

Infrared Spectra of High Polymers

Part IX. Polyethylene Terephthalate

C. Y. LIANG* AND S. KRIMM

*Harrison M. Randall Laboratory of Physics, University of
Michigan, Ann Arbor, Michigan*

Infrared spectra of polyethylene terephthalate and three of its deuterated analogs have been obtained in the region of 70 to 3600 cm^{-1} , polarized spectra having been obtained down to 330 cm^{-1} . On the basis of analysis of the predicted spectrum, and with the aid of data from benzene and substituted benzenes, a complete assignment of the spectrum has been made. This assignment suggests a modification of the proposed chain structure of this polymer. It also leads to the conclusion that the changes in the spectrum which occur upon crystallization of the polymer are not associated with different isomeric forms of the $-\text{OCH}_2\text{CH}_2\text{O}-$ portion of the chain, but rather with changes in the symmetry and resonance characteristics of the substituted benzenoid ring framework.

INTRODUCTION

The infrared spectrum of polyethylene terephthalate, $(-\text{OCH}_2\text{CH}_2\text{OOC}_6\text{H}_4\text{CO}-)_n$, has been the subject of fairly extensive investigation. Early efforts (1) were concerned with obtaining the polarized spectrum in the region above 700 cm^{-1} , and with the interpretation (2) of some of its salient features. Extension of the spectral region down to about 100 cm^{-1} was undertaken (3) in order to permit a more complete analysis. The first attempt at making an assignment of bands in the infrared spectrum was due to Miller and Willis (4), who investigated the region of 700 to 1800 cm^{-1} with polarized radiation and oriented samples. The 2600- to 3600- cm^{-1} region was subsequently studied (5). While a deeper understanding of the spectrum was achieved, a complete and satisfactory set of assignments did not emerge from this work. Subsequent efforts were concentrated mainly on elucidating the changes occurring in the spectrum as a result of crystallization. Cobbs and Burton (6) presented spectra indicating pronounced enhancement of absorption at 1340 and 972 cm^{-1} upon crystallization of the polymer, as well as smaller changes in some of the other bands. This was

* Present address: Research and Development Division, American Viscose Corporation, Marcus Hook, Pennsylvania.

confirmed by Miller and Willis (7), who also pointed out that some bands are to be specifically associated with the amorphous phase. The elucidation of the structure of crystalline polyethylene terephthalate by Daubeny *et al.* (8) provided a means for understanding a possible basis for these changes. Ward (9, 10) suggested that they arise as a result of rotational isomerism in the $-\text{OCH}_2 \cdot \text{CH}_2\text{O}-$ portion of the chain, bands at 1470, 1340, 975, and 850 cm^{-1} being attributable to the trans configuration of the CH_2 groups in the crystalline regions, while bands at 1445, 1370, 1045, and 900 cm^{-1} are to be associated with the gauche configuration of the CH_2 groups which is presumably to be found in the amorphous regions. This interpretation appeared to receive confirmation from work on linear and cyclic oligomers of polyethylene terephthalate (10, 11). Although end group assignments have been made (12), and preliminary reports on the assignments of several of the polymer modes have appeared (13, 14), the first attempt at a detailed assignment in terms of some of the normal modes of the molecule was due to Tobin (15). Despite this thorough study, many aspects of the interpretation of the spectrum remained uncertain.

That ambiguities of interpretation and assignment still exist is not surprising, since the polyethylene terephthalate spectrum is one of the most complex yet submitted to a detailed analysis. The simplifications of a factor group analysis (16-18) are not very helpful because of the large number of atoms in the unit cell. In order to assist in making assignments we have, in addition to obtaining far infrared and polarization data, obtained the spectra of various deuterated species of polyethylene terephthalate. A preliminary report on the latter has already appeared (19). In this paper we wish to examine this and other data in an effort to make a complete assignment of the spectrum.

EXPERIMENTAL RESULTS

The techniques used in the present work have been described in a previous paper (17). The film samples of normal and deuterated polyethylene terephthalate were supplied to us by E. I. du Pont de Nemours and Company. Orientation was introduced by stretching or rolling. The spectra of the various polymers are shown in Figs. 1 to 4. The numbers adjacent to the curves represent specimen thickness in inches. In the polarized spectra between 330 and 3600 cm^{-1} , the solid curve represents absorption with the electric vector perpendicular to the orientation direction and the broken curve that with the electric vector parallel to this direction. Bands are designated σ or π according as the maximum absorption occurs with perpendicular or parallel polarized light, respectively.

The frequency, relative intensity, polarization, and crystalline or amorphous origin (based on the change in intensity of the band upon crystallization) of the bands in polyethylene terephthalate are listed in Table I. The assignments given in Table I will be discussed in more detail below. In Tables II to IV are

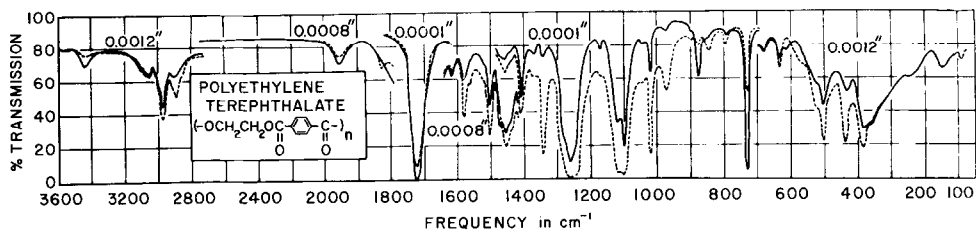


FIG. 1. Infrared spectrum of polyethylene terephthalate.

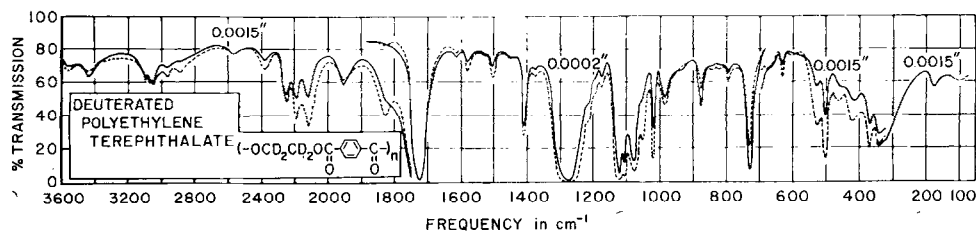
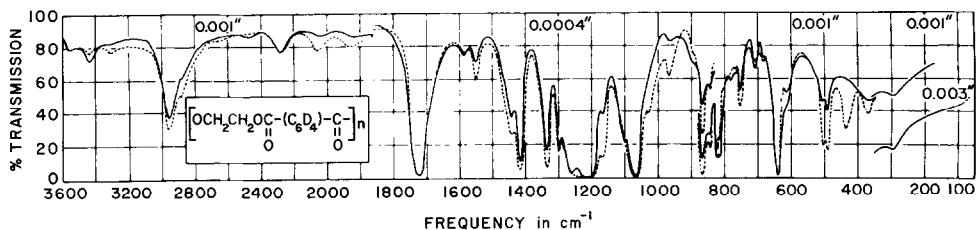
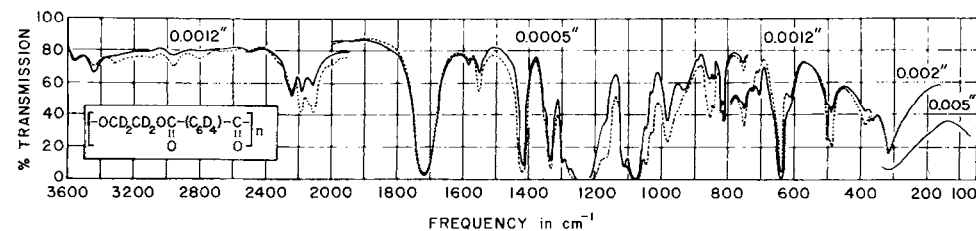
FIG. 2. Infrared spectrum of polyethylene- D_4 terephthalate.FIG. 3. Infrared spectrum of polyethylene terephthalate- D_4 .FIG. 4. Infrared spectrum of polyethylene- D_4 terephthalate- D_4 .

TABLE I
INFRARED SPECTRUM OF POLYETHYLENE TEREPHTHALATE

Frequency, cm ⁻¹	R. I.	Polarization	Assignment*
~95	vw		Skeletal (?)
145	w		$\nu_{10B}(B_{3g})$ (?)
250	vw		$\nu_{18B}(B_{3u})$
355	w	σ (?)	$\gamma_r(\text{C=O})$
383 (c)†	m	π	$\delta(\text{COC})$
430	w	σ	$\nu_{16B}(B_{1u})$
437 (c)	m	π	$\delta(\text{CCO})$
502 (a)	m	π	$\gamma_w(\text{C=O})$
525 (a)	w	π (?)	$\nu_{6A}(A_1)$
575	vw	π	$\nu_{10B}(B_{3g}:145) + \nu_{16B}(B_{1u}:430) = 575(B_{2u})$
613 (a)	vw	σ	$\nu_{6B}(B_1)$
633 (c)	w	π	$\nu_{18B} + \delta(\text{COC}) = 633$
680 (a)	vw	σ (?)	$\nu_4(B_2)$
727 } 733 }	s	σ	$\nu_{11}(B_{1u})$
796 (a)	w	π	$\left\{ \begin{array}{l} \gamma_r(\text{C=O}) + \delta(\text{CCO}) = 792 \\ \nu_{16B} + \delta(\text{COC}) = 813 \end{array} \right.$
845 (c)	w	π	$\gamma_r(\text{CH}_2)$
875	m	σ	$\nu_{17B}(B_{1u})$
898 (a)	vw	π (?)	$\delta(\text{COC}) + \gamma_w(\text{C=O}) = 885$ (?)
973 (c)	m	π	$\nu_{12}(B_{2u})$
1020	s	π	$\nu_{18A}(B_{2u})$
1043 (a)	w	—	$\nu(\text{CC})$ (?)
1100 (a)	s	π	$\left\{ \begin{array}{l} \nu_{15}(B_{3u}) \\ \nu(\text{O—C}) \text{ (amorphous)} \\ \nu(\text{O—C}) \text{ (crystalline)} \end{array} \right.$
1120 (c)	s	π	$\nu(\text{O—C}) \text{ (crystalline)}$
1172 (a)	w	π (?)	$\nu_{9A}(A_1)$
1245 } 1263 } 1280 }	vw } vs } vw }	π	$\left\ \begin{array}{l} \\ \nu(\text{C—O}) \end{array} \right.$
1343 (c)	s	π	$\nu_{13}(B_{2u})$
1370 (a)	w	π (?)	$\left\{ \begin{array}{l} \nu_2'(A_1) \text{ (?)} \\ \nu_5(B_{3g}:978) + \nu_{16A}(A_u:404) = 1382(B_{3u}) \\ \nu_5(B_{3g}:978) + \nu_{16B}(B_{1u}:430) = 1408(B_{2u}) \end{array} \right.$
1410	s	π	$\nu_5(B_{3g}:978) + \nu_{16B}(B_{1u}:430) = 1408(B_{2u})$
1435	vw	π (?)	
1455 (a?)	m	π	$\delta(\text{CH}_2)$
1473 (c)	w	σ	$\left\{ \begin{array}{l} \nu_{19B}(B_{3u}) \\ \delta(\text{CH}_2) \text{ (?)} \end{array} \right.$
1504	mw	π	$\nu_{19A}(B_{2u})$
1563	vw	—	$\nu(\text{O—C}) + \delta(\text{CCO}) = 1557$
1580 (a?)	mw	π	$\nu_{8A}(A_1)$
1617 (a)	w	σ	$\nu_{3B}(B_1)$
1724	vs	σ	$\nu(\text{C=O})$
1830	w	π	$\nu_{10A}(B_{2g}:853) + \nu_{17A}(A_u:977) = 1830(B_{2u})$
1955	mw	σ	$\nu_{17A}(A_u:977) + \nu_5(B_{3g}:978) = 1955(B_{3u})$
2852	vw	π (?)	
2890	vw	π (?)	

TABLE I—Continued

Frequency, cm^{-1}	R. I.	Polarization	Assignment*
2908	m	π	$\nu_s(\text{CH}_2)$
2970	ms	π	$\nu_a(\text{CH}_2)$
3012 (c)	vw	π	
3055 (c)	w	π	$\nu'_{20A}(B_{2u})$
3068	w	σ	$\nu(\text{C=O}) + \nu'_{13}(B_{2u}) = 3067 (?)$
3082	w	σ	$\nu_{20B}(B_{3u})$
3100	w	σ	
3130	vw	—	
3440	w	σ	$2 \times \nu(\text{C=O}) = 3448$
3560	w	π	$\nu(\text{OH})$ (end groups)

* ν = stretching, δ = bending, γ_w = wagging, γ_r = rocking.

† (a) = amorphous, (c) = crystalline (data from Refs. 6, 7, 15, and 19).

TABLE II
INFRARED SPECTRUM OF POLYETHYLENE- D_4 TEREPHTHALATE

Frequency, cm^{-1}	R. I.	Polarization	Frequency, cm^{-1}	R. I.	Polarization
~100	vw?		1196	vw	—
177	w		1218	vw	—
315	vw		1275	vs	π
340	m	π	1375	w	$\pi(?)$
370	m	π	1408	s	π
415 } 423 }	mw	π	1450	vw	$\pi(?)$
464	w	π	1504	mw	π
502	m	π	1526	vw	—
528	w	$\pi(?)$	1581	mw	π
603	vw	$\pi(?)$	1613	w	σ
633	w	π	1724	vs	σ
678	vw	$\pi(?)$	1828	w	π
728 } (734) }	s	σ	1955	mw	σ
795	w	π	2118	m	π
825	vw	π	2190	m	π
844	vw	π	2247	mw	σ
875	m	σ	2380	w	π
937	vw	σ	2570	w	$\sigma(?)$
984	m	π	2890	vw	π
1019	s	π	2965	vw	π
1052	mw	π	3055	vw	$\pi(?)$
1076	ms	π	3066	vw	$\sigma(?)$
1106	s	π	3075	vw	$\sigma(?)$
1122	s	π	3100	vw	σ
1174	w	$\sigma(?)$	3335	vw	π
			3440	w	σ
			3560	w	π

TABLE III
INFRARED SPECTRUM OF POLYETHYLENE TEREPHTHALATE- D_4

Frequency, cm ⁻¹	R. I.	Polarization	Frequency, cm ⁻¹	R. I.	Polarization
297	w		1166	w	—
370	mw	π	1215	vs	$\pi(?)$
437	m	π	1260	s	$\sigma(?)$
490	m	π	1300	m	σ
503	m	π	1335	s	π
615	w	π	1416	s	π
640	s	σ	1443	m	π
684	vw	$\pi(?)$	1551	m	π
707	w	σ	1586	w	σ
754	mw	π	1724	vs	$\sigma(?)$
768	vvw	—	1928	}	π
781	vw	σ	1918		
803	vvw	—	2060		
816	mw	σ	2045	w	π
823	m	σ	2280	w	—
844	mw	π	2472	vw	σ
867	ms	π	2648	vw	π
898	vw	—	2890	vw	$\pi(?)$
967	m	π	2960	m	π
1032	vw	π	3320	vw	π
1068	vs	π	3440	w	σ
1102	vw	σ	3560	w	$\pi(?)$

listed the frequency, relative intensity, and polarization of the bands in the various deuterated polyethylene terephthalates.

PREDICTED SPECTRUM OF POLYETHYLENE TEREPHTHALATE

1. STRUCTURE OF POLYETHYLENE TEREPHTHALATE

A necessary preliminary to the assignment of bands in the infrared spectrum is a knowledge of the number and kinds of normal modes and their expected activity. This analysis must be based on a definite molecular structure, so we turn first to a consideration of the structure of polyethylene terephthalate.

As we noted earlier, the crystal structure of this polymer has been determined from an x-ray diffraction analysis (8). The molecules are thought to be centrosymmetric, and their arrangement in the triclinic cell of the crystal is shown in Fig. 5. The molecule is nearly planar and practically fully extended. Departures from planarity arise as a result of the COO group being about 12° out of the plane of the benzene ring, and from a rotation of the CH₂—CH₂ bond (around the O—CH₂ bond as axis) of about 20° from the planar configuration. From the

TABLE IV
INFRARED SPECTRUM OF POLYETHYLENE- D_4 TEREPHTHALATE- D_4

Frequency, cm^{-1}	R. I.	Polarization	Frequency, cm^{-1}	R. I.	Polarization
317	ms		1277	m	—
365	vw		1300	m	σ
386	w	π	1335	s	π
490	m	π	1340	vw	—
502	m	π	1355	vw	π
615	w	π	1416	s	π
640	s	σ	1551	w	π
707	w	σ	1586	w	σ
728	vw	—	1718	vs	$\sigma(?)$
754	mw	π	1996	vw	π
763	vvw	—	2118	m	π
804	vvw	—	2130	vw	$\pi(?)$
816	m	σ	2190	m	π
823	m	σ	2247	mw	σ
844	mw	π	2280	vw	σ
855	m	π	2340	vw	π
894	vw	σ	2472	vw	σ
935	w	σ	2648	vw	π
982	m	π	2800	vw	π
1030	w	—	2965	vw	π
1045	mw	π	3100	vw	$\pi(?)$
1076	vs	π	3320	vw	π
1112	s	$\sigma(?)$	3440	w	σ
1166	w	$\pi(?)$	3560	w	π
1235	vs	π			

coordinates of the atoms it is possible to compute the orientation of various portions of the molecule with respect to the fiber axis. Some of these are given in Table V. The consistency between the spectrum and this structure, and the inferences from the spectrum concerning other possible structures, will be considered later.

2. NORMAL MODES UNDER THE FACTOR GROUP

On the basis of the structure of polyethylene terephthalate described above, the factor group (\mathcal{G}), or unit cell group (\mathcal{G}_1), of the space group $P\bar{1}$ is isomorphic to C_i . Because of the low symmetry of this group (the only element of symmetry being a center), the factor group analysis is not very helpful in interpreting the spectrum. It merely tells us that the mutual exclusion rule applies, and that therefore half of the normal modes of the molecule will be infrared active. In order to achieve an analysis of the spectrum we must therefore turn to a consideration of the local symmetries of portions of the molecule. This ap-

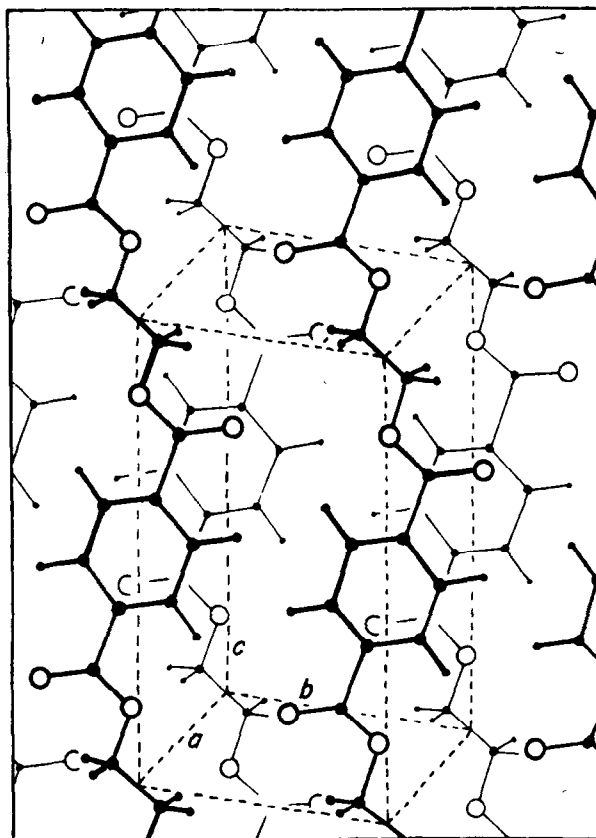


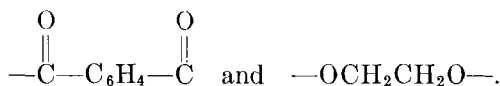
FIG. 5. Crystal structure of polyethylene terephthalate [after Daubeny *et al.* (8)].

TABLE V
ORIENTATION OF GROUPS IN POLYETHYLENE TEREPHTHALATE
MOLECULE WITH RESPECT TO FIBER AXIS^a

Direction within group	Angle with fiber axis
H—H axis of a CH ₂ group	77°
Twofold axis of a CH ₂ group	71°
—CH ₂ —CH ₂ — bond	57°
$\begin{array}{l} \diagdown \\ \text{C}=\text{O} \text{ bond} \\ \diagup \end{array}$	76°
$\begin{array}{l} \parallel \\ -\text{C}-\text{O}- \text{ bond} \end{array}$	47°
—O—CH ₂ — bond	19°
<i>Para</i> axis of benzene ring	24°

^a Calculated from structure of Daubeny *et al.* (8).

proximate method for treating the spectra of high polymers has been discussed (18) and satisfactorily applied (22). In the next paragraphs we will therefore consider the spectrum as determined by the following groups:



3. NORMAL MODES OF $\begin{array}{c} \text{O} \qquad \qquad \text{O} \\ \parallel \qquad \qquad \parallel \\ -\text{C}-\text{C}_6\text{H}_4-\text{C}- \end{array}$

The modes of this group will be considered in terms of motions in which the O atoms move with respect to a rigid C—C₆H₄—C framework, and those in which the C=O group moves as a unit. The former modes contribute six normal vibrations, of which (if we assume a center of symmetry) three are infrared active. These involve essentially the stretching of the C=O bond, $\nu(\text{C}=\text{O})$, and the deformation modes in which the O moves parallel, $\gamma_w(\text{C}=\text{O})$, and perpendicular, $\gamma_r(\text{C}=\text{O})$, to the plane of the benzene ring. (We assume the C—C₆H₄—C framework to be planar, even though the structure determination (8) indicates a slight departure from planarity.) Their polarizations in an oriented specimen are predicted (14) to be (see Table V) σ , π , and σ , respectively.

If we assume the presence of a center of symmetry, the C—C₆H₄—C framework will have the symmetry V_h . We choose the axis through the *para* substituents as the y axis and the axis perpendicular to the plane of the ring as the z -axis. The character table, including the number of normal modes under each species, n_i , and the polarization of the infrared active bands to be expected in an oriented specimen (see Table V), is shown in Table VI.

The normal modes of benzene have been computed in detail (23, 24), and those for *para* disubstituted benzenes have been estimated (25, 26). On the

TABLE VI
CHARACTER TABLE FOR C—C₆H₄—C

V_h	E	$C_2(z)$	$C_2(y)$	$C_2(x)$	i	$\sigma(xy)$	$\sigma(xz)$	$\sigma(yz)$	n_i	NULL	IR	R
A_g	1	1	1	1	1	1	1	1	6		—	p
B_{1g}	1	1	-1	-1	1	1	-1	-1	6	R_z	—	dp
B_{2g}	1	-1	1	-1	1	-1	1	-1	2	R_y	—	dp
B_{3g}	1	-1	-1	1	1	-1	-1	1	4	R_x	—	dp
A_u	1	1	1	1	-1	-1	-1	-1	2		—	—
B_{1u}	1	1	-1	-1	-1	-1	1	1	4	T_z	σ	—
B_{2u}	1	-1	1	-1	-1	1	-1	1	6	T_y	π	—
B_{3u}	1	-1	-1	1	-1	1	1	-1	6	T_x	σ	—

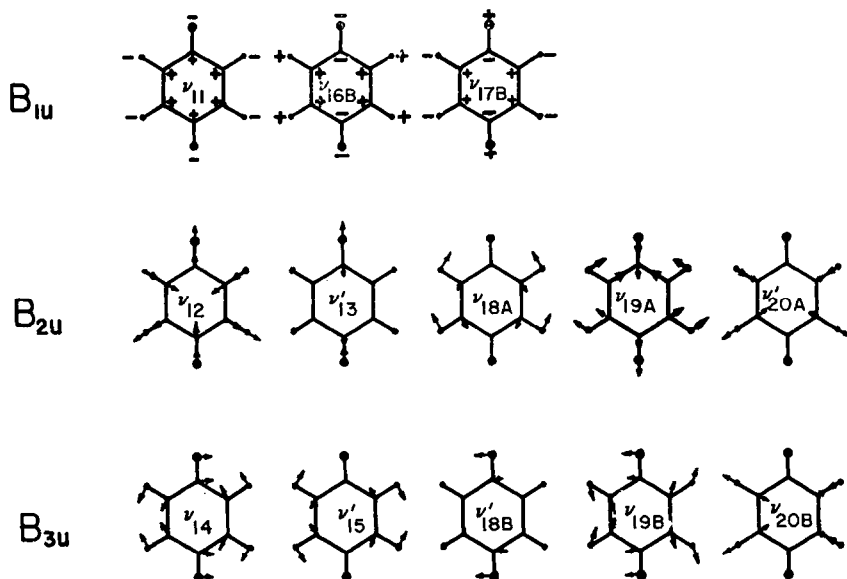


FIG. 6. Infrared active normal vibrations of *para* disubstituted benzene

basis of this work, we present in Fig. 6 a probable set of normal modes for the infrared active vibrations. The unprimed modes are benzene modes. The primed ones are modes derived from benzene modes, and represent reasonable combinations of the latter which are expected to approximate more nearly the actual normal vibrations. Although the mutual exclusion rule is expected to apply, it might be noted that the strict selection rules implied by Table VI may break down in the amorphous regions of the polymer, e.g., as a result of the two C=O groups no longer being strictly related by a center of symmetry. In this case, Raman active modes may appear weakly.

4. NORMAL MODES OF $-\text{OCH}_2\text{CH}_2\text{O}-$

In the above structure of polyethylene terephthalate (8) the configuration of the $-\text{OCH}_2\text{CH}_2\text{O}-$ portion of the chain is identical with that of a *trans* 1,2-disubstituted ethane of symmetry C_{2h} . Symmetry considerations show that 9 infrared active modes are to be expected (27). From the form of the normal vibrations (28) we can determine the approximate nature and polarization (14) of the infrared active modes in an oriented specimen. Using the data of Table V, these are given in Table VII.

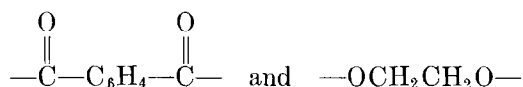
The above analysis is incomplete in that it predicts 12 null modes (translations and rotations) whereas we know that a long chain molecule has only four

TABLE VII
 APPROXIMATE NATURE AND POLARIZATION OF THE INFRARED
 ACTIVE MODES OF TRANS—OCH₂CH₂O—^a

Mode	Polarization
$\nu_a(\text{CH}_2)$	σ
$\nu_s(\text{CH}_2)$	σ
$\delta(\text{CH}_2)$	σ
$\gamma_r(\text{CH}_2)$	σ
$\gamma_w(\text{CH}_2)$	π
$\gamma_t(\text{CH}_2)$	—
$\nu(\text{O—C})$	π
Chain bending: in plane	σ
Chain bending: out of plane	σ

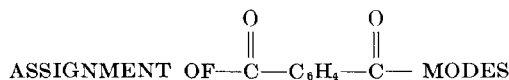
^a Based on structure of Daubeny *et al.* (8).

(17, 18). It will be readily seen that when we consider the motions of the



groups with respect to each other, 8 of the above 12 modes are internal skeletal motions. Among these are modes such as the stretching of the $\text{—}\overset{\parallel}{\text{C}}\text{—O}$ bond, $\nu(\text{C—O})$, and the deformations of the CCO and COC angles, $\delta(\text{CCO})$ and $\delta(\text{COC})$; the others are chain bending modes. We will consider these later.

In the following paragraphs we will discuss first the assignment of the benzene ring vibrations, showing that a consistent analysis is possible on the basis of the orientation of the ring in the proposed crystal structure. We will then consider the assignments of the C=O group. Finally, we will discuss the assignments for the $\text{—OCH}_2\text{CH}_2\text{O—}$ portion of the molecule. It will be shown that for the latter case the spectrum is not consistent with the proposed structure, and an alternative structure will be suggested. The question of the suggested (9, 10) gauche configuration of the $\text{—OCH}_2\text{CH}_2\text{O—}$ group will be considered at that time.



In assigning the substituted benzene ring modes we shall be guided by several principles. To begin with, we start with the assignments which have been worked out in detail for benzene (24, 29) and *para* dideuterobenzene (24–26). As will be shown below, modes in which the substituents do not move have frequencies very close to those in benzene. In some cases use can be made of calculations

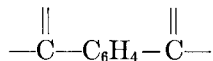
(30–32) of the effect of the substituent on the other modes. The deuteration results are of help in identifying some of the modes, as are pertinent correlations from smaller analogous molecules (33). We also utilize the polarization measurements in making assignments, seeing no clear-cut reason why they should be held in question (15). In fact it seems that a set of assignments consistent with the polarization measurements can be achieved for the benzene ring modes, which gives confidence that the polarization results are also applicable to the other modes. Finally, it must not be overlooked that relaxation of the V_h symmetry, such as could occur in the amorphous regions, will result in the appearance of some of the normally infrared inactive Raman modes.

1. ASSIGNMENT OF B_{2u} MODES

We consider first the assignment of the B_{2u} modes, since they should be readily identifiable by their π polarization. The five B_{2u} modes derive from two inactive B_{1u} modes (ν_{12} and ν_{13}) and three infrared active E_{1u} modes (ν_{18} , ν_{19} , and ν_{20}) of benzene.

The ν_{18A} mode should be readily identified since the substituents in the para position do not move. It occurs as a strong band at 1037 cm^{-1} in benzene, and we have no difficulty in assigning to it the strong π band at 1020 cm^{-1} in the polymer. It probably shifts to about 860 cm^{-1} on ring deuteration, in comparison with the shift to 819 cm^{-1} in 2,3,5,6-tetradeuterobenzene (26). The CH stretching mode, ν_{20A} , can similarly be identified with the π band at 3055 cm^{-1} . It is found at 3060 cm^{-1} in paradideuterobenzene (26). The ν_{19A} mode occurs at 1485 cm^{-1} in benzene, and the evidence seems to indicate (23, 33, 34) that it moves to slightly higher frequencies in para disubstituted benzenes. On this basis the ν_{19A} mode can be readily assigned to the π band at 1504 cm^{-1} . From its disappearance on ring deuteration, and the relative enhancement and slight shift of the band near 1410 cm^{-1} , deuteration appears to shift it to about 1415 cm^{-1} . This indicates that this mode contains a significant proportion of H motion, perhaps as shown in Fig. 6.

The identification of the ν_{12} and ν_{13} modes is less certain. The latter, as indicated, is expected (26) to be a stretching mode of the CC bond between the benzene ring and the C=O group. Because of the planarity of the



framework, and the resulting resonance in this conjugated structure, we expect this CC bond to have some double-bond character. This should place the ν_{13} mode at a higher value than if a pure CC single bond were involved (for example, in butadiene the $\nu(\text{CC})$ mode is found (35) at 1205 cm^{-1}). We believe that ν_{13} should be assigned to either of the bands at 1343 or 1410 cm^{-1} . Since we

will show later that the 1410 cm^{-1} band is most probably a combination band, we choose the band at 1343 cm^{-1} . For various reasons this band cannot be assigned to a CH_2 mode, such as has been suggested or implied by many authors (4, 9, 10, 15, 19). At present we will just note that this band is not shifted by deuteration of the CH_2 group (see Fig. 4). It may seem from Fig. 2 that deuteration has caused this band to disappear, but as we shall presently discuss, there is good reason to believe that it has merged with the band at 1263 cm^{-1} , which, in polyethylene- D_4 terephthalate (Fig. 2) has broadened and shifted to 1275 cm^{-1} , the highest value it assumes in the four polymers. The absence of a shift on ring deuteration is quite consistent with the nature of this mode.

Before proceeding with the other assignments, it is necessary to say a few words about the significant increase in intensity of the 1343-cm^{-1} band which we have noted occurs upon crystallization of the polymer. This behavior is quite consistent with the proposed assignment. If, as we shall show later, the polymer in the amorphous regions is characterized by a loss of its center of symmetry (as evidenced by the appearance of Raman active bands), we would expect this

to imply a departure from planarity of the $\begin{array}{c} \text{O} \\ \parallel \\ -\text{C}-\text{C}_6\text{H}_4-\text{C}- \\ \parallel \\ \text{O} \end{array}$ group. This in turn will be associated with a loss of resonance in the CC bond whose stretching is involved in the ν'_{13} mode, and the position and intensity of this mode would be expected to change. The increased intensity upon crystallization is then just a

reflection of the increased number of $\begin{array}{c} \text{O} \\ \parallel \\ -\text{C}-\text{C}_6\text{H}_4-\text{C}- \\ \parallel \\ \text{O} \end{array}$ groups with strict V_h symmetry. If this effect occurs for the ν'_{13} mode, we shall expect it in other modes, especially those in which the motions significantly involve this CC bond, and this in fact seems to be the case. It might be noted that the suggested merging of this band with that at 1263 cm^{-1} in polyethylene- D_4 terephthalate is not at all unreasonable. We will see that the latter band is to be associated with $\nu(\text{C}=\text{O})$, and it is quite likely that under certain conditions $\nu(\text{C}=\text{O})$ and ν'_{13} could be quite close to each other.

The final mode in the B_{2u} species, ν_{12} , is an inactive mode in benzene located at about 1010 cm^{-1} . Its assignment in polyethylene terephthalate is difficult to make with certainty, but we believe that the position, intensity, polarization, deuteration behavior, and intensity increase upon crystallization of the band at 973 cm^{-1} are consistent with its assignment to ν_{12} .

2. ASSIGNMENT OF B_{1u} MODES

The three B_{1u} modes derive from one infrared active A_u mode (ν_{11}) and two inactive E_{2u} modes (ν_{16} and ν_{17}) of benzene. The ν_{16B} mode is found at 405 cm^{-1} in benzene, and is expected in the same general region (23, 36) in *para* disub-

stituted benzenes. Since it should exhibit σ polarization in oriented polyethylene terephthalate, the only possibilities for assignment are bands at 355 and 430 cm^{-1} . The former is more reasonably assigned otherwise. Choice of the latter will be shown to be consistent with certain expected combinations. We therefore assign the band at 430 cm^{-1} to ν_{16B} .

The two out-of-plane bending modes will be expected to give rise to moderately strong σ bands in the region of approximately 600–900 cm^{-1} (24, 32, 33, 37). Despite its early misassignment (4), it soon became evident (13, 15) that the band at 730 cm^{-1} is to be associated with one of these modes. Tilting experiments on oriented specimens (13) also showed that the 875 cm^{-1} band is associated with an out-of-plane bending mode. Ring deuteration (19) confirms this assignment. From the deuterated spectra (see Figs. 1 and 3) it is clear that the 730- cm^{-1} band shifts to 640 cm^{-1} , and the 875- cm^{-1} band shifts to near 820 cm^{-1} (an assignment of the shift to 707 cm^{-1} leaves the moderately strong σ bands near 820 cm^{-1} completely unassignable). On the basis of the larger isotope shift and greater intensity of the 730- cm^{-1} band we assign it to ν_{11} , whereas ν_{17B} is associated with the band at 875 cm^{-1} .

3. ASSIGNMENT OF B_{3u} MODES

The five B_{3u} modes derive from two inactive B_{2u} modes (ν_{14} and ν_{15}) and three infrared active E_{1u} modes (ν_{18} , ν_{19} , and ν_{20}) of benzene. The ν_{20B} mode, which is found in benzene at 3080 cm^{-1} and is expected to change hardly at all in *para* disubstituted benzenes, is readily identified by its position and polarization with the band at 3082 cm^{-1} . The ν_{19B} mode should be located near 1450 cm^{-1} , but is often not found (33). We believe that it may be associated with the weak crystallization-variable band at 1473 cm^{-1} . It is the only band with appropriate polarization in the expected region, and its enhancement with increasing crystallinity is consistent with the arguments set forth above in connection with the assignment of $\nu'_{13}(B_{2u})$. (A possible assignment to a $\delta(\text{CH}_2)$ mode will be considered later.)

The assignments of two of the other three modes can be made with fair certainty. On the basis of analogy with *p*-xylene (23), where the band is thought to be located at 232 cm^{-1} , we would assign the ν'_{18B} mode in the polymer to the weak band at 250 cm^{-1} . The ν'_{15} mode should be essentially a hydrogen mode (26), and should be found near 1100 cm^{-1} (23, 26). From the appearance of π bands in this region in polyethylene terephthalate it would seem that no assignment can be made. However, it has already been noted (10) that this group of bands is of quite complex origin. In fact weak bands near this position are found in terephthalic acid (11), which would not be expected to exhibit the $\nu(\text{O—C})$ mode which is the main contributor to this region in the higher oligomers (where the intensity relative to the very strong $\nu(\text{C}=\text{O})$ mode near 1250 cm^{-1} remains

essentially constant) and in polyethylene terephthalate. We therefore feel that there is good reason to believe that ν'_{15} contributes to the band at 1100 cm^{-1} . Because of its weakness, its σ polarization is not evident; the π polarization of the overlapping band dominates. This assignment is further supported by the presence of a weak σ band at 935 cm^{-1} in the ring deuterated polymer (see Fig. 4) which bears the same isotopic shift ratio to the 1100-cm^{-1} band as is the case for the analogous CH bending mode ν_{18A} . The assignment of the remaining mode of this species, ν_{14} , is in doubt in benzene (24), and we have been unable to locate it with any assurance in our polymer spectrum.

4. ASSIGNMENT OF RAMAN ACTIVE MODES

The assignments discussed in the above paragraphs still leave many bands, which are not associated with C=O, $-\text{OCH}_2\text{CH}_2\text{O}-$, or skeletal modes, unaccounted for. We will show in this and the next section that these bands are due to Raman active modes which become infrared active as a result of loss of symmetry, and to combination bands.

As we have observed before, loss of the center of symmetry, e.g., by rotations of the C=O groups out of the plane of the benzene ring, will lead to the appearance in the spectrum of bands which are forbidden under V_h symmetry. It should be possible to identify such bands by three characteristics: knowledge of their positions from Raman data, the fact that their intensity increases with increase in amorphous content, and their polarization, which should be correlatable with the activity predicted under a lower symmetry, which would most probably be C_{2v} (22). For example, relaxation of symmetry should give rise (33) to the appearance of bands associated with ν_8 , which appears at 1585 cm^{-1} in benzene. The evidence strongly suggests that the bands at 1580 and 1617 cm^{-1} , which increase in intensity with increasing amorphous content, are due to the $\nu_{8A}(A_1)$ and $\nu_{8B}(B_1)$ modes, respectively. (For the form of these normal modes, see Refs. 22 or 23.) These modes are actually strongly mixed with ν_9 (24), which accounts for the small shift to 1551 and 1586 cm^{-1} , respectively on ring deuteration. Other modes which seem to fit into this category (33) are $\nu_{9A}(A_1)$ at 1172 cm^{-1} , $\nu_4(B_2)$ at 680 cm^{-1} , $\nu_{6B}(B_1)$ at 613 cm^{-1} , and possibly $\nu_{6A}(A_1)$ at 525 cm^{-1} . Other, less certain, possibilities are ν_2' at 1370 cm^{-1} [this is the Raman active counterpart of ν'_{13} , and is found at a slightly higher frequency than the infrared active mode in *para* dideuterobenzene (25, 26)]; $\nu(\text{CC})$, the stretching of the $\text{H}_2\text{C}-\text{CH}_2$ bond, at 1043 cm^{-1} ; and $\nu_{10B}(B_{3g})$ at 145 cm^{-1} . The reason for suggesting the latter assignment is that ν_{10B} is expected to occur at a low frequency (23), and its assignment as suggested leads to the accurate reproduction of a combination band observed in benzene (29).

5. ASSIGNMENT OF COMBINATION BANDS

It is known that in benzene (29) and in substituted benzenes (38) certain characteristic combination bands of the out-of-plane CH bending vibrations

appear with significant intensity in the infrared spectrum. This was found to be true in polystyrene (22), and we would expect a similar situation in the spectrum of polyethylene terephthalate. This will be shown to be the case, which also aids in confirming some of the assignments of the fundamentals.

In assigning combination bands, we are guided by two principles. The species of the combination should follow from those of its components according to the character table, and Raman active components should have frequencies near those of the corresponding mode in benzene when this mode is one in which there is no motion of the *para* substituents. In the latter connection it is also often possible to make use of Raman data on similar smaller molecules, such as dimethyl and diethyl terephthalate (39).

In this way, for example, we can identify two characteristic combination bands at 1830 and 1955 cm^{-1} . The former is a π band and therefore belongs to the B_{2u} species. One of the characteristic combinations is $\nu_{10} + \nu_{17}$, and it will be readily seen that $\nu_{10A} + \nu_{17A}$ ($849 + 984 = 1833$ in benzene) gives a band in the appropriate region and of the correct species. If we use the value of 853 cm^{-1} for ν_{10A} from diethyl terephthalate (39), this would place ν_{17A} at about 977 cm^{-1} . The σ band at 1955 cm^{-1} must belong to the B_{1u} or B_{3u} species. Again it can be seen that the characteristic combination $\nu_{17A} + \nu_5$ gives a band (on the basis of the benzene frequencies) which is in the appropriate range and of the correct species. Using the above value for ν_{17A} we find that ν_5 is at about 978 cm^{-1} , not far from its value of 967 cm^{-1} in *para* dideuterobenzene (25). Using this value for ν_5 and our assigned value for ν_{16B} we find that another characteristic combination, $\nu_5 + \nu_{16B}$, is accurately reproduced. It might be thought that the 1410- cm^{-1} band is too strong to be attributed to a combination band, but in fact such combinations are quite strong in benzene (29). Finally, $\nu_5 + \nu_{16A}$ may be contributing to the 1370- cm^{-1} band. The other possible combinations of these characteristic out-of-plane CH bending modes give bands which, other than the apparently absent $\nu_5 + \nu_{17B}$, overlap with other strong bands in the spectrum.

In summary, it appears that the spectrum predicted for the C—C₆H₄—C framework is satisfactorily identifiable in detail within the spectrum of polyethylene terephthalate. Since this has been based on the assumption of an orientation of the benzene ring similar to that in the crystal structure, we may presume that this orientation (*viz.*, with the *para* axis of the substituted ring oriented essentially parallel to the stretching direction) is substantiated by the spectral results. We have also seen that the intensity of certain of the ring modes is sensitive to the exact symmetry of the ring, which seems reasonably to be associated with the amorphous or crystalline state of the polymer.

In the category of modes associated with the C=O group we expect to find three bands, and their identification is not too difficult. There is no question about the location of $\nu(\text{C}=\text{O})$ at 1724 cm^{-1} . The $\gamma_r(\text{C}=\text{O})$ mode is expected to give rise to a σ band. On the basis of its assignment in ketones to a band at

390 cm^{-1} (40), we feel that it is probably to be assigned to the 355- cm^{-1} σ band in polyethylene terephthalate. The $\gamma_w(\text{C}=\text{O})$ mode is assigned to a band at 639 cm^{-1} in $\text{CH}_3\text{COOCH}_3$ (41) and at 527 cm^{-1} in $\text{CH}_3\text{COCH}_2\text{COCH}_3$ (40). The assignment in the polymer is not entirely unambiguous, but we believe this mode can reasonably be assigned to the π band at 502 cm^{-1} . Its supposed enhancement in the amorphous state (15) may be related to the interaction between the $\text{C}=\text{O}$ group and the benzene ring, which we discussed earlier.

ASSIGNMENT OF $-\text{OCH}_2\text{CH}_2\text{O}-$ AND SKELETAL MODES

In discussing these assignments, we will first try to dispose of those modes involving stretching and deformation vibrations of the $-\overset{\parallel}{\text{C}}-\text{O}-\text{C}-$ group, reserving for the subsequent discussion the assignment of the CH_2 modes and the attendant questions of the configuration of the $-\text{OCH}_2\text{CH}_2\text{O}-$ portion of the chain.

1. ASSIGNMENT OF $-\overset{\parallel}{\text{C}}-\text{O}-\text{C}-$ MODES

Esters are known (41, 42) to give rise to two strong absorption bands associated with the stretching of the $\overset{\parallel}{\text{C}}-\text{O}$ and $\text{O}-\text{C}$ bonds. These can be assigned with a fair degree of certainty to the strong π bands at 1263 and 1120 cm^{-1} , respectively. The smaller dichroism of the former is consistent with the less parallel orientation of the $\overset{\parallel}{\text{C}}-\text{O}$ bond (see Table V). The presence of two π bands in the 1100- cm^{-1} region may be an indication of the dependence of the $\nu(\text{O}-\text{C})$ mode on the configuration of the neighboring CH_2 groups with respect

to the $\text{C}_6\text{H}_4-\overset{\text{O}}{\parallel}{\text{C}}-$ portion of the chain. This is hypothetical at present, but we will shortly consider some arguments which point in this direction.

Assignments have been suggested (41) for the $\delta(\text{CCO})$ and $\delta(\text{COC})$ modes. These are consistent with the bands which we find in the 300-500 cm^{-1} region. The difficulty about making a reasonably certain assignment is that we do not know the forms of the normal vibration. It would seem, on the basis of a simple three mass model, that these deformation vibrations should exhibit σ polarization. However, it is well known (43) that the actual form of this vibration is a sensitive function of the masses, and in fact for certain mass distributions this mode will exhibit π polarization (Ref. 28, pp. 225-227). We will therefore assume that this is the case, and base our assignments on those for $\text{CH}_3\text{COOCH}_3$ (41). This leads to the assignment of the 437- cm^{-1} band to $\delta(\text{CCO})$ and the 383- cm^{-1} band to $\delta(\text{COC})$. Perhaps the apparent weakening of the 437- cm^{-1} band on ring

deuteration is associated with an interaction between this mode and one of the ring modes. We are unable to indentify with any certainty the skeletal modes, and suggest that they may be the origin of perhaps one of the weak low-frequency bands in the spectrum. Several combination bands involving these $\begin{array}{c} \parallel \\ \text{C}-\text{O}-\text{C} \end{array}$ modes seem to occur in the spectrum, and are indicated in Table I.

2. ASSIGNMENT OF CH₂ MODES

The assignments of the $\nu_s(\text{CH}_2)$ and $\nu_a(\text{CH}_2)$ modes can be made on the basis of their well-established positions in hydrocarbons (44), where they are found at 2853 and 2925 cm^{-1} , respectively. If we take into account the increase in these frequencies which occurs when the CH₂ group is adjacent to the ester linkage (45), then there is no difficulty in assigning $\nu_s(\text{CH}_2)$ and $\nu_a(\text{CH}_2)$ to bands at 2908 and 2970 cm^{-1} , respectively. What becomes immediately apparent is that their π polarization is inconsistent with the σ polarization predicted from the crystal structure (8, 14) (see Table V). We shall return to this point presently. There may be an additional σ band in this group, since a third σ band appears in CD₂ polymers (see Figs. 2 and 4). The $\delta(\text{CH}_2)$ mode is similarly (44) located with no difficulty at 1455 cm^{-1} , shifting to 1076 cm^{-1} on deuteration. Its π polarization is consistent (14) with that of the $\nu_s(\text{CH}_2)$ mode. The possible presence of a σ $\nu(\text{CH}_2)$ mode suggests that the σ band at 1473 cm^{-1} may be a $\delta(\text{CH}_2)$ mode. This is difficult to verify by deuteration because of the weakness of the band.

The assignment of the $\gamma_w(\text{CH}_2)$ mode is of especial importance, since it has been made the basis of a postulated gauche configuration for the $-\text{OCH}_2\text{CH}_2\text{O}-$ group in the amorphous regions (9, 10, 19). On the basis of the existence of similar bands in the spectra of rotational isomers of ethylene dihalides (46) and in polyethylene glycol (47), Ward (9, 10) has postulated that the 1343- and 1370- cm^{-1} bands are associated with $\gamma_w(\text{CH}_2)$ modes of the *trans* and *gauche* forms of the $-\text{OCH}_2\text{CH}_2\text{O}-$ group, respectively. We wish to point out that these bands are probably not due to CH₂ groups. First, as we have already noted, the 1343- cm^{-1} band does not shift on deuteration of the CH₂ groups. The spectra indicate that the same is true of the 1370- cm^{-1} band. Second, the $\gamma_w(\text{CH}_2)$ mode, which is located at about 1369 cm^{-1} in hydrocarbons (44), is generally very weak in polymers in comparison to the $\delta(\text{CH}_2)$ mode (22, 44, 48-50). Although in some cases its intensity appears to be enhanced (51), it is never more intense than the $\delta(\text{CH}_2)$ mode. On this basis it would be difficult to assign the 1343- cm^{-1} band to $\gamma_w(\text{CH}_2)$. Third, as we have shown (14), in terms of the strong π $\nu_s(\text{CH}_2)$ and $\nu_a(\text{CH}_2)$ modes the $\gamma_w(\text{CH}_2)$ mode should exhibit σ polarization. This also eliminates the 1343- cm^{-1} band from consideration, leaving only the 1370- cm^{-1} band. The latter may be due to $\gamma_w(\text{CH}_2)$, but at present we think this unlikely,

considering that it does not shift on deuteration of the CH_2 group. We would therefore conclude that $\gamma_w(\text{CH}_2)$ is not detected in the spectrum, and would account for the intensity changes of the 1343-cm^{-1} band not by rotational isomerism of the CH_2 groups but, as indicated in the earlier discussion, by the influence

of resonance in the $\begin{array}{c} \text{O} \qquad \qquad \text{O} \\ \parallel \qquad \qquad \parallel \\ -\text{C}-\text{C}_6\text{H}_4-\text{C}- \end{array}$ group on certain of the benzene ring modes.

On the basis of the crystal structure of polyethylene terephthalate (8) the $\gamma_r(\text{CH}_2)$ mode should give rise to a σ band. There is no band in the spectrum in the appropriate region which can thus be assigned. If, however, we follow the observed π polarization of the intense $\nu_s(\text{CH}_2)$ and $\nu_a(\text{CH}_2)$ modes in expecting (14) a π $\gamma_r(\text{CH}_2)$ mode, then the assignment of this mode to the π band at 845 cm^{-1} is a reasonable one, particularly since this band appears to shift on deuteration of the CH_2 group. The only other CH_2 mode, $\gamma_t(\text{CH}_2)$, the CH_2 twisting mode, is generally too weak to be observed, and we have not been able to assign it in the present work.

STRUCTURE OF POLYETHYLENE TEREPHTHALATE

We wish to consider now the implications of the above results with respect to the structures that have been suggested for the crystalline (8) and amorphous (9, 10) forms of polyethylene terephthalate.

It has already been noted that, whereas the spectrum is consistent with the benzene ring orientation proposed for the crystalline structure, this is not the case for the CH_2 groups. Their modes exhibit dichroism in complete disagreement with that predicted, and, if the assignment of the 845-cm^{-1} crystalline band to $\gamma_r(\text{CH}_2)$ is correct, this dichroism seems to be associated with the crystalline phase. Since we find no reason to hold the polarization data in question, nor their correlation with the transition moments of the CH_2 group, we are led to suggest that the proposed chain structure may be in error with respect to the orientation of the CH_2 groups. It is interesting to note that the authors themselves (8) point out that the location of these carbon atoms was the least reliable part of the structure determination. The dichroism of the CH_2 modes can be accounted for by a change in the structure which, molecular models indicate, is easily possible. This consists of an additional rotation of the CH_2CH_2 bond about the $\text{O}-\text{CH}_2$ bond followed by a rotation about the $\text{C}-\text{O}$ bond. This still preserves the center of symmetry and gives a fiber axis repeat essentially identical with that observed. It should be noted that such a larger rotation about the $\text{O}-\text{CH}_2$ bond is observed in polyethylene adipate (8, 52), a fact which indicates that rotation about this bond occurs with relative ease. We feel that the interpretation of the infrared spectrum is compelling enough so that the possibility of the predominant structure being such as that suggested here must be seriously considered.

The second point concerns the presence of a gauche configuration for the $-\text{OCH}_2\text{CH}_2\text{O}-$ group in the amorphous regions. As will have been gathered by now, the changes in the spectrum upon which the above conclusion is based are not associated with CH_2 modes, as claimed (9, 10, 53). Such prominently crystallization sensitive bands as those at 973 and 1343 cm^{-1} are not CH_2 modes, since they are not affected by deuteration in the expected manner. While it is possible that the chains in the amorphous regions have gauche $-\text{OCH}_2\text{CH}_2\text{O}-$ groups, we do not think that unambiguous evidence exists in the infrared spectrum in support of this. Rather we believe that the changes that occur upon crystallization are associated with changes in the symmetry and resonance characteristics

of the $-\overset{\text{O}}{\parallel}{\text{C}}-\text{C}_6\text{H}_4-\overset{\text{O}}{\parallel}{\text{C}}-$ framework. In addition, in view of the discussion of the previous paragraph, it is probably more likely that structural changes in the chains in the amorphous regions are associated with rotations around the $\text{O}-\text{CH}_2$ bonds than with discrete rotationally isomeric states about the CH_2-CH_2 bond.

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REFERENCES

1. R. BARER, A. R. H. COLE, AND H. W. THOMPSON, *Nature* **163**, 198 (1949).
2. J. MANN AND H. W. THOMPSON, *Proc. Roy. Soc.* **A211**, 168 (1952).
3. S. KRIMM AND G. B. B. M. SUTHERLAND, Symposium on Molecular Structure and Spectroscopy, Columbus, Ohio, 1952.
4. R. G. J. MILLER AND H. A. WILLIS, *Trans. Faraday Soc.* **49**, 433 (1953).
5. G. J. WESTON, *Chem. and Ind.* p. 604 (1954).
6. W. H. COBBS, JR., AND R. L. BURTON, *J. Polymer Sci.* **10**, 275 (1953).
7. R. G. J. MILLER AND H. A. WILLIS, *J. Polymer Sci.* **19**, 485 (1956).
8. R. DE P. DAUBENY, C. W. BUNN, AND C. J. BROWN, *Proc. Roy. Soc.* **A226**, 531 (1954).
9. I. M. WARD, *Chem. and Ind.* p. 905 (1956).
10. I. M. WARD, *Chem. and Ind.* p. 1102 (1957).
11. B. SEIDEL, *Z. Electrochem.* **62**, 214 (1958).
12. D. PATTERSON AND I. M. WARD, *Trans. Faraday Soc.* **53**, 291 (1957).
13. C. Y. LIANG AND S. KRIMM, *J. Chem. Phys.* **27**, 327 (1957).
14. C. Y. LIANG AND S. KRIMM, *J. Chem. Phys.* **27**, 1437 (1957).
15. M. C. TOBIN, *J. Phys. Chem.* **61**, 1392 (1957).
16. M. C. TOBIN, *J. Chem. Phys.* **23**, 891 (1955).

17. C. Y. LIANG, S. KRIMM, AND G. B. B. M. SUTHERLAND, *J. Chem. Phys.* **25**, 543 (1956).
18. C. Y. LIANG, *J. Mol. Spectroscopy* **1**, 61 (1957).
19. W. W. DANIELS AND R. E. KITSON, *J. Polymer Sci.* **33**, 161 (1958).
20. S. BHAGAVANTUM AND T. VENKATARAYUDU, "Theory of Groups and its Application to Physical Problems," Andhra University, Waltair, India, 1951.
21. D. F. HORNIG, *J. Chem. Phys.* **16**, 1063 (1948).
22. C. Y. LIANG AND S. KRIMM, *J. Polymer Sci.* **27**, 241 (1958).
23. K. S. PITZER AND D. H. SCOTT, *J. Am. Chem. Soc.* **65**, 803 (1943).
24. D. H. WHIFFEN, *Phil. Trans. Roy. Soc.* **A248**, 131 (1955).
25. N. HERZFELD, J. W. HOBDEN, C. K. INGOLD, AND H. G. POOLE, *J. Chem. Soc.* p. 272 (1946).
26. C. R. BAILEY, S. C. CARSON, R. R. GORDON, AND C. K. INGOLD, *J. Chem. Soc.* p. 288 (1946).
27. S. MIZUSHIMA, "Structure of Molecules and Internal Rotation," p. 33. Academic Press, New York, 1954.
28. K. W. F. KOHLRAUSCH, "Ramanspektren," p. 177. Akademische Verlagsgesellschaft Becker and Erler, Leipzig, 1943.
29. R. D. MAIR AND D. F. HORNIG, *J. Chem. Phys.* **17**, 1236 (1949).
30. E. HERZ AND J. WAGNER, *Monatsh. Chem.* **76**, 93 (1946).
31. E. HERZ, K. W. F. KOHLRAUSCH, AND R. VOGEL, *Monatsh. Chem.* **76**, 200 (1946).
32. A. R. H. COLE AND H. W. THOMPSON, *Trans. Faraday Soc.* **46**, 103 (1950).
33. R. R. RANDLE AND D. H. WHIFFEN, "Molecular Spectroscopy," George Sell, ed., p. 111. Institute of Petroleum, London, 1955.
34. E. E. FERGUSON, R. L. HUDSON, J. R. NIELSEN, AND D. C. SMITH, *J. Chem. Phys.* **21**, 1457 (1953).
35. C. M. RICHARDS AND J. R. NIELSEN, *J. Opt. Soc. Am.* **40**, 438 (1950).
36. E. K. PLYLER, *Disc. Faraday Soc.* **9**, 100 (1950).
37. T. SHIMANOCHI, Y. KAKIUTI, AND I. GAMO, *J. Chem. Phys.* **25**, 1245 (1956).
38. D. H. WHIFFEN, *Spectrochim. Acta* **7**, 253 (1955).
39. A. PONGRATZ AND R. SEKA, *Monatsh. Chem.* **66**, 307 (1935).
40. J. LECOMTE, *Disc. Faraday Soc.* **9**, 125 (1950).
41. J. K. WILMSHURST, *J. Mol. Spectroscopy* **1**, 201 (1957).
42. H. W. THOMPSON AND P. TORKINGTON, *J. Chem. Soc.* p. 640 (1945).
43. G. HERZBERG, "Infrared and Raman Spectra," p. 174. Van Nostrand, New York, 1945.
44. S. KRIMM, C. Y. LIANG AND G. B. B. M. SUTHERLAND, *J. Chem. Phys.* **25**, 549 (1956).
45. B. NOLIN AND R. N. JONES, *Can. J. Chem.* **34**, 1392 (1956).
46. J. K. BROWN AND N. SHEPPARD, *Trans. Faraday Soc.* **48**, 128 (1952).
47. W. H. T. DAVISON, *J. Chem. Soc.* p. 3270 (1955).
48. S. KRIMM AND C. Y. LIANG, *J. Polymer Sci.* **22**, 95 (1956).
49. S. KRIMM, C. Y. LIANG, AND G. B. B. M. SUTHERLAND, *J. Polymer Sci.* **22**, 227 (1956).
50. O. THEIMER, *J. Chem. Phys.* **27**, 1041 (1957).
51. C. Y. LIANG AND S. KRIMM, *J. Polymer Sci.* **31**, 513 (1958).
52. C. W. BUNN, *J. Polymer Sci.* **16**, 323 (1955).
53. D. GRIME AND I. M. WARD, *Trans. Faraday Soc.* **54**, 959 (1958).