Wide-Angle X-Ray Diffraction and Differential Scanning Calorimetry Study of the Crystallization of Poly(ethylene naphthalate), Poly(butylene naphthalate), and Their Copolymers

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Received 10 June 2003; revised 26 September 2003; accepted 2 October 2003

ABSTRACT: The crystallization behavior of a series of poly(ethylene-*co*-butylene naphthalate) (PEBN) random copolymers was studied. Wide-angle X-ray diffraction (WAXD) patterns showed that the crystallization of these copolymers could occur over the entire range of compositions. This resulted in the formation of poly(ethylene naphthalate) or poly(butylene naphthalate) crystals, depending on the composition of the copolymers. Sharp diffraction peaks were observed, except for 50/50 PEBN. Eutectic behavior was also observed. This showed isodimorphic cocrystallization of the PEBN copolymers. The variation of the enthalpy of fusion of the copolymers with the composition was estimated. The isothermal and nonisothermal crystallization kinetics were studied. The crystallization rates were found to decrease as the comonomer unit content increased. The tensile properties were also measured and were found to decrease as the butylene naphthalate content of the copolymers increased. For initially amorphous specimens, orientation was proved by WAXD patterns after drawing, but no crystalline reflections were observed. However, the fast crystallization of drawn specimens occurred when they were heated above the glass-transition temperature. © 2004 Wiley Periodicals, Inc. J Polym Sci Part B: Polym Phys 42: 843–860, 2004

Keywords: wide-angle X-ray diffraction (WAXD); poly(ethylene naphthalate) (PEN); poly(butylene naphthalate) (PBN); crystallization; copolymerization; mechanical properties

INTRODUCTION

Naphthalene-containing thermoplastic polyesters have attracted interest in recent years. Poly(ethylene naphthalate) (PEN or **I**), poly(butylene naphthalate) (PBN or **II**), and poly(propylene naphthalate) (PPN) are the most well known members of this family of thermoplastics.

PEN has a melting temperature (T_m) of 267 °C and a high glass-transition temperature (T_g) of 122 °C. This permits applications at temperatures much higher than those at which poly(ethylene terephthalate) can be used. PEN also exhib-

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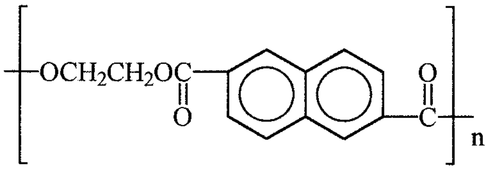
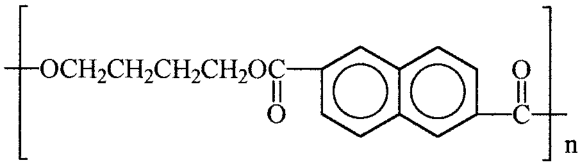
Journal of Polymer Science: Part B: Polymer Physics, Vol. 42, 843–860 (2004)

its excellent mechanical and gas barrier properties and chemical and UV resistance, which allow its use in applications for which more expensive polyimides have always been used. The thermal behavior of PEN was first studied by Cheng and Wunderlich.[1] The crystal modifications of the polymer were described by Mencik,[2] Zachmann et al.,[3] and Cakmak and Kim.[4] The mechanical properties and strange necking behavior of PEN have also attracted special interest.[5,6]

PBN is a new thermoplastic with a T_m of 241 °C and a T_g of 72 °C.[7] Among its properties, excellent chemical resistance and very fast crystallization rates have been noted.[8] It is used mainly for fiber production and containers. The thermal behavior and crystal modifications of PBN have recently been studied:[9,10]



(I)



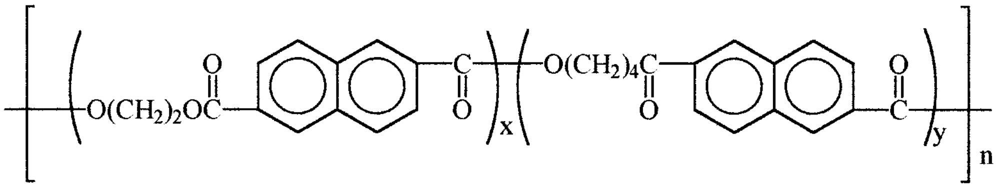
(II)

PPN is a polyester with a very short history, like poly(propylene terephthalate). This is because only in recent years has 1,3-propanediol been produced in sufficient amounts and at low cost. PPN exhibits a T_m of 201 °C and a T_g of 82 °C.[11]

Furthermore, the properties of polymeric materials are dependent on the morphology generated during their processing, and this is usually dynamic. The crystallization of a polymer may cause a volume reduction up to 20%, which, in turn, results in the generation of mechanical stresses. Knowledge of the crystallization parameters is needed for the optimization of the processing conditions and the properties of the end products.[12]

Especially for copolymers, crystallization may not be observed over the entire range of compositions. Only long sequences of the monomer in excess are anticipated to crystallize.[13] Comonomer units can only form crystal defects. In general, they are excluded from crystals.[14] Copolymer crystals have small dimensions. Lu and Windle[15] studied the crystallization behavior of poly(ethylene terephthalate-*co*-naphthalate)s and found that models first introduced to describe the behavior of liquid-crystalline polymers could be useful.

In this study, the crystalline structure of poly(ethylene-*co*-butylene naphthalate)s (PEBN or **III**) was examined with wide-angle X-ray diffraction (WAXD). A study of both the isothermal and nonisothermal crystallization kinetics was also performed with differential scanning calorimetry. Isothermal crystallization was treated with the Kolmogorov–Mehl–Avrami equation,[16–20] whereas the Ozawa[21] and modified Avrami approaches[22–25] were elaborated for nonisothermal crystallization. Finally, the mechanical properties and the effect of drawing on the morphology of the specimens were examined.



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(III)

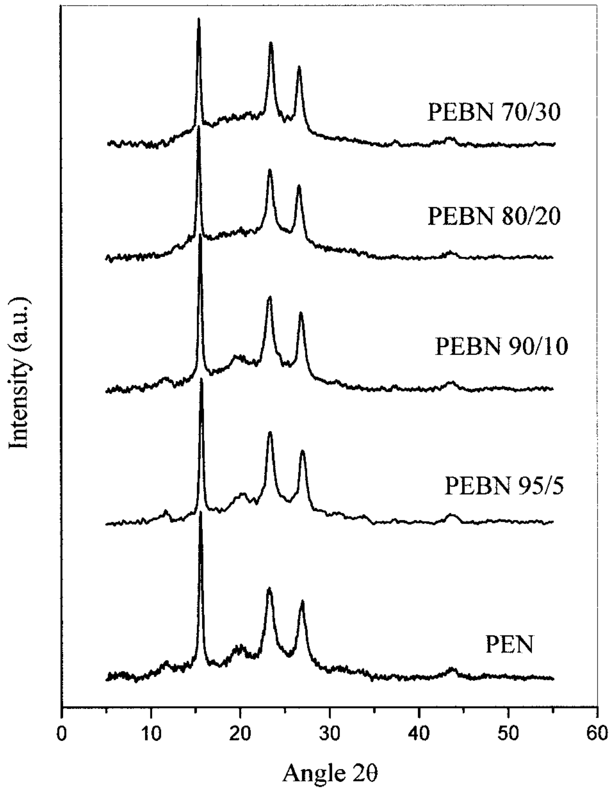

Figure 1. WAXD patterns for annealed PEN, 95/5 PEBN, 90/10 PEBN, 80/20 PEBN, and 70/30 PEBN.

EXPERIMENTAL

PEN, PBN, and PEBN copolyesters were synthesized according to the polycondensation method from dimethyl naphthalene-2,6-dicarboxylate (DMN), ethylene glycol, and 1,4-butanediol, with $Ti(OBu)_4$ as a catalyst. The synthesis is described in detail in a previous article.[26]

For the density measurements, a Davenport density measurement apparatus was used. To fill the density gradient column, tetrachloromethane (1.59 g/cm^3) and *n*-heptane (0.7 g/cm^3) were used. First, two solutions of these solvents were prepared with densities of 1.40 and 1.26 g/cm^3, respectively, and then they were added to the column via mixing with a suitable device. A set of calibrated floats (H & D Fitzgerald, Ltd.) was placed inside the column to graduate it. The densities were measured at 23 °C. For each of the polyesters, the densities of a series of semicrystalline samples were measured, and the average values were used. Quenched samples were used to determine the density of the amorphous materials.

The crystallizations of the polyester samples were performed in a PerkinElmer Pyris 1 differential scanning calorimeter. Samples of 5 ± 0.01 mg were used. It is important for crystallization experiments that the thermal lag be minimized, so samples equal to 5 mg or less should be used in differential scanning calorimetry (DSC) tests. All polyester samples were initially melted at 20 °C above the respective melting point, for 5 min, to erase the entire thermal history and then were cooled at 150 °C/min to the crystallization temperatures.

For nonisothermal crystallizations, samples were cooled at various cooling rates from T_m to 25 °C.

The crystalline structure of the polyesters was investigated by WAXD with a Seifert 3003T powder diffractometer with Cu Kα radiation at 2θ = 5–90°.

The tensile mechanical properties were studied on relatively thin films of the polymeric samples, which were prepared with an Otto Weber PW 30 hydraulic press at a temperature 20 °C above the respective melting point and under a load of 6 kN on a ram of 110 mm, followed by rapid cooling in the molds. Dumbbell-shaped tensile test specimens (central portion ~ 5 × 0.5 mm thick, gauge length = 22 mm) were cut from the sheets in a

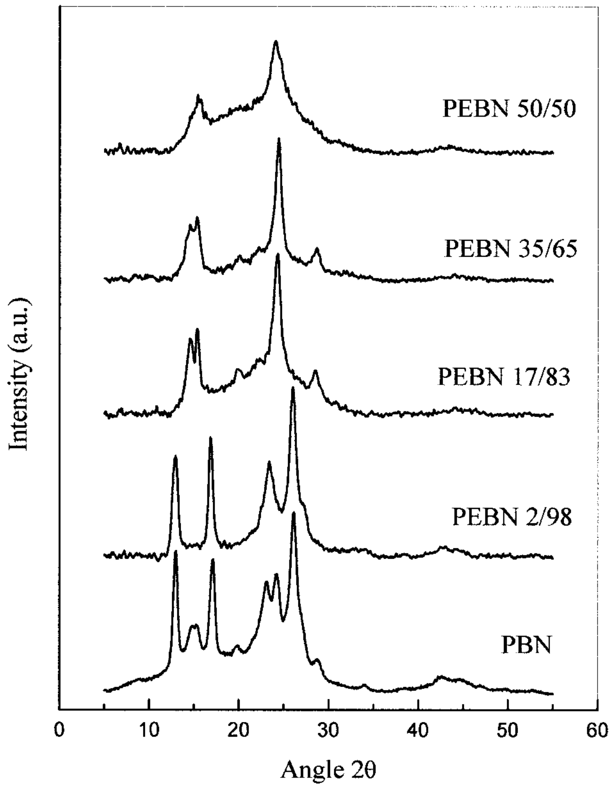

Figure 2. WAXD patterns for as-received PBN, 2/98 PEBN, 17/83 PEBN, 35/65 PEBN, and 50/50 PEBN.

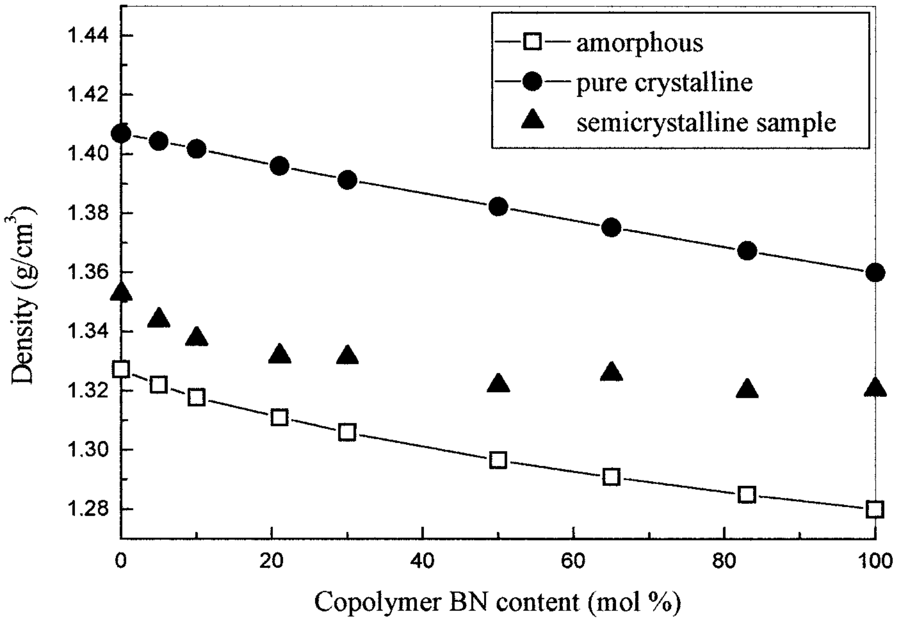

Figure 3. Variation of the density of pure crystalline and pure amorphous PEBN copolymers with the copolymer composition.

Wallace cutting press and were conditioned at 23 °C and 55–60 relative humidity for 48 h.

The stress–strain data were obtained with an Instron tensile testing machine (model 1122), which was maintained under the same conditions and operated at an extension rate of 10 mm/min.

RESULTS AND DISCUSSION

WAXD

The crystalline structure of the copolyesters was studied with WAXD. The copolymers with less

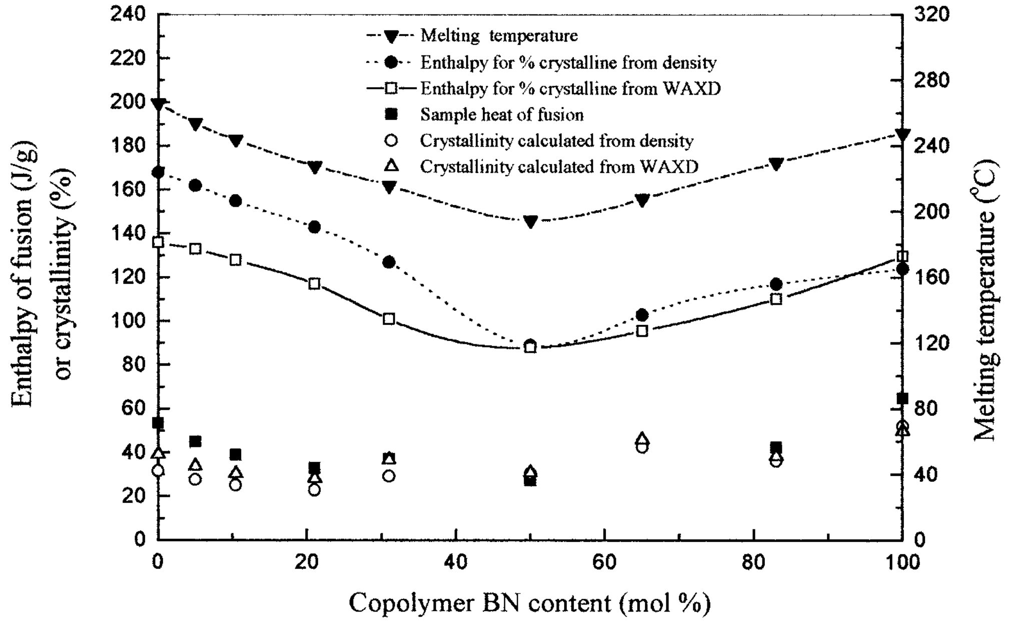

Figure 4. Enthalpy of fusion and melting temperature as a function of the copolymer composition.

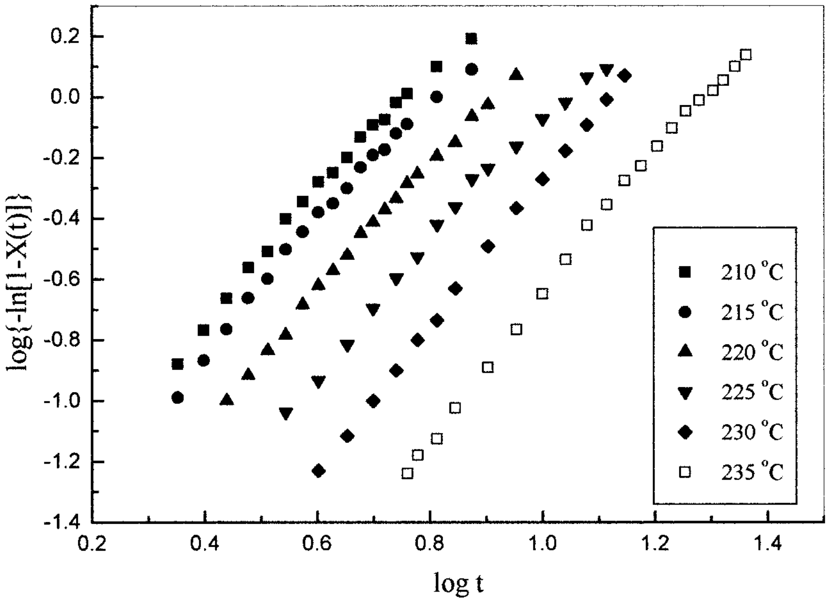

Figure 5. Avrami plots for the isothermal crystallization of PEN at various temperatures.

than 50 mol % butylene slowly crystallized, and so only an amorphous halo was observed for the samples received from the reactor. However, after proper annealing of the samples, crystalline reflections were observed. PEN was annealed at 245 °C for 1 h; 95/5 PEBN and 90/10 PEBN samples were annealed at 200 °C for 1.5 h; and annealing for 80/20 PEBN and 70/30 PEBN samples was carried out at 180 and 170 °C, respectively, for 2 h. However, crystalline reflections were observed for the as-received samples in the case of copolymers with 50 mol % or more butylene. Thus, WAXD proved crystallinity for the PEBN copolymers over the entire range of compositions.

In the WAXD patterns of copolymers with less than 30 mol % butylene naphthalate (BN), only crystalline reflections of the α-crystal form of PEN[3] were observed (Fig. 1). For the rest of the copolymers, the crystalline reflections were those associated with the α-crystal form of PBN[9] (Fig. 2). Reflections of the β-crystal form of PBN[9] were observed for the 2/98 PEBN samples crystallized after cooling in the reactor. WAXD data, supported by data for crystallization kinetics, as discussed later, led to the conclusion that for the PEBN copolymers, only the crystallization of sequences of the monomer in excess occurred, leading to one type of crystal, exclusively PEN or PBN crystals, in each case.

It is well known that cocrystallization behavior in A/B random copolymers can be divided into two types: isomorphism and isodimorphism.[27] When

Table 1. Results of the Avrami Analysis for the Isothermal Crystallization of PEN

Temperature (°C)	k	n	$t_{1/2}$ (min)[a]	$t_{1/2}$ (min)[b]
210	0.0190746	2.40	4.5	4.2
215	0.0161808	2.34	5.0	4.7
220	0.0096828	2.30	6.4	5.9
225	0.0040977	2.33	8.5	8.1
230	0.0019055	2.46	11.0	11.9
235	0.0007989	2.51	15.6	17.1

[a] Values obtained after the Avrami analysis.
[b] Direct measurement from the crystallization peak.

Table 2. Results of the Avrami Analysis for the Isothermal Crystallization of 95/5 PEBN

Temperature (°C)	k	n	$t_{1/2}$ (min)[a]	$t_{1/2}$ (min)[b]
195	0.0018030	2.37	12.3	12.9
200	0.0010691	2.38	15.1	14.3
205	0.0006902	2.45	16.8	17.2
210	0.0001429	2.75	21.9	20.8
215	0.0000548	2.84	27.8	26.6

[a] Values obtained after the Avrami analysis.
[b] Direct measurement from the crystallization peak.

Table 3. Results of the Avrami Analysis for the Isothermal Crystallization of 90/10 PEBN

Temperature (°C)	k	n	$t_{1/2}$ (min)[a]	$t_{1/2}$ (min)[b]
185	0.0013964	2.41	13.1	13.8
190	0.0009977	2.40	15.3	16.2
195	0.0005998	2.32	20.9	20.2
200	0.0002704	2.49	23.4	23.7
205	0.0000614	2.79	28.0	26.7

[a] Values obtained after the Avrami analysis.
[b] Direct measurement from the crystallization peak.

Table 5. Results of the Avrami Analysis for the Isothermal Crystallization of 2/98 PEBN

Temperature (°C)	k	n	$t_{1/2}$ (min)[a]	$t_{1/2}$ (min)[b]
208	0.054497	2.03	3.5	3.4
210	0.034041	2.10	4.2	4.4
214	0.004867	2.17	8.3	8.5
217	0.002889	2.26	11.3	11.9
220	0.000873	2.31	18	17.2

[a] Values obtained after the Avrami analysis.
[b] Direct measurement from the crystallization peak.

A and B have similar chemical structures and thus occupy approximately the same volume, the excess free energy of cocrystallization is very small, and the chain conformations of the two corresponding homopolymers become compatible with either crystal lattice. Then, only one crystalline phase is detected over all compositions. This is isomorphism. However, copolymers may show isodimorphism, in which two crystalline phases, each containing comonomer units as a minor component, are observed. In isodimorphism, the increase in the minor comonomer content in each crystalline phase results in a lowering of T_m and the crystallinity. Thus, a eutectic melting behavior is observed.

It is obvious that PEBN copolymers exhibit isodimorphism. This is confirmed by the WAXD patterns, as well as the eutectic behavior.[26] Isodimorphism was also observed for poly(ethylene terephthalate-*co*-naphthalate)[15] and poly(butylene terephthalate-*co*-naphthalate) copolymers.[28] The case of 50/50 PEBN is of special interest because a distorted PBN crystalline pattern can be observed (Fig. 2).

For PBN, the appearance of the higher density β-crystal form is associated with high crystallization temperatures.[9,10] As mentioned earlier, for as-received samples of 2/98 PEBN, the crystalline reflections observed were those of the β-crystal form of PBN. Thus, even PEBN copolymers with very low ethylene naphthalate contents can crystallize in the β-crystal form of PBN, if crystallization takes place at a high temperature. However, copolymers of higher comonomer contents cannot give crystals of the β form.

Density Measurements and Enthalpy of Fusion

The densities of a series of samples of PEN, PBN, and PEBN were measured with a tetrachloromethane/n-heptane density gradient column. The density for amorphous PEN was found to be 1.3288 g/cm^3, smaller than the value of 1.34 g/cm^3 reported by Buchner et al.[3] However, the value of 1.3288 g/cm^3 is very close to the value of 1.3274 g/cm^3 reported by Sauer et al.[29] The density of amorphous PBN could not be measured directly because amorphous PBN cannot be obtained via quenching. Therefore, in this work, the value of

Table 4. Results of the Avrami Analysis for the Isothermal Crystallization of PBN

Temperature (°C)	k	n	$t_{1/2}$ (min)[a]	$t_{1/2}$ (min)[b]
212	0.112763	2.18	2.3	2.4
215	0.030788	2.17	4.2	4.5
218	0.007346	2.20	7.9	8.5
221	0.003951	2.34	9.1	10.3
224	0.000865	2.38	16.6	17.5

[a] Values obtained after the Avrami analysis.
[b] Direct measurement from the crystallization peak.

Table 6. Results of the Avrami Analysis for the Isothermal Crystallization of 17/83 PEBN

Temperature (°C)	k	n	$t_{1/2}$ (min)[a]	$t_{1/2}$ (min)[b]
188	0.058340	1.98	4.2	4.4
191	0.013483	2.05	7.1	6.9
194	0.004970	2.10	10.5	10.1
197	0.003131	2.04	14.1	14.2
200	0.000966	2.21	19.6	19.1

[a] Values obtained after the Avrami analysis.
[b] Direct measurement from the crystallization peak.

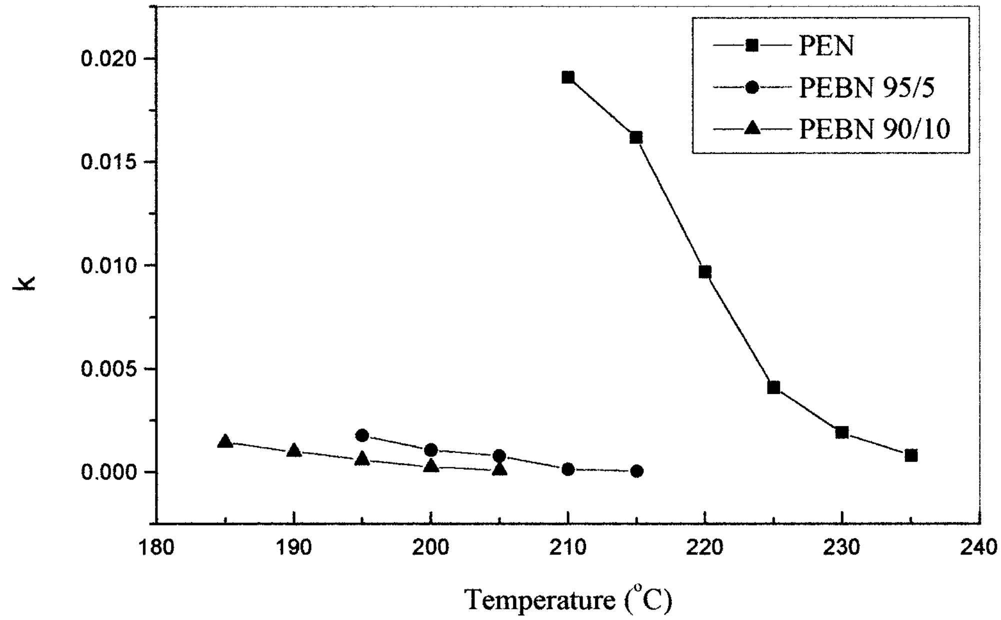

Figure 6. *k* versus the temperature for the isothermal crystallization of PEN, 95/5 PEBN, and 90/10 PEBN.

1.28 g/cm^3, which was reported earlier for amorphous PBN,[30] was accepted. For the copolymers containing more than 35 mol % ethylene naphthalate units, the density of the amorphous phase was measured with quenched samples. For the copolymers 2/98 PEBN and 17/83 PEBN, the density of the amorphous phase was calculated with a graph of the variation of the density with the comonomer unit content (Fig. 3).

The densities for pure crystalline PEN and PBN have been calculated with crystallographic data.[2,9] In the case of PEN, because only the

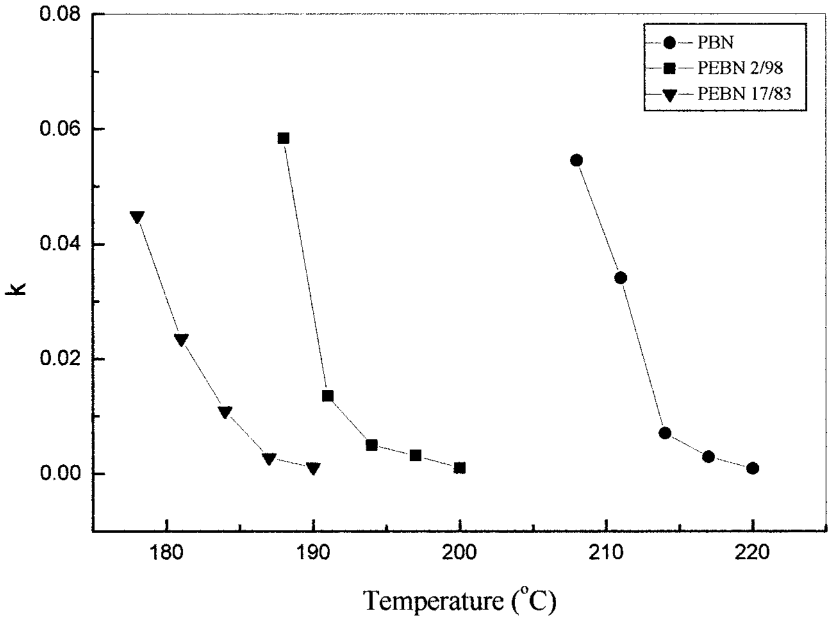

Figure 7. *k* versus the temperature for the isothermal crystallization of PBN, 2/98 PEBN, and 17/83 PEBN.

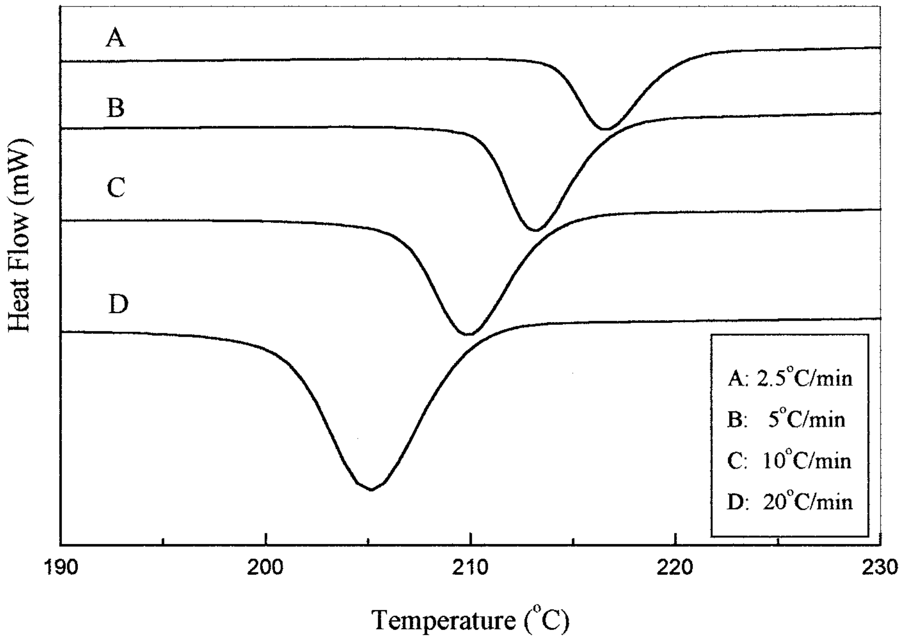

Figure 8. DSC cooling scans for 17/83 PEBN at various cooling rates.

α-crystal form was observed, the respective density value, 1.407 g/cm^3, proposed by Mencik[2] was used. For PBN,[9] the density of the α-crystal form is 1.36 g/cm^3, whereas the density of the β-crystal form is 1.39 g/cm^3. In this work, both crystal forms were observed, and thus the proper density values were used in each case. For the calculation of the density of the pure crystalline copolymers, a linear variation of the density with the comonomer weight fraction was assumed (Fig. 3).

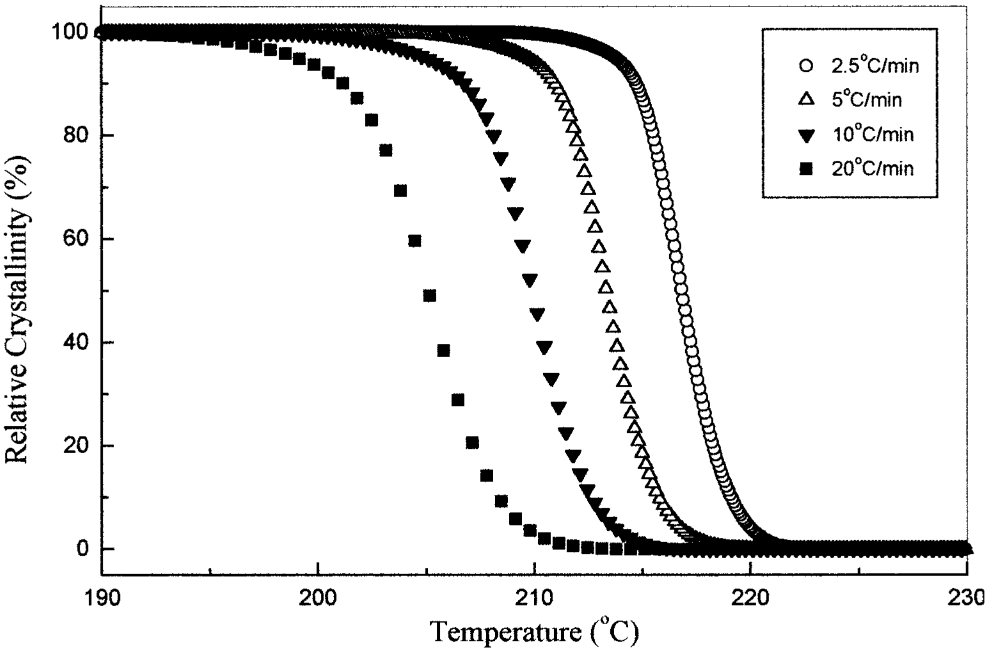

Figure 9. Variation of the relative crystallinity for 17/83 PEBN at various cooling rates.

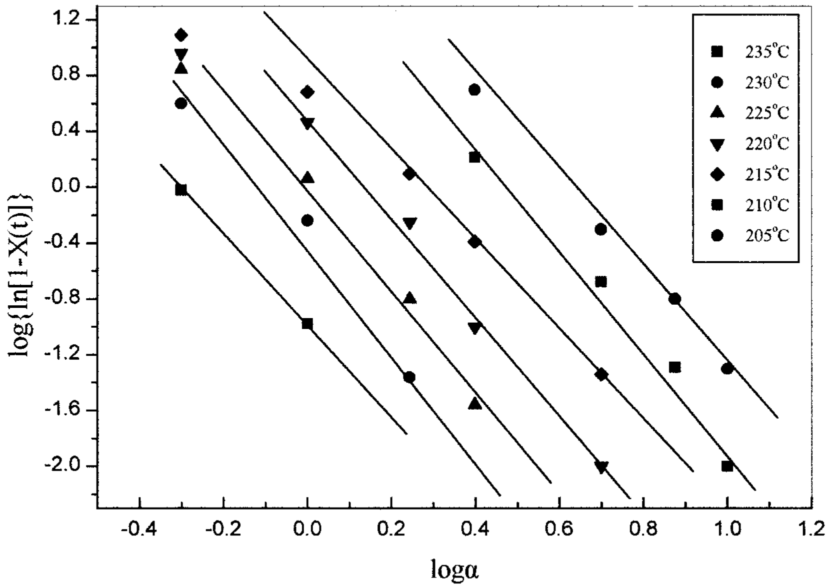

Figure 10. Ozawa plots for the nonisothermal crystallization of PEN.

The crystallinity of the samples was calculated with the density data. Moreover, the heat of fusion of the samples was measured from the DSC melting traces. In this way, values of the enthalpy of fusion for pure crystalline polymers were calculated. It is important that the enthalpy of fusion for pure crystalline PEN was found to be 168 ± 10 J/g; this is almost identical to that reported by Sauer et al.,[29] probably because the calculations were based on about the same value for the density of pure amorphous PEN. In contrast, Buchner et al.[3] reported a value of about 190 J/g, which they calculated by assuming an erroneous value of 1.34 g/cm^3 for the density of amorphous PEN. For PBN, the enthalpy of fusion was found to be 124 J/g. Even though there is still a question about the density values, especially for amorphous PBN, this first experimental finding is of

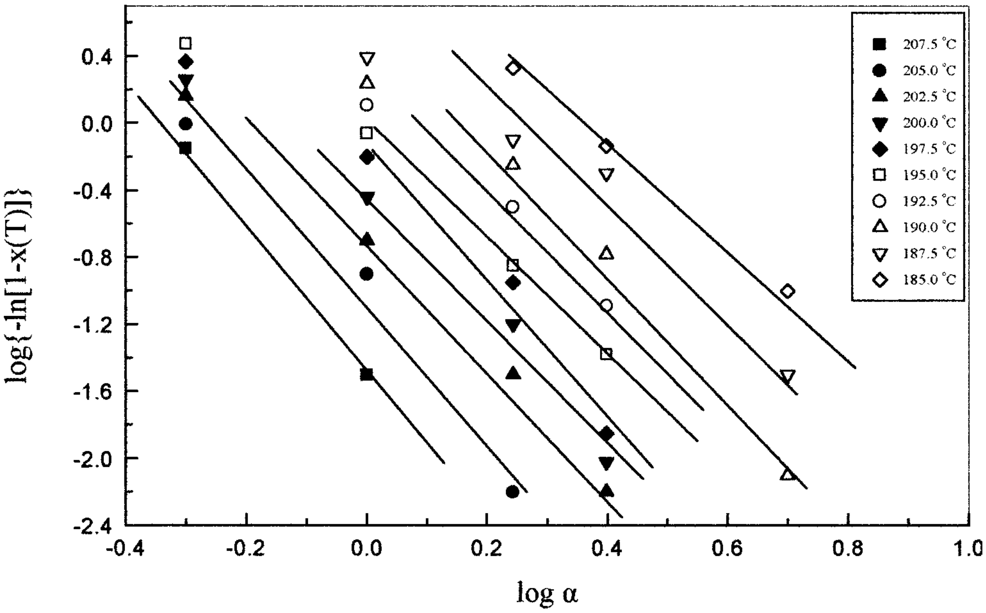

Figure 11. Ozawa plots for the nonisothermal crystallization of 95/5 PEBN.

Table 7. Results of the Ozawa Analysis for the Nonisothermal Crystallization of PEN

Crystallization Temperature (°C)	$k \times 10^7$	n	$t_{1/2}$ (min)
205	100.6467	3.17	0.21
210	51.0858	3.58	0.3
215	5.5030	3.38	0.54
220	1.8656	3.04	0.72
225	0.8423	2.91	0.94
230	0.3969	3.56	1.17
235	0.1057	3.27	1.75

special interest. The crystallinity was also measured with WAXD data. Then, a lower value for the enthalpy of fusion for pure crystalline PEN was calculated, and in general, some deviations can be seen between the values of the enthalpy to which the two methods lead. For PBN, no experimental value for the enthalpy of fusion was available in the literature up to now. The only known value arrived through a theoretical estimation with the group method of Van Krevelen.[30] However, no significant deviation between the theoretical and experimental values was observed for the enthalpy of fusion of PBN.

The estimation of the variation of the enthalpy of fusion of copolymers with the comonomer content can be observed in Figure 4. It is obvious that the enthalpy of fusion and T_m decrease in a similar way because they exhibit their minimum values for the same copolymer composition, which is about 50 mol %. Although all these enthalpy calculations are rough estimations, they have special significance. Such findings can be useful for the validation of theoretical approximations of the copolymer cocrystallization, which usually are based only on T_m measurements.[31]

Table 8. Results of the Ozawa Analysis for the Nonisothermal Crystallization of 95/5 PEBN

Crystallization Temperature (°C)	$k \times 10^7$	n	$t_{1/2}$ (min)
185.0	10.7152	2.76	0.37
187.5	3.3029	2.51	0.54
190.0	2.5621	2.79	0.63
192.5	1.3819	2.72	0.77
195.0	0.6437	3.09	1.02
197.5	0.3997	3.11	1.19
200.0	0.2624	3.16	1.36
202.5	0.1673	3.39	1.52
205.0	0.0772	3.31	1.94
207.5	0.0316	3.29	2.56

Table 9. Results of the Ozawa Analysis for the Nonisothermal Crystallization of 90/10 PEBN

Crystallization Temperature (°C)	$k \times 10^7$	n	$t_{1/2}$ (min)
180.0	2.3796	2.98	0.65
182.5	1.6765	3.50	0.78
185.0	1.1545	3.29	0.85
187.5	0.4296	2.72	1.19
190.0	0.2678	3.09	1.35
192.5	0.2026	3.11	1.48
195.0	0.1452	3.16	1.62
197.5	0.1125	3.39	1.7
200.0	0.0763	3.31	1.94
202.5	0.0549	3.29	2.15
205.0	0.0316	3.32	2.53

Crystallization Kinetics

Isothermal Crystallization

The crystallization kinetics of PEN, PBN, and the copolymers 95/5 PEBN, 90/10 PEBN, 17/83 PEBN, and 2/98 PEBN were studied via DSC. A series of isothermal crystallizations at various temperatures for each homopolymer was carried out via DSC. The relative crystallinity at time t [$X(t)$] was determined from the heat evolved as follows:

Table 10. Results of the Ozawa Analysis for the Nonisothermal Crystallization of PBN

Crystallization Temperature (°C)	$k \times 10^7$	n	$t_{1/2}$ (min)
196	436.51583	2.05	0.04
200	239.88329	2.10	0.06
204	103.99202	2.16	0.09
208	24.54709	2.11	0.18
212	2.97852	2.39	0.54
214	2.18273	2.02	0.57
216	1.46218	2.35	0.73
218	0.89125	2.41	0.90
220	0.34674	2.64	1.30
224	0.02457	3.92	2.34

Table 11. Results of the Ozawa Analysis for the Nonisothermal Crystallization of 2/98 PEBN

Crystallization Temperature (°C)	$k \times 10^7$	n	$t_{1/2}$ (min)
220	0.0199	3.15	3.08
218	0.3548	2.56	1.30
192	251.1889	2.06	0.06
196	125.8927	2.08	0.08
200	79.4328	2.12	0.11
204	12.5892	2.23	0.27
208	2.3988	2.14	0.55
212	1.9952	2.31	0.63
214	1.3182	2.45	0.77
216	0.9724	2.47	0.87
218	0.3548	2.56	1.30
220	0.0199	3.15	3.08

$$X(t) = \Delta H_t/\Delta H_\infty \tag{1}$$

where ΔH_t is the heat evolved at time t and ΔH_∞ is the heat evolved at the end of crystallization.

For the analysis of the isothermal crystallization, the so-called Avrami equation (more correctly termed the Kolmogorov–Mehl–Avrami equation) was applied.[16–20] In the Avrami equation,

$$1 - X(t) = \exp(-kt^n) \tag{2}$$

where n is the Avrami exponent, which is a function of the nucleation process, and k is the growth function, which is dependent on the nucleation and crystal growth. Plots of $\log\{-\ln[1 - X(t)]\}$ versus $\log t$ were constructed. In Figure 5, the Avrami plots for the isothermal crystallization of PEN are shown. In these plots, an initial linear part can be observed, which was used for the estimation of the parameters n and k. The deviation, which can be observed after this first linear part in the Avrami plots, is often attributed to secondary crystallization. This is possibly the explanation for the plots of the PEBN copolymers. From the slope and intersection of the Avrami plots, values of n and k, respectively, were calculated, and the results are summarized in Tables 1–6. It is known that the value of n strongly depends on both the mechanism of nucleation and the morphology of crystal growth and that ideally n will be an integer.[18–20] The values found for the PEBN copolymers ranged between 2 and 2.8, and they may possibly be related to the spherical morphology, diffusion control, and thermal nucleation. However, because crystallization is often too complex, the interpretation of the n values is not always unambiguous.

From these results, it is obvious that the crystallization half-time ($t_{1/2}$) increases with the comonomer content, and this means that the crystallization process becomes slower. In Figures 6 and 7, the dependence of k on the crystallization temperature is shown. It is obvious that this dependence is rather exponential.

The Avrami parameters calculated for PEN are close to those reported by Lee and Cakmak.[32] However, their resins were produced with a different catalyst, and this was probably responsible for the faster crystallization in their case. However, the Avrami parameters for PBN, 2/98 PEBN, and 17/83 PEBN are comparable to those reported by Lee et al.[30]

Nonisothermal Crystallization

From dynamic crystallization experiments, data for the relative crystallinity as a function of temperature can be obtained for each cooling rate. Thus, there is a need to extract data for the relative crystallinity as a function of time at various crystallization temperatures to make direct comparisons with the data from isothermal tests. For such transformations from temperature to time, the cooling rate must be taken into account.[12]

For nonisothermal crystallization studies, crystallizations at various cooling rates should be performed. In all cases for the polymers of this work, S-type curves consistent for a nucleation and growth process were obtained, representing the relative crystallinity as a function of temperature during cooling at a constant cooling rate. As

Table 12. Results of the Ozawa Analysis for the Nonisothermal Crystallization of 17/83 PEBN

Crystallization Temperature (°C)	$k \times 10^7$	n	$t_{1/2}$ (min)
172	10.2323	2.03	0.09
176	4.95496	2.15	0.40
180	1.4563	2.33	0.72
184	0.98126	2.43	0.86
188	0.6345	2.54	1.12
192	0.3041	2.68	1.37
196	0.0152	3.05	3.50

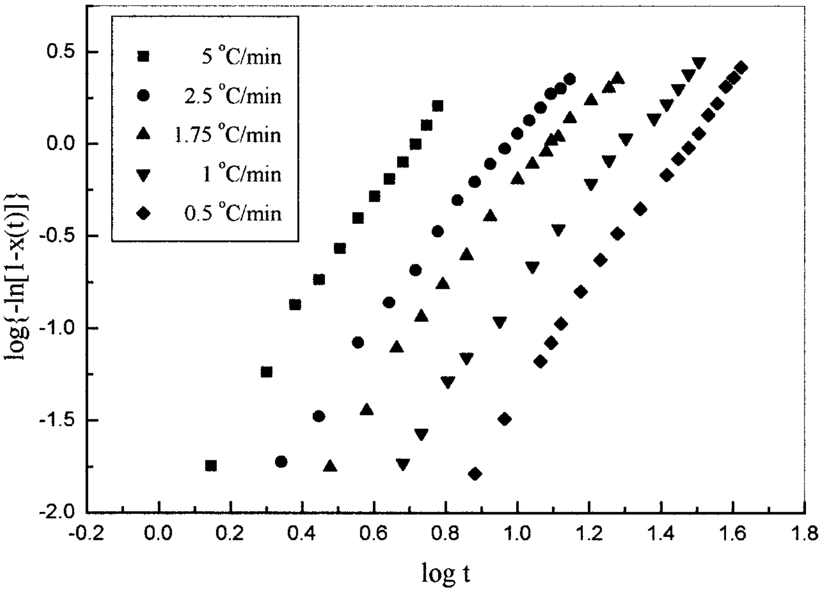

Figure 12. Avrami plots for the nonisothermal crystallization of 95/5 PEBN.

the cooling rate increases, the crystallization temperature range becomes broader, and it shifts to lower temperatures (Figs. 8 and 9).

For the analysis of the experimental results, the Ozawa approach[21] and the modified Avrami approach[22–25] were elaborated.

Ozawa Analysis of Nonisothermal Crystallization

According to the Ozawa theory,[21] the degree of conversion at temperature T [$X(T)$] can be calculated as follows:

$$\ln[1 - X(T)] = k(T)/\alpha^n \qquad (3)$$

where α is the cooling rate, n is the Avrami exponent, and k is the cooling crystallization function. k is related to the overall crystallization rate and indicates how fast crystallization occurs. From the Ozawa equation, it follows that

$$\log\{-\ln[1 - X(T)]\} = \log k(T) - n \log \alpha \qquad (4)$$

From the plotting of $\log\{[1 - X(T)]\}$ versus $\log \alpha$, a straight line should be obtained, and the kinetic parameters n and k can be achieved from the slope and intercept, respectively.

The Ozawa analysis was applied for PEN, 95/5 PEBN, and PEBN 90/10 as well as PBN and the copolymers 2/98 PEBN and 17/83 PEBN. An analysis of nonisothermal crystallization for PEN, 95/5 PEBN, and 90/10 PEBN was performed for slow cooling rates because for rates faster than 5 °C/min, no significant crystallization of these polymers occurs. For PBN, 2/98 PEBN, and 17/83 PEBN, nonisothermal crystallizations were per-

Table 13. Results of the Avrami Analysis for the Nonisothermal Crystallization of PEN

Cooling Rate (°C/min)	k	k'	n	$t_{1/2}$ (min)
0.5	0.0000398	0.0000000016	3.53	280
1	0.0000631	0.0000631	3.38	15.6
1.75	0.0003162	0.01	3.25	3.68
2.5	0.0006309	0.0524807	3.23	2.22
5	0.0015849	0.2754228	3.25	1.33

Table 14. Results of the Avrami Analysis for the Nonisothermal Crystallization of 95/5 PEBN

Cooling Rate (°C/min)	k	k'	n	$t_{1/2}$ (min)
0.5	0.0000417	0.0000000017	3.45	311
1	0.0000537	0.0000537	3.30	17.6
1.75	0.0001220	0.0055316	3.23	4.46
2.5	0.0002455	0.0359749	3.17	2.54
5	0.0004467	0.2137962	3.11	1.45

Table 15. Results of the Avrami Analysis for the Nonisothermal Crystallization of 90/10 PEBN

Cooling Rate (°C/min)	k	k'	n	$t_{1/2}$ (min)
0.5	0.00002519	0.0000000006	3.34	509
1	0.00003162	0.00003162	3.29	20.7
1.75	0.00005119	0.00349025	3.21	5.19
2.5	0.00008318	0.0233345	3.18	2.91
5	0.00019953	0.18197	3.02	1.55

formed at cooling rates ranging from 0.5 to 20 °C/min.

Ozawa plots for PEN and copolymers 95/5 PEBN and 90/10 PEBN are shown in Figures 10 and 11, respectively, and the results are summarized in Tables 7–12. In these plots, we can again see an initial linear part, whereas some curvature is observed in the upper part, as observed in the Avrami analysis for isothermal crystallization discussed previously. This is reasonable because the upper part is related to later stages during which crystallization is retarded, because it takes place in a constrained environment. Ozawa, in his approach, ignored secondary crystallization and the dependence of the fold length on the temperature.[21,12]

Lopez and Wilkes[23] claimed that during cooling, secondary crystallization could not take place because of the continuous decrease in temperature. However, it is known that the Ozawa analysis cannot describe adequately the crystallization kinetics of polymers such as polyethylene, poly(ether ether ketone), and nylon-11, for which a large part of the crystallinity is attributed to secondary crystallization.[12]

Table 16. Results of the Avrami Analysis for the Nonisothermal Crystallization of PBN

Cooling Rate (°C/min)	k	k'	n	$t_{1/2}$ (min)
0.5	0.000316	0.0000001	4.40	35.87
1.0	0.00126	0.00126	3.51	6.03
2.5	0.00631	0.1318	3.24	1.67
5	0.00794	0.3802	3.46	1.18
10	0.00900	0.6243	3.38	1.03
15	0.01000	0.7356	3.28	0.98
20	0.01580	0.8128	3.20	0.95

Table 17. Results of the Avrami Analysis for the Nonisothermal Crystallization of 2/98 PEBN

Cooling Rate (°C/min)	k	k'	n	$t_{1/2}$ (min)
0.5	0.000251	0.000000063	4.02	56.42
1.0	0.000631	0.000631	3.63	6.88
2.5	0.001	0.0631	3.31	2.06
5	0.00125	0.263	3.35	1.33
10	0.00144	0.5199	3.29	1.09
15	0.001585	0.6506	3.26	1.02
20	0.001995	0.7328	3.31	0.98

Avrami Analysis of Nonisothermal Crystallization

The Avrami equation can be modified to describe nonisothermal crystallization.[22–25] For nonisothermal crystallization at a chosen cooling rate, $X(T)$ is a function of temperature. The crystallization temperature can be converted into crystallization time t with the following equation:

$$t = \frac{(T_0 - T)}{\alpha} \tag{5}$$

where α is the cooling rate and T_o is the onset temperature of crystallization.

The Avrami parameters can be estimated from $\log\{-\ln[1 - X(T)]\}$ versus $\log t$. The rate of nonisothermal crystallization depends on the cooling rate. If there is a constant cooling rate, the crystallization rate constant can be corrected as follows:[33]

$$\log k' = \frac{\log k}{\alpha} \tag{6}$$

Table 18. Results of the Avrami Analysis for the Nonisothermal Crystallization of 17/83 PEBN

Cooling Rate (°C/min)	k	k'	n	$t_{1/2}$ (min)
0.5	0.0001259	0.000000158	4.13	70.81
1.0	0.000166	0.000166	3.49	10.90
2.5	0.001949	0.0328095	3.24	2.56
5	0.000218776	0.1853531	3.28	1.50
10	0.002512	0.4365160	3.22	1.15
15	0.000269	0.578096	3.30	1.06
20	0.00031	0.667575	3.23	1.01

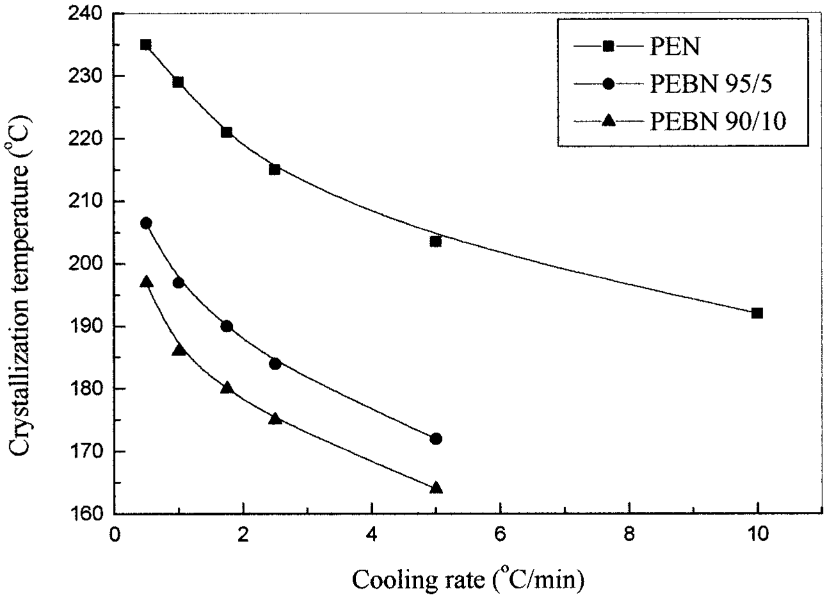

Figure 13. Crystallization peak temperature against the cooling rate for PEN, 95/5 PEBN, and 90/10 PEBN.

Thus, $t_{1/2}$ can be calculated from the corrected crystallization constant (k') with the following equation:

$$t_{1/2} = \left(\frac{\ln 2}{k'}\right)^{1/n} \tag{7}$$

As we can see in Figure 12, two regimes in crystallization exist because the slope of $\log\{-\ln[1 - X(T)]\}$ versus $\log t$ changes. This is common for all the polymers of this work. The slope in the first regime is greater than that in the second regime. The retardation of crystallization should probably

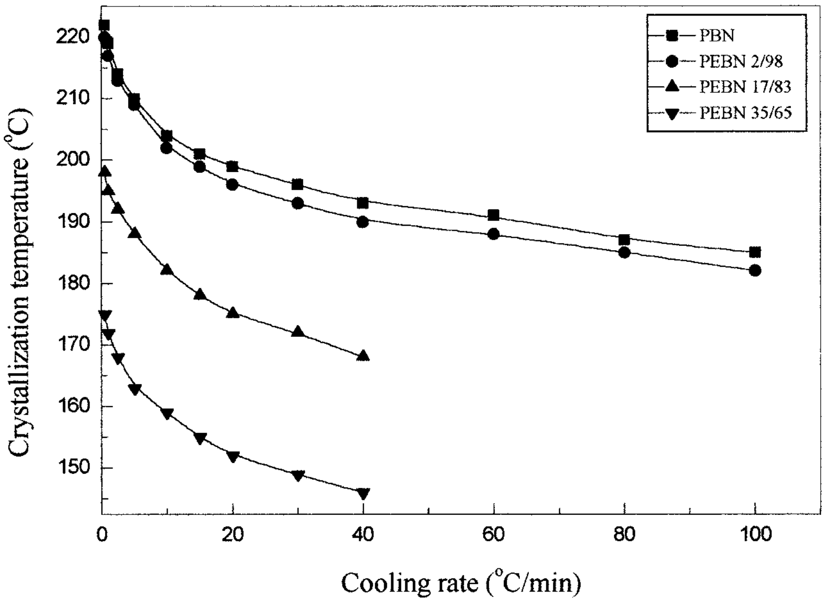

Figure 14. Crystallization peak temperature against the cooling rate for PBN, 2/98 PEBN, 17/83 PEBN, and 35/65 PEBN.

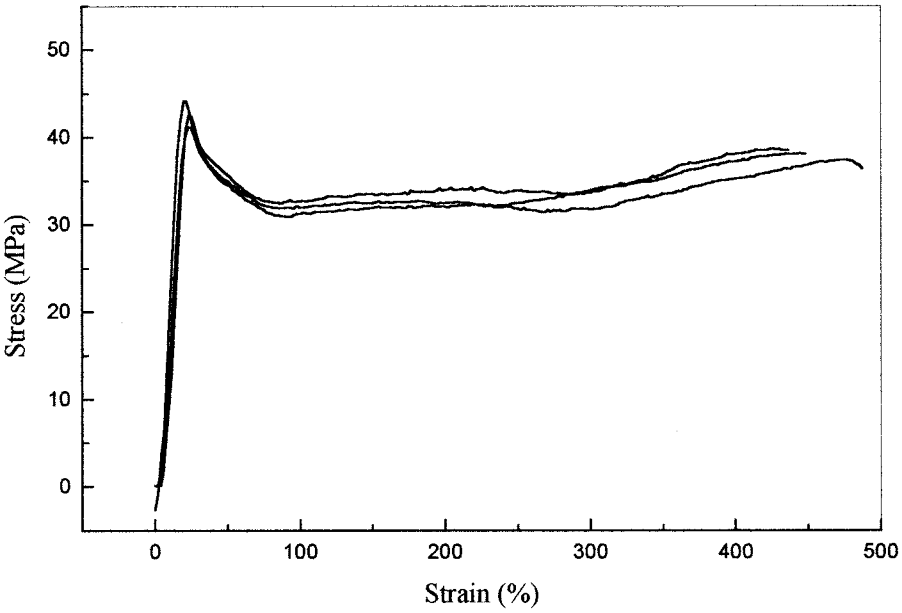

Figure 15. Stress–strain curves for 17/83 PEBN.

be attributed again to the secondary crystallization.

In general, the modified Avrami equation is valid only for the first regime in which the primary crystallization occurs. Therefore, for each cooling run, the Avrami parameters were estimated from the slope and intercept of the plot in the first regime. The Avrami exponent was found to range from 3.0 to 4.4. Values for the exponent decrease as the cooling rate increases, that is, as the supercooling increases. The results of these analyses are summarized in Tables 13–18.

The values of the Avrami exponent are larger than those found by the Ozawa analysis. This has also been reported for other polymers.[33]

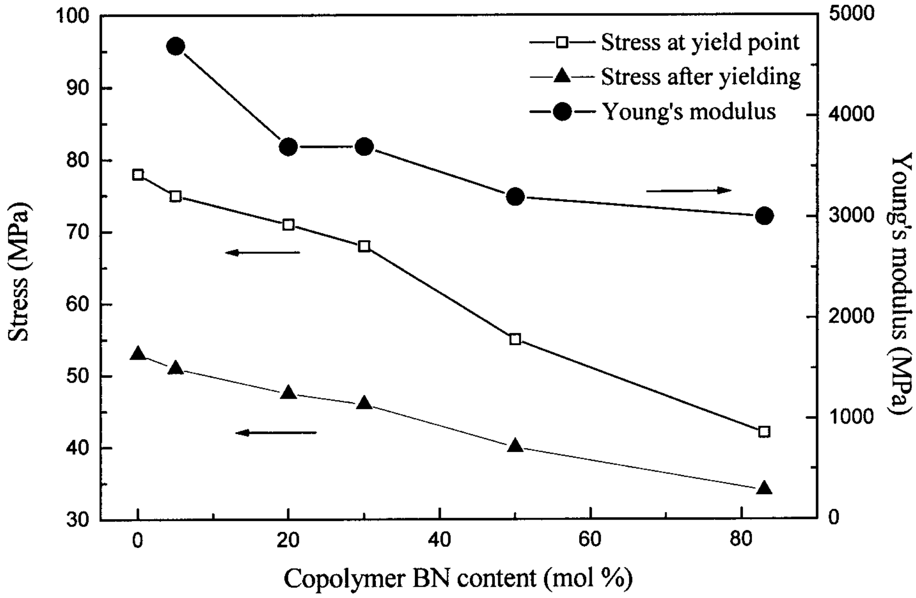

Figure 16. Stress at the yield point, stress after yielding, and Young's modulus against the PEBN copolymer composition.

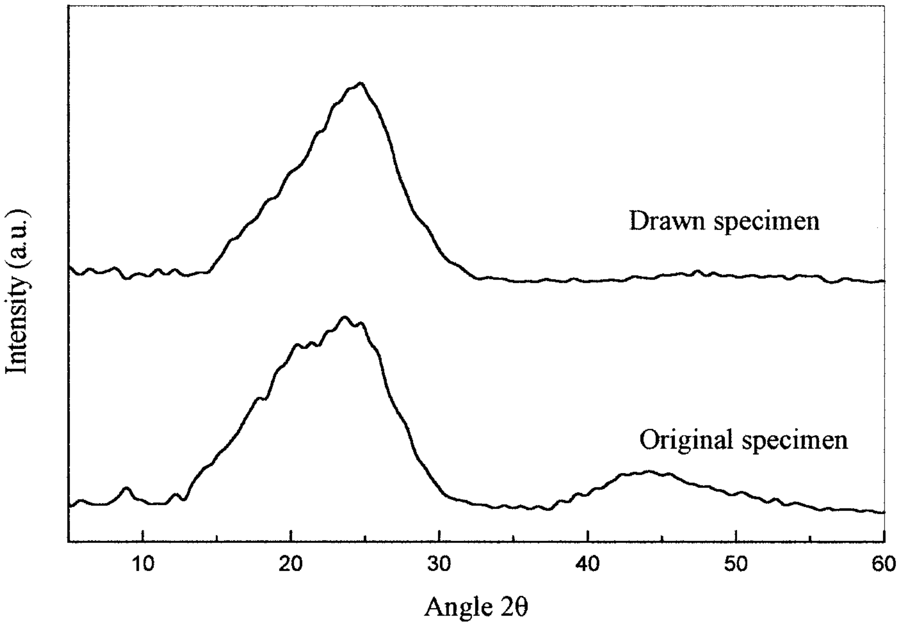

Figure 17. WAXD patterns for 80/20 PEBN specimens.

k increases with an increasing cooling rate, whereas $t_{1/2}$ decreases. This is reasonable because k (or k') and $t_{1/2}$ are measures of the crystallization rate, which becomes faster with supercooling.

From DSC thermograms at various cooling rates, the crystallization peak temperature has been found to decrease with an increasing cooling rate. The respective plots, which show the variation of the peak temperature with the cooling rate, for the PEBN copolyesters are shown in Figures 13 and 14. In these plots, it is obvious that the peak temperature at a given cooling rate decreases with increasing comonomer content, and this means that the crystallization rates de-

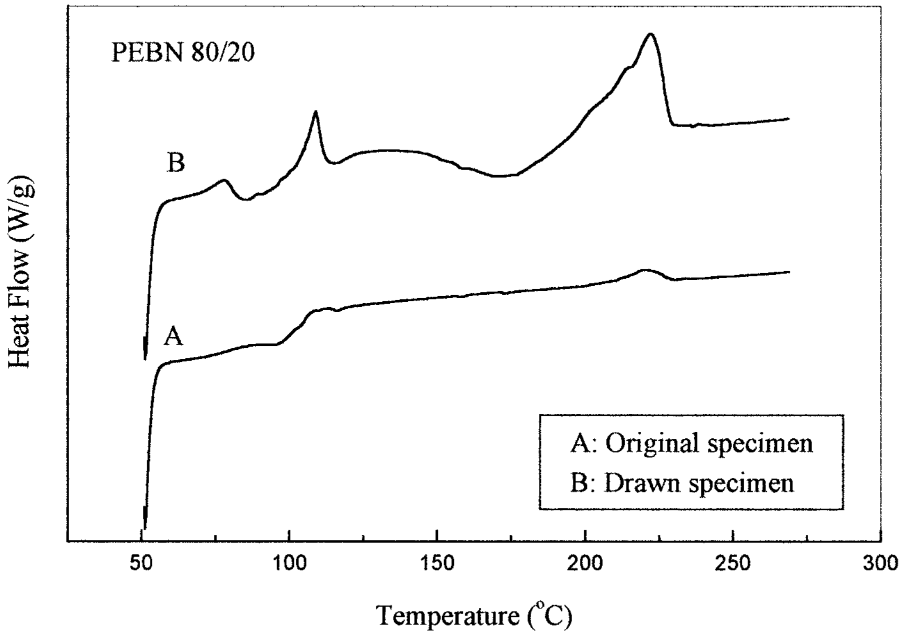

Figure 18. DSC thermograms for 80/20 PEBN specimens.

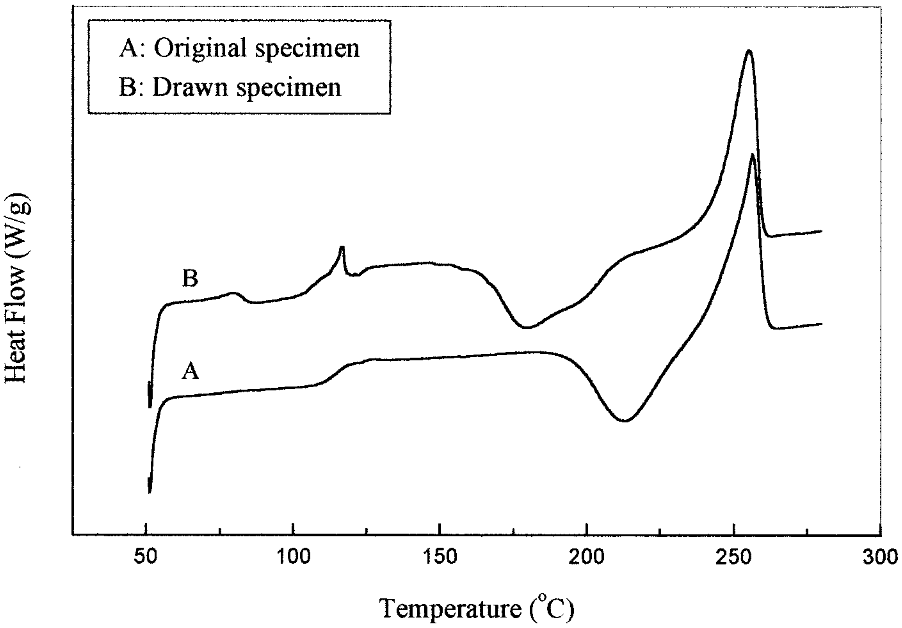

Figure 19. DSC thermograms for 95/5 PEBN specimens.

crease with the comonomer content. Furthermore, the enthalpy of crystallization decreases as the cooling rate increases, so the crystallinity obtained at the end of the experiments decreases as the cooling rate increases, and the maximum crystallinity for a given cooling rate decreases as the comonomer content increases.

Tensile Properties and Morphology of Drawn Specimens

Tensile tests for the copolymers were performed at 23 °C. In Figure 15, the stress–strain curves for the 17/83 PEBN copolymer specimens can be seen. The necking behavior of PEN has been discussed in literature.[5,6] It must be noted that copolymers containing large BN units resulted in the formation of semicrystalline specimens, whereas specimens of copolymers with large contents of ethylene naphthalate units were obtained in the amorphous state after the quenching procedure, which was followed for the specimen preparation.

The stress at the yield point and after yielding decreases steadily with increasing butylene unit content (Fig. 16). The same trend is obvious for the Young's modulus of the copolymers.

WAXD diagrams of the copolymers before and after drawing showed no crystalline reflections (Fig. 17). WAXD patterns shown in Figure 17 were taken with the X-ray beam parallel to the drawing direction. However, the profile that was obtained when the X-ray was parallel to the cross direction was similar. This is probably related to the small draw ratio. In a similar case, for PEN/PEI blends, Cakmak and Kim[34] found that the difference between the profiles of the normal and transverse directions became larger toward the final stage of deformation.

This means that crystallinity cannot be generated during drawing at temperatures lower than T_g. However, in the WAXD diagram of the original specimen, two amorphous halos were observed in contrast to the diagram for the drawn specimen, in which only one halo remained. Also, the shape of the remaining halo was sharper and more symmetrical after drawing. In the DSC traces of the specimens, a different behavior was recorded. Enhanced cold crystallization was observed for the drawn specimens, even in the case of copolymers for which cold crystallization normally would not occur (see Figs. 18 and 19). Such a finding was reported in the literature for poly(ethylene terephthalate).[35–38] In the traces of the drawn specimens, peaks were also observed below T_g. These are probably associated with relaxations of the constrained amorphous phase.

CONCLUSIONS

The WAXD patterns of PEBN random copolymers showed that the crystallization of these copolymers could occur over the entire range of compositions. PEN or PBN crystals were formed, depending on the composition of the copolymers. Melting points decreased with increasing comonomer unit content, and this resulted in eutectic behavior. This was evidence of the isodimorphic cocrystallization of the PEBN copolymers. The variation of the enthalpy of fusion of the copolymers with the composition was estimated, and the picture was found to be analogous to that of the melting points. Isothermal and nonisothermal crystallization kinetic studies showed that the crystallization rates decreased with increasing comonomer units content. The tensile properties of the copolymers were found to decrease with increasing BN content. No crystalline reflections were observed in the WAXD patterns of the initially amorphous specimens after drawing. However, fast crystallization of the drawn specimens occurred with heating above T_g. Thus, it seems that although crystallinity did not evolve during drawing at temperatures below T_g, the amorphous phase was strongly influenced.

The authors are greatly indebted to Amoco Chemicals-Fine Acids (Chicago, IL) for providing DMN.

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