Far infra-red absorption spectra of undeuterated and deuterated poly(ethylene terephthalate)

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An assignment of the absorption spectrum of undeuterated PET (PET-H) is reported, based on a model calculation which uses the moments of inertia of single molecular groups. In order to check this model the spectroscopic measurements were carried out with fully deuterated PET (PET-D). The model developed with PET-H allows a quantitative prediction of the frequency shifts by deuteration. The two absorption bands below 100 cm^{-1} are in good agreement with the calculation. A possible assignment of the bands at 139 cm^{-1} (PET-H) and 132 cm^{-1} (PET-D) to a conformationally-dependent vibration of the ethylene group is discussed.

INTRODUCTION

The low frequency i.r. absorption spectrum (below 200 cm^{-1}) of PET depends strongly on the degree of crystallinity of the sample studied. In *Figure 1* examples of the spectra of amorphous and partly crystallized undeuterated PET (PET–H) are shown, as reported previously by Frank and Knaupp[1]. The assignment of these low frequency spectra[1] is based on the assumption of coupled torsional vibrations of molecular groups as a whole, neglecting internal motion of single groups. The frequencies are dependent on the moments of inertia of the groups involved. As for PET–H these are the benzene ring, the COO group and the $(CH_2)_2$ group. Disregarding any special procedure of calculation it is clear that a change of the moments of inertia due to replacing H atoms by D atoms would lead to a change in the frequencies calculated. The comparison of observed absorption frequencies obtained from undeuterated and deuterated specimens would give a check for the validity of the model proposed for the assignment. In this paper results of far infra-red (*FIR*) spectroscopic studies on deuterated PET (PET–D) are compared with spectra of undeuterated samples.

ASSIGNMENT OF THE ABSORPTION SPECTRUM OF PET BELOW 200 cm^{-1}

In general, when interpreting the spectrum of a crystalline substance, the coupling amongst the skeletal vibrational modes and the internal rotational vibrations, as well as the external lattice modes have to be taken into account. However, an extremely simplified model using only the torsional vibrations of non-bonded groups in neighbouring chains coupled by van der Waals interactions is sufficient for an assignment. We will repeat briefly the basic ideas and the method of frequency calculation which are used to interpret the spectrum obtained from an amorphous specimen.

The broad absorption peak at 104 cm^{-1} is similar to that produced by pure liquid benzene and is observed in other materials containing benzene rings. This has been extensively reported by Frank *et al*[2]. Comparison of the spectra of undeuterated benzene with those of deuterated species leads to the conclusion that torsional and not translational vibrations generate this absorption behaviour. This gives a guide to finding a mechanism to explain the more complicated spectra of the partly crystallized substance.

The three absorption maxima observed in the crystallized samples become more and more intense with increasing degrees of crystallinity. Moreover, all absor-

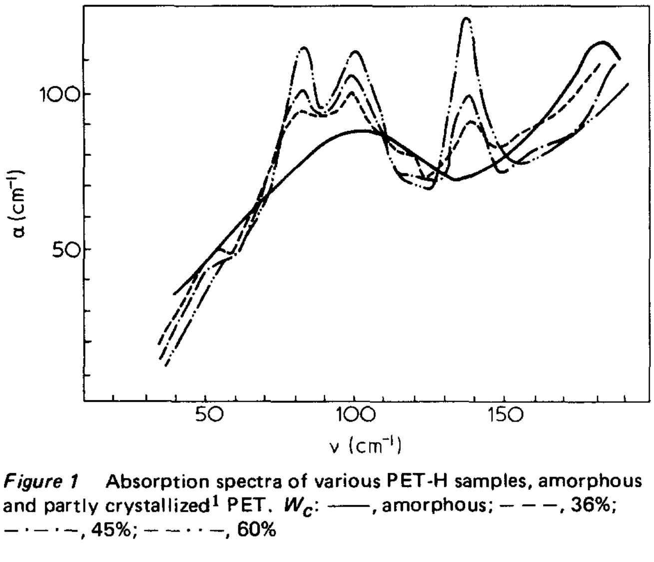

Figure 1 Absorption spectra of various PET-H samples, amorphous and partly crystallized[1] PET. W_C: ——, amorphous; — — —, 36%; — · — · —, 45%; — — · · —, 60%

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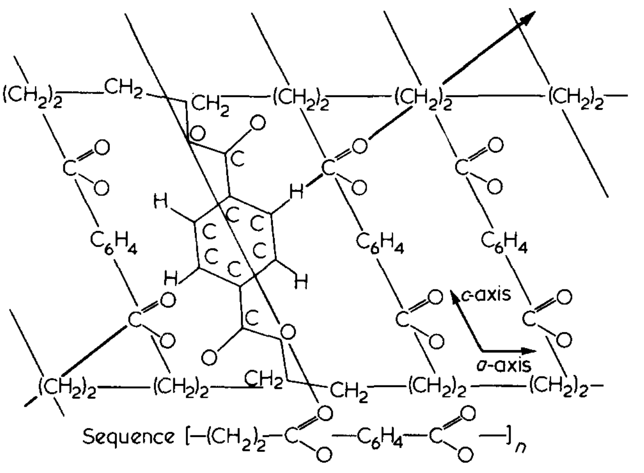


Figure 2 010 plane of the PET-H crystal lattice. Thick arrow gives the propagation direction of the torsional wave

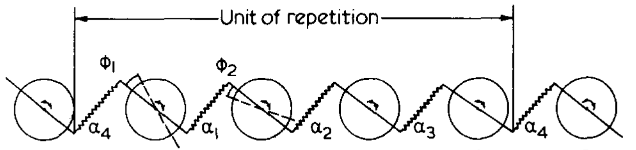


Figure 3 Linear chain of coupled rotators. Twisting elements are coupled by springs. (Axis of rotation perpendicular to the sheet). θ_i, α_i, φ_i ($i = 1 \ldots 4$) are respectively the moments of inertia, torsional constants and dislocation angles. A cyclic permutation of the indices describes the same physical state

ption maxima shift to higher frequencies when the samples are cooled down from room temperature to 12 K[9]. Thus, we can assume that the process generating this spectroscopic feature is a specific interaction within the crystalline regions only, and we can construct the following model.

The *c*-axis in the lattice is considered to be an axis of rotation around which the individual masses can perform torsional vibration (see *Figure 2*). The COO group, the benzene ring and the $(CH_2)_2$ group are taken as rotating elements. Internal motions are neglected. The moments of inertia around the rotation axis can be calculated. It is supposed that a torsion of a single element is coupled to a torsion of an element in the neighbouring chain. On the hypothesis of a cog-wheel-mechanism, a torsional wave runs through the crystal transverse to the chain as indicated. We now identify this model with a modified linear chain, where the distances between the rotating elements are constant and only the rotating angles can change. The torsional force constants will be represented as springs as shown in *Figure 3*. The equations of motion of this system are the following:

$$\begin{aligned}
\theta_1\ddot{\varphi}_1 &= -\alpha_1(\varphi_1+\varphi_2)-\alpha_4(\varphi_1+\varphi_4)\\
\theta_2\ddot{\varphi}_2 &= -\alpha_2(\varphi_2+\varphi_3)-\alpha_1(\varphi_2+\varphi_1)\\
\theta_3\ddot{\varphi}_3 &= -\alpha_3(\varphi_3+\varphi_4)-\alpha_2(\varphi_3+\varphi_2)\\
\theta_4\ddot{\varphi}_4 &= -\alpha_4(\varphi_4+\varphi_1)-\alpha_3(\varphi_4+\varphi_3)
\end{aligned}$$

θ_i ($i = 1 \ldots 4$) are the moments of inertia of molecular groups; α_i are the interaction constants represented by springs in *Figure 3*; φ_i are angles of distortion of molecular groups. Indices $i = 1$ and $i = 3$ refer to the COO group, which appears twice in the repetition unit; $i = 2$ refers to the benzene ring and $i = 4$ to the $(CH_2)_2$ groups.

The dispersion relations of this system were calculated for cyclic boundary conditions, which indicate infinitely long chains; frequencies at $k = 0$ are compared with the measured values.

The moments of inertia were calculated from the molecular geometry of the groups, and the torsional force constants taken as fitting parameters, i.e. suitable values were taken for the force constants so that the absorption frequencies both calculated and measured for undeuterated PET agreed.

The most important point is as follows. Because the coupling of neighbouring groups is given by the intermolecular interaction, we can propose that this interaction, especially in the far infra-red is essentially unchanged by deuteration of the groups involved. Thus, by deuteration we obtain a criterion for the validity of the model. Once a set of torsional force constants is determined by fitting the frequencies of the undeuterated material, there is no further free parameter for fitting the values of the deuterated sample. If the model is correct, then the frequencies of the deuterated material should be obtained directly.

EXPERIMENTAL

Sample preparation

Undeuterated samples. The material was obtained as an X-ray amorphous foil of ~100 μm thickness from Fa. Kalle, Niederlassung Hoechst AG, Wiesbaden. Samples were crystallized at 220°C with different annealing times in order to initiate crystallization with the same number of nuclei per unit volume. At the end of the annealing period they were quenched in ice water. The volume fraction of crystallinity was determined from wide-angle X-ray scattering diagrams and from density gradient measurements. The results of these two methods were found to be in good agreement and are listed in *Table 1*.

Deuterated samples. d_4-Perdeutero-terephthalic acid was prepared according to Ward and Grime[3] and Yamamoto *et al.*[4]. Deuterated ethylene glycol was a commercially available reagent from Merck AG, Darmstadt. The d_4-perdeutero-terephthalic acid was first converted to the dichloride in petrol ether using $SOCl_2$, with a yield of 61%. From this the dimethyl ester was obtained with dry CH_3OH (yield 92%) in conventional reactions. Before use all substances were characterized by proton magnetic resonance (p.m.r.) spectroscopy using a JEOL PMX 60 instrument.

The polymerization was carried out as follows. 0.02 Mole of d_4-perdeutero-terephthalic acid dimethyl ester and 0.047 mole of deutero-ethylene glycol were placed together with 6.25 mg $Ca(OOCCH_3)_2 \cdot 2H_2O$ and 1.5 mg

Table 1 Thermal history of PET films, annealing temperature T_{an} = 220°C; annealing time t_{an} and resulting degree of crystallinity W_c (%) determined by X-ray scattering

T_{an} (min)	W_c (%)
5	36
10	43
20	44
40	45
85	51
2700	60

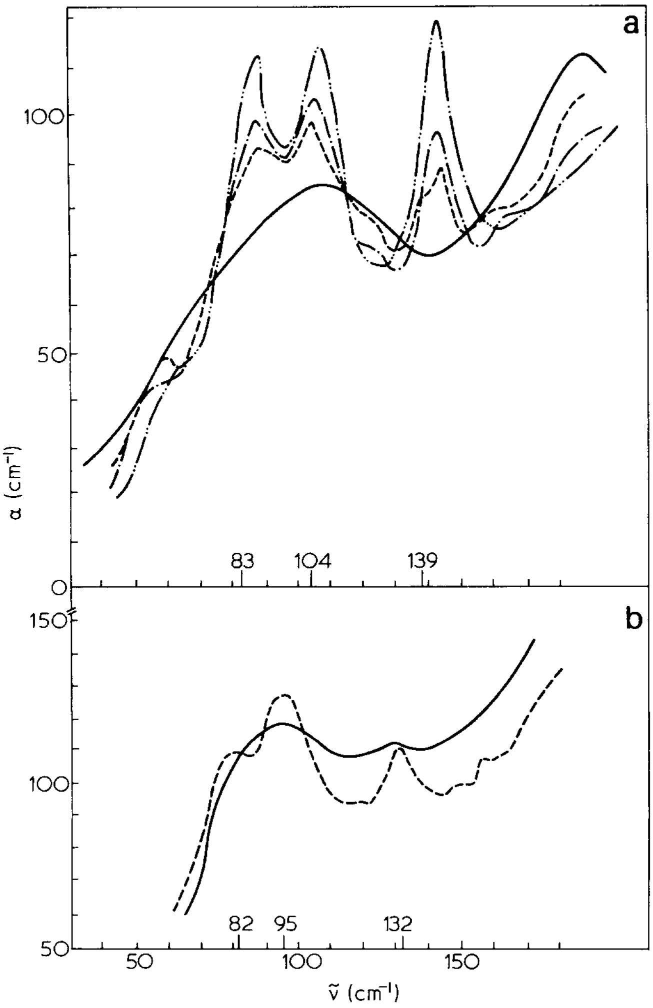


Figure 4 Comparison of the *FIR* spectra of (a) PET-H and (b) PET-D. Sample preparation see text.

(a) PET-H

	W_c
——	Amorphous
– – –	36% Crystalline
–·–·–	45% "
–··–	60% "

(b) PET-D: ——, amorphous; – – –, crystalline

Sb_2O_3 in a 100 cm^3 Schlenk tube. The material was molten at 179°C in an oil bath under a continuous flow of dry nitrogen which was directed through a capillary down to the bottom of the tube. The resulting methanol was distilled through the side arm into the tube over a period of 1 h and the temperature of the bath was raised to 197°C. After an additional 2 h it was heated up to 220°C and maintained at this temperature for 24 h. The tube was then evacuated carefully to a pressure of 0.1 torr and after raising the temperature to 280°C the mixture was kept for an additional 24 h to allow polycondensation to proceed. After the polymer had cooled to room temperature it was precipitated from a hot mixture of tetrachloroethane/phenol (40/60 wt%) by pouring into benzene. Intrinsic viscosities were determined from the above solvent mixture at 25°C, $[\eta] = 0.07$ ml mg^{-1}. The result of this procedure was a granulate which was dissolved in a 1:3 mixture of dichloromethane and trifluoroacetic acid (see d'Esposito and Koenig[5]) and carefully evaporated to prepare a foil ~200 μm thick. From its spectroscopic behaviour the sample was found to be nearly amorphous (see below). The annealing was carried out at 180°C (60 h) under vacuum because at this temperature we could be sure that the material did not become brittle. The degree of crystallinity was not determined but at this temperature after 60 h a volume percentage of at least 45% can be estimated (Zachmann[6]).

RESULTS

The absorption spectra were measured by a Beckman-RIIC Fourier spectrometer type FIR 30. *Figure 4a* shows the spectra for undeuterated samples previously reported[1]. In *Figure 4a* the new results are plotted on the same scale for an unannealed sample and a crystallized one as described above. The unannealed deuterated sample shows similar behaviour to the amorphous undeuterated one: there is only one broad peak in the region below 100 cm^{-1}, shifted to lower wavenumbers. The crystallized sample shows 3 bands, analogous to the undeuterated material. All bands shift to lower frequencies with deuteration.

DISCUSSION

In *Table 2* are shown the moments of inertia calculated for PET–H and PET–D. The sequence is the same as used in the calculation according to *Figures 2* and *3* (of course the values for the COO groups are the same in both types of sample). The last column of *Table 2* lists the interaction parameters between pairs of groups used to fit the frequencies observed for PET–H. This set has also been used in calculations on both types of material. However, it was impossible to fit the band at 139 cm^{-1} and 132 cm^{-1}, respectively. In the calculation by Frank *et al.*[1] this was included in the fit but at different ends of one frequency branch, which seems to be somewhat conjectural. Thus, we obtain only the two lowest frequencies from our calculation. This is a consequence of the restriction mentioned above. The experimental and calculated frequencies are given in *Table 3*.

Table 2 Moments of inertia around the chain axis and force constants used in the calculation of frequencies according to the sequence in *Figure 2*

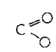
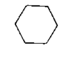
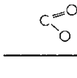
	θ_H(a.m.u. Å^2)	θ_D(a.m.u. Å^2)	α(mdyn Å/rad)
$(CH_2)_2$	15.9	24.2	
			0.15
	89.9	89.9	
			0.21
	88.6	107.0	
			0.21
	89.9	89.9	
			0.15

Table 3 Comparison of frequencies measured and calculated (cm^{-1})

PET-H		PET-D	
$\tilde{\nu}_{meas}$	$\tilde{\nu}_{calc.}$	$\tilde{\nu}_{meas}$	$\tilde{\nu}_{calc.}$
83	83	82	82
104	105	95	97
139	–	132	–

Considering the spectra of amorphous PET–H and PET–D it is clear that the shift of the broad band at 104 cm^{-1} and 93 cm^{-1}, respectively, is in good agreement with the assumption of a *torsional* vibration of the benzene ring and not with that of a translational oscillation.

For the ratio of frequencies we obtain:

$$\frac{\tilde{\nu}_D}{\tilde{\nu}_H}=\sqrt{\frac{\theta_H}{\theta_D}}$$

We compare the masses and moments of inertia of the benzene ring C_6H_6 with those of C_6D_6. The ratio of the maximum frequencies $\tilde{\nu}_D/\tilde{\nu}_H=0.912$ corresponds more closely to the square root of moments of inertia than to that of the masses:

$$(\theta_H/\theta_D)^{1/2}=0.915 \quad ; \quad (m_H/m_D)^{1/2}=0.975$$

We propose to assign the 139 cm^{-1} band to an intramolecular motion where the $(CH_2)_2$ groups move in opposite phase to the benzene ring. The condition for this motion is the *trans*-conformation of the $(CH_2)_2$ group. This is in good agreement with the observation that the integrated absorption intensity of this band depends linearly on the degree of crystallization[1] because the *trans*-conformation is an imperative condition for the crystallization of a chain segment. This agrees with the calculation of Danz, Dechant and Ruscher[7] who give an assignment on the basis of an in-plane normal coordinate analysis of a monomeric unit. It is further in agreement with the assignment of Boerio and Bahl[8] who studied the i.r. spectra of PET–H and P(Ed_4)T and PE(Td_4). For PET–H they give a similar description to Danz, but with the other materials no observation of an absorption band in this region is reported. Fully deuterated material has not been previously studied by either group of authors.

A rough estimation of the frequency shift on the basis of the molecular motion given by Danz[7] and Boerio[8] is obtained as follows. We assume that only the $(CH_2)_2$ groups oscillate whereas the rest of the molecule is fixed in space. Then we obtain for the mass relationship:

$$[(CD_2)_2/(CH_2)_2]^{1/2}=\sqrt{\frac{32}{28}}=1.07$$

For the corresponding frequencies we obtain:

$$\tilde{\nu}_H/\tilde{\nu}_D=\frac{139}{132}=1.05$$

This result supports the interpretation given above.

In *Figure 4b* a leading peak for the amorphous sample is seen at 132 cm^{-1}. This is an indication that this sample is not completely amorphous. The band at 139 cm^{-1} and 132 cm^{-1} appears to be a sensitive indicator for the onset of crystallization.

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