Conformational structure of poly(ethylene terephthalate). Infra-red, Raman and n.m.r. spectra

J. Štokr, B. Schneider, D. Doskočilová and J. Lövy
Institute of Macromolecular Chemistry, Czechoslovak Academy of Sciences, 162 06 *Prague* 6, *Czechoslovakia*

and P. Sedláček
Chemopetrol, k.p. Silon, 391 11 *Planá nad Lužnicí, Czechoslovakia*
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Infra-red and Raman spectra of unoriented samples of poly(ethylene terephthalate) in the crystalline and amorphous states and in solution were measured. The dissolved polymer was also studied by n.m.r. spectra. Digital separation of the vibrational spectra of amorphous and crystalline components made possible the detection of some new bands, the interpretation of which is presented. By comparison with the vibrational spectra of model compounds combined with analysis of n.m.r. spectra, the conformational forms present in the amorphous and liquid states of poly(ethylene terephthalate) were characterized and their populations were determined. Bands in vibrational spectra which are characteristic of various conformational forms were defined.

Keywords Spectroscopy; infra-red; Raman; poly(ethylene terephthalate); conformational structure; crystalline state; amorphous state

INTRODUCTION

Vibrational spectra of poly(ethylene terephthalate) (PET) have been studied in a number of papers[1-19]. In the crystalline state where PET is present in an almost planar form according to X-ray diffraction analysis[20], vibrational spectra have been interpreted based on a force-field calculation[9,18,19]. From infra-red spectra it was found that in the amorphous state PET has a *gauche* structure of the ethyleneglycol fragment[6,8,12-14,16], contrary to the crystalline state where the ethyleneglycol fragment of PET has a *trans* structure[20]. All major changes which are observed upon transition from the crystalline to the amorphous state, have been attributed to this conformational change[1,2,5-7]. Krimm[3,4] has expressed the assumption that some changes in infra-red spectra which are observed upon transition from the crystalline to the amorphous state may be caused by the loss of the centre of symmetry on the benzene ring which takes place in the amorphous state. Bands in amorphous and crystalline PET have been assigned to various vibrational modes[2,8,12] and bands characteristic of the crystalline and of the amorphous states have been defined. N.m.r. spectra have so far not been used in studies of the conformational structure of PET.

In our preceding studies[21-23] we have been able to characterize, by means of vibrational and n.m.r. spectra, the conformational structure of methyl benzoate, dimethyl terephthalate, ethyl benzoate, diethyl terephthalate and ethyleneglycol dibenzoate in the crystalline and liquid states of these molecules. These measurements have shown that in the most stable crystalline state all these models have a completely planar structure, and that in the liquid and glassy states there appear additional conformers generated by rotation about the bonds C_{ar}–CO or CO–O, O–CH_2 and CH_2–CH_2; for all these conformers, frequencies of characteristic bands in vibrational spectra have been found. In this paper, the results of the model compound studies are used for the characterization of the conformational forms existing in amorphous and liquid PET, and for the assignment of the corresponding vibrational spectra. As besides conformational structure, the vibrational spectra of PET are also strongly affected by orientation, infra-red and Raman spectra of completely unoriented samples have been newly measured.

EXPERIMENTAL

Sample preparation

All samples for spectral measurements were prepared from commercially polymerized PET. The powdered sample for the measurement of infra-red spectra was prepared from the dispersion which was formed by cooling of the solution of PET granules in 6-caprolactam melt[24]. The resulting sample was extracted with water until the content of 6-caprolactam in the PET powder dropped below 0.1%. The obtained PET powder consisted of particles of diameter <6 μm; the crystallinity determined by X-ray was 50–55% and the number-average molecular weight M_n was $\sim 11 \times 10^3$. The sample for the measurement of Raman spectra was prepared by spontaneous effusion of PET melt at 290°C from the reactor into an ice–water bath at 0°C. The resulting sample had the shape of a string of 3 mm diameter; its crystallinity as determined from density was within 0–1% and the number-average molecular weight M_n was

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$\sim 18 \times 10^3$. The sample for the measurement of n.m.r. spectra was prepared by melt spinning in a laboratory apparatus; its number-average molecular weight M_n was 16.5×10^3. For the measurement of solution spectra, PET was dissolved in a mixture of phenol and 1,1,2,2-tetrachloroethane in the ratio 1:3 v/w.

Infra-red spectra were measured on the infra-red spectrometer Perkin-Elmer 580 B connected with a multichannel analyser TN-4000 (Tracor Northern). The powdered sample was measured by the KBr pellet technique. Infra-red spectra of amorphous PET were obtained so that the pellet with the powdered sample was heated to ~290°C, quenched in liquid nitrogen, reground and pressed. The spectrum of dissolved PET was obtained by digital subtraction of the solvent spectrum.

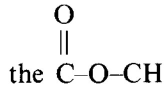
Raman spectra were measured on the spectrometer Coderg LRDH-800 connected with the computer system TN-11 (Tracor Northern). Spectra were excited by the line 514.5 nm of the argon laser CR 3 of Coherent Co. Spectra were measured in the 90° arrangement. The amorphous sample prepared for the measurement of Raman spectra in the form of a string, was quite transparent. The spectra of this sample measured at various orientations differed a little. In order to remove this effect which indicated a partial orientation of the sample, the surface of the sample was roughened. After this treatment the spectra measured in different orientations were identical. However, the resulting spectra were very weak and for obtaining good quality spectra, about 30 accumulations were necessary. Samples of medium crystallinity were obtained by heating the amorphous sample to 180°C for one hour. Spectra of these samples did not show any effects of orientation, and good spectra could be obtained after 3 accumulations. In accumulating spectra of dissolved PET a programme permitting automatic subtraction of the solvent spectrum after each scan was used. All Raman spectra discussed in this paper were once smoothed by a digital three-point binomial filter.

^{13}C n.m.r. spectra were measured with 10% w/v solutions of PET in the mixture of phenol with 1,1,2,2-tetrachloroethane-d_2 (1:3 v/w) using the spectrometer Varian XL-200 at 50 MHz and 70°C. The carbonyl band was measured with a digital resolution of 0.2 Hz (a) with selective decoupling of the aromatic and aliphatic protons of PET ($\gamma H_2 = 250$ Hz), (b) with noise decoupling of the protons, and (c) with gated decoupling yielding the fully coupled spectrum and preserving the NOE enhancement.

RESULTS AND DISCUSSION

Conformational forms of PET and their symbols

The possible conformational forms of PET are expected to be analogous to forms found in the studied model compounds of PET. Measurements of infra-red and Raman spectra of dimethyl terephthalate[21] and of diethyl terephthalate[22] have shown that in the crystalline state the ester groups of these molecules are always in a mutual *trans* orientation T_B; in the liquid state, forms with a mutual *cis* orientation of ester groups C_B (*Figure 1*) are also present. The populations of the T_B and C_B forms in the liquid state are comparable. In vibrational spectra of liquid methyl benzoate and dimethyl benzoate[21] weak bands have been found indicating that small amounts of forms with a non-planar structure of the benzyl ester group may also occur; they could be generated either by rotation about the C_{ar}–CO or about the CO–OCH$_3$ bond.

Analysis of infra-red, Raman and n.m.r. spectra of model compounds containing the  $\overset{\overset{\displaystyle O}{\|}}{C}-O-CH_2-C$ group (ethyl benzoate[22], diethyl terephthalate[22], ethyleneglycol dibenzoate[23]) has shown that in the liquid state all these compounds contain both the form with a *trans* structure of this group (t) (*Figure 1*), and the two equienergetic mirror image forms with the CH$_2$–C bond twisted out of the plane of the ester group by rotation about the O–CH$_2$ bond; these forms are designated as *gauche* (g) (*Figure 1*). From analysis of n.m.r. spectra the population of the *trans* form (p_t) and of both *gauche* forms (p_g) in ethyl benzoate and in diethyl terephthalate is $p_t = 0.71 \pm 0.04$, $p_g = 0.29 \pm 0.04$, and in ethyleneglycol dibenzoate $p_t = 0.83 \pm 0.03$, $p_g = 0.17 \pm 0.03$. In liquid ethyleneglycol dibenzoate, the ethyleneglycol fragment exists predominantly in the form of the two equienergetic mirror image *gauche* forms designated as G (*Figure 1*). From n.m.r. analysis the population of both G forms at room temperature is $p_G = 0.915$, and the population of the *trans* form (T) in the liquid state is only $p_T = 0.085$. From these data it follows[23] that ethyleneglycol dibenzoate in solution at room temperature contains predominantly the structure tGt (~63%), a considerable amount of the structure tGg (~26%), a small amount of the structure tTt (~6%), and a few per cent of the structures gGg and tTg; the content of the structure gTg is quite negligible.

Using the above introduced symbols, PET in the crystalline state has the tTt conformational structure with a mutual *trans* orientation (T_B) of ester groups.

N.m.r. spectra

The determination of the conformational structure on the bonds O–CH$_2$ and CH$_2$–CH$_2$ of PET in solution from n.m.r. spectra is more difficult than for the model compounds, mainly because of larger line width and consequently poorer resolution, even at elevated temperature. However, for the determination of the structure of the ethyleneglycol fragment, use could be made of band intensities in infra-red spectra (as will be shown further in detail), from which it followed that amorphous PET contains about 10% and PET in solution about 7% of the tTt form.

For the determination of the conformational structure on the O–CH$_2$ bond of PET we have tried to apply a

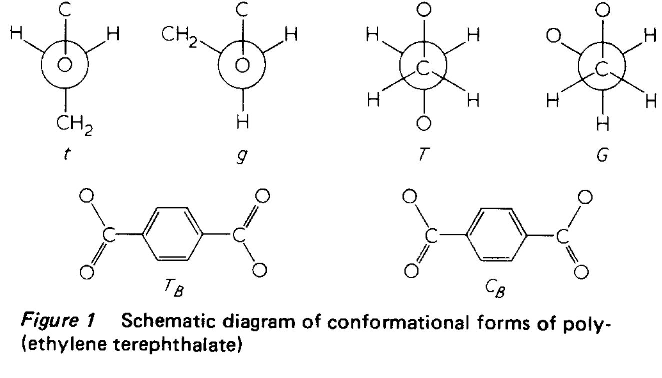


Figure 1 Schematic diagram of conformational forms of poly(ethylene terephthalate)

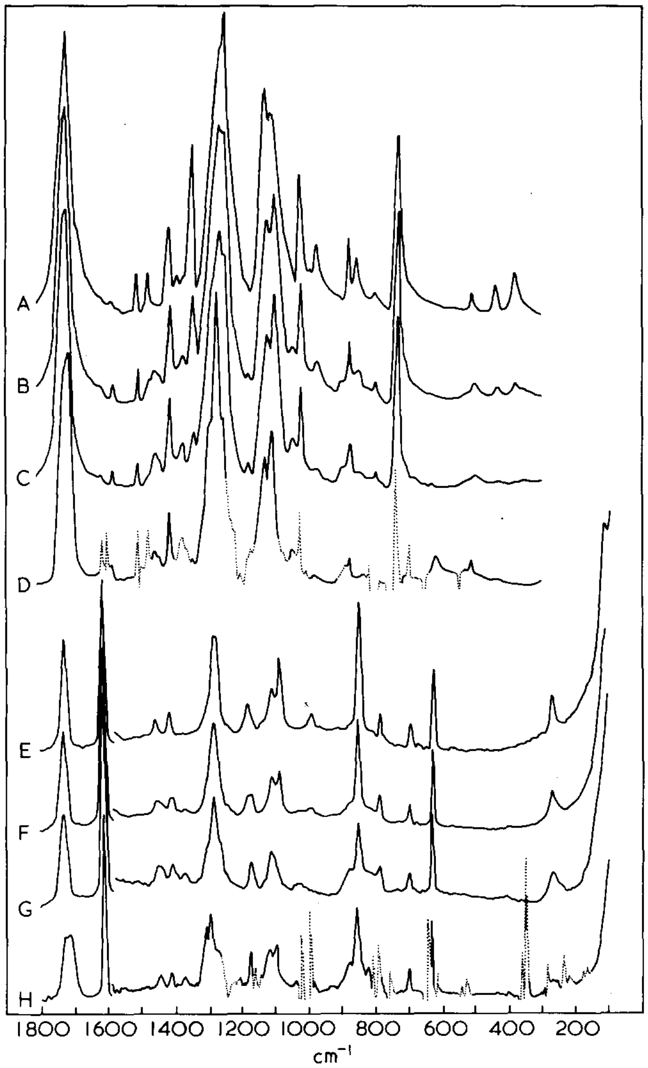


Figure 2 Vibrational spectra of poly(ethylene terephthalate). Infra-red spectra: (A) crystalline, (B) semicrystalline, (C) amorphous, (D) solution. Raman spectra: (E) crystalline, (F) semicrystalline, (G) amorphous, (H) solution. Dotted parts of the spectra indicate solvent bands

similar procedure as that used in our previous communications[22,23] for ethyl benzoate and ethyleneglycol dibenzoate, using the $^3J_{CH}$ coupling constant obtained by analysis of the carbonyl band in ^{13}C n.m.r. spectra measured with selective heteronuclear decoupling of the aromatic protons. Contrary to the model compounds, the ^{13}CO band of PET did not exhibit any fine structure in the present case. The value of $^3J_{CH}$ was determined by comparison of the experimentally measured width of the ^{13}CO band with the width of the simulated band of the AA'A''A'''X system (where X corresponds to ^{13}CO and AA'A''A''' to protons of the ethylene fragment). As mentioned above, the content of *tTt* forms in liquid PET is practically equal as in ethyleneglycol dibenzoate. As the shape of the ^{13}CO bands depends very little on the population of the *T* and *G* forms, in the present band-shape simulation the same values of interproton coupling constants within the ethylene fragment were used as those found and applied in the analysis of the ethyleneglycol dibenzoate spectra[23]. The found value of the $^3J_{CH}$ constant was corrected for the effect of the irradiating field similarly as in our preceding communications[22,23]. The corrected value of $^3J_{CH}$ was 3.0–2.6 Hz, for the considered widths of a singlet line within 2.5–4.0 Hz (the value 2.5 Hz corresponds to the width of the ^{13}CO band in a noise decoupled spectrum). By a calculation similar to our preceding communications[22,23], the corrected value of $^3J_{CH}$ yields $p_t = 0.74 \pm 0.07$. The accuracy of this result is lower than in the case of ethyleneglycol dibenzoate due to the lack of reliable information about the width of singlet lines in the ^{13}CO multiplet of PET in solution. In spite of that it is evident that even for PET, the *trans* conformation on the O–CH_2 bond strongly predominates. The value of p_t for PET is probably slightly lower than for ethyleneglycol dibenzoate, and nearer to the value found for ethyl benzoate, but the differences are not beyond experimental error.

Infra-red and Raman spectra

Infra-red and Raman spectra of crystalline, semicrystalline and amorphous PET, and of PET dissolved in the mixture of phenol and 1,1,2,2-tetrachloroethane are shown in *Figure 2*. The spectra of semicrystalline and amorphous PET and of PET in solution are directly measured spectra. The spectrum of crystalline PET was obtained by digital subtraction of the spectrum of amorphous PET from the spectrum of semicrystalline PET. In infra-red and Raman spectra obtained in this way we have detected some bands which have not been described previously for unoriented PET in the crystalline or amorphous states. This concerns the band at 1086 cm^{-1} in infra-red spectra of crystalline PET, and the bands at 1582, 975, 683 and 415 cm^{-1} in Raman spectra of crystalline PET. We have compared the character and the experimental wavenumber values of the vibrational bands of PET with wavenumber values and assignment to vibrational modes as calculated for the planar form of PET by Boerio *et al.*[19]. Based on this comparison we have refined the interpretation of some vibrational bands of the *tTt* form of PET as shown in *Table 1*.

From *Table 1* it is seen that the bands in vibrational spectra of PET can be divided into four groups: I–bands the intensity of which practically does not change upon transition from crystalline to amorphous state or solution; II–bands appearing only in infra-red and Raman spectra of crystalline PET, and bands the intensity of which is significantly higher in spectra of crystalline samples than in the spectra of amorphous or liquid samples (*Table 2*); III–bands appearing only in infra-red and Raman spectra of amorphous and liquid PET, and bands the intensity of which is significantly higher in spectra of amorphous or liquid samples than in the spectra of crystalline samples (*Table 3*); IV–bands which appear both in the infra-red and Raman spectra of amorphous or liquid PET, but which appear either only in the infra-red, or only in the Raman spectra of crystalline PET (*Table 4*).

The same classification can also be applied to vibrational bands of model compounds of PET, in which conformationally sensitive bands have been assigned to various types of conformational structures based on the comparison of vibrational spectra of various crystalline forms and of amorphous and liquid samples, and on analysis of n.m.r. spectra of liquid samples.

Bands of type I evidently correspond to vibrations

Table 1 Interpretation of infra-red and Raman spectra of poly(ethylene terephthalate). The symbol PED stands for 'potential energy distribution'

ν (cm^{-1}) This work						ν (cm^{-1}) Taken from ref. 19				
I.r.			Raman			I.r.	Raman	Calc.	Sym-metry	PED
Cryst.	Amorph.	Solution	Cryst.	Amorph.	Solution	Semicryst.		*tTt*		
			1729	1728	1724 1714		1730	1733	A$_g$	S(90)
1718	1725	1721 1711				1727		1721	B$_u$	S(93)
1684*			1690*							
		1647*								
1616	1616	1608†	1616	1616	1616		1615	1606	A$_g$	T(74), ϕ(25)
1580*	1580	1581	1582	1580	1580	—		1576	A$_g$	T(82), ϕ(13)
	1554*	1556*								
1526	1531*	1530*								
1507	1506	1504				1504		1504	B$_u$	ϕ(54), T(39)
1473	1479*	1475†				1475		1465	B$_u$	ψ'(62), α'(35)
			1463	1469*			1462	1452	A$_g$	ψ'(58), α'(44)
1458*	1456	1456		1455	1449					
1442*	1443			1443	1445					
			1419				1418	1395	A$_g$	β(62), α'(28)
1412	1412	1412		1412	1414	1410		1407	B$_u$	T(46), ϕ(39)
					1407*					
1387										
1370*	1374	1374†		1374	1375					
		1363†								
1343	1342	1341*				1337		1334	B$_u$	β(55), α'(41)
		1309*	1308	1308	1312†		1310	1316	A$_g$	ϕ(71)
								1293	B$_u$	T(138)
	1287	1286*	1288	1288	1288*		1295	1273	A$_g$	T(37), t_1(32), ϕ(18), θ(18)
			1281				—	1285	B$_g$	α'(62), β(48)
1265	1266	1266		1270	1273	1263		1254	B$_u$	t_1(50), T'(38), θ(23)
1248	1248	1250		1250*	~†			1271	A$_u$	α'(94)
			1187							
1178*	1176	1177†		1178	1180		1192	1178	A$_g$	ϕ(72), T(15)
			—				—	1174	B$_g$	β(43), α'(39)
	1139	1138*								
1126	1122	1125				1126		1126	B$_u$	Ω(26), t_1(26), ϕ(19), T(12)
			1120	1119	1124		1119	1118	A$_g$	t_1(38), r(35), γ'(15)
1112*										
1102	1101*	1102		1103*	1105*			1109	B$_u$	ϕ(56), T(33)
			1097				1096	1100	A$_g$	T(31), r(28), t_1(10)
1086*										
1043*	1043	1043								
				1031	1030*†					
1023										
1019	1018	1019†		1018*			1018	1019	B$_u$	Ω(37), T(28), ϕ(27)
			998	997*			1000	1002	A$_g$	t_2(80), r(20)
988						—		991	A$_u$	μ_2(126)
			975*				—	972	B$_g$	μ_2(136)
971	975	977				973		971	B$_u$	t_2(89)
	935*				935*					
901*	898	900*†								
			885*	886	887					
						875		871	A$_u$	μ_2(81), M(24), Z(15)
873	875	875				—		868	B$_u$	t_1(29), υ(23), θ(14)
							—	859	B$_g$	μ_2(114)
	857*		858	859	861		857	844	A$_g$	T(27), t_1(15), θ(12), T'(11), r(10)
849	842	847*				837		837	A$_u$	β(97)
		840*†								
			828	830	827†					
	811*	~†		810						
793	794	~†	795	795	797†		800	799	B$_g$	Z(48), μ_3(48), M(40)
775*	780*	776*†								
727	728	731†		732	734*	727		723	A$_u$	μ_3(60), μ_2(43)
705*	705	709*	703	703	704		701	693	A$_g$	Ω(36), θ(22), T'(14)
	680	682*†	683	683	~†		—	673	B$_g$	Z(86), μ_3(39)
667										
632*	633	636*†	632	633	633		626	628	A$_g$	Ω(60), ϕ(15)
		619		617*						
							—	559	A$_g$	γ(37), Φ(22)
524*	532	530*†		530*						
507	500	510		498*					B$_u$	T'(37), θ(19)
461*						—		470	A$_u$	Z(89), M(79)
437	429*	424*		430*		438		459	B$_u$	υ(31), γ(27), θ(16)
—						430		411	A$_u$	Z(135)
			415*	408*			—	373	A$_g$	γ'(23), Φ(21), Ω(10)
378	388*			385*		382		384	B$_u$	γ(29), γ'(18), θ(17)
	340									
	300									
	270*		280	270	265		278	282	A$_g$	θ(33), Φ(28), υ(21)
				235*						
				215*						
			121					119	B$_g$	τ_3

* Poorly defined bands

† Wavenumbers may be affected by solvent bands

Table 2 Bands of type II of poly(ethylene terephthalate) (PET), and analogous bands of ethyleneglycol dibenzoate (EDB)

PET ν (cm^{-1})		EDB ν (cm^{-1})	
I.r.	Raman	I.r.	Raman
1684*†	1690*†		
1473		1482	
	1463		1473
	1419		1418
1387†			
1343		1341	
	1281		
1248			
	1187		1184
1126			
1112*†			
	1097		1099
1086*†			
1023†			
	998		
988			
	975*		
971		981	
849		859	
667†			
507			
461*			
437			
	415*		408
		405	
378			
	280		291
	121		

All bands of PET shown in this Table are characteristic of the *tTt* forms in the crystalline state

* Poorly defined bands

† Bands which have not been assigned to calculated vibrational modes

which are not appreciably affected by conformational structure or crystallinity of PET.

Bands of type II may be either characteristic of the *tTt* conformational structure of PET, or they may be connected with the ordering of PET molecules in crystalline domains. In *Table 2* the infra-red and Raman lines of PET can be divided into two groups. The first of these contains bands and lines which correspond to those calculated by Boerio *et al.*[15] for the planar structure of PET. When bands of this type can be observed in vibrational spectra of liquid and amorphous samples, they are shifted by 1–7 cm^{-1} with respect to their positions in the crystalline state. As all these lines are sensitive to conformational and therefore also to geometrical structure of the monomeric unit, these shifts indicate that the geometrical structure of the *tTt* form of PET in the amorphous state differs somewhat from the structure in the crystalline state.

From infra-red spectra of amorphous and crystalline PET which were normalized to equal intensities of conformationally insensitive bands, the content of the *tTt* form was estimated from the factor necessary for digital subtraction of the crystalline from the amorphous component of the spectrum, yielding 10±3% of *tTt*. An analogous procedure yielded 7±3% of *tTt* form in the solution of PET.

The other group of vibrational bands of type II, marked in *Table 2* by the index †, contains those bands which cannot be assigned to any calculated mode of the *tTt* structure, and which can be observed only in the spectra of crystalline samples as weak or very weak bands. These bands can correspond either to harmonic or combination vibrations, or they may be connected with the ordering of PET molecules in crystalline domains. In this category has been included also the band at 988 cm^{-1} which, due to its behaviour, is thought to be in connection with regular folding of the polymer chain[10], even though aromatic hydrogen coordinates predominate in its vibrational interpretation as seen from *Table 1*.

Table 3 summarizes bands of group III which appear in spectra of amorphous and liquid samples of PET and which are absent from vibrational spectra of crystalline PET, and also analogous bands of liquid ethyleneglycol dibenzoate which are absent from vibrational spectra of the crystalline form with the planar structure of this model compound. From this *Table* and from *Figure 2* it can be seen that many bands characteristic of the amorphous and liquid state of PET agree by wavenumbers, intensity and activity in infra-red and Raman spectra with the bands of liquid ethyleneglycol dibenzoate. All bands of ethyleneglycol dibenzoate appearing upon dissolution of crystals with the *tTt* structure, correspond to the *G* form of the ethyleneglycol fragment, and in some cases it was possible to differentiate bands of the *Gg* and *Gt* conformational forms.

From the analogy between the vibrational spectra of ethyleneglycol dibenzoate and PET, all bands of PET shown in *Table 3* (with the exception of the band at 530 cm^{-1}) can be assigned to the *G* conformational form of the ethyleneglycol fragment, and it can also be assumed that the bands of PET which appear at equal wavenumbers as the bands of the *Gg* and *Gt* forms of ethyleneglycol dibenzoate, are also in vibrational spectra of PET characteristic of these forms. This classification of bands is given in *Table 3*.

The band appearing in infra-red and Raman spectra of amorphous and liquid PET at 530 cm^{-1} might, in

Table 3 Bands of type III of poly(ethylene terephthalate) (PET) and analogous bands of ethyleneglycol dibenzoate (EDB)

PET ν (cm^{-1})		EDB ν (cm^{-1})	
I.r.	Raman	I.r.	Raman
1554[a]			
1456[c]	1455[c]	1461	1463
1443[d]	1443[d]	1438	1440
	1412[c]		1416
	1407[asd]		1404
1374	1374	1370	1370
1139			
1043[c]		1046	1040
	1031		
935[a]	935[as]		
898		899	
	886	882	884
	830		
811[ad]	810[d]	816	813
619[a]	617[a]		
532	530[a]	522	522
	408[a]		
340[d]		335	335
300			
	235		
	215		

All bands of PET shown in this Table are characteristic of *G* conformational structures

[a] Poorly defined bands

[s] Bands appearing only in solution

[c] Bands corresponding probably to *Gt* forms

[d] Bands corresponding probably to *Gg* forms

Table 4 Vibrational bands of type IV of PET, and analogous bands of ethyleneglycol dibenzoate (EDB), diethyl terephthalate (DET) and dimethyl terephthalate (DMT)

PET ν (cm^{-1})				EDB ν (cm^{-1})				DET ν (cm^{-1})				DMT ν (cm^{-1})			
I.r.		Raman		I.r.		Raman		I.r.		Raman		I.r.		Raman	
Cryst.	Amorph.	Cryst.	Amorph.	Cryst.	Liquid	Cryst.	Liquid	Cryst.	Liquid	Cryst.	Liquid	Cryst.	Liquid	Cryst.	Liquid
1616^{ax}	1616^{e}	1616	1616					1615^{a}	1615	1614	1614	—	1616	1616	1616
1580^{ax}	1580^{e}	1582	1580					1577^{a}	1579	1578	1579	—	1577	1577	1576
1412	1412	—	1412^{e}					1411	1410	—	1410	1409	1410	—	1409
—	1287	1288	1288												
1265	1266	—	1270^{c}												
1248	1248	—	1250^{ac}												
1178^{a}	1176^{e}	1187	1178					—	1174^{a}	1170	1174	—	1178^{a}	1174	1174
				1120	1114	—	1114								
												1116	1116	—	1113
1102	1101^{a}	—	1103^{ae}												
				—	1097	1099	1095								
1019	1019	—	1018^{ae}									—	965^{a}	959	960
—	857	858	859									—	837	841	836
												817	812	—	812
								—	795	793	794	—	796	796	794
727	728	—	732					727	731	—	732	731	731	—	730
705^{ax}	705	703	703					—	704	705	704	—	704	705	704
—	680	683	683												
632^{ax}	633^{e}	632	633					—	633	634	633	—	633	633	633
507	500	—	498^{ac}												
				481	489	—	487								
437	429^{a}	—	430^{ac}												
								406	405	—	406				
378	388^{a}	—	385^{ac}												
								365	367	—	367				
				353	350	—	353								
												—	350	351	348
												323	322	—	327
—	270^{ac}	280	270	—	280	291	278								

Activity of all the bands of PET shown in this Table is affected by centres of symmetry

[a] Poorly defined bands

[e] Bands characteristic of the C_B structures

[c] Bands characteristic of *G* structures

[x] Band is evidently due to incomplete compensation of the amorphous component in experimental spectra of the crystalline sample

analogy with the vibrational spectra of model compounds, indicate a small amount of the conformational form with the plane of the ester group twisted out of the plane of the benzene ring.

Bands of type IV are summarized in *Table 4*. These bands have the property that at the wavenumber of a conformationally sensitive band in infra-red spectra, a conformationally insensitive band is found in Raman spectra, and *vice versa*. This indicates that the conformational isomers corresponding to these wavenumbers in the spectra of liquid and amorphous PET differ from the *tTt* conformational form present in the crystalline state by the activity of bands in infra-red and Raman spectra, while the vibrational interactions, and therefore also the position of the bands, remains the same as in the *tTt* conformation.

Bands of this type are also observed in vibrational spectra of model compounds[21–23]. In dimethyl terephthalate and diethyl terephthalate, these bands are sensitive to the mutual *cis–trans* isomerism of ester groups (C_B–T_B), due to the presence of the centre of symmetry in the centre of the benzene ring in T_B isomers, and to its absence in C_B isomers. Type IV bands of PET, with wavenumbers coinciding with those C_B isomers of dimethyl terephthalate and diethyl terephthalate, can also in PET be assigned to C_B isomers, and this assignment is shown in *Table 4*. This structural interpretation is in agreement with the assignment of these bands to vibrational modes (*Table 1*) in which coordinates of C and H atoms of the benzene ring predominate. All bands of the C_B isomer are very weak and therefore it is difficult to make an estimate of the population of this conformer in amorphous and liquid PET. As the ratio of the intensities of bands characteristic of the form C_B to the intensities of conformationally insensitive bands in amorphous and liquid PET is approximately equal as in DMT and DET, it may be assumed that similarly as in the model compounds, the population of the T_B and C_B conformers is approximately equal both in liquid and in amorphous PET.

Bands of type IV are also observed in ethyleneglycol dibenzoate. In crystalline ethyleneglycol dibenzoate these bands occur at 1120, 481 and 353 cm^{-1} in infra-red spectra, and at 1099 and 391 cm^{-1} in Raman spectra. In this case the described behaviour of these bands is due to the presence of the centre of symmetry in the ethyleneglycol fragment in the planar structure of the crystalline state, and by the loss of this centre of symmetry in the liquid state where practically only nonplanar conformers are present. As the loss of the centre of symmetry manifested in infra-red spectra of liquid samples of ethyleneglycol dibenzoate is almost exclusively connected with the occurrence of *G* conformational forms (the content of *tTg* and *gTg* forms is very small), the Raman bands at 1114, 487 and 353 cm^{-1} and the infra-red bands at 1097 and 280 cm^{-1} in liquid ethyleneglycol dibenzoate may be described as bands characteristic of the *G* conformational forms.

In vibrational spectra of PET, those bands of group IV which are assigned to vibrational modes in which coordinates of the ethyleneglycol fragment predominate, should be evidently interpreted as bands sensitive to the loss of symmetry on the ethyleneglycol fragment. Consideration of the population of various conformational forms of PET in the liquid and amorphous states indicates that, similarly as in ethyleneglycol dibenzoate, the bands appearing in infra-red and Raman spectra of liquid and amorphous samples in consequence of the loss of the centre of symmetry on the ethyleneglycol fragment, are bands characteristic of the occurrence of *G* forms. This interpretation is indicated in *Table 4*.

In *Table 4* are also included Raman bands at 1018 and 1103 cm^{-1} which are interpreted as characteristic of the occurrence of C_B isomers, and bands at 385, 430, 498, 1250 and 1270 cm^{-1}, which are interpreted as characteristic of the occurrence of *G* isomers, even though these bands have no analogy in vibrational spectra of model compounds. This classification has been adopted only on the basis of the vibrational interpretation of these bands (*Table 1*) and is not unequivocal.

In addition, *Table 4* also contains bands for which, even on the basis of vibrational interpretation, a decision about their connection with T_B–C_B isomerism, or occurrence of *G* forms cannot be made.

CONCLUSIONS

Bands of infra-red and Raman spectra characteristic of the various conformational forms appearing in amorphous and liquid poly(ethylene terephthalate) (PET) are summarized in *Tables 2–4*. It was found that most of these bands also appear in vibrational spectra of liquid samples of model compounds (methyl benzoate, dimethyl terephthalate, ethyl benzoate, diethyl terephthalate and ethyleneglycol dibenzoate).

The relative intensities of conformationally sensitive and conformationally insensitive bands in vibrational spectra of PET indicate that the contents of the *tTt* form in the solution of PET (7%) is equal within experimental error to the contents of this form in liquid ethyleneglycol dibenzoate; evidently also for the T_B–C_B conformers differing by mutual orientation of the carbonyl groups on the benzene ring, the population of these conformers in amorphous and liquid PET is similar as in the model compounds (DMT, DET) where the population of these conformers in the liquid state is comparable. In vibrational spectra of PET in solution, bands of *gG* and *tG* forms can be identified, similarly as in vibrational spectra of liquid ethyleneglycol dibenzoate.

Analysis of ^{13}C n.m.r. spectra of PET in solution has shown that the population of the *t* conformational forms ($p_t = 0.74 \pm 0.07\%$) and *g* conformational forms is equal, within experimental error, as in ethyl benzoate. Based on these results it may be assumed that the population of the basic conformational forms of PET in the liquid state is approximately equal as in the model compounds, with approximately 63% of form *tGt*, 26% of form *tGg*, and 7% of form *tTt*. The populations of the other conformational forms (*gGg*, *tGg*, *gTg*) are very low.

The vibrational spectra of amorphous PET indicate that the conformational structure of the amorphous state does not significantly differ from the conformational structure of PET in solution.

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