

## Bimodal Character of Polyester-Solvent Interactions.

### I. Evaluation of the Solubility Parameters of the Aromatic and the Aliphatic Ester Residues of Poly(ethylene Terephthalate)

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#### Synopsis

The Hildebrand and the Hansen solubility parameters of the aromatic and the aliphatic ester residues of poly(ethylene terephthalate), PET, are evaluated and compared to those determined experimentally. The interactions of nonaqueous solvents with the aromatic and aliphatic ester residues of PET are also described in terms of their relative basicity and acidity in the Lewis sense, where the aromatic residue may be taken as a Lewis acid and the aliphatic ester residue may be taken as a Lewis base.

#### INTRODUCTION

The solubility parameter concept of Hildebrand and Scott<sup>1</sup> and the extension of this principle by Hansen<sup>2</sup> has been shown<sup>3,4</sup> to be successful in describing the nature of the interactions between nonaqueous solvents and poly(ethylene terephthalate), PET, as represented by longitudinal shrinkage, volume swelling, and crystallization, giving rise to a bimodal solubility parameter distribution with interaction maxima at  $\delta$  values of 9.85 and 12.1 (see Fig. 1).

From a comparison of the  $\delta$  values of chemically similar compounds<sup>3</sup> and from iodine displacement studies,<sup>4</sup> it is proposed that the  $\delta$  values of 9.85 and 12.1, corresponding to the two interaction maxima (Fig. 1), may be assigned to the aromatic (A) and the aliphatic ester (B) residues of PET, respectively, as represented in Figure 2. To confirm the above assignment of  $\delta$  values and to more precisely describe the chemical structures of the aromatic and aliphatic ester residues, it is of interest to evaluate the solubility parameters of the respective residues and to compare the calculated values with those determined experimentally.

#### HILDEBRAND SOLUBILITY PARAMETER

According to Hildebrand's definition,<sup>1</sup> the total solubility parameter  $\delta$  is given by the square root of the cohesive energy density (CED) and thus is taken as a measure of the energy required to disrupt the intermolecular forces which hold the molecules in the condensed state. The CED is given by the following relation:<sup>1</sup>

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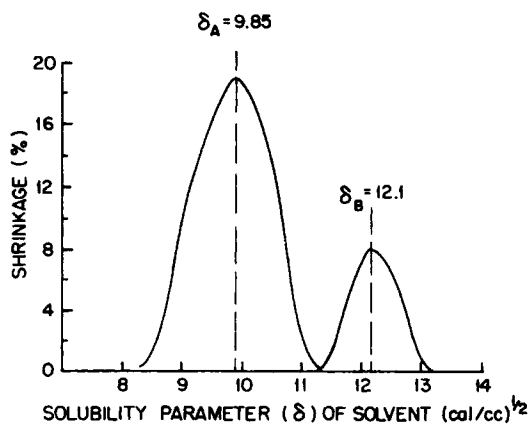


Fig. 1. Per cent shrinkage of a polyester yarn after 90 days in various organic solvents at 21°C as a function of the Hildebrand solubility parameter ( $\delta$ ) of the solvent giving rise to interaction maxima at  $\delta$ -values of 9.85 and 12.1 which correspond to the aromatic (A) and the aliphatic ester (B) residues of PET, respectively. From Knox, Weigmann, and Scott.<sup>4</sup>

$$\text{CED} = \frac{\Delta\bar{E}^v}{\bar{V}} \quad (1)$$

where  $\Delta\bar{E}^v$  is the molar energy of vaporization and  $\bar{V}$  is the molar volume of the condensed fluid. For a dense fluid (i.e., liquid or amorphous solid), the CED is experimentally determined from vapor pressure measurements which permit the evaluation of the molar enthalpy of vaporization ( $\Delta\bar{H}^v$ ) by the Clapeyron relation:<sup>5</sup>

$$\Delta\bar{H}^v = T \left( \frac{\partial P}{\partial T} \right)_V (\bar{V}_g - \bar{V}_l) \quad (2)$$

where  $P$  is the pressure,  $T$  is the absolute temperature, and  $V_{g,l}$  are the gaseous and liquid molar volumes, respectively. The molar energy of vaporization ( $\Delta\bar{E}^v$ ) is therefore given by<sup>5</sup>

$$\Delta\bar{E}^v = \Delta\bar{H}^v - \Delta(PV) \quad (3)$$

where  $\Delta(PV) \simeq RT$ , and  $R$  is the universal gas constant. From expressions (1) and (3), the CED may be determined.

Frequently, however, the fluid (or solid) in question may undergo degradation, chemical or structural rearrangement (e.g., crystallization) before vaporization occurs. Hence, it may not always be possible to measure directly the molar en-

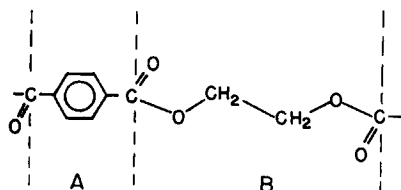


Fig. 2. Schematic representation of the bicomponent nature of the monomer repeat unit of PET; (A) aromatic residue centered around A; and (B) aliphatic ester residue centered around B. From Knox and Weigmann<sup>3</sup> and Knox, Weigmann, and Scott.<sup>4</sup>

thalpy of vaporization. This is especially true for high molecular weight materials such as polymers. Allen<sup>6</sup> suggests an alternative approach to the determination of the CED of polymeric materials. At atmospheric pressure, it may be shown<sup>1</sup> that the internal pressure ( $P_i$ ) which is taken to be a measure of the CED is given by

$$P_i = \frac{T\alpha}{\beta_T} \quad (4)$$

where  $\alpha$  is the thermal volume expansion coefficient and  $\beta_T$  is the isothermal compressibility. Frank<sup>7</sup> points out that for fluids which deviate from the behavior exhibited by a van der Waals liquid, the internal pressure ( $P_i$ ) is given by the ratio

$$\frac{P_i}{\text{CED}} = n \quad (5)$$

where  $n = 1$  for a van der Waals liquid. Allen<sup>6</sup> has shown that for fluids which are polar or hydrogen bonding in nature, the value of  $n$  is less than unity, while for hydrocarbons and fluorocarbons, the value of  $n$  is greater than unity. Only highly spherical, nonpolar molecules such as methane have a value of  $n = 1$ . Allen suggests<sup>6</sup> that the CED of polymeric materials may be evaluated given the internal pressure  $P_i$  from expression (4) and the value  $n$  for the ratio  $P_i/\text{CED}$  of chemically similar model compounds.

Hildebrand,<sup>1</sup> Walker,<sup>8</sup> and Kistiakowsky<sup>9</sup> have shown that for dense fluids with normal boiling points ( $T_b$ ) less than 600°K, the molar enthalpy of vaporization  $\Delta\bar{H}^v$  may be expressed by various analytical functions of  $T_b$ . The application of the Hildebrand rule<sup>1</sup> and the expressions proposed by Walker<sup>8</sup> and Kistiakowsky<sup>9</sup> necessitate knowing  $T_b$ , which is undefined for polymeric materials. However, a pseudoboiling point may be defined for the polymer repeat unit and evaluated by one of the expressions proposed by Meissner and Redding.<sup>10</sup>

It is apparent that the estimation of the molar enthalpy of vaporization of a chemical residue by the above approach requires successive approximations. Small<sup>11</sup> has shown that one may avoid such a multiapproximation scheme. He observed that each atomic and structural group has a characteristic cohesive energy and that the total cohesive energy of the chemical unit is simply given by the sum of the contributions of the various atomic and structural groups making up the chemical unit. Small<sup>11</sup> defined the total solubility parameter  $\delta$  by the following relation:

$$\delta = \frac{\sum_i F_i}{\bar{V}} \quad (6)$$

where  $F_i$  are the molar attractive constants of the atomic and structural groups forming the residue, and  $\bar{V}$  is the molar volume of the residue. Bondi<sup>12</sup> has evaluated a similar set of energy constants.

The above method proposed by Small<sup>11</sup> for the calculation of the solubility parameter of a chemical residue is based on the assumption of additivity which is not always observed for highly polar and hydrogen bonding compounds. However, from the comparison of experimental and calculated  $\delta$  values of

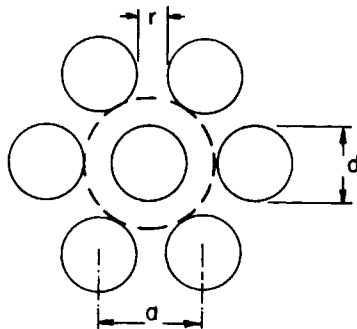


Fig. 3. Schematic representation of a spherical fluid model of a hard sphere having a diameter  $d$  and separated by a distance  $r$  ( $=d/2$ ) and generating upon free rotation a spherical cage volume of diameter  $2d$ . From Eyring.<sup>13</sup>

chemically similar compounds, the values of  $F$  may be adjusted to give a better estimate of the  $\delta$  values of corresponding chemical residues.

### Model for Volume Element of Polymeric Residue

To evaluate Small's expression for the CED, it is necessary to know the molar volume  $\bar{V}$  of the polymer residue. In the case of a polymer repeat unit, the molar volume is given by

$$\text{molar volume } \bar{V} = \frac{\text{molecular weight of repeat unit}}{\text{density of amorphous polymer}} \quad (7)$$

The measurement of the density of the bulk polymer is straightforward, but it is not possible to measure the density of a chemical residue other than that of the polymer repeat unit.

For example, the repeat unit of PET as represented in Figure 2 may be divided into two chemical residues: an aromatic residue centered around A and an aliphatic ester residue centered around B. It is not possible to assume that the densities of the aromatic and aliphatic ester residues are equal to that of the bulk amorphous polymer. This is supported by a comparison of the densities of chemically similar compounds. Benzaldehyde, taken as a model for residue A, has a density of 1.046 g/cm<sup>3</sup>; and ethylene diformate, taken as a model for residue B, has a density of 1.18 g/cm<sup>3</sup>; while dimethyl phthalate, taken as a model for the repeat unit, has a density of 1.189 g/cm<sup>3</sup>. It is more reasonable to assume the density of the bulk polymer to be given by the sum of densities  $\rho$  of the chemical residues  $i$  weighted by their volume fraction  $\phi$ :

$$\text{density of polymer (g/cm}^3\text{)} = \sum_i (\phi_i \rho_i) \quad (8)$$

To evaluate the molar volume of a chemical residue, it is first of interest to compare two different models of fluids: (i) a spherical fluid model permitting complete free rotation, and (ii) a cylindrical fluid model permitting only uniaxial rotation. In the case of the spherical fluid model schematically represented in Figure 3, Eyring<sup>13</sup> and Lennard-Jones<sup>14</sup> suggest that a single-component monomeric fluid (e.g., benzene or benzaldehyde) may be represented by a hard

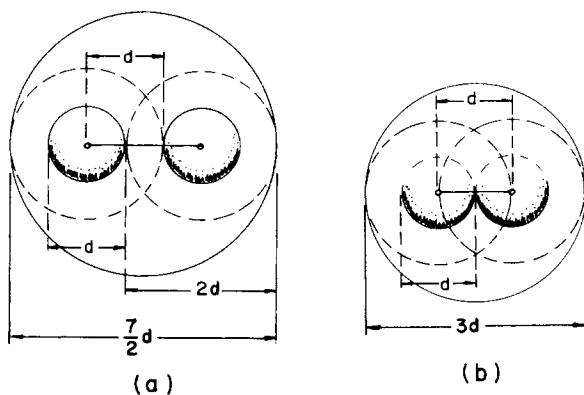


Fig. 4. Schematic representation of a bicomponent monomeric liquid (a) and a polymeric residue (b) by a spherical fluid model.

sphere having a diameter  $d$ . Upon free rotation in space, the above fluid generates a spherical "cage" volume element.

It is therefore suggested that a bicomponent monomeric fluid, such as the monomer of PET (Fig. 2), may be represented by two hard spheres separated by a distance  $d/2$ , where for simplicity the value of  $d$  is taken to be equal for both spheres. As the bicomponent fluid rotates freely in space, it generates a spherical "cage" volume element having a diameter  $7/2d$  (Fig. 4a). On the other hand, the PET residue itself is characterized as a bicomponent fluid-like segment (Fig. 4b) which may be represented by two hard spheres in contact with each other. Upon free rotation, the fluid-like segment generates a spherical "cage" volume element having a diameter  $3d$ . The spherical model of a bicomponent fluid, such as that representing the monomeric repeat unit of PET, predicts a 37% contraction in volume upon going from the monomer to the polymer, that is, upon going from a monomer volume of  $V_m = 4/3\pi(7/2d)^3 = (7/2)^3 \times 4/3\pi d^3 = (7/2)^3 V_{\text{sphere}}$  to a polymer volume of  $V_p = 4/3\pi(3d)^3 = (3)^3 \times 4/3\pi d^3 = (3)^3 V_{\text{sphere}}$ , where  $V_{\text{sphere}} = 4/3\pi d^3$  and  $\% \Delta V = (1 - V_m/V_p) \times 100$ .

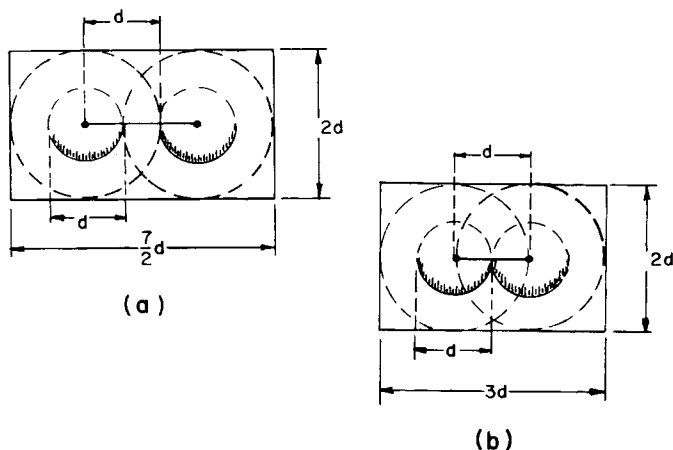


Fig. 5. Schematic representation of a bicomponent monomeric liquid (a) and a polymeric residue (b) by a cylindrical fluid model.

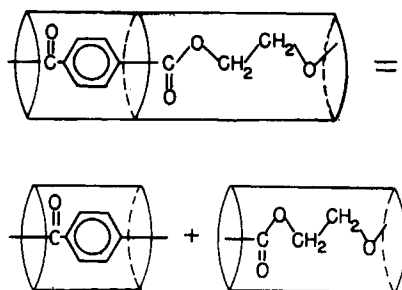


Fig. 6. Schematic representation of the PET repeat unit divided into two nonoverlapping cylindrical volume elements.

Experimentally, it is observed that PET contracts approximately 11% upon going from the monomer to the polymer as given by  $\% \Delta V = (1 - \rho_m / \rho_p) \times 100$ . It is therefore proposed that the monomer and repeat unit of PET be represented instead by a cylindrical fluid model for which rotation is restricted about the chain axis (Fig. 5a and 5b) generating cylindrical "cage" volume element of height  $7/2d$  and  $3d$ , respectively. The cylindrical fluid model predicts a 14% contraction in volume upon going from the monomer,  $V_m = \pi d^2 \times 7/2d = (7/4)V_{\text{cylinder}}$ , to the polymer,  $V_p = \pi d^2 \times 3d = 3/2(2\pi d^3) = (3/2)V_{\text{cylinder}}$ , where  $V_{\text{cylinder}} = 2\pi d^3$ , the volume of a single component monomeric fluid analogous to that represented in Figure 3. The cylindrical fluid model appears to describe well the molecular packing of PET and its monomer. The cylindrical fluid model shall be used in all further discussions.

The repeat unit of PET is now divided into nonoverlapping cylindrical volume elements as represented in Figure 6. It is important to require that the cylindrical volumes not overlap in order that the sum of the volumes of the cylindrical elements be equal and not greater than the total volume of the repeat unit. This is illustrated partly in Figure 7 and will be discussed in a later section.

To carry out a cylindrical sectioning of the PET repeat unit, the rigid phenylene ring is taken as the reference structure (Fig. 7). As a result of the symmetry of the phenylene ring, uniaxial rotation generates a cylindrical volume element (Fig. 7b) and free rotation generates a spherical volume element (Fig. 7c) which are taken to be equivalent. The cylindrical volume element of the remaining PET residue (i.e.,  $\bar{V}_{\text{PET}} - \bar{V}_{\text{phenylene ring}} = \bar{V}_{\text{ethylene diformate residue}}$ ) and other PET residues are calculated according to the scheme given in Table I.

In Figure 7d, it is observed that the cylindrical volume element of the flexible aliphatic ester residue is less than that of the freely rotating volume element. Hence, if the flexible aliphatic ester residue had been taken as the reference structure instead of the rigid phenylene ring, the calculated cylindrical volume of the phenylene ring would be unrealistically low. From Figure 7d, it is apparent that  $(\bar{V}_A)_{\text{spherical}} + (\bar{V}_B)_{\text{spherical}} > (\bar{V})_{\text{PET}}$ .

### Calculation of Molar Volume of Polymeric Residues

It has been shown that a long-chain molecule, such as PET, may be represented as a "segmented chain molecule" of nonoverlapping cylindrical volume elements. The molar volume of any one of the above volume elements may be calculated

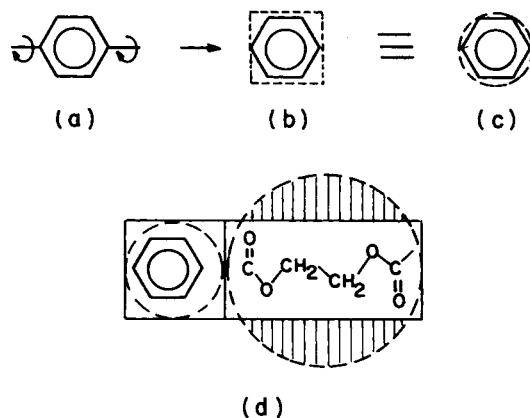


Fig. 7. Schematic representation of the cylindrical (b) and spherical (a) volume elements generated upon free rotation of the *p*-phenylene ring (a) which is taken as the reference structure in the representation of the PET repeat unit by the cylindrical fluid model (d). (////) = the spherical fluid volume.

from the definition of the packing coefficient  $K_p$  for long-chain molecules by Slonimskii:<sup>15</sup>

$$K_p = \frac{\bar{V}^0}{\bar{V}} \quad (9)$$

where the intrinsic volume  $\bar{V}^0$  is given by

$$\bar{V}^0 = N_{AV} \sum_i \Delta v_i \quad (10)$$

and the molar volume  $\bar{V}$  is given by expression (8).  $N_{AV}$  is the Avagadro number and  $\Delta v_i$  are the volume increments of the atomic and structural groups forming

TABLE I  
Scheme for the Calculation of the Cylindrical Volumes of PET Residues

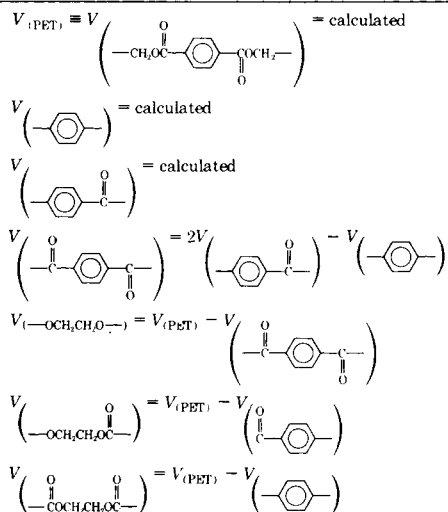
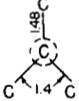



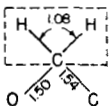

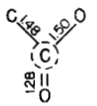
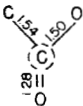


TABLE II  
The Intrinsic Volumes of Atom or Atomic Groups Forming the PET Residues<sup>a</sup>

Atom or atomic group	Volume increment, Å <sup>3</sup>	Atom or atomic group	Volume increment, Å <sup>3</sup>
	8.4		5.85
	14.7		3.45
	20.2		2.7
	15.7		15.8

<sup>a</sup> From Slonimskii.<sup>15</sup>

the repeat unit. Values of  $\Delta v_i$  used in the evaluation of the intrinsic volumes of various PET residues are listed in Table II.

The calculation of  $\Delta v_i$  is based on the representation of the volume of an atom<sup>16</sup> by a sphere with a radius  $R$ . If this atom is covalently bonded to other atoms, these adjacent atoms cut off part of the spherical volume of the first atom as a consequence of the sum of the atomic radii of the two-valent bonded atoms always being greater than the distance between the centers (see Fig. 8). This distance is the bond length  $d_i$ . The volume of the increment  $\Delta v_i$  for the given atom is calculated as the volume of the sphere of this atom minus the volume of the spherical segment cut off by the adjacent valent bonded atom. To evaluate  $\Delta v_i$ , values of atomic radii and bond length were taken from measurements made by Bondi.<sup>17</sup>

Experimentally, Slonimskii<sup>15</sup> observed the packing coefficient for a variety of polymers to be approximately the same having a mean value of 0.681. For PET, the value of  $K_p$  is found<sup>15</sup> to be 0.694. In evaluating the packing coefficient

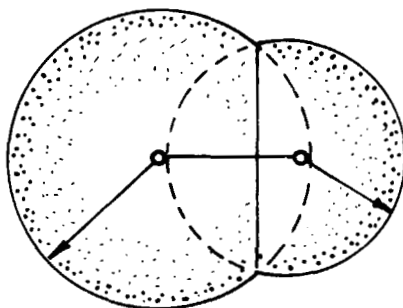

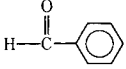
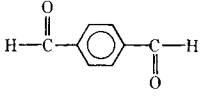
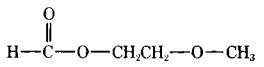
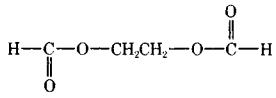
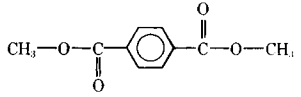


Fig. 8. Schematic representation of two atoms covalently bonded to each other. From Slonimskii.<sup>15</sup>



TABLE III  
Comparison of the Experimental and Calculated Molar Volumes of Monomeric  
Liquids Chemically Similar to the PET Residues

Chemical units	$\bar{V}_l$ , cc/mole	$\bar{V}_l$ , cc/mole	$\bar{V}_l$ , cc/mole
	89.4 <sup>a</sup>	88.0 <sup>a</sup>	89.4 <sup>c</sup>
	101.45	104.0	104.6
	114.3	116.9	115.57
$\text{CH}_3\text{---O---CH}_2\text{CH}_2\text{---O---CH}_3$	104.5	99.3	106.0
	99.33	98.4	101.5
	100.0	104.7	105.6
	162.9	165.6	163.3

<sup>a</sup> Experimental value found in literature.

<sup>b</sup> Calculated value according to the LeBas method.<sup>18</sup>

<sup>c</sup> Calculated value according to the Traube method.<sup>19</sup>

for the various chemical residues making up the polymer repeat unit, Slonimskii<sup>15</sup> assumed a single-valued  $K_p$ ; that is, he took the value of  $K_p$  of the chemical residues making up the polymer repeat unit to be equal to that of the polymer repeat unit. It is proposed here that the above assumption of a single-valued packing coefficient for all atomic and structural groups forming a long-chain molecule is an unnecessary assumption. The assumption of a single-valued  $K_p$  would require, for example, that two structural groups having the same molar intrinsic volume, but of different functionality, to have the same molar volume when part of a long-chain molecule.

In light of the proposed bicomponent cylindrical model for PET as depicted in Figures 5-7, the repeat unit of PET may be treated as being composed of  $i$  nonoverlapping cylindrical residues. The total molar volume of the PET repeat unit is therefore given by eqs. (11) and (12):

$$(\bar{V}_p)_{\text{PET}} = \sum_i (\bar{V}^0/K_p)_i = \sum_i (\bar{V}_p)_i \quad (11)$$

and

$$(\bar{V}_p)_{\text{PET}} = \sum_i [\bar{V}_l/(K_p/K_l)]_i \quad (12)$$

where

$$K_p \bar{V}_p = K_l \bar{V}_l = \bar{V}^0 \quad (13)$$

and  $p$  and  $l$  denote the polymer and liquid monomer, respectively.

The equivalency of expressions (11) and (12) suggests that upon going from the liquid monomer ( $l$ ) to the polymer ( $p$ ), each cylindrical volume element contracts by the ratio  $(K_p/K_l)_i^{-1}$ . It is proposed that the fractional volume contraction of each residue  $i$  may be taken to be equal to the fractional volume contraction of the polymer repeat unit. Hence, the value of  $(K_p/K_l)_i$  of each residue making up the repeat unit is taken to be equal to that of  $(K_p/K_l)$  of the polymer. The assumption that the value of  $(K_p/K_l)$  is a characteristic constant of the given polymer is a less rigid assumption than that of a single-valued  $K_p$  for all polymeric residues made by Slonimskii.<sup>15</sup>

The molar volume of any residue  $i$  may now be evaluated by the following relation:

$$(\bar{V}_p)_{\text{PET}} = (K_p/K_l)^{-1} \sum_i (\bar{V}_l)_i \quad (14)$$

where  $\bar{V}_l$  are cylindrical nonoverlapping liquid volume elements as calculated according to the scheme listed in Table II. For PET, the value of  $(K_p/K_l)$  is given by ratio of volumes,  $\bar{V}_l/\bar{V}_p$ , according to expression (13) and is found to be approximately 1.0904.

The packing coefficients  $K_p$  of the various PET residues may be evaluated from expression (13) if the cylindrical molar liquid volume,  $\bar{V}_l$  is known. LeBas<sup>18</sup> and Traube<sup>19</sup> have shown that the molar liquid volume of a chemical unit may be expressed as the sum of the atomic and structural contributions. LeBas<sup>18</sup> evaluated the molar liquid volumes at the normal boiling point  $T_b$ . To find the value of  $\bar{V}_l$  at a temperature below  $T_b$ , one may make use of the Goldhammer expression<sup>20</sup> which requires the value of the critical temperature  $T_c$ . The method outlined by Eduljee<sup>21</sup> may be used to evaluate an approximate value of  $T_c$  and enable the molar volume to be evaluated for  $T < T_b$ . A more direct approach is taken by Traube.<sup>19</sup> Traube<sup>19</sup> showed that the molar volume at room temperature, for example, is given by the sum of atomic and structural contributions plus a constant called the covolume. The value of the covolume may be treated as an adjustable parameter for a group of model compounds so as to better estimate the molar liquid volume of chemically similar polymer residues.

In Table III, experimental values of  $\bar{V}_l$  for various model compounds for PET residues are listed and are compared with those evaluated by methods outlined by LeBas<sup>18</sup> and Traube.<sup>19</sup> The agreement of the calculated and experimental values of  $\bar{V}_l$  gives confidence to the estimated values for the various PET residues. Values of  $\bar{V}_l$ ,  $\bar{V}^0$ ,  $K_p$ ,  $K_l$ , and  $\bar{V}_p$  for various PET residues are listed in Table IV.


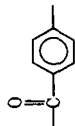
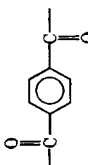
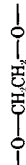
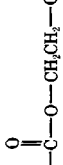
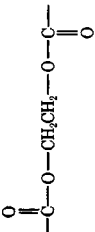
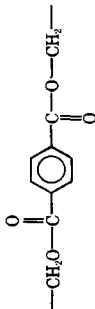
The total Hildebrand solubility parameters  $\delta$  of the various PET residues may now be calculated using expression (6) proposed by Small<sup>11</sup> and the values of the molar volumes  $\bar{V}_p$  as given by expression (14). The values of  $\delta$  for the various PET residues are listed in Tables V-VII.

## HANSEN SOLUBILITY PARAMETERS

### Simple Monomeric Fluids

Van Arkel<sup>22</sup> showed that the mutual solubility of liquids possessing permanent dipoles is not adequately described by the Hildebrand solubility parameter

TABLE IV  
The Calculated Molar Volumes and Packing Coefficients of the Spherical and Cylindrical Volume Elements of Liquid and Polymeric Residues Forming the Poly(ethylene Terephthalate) Repeat Unit

Chemical units	$\bar{V}_1$ , cc/mole	$\bar{V}_1$ , cc/mole	$\bar{V}_1$ , cc/mole	$\bar{V}_1$ , cc/mole	$K_I$	$K_p$	$\bar{V}_p$ , cc/mole
	81.0a	83.2b	82.1c	82.1d	0.547	0.577	75.93e
	97.06	95.25	96.16	96.16	0.609	0.644	88.23
	108.59	110.65	109.12	109.12	0.656	0.715	100.13
	56.6	68.62	68.62	48.0	0.591	0.645	44.02
	81.36	84.02	82.6	60.96	0.679	0.741	55.91
	106.5	98.4	102.45	73.92	0.737	0.803	67.83
	160.31	157.12	158.72	158.72	0.637	0.694	144.1

a Calculated spherical volume by LeBas method.<sup>18</sup>




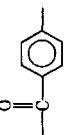
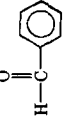

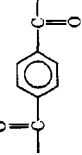
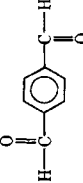

b Calculated spherical volume by Traube method.<sup>19</sup>

c Average of values 1 and 2.

d Cylindrical volume calculated according to the proposed scheme in Table I and using the average values given in column 3.

e Cylindrical volume of polymeric residues calculated according to the proposed scheme in Table I, using the van der Waals (intrinsic) volumes in Table II and the packing coefficients  $K_{I,p}$  as defined by Slonimskii.<sup>1,5</sup>

TABLE V  
The Molar Volumes, the Boiling, Critical, and Reduced Temperatures, and the Hansen Solubility Parameters of the Various Polymeric Residues and of the Corresponding Chemically Similar Monomeric Liquids and Homomorphs which Form the Aromatic (A) Residue of Poly(ethylene Terephthalate)<sup>a</sup>

Chemical units	$\bar{V}$ , cc/mole	$T_B$ , °K	$T_C$ , °K	$T_R$ , (T = 298)	$\delta$ , (cal/cc) <sup>1/2</sup>	$\delta_d$ , (cal/cc) <sup>1/2</sup>	$\delta_a$ , (cal/cc) <sup>1/2</sup>
(I) 	(75.93)	—	—	—	(8.67)	(8.56)	(1.35)
(II) 	89.4	353.1	562.1	0.809	9.15	9.03	1.48
(III) 	108.7	353.9	553.1	0.790	8.18	8.18	0
(I) 	(88.23)	—	—	—	(10.40)	(9.19)	(4.75)
(II) 	101.45	452.1	625.1	0.477	10.07	8.90	4.60
(III) 	128.3	374.1	572.1	0.521	7.82	7.82	0
(I) 	(100.13)	—	—	—	(11.57)	(9.62)	(5.29)
(II) 	115.67	520.1	(706.8)	(0.422)	11.49	9.55	6.91
(III) 	144.0	397.8	(567.5)	(0.525)	8.89	8.89	0

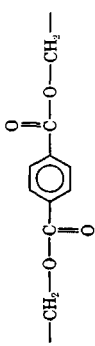
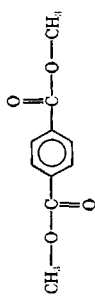
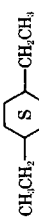
<sup>a</sup> ( ) = Calculated values; (I) polymer residue; (II) monomer; (III) homomorph.

TABLE VI  
The Molar Volumes, the Boiling, Critical, and Reduced Temperatures, and the Hansen Solubility Parameters of the Various Polymeric Residues and of the Corresponding Chemically Similar Monomeric Liquids and Homomorphs which Form the Aliphatic Ester (B) Residue of Poly(ethylene Terephthalate)<sup>a</sup>

	Chemical units	$\bar{V}$ , cc/mole	$T_B$ , °K	$T_C$ , °K	$T_R$ , ( $T = 298$ )	$\delta$ , (cal/cc) <sup>1/2</sup>	$\delta_d$ , (cal/cc) <sup>1/2</sup>	$\delta_a$ , (cal/cc) <sup>1/4</sup>
(I)	$-\text{O}-\text{CH}_2\text{CH}_2-\text{O}$	(44.02)	—	—	—	(9.22)	(6.05)	(6.92)
(II)	$\text{CH}_3-\text{O}-\text{CH}_2\text{CH}_2-\text{O}-\text{CH}_3$	104.5	366.1	536.1	0.566	11.88	7.85	8.92
(III)	$\text{CH}_3-\text{CH}_2\text{CH}_2-\text{CH}_3$	101.43	272.6	(438.9)	(0.679)	6.72	6.72	0
(I)	$-\text{O}-\text{CH}_2\text{CH}_2-\text{O}-\overset{\text{O}}{\parallel}{\text{C}}-$	(55.91)	—	—	—	(11.55)	(8.98)	(7.28)
(II)	$\text{CH}_3\text{O}-\text{CH}_2\text{CH}_2-\text{O}-\overset{\text{O}}{\parallel}{\text{C}}-\text{H}$	99.33	404.4	(574.2)	(0.519)	(10.08)	(7.78)	(6.65)
(III)	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$	116.1	309.2	469.5	0.635	7.02	7.02	0
(I)	$-\overset{\text{O}}{\parallel}{\text{C}}-\text{O}-\text{CH}_2\text{CH}_2-\text{O}-\overset{\text{O}}{\parallel}{\text{C}}-$	(67.83)	—	—	—	(13.06)	(10.62)	(7.6)
(II)	$\text{H}-\overset{\text{O}}{\parallel}{\text{C}}-\text{O}-\text{CH}_2\text{CH}_2-\text{O}-\overset{\text{O}}{\parallel}{\text{C}}-\text{H}$	105.62	447.1	618.2	0.482	10.09	8.2	5.2
(III)	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$	131.6	341.9	508	0.587	7.24	7.24	0

<sup>a</sup> ( ) = Calculated values; (I) polymer residue; (II) monomer; (III) homomorph.

TABLE VII  
 The Molar Volumes, the Boiling, Critical, and Reduced Temperatures, and the Hansen Solubility Parameters of the Polymeric Residue  
 and the Corresponding Monomeric Liquid and Homomorph which Form the Monomer Repeat Unit of Poly(ethylene Terephthalate)<sup>a</sup>

Chemical units	$\bar{V}$ , cc/mole	$T_B$ , °K	$T_C$ , °K	$T_R$ ( $T = 298$ )	$\delta$ , (cal/cc) <sup>1/2</sup>	$\delta_d$ , (cal/cc) <sup>1/2</sup>	$\delta_{d_1}$ , (cal/cc) <sup>1/2</sup>
(I) 	144.1	—	—	—	(10.71)	(9.36)	(5.20)
(II) 	163.3	>573	>850	<0.350	10.45	9.13	5.08
(III) 	157.1	(398)	(568)	(0.524)	8.75	8.75	0

<sup>a</sup> ( ) = Calculated values; (I) polymeric residue; (II) monomer; (III) homomorph.

concept.<sup>1</sup> In considering liquids whose molecules possess permanent dipoles, Van Arkel<sup>22</sup> found it useful to separate the CED into polar and nonpolar contributions. The nonpolar contribution to the CED is taken as that arising from dispersion forces and the polar contribution is therefore taken as a residual contribution to the CED arising from dipole-dipole forces and other associative forces. More recently, Hansen<sup>2</sup> has shown that the polar contribution to the CED as defined by Van Arkel<sup>22</sup> may be separated into contributions from permanent dipole-dipole forces and from hydrogen bonding-type forces. Hansen<sup>2</sup> expressed the total Hildebrand solubility parameter  $\delta$  by the sum

$$\delta = (\delta_d^2 + \delta_p^2 + \delta_h^2)^{1/2} \quad (15)$$

where  $d$ ,  $p$ , and  $h$  denote dispersion, polar (dipole-dipole), and hydrogen bonding, respectively. The polar contribution to the CED as defined by Van Arkel<sup>22</sup> is given by the associative parameter  $\delta_a$ :

$$\delta_a = (\delta_p^2 + \delta_h^2)^{1/2} \quad (16)$$

of the Hansen two-dimensional solubility parameter approach<sup>2</sup> and, therefore, the total Hildebrand solubility parameter  $\delta$  may also be given by the sum

$$\delta = (\delta_d^2 + \delta_a^2)^{1/2} \quad (17)$$

Bondi and Simkin<sup>23</sup> have shown that the energies of vaporization of polar liquids can be divided into polar (associative) and nonpolar (dispersion) contributions by using the homomorph idea of Brown.<sup>24</sup> The homomorph of a polar molecule is defined as a nonpolar molecule having very nearly the same size and shape as those of the polar molecule. For example, the homomorph of chlorobenzene might be toluene. Blanks and Prausnitz<sup>25</sup> have shown that the nonpolar dispersion solubility parameter  $\delta_d$  of a polar molecule may be calculated by representing the polar molecule by its corresponding hydrocarbon homomorph and taking the total solubility parameter  $\delta$  of the homomorph to be equivalent to the dispersion solubility parameter  $\delta_d$  of the polar molecule. It must be remembered, however, to evaluate the molar energy of vaporization of the homomorph at the same reduced temperature as that of the polar molecule and to compare the molar volumes at this same reduced temperature also. The temperature dependence of the energies of vaporization is given by the expression proposed by Haggemacher<sup>26</sup> and that of the molar volumes by the expression proposed by Goldhammer.<sup>20</sup> The polar energy of vaporization is, therefore, simply the difference between the experimentally determined total energy of vaporization and the energy of vaporization of the homomorph at the same reduced temperature. And, therefore, the associative solubility parameter  $\delta_a$  of the polar molecule is given by

$$\delta_a(\text{polar molecule}) = [\delta^2(\text{polar molecule}) - \delta^2(\text{homomorph})]^{1/2} \quad (18)$$

where  $\delta^2$  of the homomorph has been evaluated at the same reduced temperature as that of the polar molecule.

As discussed earlier, Hansen<sup>2</sup> has shown that the associative solubility parameter  $\delta_a$  as given by expression (18) may, in turn, be separated into polar (dipole-dipole) and hydrogen-bonding contributions according to expression (16). To evaluate the contribution of the permanent dipole to the total CED, Hansen<sup>2</sup> made use of the expression proposed by Böttcher<sup>27</sup> from the theory of

polarization. The polar solubility parameter  $\delta_p$  is, therefore, the square root of the contribution of the permanent dipoles to the total CED and is given by [6]:

$$\delta_p = \left[ \left( \frac{12108}{\bar{V}} \right) \left( \frac{\epsilon - 1}{2\epsilon + N_D^2} \right) (2 + N_D^2) \mu^2 \right]^{1/2} \quad (19)$$

where  $\bar{V}$  is the molar volume ( $\text{cm}^3/\text{mole}$ ),  $\epsilon$  is the static dielectric constant,  $N_D$  is the index of refraction for the sodium  $D$  line, and  $\mu$  is the dipole moment in debyes.

Expression (19) assumes a spherical model with a point dipole at the center of the molecule. The extent to which the idealized model can be in error has been calculated by Böttcher<sup>27</sup> for the situation where the center of the dipole is removed a distance  $s$  from the center of the spherical molecule of radius  $r$  and is found to be appreciable for asymmetric molecules. Keesom<sup>28,29</sup> points out that the polar cohesive energy should also be corrected for hindered rotation of the dipole moment. Hansen<sup>2</sup> takes into account deviations from expression (19) by comparing the calculated values with experiment.

The hydrogen-bonding solubility parameter  $\delta_h$  is found to be given by the following expression for alcohols:<sup>30,31</sup>

$$\delta_h = \left[ \frac{5000}{\bar{V}} N_{\text{OH}} \right]^{1/2} \quad (20)$$

where  $N_{\text{OH}}$  denotes the number of hydroxyl groups. For compounds other than alcohols, Hansen<sup>2</sup> treats the value of  $\delta_h$  as a residual parameter given by the following relation:

$$\delta_h = [\delta^2 - \delta_d^2 - \delta_p^2]^{1/2} \quad (21)$$

### Polymeric Residues

In order to calculate the Hansen solubility parameters of a polymeric residue, one may make use of the approximation proposed by Blanks and Prausnitz.<sup>25</sup> Blanks and Prausnitz<sup>25</sup> assume that the fractional contribution of the dispersion forces, for example, to the total CED of the given polymeric residue may be taken to be equal to that of a chemically similar monomeric fluid. That is,

$$(\delta_j^2)/(\delta^2)_{\text{polymer}} \approx [(\delta_j^2)/(\delta^2)]_{\text{monomer}} \quad (21)$$

where  $j$  denotes the Hansen solubility parameter in question.

Expression (21) is found to be very useful in calculating the values of the dispersion and associative solubility parameters of the various PET residues which are given in Tables V–VII. Unfortunately, not all values of the necessary constants required to solve expression (19) for the polar solubility parameter are known for the various monomeric fluids given in Table III. It is, therefore, not possible to calculate directly the polar and hydrogen-bonding contributions to the total CED of the various PET residues. Values of the polar and hydrogen-bonding contributions to the total CED may be estimated if one takes the experimentally determined fractional contribution of the polar solubility parameter to the total CED, for example, to be equal to that determined according to ex-



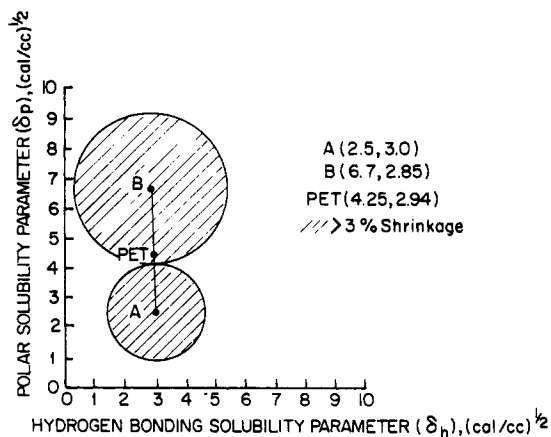


Fig. 9. Hansen solubility parameter plot of areas of high PET-solvent interaction (//// > 3% shrinkage). The coordinates of the centers of the interaction circles A and B are the experimental values of  $\delta_p$  and  $\delta_h$ , respectively, of the aromatic (A) and aliphatic ester (B) residues of PET. The volume fraction average of residues A and B is taken as the center of the interaction circle for the monomer repeat unit, PET.

pression (21). Therefore, a value of  $\delta_p$  (or  $\delta_h$ ) may be evaluated based on the calculated value of  $\delta$  and the experimental value for the fractional contribution  $(\delta_j^2)/(\delta^2)$ . That is,

$$(\delta_j^2)_{\text{calc}} \approx (\delta^2)_{\text{calc}} \times [(\delta_j^2)/(\delta^2)]_{\text{exp}} \quad (22)$$

where  $j$  denotes the polar and hydrogen-bonding contributions to  $\delta^2$ .

### EXPERIMENTAL EVALUATION OF THE HANSEN SOLUBILITY PARAMETERS OF PET RESIDUES

To determine experimentally the Hansen solubility parameters of the PET residues, the PET-solvent interactions as indicated by shrinkage, swelling, and crystallization are represented graphically<sup>3,4</sup> as a circle of interaction by a Hansen two-dimensional plot with fixed coordinates  $\delta_p$  and  $\delta_h$  and a floating axis  $\delta_d$  (see Fig. 9). The coordinates of the center of the circle of interaction are taken as the experimental values of  $\delta_p$  and  $\delta_h$  of the given PET residue. The value of the associative solubility parameter  $\delta_a$  is calculated from expression (16) and that of the dispersion solubility parameter  $\delta_d$  from expression (17) in which the values of the total Hildebrand solubility parameter  $\delta$  are taken to be those of the interaction maxima of a Hildebrand solubility parameter plot (see Fig. 1). The experimental values obtained for the Hansen solubility parameters for the aromatic (A) and aliphatic ester (B) residues of PET are given in Table VIII.

The center  $(\delta_d, \delta_p, \delta_h)$  and the radius  $R$  of the polymer-solvent interaction sphere is used by Hansen<sup>2</sup> to characterize the material in question. Hansen<sup>2</sup> suggests that the value of  $R$  may be given by

$$R_{\text{Hansen}} = [2(\delta_2 - \delta_1)_d^2 + (\delta_2 - \delta_1)_p^2 + (\delta_2 - \delta_1)_h^2]^{1/2} \quad (23)$$

where 1 denotes the "borderline" solvent and 2 denotes the polymeric material (residue). Hansen incorporates the factor 2 before the dispersion term  $(\delta_2 - \delta_1)_d^2$  based on the empirical observation that the polymer-solvent interaction

domains may be made spherical if the unit distance on the  $\delta_d$  axis is made equal to twice that along the  $\delta_p$  and  $\delta_h$  axes. The definition of the value of  $R$  by Hansen is inconsistent with the definition of  $\delta$  as given by expression (15) and with the thermodynamic definition of  $R$  by Hildebrand and Scott:<sup>1</sup>

$$R_{\text{Hildebrand}} = \left[ \sum_i (\delta_2 - \delta_1)_i^2 \right]^{1/2} \quad (24)$$

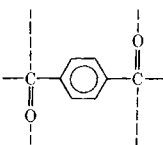
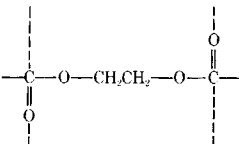
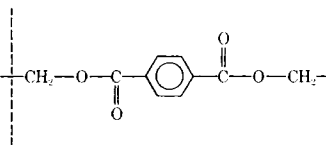
and

$$R^2_{\text{Hildebrand}} = \overline{\Delta G^E_{\text{mix}}} / \bar{V}_{\text{mix}} \phi_1 \phi_2 \quad (25)$$

where  $\overline{\Delta G^E_{\text{mix}}}$  is the molar free energy of mixing polymer (2) and solvent (1);  $\bar{V}_{\text{mix}}$  is the molar volume of the mixture, and  $\phi$  is the volume fraction. The value of  $R$  as given by expression (24) assumes the validity of the geometric mean additivity rule and is consistent with the definition of  $\delta$  as given by expression (15).

The incorporation of the factor 2 by Hansen is not needed to make the polymer-solvent interaction domain spherical in shape. The spread in the values of  $\delta_d$  for most solvents is small compared to that of  $\delta_p$  and  $\delta_h$ —hence giving the observed “apparent” nonspherical representation of the data. Presumably, if solvents could be found (and had been used) with  $\delta_d$  values smaller and larger than those used by Hansen, then the resultant polymer-solvent interaction domain would approach that of a sphere as defined by expressions (15) and (24). For PET-solvent interactions, the values of  $R_A$  and  $R_B$  are found to be 1.88 and 2.22, respectively. These values are slightly different than values reported earlier.<sup>4</sup> Therefore, solvents which fall within one of the interaction spheres defined by  $R_{A,B}$  (i.e.,  $R_{\text{solvent}} < R_{A,B}$ ) would be expected to interact with PET

TABLE VIII  
The Experimental Hansen Solubility Parameters of the Aromatic Residue (A),  
of the Aliphatic Ester Residue (B), and of the Monomer Repeat Unit  
of Poly(ethylene Terephthalate) (PET)<sup>a</sup>

PET residues	$\delta$ , (cal/ cc) <sup>1/2</sup>	$\delta_d$ , (cal/ cc) <sup>1/2</sup>	$\delta_p$ , (cal/ cc) <sup>1/2</sup>	$\delta_h$ , (cal/ cc) <sup>1/2</sup>	$\delta_a$ , (cal/ cc) <sup>1/2</sup>
(A) 	9.85	9.04	2.50	3.00	3.91
(B) 	12.10	9.66	6.70	2.85	7.29
(PET) 	10.78	9.30	4.25	2.94	5.32

<sup>a</sup> (A) = aromatic residue; (B) = aliphatic ester residue; PET = monomer repeat unit.

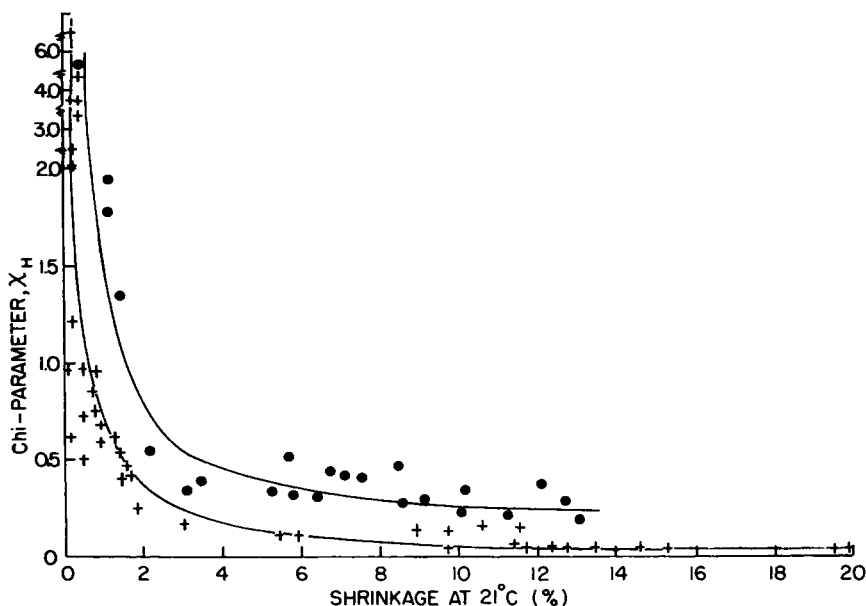


Fig. 10. Plot of the Flory-Huggins chi-parameter of nonaqueous solvents interacting with either the aromatic (A) or the aliphatic ester (B) residue of poly(ethylene terephthalate) as a function of the percent shrinkage at 21°C after 90 days. (+) Residue A; (●) residue B.

bringing about volume swelling, longitudinal shrinkage, and crystallization of the polyester structure.

Based on expression (25), the extent of the particular PET residue-solvent interaction should be related to the value of  $R$  for the given residue-solvent pair. It may be shown that the value of  $R^2$  is related to the Flory-Huggins chi-parameter ( $\chi$ ) which is frequently taken as a relative measure of the "compatibility" of the polymer and solvent.<sup>1</sup> The value of  $\chi$  as modified by the Hansen three-dimensional solubility parameter principle may be given by the following expression:

$$\chi = \chi_s + \frac{\bar{V}_1}{RT} [\Sigma(\delta_1 - \delta_2)^2_{d,p,h}] \quad (26)$$

where  $\bar{V}_1$  is the molar volume of the solvent,  $R$  is the universal gas constant,  $T$  is the absolute temperature, and  $\chi_s$  is the entropic contribution to  $\chi$ , representing the packing geometry of the solvent molecules and the particular polymeric residue and is usually taken as a constant for a given polymeric residue. The term in brackets is the value of the square of the radius for the given solvent-PET residue pair as previously defined by expression (24).

In Figure 10, the values of  $\chi$  for various PET-solvent systems, as calculated according to expression (26) assuming  $\chi_s$  is zero, are plotted as a function of shrinkage of a drawn PET yarn. A smooth relationship between  $\chi$  and shrinkage is observed for the interaction of solvents with the aromatic (A) and the aliphatic ester (B) residues of PET, respectively. The vertical displacement of curve B from that of curve A is attributed to having neglected the contribution of  $\chi_s$ , which is most likely different for the two PET residues, to the total chi-parameter  $\chi$ .

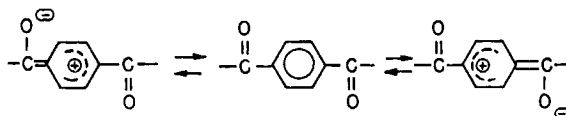


Fig. 11. Schematic representation of the deactivation of the benzene ring of the aromatic residue (A) by the 1,4-carbonyl groups.

## THE CHEMICAL NATURE OF THE PET RESIDUES

The nature of residues A and B has so far been described in terms of intermolecular cohesive forces as given by the Hansen solubility parameters from which it was possible to make structural assignments. It is of interest to supplement this description of the chemical association that exists between the solvent and a given PET residue in terms of the Lewis concept of basicity and acidity.<sup>32,33</sup> Here, it is suggested that the interaction of a solvent and a PET residue may be described as an interaction of a Lewis base and acid forming a "salt." In keeping with the bimodal character of PET-solvent interactions, it is proposed that one of the residues may be considered as a Lewis base and the other, as a Lewis acid.

The benzene ring is represented by a cyclic cloud of delocalized  $\pi$ -electrons above and below the plane of the ring. The 1,4-carbonyl groups are able to deactivate the benzene ring by extended electron delocalization through resonance structures<sup>34</sup> permitting the overlap of the  $p$ -orbitals of the aromatic carbon adjacent to the carbonyl carbon and of the carbonyl group (Fig. 11). As a result of the deactivation of the benzene ring by the 1,4-carbonyl groups, the benzene ring is electron deficient (+) and may be considered as a Lewis acid. The ester group is, in turn, electron rich (-) and may be considered as a Lewis base.

The view that the aromatic residue may be characterized as a Lewis acid and that the aliphatic ester residue may be characterized as a Lewis base is in slight disagreement with that proposed by Moore and Sheldon<sup>35</sup> who attributed the acidity of the PET monomer unit to the methylene groups rather than to the benzene ring.

From what has been said about the differences in the relative acidity and basicity of the aromatic and aliphatic ester residues, the solvents that would be expected to interact with a given PET residue are listed according to their functionality and extent of interaction with PET in Table IX. From Table IX, it is observed that the concept of acidity and basicity as defined in the Lewis sense describes well the interactions of nonaqueous solvents with PET.

In several instances, however, the concept of acidity and basicity fails to predict the observed behavior with PET. For example, although alcohols and alkanes are expected to interact with the aromatic residue, it is observed that, with a few exceptions (e.g., furfuryl alcohol and tetralin), alcohols and alkanes are relatively poor solvents for PET and do not show any significant interaction with PET. The relative inertness of alcohols and alkanes to interaction with PET is attributed to the intermediate hydrogen bonding nature of PET. Alkanes from weak or no hydrogen bonds with PET, while alcohols are very strong hydrogen-bonding solvents and exhibit self-association which prevents interassociation with PET.

As has been shown previously,<sup>4</sup> the multidimensional solubility parameter principle of Hansen which takes into account the relative contributions of polar and hydrogen bonding to the determination of solvent-polymer compatibility describes well the interactions of nonaqueous solvents with PET residues. As has been shown above, the effects of specific forces, e.g., hydrogen bonding, may override the primary effects of acidity and basicity.

### CONCLUSIONS

It has been shown that the volume element of a polymeric residue is best represented by a cylindrical fluid model. The total Hildebrand solubility parameter of the polymeric residue may then be calculated according to the method outlined by Small<sup>11</sup> for which the value of the molar volume may be evaluated from that of the corresponding monomeric fluid by the methods of LeBas<sup>18</sup> and Traube<sup>29</sup> and the ratio of the respective packing coefficient, ( $K_l/K_p$ ). The total Hildebrand solubility parameter may be separated into nonpolar and associative contributions using the homomorph method of Brown et al.<sup>24</sup> as applied to polymers by Blanks and Prausnitz.<sup>25</sup> The associative solubility parameter may, in turn, be separated into polar and hydrogen-bonding contributions by extending the approach taken by Blanks and Prausnitz.<sup>25</sup> The experimental values of the Hildebrand and Hansen solubility parameters may be evaluated by graphically representing the polyester-solvent interactions, as described previously<sup>3,4</sup> by Hildebrand and Hansen solubility parameter plots (Figs. 1 and 9). From a comparison of the calculated and experimental  $\delta$ -values, the initial assignment of the  $\delta$ -values of 9.85 and 12.1 to the aromatic (A) and to the aliphatic ester (B) residues, respectively, is supported here. It will be shown in part II of this series that the structures of residues A and B are best described by "hy-

TABLE IX  
Interaction of Lewis Acids and Bases with Polyester Residues<sup>a</sup>

Solvent class	Aromatic residue	Aliphatic ester residue
<i>Lewis Acids</i>		
nitriles		++
nitro		++
esters	+b	+++
ketones		++
aldehydes		++
carboxylic acids		++
amides		+++
<i>Lewis Bases</i>		
chlorohydrocarbons	++++	
bromohydrocarbons	++	
arenes	+	
alkanes	+	
ethers	++	
alcohols	+	
amines	+++	+b

<sup>a</sup> Levels of interaction: + (0-5%); ++ (5-10%); +++ (10-15%); ++++ (15-20%) shrinkage after 90 days at 21°C.

<sup>b</sup> Borderline solvents.

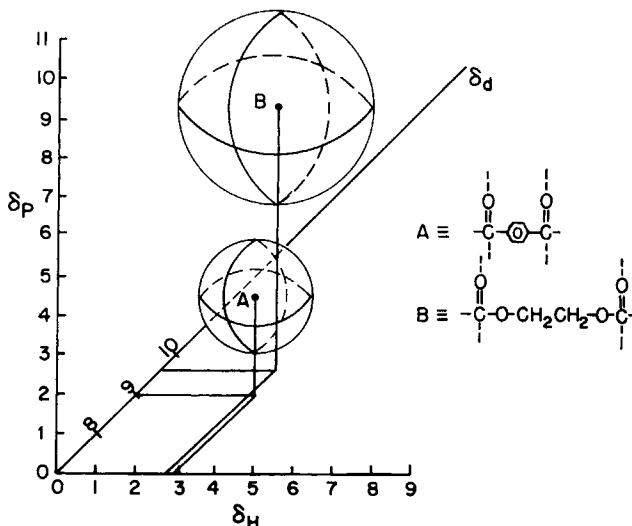


Fig. 12. Three-dimensional Hansen solubility parameter plot of the interaction of nonaqueous solvents with the aromatic (A) and the aliphatic ester (B) residues of PET.

brid" 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 groups effectively act as a common plane between the two residues and are "shared" by both residues.

It has also been shown that the bimodal character of polyester-solvent interactions may be described in terms of the relative basicity and acidity in a Lewis sense of the aromatic and aliphatic ester residues.

In conclusion, the nature of the PET-solvent interactions is believed to be bimodal in character giving rise to two spheres of interaction when represented by the Hansen solubility parameter concept (see Fig. 12). Solvents which fall within one of the PET spheres are expected to interact with the given residue bringing about volume swelling, longitudinal shrinkage, and crystallization of the polyester structure. The solubility parameter concept is found to be useful in describing the ability of a solvent medium to bring about changes in polyester.

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