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Polymer 42 (2001) 8197–8205

polymer

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Observations during crystallisation of poly(ethylene-*co*-butylene naphthalene-2,6-dicarboxylate)s

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Received 9 March 2001; accepted 30 April 2001

Abstract

The crystallisation behaviour of poly(ethylene-*co*-butylene naphthalene-2,6-dicarboxylate)s (PEBN copolyesters) was studied by means of differential scanning calorimetry (DSC). A eutectic behaviour was found, and the composition related with the lower melting point was about 50/50 mol%. On the other hand, the crystallisation kinetics was faster for copolymers with high butylene-naphthalate content, while the slower crystallisation rates were observed for the PEBN 70/30. Crystallisation and melting of PEBN 50/50 and PEBN 70/30 copolymers are of special interest. Despite its composition, the PEBN 50/50 copolyester exhibited significant crystallinity and fast crystallisation rates. Cooling from the melt resulted in crystallisation at $T_c = 106°C$, quite close to the glass transition temperature ($T_g = 92°C$). On isothermal crystallisation at temperatures near T_c region, double exothermic peaks in the heat flow vs. time plot were observed. For amorphous samples, in the DSC traces on heating, a sharp cold-crystallisation peak ($T_{cc} = 125°C$), followed by a second exothermal peak, was observed. The relatively low melting point ($T_m = 196°C$), comparing with those of the other PEBN copolymers was attributed to limited crystal lamellar thickness. For the PEBN 70/30, crystallisation was very slow. Even after prolonged crystallisation times, a quadruplicate melting peak was observed which was attributed to melting of metastable crystalline phases initially formed.

Keywords: Poly(ethylene naphthalate); Poly(butylene naphthalate); Isothermal crystallisation

1. Introduction

The crystallisation of polymers involves complicated molecular processes, and the understanding of the molecular mechanisms has long been hindered. There still remain many basic questions unanswered. The polymer crystallisation has hitherto been mostly investigated for simple polymers, such as polyethylene, which have large structural flexibility [1]. Strobl and co-workers [2], finishing their excellent paper dealing with crystallisation of propylene copolymers, formulated the main questions as follows:

1. What is the macroscopic structure of the high surface free energy (native) crystal form?
2. What is the nature of the relaxation processes that are responsible for the stabilisation showing up in the difference between the temperatures of crystallisation and melting?
3. Since crystal thickness and growth rates are independent properties, which is the rate-determining step and which is the pathway followed in the formation of the native crystals?

The introduction into a polymer chain of units that differ chemically or structurally from the predominant chain-repeating elements imposes restrictions on crystallisation and influences the melting process. In general, for copolymers, the degree of crystallinity decreases as the fraction of the minority comonomer increases, because of the exclusion of the comonomer units from the crystals, leading often to fully amorphous materials, even at low concentrations of the comonomer [3,4]. However, there are copolyesters containing naphthalene or benzene rings in the main chain, where some crystallinity can be observed over the entire range of constitution, as well as copolyesters in which both the comonomer units participate in the formation of crystals [5–9].

Metastable behaviour is observed in phase transformations that are impeded by kinetic limitations along the pathway to thermodynamic equilibrium. This is illustrated in structural and morphological investigations of crystallisation [10–12].

PEN and PBN, these two engineering plastics have superior thermal, mechanical, electrical and other properties, comparing with PET and PBT, respectively, leading to an extension of the use of polyesters. Since properties of polymers are dependent on their morphology,

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0032-3861/01/$ - see front matter
PII: S0032-3861(01)00318-4

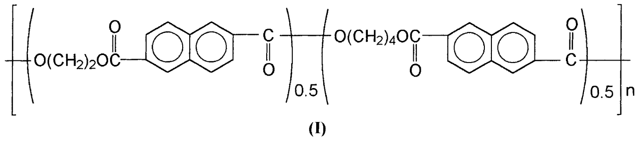
Table 1
Intrinsic viscosities and thermal parameters of PEBN copolymers

Polymer	Intrinsic viscosity [η] (dl/g)	BN (mol%)	T_g (°C)	T_m (°C)	T_m^∞ (°C)
PEN	0.46	0.0	122	268	337
EB1	0.60	5.0	118	253	315
EB2	0.53	10.6	113	243	296
EB3	0.56	21.4	107	222	267
EB4	0.60	31.3	100	220	237
EB5	0.58	50.2	92	195	212
EB6	0.50	65.0	80	208	247
EB7	0.70	83.0	77	230	270
PBN	0.61	100.0	71	242	294

phase transformations are of special interest. Crystallisation of PEN and PBN has been studied in some extent [13–18].

Ungar and Keller [19–22] first observed double exothermal peaks, in differential scanning calorimetry (DSC) traces on isothermal crystallisation for ultra-long paraffins. They proposed that the first increase and subsequent decrease correspond to extended-chain crystallisation, whilst the renewed increase beyond the minimum corresponds to chain-folded crystallisation. The anomalously retarded crystallisation with increasing crystallisation time was supposed to arise through competition between extended and folded chain deposition. Non-integral and integral folding crystal growth was proposed by Cheng [23] for the interpretation of double exothermal peaks observed on isothermal crystallisation of low-molecular mass poly(ethylene oxide). Anomalous two-stage spherulite growth in poly(aryl ether ketone)s during isothermal crystallisation was also observed near the maximum growth rate region and according to Schultz [24,25], a possible explanation is the interface breakdown caused by large perturbations of local composition and/or stress fields. Interesting works dealing with PEEK, poly(aryl ether ketone ketone) copolymers [26–28], as also with special poly(ether ether ketone)s [29] have been published. A double cold-crystallisation peak was also reported for poorly crystallised PET [30–32], while secondary crystallisation is always a popular subject for investigation.

PEBN copolymers were found to crystallise and exhibit eutectic behaviour [33,34]. In this work, crystallisation rates of the PEBN copolymers were measured. Especially some peculiarities of cold, as well as of isothermal crystallisation of PEBN 50/50 (**I**), which corresponds to the eutectic point of PEBN copolymer series, and the unusual melting of PEBN 70/30 crystals were studied using DSC.



(I)

2. Experimental

Synthesis of the PEBN copolymer series was presented in a previous paper [33]. The intrinsic viscosity of the homopolymers and copolymers were measured in a mixture of solvents phenol/tetrachloroethane, 60/40% (w/w). Viscosities, glass transition and melting temperatures are listed in Table 1.

Crystallisation studies of the copolymers were carried out using a Perkin–Elmer Pyris 1 DSC. For preliminary studies, a Perkin–Elmer DSC-2 calorimeter was also used. Isothermal crystallisations were performed at a series of temperatures below the melting point of the homopolymers or copolymers in the DSC pan. Crystallisation temperatures for each material were selected in a broad temperature range from the T_g region up to the vicinity of T_m. The experimental cycle that was followed for each set of tests was the same. Each sample was first heated at a temperature of about 30°C above its melting point for a holding time of 5 min. After that, every crystal nuclei was supposed to be destroyed. The second step of the procedure involved a rapid cooling to the desired crystallisation temperature, at a cooling rate 150°C/min. When the sample got the desired temperature, it was let to crystallise. The holding times were not selected. Instead, the crystallisation exotherms were recorded as a function of time, until no change was observed. Then, it was supposed that the isothermal crystallisation process was completed and the sample was rapidly cooled to the ambient temperature, also at a cooling rate 150°C/min. At last, the heating scan of the crystallised sample was recorded.

Non-isothermal crystallisation on cooling at slow cooling rates was also performed. In order to obtain amorphous samples, melt quenching in liquid nitrogen was used. In most heating scans, the heating rate was 20°C/min.

Samples of less than 5 mg were used for minimising thermal lag. Where some other procedure was followed, this will be described in detail in the text.

3. Results and discussion

PEN is a slowly crystallising polymer because of the presence of a rigid segment, the rigid naphthalene ring and a short flexible ethylene group in the repeating unit. In contrast, PBN is rapidly crystallising, because of the presence of the long flexible butylene unit [16].

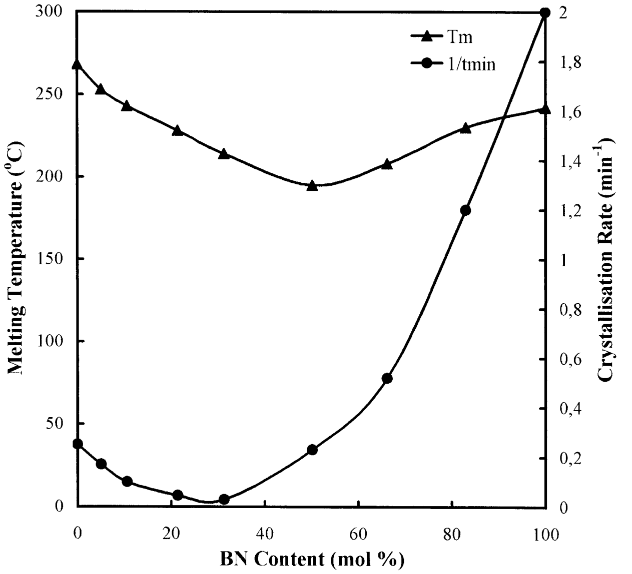


Fig. 1. Melting temperatures and maximum crystallisation rates (as the inverse crystallisation half-time) of PEBN copolymers.

At a fixed crystallisation temperature, variation in the comonomer concentration results in a preferential exclusion of the minority component from the crystal because of the energy penalty. At exactly equal amounts of the comonomers, the melting temperature is expected to be minimum and also the crystal growth rate is anticipated to have a minimum at this point [35]. For PEBN copolyesters actually a deviation from the behaviour described above was found. The composition of the copolymers was determined using ^{1}H NMR and the results are shown in Table 1. EN stands for ethylene-naphthalate and BN for butylene-naphthalate units. Though a eutectic behaviour was found, the eutectic point corresponding to the PEBN 50/50 copolymer, the specific copolymer had not the minimum crystallisation rates observed (Fig. 1).

It must be noted that this copolymer had faster crystallisation rates even than the PEN homopolymer. Copolymers with large EN content were those crystallising slower. In Fig. 1, the melting point and the crystallisation rates (as the inversed crystallisation half-times) are plotted against BN content. From these plots, it is obvious that the eutectic point is for 50 mol% BN content, while the minimum in crystallisation rates is for 30 mol% BN content.

The temperature window for crystallisation is the range between the T_g and T_m. For the PEBN copolymers as one can see in Fig. 2, a significant drop in the T_m was observed, while the drop in the respective T_g was small, and thus the temperature window for crystallisation gets narrower as the comonomer content increases. Usually, the maximum crystallisation rates, or the minimum crystallisation half-times, for polymers are observed at about the midway from T_g to T_m. This is because at low temperatures nucleation is favoured, while at higher temperatures, the diffusion rates are increased leading to faster crystal growth rates.

As it is shown in Fig. 3, crystallisation half-times $t_{1/2}$ increase dramatically with the BN content in copolymers up to 30 mol%. In Fig. 4, one can see that copolymers with more than 50 mol% BN content exhibit a different behaviour. They all have fast crystallisation rates, just because of the large BN content, which is responsible for the significant flexibility of the chains even at low temperatures. Thus, PBN, PEBN 17/83 and PEBN 35/65 showed no minimum in their crystallisation rates. That is, crystallisation rates increase with supercooling. It is worthwhile

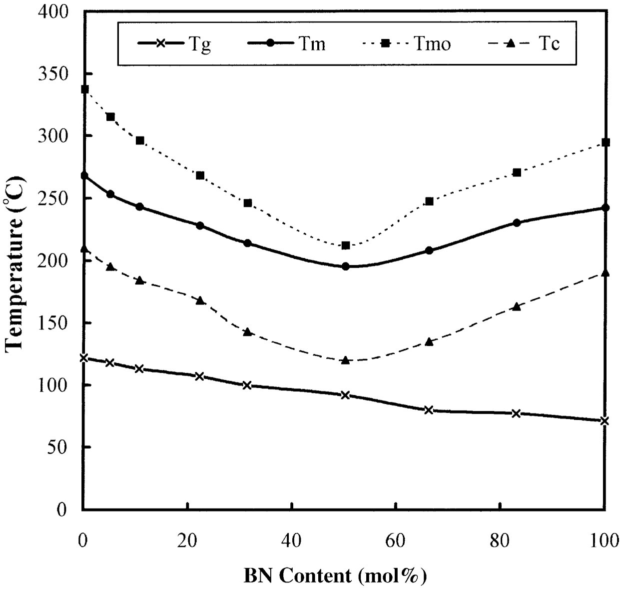


Fig. 2. Glass transition temperatures, crystallisation temperatures for maximum rate, melting temperatures and equilibrium melting temperatures for PEBN copolymers.

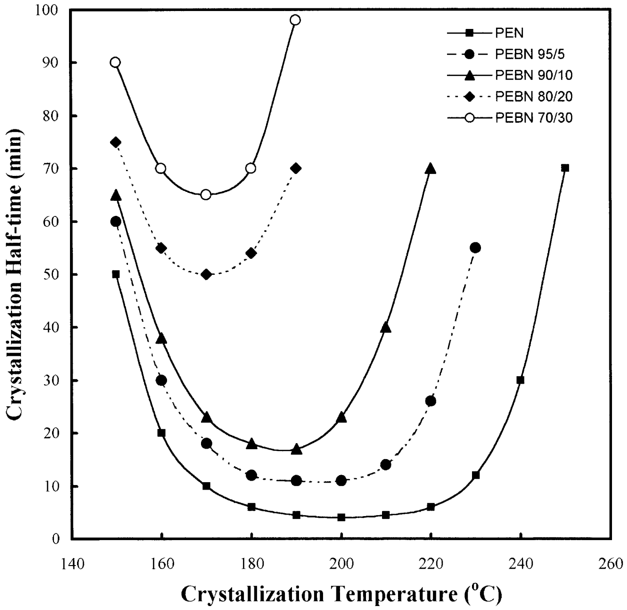


Fig. 3. Crystallisation half-time against crystallisation temperature for PEBN copolymers with low BN content.

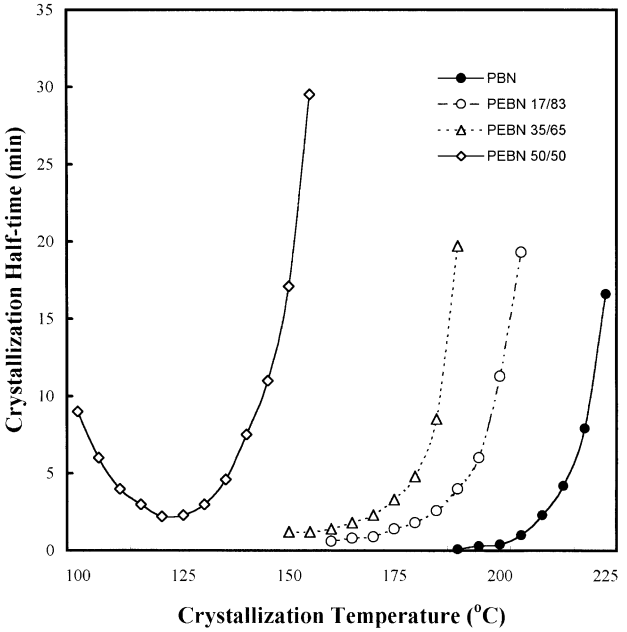


Fig. 4. Crystallisation half-time against crystallisation temperature for PEBN copolymers with large BN content.

noting that isothermal crystallisation of these copolymers could not be performed at very low temperatures, since they start to crystallise during cooling. For PEBN 50/50, however, a maximum in the crystallisation rates is observed at about 120–130°C.

For PBN and the PEBN 17/83, it was found that they could not be got amorphous even by quenching into liquid nitrogen. For the rest of the copolymers as well as for PEN, a cold-crystallisation was observed on heating the quenched samples. Especially, quenched PEBN 35/65 exhibited a sharp cold-crystallisation peak in its DSC trace on heating, just as the temperature overpassed the T_g. It seems that PEBN copolymers with equal or more than 50 mol% BN content exhibit features that are combination of those of PEN and PBN, that is, they retain some of the characteristics of the homopolymers, at least from the aspect of crystallisation rates, as well as from the aspect of the T_g value, though the melting points are lower than those of the homopolymers. Instead, the copolymers with greater EN than BN content have their own specific behaviours, from the aspect of crystallisability and crystallisation rates, though their T_gs fall between those of the homopolymers. It is known that as comonomer units are introduced into the homopolymer chains the crystallisability is reduced since the regularity is reduced. So what was found for PEBN copolymers was the rule for copolymers. But, it is very important that two classes of PEBN copolymers are available, each one having its' own advantages. It is known that PBN is rapidly crystallising and the effort was made to control its' crystallisation rates. From the above mentioned, it was made clear that PEBN 35/65 has also fast crystallisation, but it offers the advantage that even amorphous specimens can be made from this material. On the other hand for PEBN 95/5 or PEBN 90/10, the reduction in T_ms, which are lower than that of PET, combined with a reduction in the melt viscosity due to the introduction of the flexible butylene units into the chains, can offer advantages in processing. The melt viscosity is high for PEN comparing to PET. It must be noted here that the T_gs are slightly reduced, comparing to PEN, while they are at least 30°C higher than that of PET. It is true that crystallisation rates are somehow reduced comparing with PEN. But however, PEN itself crystallises slowly, so that some nucleation agent is incorporated to speed up its crystallisation, when this is needed.

For PEN, nucleation controls the overall crystallisation rates, since it is the slower process. The same is met for EN-rich copolymers. Instead, PBN and BN-rich copolymers have fast nucleation rates. In general, for fast nucleation rates, large supercoolings are demanded. Supercooling is defined as the temperature difference between T_m and T_c, ($\Delta T = T_m - T_c$), or more correct, as the difference between the equilibrium melting point T_m^o and T_c, ($\Delta T = T_m^o - T_c$). Since there is a drop in the melting point of copolymers with comonomer content, the same supercooling is achieved at lower T_cs for copolymers. So, as the comonomer content increases the maximum crystallisation rates is anticipated to be observed at lower T_cs, and this is the reason for the shift of the curves observed in Figs. 3 and 4 to lower temperatures. However, as it can be seen in these figures, the curves are also shifted upwards to larger crystallisation half-times, as the comonomer content increases.

In Fig. 2, it can be observed that T_cs at which the maximum crystallisation rates are achieved have a more significant decrease than the respective apparent T_ms, so that the supercooling ΔT_{max} demanded to achieve the maximum crystallisation rates are generally larger for the copolymers and the larger observed is that for PEBN 50/50. However, one can see that the drop of T_cs goes rather in parallel to the drop of the equilibrium melting points calculated after the Hoffmann–Weeks method [36]. So, if for the calculation of supercooling the equilibrium melting point is used, ΔT_{max} is found to be more or less the same for all copolymers. For PBN and BN-rich copolymers, the T_c represents the temperature at which the material practically crystallises almost immediately.

Finally, in the same Fig. 2, one can see that the difference between equilibrium and the apparent melting point decreases with the comonomer content. This is because the probability for a defect to appear in copolymer crystals increases with comonomer content, and thus even by crystallisation at elevated temperatures a large number of defects is present in crystals, leading to lower equilibrium melting points.

3.1. The behaviour of PEBN 50/50

The PEBN 50/50 can be obtained in the glassy state after melt-quenching. The corresponding DSC traces of quenched amorphous samples at different heating rates are shown in Fig. 5.

In these DSC traces, double cold-crystallisation peaks were observed. For a heating rate 20°C/min (trace C), first a sharp cold-crystallisation peak appeared, the peak temperature being 125°C, followed by a second, broad, exothermal peak. For a heating rate 10°C/min (trace B) also, a second peak was observed after the main peak, but in this case, the second peak was sharp, while for a heating rate 5°C/min (trace A), the two peaks were not well resolved. However, on heating by 40°C/min, only one cold-crystallisation peak was observed, and the melting point was found to be 185°C, while for slower heating rates it was about 196°C. Low melting point was found after isothermal crystallisation at very low T_c (100°C), indicating similarities in the morphologies of the samples.

The double peaks observed are indications of sequential crystallisation processes. The lower-temperature peak is the main one. It was observed quite close to the T_g. As the heating rate was reduced, the position of the main peak shifted to lower temperature. But the second, higher temperature peak was more strongly affected by the heating rate reduction. The second peak's position shifted downwards, so that the two peaks finally coincided.

When PEBN 50/50 was cooled from the melt at a cooling rate 10°C/min (Fig. 6, trace A), a crystallisation peak was observed at the temperature region 120–100°C that is just above the T_g, resulting in low crystallinity. Thus, on subsequent heating, a cold-crystallisation occurred (trace B). It is worth noting that a shoulder, which could be related with the aforementioned double cold-crystallisation peak for amorphous samples, accompanied the cold-crystallisation peak. On cooling at slower rates (5°C/min), crystallisation started at higher temperatures (trace C). In this case, higher crystallinity was achieved and almost no cold-crystallisation appeared on subsequent heating (trace D).

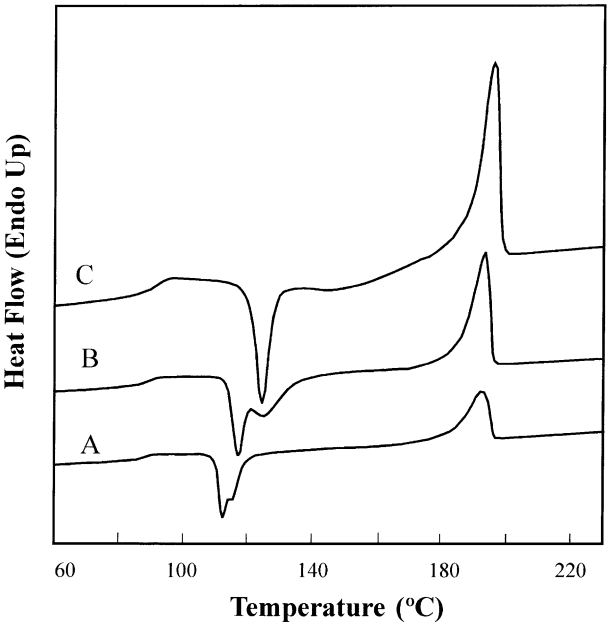


Fig. 5. DSC traces of quenched PEBN 50/50 samples at different rates: (A) 5°C/min; (B) 10°C/min; (C) 20°C/min.

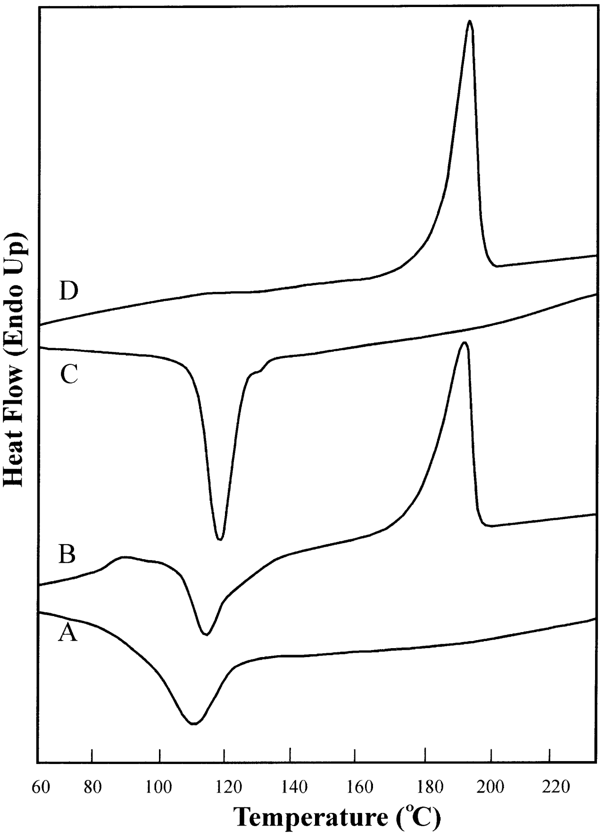


Fig. 6. DSC traces for PEBN 50/50: (A) on cooling at 10°C/min; (B) on heating at 20°C/min after cooling at 10°C/min; (C) on cooling at 5°C/min; (D) on heating at 20°C/min after cooling at 5°C/min.

When the PEBN 50/50 copolymer was subjected to isothermal crystallisation, at T_cs between 112 and 128°C, a strange double exothermal peak appeared in the heat flow vs. time plot (Fig. 7). At these temperatures, the crystallisation rates are the faster obtained, as proved by the shortest crystallisation half-times.

In the following paragraphs, it is attempted to deal with probable reasons that may be responsible for the appearance of double peaks in both cold-crystallisation and isothermal crystallisation.

One may ascribe the first peak as a crystallisation process, which results in some kind of original metastable crystals. According to Keller and Cheng, a metastable phase is favoured by kinetics, though it is not the most stable phase from the aspect of thermodynamics. The stability of a state is associated with phase size. A phase domain limited to small regions such as a fine grain structure in a polycrystalline solid, is by definition metastable. These domains develop towards their state of ultimately stability, the single-phase domain, by coalescence of the smaller phase regions [37]. The second peak in cold-crystallisation or isothermal crystallisation of PEBN 50/50 may be related

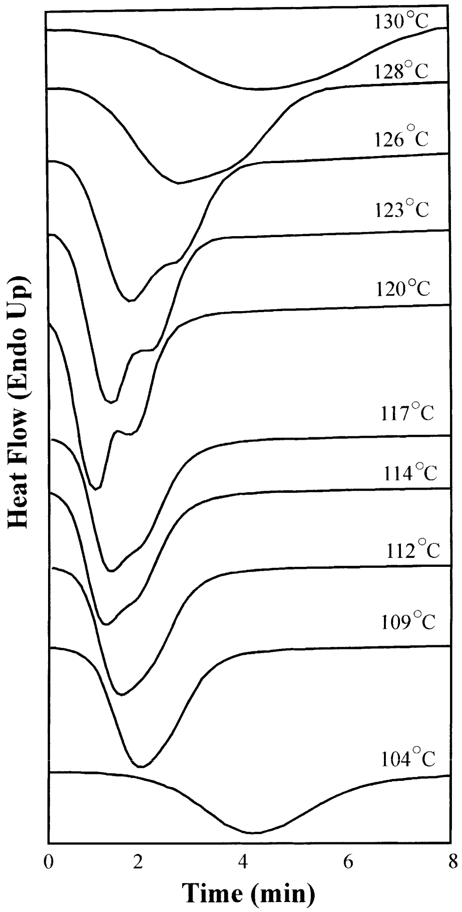


Fig. 7. DSC traces for isothermal crystallisation of PEBN 50/50 at various temperatures.

with a process leading to the formation of a more stable crystalline phase. Since only one large melting peak was observed on heating, it could be assumed that only one crystal population remained after the double crystallisation process. That is, the original metastable crystalline phase transformed to another more stable phase, and this means that the crystallisation of the copolymer goes through the forming of a first metastable crystalline phase.

During the second crystallisation process, it is obvious that crystallinity increases. An additional fraction of the material that was first remained out of the crystals was crystallised in the second stage. This was probably non-crystallising chain segments, excluded from the crystals at the early stage of crystallisation, or material that could not reach the growth surfaces of the crystals.

It is known that PBN has very fast crystallisation rates and this is mainly due to fast nucleation rates [16]. For PEBN copolymers with low EN content also very fast crystallisation was observed and one might assume that for these, as well as for PEBN 50/50, nuclei in which sequences BN are dominant are formed. Hoffman et al. [38–40] have observed distinct kinetic regimes in the crystallisation of polymers from the quiescent melt. At relatively low supercooling, the rate of nucleation is relatively small, compared to the growth rate (regime I). In this case, once a new layer nucleates, layer growth to complete the layer occurs very rapidly and then a new layer must once again be nucleated. At large supercooling (regime II), the absolute rates of nucleation and layer growth become competitive, and new layers nucleate on growing layers. It must be noted that the double peaks were observed at large supercooling. So, one could assume that they are connected with a transition from regime I to regime II. It was found that at even lower T_cs, that is, in even larger supercoolings, for PEBN 50/50 crystals of lower melting point formed during isothermal crystallisation. This probably occurred because the larger nucleation rates resulted in a larger number of crystals and finally to small crystal size and limited degree of perfection.

Crystal growth is strongly depended on the nature of the polymer chains. Symmetry and also flexibility are crucial to achieve adequate diffusion rates. According to Sadler and Gilmer [41] as a chain molecule attaches to a rough growth face it does not necessarily choose a conformation which is suitable for later stages of growth, and this is the 'blind-attachment'. It forms chain folds and loops, which constitute 'pinned' surface sites, onto which further attachment is impossible. Net advance of the growth face can only occur by a constant onto off flux of segments, which gradually sorts out chain conformations suitable for incorporation into the body of the crystal. It is very important that the concepts of 'blind attachment' and 'pinning' lend themselves to an application to copolymer crystallisation. When a copolymer is crystallised, the remaining melt progressively gets poorer in crystallisable species and sequences, so that some kind of fractionation of polymer chains, may also occur during crystallisation and if the crystallisation follows the order of decreasing sequence length, the shorter crystallisable sequences will be incorporated after longer sequences have been consumed.

For the explanation of the double crystallisation peaks for PEBN 50/50, the concept of 'solute' introduced by Schultz [24,25] may be useful. This is outlined here. During the crystallisation, a crystal/non-crystal growth front must move forward, liberating at the interface the heat of fusion and any non-crystallising species. The heat of fusion and the non-crystallising material, 'solute', must be conducted away. A thermodynamic force, which increases with supercooling, drives the crystal/non-crystal front forward. Thermal diffusion can be important only when the driving force is very high. When the supercooling increases, so do the driving force and the natural velocity V_n of the growth front. The diffusion limited velocity V_d, consistent with maintaining thermal and chemical equilibrium at the interface, is that which would be taken by the system, when V_n is so much greater than V_d that growth dynamics are determined only by V_d. At very high driving forces, $V_n > V_d$ and the transport of solute controls the behaviour. A solute-rich boundary layer will build up in front of the growing interface and the growth rate will be reduced. But the interface may break down spontaneously into narrow fingers extending into more distant melt and the growth may suddenly increase.

At high supercoolings, the critical size for a crystal embryo to become a nucleus able to lead to crystal growth is small. To explain the fast crystallisation rates of the PEBN 50/50, the assumption that even short, since flexible, BN sequences can form small crystals seems reasonable. Large number of crystals with very limited lamellar thickness may form. However, the incorporation of shorter sequences may lead to increase of lamellar thickness, for such a copolymer for which in general only short homopolymer sequences may be observed and large differences in sequence length are not expected. Thickening and stabilisation of the crystal will cause the increase of melting temperature, because the melting point is a function of lamellar thickness and heat of fusion. According to Blundell et al. [29] who studied the behaviour of a poly(ether ether ketone) having both biphenyl and meta-phenyl units, an increase in lamellar thickness occurs as meta-phenyl units excluded from the crystallising sequences in a first stage, can be incorporated into the crystallising sequences, in the second stage.

At this point, secondary crystallisation must be discussed. It may start after the completion of primary crystallisation, or during primary crystallisation. Secondary crystallisation is related with processes that take place within the spherulites [42–45]. However, secondary crystallisation is a slow process involving formation of new crystals, lamellar thickening or formation of new lamellar stacks [45]. Secondary crystallisation leads to the appearance of a low-temperature melting peak on subsequent heating, the peak position being 10 up to 30°C higher than the crystallisation temperature. Secondary crystals are related with the fringed micelle model when they form at low crystallisation temperatures, while primary crystals are assumed to be of lamellar type [44]. On the other hand for primary crystals, the concentration of defects that enter the crystal is strongly dependent on supercooling. At high supercoolings, the free energy driving force is so strong that the defects are incorporated into the crystal at almost the same concentration as they occur along the chain. At lower supercoolings, growth is slower, so that there is time to sort out energetically more favourable configurations. According to Strobl and co-workers [2] when the concentration of non-crystallisable segments in the interface between the crystal growth face and the melt is so large that primary crystallisation is no more possible to occur, secondary crystallisation occurs, especially under large supercoolings. It would be very plausible to attribute the second peak especially in the isothermal crystallisations to secondary crystallisation. This is because both the chemical structure and the low T_cs favour formation of secondary crystals. In fact, secondary crystallisation can be a process for stabilisation of crystals, since it leads to a reduced surface energy especially by crystal thickening. Thickening may be caused by the incorporation of new random sequences. On the other hand, the concept of 'solute' that Schultz described can be elaborated to explain why primary crystallisation is limited and secondary crystallisation is favoured.

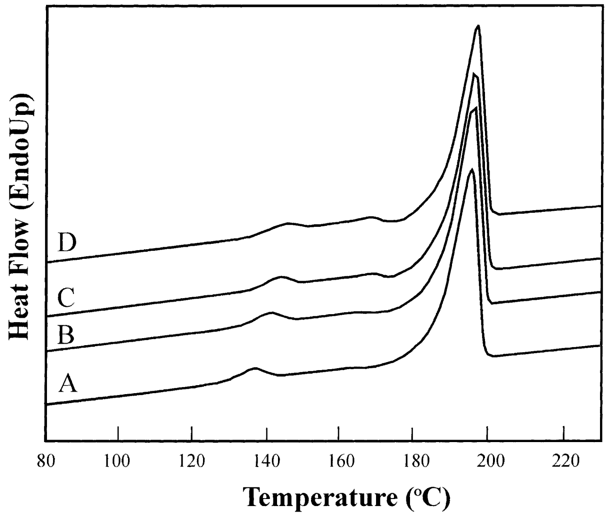


Fig. 8. DSC traces on heating of PEBN 50/50 isothermally crystallised at various temperatures: (A) at 126°C for 15 min; (B) at 130°C for 20 min; (C) at 134°C for 30 min; (D) at 140°C for 30 min.

At this point, it would be very helpful to discuss the melting behaviour of the copolyester. In the DSC traces of the isothermally crystallised samples of PEBN 50/50 up to three melting peaks may appear (Fig. 8). The lower-temperature melting peak is attributed to the melting of secondary crystals. The middle-melting peak is related with the melting of the primary crystals, grown during the isothermal stage. The highest peak is attributed to the final melting of primary crystals that were perfected during the heating scan. The multiple melting peak behaviour of PEN and PEBN copolyesters was described in detail in a previous paper [34]. However, this behaviour is much less pronounced for PEBN 50/50 than for PEN and other PEBN copolymers (Fig. 9). This deviation is attributed to the unique chemical structure of the PEBN 50/50 itself. For such a copolymer, crystals of low stability (low enthalpy of fusion) based on both comonomer units should be supposed in accordance to what Lu and Windle [5,46] proposed for PET/PEN copolymers.

For the primary crystals of PEN, PBN and the PEBN copolymers, it was found that recrystallisation is very important [34,47]. For PBN and fast crystallising copolymers, recrystallisation is faster than melting and thus the middle-melting peak often does not appear, or instead of the middle-melting endotherm a recrystallisation exotherm appears. In fact, what is recorded in a standard DSC trace on heating, is the sum of a melting and recrystallisation peak. For PEN, as well as for slowly crystallising copolymers, the middle-melting peak is large because melting is much faster than recrystallisation.

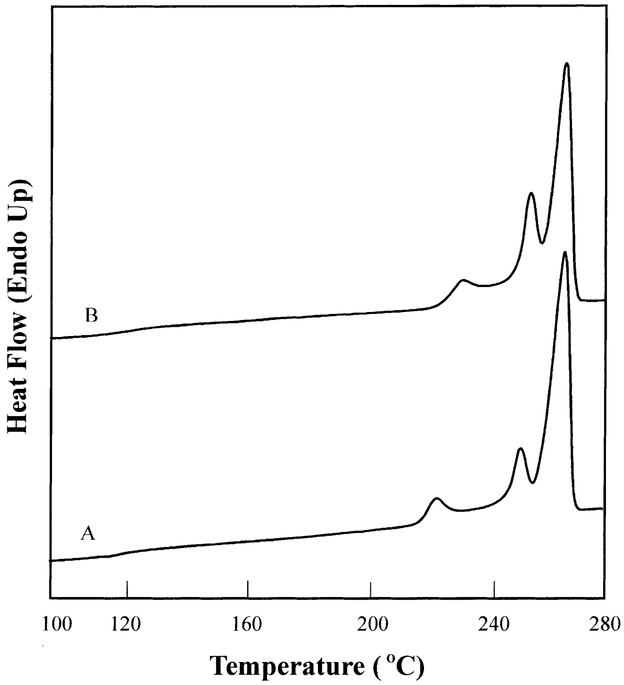


Fig. 9. DSC traces on heating at 20°C/min for PEN isothermally crystallised: (A) at 210°C for 12 min; (B) at 220°C for 20 min.

For PEBN 50/50 isothermally crystallised at temperatures from 110 up to 130°C, the low-temperature melting peak appeared even after short crystallisation times. After crystallisation at 100°C, a large low-temperature melting peak was observed starting at about 105°C, as well as a final melting of only about 188°C. It is obvious that at such a low T_c, secondary crystallisation was increased. However, only one crystallisation peak was observed during crystallisation at 100°C. The whole picture for PEBN 50/50 crystallisation supports the assumption that the second peak should be strongly connected with secondary crystallisation.

3.2. The behaviour of PEBN 70/30

For PEBN 70/30, it was found that crystallisation is very slow and the resulting morphology is connected with a very broad melting temperature region. PEBN 70/30 shows very low crystallinity and thus even after prolonged crystallisation times, the glass transition is very pronounced as it is shown in Fig. 10. Note the large enthalpy relaxation of a sample that was cooled to the room temperature in the reactor in which it was synthesised, dried at 70°C for a day and then stored for about 4 years at room temperature.

Actually, up to four melting peaks were observed after isothermal crystallisation for PEBN 70/30, the peak multiplicity depending on the temperature and the time of crystallisation, as one can see in Fig. 10. This should be attributed to a crystallisation process involving formation of metastable crystalline phases and transformation to more stable ones, as well as formation of different crystal distributions of various degrees of perfection.

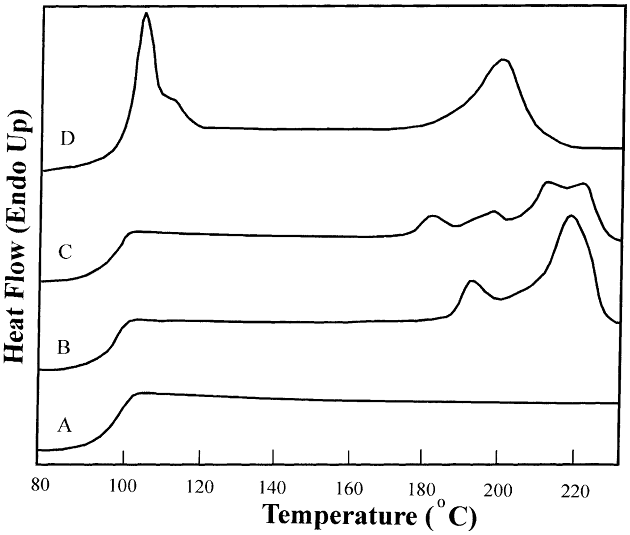


Fig. 10. DSC traces on heating at 20°C/min for PEBN 70/30: (A) quenched; (B) crystallised at 180°C for 2 h; (C) crystallised at 170°C for 1.5 h; (D) sample stored for 4 years.

In contrast to the model of homopolymer sequence matching, Windle and co-workers [5,46,48] suggested that, crystallinity in some random poly(ethylene terephthalate-*co*-2,6-naphathlate)s (PETN copolymers) results by segregation and lateral matching of similar yet random sequences of the neighbouring molecules. The crystals themselves thus contain mixtures of different monomer units and lack periodicity in the chain direction. They are called non-period-layer (NPL) crystals. Parallel with the NPL model, the 'plane start register model', was proposed by Gutierrez et al. [49]. In this model, the three-dimensional order is seen to arise from the parallel arrangement of a number of random but non-identical sequences with just one monomer in register at the centre of each sequence. These models were initially proposed for the case of liquid-crystalline copolymers, but it was found that they could be used for conventional copolymers, such as PETN copolyesters. Probably, they can also be used to explain crystallinity for PEBN copolymers with large comonomer content, such as the PEBN 70/30.

Acknowledgements

We are greatly indebted to Amoco Chemicals-Fine Acids (Chicago, IL) for providing the dimethyl naphthalene-2,6-dicarboxylate (DMN) samples.

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