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Dielectric and dynamic mechanical relaxation behaviour of poly(ethylene 2,6-naphthalene dicarboxylate). II. Semicrystalline oriented films

L. Hardy[a,1], I. Stevenson[b,*], A. Fritz[c], G. Boiteux[b], G. Seytre[b], A. Schönhals[d]

[a]*CERSIM/Department of Chemistry, Pavillon A. Vachon, Université Laval, Québec, Canada GIK 7P4*
[b]*Laboratoire des Matériaux Polymères et Biomatériaux (UMR CNRS 5627), Université Claude Bernard, Lyon 1, ISTIL; 15, Bd Latarjet, F-69622 Villeurbanne Cedex, France*
[c]*University of Applied Sciences Wildau, Bahnhofstraße, D-15745 Wildau, Germany*
[d]*Bundesanstalt für Materialforschung and -prüfung, Unter den Eichen 87, D-12205 Berlin, Germany*

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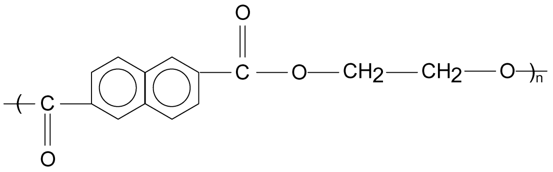
Abstract

The dielectric and dynamic mechanical behaviour of bi-stretched non-treated and annealed semicrystalline poly(ethylene 2,6-naphthalene dicarboxylate) (PEN) films are studied as a function of different morphologies obtained by thermal treatments at temperatures close to the melting temperature of a semicrystalline film. Differential scanning calorimetry (DSC) shows that the glass transition temperatures do not change significantly with the thermal treatment for bi-stretched films. However, the melting temperatures and the degree of crystallinity increase with the value of annealing temperature. Both dielectric relaxation spectroscopy (DRS) and dynamic mechanical analysis (DMA) display three relaxation processes. In order of decreasing temperature, can be observed: the α-relaxation due to the glass transition, the β^*-process assigned to cooperative molecular motions of the naphthalene groups which aggregate and the β-relaxation due to local fluctuations of the carbonyl groups. The α-relaxation process shifts to higher temperatures for the 250 and 260 °C treated bi-stretched semicrystalline samples compared to the sample thermally treated at 240 °C according to DRS data but shifts to lower temperatures according to the DMA measurements for the three annealed samples. This discrepency results from the different sensitivity of each methods with regards to the release of orientation. At a fixed frequency the temperature associated to β^*-relaxation is lower for the non-treated bi-stretched semicrystalline samples than for the treated ones using DMA but no difference can be seen in DRS. The associated apparent activation energies are rather high which suggest cooperative motions. It is assumed that the orientation of the samples prevents coupling between the naphthalene groups due to the stretched chain configuration in the amorphous phase. The activation energy for the β-process given by DRS is independent of the thermal treatment and the value agrees with those found for poly(ethylene terephthalate) (PET) and amorphous PEN. Evidence of the decrease of orientation in the sample with thermal treatment can be seen via the onset of mobility, both by DRS and DMA. Thus, the orientation induces a greater change of properties compared to the crystalline samples obtained from the thermal treatment of an amorphous sample. Finally, a three phase model is proposed since there is evidence of a rigid amorphous phase present in PEN biaxially stretched samples which was favoured by the dependence of dielectric relaxation strengths on the degree of crystallinity for the β^*- and α-relaxation.

Keywords: Poly(ethylene 2,6-naphthalene dicarboxylate); Dielectric relaxation spectroscopy; Dynamic mechanical analysis

1. Introduction

Poly(ethylene 2,6-naphthalene dicarboxylate) or PEN is a thermoplastic polyester with the formula



It combines thermal stability, degradation resistance, weak permeability, excellent mechanical and dielectric properties [1,2]. In general, PEN has more favourable properties compared to poly(ethylene terephthalate) (PET)

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* Corresponding author. Tel.: +33-4-72-44-62-13; fax: +33-4-72-43-12-49.
E-mail address: isabelle.stevenson@univ-lyon1.fr (I. Stevenson).

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which has only a phenyl group in the repeating unit instead of a naphthalene structure. Like PET, PEN can be used in the packaging industry as well as a base film support for thin (down to 1 μm) gauge electromagnetic tapes for audio, video and computer applications [3,4] and also in capacitors. In such applications it should be noted that PEN has a smaller dielectric permittivity, a lower dielectric loss and a 25% higher breakdown voltage than PET. As an aromatic co-polyester PEN exhibits photoconduction and electroluminescence due to the π electron systems as investigated by Kojima et al. [5] who reports that photoconductivity increases with crystallinity.

In general the properties of PEN depend strongly on the morphology of the sample. Therefore in order to tailor its properties to a given application it is important to know the structure–property relationships and to control the morphology. During the last two decades, several articles concerning PEN have been published which have dealt mainly with semicrystalline biaxially stretched and amorphous samples [6–8] as well as with structure and texture [9], orientation factor measurements [10], dielectric and photoluminescence properties [11].

WAXS indicates that the PEN can crystallise in two triclinic forms; the α [12] and the β [13] form. The latter is characterised by four chains per unit cell and can only be obtained under special conditions of rapid quenching and annealing. Generally, PEN is crystallised from the melt at 160 °C in the α form—also referred to as the low temperature modification—which corresponds to one chain per unit cell. During annealing the crystallinity increases and additionally the crystallites and amorphous regions can be oriented by stretching. As a consequence of two-way stretching, the properties become anisotropic and an orientation of the chains in the machine direction (MD) and the transverse direction (TD) is observed [14,15]. Typical differences in characteristic values of the mechanical properties for biaxially stretched PEN and PET films are also reported elsewhere [16].

Chen and Zachman reported dynamic mechanical analysis (DMA) measurements in PEN and random copolymers of PET and PEN in which the β-, β^* and α-relaxation in order of increasing temperature were revealed [17]. This work was completed later using dielectric measurements done by the same authors [18] and by Bellomo et al. [19]. The high temperature relaxation was associated to the glass transition, which is due to the micro-Brownian motions of the chain segments, originating from conformational rearrangements of the chains in the amorphous regions of the sample. If amorphous or semicrystalline non-oriented PEN samples are thermally treated at temperatures higher than T_g, the amplitude of the α-relaxation peak decreases due to the decrease in the amount of the amorphous phase because crystallinity increases and induces further structural changes [7,18]. According to Bellomo et al. [19], the β^*-relaxation process is probably associated to out-of-plane motions of the naphthalene cycle. The reported value of the activation energy estimated from dielectric measurements is rather high. This may imply that the underlying motional process is cooperative in nature. Experimental evidence suggests that the β^*-relaxation should be assigned to the molecular fluctuations of aggregates of the naphthalene rings [6] which have also been revealed by vibrational spectroscopy [20,21].

The β-relaxation is related to local fluctuations of the ester groups [22] because the location and the activation energy of this process is similar to that of PET [23]. Cañadas et al. have made a comparative study of the amorphous and partially crystalline PEN samples by TSDC, dielectric relaxation spectroscopy (DRS), DMA and differential scanning calorimetry (DSC) [1,24]. Investigations on the effect of ageing on copolymers of PET and PEN were also published [25], but surprisingly no β^*-process was discussed even for pure PEN indicating again the complexity of the structure–property relationships of PEN and the influence of process conditions and the thermal history of the sample. Nogales et al. [26] have shown by dielectric spectroscopy the influence of the crystalline nanostructure on the segmental mobility of semicrystalline polymers (such as PEN) of different crystallinity. Two different levels of restrictions have been found for samples having low and high crystallinities. The results from dielectric spectroscopy and DSC indicate that the amount of material involved in the α-process is lower than that calculated on the basis of crystallinity. It supports the idea of a heterogeneous amorphous phase with regions of different mobility that may become more mobile as temperature increases as in the case of a semicrystalline rigid aromatic polymer such as PEN. The work of Sauer et al. [27] is an example of the existence of constrained amorphous motions in flexible polymers. Such polymers including poly(oxymethylene) and its miscible blends have shown such motions as evidenced by dielectric and TSDC studies. Shafee [28] has described the influence of the semicrystalline morphology on the dielectric relaxation properties of poly(3-hydroxybutyrate) or PHB. The constraining influence of the crystallites produces a progressive α-relaxation broadening and a positive offset of this relaxation temperature. An increase of relaxation strength as the temperature increases above T_g was observed. The explanation can only be the existence of a rigid amorphous phase (RAP) which relaxes gradually above the T_g of the mobile amorphous material. The work of Xin Lu et al. [29] concerns the effects of annealing on the disappearance and re-creation of constrained amorphous phase in polyphenylene sulfide (PPS). The location of this RAP is suggested to be within the amorphous phase rather than separated from the liquid-like amorphous phase. Krishnaswamy and Kalika [30] have worked on the glass transition characteristics of poly(aryl ether ketone ketone) and its copolymers. Its glass transition temperature has been investigated as a function of the backbone structure and crystallisation history. Homo- and copolymers with different terephthalic/isophthalic ratios were studied. A measurable quantity of RAP was observed. It is important to point out that this RAP was only observed in low crystallinity thermoplastics, which have a slow crystallisation process, so are easily obtained as 100% amorphous material. Nogales et al. [31] have investigated the structure–dynamics relationships of the α-relaxation in flexible copolyesters during crystallisation as revealed by real time methods. The evolution of an α-relaxation during an isothermal crystallisation for copolyesters of hydroxybutyrate (HB) and hydroxyvalerate (HV) has been monitored by WAXS and dielectric measurements. Dielectric measurements suggest that the progressive immobilisation of polymer segments as crystallisation proceeds cannot be exclusively associated with the amount of crystalline material.

Such a three phase model can be proposed for semicrystalline PEN:

1. a crystalline phase (spherulite superstructure in the annealed amorphous PEN or dispersed lamellae in the biaxially drawn semicrystalline PEN),
2. a ‘mobile’ amorphous phase which is in a more or less random chain conformation,
3. a restricted or RAP whose existence is an opened question for PEN and which is a phase close to the crystallites.

To summarize all discussed results concerning mechanical and dielectric relaxation experiments, the understanding of the structure–properties relationships in PEN have not yet been achieved, illustrated by a certain amount of contradictory results in the published literature. It is clear that the morphology of such a material can be quite complicated depending on the synthesis and processing conditions including thermal history. It is therefore necessary to re-examine the properties of PEN carefully starting with the study of a biaxially stretched PEN film non-treated and thermally treated. DMA and DRS techniques were used since they have shown previously [6,7] their complementarity to other techniques by considering molecular mobility as a probe for structure elucidation. In the first part of Ref. [7], the samples under investigation were amorphous or crystalline after thermal treatment of the amorphous film and the evolution of their properties with their change in morphology has been studied. The DSC experiments show no significant change in the glass transition temperature with thermal treatment. However, the α-relaxation process observed by dielectric and dynamic mechanical analysis shifts to a higher temperature by a few degrees for the semicrystalline samples compared to the amorphous sample as expected [7]. The β^*- and the β-relaxation which occur at lower temperatures (or higher frequencies) than the α-relaxation have been analysed in terms of the variation of the activation energies and of the variation of enthalpies and entropies (Starkweather formalism), as a function of morphology (amorphous and semicrystalline).

In this paper, dielectric and viscoelastic measurements are compared between samples which are semicrystalline and oriented then thermally treated, thus including the study of orientation effects on the properties. These investigations are supplemented by thermal analysis. A dielectric study of oriented biaxially stretched PEN samples which compares the results as a function of the position of the samples within the width of a processed sheet can be found in Ref. [32]. Further work concerning WAXS studies [9] as well as a polarized FTIR experiments to investigate the structure has been recently published [10]. Pole figures [9] have shown that the texture was modified and that the disorientation of the crystallites is mainly complete at 260 °C. The orientation factor calculations showed [10] that the amorphous phase is disoriented. Consequently, it seems possible to investigate the disorientation process under thermal treatment of the oriented amorphous phase of a bi-stretched material by dielectric and mechanical spectroscopy.

2. Experimental

PEN samples were obtained from Du Pont de Nemours as semicrystalline biaxially stretched films with a thickness of 25 μm. The samples were cut from different positions of a 2.38 m wide sheet but it was checked in Ref. [32] that there was no big differences in terms of dielectric properties between the samples. The draw ratio (MD and TD, machine direction and transverse direction, respectively) was comprised between 3.5 and 4. Bi-oriented PEN films were obtained by a sequential bi-stretching in two directions (at 90° to each other) with a first stretching in the MD direction then in the TD direction from the 300 μm thick amorphous film studied in the first part of this paper [7].

This paper focuses on the results obtained on semicrystalline bi-stretched PEN and three semicrystalline bi-stretched samples ‘as received’ obtained by annealing this semicrystalline bi-stretched material at 240, 250 and 260 °C. It is clear that the PEN samples studied, summarised in Fig. 1, can present different relaxation behaviours due to different morphological characteristics in the neat and in the annealed state.

The thermal treatments were performed in the oven of the dynamic mechanical instrument (2980 TA instruments) described in Refs. [7,32] to achieve the same controlled conditions for each sample. The films were heated from room to the annealing temperatures at a rate of 20 K/min. The annealing time was 1 h and after that period the sample was slowly cooled down to room temperature at a rate of −5 K/min.

DSC measurements were carried out using a 2920 TA Instruments device in the temperature range from 50 to 300 °C with a heating rate of 10 K/min. Sample weights were approximately 10 mg. The temperature calibration was

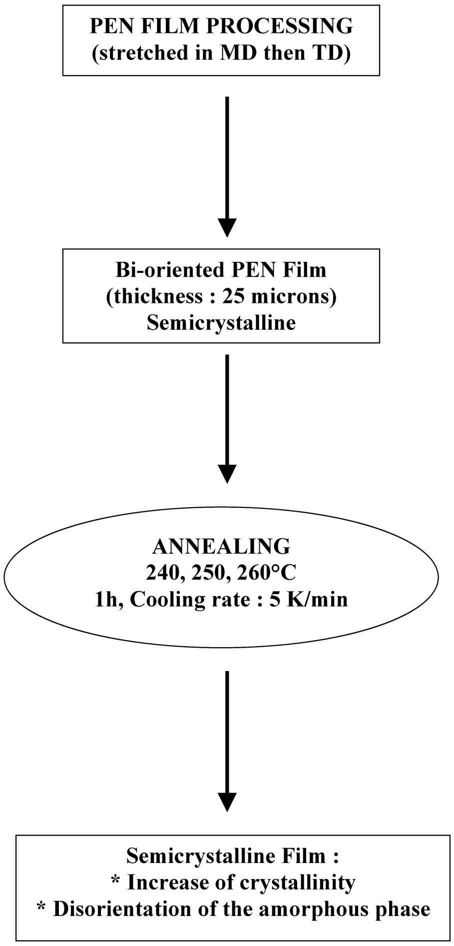

Fig. 1. Processing of the different biaxially stretched PEN samples and morphology studied.

achieved using indium. All samples were sealed in aluminium pans and the measurements were performed under a high purity nitrogen atmosphere. The glass transition temperature T_g has been estimated from the onset temperature. Crystallisation and melting temperatures were taken from the maximum positions of the peaks in the thermograms. The corresponding enthalpies were calculated by the area under the peak using standard procedures. The degree of crystallinity has been estimated using the crystallisation enthalpy of a 100% crystalline sample $\Delta H_\infty = 190$ J/g [33].

The dynamic mechanical properties of PEN samples were studied with a DMA 2980 TA Instruments analyser applying tensile stress. The complex elastic modulus $E^* = E' + iE''$ (E', real part or storage modulus; E'', loss part; $\tan\delta_{DMA} = E''/E'$, $i^2 = -1$) was measured at 1, 3, 5, 7, 10, 12 and 15 Hz. During the measurements, the temperature was raised from −90 to 230 °C at a rate of 1 K/min. The dimensions of the samples were 15 mm in length and 5 mm in width. The comparison will be made between dielectric measurements and the results obtained in DMA on the TD samples.

For the dielectric measurements, circular aluminium electrodes (20 mm diameter) were evaporated on the top and the bottom of the sample.

The complex dielectric function

$$\varepsilon^*(f) = \varepsilon'(f) - i\varepsilon''(f) \tag{1}$$

(f, frequency; ε', real part or permittivity; ε'', imaginary or loss part) was measured in the frequency range from 10^{-1} to 10^5 Hz by a lock-in amplifier (Stanford Research 810) interfaced to the sample by a broadband dielectric interface (BDC, Novocontrol). The temperature of the sample was varied from 173 to 483 K by a custom made liquid nitrogen cooled cryostat and was controlled with an accuracy of $\Delta T = 0.02$ K. A detailed specification of the dielectric equipment used to measure the dielectric function is described elsewhere [34].

3. Results and discussion

3.1. Thermal behaviour

The glass transition temperature (T_g), the melting temperatures (T_{m_1} and T_{m_2}) and the degree of crystallinity [X_c (%)] determined from DSC measurements are given in Table 1 and are shown in Fig. 2. The T_g for the non-treated material was not clearly detectable. However, due to the thermal treatment which contributes to the disorientation of the amorphous phase, T_g becomes detectable for thermally treated films and is approximately equal to 118 °C. There is no significant variation of T_g with thermal treatment as is also the case for the amorphous samples [6,7]. It should also be noticed that two different populations of crystallites appear randomly in this type of sample under annealing at 240 °C, leading to two distinct melting temperatures (the so called T_{m_1} and T_{m_2}). T_{m_1} (at around 255 °C) is a small peak and it is only observed for the sample annealed at 240 °C. As it is not observed from $T_{ann} = 250$ °C, it is expected to reflect the previous temperature of annealing of the PEN film either for the first annealing treatment at 240 °C (T_{m_1} observed at 257 °C) or in the industrial process at around 230 °C (also known as the thermosetting temperature and set at 10–30 K below melting temperature, its purpose being to improve the heat shrinkage stability of the film).

Table 1
DSC values for biaxially stretched samples (non-treated and thermally treated). T_g is the glass transition temperature and T_{m_1} and T_{m_2} are the melting temperatures. NT = non-treated and for example $T = 240$ °C means sample treated at 240 °C

PEN sample	T_g onset (+/− 1 °C)	T_{m_1} (+/− 1 K)	T_{m_2} (+/− 1 K)	X_c (%)
NT	Not determined	230	268	17 ± 1
$T = 240$ °C	119	257	265	23 ± 2
$T = 250$ °C	120	–	266	25 ± 3
$T = 260$ °C	118	–	269	24 ± 2

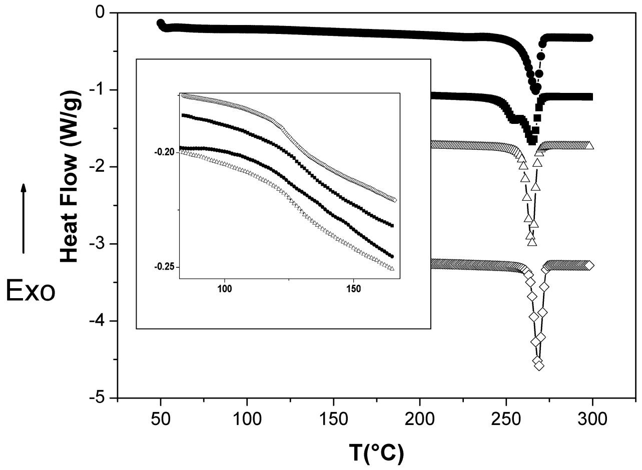

Fig. 2. DSC thermograms of PEN samples. Biaxially stretched non-treated sample (●) and thermally treated sample at 240 °C (■), at 250 °C (△) and at 260 °C (◇). The insert shows the glass transition for the non-treated and thermally treated biaxially stretched samples (same symbols).

T_{m_2} is the melting point temperature of crystallised PEN (265–269 °C). From the values of X_c (%) shown in Table 1, it can be concluded that non-treated samples have a lower degree of crystallinity (17%) than the thermally treated ones (25%). Such results could suggest that it is a consequence of the increase of the number of crystallites or that it is due to the perfection of the crystallites. For the following discussion it is important to point out that the increase of X_c (%) with thermal treatment is evident in the thermally treated samples compared to non-treated ones despite the simultaneous disorientation of the amorphous phase of these samples [10] and the modification of texture from 260 °C [9].

3.2. Relaxation behaviour

Fig. 3 (insert) shows the loss modulus E'' for the biaxially stretched non-treated samples and the thermally treated samples at 260 °C versus temperature at a frequency of 10 Hz. Three relaxation processes are indicated by peaks observed in loss modulus E'' which are designated β-, β*-, α-relaxation in order of increasing temperature or decreasing frequency. Fig. 3 shows the dielectric data at 1 kHz (variation of log ε'' as a function of temperature) in comparison with DMA data. In agreement with the mechanical relaxation behaviour measured by DMA, the dielectric spectra also show three relaxation processes. As a further example of dielectric measurements, a 3D plot ($\log \varepsilon'' - \log f - T$) for the non-treated sample is shown in Fig. 4 to visualize the evaluation of the relaxation processes.

The annealing process increases the crystallinity (Table 1) and consequently, significantly decreases the intensity of the α-relaxation since the amount of the amorphous phase is reduced. Also the intensities of the β-relaxation which are related to short distance motions and that of the β*-process which is assigned to partially cooperative motions should decrease because both relaxation processes take place in the amorphous phase. Regarding the dielectric results in Fig. 3: the α-relaxation displays a slightly different behaviour. However, it has to be mentioned that the effect of disorientation of the chain extended amorphous phase involves more chain mobility and thus an increase of the E'' peak amplitude which is observed for the α-relaxation detected by DMA (see insert in Fig. 3). Hence, the consequence of the disorientation effect dominates the effect of increasing crystallinity when annealing in terms of viscoelastic relaxation behaviour. This supports the idea that the annealing leads rather to crystallite perfection than to nucleation of new crystallites.

The data have been analyzed by the fitting of the Havriliak–Negami [35,36] function. From this fit, the positions of the maximum of dielectric loss (relaxation rate f_{max}) and the dielectric relaxation strength $\Delta\varepsilon$ have been extracted for each process.

For the mechanical experiments the temperature of maximal loss can be extracted and plotted with corresponding measured frequently in the relaxation map as shown in Fig. 5 where both DMA and DRS data are displayed. The mechanical data are shifted slightly towards higher temperatures for the three relaxation processes compared to those for the dielectric data. In other words, the mechanical relaxation processes are observed at temperatures 10–15 K higher than the corresponding dielectric loss peaks (Fig. 5). This behaviour has already been observed for other materials [37–39] and also discussed for PEN in Ref. [6]. Dielectric spectroscopy is sensitive to fluctuations of dipole moments but a mechanical experiment monitors the fluctuations of internal stresses [40]. It has therefore been concluded that each method measures different aspect of the same relaxation process. This is verified again in the case of biaxially stretched PEN samples. In the next three sections the results obtained for each relaxation by both dynamical methods are discussed separately.

3.2.1. β-relaxation

The molecular assignment of the β-relaxation has been proved somewhat controversial in the literature [6,7,32] even for PET. Maxwell et al. [41] concluded that the β-relaxation peak in PET is perhaps due to two molecular processes. Moreover dielectric and mechanical spectroscopy have been applied to a group of three polyesters containing naphthalene groups [42]. A systematic absence of the dielectric β-relaxation is regarded as an indication that the process is associated with the naphthalene groups and neighbouring carbonyl groups undergoing a coordinated rotation motion about the main polymer axis. In Fig. 6 the relaxation map for the β-relaxation is given. Both sets of data fit well to an Arrhenius equation of the form

$$f_{\beta,\max} = f_\infty \exp\left[-\frac{E_A}{kT}\right] \qquad (2)$$

where E_A is the activation energy, f_∞ is the pre-exponential

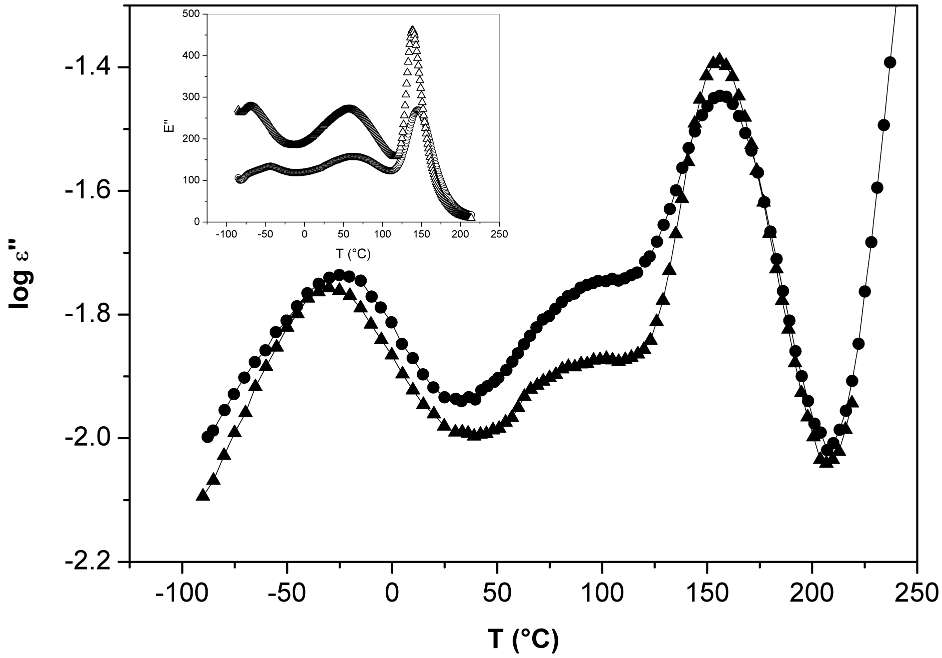

Fig. 3. DRS data (1 kHz)—log ε''—(filled symbols) and DMA data (10 Hz)—E''—(open symbols) in the insert for the biaxially stretched non-treated (○, ●) and thermally treated at 260 °C (△, ▲) biaxially stretched samples versus temperature.

factor, k is the Boltzmann constant and T is the temperature. The estimated activation energies are given in Table 2.

An alternative approach to describe the data is the Eyring theory [43] which gives:

$$f_{\beta,\max} = \frac{kT}{2\pi h}\exp\left[-\frac{\Delta H}{kT}\right]\exp\left[-\frac{\Delta S}{kT}\right] \qquad (3)$$

Here h is Planck's constant, ΔH and ΔS denote the activation enthalpy and entropy, respectively. Applying the general relationship $E_A = \Delta H + kT$, these quantities can be estimated from Eqs. (2) and (3) and are collected in Table 2.

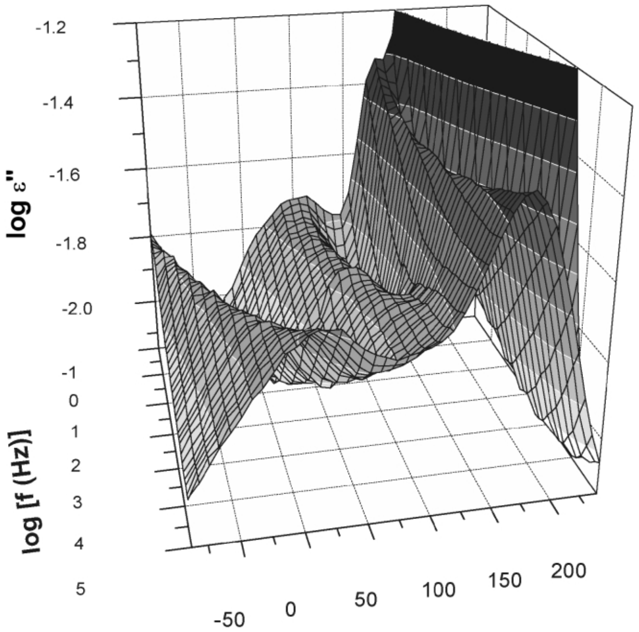

Fig. 4. 3D plot showing log ε'' for the non-treated biaxially stretched sample as a function of frequency (ranging from 0.1 to 10^5 Hz) and temperature (from -100 to 250 °C).

The estimated activation parameters are given in Table 2. The data for the mechanical measurements show a relatively big scatter. This might be due to the frequency range, which is limited in comparison to the one used in dielectric measurements. For all annealing temperatures the activation

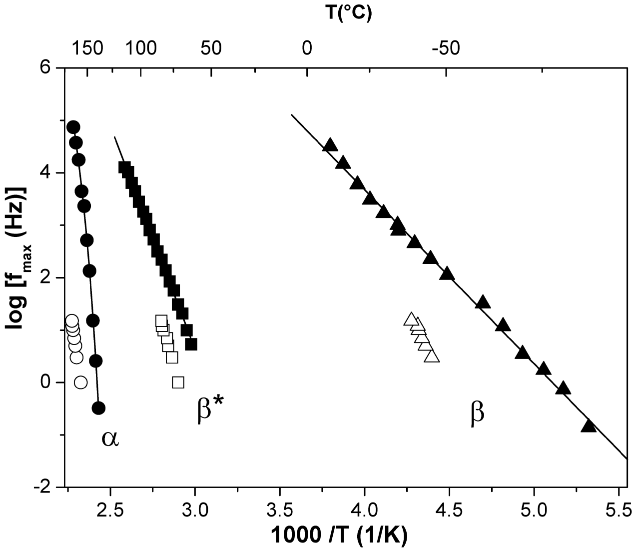

Fig. 5. Relaxation map for the α-(○, ●), β^*-(△, ▲) and β-relaxation (□, ■) obtained from DMA (open symbols) and from DRS data (filled symbols) for the non-treated biaxially stretched sample. Lines are fits to the Arrhenius equation to the dielectric β- and β^*-process and the Vogel–Fulcher–Tammann formula for the dielectric α-relaxation.

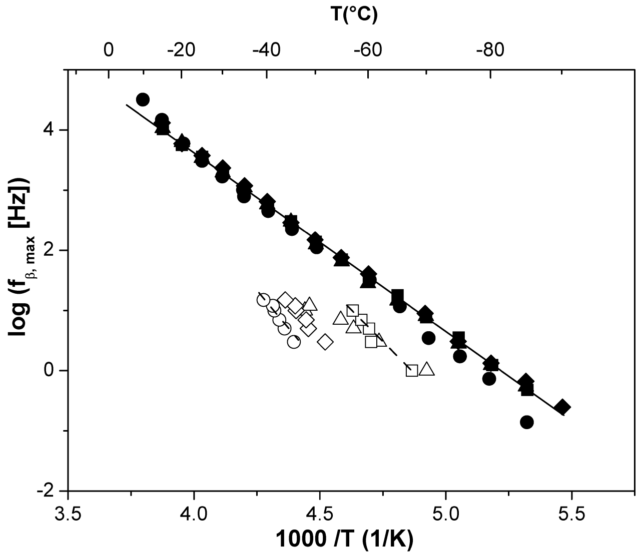

Fig. 6. Relaxation map for the β-relaxation. Filled symbols represent DRS open symbols DMA: non-treated (○, ●), thermally treated at 240 °C (△, ▲) at 250 °C (□, ■) and at 260 °C (◇, ◆). The solid line is a fit of the Arrhenius equation to the dielectric data of the sample treated at 240 °C. The dashed lines are fits of the Arrhenius equation to mechanical data for the sample treated at 250 °C and for the non-treated one. The other fit lines are omitted for seek of simplicity.

energy appears to be lower than the activation energy found for the non-treated sample (Table 2) which are 68 kJ/mol (DRS) and 96 kJ/mol (DMA). The value obtained by mechanical spectroscopy is relatively high compared to those given in the literature [17,22,44] and they differ significantly from those previously found [6,7,32]. This may be due to the fact that the thickness of the samples is only 25 μm which is close to the minimum limit for the accuracy of the DMA apparatus (300 μm in Refs. [6,7]).

Compared to the values obtained by mechanical spectroscopy DRS gives activation energies which are similar to that obtained for PET indicating a local motional process. Therefore it is concluded that the β-relaxation as already described before [6,7,32] is due to local molecular motions (associated to ester group motions alone or motions of ester groups associated to flips of the phenyl ring [41,42,45] as in the case of PET or associated to naphthalene ring in the case of PEN). The activation energy of the non-treated biaxially semicrystalline samples (63 kJ/mol) decreases by 6 kJ/mol for the treated samples (57 kJ/mol). Boyd et al. [44] have shown for PET that the activation energy for the β-relaxation was equal to 53 kJ/mol for the amorphous material and equal to 62 kJ/mol for the semicrystalline PET (the same value was found for amorphous PEN [32]). It seems that the activation energy decreases with annealing to a value similar to that obtained for the amorphous PEN sample. This leads again to the assumption that the annealing leads to a perfection of crystallites rather than the nucleation of new ones.

The values of activation energy for the non-treated and treated amorphous samples were found to be approximately 50 kJ/mol [6,7] with an increase when comparing non-treated to treated material according to DMA data but a decrease according to DRS. This tendency in DMA is not found with the biaxially stretched samples but it has to be kept in mind that the narrow range of frequency available can involve an incertitude in the calculation of the slope of the straight line leading to the activation energy values. In addition, the activation energy decreases with thermal treatment. It can be speculated that orientation in both directions disturbs the relaxation of local dipoles such as ester groups and thus increases significantly the apparent activation energy associated with ester (carbonyl) motions. However, the tendency found in Refs. [6,7] using DRS is more in agreement with the biaxially stretched PEN samples although the energy values are slightly higher (57–63 kJ/mol) but of the same order of magnitude.

3.2.2. β^*-relaxation

Fig. 7 shows the relaxation map for the β^*-relaxation. As for the β-process, the data for the β^*-process can be described by an Arrhenius equation. The activation parameters are collected in Table 3. The activation energy for the β^*-process is essentially higher than the value obtained for the β-relaxation. So they should be considered as apparent activation energies. In addition, the values of the estimated activation entropy ΔS and enthalpy ΔH are high (Table 3). This indicates that the molecular motions which are responsible for the β^*-process are cooperative or at least coordinative in nature.

For the thermal treated samples the β^*-relaxation strength as seen by DMA is higher than that of the non-treated sample (Fig. 3). As this relaxation is partially

Table 2
Activation energies calculated with Arrhenius equation, variation of enthalpy and entropy calculated with Starkweather formalism in the case of the β relaxation for the non-treated (NT) and the annealed at 240, 250, 260 °C biaxially stretched samples obtained from viscoelastic (MD) and dielectric measurements

PEN sample	DRS (β)			DMA (β)		
	E_A (kJ/mol)	ΔH (kJ/mol)	ΔS (J/mol/K)	E_A (kJ/mol)	ΔH (kJ/mol)	ΔS (J/mol/K)
NT	63 ± 6	62 ± 6	88 ± 9	96 ± 10	94 ± 24	200 ± 100
$T = 240$ °C	58 ± 6	56 ± 6	64 ± 9	45 ± 4	70 ± 2	0
$T = 250$ °C	57 ± 6	55 ± 6	61 ± 6	80 ± 11	78 ± 11	153 ± 53
$T = 260$ °C	57 ± 6	55 ± 6	61 ± 6	77 ± 13	76 ± 13	125 ± 56

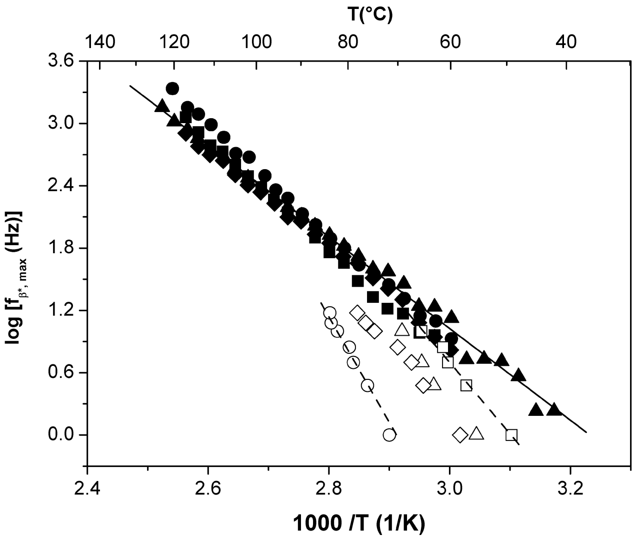

Fig. 7. Relaxation map for the β^*-relaxation. Open symbols represent DMA data, filled symbols DRS data. (○, ●) non-treated, (△, ▲) thermal treatment at 240 °C, (□, ■) thermal treatment at 250 °C, (◇, ◆) thermal treatment at 260 °C. The solid line is a fit of the Arrhenius equation to the dielectric data of the sample treated at 240 °C. The dashed lines are fits of the Arrhenius equation to mechanical data for the sample treated at 250 °C and for the non-treated one. The other fit lines are omitted for seek of simplicity.

cooperative, it should decrease in amplitude with increasing temperature due to the thermal treatment. The observed results can thus be explained by either the release of mobility generated by the disorientation of the amorphous phase leading to an increase in amplitude of the β^*-peak or reflects the incertitude of measurements on the modulus with the use of small dimension samples. Also, for the thermal treated samples the β^*-relaxation region is shifted to lower temperatures (Fig. 7). It appears that the annealing procedure causes a decrease of the apparent activation energy. The corresponding values of ΔS and ΔH are also essentially lower. This can be regarded as evidence that the cooperative nature of the molecular motions are responsible for the decrease in the β^*-relaxation with thermal treatment. Referring to the amorphous samples studied in our previous work [6,7], it was clear that the value of the energy for the non-treated amorphous sample was due to the presence of chains with strong interactions via aggregation of the naphthalene rings, which subsequently vanishes during annealing. In the case of biaxially stretched samples, the amorphous phase oriented chain conformation may promote the formation of naphthalene aggregates, leading to a higher number of aggregates for the biaxially stretched untreated samples compared to the thermally treated ones. Disorientation of the amorphous phase leads to a decrease of activation energy since aggregates are destroyed and fewer aggregates can be formed.

Fig. 3 shows that the dielectric β^*-relaxation is more separated from the α-relaxation than in the case of the amorphous samples [6,7]. The thermal treatment causes a strong decrease of the intensity of the dielectric β^*-relaxation but there is non-significant difference in the activation energies between non-treated and treated samples on the relaxation map (Fig. 7), in contrast to the results obtained by DMA.

There is no dielectric relaxation process in PET similar to the β^*-relaxation found for PEN. It must therefore be concluded that the β^*-process must be associated to naphthalene units [18]. Furthermore, in order to assign a molecular origin to this dielectric relaxation process, it is necessary to consider the relaxation behaviour of rigid main chain polymers from a general point of view, which can be more complex than that of flexible amorphous macromolecules. The existence of an additional process in-between the β- and α-relaxation with a high activation energy has been demonstrated by several other authors for rigid aromatic main chain polymers [46,47]. For instance, PET/xPHB co-polyesters with a liquid crystalline phase show two dynamic glass transitions which indicate a microphase separated structure [46]. Moreover for poly(amide imides), in addition to the β-relaxation, a β^*-relaxation process has been observed at temperatures below the glass transition [47] with a high value of activation energy. It has been shown that the behaviour of this β^*-process, like the dielectric strength and the apparent activation energies, depends on the chain structure of the poly(ester imides) [48]. Hence, the β^*-relaxation found for PEN (Fig. 3) can be regarded as a general feature of main chain aromatic polymers. Even if the β^*-relaxation is close to the α-process, it is obvious from Fig. 3 that its amplitude depends strongly on the thermal treatment.

The activation energies estimated (Table 3) for the β^*-process are essentially higher than that for the β-relaxation, being of the order of 100 kJ/mol. Correspondingly the

Table 3
Activation energies calculated with Arrhenius equation, variation of enthalpy and entropy calculated with Starkweather formalism in the case of the β^*-relaxation for the non-treated (NT) and the annealed at 240, 250, 260 °C biaxially stretched samples obtained from viscoelastic (MD) and dielectric measurements

PEN sample	DRS (β^*)			DMA (β^*)		
	E_A (kJ/mol)	ΔH (kJ/mol)	ΔS (J/mol/K)	E_A (kJ/mol)	ΔH (kJ/mol)	ΔS (J/mol/K)
NT	97 ± 10	94 ± 9	68 ± 7	222 ± 25	242 ± 25	473 ± 47
$T = 240$ °C	83 ± 8	80 ± 8	28 ± 3	147 ± 15	144 ± 15	212 ± 21
$T = 250$ °C	101 ± 10	98 ± 10	77 ± 8	132 ± 13	125 ± 13	154 ± 22
$T = 260$ °C	88 ± 9	85 ± 8	42 ± 4	141 ± 14	138 ± 14	190 ± 43

estimated values for the activation entropy ΔS are also high. They are almost identical for the three annealed samples (Table 3). This indicates that the molecular motions which are responsible for the β^*-process are partially cooperative in these materials as it was the case for the amorphous sample [6,7]. The activation energy for the β^*-process of the amorphous PEN sample [6,7,32], where naphthalene aggregates are free to fluctuate, are of the same order of magnitude than those found for the non-treated biaxially stretched samples (97 kJ/mol which is slightly higher than in Ref. [32]: 92 kJ/mol and lower than in Ref. [7]: 152 kJ/mol). The naphthalene ring is less polar than the ester group [49] therefore its molecular fluctuations cannot lead to a significant dielectric response. Thus, the observed dielectric response should be related mainly to the polar ester groups close to the naphthalene aggregates as it was previously discussed for on amorphous PEN [6,7]. This assumption was supported by the work of Spies [20] and Jones [21] which found aggregates in PEN by applying fluorescence spectroscopy in solution and also in the solid state. Moreover, Wübbenhorst et al. [8] have argued on quenched and amorphous PEN sample in favour of the assignment of the β^*-relaxation to motions of a naphthalene/ester sequence around their collinear outer bonds in an assumed liquid crystalline state. This assignment is quite similar than the interpretation given above using the term aggregates. This particular conformational state should be sensitive to local orientational order of PEN.

The dielectric strength $\Delta\varepsilon_{\beta^*}$ of the β^*-relaxation decreases with increasing temperatures (Fig. 8). This is quite different to the behaviour of β-relaxation processes which corresponds to localized fluctuations where generally an increase of the dielectric relaxation strength with temperature is found as can be seen in Chapter 7 of Ref. [50]. This points also to a cooperative character of the β^*-relaxation. Moreover $\Delta\varepsilon_{\beta^*}$ does not vary systematically with the annealing temperature (Fig. 8). A change of the dielectric strength of the β^*-peak between ‘as received’ and the thermally treated samples can be explained by at least three different reasons: firstly the number of fluctuating moieties and/or secondly the angle of fluctuation decreases when the material is thermally treated. Thirdly it is possible that the Kirkwood/Fröhlich correlation factor decreases due to the annealing procedure (see definition in Chapter 1 of Ref. [50]). In order to check which of these possibilities best suits the experimental data, $\Delta\varepsilon_{\beta^*}$ is plotted as a function of crystallinity in Fig. 9 (insert). In addition, data for the amorphous sample are included which are taken from Ref. [7]. This figure shows that $\Delta\varepsilon_{\beta^*}$ decreases with the increase of the degree of crystallinity which indicates that the change of $\Delta\varepsilon_{\beta^*}$ is due to the decrease of the amount of the amorphous phase and therefore to a decrease of the number density of contributing dipoles. To discuss the dependence of the relaxation strength on the degree of crystallinity X_c it is useful to consider its value normalised by that measured for the complete amorphous state $\Delta\varepsilon_{\mathrm{red},\beta^*} = \Delta\varepsilon_{\beta^*}/\Delta\varepsilon_{\beta^*,\mathrm{amorphous}}$ (Fig. 9). The data does not correspond to a simple two phase model, i.e. $\Delta\varepsilon_{\mathrm{red},\beta^*} = 1 - X_c$. The extrapolation of $\Delta\varepsilon_{\mathrm{red},\beta^*}$ to zero gives a value of approximately 35% meaning that only a fraction of the amorphous phase which is amorphous in structure contributes to the β^*-relaxation. The remaining fraction must be related to the restricted amorphous phase RAP. This is further evidence that the β^*-relaxation is a complicated relaxation process which can only take place in the amorphous phase which is not restricted in mobility. Secondly, compared to PET [50] the amount of RAP appears to be very high for biaxial stretched PEN. It can hence be concluded that the process of biaxial stretching leads to a high amount of RAP.

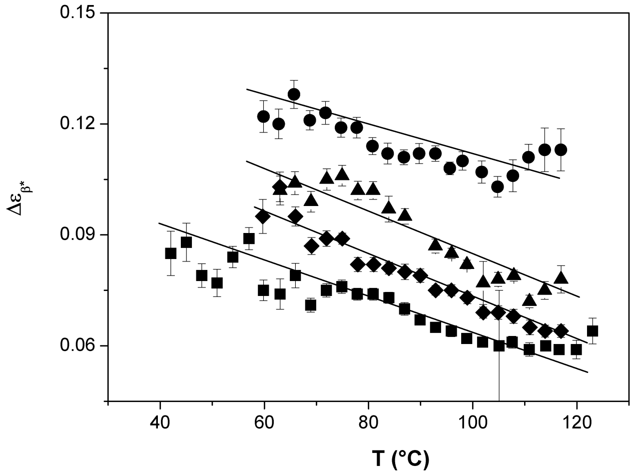

Fig. 8. Dielectric strength $\Delta\varepsilon_{\beta^*}$ for the β^*-relaxation in the case of the non-treated (●) and thermally treated samples at 240 °C (▲), at 250 °C (■) and at 260 °C (◆). Lines are guide to the eyes.

It should be further mentioned that as crystallinity increases under annealing, the orientation of the amorphous phase decreases (see shrinkage from TMA results [9] or the calculation of the orientation functions by polarized FTIR [10]). Hence, two opposing effects on the molecular mobility occur at the same time but the main effect on the change of $\Delta\varepsilon_{\beta^*}$ is related to the increase of crystallinity.

Hence, it can be speculated that the disorientation of the oriented amorphous phase in the bi-stretched sample and the RAP may have changed the nature of the naphthalene aggregates and influenced the activation energy of the β^*-relaxation process. This has been further revealed by the DMA results shown in this paper, since this technique probes the effect of naphthalene aggregates on the internal stresses in the sample whereas the DRS is only sensitive to fluctuations of polar groups close to naphthalene aggregates. Thus, DRS indirectly probes the naphthalene motions. This can explain the difference in activation energy calculated for the β^* relaxation with both techniques.

3.2.3. α-relaxation

The relaxation map of the α-relaxation is shown in Fig. 10. As expected the temperature dependence of the relaxation rate $f_{\alpha,\max}$ for the α-relaxation is curved as a

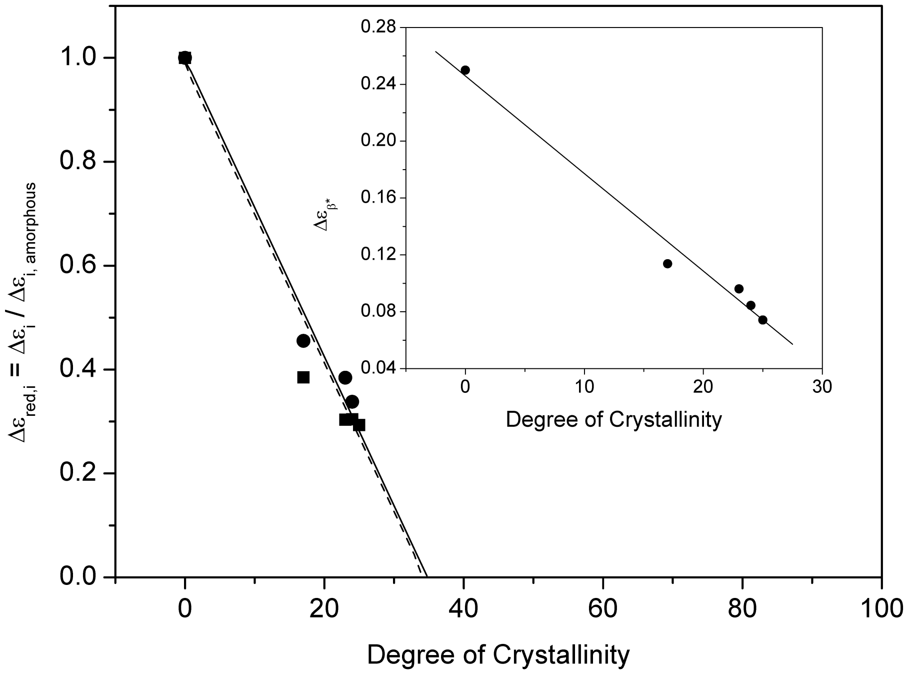

Fig. 9. Normalized dielectric relaxation strength $\Delta\varepsilon_{red,i} = \Delta\varepsilon_i/\Delta\varepsilon_{i,amorphous}$ versus degree of crystallinity for the β^*- (●, $i = \beta^*$, solid line) at $T = 80$ °C and for the α-relaxation (■, $i = \alpha$, dashed line) at $T = 150$ °C. Lines are linear regression to the data. The insert shows $\Delta\varepsilon_{\beta^*}$ versus degree of crystallisation at 80 °C. The line is a linear regression to the data.

function of $1/T$ and can be described by a VFT (Vogel–Fulcher–Tammann) equation [51–53].

$$f_{\alpha,\max} = f_\infty \exp(-B/(T - T_0)) \tag{4}$$

where B, activation parameter; f_∞, pre-exponential factor; T_0, ideal glass transition temperature $T_0 \approx T_g - 30\cdots 50$ K.

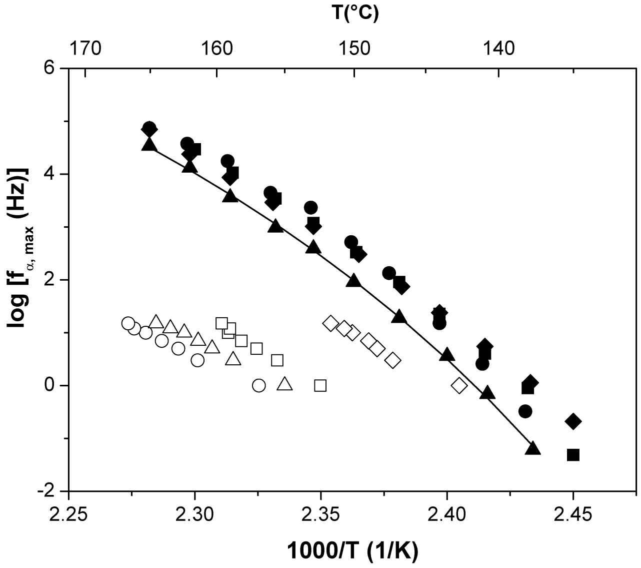

Fig. 10. Relaxation map for the α-relaxation. Open symbols represent DMA data, filled symbols DRS data. (○, ●) non-treated, (△, ▲) thermal treatment at 240 °C, (□, ■) thermal treatment at 250 °C, (◇, ◆) thermal treatment at 260 °C biaxially stretched samples. The line presents a fit of the VFT-equation to the dielectric data of the sample treated at 240 °C. The other fit lines are omitted for seek of simplicity.

Due to the limited range of frequencies available for the mechanical measurement the parameter of the VFT equation could not be estimated reliably. For the annealed samples, the $\log f_{\alpha,\max}$ versus $1/T$ curves shift systematically to lower temperatures. In contrast to the amorphous samples [6,7], it seems that these results can be explained by the decrease of the orientation which favours an increase in molecular mobility within the material and explains the decrease of T_α. This increase in mobility is in agreement with the large increase of the amplitude of E'' for the α-relaxation as shown in Fig. 3.

As in the case of the mechanical measurements, the trace of the dielectric α-relaxation is curved versus $1/T$ in the Arrhenius plot. The VFT equation (Eq. 4) can be used to describe the data and the VFT equation parameters are expressed in Table 4. Extrapolated to low frequencies the curve at 240 °C gives T_α values in good agreement (136 °C) with the glass transition temperature measured by DSC (120 °C).

Table 4
VFT parameters calculated with VFT equation obtained from dielectric measurements. Variation of B (K), $\log f_0$ and T_0 (K) in the case of the α-relaxation for the non-treated (NT) and the annealed at 240, 250, 260 °C biaxially stretched samples

PEN sample	B (K)	$\log f_0$	T_0 (K)
NT	424 ± 68	12 ± 1	377 ± 3
$T = 240$ °C	862 ± 15	15 ± 2	358 ± 6
$T = 250$ °C	595 ± 130	13 ± 1	366 ± 5
$T = 260$ °C	785 ± 151	14 ± 1	355 ± 4

For the annealed samples the α-relaxation process shifts to higher temperatures for the samples annealed at 240 °C. This fact can be understood by the increase of crystallinity (Table 1). If T_{ann} is increased further (250, 260 °C) the relaxation rate shifts back to lower temperatures due to the increase of mobility during the release of orientation. Hence, the behaviour of the rate of the dielectric α-relaxation during thermal treatment can be understood by a competition between the increase of crystallinity and the release of orientation during annealing whereas the mechanical behaviour is more sensitive to the release of orientation. This becomes more clear in Fig. 11 where the difference of T_α for the 'as received sample' and the annealed samples at a frequency of 10 Hz is plotted versus annealing temperature. For the dielectric α-relaxation the data show small variation indicating that DRS as a more localized probe is less sensitive to orientation than mechanical spectroscopy where a strong variation of T_α was found with annealing temperature. In the insert of Fig. 11, the difference between the dielectric and the mechanical is plotted versus T_{ann}. For low annealing temperatures there is an almost parallel variation of the dielectric and mechanical data. At $T_{ann} = 260$ °C strong difference of the both data sets is observed. It is known from shrinkage and X-ray experiments (pole figures) [9] that at this annealing temperature the disorientation of the chains is almost complete.

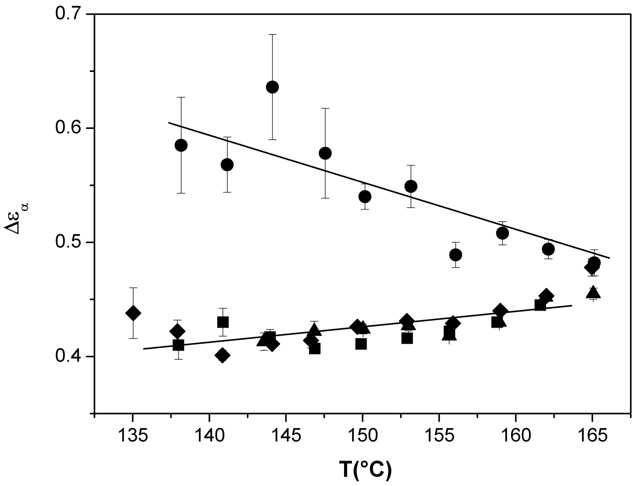

Fig. 12. Dielectric strength $\Delta\varepsilon_\alpha$ for the α-relaxation for non-treated (●) and thermally treated at 240 °C (▲) at 250 °C (■) and at 260 °C (◆) biaxially stretched samples. Lines are guides to the eyes.

Fig. 12 gives the temperature dependence of the dielectric relaxation strength $\Delta\varepsilon_\alpha$ for the samples studied. For the 'as received' material $\Delta\varepsilon_\alpha$ decreases with increasing temperature. The annealing procedure leads to a reduction of $\Delta\varepsilon_\alpha$ and $\Delta\varepsilon_\alpha$ increases with increasing temperature. In Fig. 9: $\Delta\varepsilon_{red,\alpha} = \Delta\varepsilon_\alpha/\Delta\varepsilon_{\alpha,amorphous}$ is plotted versus the degree of crystallinity. This figure shows that $\Delta\varepsilon_\alpha$ scales with crystallinity. Like for the β^*-process also for the α-relaxation the dependence of $\Delta\varepsilon_\alpha$ on the degree of crystallinity do not follow a two phase model which gives again evidence for the restricted amorphous phase. The extrapolation $\Delta\varepsilon_{red,\alpha}$ to zero gives a value for the amount of RAP which is quite consistent with that obtained from that of the β^*-relaxation.

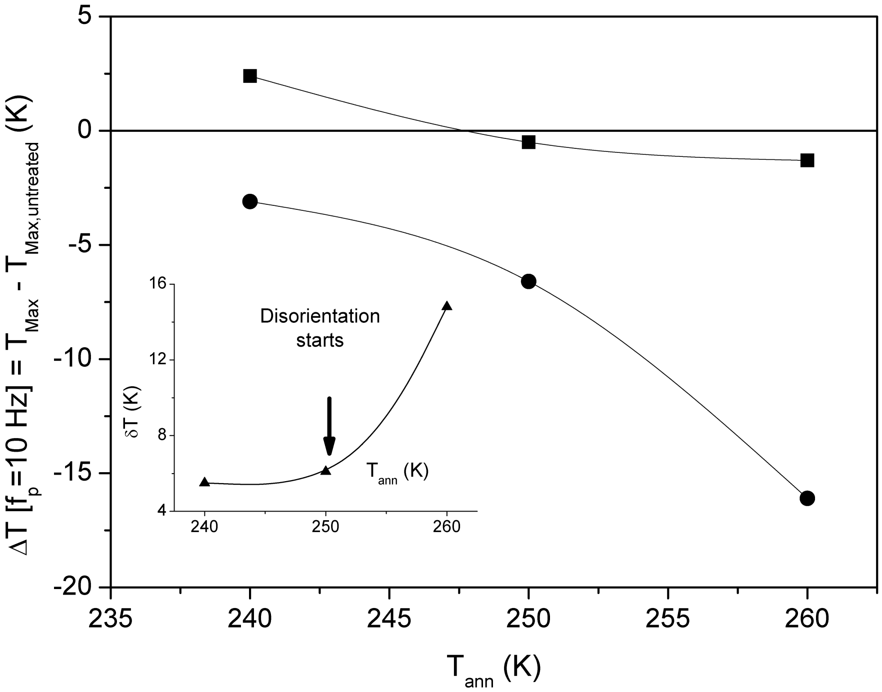

Fig. 11. Difference of the temperatures where the relaxation rates are 10 Hz versus annealing temperature for the treated and untreated samples: (■) DRS; (●) DMA. The lines are guides to the eyes. The insert gives the difference of the dielectric and mechanical values versus annealing temperature. The line is a guide to the eyes.

Schlosser and Schönhals [54] have studied the evolution with temperature of $\Delta\varepsilon_\alpha$ for PET. It was found that $\Delta\varepsilon_\alpha$ decreases with increasing temperature for amorphous samples and that $\Delta\varepsilon_\alpha$ increases with temperature for semicrystalline samples. The same was also found for other semicrystalline polymers [50, Chapter 7]. The reason why $\Delta\varepsilon_\alpha$ decreases with increasing temperatures for the non-treated semicrystalline sample but increases for the annealed ones involving only a small change in crystallinity is not well understood and needs more experiments. However, the change in the temperature dependence implies a change in structure induced by the annealing process.

Due to the more rigid chain structure of PEN the glass transition temperature is higher than that of PET. It is also well known that the T_g of polymers with a semicrystalline morphology is higher than for the corresponding amorphous state. Such a comparison cannot be made here since the non-treated sample is semicrystalline already and the treated sample is more crystalline but disoriented. The DMA measurements give a systematic decrease of the dynamic glass transition temperature with the annealing temperature (Fig. 10) which was not the case for the viscoelastic behaviour of the amorphous sample [6,7]. However, the dynamic glass transition temperature extracted from the dielectric measurements increases firstly with the annealing temperature (240 °C) but decreases for higher annealing temperatures (250, 260 °C). It can be argued that this difference comes from the competition between the modification of the crystalline phase (size, perfection) and the release of mobility generated by the disorientation of the amorphous phase. This is also supported by the fact that the amplitude of log ε'' (DRS) and E'' (DMA) is higher for the treated material compared to the non-treated one.

4. Conclusions

The dielectric and dynamic mechanical behaviour of biaxially stretched poly(ethylene 2,6-naphthalene dicarboxylate) (PEN) and of thermally annealed samples has been reported as a function of the morphology. The DSC study shows that the glass transition temperatures and the melting temperatures do not change significantly with the thermal treatment. However, the degree of crystallinity increases at low annealing temperatures but decreases at higher ones. Both dynamic mechanical and DRS display the main α-relaxation process associated to glass transition and two processes: β^*- and β-relaxation at lower temperatures (or higher frequencies) than the α-relaxation. These latter relaxations are analysed in terms of the activation energies (Arrhenius plot), the variation of enthalpies and entropies (Starkweather formalism) as a function of morphology (semicrystalline oriented and semicrystalline disoriented). It has been confirmed that for this textured material the β-relaxation is also due to local movements. The molecular mechanism is assumed to be similar to that of the β-relaxation in PET, i.e. to local fluctuations of carbonyl groups. The high values found for the activation energies, enthalpies and entropies of the β^*-process leads to the conclusion that this relaxation process should be due to partially cooperative molecular motions. If the non-treated biaxially stretched samples are thermally treated, the polymer crystallises. Experimentally the activation energy of the mechanical β^*-relaxation decreases dramatically and the peak shifts to lower temperatures for the DMA data. This experimental fact can be regarded as a further hint for the assignment of the β^*-relaxation to cooperative motional processes, because local molecular motions are in general not influenced by a change in the supramolecular structure in amorphous phase. However, the relaxation peaks are in the same position and the activation energies do not vary so much in the DRS data, which appears less sensitive regarding the detection of this change of supramolecular structure in the amorphous phase. Nevertheless, the dielectric strength of the β^*-process depends systematically on the degree of crystallinity.

The chains will be stretched in the amorphous regions because of the semicrystalline oriented morphology. This process will also influence the proposed aggregation, which is less likely to occur than in the case of an amorphous sample. This means that the number, the extent and the size of the aggregates are smaller in the semicrystalline disoriented state than in the oriented semicrystalline one. Therefore the activation energy of the β^*-relaxation is decreased in the treated state compared to the non-treated one and this fact is observed in both techniques, but to a greater degree in DMA. The main difference between the amorphous material behaviour and that of the annealed disoriented semicrystalline samples is the release of mobility seen in DMA through the increase of amplitude of E''.

The dielectric α-relaxation shifts to higher temperature for the semicrystalline samples treated at 240 °C compared to the non-treated oriented one. However, the viscoelastic behaviour is different and reveals firstly that the α-relaxation shifts to lower temperature and secondly that the maximum height for the annealed samples increase compared to the non-treated one. These two observations prove that the increase of mobility generated when the amorphous phase becomes disoriented is predominant over the change in crystallinity. Like for the β^*-relaxation the dielectric strength decreases with increasing degree of crystallinity. Its extrapolation to zero leads to the conclusion that the amount of restricted amorphous phase is quite high for biaxial stretched PEN materials. This is quantitatively consistent with the dependence of the relaxation strength of the β^*-process.

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