Bimodal Character of Polyester–Solvent Interactions. II. Evaluation of the Chemical Structures of the Aromatic and Aliphatic Ester Residues of Poly(ethylene Terephthalate)

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Synopsis

The chemical structures of the aromatic (A) and the aliphatic ester (B) residues of poly(ethylene terephthalate), PET, are evaluated from a comparison of their Hansen solubility parameters, as determined experimentally, and with those calculated for the various residues of PET. From such a comparison it is proposed that the structures of residues A and B are best represented by "hybrid" structures which may be taken as linear combinations of two or more structures rather than by single chemical structures. That is, the 1,4-carbonyl group which separates the benzene ring of the aromatic residue and the ethylene group of the aliphatic ester residue effectively acts as a common plane between the two residues and is "shared" by the benzene ring and the ethylene glycol group. It is proposed that the extent to which the 1,4-carbonyl group is "shared" by residues A and B is 0.33 and 0.67, respectively, which is consistent with the most probable molecular conformation of the 1,4-benzenoid residue of PET as calculated from the data of Tonelli[23] and Daunbeny et al.[21] and which gives support to the view that the bond connecting the benzene ring and the carbonyl group is not rigid, but free to rotate as proposed earlier by Flory[27] and by Tonelli.[23]

INTRODUCTION

It has been shown previously[1,2] that the interaction of nonaqueous solvents with poly(ethylene terephthalate) (PET) may be characterized as bimodal in nature giving rise to two interaction maxima at δ values of 9.85 and 12.1 (Fig. 5) as a consequence of the preferential interaction of solvents with the aromatic (A) and aliphatic ester (B) residues of the PET monomer repeat unit (Fig. 1). In part I of this series,[3] the Hansen solubility parameters for the various chemical residues of PET (see Table I) were evaluated and compared to those determined experimentally (see Table II) in order to give support to the structural assignment of the aromatic (A) residue to the δ value of 9.85 and the aliphatic ester (B) residue to the δ value of 12.1.[1,2] From the comparison of the calculated and experimental δ values, it was proposed[3] that the chemical structures of residues A and B are best described by "hybrid" structures taken as linear combinations of two or more structures, rather than by single chemical structures. This is equivalent to saying that the 1,4-carbonyl group which separates the benzene ring of residue A and the ethylene glycol group of residue B effectively act as a common plane, as represented by the dotted line in Figure 1, between the two

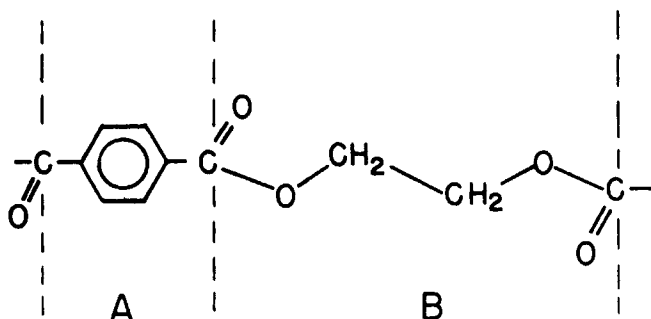* Present address: E. I. du Pont de Nemours & Co., Inc., Kinston, North Carolina 28501.

Fig. 1. Schematic representation of the bicomponent nature of the monomer repeat unit of PET: (A) aromatic residue centered around A; and (B) aliphatic ester residue centered around B. Ref: Knox, Weigmann, and Scott.[2]

residues and is "shared" by both residues. The intent of this study is to determine the "extent" to which the 1,4-carbonyl group is "shared" by examining different hybridization schemes, i.e., different linear combinations of the various chemical residues listed in Table I, and by comparing the corresponding δ values with those determined experimentally in part I of this series[3] (see Table II).

Finally, to give support to the proposed bimodal character of PET–solvent interactions and the "hybrid" structures of the aromatic (A) and aliphatic ester (B) residues of PET, it is of interest to evaluate the structures of residues A and B by an approach which does not depend on the particular representation of the effects of solvents (e.g., solubility parameter plot) on the polyester structure and thereby show that the bimodal character of PET–solvent interactions is a consequence of the particular stereochemical nature of the PET monomer repeat unit and is not, therefore, a consequence of the particular configurations of the molecular chains which describe the given fiber structure. The approach taken here is based on the comparison of the results of spectroscopic and theoretical studies reported in literature on the molecular conformations of the 1,4-benzenoid and the ethylene glycol residues of the PET monomer repeat unit.

MOLECULAR STRUCTURE OF POLYESTER RESIDUES

The exact structures of residues A and B are not apparent from Figure 1. If the two residues are considered as distinct chemical units, then it may be shown[3] that there are several structural assignments possible for both residues (see Table I). It is not possible without additional information to assign specific structures to residues A and B.

The calculated δ values of the six possible chemical structures listed in Table I for residues A and B are compared to the experimental δ values[3] listed in Table II. Such a comparison suggests that the chemical structures of the aromatic and aliphatic ester residues of PET (Fig. 1) giving rise to the bimodal solubility parameter distribution for PET–solvent interactions (Fig. 5) are not represented by single chemical structures, but by "hybrid" structures defined as linear combinations of two or more structures. This is equivalent to saying that the 1,4-carbonyl groups effectively act as a common plane between the aromatic and aliphatic ester residues and are "shared" by both residues. A measure of the relative degree to which the 1,4-carbonyl groups are "shared" by the respective

TABLE I

The Molar Volume, Cohesive Energy Density, Cohesive Energy, and Hansen Solubility Parameters of the Polymeric Residues and Repeat Unit of Poly(ethylene Terephthalate)
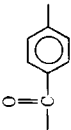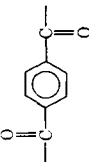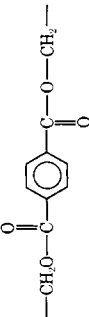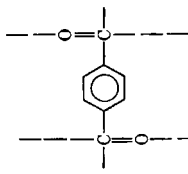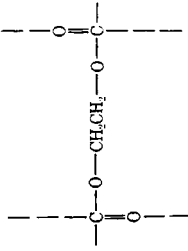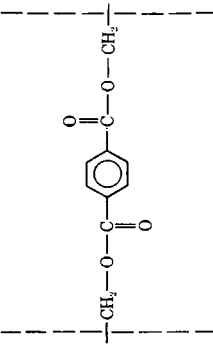
Chemical units	$\overline{V}$, cc/mole	CED, (cal/cc)	E_c, (kcal/mole)	δ, $(cal/cc)^{1/2}$	δ_d, $(cal/cc)^{1/2}$	δ_a, $(cal/cc)^{1/2}$
(aromatic ring, $-CH_3$)	75.93	75.34	5.72	8.67	8.56	1.35
$O=C-\bigcirc-C=O$	88.23	108.16	9.54	10.40	9.19	4.75
$O=C-\bigcirc-C-O$	100.13	133.86	13.40	11.57	9.62	5.29
$-O-CH_2CH_2-O-$	44.02	85.01	3.74	9.22	6.05	6.92
$O=C-O-CH_2CH_2-O-$	55.91	133.40	7.46	11.55	8.98	7.28
$O=C-O-CH_2CH_2-O-C=O$	67.83	170.56	11.57	13.06	10.62	7.60
$-CH_2O-C(=O)-\bigcirc-C(=O)-O-CH_2-$	144.10	114.70	16.53	10.71	9.36	5.20
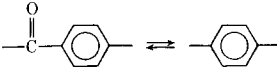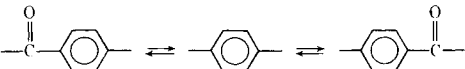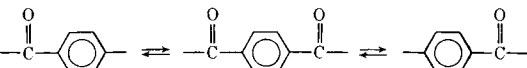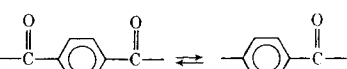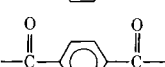
TABLE II

Comparison of the Experimental and of the Calculated Hansen Solubility Parameters of the Aromatic Residue (A), of the Aliphatic Ester Residue (B), and of the Monomer Repeat Unit of Poly(ethylene Terephthalate)[a]

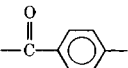| PET residues	δ, (cal/cc)$^{1/2}$	δ_d, (cal/cc)$^{1/2}$	δ_p, (cal/cc)$^{1/2}$	δ_h, (cal/cc)$^{1/2}$	δ_a, (cal/cc)$^{1/2}$
(A)	9.85	9.04	2.50	3.00	3.91
	9.885	9.02	2.58[b]	3.11[b]	4.04
(B)	12.10	9.66	6.70	2.85	7.29
	12.12	9.60	6.72[b]	2.87[b]	7.40
(PET)	10.78	9.30	4.25	2.94	5.32
	10.71	9.36	4.16[b]	3.12[b]	5.20

[a] (A) = Aromatic residue; (B) = aliphatic ester residue; PET = monomer repeat unit. First row = experimental values; second row = calculated values.

[b] Based on experimental ratios $(\delta_p/\delta_a)^2$ and $(\delta_h/\delta_a)^2$.

TABLE III
The Calculated Hansen Solubility Parameters of Various Aromatic Residues of
Poly(ethylene Terephthalate) as a Function of the Fractional Carbonyl Content

F_c	Hybridization schemes	$\delta,$ (cal/ cc)$^{1/2}$	$\delta_d,$ (cal/ cc)$^{1/2}$	$\delta_a,$ (cal/ cc)$^{1/2}$
0		8.67	8.56	1.35
0.25		9.60	8.90	3.18
0.33		9.88	9.02	4.04
0.50		10.40	9.19	4.75
0.67		10.82	9.35	4.95
0.75		11.02	9.42	5.15
1.00		11.57	9.62	5.29

residues is given by the fractional carbonyl content, f_c, defined by the following relation:

$$f_c = \frac{\text{total no. of } \overset{\displaystyle O}{\underset{\displaystyle /\ \backslash}{\overset{\displaystyle \|}{C}}} \text{ groups per hybrid scheme}}{2 \times \text{no. of residues per hybrid scheme}} \tag{1}$$

In Tables III and IV, the values of f_c for the various hybridization schemes are given with corresponding δ values. The general expression for the value of a given δ_j for a hybrid residue is given by the following expression:

$$(\delta_j)_{\text{hybrid}} = \sum_i \phi_i (\delta_j)_i \tag{2}$$

where j denotes the particular solubility parameter of interest; i denotes the polymeric residues forming the hybrid residue; and ϕ_i is the volume fraction of the ith polymeric residue as defined by

$$\phi_i = \frac{\bar{V}_i}{\sum_i \bar{V}_i} \tag{3}$$

and $\bar{V}_i$ is the molar volume of the ith polymeric residue. The value of δ_j for the entire PET monomer repeat unit may now be represented by an average of the

TABLE IV

The Calculated Hansen Solubility Parameters of Various Aliphatic Ester Residues of Poly(ethylene Terephthalate) as a Function of the Functional Carbonyl Content

F_c	Hybridization schemes	δ, $(cal/cc)^{1/2}$	δ_d, $(cal/cc)^{1/2}$	δ_a, $(cal/cc)^{1/2}$
0	—O—CH₂CH₂—O—	9.22	6.05	6.92
0.25	—O—CH₂CH₂O—C— ⇌ —O—CH₂CH₂—O— (C=O)	10.52	7.69	7.12
0.33	—C—O—CH₂CH₂—O— ⇌ —O—CH₂CH₂—O— (C=O)	10.92	8.15	7.18
0.50	—C—O—CH₂CH₂—O— (C=O)	11.55	8.98	7.28
0.67	—C—O—CH₂CH₂—O— ⇌ —C—O—CH₂CH₂—O—C— (C=O)	12.12	9.60	7.40
0.75	—C—O—CH₂CH₂—O— ⇌ —C—O—CH₂CH₂—O—C— (C=O)	12.38	9.88	7.46
1.00	—C—O—CH₂CH₂—O—C— (C=O)	13.06	10.62	7.60

Fig. 2. Hildebrand solubility parameter (δ) of the aromatic residue (A) and the aliphatic ester residue (B) as a function of the fractional carbonyl content (f_c) of residue A.

δ_j values of the aromatic (A) and aliphatic ester (B) "hybrid" residues:

$$(\delta_j)_{\text{PET}} = \phi_A(\delta_j)_A + \phi_B(\delta_j)_B \qquad (4)$$

where $(\delta_j)_{A,B}$ and $\phi_{A,B}$ are given by expressions (2) and (3), respectively.

In Figures 2–4, the calculated values of δ, δ_d, and δ_a for the various hybrid structures are plotted as a function of the fractional carbonyl content f_c. It is observed that the best agreement between the calculated and the experimental δ values is given for the hybridization schemes corresponding to f_c values of 0.33

Fig. 3. Hansen dispersion solubility parameter (δ_d) of the aromatic residue (A) and the aliphatic ester residue (B) as a function of the fractional carbonyl content (f_c) of residue A.

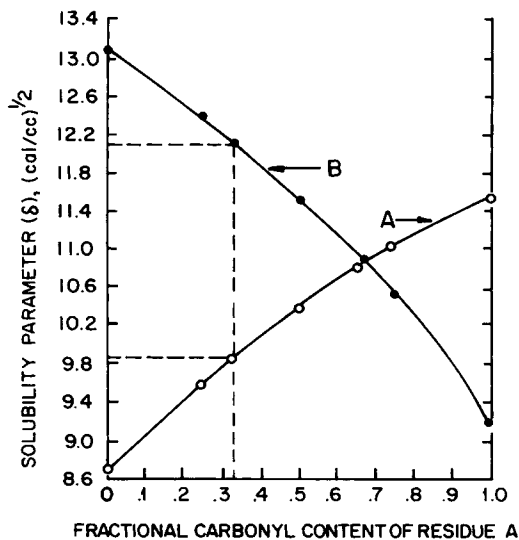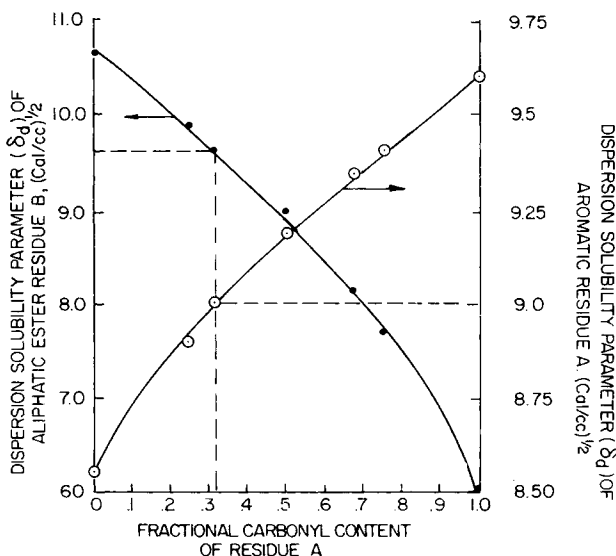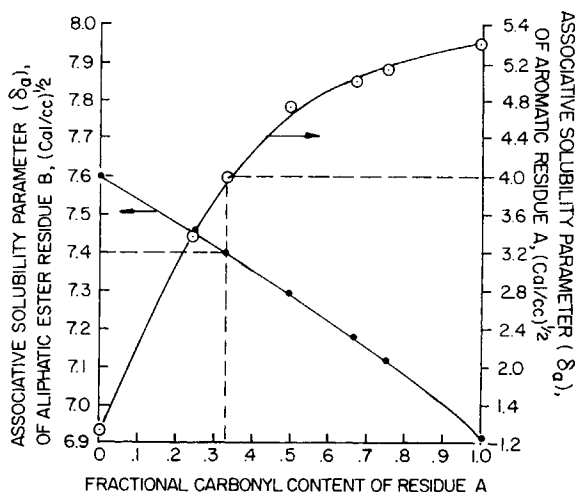Fig. 4. Hansen associative solubility parameter (δ_a) of the aromatic residue (A) and the aliphatic ester residue (B) as a function of the fractional carbonyl content (f_c) of residue A.

and 0.67 for residues A and B, respectively (see Tables III and IV). In Table II, the experimental and calculated δ values, based on the above proposed hybridization schemes, for residues A and B and for the PET repeat unit are compared. The excellent agreement between the calculated and experimental values gives support to (i) the bimodal character of PET–solvent interactions; (ii) the concept of "hybrid" polymeric residues rather than discrete chemical units; and (iii) the Hansen multidimensional solubility parameter concept as an approach to characterizing the chemical nature of fiber–solvent interactions.

Bimodal Solubility Parameter Distribution

Intuitively, the concept of hybridization must also affect the bimodal solubility parameter distribution. Two important characteristics of any distribution are the height (amplitude) and breadth (base width). It is of interest to briefly describe the dependence of the height and breadth of the solubility parameter distribution on the nature of PET–solvent interactions.

The difference in the extent of PET–solvent interactions for residues A and B is represented by the difference in the heights of the maxima of the Hildebrand plot in Figure 5. The extent of solvent interaction is greater for residue A than for residue B. It is suggested here that the extent of solvent interactions is related to the solvent's ability to overcome the interchain cohesive energy (E_c) and thus permit local segmental motion to take place. It is proposed that the interchain cohesive energy E_c is defined by the product of the cohesive energy density (CED) of the given residue and its molar volume:

$$E_c = \text{CED} \times \bar{V} \tag{5}$$

and from the definition of CED,[4] E_c is found to be equivalent in value to the molar energy of vaporization ($\Delta \bar{E}^v$) of the given residue and should, therefore, be independent of changes in density, i.e., molecular packing and order, and only
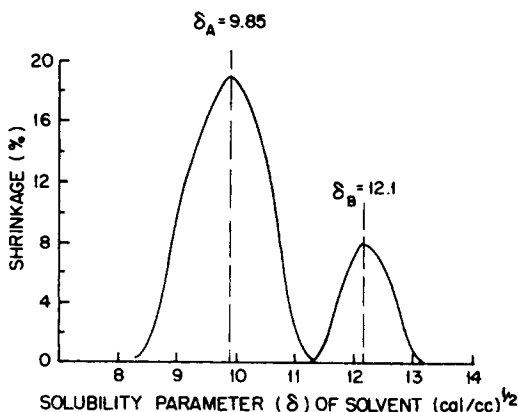
Fig. 5. Percent shrinkage of a polyester yarn after 90 days in various organic solvents at 21°C as a function of the Hildebrand solubility parameter (δ) of the solvent giving rise to interaction maxima at δ-values of 9.85 and 12.1 which correspond to the aromatic (A) and the aliphatic ester (B) residues of PET, respectively. Ref: Knox, Weigmann, and Scott.[2]

dependent on changes in the chemical structure of the polymeric residue (i.e., CED and molar volume, $\bar{V}$).

In Figure 6 the values of E_c for residues A and B are plotted as a function of the carbonyl content (f_c) taken as a measure of change in the chemical structure of the polymeric residues as given in Table I. The values of CED and $\bar{V}$ required to calculate E_c are listed in Table I. From Figure 5 it is observed that the extent of solvent interaction is greater for residue A than for residue B, which indicates that it is easier to break a "residue A" interchain bond than a "residue B" interchain bond; and therefore, the value of $(E_c)_A$ is taken to be less than that of $(E_c)_B$. Hence, from Figure 6 the only possible values of $(f_c)_A$ and $(f_c)_B$ which satisfy the condition that $(E_c)_A < (E_c)_B$ are given by $(f_c)_A \leq 0.38$ and $(f_c)_B \geq 0.62$, respectively, which are in good agreement with the observed values of 0.33 and 0.67, respectively.

The breadth of the solubility parameter distribution denoted by $\Delta\delta$ is frequently defined by the Flory expression[27a] for the critical conditions of polymer-liquid interactions:

$$\Delta\delta = (2RT/\bar{V}_l)^{1/2}[1 + 1/x]^{1/2} \tag{6}$$

where R is the universal gas constant, T the absolute temperature, $\bar{V}_l$ the molar volume of solvent, and x the degree of polymerization. For large values of x, the value of $\Delta\delta$ approaches the limiting value of

$$\Delta\delta = (2RT/\bar{V}_l)^{1/2} \tag{7}$$

In evaluating expression (7) for $\Delta\delta$, it shall be assumed that the largest value of $\bar{V}_l$ which may be taken (i.e., defines the boundary limits) and still permit one to represent the solvent–PET interaction as a solvent–residue solvate "complex" in which the solvent molecules pack (coordinate) around the given residue to form a cylindrical volume element is $\bar{V}_{solvent} \equiv \bar{V}_{residue}$. Thus, the critical conditions for solvent–PET interaction is given by expression (7) in which the value of $\bar{V}_l$ is now taken as that of the given residue. Therefore, it is possible to express $\Delta\delta$ as a function of the fractional carbonyl content f_c.

Fig. 6. The cohesive interchain energy (E_c) of the aromatic.(A) and the aliphatic ester (B) residues as a function of the fractional carbonyl content (f_c) of residue A.

In Figure 7, the values of $\Delta\delta$ are plotted as a function of f_c for residues A and B. For all values of f_c, $(\Delta\delta)_A < (\Delta\delta)_B$. Experimentally, the values of $\Delta\delta_{A,B}$ are found to be 3.75 and 4.43 $(cal/cm^3)^{1/2}$, respectively (see Fig. 8). Comparison of the experimental values of $\Delta\delta$ with those in Figure 7 plotted as a function of f_c

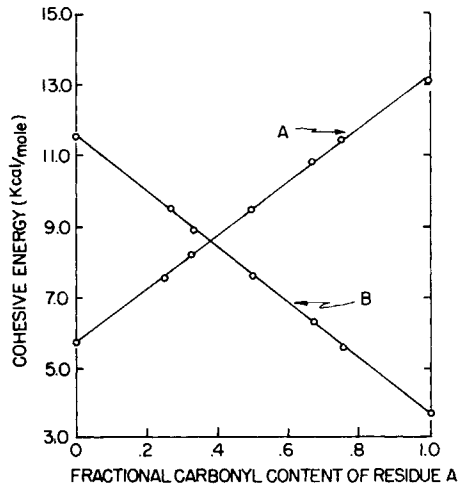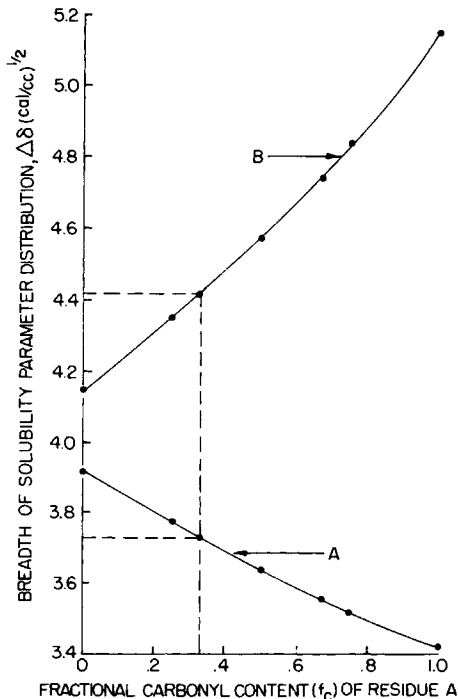Fig. 7. Breadth of the solubility parameter distribution (i.e., diameter of Hansen circle of PET-solvent interaction) of the aromatic (A) and the aliphatic ester (B) residues as a function of the fractional carbonyl content (f_c) of residue A.
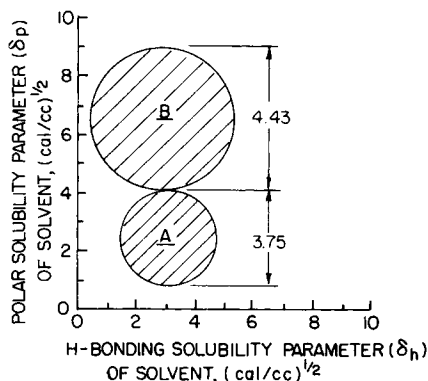
Fig. 8. Hansen solubility parameter plot of areas of high PET-solvent interaction (/// > 3%-shrinkage). Ref: Knox, Weigmann, and Scott.[2]

again give support to the proposed hydridization schemes in which $(f_c)_A = 0.33$ and $(f_c)_B = 0.67$.

The observation that $(\Delta\delta)_A$ is always less than $(\Delta\delta)_B$ for all values of $(f_c)_{A,B}$ (see Fig. 7) is in direct opposition to that obtained by representing the shrinkage data, for example, by a Hildebrand plot in Figure 5. The inability of the Hildebrand plot to quantitatively represent PET–solvent interactions was discussed previously[1,2] and is again supported here.

The anomalous broadening of the solubility distribution curve associated with residue A is schematically illustrated by Figure 9 in which the chemical structures comprising the "hybrid" structures are positioned on the bimodal plot in Figure 5 at their respective total solubility parameters.

CONFORMATION ANALYSIS OF POLYESTER

It has been shown from comparison of the experimentally determined and calculated δ values for the various possible structures of the PET residues that
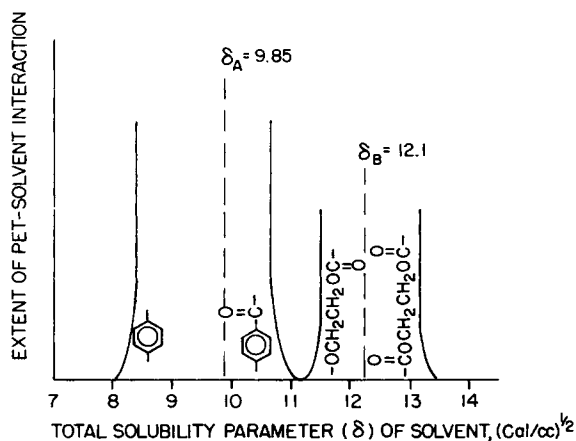

Fig. 9. Schematic representation of the anomalous broadening of the Hildebrand solubility parameter distribution curve associated with the aromatic residue A in which the chemical structures comprising the "hybrid" structures are positioned on the bimodal plot at their respective total solubility parameters (δ).
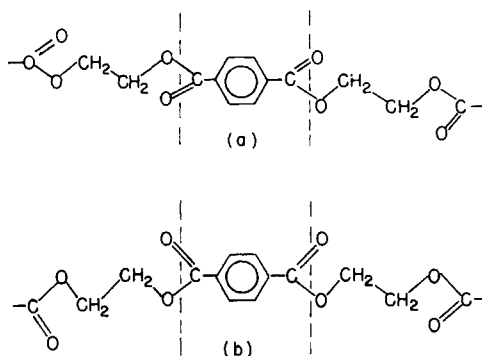
Fig. 10. Schematic representation of the planar *trans* (a) and *cis* (b) configurations of the 1,4-benzenoid residue of the PET monomer repeat unit. Ref: Reddish.[17]

the structures are best represented by hybrid structures in which the carbonyl group is taken as a common plane, shared by both residues A and B. The degree of sharing was expressed in terms of the fractional carbonyl content f_c and found to be 0.33 and 0.67 for residues A and B, respectively. This observation is in conflict with the concept of electron delocalization which would favor, according to the $4n + 2$ Hückel rule,[5,6] a coplanar *cis,trans* 1,4-benzenoid structure as shown in Figure 10. This view of a rigidly planar 1,4-benzenoid structure would give rise to values of $(f_c)_{A,B} = 1.0$ and 0, respectively, and has formed the basis of many spectroscopic studies[6-20] in which the changes in PET upon crystallization are

(a)

(b)

OXYGEN   CARBON   HYDROGEN

Fig. 11. Schematic representation of the configuration of the ethylene glycol residue of PET in the (a) crystalline state and the (b) amorphous state. Ref: Ward.[20]
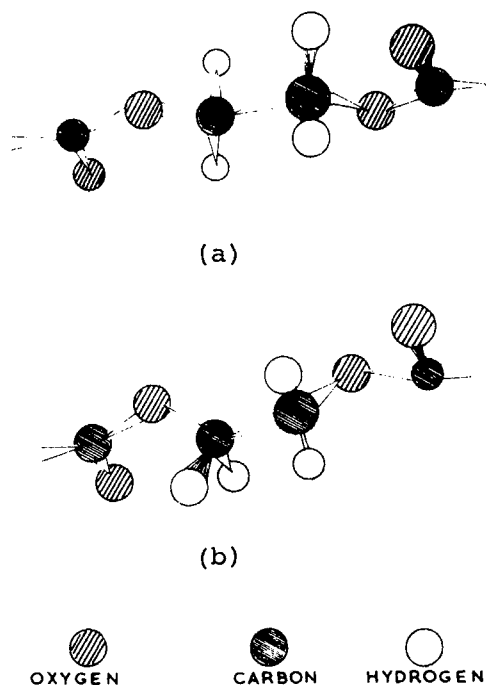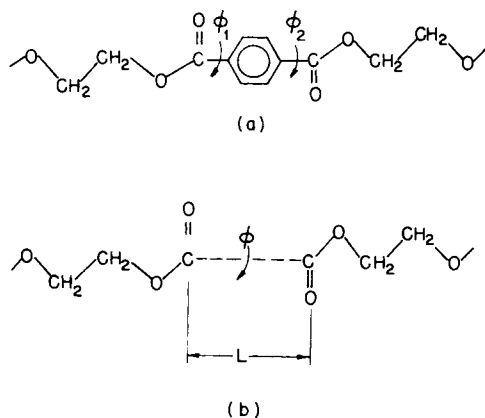
Fig. 12. (a) Schematic representation of the 1,4-benzenoid residue of the PET monomer repeat unit. The planar zigzag conformation is taken as the reference state, where rotation angles $\phi_1 = \phi_2 = 0°$ in this state, and the angles are positive for the right-handed rotations [27]. (b) PET chain as in (a) except the benzene ring in the 1,4-benzenoid residue is replaced by the virtual bond L: rotation angle ϕ is $0°$ in this reference *trans* state and positive for right-handed rotations [27]. Ref: Tonelli.[23]

attributed to the rotational isomerism of the ethylene glycol residue (—O—CH$_2$—CH$_2$—O—). That is, in the completely amorphous state, the ethylene glycol residue exists in the gauche configuration; while in the completely crystalline state, as given by the unit cell,[21] the ethylene glycol residue exists in the *trans* configuration[21] (see Fig. 11).

This view of the PET monomer repeat unit as being composed of an inflexible 1,4-benzenoid residue and a flexible ethylene glycol residue is in contrast to what was deduced from the previous discussions concerning the calculation of the Hansen δ values of residues A and B. The inherent difference of the two models of PET is based on the rigidity of the 1,4-benzenoid structure and the rotational freedom of the 1,4-carbonyls. Recent configurational analyses of amorphous PET by Williams and Flory[22] and by Tonelli[23] and recent studies of the vibrational spectra of PET[24–26] give support to the view taken here that the 1,4-benzenoid structure is flexible and cannot be considered rigidly planar in the amorphous state. A brief review of the arguments given in the above conformational analyses are repeated below in order to provide the background necessary to evaluate the most probable conformation of the 1,4-benzenoid structure; that is, to evaluate the values of the fractional carbonyl content f_c of residues A and B by an approach which is not dependent on the behavior of PET in the swollen state and therefore to show that the fractional carbonyl content and thus the conformation of the 1,4-benzenoid structure are inherent molecular properties of polyester and not of the given solvent system or fiber morphology.

Williams and Flory[22] have shown that the planar cis and trans isomers of the 1,4-benzenoid structure are equally probable and are the most probable of the rotational isomers. Consequently, Williams and Flory conclude that the *p*-phenylene ring may be treated as a virtual bond connecting the 1,4-carbonyl carbons (Fig. 12) and behaves as a statistical freely rotating link[27] between the ethylene glycol residues. This model of the 1,4-benzenoid structure is shown to yield calculated chain dimensions in agreement with the values obtained from intrinsic viscosity studies.[19,28]
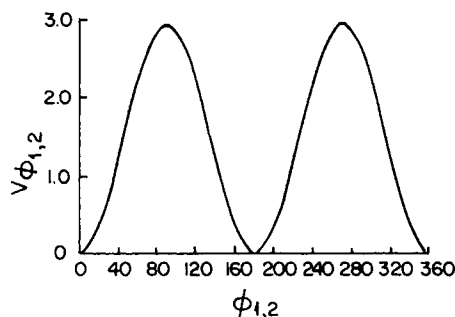
Fig. 13. Potential energy $V_{\phi 1,2}$ for rotations $\phi_{1,2}$ about the —C_6H_4—CO— bonds in the 1,4-benzenoid residue of the PET monomer repeat unit. Ref: Tonelli. [23]

Inspection of space-filling molecular models made by Tonelli[23] supports the view taken by Williams and Flory[22] that the rotation about the bond connecting the carbonyl carbon and the benzene ring is independent of the rotations about the para carbonyl group and the methylene groups of the ethylene glycol residue.

Using the above model for the 1,4-benzenoid structure of PET, Tonelli[23] proposes that the resistance to rotation, $V_{\phi 1,2}$ (subscript meaning ϕ_1 or ϕ_2), about the benzene–carbonyl bonds is given by the sum of two independent contributions: (i) the intrinsic twofold torsional potential V_π resulting from the delocalization of π-electrons over the 1,4-benzenoid structure; and (ii) the nonboned interactions V_{nb} of the carbonyl group with the carbon and hydrogen atoms ortho to the carbonyl group. Therefore, the net barrier to rotation, $V_{\phi 1,2}$, is given by the sum

$$V_{\phi 1,2} = V_{nb} + V_\pi \qquad (8)$$

and is found to be approximately 3.0 kcal/mole. The maximum energy difference between any two rotational states is approximately 1.65 kcal/mole (Fig. 13).

The rotation barrier about a 1,4-benzenoid residue is a sum of the two independent rotations[23] $\phi_1 + \phi_2$ about the benzene–carbonyl bonds. Therefore, the probability p_ϕ of a virtual bond rotational state ϕ is given by the product of the

TABLE V
Probabilities of Rotational States About the Virtual Bond Spanning
the 1,4-Benzenoid Residue PET[a]

ϕ, degrees	p_ϕ	$P_x \ (= \Sigma p_\phi)$
0, 180	0.0574	0.1184
10, 170, 190, 350	0.0550	0.2200
20, 160, 200, 340	0.0487	0.1948
30, 150, 210, 330	0.0399	0.1596
40, 140, 220, 320	0.0302	0.1208
50, 130, 230, 310	0.0209	0.0836
60, 120, 240, 300	0.0130	0.0520
70, 110, 250, 290	0.0076	0.0304
80, 100, 260, 280	0.0044	0.0176
90, 270	0.0035	0.0140

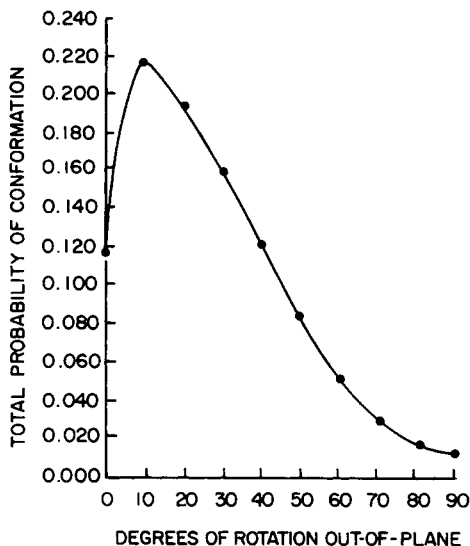[a] From ref. 23; p_ϕ = probabilities of rotational states; P_x = probabilities of conformational states.

Fig. 14. Total probability of the rotational conformations P_x $(=\Sigma_{p_\phi})$ of the —C_6H_4—CO— bonds in the 1,4-benzenoid residue of the PET monomer repeat unit as a function of the degrees of rotation out-of-plane with respect to the benzene ring. Data: Tonelli.[23]

two independent probabilities of the rotational states ϕ_1 and ϕ_2. Tonelli[23] calculates the probabilities of the rotational states about the virtual bond L spanning the 1,4-benzenoid structure (Fig. 12) and shows that although the *trans* (0°) and *cis* (180°) isomers are the most probable rotational states, the nonplanar conformers are also nearly probable (Table V).

The calculated values of the probabilities of the rotational states given by Tonelli[23] may be used to determine the most probable rotational conformational state. The total probability of a conformational state $x°$ out of plane, P_x, is given by the following relation:

$P_x = \Sigma p_\phi$ = (no. nondegenerate rotational conformers $x°$ out of plane)
$$\times \text{(probability of conformer } p_\phi) \quad (9)$$

where the probability of the nondegenerate conformers, for example, 10°, 170°, 190°, and 350° out of plane are taken as being equal and denoted by p_ϕ in the above expression. Therefore, the total probability of the rotational conformation 10° out of plane is given by

$$P_{10°} = p_{10°} + p_{170°} + p_{190°} + p_{350°} = 4p_{10°}$$

Values of P_x for the other rotational conformations are calculated in a similar manner and the results of these calculations are given in Table V.

In Figure 14, the values of P_x are plotted as a function of the degrees (x) of rotation out of plane of the benzene ring. It is observed that the conformational state corresponding to 10° rotation out of plane (i.e., 10°, 170°, 190°, 350°) is the most probable rotational conformation for the 1,4-benzenoid structure.

The observation that the 10° conformational state is more probable than the planar conformation state despite $p_\phi(0°) > p_\phi(10°)$ is at first surprising, but is a direct consequence of the 10° conformational state having four nondegenerate
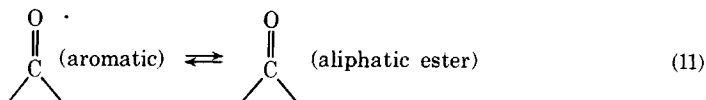
rotational conformers (10°, 170°, 190°, and 350°) while the planar conformational state has only two nondegenerate rotational conformers (0° and 180°).

The observation that the 10° conformational state is the most probable state is also supported by x-ray diffraction studies by Daunbeny et al.[21] on the unit cell of PET. Daunbeny showed that even in the completely crystalline state, the 1,4-carbonyls may exist as much as 10–12° out of plane, most likely as a consequence of nonbonded interactions between the carbonyl oxygens and the ortho carbons and hydrogens of the benzene ring.

The above observations strongly suggest that the 1,4-benzenoid structure may be considered as a "freely" rotating structural unit in which the 1,4-carbonyl groups may exist out of plane. Therefore, the fractional carbonyl content f_c of the 1,4-benzenoid structure is expected to be less than unity and may be given by

$$f_c = \sum_i (P_x)_i \tag{10}$$

where i denotes the "allowed" conformational states $x°$ out of plane describing the 1,4-benzenoid structure, and $(P_x)_i$ is the total probability of the ith conformational state as given by expression (9). In the case of PET the carbonyl group may be treated as being in dynamic equilibrium between the aromatic and aliphatic ester residues:

$$\underset{/\backslash}{\overset{\overset{\textstyle O}{\|}}{C}} \text{(aromatic)} \;\rightleftharpoons\; \underset{/\backslash}{\overset{\overset{\textstyle O}{\|}}{C}} \text{(aliphatic ester)} \tag{11}$$

where f_c (aromatic) $+ f_c$ (aliphatic ester) $= 1.0$.

To evaluate the values of f_c for the aromatic and aliphatic ester residues, it is necessary to determine the "allowed" conformational states, i.e., those which define the aromatic and aliphatic ester residues. Intuitively, for the 1,4-carbonyls to be resonance stabilized, they must be nearly planar with respect to the benzene ring for proper overlap of the p-orbitals of the benzene ring and of the 1,4-carbonyls. From Daunbeny's observation[21] that the 1,4-carbonyls in the unit cell may exist as much as 10° out of plane and from the observation (Fig. 14) that the conformational state 10° out of plane is found to be the most probable state, it is proposed that the conformational states which characterize the aromatic carbonyl group are given by the arc of rotation $0° \rightarrow 10°$ and that the conformational states which characterize the aliphatic ester carbonyl group are given by the complementary arc of rotation $10° \rightarrow 90°$. Inherent in the above argument is the assumption that the definition of aromaticity, i.e., overlap of successive p-orbitals, is not dependent on molecular orientation, local ordering effects, and crystallinity. The possible effects of morphology on the extent of carbonyl rotation and the fractional carbonyl content will be discussed in part III of this series.[29]

The corresponding values of f_c may now be determined by evaluating expression (10). It is found that the values of f_c for the aromatic and aliphatic ester residues are 0.33 and 0.67, respectively, which are in excellent agreement with the values of $(f_c)_{A,B}$ determined previously. The above results give support to

the proposed "hybrid" character of the structures of the aromatic (A) and the aliphatic ester (B) residues of PET.

CONCLUSIONS

It has been shown previously[1,2] that the interaction of nonaqueous solvents with PET may be characterized as bimodal in nature giving rise to two interaction maxima for solvents having δ values near 9.85 and 12.1. It was proposed[1] by the comparison of chemically similar compounds that the PET monomer repeat unit may be represented as being composed of an aromatic and an aliphatic ester residue having δ values of 9.85 and 12.1, respectively. This assignment was supported by iodine displacement studies[2] and by the consideration that the interaction of solvents and PET residues may be described as an interaction of Lewis acids and bases.[3] To give support to the above indirect evidence, it was of interest to calculate the Hansen solubility parameters of the various chemical residues forming PET and compare the calculated values with those determined experimentally. This was done in part I of this series.[3]

It has been shown here that the comparison of the calculated and experimental δ values suggests that the structures of residues A and B be best represented by "hybrid" structures which are taken as linear combinations of two or more single chemical structures rather than by single chemical structures. The concept of a "hybrid" structure assumes that the 1,4-carbonyl group is "shared" by the two residues, which suggests that the bond connecting the benzene ring of the aromatic residue and the ethylene glycol group of the aliphatic residue is free to rotate and not rigid, i.e., the carbonyl group is not necessarily in the plane of the benzene ring as previously assumed.[6–20]

Using Tonelli's data[23] for the probabilities of the various rotational conformations of the 1,4-benzenoid structure of PET, it has been shown that the most probable rotational conformation is for a 10° rotation of the 1,4-carbonyl groups out of the plane of the benzene ring. Daunbeny[21] has shown that in the crystalline state the 1,4-carbonyl groups, which are taken to be aromatic in nature (i.e., in the plane of the benzene ring), may exist as much as 10–12° out of the plane as a result of nonbonded interactions. Using the unit cell[21] as a reference, the criterion for "aromaticity" of the 1,4-carbonyl groups (i.e., "shared" by the aromatic residue A) is defined by the arc of rotation 0°→10°; and that criterion for "nonaromaticity" (i.e., "shared" by the aliphatic ester residue B) is given by the complementary arc of rotation, 10°→90°. Using Tonelli's data for the probabilities of the various rotational conformations[23] and the above arbitrary definition of "aromaticity" and "nonaromaticity" of the 1,4-carbonyl groups of the 1,4-benzenoid structure of PET, it is found that the fractional carbonyl contents of residues A and B are 0.33 and 0.67, respectively, which is in agreement with those evaluated by the comparison of the calculated and experimental δ values of the various PET residues.

Hence, it has been shown that the interaction of a solvent with a given PET residue is an inherent molecular property of the PET repeat segments which make up the macromolecular structure and not a result of the particular representation of PET–solvent interactions, nor should it be affected by the bulk fiber structure (i.e., crystallinity, draw ratio, etc.). The effects of fiber morphology on the molecular conformation of the 1,4-benzenoid residue and hence on the

fractional carbonyl content and the corresponding δ values of the PET residues A and B are the subject of part III of this investigation.[29]

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