

Infrared Studies of Cryogenic Transitions in Poly(ethylene Terephthalate) and Polystyrene

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Synopsis

Infrared absorbance measurements as a function of temperature down to 13°K have been made on poly(ethylene terephthalate) and polystyrene. Transition temperatures are assigned to the temperatures where there are abrupt changes in the absorbance or integrated band intensities. Bands of known structural origin arising from either crystalline or amorphous phases are studied to probe the structure basis and environment effect for each transition. Transitions are found around 50, 120, 180, and 220°K for PET and around 50° and 235°K for polystyrene.

INTRODUCTION

Relaxation mechanisms in PET have been studied extensively. The β -peak of poly(ethylene terephthalate) (PET) was resolved by Illers and Breuer¹ into three maxima at 108°, 168°, and 200°K. The 108°K peak was attributed to the motion of the methylene groups on the basis of NMR measurements, and the other two were suggested to be due to motions of the COO groups in the presence of two different hindrance potential.¹ Recent torsional pendulum studies by Armeniades and co-workers² have confirmed the existence of these multiple transitions. They also reported the existence of two peaks at 48° and 20°K for some specimens. The peak at 48°K is reported to be accentuated by orientation, while the other peak is related to the presence of crystallinity.² Dilatometric studies by Haldon and co-workers³ also confirmed the existence of multiple β -transitions. Infrared studies by Hannon and Koenig⁴ showed that location of the β -transition varied with the degree of mechanical treatment or orientation. However, the method of data treatment could only detect a single transition for an IR band in a given temperature range. Since the vibrational modes studied are in the skeletal vibrational region where molecular motions are rather mixed, it is believed that multiple rather than single transitions should be detected for each mode. Therefore, a different approach for the data analysis is adopted in this work.

Polystyrene represents the class of polymers with pendant side groups. This polymer has also been extensively studied.⁵ The δ -peak near 50°K has been attributed to motions of the phenyl side groups, while the γ -peak

at 100–150°K and the β -peak around 300°K have been associated with motions of special main chain segments.

Despite the abundance of literature for this type of study, the structural basis for each transition in most cases is still an open question. Since infrared spectroscopy has long been established as an effective tool for probing molecular structure, it seems to be ideal for the study of structure and transition temperature correlations.

However, the use of infrared spectroscopy for these types of studies has only recently been attempted. Several authors have reported the detection of abrupt changes in the infrared absorbance in the temperature region of transitions in a variety of polymers.^{4,6,7,8} However, most of the infrared studies have been limited in temperature range. In our laboratory, Hannon and Koenig⁴ have studied PET down to liquid nitrogen temperature, and in the present work we have continued the study of PET down to 13°K by using a new cryogenic cell. Results for atactic polystyrene down to 13°K are also included in this report.

By using the coupled oscillator model, Hexter⁹ has shown that infrared absorption intensity will be greatly increased when two molecules come closer together.

When molecules are brought closer together, one would expect the intermolecular forces to play an important role in the vibrational spectrum. We may expect the derivative of the dipole moment with displacement and the resultant infrared absorption intensity to be very sensitive to changes in molecular environment.

Ovander^{10,11} has shown in two theoretical treatments that in a condensed phase the integrated band intensity and the absolute temperature should have the following linear relationship:

$$I = I_0 + \alpha T \quad (1)$$

where α , the temperature coefficient, is generally negative. This relationship has been shown to hold experimentally for some low molecular weight molecules.^{12,13}

Since thermoexpansion measurements have shown abrupt changes in the region of the transition temperatures,³ one would expect the intermolecular force field to show abrupt changes in the same region. Based on the previous analysis, it is reasonable to expect that infrared intensity should decrease with increasing temperature and show abrupt changes in the region of transition temperatures. Infrared spectroscopy also offers an unique possibility for correlating molecular structure with the transition temperatures, since it is uniquely sensitive to a particular portion of the molecule and the environmental changes in this particular structural entity.

EXPERIMENTAL

Apparatus

A simplified schematic drawing of the cryogenic cell used is shown in Figure 1. The tail section can be removed for changing the sample. The

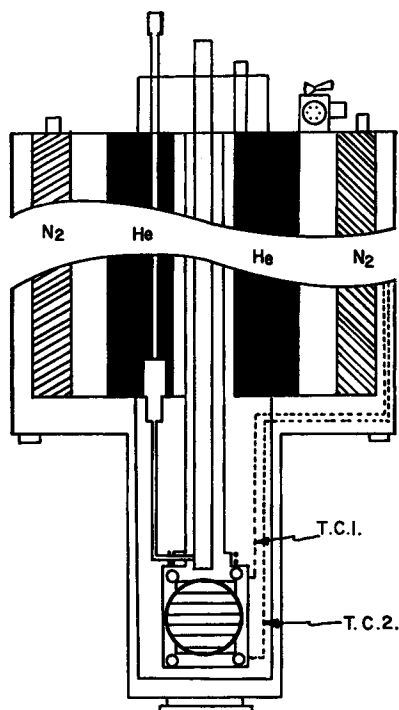


Fig. 1. Schematic drawing of the cryogenic cell used for IR studies.

sample holder is next to the cold finger. The copper screen across the sample holder is used to enhance the uniformity in temperature across the entire sample. The needle valve controls the amount of helium flowing through the capillary tube, and the rate of flow determines the temperature. The exhaust gas line is vented to the atmosphere. Two copper-Constantan thermocouples were used to measure temperatures. Both thermocouples are attached to the sample holder, one at the top and the other at the bottom, and are touching the sample film. The temperature readings are believed to be accurate to $\pm 0.5^\circ\text{K}$. A $20\text{-}\Omega$, 5-watt heating coil is used to heat the sample. A Perkin Elmer IR 521 spectrometer is used for the experiment. A Perkin Elmer DDR-2C digital data recorder with paper tape punch output is connected to the spectrometer. This allows us to record the spectra in a digitized form at any preset interval. Experiments are run between 13° and 300°K . Data are taken at every 4° or 5°K . Each band was scanned at a scanning speed of 20 cm^{-1} per minute.

Samples

PET samples were obtained from du Pont de Nemours and Company. They were run as received. The PET sample designated sample 1 is Mylar A, which was biaxially stretched and heat set at 200°C . The PET sample designated sample 2 is an amorphous sample obtained by solvent casting. Polystyrene sample was from Dow Chemical Company and designated Styron 690. It was compression molded at 150°C .

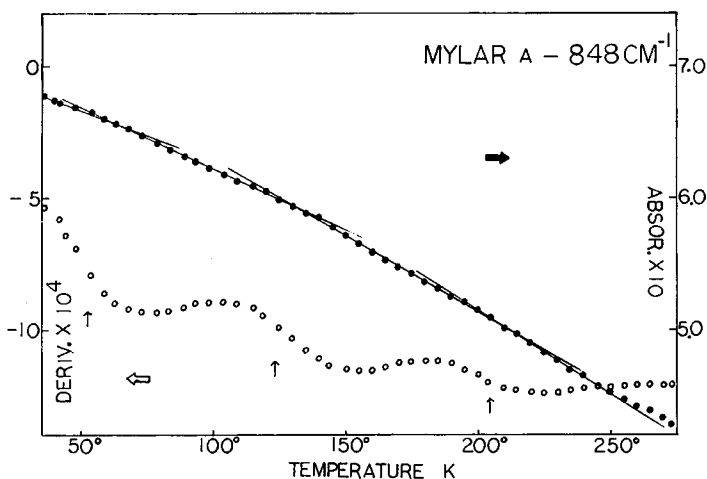


Fig. 2. Absorbance and derivative of absorbance with respect to temperature as a function of absolute temperature for 848 cm^{-1} band of Mylar A.

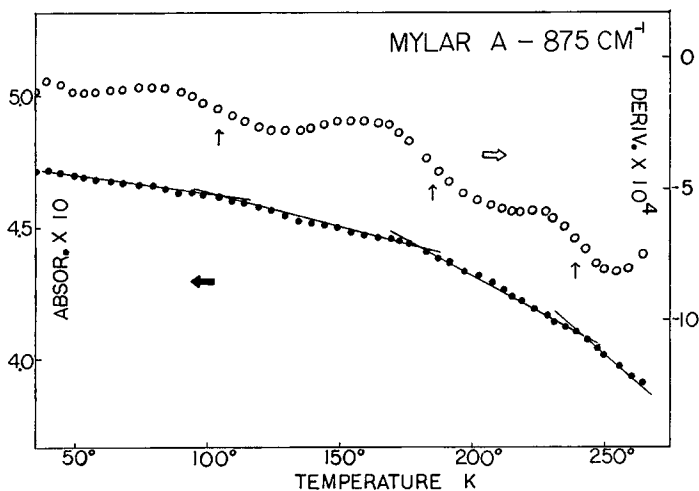


Fig. 3. Absorbance and derivative of absorbance with respect to temperature as a function of absolute temperature for 875 cm^{-1} band of Mylar A.

Data Treatment

The digitized data from the punched paper tapes are transferred to magnetic tape for computer use. The data points are then smoothed, differentiated, and interpolated to locate the exact peak and valley locations of the transmission curve. The absorbances are then calculated. We also calculated the integrated band intensity for the polystyrene experiments. The major parts of the computer programs were obtained from National Research Council of Canada. However, the programs were modified to fit

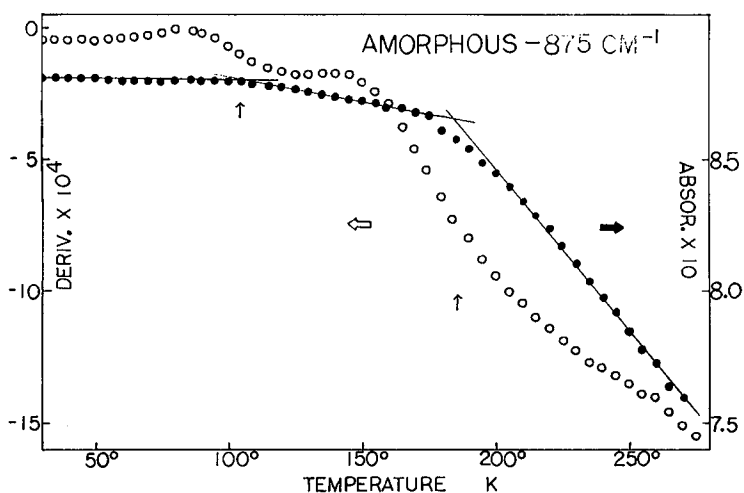


Fig. 4. Absorbance (●) and derivative of absorbance (O) with respect to temperature as a function of absolute temperature for 875 cm^{-1} band of amorphous PET.

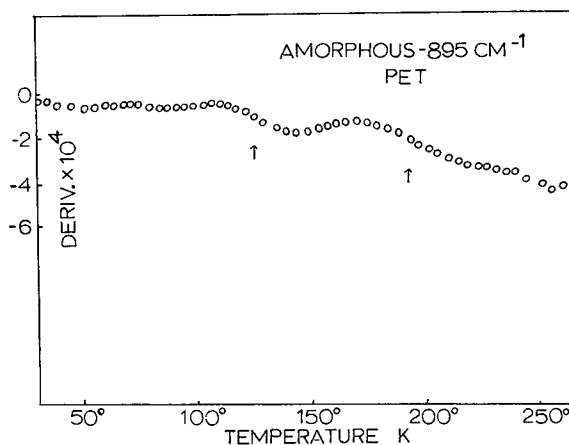


Fig. 5. Derivative of absorbance with respect to temperature as a function of absolute temperature for 895 cm^{-1} band of amorphous PET.

our particular need. Intensity data for the entire temperature range was processed with a curve-smoothing program utilizing the moving arc method. The purpose of the process was to remove random noise. The slope at each point and the error of slope¹⁴ were also calculated. The transition temperatures were assigned to the locations where there is a sudden change in intensity. These locations can be seen more clearly in the derivative curves shown in Figures 2 to 4.

RESULTS

The infrared absorption bands chosen for intensity studies are those bands with known structural and vibrational origins. The intensity and

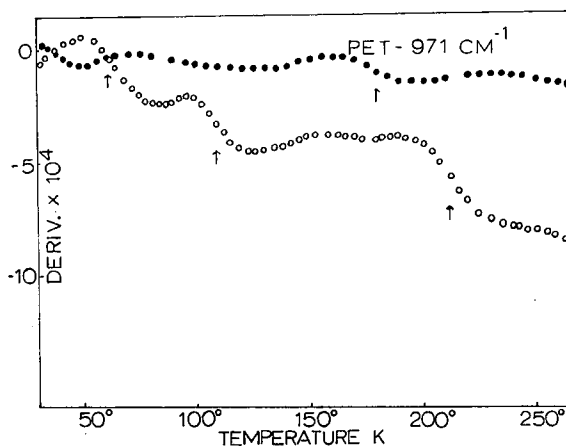


Fig. 6. Derivative of absorbance with respect to temperature as a function of absolute temperature for 971 cm^{-1} band of Mylar A (O) and amorphous PET (●).

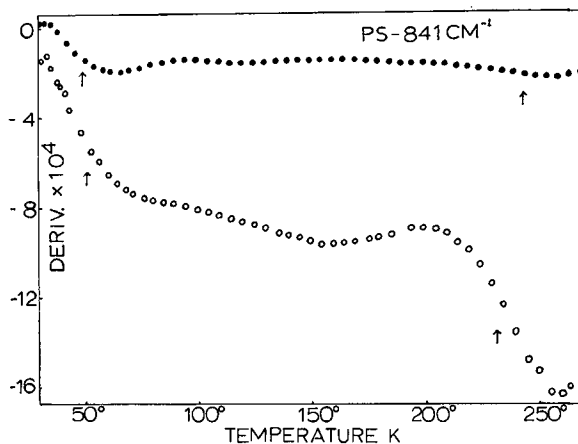


Fig. 7. Derivative of absorbance (●) and integrated band intensity (O) with respect to temperature as a function of absolute temperature for 841 cm^{-1} band of polystyrene.

derivative-versus-temperature plots for these IR bands are given in Figures 2 through 8 where each data curve has been subjected to a 9-point smoothing process. A summary of the results is given in Tables I and II. The blank spaces in the tables indicate that the IR band involved is too weak to make any intensity study, and the dashed lines indicate that no transition was detected. Results are fairly reproducible, although some of the transitions may be shifted by as much as 10° from one experiment to the other. Our results are in good agreement with those from other methods.

DISCUSSION

From Table I one can see that the transition temperature around 50°K for PET only appears in the crystalline bands. This transition is believed

to correspond to the loss peak observed by the torsional pendulum method at 48°K, which has been suggested to arise from crystal defect structures.² In view of the fact that this polymer does not have a pendant side group and that the transition occurs in the low temperature region, this assumption seems to be reasonable.

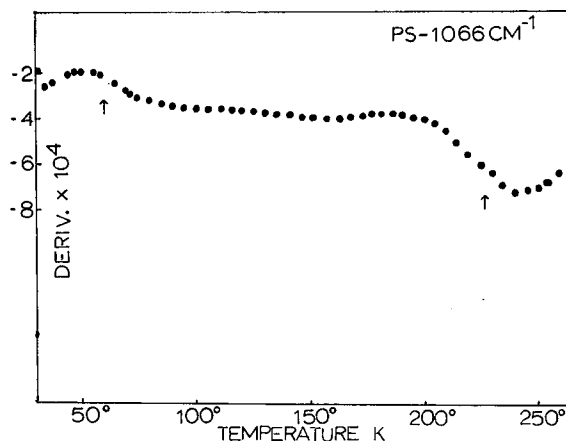


Fig. 8. Derivative of integrated band intensity with respect to temperature as a function of absolute temperature for 1066 cm^{-1} band of polystyrene.

TABLE I
Transition Temperatures Observed for PET by IR Method

Band, cm^{-1}	IR Band assignment ^{15,16,17}	Predominant phase ¹⁷	Sam-ple ^a	Transition temperatures, °K			
848	CH_2 rock (<i>trans</i>)	crystalline	1	208	—	123	50
			2				
895	CH_2 rock (<i>gauche</i>)	amorphous	1				
			2	—	195	120	—
971	C—O stretch (<i>trans</i>)	crystalline	1	214	—	110	60
			2	—	175	—	—
875	O=C—O out-of-plane bending and out-of-plane bending of H on the phenyl group	both	1	235	183	108	—
			2	—	180	105	—

^a Sample 1 = Mylar A; sample 2 = amorphous.

TABLE II
Transitional Temperatures Observed for Atactic Polystyrene by IR Method

Band, cm^{-1}	IR Band assignment ¹⁹	Transition temperatures, °K		
841	out-of-plane bending of H on phenyl group	235	—	45
1066	skeletal vibration	230	—	60

Also in Table I, the transition temperature around 120°K for PET shows up in both the crystalline and amorphous samples. NMR results¹⁸ suggest that the origin of this transition is the hindrance of the torsional motion of the methylene group. Our results from the 848 cm⁻¹ and 895 cm⁻¹ bands, which are assigned to the methylene rocking mode in the crystalline and amorphous regions, respectively, show that the methylene group is involved. However, one can also observe from Table I that this transition shows up in the results of other bands which are assigned to other types of vibrations. This may be due to the fact that these modes are mixed with the methylene vibrations.

The transition around 220°K seems to arise mainly from the crystalline phase and the transition around 180°K from the amorphous phase, as can be seen in Table I. Figures 3 and 4 show the results for the 875 cm⁻¹ band of PET. By comparing these two figures, one can see that the change in the slope for the transition at 180°K is greatly increased for the amorphous sample. This fact also indicates that the structure involved with this transition must originate in the amorphous region where the greater degree of thermoexpansion occurs. Since it was established by Miyake¹⁷ in his IR study of this compound that the *trans* conformation in ethylene glycol was favored in the crystalline phase and the *gauche* conformation in the amorphous phase, one can therefore conclude from our results that these two transitions originate from a similar type of molecular segments where the ethylene glycol group is in a different conformation.

For atactic polystyrene, the transition around 50°K has also been found by other methods.⁵ The band at 841 cm⁻¹ studied has been assigned to a hydrogen out-of-plane bending motion of the phenyl group.¹⁹ These results indicate that the δ -peak around 50°K is very likely due to the hindrance of the motion of the phenyl group.

Another transition for polystyrene around 240°K which shows up more clearly in integrated band intensity plot of Figure 7 is believed to be the β -transition found by other methods.^{5,20} The fact that it is more pronounced in the integrated band intensity plots implies that less regular structures contribute more to the transition. The less regular structures would tend to lower the transition temperature. This is actually the case, as can be seen from Figure 7. Here, the temperature shifts from 245° to about 235°K. This particular transition also appears in the change in intensity of the 1066 cm⁻¹ band which has contributions from the skeletal motion and the hydrogen in plane motion of the phenyl group.¹⁹ This transition is very likely contributed by skeletal motion. The question whether the phenyl group is involved for this transition or not cannot be answered by our results.

Our present method of data analysis depends on the validity of eq. (1). This relationship is only an approximation. This is also the case for the relationship between thermoexpansion and temperature.²¹ It is our present feeling that eq. (1) should hold except for the extremely low temperature region. Further research in the temperature and absorption intensity relationship for molecular crystals will be helpful.

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