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RELAXATIONS IN AMORPHOUS AND SEMI-CRYSTALLINE POLYESTERS
A study by thermally stimulated depolarization currents

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Abstract

Thermally stimulated depolarization currents and differential scanning calorimetry are performed on thermoplastic polyesters to characterize both α and β relaxations. The influence on the different relaxations phenomena of the chemical structure (size of the naphthalene groups, presence of cyclohexane, length of the aliphatic group, ...) as well as the influence of the crystallinity are discussed. The three phases model with a crystalline part, a rigid amorphous part unable to relax and an amorphous phase able to relax at various temperatures depending on the distribution of the relaxation times is used to explain the evolution of the main α relaxation while the standard two-phases model is sufficient to explain the variations of the β relaxation mode. Elementary analysis of both α and β relaxations show that the β relaxation characterized by a continuous variation of activation energies as a function of temperature follows the activated state equation with a zero activation entropy while the cooperative α relaxation exhibits a prominent maximum of the activation energies at the glass transition temperature.

Keywords: DSC, relaxation, saturated polyester, thermally stimulated depolarization current (TSDC)

Introduction

Analysis by thermally stimulated depolarization currents (TSDC) has been frequently employed since Van Turnhout's pioneer works [1] to investigate the molecular motions in polymeric materials [2, 3]. The great interest of TSDC results is due in part to the low equivalent frequency of about 10^{-3} Hz [4] and its capability to resolve complex dielectric transitions into narrow distributions of relaxations [3, 5]. Moreover, the high sensitivity makes TSDC quite useful for the study of main and secondary relaxations in amorphous or semi-crystalline polymers. The α and β relaxation

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transitions are known to be typical of all polymers [6]: the α relaxation characterizes the liquid to the glassy state transition upon cooling (glass transition) while the β relaxation is also a universal phenomenon and is a matter for local or short scale process. For some polymers, these relaxations are well-separated (as example poly(ethylene terephthalate) [7]) whereas for other polymers they are overlapped (as example poly(methyl α-*n*-pentyl acrylate) [8]). When the repeating units have different fragments, several β-relaxation transitions can be observed [6, 9]. In this work, we propose new results given by differential scanning calorimetry and thermally stimulated depolarization current measurements on α- and β-relaxations in various thermoplastic polyesters (a schematic view of the repeating units is presented Fig. 1). They lead to characterize the influence of the chemical structure on the motions at the origin of the TSDC modes.

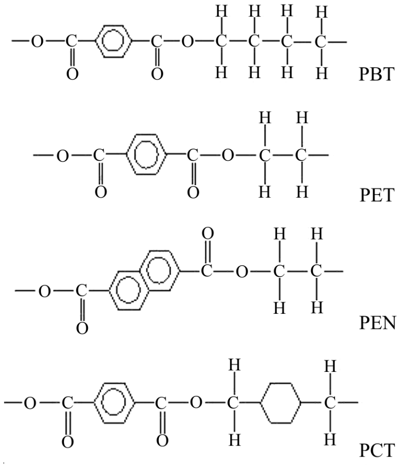

Fig. 1 Repeating units of the polyesters

Poly(ethylene terephthalate) 'PET' is one of the most studied polymers because of its important commercial significance on the one hand and because of the very wide possibilities of physical state (wholly amorphous, thermally or strain induced semi-crystalline states) [10–12]. Several workers [7, 13] have reviewed dielectric properties of different PET generally focused on the glass transition.

Poly(cyclohexane 1,4-dimethylene terephthalate), 'PCT', is a less studied semi-crystalline polyester. Compared to PET, its repeating unit includes a cyclohexane group between the methylene groups. Due to its good thermal properties (the temperatures of glass transition and melting are higher than those observed for PET), PCT is principally used in injection molding process for electronic and automotive markets.

Poly(ethylene glycol-co-cyclohexane-1,4-dimethanol terephthalate), 'PETG' is a wholly amorphous copolyester where CHDM (cyclohexane-1,4-dimethanol, also present in PCT) has replaced some of the ethylene glycol present in PET. Due to its clarity, toughness and good melt strength at processing temperature qualities, PETG is useful in many processes and applications: film extrusion and extrusion blow molding for packaging, injection molding for medical applications.

Poly(ethylene naphthalene 2,6-dicarboxylate), 'PEN' is an aromatic polyester in which the benzene group of PET is replaced by a naphthalene group. It has been shown that PEN has better physical properties (heat resistance, elastic modulus, tensile strength and barrier properties) than PET [14, 15]. PEN is now used as the base film of long-playing videotapes, as well as insulating in electronics industry or also in packaging.

Poly(butylene terephthalate), 'PBT' is a semi-crystalline polyester with many engineering applications. The molecule has both flexible segments (four methylene groups) and a hard segment (terephthalate group) in the repeating unit. Due to its longest flexible segment, PBT has a high crystallization rate and exists only on a semi-crystalline form at room temperature. Because of the insulating properties, it is widely used in electronic technologies.

The glass transition in the amorphous phase of semi-crystalline polyesters is often influenced by the presence of a crystalline phase even if the degree of crystallinity is low for these polyesters (around 30%) [16, 17]. Furthermore, the crystallinity rate of PET and PEN is low and amorphous materials can be obtained by rapid quenching from the melt while annealing above the glass transition temperature induced «cold» thermal crystallization. A three phases model has been often proposed to explain the results obtained on the most studied semi-crystalline polyesters as PET [18], PBT [19] and PEN [20]. It consists in crystalline, amorphous and intermediate rigid amorphous fractions [18, 21]. The last fraction, constrained, cannot participate in the relaxations associated with the normal amorphous phase [18, 22]. This paper deals with the influence of the crystalline phase on the α and β relaxations in thermoplastic polyesters and discusses the validity of the three phases model.

Experimental

Materials

PET films with a number average molecular mass, M_n of 31000 g mol^{-1} were isotropic and amorphous judging from birefringence, density and X-ray diffraction measurements. From these amorphous PET films (a-PET), semi-crystalline films (sc-PET) were obtained by an annealing at 133°C during 1 h. Using the calculated melting enthalpy of a wholly crystalline PET (ΔH_f^0=140 J g^{-1} [23]), there degree of crystallinity X_c=26% were determined by DSC from the melting enthalpy (Fig. 2).

PEN (from Amoco Co.) was used, as PET, under amorphous form and semi-crystalline forms (a-PEN, sc-PEN, respectively) obtained by annealing amorphous films at 183°C during 1 h. The degree of crystallinity X_c=35% is also calculated from the melting enthalpy and from ΔH_f^0(=103 J g^{-1} [14]).

PCT (Thermx 11440 from Tennessee Eastman Co., M_n=25000 g mol^{-1}) was used in its amorphous form (a-PCT).

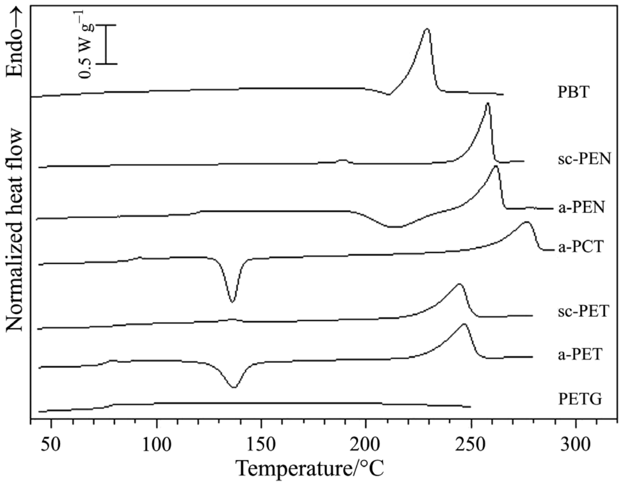

Fig. 2 DSC curves obtained for each sample. The curves are normalized to 1 g of matter and shifted on the ΔC_p axis for legibility. The heating rate is 10 K min^{-1}

PETG (6763 from Tennessee Eastman Co.) is an amorphous copolymer with $M_n \cong 26000$ g mol^{-1}. It consists of cyclohexane dimethanol, ethylene glycol and terephthalic acid with a molar ratio of approximately 1:2:3. PBT (Celanex 2500, Hoechst Co.) is a semi-crystalline polyester and the degree of crystallinity is measured by DSC $X_c=32\%$ ($\Delta H_f^0=142$ J g^{-1}) [19].

Methods

For thermally stimulated depolarization currents, samples were disk shaped with about 0.5 mm thick and areas of 150 mm^2. Before experiments, samples were stored under vacuum in the presence of P_2O_5 during two weeks at 20°C in order to avoid moisture sorption. TSDC measurements were performed with an apparatus developed in our laboratory [24]. The samples were submitted to an electric field ($E=10^6$ V m^{-1}) during 2 min (t_p) at a polarization temperature T_p just above their respective glass transition temperatures T_g. These experimental conditions lead to saturate the orientation of dipoles whose relaxation times are less or equal than the duration of polarization. Then, the decrease of temperature down to –150°C at constant cooling rate freezes in the matter in this new configuration. At this temperature, the electric field is cut off and a short circuit is set up. Then, the increase in temperature (at constant rate $r=10$°C min^{-1}) allows gradual relaxation of the different polarized units which results in a depolarization current I. The conductivity σ (in Siemens per meter) is used as a normalized quantity instead of I ($\sigma=I/ES$ where S is the surface of the sample). Using this method, the so-called 'complex' spectra $\sigma=f(T)$ are obtained and consist of several peaks.

'Elementary' TSDC spectra are obtained by means of the fractional polarization method which allows the selection of a small range of relaxing elements for each spectrum. The sample is submitted to the same electric field during 2 min at a temperature T_p'. The temperature is then lowered to $T_d=T_p'-5°C$ and a short circuit is performed during 2 min. Under these conditions, mobile dipolar units whose relaxation times are greater than 2 min at T_p' were not orientated by the electric field while those with relaxation times shorter than 2 min at T_d are randomized by the short-circuit. The sample, short-circuited, is finally cooled down to $T_0=T_p'-40°C$, and then, the depolarization current was measured during reheating (r=10°C min^{-1}) up to T_p'. By increasing polarization temperature T_p' the same procedure is performed allowing an exploration of all the transitions.

Enthalpic analysis are performed with the help of a Perkin Elmer DSC7 apparatus. Calibration is achieved from the determination of the temperature and the enthalpy of fusion of indium and zinc. Calorimetric measurements are made under nitrogen ambience with a heating rate of 10°C min^{-1}. The DSC curves were normalized to 1 mg of matter. To compare ‘complex’ TSDC and DSC data in the best conditions and principally in order to have the same aging, the following thermal cycles are performed by DSC: the samples are annealing just above T_g during 2 min, then they are cooled down to 40°C before the scans. By this way, these thermal cycles limit the aging of the various samples to 5 min.

Results and discussion

DSC investigations

The DSC behaviors of the different materials are displayed on Figs 2 and 3 (Fig. 3 is an expended view in the glass transition temperature range) and the different thermal data are reported in Table 1. For shake of clarity, the different curves have been

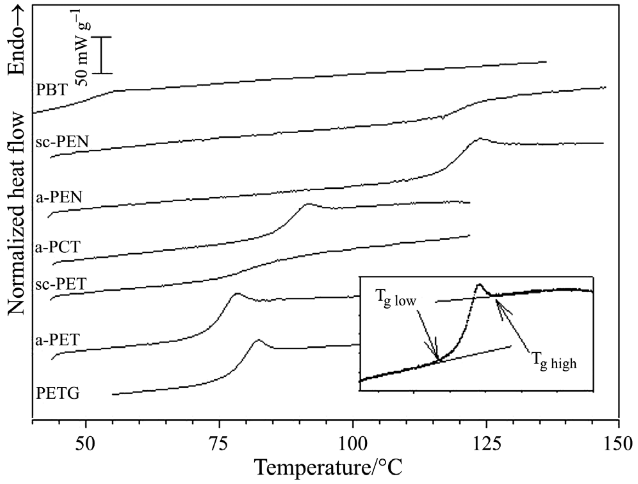

Fig. 3 DSC curves obtained for each sample in the glass transition temperature region. The curves are normalized to 1 g of matter and shifted on the ΔC_p axis for legibility. The heating rate is 10 K min^{-1}

shifted along the heat flow axis. They show different thermal behavior for each sample. Except for PETG, at high temperature all the DSC curves exhibit an endothermic peak due to the melting of the crystalline phase existing before or appeared during the DSC scan. Between the glass transition and the melting temperature range, one can observe an exothermic peak for a-PET, a-PCT and a-PEN samples [25]. This peak is due to the cold crystallization of a part of the amorphous phase during the heating. This crystallization is not observable for PETG sample (amorphous copolyester) and, of course, for sc-PET and sc-PEN because these samples are fully crystallized prior the DSC scan. For these semi-crystalline samples, supplementary weak endothermic peaks are observed (at 136°C for sc-PET and at 189°C for sc-PEN). Depending on the annealing conditions (time, temperature) [26] these peaks are due to the melting of crystals formed during the annealing treatment by partial melting and recrystallization mechanisms. They could be attributed to crystal thickening as well as to crystal perfection and fold-surface smoothing of the crystalline layers [27]. This phenomenon is not observed for PBT because this material is crystallized from the melt and not by annealing an amorphous material. The weak exothermic peak observed just before melting is indicative of recrystallization. It is often observed when the specimen crystallizes while being quickly cooled [19].

Table 1 DSC parameters. The enthalpy and temperature crystallization parameters correspond to the cold-crystallization

	X_c*/%	T_g onset/ °C	ΔC_p/ J g^{-1} K^{-1}	ΔT_g/ °C	T_{crys}/ °C	ΔH_{crys}/ J g^{-1}	T_f/ °C	ΔH_f/ J g^{-1}
a-PET	0	73	0.31	10	137	24	247	38
sc-PET	26	76	0.11	15			245	37
a-PEN	0	117	0.29	15	213	33	262	34
sc-PEN	35	117	0.16	22			262	37
PBT	32	47	0.08	17			229	45
a-PCT	0	86	0.22	10	136	24	277	33
PETG	0	71	0.28	11				

* before DSC scan

In the temperature range of the glass transition (Fig. 3), a change of heat capacity called ΔC_p indicates the glass transition and an overshoot is observed for the amorphous samples. This phenomenon is due to the structural relaxation that arises during the thermal cycle (the same for all the samples). The values of ΔC_p (in J g^{-1} K^{-1}) are given in Table 1 and the mass used for the calculation are the whole masses of samples. However, for semi-crystalline samples it is obvious that the crystalline phase does not participate to the glass transition and it is usual in a two phases model (a crystalline phase with a degree X_c and an amorphous phase with a degree $X_a=1-X_c$) to write that $\Delta C_p=(1-X_c)\Delta C_{p0}$ where ΔC_{p0} is the jump at the glass transition T_g of the thermal heat capacity of the wholly amorphous sample.

It is clear that PET and PEN do not follow this classical rule. Indeed, for these samples, there is no correlation between the increase of the degree crystallinity and the decrease of ΔC_p. For example, ΔC_p decrease of 64% when X_c increase of 26% in PET and ΔC_p decrease of 45% when X_c increase of 36% in PEN. These results are not surprising because in a previous work on drawn PET and PCT [28, 29], we had shown that ΔC_p is lower than $(1–X_c)\Delta C_{p0}$. It has been suggested in the three-phase model that this deviation is caused by molecules whose mobility has been hindered although located in the amorphous phase [12, 30, 31].

The width of the glass transition zone could be characterized by $\Delta T_g=T_{g\,high}–T_{g\,low}$ where $T_{g\,low}$ is the temperature which corresponds to the beginning of the glass transition phenomena and $T_{g\,high}$ is the temperature at which the glass transition phenomena are finished (as shown in the insert of Fig. 3). ΔT_g is often related to the width of the distribution of the spectrum of relaxation times. From data collected in the literature, Saiter *et al*. had shown that the greater the T_g, the lower the non-exponential parameter β [32] which is inversely related to the width of the distribution of relaxation times through the stretched exponential response function for structural relaxation [32]. Due to the increase of $T_{g\,high}$, the value of ΔT_g is larger for the semi-crystalline samples than for the amorphous ones (Fig. 3) showing that the presence of the crystalline phase modified the distribution of time constants of the relaxation of the material. The widening of the glass transition zone evidences the heterogeneity of the amorphous phase. In the classic three-phase model, one must consider a possible evolution of the amorphous phase due to the presence of the crystalline phase.

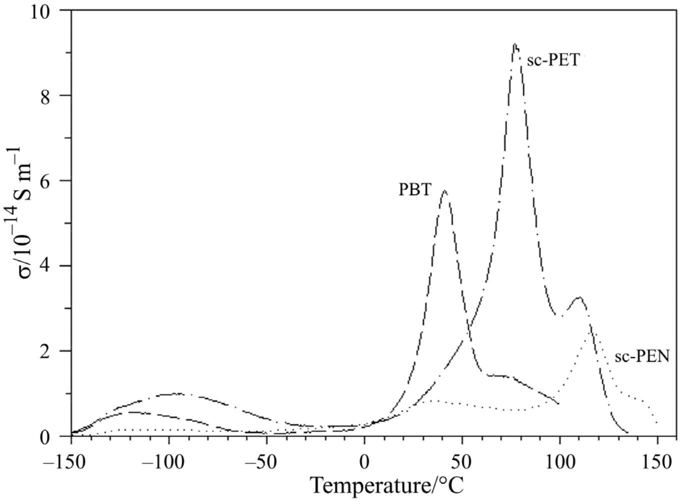

Fig. 4 Complex TSDC spectra for the semi-crystalline polyesters ($E=10^6$ V m^{-1}, T_p just above T_g, T_d=–150°C, r=10°C min^{-1})

TSDC investigations

Complex TSDC spectra

Between –150°C and +150°C the complex TSDC spectra of semi-crystalline polymers shows several current maxima (Fig. 4). In the –150 to 0°C region, one can observe the secondary β relaxation modes of these polyesters that have low values of the current while in the 0 to +150°C, one can observe the main α mode and others current maxima. In a first time, focus is made on the β relaxation.

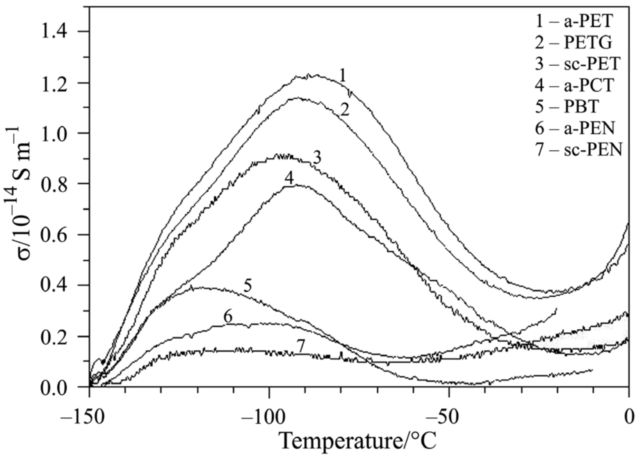

Fig. 5 Complex TSDC spectra in the β temperature range (E=10^6 V m^{-1}, T_p just above T_g, T_d=–150°C, r=10°C min^{-1})

The β relaxation modes differ from one polyester to another one (Fig. 5) and we can categorize these peaks in three groups: firstly the peaks of a-PET, sc-PET, PETG and a-PCT, secondly the peak of PBT and thirdly the peaks of a-PEN and sc-PEN. For the first group, the β relaxation mode clearly appear and its temperature at the maxima T_β is close to –92°C (Table 1). Moreover one can observe a shoulder on the low temperature side (near –130°C). The shapes of the β relaxation peaks are very similar for a-PET, PETG and a-PCT while their magnitudes are different.

The studied polyesters, considered as polar polymers, are constituted with polar groups as carboxyl groups with a dipolar moment of 0.7 Debye and aliphatic groups with a dipolar moment in the order of 0.1 Debye [33]. Then, neglecting this contribution, one can consider the studied polyesters have a single kind of dipoles (the carboxyl groups). In the one hand, as asserted by Van Turnhout [1], these groups are responsible of the β relaxation modes in the material. It follows that the area under the depolarization peak is proportional to the number of carboxyl groups oriented during the polarization duration at T_p and depolarized during the heating. The values of P_β are obtained from:

$$P(T)=\frac{1}{rS}\int_{T_1}^{T_2} I(T')\mathrm{d}T' \tag{1}$$

with r the heating rate and S the sample surface. P_β is given in Table 2 for $T_1=-150°\text{C}$ and $T_2=-20°\text{C}$. In the other hand we could calculate the relative concentration, called Cc, of the carboxyl groups (–COO–) in each materials considering only the carboxyl groups of the non-crystalline part of the materials. Indeed, the carboxyl groups linked in the crystalline phase could not be orientated by the electric field at T_p. The values of Cc are calculated as $(1–X_\text{c})$ multiply by the ratio of the molar mass of the carboxyl group on the molar mass of the repeating units M_0 shown Fig. 1: $Cc=(1–\text{X}_\text{c})M_{(\text{coo})}/M_0$ and are gathered in Table 2.

Table 2 Polarizations P_α and P_β, temperatures T_β and T_α of the maximum of the peaks, relative concentration of carboxyl group of the a-phase Cc in each materials, width $\Delta T_{1/2}$ at half maximum of the α peaks and maximum activation enthalpies ΔH^* for each polyester

	P_β/ μC m^{-2}	T_β/ °C	P_α/ μC m^{-2}	T_α/ °C	Cc/ %	$T_{1/2}$/ °C	H^*/ kJ mol^{-1}
a-PET	5.9 1.5	–91 4	26 1.5	69 1	46	8	457
sc-PET	4.0 1.5	–96 2	18 1.5	77 1	34	23	378
a-PEN	1.4 1.5	–98.8 5	13 1.5	113 1	36	15	365
sc-PEN	0.9 1.5	–96 10	6 1.5	116 1	23	26	412
PBT	1.4 1.5	–120 1.5	10.5 1.5	41 1	22	21	246
a-PCT	3.4 1.5	–91.6 1	22 1.5	80 1	32	10	277
PETG	5.3 1.5	–92.5 1.5	23 1.5	70 1	41	9	369

Due to the simplistic hypothesis (a single kind of mobile unit) it follows that the relative concentration Cc must be proportional to the β peak area whatever the material. Thus, if we have to keep in mind that this is a simplistic way and that the β mode has at least two molecular origins revealed by the main peak and the soulder on the low temperature side, we could now compare the influence of structure on the β mode. For the first group of polymers, PET has the highest P value, followed by PETG, sc-PET and finally PCT. It varies in the same way that the values of Cc: PET has the highest value followed by PETG, sc-PET and PCT. Moreover, as shown in Fig. 6, there is a correct proportionality between P and Cc $[(P_\beta(\mu\text{C m}^{-2})\approx 0.123Cc(\%)]$. The simplification seems to be confirmed by the signal observed on PETG. Indeed, for this copolyester (67% PET and 33% PCT), using the additive law the recalculated TSDC signal is very close to the real one (Fig. 7). Confirming the localization of the motion at the β relaxation, PETG could be considered as well as statistical copolyester or as a blend of amorphous PCT and PET. In an identical way, the β relaxation peak of sc-PET is also recalculated from the β peak of a-PET considering that the β relaxation occurs only in the non-crystalline part of the material. So the recalculated peak is obtained by multiplication the PET β relaxation peak by $(1–X_\text{c})$. Although there is a weak shift of

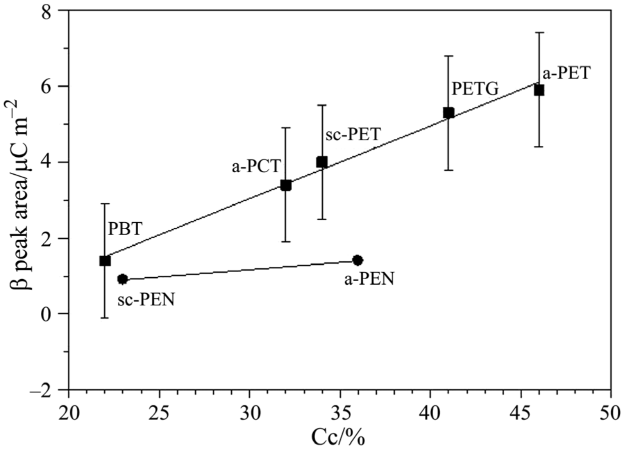

Fig. 6 Polarization of the peaks (between –150 and –20°C) *vs. Cc*, concentration of carboxyl groups of the amorphous phase in each sample

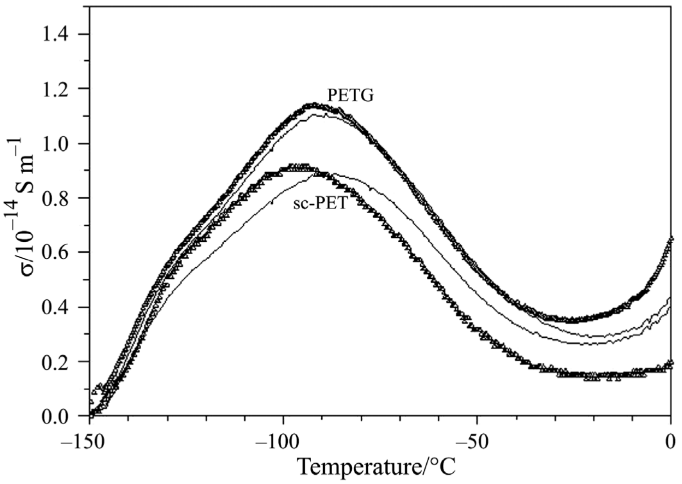

Fig. 7 Experimental complex TSDC spectra of PETG and sc-PET (Δ) and calculated spectra (in lines)

the maxima of the two peaks, their shapes look similar (Fig. 7). Moreover *P* decreases of 32% from amorphous PET to semi-crystalline PET while the degree of crystallinity increase of 26% (and for PEN a diminution of 36% for *P* between amorphous and semi-crystalline states while X_c increase of 35%). For these polyesters (first group) the localized relaxations in the amorphous phase are not, or very few, constricted by the crystalline phase and the classical two-phase model is sufficient to explain variations of the β relaxation mode.

The weakening (in magnitude and area) of the β peak observed for PBT samples could be attributed to a lower concentration of dipoles which can be oriented by the electric field (dipoles of the amorphous phase). The local motions that occur during the β mode appear at lower temperature but have probably the same origin. The lowering of temperature is due to the lengthening of the aliphatic part of the macromolecules (four methylene groups for PBT instead of two for the other polyesters) which enhances the mobility and the local motion. Boyer [34] has observed that the lengthening of the polyglycol unit forces the β transition down to about the value characteristic of the polyethylene secondary transition (while at the same time depressing T_g). The crankshaft motion (Boyer, Schatzki or Wunderlich models [34–36]) which is a general phenomenon in high polymers appears in the same temperature range than the side chain motions of polar carboxyl groups of PET, PCT and PETG. Presence of cyclohexane between the two methylene groups in PCT does not seem modify the temperature at which these intra-chain local motions (2–10 consecutive atoms) occur (no modification of the β peak shape). For the PEN materials, β modes are difficult to observe and drastically weaker than for the other polymers. If we consider that the β peak is principally due to the motion of carboxyl groups [1], the values of P_β must vary in the same way as the relative concentration of carboxyl groups *Cc* in the materials (Table 1 and Fig. 6). It turns out that the value of P_β for a-PEN is too low (concentration of carboxyl groups is higher in a-PEN than in a-PCT). The drastic decrease of the magnitude of the peaks for a-PEN and sc-PEN is probably due to the size of the naphthalene groups, which impedes the local crankshaft motion and the polarization of the carboxyl groups at high temperature.

Now, we will focus our attention on the α relaxation mode. The main transition, characterized by the α peak is clearly observed on the different TSDC complex spectra (Fig. 4 for semi-crystalline samples and Fig. 8 for amorphous ones). Temperatures T_α at the maximum of the relaxation peak are close to those observed by DSC measurements for the glass transition temperature in such a way that the α peak is considered as the dielectric manifestation of the glass transition and corresponds to cooper-

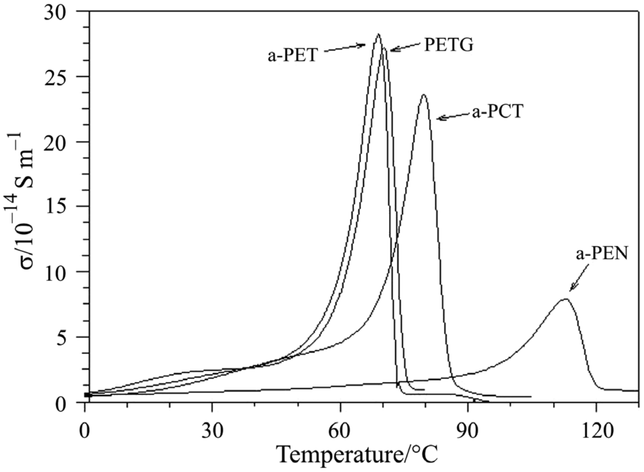

Fig. 8 Complex TSDC spectra for the amorphous polyesters in the α temperature range ($E=10^6$ V m^{-1}, T_p just above T_g, T_d=–150°C, r=10°C min^{-1})

ative movements of the macromolecules. If the temperature T_α varies very weekly (as T_g onset) with the degree of crystallinity, the shape and the polarization of these peaks depend greatly of X_c. The width at half maximum $\Delta T_{1/2}$ of the α peak temperature zone is larger for semi-crystalline samples than for amorphous ones, similarly to the width ΔT_g observed by DSC. This is probably due to an increase of the relaxation time distribution. The polarization P_α decreases with X_c of 31 and 54% for sc-PET and sc-PEN, respectively, which is larger than the increase of the degree of crystallinity. It follows that a part of the amorphous phase of the semi-crystalline samples could not be polarized at T_p. Moreover, in opposition to the β relaxation peak, the shape of the α peaks of sc samples differs from this obtained for amorphous samples. For semi-crystalline polyesters an extra-peak is observed at a temperature higher than T_p. This transition generally attributed to space charges [1] will not be discussed here.

As in DSC, the two-phase model is not adequate to the described TSDC data of the sc-samples. This loss of the ability to polarize, observed between a- and sc-samples, is attributed to a part of the material which is not able to be mobile at high temperature although being not in a crystalline state. This is the base of the three-phase model [19]. The intermolecular cooperative motions which occur at the glass transition (20–50 consecutive atoms) are probably constricted (specially for sc-PEN for which the decrease of the polarization is very important).

Elementary TSDC spectra

Figure 9 shows, as example, elementary spectra obtained on PETG sample in the α and β regions. Because of the narrowness of the T_p–T_d window, each elementary

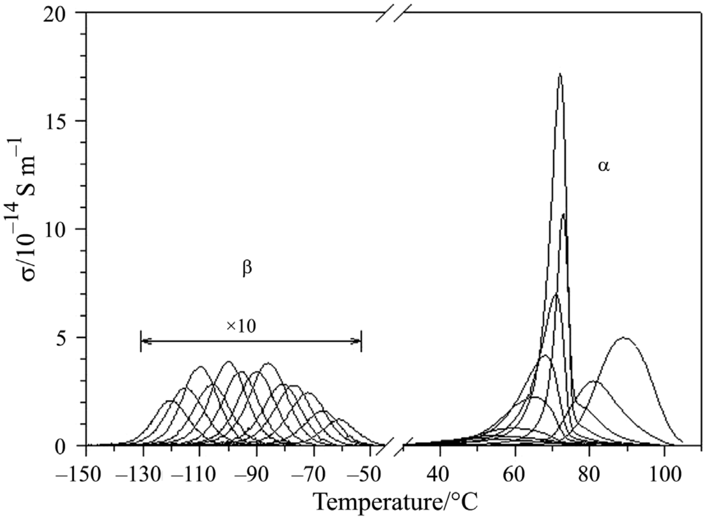

Fig. 9 Elementary spectra in the β and α temperature range for PETG. T_p varies from –130 to +80°C

spectrum could be considered as characteristic of sequences relaxing with the same relaxation time constant. Debye analysis of the current-temperature curve gives the relaxation time $\tau(T)$ using the standard Bucci method [1]. Below the glass transition temperature, it is established that the relaxation in polymers shows an Arrhenius temperature dependence of the relaxation time $\tau(T)$:

$$\tau(T)=\tau_0\exp\left(\frac{E_a}{RT}\right) \tag{2}$$

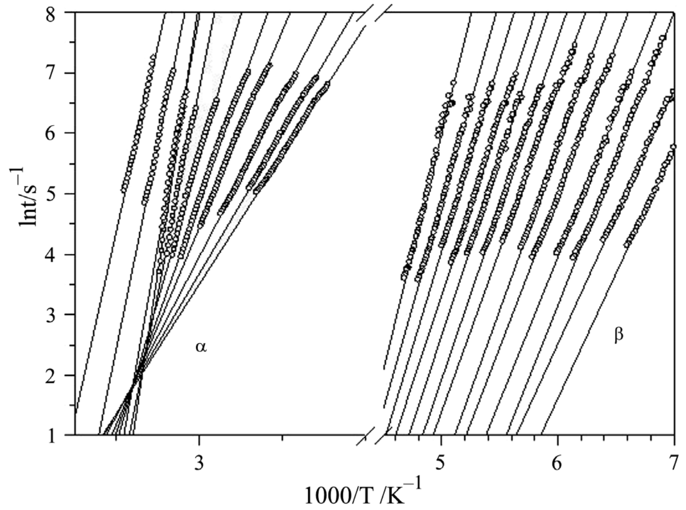

Fig. 10 Arrhenius plots for each elementary spectrum of PETG

where E_a is the apparent activation energy, R is the ideal gas constant and τ_0 is the pre-exponential factor. Thus, each elementary process could be described by an Arrhenian plot of $\ln\tau$ *vs.* $1/T$ (as example, Fig. 10 for PETG). For each sample and for each elementary spectrum, we observe a quasi-linear dependence and E_a is derived from the slope of these straight lines.

For the β region, the straight lines are quasi-parallels while for the glass transition of polymeric materials, they converge to a single point called compensation point of coordinates (T_c,τ_c) [12]. This behavior is similar for the other studied polyesters. The compensation behavior is observed quasi-systematically in the glass transition of polymeric materials. The physical significance of the compensation point is not yet well elucidated [37]. Some authors claim that a compensation point is indicative of cooperative molecular movements and that T_c is the temperature at which all the relaxations involved in the process occur with the same relaxation time τ_c [4, 38]. Read [39] has refuted the idea of this unique relaxation at T_c. In a recent work [37], Sauer and Moura Ramos have shown that compensation is a natural result of the sharp increase of E_a as one approach T_g from the low temperature side, and not its cause. Following the Eyring's activated states equation, τ_0 could be related to the variation of entropy by

$$\tau(T)=\left(\frac{h}{kT}\right)\exp\left(\frac{\Delta G^{*}}{RT}\right)=\left(\frac{h}{kT}\right)\exp\left(\frac{-\Delta S^{*}}{R}\right)\exp\left(\frac{\Delta H^{*}}{RT}\right) \tag{3}$$

where the relaxation time is associated with the crossing of a barrier of height ΔG^{*}, h, k and R are, respectively, the Planck, Boltzμann and gas constants. ΔS^{*} and ΔH^{*} are the activation entropy and the activation enthalpy respectively. ΔH^{*} and E_a are related by:

$$E_a=\Delta H^{*}+RT \tag{4}$$

In order to decide whether the relaxations are cooperative or non-cooperative, Starkweather [40] has rewritten the activated states equation:

$$\Delta G^{*}\quad H^{*}-T\Delta S^{*}=RT[\ln(k/h)+\ln(\tau T)] \tag{5}$$

Taking into account the values of the constants, Eq. (6) can be written as:

$$\Delta H^{*}\quad RT[21.92+\ln(T/f)]+T\Delta S^{*}\text{or } E_a=RT[22.92+\ln(T/f)]+T\Delta S^{*} \tag{6}$$

with f=1/2πτ is the equivalent measurement frequency of TSDC. This equivalent frequency was calculated using Van Turnhout's method (it links the strength of the TSDC mode to the ac dielectric mode [1]) and was for our studies of $5\cdot10^{-3}$ Hz. The transitions are categorized as cooperative or not based on their activation entropy [40]: a finite activation entropy is equivalent to a «high» activation energy and is known to be associated to cooperative transitions (generally the glass transition) [41, 42]. The solid curve drawn through the experimental data in Fig. 11 was calculated using Eq. (6) with the apparent activation entropy equal to zero and a frequency of $5\cdot10^{-3}$ Hz. It appears that the activa-

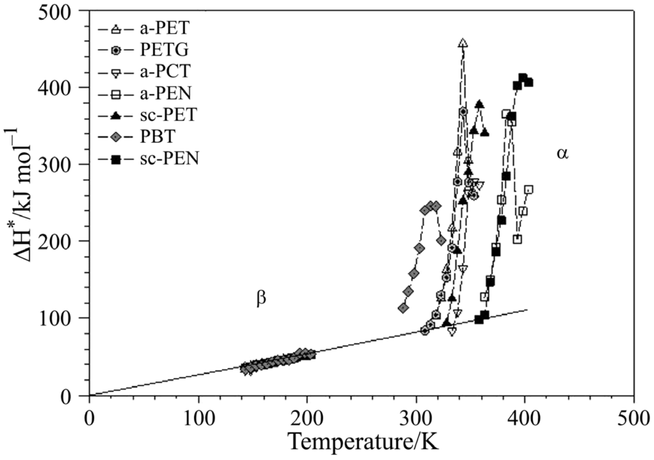

Fig. 11 Activation energies ΔH^{*} *vs*. polarization temperature T_p. The values of ΔH^{*} are derived from the slopes of the Arrhenius lines in Fig. 10 and the solid curve was calculated using the activated states equation with ΔS^{*}=0 and f=$5\cdot10^{-3}$ Hz

tion energies agree with the zero apparent entropy prediction for the polymers studied in the β region. Recently, similar results were done by Moura Ramos for liquid crystalline polymers [43]. In agreement with Sauer and Avakian, we may conclude that the motions that occur during the β relaxation are localized and non-cooperative. The activation energies are between 32 and 55 kJ mol^{-1} for the β region. For the α relaxation, the data deviated significantly from the zero entropy prediction at a temperature which could be considered as the beginning of the α TSDC relaxation mode. Maximum values of ΔH^* are observed in Fig. 11 for the α peak temperature range and are reported in Table 2. In the α peak region, the calculated values of ΔH^* do not show significant differences between a- and sc-samples and between the various polyesters.

Conclusions

For the β contribution, motions involving several units (crankshaft motion) and polar carboxyl units occur. In PEN, these motions are impeded by the bulkiness of the naphthalene rings while in PCT, presence of cyclohexane do not modify these motions. Augmentation of the length of the aliphatic part (i.e. PBT) diminishes the temperature of the β peak by increasing the local mobility. The variations of the activation energies follow the activated state equation with apparent activation entropy equal to zero. The different motions that occur at T_β are therefore localized and non-cooperative. Due to their nature, the β relaxations of the amorphous are independent of the degree of crystallinity. Presence of a crystalline phase modifies the main α relaxation. The cooperative movements are constricted and the presence of rigid fractions is confirmed. The drastic decrease of the magnitude of the peaks for PEN is due to the size of the naphthalene groups that impedes also the cooperative motions. The cooperative α relaxations show prominent maximum of the activation energies at the glass transition temperature.

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