

Spectroscopic analysis of the structure of repeat unit of polyethylene terephthalate (PET)

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The proper use of FTIR and laser Raman to study the structure of repeat unit of polyethylene terephthalate (PET) has been presented. A normal co-ordinate analysis of crystalline poly ethylene terephthalate (PET) (*trans* form) has been carried out. A systematic set of potential constants has been computed using the method of kinetic constants on the basis of C_{2h} symmetry. The potential energy distribution confirms the correctness of the assignments made.

[**Keywords:** Polyethylene terephthalate (PET), FTIR, and Laser Raman spectra, Normal coordinate analysis

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1 Introduction

Extensive research work has been carried out on structure related physical and thermal properties^{1,2}, prediction of polyethylene terephthalate (PET) container properties from film data, effect of temperature profiles of PET containers, reinforcement of PET fibres in rubbers and other thermo-plastics^{3,4} etc., on this highly crystalline, rigid, thermoplastic polymer which is rolled as a film, groomed to a container, spun as a fibre and as a moulding material. The PET structure $(-OCH_2CH_2OOC-C_6H_4-CO)_n$ is centrosymmetric. The PET structure exists both in the *gauche* and *trans* form. It is the heating process which mainly affects the orientation of the OCH_2CH_2O group which is chiefly responsible for the crystalline and amorphous nature⁵ of PET. When the polymer is heated and annealed under at 160°C for several hours the *trans* form sets in. Rapid quenching of the molten polymer introduces irregularity in the arrangement of atoms leading to a polymer configuration in which adjacent bonds are coplanar and on the same side of the C-C double bond (Gauche confirmation) assuming an amorphous state due to the rotation of the C-C axis by 120°. It is the *trans* form PET structure which accounts for the crystalline nature⁶ of PET. Hence the structure of

elucidation of repeat unit of PET that is OCH_2CH_2O has been carried out in this paper.

2 Experimental Details

Spectroscopically pure sample of polyethylene terephthalate has been procured from Central Institute of Plastic Engineering and Technology (CIPET), Chennai, India and has been used as such as the source. The Fourier *trans* form infrared spectra were recorded in the range 4000-400 cm^{-1} using PerkinElmer spectrophotometer at Medophann, Chennai, India. The laser Raman spectrum over the region 4000 - 50 cm^{-1} has been recorded using the DILOR Z 24 Raman spectrophotometer, at Regional Sophisticated Instrumentation Centre (RSIC), IIT, Chennai, India. Both the spectra have been recorded at 330K. The frequencies of all the sharp bands are accurate to ± 1 cm^{-1} . The FTIR and Laser Raman spectra are presented in Figs 1 and 2 respectively.

3 Interpretation of the Spectra

The region in 1430-910 cm^{-1} range contains many absorption bands which are caused by the C-C, C-O stretching vibrations⁷. However this is also the region rich in bending vibration bands as there are always more bending vibrations than stretching in a molecule.

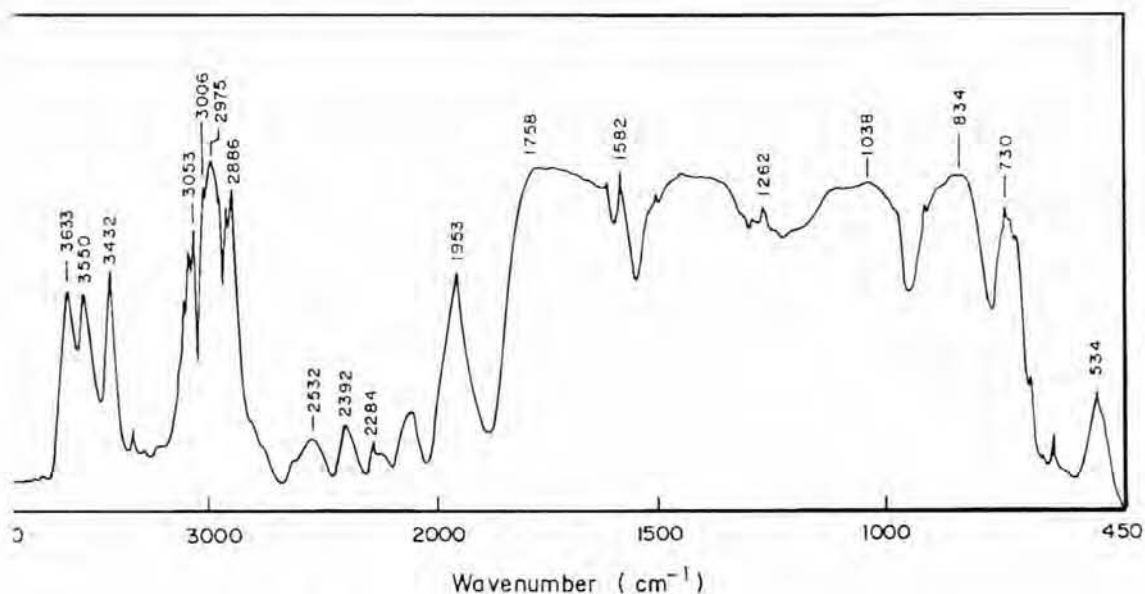


Fig. 1- FTIR spectrum of polyethylene terephthalate

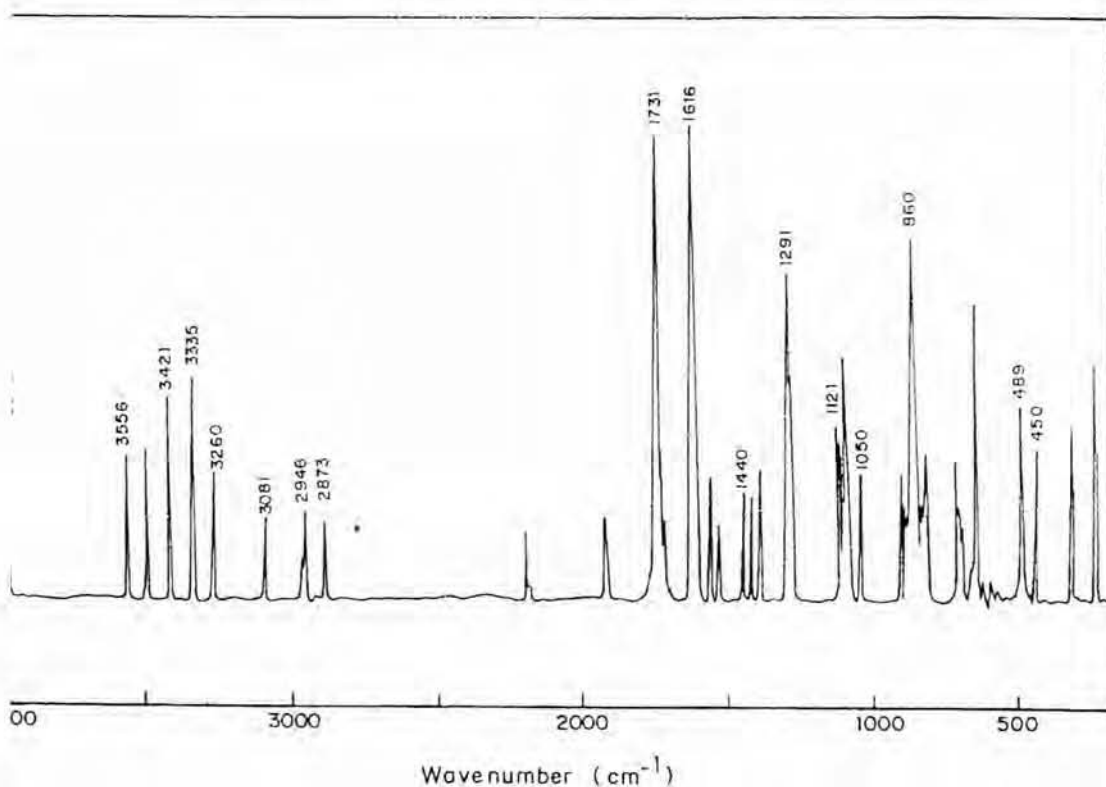


Fig. 2- Laser Raman spectrum of polyethylene terephthalate

son, this region is referred to as a fingerprint region. The infrared spectrum shows a peak at 1038 cm^{-1} attributed to the C-C stretching vibration. In the Raman spectrum of PET there is a strong broad band at 1038 cm^{-1} which means the compound certainly contains a carbonyl functional group (C=O), which is the

predominant stretching vibration of esters⁸ and C-O stretching vibration occurs at about 1064 - 1030 cm^{-1} for esters of primary alcohols and for esters of secondary alcohols⁹ it occurs at about 1100 cm^{-1} . In PET the presence of bands at 1121 cm^{-1} and 1082 cm^{-1} in laser Raman may be an indication of the dependence

Table 1— Normal modes of vibration, potential constants and PED of repeat unit of polyethylene terephthalate

Frequencies (cm ⁻¹)			Potential constant			
Fundamental			Assignment	(10 ³ N/m)		PED
mode	FTIR	Laser Raman		Initial	Final	%
$\nu_1 (A_g)$	-	2873(w)	ν_{CH_2}	5.5941	6.9800	96
$\nu_2 (A_g)$	-	1082(ms)	ν_{C-O}	6.2409	6.9996	98
$\nu_3 (A_g)$	-	707 (w)	δ_{CH}	0.8176	0.9095	99
$\nu_4 (A_g)$	-	1291 (s)	ρ_{CH_2}	0.5301	0.8281	74
$\nu_5 (A_g)$	-	1050(mw)	δ_{CCH}	0.4582	0.4973	40
$\nu_6 (A_g)$	-	408(mw)	δ_{CCO}	0.5110	0.5122	41
$\nu_7 (B_g)$	-	1440(w)	ρ_{CH_2}	0.5385	0.9843	81
$\nu_8 (B_g)$	-	1121(ms)	$\nu_{CH_2} C-O$	6.4935	7.2024	99
$\nu_9 (B_g)$	-	489(mw)	$\delta_{asy} CCO$	1.0105	1.0257	48
$\nu_{10} (A_u)$	2975(vs)	-	$\nu_{asy} CH_2$	5.6198	6.9856	97
$\nu_{11} (A_u)$	1100(s)	-	$\delta_{asy} CCH$	0.6197	0.6974	45
$\nu_{12} (A_u)$	834(vs)	-	$\delta_{asy} OCH$	0.9110	0.9192	97
$\nu_{13} (A_u)$	850(ms)	-	$\delta_{asy} OCH$	0.9110	0.9195	99
$\nu_{14} (B_u)$	3006(s)	-	$\nu C-H$	6.6198	6.9745	97
$\nu_{15} (B_u)$	3053(ms)	-	$\nu C-H$	6.6198	6.9853	97
$\nu_{16} (B_u)$	1038(ms)	-	$\nu C-C$	6.0785	6.0993	99
$\nu_{17} (B_u)$	1119(ms)	-	$\delta_{asy} CCH$	0.6197	0.7877	46
$\nu_{18} (B_u)$	730(ms)	-	$\delta_{asy} OCH$	0.8176	0.9099	98

MW- medium weak, W-weak, MS-medium strong, S-strong, VS-very strong

of the C-O asymmetric and symmetric stretching vibration on the neighbouring methylene group in the chain. Whilmhurst¹⁰ has shown that the CCO bending for similar compounds is in the region 300-500 cm⁻¹. However, bands centred at 489 and 408 cm⁻¹ of medium intensity in laser Raman are due to asymmetric and symmetric deformations, CCO. Absorption arising from C-H stretching in alkanes occurs in the general region 3050-2840 cm⁻¹. The positions¹¹ of the C-H stretching vibrations are the most stable ones in a spectrum occurring around 3050 cm⁻¹. In this polymer two pronounced peaks in FTIR of strong intensity at 3053 and 3006 cm⁻¹ are due to the asymmetric C-H stretching vibrations. The positions of the methylene group symmetric stretching (ν_{CH_2}) and asymmetric stretching ($\nu_{asy} CH_2$) occur respectively at 2886 and 2975 cm⁻¹ in FTIR and 2873 and 2946 cm⁻¹ in laser

Raman¹². The next important methylene group vibration is the bending. The alkane substituted compounds with an acyclic structure show a band at 1465 cm⁻¹ due to scissoring and the band at 1340 cm⁻¹ is due to the twisting vibration of the methylene group. Bands at 720 cm⁻¹ and those between 1350 and 1250 cm⁻¹ are generally due to the rocking, twisting and wagging vibrations of the methylene groups. Series of bands in this region are characteristic of the esters. The bands at 1440 cm⁻¹ in laser Raman of medium intensity are attributed to methylene scissoring. The sharp peak at 1291 cm⁻¹ in laser Raman is due to the CH₂ wagging¹³. The band around 1100 cm⁻¹ in FTIR has been assigned to the CCH bending by Miyake¹⁴. Krimm and Liang¹⁵ have reported the OCH symmetric and asymmetric deformation vibrations in the region 700-860 cm⁻¹ for the ethylene groups which

occur in the present compound as expected. Table I shows an analysis on the vibrational frequencies of the repeat unit of PET. Characterization, confirmation of crystalline states and their inter conversion have been made by infrared spectroscopy and absorption at 896 and 973 cm^{-1} have been assigned to the *gauche* and *trans* conformers respectively¹⁶. The intensity change at 988 cm^{-1} can be used as a measure of the extent of chain folding. An increase in intensity of the peak at 1470 and 973 cm^{-1} during crystallization process has been assigned to the *trans* ethylene glycol segments present in the crystalline region. This increased intensity may be due to the planarity of the $-\text{C}-\text{C}_6\text{H}_4-\text{C}-$ and the rejuvenation of the inversion symmetry. The decrease in intensity of the bands near 1443 and 896 cm^{-1} during crystallization process is assigned to the *gauche* ethylene glycol segments present in the amorphous region. Thus many similar mechanisms of occurrence of new bands and broadening of existing bands during crystallization have been reported by Ward and Krimm¹⁷. A necessary preliminary to the assignment of bands in the infrared and laser Raman spectra is a thorough knowledge of the number and kinds of normal modes of vibration and their structure¹⁸. Hence in the present investigation a detailed work is done on the analysis of the force constant and molecular structure of the repeat unit ($\text{OCH}_2\text{CH}_2\text{O}$) which plays a lead role in deciding the crystallinity of the compound.

4 Normal co-ordinate analysis

PET ($\text{OCH}_2\text{CH}_2\text{OOC}-\text{C}_6\text{H}_4-\text{CO}$)_n belongs to Cs symmetry. The configuration of the repeating unit of

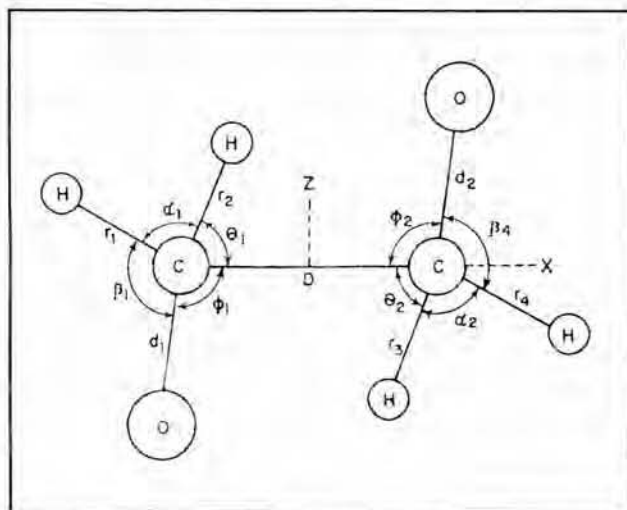


Fig. 3—Structure of polyethylene terephthalate

PET namely, $-\text{[OCH}_2\text{-CH}_2\text{O]}_n$ is identified to have C_{2h} symmetry⁸. The *trans* form of the repeat unit of PET is shown in Fig. 3. O-C-C-O atoms are assumed to lie on the XZ plane, namely the paper plane. One set of hydrogen atoms is considered below the plane of paper and the other set of hydrogen atoms above the plane of paper. The hydrogen atoms are inclined to the Y plane. Activity table for the repeating unit shows that PET has 18 fundamental modes of vibration under C_{2h} point group and can be represented as:

$$\Gamma_{\text{vib}} = 6 \text{ Ag (R)} + 3 \text{ Bg (R)} + 4 \text{ Au (IR)} + 5 \text{ Bu (IR)}.$$

Since the modes are either *g* or *u* type, the infrared and Raman activity reveal that *g* (gerade) modes are active in Raman whereas all the *u* (ungerade) modes are active in infrared. Mutual exclusion principle is operative in this molecule.

Symmetry Co-ordinates – The orthonormal set of symmetric coordinates have been constructed for in-plane and out-of-plane vibrations on the basis of the wellknown group theoretical considerations using the internal co-ordinates¹⁹. All the 18 fundamental modes of vibration are considered here and the symmetry co-ordinates are listed forthwith.

Ag species:

$$S_1 = (1/2) (\Delta r_1 + \Delta r_2 + \Delta r_3 + \Delta r_4); S_2 = (1/\sqrt{2}) (\Delta d_1 + \Delta d_2)$$

$$S_3 = (1/2) (\Delta \beta_1 + \Delta \beta_2 + \Delta \beta_3 + \Delta \beta_4); S_4 = (1/\sqrt{2}) (\Delta a_1 + \Delta a_2)$$

$$S_5 = (1/2) (\Delta \theta_1 + \Delta \theta_2 + \Delta \theta_3 + \Delta \theta_4); S_6 = (1/\sqrt{2}) (\Delta \phi_1 + \Delta \phi_2)$$

B_g species:

$$S_7 = (1/\sqrt{2}) (\Delta a_1 - \Delta a_2); S_8 = (1/\sqrt{2}) (\Delta d_1 - \Delta d_2); S_9 = (1/\sqrt{2}) (\Delta \phi_1 - \Delta \phi_2)$$

A_u species:

$$S_{10} = (1/2) (\Delta r_1 - \Delta r_2 - \Delta r_3 + \Delta r_4); S_{11} = (1/2) (\Delta \theta_1 - \Delta \theta_2 - \Delta \theta_3 + \Delta \theta_4)$$

$$S_{12} = (1/2) (\Delta \beta_1 - \Delta \beta_2 - \Delta \beta_3 + \Delta \beta_4); S_{13} = (1/2) (\Delta \beta_1 + \Delta \beta_2 - \Delta \beta_3 - \Delta \beta_4)$$

B_u species:

$$S_{14} = (1/2) (\Delta r_1 - \Delta r_2 + \Delta r_3 - \Delta r_4); S_{15} = (1/2) (\Delta r_1 + \Delta r_2 - \Delta r_3 - \Delta r_4)$$

$$S_{16} = \Delta D; S_{17} = (1/2) (\Delta \theta_1 - \Delta \theta_2 + \Delta \theta_3 - \Delta \theta_4)$$

$$S_{18} = (1/2) (\Delta \beta_1 - \Delta \beta_2 + \Delta \beta_3 - \Delta \beta_4)$$

The structural parameters used in the present work have been taken from Sutton table²⁰ of related compounds. The normal co-ordinate analysis is very useful in correlating the theoretical considerations based on the structure and nomenclature of the molecule with the qualitative analysis of the spectrum leading to the potential energy distribution which comes as a final check on the frequency assignment.

The elements of the inverse kinetic energy matrix (G) have been derived from the relation $G = B^{-1} \mu B^{-1}$ where B is the matrix formulated using the vectors which have been evaluated from the expression of the symmetry co-ordinates in terms of the Cartesian displacement co-ordinates²¹. B^{-1} is the transpose of matrix B and μ is the diagonal matrix of the reciprocal masses of the atoms in the molecule. The elucidation of the structure of many simple and complex molecules has been carried out successfully by many researchers by using the method of kinetic constants for solving the secular equation. The method of kinetic constants²² relates the off diagonal elements of the F matrix to the diagonal elements through the relation $F_{ij}/F_{jj} = K_{ij}/K_{jj}$ ($i < j$; $i, j = 1, 2, 3, 4, \dots$). The knowledge of the transformation matrix (L) and the kinetic energy matrix (K) leads to the solution of the secular equation due to Wilson²³ yielding the elements of the force constant matrix (F). This is done by fixing an initial value of force constant²⁴ which has been chosen from the work on related molecules. This set of force constant has been subsequently refined by giving step increments and iterations till convergence takes place^{25,26}. The frequency assignment is henceforth verified by evaluating the PED using the relation $\% \text{ PED} = F_{ij} L_{ij} / \lambda_j$, where PED is the contribution of the symmetry co-ordinate to the potential energy of the vibration whose frequency is ν_i . F_{ij} is the force constant, L_{ij} is the matrix element and $\lambda_j = 4 \pi^2 C^2 \nu_j^2$. The infrared and Raman frequency assignments, the initial and final values of force constants and PED for the 18 fundamental modes of vibration of repeating unit of PET are presented in Table 1.

5 Conclusion

A satisfactory vibrational band assignment has been made available for polyethylene terephthalate

through infrared and Raman spectral measurements. A systematic set of potential constants has been computed using the method of kinetic constants on the basis of C_{2h} symmetry. To check whether the chosen set of symmetric co-ordinates contributes maximum to the potential energy associated with the normal co-ordinates of the molecules, the potential energy distribution has been carried out. The potential energy distribution for all the methyl and methylene stretching and bending modes were found to be especially very satisfactory.

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