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Polymer 46 (2005) 845–857

polymer

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Thermal analysis and Raman spectroscopic studies of crystallization in poly(ethylene 2,6-naphthalate)

Gustaaf Schoukens*, Karen De Clerck

Department of Textiles, Faculty of Applied Sciences, University of Ghent, Technologiepark 907, B-9052 Zwijnaarde (Gent), Belgium

Received 9 September 2004; received in revised form 25 November 2004; accepted 30 November 2004
Available online 19 December 2004

Abstract

The combination of Fourier transform Raman spectroscopy and thermal analysis has been proved to be adequate for the study of the quantitative structural changes which take place in amorphous poly(ethylene 2,6-naphthalate) on annealing. Different conformer contents were found in the annealed samples depending on annealing conditions. In general, annealing of the amorphous poly(ethylene 2,6-naphthalate) from the glassy state induces a conformational transition of *gauche* to *trans*. The structure obtained during crystallization is characterized by a three-phase conformational model, including an amorphous phase, a rigid amorphous phase and a crystalline phase. The crystallization is further characterized by a three-zone process, firstly a primary crystallization process, secondly a variation of the rigid amorphous phase with a constant value of the crystalline phase and thirdly a secondary crystallization process. The bandwidth at half intensity at 1721 cm^{-1} in the Raman spectrum varied between 32 cm^{-1} for the complete amorphous phase and 7 cm^{-1} for the total rigid phase, the sum of the rigid amorphous and crystalline phase. The bandwidth at half intensity at 1721 cm^{-1} was directly related to the amount of the total rigid phase and confirmed by the variation of the heat capacity increase at the glass transition temperature. Two complementary bands in the Raman spectrum, at 1107 and 1098 cm^{-1}, were found to be related to the *trans* and *gauche* isomers. A difference was measured between the total *trans* content and the amount of rigid phase due to the presence of some *trans* conformations in the amorphous phase. The extrapolation of the bandwidth at half intensity at 1721 cm^{-1} to the value of zero, corresponding to the complete crystalline phase, gave a melting enthalpy of 196 J/g and the corresponding density of the crystalline phase was 1.4390 g/cm^3. A complete rigid phase structure was obtained by a melting enthalpy of 144 J/g and a density of 1.4070 g/cm^3.

Keywords: Temperature modulated calorimetry; Raman; Poly(ethylene naphthalate)

1. Introduction

Poly(ethylene 2,6-naphthalate) (PEN) is a polyester for which the preparation was first reported as long ago as 1948 [1]. PEN is produced by the condensation polymerisation of 2,6-naphtalenedicarboxylic acid and ethylene glycol [2–4]. There has, however, been increasing interest in its commercial use because of recent indications [5,6] that the dicarboxylic acid monomer will become available in large quantities. PEN molecules contain naphthalene rings, which are stiffer than those of poly(ethylene terephthalate) (PET). The important aspect of PEN is the influence of increased chain stiffness on the mechanical and thermal properties of the polymer. This polymer, like PET, can be formed into an amorphous form by being quenched from the melt, or it can be crystallized either by slow cooling from the melt or by stretching between the glass transition temperature (T_g) and the cold-crystallization temperature. PEN exhibits a T_g value of about 120 °C, and this makes it quite attractive as a high-temperature polymer for film, tape, and moulding applications. The high T_g value of PEN results in enhanced mechanical properties (elastic modulus, hardness, creep resistance, lower shrinkage, etc) and makes this polymer attractive for engineering purposes. PEN possesses oxygen barrier properties four to five times higher than those of PET, and this makes PEN attractive for packaging applications.

One of the unusual characteristics of PEN, obtained by melt polycondensation without solid-phase post-polycondensation,

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* Corresponding author. Tel.: +32 9 264 57 51; fax: +32 9 264 58 46.
E-mail address: gustaaf.schoukens@ugent.be (G. Schoukens).

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doi:10.1016/j.polymer.2004.11.106

is that it shows necking behaviour upon stretching from the amorphous state above T_g [7,8]. Some authors have reported that this neck formation is a result of a highly cooperative orientation of the naphthalene planes parallel to the surface of the film. This behaviour resembles an isotropic-nematic structural transition that occurs at highly localized regions of the sample.

It has been reported that PEN also has two crystal forms (α and β), and both are triclinic, depending on the crystallization temperature [9]. Crystallizing at 180 °C yields the α form, as reported by Mencik [2], whereas crystallizing at 240 °C from the melt yields the β form. Recent X-ray work [10] has suggested the presence of a mesophase in addition to the crystal form. In the mesophase structure, the molecular chains are in registry with each other in the meridional direction but not fully crystallized in the equatorial direction. The emergence of this structure is due to the drawing of PEN at temperatures of 120 or 150 °C [11]. This structure persists upon annealing at 180 or 200 °C, and this leads to the conclusion that the mesophase is stable at high temperatures.

There have been several other reports [12,13] of a mesophase occurring in both oriented PET and PEN prepared under specific conditions. Both nematic and smectic states were recognized in a series of stretching experiments on PET [14], and these mesophase states characterized stages in the crystallization process.

There have been many efforts devoted to understanding the complexity of the melting and recrystallization behaviour of PEN [9,15–19]. Complementary techniques such as DSC and temperature scanning X-ray were used to detect melting and recrystallization events [20–22].

One of the first studies of PEN was that of Chen and Wunderlich [15] using standard DSC to describe the thermal analysis of various glass and melt crystallized samples. Buchner et al. [9] investigated the formation of the two different crystal modifications of PEN (α and β) under various crystallization conditions. Denchev et al. [18] studied isothermally crystallized PEN from the glass at different times and temperatures. Slow heating (2 °C/min) from the amorphous glass to the isothermal annealing temperature allows one to develop an unstable morphology, due to the formation of a broad range of crystals with different melting points as one slowly heats through the crystallization region to the desired annealing temperature. The unstable morphology then evolves considerably with time. Rapid heating (200 °C/min) from the amorphous glass to the isothermal annealing temperature provides a more stable morphology similar to melt crystallization, but we will show that some basic properties of the crystallization process are not influenced by the heating rate but influenced by the annealing time and temperature. The recrystallization and melting processes in PEN were examined along with the morphological features by small angle X-ray scattering. Dual lamellar populations were observed depending on the temperature and time of crystallization [18].

There is still some controversy in the determination of the heat of fusion of 100% crystalline PEN (ΔH_m) with values of 103 [15], 190 [9] and 170 J g^{-1} [17]. The value of ΔH_m and the corresponding density of the crystalline phase is very important for calculating percent crystallinities and various rigid fractions [15,19].

In previous articles [23,24], we represented the amount of the rigid phase structure, f_r, which represents the sum of the crystalline phase and the mesophase, as a function of I_{1e}, the extra first strain invariant, which is equal to I_1-3, and a correlation between these two was experimentally obtained, so that f_r varied between 0 and 1 with I_{1e}. The first strain invariant I_1 equals $\lambda_1^2+\lambda_2^2+\lambda_3^2$, with λ_i being the draw ratios in the three principal directions and I_{1e} equalling I_1-3. In a previous article [23], we compared the stress-strain curve with f_r during drawing. When f_r was reaching 50%, for a draw ratio of 4, a dramatic increase in the stress was observed. The dramatic increase in stress suggested a critical degree of the rigid phase structure, similar to a percolation threshold accompanied by an inversion of the continuous phase. When f_r was less than 50%, the amorphous phase was the continuous phase, with the rigid phase dispersed therein. If f_r was greater than 50%, phase inversion took place, and the rigid phase formed the continuous phase, with an amorphous phase dispersed therein.

In this study, a combined use of conventional DSC, temperature modulated DSC (MDSC) and Laser–Raman spectroscopy was used to investigate the structure variations in PEN during crystallization of PEN.

The vibrational spectrum of poly(ethylene terephthalate) (PET) has been extensively studied. For PET, the bandwidth at one-half maximum intensity of the Raman-active C=O stretching vibration at 1725 cm^{-1} was found to correlate with density [25]. This correlation was valid for unoriented as well as highly oriented samples. It was suggested that a number of rotational states of the terephthalate segment occur in the amorphous polymer. Crystallization caused a transformation of the successive carbonyl groups on a benzene ring to a *trans* structure in the crystals and resonance-stabilized planar conformation. There have been attempts to explain the changes in the Raman spectrum of PET that occur upon annealing of amorphous samples. These changes, though considered to be related to the development of crystallinity, are explained as being due to conformational changes in either the carbonyl groups or the glycol linkage. Since it is assumed that these conformational changes go hand in hand with crystallinity development, the extension is both logical and reasonable.

A more complete picture of polymer structure can be obtained by an appropriate choice and combination of different methods. Then, in this work, differential scanning calorimetric (DSC and MDSC) measurements were correlated with FT-Raman spectroscopy in order to quantify the amount of *trans* isomer and of the different phases during annealing of amorphous poly(ethylene 2,6-naphthalate)

Table 1
Half bandwidth at 1721 cm^{-1} as function of the melting enthalpy of the annealed PEN samples

Sample	Annealing temperature (°C)	Annealing time (min)	Melting enthalpy (J/g)	Bandwidth at one-half maximum intensity 1721 cm^{-1}
Starting sample	23	–	2.35	25.97
	165	3	6.59	25.78
	170	3	13.9	24.71
	175	3	32.75	22.06
	180	3	41.4	20.63
	210	3	43.47	19.53
	210	30	42.12	19
	210	60	46.25	18.62
	210	240	50.16	17.74
	210	720	55.0	17.28
	210	1440	58.4	16.74
	170	60	48.10	20.17
	180	30	45.42	19.95

from its glassy state. Temperature modulated DSC (MDSC) is a technique that superimposes a low frequency small amplitude oscillation onto a linear heating ramp of standard DSC. By deconvolution the total heat flow can be separated into a heat capacity-related (reversing) component and a time-dependent non-reversing component. The reversing signal provides excellent resolution of the glass transition by separating the heat capacity from other non-reversing processes such as enthalpy relaxation and crystallization as is well known in the literature.

2. Experimental

2.1. Materials

Poly(ethylene 2,6-naphthalate) (PEN) with an intrinsic viscosity of 0.65 dl/g used in this study was provided in film form and pellet form by ICI plc. The thickness of the film was 0.65 mm and the film was in its amorphous glassy state due to its quenching after extrusion.

Crystallizations of the amorphous PEN-film were performed at temperatures between 165 and 210 °C and crystallization times between 3 and 1440 min. The amorphous PEN-film was heated at a rate of 20 °C/min under a dry nitrogen atmosphere to the desired crystallization temperature and held at that temperature for a defined time. Afterwards, the annealed sample was rapidly cooled at a rate of 200 °C/min to ambient temperature.

2.2. Differential scanning calorimetry

Conventional and modulated DSC measurements were performed in non-hermetic aluminum pans on a TA Instruments DSC 2920 with MDSC® option. The purge gas was nitrogen (25 ml/min). The temperature was calibrated with gallium, indium and tin. Indium was used for enthalpy calibration. For the conventional DSC experiments, a heating rate of 10 °C/min and for the modulated experiments(MDSC) a 2 °C modulation amplitude and a 60 s modulation period was used. The heat capacity (C_p) was calibrated with poly(methyl methacrylate), using the same modulation conditions as in the experiments. Sample masses of 8 ± 0.5 mg were used for all experiments.

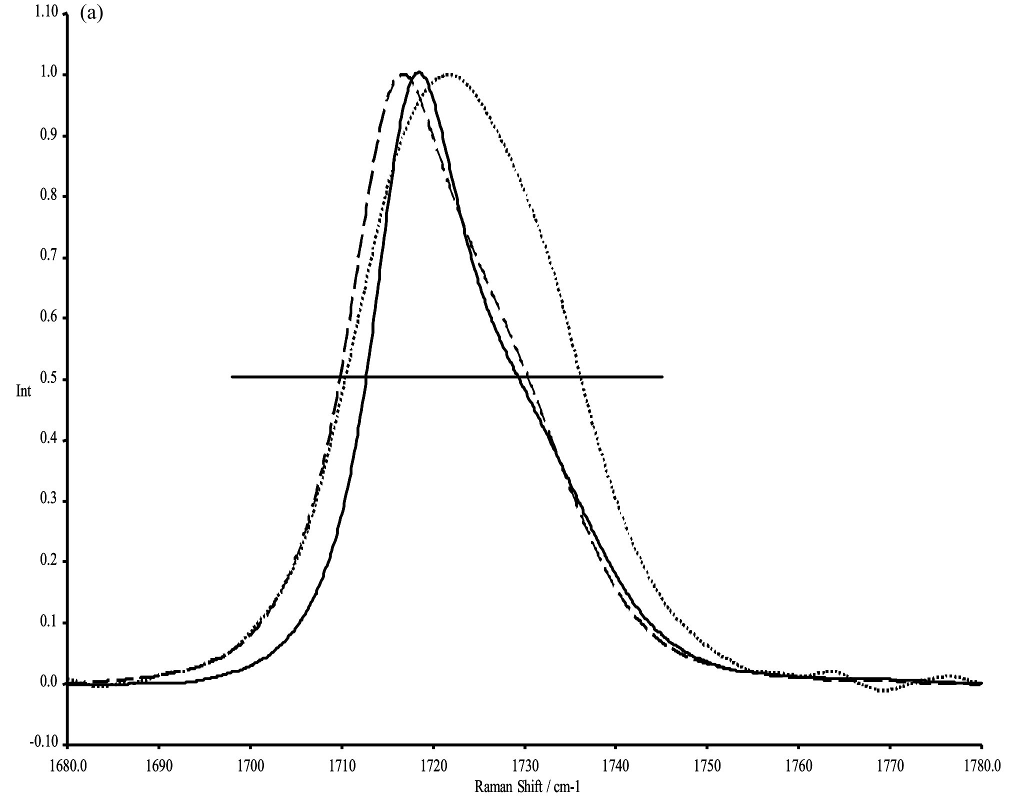
In the experimental MDSC conditions of this work, for the T_g region, the variation in the corrected heat flow phase angle was always limited to a few degrees. The modulus of the complex heat capacity and the in-phase heat capacity component are thus nearly coinciding [22]. The term (specific) heat capacity (C_p), without further specification, will therefore be used throughout this work.

The MDSC experiments were used to characterize the glass transition region. The glass transition region and heat capacity increase (ΔC_p) were calculated by using the half extrapolated tangents option in the TA Instruments software.

The melting enthalpy ΔH_m of the samples, before and after annealing, was determined with DSC thermograms. The crystallization exothermic enthalpy, $\Delta H_{\text{cold crystallization}}$ or ΔH_c, was substracted from the melting endotherm, $\Delta H_{\text{melting}}$, to determine the value of the melting enthalpy ΔH_m corresponding with the amount of apparent crystallinity initially present in the samples.

$$\Delta H_m = \Delta H_{\text{melting}} - \Delta H_{\text{cold crystallization}}$$

PEN provides a new example of a polymer that may possess a crystalline and a rigid amorphous fraction, which may be a nematic and/or mesophase structure. The rigid amorphous fraction does not contribute to the increase in the heat capacity at T_g and devitrifies only at temperatures well above T_g. Similar behaviour was found in several high-melting polymers with phenylene groups in the main chain. The overall rigid fraction f_r, comprising the rigid amorphous phase and the crystalline phase, is computed from the heat capacity increase ΔC_p by setting



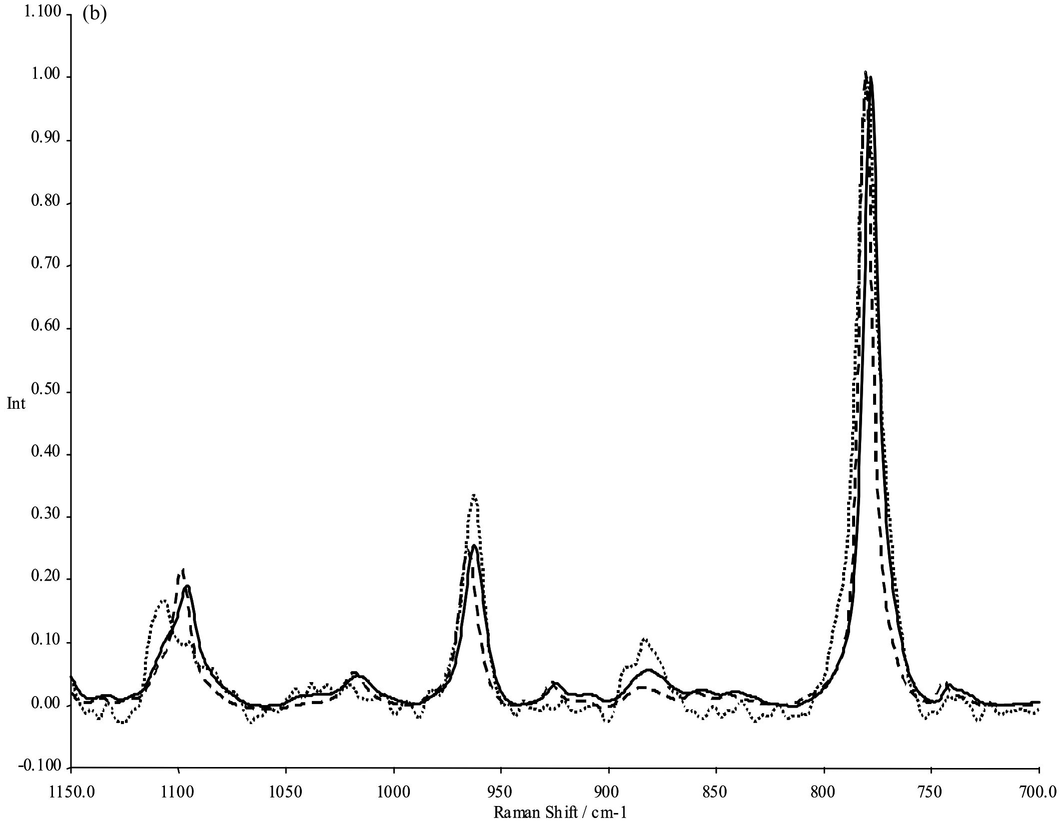


Fig. 1. (a) Raman spectra of three samples representing the recorded relative Raman intensity around the wave number of 1721 cm^{-1}; dotted lines = starting sample, continuous line = PEN annealed 3 min at 180 °C, dashed line = PEN annealed 1440 min at 210 °C. (b) Raman spectra of three samples representing the recorded relative Raman intensity in the region of wave numbers from 700 to 1150 cm^{-1}; dotted lines = starting sample, continuous line = PEN annealed 3 min at 180 °C, dashed line = PEN annealed 1440 min at 210 °C.

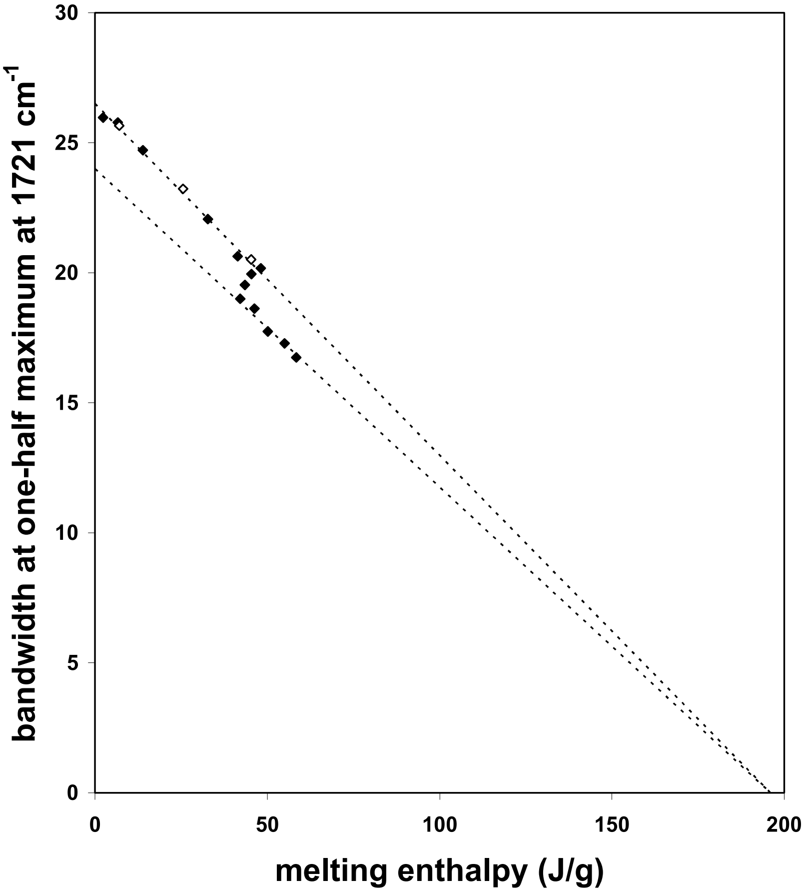


Fig. 2. Measured values of the bandwidth at one-half maximum intensity at 1721 cm^{-1} as function of the melting enthalpy; ■ for samples described in Table 1, □ for supplementary samples added afterwards.

$$f_r = 1 - [\Delta C_p(m)/\Delta C_p(a)]$$

where ΔC_p(m) and ΔC_p(a) represent the measured and total amorphous heat capacity increase at T_g, respectively.

2.3. Fourier transform Raman spectroscopy

Raman spectra were recorded on a PerkinElmer GX 2000 Fourier transform spectrometer, equipped with a Raman sample accessory A diode-pumped YAG near infrared laser (1064 nm, variable power from 10 to 2000 mW), an InGaAs detector and a Raman beamsplitter was used. The measurements were performed in back-scattering mode (180° excitation optics) with 16 scans, a resolution of 4 cm^{-1} and a laser power of 300 mW in the spectral range 300–3500 cm^{-1} with a data interval of 1 cm^{-1}.

3. Results and discussion

Raman spectra were obtained for samples with different degree of crystallinity as described in Section 2 and in Table 1.

The bandwidth at one-half maximum intensity of the Raman-active C=O stretching vibration at 1721 cm^{-1} was measured for the different samples, obtained after annealing of the amorphous film samples. The results are summarized in the following table, together with the measured values of the melting enthalpy ΔH_m (J/g).

In Fig. 1a and b, some representative Raman spectra recorded on three different samples are reported. In Fig. 1a, the variations of the bandwidth at 1721 cm^{-1} for the three different samples and in Fig. 2a, the variations of the measured intensities in the region comprising the wave numbers 780, 1098 and 1107 cm^{-1} are clearly demonstrated.

Fig. 2 is a plot of the bandwidth at one-half maximum intensity for the C=O stretching vibration at 1721 cm^{-1} versus the melting enthalpy for the collection of samples described in Table 1 and some supplementary samples added afterwards in order to complete and confirm the different relationships.

It may be seen that there is a linear correlation of the bandwidth with the corresponding values of the melting enthalpy up to a value of the melting enthalpy of 42 J/g. The second zone in the figure is corresponding with a decrease in the bandwidth for the C=O stretching at a constant value of the melting enthalpy. A third zone is characterized by a linear correlation of the measured bandwidth with the

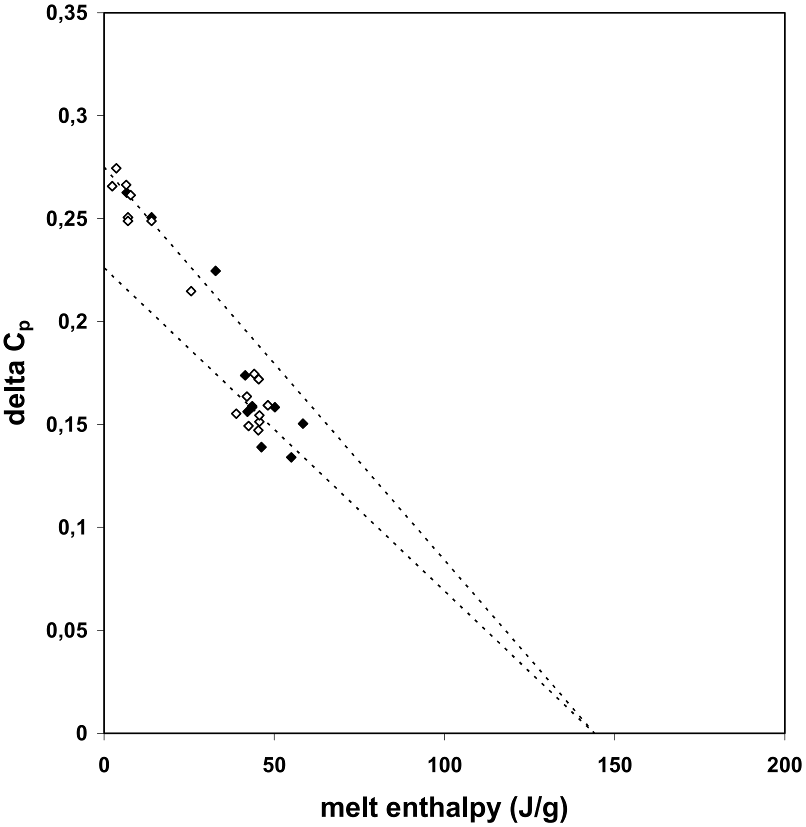


Fig. 3. Measured heat capacity increases $\Delta C_p(m)$ as function of the melting enthalpy; ■ for samples described in Table 1, □ for supplementary samples added afterwards.

melting enthalpy. The relation between the measured bandwidth and the corresponding melting enthalpies is characterized by three zones. The extrapolated value of the measured values of the bandwidth at one-half maximum intensity at 1721 cm^{-1} gave a value of 196 J/g for the zero value of the corresponding bandwidth and this value corresponded to the melting enthalpy of the complete crystalline phase. Following these results, the melting enthalpy of the complete crystalline phase was 196 J/g, a value close to one of the already published values [9] of the melting enthalpies of the complete crystalline phase.

The same three zones were found in the correlation between the measured heat capacity increase $\Delta C_p(m)$ at T_g and the melting enthalpy, as reproduced in Fig. 3.

The measured values of the heat capacity increase $\Delta C_p(m)$ are characterized by a larger scatter around a mean value than the Raman measurements. This is a general observation for measurements of heat capacity increases, result of the used techniques to calculate the heat capacity increase and the observed scatter may also be influenced by a possible shift of the glass transition temperature as function of the amount of crystallization in the samples. The represented values are already the mean values of three measurements. Even there is some scatter in the measured values, some general trends could be observed between the heat capacity increases and the melting enthalpy.

A linear decrease of the measured heat capacity increase $\Delta C_p(m)$ with the melt enthalpy is observed till the melting enthalpy reached the value of 42 J/g, where after the value of $\Delta C_p(m)$ is sharply decreased to lower values. In the third zone, a linear correlation between the measured heat capacity increase $\Delta C_p(m)$ and the melt enthalpy was again observed.

The extrapolated values of the two linear relations between the measured values of the heat capacity increase and the melting enthalpy at a value of zero for the melting enthalpy gave respectively a value of 0.2710 J/(g K) for the first one and 0.2260 J/(g K)for the second one.

The extrapolated values of the melting enthalpy for the products without an amorphous phase, heat capacity increase $\Delta C_p(m)$ equal to zero, were equal to 144 J/g for the first zone and the second zone. The combination of the results of the measured heat capacity increase with the measured values of the half bandwidth at 1721 cm^{-1} was given a linear relationship between these two measured parameters, with the measured value of the heat capacity increase becoming zero for a half bandwidth at 1721 cm^{-1} of 7 cm^{-1} and a value of the heat capacity increase of 0.2710 J/(g K) for a half bandwidth at 1721 cm^{-1} of 26.5 cm^{-1}. Due to this linear relationship and the linear relationship between the heat capacity increase and the amount of the total rigid phase, the half bandwidth at

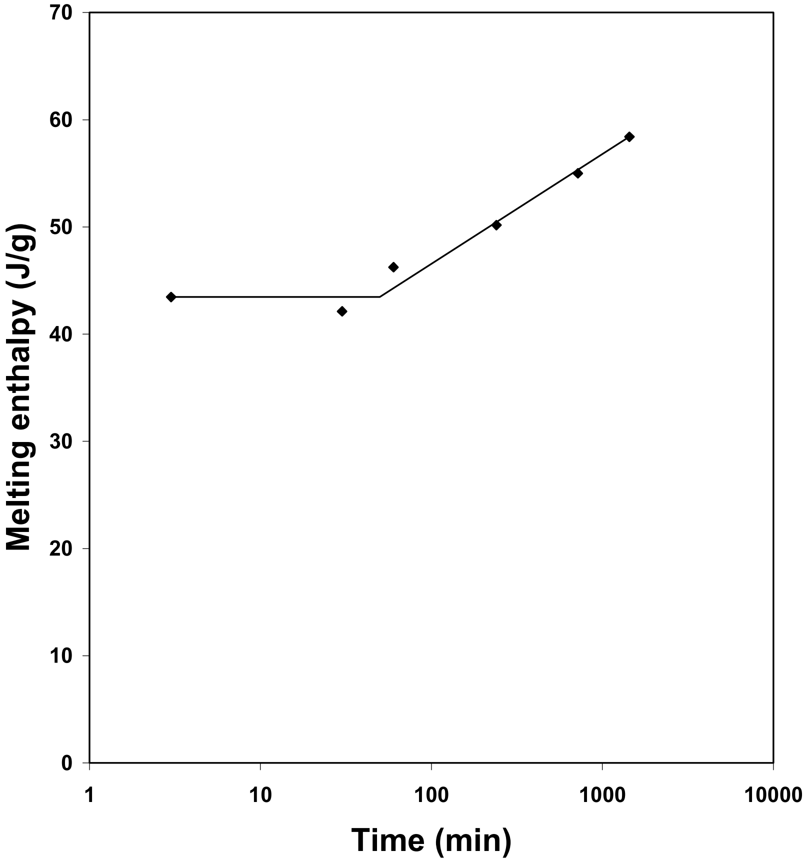


Fig. 4. The measured melting enthalpy as function of the crystallization time at 210 °C after the primary crystallization zone. The zone of primary crystallization is not represented on this figure.

1721 cm^{-1} could be linearly related to the amount of the total rigid phase. With the assumption of a three phase model for the semi crystalline structure PEN, the bandwidth at one-half maximum intensity of the1721 cm^{-1} band is a measure of the total amount of the total rigid phase, comprising the crystalline and the rigid amorphous phase.

The three zones of crystallization could also been observed in the relation between the melting enthalpy and the used crystallization time, as represented on the following Fig. 4.

The first zone is corresponding with the primary crystallization, very quick at the used annealing temperature of 210 °C, complete after 3 min and not represented on this figure, was followed by a rather constant value of the melting enthalpy up to an annealing time of 50 min, which is accompanied by an increase of the rigid amorphous phase, and followed by an increase of the melting enthalpy afterwards in the third zone. The same three zones as in the Raman spectra are observed in the crystallization behaviour as function of the annealing time. Typical is the increase of the rigid amorphous phase in the second zone before starting the secondary crystallization. These second zone corresponds to the second zone in the Raman measurements for the C=O stretching, whereby the melting enthalpy was a constant value of 42 J/g and the bandwidth at one-half maximum intensity at 1721 cm^{-1} decreased from 20.5 to 19 cm^{-1}.

In partially crystalline PEN, containing a rigid amorphous and a crystalline phase, the half bandwidth at 1721 cm^{-1} was directly related to the amount of the overall rigid fraction. This method requires no internal intensity standard and therefore requires no assumptions regarding band sensitivity to sample treatment. With this assumption and as already mentioned, the extrapolation of the linear relation between the bandwidth and the melting enthalpy in the first zone for a value of the melting enthalpy of 144 J/g gave a value of the half bandwidth at 1721 cm^{-1} of 7 cm^{-1}, the same as the value obtained for the third zone. For these values of the melting enthalpy, the total rigid fraction f_r was equal to 1. So the half bandwidth at 1721 cm^{-1} for a complete rigid phase structure was equal to 7 cm^{-1}.

To quantify the amount of the total rigid phase and the amount of amorphous phase present in the partial crystalline PEN samples the value of the half bandwidth of a complete amorphous phase has to be known. This value is not known and this value will be obtained in the following by using other bands of the Raman spectrum, especially those bands which are characterizing the complete amorphous structure or the structure containing only *gauche* isomers. A normalizing band should be chosen such that it remains constant

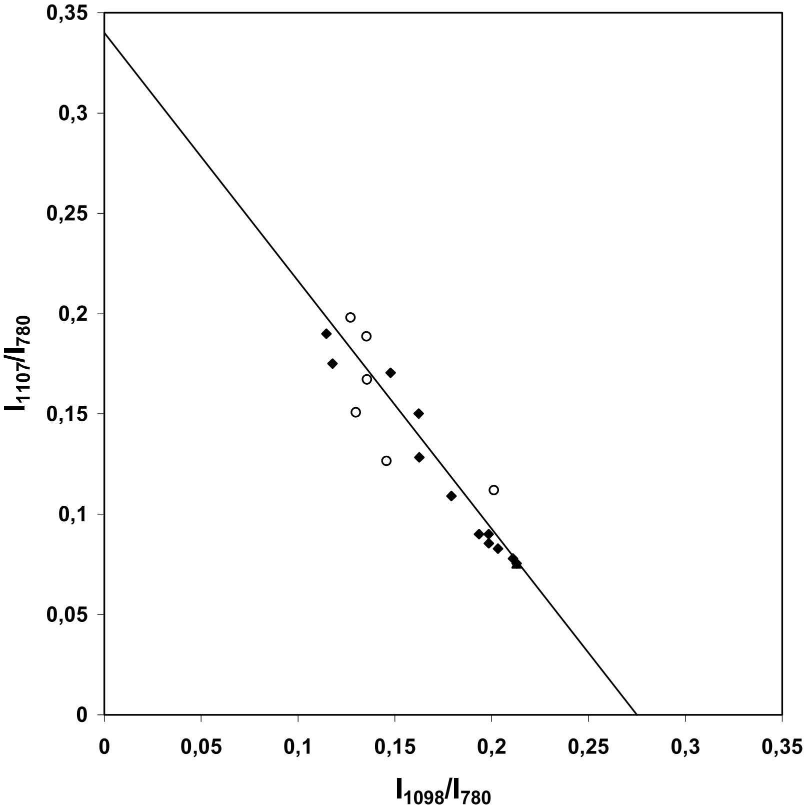


Fig. 5. The measured relative intensities of the 1107 cm^{-1} band in the Raman spectra as function of the measured relative intensities of the 1098 cm^{-1} band; ■ for samples described in Table 1, □ for supplementary samples added afterwards.

over the different samples. The band that seemed to be remaining relatively constant was the band at 780 cm^{-1}. This band is an isolated band, well separated from the other bands in the Raman spectrum. Hence, the intensity of this band can be measured fairly accurately. The intensities of the other bands in the Raman spectra were normalized to the intensity of the 780 cm^{-1} band.

In the Raman spectra of PEN, some bands were adequate to study the isomer content as function of the annealing conditions. By a first inspection of the spectra, some results could be advanced: The amorphous sample showed high values of the band at 1107 cm^{-1} and during annealing the Raman spectra showed an increase of the band at 1098 cm^{-1} and a decrease of the band at 1107 cm^{-1}. This indicated that the band at 1107 cm^{-1} could be related to the *gauche* isomer and the band at 1098 cm^{-1} to the *trans* isomer. For a quantitative analysis of the amount of *gauche* and *trans* isomers, the intensity of the already mentioned band at 780 cm^{-1} was used as the internal reference band.

Since two conformational isomers, *gauche* and *trans*, are possible in PEN samples, the sum of the amount of *gauche* and *trans* isomers must be equal to 1. For the described Raman bands, the following relationship should hold:

$$p_1 \frac{I_{1107}}{I_{780}} + p_2 \frac{I_{1098}}{I_{780}} = 1$$

where p_1 and p_2 are the 1107 and 1098 cm^{-1} band weights, respectively.

If the preceded relationship holds, a graphical representation of the relative intensity of the 1107 cm^{-1} band versus the relative intensity of the 1098 cm^{-1} must be a linear one. The measured values of the relative intensity of the 1107 cm^{-1} band versus the relative intensity of the 1098 cm^{-1} band were represented in Fig. 5. The relationship between the relative intensity values of these two bands was indeed linear, indicating that these bands are representative of the *gauche* or *trans* conformation. Form this figure, the value of p_1 was equal to 2.941 and the value of p_2 equal to 3.64.

By using these two weight factors, the amounts of the *gauche* and *trans* conformation were calculated as function of the melting enthalpy. These amounts of the two conformations are graphically represented in Fig. 6.

A decrease of the amount of *gauche* isomer and a corresponding increase of *trans* isomer is observed with increasing values of the melt enthalpy.

As already mentioned, the half bandwidth at 1721 cm^{-1} was directly related to the amount of the total rigid phase. By using the calculated values of the amount of *trans* isomers as function of the melting enthalpy, using the linear relation between the amount of rigid phase and the amount of *trans* isomers, and the corresponding values of the half bandwidth at 1721 cm^{-1}, a plot could be constructed

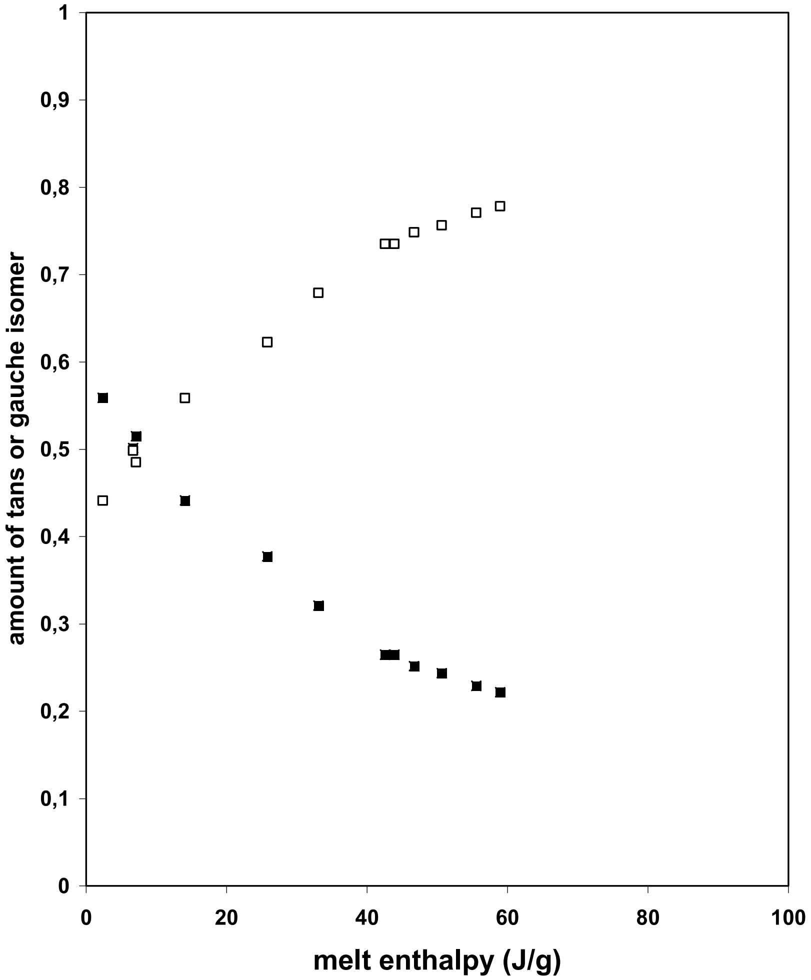


Fig. 6. The calculated amounts of the *gauche* and *trans* isomers as function of the melting enthalpy; ■ amount of *gauche* isomers, □ amount of *trans* isomers.

relating these two parameters of the partial crystalline structure of the PEN samples. This relation is graphically represented on the following Fig. 7.

The relation between the amount of *trans* isomers and the half bandwidth at 1721 cm^{-1} is characterized by two zones. A first zone at high values of the half bandwidth, characterized by a linear decrease of the amount of *trans* isomers with increasing values of the half bandwidth at 1721 cm^{-1} and whereby the amount of *trans* isomers was reaching a value of zero for a half bandwidth at 1721 cm^{-1} of 32 cm^{-1}. This can be regarded as the value corresponding to the complete amorphous phase. The amount of *trans* isomers is reaching 1, complete rigid fraction structure, for a value of the half bandwidth of 7 cm^{-1} corresponding with the limit value for the heat capacity increase. So the two limit values were known corresponding to the complete amorphous phase and the complete rigid structure.

With these values and the known values of the heat capacity increase as function of the half bandwidth, for example the measured values of 0 J/(g K) for 7 cm^{-1}, 0.2260 J/(g K) for 24 cm^{-1} and 0.2710 J/(g K) for 26.5 cm^{-1}, these latter two values corresponding to the extrapolated values in Fig. 3, the value of the heat capacity increase for the complete amorphous phase could be calculated corresponding to the half bandwidth at 172 cm^{-1} of 32 cm^{-1} and was equal to 0.34 J/(g K). This value is somewhat higher but comparable with the already published value of 0.3360 J/(g K) for the heat capacity of the complete amorphous phase [15] and this may be an indication that the used method to estimate the bandwidth at half-intensity at 1721 cm^{-1} for the complete amorphous phase is justified. Comparable values between 0.3360 and 0.3455 J/(g K) were already measured previously [23], indicating that the actual calculated value of the heat capacity increase is indeed a good value for the complete amorphous phase.

Following these results, the crystallization process of PEN from its glassy state can be divided in three zones, as represented in Fig. 8 where the amounts of *trans* isomers and rigid phase structure are plotted as function of the melting enthalpy.

In the first zone or zone of primary crystallization, the content of the total rigid phase was increasing from its initial value of 22% to an amount of 46% at the end of the primary

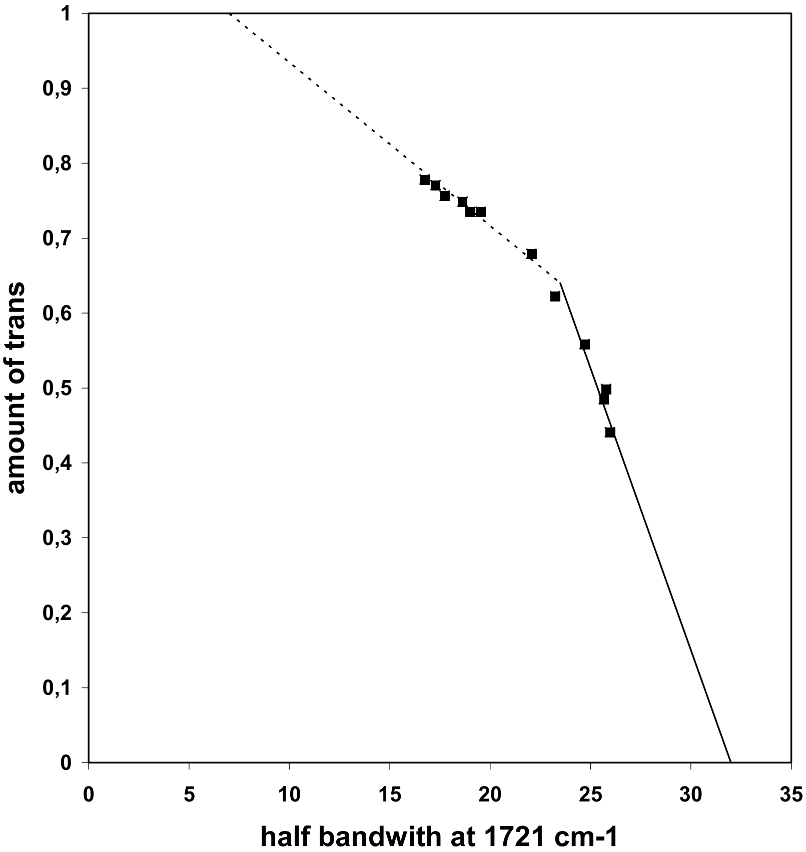


Fig. 7. The calculated amounts of *trans* isomers as function of the bandwidth at one-half maximum intensity at the 1721 cm^{-1} Raman band.

crystallization zone, reaching a melting enthalpy of 42 J/g. After reaching this value of rigid phase content, the amount of rigid phase increased from a value of 46% to a value of 52% in the second zone with constant melting enthalpy. After reaching this value of the rigid phase, the amount of rigid phase is again increasing in function of the crystallization time and temperature during the second crystallization process. These results confirmed that the crystallization behaviour of PEN was more complex than this of PET.

Typically is the value of 46% at the end of the primary crystallization zone, suggesting a critical degree of rigid phase structure. This is comparable to a percolation threshold accompanied by a possible inversion of the continuous phase. If the amount of rigid phase is of the order of 46%, phase inversion could take place and with the amount of f_r less than 46%, the amorphous phase was the continuous phase with the rigid phase dispersed therein. If f_r was greater than 46%, the rigid phase can be the continuous phase with the amorphous phase dispersed therein. A modification of the rigid amorphous phase was necessary in the second zone probably accompanied with a phase inversion, before the secondary crystallization could start with an increase in the melting enthalpy.

The total amount of *trans* isomers is changing continuously with the density or the melting enthalpy. The total amount of *trans* isomers corresponds with the *trans* isomers in the crystallised phase, the rigid amorphous phase and finally with the *trans* isomers dispersed in the amorphous phase.

The polymer PEN is characterised by a possible equilibrium structure, containing a certain amount of a crystallised, rigid amorphous and amorphous phase. This equilibrium can be reached after a certain time, in the limit after an infinite long annealing time. The crystallisation process is a dynamic process, function of time and temperature. As already mentioned, the crystallisation process of PEN is characterised by three zones. The primary crystallisation, first zone, is a very fast process converting a certain amount of the polymer chains into a chain-folded lamellar structure. The amount of crystal structure at the end of the first zone equals 21.4% (42 J/g) and the amount of rigid amorphous phase equals 24.6, 2.6% more than the original amount of rigid amorphous phase. The interface between the crystallised lamellar structure and the amorphous phase is characterised by the presence of a rigid amorphous phase, transition phase between the fully crystallised and the amorphous phase. The primary crystallisation process is so fast that the equilibrium between the amount of crystallised phase and rigid amorphous phase at the interface of the lamellar structure is not obtained. The amount of the rigid amorphous phase at the interface of the

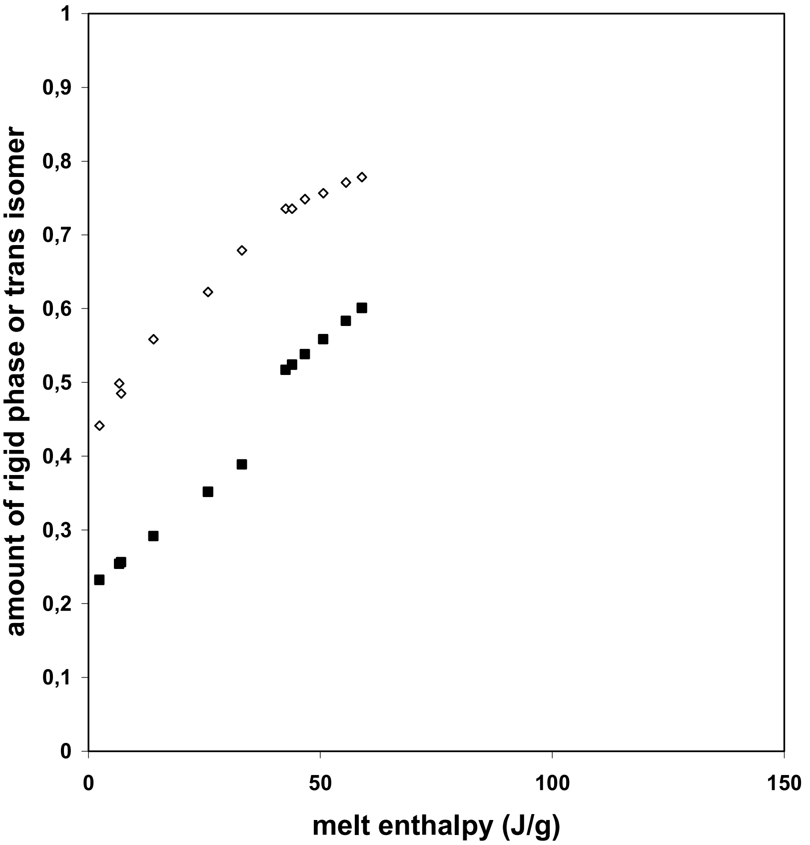


Fig. 8. The calculated amounts of *trans* isomers and rigid phase as function of the melting enthalpy; ■ amount of rigid phase, □ amount of *trans* isomers.

crystallised lamellar structure increases during the second zone, between the primary and the secondary crystallization, reaching a value of 8.6% at the end of these zone or from 12 to 40% relative to the amount of the crystallised phase, due to the transformation of the already present dispersed *trans* isomers in the amorphous phase into these rigid amorphous phase. At the end of the second zone, an equilibrium situation is reached and the secondary crystallisation is starting. The disequilibrium in amounts between the crystallised phase and the rigid amorphous phase at the interface during the primary crystallisation may be another important parameter, besides the phase inversion, that induces two different zones of crystallization.

Other interesting phenomena are the possible variations of the different structures as function of the density. From the published results of the measured densities of cold-crystallized PEN as function of the measured melting enthalpies by Hu et al. [26], a linear relationship between the resulting density and the melting enthalpy could be observed. This linear relationship can be expressed by the following equation:

$$d = 1.3270 + (0.112) * \left(\frac{\Delta H}{196}\right)$$

with d the density (g/cm^3) and ΔH the melting enthalpy (J/g).

The extrapolated value of the density, corresponding to a melting enthalpy of 196 J/g, is equal to 1.4390 g/cm^3. From the Raman spectra and the corresponding values of the melting enthalpies and densities, a crystalline phase with a density of 1.4390 g/cm^3 and a melting enthalpy of 196 J/g is obtained during the annealing of the amorphous film samples.

Fig. 9 is a plot of the linear relationship, represented as a full line in the figure, between the degree of crystallinity and the density according to the Raman and DSC measurements assuming a density of the crystalline phase of 1.4390 g/cm^3 and a melting enthalpy of 196 J/g, together with the recalculated degrees of crystallinity measured by Garcia Gutierrez et al. by using X-ray scattering methods [27].

A very good correlation is observed in the crystallinity degrees obtained by these two different methods and supporting the hypothesis that the true crystallinity of the annealed samples was obtained by using the extrapolated value of the bandwidth at half intensity at 1721 cm^{-1}.

By using the relationship between the melting enthalpy and the density, the already measured and calculated amounts of *trans* isomers and total rigid phase can be

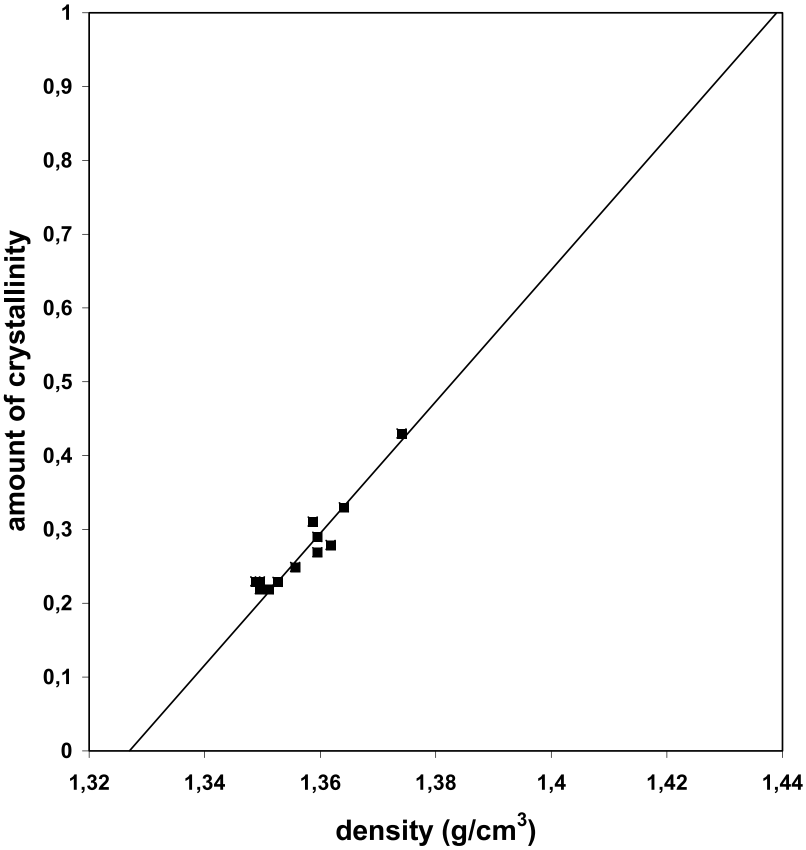


Fig. 9. The calculated amounts of crystallinity as function of the density; full line calculated in this work from Raman and DSC measurements, ■ calculated according to the X-ray measurements by Hu et al.

expressed as function of the density of the related PEN samples. This is graphically done in Fig. 10.

The same general trends as already discussed were also present in this picture. From Fig. 10, it became clear that the extrapolated value of density for a complete amorphous phase, with no *trans* isomers and a zero value of the rigid phase, was equal to 1.3060 g/cm^3 and that the extrapolated value of a complete rigid phase was equal to 1.4070 g/cm^3. Surprisingly, this corresponds to the density of the published value of the α-crystal form [2]. From this study, this value of density is more corresponding with the density of the rigid phase, a combination of the crystalline phase and the rigid amorphous phase. Also typically is the constant value of the density of the rigid phase, result of the linear variation of the density with the degree of the rigid phase in the primary crystallization zone. The relative degree of crystalline and rigid amorphous phase changed with the obtained density of the samples, but the total density of the rigid phase was remaining constant at his value of 1.4070 g/cm^3. The limit value for the secondary crystallization was also the same value of density. As can be observed from the different curves plotted in Fig. 10, a difference is observed between the amount of *trans* isomers and the amount of rigid phase. This means that a certain amount of *trans* isomers is still present in the amorphous phase, but the density of the amorphous phase is staying constant a value of 1.3060 g/cm^3. The presence of isolated *trans* isomers, distributed homogeneously into the *gauche* isomers, has no influence on the density of the amorphous phase.

4. Conclusions

The structure obtained after crystallization of PEN from its glassy state is rather complex, composed in a general way of three phases: an amorphous phase, a rigid amorphous phase and a crystalline phase. A complex variation of these structures in function of the crystallization conditions was measured. With a combined use of conventional DSC, temperature modulated DSC (MDSC) and Laser–Raman spectroscopy an analysis of the structure variations in PEN during its crystallization into α-crystals from its glassy state was possible. Clearly there was more than only a transformation into its α-crystal form. A variation of the amount of rigid phase, of amorphous phase and of *trans* isomers was observed during its crystallization. It was also possible to obtain some limiting values of the density of the different phases obtained during its crystallization.

These limiting values of the densities of the three phases together with the behaviour of the intensities of the Raman

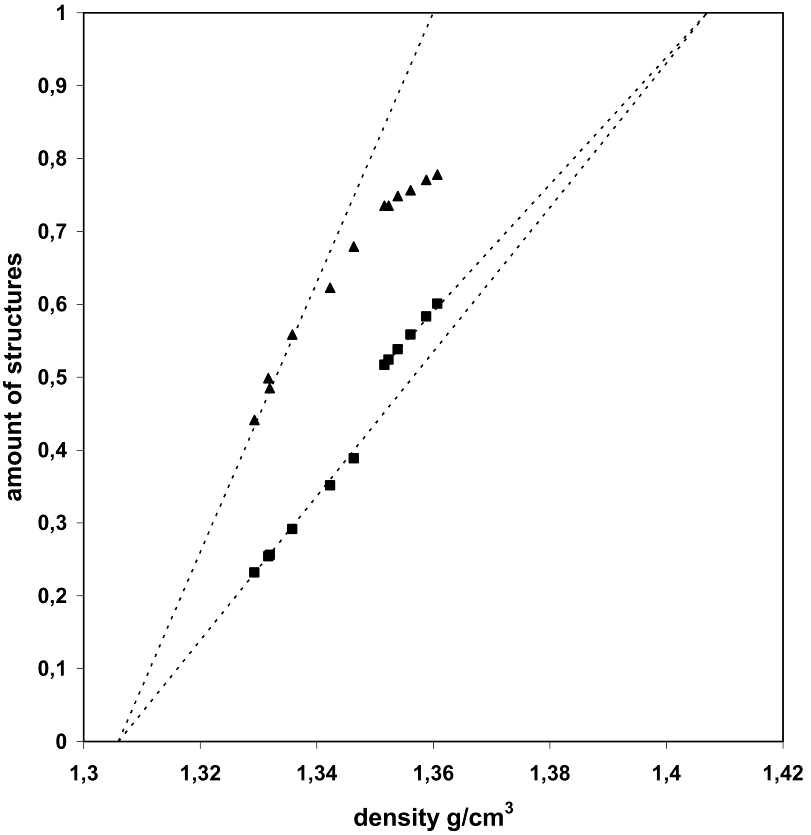


Fig. 10. The calculated amounts of the rigid phase and *trans* isomers as function of the density; ■ amount of rigid phase, ▲ amount of *trans* isomers.

bands will be used to analyse the structure variations during the orientation of PEN from its glassy state.

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