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# Comparative study of amorphous and partially crystalline PEN by TSDC, DEA, DMA and DSC

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## *Abstract*

A comparative study of the relaxational behaviour of amorphous and partially crystalline poly(ethylene-2,6-naphthalene dicarboxylate) (PEN), has been carried out by thermally stimulated depolarization currents (TSDC), differential scanning calorimetry (DSC), dynamic mechanical analysis (DMA) and dynamic electric analysis (DEA). As received, PEN (partially crystalline) shows, in the temperature range from -150 °C to 200 °C, four relaxations located, in increasing temperature order, around -70 °C( $\beta$ ), 60 °C( $\beta^*$ ), 130 °C( $\alpha$ ) and 170 °C( $\rho$ ). Amorphous PEN has been crystallized thermally heating up to different temperatures between 170 °C and 200 °C. DSC measurements of these samples show a small endothermic premelting peak, once the crystallization of the sample is completed. This peak increases and shifts towards higher temperatures as the sample is further thermally treated. Associated with the presence of this endothermic peak, the  $\rho$  relaxation passes through a maximum and

presents a sharp decrease as it is further thermally treated. The  $\alpha$ -relaxation detected by dynamic mechanical as well as dielectric (ac) measurements shifts to higher temperatures and broadens as the degree of crystallinity increases. The kinetic parameters of the observed relaxations have been determined fitting experimental data to standard models.

### *Key words:*

Crystallinity, thermostimulated depolarization current, dynamic mechanical analysis, relaxations

### *Introduction*

Interest in the study of polyesters, showing high-performance physical and chemical properties, arises from growing electronics and electrical engineering demands. From this family of polymers, poly(ethylene-2,6-naphthalene dicarboxylate) (PEN), is a new aromatic polyester that differs from poly(ethylene terephthalate) (PET) in the double aromatic ring of naphthalate group instead of the single one present in PET. Their properties improves those of the PET. For example, among other physical properties PEN is characterized<sup>1-3</sup> by a melting point of  $T_m=267$  °C that is about 10 °C higher than the one for PET, and a glass transition temperature  $T_g=122$  °C that is 50 °C higher than the one for PET<sup>4</sup>. This polymer, as in the case of PET, can be obtained in the amorphous state by quenching in iced water. Because of the increased stiffness of the polymer backbone, PEN exhibits superior thermal stability and better mechanical and tensile properties than other polyesters. These improved properties give response to high demanding mechanical and electrical engineering requirements, as insulating in surface mounted technology, miniaturization of capacitors or, for instance, as a base film for long-playing videotapes. These applications require however a wide knowledge of the electrical relaxations that the material can undergo, and its electrical

behavior in a broad spectrum of environmental conditions. In this sense, thermally stimulated currents technique<sup>5,6</sup> (TSDC) combined with other characterization techniques such as dielectric spectroscopy analysis (DEA), dynamic mechanical analysis (DMA) and differential scanning calorimetry (DSC) represent powerful experimental tools in order to characterize the material.

The aim of the present work is to study the effect of the crystallinity degree on different electrical and mechanical relaxations present in commercial semicrystalline PEN (Kaladex) by TSDC, DSC, DMA and DEA. From the complete spectrum obtained for each high temperature relaxation, various kinetic parameters have been determined fitting the curves to the usual empirical models. The evolution of these relaxations with the crystallinity degree of the material is analyzed in partially crystallized samples obtained from the amorphous state.

### *Experimental*

Commercial PEN (Kaladex) sheets were used for the experiments. Amorphous samples were prepared quenching the molten sheet in water at room temperature. Calorimetric measurements (DSC) were performed with a Mettler TC11 thermoanalyser equipped with a Mettler-20 Differential Scanning Calorimeter module. DSC curves were obtained from 10 mg samples, sealed in aluminum pans, at 10°C/min controlled heating rate.

Depolarization current measurements (TSDC) were carried out on 130  $\mu\text{m}$  thick circular samples, 2 cm diameter Al electrodes were prepared on both sides of the sheet by vacuum deposition. A Kottermann-2715 air forced circulation oven, controlled by an Eurotherm-818 programmer was used for the measurements. Temperature during annealing and measurements was measured to an accuracy of 0.1 °C by Pt-100 probes located near to the sample. Current intensity measurements were performed by means of a Keithley-610C electrometer. The full description of the TSDC experimental setup technique has been reported in previous works.<sup>7</sup>

Dielectric measurements were performed in the frequency range from  $10^{-1}$  to  $10^4$  Hz with a dielectric analyzer DEA 2970 from TA Instruments. The samples used were prepared in the same way as for TSDC measurements. Data were collected between  $-150^{\circ}\text{C}$  and  $100^{\circ}\text{C}$  at a constant heating rate of  $1^{\circ}\text{C}/\text{min}$ . From  $100$  to  $200^{\circ}\text{C}$ , the isothermal step method was used, in which data is collected isothermally at several frequencies, increasing the temperature at  $5^{\circ}\text{C}$  steps.

PEN samples of  $0.13 \times 6.5 \times 2$  mm were investigated in a range from  $0.1$  Hz to  $30$  Hz using a dynamic mechanical thermal analyzer DMTA-MARK II. The heating rate was  $1^{\circ}\text{C}\cdot\text{min}^{-1}$  up to  $100^{\circ}\text{C}$ . As it was done with DEA measurements, from  $100$  to  $200^{\circ}\text{C}$ , the isothermal step method was used, increasing the temperature at  $5^{\circ}\text{C}$  steps.

Amorphous sheets of PEN were prepared quenching the molten material in water at room temperature. Different degrees of crystallization were obtained by subsequent heating processes up to different final temperatures. This method, called *Thermal Step Stimulation* (TSS)<sup>8,9</sup>, is represented schematically in figure 1. During the first heating process (section "a" of the figure) the amorphous sample is heated up to a temperature  $T_{f1}$  that produces some degree of crystallinity in the material. The partially crystallized sample is then cooled down to temperatures below  $T_g$  (section "b") and heated up again to  $T_{f2} > T_{f1}$  (section "c"), increasing further the crystallinity degree. This process is repeated to ever increasing final temperatures ( $T_{f3}$ ,  $T_{f4}$ , ...) raising gradually the crystallinity degree of the material. One interesting advantage of this method is that when the sample is at low temperatures (around  $T_g$ ) it can be polarized in the usual way, and the TSDC discharge, DEA and DMA measurements can be performed during the heating ramps.

## *Results and Discussion*

### *DSC*

Previous to TSDC, DEA and DMA studies, DSC measurements have been carried out

from 30 °C to 300 °C, in order to characterize the glass transition, melting point and the crystallinity degree of the material. Figure 2 shows results obtained for samples treated by the TSS method up to different final temperatures. The glass transition, clearly observable in the scan corresponding to the amorphous sample, lies at  $T_g = 125$  °C approximately.

During the crystallization of the material a phase transformation occurs in which the polymer chains move towards a lower energy configuration. These transformations involve important heat transfer processes between sample and environment, which can be measured by DSC. If the sample is heated at a constant rate and the heat flow measured, an exothermic peak will arise whose area is directly related to the amount of crystallized polymer. The exothermic crystallization process of amorphous PEN can be observed for curves 1 to 4 of figure 2 ( $T_f$  up to 166 °C) at temperatures around 180 °C, before the melting process at 270 °C approximately. Curves 5 to 10 ( $T_f$  from 172 °C to 190 °C) do not show ulterior crystallization process. This indicates that these samples already have the highest degree of crystallinity achievable by TSS. From the area of the exothermic and endothermic peaks and the extrapolated heat of fusion for a pure PEN crystal ( $\Delta H_f = 103.3$  J/g), the crystallinity degree of each sample can be estimated and is reproduced in table 1. Table 1 is subsequently used to relate the final temperature of any experiment to the corresponding degree of crystallinity.

It can be noted in figure 2 the presence of a small endothermic peak in those samples fully crystallized. This endothermic peak increases in area and shifts towards higher temperatures as  $T_f$  is increased. This behavior is related to important changes in the  $\rho$  relaxation (associated to free charge trapped in the material) as will be discussed below.

### *TSDC*

Amorphous PEN shows, in the temperature range from 20 °C to 200°C, three relaxations located, in increasing temperature order, at 80 °C( $\beta^*$ ), 130 °C( $\alpha$ ) and 150

$^{\circ}\text{C}(\rho)$ .<sup>1</sup> It is interesting to compare these results with those obtained with a similar polymer as PET<sup>8</sup>. For PET only two relaxations, the  $\alpha$  peak corresponding to the glass transition of the material and the  $\rho$  relaxation associated to free charge, are observable. The absence of the  $\beta^*$  peak suggests that this relaxation is probably due to the relative motion of the two naphthalene rings present in the PEN polymer chain and not present in PET.

Amorphous PEN has been crystallized to different crystallinity degrees by the TSS process. TSDC discharges of partially crystallized samples are reproduced in figure 3 for the  $\beta^*$  relaxation and in figure 4 for  $\alpha$  and  $\rho$  relaxations. In these figures the plotted spectra corresponds to conventionally polarized samples

Polarization temperature has to be carefully chosen in order to observe the desired relaxations. In the case of the  $\beta^*$  relaxation, the employed polarization temperature was  $67^{\circ}\text{C}$ , since in a previous work<sup>1</sup> it was found that it corresponds to the optimal polarization temperature  $T_{po}$ . To observe simultaneously  $\alpha$  and  $\rho$  relaxations, a polarization temperature of  $130^{\circ}\text{C}$  was used, which is located between their respective  $T_{po}$  ( $\alpha$ :  $120^{\circ}\text{C}$ ,  $\rho$ :  $150^{\circ}\text{C}$ )

As shown in the figures, for  $\beta^*$  and  $\alpha$  relaxations, a decrease in the area and in the intensity of both peaks is observed associated to the decrease of the total amorphous fraction in the sample. Somehow more interesting is the behavior of the  $\rho$  relaxation, associated to free charge detrapping in the material, that increases at the beginning (curves 1 to 3 of figure 4), decreasing afterwards as  $T_f$  is increased. In this case the maximum in intensity is observed for samples heated up to temperatures between  $166^{\circ}\text{C}$  and  $172^{\circ}\text{C}$ , that are already fully crystallized. This fact indicates an important increase in the number of trapping centers in the material. When  $T_f$  is further increased the sample stays fully crystallized, however the  $\rho$  relaxation decreases drastically. This behavior occurs at the same time as a small endothermic peak appears in the DSC measurements, and as this peak shifts towards higher temperatures. X Ray diffraction

measurements of these samples showed that the decrease in the  $\rho$  peak can be associated to the improvement of the amorphous-crystal interphases, as will be discussed below.

It can be noted, in the  $\alpha$  and  $\rho$  relaxations, a slight shift of the temperature of the peak maximum towards higher temperatures. This behavior can be seen more clearly in Fig 5. In this figure the peak maximum is plotted versus the final temperature of each relaxation. In fact, the  $\alpha$  peak is made up of contributions coming from dipoles placed in two different amorphous fractions (interspherulitic and interlamellae). As shown for other polymers as PET,<sup>10</sup> each one of these fractions has its own  $T_g$  which is lower in the interspherulitic than in the interlamellae fraction. Therefore, a shift of the  $\alpha$  peak towards higher temperatures can be explained in terms of an increase of the interlamellae fraction respect to the interspherulitic one. The  $\rho$  peak also shifts to the right, due to an increase in the depth of the traps. From  $T_f = 179$  °C onwards it is difficult to distinguish between the  $\alpha$  and the  $\rho$  relaxations due to the broadening of their peaks.

### *DEA*

In order to compare with results obtained by TSDC, we have carried out similar DEA measurements with an initially amorphous PEN sample crystallized by subsequent heating processes (in ten degree steps) to different crystallinity degrees.

In figure 6 we can see the evolution of the loss permittivity at a frequency of  $10^3$  Hz as the final temperature of the scan increases gradually. This evolution implies an increase in the crystallinity degree according to the table 1. In the experimental range of temperatures and frequencies studied we have detected the presence of three relaxations,  $\sim -40$  °C ( $\beta$ ),  $\sim 90$  °C ( $\beta^*$ ) and  $\sim 145$  °C ( $\alpha$ ), however no  $\rho$  relaxation can be observed in this case. Because we are interested only in the zone close to the glass transition,  $\beta$  relaxation lies out of scale in figure 6. Again a decrease in the intensity of



$\beta^*$  and  $\alpha$  relaxations is observed as the crystallinity degree is increased.

### *DMA*

We have reported previously<sup>1</sup> results obtained on amorphous PEN. This material presents three peaks in  $\tan \delta$  (1Hz) at  $\sim -70$  °C ( $\beta$ ),  $\sim 60$  °C ( $\beta^*$ ) and  $\sim 130$  °C ( $\alpha$ ), respectively. Moreover, at about  $\sim 180$  °C, a strong increase of  $E'$  is observed as temperature increases, which is correlated with a further small maximum in  $\tan \delta$ .

Figure 7 shows the evolution of the  $\tan \delta$  at 10 Hz for a sample of amorphous PEN heated up to progressively higher final temperatures. We can observe that the maximum in  $\tan \delta$  corresponding to the dynamic glass transition at about 135°C is not modified when the final temperature is smaller than 180°C. However, when the sample is heated to final temperatures higher than 180 °C, the maximum of the  $\alpha$  relaxation decreases, its width increases and an additional small maximum appears as a shoulder at  $\sim 165$  °C. This peak has to be attributed to the crystalline fraction of polymer.<sup>11</sup> When the sample is heated at higher temperatures we can not clearly observe this additional peak but since the width of the peak increases we can assume that these two peaks overlap. Thus, in this case, also the intensity of  $\beta^*$  and  $\alpha$  relaxations decrease when the crystallinity increases. As it was done in the case of mechanical measurements we correlate the final temperature of the scan with the crystallinity degree according to table 1.

### *Kinetic Parameters*

The activation energies ( $E_a$ ) for the dipolar relaxations ( $\alpha$  and  $\beta^*$ ), can be evaluated from TSDC curves assuming for the discharge process a first order kinetic model, leading to the so called "Bucci and Fieschi" equation<sup>12,13</sup>:

$$I(t) = \frac{SP(\infty)}{\tau_0} \exp\left(-\frac{E_a}{kT}\right) \exp\left(-\frac{1}{\nu\tau_0} \int_{t_0}^t \exp\left(-\frac{E_a}{kT}\right) dT\right). \quad (1)$$

In this model the intensity of depolarization is expressed by equation (1), where  $S$  is the area of the sample,  $P(\infty)$  is the equilibrium polarization,  $1/\tau_0$  is the natural frequency,  $T$  the temperature,  $k$  the Boltzman constant and  $\nu$  is the heating rate. Mathematical fitting of the calculated discharges to the experimental ones allows to determine some kinetic parameters of the process, such as  $E_a$  and  $\tau_0$ .

Within this model,  $E_a$  was calculated from discharges obtained for the  $\beta^*$  relaxation, and is reproduced in figure 8. We can observe a significative tendency of its value to decrease as  $T_f$  is increased. We can understand this behavior assuming that long polymer chain segments motion is restricted in the interlamellae amorphous regions in which the polarization is mainly due to short polymer chain segments. When crystallization proceeds in the material, interlamellae amorphous regions increase respect to the interspherulitic amorphous regions, and thus the observed discharge is mainly due to short segments with lower  $E_a$ . In the case of  $\alpha$  relaxation the value of  $E_a = 1.5$  eV is approximately constant.

It is possible to calculate  $E_a$  from DEA measurements from an Arrhenius law for the relaxation time of the dipoles, and an expression of  $\varepsilon''$  for a given frequency as a function of temperature, for the  $\beta^*$  relaxation, can be postulated according to Fuoss-Kirkwood as equation (2)<sup>14,15</sup>.

$$\varepsilon''(T) = \frac{\frac{m}{2}(\varepsilon_s - \varepsilon_\infty)}{\cosh\left[\frac{m \cdot E_a}{R} \left(\frac{1}{T} - \frac{1}{T_{max}}\right)\right]}, \quad (2)$$

were  $\epsilon_s$  and  $\epsilon_\infty$  are respectively the static and optic dielectric constants, the parameter  $m$  ( $0 < m < 1$ ) gives account for the broadness of the relaxation and  $T_{max}$  is the temperature at which  $\epsilon''$  has the maximum.

In this way,  $E_a$  was calculated for the  $\beta^*$  relaxation from measurements performed with different samples (see figure 6), and the results are reproduced in figure 9. We can observe a significative tendency to decrease  $E_a$  with the crystallinity degree, as in the case of the TSDC measurements. On the other hand the parameter  $m$  increases from 0.25 for the amorphous material to 0.42 for the polymer containing the highest degree of crystallinity (48%).

It is interesting to study the effect of the crystallinity degree in the value of the activation energy associated to the  $\alpha$  process. For this reason we have represented in figure 10  $\ln f$  vs  $1/T$ . We can observe that, as the slope of the curves decreases, the value of  $T_f$  (and consequently the degree of crystallinity) increases, as it was observed in the case of the  $\beta^*$  relaxation.

Moreover, the effect of an increase of the degree of crystallinity on  $E_a$  is less important in the case of the  $\alpha$ -relaxation. This result is in accordance with the TSDC analysis reported previously.

We could also carry out a similar analysis of the results obtained by DMA. However, by this technique we only have a narrow range of frequencies and this study is, therefore, not reported.

## *Conclusions*

TSDC, DEA and DMA measurements of as received PEN Kaladex (R) (partially

crystalline) show in the temperature range from  $-150^{\circ}\text{C}$  to  $200^{\circ}\text{C}$  four relaxations located, in increasing temperature order, around  $-70^{\circ}\text{C}(\beta)$ ,  $60^{\circ}\text{C}(\beta^*)$ ,  $130^{\circ}\text{C}(\alpha)$  and  $170^{\circ}\text{C}(\rho)$ . The evolution of these relaxations with the crystallinity degree of the material was investigated in samples thermally crystallized to different degrees from the amorphous state.

The  $\beta^*$  and  $\alpha$  relaxations show a decrease in the peak area and intensity of the maximum as the crystallinity degree increases in the material. This behavior is explained in terms of the decrease of the total amorphous fraction present in the material, where the  $\beta^*$  relaxation is active. In the case of the  $\alpha$  relaxation a slight shift of the peak maxima temperature towards higher values is observed when the crystallinity degree increases. This evolution is explained assuming for the partially crystallized polymer two separated amorphous zones, one between the growing spherulites and the second one between the crystalline lamellae inside the spherulites. The amorphous fraction within the spherulites presents a higher glass transition temperature than the amorphous fraction between them, resulting in the shift of the  $\alpha$  peak.

The fit of experimental TSDC and DEA data to conventional models for the  $\beta^*$  peak, shows a significative tendency to decrease in  $E_a$  as the crystallinity degree increases in the material. The obtained values range in both cases from approximately  $0.7\text{eV}$  for the amorphous material to  $0.3\text{eV}$  for the fully crystallized material ( $\approx 48\%$ ). In the case of the  $\alpha$  relaxation, the activation energy calculated from the TSDC results lies around  $1.5\text{eV}$ , and is approximately independent from the crystallinity degree.

The  $\rho$  relaxation, only detectable by TSDC, shows a complex evolution with an initial increase in the peak area that reaches its maximum value when the crystallization process (detected by DSC) concludes. This fact indicates an important increase in the

number of trapping centers in the material while the crystallization takes place. Further thermal treatment of the sample produces a sharp decrease of the peak, at the same time as a small endothermic peak appears in DSC measurements.

Table 1. Calculated crystallinity degree as a function of  $T_f$ 

<i>Curves</i>	$T_f$ ( $^{\circ}\text{C}$ )	$T_g$ ( $^{\circ}\text{C}$ )	$T_m$ ( $^{\circ}\text{C}$ )	$\chi_c$ %
1	158	119.8	200.5	5.4
2	160	119.8	194.6	9
3	163	120.9	191.1	11.5
4	166	121.4	183.9	29
5	172	124.6	179.1	$\approx 48$
6	175	124.8	180.2	$\approx 48$
7	177	128.7	183.7	$\approx 48$
8	178	128.4	184.8	$\approx 48$
9	180	130.7	186.0	$\approx 48$
10	190	132.0	195.3	$\approx 48$

### *Figure captions*

**Figure 1.** Schematic representation of the electric field and temperature program developed in the TSS process: (a), (c) TSDC measurements and partial crystallization, (b) polarization

**Figure 2.** DSC scans at 10 °C/min for different samples of PEN treated by the TSS method (see table 1 for details)

**Figure 3.** TSDC scans of the  $\beta^*$  relaxation for samples with different crystallinity degree: (1)  $T_f=160$  °C, (2)  $T_f=166$  °C, (3)  $T_f=169$  °C, (4)  $T_f=172$  °C, (5)  $T_f=177$  °C, (6) 182 °C. ( $T_p=67$  °C,  $V_p=1.5$  kV,  $t_p=30$  min) (see table 2 for details)

**Figure 4.** TSDC scans of the  $\alpha$  and  $\rho$  relaxations for samples with different crystallinity degree: (1)  $T_f=160$  °C, (2)  $T_f=166$  °C, (3)  $T_f=172$  °C, (4)  $T_f=175$  °C, (5)  $T_f=177$  °C, (6)  $T_f=178$  °C, (7)  $T_f=179$  °C. ( $T_p=130$  °C,  $V_p=1.5$  kV,  $t_p=30$  min)

**Figure 5.** Evolution of  $T_m$  for  $\alpha$  and  $\rho$  relaxations versus the final temperature  $T_f$  reached in the TSS process

**Figure 6.** Dielectric loss for PEN at 1000 Hz for samples after heated to different final temperatures (1)  $T_f=158$ °C, (2)  $T_f=173$ °C, (3)  $T_f=189$ °C, (4)  $T_f=198$ °C, (5)  $T_f=219$ °C, (6)  $T_f=228$ °C, (7)  $T_f=238$ °C.

**Figure 7.** Tan  $\delta$  for PEN at 10 Hz for samples after heated to different final temperatures (■) 150°C, (○) 170°C, (▲) 200°C, (▽) 210°C, (◆) 240°C.

**Figure 8.** Calculated activation energies versus  $T_f$  for the  $\beta^*$  relaxation measured by TSDC

**Figure 9.** Calculated activation energies versus  $T_f$  for the  $\beta^*$  relaxation measured by DEA

**Figure 10.**  $\alpha$  relaxation dielectric map ( $\ln f$  versus  $1/T$ ) of partially crystallized PEN in the studied temperature and frequency range.



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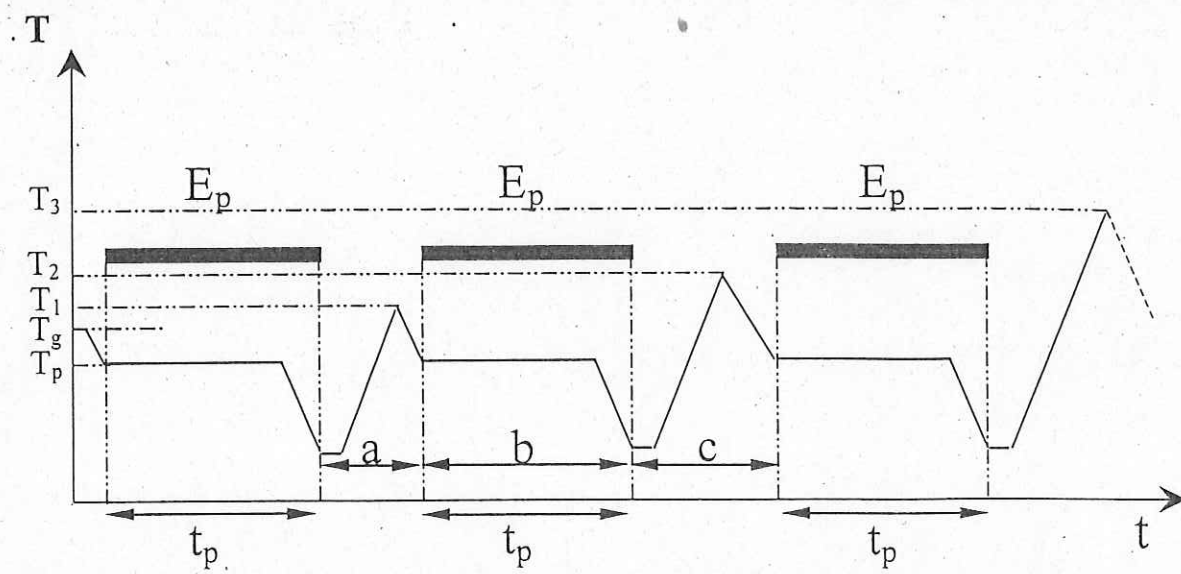


Fig. 1

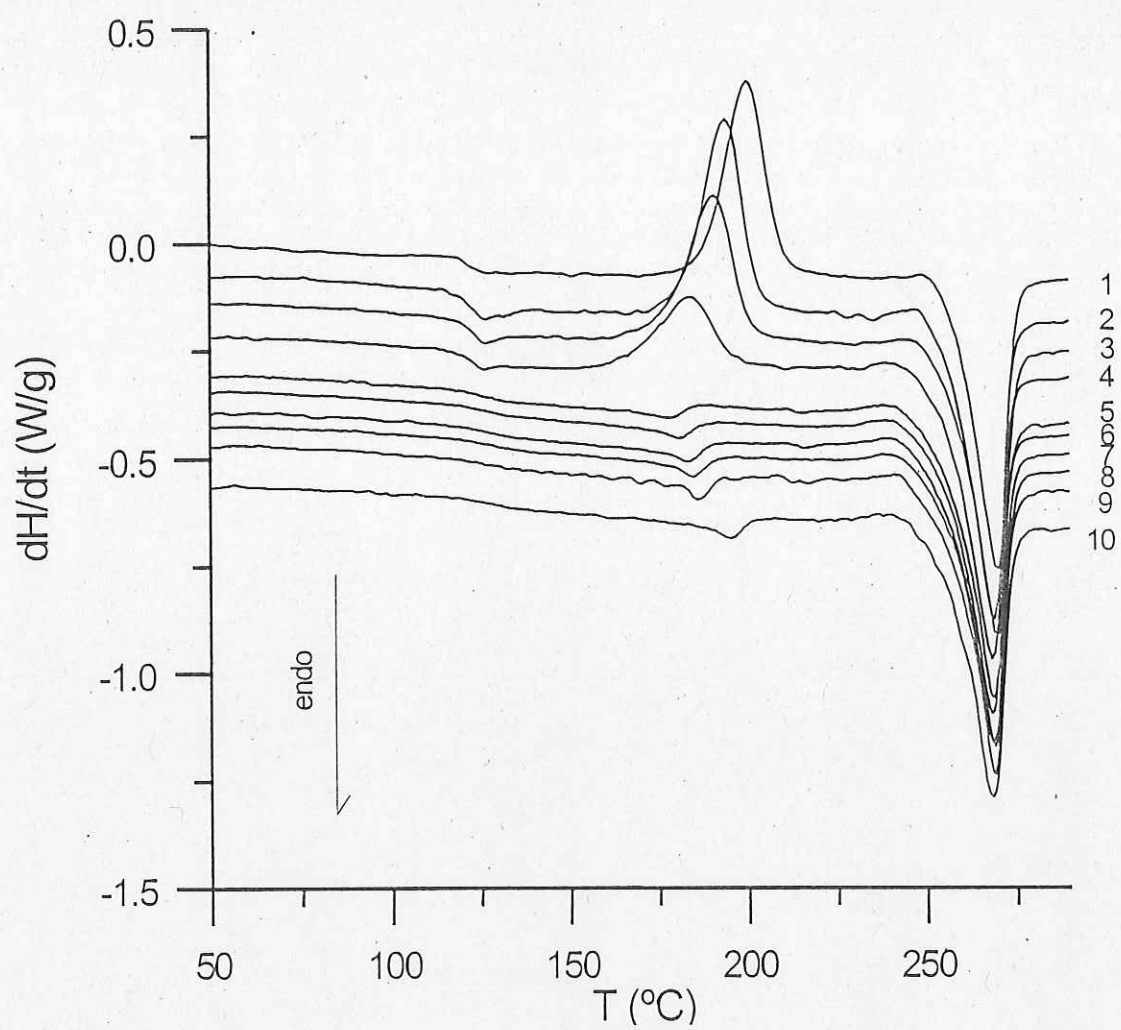


Fig. 2

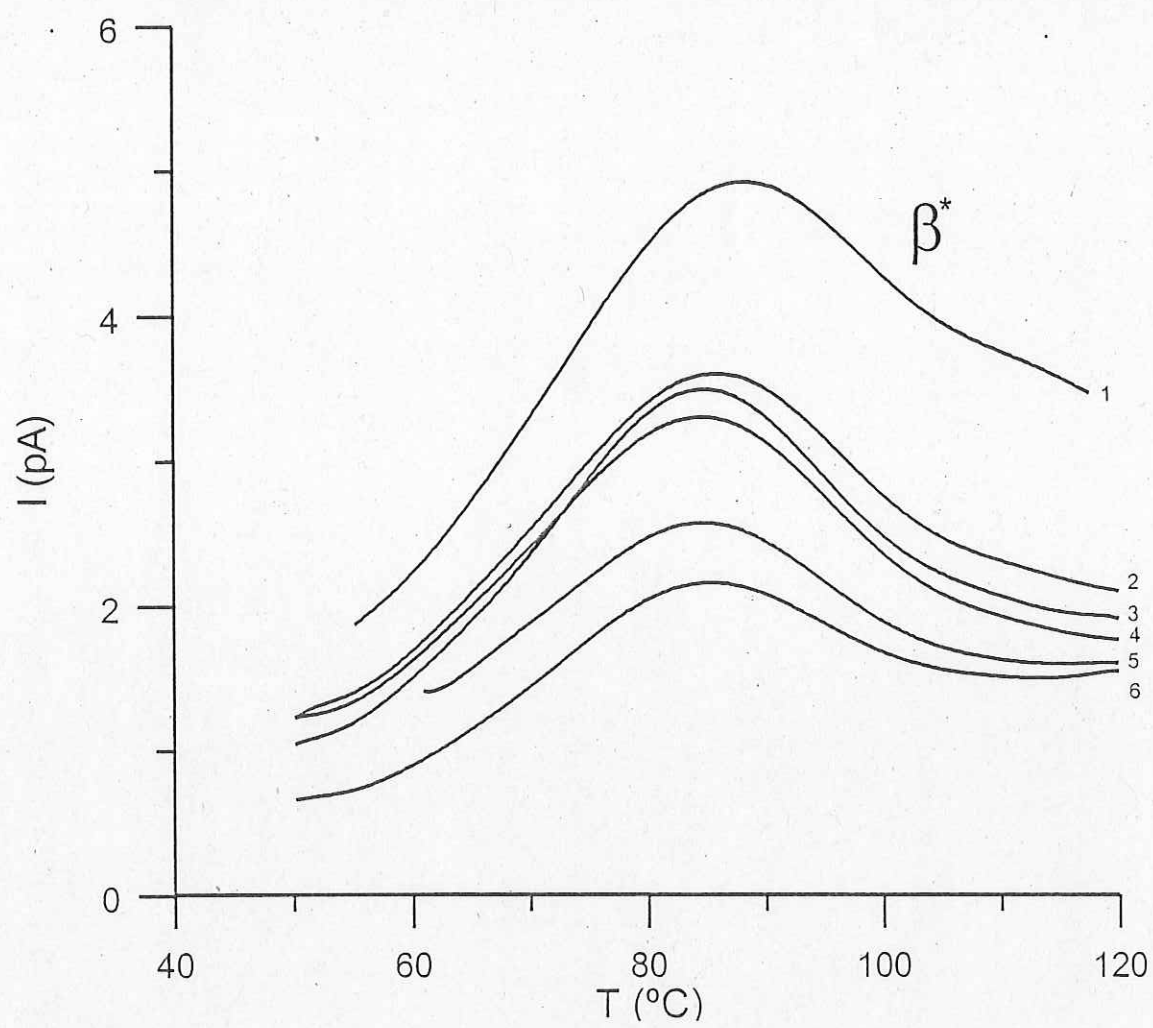


Fig 3

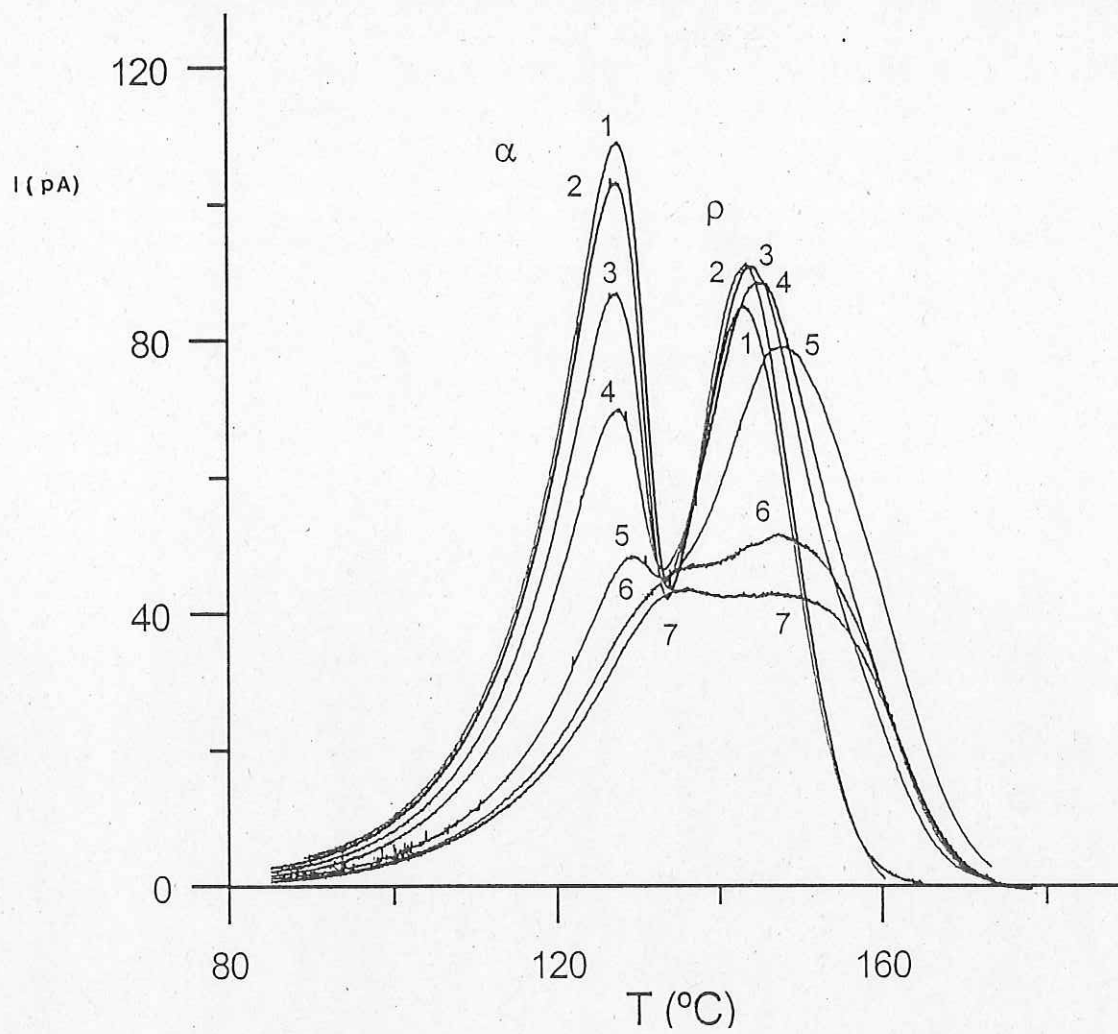


Fig. 4

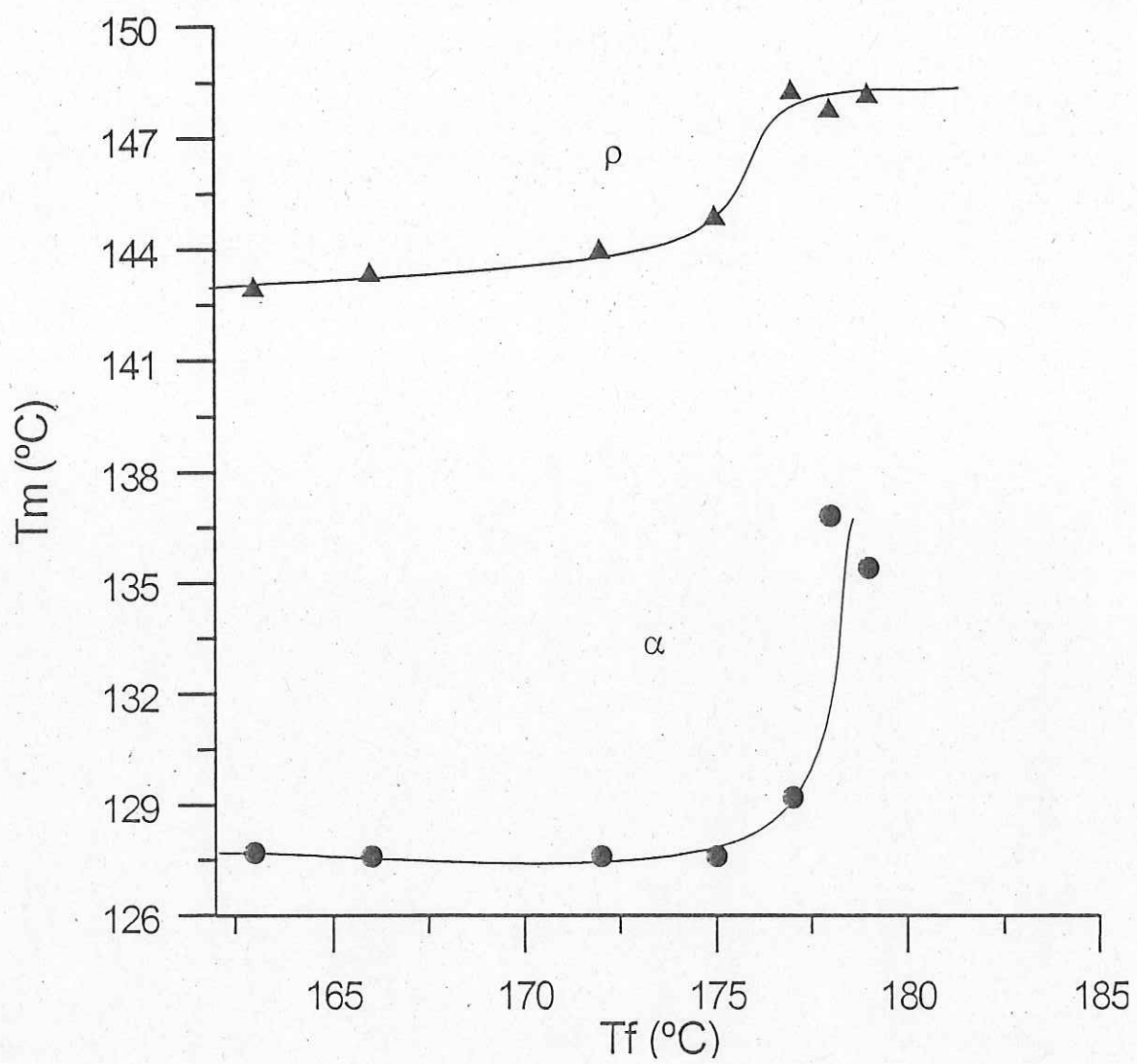


fig 5

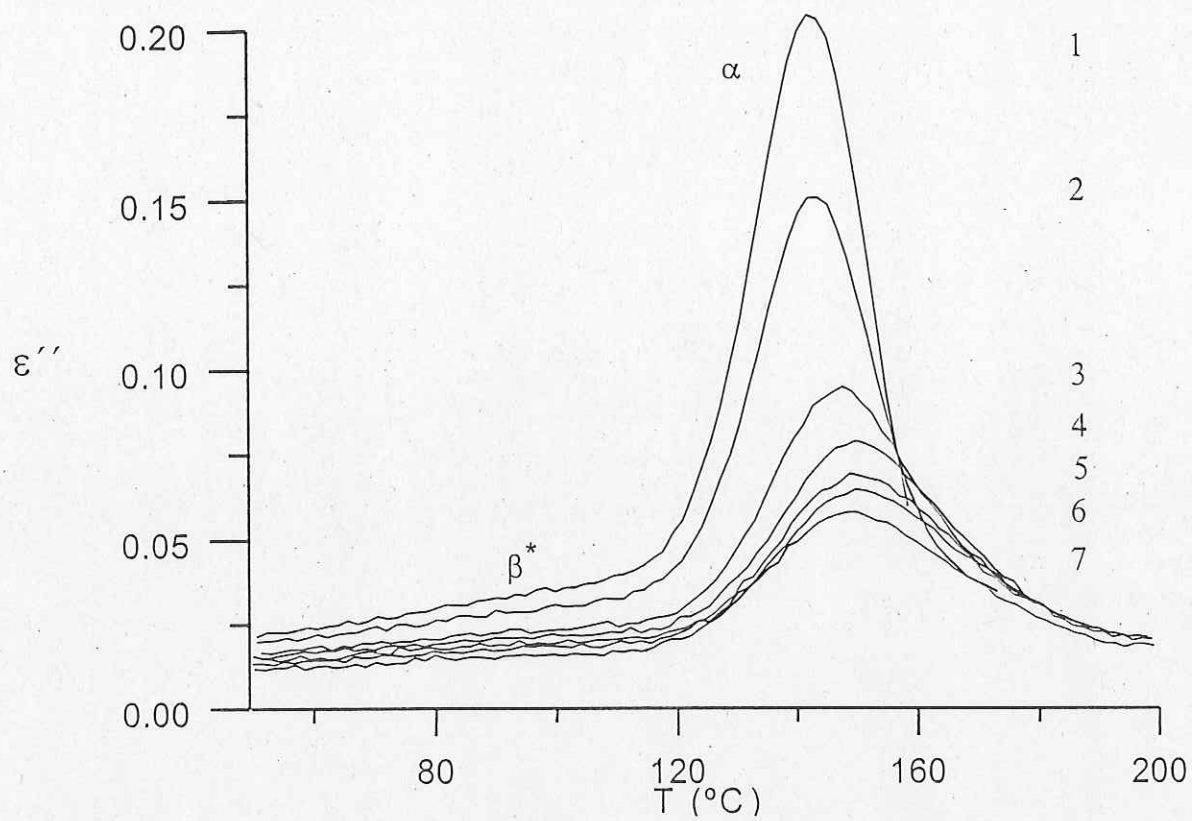
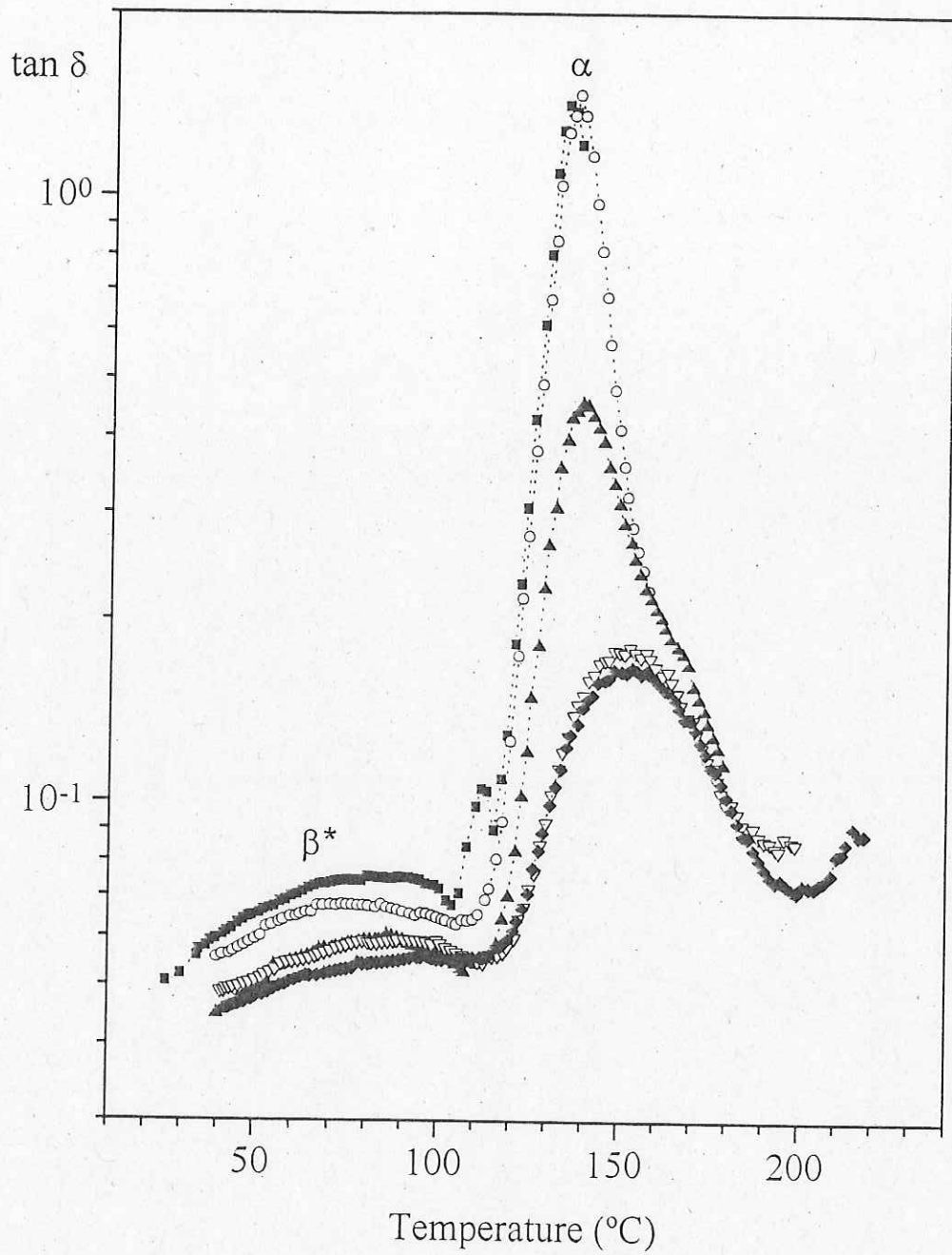


Fig.6





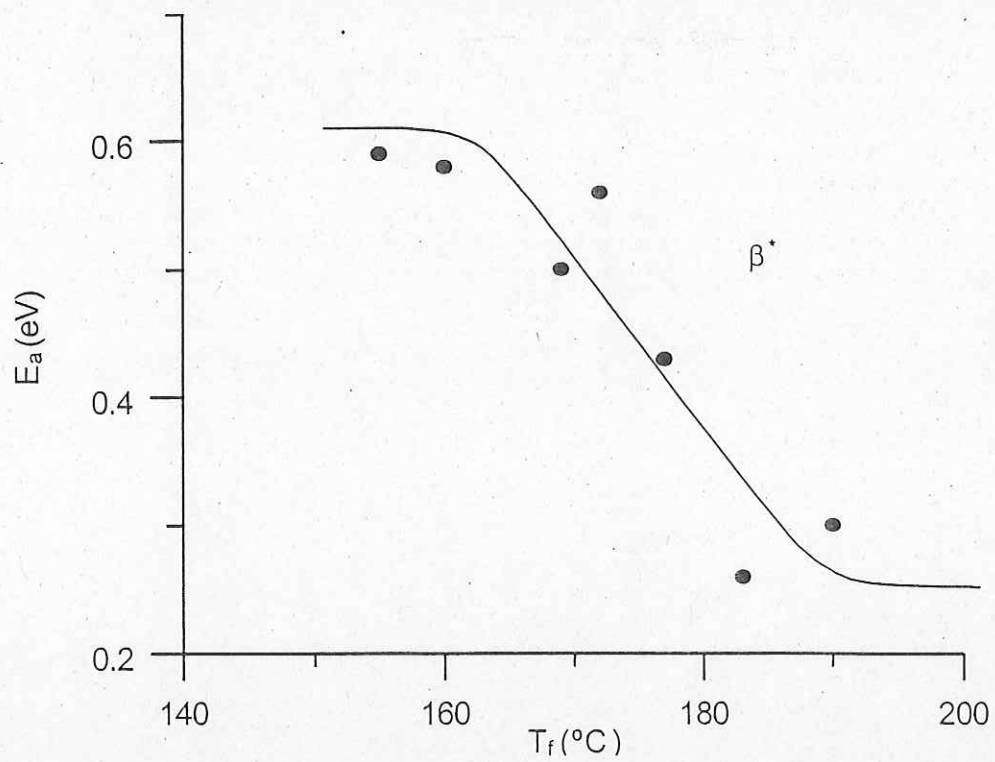


Fig. 8

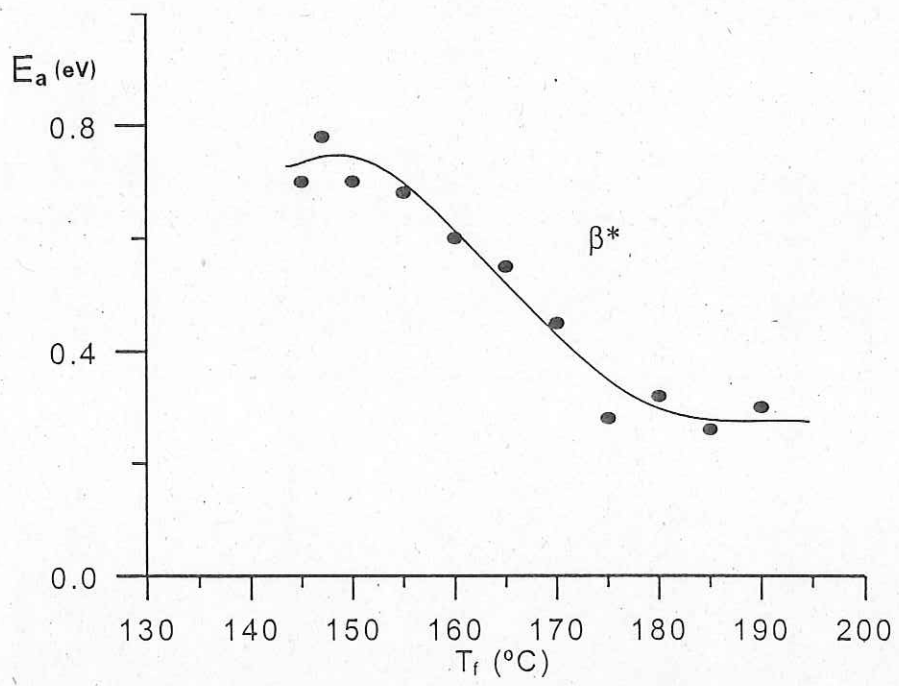


Fig. 9

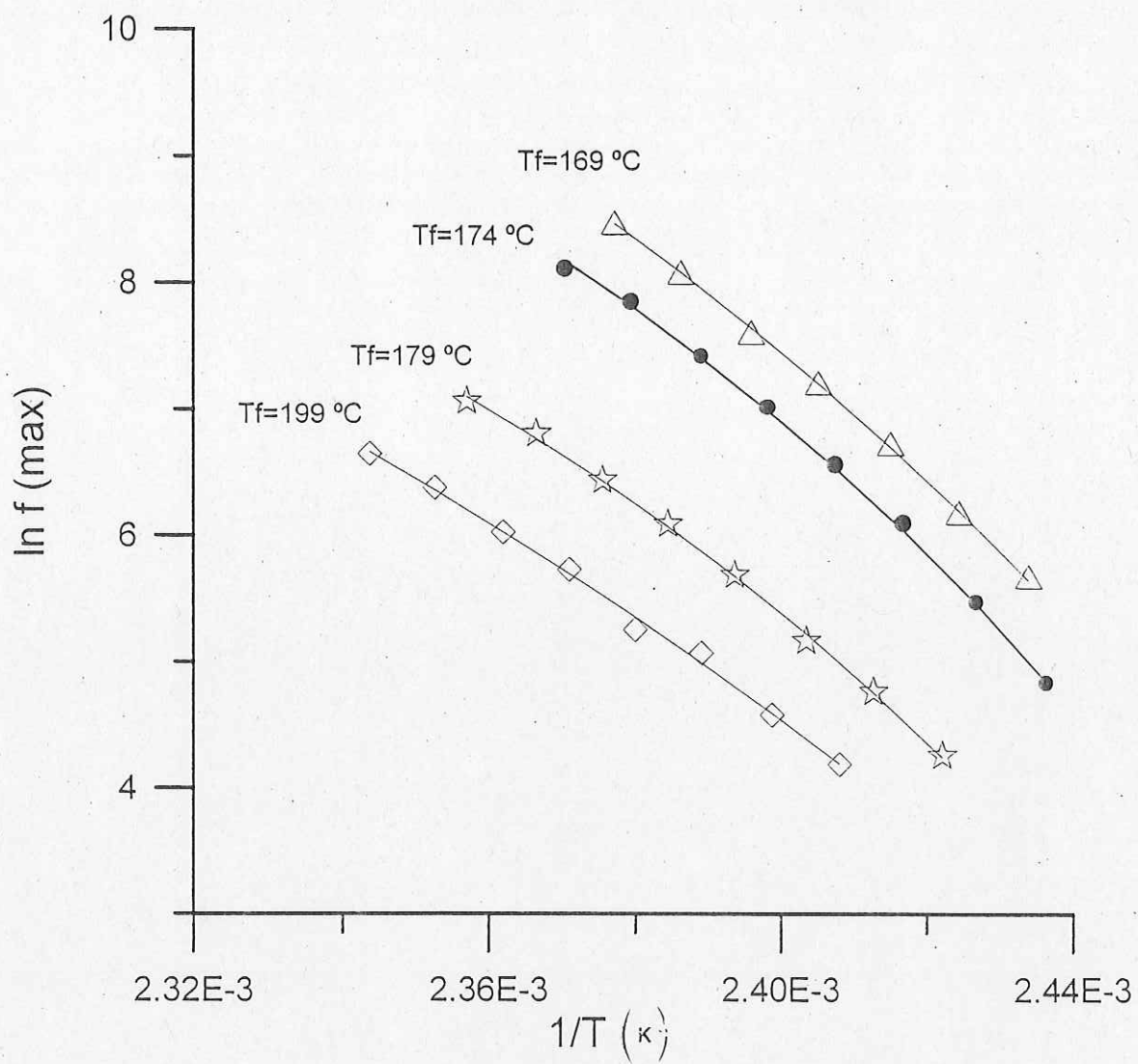


Fig 10

