stretching vibration measured. McGraw<sup>10</sup> studied the effects of high-temperature annealing on the Raman spectrum of poly(ethylene terephthalate). He found that the intensity of the 1096 cm<sup>-1</sup> band in comparison to the internal reference band at 632 cm<sup>-1</sup> correlated linearly with density of the samples. However, it is clear from the table that the density derived from the ratio of the 1096 to 632 cm<sup>-1</sup> band does not correlate with the density derived from the half-width of the 1730 cm<sup>-1</sup> band. This is consistent with Melveger's observation.<sup>11</sup> The changes in morphology on thermal and solvent treatments can be related to the macroscopic changes in shrinkage and dimensional stability (residual shrinkage in boiling water, breaking strength, and extension).<sup>16-18</sup>

As seen in Table II, significant variations in the macroscopic properties were found for samples treated under different conditions. The slack treatment produces the highest shrinkage and breaking extension in silicone oil and the lowest shrinkage and breaking extension in methylene chloride. Constant-length treatments result in a marginal decrease, if at all, in breaking extension. Long-duration treatments either in slack or constant-length conditions lead to substantial decreases in breaking extension, implying development of higher crystallinity. The residual shrinkage data indicate that when annealed in the slack condition in nitrogen atmosphere, silicone oil, or solvents, satisfactory dimensional stability can be achieved (i.e., the treated fibers show less than 2% residual shrinkage in boiling water). The constant-length treatment in silicone oil also confers satisfactory dimensional stability on the treated fibers. On the other hand, the constant-length treatment in solvents produces only marginal improvement in the dimensional stability of the treated material. The conclusions drawn from the Raman data of the thermally annealed samples are consistent with those derived from the shrinkage and residual shrinkage studies, i.e., the higher the shrinkage and the lower the residual shrinkage, the narrower the carbonyl half-width. On the other hand, the conclusions on the solvent-treated samples, especially those treated in the slack condition, appear to be contradictory. From Table II it is seen that the improved dimensional stability is not accompanied by a decrease in the bandwidth. This apparent contradiction is resolved if it is accepted that the shrinkage and the crystallization are two different processes and that though an increase in crystallinity can lead to better dimensional stability, it is not a prerequisite for achieving better dimensional stability. In the case of high-temperature annealing, the rates of shrinkage and crystallization both are fast, and the improvement in crystallinity stabilizes the structure even when the heat treatment is carried out at constant length. In the case of solvents, the rate of crystallization is much slower, especially at temperatures as low as 5°C, than that in the case of high-temperature thermal treatment.

It should be pointed out here that while the carbonyl band in the Raman spectrum sharpens on thermal or solvent treatment, the same band, for reasons

TABLE II  
Raman Spectral Data, Shrinkage, and Mechanical Properties of PET

Medium	Conditions of treatment		Free shrinkage, %	Residual shrinkage, %	Breaking strength, g/d <sup>a</sup>	Breaking extension, %	$\Delta\nu_{1/2}$ (1730 cm <sup>-1</sup> ), cm <sup>-1</sup>
	Temp., °C	Tension					
Control	—	—	—	7.7	5.1	45	18.5
Nitrogen	200	slack	16.5	0.7	5.1	75	12.5
Nitrogen	200	constant length	—	3.1	5.1	37	16.4
Silicone oil	200	slack	33.0	1.3	4.8	79	11.5
Silicone oil	200	constant length	—	1.9	5.2	50	14.0
Methylene chloride	5	slack	12.2	0.8	5.1	52	16.4
Methylene chloride	5	constant length	—	6.5	5.1	37	20.9
s-Tetrachloroethane	70	slack	18.2	1.6	4.9	64	17.9
s-Tetrachloroethane	70	constant length	—	5.2	5.2	35	20.3

<sup>a</sup> g/d: gram/denier.

unknown at present, broadens out in the IR spectrum. Figure 2 shows the infrared spectra of the control film (draw ratio of 4, courtesy du Pont de Nemours Co., USA) and the sample heat set at 200°C for 30 min in the slack condition. The broadening observed cannot be attributed to the emergence of an additional weak band at 1685  $\text{cm}^{-1}$ . The existence of such a band has been reported by Miyake.<sup>1</sup> Its assignment is at present not clear.

Because of the higher signal-to-noise ratio obtained in the present experiment, it was possible to resolve additional broad features at 1287 and 1317  $\text{cm}^{-1}$ , near the strong 1296  $\text{cm}^{-1}$  band (Fig. 1), which were not readily resolved earlier.<sup>10,11,13</sup> It is interesting to note that the relative intensities of the 1287 and 1317  $\text{cm}^{-1}$  bands compared to the 1296  $\text{cm}^{-1}$  band were different for various samples. In particular, the 1287  $\text{cm}^{-1}$  component possesses nearly the same intensity as the 1296  $\text{cm}^{-1}$  component in sample 2. As discussed earlier, this sample showed the narrowest 1730  $\text{cm}^{-1}$  band. Boerio et al.<sup>13</sup> assigned the 1296  $\text{cm}^{-1}$  band to be predominantly C—C stretching of the backbone. Therefore, it should be sensitive to the conformation of the polymer chain. The origin of the 1287 and 1317  $\text{cm}^{-1}$  bands is not clear at present. However, similar bands were observed by D'Esposito and Koenig<sup>9</sup> in the IR spectra of annealed PET samples. They assigned the 1280  $\text{cm}^{-1}$  band to be a band that exists only in samples of high crystallinity. Therefore, the high crystallinity of sample 2 is evidenced by both the narrowness of the carbonyl frequency and the high intensity of the 1287  $\text{cm}^{-1}$  band. In the present work, spectral components were seen in the neighborhood of 1287 and 1317  $\text{cm}^{-1}$  in various samples. In particular, a clear correlation can be noted in samples 4, 11, 14, 15, 18, and 19, whose Raman spectra were recorded with 6471 Å laser excitation, between the carbonyl half-widths and the intensities of the 1282 and 1292  $\text{cm}^{-1}$  components. For the narrow carbonyl bands, four out of six samples showed approximately equal component intensities. For the broad carbonyl bands, three out of six samples showed components in the intensity ratio of approximately 3:4 for the 1282 to the 1296  $\text{cm}^{-1}$  bands. For other samples, resolution was not good enough to determine band components in this region. The 1310  $\text{cm}^{-1}$  band, when observed, gave no additional information. A clearer understanding of the origin of the 1286 and 1317  $\text{cm}^{-1}$  vibrations would

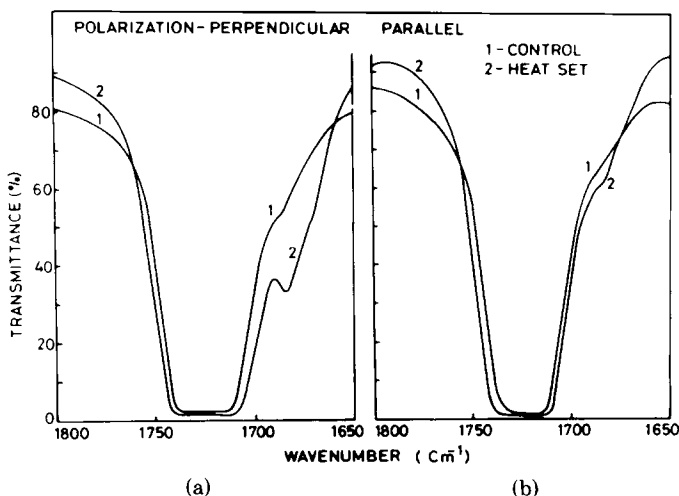


Fig. 2. Infrared transmission spectra of PET film: (a) untreated; (b) heat treated at 200°C.

be useful in further clarifying the various conformational states that exist in PET.

## CONCLUSIONS

Crystallinity, as evidenced by the width of the carbonyl stretching vibration observed at  $1730\text{ cm}^{-1}$ , affects the macroscopic properties of the oriented PET filaments, namely, the residual shrinkage and the breaking extension. These spectroscopic results, together with shrinkage measured, suggest that the rates at which the shrinkage and the crystallization processes proceed are different depending on the medium as well as the temperature of annealing.

## References

1. A. Miyake, *J. Polym. Sci.*, **38**, 479 (1959).
2. C. Y. Liang and S. Krimm, *J. Mol. Spectrosc.*, **3**, 554 (1959).
3. G. Farrow and I. M. Ward, *Polymer* **1**, 330 (1960).
4. T. R. Manley and D. A. Williams, *Polymer*, **10**, 339 (1969).
5. W. O. Statton, J. L. Koneig, and M. Hannon, *J. Appl. Phys.*, **41**, 4290 (1970).
6. D. C. Prevorsek and J. P. Sibilial, *J. Macromol. Sci. Phys.*, **5**, 617 (1971).
7. J. P. Sibilial, P. J. Harget, and G. A. Tripak, *Polym. Prepr. Am. Chem. Soc. Div. Polym. Chem.* **15**, 660 (1974).
8. A. Cunningham, I. M. Ward, H. A. Willies, and V. Zichy, *Polymer*, **15**, 749 (1974).
9. L. D'Esposito and J. L. Koenig, *J. Polym. Sci. Polym. Phys. Ed.*, **14**, 1971 (1976).
10. G. E. McGraw, in *Polymer Characterization: Interdisciplinary Approaches*, C. D. Craver, Ed., Plenum, New York, 1971.
11. A. J. Melveger, *J. Polym. Sci. Part A-2*, **10**, 317 (1972).
12. S. K. Bahl, D. D. Cornell, F. J. Boerio, and G. E. McGraw, *J. Polym. Sci., Polym. Lett. Ed.*, **12**, 13 (1974).
13. F. J. Boerio, S. K. Bahl, and G. E. McGraw, *J. Polym. Sci. Polym. Phys. Ed.*, **14**, 1029 (1976).
14. J. Purvis and D. I. Bower, *J. Polym. Sci. Polym. Phys. Ed.*, **14**, 1461 (1976).
15. A. E. Tonelli, *J. Polym. Sci., Polym. Lett. Ed.*, **11**, 441 (1973).
16. G. M. Venkatesh, P. J. Bose, R. V. Shah, and N. E. Dweltz, *J. Appl. Polym. Sci.*, **22**, 2357 (1978).
17. G. M. Venkatesh, P. J. Bose, and R. V. Shah, *J. Appl. Polym. Sci.*, to appear.
18. G. M. Venkatesh, P. J. Bose, A. H. Khan, and G. L. Madan, *J. Appl. Polym. Sci.*, **25**, 1601 (1980).
19. E. W. Fischer and S. Fakirov, *J. Mat. Sci.*, **11**, 1041 (1976).
20. H. D. Weigmann, M. G. Scott, A. S. Ribnick, and L. Rebenfeld, *Text. Res. J.*, **46**, 574 (1976).

Received May 15, 1980

Accepted June 5, 1980