Kinetics of crystallization and melting behaviour of poly(ethylene naphthalene-2,6-dicarboxylate)

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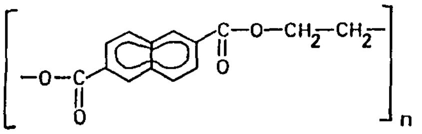
The crystallization and melting of poly(ethylene naphthalene-2,6-dicarboxylate) (PEN) has been investigated by differential scanning calorimetry and by wide angle X-ray scattering using synchrotron radiation. The material can be crystallized in two different crystal modifications called α and β. At crystallization temperatures up to 200°C only the α-modification is formed. Above this temperature, the β-modification is obtained if the material had been molten at 280°C, while the α-modification is formed if the temperature of the melt was raised to 320°C. The half times of crystallization as a function of temperature show a broad minimum ranging from 180 to 240°C. Under usual conditions, both modifications melt at 272°C. However, by applying a special annealing procedure, the melting points of both modifications can be raised to up to 290°C.

(Keywords: poly(ethylene naphthalene-2,6-dicarboxylate); crystal modifications; kinetics of crystallization; melting point; d.s.c.; synchrotron radiation)

INTRODUCTION

The crystallization and melting behaviour of poly(ethylene terephthalate) (PET) has been studied by various authors[1–3]. There also exist investigations on the influence of an increasing number of CH_2 units on the properties of PET[4]. For example, the glass transition temperature, the melting point, and the half time of crystallization are decreased considerably by such atomic units. Another important aspect is the influence of an increase in stiffness of the molecules on the properties of the material. A material with molecules which are stiffer than those of polyethylene terephthalate is poly(ethylene naphthalene-2,6-dicarboxylate) (PEN), which contains a naphthalene ring instead of the benzene ring in PET:



The synthesis of PEN has been described in the patent literature[5]. There it is reported, that PEN may crystallize. The unit cell was determined by Mencik[6]. It is triclinic ($a=0.651$, $b=0.575$, $c=1.32$ nm, $\alpha=81.33$, $\beta=144$ and $\gamma=100°$). The density is $1.407\ \mathrm{g\,cm^{-3}}$. The chains lie parallel to the c-axis. One chain passes through each unit cell. It is also reported in the patent literature that, by means of a special spinning process[5] or special annealing process[7], a material with a higher melting point and with better mechanical strength is obtained, which crystallizes in another crystal modification.

In a previous publication[8] we have shown that the second crystal modification can also be obtained under usual crystallization conditions. The unit cell was determined[9]. It is triclinic too ($a=0.926$, $b=1.559$, $c=1.273$ nm, $\alpha=121.6$, $\beta=95.57$, $\gamma=122.52°$, density $=1.439\ \mathrm{g\,cm^{-3}}$). Four chains pass through each cell. The chains are not completely extended; every naphthalene ring is twisted by 180°. We call the modification mentioned first and determined by Mencik α, and the other one β.

In this paper, we report some results on the kinetics of crystallization, on the melting behaviour, and on the crystallization conditions leading to the different crystal modifications.

EXPERIMENTAL METHODS

The glass transition temperature and the crystallization during heating and cooling as well as the melting was investigated by a Perkin Elmer DSC IV. The melting point was determined as the temperature at which melting was completed. The observed temperatures were extrapolated to zero heating rate. Densities were measured in a density gradient column containing a mixture of carbon tetrachloride and n-hexane. Gel permeation chromatography (g.p.c.) measurements were performed at 20°C using Bondagel columns manufactured by Waters. The solvent used was hexafluoroisopropanol-2. The intrinsic viscosity was determined in the same solvent at 30°C. Previously it has been shown that no degradation takes place in this solvent, if it is purified in a special way[10].

Films were obtained by using a heating press and a special device for keeping the samples *in vacuo* during heating and pressing[11]. The rate of isothermal crystallization was determined by means of wide angle X-ray scattering employing synchrotron radiation. The measurements were performed in the EMBL-laboratory at DESY in Hamburg in collaboration with Dr M. Koch using a double focusing camera[12] and a position sensitive one-dimensional Gabriel counter. The samples were

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heated in a vacuum furnace with low heat capacity so that temperature changes of 100°C could be obtained in less than 30 s. Further details are given in other publications[13,14].

The wide angle X-ray scattering of samples crystallized in different ways was also observed by using a conventional goniometer (Siemens D 500).

SYNTHESIS OF THE MATERIAL

The polymer was synthesized from naphthalene-2,6-diaciddimethyl-ester and ethylene glycol using 0.03 mol% antimony trioxide and 0.112 mol% manganese acetate as catalysts. The mol% values refer to the amount of ester. In a first process a transesterification between the two substances took place followed by polycondensation. The apparatus used was the same as that for the polycondensation of polyethylene terephthalate described earlier[15]. Both steps of the reaction occur without interruption in the same tube. The temperatures applied are shown in *Figure 1*. The decrease of pressure before polycondensation was performed very slowly to avoid an extraction of the material. The polycondensation times were 20 and 60 min.

To get large molecular weights, extremely pure materials had to be used for the synthesis. Dimethyl naphthalene-2,6-dicarboxylate was obtained from EGA-Chemie and was modified by sublimation at 160°C and 2 mbar. The ethylene glycol was obtained from Merck and was purified by boiling with metallic sodium for 1.5 h followed by distillation.

RESULTS

Characterization of the material

The intrinsic viscosities of the PEN in hexafluoroisopropanol at 30°C were 0.480 for the material polycondensed for 20 min and 0.565 for that polycondensed for 60 min.

The g.p.c. curves of the two materials are shown in *Figure 2* together with the curves of two polyethylene terephthalate samples having comparable elution times and known molecular weights. One can see that the PEN samples show similar molecular weight distributions to the PET samples and that the distribution is uniform. The peak at small elution time corresponds to dimethyl terephthalate (DMT) which was added as a standard. The peak next to the one for DMT is probably due to a small amount of oligomer present in the sample.

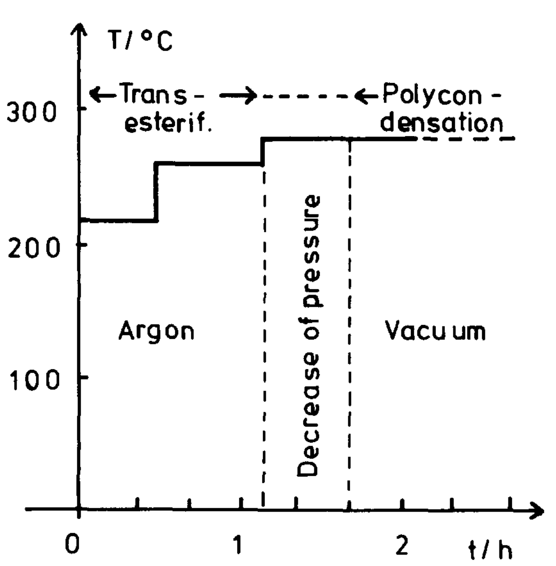

Figure 1 Change of temperature during transesterification and polycondensation

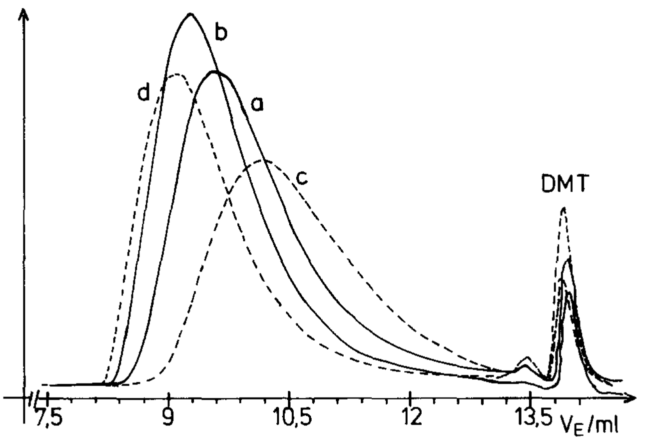

Figure 2 G.p.c. curves of PEN samples in comparison with PET samples. a, PET, polycondensation time 20 min; b, PEN, polycondensation time 60 min; c, PET, $M_w = 14200$; d, PET, $M_w = 48000$

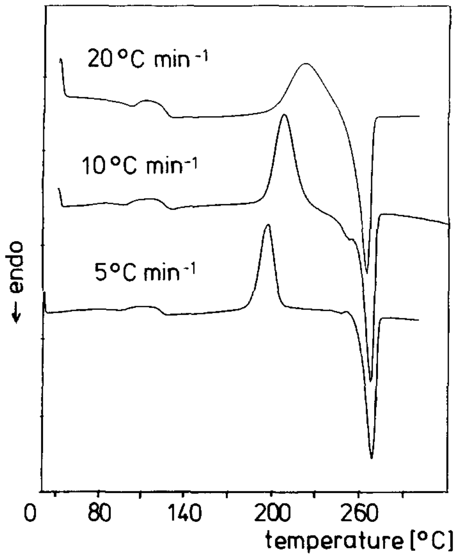

Figure 3 D.s.c. curves of amorphous PEN obtained at three different heating rates

D.s.c. measurements

Figure 3 shows the differential scanning calorimetry (d.s.c) curves obtained with different heating rates for PEN samples which had previously been molten at 280°C and quenched in ice water. One can see a step in the specific heat at 120.4°C corresponding to the glass transition temperature. The peak in the region from 170 to 240°C is caused by crystallization. The end of the following endothermal peak corresponds to the melting point (271°C). While the melting peak and the glass transition step are only weakly influenced by heating rate, the peak caused by crystallization depends strongly on the rate. From this dependence, one can estimate that the half time of crystallization as a function of temperature must have a broad minimum extending from 170 to at least 240°C; the values within this minimum must lie in the range of a few minutes.

Figure 4 shows the d.s.c. curves of PEN samples which, previously, were quenched from the melt and crystallized at different temperatures. The sample crystallized at 180°C shows a melting point at 270°C. In addition a small peak is observed just above the crystallization temperature. As the intensity of this peak changes with heating rate it is attributed to partial melting and recrystallization. According to X-ray investigations this sample is crystallized in the α-modification.

The sample crystallized at 240°C has the same melting point as the sample crystallized at 180°C. According to X-ray scattering, this sample is crystallized mainly in the β-modification.

An interesting effect is observed if the sample crystallized at 240°C is annealed for longer at temperatures close to the melting point, for example for 20 min at 268°C followed by 4 h at 272°C. As shown in *Figure 4*, an increase of the melting point to 287°C is observed. No recrystallization is observed if the sample is heated up immediately to 272°C or if the annealing takes place at temperatures lower than about 262°C. A more detailed study of this effect was performed by X-ray scattering and is reported below.

With the crystalline samples, the step corresponding to the glass transition is very small though the degree of crystallinity is < 50 % (see below). The transition seems to be broader and shifted to higher temperatures (125–140°C) than for the amorphous samples. This shows that the formation of crystals affects the mobility of the chains in the amorphous regions, similar to the effect observed with poly(ethylene terephthalate)[16,17].

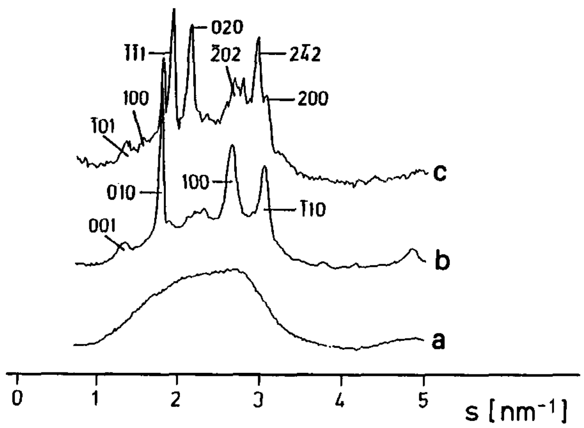

Figure 5 Wide angle X-ray scattering of PEN. a, Sample quenched from 290°C in ice–water, amorphous; b, sample quenched as in a and then crystallized for 2 h at 210°C, α-modification; c, sample crystallized from the melt for 45 min at 240°C, mainly β-modification

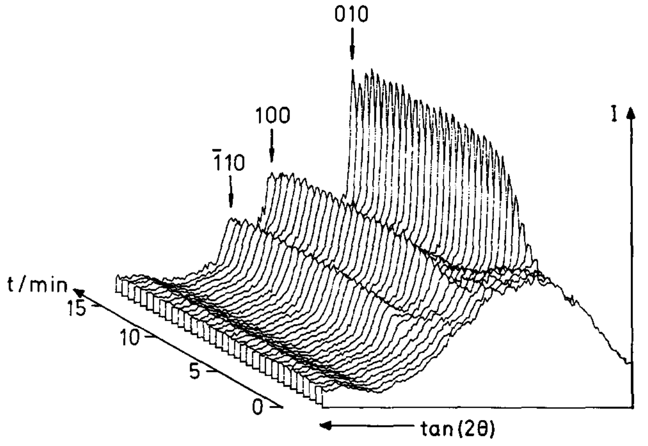

Figure 6 Change of wide angle X-ray scattering during crystallization of PEN at 190°C after heating from the glassy state. The diagram was obtained by using synchrotron radiation

X-ray scattering

Isothermal crystallization. Figure 5 shows the scattering curves of a sample quenched in ice–water after melting at 290°C for 10 min, of a sample crystallized for 2 h at 210°C after quenching and of a sample crystallized for 45 min at 240°C after quenching. The quenched sample can be considered to be amorphous. The sample crystallized at 210°C shows the crystal reflections reported by Mencik[6], which are consistent with the unit cell of the α-modification described in the Introduction. The sample crystallized at 240°C shows crystal reflections which have positions other than those of the former sample. The only exception is the reflection corresponding to the very strong 010-reflection of the α-modification. This sample is crystallized mainly in the β-modification. However, according to the 010-reflection just mentioned, a small amount of α-modification seems to be present in this sample too.

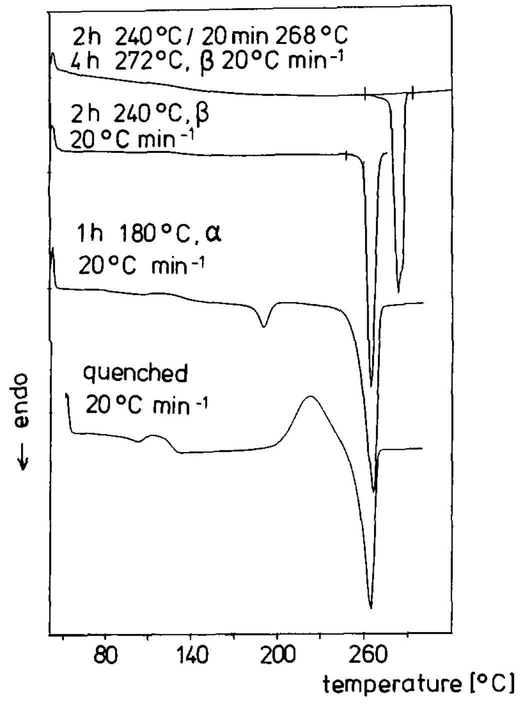

Figure 4 D.s.c. curves of PEN quenched from the melt and crystallized at different temperatures. Heating rate: 20°C min^{-1}

A suitable method for studying the kinetics of crystallization as well as the conditions under which the β-modification is formed is to measure the change of wide angle X-ray scattering during isothermal crystallization using synchrotron radiation. *Figure 6* shows the change of the scattering curve with crystallization time. Such curves allow the determination of kinetic parameters like the half-time of crystallization, and at the same time show which crystal modification is formed.

Figure 7 shows the half-time of crystallization τ as a function of the crystallization temperature T_c after melting the samples at $T_m = 280°C$ for 5 min. In the case when the α-modification was formed, τ was determined by measuring the increase of the intensity of the α-010

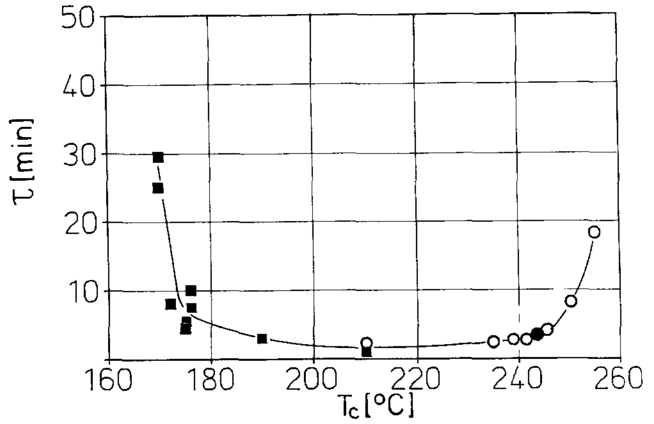

Figure 7 Half-time τ of crystallization of PEN as a function of the crystallization temperature T_c after melting at 280°C. ■, α-modification, crystallized from the glass; ○, β-modification, crystallized from the melt; ●, β-modification, crystallized from the glass

reflection. For the β-modification τ was determined from the β-020 reflection. Square symbols indicate that the samples crystallized in the α-modification, while circles are used if crystallization occurred mainly in the β-modification. Open symbols show the results of samples directly cooled from the melt to the crystallization temperature T_c, while full symbols represent the results obtained from samples which were first quenched from the melt to 0°C and afterwards heated to T_c.

A curve showing a broad minimum is obtained. The values of the β-modification continue from those of the α-modification. One can also see that the half time of crystallization is the same no matter whether the sample is directly cooled to the crystallization temperature from the melt or whether it is first quenched to room temperature and afterwards heated rapidly to the crystallization temperature. This is due to the fact that, even at the minimum of the curve, the half-time of crystallization is comparatively large, so that it is possible to freeze in completely the molten state without any nucleation taking place during quenching.

Figure 8 represents the results obtained after melting for 5 min at $T_m = 300$°C. The results are similar to those in *Figure 7*, but the half-times of crystallization are slightly larger.

Figure 9 represents the half-times of crystallization measured after melting for 5 min at $T_m = 320$°C. In this case, at all crystallization temperatures, only the α-modification is obtained. The half-times of crystallization measured after transferring the samples from the melt directly to the crystallization temperature are much larger than after melting at 280 or 300°C. If, however, the samples are quenched in ice–water before being crystallized, the half times of crystallization are similar to those in *Figures 7* and *8*. Obviously, at 320°C crystal nuclei are destroyed to a larger extent than at 300 and 280°C. During quenching below 180°C, new crystal nuclei are formed, which markedly enhance the crystallization after subsequent heating.

Recrystallization and melting. An amorphous sample of PEN was crystallized for 16 min at 240°C. Afterwards the temperature was raised to 275°C at a rate of 3°C min^{-1}. During the whole procedure the change in wide angle X-ray scattering was observed using synchrotron radiation. *Figure 10* shows the results. In *Figure 10(a)*, one can see the change of the scattering pattern during the period of heating from 240 to 275°C. In *Figure 10(b)*, temperature and intensity of the 020-reflection are plotted as functions of time. As the scattering patterns demonstrate, at 240°C, the sample mainly crystallized in the β-modification. During the subsequent heating the crystals remained stable up to about 270.5°C. At this temperature melting occurred in agreement with the results obtained by d.s.c. (see *Figure 3*).

A different result is obtained when the heating is interrupted by annealing at constant temperatures (see *Figure 11*). After crystallization at 240°C the sample was heated to 270°C, annealed at this temperature for 45 min, then heated to 280°C, annealed at this temperature for 5 min, and finally heated to 295°C. At 270°C, one recognizes a decrease of the intensity of the crystal reflections (partial melting) followed by an increase (recrystallization). Due to this process the melting point is raised to 286°C, similar to the result obtained by d.s.c. (see *Figure 4*). During recrystallization no change in the crystal modification and no considerable change in the half width of the crystal reflections could be observed.

To get more information on the recrystallization process, small angle X-ray scattering was measured in a similar experiment. *Figure 12* shows the result. In this case the annealing was performed at 265°C. In *Figure*

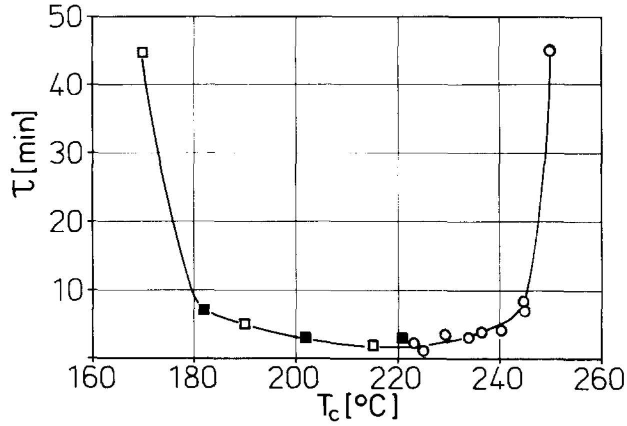

Figure 8 Half-time τ of crystallization of PEN as a function of the crystallization temperature T_c after melting at 300°C. □, α-modification, crystallized from the melt; ■, α-modification, crystallized from the glass; ○, β-modification, crystallized from the melt

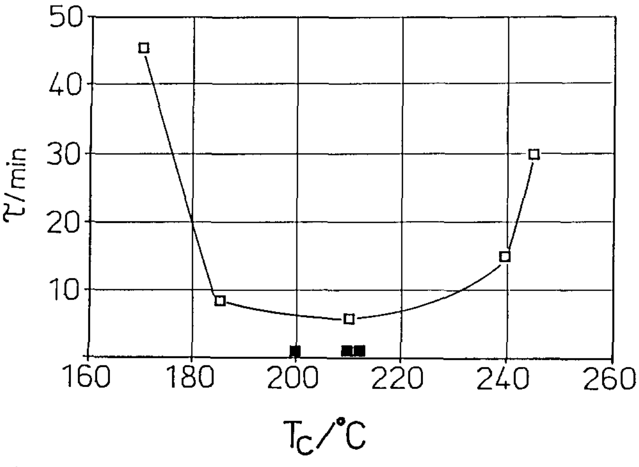

Figure 9 Half-time τ of crystallization of PEN as a function of the crystallization temperature T_c after melting at 320°C. □, α-modification, crystallized from the melt; ■, α-modification, crystallized from the glass

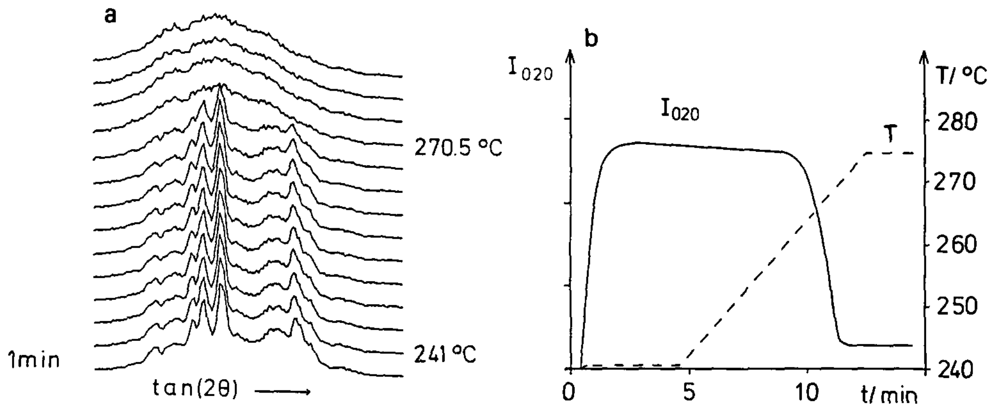

Figure 10 Change of wide angle X-ray scattering during heating and annealing of PEN previously crystallized for 16 min at 240°C in the β-modification. (a) X-ray scattering patterns. (b) Temperature T and intensity of the 020-reflection, I_{020}, as a function of time

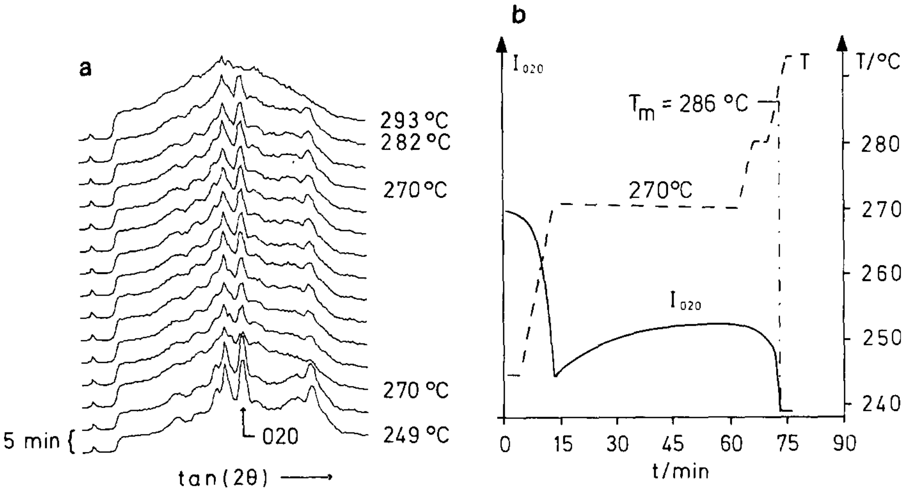

Figure 11 Change of wide angle X-ray scattering during heating and annealing of PEN previously crystallized for 16 min at 240°C in the β-modification. (a) X-ray scattering patterns. (b) Temperature T and intensity of the 020-reflection, I_{020}, as a function of time

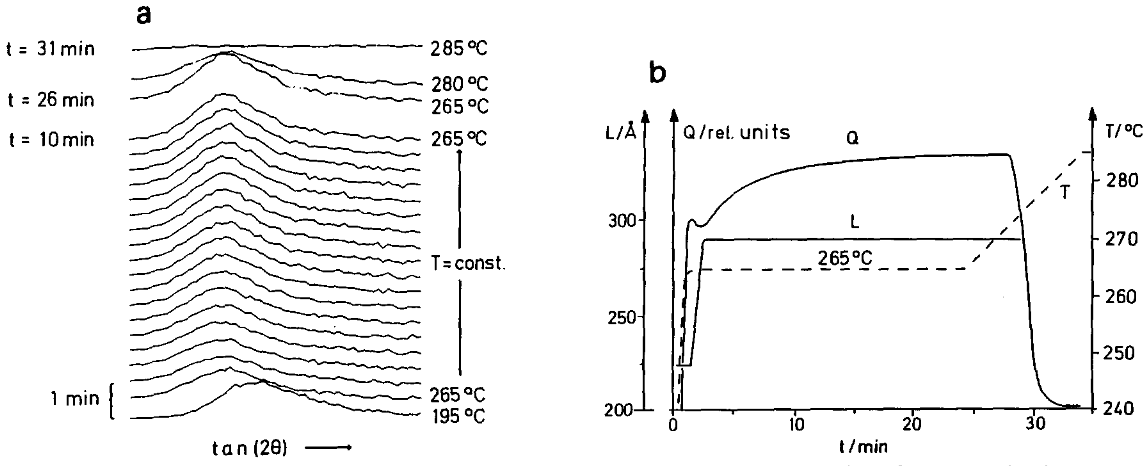

Figure 12 Change of small angle X-ray scattering during heating and annealing of PEN previously crystallized for 16 min at 240°C in the β-modification. (a) X-ray scattering patterns. (b) Temperature T, long period L and integrated scattering intensity Q (in arbitrary units) as a function of time

12(a), one can see the measured scattering curves. In *Figure 12(b)*, temperature T, long period L and integrated scattering intensity Q are plotted as functions of time. Immediately after the temperature is raised to 265°C, the long period L increases from 22.5 nm to 27 nm. During annealing at this temperature, L remains constant, while the integrated scattering intensity Q, which can be considered to be a measure of the degree of crystallinity, first decreases slightly (corresponding to melting) and then increases considerably (corresponding to recrystallization). The sample melts at 283°C, which corresponds to a melting point increase of 12°C. Obviously some increase of the crystal thickness occurs; one may doubt, however, that this increase is large

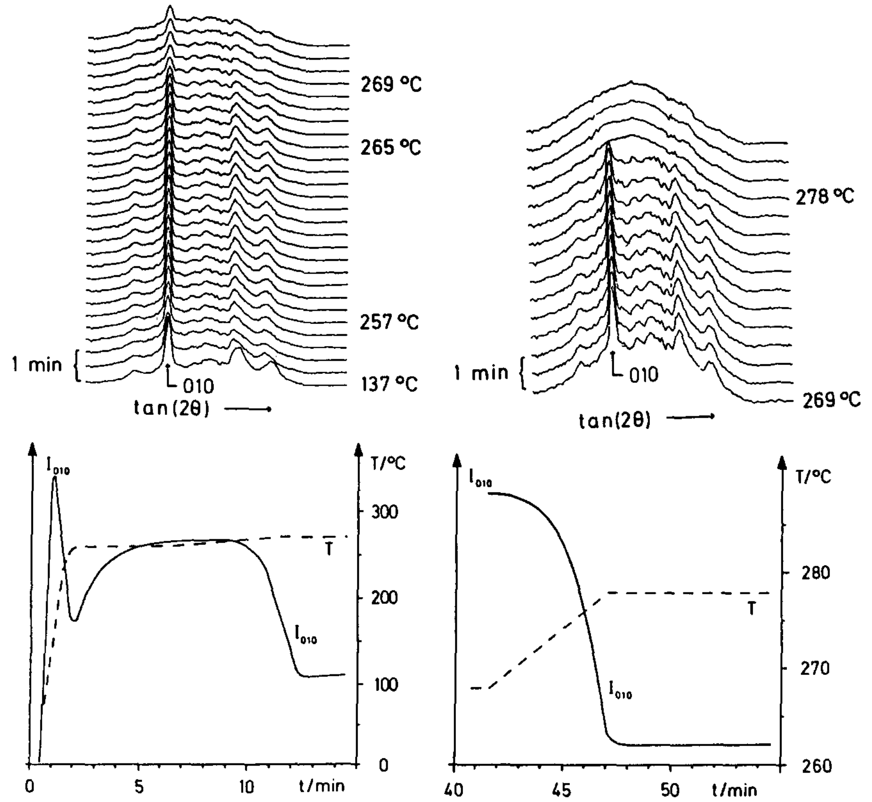

Figure 13 Change of wide angle X-ray scattering during heating and annealing of PEN previously crystallized for 16 min at 240°C in the α-modification. X-ray scattering patterns (above). Temperature *T* and intensity of the 010-reflection, I_{010}, as a function of time (below)

enough to explain the observed rise in the melting point (see Discussion).

A rise in the melting temperature by annealing was also observed with samples which were crystallized in the α-modification. *Figure 13* shows one of the results obtained by wide angle X-ray scattering. The sample was crystallized for 2 h at 207°C. By annealing at 269°C, the melting point is raised to 278°C. Again, no change of the crystal modification is observed during annealing.

One could conjecture that, during annealing, the lateral dimensions of the crystals increase or the crystals become more perfect. The wide angle scattering diagrams in *Figures 10, 11* and *13* do not indicate any change in the half width of the crystal reflections. However, the resolution of the synchrotron beam line used for these measurements was not sufficient to detect small changes in the line shape. To measure the shape of the reflections with higher accuracy and, in addition, to elminate any temperature effects, we performed another experiment in which the sample was quenched after each step of annealing. After quenching each time, wide angle X-ray scattering was measured by a conventional goniometer (Siemens D 500) at room temperature. The results are represented in *Figure 14*. No decrease of the half width of the crystal reflections can be observed while the melting point increases to 293°C.

In *Table 1*, results concerning the influence of annealing conditions on melting point are summarized. One can see that T_m increases with increasing annealing temperature T_a. The increase is larger for the β-modification than it is for the α-modification.

Density and degree of crystallinity

According to our measurements, the density of the quenched sample ρ_a is 1.3400 g cm^{-3} and that of a sample

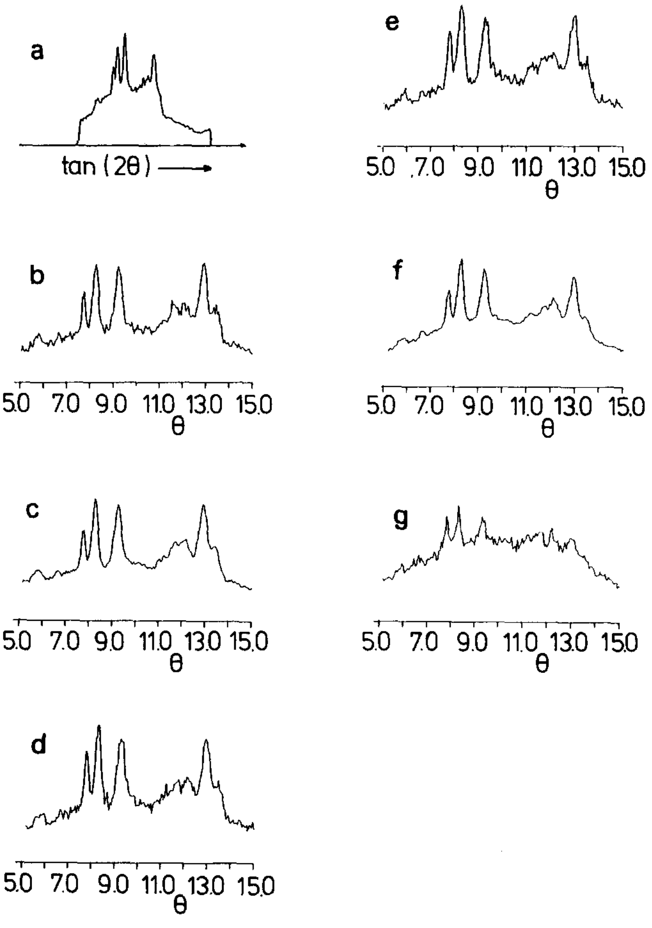

Figure 14 Wide angle X-ray scattering of PEN subsequently annealed for 20 min at different temperatures T_a and quenched, measured at room temperature after each annealing. T_a (°C): (a) 240; (b) 270; (c) 280; (d) 286; (e) 288; (f) 290; (g) 292

Table 1 Melting points of samples crystallized and annealed under different conditions

Crystallization				
Temperature (°C)	Time (min)	Modification mainly formed	Annealing	Melting point (°C)
240	16	β	–	270.5
240	30	β	25 min at 265°C 20 min at 268°C	281 284
240	16	β	40 min at 270°C	288
207	120	α	40 min at 269°C	278
240	20	β	25 min at 270, 280, 286, 288, 290, 292°C	293

crystallized at 180°C for 15 h is 1.3660 g cm^{-3}. For the completely crystalline material a density $\rho_a = 1.4007$ g cm^{-3} has been calculated from the dimensions of the unit cell of the α-modification[6]. If one assumes that the density of the quenched sample is that of the amorphous regions one can calculate the degree of crystallinity for the crystallized material by means of the equation

$$x_c = (1/\rho)(\rho - \rho_a)/(\rho_c - \rho_a)$$

One obtains $x_c = 0.43$.

DISCUSSION

Melting behaviour

We have found that the melting point of PEN can be increased by 20°C and more by annealing the sample at temperatures just below the normal melting point. As PEN is able to crystallize in two different crystal modifications one might assume that the melting point increase is caused by a change of the crystal modification. Actually, in a patent[6], the higher melting point is considered to be associated with the appearance of the β-modification. The results represented in *Figures 10, 11, 12, 13* and *14* do not support this assumption. On the contrary, they prove that:

(1) the normal melting point of the two crystal modifications is almost the same;

(2) the melting point of both crystal modifications is increased by annealing;

(3) no change of crystal modification is observed during annealing.

It seems, however, that the melting point of the α-modification is increased less by annealing than that of the β-modification. As a consequence, after annealing a material which contained both crystal modifications, the α-crystal reflections disappeared at a temperature 2°C lower than that at which the β-reflections disappeared (282 and 286°C, respectively).

As it is not a change of the crystal modification which is responsible for the increase of the melting point, one has to look for another explanation. It is well known that the melting point of polymers depends on crystallization temperature. This is attributed to the finite thickness of the crystals. According to Hoffmann[18], for lamellar crystals with thickness l_c and infinite lateral dimensions, the melting point T_m is given by

$$T_m = T_m^\circ \left(1 - \frac{\sigma_e}{l_c \Delta H_m}\right) \qquad (1)$$

where T_m° is the melting point of a crystal with infinite thickness, ΔH_m is the enthalpy of melting and σ_e is the surface free energy. The lower the temperature of crystallization T_c, the thinner the crystals and the lower the melting point. By annealing a crystallized sample at a temperature above that of crystallization, the crystals become thicker and the melting point increases.

Such recrystallization effects have been observed with different polymers[19,20]. They usually occur at temperatures far below the highest melting point T_m obtained under 'normal' heating conditions and, as a consequence, they increase the melting point, which was initially much lower than T_m, towards T_m. The temperature T_m is considered to be lower than the equilibrium melting point T_m°, which cannot be directly measured because it is impossible to grow crystals of infinite thickness. For some polymers, T_m° has been determined by measuring T_m as a function of l_c and extrapolating the results to infinite values of l_c.

In the case of PEN, the 'normal' melting point T_m seems to be at 573 K (=300°C). The recrystallization far below T_m occurs so quickly that the initial lower melting temperature T_m could not be observed in our experiments. Sometimes T_m manifests itself in d.s.c. measurements by a small melting peak just above the crystallization temperatures. If the material is brought to a temperature slightly above 270°C it melts and never crystallizes again. However, an increase of the melting point to temperatures far above 270°C is observed upon annealing of the almost completely molten material at temperatures close to T_m. This melting behaviour is different to that usually observed.

Is it possible to explain the observed increase of the melting point by an increase of the crystal thickness in spite of this difference?

To investigate this problem, in *Figure 15* the melting point calculated by means of equation (1) is plotted against the crystal thickness l_c, assuming $T_m^\circ = 573$ K (corresponding to 300°C) and $\Delta H_m = 190$ J g^{-1}. The calculation has been performed using different values of the surface free energy σ_e, which are given as parameters for the curves. Let us now consider the sample in *Figure 13*. From density measurements it is known that, before the annealing, the sample had a degree of crystallinity of 0.35. With a value of 22.5 nm for the long period L, a crystal thickness $l_c = 7.8$ nm is deduced. The long period

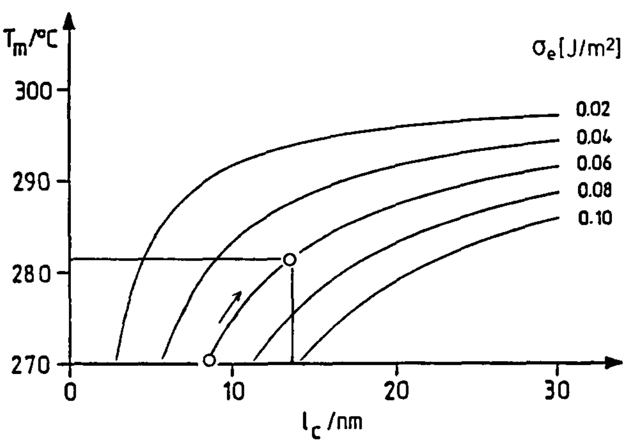

Figure 15 Melting point as a function of crystal thickness calculated by means of equation (1) for different values of the surface free energy σ_e, assuming $T_m^\circ = 573$ K and $\Delta H_n = 190$ J g^{-1}

after annealing ($L=27.0$ nm) corresponds to a crystal thickness $l_c=9.6$ nm, if x_c is assumed to be 0.35, and to $l_c=13.5$ nm if x_c is assumed to have increased to 0.50, the maximum possible value according to our investigations. From these values and by using the results plotted in *Figure 15*, we can learn the following. The observed melting point of 271°C together with a crystal thickness of 7.8 nm corresponds to a value of 0.06 J m^{-2} for σ_e, which seems reasonable. The increase of l_c to 13.5 nm, the largest value which can be brought into agreement with our results, corresponds to an increase of the melting point to 281°C. This is in good agreement with the experimental result ($T_m=555$ K, corresponding to 282°C, see *Figure 13*).

The values of the crystal thickness l_c mentioned above must be considered as a lower bound of l_c because not all of the amorphous material must necessarily be situated between the crystal lamellae. If the value of l_c before annealing is larger than 22.5 nm, then according to *Figure 15* a larger value of σ_e has to be assumed. In addition, the maximum crystal thickness after annealing is larger than 13.5 nm. Overall, due to the curvature of the curve representing σ_e as a function of l_c, the increase of the melting point is a little smaller.

Because of the ambiguities involved in the calculation (e.g. the values of T_m^0, l_c, σ_e), the result just obtained does not prove that the change of l_c is the reason for the increase of the melting point. It only illustrates that an explanation in terms of an increase of the crystal thickness might be possible. Actually, one has to point out that the unknown values of the parameters were chosen in such a way that the increase of the melting point became as large as possible. In addition, there is also the problem that the melting point increase takes place only after annealing at a temperature very close to T_m and that no recrystallization is observed if a sample is suddenly brought to a temperature above 270°C. We therefore think that one has to consider another important effect taking place during annealing: a change of surface morphology by transesterification reactions. For example, by such chemical reactions ideal chain folds on the crystal surfaces may be transformed to loose loop or loose tie molecules. These reactions may promote an increase of the melting point in two ways:

(1) They eliminate chain conformations which act as obstacles to the growing of the crystals (e.g. ideal folds).

(2) They decrease the surface free energy by changing the existing surface morphology into one with less free energy, e.g. one with less restricted chains. As has been shown previously[21,22], the value of the surface free energy of the crystals is strongly influenced by the morphology of the adjacent amorphous phase.

In support of this assumption, it may be pointed out that an increase of the melting point similar to that in PEN was observed[23] in poly(ethylene terephthalate) (PET). In addition, by neutron scattering experiments with blends of deuterated and non-deuterated PET, it has been shown that transesterification proceeds very quickly in this material[11,24,25]. We found that, at 260°C, five transesterification reactions occur per molecule per minute. However, as the increase of crystal thickness and degree of crystallinity during annealing is limited, not all obstacles hindering the improvement of crystallinity can be removed by transesterification.

It has been reported in the patent literature[7] that for an oriented copolyester of PEN, the time of annealing t_a (in minutes) necessary to obtain an increase of the melting point is related to the annealing temperature T_a (in °C) by the approximate equation

$$T_a \sim \frac{3}{T-250}$$

For $T<250$°C no melting point increase was observed. This relation is in good agreement with our results if we replace the number 250 by 260.

Crystal modification

Our results concerning the influence of crystallization conditions on crystal modification show the following. After melting at 280 and 300°C, the α-modification is formed at crystallization temperatures below 200°C, while mainly β-modification is formed above this temperature, irrespective of which modification was present before melting. If, however, the melting occurred at 320°C, the α-modification was also obtained above 200°C. It did not make any difference whether the samples were directly brought to the crystallization temperature from the melt or whether they were first quenched to room temperature and heated up quickly afterwards. Furthermore, in a sample crystallized in one of the two modifications no change in the crystal modification could be induced by any annealing below the melting temperature. In addition, if a sample was crystallized partly in the α-modification crystallization continued in this modification even if it took place above 200°C.

Each of the two crystal modifications, after it has been formed, behaves as if it were stable up to the melting point. Therefore, kinetic factors seem to determine which of them is obtained during crystallization. Therefore, important factors are the rates of nucleation and of spherulitic growth. In addition, one has to consider that, above the melting point in thermodynamical equilibrium, fluctuating crystal embryos[26] occur. If these embryos are larger than the critical crystal nucleus, they may act as crystal nuclei, after the melt has been cooled down below the melting point (athermal nucleation).

With this in mind, it seems to be possible to explain the observed results if we assume first, athermal nucleation, and second, a non-equilibrium crystal embryo distribution below 300°C, while the distribution may be in equilibrium above 300°C. Examples for such crystal embryo size distributions are shown in *Figure 16* for melt temperatures of 280 and 320°C. The number $N(l_c)$ of crystal embryos of thickness l_c is plotted as a function of l_c. The values l_c' and l_c'' represent the thickness of the critical crystal nucleus at 180 and at 220°C respectively. When the temperature of the melt is 280°C, it is assumed that a certain amount of non-equilibrium β-embryos with a thickness in the region of l_c'' is present. Similar non-equilibrium distributions have also been considered by other authors, for example Morgan[27]. In contrast, no such non-equilibrium embryos are present at 320°C. Now, if the material crystallizes at 220°C, all crystal embryos with a thickness $>l_c''$ become crystal nuclei. When the temperature of the melt is 320°C, these embryos are mainly in the α-modification, while when the melt temperature is 280°C, the embryos large enough to be nuclei are mainly in the β-modification. On the other

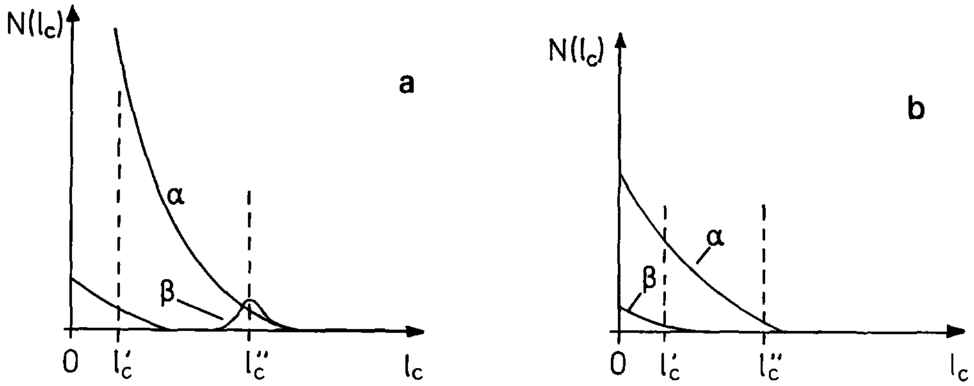

Figure 16 Schematic representation of the number of fluctuating crystal embryos of the α- and β-modifications in the melt at (a) 280°C and (b) 320°C

hand, if the material crystallizes at 180°C, all embryos having a thickness $>l_c'$ become crystal nuclei. For both temperatures of the melt these are predominantly embryos in the α-modification.

Thus, by assuming the crystal embryo distributions in *Figure 16*, agreement with the experimental results is obtained. We must admit, however, that it seems difficult to explain why the distributions for α- and β-embryos are different from each other.

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