

Bimodal Character of Polyester-Solvent Interactions.

III. The Effects of Morphology on the Nature of the Interaction of Nonaqueous Solvents with the Aromatic and the Aliphatic Ester Residues of Poly(ethylene Terephthalate)

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Synopsis

The extent of solvent-induced shrinkage, swelling, and crystallization of polyester is found to be dependent on the initial morphology of the material. However, the nature of the interaction of nonaqueous solvents with the aromatic and the aliphatic ester residues of poly(ethylene terephthalate) is found to be independent of morphology and only dependent on the differences in the stereochemical nature of the given solvent and polyester residue.

INTRODUCTION

In part I of this series,¹ the Hildebrand and Hansen solubility parameters were calculated for the various residues of the monomer repeat unit of poly(ethylene terephthalate) (PET) and compared to those determined experimentally. From such a comparison, it was proposed in part II of this series² that the structures of the aromatic (A) and the aliphatic ester (B) residues of the PET repeat unit (see Fig. 1) may be represented by "hybrid" structures defined as linear combinations of two or more structures. This is equivalent to saying that the 1,4-carbonyl groups of the 1,4-benzenoid residue ($-\text{OC}-\text{C}_6\text{H}_4-\text{CO}-$) effectively act as a common plane between the aromatic and the aliphatic ester residues and are "shared" by both residues. A measure of the extent to which the 1,4-carbonyl groups are "shared" by the respective residues is given² by the fractional carbonyl content f_c defined by the following relation:

$$f_c = \frac{\text{total no. of } \begin{array}{c} \text{O} \\ \parallel \\ \text{C} \end{array} \text{ groups per hybrid scheme}}{2 \times \text{no. of residues per hybrid scheme}} \quad (1)$$

In part II,² it was shown that the values of f_c giving the best agreement between the calculated and experimental Hildebrand and Hansen solubility parameters of residues A and B are 0.33 and 0.67, respectively.

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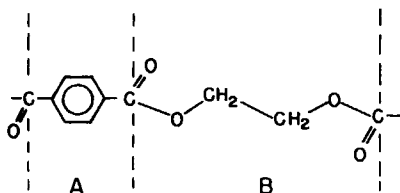


Fig. 1. Schematic representation of the bicomponent nature of the monomer repeat unit of PET: aromatic residue (A); aliphatic ester residue (B).

It was previously shown² that the observed values of f_c are also consistent with the proposed preferred molecular conformation of the 1,4-benzenoid residue of amorphous PET, which supports the view that the solvent molecules interact (at least moderate temperatures) only with the noncrystalline polymer regions. And, therefore, in the calculations of the solubility parameters δ of the residues of PET, the density of the PET repeat unit is taken to be that of the amorphous state. That is, it is assumed that there is no effect of molecular chain orientation nor of the presence of crystallites on the "stereochemical nature" of the interaction of solvents with PET. Hence, the fractional carbonyl content f_c is taken as a molecular parameter which is independent of changes in the morphology of the PET structure. Therefore, the chemical structures and the corresponding solubility parameters of the aromatic and aliphatic ester residues of PET are also taken to be independent of changes in the morphology of the PET structure.

It is of interest to test the above assumptions by examining the effects of changes in PET morphology on the "nature" and "extent" of PET-solvent interactions (e.g., shrinkage and crystallization) as represented by the bimodal solubility parameter distribution and by examining the effects of changes in PET morphology on the molecular conformations of residues A and B (i.e., the fractional carbonyl content) in the absence of solvent interactions.

RESULTS AND DISCUSSION

Cohesive Energy Density of PET Residues

The paracrystalline model of fiber structure³ suggests that there exists a distribution of local lateral order between chain segments and hence a continuum of polymer density varying from that of the completely amorphous to the completely crystalline state. A distribution of cohesive energy densities should therefore exist⁴ for drawn PET. If this is the case and if the nature of the interaction between solvent and PET is described by the degree of local lateral order, then, as the fiber is drawn, the cohesive energy density would also be expected to increase.

The increase in extensional strain would also be expected to hinder the rotation of the 1,4-carbonyls as the result of increased molecular orientation and local lateral ordering, and thereby increase the probability that a carbonyl group lies in the plane of the benzene ring. As a result, the rotational conformations, greater than 10° out of plane, would not be expected to become more hindered and less favored. Hence, as extensional strain increases, rotation about the bond connecting the benzene ring and the carbonyl group would be expected to de-

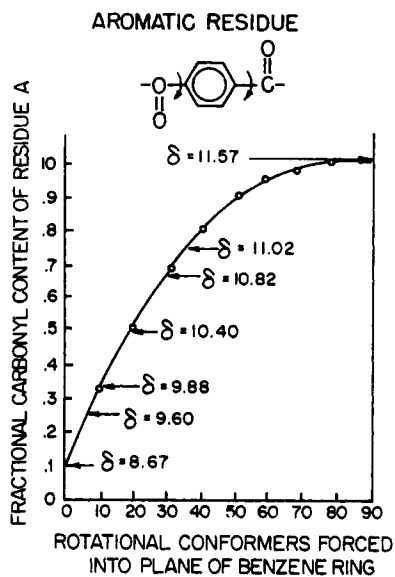


Fig. 2. The effect of the fractional carbonyl content f_c on the corresponding total solubility parameter δ as the result of rotational conformers forced into the plane of the benzene ring of the 1,4-benzenoid residue of PET due to rotational hindrance of the 1,4-carbonyls from increased molecular ordering and orientation.

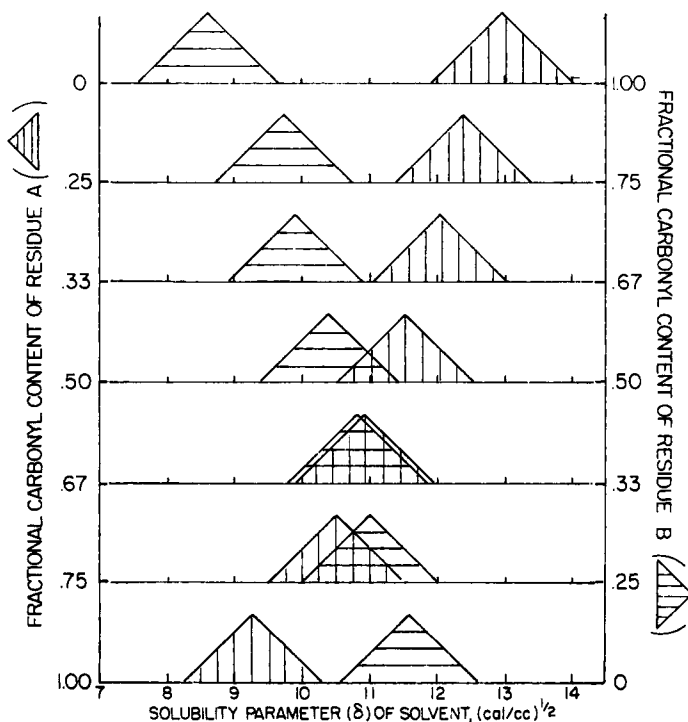


Fig. 3. Schematic representation of the effect of changing fractional carbonyl content f_c on the bimodal character of the Hildebrand solubility parameter distribution of PET-solvent interactions.

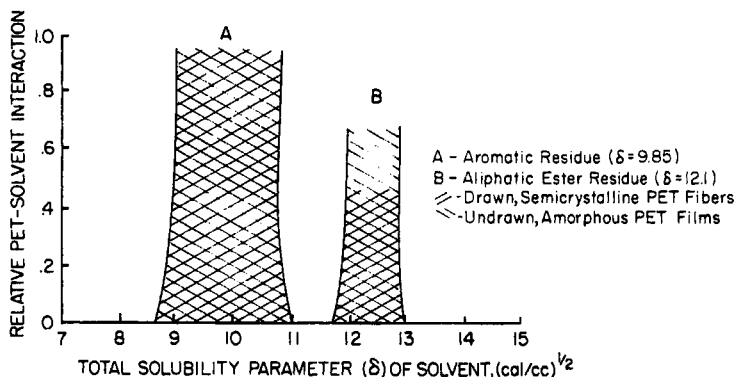


Fig. 4. Hildebrand solubility parameter distributions of interaction of nonaqueous solvents with amorphous PET films^{5,6} and with drawn, semicrystalline PET fibers.⁷

crease; and an increasing number of the rotational conformers, initially greater than 10° out of plane, would be expected to become restricted to smaller rotations. Thereby, as a greater fraction of rotational conformers become restricted to the plane of the benzene ring, the fractional carbonyl content f_c would increase and approach a limiting value of unity. The δ value of the 1,4-benzenoid residue would be expected to increase from a value of 8.67 to a value of 11.57. This is illustrated in Figure 2 in which the δ value of the "hybrid" 1,4-benzenoid residue is plotted versus the rotational conformers now restricted to the plane of the benzene ring.

The effect of increasing fractional carbonyl content (Fig. 2) would thus be to increase the δ value of residue A and decrease the δ value of residue B. Hence, with increasing chain orientation, one might expect that the δ -values of residues A and B would change in such a way that the corresponding solubility parameter distribution describing the interaction of nonaqueous solvents with the PET residues would be initially bimodal in character, having two interaction maxima; but that with increasing chain orientation (i.e., draw ratio), the two interaction maxima would merge and finally become reversed in order at the completely extended state. This is schematically represented in Figure 3.

The expected behavior depicted in Figure 3 is compared to the observed behavior for amorphous^{5,6} and drawn, semicrystalline⁷ PET in Figure 4. Except for differences in the extent of interaction, the normalized solubility parameter distributions for solvent-induced shrinkage and crystallization of drawn, semicrystalline and undrawn amorphous PET, respectively, are the same. This similar behavior strongly supports the view that the nature of the interaction between the solvent and the polymer is described in terms of their chemical nature and not in terms of fiber morphology.

Extent of PET-Solvent Interactions

As discussed previously,² the differences in the relative extents of polyester-solvent interaction is attributed to differences in the cohesive energies (E_c) of the aromatic and aliphatic ester residues. From Figure 4 it is found that the normalized solubility parameter distributions for solvent interaction with amorphous and drawn, semicrystalline PET are similar, for example, as to the "breadths" of the interaction maxima. This gives support to the view that the

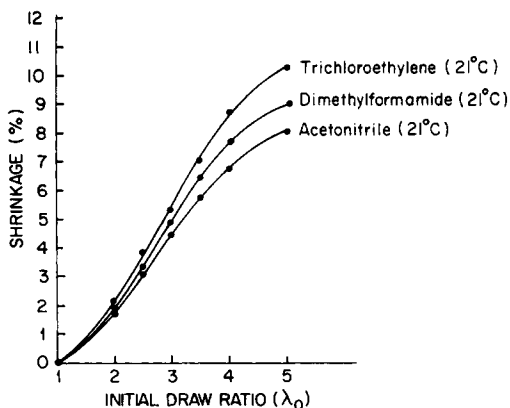


Fig. 5. Shrinkage of a drawn polyester yarn in trichloroethylene, dimethylformamide, and acetonitrile at 21 °C for several days as a function of the initial draw ratio.

structures of residues A and B are not affected by differences in fiber morphology.

The distribution curves in Figure 4 are different in one respect: the extent of solvent interaction with residues A and B are slightly different for amorphous and drawn, semicrystalline PET. If the solubility parameter distribution curves for the interaction of solvents with amorphous^{5,6} and drawn⁷ PET are normalized such that the heights of the interaction maxima associated with residue A are set to unity, then it may be shown that the difference between the interaction of solvents with residues A and B is greater for the drawn PET structure. It is believed that the "apparent" increase in solvent interaction with residue A over that with residue B is due to the preferential increase in the degree of local segmental orientation with respect to the fiber axis of the 1,4-benzenoid residues over that of the ethylene glycol residues. This view is supported by recent NMR and linear dichroism studies of drawn PET⁸ which support the belief that the 1,4-benzenoid structure is first to become oriented with respect to the fiber axis with extension, while the more flexible ethylene glycol structure becomes oriented only at much higher levels of extension.

In support of the independence of the CFD of molecular orientation, the per cent shrinkage was measured as a function of the initial draw ratio (λ_0) for PET yarn treated in three good plasticizers: trichloroethylene ($\delta = 9.3$), dimethylformamide ($\delta = 12.1$), and acetonitrile ($\delta = 11.9$), and the results are plotted in Figure 5. From Figure 5, it is expected that the degree of shrinkage for trichloroethylene would rise sharply at low draw ratios, reaching a maximum and then decrease with increasing draw ratio passing through a broad minimum and once more increase with increasing draw ratio. For acetonitrile, the shrinkage would rise continuously with increasing draw ratio reaching a maximum and then decrease with increasing draw ratio; and for dimethylformamide, the shrinkage would rise sharply to a maximum at low draw ratio and then pass through a shallow minimum and continue to rise with increasing draw ratio. The paracrystalline model, discussed previously, suggests that the degree of shrinkage for the above three solvents would decrease with increasing draw ratio (i.e., with molecular packing). Instead, the degree of shrinkage for all three solvents is observed to increase with increasing draw ratio.

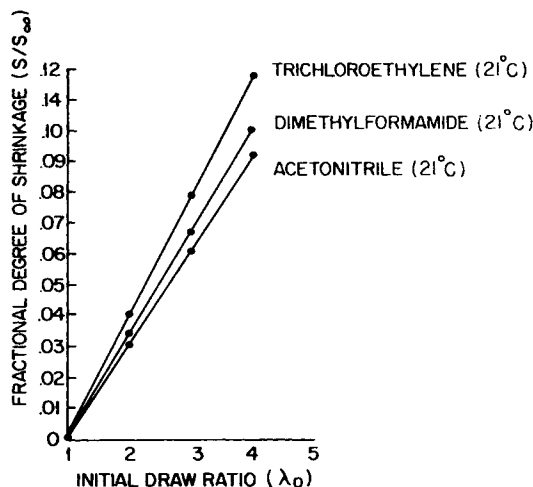


Fig. 6. Fractional degree of shrinkage of a drawn polyester yarn in trichloroethylene, dimethylformamide, and acetonitrile at 21°C for several days as a function of the initial draw ratio.

This gives support to the view that the extent of solvent interaction is primarily a consequence of the increase in the configurational entropy of the polyester structure as a result of increased chain disorientation, and not as a consequence of changes in the cohesive energy densities of the PET residues. This may be illustrated if shrinkage is considered to be primarily a result of the relaxation of orientational forces. If, for simplicity, an oriented PET yarn is treated as a stiff Hookean spring, then it may be shown that the net extensional force as a result of drawing and shrinkage (S) is given by the following:

$$\text{force} = \text{constant} [\lambda_0(1 - S) - 1] \quad (2)$$

At equilibrium,

$$\left[\frac{\partial \text{force}}{\partial (S/S_\infty)} \right]_T = 0 \quad (3)$$

and therefore,

$$\left(\frac{S}{S_\infty} \right)_{eq} = \text{constant} (\lambda_0 - 1) \quad (4)$$

where

$$S_\infty = [(\lambda_0 - 1)/\lambda_0] \times 100 \quad (5)$$

In Figure 6, the fractional shrinkage S/S_∞ of drawn PET is found to be a linear function of draw ratio. This is in support of the view that the "degree of interaction" may be related to morphology, but that the "nature of interaction" is only dependent on the chemical nature of the individual polymeric residues and of the solvent molecules.

Okajama⁹ has studied the dichroism of a PET-dye system, for which the dye may be taken as a weak plasticizer, as a function of draw ratio. He concluded that (i) there exists a distribution of local lateral order in the amorphous regions

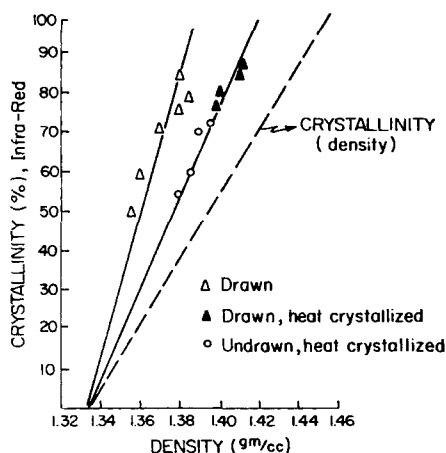


Fig. 7. Degree of crystallinity as determined by the measurement of the *trans* content of the ethylene glycol ($-\text{O}-\text{CH}_2-\text{CH}_2-\text{O}-$) residue by infrared spectroscopy for drawn and undrawn polyester films.¹¹

and that the dye molecules do not distribute themselves homogeneously throughout the entire amorphous regions, but exist only within the regions of the lowest lateral order; (ii) the relaxation and disordering of the polymer chains start preferentially in the region of the lowest lateral order; and (iii) the dye molecules combine with the polymer chains by a definite geometric relation and the angle of the dye axis with the chain axis is kept unchanged during deformation and heat treatments. The conclusions made by Okajama⁹ suggest that the interaction of a molecule with a polymer chain is defined by their respective individual stereochemical natures in such a way as to produce a minimum in the interaction energy. Thus, the "nature" of the interaction between the polymer chain residue and the penetrant is not expected to change with changes in the fiber (bulk) morphology, while the "extent" of interaction may be dependent on such changes.

Molecular Conformation of PET Residues

It has been shown above that the CED of the PET residues, and thereby their chemical structures, do not change with changes in fiber morphology. It is of interest to reexamine the possible changes in the molecular conformations of the various PET residues upon extension and crystallization to give support to the conclusions of the above discussion.

There is spectral evidence in the literature¹⁰⁻¹⁴ that the conformation of the ethylene glycol residue ($-\text{O}-\text{CH}_2-\text{CH}_2-\text{O}-$) changes upon crystallization from the *gauche* conformer to the *trans* conformer. Frequently, the *trans* content is taken to be a linear function of crystallinity (i.e., density), which is a measure of the extent of lateral molecular packing. Cunningham et al.¹⁰ and Schmidt¹² have shown that the *trans* content is not directly a measure of crystallinity as previously assumed,^{11,13,14} but that it is, in a more general sense, a measure of local lateral order which is expected to depend on chain extension

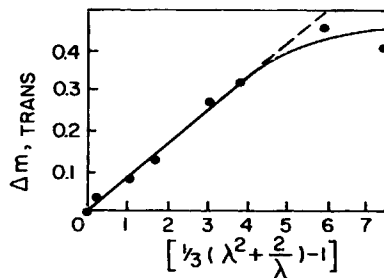


Fig. 8. The change in the content of the trans conformation of the ethylene glycol residue ($-\text{O}-\text{CH}_2-\text{CH}_2-\text{O}-$) of poly(ethylene terephthalate) as a function of the configurational entropy of the extended molecular chains $[\frac{1}{3}(\lambda^2 + \frac{2}{\lambda}) - 1]$.¹⁵

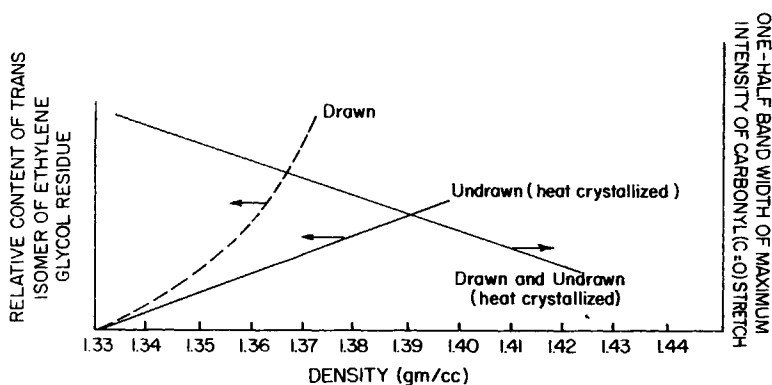


Fig. 9. Comparison of the change in the content of the trans isomer of the ethylene glycol residue ($-\text{O}-\text{CH}_2-\text{CH}_2-\text{O}-$)¹² and of the bandwidth of the carbonyl stretch⁵ for drawn and undrawn polyester films.

as well as on crystallinity. Farrow and Ward¹¹ show that upon thermal annealing, the drawn film relaxes and the *trans* content decreases in accord with molecular disordering and is now a reasonable measure of crystallinity as was found for the heat crystallized amorphous sample. This is illustrated in Figure 7.

Recently, Cunningham et al.¹⁰ have shown that the increase in the *trans* content in excess of that which may be attributed to crystallinity is directly related to the change in the configurational entropy of the polymer chain. That is, as the chain is extended, the configurational entropy decreases and the relative retractive forces increases. As a result of this increase in the "internal" orientational forces, the *trans* conformer is more favored. The increase in the *trans* conformer, Δm_{trans} , is found to be given by the following expression:¹⁵

$$\Delta m_{\text{trans}} = \nu D_2 \left[\frac{1}{3} \left(\lambda^2 + \frac{2}{\lambda} \right) - 1 \right] \quad (6)$$

where ν is the total number of network chains, D_2 is a constant of proportionality, and λ is the extensional strain (i.e., draw ratio). The increase in the *trans* content as given by the above expression is compared to experiment¹⁰ in Figure 8. Up

to values of $\lambda = 4.0$, the molecular conformation of the ethylene glycol residue is found to be sensitive to changes in fiber morphology.

Cunningham et al. have also shown¹⁰ that the 795 cm^{-1} and the 875 cm^{-1} infrared absorption bands which are associated with distortions of the benzene ring of the 1,4-benzenoid structure are sensitive to changes in extensional strain and give good agreement with optical birefringence measurements of molecular orientation even for values of λ greater than 4.

In contrast to the sensitivity of the conformation of the *trans* ethylene glycol residue and of the distortions of the benzene ring with extensional strain and crystallinity, Melveger has shown¹⁶ that the rotational conformation of the 1,4-benzenoid structure is not sensitive to extensional strain; that is, the rotations of the 1,4-carbonyl groups are not affected by increasing chain orientation (and presumably local lateral order) but are only sensitive to changes in phase (i.e., crystallization). This is shown in Figure 9. Melveger showed¹⁶ that the half-width of the maximum intensity of the carbonyl stretch is directly proportional to density (here to be taken as a measure of crystallinity) for drawn, as well as for undrawn, heat crystallized PET samples.

The results of Ward¹⁰ and of Melveger¹⁶ indicate that the rotational conformation of the benzene-carbonyl bond is not appreciably hindered by chain orientation and changes only upon a change in phase (i.e., crystallization). Therefore, the fractional carbonyl content f_c of the noncrystalline chains is expected to be independent of drawing and other extensional processes. Hence, the δ values of the PET residues A and B can be considered to be taken as molecular parameters which are not sensitive to changes in the supramolecular structure of the fiber.

CONCLUSIONS

The assignment of chemical structures to residues A and B is based on the assumption that the nature of the interaction of solvents with polyester does not depend on fiber morphology, but is an inherent molecular property of the polyester monomer repeat unit, which should be independent of molecular orientation and crystallinity. To test this assumption, the nature of the polyester-solvent interactions were compared for different fiber morphologies.

Although the "extent" of interaction is found to be dependent on changes in fiber morphology, the "nature" of the interaction is found to be dependent only on the relative differences in the stereochemical nature of the solvent and the given PET residue. This is in support of the proposed view that the CED of the polymer residue in the "swollen" state which the solvent "sees," and therefore the CED of the polymer residue should not be dependent on changes in crystallinity, density, chain orientation, or any other morphologic changes, but should only be described by the stereochemical nature of the amorphous state. This is reasonable, for a good solvent will associate with the polymer residue and form a solvate sphere. The nature of the solvate sphere should be independent of the original morphology and only dependent on the molecular and chemical nature of the given polymer residue and the surrounding solvent molecules.

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