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Structural and Conformational Characterization of Poly(ethylene 2,6-naphthalate) by Infrared Spectroscopy

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ABSTRACT: X-ray diffraction analysis demonstrated that a PEN film annealed from 160 to 260 °C crystallizes in the α crystal form while crystallization of PEN directly from the melt results in the *β* crystal form when $T_c > 200$ °C and in the α form at lower T_c. Infrared spectra from PEN samples containing α, *β*, and amorphous phases were obtained, and digital subtraction of the amorphous contribution from the semicrystalline spectra provided characteristic spectra of amorphous, α, and *β* crystalline spectra. The bands at 1004, 1332, and 814 cm^{-1} were attributed to the all-trans conformation in the α crystalline phase, and the bands at 975 and 1348 cm^{-1} were attributed to the *β* crystalline phase. Our infrared spectroscopic investigation suggests that the α crystal form adopts an all-trans conformation while the *β* crystal form adopts a conformation with appreciable gauche character. Conformational changes occurring in PEN not only are due to the rotation of the ethylene glycol unit but also arise from the rotation of the naphthalene ring. This is different from PET, where conformational changes have been observed to occur only in the ethylene glycol unit. The normalized absorbances of the band at 824 and 814 cm^{-1} were correlated to polymer density, showing that these bands can be used unambiguously to represent the amorphous and α crystalline phases, respectively. Using drawn PEN film, the assignment of the amorphous 1338 cm^{-1} band to the trans conformation was explored.

Introduction

Poly(ethylene 2,6-naphthalate) (PEN) is a crystallizable polymer of increasing commercial interest that can be used in higher temperature applications than poly(ethylene terephthalate) (PET). The naphthalene ring provides greater rigidity to the polymer backbone than the benzene ring in PET, elevating the glass transition temperature and melting point and enhancing the mechanical properties such as tensile modulus and creep resistance. As with PET, PEN can be formed into amorphous glasses by rapid quenching from the melt and then can be crystallized by stress and/or thermal energy.[1−4]

The synthesis of PEN has been described in the patent literature.[5] In a recent study, Zachman et al.[6] reported that PEN can crystallize into two different crystal modifications. The α crystal form can be obtained by annealing amorphous PEN in the solid state, and the other crystal form (*β*) can be obtained by crystallizing directly from the melt. The unit cell of the α crystal form, determined by Mencik et al.,[7] is triclinic with $a = 0.651$, $b = 0.575$, $c = 1.32$ nm, $\alpha = 81.33°$, $\beta = 144°$, and $\gamma = 100°$ and a density of 1407 kg/m^3. The chains lie parallel to the *c*-axis, and a single chain passes through the unit cell. A triclinic unit cell was also proposed for the *β* crystal form,[8] with $a = 0.926$, $b = 1.559$, $c = 1.273$ nm, $\alpha = 121.6°$, $\beta = 95.57°$, and $\gamma = 122.52°$. Four chains pass through each unit cell of the *β* form, and since every naphthalene ring is rotated by 180 °C, the chains are not completely extended. The density of the *β* crystal form was reported as 1439 kg/m^3.

The glass transition, crystallization, and melting behavior of various polyesters have been studied,[9,10] including the influence of the length of the glycol unit. However, the nature of the ring structure will also effect the chain mobility and crystallization behavior. Therefore, the comparison of PET and PEN which have the same number of carbons in the glycol unit is of particular interest. During the past decade PEN has been the subject of many morphological studies using X-ray diffraction,[11] differential scanning calorimetry,[12] and solid-state NMR spectroscopy.[13] Recently, solid-state NMR spectroscopy has been used to investigate amorphous and semicrystalline PEN in the α form. It was shown that the line shape of the ethylene carbon indicates two components, assigned to trans and gauche conformations. The first component mainly arises from the crystalline component and the second one from the amorphous component.

Microstructure characterization of PEN has been carried out to some extent by IR spectroscopy.[14,15] Ouchi et al. investigated some poly(methylene terephthalates) and poly(methylene 2,6-naphthalates) by IR spectroscopy.[14] It was found that a number of vibrational bands associated with PEN behaved differently from other polyesters, and those bands were attributed to the intermolecular interactions arising from tight packing. In situ FTIR characterization was carried out to obtain conformational changes occurring during isothermal melt crystallization, and the bands associated with crystalline and amorphous trans conformations were identified.[15] Vibrational characteristics of molecular packing of the polymer chain appear in the infrared region between 1000 and 800 cm^{-1} for PEN. The bands associated with molecular packing may be useful to determine structure−property relationships in PEN. In the present work we report IR studies of the two crystalline phases and the amorphous phase of PEN. Changes in the infrared spectrum are interpreted in terms of conformational changes, crystallinity changes, and packing differences.

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Experimental Section

Samples. Amorphous PEN films were supplied by Eastman Chemical Company. Crystallization of polyethylene naphthalate was carried out by two different methods. (1) Amorphous films were melted at 310 °C for 10 min in the convection oven, and crystallization was carried out for 15 min at various crystallization temperatures (T_c) from 200 to 250 °C, followed by quenching to room temperature. (2) Crystallization was carried out by annealing the amorphous film for half an hour at various annealing temperatures (T_a) from 160 to 260 °C followed by quenching at room temperature. Samples prepared by melt crystallization were in the β form when $T_c > 200$ °C and in the α form at $T_c = 190$ °C. Samples prepared by annealing were in the α form at all T_a. For the study of drawn PEN, samples of the amorphous film (8 mm gauge length by 75 mm wide) were stretched in the furnace of an Instron tensile tester, as described elsewhere,[16] to draw ratios in the range 1−3.5 at a temperature of 140 °C and at a nominal strain rate of 0.42 s^{-1}. Specimens cut from the center of the drawn film were used for structure characterization.

Density. Polymer density ρ was determined on small pieces of the film using a density gradient column at 23 °C. Each density value is the average of three determinations. The column liquids used were carbon tetrachloride and *n*-heptane. Samples were allowed 16 h for equilibration in the gradient column before a reading was taken. Apparent volume fraction crystallinity χ was determined from $\chi = (\rho - \rho_a)/(\rho_c - \rho_a)$. The values for the density of the amorphous, α crystalline, and β crystalline phases were taken as 1325, 1407, and 1439 kg/m^3, respectively.[7,8] An amorphous density of 1330 kg/m^3 was determined in our laboratory.

Differential Scanning Calorimetry. Thermal analysis was carried out on a Perkin-Elmer DSC 7 differential scanning calorimeter using 2−5 mg sample. Each thermogram was obtained from 30 to 300 °C at a heating rate of 10° C/min. Calibration was performed using indium and zinc.

FTIR Spectroscopy. Infrared spectra were taken using the ATR mode on a Nicolet 560 FTIR spectrometer equipped with an Advantage microscope using a liquid nitrogen cooled mercury cadmium telluride (MCT) detector. All ATR spectra were obtained using the ATR accessory at an incident angle of 45°. At least 256 scans were obtained to achieve an adequate signal-to-noise ratio. Samples were prepared very carefully with smooth surface to ensure good contact. All subtractions were carried out using standard Ominic software. Selected IR bands were resolved using a peak fitting program (Jandell) to determine the area under the peaks. The bands were assumed to be Lorentzian with a linear baseline.

Results and Discussion

Density and X-ray Diffraction. Figure 1 shows the wide-angle X-ray diffraction patterns of PEN (a) quenched quickly from the melt to room temperature (amorphous), (b) crystallized from the melt by cooling from 310 to 230 °C, and (c) annealed at 250 °C. These diffraction patterns suggest that the melt crystallized sample crystallizes mainly in the β crystal form, and the annealed sample crystallizes predominantly in the α crystal form. The α crystal form shows three strong reflections at $2\theta = 15.6°$, 23.3°, and 27.0° corresponding to 010, 100, and 110 diffraction planes, and the β crystal form shows strong reflections at $2\theta = 16.4°$, 18.6°, and 25.5° corresponding to 111, 020, and 242 diffraction planes. These reflections were used to identify the crystal forms and purity of the samples. Table 1 shows the effects of crystallization conditions on volume fraction crystallinity (from density measurements), the crystal form (from WAXS), and the melting temperature (from DSC). Most of the β samples were found to contain a very small amount of α form, but the β sample used for the subsequent IR spectroscopic investigation, which was crystallized from the melt at 230 °C, does not have any detectable α form. The volume fraction crystallinity of the α samples increases as a function of annealing temperature while the crystallinity of the β samples is essentially independent of crystallization temperature. It is apparent that melting temperature increases as a function of crystallization temperature for the β crystal form. For the α form, however, the melting point stays almost constant up to the annealing temperature of 240 °C and then increases at 260 °C.

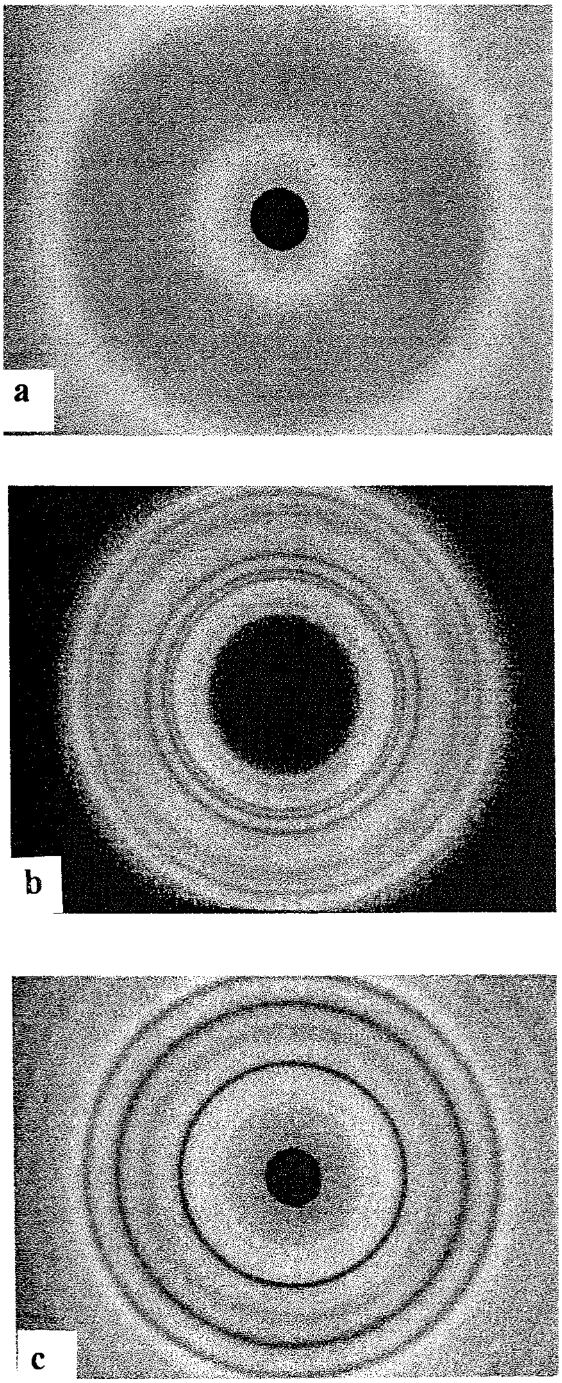

Figure 1. Wide-angle X-ray diffraction pattern of PEN: (a) amorphous film as received; (b) sample annealed at 250 °C for 30 min, α crystal form; (c) sample crystallized from the melt at 230 °C, β crystal form.

FTIR Spectroscopy. The infrared spectra taken in the region between 600 and 1800 cm^{-1} at room temperature for amorphous PEN and for semicrystalline PEN containing the α crystal form and the β crystal

Table 1. Density, Crystallinity, Crystal Form, and Melting Points of PEN Samples Crystallized under Different Conditions

method	T_c (°C)	density (kg/m^3)	crystallinity (%)	crystal form	T_m (°C)
melt	190	1354	38	α	267.8
	200	1358	30	β	265.2
	210	1361	31	β	268.5, 260.1
	220	1361	32	β	268.3, 263.5
	240	1359	30	β	267.6
	250	1360	31	β	271.5
annealed	160	1331	9	α	263.0
	170	1346	28	α	264.2
	180	1348	30	α	264.5
	200	1349	32	α	265.0
	220	1351	34	α	265.0
	240	1354	38	α	265.5
	260	1357	43	α	270.0

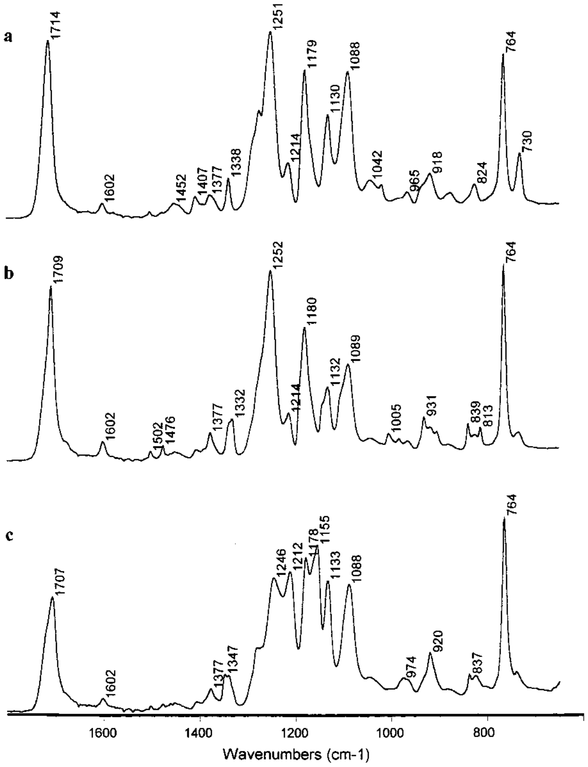

Figure 2. Infrared spectra of PEN in the 600−1800 cm^{-1} region: (a) amorphous film as received; (b) sample annealed at 250 °C for 30 min, α crystal form; (c) sample crystallized from the melt at 230 °C, β crystal form.

form are shown in Figure 2a−c, respectively. A comparison of these spectra shows distinctive features that can be used to identify the three phases as discussed below. Vibrational modes in the infrared spectra of PEN can be classified into the bands associated with the naphthalene ring and the bands associated with the ethylene glycol unit. Both units are connected by a C=O group, and the C=O stretching vibration influences both classes of vibrations and vice versa. It is clear from the comparison of the amorphous spectrum and semicrystalline spectra that the crystallization of PEN effects both classes of vibrations that are associated with the aromatic ring and ethylene glycol unit. Effects of crystallization on the IR spectra of PET have been studied extensively,[17−20] and it has been reported that bands associated with the aromatic ring are not affected by crystallization and that spectral changes in PET occur only due to changes in the conformation of the ethylene glycol unit.[17] However, the crystallization of PEN alters the conformation of the ethylene glycol unit as well as the naphthalene ring.

The first striking feature is the difference in the C=O stretching frequency. The amorphous spectrum shows a band at 1714 cm^{-1}, associated with the C=O stretching vibration, while it appears at 1709 cm^{-1} for the α crystalline phase and at 1707 cm^{-1} for the β crystalline phase. Both semicrystalline samples show a shoulder at 1714 cm^{-1}, due to the presence of a substantial amorphous fraction. (It will be shown later that, after subtraction of the amorphous spectrum from the semicrystalline spectra, the carbonyl stretching vibration appears at 1708 cm^{-1} for the α crystalline phase and at 1704 cm^{-1} for the β crystalline phase.) The band shift for the C=O vibration in the α crystalline phase was also observed by Kimura et al.[15] and explained by the differences in the conjugation between the carbonyl group and naphthalene ring. Conjugation has a strong electron-withdrawing effect on the C=O group, leading to a downward shift in the vibration. Since we observe a larger shift for the β crystal structure than the α crystal structure, we can conclude that the conjugation between the naphthalene ring and the carbonyl group is greater for the β crystal structure than the α crystal structure. By contrast, the C=O stretching band occurs at 1714 cm^{-1} for both crystalline and amorphous phases (not shown) of PET, suggesting that crystallization of PET does not effect the interaction between the aromatic ring and C=O group.[18]

Another important feature is that the amorphous spectrum shows a strong broad band at 824 cm^{-1}, assigned previously to the CH_2 rocking vibration, while three new bands at 839 and 814 cm^{-1} appear for the α crystal form and one band appears at 837 cm^{-1} for the β crystal form of PEN. From similar evidence, Kimura et al.[15] attributed the band at 824 cm^{-1} to the amorphous phase, the band at 839 and 814 cm^{-1} to the α crystalline phase, and the band at 837 cm^{-1} to the β crystalline phase. Both α and β samples show a broad band at 824 cm^{-1}, confirming the presence of a significant amorphous component. Ouchi et al.[14] also observed the appearance of 839 and 814 cm^{-1} after crystallization by annealing. They showed that the band at 824 cm^{-1} is present in all naphthalene-containing polyesters, whereas the formation of new bands due to crystallization occurs only for PEN and not for other naphthalene-containing polyesters.[14]

To confirm these assignments, we have correlated the density with the absorbance of crystalline and amorphous bands (824 and 814 cm^{-1}). The absorbance of each band used was obtained by using a peak fitting program, as shown in Figure 3. The absorbance ratio of the 814 and 824 cm^{-1} to the internal reference band at 1602 cm^{-1}, attributed to naphthalene ring vibration, was plotted against the measured density (Figure 4) and fitted by liner regression. A linear dependence of the normalized absorbance with respect to density is observed. The extinction of the crystalline sensitive band at 814 cm^{-1} gave a density of 1324 kg/m^3, in close agreement with the reported amorphous density of 1325 kg/m^3. The extrapolation of the amorphous sensitive band at 824 cm^{-1} provided a density of 1404 kg/m^3, which is in very close agreement with the reported α phase crystalline density of 1407 kg/m^3. However, when the band at 839 cm^{-1} was plotted against density (not shown), extinction of this band provided a density of 1300 kg/m^3, much lower than the reported amorphous

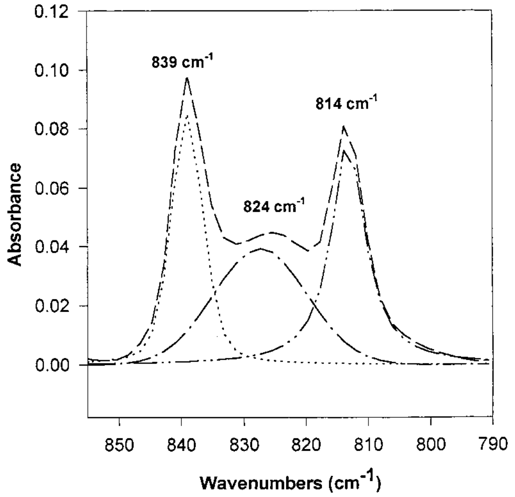

Figure 3. Curve fitting of the IR spectra in the region between 800 and 900 cm^{-1}.

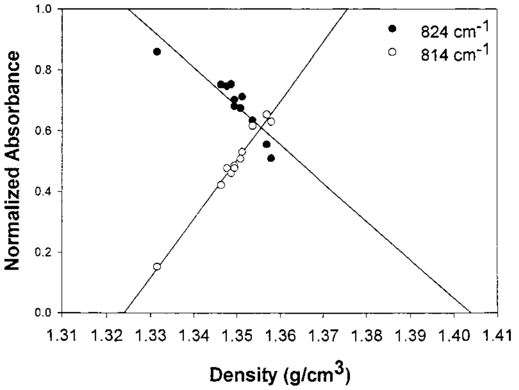

Figure 4. Normalized absorbance of crystalline band at 814 cm^{-1} and the amorphous band at 824 cm^{-1} vs polymer density.

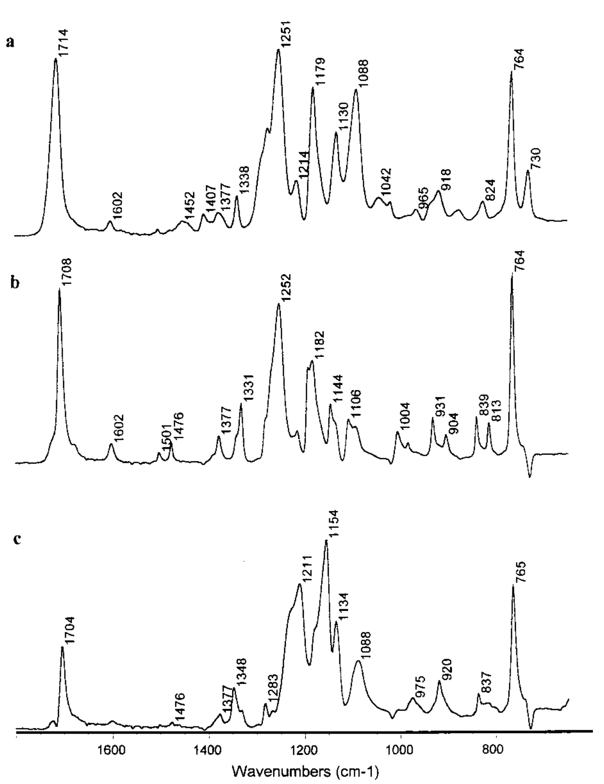

Figure 5. Infrared spectra of PEN in the 600–1800 cm^{-1} region: (a) amorphous; (b) α crystal form; (c) *β* crystal form.

density. This suggests that the band at 839 cm^{-1} cannot be fully attributed to the crystalline phase.

Whereas the band at 824 cm^{-1} is observed for all the naphthalene-containing polyesters, the new bands appearing during crystallization occur only for PEN, suggesting that the crystal chain packing in PEN may be different from the other naphthalene-containing polyesters. Moreover, similar behavior has not been observed in PET. Intermolecular interaction of neighboring chains in PEN may lead to crystal field splitting, giving birth to new bands in the crystalline spectrum. We have demonstrated for the first time that the bands associated with packing in the α crystalline phase are different from in the *β* crystalline phase, indicating that the chains in the two crystal phases pack differently. These bands (814 cm^{-1} for α and 837 cm^{-1} for *β* crystalline phase) can be considered “true” crystallinity bands. True crystallinity bands, caused by intermolecular interaction in the crystalline state, have been observed in only a few semicrystalline polymers such as polyethylene.[21] In PE, for example, the splitting of a band at 720 cm^{-1}, associated with CH_2 rocking vibration, is due to intermolecular interaction in the crystalline state. Since it is unusual to identify bands directly associated with crystallinity in semicrystalline polymers, bands associated with certain conformational arrangements are often used on the assumption that these conformational arrangements are required for crystallization. Taking advantage of “true” crystallinity bands observed in PEN, we can explore infrared spectroscopic methods to obtain crystallinity and crystalline orientation without calibration against other techniques.

Digital subtraction of the amorphous spectrum from the semicrystalline spectra was carried out to obtain the 100% crystalline spectra of the α and *β* crystal phases. The procedure for obtaining crystalline spectra from semicrystalline spectra was reported previously for various semicrystalline polymers, including *trans*-1,4-polyisoprene,[22] polypropylene,[23] PEEK,[24] poly(ethylene terephthalate),[17] and poly(ethylene naphthalate).[15] In the case of PET, the subtraction method was used to separate and quantify trans and gauche conformations.[25] In combination with density or X-ray determinations, it can also be used to separate the crystalline and amorphous trans conformations.[26] In the present study, subtraction of amorphous PEN from the semicrystalline spectra was performed by observing the disappearance of the amorphous band at 824 cm^{-1}. The subtracted spectra representing α and *β* crystalline phases of PEN are shown in Figure 5 along with the amorphous spectrum. The observed frequencies of the amorphous, α crystalline, and *β* crystalline spectra are presented in the Table 2, together with tentative band assignments.

By comparing the amorphous spectrum with α and *β* crystalline spectra (Figure 5), the bands characteristic of the amorphous, α, and *β* crystalline phases were identified. The bands at 1714, 1452, 1407, 1338, 1042, 965, and 824 cm^{-1} disappeared completely in both α and *β* crystalline spectra, confirming that these bands can be attributed to amorphous phase.[14,15] Since the bands at 1452 and 1042 cm^{-1} were previously assigned to the gauche conformation of PET,[21] it is reasonable to assign these bands to the gauche conformation of the ethylene glycol unit in PEN.[14] The bands at 1708, 1476, 1331, 1004, 839, and 814 cm^{-1} are characteristic of the α crystalline phase, and the bands at 1704, 1348, 1154,

Table 2. Infrared Absorption Frequencies (cm^{-1}) of Poly(ethylene naphthalate) in the Amorphous Phase and α and β Crystalline Phases[a]

amorphous	α crystalline	β crystalline	assignment
1714 vs	1708 vs	1704 vs	C═O stretch
1602 s	1602 s	1602 s	naphthalene
1570 w	1570 w	1570 w	naphthalene
1501 m	1501 m	1501 m	naphthalene
1477 m	1477 m		trans CH_2
1452 m			gauche CH_2
1407 m			
1376 m	1376 m	1376 m	
1338 s	1341 sh	1347 sh	
	1332 s	1332 s	trans CH_2
1275 sh	1252 vs	1282 vs	=C−O + aromatic
1252 vs		1258 vs	=C−O + aromatic
		1230 sh	
1214 m	1214 m	1214 m	aromatic
1179 vs	1191 vs	1179 vs	naphthalene
	1182 vs		
1130 s	1144 s	1133 s	naphthalene
	1134 sh		
	1106 s		
1088 vs	1088 sh	1086	
1042 m			gauche
1018 m			
	1004		trans
984 sh	984 m	984 sh	
964 m		975	
931 sh	931 s	919 s	
918 s			amorphous
	905 s		crystalline
874 sh			
824 m			amorphous
	839 m, 813 m	836 m	crystalline
764 vs	764 vs	764 vs	naphthalene
730 s			amorphous

[a] Abbreviations: vs = very strong, s = strong, w = weak, m = medium, sh = shoulder.

Table 3. Normalized Absorbance of the Bands at 1338 and 1332 cm^{-1} to the Band at 1602 cm^{-1} Changes as a Function of Draw Ratio

draw ratio	band at 1338 cm^{-1}	band at 1332 cm^{-1}	draw ratio	band at 1338 cm^{-1}	band at 1332 cm^{-1}
1.0	2.47		2.0	2.57	
1.1	2.50		2.3	1.84	0.53
1.3	2.60		2.5	1.74	0.59
1.5	2.50		3.3	1.78	0.78
1.7	2.52				

975, and 837 cm^{-1} are characteristic of β crystalline phase, confirming the assignments in refs 14 and 15. These bands can be used to determine the crystal form and purity of the sample.

The band at 1338 cm^{-1} in the amorphous spectrum is shifted to 1332 cm^{-1} in the α crystalline phase while it is shifted to 1347 cm^{-1} in the β crystalline phase. The bands at 1338 and 1370 cm^{-1} were observed in PET and attributed to the trans and gauche conformation of the CH_2 wagging mode,[17] respectively. Since we have seen a strong band at 1338 cm^{-1} in the amorphous spectrum of PEN that disappears completely in the crystalline spectrum, it can be assigned to the CH_2 wagging vibration associated with the amorphous phase. In a recent infrared study, the band at 1338 cm^{-1} was attributed to the amorphous trans conformation, and it was suggested that at a crystallization temperature of 255 °C formation of the amorphous trans conformation precedes crystallization.[15] To explore the nature of the 1338 cm^{-1} band further, we have obtained IR spectra of drawn PEN films as a function of draw ratio. We have found that the absorbance of the 1338 cm^{-1} band (relative to the “reference” band at 1602 cm^{-1}) stays constant as the draw ratio is increased from 1 to 2 (Table 3). Density measurements (to be published elsewhere) indicate that crystallization starts at a draw ratio somewhat greater than 2 under the drawing conditions used, and this is confirmed by the emergence of the 1332 cm^{-1} (α crystalline) band at a draw ratio of 2.3 (Table 3). It would be reasonable to expect an increase in amorphous trans content during drawing, prior to the onset of crystallization, and the absence of an increase in absorbance of the 1338 cm^{-1} band in this draw ratio region may cast doubt on its assignment to the trans conformation. Unpublished data from our laboratory, using the 1338 cm^{-1} trans band in PET, indicates a roughly 20% increase in amorphous trans content when amorphous, unoriented PET is drawn (above T_g) to a draw ratio of 2 at a nominal strain rate of 0.56 s^{-1}. Roland and Sonnenschein,[27] on the other hand, show a negligible increase in the trans content of PET in this draw ratio region, but this may be due to the much lower strain rate (0.003 s^{-1}) used in their study. It could be argued that the decrease in the absorbance of the 1338 cm^{-1} band after stress-induced crystallization of PEN (Table 3) arises from crystallization of amorphous trans segments, but this could equally arise from a decrease in the total amorphous content. Moreover, in the case of PET, increasing the draw ratio from 3 to 6 was found by Padibjo and Ward to cause a modest increase in amorphous trans content *together with* a rapid increase in crystallinty.[28] These observations certainly do not rule out the amorphous trans assignment of the 1338 cm^{-1} band, since they may rather indicate differences in deformation behavior between PET and PEN, but they indicate a need for further investigation of this band.

The frequency distribution for six possible conformational models of poly(ethylene glycol) was calculated by Matsuura and Miyazawa.[29] There are three chain bonds per repeat unit ($O-CH_2-CH_2-O$), and assuming that each bond can adopt the trans (T) or gauche (G) form, possible conformational models are TTT, TGT, TTG, TGG, GTG, and GGG. The calculations predict that a band will be seen at 1330−1340 cm^{-1} for the trans CH_2-CH_2 bond and at 1350−1360 cm^{-1} for the gauche CH_2-CH_2 bond. It is therefore reasonable to assign the band at 1332 cm^{-1} to the trans CH_2 wagging vibration in the α crystalline phase and the band at 1347 cm^{-1} to the gauche CH_2 wagging in the β crystalline phase. A shoulder at 1332 cm^{-1} in the β crystalline spectrum suggests that part of the chain adopts the trans CH_2 bond. We therefore deduce that the β crystalline form contains both trans and gauche components.

It is to be hoped that future investigations will pin down the conformational assignment of the 1338 cm^{-1} band in PEN. If it can be definitively assigned to amorphous trans, this would permit *direct* measurement of the trans conformer orientation in the amorphous phase of PEN, even in the presence of crystallinity. In PET, trans conformers in both the crystalline and noncrystalline phases contribute to the 1338 cm^{-1} band, and orientation of the amorphous trans component cannot be determined directly for this polymer.

In addition to the band at 1338, bands at 973 and 1470 cm^{-1} have been attributed to the trans conformation of PET,[17] and significant absorption at these wavenumbers in the infrared spectrum from the (unoriented) amorphous PET spectrum suggests that small amounts of trans conformation are present in amorphous PET. If we accept the attribution of the 1338 cm^{-1} band in PEN to amorphous trans conformers, the presence of this band in the amorphous spectrum suggests that there is a significant amount of trans conformers in amorphous PEN. The only other band in the amorphous spectrum that is attributable to the trans conformation is at 1476 cm^{-1} [15]. It is very small and poorly resolved in the amorphous spectrum, but it is clearly visible in the α crystalline spectrum. It can be assigned to the CH_2 scissoring vibration of the trans conformation, and its presence in the amorphous spectrum provides independent evidence that there is a small fraction of trans conformers in the amorphous phase of PEN.

A broad band at 964 cm^{-1} appears in the amorphous spectrum but is completely absent in the subtracted (crystalline) spectra. New bands at 992 and 1004 cm^{-1} appear in the α crystalline spectra while a band at 975 cm^{-1} appears in the β crystalline spectra. The band at 964 cm^{-1} was previously attributed to the gauche conformation of C−O stretching in ethylene glycol.[22] A band at 1005 cm^{-1} is predicted to appear in poly(ethylene glycol) when the conformation of ethylene glycol unit is TTT.[29] Therefore, we assign the band at 1004 cm^{-1} to the TTT conformation of the ethylene glycol unit in the α crystalline phase. The fact that we do not see this band in the β crystalline spectrum provides further evidence that the β crystalline phase adopts a different conformation from the all-trans conformation. The band at 1042 cm^{-1} in the amorphous spectrum has been attributed to the asymmetric stretching vibration of the C−O bond in the gauche conformation.[18] This disappears in the subtracted α and β spectra, confirming that this band is associated with gauche conformation of the ethylene glycol unit in the amorphous phase.

Solid-state NMR spectroscopy has been used in the past to determine the conformational changes in polymers. Changes in the conformation of the C−C bond can be easily seen in the spectra due to the γ-gauche effect,[30] provided the chains have more than three carbons. Since PEN has only two carbons in the ethylene glycol unit, it is impossible to observe the γ-gauche effect in the NMR spectra of this polymer. However, selectively deuterated PEN has been investigated recently by solid-state deuterium NMR spectroscopy.[31] It was found that molecular mobility of the ethylene groups is higher for amorphous PEN than amorphous PET. Also, trans−gauche jumps occurred in almost equal population for β crystals, whereas this is not the case for α crystals of PEN or PET crystals. The latter effect confirms our infrared results showing that the ethylene glycol unit has a considerable amount of gauche conformation in the β crystal form. These findings from IR and NMR analysis of the trans−gauche nature of the ethylene glycol unit in the α and β crystal forms are supported by X-ray diffraction studies showing that the α crystal structure adopts an all-trans conformation,[7] while the repeat distance for the β crystal form is shorter than the α crystal form.[8]

The bands associated with the naphthalene ring can be seen in three regions: 700−800, 1000−1300, and 1500−1600 cm^{-1}. The bands at 765 and 730 cm^{-1} are assigned to the out-of-plane bending vibration, and the corresponding vibration can be seen at 730 cm^{-1} for PET. The band at 730 cm^{-1} was first assigned to the C−O−C bending vibration,[32] but since it appears in the spectra of terephthalic acid and other compounds that do not have the C−O−C linkage, it was concluded that the band at 730 cm^{-1} may be assigned to aromatic C−H out-of-plane bending vibration.[20] Bands due to the in-plane bending vibration can be seen in the region between 1300 and 1000 cm^{-1}. The bands at 1130, 1178, and 1214 cm^{-1} in the amorphous spectrum are assigned to the naphthalene in-plane vibration. These bands are shifted to 1144, 1190, and 1207 cm^{-1} in the α crystalline spectrum and 1134, 1152, and 1207 cm^{-1} in the β crystalline spectrum, suggesting that the naphthalene ring adopts a different conformation in each phase. Skeletal vibrations involving aromatic C−C stretching frequency can be seen at 1500 and 1600 cm^{-1}, and neither of these bands is affected by crystallization.

From these results, it should be noted that bands associated with the naphthalene in-plane vibrations are influenced by the crystallization of PEN, whereas bands associated with the phenyl ring in PET are not affected by crystallization at all. The changes in the vibrations associated with the naphthalene ring suggest that there are significant differences in the naphthalene ring conformation in the three phases. Besides the ethylene glycol unit, there are three more possible rotational axes present in PET and PEN (C^{ar}−C, CO−O, and O−C). It has been established that these rotations do not occur in PET because the vibrations associated with the phenyl ring and carbonyl stretching do not depend on whether PET is crystalline or amorphous.[18] On the other hand, we have seen dramatic changes in the bands associated with the naphthalene ring and carbonyl stretching vibration in the infrared spectra of the α, β, and amorphous phases of PEN, indicating that rotations do not only occur in the ethylene glycol unit of the chain. In fact, X-ray diffraction studies suggest that the naphthalene ring in the β crystal structure is rotated by 180°.[6] Our infrared results confirm that the naphthalene ring takes different arrangements in each phase, and these arrangements may be associated with the rotation of the bond between the naphthalene ring and carbonyl group. The rotation would bring this carbonyl group in to different positions with respect to other carbonyl groups in the monomer unit, leading to a shift in the carbonyl stretching vibration.

Conclusions

Infrared spectra of the α, β, and amorphous phases of PEN have been obtained by a digital subtraction method, and the bands associated with each phase have been identified. Correlation between the polymer density and the normalized absorbance of bands at 824 and 814 cm^{-1} permits definitive attribution of these bands to the amorphous and α crystalline phases, respectively. Differences in the carbonyl stretching vibration were found between the amorphous and crystalline spectra, and it was shown that conjugation between the naphthalene ring is higher for the β crystalline phase than the α crystalline phase or amorphous phase. Interchain interaction and conformational changes are responsible for the birth of new bands in the crystal phase. From our infrared results we confirm that the α crystal form adopts an all-trans conformation, and we provide evidence that the β crystal form includes appreciable gauche conformation. Observations of band shifts associated with both the naphthalene ring and the ethylene glycol unit as a result of crystallization suggest that bond rotation occurs in the bond between the naphthalene group and the carbonyl bond ($C^{ar}-C$) as well as in the C−C bond of the ethylene glycol unit.

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