Multiple melting behaviour of poly(ethylene-co-butylene naphthalene-2,6-dicarboxylate) s

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Abstract

The multiple melting behaviour of poly(ethylene naphthalene-2,6-dicarboxylate) (PEN) and poly(butylene naphthalene-2,6-dicarboxylate) (PBN) as well as of eight random poly(ethylene-co-butylene naphthalene-2,6-dicarboxylate)s (PEBN) copolymers was studied using differential scanning calorimetry. The isothermally crystallized samples showed up to three melting peaks, depending on the crystallization temperature. Especially, the PEBN 70/30 copolymer showed a four-fold melting peak. Recrystallization exotherm is observed in some cases just before the ultimate melting peak of polymers. This multiple melting, as well as the effect of crystallization temperature on this behaviour, is discussed in detail in this work.

Keywords: Poly(ethylene naphthalene-2,6-dicarboxylate) or poly(ethylene 2,6-naphthalate); Poly(butylene 2,6-naphthalate); Multiple melting behaviour

1. Introduction

A detailed thermal study of poly(ethylene 2,6-naphthalate) (PEN) was carried out by Cheng and Wunderlich [1] using differential scanning calorimetry (DSC). The crystallization and melting behaviour of this polymer was also investigated by Zachmann et al. [2] and Buchner et al. [3] using DSC and synchrotron radiation. Kimura et al. [4] studied the crystallization process of PEN using FTIR spectroscopy, whilst Wang et al. [5] studied the melting behaviour of PEN using infrared spectroscopy and found that the phenomenon of multiple endothermic melting peaks is due to the melting of imperfect crystalline conformation formed during crystallization.

On the other hand, there are only a few respective studies published on poly(butylene 2,6-naphthalate) (PBN), such as those by Lee et al. [6] and Yamanobe et al. [7].

Some interesting studies were also carried out dealing with naphthalene based copolymers [8–14].

In our previous paper [8], the synthesis and some thermal parameters of eight PEBN copolyesters were presented. In that work, some DSC thermograms showed more than one melting peak, while the glass transition of PBN and some adjacent copolymers could not be determined.

Multiple melting endotherms have been observed during calorimetric analysis for most semicrystalline polymers. There have been many extensive studies on multiple melting behaviour of PET [15,16], PBT [17], PEEK [18,19], poly(1,4-phenylene sulfide) (PPS) [20], and other semicrystalline polymers. Attempts to explain the origin of the multiple melting peaks in certain semicrystalline polymers have been made by various researchers. These multiple melting peaks could be ascribed to a variety of reasons [21]: (a) the presence of more than one crystal modification, (b) molecular weight segregation accompanying crystallization, (c) variation in morphology, (d) orientation effects, and (e) melting, recrystallization and annealing processes occurring during the DSC run.

In this work the interesting thermal behaviour of poly(ethylene-co-butylene naphthalene-2,6-dicarboxylate) copolymers, as well as of their homopolymers PEN and PBN, is studied by a plethora of differential scanning calorimetry thermograms.

2. Experimental

DSC runs were performed on a Perkin-Elmer DSC-2 calorimeter, and from their traces the glass transition temperatures (\(T_g\)) and melting points (\(T_m\)) of copolymers and homopolymers were determined.

For the determination of \(T_g\) values, samples were melt-quenched into liquid nitrogen and then heated at a rate of 20°C min\(^{-1}\).
Table 1

<table>
<thead>
<tr>
<th>Polymer</th>
<th>BD unit</th>
<th>T_g (°C)</th>
<th>T_w (°C)</th>
<th>T_m (°C)</th>
<th>T_m (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PEN</td>
<td>0.0</td>
<td>122</td>
<td>218</td>
<td>268</td>
<td>337</td>
</tr>
<tr>
<td>EB1</td>
<td>5.0</td>
<td>118</td>
<td>—</td>
<td>253</td>
<td>315</td>
</tr>
<tr>
<td>EB2</td>
<td>10.6</td>
<td>113</td>
<td>—</td>
<td>243</td>
<td>296</td>
</tr>
<tr>
<td>EB3</td>
<td>21.4</td>
<td>107</td>
<td>—</td>
<td>222</td>
<td>267</td>
</tr>
<tr>
<td>EB4</td>
<td>31.3</td>
<td>100</td>
<td>—</td>
<td>200</td>
<td>250</td>
</tr>
<tr>
<td>EB5</td>
<td>50.2</td>
<td>92</td>
<td>126</td>
<td>195</td>
<td>212</td>
</tr>
<tr>
<td>EB6</td>
<td>65.0</td>
<td>80</td>
<td>94</td>
<td>204</td>
<td>247</td>
</tr>
<tr>
<td>EB7</td>
<td>83.0</td>
<td>77</td>
<td>—</td>
<td>236</td>
<td>279</td>
</tr>
<tr>
<td>EB8</td>
<td>100.0</td>
<td>72</td>
<td>—</td>
<td>240</td>
<td>292</td>
</tr>
<tr>
<td>PBN</td>
<td>100.0</td>
<td>71</td>
<td>—</td>
<td>242</td>
<td>294</td>
</tr>
</tbody>
</table>

DSC runs on cooling at a rate of 10°C min^{-1} and subsequent runs on heating at a rate of 20°C min^{-1} were recorded in order to determine the T_m values of non-isothermally crystallized samples.

The melting behaviour of the isothermally crystallized samples was studied using the following procedure. The samples were heated to a temperature of about 30°C above their melting temperature, in order to melt all crystal nuclei, and then remained at that temperature for 5 min, before quenching to the desired crystallization temperature at a rate of 320°C min^{-1}. The crystallization exotherms were recorded as a function of time until no change was observed. Subsequently, the samples were cooled to room temperature at the same cooling rate of 320°C min^{-1} and then heated at a rate of 20°C min^{-1}.

The weight of samples was in all cases 12 ± 0.001 mg. If some other procedure was used in some cases, this will be described in the appropriate section.

3. Results and discussion

PEN is a slowly crystallizable polymer, in contrast to PBN which crystallizes rapidly. Yamanobe et al. [7] reported that the structure of PEN is independent of the process by which the specimen was prepared, although the structure of most crystalline polymers is governed by crystallization conditions. Because of the fact that the rate of crystallization of PEN increases with decreasing crystallization temperature, quenching from the melt cannot produce amorphous PBN but a crystalline one. Thus, the high chain mobility of PEN may give fast nucleation and growth of PBN crystals from the melt. This difference in chemical structure can give rise to a fast crystallization of PBN from the melt, while PEN chains are not so mobile, so they may be frozen into an amorphous state even at a cooling rate of 20°C min^{-1}.

Copolymers with high ethylene unit content were found to be slowly crystallizable, like PEN. They can be obtained almost completely amorphous, if they are cooled from the melt at a relatively fast rate. However, for some compositions a cooling rate of 20°C min^{-1} or even 10°C min^{-1} is fast enough for them to be frozen into an amorphous state.

On the contrary, copolymers with high butylene unit content cannot easily be obtained amorphous, even when they are melt-quenched. This is due to their fast crystallization rate.

3.1. Glass transition temperatures

From the DSC traces on heating of melt-quenched samples, at a heating rate of 20°C min^{-1} the T_g values were determined. These decrease monotonically from that of the homopolymer PEN, to that of the homopolymer PBN.

The T_g of PEN was found in this work to be 122°C (Table 1). This is in good agreement with those values reported by Cheng and Wunderlich [1].

In the literature, various different T_g values of pure PBN have been reported, such as 41°C [7], 48°C [22], 52°C [6], 66°C [10] and 82°C [23]. The dispersity of the reported T_g is not so strange, since PBN cannot in fact be obtained quite amorphous and the only evidence for T_g in DSC traces is a small displacement of the baseline, as has also been reported by other authors [7]. So, a series of DSC runs of quenched PBN samples during heating was recorded. Tests were performed using various sensitivities (a range of 5, 2, 1 and 0.5 mcal s^{-1}) and also heating rates (10, 20, and 40°C min^{-1}). Finally, a T_g of 71°C was revealed at a heating rate of 20°C min^{-1} and range 1 mcal s^{-1}. Of course this, as well as the values reported by other authors, is not the T_g of pure amorphous PBN samples.

However, a quick calculation using the empirical Fox relationship on the seven samples in Table 1 suggests a figure of 66°C is more appropriate to be put alongside the 122°C for PEN.

3.2. Melting behaviour

The introduction into a polymer chain of units that differ chemically or structurally from the predominant chain repeating elements imposes restrictions on crystallization and influences the melting process [24,25].

In a random copolymer chain, two different types of chemical copolymer units are joined together at random, so that it is unlikely that such chains can be packed into a three-dimensional long-range order lattice to form an ideal crystalline structure. However, numerous experiments have verified that crystallites can form in random copolymers under some circumstances.

The PEBN copolysteres have been proved to be crystallizable, although some of them exhibit very slow crystallization rates or low degree of crystallinity, due to their composition.

3.3. Melting behaviour after non-isothermal crystallization

In DSC traces of PBN and its adjacent copolymers, that is those having high butylene unit content (samples PBN,
EB8–EB6, a sharp crystallization exotherm appears on cooling, in contrast to the absence of crystallization exotherm for copolymers having high ethylene unit content. After non-isothermal crystallization a single sharp melting peak in the DSC trace on heating is usually observed, as shown in Fig. 1, reflecting rather a narrow crystal size distribution. This melting process is accompanied by a recrystallization process resulting in more perfect crystals; this is revealed by a small exotherm that appears just before the main melting endotherm.

Copolymers EB3 and EB4 are almost amorphous, since no crystallization on cooling and no melting peaks are observed in DSC runs on heating.

The large area under the melting peak as well as the small displacement in baseline in the $T_g$ region prove that under the experimental conditions PBN and its adjacent copolymers possess a significant degree of crystallinity.

It is worthwhile noting that the cold crystallization appeared only in samples PEN and EB5. Samples EB6–PBN did not show cold crystallization, because of their enhanced crystallizability. However, for copolymer EB6 a cold crystallization exotherm was observed, when the sample was melt-quenched in liquid nitrogen [8].

All polyester samples after quenching in liquid nitrogen, or cooling at a slow rate ($10^8$C min$^{-1}$) showed up to one melting peak during heating scan. This is because even amorphous samples can crystallize during heating scan (cold crystallization). It is interesting to note that the crystals formed during slow cooling or cold crystallization are defective and undergo crystal perfection during the heating scan, resulting in a single melting peak.

3.4. Melting behaviour after isothermal crystallization

DSC traces of isothermally crystallized samples are shown in Fig. 2. As shown, three melting peaks appear in these thermograms on heating, while four-fold melting peaks are observed for the EB4 copolymer. This behaviour occurs when the crystallization temperature ($T_c$) lies within a definite range at which the crystallization rate is fast.

Crystallization at lower $T_c$ values than the aforementioned range is slower and results in two melting peaks, while when this process takes place at higher $T_c$s it is also slow and results in two melting peaks that progressively get closer and finally coincide. In some cases a shoulder appears before or after the main melting peak, depending on the crystallization temperature.

Multiple melting peaks in DSC traces of isothermally crystallized PEN were first reported by Cheng and Wunderlich [1]. Wang et al. [5] studied the melting process of PEN by means of FTIR and showed that multiple endothermic peaks are due to the melting of imperfect crystalline conformation formed during crystallization.

The lowest small melting peak is similar to the annealing peak [1], and hereafter will be referred to as the lowest peak. Its position is affected by the crystallization temperature and it is discussed later. It appears at 10–15°C above the crystallization temperature. This peak must be attributed to the melting of defective crystals formed during secondary crystallization, as has also been reported for other polymers by Yagpharov [16].

The middle melting peak is associated with the melting of primary crystals formed during the isothermal crystallization [14], and hereafter will be referred to as the middle peak. Its position depends also on the crystallization temperature. Medellin-Rodriguez and Phillips [26] studied the analogous behaviour of PET and proposed that the middle peak is associated with secondary crystallization.

The highest melting peak is due to the melting of crystals of higher stability formed due to recrystallization or reorganization of crystals initially formed during isothermal crystallization, and hereafter will be referred to as the highest peak. Medellin-Rodriguez and Phillips attributed the
ultimate peak of PET to the melting of original primary crystals that have high melting temperature, but they also accept that in the case of PEN the recrystallization process is significant.

3.5. Effect of crystallization temperature ($T_c$)

The effect of crystallization temperature on the relative areas under the lowest, middle and highest peaks for a given heating rate is shown in Fig. 3, where the different curves represent the melting behaviour of the samples of the EB1 copolymer crystallized at various temperatures. In these curves it is obvious that with increasing $T_c$, within a temperature range (175–225°C), the area under the middle and to some extent the lowest peak increase, while the area under the highest temperature melting peak decreases. It is evident that at higher $T_s$ the crystallization proceeds at a slower rate, accompanied by a simultaneous annealing, resulting in more perfect crystals. So, with increasing $T_c$, larger and larger fractions of the sample crystallize in the form of more perfect crystals, and thus the fraction which would undergo recrystallization on heating decreases. This results in a decrease of the area under the highest peak, and in an increase of the area under the other two melting peaks.

The height ratio of the two ultimate melting peaks progressively changes with $T_c$. The lower peak shifts to higher temperatures and its height increases as $T_c$ increases. In contrast, the higher peak, that always appears at the same temperature, reduces in height, being finally overlapped by the lower temperature melting peak.

For the investigation of the nature of the lowest and the middle peaks, a cycle of recordings was followed, as shown in Fig. 4 for the homopolymer PEN. First, the sample was crystallized at an appropriate temperature (220°C for 15 min) in order to result in three well-resolved melting peaks, and then the whole melting process was recorded on heating (trace A). The sample was crystallized again under the same previously reported conditions, and heated as previously, but this time heating was interrupted just after the lowest peak (trace B). The sample was then cooled at a rate of 320°C min$^{-1}$ to 100°C (below $T_g$) and the melting behaviour of the sample was recorded (trace C). The lowest peak in this case was not observed. The sample was crystallized again and the heating was interrupted just after the middle peak (trace D). The same procedure as before was followed, and then only the highest peak was observed. The conclusion derived from the above work is that the lowest and the middle peaks are due to the melting of crystals that cannot be formed during scan heating, but only during the isothermal crystallization stage.

It is known for polymers that at temperatures lower than the equilibrium melting temperature ($T_m^e$), the crystalline structure is thermodynamically favoured more than the liquid, since the crystal surface energy is less. So, if kinetics permit the crystallization or recrystallization to proceed to a significant extent, during a definite time, the polymer gets significant crystallinity. A major factor in recrystallization is the supercooling, that is the difference between $T_m^e$ and the recrystallization temperature. If this difference is large, the recrystallization process is faster [19].

Crystallization at low $T_s$ results in a broad melting point distribution, since the crystals formed are less perfect. But their melting is accompanied by recrystallization. It was referred to previously that low $T_c$ results in a low peak temperature for the lowest and the middle peak. In this case the supercooling is large and recrystallization may result in a significant amount of perfect crystals that are associated with the highest peak. So, a low $T_c$ results in increase of the highest peak area.

At slow heating rates more time is available for the crystals to anneal, or for the material formed after melting

Fig. 2. DSC runs of isothermally crystallized samples from the melt. Heating rate 20°C min$^{-1}$. 
of poor crystals to recrystallize. This also results in an increase of the highest peak area.

For PEN and its adjacent copolymers the triple melting peak behaviour is more pronounced, as seen in Fig. 5. For PBN and its adjacent copolymers a triple melting peak behaviour is also observed, but for the latter polyesters a characteristic recrystallization exotherm just before the highest peak is observed in DSC traces, as seen in Fig. 6. This behaviour is also observed for the homopolymer PEN, if the \( T_c \) lies between 200 and 210°C. At such \( T_c \)s crystallization rates of PEN are maximum.

It has been noted that in PEBN copolymers with an ethylene naphthalate unit content less than 12.5 mol% only PBN crystals are observed [6]. For copolymers with little butylene naphthalate unit content it might be supposed that only PEN crystals are formed. Mixed types of crystals should be supposed to form in any other case [13].

The EB4 copolymer, having a composition PEBN 70/30 mol%, exhibits a broad range of melting points and an interesting four-fold melting peak behaviour. This copolymer is very slowly crystallizable and its crystals are poor. The middle peaks are not always well resolved. The highest peak is not easily observable after non-isothermal crystallization, and this is a significant difference from the other polymers studied in this work. At slow heating rates the
highest peak area increases, so some kind of crystal perfection or annealing may occur (Fig. 7).

The EB5 copolymer, that has a PEBN 50/50 mol% composition, is in contrast to the EB4, which is rather easily crystallizable, as revealed by the cold crystallization of the amorphous sample just after the glass transition. It exhibits a weaker trend for triple melting peak behaviour. Besides, it has low melting point (196°C), the lowest observed for copolymer in this work, despite its crystallizability. The eutectic behaviour for copolymers is well known. The limitation for lamellar thickness of copolymers, resulting in a melting point depression, has been referred to [27] (Fig. 8).

3.6. Equilibrium melting temperatures

As mentioned in a previous section, isothermal crystallization at elevated temperatures, that is close to the melting point of the polymers, results in a single melting peak. Melting temperatures of samples isothermally crystallized at such elevated temperatures for 24 h, that is of samples annealed at elevated temperatures, were used for the estimation of the equilibrium melting points of polymers.

The equilibrium melting temperatures of polymers were estimated by extrapolating the experimental relation between the observed melting temperature and the crystallization temperature to the line representing \( T_m = T_c \) following the Hoffmann and Weeks approach [28]. \( T_m^{\infty} \) for PEN was found to be about 337°C, as was first reported by Cheng and Wunderlich [1], while the \( T_m^{\infty} \) for PBN was found
to be in agreement with that reported by Lee et al. [6], that is about 294°C. Equilibrium melting temperatures for copolymers lie between these two extremes (Table 1), following a eutectic behaviour.

Fig. 6. DSC runs of PBN isothermally crystallized samples at different temperatures. Heating rate 20°C min⁻¹.

Fig. 7. DSC runs of the EB4 copolymer isothermally crystallized at different temperatures. Heating rate 20°C min⁻¹.

Fig. 8. DSC runs of the EB5 copolymer isothermally crystallized at different temperatures. Heating rate 20°C min⁻¹.

References