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Synthesis and thermal behaviour of poly(ethylene-co-butylene naphthalene-2,6-dicarboxylate)s

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Poly(ethylene naphthalene-2,6-dicarboxylate) and poly(1,4-butylene naphthalene-2,6-dicarboxylate) homopolymers were synthesized by the two-step melt polycondensation process of dimethyl naphthalene-2,6-dicarboxylate and ethylene glycol (EG) or 1,4-butanediol (BD) respectively. Eight copolymers of the above three monomers were also synthesized by varying the mol% of BD with respect to EG in the initial monomer feed. The copolymer composition was determined by ^{1}H n.m.r. spectroscopy. The thermal behaviour was investigated over the entire range of copolymer composition by differential scanning calorimetry and thermomechanical analysis. The glass transition (T_g), cold crystallization (T_{cc}), melting point (T_m) and crystallization (T_c) temperatures have been determined. The melting temperature of the above copolymers was depressed gradually at first with the increase of BD in the composition and eutectic behaviour appeared with a minimum at about 40 mol% BD content. © 1998 Published by Elsevier Science Ltd. All rights reserved.

(Keywords: poly(ethylene-co-butylene naphthalene-2,6-dicarboxylate); poly(ethylene-co-butylene 2,6-naphthalate); ^{1}H n.m.r. spectroscopy)

INTRODUCTION

Poly(ethylene 2,6-naphthalate) (PEN), the thermoplastic homopolymer derived from dimethyl 2,6-naphthalate (DMN) and ethylene glycol (EG), has thermal, mechanical, chemical and dielectric properties which are generally superior to those of poly(ethylene terephthalate) (PET). Compared to PET, PEN demonstrates a 43°C higher glass transition temperature, 50% higher modulus, 33% higher tensile strength, a five-fold improvement in gas barrier (measured on biaxially oriented films), a four-fold improvement in moisture barrier and greater chemical resistance[1]. Unfortunately, the production cost of PEN until now has been much higher than that of PET, and this has limited its use. The applications of PEN include films for photography, recording audio, video and data storage, food packaging and insulating material for capacitors, and fibres for the reinforcement of car radial tyre carcasses and belting, and for soft-drink bottles or returnable/refillable water bottles.

Another thermoplastic polyester, poly(butylene 2,6-naphthalate) (PBN), derived from DMN and 1,4-butanediol (BD), has a more rapid rate of crystallization compared to that of poly(butylene terephthalate) (PBT), and excellent mechanical, thermal and electrical properties. The applications of PBN include biaxially oriented films, fibres, connectors, switches, coil bobbins, ignition coils, fuel sensors, fuel tanks and hoses.

The most important feature of the two aforementioned polymers compared to polyalkylene terephthalates is the increased stiffness of their macromolecular chains due to the presence of a naphthalene ring (see *Figure 1*) instead of a benzene ring[2]. This difference, in the case of PEN and PET, was attributed to the difference in the deformability between the naphthalene and phenyl rings, because in contrast to the conformation of PET, all atoms of the PEN chain, including O–CH$_2$, are coplanar[3].

Blends of PEN/PBN should also be useful in engineering plastics, if of course they are miscible. Unfortunately, in contrast to the blends of PET/PBT which are miscible in the amorphous phase, as was shown by the observation of a single glass transition temperature over their entire composition range[4], blends of PEN/PBN have been found to be immiscible except when the PBN content exceeds 80 wt% or 78 mol%[5].

For this reason, it was of interest to prepare the homopolymers PEN and PBN and copolymers from DMN and EG : BD with initial molar glycol feed ratios of 95:5, 90:10, 80:20, 70:30, 60:40, 50:50, 30:70 and 10:90, and to study their thermal behaviour.

The preparation of copolyesters from the above monomers was first reported in the literature by Prof. Seung Soon Im *et al.* (published in the Korean language)[6]. Copolyesters (PEN/PBN, 5-40/95-60) have also been reported in a Japanese patent prepared by transesterification of previously prepared PEN and PBN[7].

EXPERIMENTAL

Synthesis of PEN/PBN homopolymers and their copolymers

PEN and PBN homopolymers and their copolymers were synthesized from DMN, EG and/or BD. The starting materials were of commercial grade and were used without further purification. DMN was a gift from Amoco Chemicals-Fine Acids (Chicago, IL, USA).

The preparation of PEN from DMN is similar to that of

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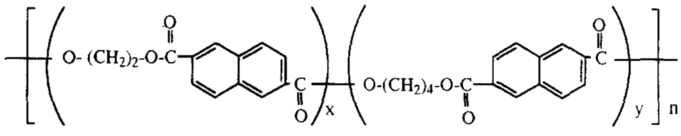

Where x + y = 1

Figure 1 Structure of PEN/PBN copolymers

Table 1 Ultimate temperature of transesterification and polycondensation, intrinsic viscosities of the polyester samples prepared measured at 25°C in a phenol/tetrachloroethane mixture, comparison of feed composition and ^1H n.m.r. composition of PEN/PBN copolymers

Polymer	Transesterification temperature (°C)	Polycondensation temperature (°C)	Intrinsic viscosity $[\eta]$ (dl g^{-1})	Feed composition (mol%)		^1H n.m.r. composition (mol%)	
				EG	BD	EG	BD
PEN	260	290	0.46	100	0	100.0	0.0
EB1	255	288	0.60	95	5	95.0	5.0
EB2	250	284	0.53	90	10	89.4	10.6
EB3	245	279	0.56	80	20	78.6	21.4
EB4	240	275	0.60	70	30	68.7	31.3
EB5	235	271	0.58	60	40	49.8	50.2
EB6	230	267	0.50	50	50	35.0	65.0
EB7	225	263	0.70	30	70	17.0	83.0
EB8	220	259	0.60	10	90	0.0	100.0
PBN	215	255	0.61	0	100	0.0	100.0

PET from dimethyl terephthalate (DMT) by the use of the catalytic system $M^{2+}(CH_3COO)_2^-/Sb_2O_3$, where M can be Zn, Mn, Ca, etc. On the other hand, the preparation of PBN from DMN is similar to that of the preparation of PBT from DMT, where tetrabutyl titanate (Tizor) is usually used as a catalyst for both steps (transesterification and polycondensation). This catalyst can also be used in the case of PET, but it gives a pale yellow discoloration to the polymer, while the catalytic system zinc acetate/antimony trioxide does not work satisfactorily in the case of PBN[6]. So, for all of the above reasons, it was decided to use tetrabutyl titanate for the preparation of all polymeric samples (homopolymers and copolymers) in this work.

In each preparation, the reaction mixture comprised 50 g (0.205 mol) of DMN, and the various amounts (mol%) of EG and/or BD (molar ratio of DMN/diol = 1:2) and the catalyst (60 ppm Ti) on DMN. Other additives, such as heat stabilizer etc., were not charged into the reaction tube of the polyesterification apparatus, which was similar to that used by Günter and Zachmann[8]. The reaction mixture was heated in a programmed fashion to the final temperature (*Table 1*) under an argon atmosphere and stirred at a constant speed (500 rpm). This first step (transesterification) is considered to be complete after ≈ 3 h, when the theoretical amount of methanol (16.4 ml) was collected.

In the second step (polycondensation), a vacuum (4.0 Pa) was applied slowly over a period of time, about 30 min, to avoid excessive foaming and to minimize oligomer sublimation, which is a potential problem during the melt polycondensation. The temperature was increased simultaneously such that when full vacuum was reached the final polycondensation temperature was also reached (30 min). The final temperatures that were selected for transesterification and polycondensation are shown in *Table 1*. The polycondensation was continued for about 1.5 h until the agitator speed decreased to 350 rpm. After the polycondensation reaction was complete, the reaction tube had to be broken to get the product out of the tube. In most of the polymerizations, the tube was broken due to the adhesion of the polyester to the glass and its shrinkage during cooling. All polyester samples, which had a white to yellowish colour, after the glass particles were removed with a grinder, were ground in a mill, sieved, washed with methanol and dried at 110°C for 12 h.

Measurements

Intrinsic viscosity $[\eta]$ measurements were performed using an Ubbelohde viscometer at 25°C in a mixture of phenol and tetrachloroethane (60:40, w/w). The samples were maintained in the above mixture of solvents at 120°C for 20 min to achieve a complete solution. The solution was then cooled to room temperature and filtered through a disposable membrane filter (Teflon).

^1H n.m.r. spectra at 300 MHz were obtained on a Bruker AMX-300 *FT*-n.m.r. spectrometer for copolymer composition determination. The samples were dissolved in a mixture of $CF_3COOH/CDCl_3$ (7:3, v/v) using tetramethylsilane (TMS) as an internal reference ($\delta = 0$ ppm). The concentration of the sample solutions was 10% w/v.

Thermal analyses (differential scanning calorimetry, d.s.c.) were performed on a Perkin–Elmer DSC-2 using the following parameters: heating rate 20°C min^{-1}, cooling rate 10°C min^{-1}, sample weight 12.00 ± 0.01 mg, nitrogen flow rate 1.5 l h^{-1}, sensitivity 5 mcal s^{-1}.

Three runs were recorded for each sample:

First run:	heating (0–300°C) of the initial sample at a heating rate of 20°C min^{-1}.
Second run:	reheating (0–300°C) of the previous sample quenched from the melt, just after the completion of the first run, in liquid nitrogen.
Third run:	cooling (from 300 to 0°C) of the previous melted samples at a cooling rate of 10°C min^{-1}.

The determination of the glass transition temperature was also done on the TMS-2 (Perkin–Elmer), using a penetration probe, in the following way. The samples were prepared by melting the polymer, at a temperature 30°C higher than its melting point, into a large-volume stainless steel capsule without a cover and heated into the holder of a differential scanning calorimeter under a nitrogen

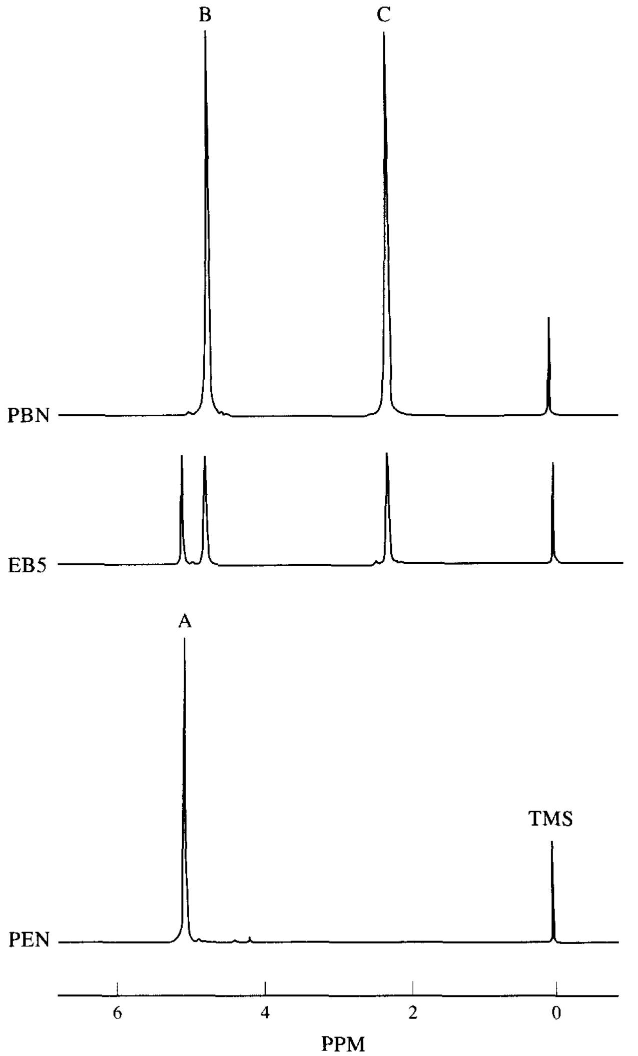

Figure 2 ^{1}H n.m.r. spectra of homopolymers PEN and PBN, and copolymer EB5

atmosphere and subsequent quenching at the temperature of dry ice (− 70°C). The above capsules are manufactured by Perkin–Elmer (Part No. 319-0218) and are recommended for liquid samples in d.s.c. analysis. After quenching, the samples remained in the capsules and were used for penetration measurements as a whole.

The penetration probe made contact with the sample's upper surface, whose temperature was controlled exactly by a linearized resistance thermometer in a low mass furnace. As the sample softened (T_g), the probe penetrated into it and this new position was accurately monitored by a linear variable differential transformer (LVDT). The penetration probe[9], with a flat tip whose surface area was 0.621 mm^2, was used and a weight of 31.05 g was added to the loading platform, corresponding to a pressure on the sample of 4.9 MPa. All runs were performed under a helium atmosphere at a heating rate of 5°C min^{-1}.

RESULTS AND DISCUSSION

Copolymer composition

The compositions of PEN/PBN copolymers were determined from ^{1}H n.m.r. spectra, as shown in *Figure 2*. Three main peaks were used for this determination: one for the ethylene unit (A: 5.02 ppm) and two for the butylene unit (B: 4.71 ppm; C: 2.24 ppm). Thus, the molar compositions were found using the following equations:

$$\text{PEN (mol\%)} = [\text{A}/(\text{A} + \text{D})] \times 100$$

$$\text{PBN (mol\%)} = [\text{D}/(\text{A} + \text{D})] \times 100$$

where D = (B + C)/2.

The compositions found are listed in *Table 1*. It can be seen from these results that the actual molar composition is about the same as that of the feed composition for the first five samples (PEN–EB4). However, a discrepancy between copolymer and feed composition was observed for samples EB5–EB7, and especially for sample EB8, taken from a monomer feed 10:90, which is pure PBN. Such a discrepancy was also reported[10] for copolymers prepared from DMN, EG and 1,6-hexanediol.

It is worth noting that EG has a lower boiling point (198°C) compared to that of BD (230°C) and 1,6-hexanediol (250°C). These diols are used in double molar quantity compared to DMN, so that at the end of the first step (transesterification) their whole amount should have been reacted with DMN, producing the corresponding bis-hydroxyalkyl naphthalates. However, a small amount (≈ 0.5m*l*) of diol appeared with the final drops of the evolved methanol. This is concluded from the fact that, while the theoretically expected amount of methanol is 16.4 ml (see Experimental), the distilled amount was about 17 ml. When the refractive index of these final drops was determined, it was found to be equal to 1.425, which coincides with the refractive index of EG (1.432) rather than with that of BD (1.446) or methanol (1.329). This loss of EG should cause a discrepancy in the feed composition of diols compared with that used initially. The amount of distilled EG was found to be about the same for all the feed compositions of diols used, so the discrepancy in feed composition of diols should be higher for the feed EG : BD = 10:90 than that for the feed 90:10. The difference between copolymer and feed composition could also be caused during the polycondensation process, when bis-hydroxyalkyl naphthalates are condensated with concurrent evolution of an EG or BD molecule. The evolution of EG should occur more readily than that of BD, due to its higher volatility, enriching the copolymer composition with butylene units.

Thermal properties

The glass transition temperature (T_g), the cold crystallization temperature (T_{cc}), the melting temperature (T_m) and the crystallization temperature (T_c) of the samples prepared were studied in this work and are shown in *Table 2*.

T_g and T_{cc} values were determined from the d.s.c. thermograms on heating of the quenched samples (second run), which are shown in *Figure 3*. The quenching of melted samples (300°C) just after the first run in liquid nitrogen was chosen in order to determine the T_g and T_{cc} values of all samples with greater accuracy, but even after this treatment, samples EB7, EB8 and the homopolymer PBN did not reveal their T_g. This is due to the very rapid crystallization of these samples; in addition, EB8 is pure PBN, as revealed by ^{1}H n.m.r. The T_g determination of the latter three samples was also impossible when thermomechanical analysis (t.m.a.) was used for this purpose, because of their high crystallinity. In the literature, various different T_g values of pure PBN have been reported, such as 41°C[11], 48°C[12], 52°C[13] and 82°C[1,14].

In *Figure 4*, the T_g of amorphous PEN (125°C) obtained

Table 2 Thermal parameters of PEN/PBN copolyesters determined by differential scanning calorimetry and thermomechanical analysis

Polymer	BD unit	Thermal parameters				
		T_g (°C)[a]	T_g (°C)[b]	T_{cc} (°C)[a]	T_m (°C)[a]	T_c (°C)[a]
PEN (100:0)	0.0	122	125	218	268	—
EB1 (95:5)	5.0	118	117	—	253	—
EB2 (90:10)	10.6	113	111	—	243	—
EB3 (80:20)	21.4	107	105	—	222	—
EB4 (70:30)	31.3	100	102	—	200	—
EB5 (60:40)	50.2	92	91	126	195	—
EB6 (50:50)	65.0	80	82	94	208	159
EB7 (30:70)	83.0	—	—	—	230	175
EB8 (10:90)	100.0	—	—	—	242	208
PBN (0:100)	100.0	—	—	—	246	210

[a] Determined by d.s.c.
[b] Determined by t.m.a.

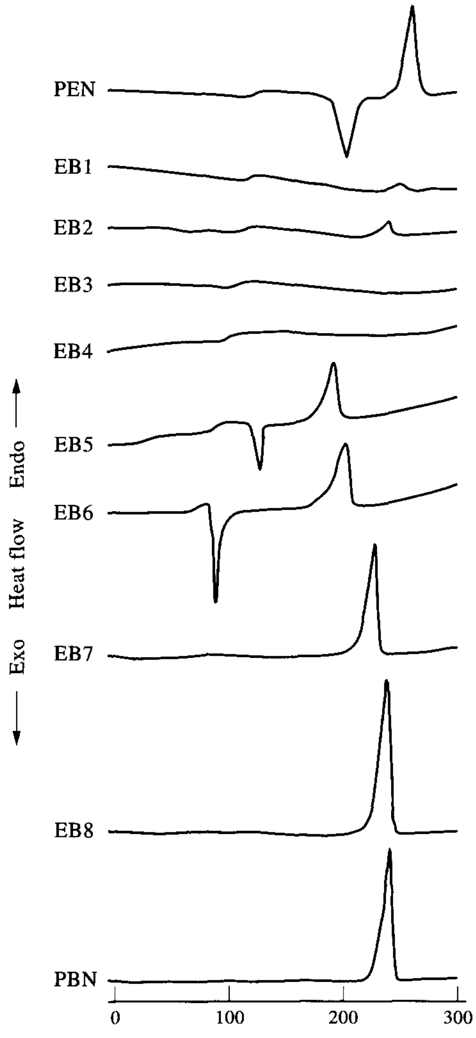

Figure 3 D.s.c. curves of the quenched PEN/PBN copolymers and their homopolymers

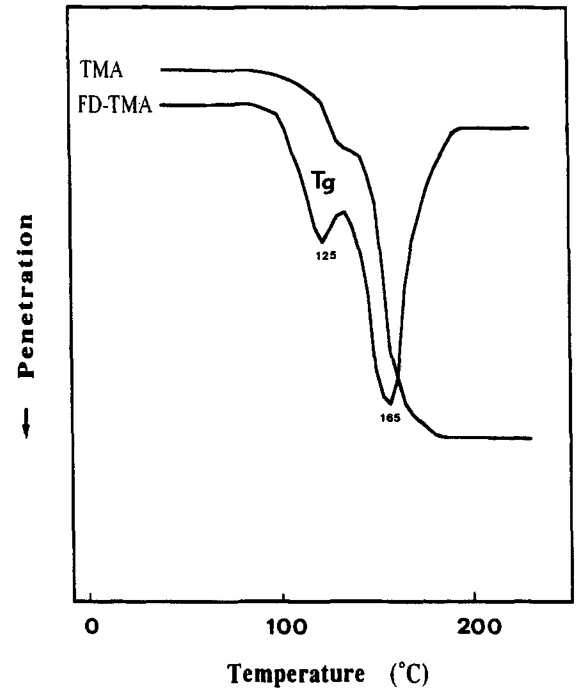

Figure 4 PEN's T_g determination by penetration measurements at a heating rate of 5°C min^{-1} and a pressure on the sample of 4.9 MPa. TMA, thermomechanical analysis curve; FD-TMA, first derivative thermomechanical analysis curve

from the first derivative (curve FD-TMA) is shown. It is remarkable that the penetration curve shows two steps near the T_g region. These steps are better shown by the first derivative curve as two distinct peaks (peak 1 at 125°C and peak 2 at 165°C). The temperature corresponding to peak 1 coincides with T_g as obtained by d.s.c., while peak 2 represents a penetration in the beginning of the cold crystallization region, where a reorganization of macromolecules begins to take place. This process could be related to cold crystallization, because the polymeric sample was found to be under stress and at a temperature higher than that of T_g. A confirmation of this hypothesis is that no other penetration is observed on further heating, for example in the region of cold crystallization $\approx$ 220°C, except that in the region of the melting temperature. Similar behaviour was observed[15] when we tried to study the T_g values of the chain-extended PET samples by t.m.a. This behaviour was also observed by other investigators[16], who relied on dielectric measurements. Two relaxation regions were observed by using the dielectric analyser: the relaxation region from the pure amorphous phase of the PET sample and the relaxation region from the spherulitic phase. This second penetration step needs further investigation.

The T_g values obtained from the two thermoanalytical techniques (d.s.c. and t.m.a.) are in good agreement (*Table 2*).

T_g values decreased linearly with increasing content of the flexible butylene units in the copolymer, as shown in *Figure 3* and even more clearly in *Figure 5*. The increased

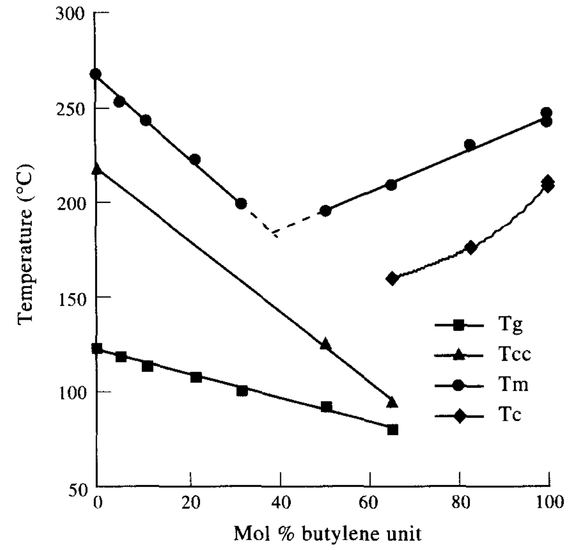

Figure 5 Glass transition temperature (T_g), cold crystallization temperature (T_{cc}), melting temperature (T_m) and crystallization temperature (T_c) as a function of copolymer composition, expressed as BD molar fraction

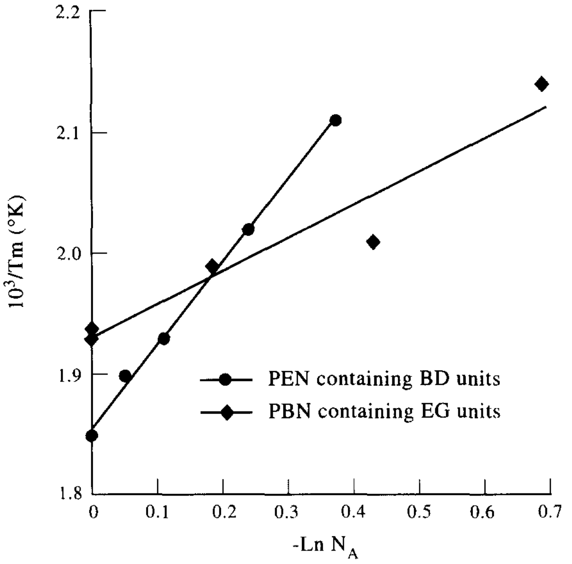

Figure 7 Plot of $1/T_m$ *versus* $-\ln N_A$ for PEN/PBN copolyesters

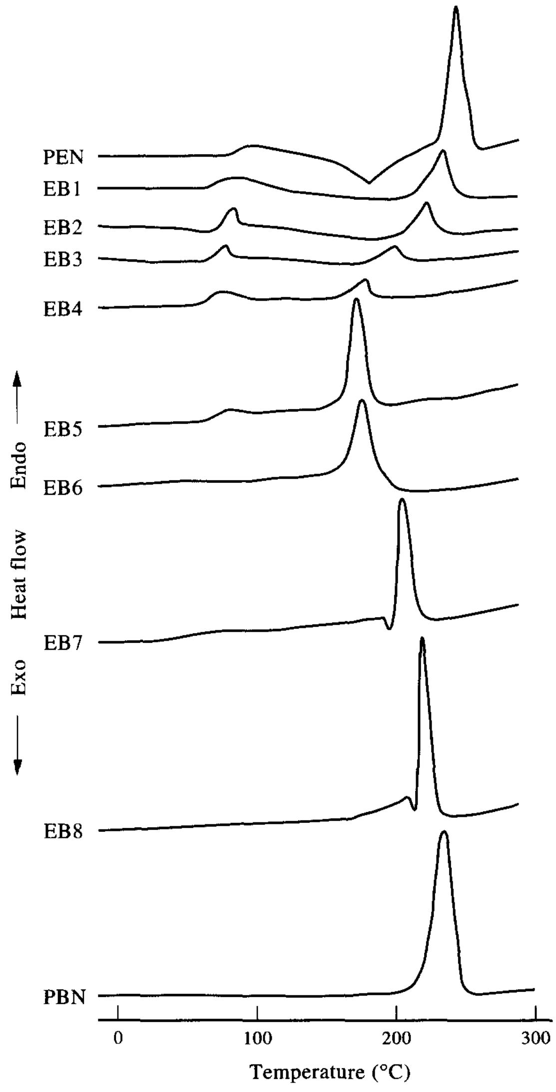

Figure 6 D.s.c. curves of the initial samples of PEN/PBN copolymers and their homopolymers

BD content of PEN/PBN copolymers will result in a reduced density. Thus, the PEN/PBN copolymers which have more flexible butylene units have lower T_g and T_{cc} values.

It is worthwhile noting that the cold crystallization appeared only in the samples PEN, EB5 and EB6. Samples EB1–EB4 did not show cold crystallization because they cannot crystallize easily, while samples EB7–PBN did not show cold crystallization because of the very rapid crystallization, even on quenching, i.e. they were crystallized on quenching.

T_m values were determined from the first run d.s.c. thermograms (*Figure 6*) of the initial samples, which were proven to be highly crystalline materials. This was deduced from the fact that, when some initial samples were annealed for 2 h at 200°C, thermograms similar to those observed from the first run were obtained.

From these thermograms, one can observe a single melting temperature for all samples; these values decreased at first and then increased again with butylene content. These T_m values are listed in *Table 2* and are plotted in *Figure 5*. At 40 mol% butylene units, a minimum in T_m values (eutectic point) was observed, at about 185°C.

Using the theory of melting point depression of copolymers, the heat of fusion (ΔH_f) of PEN and PBN could be calculated from the copolymer melting points. According to this theory, the component which brings about the depression in T_m of a polymer may be a constituent of the polymer itself. In a copolymer consisting of *A* units which crystallize and *B* units which do not, with the two units occurring in random sequence along the chain, the latter should depress the melting point of the former according to Flory's equation[17]:

$$\frac{1}{T_m} - \frac{1}{T_m^\circ} = \frac{R}{\Delta H_f} \ln N_A$$

where T_m° is the melting point of homopolymer with *A* units, T_m the melting point of the copolymer, N_A the molar fraction of *A* units, R the gas constant (8.314 J mol^{-1}) and ΔH_f the heat fusion per repeating unit of the homopolymer with *A* units.

If this equation is applied twice for our copolymers, considering first that PEN represents the *A* units and second that PBN represents the *A* units, we obtain the lines shown in *Figure 7*.

From the slope of the $1/T_m$ *versus* $-\ln N_A$ plot, $R/\Delta H_f$ values were determined. The heats of fusion found were 12.3 kJ mol^{-1} for PEN and 30.6 kJ mol^{-1} for PBN. The theoretical values of ΔH_f were calculated as about 25 kJ mol^{-1} for PEN and 41 kJ mol^{-1} for PBN by the group contribution method[18]. Such discrepancies between the theoretical values of ΔH_f and those determined based on the above equation of Flory were also observed by other investigators[10,19,20], and were attributed to the dependence of T_m depression not on the molar fraction N_A, but rather on the sequence propagation probability. The higher difference in the ΔH_f value for PEN than that for PBN is rather due to the higher crystallizability of the latter. Indeed, when A units represent PBN units, which crystallize more easily than PEN units, this is true, but the converse is not.

T_c values were determined from the third run d.s.c. thermograms on cooling (300 to 0°C) from the melt at a cooling rate of 10°C min^{-1}. As one can see from *Table 2*, only the last four samples, EB6, EB7, EB8 and PBN, showed crystallization on cooling; the other samples could not crystallize. It is also interesting to note that the very close values (208, 210°C) of T_c for the samples EB8 and PBN is also proof that sample EB8 is pure PBN.

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