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Nirmala R. James^a; E. Bhojgowd^a; C. Ramesh^a; S. Sivaram^a

^a Division of Polymer Chemistry, National Chemical Laboratory, Pune, India

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Studies on the Crystallization and Melting Behavior of Poly(ethylene 2,6-naphthalate)*

NIRMALA R. JAMES, E. BHOJE GOWD, C. RAMESH[†]
and S. SIVARAM

*Division of Polymer Chemistry, National Chemical Laboratory,
Pune 411008, India*

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Crystallization behaviour of low molecular weight (oligomeric) and high molecular weight poly(ethylene 2,6-naphthalate)s (PEN) was studied using wide angle X-ray diffraction (WAXS) and differential scanning calorimetry (DSC). It was found that the crystallization conditions determine the nature of crystalline modification. Crystallization from the glassy state gives α -modification, whereas, crystallizing from the melt above 220°C results in β -modification. In contrast, the oligomers gives both the modifications up on crystallizing from the melt. The equilibrium melting temperatures of PEN were determined from DSC experiments, based on conditions of crystallization of α and β -modifications.

Keywords: Poly(ethylene 2,6-naphthalate); Crystallization; Crystalline modifications

INTRODUCTION

Poly(ethylene 2,6-naphthalate)s (PEN) is a thermoplastic polyester which exhibits an oxygen barrier approximately five times greater than that of PET and a glass transition temperature of 120°C, which is 45°C higher than that of PET. These desirable properties of PEN have led to new markets and applications [1]. PEN is also well-known for its

* Dedicated to Professor Fakirov on his 65th birthday.

[†] Corresponding author. e-mail: ramesh@poly.ncl.res.in

photochemical and electrical properties as well as its ability to form liquid crystalline polymers with suitable comonomers [2, 3].

Many workers have investigated the crystallization behavior and crystal structure of PEN. Two crystal modifications, α and β are reported for PEN. The unit cell dimensions of α -form of PEN were determined by Mencik [4]. He suggested it to be triclinic ($a=0.651$, $b=0.575$, $c=1.32$ nm, $\alpha=81.33$, $\beta=144$ and $\gamma=100^\circ$) with a density of 1.407 g/cm³. The chains lie parallel to the c -axis and one chain passes through each unit cell. Zachmann *et al.* [5, 6] noted that the β -form could be formed during crystallization and the unit cell dimensions of which was determined to be $a=0.926$, $b=1.559$, $c=1.273$ nm, $\alpha=121.6$, $\beta=95.57$ and $\gamma=122.52^\circ$ with density of 1.439 g/cm³. Four chains pass through each cell. The chains are not completely extended since every naphthalene ring is twisted by 180° . Subsequently attempts were made to determine the specific conditions under which α and β forms are obtained. However, there is no agreement among different reports [6, 7]. The modifications are thermally stable but under severe thermo-mechanical treatment the β -modification can irreversibly transform into α -modification [8].

In the present work, we have carefully examined the crystallization and melting behaviour of α and β crystal modifications of oligomeric PEN ($[\eta] \sim 0.2$ dL/g) as well as for high molecular weight PEN ($[\eta] \sim 0.6$ dL/g). The equilibrium melting temperatures of α and β crystal forms are also computed from the melting behaviour of these two modifications.

EXPERIMENTAL

Materials

High molecular weight PEN ($[\eta]$ 0.6 dL/g) was obtained from Aldrich Chemicals, USA and used as received.

Preparation of Oligomers

PEN oligomer were prepared using standard melt polycondensation chemistry. Bis(hydroxyethyl) naphthalate (BHEN) was prepared from 2,6-dimethyl naphthalate (DMN) and EG according to the reported

procedure [9]. Oligomers were prepared from BHEN in presence of Sb_2O_3 (300 ppm) as catalysts.

Crystallization

The PEN sample ($[\eta]$ 0.6 dL/g) (about 10 mg) was crystallized in a Perkin Elmer DSC-7. The sample was first melted at 330°C and then cooled to the crystallization temperature at 100°C/min. and crystallized for about 120 minutes. The crystallization temperature was between 200°C to 250°C. In the case of oligomer a different method was followed because of the high crystallization rate of the oligomer samples. A small thin film of the oligomer sample was formed on a small copper plate and melted to temperature 330°C. Then the copper plate along with the melt sample was quickly transferred to a hot silicon oil bath maintained at temperatures between 190°C to 240°C. This technique ensured that the sample crystallized at the intended crystallization temperature only. The oil bath was maintained within 1°C of the set temperature.

WAXS Studies

In the case of high molecular weight PEN samples crystallized in a DSC-7 cell, WAXS pattern was obtained in the transmission mode. A small piece of the sample (sample size ~ 1 mm) was set in the goniometer head. The X-ray diffraction pattern was obtained using a DIP 1000 imaging plate (MAC Science Co. Ltd, Japan). The incident beam was graphite monochromatized $\text{Cu-K}\alpha$ and the generator was operating at 40 KV 200 mA (SRA 18, Mac Science, Japan).

In the case of oligomer samples crystallized in the copper plate, the WAXS pattern was obtained in reflection mode using a Rigaku Dmax 2500 diffractometer fitted with a diffracted beam graphite monochromator. The radiation was $\text{Cu-K}\alpha$ and scanned between $2\theta = 10$ to 35 deg. The generator was operated at 40 KV and 150 mA.

DSC Studies

The crystallization and melting behaviour studies were performed on Perkin Elmer DSC-7 which had been calibrated using an Indium

standard. About 8 mg of sample was initially melted at 330°C for 1 minute and cooled rapidly to the crystallization temperature and crystallized isothermally for 120 minutes. After crystallization the sample was heated to melting without cooling down to room temperature. In another series of experiments amorphous PEN samples (polymer and oligomer) were heated from room temperature to the crystallization temperature and crystallized for 120 minutes and then heated to melting without cooling to room temperature and the melting endotherms were recorded.

RESULTS AND DISCUSSIONS

Figure 1 shows the X-ray diffraction patterns of high molecular weight PEN samples crystallized from the melt in DSC. The patterns show characteristics of α -form or β -form depending on the crystallization

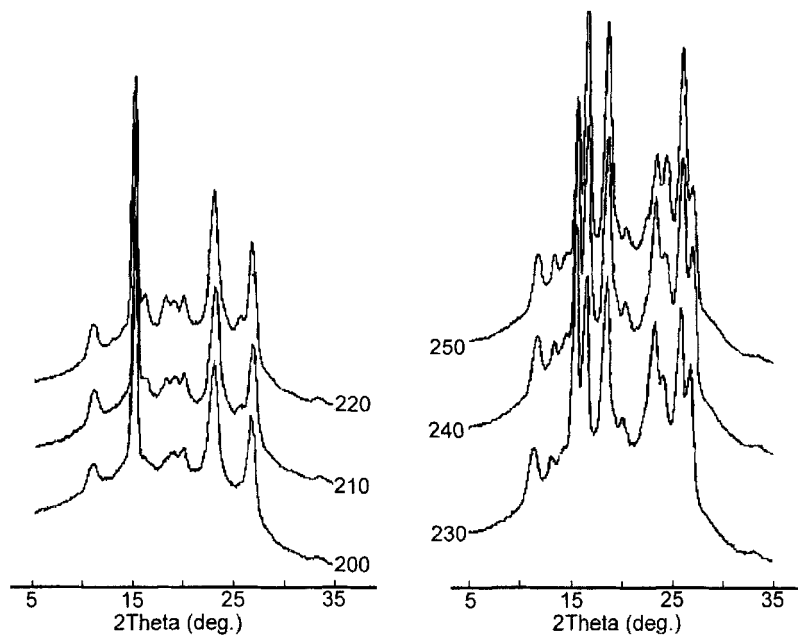


FIGURE 1 X-ray diffraction patterns of HMPEN crystallized from the melt. The crystallization temperature (°C) is indicated near the pattern.

conditions. In general samples crystallized at 220°C and below show reflections at $2\theta = 15.6, 23.3$ and 27.0 corresponding to 010, 100 and 110 diffraction planes which belong to α -modification. The samples crystallized above 220°C show peaks at $2\theta = 16.4, 18.6$ and 25.5 corresponding to 111, 020 and 242 reflections of β modification. In these samples the peak at $2\theta = 15.6$ indicates the presence of small amount of α -modification. The small α -modification could arise from the crystallization of the polymer occurring during cooling from the crystallization temperature. Similar results are obtained when the melt temperature is varied from 290°C to 340°C, indicating that the melt temperature does not influence the type of the structure. The crystallization temperature appears to be a more critical parameter. These results are similar to the data reported by Vasanthan and Salem [7], however they report formation of β modification at temperatures above 200°C. In contrast, we observed formation of β -modification only above 220°C. On the other hand our observation differ from Zachmann *et al.* [6] who reported α -modification for samples only when the melt temperature exceeds 320°C. In our work samples crystallized below 220°C show α -modification.

Figure 2 shows the X-ray diffraction patterns of the oligomer samples crystallized from the melt. It is seen that, in the temperature range studied (190 to 230°C), the samples crystallized in both α and β -modifications, with α -modification being the predominant fraction. Thus, the crystallization behavior of the oligomer differs from that of high molecular weight polymer. Both the oligomer and polymer crystallize in α modifications if crystallized from the glassy state instead of crystallizing from the melt. Figure 3 shows selected XRD patterns of oligomer and polymer crystallized from the glassy state. This behaviour is consistent with the observation made by Vasanthan and Salem [7].

The crystallization peak temperature (T_{CC}) on cooling from melt has been taken as a measure of crystallization rate [10]. The oligomer PEN exhibits a T_{CC} of 220°C indicating very high rate of crystallization. However, the melting temperature is 246°C. On the other hand the high molecular weight PEN has a T_{CC} of 200°C, indicating lower crystallization rate but melts at 265°C. The melting endotherms of the high molecular weight PEN crystallized from the melt at temperatures between 230 and 250°C is shown in Figure 4. These

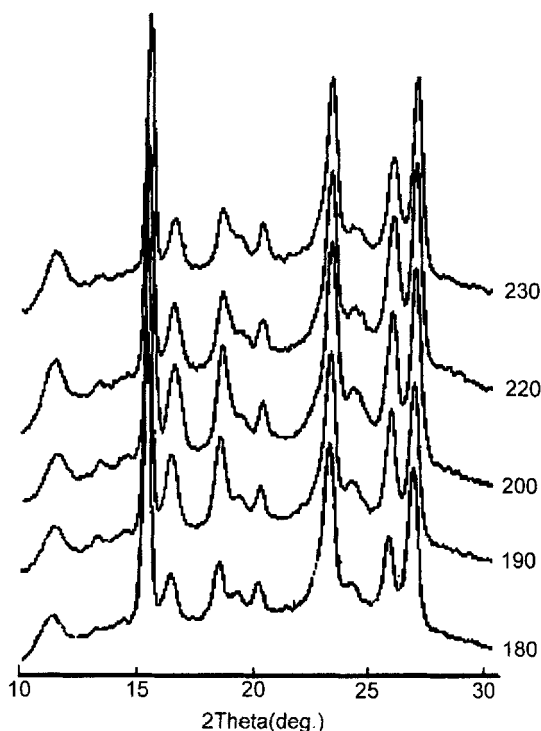


FIGURE 2 X-ray diffraction patterns of oligomer PEN crystallized from the melt. The crystallization temperature ($^{\circ}\text{C}$) is indicated near the pattern.

endotherms represent the melting of predominantly β modification. The melting endotherms of α -modification are given in Figure 5. In this case the samples are crystallized between 230 and 250 $^{\circ}\text{C}$ by heating the amorphous samples from room temperature. In both the cases the endotherms shift towards higher temperature on increasing crystallization temperature. The melting temperatures and heat of fusion of both the modifications are given Table I. It is seen from the table that the β -modification melts a higher temperature than that of α -modification by 2 to 3 $^{\circ}\text{C}$. However, the α -modification has higher heat of fusion than β -modification.

The crystallization temperatures employed in the present investigations are well above the maximum crystallization rate and after crystallization the samples are directly heated to melting without cooling to room temperature. Hence, structural rearrangement on

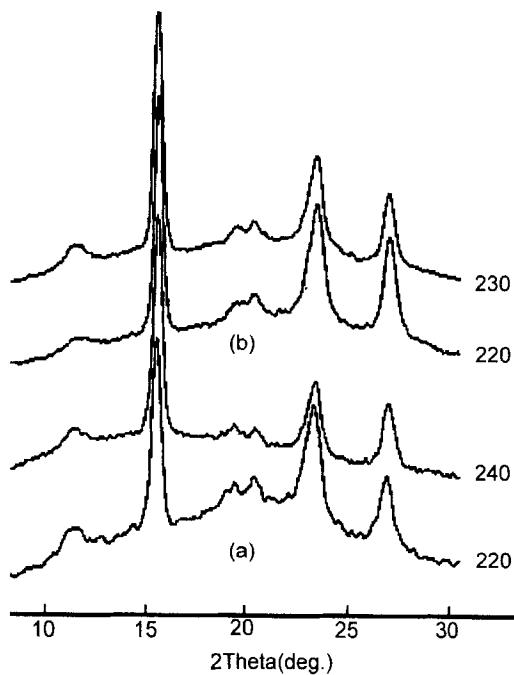


FIGURE 3 X-ray diffraction patterns of (a) HMPEN and (b) Oligomer PEN crystallized from the glassy state. The crystallization temperature ($^{\circ}\text{C}$) is indicated near the pattern.

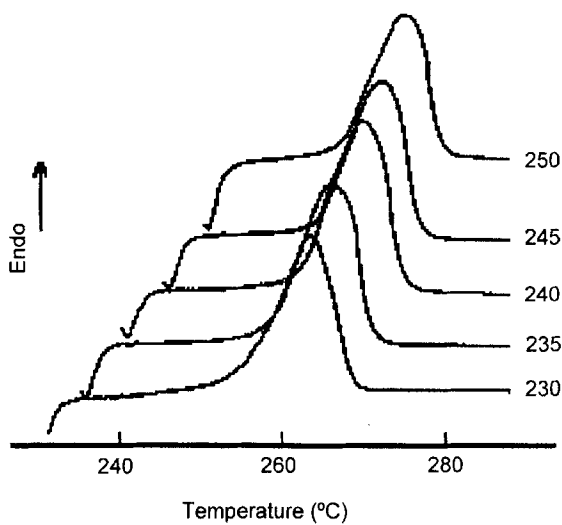


FIGURE 4 Melting endotherms of α -modification (HMPEN).

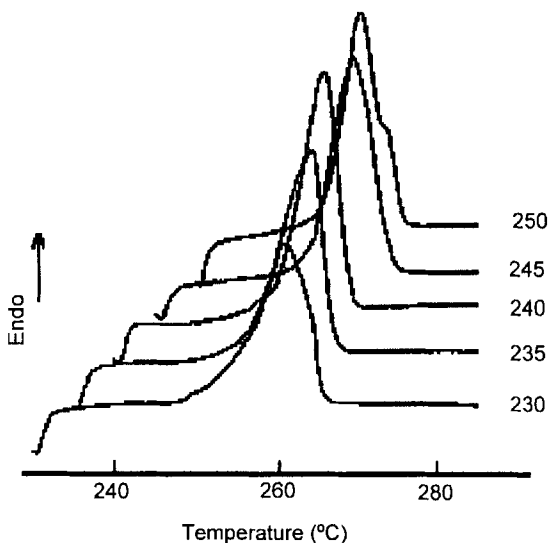


FIGURE 5 Melting endotherms of β -modification (HMPEN).

TABLE I Melting temperature and heat of fusion of the α and β modifications of high molecular weight PEN

Crystallization temperature (°C)	T_m (°C)		ΔH (J/g)	
	β -form	α -form	β -form	α -Form
230	263	261	45	49
235	266	265	45	52
240	269	266	48	53
245	272	270	43	53
250	275	271	40	49

heating will be minimized and the endotherms truly represent the material crystallized at the crystallization temperature. The melting temperatures are plotted as a function of crystallization temperature for α and β -modifications in Figure 6. The equilibrium melting temperatures of the α and β -modifications can be determined by intersecting these straight lines with that of $T_c = T_m = T_m^0$ line [11]. The values obtained are 293 and 312°C respectively for α and β -modifications. Zachmann *et al.* [6] report a melting point of 300°C but the nature of the crystalline modification is unknown. The equilibrium melting temperature reported in this work for α -modifications is

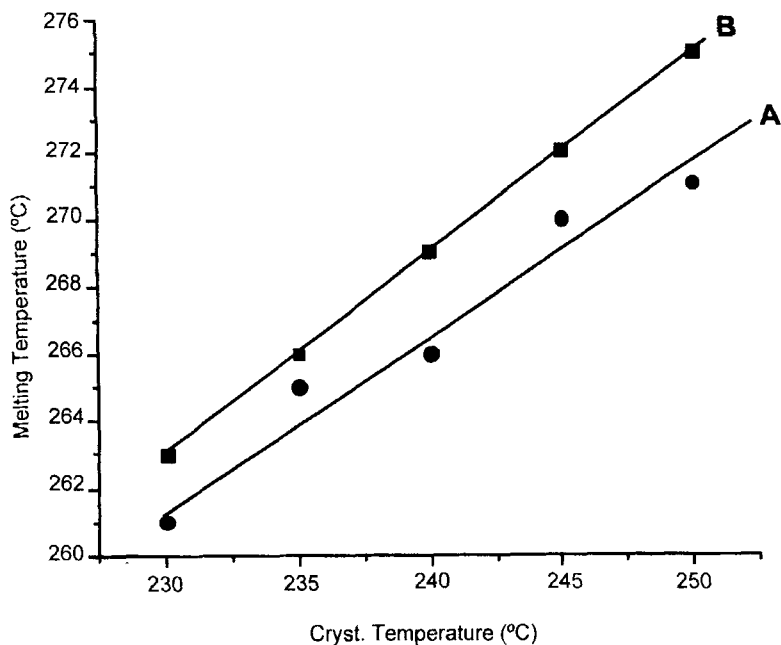


FIGURE 6 The plot between crystallization temperature and melting temperature. (A) α -modification. (B) β -modification.

almost 17°C less than the value reported for PET by Fakirov [12] *et al.* Heuvel and Klop [8] reported melting temperatures over 300°C for β -modifications during draw spinning. This was attributed to crystallites with fewer chain folded molecules. These crystallites are formed under orientation induced crystallization at high temperatures and high stress levels during spinning. In the β -modification the naphthalene ring is rotated by 180°C and the chains are not fully extended. Hence there will be relatively less change in entropy during melting compared to α -modification. This will lead to higher melting temperature and equilibrium melting temperature for β -modification.

CONCLUSIONS

PEN was melted at temperatures (T_m) ranging from 340 to 290°C followed by rapid cooling to crystallization temperatures (T_c) ranging

from 220 to 250°C. The crystal modification formed in each case was determined from WAXD patterns. It is found that whenever T_c was 230°C and above, β -modification was formed, while crystallization at 220°C and below yielded α modification. The melt temperature from which the material was brought to the crystallization temperature (T_c) does not seem to influence the type of modification. The low molecular weight oligomer PEN crystallizes in both modifications under similar conditions. However, when crystallization is performed by heating from glassy state, then both the high molecular weight PEN and the oligomer PEN crystallize in the α -modification only. The equilibrium melting temperature of α -modification is 293°C while for the β -modification it is 312°C.

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