

Solvent-Induced Structural Changes in Sulfonated Poly(ethylene terephthalate) (SPET) Fibers

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SYNOPSIS

The microstructure and macrostructure of sulfonated poly(ethylene terephthalate) (SPET) fibers were studied by subjecting them to solvents with solubility parameters similar to those of the PET. Dimethyl sulfoxide (DMSO), methylene chloride (MeCl_2), and pyridine, whose solubility parameters (δ) are close to those of the flexible aliphatic ester segment ($-\text{CO}-\text{O}-\text{CH}_2-\text{CH}_2-$), the semirigid aromatic segment ($-\text{CO}-\text{C}_6\text{H}_4-$), and the average δ of the PET repeating unit, respectively, were used. The solvent uptake levels of these three solvents, which were not affected by crimping or relaxing processes of the fibers, were related to their sizes, shapes, and solubility compatibility with SPET. The solvent-induced effects were strongly dependent upon the fiber structure caused by the fiber-forming processes, but were generally not as strong as the processes. The most distinct changes brought about by the solvents include overall orientation determined by birefringence and the *trans-gauche* ratio and extent of chain fold by FTIR measurements. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

The sulfonated poly(ethylene terephthalate) (SPET) has a main-chain structure similar to the poly(ethylene terephthalate) (PET) homopolymer with 2–3 mol % of the aromatic rings being sulfonated ($-\text{SO}_3^- \text{Na}^+$).¹ Previously, we have reported on the structure of the sulfonated PET (SPET) fibers as affected by processing.² The SPET fibers have a viscosity-average molecular weight (M_v) of 19,600 g/mol. At an average degree of polymerization (DP) of 102, the SPET polymer contains an average of two to three sulfonated units per molecule. Compared to the PET fibers, the SPET chains in the undrawn fibers have higher mobility, are easier to crystallize, and form smaller crystals upon drawing and heating. The differences in physical and thermal properties between the analogous PET and SPET fibers are attributed to their different responses to processing because of the molecular weights and sulfonated side-group effects.

The model of semicrystalline PET fibers as the coexistence of folded-chain crystalline domains in an amorphous matrix is believed to be applicable to the SPET fibers. However, the sulfonated side groups, being irregular along the chain, have to be excluded from the crystalline domains. The sulfonated segments should be found only in the noncrystalline regions and on crystal surfaces. Better understanding of the noncrystalline domains in the SPET fiber should contribute to knowledge of the internal structure of these fibers.

Although modern instrumentation has provided some excellent tools for characterizing the crystalline domains in polymers, obtaining structural information in the noncrystalline regions is much more challenging. The glass transition temperature (T_g) of a polymer is related to the segmental mobility of polymer chains in the noncrystalline domains. Above this temperature, the thermal energy input causes disruption of intermolecular cohesive forces and mobilizes the chains. Solvents with solubility parameters close to those of the polymer are also known to provide sufficient energy for chain interaction^{3,4} and to facilitate molecular mobility or rearrangement by lowering the T_g .⁵

The solubility parameter values (δ) of PET ho-

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mopolymer are 12.1, 9.8, and 10.7 (cal/cm³)^{1/2} for the aromatic segment (—CO—C₆H₄), the aliphatic segment (—CO—CH₂—CH₂), and the repeating unit, respectively.⁵ The majority of work on the PET–solvent interaction has been on the solvent-induced crystallization (SINC). SINC has been described as the formation of new crystallites in glassy polymers and the perfection and growth of existing crystallites in semicrystalline polymers. Strong interacting solvents such as dimethylformamide and methylene chloride are known to cause SINC on PET films^{6–11} and PET fibers.^{12–14} The fundamental molecular event during solvent-induced crystallization is the input of chemical energy, which results in a localized “chemical melting” of the internal structure and promotes chain mobility.

This article reports the solvent–polymer interaction in SPET fibers to further discern the fiber structure, particularly in the noncrystalline domains. Structural changes in the solvent-treated fibers were analyzed to provide additional information about the polymer structures generated from the various fiber-forming processing stages.

EXPERIMENTAL

Materials and Reagents

The sulfonated poly(ethylene terephthalate) (PET) fibers used were Dacron 64 filaments donated by E. I. du Pont de Nemours and Co., Wilmington, Delaware. Fibers from four consecutive commercial processing stages, i.e., spinning, drawing, crimping, and relaxing, were used. These fibers are referred to as “processed” fibers here. Isothermal annealing at 172°C was also performed on the drawn fibers for 10 min without tension. The fiber-forming processes and characterization of these fibers have been detailed elsewhere.²

Three organic solvents chosen for the study were dimethyl sulfoxide (DMSO) (Aldrich, 99+% grade), methylene chloride (Fisher, Optima grade), and pyridine (Aldrich, spectrophotometric grade). The solubility parameters (δ 's) of these solvents are 12.9, 9.7, and 10.6 (cal/cm³)^{1/2}, respectively, and are close to the δ 's of the flexible aliphatic ester segment, the semirigid aromatic segment, and the average δ of the PET molecule, respectively.³

Solvent Treatment

Approximately 1000 filaments at 15 cm in length were tied in bundles at one end with a thread. Each

fiber bundle weighed approximately 0.1 g. Carbon tetrachloride (certified ACS grade), which is known not to crystallize PET,¹⁵ was used to remove organic matter and processing residuals from the fiber bundles. Fiber bundles were then dried in a vacuum at 23°C ($\pm 2^\circ\text{C}$) for 24 h and their weights and lengths measured. The fiber length was taken to be the average of three fiber-length measurements from each bundle.

All solvent treatments were performed at 23°C ($\pm 2^\circ\text{C}$). Each fiber bundle was immersed in 35 mL of the specified solvent for various lengths from 1 min to 48 h. The fiber bundles were removed from the solvents, drained for 30 s, and then centrifuged at 2500 rpm for 5 min. The centrifuge tubes were lined with mesh screens to facilitate separation of the fibers from the excess solvent. The fibers were then rinsed in an appropriate solvent for each of the treatment solvents for 1 min: doubly distilled and deionized (DDD) water for DMSO, methanol for pyridine, and CCl₄ for MeCl₂. Fiber bundles were again centrifuged for 5 min and then stored in a vacuum desiccator. The fiber weights were monitored at regular intervals up to 2 weeks. Stabilized fiber weights and lengths were taken when no changes were observed in fiber weights during this period. Solvent uptake was calculated based on weight percentage (w/w %) of weight increase in fibers of the original fiber weight.

Structural Characterization

The fiber diameter, density, refractive index (RI), and differential thermal analysis (DTA) of the solvent-treated SPET fibers were performed as previously described.² Student *t*-tests were performed on the above data to determine significant differences at the .01 confidence level.

Fourier Transform Infrared Spectroscopy (FTIR)

The FTIR spectra of the PET fibers were scanned in the 4000 to 400 cm⁻¹ region with an attenuated total reflectance (ATR) accessory using a KRS-5 crystal. The interface angle of the KRS-5 crystal was 45° and the index of refraction at 25°C was 2.37. The fibers were aligned on both parallel faces of the crystal. The total weight of each fiber sample used for ATR–FTIR was approximately 30 mg. A nujol oil was placed on the fibers to ensure good contact with the ATR crystal. The background spectrum of the nujol alone on the crystal was run and subtracted from the fibers' spectra. Sixty-four scans of each sample in the transmission mode were

obtained, and two spectra were obtained for each fiber sample. The average of two scans is reported.

Peak intensities in percent transmission were taken from the average of the two spectra at wavelengths of 988 cm^{-1} (chain fold), 973 cm^{-1} (*trans*), 898 cm^{-1} (*gauche*), and 795 cm^{-1} (internal reference). Measurement of the 988 , 973 , and 898 cm^{-1} bands were normalized over the intensity of the 795 cm^{-1} band. Since the aliphatic ester segments are in either *trans* or *gauche* conformation, the relative percentage of each conformation was calculated assuming the summation of the two being 1.

Wide-angle X-ray Scattering (WAXS)

The WAXS patterns of the fibers were made on an X-ray diffractometer equipped with a graphite monochromator that gave $50\text{ kV CuK}\alpha$ at 15 mA .

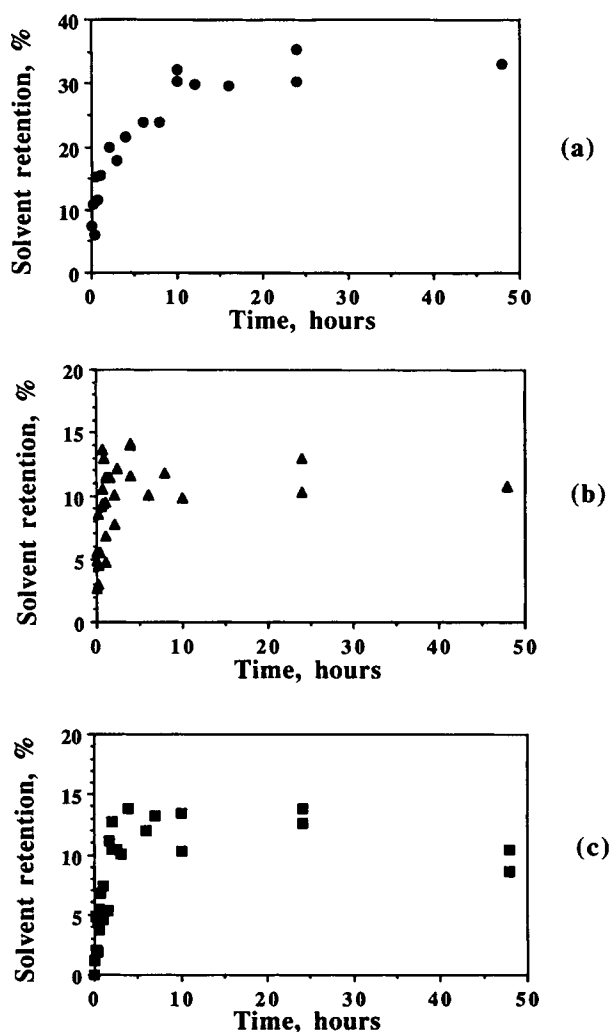


Figure 1 Solvent retention in drawn SPET fibers: (a) DMSO; (b) methylene chloride; (c) pyridine.

Table I Solvent Uptakes (w/w %) in SPET Fibers

Solvent Process	DMSO 16 h	MeCl ₂ 6 h	Pyridine 6 h
Drawn	29.5	10.6	12.0
Crimped	30.8 (1.6)	9.6 (2.1)	—
Relaxed	30.5 (2.3)	9.6 (2.1)	—
Annealed	38.6	18.0	17.2

Nos. in () represent standard deviations for those fibers treated in duplicate ($n = 2$).

Scanning of the fiber samples was done in the reflectance mode from 10° to 32° (2θ angle) at a rate of $1.6^\circ/\text{min}$. Samples were prepared by laying out a random array of fibers on a glass slide. A window-type frame was cut from PET film and placed over the glass slide, outside of the incident beam, sandwiching the fibers. The frame was heat fused to the slide to secure the fibers.

A graphic multiple-peak resolution method for estimating crystalline structures was used.¹⁶ The X-ray diffraction scan was resolved into its four separate apparent peaks, i.e., 100, 010, 110, and amorphous peaks. The 100, 010, and 110 peaks represent the *c*, *a*, and *b* directions in the unit cell structure of the crystals, or the "axial," "ring stacking," and "side-by-side" direction, respectively.

RESULTS AND DISCUSSION

Solvent Retention

With the drawn fibers, solvent uptakes increase with increasing length of time in each of the three solvents (Fig. 1). The MeCl₂ and pyridine uptakes in the drawn fibers are more scattered between 1 and 10 h of solvent treatment. Maximum levels of MeCl₂ and pyridine uptake are reached at approximately 10–15% after 4 h. Maximum uptake of DMSO is higher (30%) and takes longer (10 h) to reach. Based on the solvent uptake data for the drawn fibers, a 16 h solvent time was chosen for DMSO, whereas a period of 6 h was used for both pyridine and MeCl₂ to achieve optimal uptake.

The uptake of each solvent in the fibers did not vary among the drawing, crimping, and relaxing processes (Table I). Solvent uptakes in the annealed drawn fibers, however, were considerably higher than in the other processed fibers. Differences among the solvents were also observed. The optimal DMSO uptakes in processed SPET fibers were al-

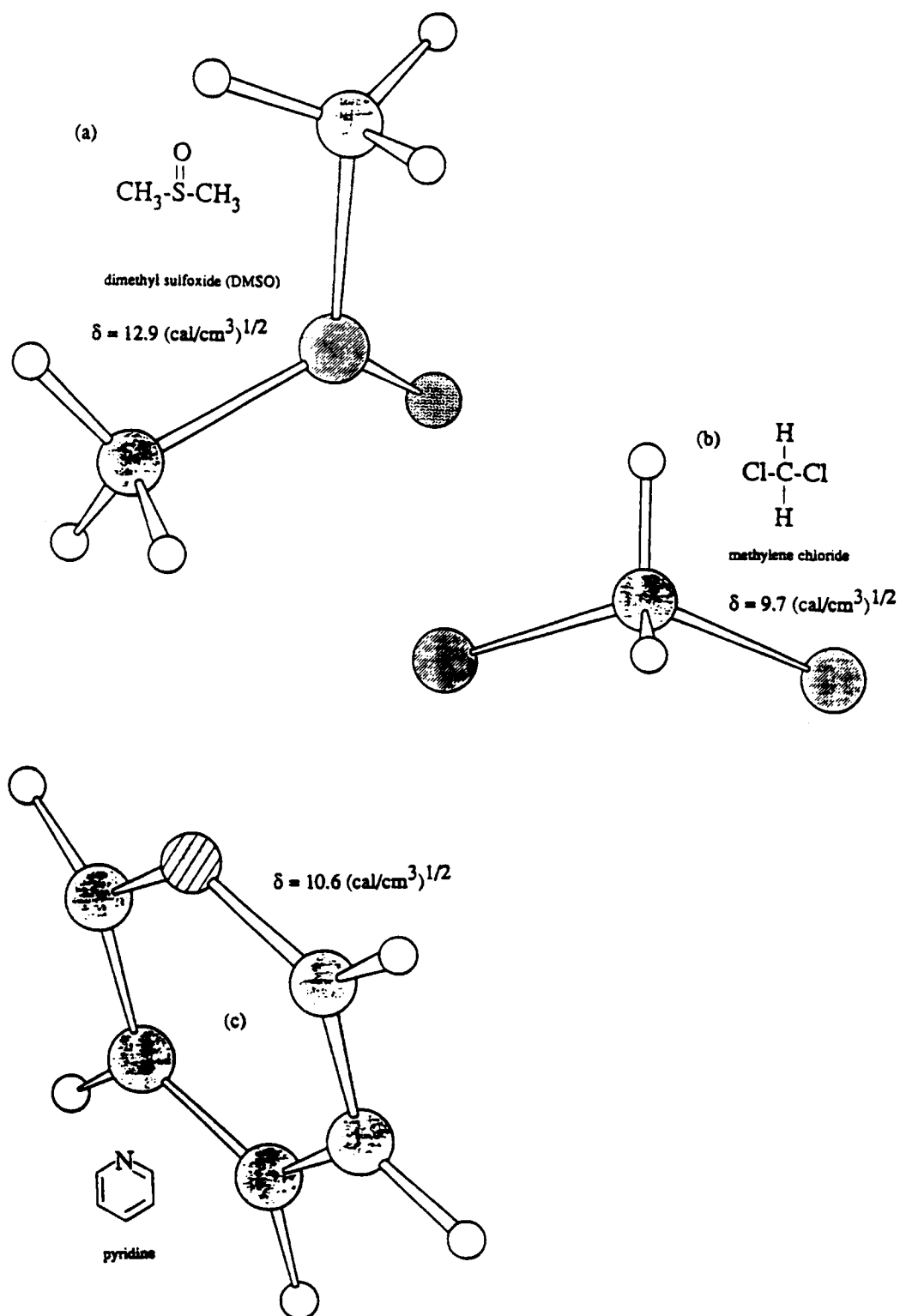


Figure 2 Three-dimensional diagrams of solvent molecules: (a) DMSO; (b) methylene chloride; (c) pyridine.

most three times as much as those of MeCl_2 and pyridine, the latter two of which were similar.

Diffusive transport, which is proportional to the fractional free volume, is believed to take place in the noncrystalline regions in the polymer.¹⁷ Diffusion of molecules, such as most swelling or solvating organic liquids, which interact weakly thermodynamically with polymer chains, has been described by the "hole" concept.¹⁸ Holes are defined as intermolecular or intramolecular spaces in the polymer. Molecules smaller than the monomer units of a polymer are considered smaller than the average hole size and diffuse into the polymer through the unoccupied holes. Smaller solvent molecules have been shown to more easily gain access to areas of disorder in the PET polymer.^{18,19}

Differences in the rates and the uptakes of these solvents in SPET fibers can be explained by their sizes and shapes. The DMSO molecules are rod-shaped with approximate dimensions of $1 \times 2 \times 5.8$ Å (Fig. 2). The MeCl_2 molecules are tetrahedral ($\sim 2 \times 2 \times 3.5$ Å), whereas pyridine molecules are flat square ($\sim 1 \times 4 \times 4$ Å). The overall solvent uptakes in the drawn SPET increased in the order of pyridine, MeCl_2 , and DMSO. The significantly higher rate and level of DMSO uptake can be related to its smaller overall size and linear form.

Another explanation for the diffusion of solvents and their uptake behavior is their solubility compatibility with the polymer. The solubility compatibility of these solvents with the PET varies. DMSO has a δ similar to the aliphatic segments of PET, whereas MeCl_2 and pyridine have δ 's close to those of the aromatic segments and the average δ of PET, respectively. Among the three solvents studied, the better diffusion and uptake of DMSO in PET may also be associated with the similarity in δ to the aliphatic segment of the PET molecules.

In our earlier article, crimping and relaxing were shown to lower chain mobility and increase fiber density and orientation without affecting the overall

crystalline content.² Annealing, on the other hand, not only increased fiber density and overall orientation but also caused chain relaxation in the noncrystalline regions. The solvent-uptake levels do not seem to be associated with process-induced changes in either density or orientation in the SPET structure. The much higher solvent uptakes in the annealed fibers suggest that the holes are made more accessible to the solvents by annealing. The one structural difference between the processed and annealed fibers is the increased chain relaxation in the noncrystalline domains. Diffusion is aided when more intermolecular and intramolecular spaces become available to the penetrant through rotation and/or bond stretching of the more relaxed noncrystalline chain segments.

Fiber Dimension

All untreated fibers, i.e., the processed and annealed, have similar diameters (Table II). Solvent treatments increased fiber diameters in some cases. Following DMSO treatment, the diameters of the crimped and relaxed fibers are increased by about 4%. The MeCl_2 treatment increased the diameters of all processed fibers. These diameter increases are less on the further processed fibers or in the descending order of drawn ($\sim 15\%$), crimped ($\sim 9\%$), and relaxed ($\sim 2\%$) fibers. Pyridine also increases the diameters of the drawn fibers by about 8%. The diameters of the annealed fibers were not affected by any of the solvents.

With the drawn fibers, the lengths of DMSO-treated fibers remained unchanged with increasing solvent time. The majority of the MeCl_2 -treated samples showed reduced fiber lengths by 13–17%, but no clear relationship was found with the lengths of solvent time [Fig. 3(a)]. The lengths of pyridine-treated fibers decreased with increasing solvent time during the first 2 h, then leveled at around 6–8% [Fig. 3(b)].

Table II Fiber Diameter (μm)^a of SPET Fibers

Process Treatment	Untreated	DMSO	MeCl_2	Pyridine
Drawn	17.7 (1.1)	17.9 (0.7)	20.4 (0.5) ^b	19.1 (0.2) ^b
Crimped	18.0 (0.4) ^c	18.7 (0.8) ^b	19.7 (0.9) ^b	—
Relaxed	17.9 (0.4)	18.6 (0.6) ^b	18.3 (0.5) ^b	—
Annealed	18.1 (0.5) ^c	18.3 (0.5)	18.5 (0.6)	18.2 (0.5)

Nos. in () represent standard deviation.

^a Value represents a mean of 12 ($n = 12$).

^b Significant difference between the solvent-treated and the untreated.

^c Significant difference between the further-processed and the drawn fibers.

It is clear that, in addition to differences in their uptake, these solvents also have different effects on fiber dimensions. Although DMSO uptakes in the fibers are highest among solvents, neither fiber length nor diameter of the drawn fibers was affected by DMSO. The MeCl_2 and pyridine treatments, on the other hand, increased fiber diameters by 15 and 8%, respectively, while decreasing fiber lengths by similar extents. The annealed fibers retained most solvents, but neither fiber diameter nor fiber length, were affected by any of the solvents. Length reduction and diameter enlargement of the MeCl_2 - and pyridine-treated fibers at lower solvent uptake levels and little change in fiber dimensions of the DMSO-treated fibers at higher uptake levels suggest that these solvents interact differently with the non-crystalline chains to cause different dimensional changes.

Fiber Density

The drawn SPET fibers have an average density of 1.3788 g/cc. The densities remained unchanged for DMSO-treated fibers, whereas both the MeCl_2 - and pyridine-treated fibers had increased densities (Fig.

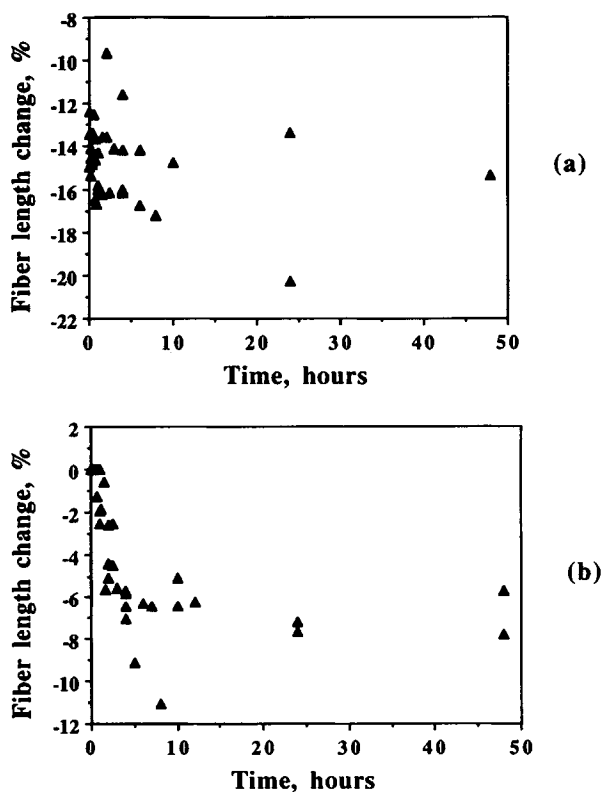


Figure 3 Length change (%) of solvent-treated drawn SPET fibers: (a) methylene chloride; (b) pyridine.

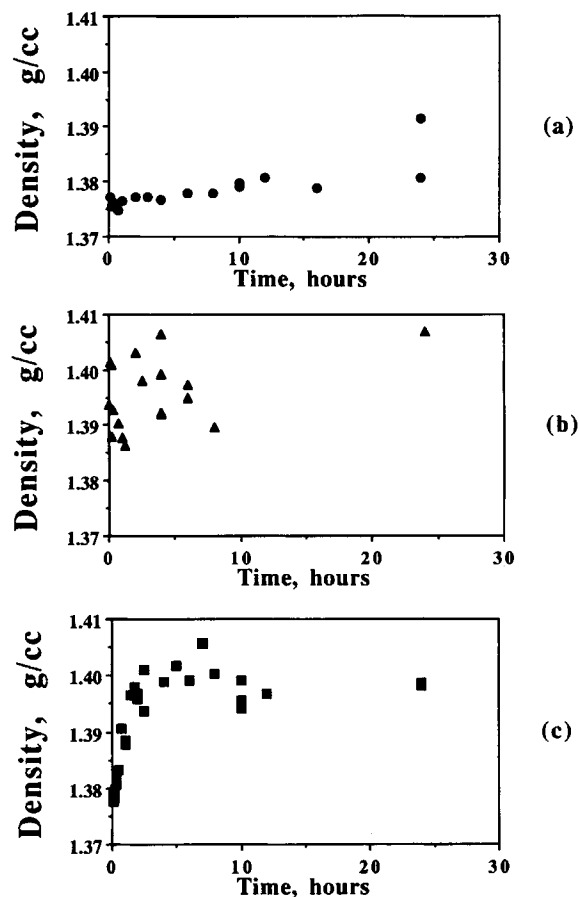


Figure 4 Density of solvent-treated drawn SPET fibers: (a) DMSO; (b) methylene chloride; (c) pyridine.

4). MeCl_2 treatment increased the densities of the drawn fibers by 0.01–0.03 g/cc without a clear relationship to the lengths of the treatments. The densities of the pyridine-treated fibers showed drastic increases with solvent time up to about 4 h before leveling off at a density of about 1.40 g/cc.

Fiber densities were increased significantly upon crimping, relaxing, and annealing (Table III). The effects of these three solvents on the density of the drawn SPET fibers are strongly influenced by the fiber structure resulting from the fiber-forming processes and annealing. The solvents have been shown to increase the densities of drawn and relaxed fibers, whereas the opposite is observed on the crimped fibers. The influence of solvents on fiber density is least on the annealed fibers.

Refractive Index and Birefringence

Upon solvent treatments, refractive indexes (RIs) with the fiber aligned perpendicular to plane-polarized light (n_{\perp}) of the fibers were either not changed

Table III Fiber Density (g/cc) of SPET Fibers

Process Treatment	Untreated	DMSO	MeCl ₂	Pyridine
Drawn	1.3788 (0)	1.3789 (.0009)	1.3972 (0) ^a	1.3991 (.0002) ^a
Crimped	1.3914 (.0005) ^b	1.3907 (.0006) ^a	1.3890 (.0006) ^a	—
Relaxed	1.3890 (.0004) ^b	1.3915 (.0006) ^a	1.3897 (.0004) ^a	—
Annealed	1.4066 (.0004) ^a	1.4063 (0) ^a	1.4065 (.0002)	1.4058 (.0004) ^b

Nos. are a mean of four readings ($n = 4$). Nos. in () indicate standard deviation.

^a Significant difference between the solvent-treated and the untreated.

^b Significant difference between the further-processed and the drawn fibers.

or only slightly reduced (Table IV). The RIs aligned parallel to plane-polarized light (n_{\parallel}) of the fibers were increased by processing and annealing. The solvents also increased the n_{\parallel} 's of the processed fibers but not those of the annealed fibers. The increases in the n_{\parallel} 's resulted in the increased birefringences (Δn) on processed, annealed, and processed fibers with solvent treatments (Table V). The improvement of the overall orientation in fibers by the solvents is much more distinct than are changes in fiber dimension and density. All three solvents increased the Δn of the drawn fibers similarly. With the crimped and relaxed fibers, the Δn 's were increased more by DMSO than by MeCl₂. The MeCl₂ treatment actually reduced the Δn of the annealed fibers.

The densities and Δn 's of the crimped and relaxed fibers are higher than those of the drawn fibers, indicating better overall chain packing and orientation in these fibers. However, the levels of solvent uptake are similar among these processed fibers. As stated

earlier, the solvent uptake in the SPET fibers is not affected by the levels of overall chain packing or the orientation of the fiber.

Solvent uptake in SPET fibers has been related to their solubility compatibility with the PET and solvent shapes. The levels of solvent effects also appear to be solvent-type dependent. DMSO treatments on the processed fibers cause significant increases in birefringence, but have little or no effects on fiber dimensions and densities.

The annealed fibers have the highest solvent uptakes, but none of the solvents appreciably changed their dimensions, densities, or birefringences. That the annealed fibers had much higher density than other processed fibers indicates a more regular packing of the crystals and of the chains in the non-crystalline regions. The lack of solvent effects indicates a highly stable structure of the annealed fibers.

Differential Thermal Analysis (DTA)

The melting temperatures (T_m) of the fibers were not affected by any of the solvents. On the drawn fibers, one observed thermal behavior change was the increased relative intensity of the low melting temperature (LM) to high melting temperature (HM) peak ratio (Fig. 5). The effects of solvents on the enthalpy of fusion (ΔH_f) of the fibers were small.

The effects of processing and solvents on the heat capacity value (C_p) were more distinct. The C_p of a polymer indicates the chain mobility in the non-crystalline regions. The C_p 's in the SPET fibers decreased significantly with drawing and crimping processes (Table VI). The reduced molecular mobility in the noncrystalline regions is consistent with the increased density and orientation of these processed fibers. The C_p 's were not changed with subsequent processes. The solvents also reduced the C_p 's of the drawn fibers, but increased those of the relaxed and annealed fibers. The C_p 's of the crimped

Table IV Refractive Indices of SPET Fibers

Process/treatment	n_{\parallel}	n_{\perp}
Drawn, untreated	1.665 (.001)	1.556 (0)
DMSO-treated	1.680 (.003)	1.556 (.001)
MeCl ₂ -treated	1.677 (.005)	1.553 (.004)
Pyridine-treated	1.680 (.003)	1.554 (0)
Crimped, untreated	1.668 (0)	1.550 (0)
DMSO-treated	1.697 (0)	1.548 (0)
MeCl ₂ -treated	1.689 (0)	1.551 (0)
Relaxed, untreated	1.673 (0)	1.555 (0)
DMSO-treated	1.691 (0)	1.547 (0)
MeCl ₂ -treated	1.689 (0)	1.550 (0)
Annealed, untreated	1.711 (.009)	1.554 (.003)
DMSO-treated	1.711 (.009)	1.554 (.003)
MeCl ₂ -treated	1.704 (.002)	1.559 (.010)
Pyridine-treated	1.711 (.009)	1.554 (.003)

Nos. are the mean of nine measurements ($n = 9$). Nos. in () represent standard deviations.

Table V Birefringence (Δn) of SPET Fibers

Process Treatment	Untreated	DMSO	MeCl ₂	Pyridine
Drawn	0.109 (0)	0.124 (.001) ^a	0.124 (.001) ^a	0.126 (.003) ^a
Crimped	0.113 (0) ^b	0.149 (0) ^a	0.138 (0) ^a	—
Relaxed	0.118 (0) ^b	0.144 (0) ^a	0.139 (0) ^a	—
Annealed	0.157 (.001) ^b	0.157 (.001)	0.145 (.008) ^a	0.157 (.001)

Nos. are the mean of nine measurements ($n = 9$). Nos. in () represent standard deviations.

^a Significant difference between the solvent-treated and the untreated.

^b Significant difference between the further-processed and the drawn fibers.

fibers were the lowest and were not affected by any of the solvents. On the relaxed and annealed fibers, increased chain mobility in the noncrystalline regions was observed.

Fourier Transform Infrared Spectroscopy (FTIR)

In the SPET structure, the ethylene glycol (EG) segment can exist in either *gauche* or *trans* conformations. The more stable *trans* conformation can be present in crystalline and noncrystalline domains in the fibers. The less stable *gauche* conformation, however, exists only in the noncrystalline regions, such as amorphous regions, crystal surfaces, and folds. Because crystalline regions contain only *trans* conformation, the proportion of *trans* or the *trans* /

gauche (*T/G*) ratio can be used to indicate the extent of crystalline content in the fibers.

Sixty percent of the EG chains in the spun fibers is in the more stable *trans* conformation (Table VII). Drawing increased the extent of the *trans* form of the EG segments in the fibers to around 79%. The level of *trans* conformation was decreased by crimping but returned to a level similar to that of the drawn fibers after relaxing. The *trans* form was further increased to 84% upon annealing. The *T/G* ratio in the fibers was increased by all solvent treatments at all processing stages except for the DMSO-treated drawn fibers.

The band at 988 cm⁻¹ representing chain fold was not identifiable on the spun and the drawn fibers (Fig. 6). This band became observable on the crimped fibers and on solvent-treated drawn fibers, but was still too small to be measured. These chain-fold bands were measurable for the annealed as well as all the processed fibers treated with solvents. The increased *T/G* ratio and percentage of chain fold are consistent with the increased chain packing and orientation of the processed and solvent-treated fibers.

Wide-angle X-Ray Scattering (WAXS)

The crystallite dimension (L) and interplanar spacing (d) of the SPET fibers were calculated. The unit cell dimensions of the SPET crystalline structure, which are similar to those of PET,²⁴ remain constant among the processed and solvent-treated fibers. The most apparent differences at these processing stages are the relative intensity and resolution between the peaks representing the 110 and 100 planes (Fig. 6).

Crystallite dimensions of the crimped fibers were reduced in all directions, particularly in the axial and stacking directions (Table VIII). The change brought about by the relaxing process was mainly in increasing the crystal dimension in the axial direction. Annealing of the drawn fibers caused significant increases in all three crystallite dimensions.

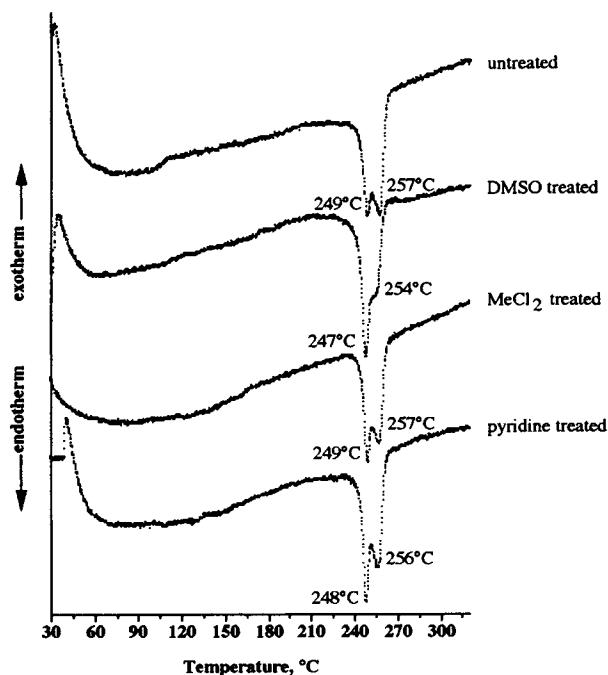


Figure 5 DTA thermograms of drawn and solvent SPET fibers.

Table VI Heat Capacity [C_p (J/g °C)] of SPET Fibers

Process Treatment	Untreated	DMSO	MeCl ₂	Pyridine
Undrawn	19.84 (4.45)	—	—	—
Drawn	7.84 (2.57)	3.10 (0.79)	3.74 (1.07)	2.89 (0.01) ^a
Crimped	1.67 (2.25)	1.17 (1.20)	0.57 (0.68)	—
Relaxed	2.19 (1.28)	5.11 (0.03) ^a	3.46 (3.58)	—
Annealed	1.84 (0.52) ^b	2.80 (0.89)	6.29 (0.67)	4.07 (3.75)

Nos. are a mean of 2 ($n = 2$). Nos. in () indicate standard deviations.

^a Significant difference between the solvent-treated and the untreated.

^b Significant difference between the further-processed and the drawn fibers.

In the drawn fibers, DMSO and pyridine caused a slight reduction in crystallite dimensions in the 100 and 110 directions, whereas MeCl₂ significantly increased the 010 dimension. In the crimped fibers, DMSO and MeCl₂ increased the axial and stacking directions of the crystal dimensions. The effects of these two solvents on the crystal dimensions of the relaxed fibers are very different, i.e., both solvents decreased the crystal dimensions along the axial direction and 110 directions. With the annealed fibers, the solvents did not affect the axial crystal dimensions, but increased the crystal dimensions in the 010 and 110 directions in some cases.

The effects of solvents on the crystallite dimensions vary with solvents as well as with the pro-

cessing stages of the fibers. The different solvent effects on fibers from different processing states indicate that not only does each solvent interact differently with the crystals in the fibers, but also that the effects of each solvent on the PET crystals are strongly dependent on the process or microstructure of the PET fibers.

CONCLUSION

Our previous study shows that the microstructure and macrostructure of the SPET fibers are highly dependent upon the drawing and heat processes, particularly upon untensioned annealing.² This

Table VII *Trans* (*T*) and *Gauche* (*G*) by % and Chain-fold Conformations of SPET Fibers

Process/Treatment	Chain Fold A988/A795 (%)	<i>Trans</i> A973/A795 (%)	<i>Gauche</i> A896/A795 (%)	<i>T/G</i> Ratio
Spun, untreated	^a	60.3	39.7	1.5
Drawn, untreated	^a	78.5	21.5	3.7
DMSO-treated	^b	75.8	24.2	3.1
MeCl ₂ -treated	^b	82.1	17.9	4.6
Pyridine-treated	^b	80.5	19.5	4.1
Crimped, untreated	^b	69.2	30.8	2.3
DMSO-treated	0.07	85.5	14.5	5.9
MeCl ₂ -treated	0.09	85.0	15.0	5.7
Relaxed, untreated	^b	79.6	20.4	3.9
DMSO-treated	0.08	84.2	15.8	5.3
MeCl ₂ -treated	0.07	81.2	18.8	4.3
Annealed, untreated	0.15	84.4	15.6	5.4
DMSO-treated	0.18	87.0	13.0	6.7
MeCl ₂ -treated	0.21	87.4	12.6	6.9
Pyridine-treated	0.14	87.9	12.1	7.2

Visual average of two scans.

^a Not apparent.

^b Observable but not measurable.

study uses strongly interacting solvents to gain further structural information on the SPET fibers. The uptake levels of any one solvent in SPET fibers are not affected by crimping or relaxing processes, but uptakes of the three solvents studied are related to their overall sizes and shapes. Stronger solvent effects on fiber structures were observed on the drawn fibers than on the further processed, i.e., crimped and relaxed fibers. The annealed fibers, which have fewer but larger crystals that are highly oriented, densely packed, and very stable, show the highest levels of solvent uptakes but the least effects on their physical properties. This study shows that solvent-SPET interaction was highly dependent upon the existing fiber structures. The solvent-polymer in-

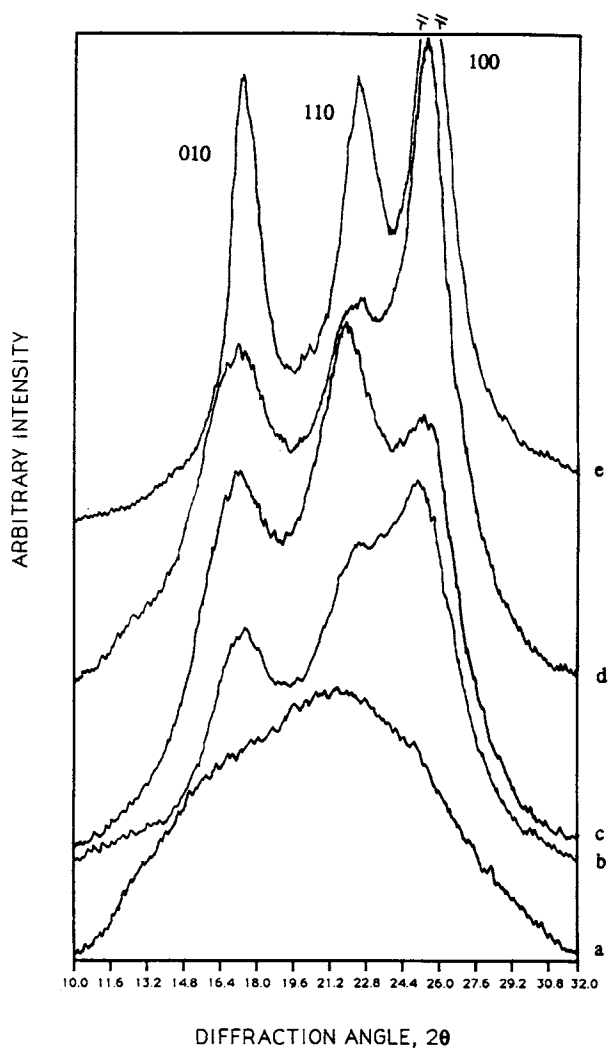


Figure 6 X-ray diffractograms of SPET fibers: (a) undrawn; (b) drawn; (c) crimped; (d) relaxed; (e) annealed.

Table VIII Crystallite Dimensions, L (Å), of SPET Fibers

Process/ Treatment	Axial 100	Stacking 010	Side-by-Side 110
Drawn/ None	34.3	34.7	33.8
DMSO	27.6	34.7	22.5
MeCl ₂	37.8	48.0	35.0
Pyridine	29.2	34.7	24.8
Crimped/ None	27.6	27.2	30.7
DMSO	60.2	40.3	35.0
MeCl ₂	48.7	40.3	30.8
Pyridine	—	—	—
Relaxed/ None	40.8	28.8	27.4
DMSO	29.1	30.5	22.5
MeCl ₂	35.2	30.5	22.5
Pyridine	—	—	—
Annealed/ None	48.7	59.3	44.9
DMSO	47.0	65.6	59.8
MeCl ₂	48.7	59.4	48.4
Pyridine	48.7	67.3	48.4

teraction in the processed fibers was found to be related to the chain mobility, packing, and orientation in the noncrystalline domains, but not necessarily to crystallite size or content. The solvent-induced changes provide additional structural information of the fibers, including their overall orientation, *trans-gauche* ratio, and extent of chain fold.

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