

Infrared Spectroscopic Studies of Melting Behavior of Poly(ethylene 2,6-naphthalenedicarboxylate)

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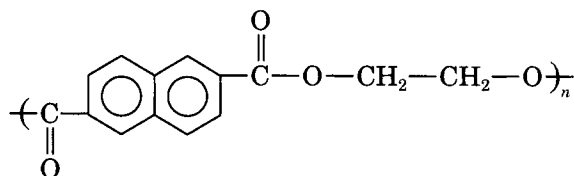
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SYNOPSIS

The FTIR method was used to study the melting behavior of poly(ethylene 2,6-naphthalenedicarboxylate) (PEN) samples of different thermal history of crystallization. With subtraction of the spectra of PEN samples of different crystallinities and amorphous PEN, the spectra of crystalline trans conformers, amorphous trans conformers, and amorphous gauche conformers were obtained. By following the changes in intensity of various gauche and crystalline bands during heating, the phenomenon of multiple melting endothermic peaks was shown to be due to the melting of imperfect crystalline conformation formed during crystallization. For two-step annealed samples, the crystalline conformational defects change into a more perfect one during annealing at higher temperatures. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

Poly(ethylene 2,6-naphthalenedicarboxylate) (PEN) with repeat unit was developed in the 1970s as a kind of heat resistant insulating film. Several studies about



its structure and properties were published.¹⁻³ Solvents like dioxane, aniline, and methylene chloride were found to induce crystallization.^{4,5} The crystal structure of PEN was reported to be triclinic with unit cell dimensions $a = 0.651$ nm, $b = 0.575$ nm, $c = 1.32$ nm, and $\alpha = 81^\circ 21'$, $\beta = 144^\circ 00'$, and $\gamma = 100^\circ 00'$.⁶ There are only a few studies about the behavior of crystallization and melting of PEN.^{7,8} PEN has a structure similar to PET. The $-\text{O}-\text{CH}_2-\text{CH}_2-\text{O}-$ moiety adopts trans conformation in the crystal regions and both gauche and trans conformation in the amorphous regions.⁷

The phenomenon of multiple melting endothermic peaks exists for many crystalline polymers.⁹ This phenomenon has been attributed to different factors for different polymers, including different crystal structure,¹⁰⁻¹² different crystal size,¹³ crystal reorganization, and perfection¹⁴ during the heating up DSC run. Amorphous PEN samples annealed at certain temperatures for crystallization exhibit some small premelting peaks in the DSC curves.¹⁵

FTIR, which is sensitive to both structural conformation and molecular environment, has become an important tool in characterizing semicrystalline polymers.¹⁶ In FTIR studies of poly(ethylene terephthalate) (PET), the pure spectra of the trans conformers in the crystalline region (T_c), the trans conformers in the amorphous region (T_a), and the gauche conformers (G) were obtained.¹⁷⁻¹⁹ In this study we isolated the infrared spectral features of the crystalline and amorphous phase by means of spectral subtraction,¹⁷ that is, subtracting the gauche conformational spectrum of PEN from the spectra of PEN samples of various crystallinities to obtain the spectrum of the trans conformer of PEN. Then the spectra of trans conformers at different crystallinities were subtracted from each other to obtain the spectrum of trans conformers in the crystalline region and in the amorphous region. Through monitoring the change of absorbance of these bands, we can further understand the crystallization and melting behavior of PEN.

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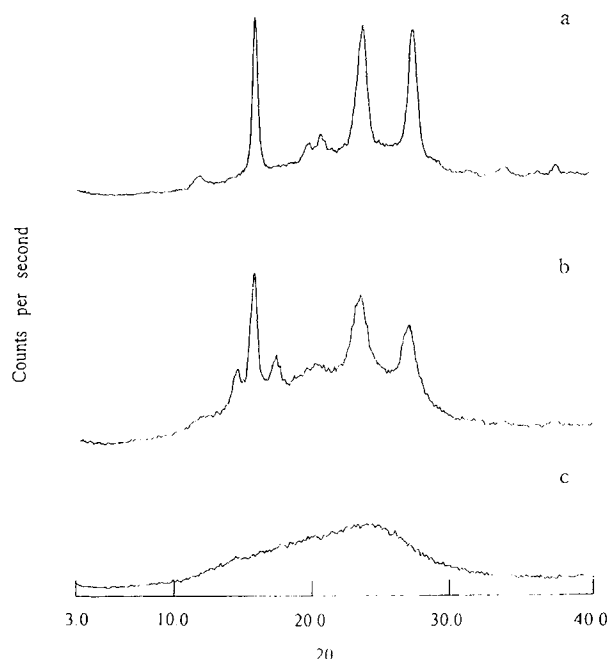


Figure 1 WAXD of PEN. (a) Sample of high crystallinity (annealed at 240°C for 1 h); (b) sample of lower crystallinity (annealed at 160°C for 1 h); and (c) amorphous sample.

EXPERIMENTAL

The PEN sample used in this study was kindly supplied by Prof. Deben Chen of Sichuan University. Amorphous PEN films of about 5- μm thickness were prepared by solution casting onto glass plates from a 5% solution of PEN in CHCl_3 — CF_3COOH (7 : 3) at 80°C. The films were air dried, then extracted with ethyl alcohol at room temperature, and dried in a vacuum at 40°C for 24 h. The films proved to be amorphous by their WAXD [Fig. 1(c)].

The dried amorphous films were annealed at various temperatures to get samples of different crystallinities and then were air quenched to room temperature. FTIR spectra were taken for each sample film after each step of annealing on a Bruker model IFS-113v spectrometer at 2- cm^{-1} resolution for 256 scans. WAXD data of these samples were recorded on a Rigaku DImax-3B Automatic X-ray Powder Diffractometer with Ni-filtered CuK_α radiation (40 kV, 30 mA).

PEN samples A, B, C, and D of different crystallinities were prepared by annealing amorphous PEN films at: 180°C for 1 h; 200°C for 0.5 h; 210°C for 0.5 h; and 180°C for 1 h and then 210°C for 0.5 h, respectively. FTIR spectra of these films were measured *in situ* and recorded every 4 min at a heating rate of 1°C/min.

DSC curves were recorded for the amorphous PEN films and films annealed under the same conditions as above. A Perkin-Elmer DSC-4 was used and the scan rate was 10°C/min.

RESULTS AND DISCUSSION

The —O—CH₂—CH₂—O— moiety adopts trans conformation in the crystalline regions. In amorphous regions it is mainly in gauche conformation and a small contribution of trans conformation. Figures 1 and 2 shows the WAXD data and infrared spectra of PEN under different degrees of crystallinity: one of high crystallinity from an amorphous sample annealed at 240°C for 1 h [Fig. 1(a)], one of lower crystallinity from an amorphous sample annealed at 160°C for 1 h [Fig. 1(b)], and one of an amorphous sample [Fig. 1(c)]. The spectra of partially crystalline S_c [Fig. 2(a,b)] and amorphous S_a [Fig. 2(c)] PEN can be expressed by

$$S_c = T_c + T_a + G$$

and

$$S_a = T_a + G$$

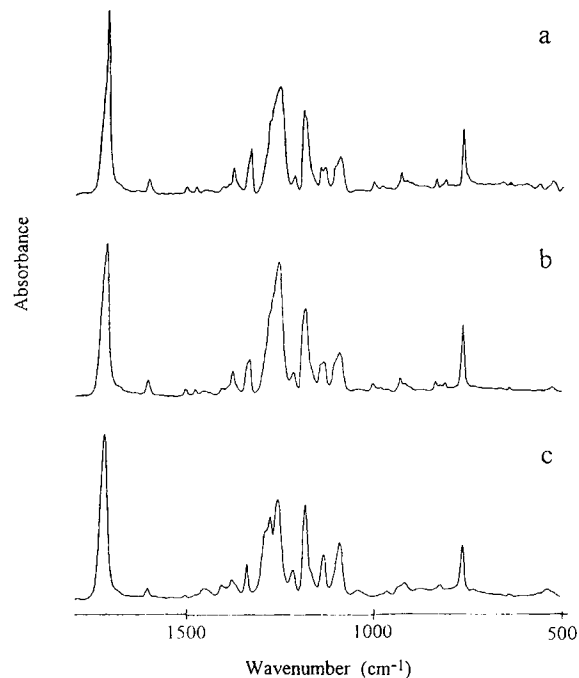


Figure 2 Infrared spectra of PEN. (a) Sample of high crystallinity (annealed at 240°C for 1 h); (b) sample of lower crystallinity (annealed at 160°C for 1 h); and (c) amorphous sample.

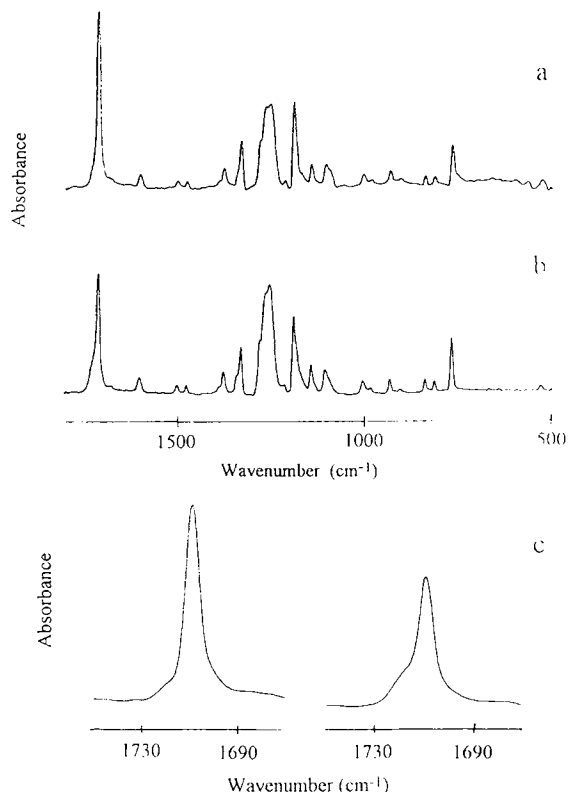


Figure 3 Infrared spectra of the trans conformers of PEN. (a) Sample of high crystallinity (annealed at 240°C for 1 h); (b) sample of lower crystallinity (annealed at 160°C for 1 h), and (c) expanded spectra of (a) and (b) in the 1670–1750 cm^{-1} region.

So the spectrum of the trans conformer S_T can be obtained by

$$S_T = S_c - k_1 S_a$$

where k_1 is an adjustable coefficient which is tuned to completely eliminate the gauche bands from the subtraction spectrum. Thus by subtraction of spectra (a – c) and (b – c) in Figure 2 one obtains the spectra of trans conformers in the samples of high crystallinity (S_{Th}) as shown in Figure 3(a) and of low crystallinity (S_{Tl}) as shown in Figure 3(b). Figure 3(c) shows the expanded spectra of Figure 3(a,b) in the 1670–1750 cm^{-1} region. In Figure 3(c) the strong band at 1712 cm^{-1} can be assigned as the C=O stretching vibrational mode of T_c and the shoulder band at 1720 cm^{-1} can be assigned to T_a . This fact indicates that the ratio of G and T_a in the amorphous sample is higher than that in the crystalline sample, so the amorphous trans bands could not be eliminated completely from the subtraction spectrum. We can see there are more T_c and fewer

T_a in the spectrum S_{Th} than that in the spectrum S_{Tl} , further subtraction of spectra (a – b) in Figure 3 gives the spectrum of the trans conformer in the crystalline regions (T_c) as shown in Figure 4(a). Subtraction of spectra (b – a) in Figure 3 gives the spectrum of the trans conformer in the amorphous regions (T_a) as shown in Figure 4(b), that is

$$T_c = S_{Th} - k_2 S_{Tl}$$

$$T_a = S_{Tl} - k_3 S_{Th}$$

where the coefficient k_2 is adjusted to eliminate amorphous trans bands and the coefficient k_3 is adjusted to eliminate crystalline trans bands. While subtraction of spectra c in Figure 2 minus b in Figure 4 gives the spectrum of the gauche conformer (G) as shown in Figure 4(c), that is

$$G = S_a - k_4 T_a$$

where the coefficient k_4 is adjusted to eliminate amorphous trans bands.

The main bands of these three conformers are summarized in Table I. By comparison of these spectra one obtains the PEN crystalline bands 1712, 1332, 1193, 1145, 1107, 1005, 933, 839, and 814 cm^{-1} ,

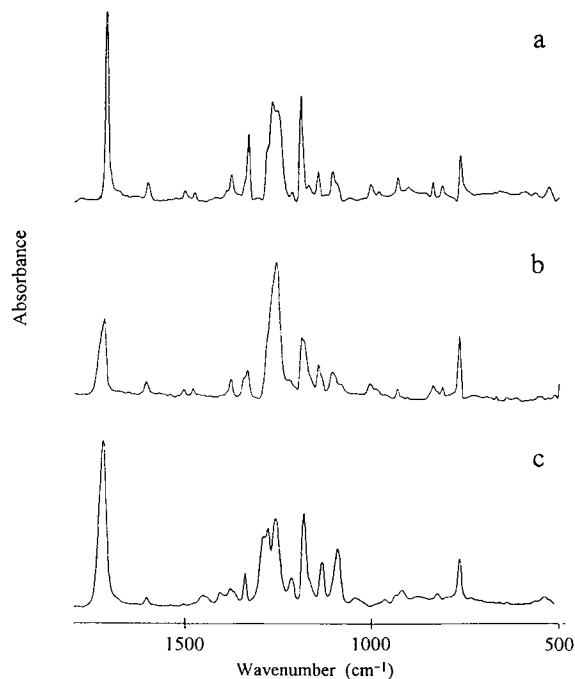


Figure 4 Infrared spectra of different conformers of PEN. (a) Trans conformer in the crystalline regions; (b) trans conformer in the amorphous regions; and (c) gauche conformer.

Table I Infrared Bands of Conformers of PEN

Band Frequency (cm ⁻¹)			
<i>T_c</i>	<i>T_a</i>	<i>G</i>	Tentative Assignment ⁷
1712	1720	1720	ν (C=O)
1601	1603	1603	Arom. ring vibration
1502	1502	1503	Arom. ring vibration
1475	1475	1455	δ (CH ₂)
1377	1377	1379	ω (CH ₂)
		1278	
1268	1257	1257	ν (=C—O)
1215	1215	1215	Arom. ring vibration
1193	1190	1182	Naphthalene ring vibration
1145	1144	1132	Naphthalene ring vibration
1107	1105		
		1091	ν_s (C—O) gauche
		1042	ν_a (C—O) gauche
933	932	918	δ (arom. CH out of plane)
839	837	825	
814	812		
766	766	766	δ (arom. CH out of plane)

and the PEN amorphous bands 1720, 1339, 1278, 1182, 1132, 1091, 1042, 918, and 825 cm⁻¹.

From WAXD experiments⁶ it is known that the PEN crystal lattice is triclinic; the —O—CH₂—CH₂—O— moiety takes the trans conformation completely in the crystalline region. The bands at 1091 and 1044 cm⁻¹ can be assigned as antisymmetric and symmetric —C—O— stretching vibrations, respectively, of the gauche conformer. The 1091-cm⁻¹ band decreased in absorbance significantly during crystallization. The 825-cm⁻¹ band in the amorphous sample decreased its intensity greatly after annealing at 160°C, and two sharp bands were created at 839 and 814 cm⁻¹. Ouchi et al.⁷ attributed these two bands to crystalline splitting due to intermolecular interactions.

The changes of absorbance of the 1091-cm⁻¹ gauche band on heating at 1°C/min for the four samples of different thermal history, A (annealed at 180°C for 1 h), B (annealed at 200°C for 0.5 h), C (annealed at 210°C for 0.5 h), and D (annealed at 180°C for 1 h + 210°C for 0.5 h) are shown in Figure 5. A step increase of the absorbance occurred at 180°C for A, at 192°C for B, at 200°C for C, and at 196°C for D. These temperatures, corresponding to the onset of a small endothermic peak, occurred before the melting point as previously observed by Cheng and Wunderlich¹⁵ for PEN. Very step increases of the absorbance then occurred near the respective melting points of these samples. The appearance of a small peak on the DSC curve (Fig. 6)

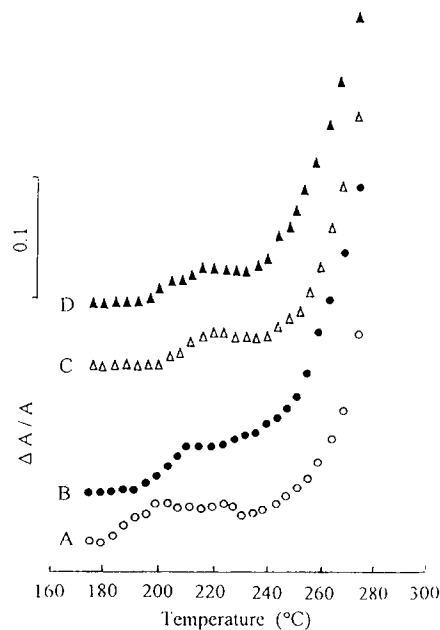


Figure 5 The changes of absorbance of the 1091-cm⁻¹ band on heating for the four samples of PEN of different thermal histories. Amorphous samples annealed at (A) 180°C for 1 h; (B) 200°C for 0.5 h; (C) 210°C for 0.5 h; and (D) 180°C for 1 h + 210°C for 0.5 h.

and a step increase of the infrared gauche band intensity are probably related to imperfect crystallization of PEN so that not all crystalline chains are in TTT conformation but some segments are in GTG or GTT conformational defects that lead to

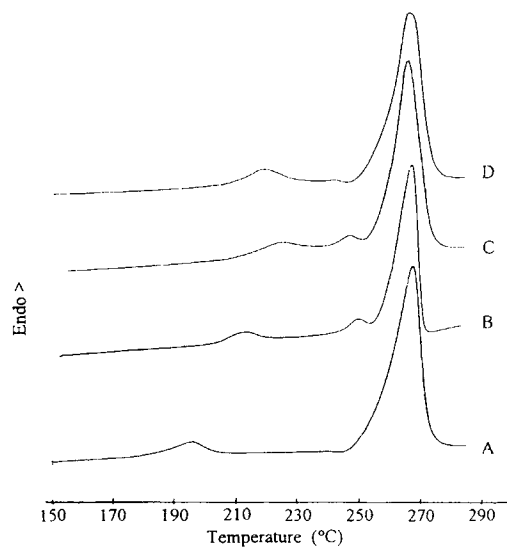


Figure 6 DSC curves for the four samples of PEN of different thermal history. Amorphous samples annealed at (A) 180°C for 1 h; (B) 200°C for 0.5 h; (C) 210°C for 0.5 h; and (D) 180°C for 1 h + 210°C for 0.5 h.

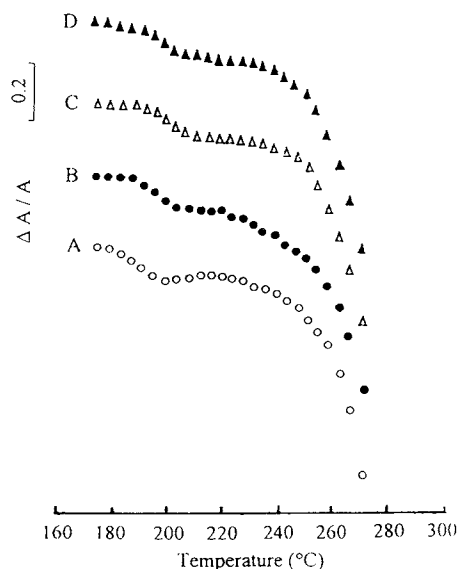


Figure 7 Changes of absorbance of the 839-cm^{-1} band on heating for the four samples of PEN at different thermal histories. Amorphous samples annealed at (A) 180°C for 1 h; (B) 200°C for 0.5 h; (C) 210°C for 0.5 h; and (D) 180°C for 1 h + 210°C for 0.5 h.

somewhat lower melting temperature. A comparison of the absorbance changes on heating of samples A and D indicates that the conformation defect that melts at 180°C in A was removed by the second step annealing at 210°C so that the absorbance changes of D and C on heating are almost identical. The increase of the gauche band absorbance at 1091 cm^{-1} on heating of the samples was accompanied by the decrease of the crystalline trans band absorbance at 839 cm^{-1} as shown in Figure 7. This confirms that the small absorbance steps or the small endothermic peaks on the DSC curves originate from the melting of the imperfect crystalline regions. For the two-step annealed samples the results are in accord with the interpretation of Cheng et al.²⁰ that the lower melting crystals grown during the first isothermal crystallization must melt in the second crystallization step. During melting of the first isothermally crystallized regions, the thermal history of the sample must have been lost to some degree. Recrystallization at the second crystallization step led to a new low temperature melting peak, governed by the higher crystallization temperature of the second step.

CONCLUSIONS

By using subtraction of infrared spectra of samples of different crystallinities, the spectra of crystalline

trans conformation, amorphous trans conformation, and gauche conformation of PEN were obtained. Conformational defects of crystallized samples were detected. The small endothermic peak below the melting point was identified as the melting of the imperfect crystalline region. In the two-step annealed sample, the imperfect crystalline regions formed in the first-step crystallization changed into more a perfect structure through recrystallization when annealed at higher temperatures.

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