**On the Origin of the Multiple Melting Behavior in Poly(ethylene
naphthalene-2,6-dicarboxylate): Microstructural study as Revealed by
Differential Scanning Calorimetry and X-Ray Scattering**

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SYNOPSIS

In this paper a study on the melting behavior and microstructure of semicrystalline poly(ethylene naphthalene-2,6-dicarboxylate) (PEN) prepared by crystallization from the glass under different annealing conditions is presented. The influence of the annealing temperature (T_a), annealing time (t_a) and the heating rate (R_h) at which T_a is reached on the endothermic behavior of the samples was investigated by means of differential scanning calorimetry (DSC). A dual melting behavior appeared for low R_h values (2 deg.min⁻¹) within the range of $145^{\circ}\text{C} < T_a < 250^{\circ}\text{C}$ and $1 \text{ min} \leq t_a \leq 16 \text{ h}$. Samples subjected to fast heating rates ($R_h = 200 \text{ deg.min}^{-1}$) to reach a $T_a \geq 230^{\circ}\text{C}$ showed DSC traces in which a transition is observed from three peaks to a single melting peak when t_a increases in the 30-240 min range. On the basis of the DSC results, PEN samples were prepared displaying single or dual endothermic behavior. The microstructure of these samples was studied by wide (WAXS) and small-angle X-Ray scattering (SAXS) techniques. The SAXS data were analyzed using the correlation function and interface distribution function formalisms, respectively. In samples with a single melting behavior, microstructural parameters such as the long spacing, the amorphous and the crystalline phase thicknesses are consistent with a lamellar stacking model in which the thickness distributions of both phases are almost the same. For samples exhibiting two melting endotherms, a dual lamellar model which is in agreement with the experimental results is proposed.

Key words: PEN, DSC, dual melting, correlation function, interface distribution function

INTRODUCTION

Poly(ethylene naphthalene-2,6-dicarboxylate) (PEN) is a semirigid polyester, similar to poly(ethylene terephthalate) (PET), containing naphthalene instead of benzene rings in the main chain. The molecular structure of PEN is, consequently, stiffer and its glass transition temperature (T_g) significantly higher than that of PET (about 120°C compared to 70°C). The high T_g - value contributes to an enhancement of the mechanical properties of PEN – tensile modulus, hardness, creep resistance and lower shrinkage^{1,2} – making this polymer attractive for engineering purposes.

The physical properties and morphology of PEN have been studied by several authors, although not so extensively as those of PET. Two different crystal modifications, α and β , are found in the PEN's triclinic unit cell³. Buchner et al.⁴ investigated the structure development from the glass using synchrotron radiation. The influence of crystallization conditions on polymorphism was also studied by these authors. An important conclusion of this study is that both modifications exhibit similar melting temperatures (T_m), that increase upon annealing with no change in crystal modification during or after annealing⁴.

Recent studies have been reported on the physical aging of PEN⁵ and on the emerging morphology as revealed by electron microscopy, during the first stages of crystallization⁶. The latter studies reveal that annealing of an amorphous sample for short times and relatively low temperatures results in a phase separation of non-crystallizable and crystallizable regions giving rise to an incipient dendritic superstructure. Increasing the annealing time provokes further phase separation within the crystallizable regions with the formation of crystalline lamellae and amorphous zones. Even longer annealing times or

higher annealing temperatures leads to an increase in number and size of the crystalline lamellae⁶.

Furthermore, studies on the melting and crystallization behavior of PEN by means of differential scanning calorimetry (DSC) provide evidence for a dual melting behavior induced by annealing^{7,8}. When heated in a DSC apparatus, PEN semicrystalline samples reveal two melting endotherms. The position of the low temperature endotherm was found to be highly dependent upon the time and temperature of annealing. On the contrary, the high temperature endotherm was found to be independent of both parameters⁷. No structural model was proposed at that time to explain sufficiently well the double melting behavior of PEN.

Previous studies on the melting and crystallization peculiarities, mostly in PET and poly(aryl ether ether ketone) (PEEK) samples, suggest that the multiple melting behavior⁸⁻¹¹ is a general feature of the semirigid semicrystalline polymer systems. However, there is still a considerable controversy concerning the structural explanation of the low melting endotherm. As summarized in ref. 9, the morphological models proposed can be categorized into three groups: (i) dual lamellar population, (ii) physical aging and (iii) melting-recrystallization. The first group encompasses two variants, namely the dual lamellar stack model with thin and thick lamellae in *separate* stacks, and the lamellar insertion model where the thin lamellae are inserted between the thicker ones in the *same* stack¹². Despite the fact that many experiments support the dual lamellar stack hypothesis as origin of the low endotherm in PEEK^{9,12} or poly(butylene terephthalate) (PBT)¹⁴, a model which may be valid for all semirigid polymers has not yet emerged. Furthermore, there is still a need for systematic investigations on the melting and crystallization of other polymers, such as PEN, the samples being prepared under various annealing conditions.

The aim of the present paper is to complement the above studies offering a novel analysis of the crystallization and melting behavior of PEN by means of DSC and X-ray scattering methods. Contrary to similar studies where crystallization was conducted from the melt, here we investigated initially amorphous PEN samples, isothermally crystallized at a T_a in the range $T_g < T_a < T_m$ from the glassy state (cold crystallization). The crystallization conditions including temperature and annealing time, as well as heating rate at which the annealing conditions were attained, were varied in a relatively broad range. In this way, samples with different thermal history were prepared displaying either dual or single endothermic behavior. An attempt was also made to shed more light on their supposedly different morphologies by employing DSC and X-ray scattering techniques.

EXPERIMENTAL

Materials and sample preparation

The PEN used in this study (Eastman Chemicals, ref. No PLS 14991) was provided in the form of pellets. The intrinsic viscosity, measured in *o*-chlorophenol at 25°C, was 0.4968 g/dL. The viscosity-average molecular weight $\bar{M}_v = 25.000$ was obtained from the following relation which was shown to be valid for PET¹⁵:

$$[\eta] = 6.31 \times 10^{-4} \bar{M}_v^{0.658} \quad (1)$$

Fully amorphous PEN films with a thickness of 0.2 mm were prepared by mold pressing in the following way. The PEN pellets were firstly dried in vacuum for 24 h at 100°C. Subsequently, they were pressed at 300°C for 2-3 minutes and then quenched to room temperature within 20-30 sec. by letting cold water pass through the pressing plates. To perform cold crystallization experiments, the amorphous PEN films were introduced into

a tightly closing stainless steel chamber that was placed into a vacuum oven. These experiments were carried out in two different modes: (i) gradual heating of the polymer specimen at a rate $R_h = 2 \text{ deg.min}^{-1}$ from room up to the annealing temperature (T_a) and annealing at T_a for various times, or (ii) placing the sample instantly at T_a ($R_h \approx 200 \text{ deg/min}$) with subsequent annealing for a given time t_a . In doing so, the temperature of the PEN sample was controlled with an accuracy of $\pm 0.5^\circ\text{C}$.

Techniques

The density, ρ , of the PEN samples was measured in a density gradient column containing a mixture of carbon tetrachloride and *n*-hexane. The ρ values were employed to calculate the volume crystallinity fraction, χ_c^{vol} , by using the equation:

$$\chi_c^{vol} = \frac{\rho - \rho_a}{\rho_c - \rho_a} \quad (2)$$

where the density of the amorphous PEN regions ρ_a was assumed to be 1.3301 g/cm^3 . The density of the crystalline regions ρ_c was given the value of 1.4007 g/cm^3 derived from the unit cell dimensions of the α -modification³.

The DSC traces were obtained in an indium calibrated Perkin-Elmer DSC-7 instrument at a heating rate of 10 deg.min^{-1} in dry nitrogen atmosphere. Sample weights varied typically in the 8-10 mg range.

Wide angle X-ray scattering (WAXS) patterns of PEN samples with different crystallinities and thermal history were recorded at room temperature on a $\theta - 2\theta$ goniometer Seifert C 3000 using Ni-filtered $\text{Cu-K}\alpha$ radiation. The degree of crystallinity, χ_c^{WAXS} , was calculated by means of the curve fitting procedure given by Blundell and Osborn¹⁶. Two broad Gaussian peaks were used to describe the amorphous halo. The

crystalline peaks were also fitted with Gaussian functions. The value for χ_c^{WAXS} was derived by dividing the sum of the crystalline reflection intensities to the overall intensity (see ref. 14).

Small angle X-ray scattering (SAXS) measurements of PEN samples were performed on the A2 beamline at HASYLAB (Hamburg, Germany). The wavelength of the pinhole collimated X-rays from the synchrotron source was 0.15 nm. The scattered radiation was monitored by a gas-filled, position sensitive detector. The sample-to-detector distance was set at 1450 mm. The samples studied were 0.2 mm thick films with varying crystallinities. In this paper, the SAXS patterns obtained at 50°C are discussed. No difference was observed between them and those obtained at room temperature.

SAXS data analysis

To derive the structural parameters of the semicrystalline samples under investigation, we used the following three methods of evaluation:

Bragg's Law

From the Lorentz corrected SAXS profile, the position of the maximum, q_{max} , was determined and used for calculation of the Bragg's long period, L_B :

$$L_B = \frac{2\pi}{q_{max}} \quad (3)$$

where $q = (4\pi/\lambda) \cdot \sin\theta$ is the scattering vector, and 2θ the scattering angle. L_B represents the sum of the average thickness of the crystal lamellae, l_c , and of the interlamellar amorphous regions, l_a . This method does not directly provide any values for l_a or l_c .

Correlation Function

According to the more elaborated approach of Kortleve and Vonk^{17,18}, in case of isotropic polymers, one can obtain the Fourier transform of the Lorentz corrected SAXS profile, namely the linear correlation function $\gamma_{l,r}$ (CF) as:

$$\frac{\gamma_{l,r}}{Q} = \frac{\int_0^\infty (I - I_b) q^2 \cos(qr) \exp(\sigma^2 q^2) dq}{\int_0^\infty (I - I_b) q^2 dq} \quad (4)$$

Here, I_b is that contribution to the total scattering arising from density fluctuations (liquid scattering), and σ is a term, related to the thickness of the crystal/amorphous interface. Q is the so-called scattering invariant that can be determined by integrating the SAXS profile over all scattering angles, *i.e.*:

$$Q = \int_0^\infty (I - I_b) q^2 dq \quad (5)$$

One advantage of the CF method in contrast to Bragg's law is that, in addition to the long period L , the values for I_a and I_c , the degree of crystallinity within the lamellar stacks (x_{cl}) and the thickness of the boundary between a crystal and the adjacent amorphous region can be obtained¹⁷⁻¹⁹. When considering the structure of an ideal two-phase model, Q can be related to the following morphological variables¹²:

$$Q = k x_{sph} x_{st} \frac{I_c}{I_c + I_a} \frac{I_a}{I_c + I_a} (\rho_c - \rho_{ila})^2 \quad (6)$$

Here, k is a calibration constant, x_{sph} is the volume fraction of the spherulites in the material, x_{st} is the volume fraction of lamellar stacks within the spherulite, ρ_c and ρ_{ila} are the electron densities in the two phases – crystalline and interlamellar, respectively.

Interface Distribution Function

In addition to $\gamma_{l,r}$, one may also calculate the interface distribution function $g_{l,r}$, introduced by Ruland²⁰:

$$\frac{g_{l,r}}{Q} = \frac{\int_0^\infty G_q \cos(qr) \exp(\sigma^2 q^2) dq}{\int_0^\infty (I - I_b) q^2 dq} \quad (7)$$

where G_q is the interference function of the two phase system:

$$G_q = K - (I - I_b) q^4 \exp(\sigma^2 q^2) \quad (8)$$

and K is the Porod constant. It is worth mentioning that $g_{l,r}$ (or IDF) represents a Fourier transform of G_q . On the other hand, IDF is the second derivative of $\gamma_{l,r}$ and gives the probability distribution of finding two interfaces (located between a crystal and the adjacent amorphous region) at a certain distance between each other. The values of IDF are negative if the sequence of the phases is the same at both considered interfaces, *i.e.*, when considering the distance representing L . Positive values of IDF appear in the case when the said sequence is not the same as it is for the distance denoting the crystal thickness²¹. As shown by Stribeck and Ruland²², analyzing the IDF function, one can calculate not only L , l_c , l_a , but also the breadth of their distributions.

CF and IDF can be calculated once the Porod constant K , the liquid scattering profile I_b and the interface correction term σ are estimated. The principles of the subsequent analysis and the evaluation of both CF and IDF are discussed in detail elsewhere²³⁻²⁵. For the data processing in this study the SASDAP software²⁶ was employed. Fig. 1 illustrates an example of CF, IDF and of the structural parameters that can be obtained from these functions.

Data interpretation

In addition to the L_B values obtained from the Lorentz corrected SAXS profile, additional estimates for the long spacing: (1) – from the position of the first maximum of CF (denoted as L_c^M); (2) – from twice the position of the first minimum of CF (L_c^m) and (3) – from the position of the first minimum of IDF (L_I) may be obtained.

From IDF it is also possible to calculate l_a and l_c . Its maxima (Figure 1 shows a sample with only one maximum) correspond to certain lengths. As pointed out by Santa Cruz et al.²¹, the IDF analysis does not identify directly which one of these lengths can be assigned to l_c and which one to l_a . If the number of maxima are two, one may denote the larger length as l_1 , and the smaller as l_2 . The l_1 value will be then the thickness of the more abundant phase within the stack (either amorphous, or crystalline, depending on the sample structure), and l_2 – the less abundant one. For the final assignment of l_1 to l_a or l_c , determination of the volume crystallinity fraction in the sample studied is often appropriate.

In many cases it is advantageous to compare the IDF values for l_c and l_a to those calculated on the basis of the CF. There are several calculation methods based on CF analysis²⁴ from which we employed the one described by²¹:

$$\frac{B}{L_c^M} = x_1(1 - x_1) \quad (9)$$

where B is the position of the first intercept of CF with the r -axis (Figure 1). From the two solutions of the above quadratic equation, the one with the higher value should be ascribed to the larger fraction of the two phases found within the lamellar stacks. For example, in highly crystalline samples, x_1 would correspond to the crystal fraction within the lamellar stacks (denoted as x_{cl}) and $1-x_{cl}$ would, then, represent the amorphous fraction within the stack.

Once the assignment of x_l is made for each particular case, one may calculate the l_a and l_c from the values of L employing the following equations:

$$l_c = x_{cl}L \quad \text{and} \quad l_a = (1 - x_{cl})L \quad (10)$$

where L , as indicated in ref. 21, may take the values of L_c^M , or L_c^m .

RESULTS

Wide Angle X-ray Diffraction

The WAXS patterns of selected PEN samples annealed under different conditions are shown in Fig. 2. The lower curve shows the scattering profile of the starting amorphous sample obtained after melting the PEN pellets for 3 min. at 300°C and quenching at 16-18°C. Cold crystallization of amorphous PEN at $T_a = 145^\circ\text{C}$ for $t_a = 200$ and 400 min leads to degrees of crystallinity χ_c^{WAXS} in the range of 0.1 - 0.2. Prolonged annealing at higher temperatures results in higher crystallinities: for instance, 24 h annealing at 165°C gives $\chi_c^{WAXS} = 0.27$, and annealing for 2 h at 240°C furnishes $\chi_c^{WAXS} = 0.31$. The larger χ_c^{WAXS} - value of 0.40 was obtained when the starting amorphous sample was placed instantly at $T_a = 240^\circ\text{C}$ and kept there for 4 hours. A slower heating rate under the same conditions induced only a value of $\chi_c^{WAXS} = 0.32$. Irrespective of the annealing conditions, all semicrystalline samples show reflections consistent with the α -modification of the unit cell which is characterized by the strong (010) reflection.

Differential Scanning Calorimetry

The calorimetric experiments were grouped into two sets of data: (i) DSC traces of samples of amorphous PEN films annealed in a vacuum oven (see Experimental part), and

(ii) traces of samples crystallized in the DSC apparatus by modeling the same annealing conditions as those of set (i).

Fig. 3 shows the DSC curve of the amorphous PEN used in all annealing experiments. One can see the following thermal transitions: 1) the step at $\approx 120^\circ\text{C}$ attributed to the glass-to-rubber transition, 2) a broad crystallization exotherm in the range of $150\text{--}230^\circ\text{C}$ with an enthalpy $\Delta H_c = -47.8 \text{ J/g}$, and 3) a melting endotherm centered at 268°C , with $\Delta H_m = 49.4 \text{ J/g}$. The annealing temperatures of all cold crystallization experiments covering the range $145\text{--}250^\circ\text{C}$, are indicated in Fig. 3 by arrows.

Influence of the heating rate R_h and annealing temperature T_a .

The thermograms of figures 4a-c (scan rate 10 deg.min^{-1}) illustrate the influence of the annealing temperature T_a and the heating rate R_h on the melting behavior of three glassy samples annealed in vacuum for $t_a = 2 \text{ h}$.

Fig. 4a exhibits the DSC traces obtained for a sample heated at $T_a = 185^\circ\text{C}$. These curves are characteristic of all other samples crystallized for $t_a = 2 \text{ h}$ and $T_a = 165\text{--}200^\circ\text{C}$. In all these cases, two melting endotherms are observed, the higher one having significantly larger intensity. Raising the heating rate R_h from 2 deg.min^{-1} (solid line) up to 200 deg.min^{-1} (dashed line) does not produce in these experiments a significant change in either the intensity of the melting endotherms or the peak temperature of the higher endotherm. The increase of T_a from 145 up to 200°C results, however, in an upward shift of the lower melting endotherm..

Figs. 4b and 4c show the DSC traces of PEN samples, cold crystallized from the glass for $t_a = 2 \text{ h}$ at $T_a = 230^\circ\text{C}$ (4b) and 240°C (4c), respectively. Here, unlike the DSC traces of Fig. 4a, the important influence of R_h on the magnitude of the lower endotherm is

evident: the use of a slow heating rate ($R_h = 2 \text{ deg.min}^{-1}$, solid lines) results in a dual endothermic behavior which is different from that observed in the samples in Fig. 4a. The lower endotherms in Figs. 4b and 4c were found to be sharper and much more intense than those of the samples annealed at $T_a \leq 200^\circ\text{C}$.

The use of a fast heating rate ($R_h = 200 \text{ deg.min}^{-1}$) results in a very different melting behavior (dashed lines). Apparently, for $T_a \geq 230^\circ\text{C}$, R_h strongly affects the melting behavior of PEN. For constant t_a and T_a , a slow heating to T_a gives rise to a dual endothermic behavior, while a fast temperature ramp to the same T_a favors the appearance of a single melting peak. The latter trend is quite evident in Fig. 4c for $T_a = 240^\circ\text{C}$.

Figure 5 comparatively illustrates the DSC traces of amorphous PEN samples crystallized in the range $165^\circ\text{C} < T_a < 250^\circ\text{C}$ for $t_a = 2 \text{ h}$, and $R_h = 2 \text{ deg.min}^{-1}$. A sample annealed at 145°C for $t_a = 16 \text{ h}$ is also shown for completeness. Here, the cold crystallization experiments were performed in the DSC apparatus. A close inspection of the curves in Fig. 5 shows that they reproduce the results obtained in the vacuum oven. For annealing experiments at $T_a \leq 200^\circ\text{C}$ the lower endotherm shifts to higher temperatures without a clear increase in intensity or sharpness. However, for $T_a \geq 230^\circ\text{C}$ there appears an abrupt increase of the low endotherm which becomes sharper and eventually more intensive than the higher endotherm. Fig. 6 represents the temperatures of both endotherms as a function of T_a at a constant $t_a = 2 \text{ h}$. One sees that the melting temperature for the higher endotherm (solid symbols) remains constant at $T_m = 268^\circ\text{C}$, whereas the temperature for the lower endotherm (open symbols) linearly increases from 165°C up to temperatures higher than 250°C .

Influence of the annealing time t_a

The above effects are further examined in the light of the DSC curves as shown in Fig. 7. Curve (a) corresponds to the starting amorphous sample. Curves (b) – (e) depict the DSC traces of samples annealed at $T_a = 145^\circ\text{C}$ for $100 \text{ min} < t_a < 920 \text{ min}$, which were subsequently quenched in ice water. One sees that as t_a increases, the minimum of the exotherm characterizing the dynamic crystallization of the polymer (T_{dc}), first shifts to lower temperatures and then decreases in magnitude. A low melting endotherm appears only in the sample that does not exhibit a clear crystallization peak (curve (e)). The inset in Fig. 7 presents the evolution of χ_c^{WAXS} as a function of t_a within the above interval. One sees that the curve has a sigmoidal shape which shows saturation after $t_a = 400 \text{ min}$.

Fig. 8 displays the evolution of the higher and lower melting endotherms as a function of the annealing time at $T_a = 230^\circ\text{C}$. Here the lower melting endotherm appears during the slow heating ramp to T_a . This endotherm increases in intensity with annealing time at this temperature, this increase being accompanied by a general shift to higher temperatures. The complex shape of the DSC curves obtained after $t_a = 1$ and 120 min . suggests simultaneous occurrence of melting and recrystallization processes.

The plot in Fig. 9 is derived from the DSC curves in Fig. 8 and illustrates the melting temperature variation of, both, the lower (open symbols) and higher (solid symbols) endotherms as a function of $\log(t_a)$ at $T_a = 230^\circ\text{C}$, and $R_h = 2 \text{ deg.min}^{-1}$. While the lower endothermic peak temperature gradually increases following a linear increase, the temperature characterizing the higher endotherm remains nearly constant with t_a .

Fig. 10 shows the DSC traces of cold crystallized PEN in the DSC apparatus at 230°C for different annealing times t_a using a heating rate $R_h = 200 \text{ deg.min}^{-1}$. It is noteworthy that none of these curves displays a low melting, low intensity endotherm such

as in Fig 5 ($T_a = 145\text{-}200^\circ\text{C}$). It is seen that short annealing times (30 and 60 min.) result in a multiple melting behavior. These curves may be considered as being composed of, at least, three melting peaks with different temperature and width. Longer annealing times lead to a dual endothermic behavior. Finally, the 240 min annealing at 240°C induces the appearance of a sharp single melting peak. In all curves the melting temperature of the most intensive peak does not change significantly ($T_m^{peak} = 260 \pm 1^\circ\text{C}$). Up to $t_a = 120$ min, a higher melting shoulder at $T_m^{peak} = 266^\circ\text{C}$ is also observed in the DSC traces.

Preparation of samples with annealing controlled melting behavior

From our DSC studies, we could follow the influence of the annealing conditions – T_a , t_a and R_h – on the melting behavior. Fig. 11 shows the transition from a multiple to a single endothermic behavior, induced by choosing the appropriate annealing conditions. Sample (a) in Fig. 11 was prepared in the vacuum oven by annealing an amorphous PEN specimen for 5 h at 230°C , with $R_h = 2^\circ\text{C}^{-1}$. It reveals two melting peaks: a very sharp one at $T_m = 251^\circ\text{C}$ and a broader endotherm at $T_m = 266^\circ\text{C}$. One should also mention the appearance of a crystallization peak at about 253°C and the rather complex shape of the broader endotherm. Similarly, in Fig. 8 this behavior seems to incorporate the melting of two populations of crystals, as well as melting and recrystallization of the lower melting crystalline phase.

To obtain sample (b), a piece of (a) was additionally annealed for 12 h at $T_a = 225^\circ\text{C}$. As a result, the two endotherms of (a) almost merged into one with a $T_m = 269^\circ\text{C}$. Another 4 h heat treatment of (b) at the same conditions gave rise to sample (c) that displayed a single melting peak with $T_m = 266^\circ\text{C}$ which was quite similar that of the sample in Fig. 4c (2 h at 240°C , dashed lines) and also to sample (e) in Fig. 10 (240 min at 230°C , R_h

= 200 deg.min⁻¹). The corresponding χ_c^{WAXS} values for samples (a), (b) and (c) from Fig. 11 were found to be 0.32, 0.38 and 0.40, respectively. Besides this observation, it is to be noted that $T_a = 225^\circ\text{C}$ used in the additional annealing of sample (a) was well below the T_m of its crystalline phase though above the T_{dc} of the amorphous phase (see Figs. 3 and 7).

Small Angle X-ray Scattering Experiments

The samples used for the SAXS measurements were prepared by annealing the glass in a vacuum oven (see Experimental part). Their annealing conditions, crystallinity and endothermic behavior are summarized in Table 1.

Fig. 12a illustrates the SAXS patterns, showing well defined Bragg peaks, and Fig. 12b – the Lorentz corrected SAXS profiles of the samples.

The values of the long spacings L_B as determined from the curves in Fig. 12b, are given in Table 2. This table also contains values of the two long spacings L_c^m and L_c^M derived from the CF curves depicted in Fig. 13a. A comparison between the long spacing values obtained from CF and Lorentz corrected SAXS profile shows that in all cases $L_B > L_c^M > L_L$. Similar data were reported for PET²¹, PEEK¹² and PBT¹⁴ samples.

The IDF functions of the samples studied are illustrated in Fig. 13b. These functions differ in shape, as well in the position of their maxima and minima. This figure also shows that the IDF of sample 1 (with the single DSC melting endotherm) exhibits the broadest negative and positive peaks, each one comprising two unresolved extremes. Samples 2, 3, 4 displaying dual melting behavior with high magnitude of the lower endotherm, are characterized by smooth curves significantly narrower than those of sample 1. Sample 5 (lower endotherm with lower intensity) reveals the narrowest and smoothest IDF.

DISCUSSION

Differential Scanning Calorimetry

It is generally accepted²⁷ that the occurrence of a double melting behavior of semicrystalline polymers can be due to various reasons. In non-oriented samples these may include 1) reorganization of metastable crystals; 2) recrystallization effects; 3) coexistence of crystals with different structure; 4) coexistence of two populations of crystal lamellae with different thicknesses. On the basis of our WAXS studies (Fig. 2) we can rule out the coexistence of different polymorphic structures or their transition from one to another as a source of multiple melting peaks.

The present DSC experiments reveal the influence of three main factors – t_a , T_a , and R_h – on the number and shape of the endotherms. For PEEK^{9,12} and melt crystallized PEN samples⁷, annealing time has been shown to affect the position and intensity of the low melting endotherm only^{9,12}, without changing significantly the position of the higher melting endotherm. The DSC curves in Fig. 8 show the occurrence of a similar effect in the PEN samples studied here. The plot of Fig. 9 confirms the linear dependence of T_m from the lower endotherm on $\log t_a$ for PEN obtained by cold crystallization. Our DSC experiments reveal in addition, the linear dependence of T_m from the low endotherm on T_a (Fig. 6).

A new finding in the present study is the combined influence of R_h and T_a on the nature of the melting behavior (Figs. 4, 5, 10). Thus, the use of lower rates ($R_h = 2 \text{ deg. min}^{-1}$) always results into two melting endotherms with quite different intensities and melting temperatures (Figs. 4a-4c, Fig. 5, Fig. 8). On the other hand, high heating rates ($R_h = 200 \text{ deg. min}^{-1}$) do not give rise to a low intensity lower melting endotherm (Fig. 10).

As regards the lower intensity endotherm, there are three important aspects to be addressed to: a) its appearance, b) its shift to higher temperatures with the increase of T_a ,

and c) its growth in intensity when $T_a > T_{dc}$ of the amorphous PEN. Curve (e) in Fig. 7 shows that the low melting endotherm appears only after the primary crystallization process at $T_a = 145^\circ\text{C}$ is completed which corresponds to stabilization of the χ_c^{WAXS} - values around 0.20. This behavior can be explained assuming that at low t_a values the incipient crystallizing morphological units (dendrites or axialites)⁶ are surrounded by relatively large areas of amorphous material. As t_a increases at 145°C , the morphological entities start growing and gradually filling the volume of the sample. At the same time, the interstack amorphous phase can crystallize dynamically during the DSC scan at 10 deg. min^{-1} (curves (b)-(d) in Fig 7). The crystallization process slows down significantly when $t_a > 400 \text{ min}$ most probably because of the impingement of morphological units with one another. It is noteworthy that the rest of the amorphous phase between the crystal stacks practically does not crystallize during the DSC scan (Fig. 7, curve (e)). It is at this moment when the low melting endotherm appears for the first time in the DSC traces.

As seen from Fig 5, the increase of T_a in the range of $145\text{-}200^\circ\text{C}$ is not sufficient to induce any change in the intensity of the lower endotherm, irrespective of the R_h value. However, if the annealing temperature surpasses the maximum temperature of the dynamic crystallization T_{dc} registered in the amorphous sample (Fig. 3, Fig. 7 (a); $T_{dc} = 210^\circ\text{C}$), then an increase in T_m and intensity (Figs. 5, 6, 8) is induced in the existing lower endotherm.

From the above results one may conclude that the lower melting endotherm: (i) only appears after some preliminary (or primary) crystallinity is present in the sample, and (ii) originates from the amorphous phase which was not included in the primary crystallization regions. Fig. 14 illustrates schematically the isothermal process of structure development at shorter (primary crystallization) and at longer times (secondary crystallization).

The above conclusions are in agreement with the findings of Krüger and Zachmann²⁸ who provided evidence that in PEEK samples the lower endotherm was caused by melting of some thinner crystals between the lamellar stacks and not by melting of the lamellar stacks themselves. This is in favor of the concept of the so-called dual lamellar stack model^{9,12}.

Small angle X-ray Scattering: Analysis of the Data in the Light of the Dual Lamellar Stack Model

According to the dual lamellar stack model, the amorphous phase is not only located between adjacent lamellae within the lamellar stacks, but also between the stacks, forming the so-called “liquid pockets”. The latter amorphous-rich formations are of considerable size with respect to the long spacing (2000-5000 Å). Secondary lamellae may form out of this interstack material under appropriate crystallization conditions giving rise to a dual lamellar stack structure^{9,12}.

Since the DSC data analysis favors the view of the dual lamellar stack structure, we shall consider this model for the discussion of the SAXS data. The observation that $L_c^M > L_c^m$ derived from the CF analysis (Table 2) leads to the conclusion that the half-widths of the distribution functions of the thicknesses of the amorphous and crystalline phase in the stacks are different. As pointed out by Strobl et al.¹⁸, for an ideal two phase model (*i.e.*, in which the thicknesses of both phases are the same), $L_c^M = L_c^m$. Therefore, the difference $\Delta L = L_c^M - L_c^m$ might be used as a quantitative estimate of the degree of deviation from the ideal two-phase model. As seen from Table 2, the samples crystallized at $T_a = 240$ C, $R_h = 200$ deg.min⁻¹ and $T_a = 225^\circ\text{C}$ display the smallest ΔL values and appear to be closer to the ideal two phase model than the rest of the samples. It is worth noting here, that the former sample

is the only one that shows a clear single melting DSC endotherm (Fig. 11, (c)), while in the latter one the two endotherms merge almost completely (Fig. 11, (b)).

The ΔL values for all other samples are larger. In their DSC traces (Fig. 5, Fig. 11, (a)), the samples annealed at $T_a = 165^\circ\text{C}$, $T_a = 230^\circ\text{C}$ and $T_a = 240^\circ\text{C}$ ($R_h = 2 \text{ deg.min}^{-1}$) respectively, show dual melting behavior. A closer inspection of these data shows that whenever the lower endothermic peak is sharper and higher in magnitude (e.g., in the two latter samples), ΔL in Table 2 is progressively smaller and much closer to that of the samples displaying single melting peak.

If the thickness of, both, crystalline and amorphous phases, and that of the long spacing $L = l_a + l_c$ were constant throughout the entire sample, then IDF would consist of separate positive and negative peaks. On the contrary, smooth curves indicate the occurrence of a broad distribution of these values²¹. Fig. 15a-c shows the fittings of the IDF for three selected PEN samples with different thermal history and melting behavior. Gaussian distributions are assumed for L (first IDF minimum), l_a (first IDF maximum) and l_c (second IDF maximum). The positive parts of the IDF functions of the two samples annealed at $T_a = 240^\circ\text{C}$ are fitted with two Gaussians. For the sample annealed at $T_a = 165^\circ\text{C}$, the positive part of IDF is fitted with a single Gaussian. The results obtained are in agreement with those from the CF and reveal the occurrence of a narrower distribution of crystal thicknesses throughout the sample annealed at $T_a = 240^\circ\text{C}$ ($R_h = 200 \text{ deg.min}^{-1}$), a very broad variance in the sample annealed at $T_a = 165^\circ\text{C}$. The sample annealed at $T_a = 240^\circ\text{C}$ ($R_h = 2 \text{ deg.min}^{-1}$) displays somehow medium variances of size distribution. In the present study we have used IDF analysis to determine the average L , l_a and l_c values and have compared them to those obtained from CF.

The long spacing L_I was determined for each sample as the r - position of the first minimum of IDF (Fig. 13b) (see Tab. 2). The thickness of the less abundant phase within the lamellar stacks, l_i , was also determined from IDF as the r - position of its first maximum (Fig. 1). To enable comparison between data from CF and IDF, the latter parameter was calculated from CF (Fig. 13a) by means of Eqs.(9, 10) assuming that $L = L_c^M$ (denoted in Table 2 by l_i^{calc}). The symbol x_I in Table 2 stands for the fraction of the more abundant phase within the lamellar stacks as calculated from Eq. (9). Then clearly,

$$l_i^{calc} = (1-x_I) L_c^M \quad \text{and} \quad (11)$$

$$l_m^{calc} = x_I L_c^M \quad (12)$$

wherein l_m^{calc} is the thickness of the larger phase within the stacks.

One observes a good agreement between the thicknesses of the less abundant phase within the stacks as calculated from CF (Tabl.2, l_i^{calc}) and those derived from IDF (l_i). Moreover, the data obtained show that this phase does not change its thickness significantly as a function of annealing conditions. On the contrary, the changes in the thicknesses of the more abundant phase (l_2^{cal}) are significantly larger.

At this point the question arises concerning the assignment of l_i and x_I . For this reason, the crystal volume fraction values, χ_c^{vol} , were determined. As seen from Table 2, the χ_c^{vol} values significantly increase with T_a , while all x_I are almost independent on the thermal treatment of the sample showing a value around 0.70. Similar behavior was already reported in earlier studies on PET^{21,29}.

All samples in Table 2 display χ_c^{vol} values in the range between 0.33 and 0.50, being always lower than the corresponding x_I values. It seems logical to accept that for these samples $x_I = x_{cl}$. The physical meaning of this assumption could be that there is a certain amount of amorphous material outside the stacks in which these are embedded, *i.e.*, the

microstructure of these samples would be in agreement with the lamellar stack model. The other option (*i.e.*, $1-x_l = x_{cl}$) would mean that the linear crystallinity within the stacks is lower than the average sample crystallinity which apparently has no physical meaning.

One may assume that in the sample annealed at $T_a = 165^\circ\text{C}$, where the difference $x_{cl} - \chi_c^{vol}$ is the largest of all, the interstack amorphous regions are larger than those within the stacks causing this drastic difference.

Table 2 includes two estimates for the thickness of the crystalline phase. For all samples $l_2^{calc} = l_c$ (derived from CF data), and $L_l - l_l = l_c$ representing the second estimate determined by IDF analysis. These two estimates differ significantly owing to the lower values of L_l as compared to L_c^M . As pointed out by Santa Cruz et al.²¹, the real long spacing L_{true} should be even smaller than L_l , if the values of the variances of l_a and l_c are different, as in our case.

Summarizing, from the SAXS data for the first four samples in Table 2, the following trend is demonstrated:

$$L_B > L_c^M > L_c^m > L_l. \quad (13)$$

For the sample annealed at $T_a = 165^\circ\text{C}$, the order is slightly different:

$$L_B > L_c^M > L_l > L_c^m. \quad (14)$$

The model analyses performed by Verma et al.^{12,30} show that both trends are best described by a dual lamellar stack model. The same authors also demonstrate using model calculations that the absence of a clear second minimum in the IDF function (as with all samples in Table 2) can be explained with overlap effects rather than with the absence of a bimodal lamellar size distribution.

The studies of Santa Cruz et al.²¹ offer a more detailed interpretation of Eqs. 12 and 13. By means of model calculations these authors demonstrated that L_l and L_c^M are always larger than the true value of the long spacing, L_{true} , i.e.,

$$L_c^M > L_l > L_{true}. \quad (15)$$

Furthermore, as regards the L_c^m values and their relation to L_{true} , there are two possibilities:

$$\text{either } L_c^m < L_{true} \text{ or } L_c^m > L_{true} \quad (16)$$

If we combine Eqs. 15 and 16 to exclude the L_{true} value, in the first case when $L_c^m < L_{true}$ Eq. 14 is reproduced. When $L_c^m > L_{true}$ one may obtain an expression equal to Eq. 13. According to the conclusions drawn in ref. 21, this means that for the sample with $T_a=165$ C the variance of the larger thickness (i.e. that of the crystal lamellae) is larger than the variance of the lower thickness which is that of the amorphous phase. For the other samples the opposite trend is established – that the width of the amorphous layer size distribution is greater than that of the lamellar size distribution. These considerations are in agreement with the DSC results. Only the sample with $T_a = 165^\circ\text{C}$ exhibits a dual melting behavior with the lower endotherm being much lower in magnitude and temperature than the higher one (see Fig. 5). Generally, one has to expect such a behavior for all samples annealed at $T_a < 210^\circ\text{C}$ implying large differences in thickness and perfection between the primary and secondary lamellae (see Fig. 16, left). The rest of the studied samples were with a $T_a > 210^\circ\text{C}$ and exhibit either a single melting behavior, or the two endotherms are much closer as to their magnitude and melting temperature than those in the previous case, which results in a narrower variance of the lamellar thickness (see Fig. 16, right).

CONCLUSIONS

1. The melting behavior of PEN samples crystallized from the glass depends not only on annealing temperature and time alone, but also on the heating rate. When crystallization is performed above 210°C, the rate R_h at which this temperature is reached has a major influence on the number of melting peaks in the DSC traces.
2. By conveniently changing the values of T_a , t_a and R_h , it is possible to obtain, at will, semicrystalline PEN displaying single, dual or multiple melting peaks.
3. The present DSC results show that when $T_a < T_{dc}$, the low melting endotherm only appears after certain preliminary crystallinity is already created in the sample. Under such conditions, the low melting endotherm does not increase in intensity even after prolonged annealing times, but only shifts to higher melting temperatures. When $T_a > T_{dc}$, the latter effect is accompanied by an abrupt growth of the low melting peak at low R_h values.
4. If one uses high R_h values, which corresponds to a steep heating ramp, a transition is observed from multiple to single melting endotherm, depending on the annealing time. The DSC data suggest a superimposition of melting and recrystallization on the thermal behavior. This effect deserves special attention and will be elucidated in a forthcoming study.
5. A reasonable explanation about the influence of R_h on the observed melting behavior could be as follows: is when T_a is reached slowly ($R_h = 2 \text{ deg.min}^{-1}$), simultaneous partial cold crystallization and molecular reorganization start taking place below T_a , this process being completed at T_a . When fast heating up to T_a is applied ($R_h = 200 \text{ deg.min}^{-1}$), overall crystallization and reorganization occur at T_a .

6. A direct connection between the endothermic behavior and the microstructure of PEN as revealed by SAXS is highlighted: dual melting DSC peak is shown to correspond to a morphology which is best described by a dual lamellar stack model, the crystalline phase being thicker than the amorphous one. On the contrary, a single melting peak appears to correspond to a morphology more consistent with the finite lamellar stack model having similar thickness distributions in both phases.

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Figure captions

Figure 1 Typical correlation function (CF) and interface distribution function (IDF) showing the main parameters to be used (see the text)

Figure 2 WAXS patterns of PEN samples obtained under different annealing temperature T_a , annealing time t_a and heating rate. χ_c^{WAXS} represents the resultant crystallinity fraction as determined by WAXS.

Figure 3 DSC curve of the starting amorphous PEN obtained at 10 deg.min⁻¹ heating rate. (T_m^{peak} = peak melting temperature). The arrows indicate the temperature at which annealing were performed: (a) - 145°C; (b) - 165°C; (c) - 185°C; (d) - 200°C; (e) - 230°C; (f) - 240°C; (g) - 250°C.

Figure 4 Melting behavior of PEN samples as a function of annealing temperature T_a and heating rate and R_h : solid lines for T_a reached at $R_h = 2$ deg.min⁻¹; dashed lines: - at maximum heating rate ($R_h \sim 200$ deg.min⁻¹).

Figure 5 DSC traces of amorphous PEN films annealed at various T_a for $t_a = 120$ min. and $R_h = 2$ deg.min⁻¹. Only for the bottom curve ($T_a = 145^\circ\text{C}$) t_a was 960 min.

Figure 6 Melting of the low (open symbols) and high temperature endotherms (solid symbols) as a function of T_a . The data are derived from Fig. 5.

Figure 7 DSC traces of PEN samples obtained by annealing of amorphous specimens at $T_a=145^\circ\text{C}$ for $0 < t_a < 960$ min range. (a) - starting sample; (b) - 100 min; (c) - 200 min; (d) - 400 min; (e) - 960 min. The inset represents the evolution of χ_c^{WAXS} as a function of t_a .

Figure 8 DSC traces of amorphous PEN samples annealed at $T_a = 230^\circ\text{C}$ for different times t_a . The annealing temperature was reached at $R_h = 2 \text{ deg. min}^{-1}$.

Figure 9 Time dependence of the low (open symbols) and high (solid symbols) endotherm temperature peaks in PEN samples annealed at $T_a = 230^\circ\text{C}$ for different t_a : (a) - 1 min; (b) - 30 min; (c) - 60 min; (d) - 120 min; (e) - 300 min; (f) - 720 min; T_a reached at a low heating rate (2 deg. min^{-1})

Figure 10 DSC traces of amorphous PEN samples annealed at 230°C for different times t_a . The annealing temperature was reached at $R_h = 200 \text{ deg. min}^{-1}$.

Figure 11 Transition from multiple to single melting peak behavior in semicrystalline PEN: (a) - initially amorphous PEN film annealed for 5 h at 230°C ; (b) - sample (a) after additionally annealing it for 12 h at 225°C ; (c) - sample (b) after 4 further hours at 225°C . In all cases $R_h = 2 \text{ deg. min}^{-1}$.

Figure 12 (a): Experimental SAXS curves and **(b):** Lorentz-corrected SAXS patterns of samples with various χ_c^{WAXS} -values. (For sample designation see Table 1). The patterns are normalized in respect to the primary beam. The intensity scaling is given in arbitrary units.

Figure 13 (a): Linear correlation function curves and **(b):** interface distribution function curves for PEN samples obtained at 50°C. (For sample designation see Table 1).

Figure 14 Schematics showing the effect of the annealing time t_a on microstructure annealing isothermally at $T_a = 145^\circ\text{C}$. At $t_a < 400$ min, primary crystallization takes place (left). When $t_a > 400$ min, primary crystallization is completed and secondary crystallization starts by formation of thinner lamellae located within the interstack amorphous regions.

Figure 15 Interface distribution functions of three PEN samples with different thermal history and melting behavior: **(a):** single DSC peak; **(b):** dual endothermic behavior; **(c)** - two endotherms. (see the text).

Figure 16 Schematic representation showing the effect of annealing temperature T_a on microstructure. At a $T_a \leq 210^\circ\text{C}$ (left), a dual lamellar stack distribution is to be expected inducing the appearance of two melting peaks in the DSC traces. At $T_a > 210^\circ\text{C}$ (right), high values of the heating rate R_h and when t_a is long enough, a more homogeneous distribution of thicker lamellae appears giving rise to a single melting behavior.

Table 1 Designation and characterization of the PEN samples used for SAXS measurements. (t_a = annealing time; T_a = annealing temperature; R_h - rate at which T_a was reached, χ_c^{WAXS} - WAXS crystallinity fraction).

Sample	Annealing conditions			χ_c^{WAXS}	Endothermic behavior (DSC)
	t_a , h	T_a , °C	R_h , deg/min		
1	4.0	240	200	0.40	single, ^{a)}
2	4.0	240	2	0.38	double ^{b)}
3	4.0	230	2	0.32	multiple ^{c)}
4 ⁺⁾	12.0	225	2	0.38	double, merging ^{d)}
5	24.0	165	2	0.27	double ^{e)}

NOTES: ⁺⁾ Sample 4 produced from sample 3 applying the conditions indicated

^{a)} DSC curve identical to curve (c) in Figure 11

^{b)} DSC curve identical to the curve with $T_a = 240^\circ\text{C}$ in Figure 5

^{c)} Curve (a) in Figure 11

^{d)} Curve (b) in Figure 11

^{e)} DSC curve identical to curve with $T_a = 165^\circ\text{C}$ in Figure 5

Table 2 Structural parameters of the PEN samples studied, as derived by various methods of SAXS data processing:

L_B – the long spacing as computed from the Lorentz-corrected SAXS curves in Fig. 12b;

L_c^m and L_c^M – long spacings calculated from the CF functions in Fig. 13a;

L_{I1} – long spacing as obtained from IDF in Fig. 13b

x_I – fraction of the more abundant phase within the lamellar stacks as calculated from Eq (9)

χ_c^{vol} – volume crystallinity fraction derived from Eq (1)

l_I – thickness of the less abundant phase within the lamellar stakes as determined from IDF

l_I^{calc} – thickness of the less abundant phase within the lamellar stakes as calculated from Eq (10)

l_2^{calc} – thickness of the more abundant phase within the lamellar stacks as calculated from Eq (10)

Sample ^{a)}	L_B^* Å	L_c^m Å	L_c^M Å	ΔL_c Å	x_I	$1-x_I$	χ_c^{vol}	L_{I1} Å	l_I^{calc} , Å	l_2^{calc} Å	$L_{I1}-l_I$ Å
1	135	118	126	8	0.69	0.31	0.48	103	37	87	66
2	126	100	117	17	0.70	0.30	0.43	96	34	82	62
3	119	96	111	15	0.68	0.32	0.45	91	35	76	56
4	123	108	114	6	0.69	0.31	0.50	95	35	78	60
5	106	82	102	20	0.71	0.29	0.33	91	35	70	56

NOTE: For further details about the annealing conditions and sample designation see Table 1

Figure 1 Z. Denchev et al., On the Origin of the Multiple Melting Behavior...

Figure 2, Z. Denchev et al., On the Origin of the Multiple Melting Behavior...

Figure 3 Z. Denchev et al., On the Origin of the Multiple Melting Behavior...

Figure 4 Z. Denchev et al., On the Origin of the Multiple Melting Behavior...

Figure 5 Z. Denchev et al, On the Origin of the Multiple Melting Behavior...

Figure 6 Z. Denchev et al., On the Origin of the Multiple Melting Behavior...

Figure 7 Z. Denchev et al., On the Origin of the Multiple Melting Behavior.....

Figure 8, Z. Denchev et al., On the Multiple Melting Behavior of ...

Figure 9 Z. Denchev et al., On the Origin of the Multiple Melting Behavior...

Figure 10 Z. Denchev et al, On the Origin of the Multiple Melting Behavior...

Figure 11 Z. Denchev et al., On the Origin of the Multiple Melting Behavior...

Figure 12 Z. Denchev et al., On the Origin of the Multiple Melting Behavior...

Figure 13 Z. Denchev et al., On the Origin of the Multiple Melting Behavior...

Figure 14 Z. Denchev et al., On the Origin of the Multiple Melting Behavior...

Figure 15 Z. Denchev et al., On the Origin of the Multiple Melting Behavior...

$t_a = 240 \text{ min}$

$T_a \leq 210^\circ\text{C}$

$T_a > 210^\circ\text{C}$, fast heating

Figure 16 Z. Denchev et al., On the Origin of the Multiple Melting Behavior...