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ORIGINAL CONTRIBUTION

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New dielectric relaxation process reveals mesomorphic ordering in rapidly cooled poly(ethylene naphthalate)

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Abstract A curious, strong dielectric relaxation process (δ) was found in rapidly cooled poly(ethylene naphthalate). This process, which is located between two known β and β^* relaxations of PEN, appears predominantly after rapid cooling and remains present even after heating above the glass transition temperature. In view of its very low activation energy of ~10 kJ/mol, its markedly high relaxation strength of up to $\Delta\varepsilon = 5$, and its Debye-like peak shape, a collective relaxation mechanism is proposed, which involves collective crankshaft motions of the -O-CH$_2$-CH$_2$-O- sequences in a regular arrangement of the main chains. The analogy between this δ-relaxation and an ultra-slow relaxation recently found in the smectic E phase of a side-chain liquid crystalline polymer suggests a (close-to) hexagonal smectic ordering in PEN. The very existence of liquid-crystalline order in PEN is corroborated by the observation of a thermo-reversible discontinuity in the relaxation parameters around −90 °C, which resembles a broadened LC-LC phase transition. Re-evaluation of experimental data of the β^* relaxation, which occurs in the non-crystalline fraction of PEN, suggests that this relaxation is sensitive to the local orientational order, which extends from nematic to isotropic. The shift in the temperature of the β^* peak and even the splitting of this peak found by other authors can be ascribed to the lowering of the activation energy by the local ordered packing of the PEN chains in line with a lower activation energy in the nematic order. The coexistence of isotropic and nematic regions in PEN is put in the context of orientational order fluctuations during the induction period of cold crystallisation of semi-flexible polymers.

Key words Poly(ethylene naphthalate) (PEN) · Dielectric relaxation spectroscopy · Low temperature cooperativity · Hexagonal smectic order · Liquid crystallinity · Quenching

Introduction

Poly(ethylene naphthalate) (PEN, cf. Fig. 1) is a semi-flexible polymer with superior properties compared to those of PET [poly(ethylene terephthalate)] viz., a higher glass-transition temperature (115 instead of 75 °C for PET), excellent mechanical properties, such as tensile properties and dimensional stability, and a higher refractive index. Unfortunately, the maximum crystallisation rate of PEN is only 1/5 of that for PET, which hampers its application for fast injection molding. Although PEN shows typical lamellar growth at temperatures just below the melting temperature ($T_m \sim 260$ °C), its cold crystallisation behaviour and slow crystallisation kinetics are far from being understood.

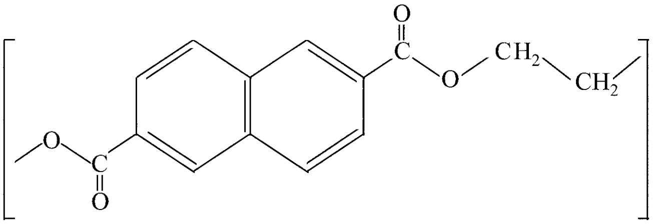

Fig. 1 Chemical structure of poly(ethylene-2,6-naphthalene)

A popular view that explains the unexpected high E-modulus and the slow crystallisation kinetics, assumes the presence of a third phase, "*rigid* amorphous phase" (RAP) [1–3], which involves oriented and constrained "non-crystalline" polymer chain sequences close to the crystalline lamellae. However, recent studies on PEN rather reveal the existence of highly ordered, non-crystalline domains, both in drawn PEN fibres [4, 5] and PEN films [6] or as a result of cold crystallisation [7]. These structures show X-ray patterns typical for *mesomorphic* structures and have a thermal stability of more than 180 °C [5]. Additional support for the existence of mesomorphic ordering in PEN comes from Sata et al. who deduced a nematic-like order from magnetic orientation studies just below the melting temperature [8]. These findings refute the RAP model and imply that, under certain conditions, an amorphous phase, a crystalline phase, and a mesophase coexist in spatially separated regions of PEN.

The occurrence of mesomorphic order in PEN is a point of on-going debate. In contrast to several truly liquid crystalline thermotropic (LC) copolyesters like Vectra, PEN crystallises in two genuine triclinic crystal structures, the α and β modifications, and its degree of crystallinity reaches ~35%, which is a rather low value for a semi-crystalline polymer. Proper liquid crystalline behaviour in the sense of stable mesophases has so far not been observed in PEN, the chain structure of which shows a concentration v of rod-like segments below the critical concentration v^* at which the isotropic liquid becomes unstable, i.e., would undergo an isotropic-nematic phase transition [9].

Nevertheless, Imai et al. [10] and others have shown that fluctuations in density and in local chain ordering occur in the induction period prior to crystallisation of PET, PEN, or syndiotactic PS [6, 10, 11]. Based on arguments from statistical thermodynamics about the crystallisation process of semi-flexible chain molecules, Flory already proposed a two-step crystallisation model. In the first step, ordering of chains into a parallel alignment (a nematic order) is established, which is followed by improvements of the molecular packing by longitudinal adjustments of the chains in the parallel state [12]. Recent experimental results on PEN and PET with time-resolved FTIR, SANS, SAXS, and depolarised light scattering seem to justify this two-step concept [10, 13].

If one links the nucleation process with the spatial orientational fluctuations in the polymer melt, discussed in the framework of spinodal decomposition in "amorphous" and "nematic" regions, it is likely that crystal nucleation starts in regions with higher orientational order. Baltá-Calleja et al. [7], however, showed by high-resolution transmission electron microscopy on cold-crystallised PEN that, after an initial phase separation of PEN into regions of medium density (non-crystalline, unknown structure) and low density (identified as "real" amorphous phase), crystallisation occurs solely in the (low density) amorphous phase. If one supposes that the non-crystallisable phase corresponds with a (dense) mesophase, one can explain the relative stability of such mesomorphic structures.

In contrast to PET, only a few studies have appeared about the molecular and cooperative dynamics of PEN by dynamic mechanical analysis (DMA) or dielectric relaxation spectroscopy (DRS) [14–17]. According to Bellomo and Lebey [14], three relaxation processes (β, β^*, and α) can be distinguished. The low-temperature (β) process, for which activation energies between 39 and 45 kJ/mol have been found by DRS [16], is related to local motions involving the ester groups. This assignment is confirmed by the occurrence of a β-process with almost the same activation parameters as in the structurally similar PET. At high temperatures, the α-relaxation can be observed, which is associated with the dynamic glass transition. This relaxation process reflects the co-operative segmental motions of the amorphous fraction of PEN and thus decreases in intensity when the degree of crystallinity increases.

The β^* relaxation is the least understood relaxation process in PEN and does not exist in PET. It was attributed to specific out-of-plane motions of the naphthalene group [14]. Recent studies yielded activation energies in the range between 125 and 270 kJ/mol, which are far too high for local molecular motions in general. Furthermore, these values depend strongly on the thermal history of the PEN as well on the technique used (DRS, DMA) [16]. Since a high activation energy implies a co-operative molecular mechanism, Hardy et al. [16] discussed the β^* process in terms of aggregates of PEN chains being present in the amorphous state.

In the present paper, we report on unexpected results from dielectric relaxation spectroscopy on *rapidly* cooled PEN, which give additional support for the existence of LC-like local ordering [18].

Materials and methods

Samples for the dielectric experiments were prepared by melting of PEN ($\eta_{\mathrm{rel}} = 1.6$ in *m*-cresol at 25 °C) at 290 °C together with quartz fibres between circular aluminium electrodes (diameter 30 mm).

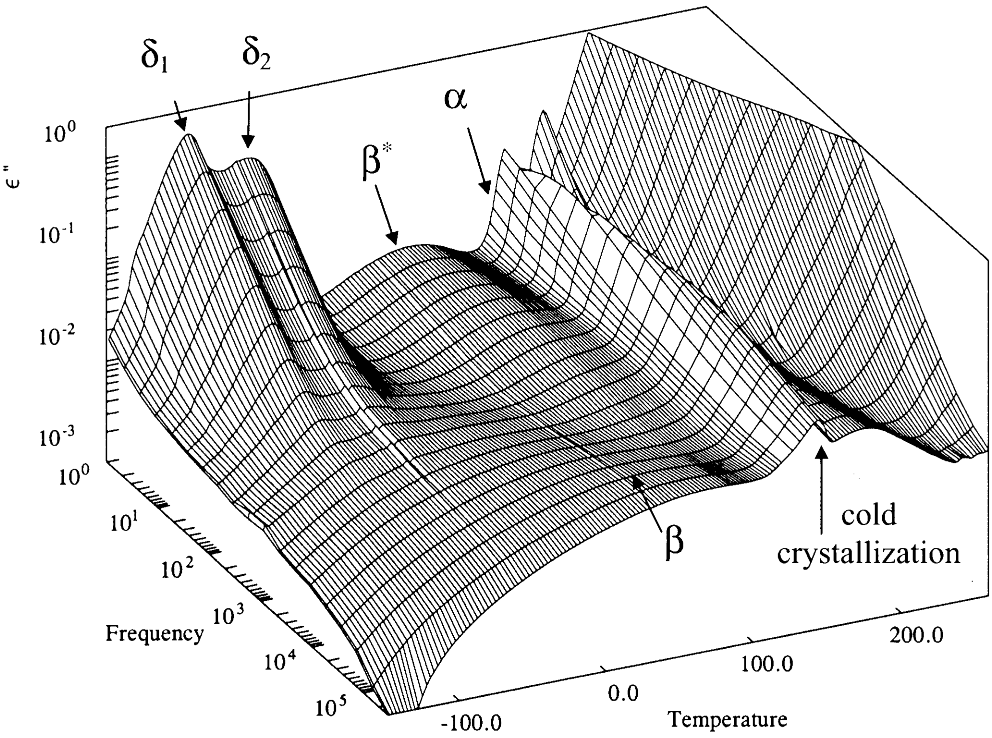

Fig. 2 Dielectric loss ε'' of a rapidly cooled PEN sample 2 during slow heating with 0.5 K/min. Two prominent peaks δ_1 and δ_2 are visible together with the β, β^*, and α relaxation process

This resulted in 300–600 μm thick PEN layers in disk-shaped Al-PEN-Al sandwiches. In order to obtain amorphous material (which was confirmed by DSC), samples 1 and 2 were quenched from the melt by placing the hot samples (T = 290 °C) on a massive metal plate (at room temperature). This resulted in a cooling rate of ~70 K/min in the crystallisation temperature range of 150–270 °C. Alternatively, another sample 3 was quenched in the dielectric cell by cold nitrogen gas leading to a lower cooling rate of 30–40 K/min. Semi-crystalline PEN samples were prepared by rapidly placing a molten sample in the pre-equilibrated dielectric cell followed by isothermal crystallisation for 4 h at 180 (sample 4) and 240 °C (sample 5). All preparation steps took place under flowing nitrogen gas.

Dielectric measurements on PEN samples were performed using a combination of two dielectric analysers covering a frequency range from 10^{-2} to 10^6 Hz:

1) a frequency response analyser (Schlumberger 1260) equipped with a custom made dielectric interface (developed by TNO) for frequencies between 10^{-2} and 10^3 Hz, and
2) a Hewlett-Packard 4284A precision LCR-meter for frequencies between 10^3 and 10^6 Hz.

The sample was placed in a cryostat (Novocontrol), the temperature of which was controlled with nitrogen gas with a stability of better than ±50 mK. More details about the experimental setup can be found in Ref. [19].

In order to determine the relaxation time $\tau(T)$ from the dielectric loss curves we have fitted the frequency spectra $\varepsilon''(\omega)$ by a set of two Havriliak-Negami relaxation functions (Eq. 1) using the Levenberg-Marquardt algorithm:

$$\varepsilon'' = -\sum_{k=1}^{2} \mathrm{Im}\left\{\frac{\Delta\varepsilon_k}{\left(1+(i\omega\tau_k)^{a_k}\right)^{b_k}}\right\} + \frac{\sigma}{\varepsilon_0\omega} \tag{1}$$

where $\Delta\varepsilon_k$ and τ_k correspond to the relaxation strength and the mean relaxation time of the kth process. The two shape parameters a_k and b_k, which determine the logarithmic slope of the low frequency loss tail a and the high frequency loss tail $-a \cdot$ b, are determined by the underlying distribution in relaxation times. The 2nd term in Eq. 1 accounts for pure ohmic conduction.

Results and discussion

Figure 2 shows a 3D representation of the loss ε'' of amorphous sample 2 measured during slow heating from −150 to +250 °C. As expected, the three well known relaxation processes of PEN (β, β^*, and α) appear. Above T_g, a clear drop in ε'' indicates the onset of cold crystallisation, which also gives rise to an additional peak (often called the ρ peak) above the α-process, caused by interfacial polarisation at the crystalline lamellae.

The most intriguing phenomenon, however, is the appearance of two additional strong and unusual relaxation peaks (δ_1 and δ_2)[1], the peak maxima of which show up around −100 and −60 °C, respectively.

These odd relaxations have so far not been reported. In order to ensure that no experimental artifacts are playing a role in our experiments, we have performed dielectric experiments on a series of differently prepared

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[1] The symbol δ has been chosen in order to distinguish this strong process from both segmental and local relaxation processes, usually denoted by α, γ, and β. Note that this δ-process should not be confused with the notation for fluctuations around the short molecular axis of mesogens.

amorphous and semi-crystalline PEN samples (cf. Table 1). A comparison of all temperature-dependent loss curves, measured at 1.5 Hz, is made in Fig. 3a. For a better illustration of the strength of the relaxation processes we have shown the permittivity $\varepsilon'(T)$.

Let us first ignore the peculiar δ-peaks occurring only for samples 1 and 2. If not affected by the δ-peaks, the β, β^*, and α relaxation peaks reflect the trends described by other authors [15–17]. With increasing crystallinity, the intensities of the β and β^* processes decrease, which again confirms the assignment of both relaxations to molecular motions in the *non-crystalline* phase. As expected, the semi-crystalline sample 5 possesses the highest crystalline fraction, since it was crystallised at the highest temperature (T = 240 °C). For the α-relaxation peak, we can recognize a similar trend: the highest peak maxima originate from fully amorphous samples. As an exception, the stepwise heated sample 1 deviates from the other two amorphous samples for unknown reasons.

A second trend visible in Fig. 3a concerns the peak position of the β^* process. Compared to the amorphous samples, which demonstrate a neat reproducibility of their β^*-peaks, the peak positions of both semi-crystalline samples are shifted to lower temperatures by about 10 K. This finding is in qualitative agreement with results from Hardy et al. [16], who also noted shifts in the dielectric and mechanical β^*-relaxation maxima, which are linked to a strong reduction in the activation energy of the mechanical β^*-peak from 269 kJ/mol (amorphous PEN) down to ~130 kJ/mol (for semi-crystalline PEN) [16, 17]. Their activation energy for the dielectric β^*-peak of amorphous PEN was slightly higher (152 kJ/mol) and agrees nicely with our Arrhenius parameters with $E_a = 147$ kJ/mol from sample 3, the relaxation times of which are shown in Fig. 7.

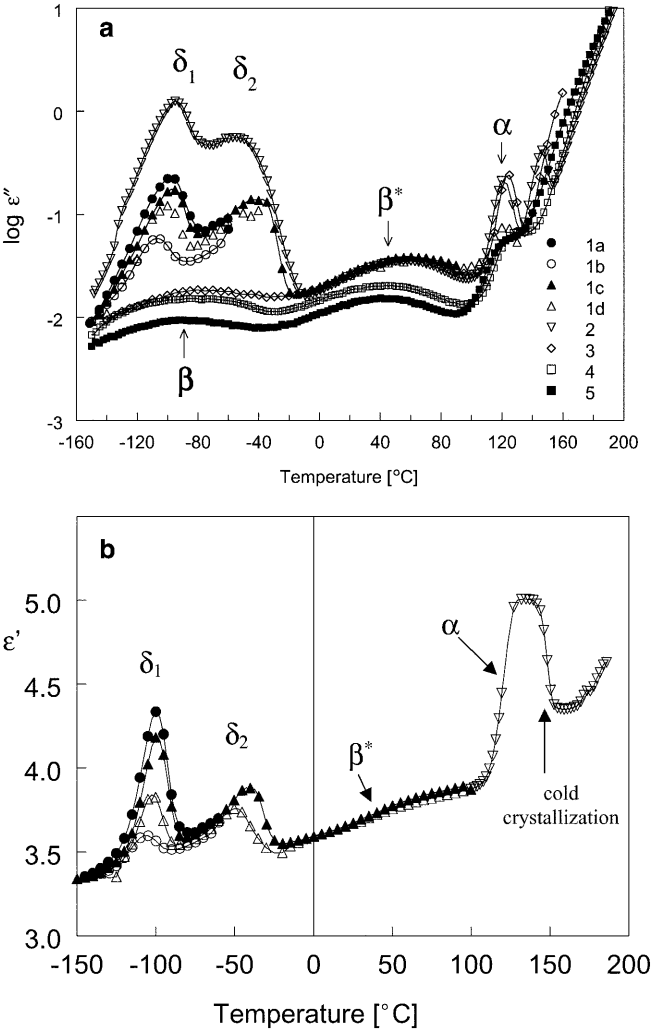


Fig. 3 (*a*) Dielectric loss ε'' at about 1.5 Hz as a function of temperature for various amorphous (samples 1–3) and semi-crystalline (samples 4, 5) PEN specimens (cf. Table 1). (*b*) Permittivity ε' at 0.1 Hz as a function of temperature for amorphous samples 1 and 2. The symbols are the same as in Fig. 3a

We will now discuss the strong, unexpected peaks visible in Figs. 2, 3a, and 3b, for convenience we have labelled them as δ_1 and δ_2 relaxation. They were first observed by us on the rapidly cooled sample 2 and could also be detected in other PEN samples not described in this paper. In order to study the reproducibility and thermal stability of the δ-peaks, we performed a stepwise heating/cooling procedure (see Fig. 4) on a sample, which was quenched in a very similar way as sample 2. Apart from the somewhat lower δ-peak intensity in sample 1 compared to that of sample 2, one sees that a thermal treatment up to 100 °C (sample 1d) has only a marginal effect on the δ-peak position and intensity. In

Table 1 Sample overview and preparation details for dielectric experiments

Sample	Initial preparation	Temp. interval	Heat./cool. rate [K/min]
1a	quenched to 25 °C	−150 °C…−60 °C	+1
1b		−60 °C…−150 °C	−1
1c		−150 °C…100 °C	+1
1d		−150 °C…250 °C	+1
2	quenched to 25 °C	−150 °C…250 °C	+1
3	quenched to −140 °C	−140 °C…160 °C	+0.7
4	crystallised at 180 °C for 120 min	−150 °C…250 °C	+1
5	crystallised at 240 °C for 140 min	−150 °C…250 °C	+1

fact, the largest discrepancy was found between the first heating (sample 1a) and cooling run (sample 1b), both taking place below −60 °C.

For a more quantitative analysis, we modelled the dielectric loss data in the δ-relaxation region by means of a Cole-Cole fit, using a symmetric HN-function (b = 1). The constraint b = 1 was necessary because no relaxation data at frequencies below the peak frequency were available. On the same grounds, the peak shape parameter, actually describing the high-frequency slope of the δ-process, represents the most accurate fit parameter. Both Figs. 4 and 6 indicate the existence of two temperature regions (−150...−100 °C and −80...−25 °C) each characterised by weak changes in the relaxation time and nearly constant shape parameters. These two regions are separated by a clear discontinuity in τ and a minimum in a. Such abrupt changes in the relaxation parameters τ and a indicate a phase transition between different liquid-crystalline phases. This idea is supported by the hysteresis found between repeated heating and cooling due to undercooling of the LC-LC phase transition.

A second surprising feature of the δ-relaxation is its very low activation energy of 10 kJ/mol, which was determined by a fit of the relaxation times in the lower interval (δ_1-peak) according to an Arrhenius law, $\tau(T) = \tau_\infty \exp[E_a/RT]$. The fit is shown in the relaxation map (Fig. 7) together with fitted curves and mean relaxation times of all the other relaxations encountered in PEN.

From Fig. 5 we can see that the relaxation strength $\Delta\varepsilon_\delta$ reaches values of up to 5, which is of the order of that of the α-process. Such high relaxation strengths are indicative for collective relaxation processes in highly ordered molecular ensembles which are characterised by a strong correlation of the individual molecular motions. Collective relaxation processes are known, e.g., from ferroelectric materials and liquid crystals. Owing to the motional average over an entire molecular ensemble, these relaxation processes can often be portrayed by a single relaxation time, resulting in Debye relaxations. In

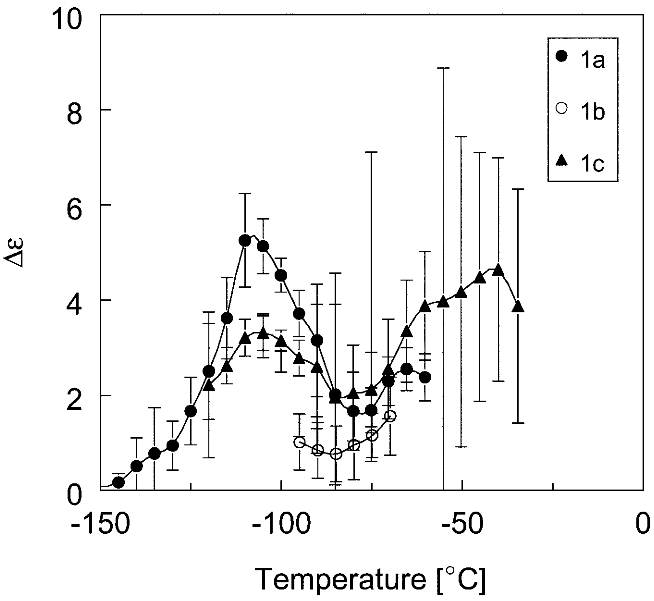
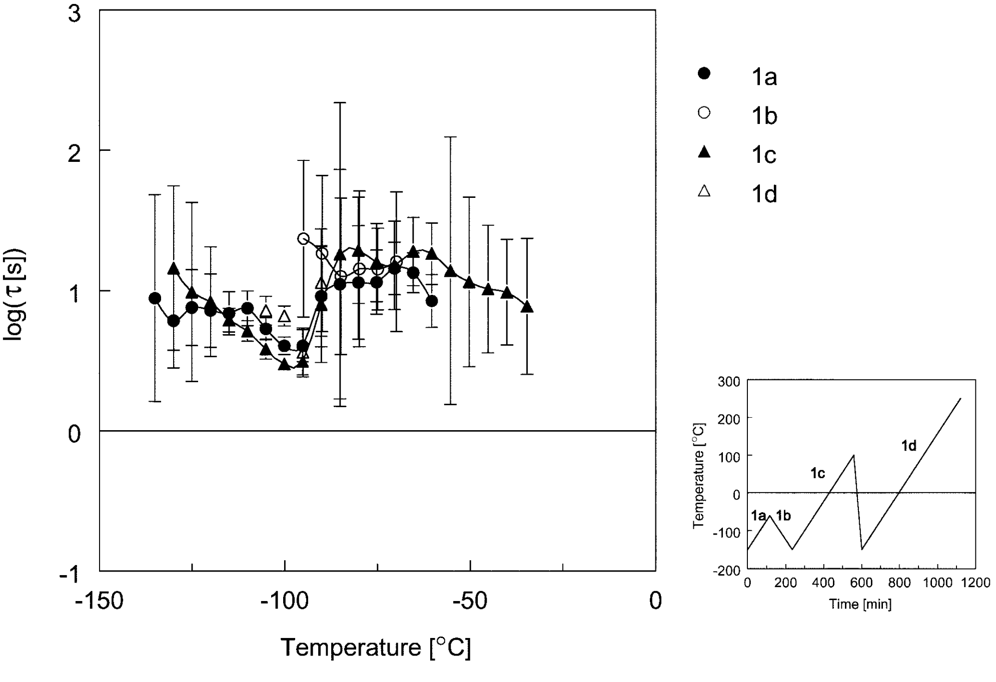


Fig. 5 Relaxation strength Δε(T) of the δ-process of sample 1a–1c

Fig. 4 Mean relaxation time τ_δ obtained by a HN-fit to the loss spectrum of amorphous sample 1a–1d for various consecutive heating and cooling runs. The temperature profile is given on the right of the figure



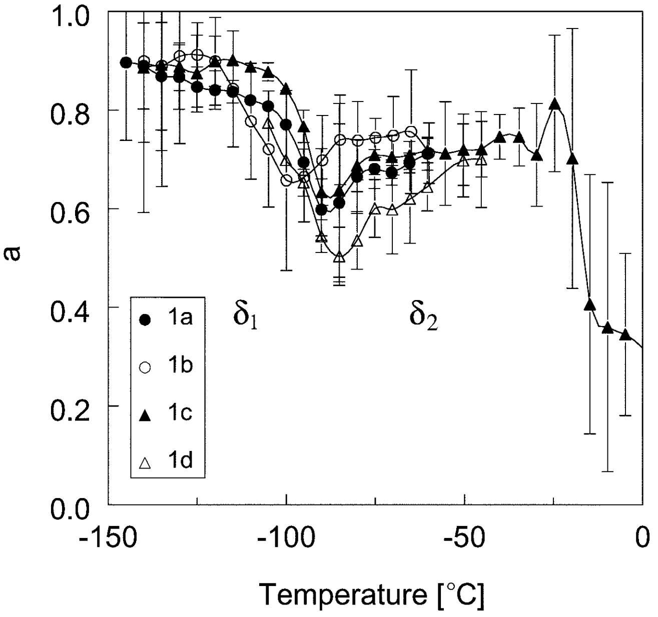


Fig. 6 Shape parameter a_{HN} of the δ-process of sample 1a–1d

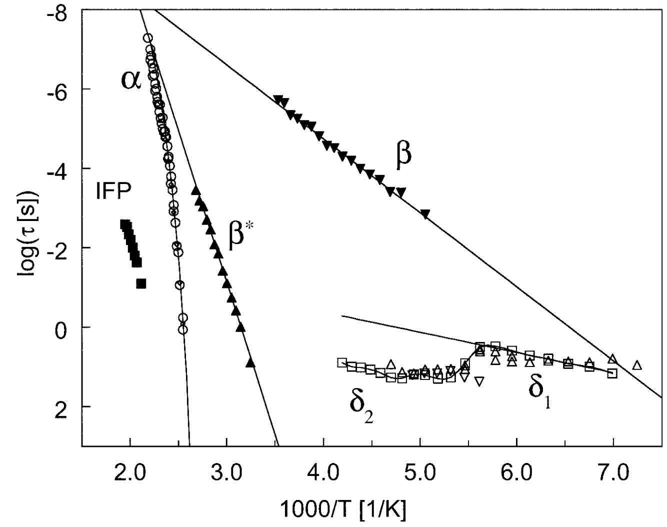


Fig. 7 Relaxation map showing all dielectric relaxation processes encountered in PEN. The relaxation data were obtained from HN-fits on different samples: α and interface polarisation (IFP) – samples 2 and 3; β and β^* relaxation – sample 3; δ_1 and δ_2 process – samples 1 and 2. Activation parameters: $E_{a\beta} = 36$ kJ/mol, $\log(\tau_{\infty\beta}[s]) = -12.2$; $E_{a\beta^*} = 147$ kJ/mol, $\log(\tau_{\infty\beta^*}[s]) = -24$; $E_{a\delta} = 10$ kJ/mol, $\log(\tau_{\infty\delta}[s]) = -2.4$

this view, we may interpret the shape parameters between 0.7 (δ_2) and (δ_1) as an additional hint for the collective nature of the δ-relaxation.

Here we want to recall that cooperative motions involving naphthalene groups have been suggested as a likely molecular reason for the high activation energy of the β^* process of PEN [16]. It is helpful to compare this β^* process with a very similar relaxation process (labelled β in Ref. [20]) found for a thermotropic liquid-crystalline terpolyester, which contains 60% HNA (hydroxynaphthoic acid) groups (Vectra B950) [20]. Boersma et al. assigned their β_{Vectra}-process to a combined rotation of a naphthalene/ester sequence around their collinear outer bonds. This process surprisingly shows an activation energy of 131 kJ/mol close to values given by Hardy et al. for $E_{a\beta^*}$ of semi-crystalline PEN. This striking agreement suggests that the β^* process is sensitive to the local orientational order, which spans from nematic to isotropic. An improvement of the orientational order of PEN chains, which is accompanied by changes into the *trans*-conformation [13], causes a decrease in the activation energy due to the reduction in sterical hindrance. A strong hint for this assignment can be drawn from the fine structure of the activation energy landscape of some β^*-relaxation peaks presented in Refs. [16, 17] which clearly shows a splitting of the β^*-peak into two individual relaxation processes, implying the coexistence of two differently ordered non-crystalline phases in PEN.

It is obvious that the very origin of the δ-relaxation must be different from that of the β^*-relaxation. In particular, its small activation energy $E_{a\delta}$, which merely equals twice the rotational potential for an aromatic ether bond rotation (~5 kJ/mol [21]) favours collective crankshaft motions of the -O-CH$_2$-CH$_2$-O- sequences in a suitable regular arrangement without any sterical hindrance. Recently, we have found an ultra-slow relaxation in the smectic-E state of a side-chain liquid crystalline polymer with alkoxy-biphenyl mesogens [22], the activation parameters [$E_a = 19$ kJ/mol, $\log(\tau_\infty) = -2.1$] of which resemble those of the δ-process. From this strong analogy we conclude that PEN chains can organise themselves, at least at low temperatures, in a (close-to) hexagonal layer structure, like a smectic B or smectic E phase. The short-range positional order in all three dimensions of such a smectic phase in combination with conformational regularity provides a likely explanation for the existence of the δ-relaxation in PEN. We therefore attribute the phase transition at around −90 °C to a smectic-smectic phase transition, which is accompanied by a step in the relaxation time. Another reasonable assumption is that the relaxation time increases with the size of the smectic domains. This might explain the absence of the δ-process in most semi-crystalline and amorphous PEN samples. Those samples probably have too large LC domains which result in a shift of the δ-relaxation beyond the frequency window of the DRS experiment.

Low-temperature WAXS, DSC, solid-state NMR and time-domain dielectric experiments on PEN are in progress to study the mesomorphic properties of PEN in detail.

Conclusions

The dynamic properties of amorphous and semi-crystalline poly(ethylene naphthalate) samples have been analysed with broad-band dielectric spectroscopy. This study confirms first of all the typical properties of the three well known β, β^*, and α relaxation processes, the behaviour of which was found to agree with recent dielectric and dynamic-mechanical studies on PEN.

Secondly, a novel strong dielectric relaxation process (δ) was observed in rapidly cooled samples. From its striking low activation energy of $\sim$10 kJ/mol, large relaxation strength of up to $\Delta\varepsilon = 5$, and Debye-like peak shape, a collective relaxation mechanism is proposed, based on collective crankshaft motions of the -O-CH_2-CH_2-O- sequences in a regular, liquid crystalline arrangement. Although the particular LC structure has not yet been identified by X-ray diffraction measurements, the existence of a (close-to) hexagonal smectic phase providing for three-dimensional short-range positional order of the PEN chains, is the most likely.

The assignment of the β^* relaxation was discussed in view of its dependence on the local orientational order and remarkable analogy with main-chain liquid-crystalline polymers. Splitting and characteristic shifts of the β^* peak described by some authors imply the coexistence of isotropic and nematic regions in amorphous and even semi-crystalline PEN.

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References

1. Huo PT, Cebe P (1992) Macromolecules 25:902
2. Kalika DS, Krishnaswamy RK (1993) Macromolecules 26:4252
3. Chaps. 2–5, 9 In: Mathot, VBF, ed., Calorimetry and Thermal Analysis of Polymers. Carl Hanser Verlag, München, 1994
4. Saw CK, Menczel J, Choe EW, Hughes OR (1997) In: ANTEC ‘97, p 916
5. Jakeways R, Klein JL, Ward IM (1996) Polymer 37:3761
6. Carr PL, Nicholson TM, Ward IM (1997) Polym Adv Technol 8:592
7. Baltá Calleja FJ, Rueda DR, Michler GH, Naumann I (1998) J Macromol Sci- Phys B37:411
8. Sata H, Kimura T, Ogawa S, Yamato S, Ito E (1996) Polymer 37:1879
9. Doi M, Shimada T, Okano K (1988) J Chem Phys 88:4070
10. Imai M, Kaji K, Kanaya T, Sakai Y (1995) Phys Rev B 52:12696
11. Matsuba G, Kaji K, Nishida K, Kanaya T, Imai M (1999) Macromolecules 32:8932
12. Flory PJ (1956) Proc R Soc London A 234:60
13. Kimura F, Kimura T, Sugisaki A, Komatsu M, Sata H, Ito E (1997) J Polym Sci B: Polym Phys 35:2741
14. Bellomo JP, Lebey T (1996) J Phys D: Appl Phys 29:2052
15. Canadas JC, Diego JA, Mudarra M, Belana J, Diaz-Calleja R, Sanchis MJ (1999) Polymer 40:1181
16. Hardy L, Stevenson I, Boiteux G, Seytre G, Schönhals A (2000) Polymer submitted
17. Stevenson I, Hardy L, Boiteux G, Seytre G, Schönhals A (2000) In: 8th Intern. Conf. on Dielectric Materials, Measurements and Applications. Heriot-Watt University, Edinburgh
18. de Rooij AL (1999) M.Sc thesis, TU Delft
19. Mertens IJA, Wübbenhorst M, Oosterbaan WD, Jenneskens LW, van Turnhout J (1999) Macromolecules 32:3314
20. Boersma A, van Turnhout J, Wübbenhorst M (1998) Macromolecules 31:7453
21. Hummel JP, Flory PJ (1980) Macromolecules 13:479
22. Wübbenhorst M, Nieuwhof RP, Marcelis ATM, Sudhölter EJR, van Turnhout J (2000) Macromolecules submitted