

# Cold crystallization effect on $\alpha$ and $\rho$ amorphous poly(ethylene terephthalate) relaxations by thermally stimulated discharge currents

J. Belana and M. Pujal

*Laboratorio de Fisica Aplicada, Escuela Tecnica Superior de Ingenieros Industriales de Terrassa (U.P.C.), Colon 11, Terrassa 08222, Barcelona, Spain*

and P. Colomer and S. Montserrat

*Laboratorio de Termodinamica y Fisicoquimica, Escuela Tecnica Superior de Ingenieros Industriales de Terrassa (U.P.C.), Colon 11, Terrassa 08222, Barcelona, Spain*

*(Received 1 June 1987; revised 15 March 1988; accepted 22 March 1988)*

The thermally stimulated discharge currents (TSDC) of crystalline poly(ethylene terephthalate) (PET-c) show two clearly differentiated relaxations,  $\alpha_c$  and  $\rho_c$ , which could result from the  $\alpha$  and  $\rho$  relaxations of amorphous PET as a consequence of the crystallization process. The evolution of  $\alpha$  and  $\rho$  relaxations of amorphous PET has been studied by the application of a method which we have called thermal stimulation by steps (TSS) and by isothermal crystallization of amorphous samples for different times. The  $\rho$  relaxation increases due to progressive nucleation and subsequent growth of the nuclei until a maximum value is reached; from then on until extinction  $\rho$  is mainly affected by growth. The  $\alpha$  relaxation decreases progressively until its total extinction following the increase of restrictions. For a certain degree of crystallinity, by applying the TSS method, simultaneous occurrence of  $\alpha$ ,  $\rho$ ,  $\alpha_c$  and  $\rho_c$  is achieved, which implies that  $\alpha_c$  and  $\rho_c$  do not proceed from  $\alpha$  and  $\rho$  and, consequently, that their origin is different.

**(Keywords: poly(ethylene terephthalate); relaxations; cold crystallization; thermally stimulated discharge currents; thermal stimulation by steps)**

## INTRODUCTION

The technique of thermally stimulated discharge currents (TSDC) has proved most useful in studying the relaxations of polymeric materials, particularly in determining their origin (dipolar or space charge) and their association to concrete movements of the chains and/or changes in the material morphology. In this sense, the literature for poly(ethylene terephthalate) (PET) is vast<sup>1-22</sup>.

The TSDC curves resulting from amorphous PET electrets show, in the range room temperature–100°C, two relaxations situated approximately at 80 and 90°C, called  $\alpha$  and  $\rho$ , respectively. The first, associated with the glass transition, is dipolar while the other is of the space charge. Both relaxations have been studied previously<sup>19-21</sup>.

Some changes in both relaxations, which must be related to the degree of crystallinity of the sample, can be seen on comparing the TSDC curves of semicrystalline PET and amorphous PET. The crystallization of the material involves an increase of the mobility restrictions of the chains, which influences both the dipolar relaxation and the detrapping of the free charge.

The effect of crystallinity on the  $\alpha$  relaxation has been thoroughly studied over the last two decades by dynamic mechanical analysis and dielectric analysis. Dynamic mechanical analysis<sup>23,24</sup> shows displacement of the  $\alpha$

relaxation to higher temperatures when the degree of crystallinity increases, while the height of the dispersion decreases and its width increases. However, for a given degree of crystallinity the relaxation tends to displace in the opposite direction<sup>25-28</sup>. This behaviour is believed to result from the effect of crystal size on the amorphous region. At low crystallinities, the many small spherulites act like crosslinks and inhibit the movement of the segments in the amorphous domains while, at high crystallinities, the smaller number of large spherulites makes these domains more mobile. When the degree of crystallinity is the same, the effect of small but numerous spherulites inhibits these movements more than a few larger spherulites. Consequently, the method of preparing semicrystalline samples, with different morphology, may give rise to considerable changes in relaxation behaviour<sup>28,29</sup>.

Dielectric measurements<sup>30-32</sup> give similar behaviour to dynamic mechanical measurements with respect to relaxation displacement towards higher temperatures and the decrease of its height, on increasing the degree of crystallinity, although the relaxation tends to disappear. McCrum<sup>23</sup> and Boyd<sup>33</sup> have compared the dynamic mechanical and dielectric results and have re-examined the behaviour of the relaxation in semicrystalline material.

Papers concerning the effect of the degree of crystallinity on  $\alpha$  and  $\rho$  relaxations of amorphous PET

studied by TSDC are few. With regard to  $\alpha$  relaxation, Sacher<sup>10,11</sup> discussed relaxation displacement to higher temperatures when a sample is annealed at 130°C. Vanderschueren<sup>34</sup> proved equally the displacement of  $T_\alpha$  and its fall in intensity on polarizing at 110°C, showing the greater extent of the relaxation and the decrease of the apparent activating energy on increasing the crystallinity while the  $T_\alpha$  displacement is parallel to the  $T_g$  displacement of the material. Schneider<sup>22</sup>, using samples annealed at 80 and 90°C with annealing times of 1 and 100 h, observed a  $T_\alpha$  displacement from 70 to 80°C for the samples annealed for 100 h at 90°C ( $x_c = 10\%$ ) as well as a fall in intensity and an increase in relaxation width.

With respect to  $\rho$  relaxation, Vanderschueren<sup>34</sup>, Asano and Suzuki<sup>13</sup> and Van Turnhout<sup>1</sup> demonstrated the increase of  $T_\rho$  with polarization temperature and the further decrease of  $I_\rho$  for higher polarization temperatures. They suggested that this effect may be caused by a likely injection of carriers which may neutralize the space charge, the  $\rho$  evolution being a result of a likely crystalline rearrangement. Schneider<sup>22</sup> pointed out a marked displacement of  $T_\rho$  in samples annealed for 100h at 90°C ( $T_\rho$  increased from 92 to 109°C), and believed it to be due to charge detrapping from increasingly deeper levels.

Apart from the question of whether amorphous PET shows 'paracrystalline' structures, undetectable by X-rays, which has given rise to some controversy<sup>35-40</sup>, the beginning of the cold crystallization has been shown to be between 80 and 100°C, according to the measurement system used<sup>41-46</sup>. By differential scanning calorimetry (d.s.c.), the beginning of crystallization can be detected above 100°C, the exothermic peak being placed between 120 and 130°C<sup>47-50</sup>.

Isothermal crystallization for low annealing temperatures ( $T_c < 100^\circ\text{C}$ ) takes place by formation of new crystallites before the existing ones start growing, the size having no relation to temperature. Crystallization for high  $T_c$  results from diffusion, which makes the crystallites grow with little or no formation of new nuclei, the size of the crystal depending on temperature. For intermediate temperatures both effects occur simultaneously<sup>41,45,51,52</sup>.

During non-isothermal crystallization and for a constant heating rate, the nuclei only form at low temperatures, their numbers being inversely proportional to the rate, while the crystals grow in size at higher temperatures with no increase in their number<sup>53-56</sup>.

The aim of this Paper is to study the behaviour of  $\alpha$  and  $\rho$  relaxations of amorphous PET by TSDC during cold crystallization of the material. The samples, with different crystallinity, will be formed either non-isothermally by breaking up depolarization at given temperatures or isothermally at temperatures at which nucleation or growth are dominant. In other words this is an approach to the evolution of relaxations *versus* the increase of crystallinity and its comparison with dielectric and dynamic mechanical measurements. It is also an attempt to see whether the  $\alpha_c$  and  $\rho_c$  relaxations of crystalline PET result from a continuous displacement of  $\alpha$  and  $\rho$ . The evolution of these relaxations will be correlated with the nucleation and/or growth occurring during crystallization.

## EXPERIMENTAL

The experiments were carried out on commercial PET,

with a number average molecular weight  $M_n$  of 20 000.  $M_n$  was determined by viscosimetric measurements using *o*-chlorophenol, at 25°C, as a solvent.

Amorphous PET films were prepared, with a diameter of 2 cm and thickness of  $\approx 250 \mu\text{m}$ , by fusion and quenching in moulds. The films were conditioned for a few days in a vacuum chamber, at 40°C. The samples were heated to a temperature  $\leq 90^\circ\text{C}$  to eliminate likely internal stresses originating during the manufacturing process which could give rise to polarization. Density measurements after this heating process gave, in all cases, a degree of crystallinity  $< 1\%$ . The conditioned samples, without internal stresses, were metallized on both sides with aluminium in a vacuum chamber.

To form the electrets, the samples were heated from  $T_0$  to the polarization temperature  $T_p$  and then a field  $E_p$  was applied to them for an isothermal time  $t_{pi}$ . Subsequently, the samples were cooled to a temperature  $T_0 < T_p$  at a controlled rate  $v$  ( $2^\circ\text{C min}^{-1}$ ). The field was then withdrawn and the short-circuited electrets were kept for a time  $t_d$  before discharge was initiated.

The electret samples were discharged by heating at a rate  $v$  up to a final temperature  $T_f$ .

The experimental equipment used was formed by a measuring cell placed in an air-forced Heraeus oven modified to be controlled by a Setaram PID RT-3000 temperature programmer. The temperature was measured by means of Pt-100 probes located very near the sample with a digital thermometer Mettler TM-15 with an approximate accuracy of  $0.1^\circ\text{C}$ . The discharge current was measured with a digital electrometer Kheitley 616 whose accuracy is  $\pm 5\%$  of reading in the range  $10^{-9}$ – $10^{-11}$  A. The current was recorded as a function of temperature in an H.P. 7046 A. Previous experiments show that the temperature gradients across the sample are lower than  $0.2^\circ\text{C}$  in the temperature range used in this work.

The trials developed to establish the effect of cold crystallization on the relaxations were done according to a method which we have called thermal stimulation by steps (TSS). Figure 1 shows a TSS operating diagram.

The purpose of this method is to make electrets cyclically at a fixed  $T_p$  and then to apply to them a discharge up to a temperature  $T_f$  whose value increases by  $\Delta T$  in each cycle. This increase should be as small as possible,  $< 1^\circ\text{C}$  in the temperature ranges where the most significant changes are expected. This process leads to gradual crystallization in the amorphous sample and the crystallinity is determined by density measurements using

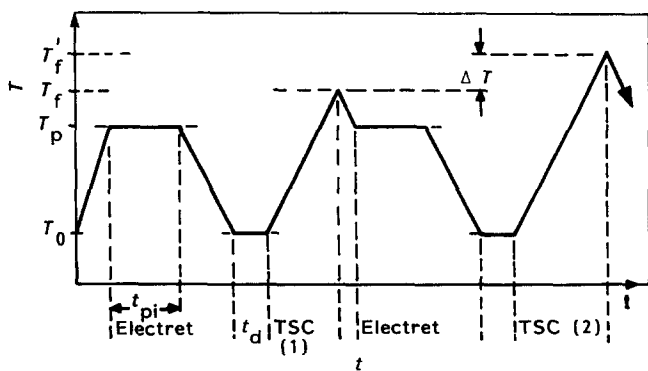


Figure 1 Operating diagram for the thermal stimulation by steps (TSS) method

a density gradient column. Characterization of the sample, before the TSDC trials, was performed by d.s.c. using a Mettler TA-3000 calorimeter.

## RESULTS AND DISCUSSION

Figure 2 shows the discharge of PET amorphous and semicrystalline electrets, formed under the conditions mentioned above. In the amorphous PET three peaks can be seen, at  $\approx 83$ , 95 and 128°C ( $\alpha$ ,  $\rho$  and cc, respectively), while in the crystalline PET only two relaxations are distinguished, at 93 and 118°C ( $\alpha_c$  and  $\rho_c$ ), both of lower intensity than  $\alpha$  and  $\rho$  and also more symmetric.

The peak cc occurring on heating the amorphous PET is thought to be due to the non-isothermal crystallization process. This assumption is based on the d.s.c. tests, which let us observe one exothermal peak in the same region of temperatures, and also on the degree of crystallinity before and after heating ( $x_{ci}=0.3\%$ ,  $x_{cf}=40\%$ ). Obviously, the peak cc does not appear in the TSDC and DSC curves of the crystalline PET ( $x_c=40\%$ ), Figure 3.

Since  $\alpha_c$  and  $\rho_c$  relaxations are characteristics of the crystalline PET, the question arises whether  $\alpha$  and  $\rho$  of the amorphous PET evolve continuously with the increase in crystallinity until  $\alpha_c$  and  $\rho_c$  are formed, or whether the latter result from mechanisms other than  $\alpha$  and  $\rho$ .

Initially, the influence of the polarization temperature  $T_p$  on  $\alpha$  and  $\rho$  was examined in the temperature range 75–130°C. The curves shown in Figure 4 were obtained.

With regard to  $\alpha$  relaxation it can be observed that neither  $I_\alpha$  nor  $T_\alpha$  change significantly for  $T_p < 90^\circ\text{C}$ , while for  $90 \leq T_p \leq 110^\circ\text{C}$   $I_\alpha$  begins to fall and  $T_\alpha$  tends to move slightly towards higher temperatures. On the other hand, during this range of polarization temperatures,  $I_\rho$  increases progressively as  $T_p$  increases. Polarizations made at  $T_p > 110^\circ\text{C}$  originate significant changes in both relaxations. While the  $\alpha$  intensity falls sharply and its temperature increases, the  $\rho$  relaxation grows progressively, reaching a maximum, to decrease later, sharply increasing its position very clearly. For  $T_p = 130^\circ\text{C}$ ,  $\alpha_c$  and  $\rho_c$  are already perceptible (Figure 5).

The most significant changes in both relaxations take place in the domain of polarization temperatures in which cold crystallization occurs, which is a reason to assume they result from it. However, these results do not clarify whether  $\alpha$  and  $\rho$  evolve continuously to  $\alpha_c$  and  $\rho_c$ .

Experiments in which the crystallinity of the samples were progressively increased have been carried out by the thermal stimulation by steps (TSS) method. Density was measured after each stage and, afterwards, crystallinity was evaluated.

Results for  $T_p = 90^\circ\text{C}$  are shown in Figure 6. Figure 7 shows the evolution of crystallinity versus final temperature reached in each TSS cycle. Figures 8 and 9 show the evolution of the intensity and position of both relaxations versus the final temperature reached in the former discharge as well as the crystallinity of the samples.

For  $T_f < 105^\circ\text{C}$  ( $x_c < 3\%$ ) no significant changes have been observed in either relaxation, although  $I_\rho$  tends to increase smoothly. In the  $T_f$  range between 105 and 120°C, changes are important and coincident with a marked increase in the crystallinity ( $x_c$  increases from  $\approx 3$  to 32%). The  $\alpha$  relaxation tends to increase progressively the temperature of the maximum, while a marked fall of

intensity begins to occur; equally, the  $\rho$  relaxation increases sharply in intensity, going through a maximum, and also increases its position. For  $T_f > 120^\circ\text{C}$ , with a small increase of crystallinity,  $\rho$  relaxation initiates a fast decrease in intensity while  $I_\alpha$  falls sharply.

When this decrease is taking place, once crystallization has finished for the conditions mentioned, the occurrence of the  $\alpha_c$  relaxation is emphasized, weak at first, placed at  $\approx 10^\circ\text{C}$  above  $\alpha$  and then becoming stronger when  $I_\alpha$  begins to decrease.  $I_\alpha$  and  $I_{\alpha_c}$  are practically identical for a final temperature of 122°C ( $x_c = 32\%$ ), while a weak  $\rho_c$  relaxation at about 116°C can be observed. For  $T_f > 123^\circ\text{C}$ , both  $\alpha$  and  $\rho$  disappear from the spectrum and only  $\alpha_c$  and  $\rho_c$  remain visible.

The results found for the variation of both relaxations with polarization temperature and from the application of the TSS method show – after an insensitivity period for crystallinities  $< 3\%$  – that  $\alpha$  relaxation moves to higher temperatures and reduces its height, in accordance with

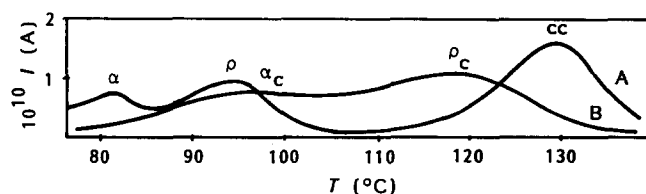


Figure 2 TSDC curves for PET samples with different crystallinities. A, PET-a,  $x_c = 0.33\%$ ;  $T_p = 88^\circ\text{C}$ ;  $E_p = 90 \text{ kV cm}^{-1}$ ;  $t_{pi} = 3 \text{ min}$ ;  $v = 2^\circ\text{C min}^{-1}$ . B, PET-c,  $x_c = 40\%$ ;  $T_p = 108^\circ\text{C}$ ;  $E_p = 108 \text{ kV cm}^{-1}$ ;  $t_{pi} = 60 \text{ min}$ ;  $v = 2^\circ\text{C min}^{-1}$ .

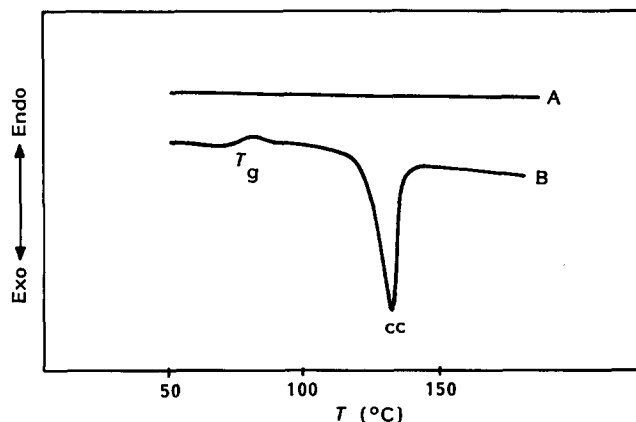


Figure 3 D.s.c. curves for, A, PET-c and, B, PET-a. Heating rate  $2^\circ\text{C min}^{-1}$ .

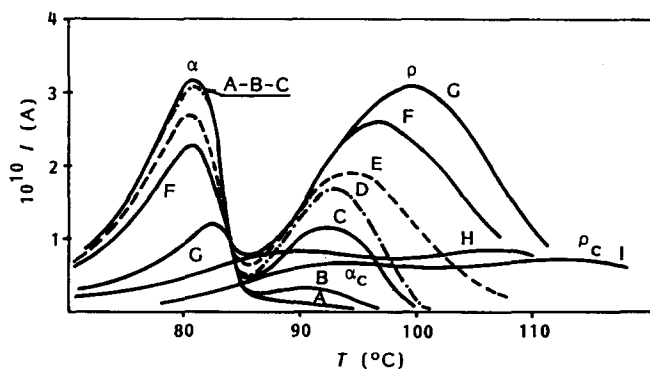


Figure 4 TSDC curves of amorphous PET samples at different polarization temperatures  $T_p$ ;  $E_p = 120 \text{ kV cm}^{-1}$ ;  $t_{pi} = 5 \text{ min}$ .  $T_p$  (°C): A, 75; B, 80; C, 85; D, 90; E, 100; F, 110; G, 118; H, 122; I, 130

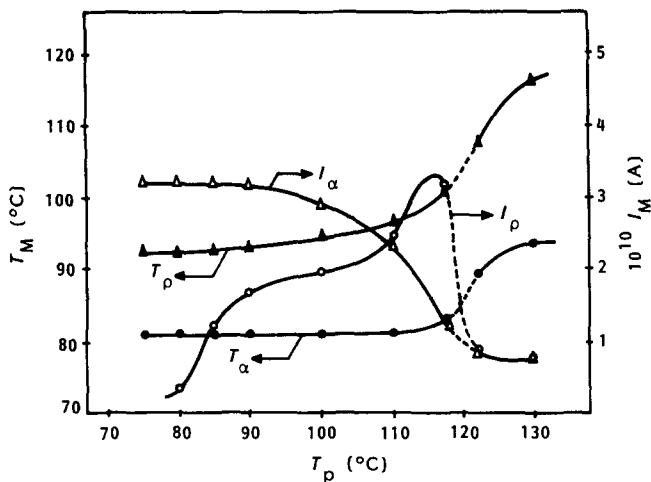


Figure 5 Evolution of  $\alpha$  and  $\rho$  amorphous PET relaxation versus polarization temperature  $T_p$

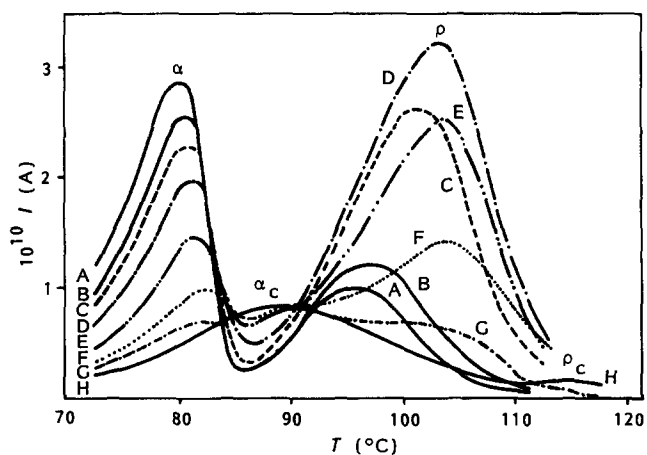


Figure 6 TSDC curves obtained by TSS;  $T_p = 90^\circ\text{C}$ ;  $E_p = 90 \text{ kV cm}^{-1}$ ;  $t_{pi} = 30 \text{ min}$ ;  $t_d = 5 \text{ min}$ .  $T_f$  (°C): A, 112; B, 116.5; C, 117.5; D, 121; E, 122; F, 122.5; G, 123; H, 130

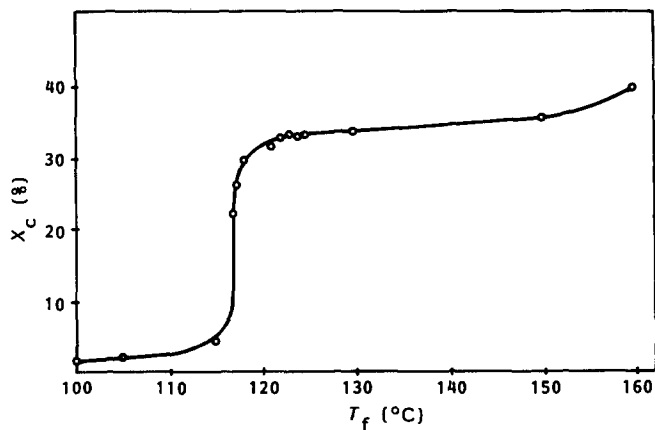


Figure 7 Percentage crystallinity  $x_c$  versus final temperature  $T_f$  reached in each TSS cycle

the results from dynamic mechanical and dielectric analyses, although such a displacement is very reduced. For crystallinities of 30%, the intensity of the relaxation falls sharply until its extinction. This is in agreement with the results given by Wissler<sup>37</sup> in polycarbonate by TSC measurements. The fall of  $I_x$  shows the simultaneous

occurrence of the  $\alpha_c$  relaxation, wider and symmetric, which will remain later as a typical relaxation of the crystalline sample. This  $\alpha_c$  relaxation becomes slightly displaced with further increase in crystallinity.

The fact that at no time is the displacement of the relaxation observed in the opposite direction, towards lower temperatures, as happens with other analytical methods<sup>24,25,27,28</sup>, could be a consequence of different ways of preparing the samples and, thus, of a different morphology. The samples used in this work are presumably composed of a large number of small spherulites, since nucleation predominates over growth, while in the samples used by other authors the reverse displacement takes place in samples whose morphology is a small number of large spherulites.

The progressive presence of a large number of small spherulites in the material implies an important reduction of the chain movements in the amorphous region; consequently, the intensity of the relaxation must diminish until extinction when the crystallinity is high. The  $\alpha_c$  relaxation resulting in the crystalline sample may have a different origin from the  $\alpha$  relaxation and it may be related

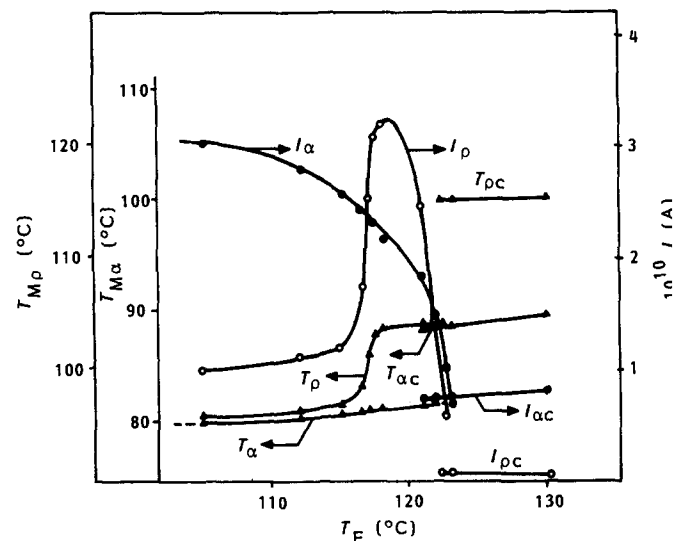


Figure 8 Evolution of  $\alpha$  and  $\rho$  relaxations versus final temperature  $T_f$  reached in each TSS cycle

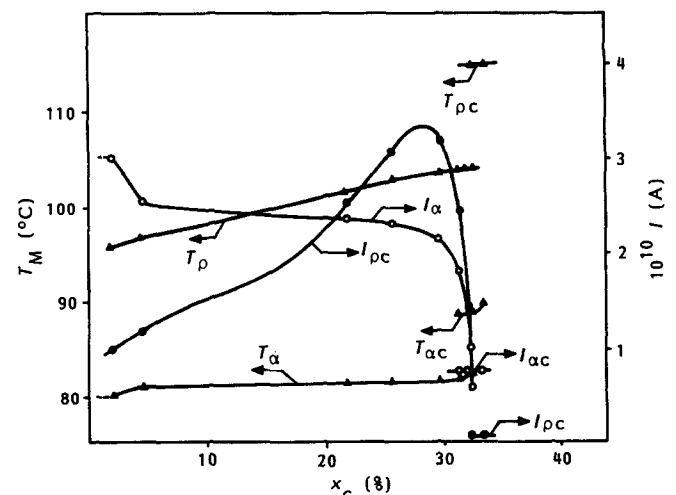
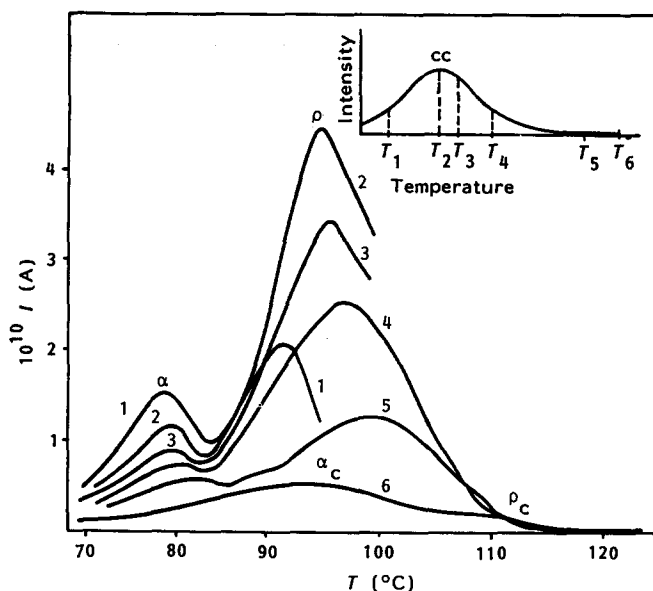


Figure 9 Evolution of  $\alpha$  and  $\rho$  relaxations versus percentage crystallinity  $x_c$



**Figure 10** Correspondence between the evolution of the  $\rho$  relaxation and the cold crystallization peak cc;  $T_p=90^\circ\text{C}$ ;  $E_p=90\text{ kV cm}^{-1}$ ;  $t_{pi}=15\text{ min}$ . Numbers on curves relate to temperatures  $T_1-T_6$  on inset

to the movements of the interlamellar amorphous region; this matter will be dealt with in detail in a future paper.

Another aspect to consider is the possibility of a double  $T_g$  ( $T_g(L)$  and  $T_g(U)$ ), according to the nomenclature used by Boyer<sup>58</sup>, so that the  $\alpha$  relaxation would be associated with  $T_g(L)$ . Boyer<sup>58</sup>, based on the  $v-T$  curves found by Hellvege<sup>59</sup>, suggests that  $T_g(L)$  is essentially independent of crystallinity, while  $T_g(U)$  is dependent, both becoming apparent for a crystallinity of 33%. He also suggests that Illers and Breuer's<sup>25</sup> measurements with a torsion pendulum at 1 Hz, where relaxation is strongly influenced by crystallinity with greater amplitude and marked displacement, could well be a joint occurrence of  $T_g(L)$  and  $T_g(U)$  since the  $T_g/T_M$  ratio in the PET seems unfavourable to their resolution by mechanical measurements. In this connection, our results show, on one hand, the small displacement of  $\alpha$  with crystallinity and the simultaneous appearance of  $\alpha$  and  $\alpha_c$  with 32% crystallinity, which is in accordance with the Boyer hypothesis. On the other hand,  $\alpha_c$  varies, although not very markedly, with crystallinity for  $x_c > 33\%$ . For  $x_c < 33\%$ ,  $\alpha_c$  does not become apparent in the discharge curves and, therefore, its evolution cannot be described. However, if  $\alpha_c$  does not proceed from  $\alpha$  as indicated, a more careful analysis could reveal an overlapped relaxation at  $\alpha$  or, else,  $\rho$  which could give rise to  $\alpha_c$  by evolution of crystallinity.

The possibility of a double transition has also been mentioned by Groeninckx *et al.*<sup>28</sup> in PET samples isothermally crystallized as a function of time. This situation is due to the fact that spherulites are not totally developed and to the existence of an inter-spherulite amorphous region. One transition could be, then, due to the amorphous phase between lamellae constituting the spherulites and the other to the inter-spherulite amorphous region.

The  $\rho$  relaxation is strongly influenced by the crystallinity, not only in its position but also in its intensity. Its behaviour can be attributed to charge

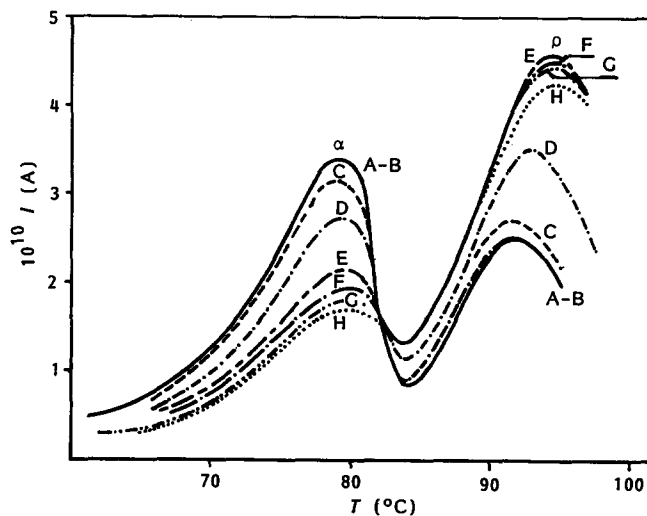
detrapping associated with progressive nucleation and further growth by chain incorporation to these nuclei. The self-accelerated crystallization process starts, in a first stage, the increase of intensity up to a maximum; the subsequent decrease will be a result of strong limitations on mobility imposed by the crystalline medium. The displacement will result from the higher thermal stability of charges and from the higher amount of energy required. This hypothesis seems possible if we consider the sharp fall of  $\alpha$  and  $\rho$  almost simultaneous until their extinction.

To establish a connection between  $\rho$  evolution and the crystallization process, different samples of amorphous polymer have undergone a cycle of trials with the purpose of forming electrets and applying to them a discharge until a final temperature  $T_i$  was reached. Such a temperature belongs to the thermal range covered by the cc cold crystallization peak. The selected temperatures and the results obtained are shown in Figure 10.

In each discharge a  $\rho$  evolution is perceptible parallel to that followed by the cc peak, so that the ascending branch of cc fits in with the increase of  $\rho$  intensity, giving a maximum at  $T_2$ , which corresponds to the maximum of the cc peak. The severe fall of  $\rho$  accompanies the decrease in cc until  $T_5$ , where the four relaxations already indicated ( $\alpha$ ,  $\rho$ ,  $\alpha_c$  and  $\rho_c$ ) appear simultaneously. At  $T_6$ , only  $\alpha_c$  and  $\rho_c$  appear in the spectrum. Therefore, everything seems to indicate that  $\rho$  manifests the changes in the material during non-isothermal crystallization.

To go further into these aspects, the behaviour of  $\rho$  has been studied during annealing at temperatures low enough to ensure that nucleation is the dominant process and growth null or most limited. Annealing was done at  $T_a=85^\circ\text{C}$  for times between 1 and 208 h. Samples were polarized at the same temperature under the conditions indicated in Figure 11. Figure 12 shows the evolution of  $I_\alpha$  and  $I_\rho$  with an annealing time  $t_a$ .

The  $\alpha$  and  $\rho$  relaxations do not change significantly for  $t_a < 30$  h. After this time, a gradual fall of  $I_\alpha$  is initiated with no significant changes in its position while  $I_\rho$  grows, the maximum being displaced to higher temperatures. For  $t_a = 140$  h the maximum value of  $I_\rho$  is reached and the



**Figure 11** TSDC curves of amorphous PET samples annealed at  $T_a=85^\circ\text{C}$  for different times  $t_a$ ;  $T_p=85^\circ\text{C}$ ;  $E_p=90\text{ kV cm}^{-1}$ ;  $t_{pi}=15\text{ min}$ .  $t_a$  (h): A, 20; B, 30; C, 40; D, 112; E, 136; F, 160; G, 184; H, 208

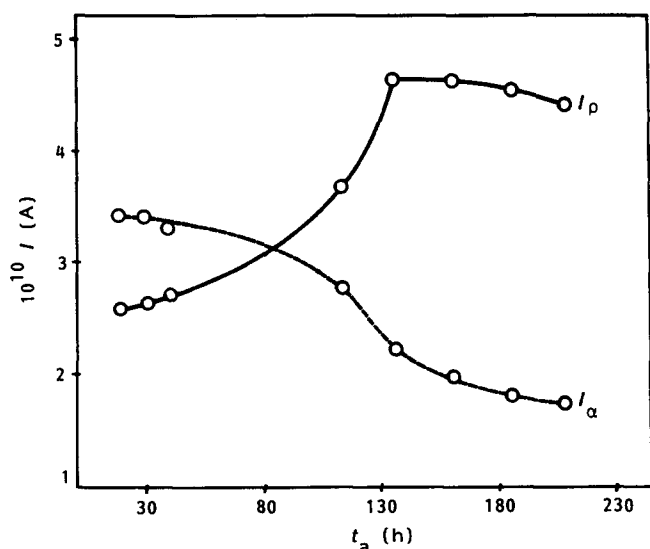


Figure 12 Evolution of  $\alpha$  and  $\rho$  relaxations versus annealing time  $t_a$  for  $T_a = 85^\circ\text{C}$

intensity begins to fall mildly without important modifications in its position, while  $I_\alpha$  falls a little and tends to stabilization.

The parallelism found in the results is marked in these experiments and the TSS experiments, although in this case the relaxations  $\alpha$  and  $\rho$  do not disappear and the simultaneity of the four relaxations does not take place, as it did with the TSS method. Because of the low crystallinity achieved, the experiments suggest that  $\alpha_c$  and  $\rho_c$  become visible with higher crystallinities, the behaviour of relaxations depending on the type of crystallization.

The fact that nucleation is the only possible process at low temperatures of annealing facilitates the association with this process of the changes observed in both relaxations. After a period with no noticeable changes, the increase of the number of nuclei with time gives rise to a fall of  $I_\alpha$  and to the displacement of  $T_\alpha$  for the restrictions imposed. The fact that this nuclei increase is limited makes  $I_\alpha$  tend to stabilization for high annealing times and, since growth is most unlikely, the displacement of  $T_\alpha$  will not be important. The sharp fall of  $I_\alpha$  in the curves resulting from the application of the TSS method would be consequent on the strong restrictions imposed by the crystallites during their growth. On the other hand, the fact that  $I_\rho$  passes by a maximum in its evolution could result from the limitation in the detrapped charge due to the limitation in the nuclei formation.

Since, during non-isothermal crystallization, nucleation and growth may occur together, the behaviour of  $\alpha$  and  $\rho$  relaxations (Figures 8, 9 and 10) shows three zones in relation to crystallinity:

In the first zone ( $x_c < 3\%$ ), with temperature  $\leq 100^\circ\text{C}$ , the insensitivity of the  $\alpha$  relaxation suggests that the restrictions are almost null because of the small number of nuclei, although their formation becomes more apparent by the growth of  $\rho$  resulting from the associated charge detrapping.

In the second zone ( $3 \leq x_c \leq 30\%$ ), with heating up to  $\approx 121^\circ\text{C}$  (up to the maximum of the cc peak), there is a strong increase in the number of nuclei, with a likely beginning of growth, which is perceptible because of the increase of restrictions on the amorphous region. This, in

turn, originates the fall of  $I_\alpha$  and the displacement of  $T_\alpha$ , while the liberation of charge becomes more marked by the effect of the process, which leads to the increase of  $I_\rho$  up to its maximum.

Finally, in the third zone ( $x_c > 30\%$ ), which corresponds to the descending branch of the cc peak, nucleation is possibly less and less effective. The growth of the nuclei formed causes the restrictions, so important in the amorphous region, that provoke the sharp fall of  $I_\alpha$  to its extinction, as well as a more marked displacement of  $T_\alpha$ . On the other hand, the mobility of the chains for its incorporation will be less, and this will give rise to a fall in  $I_\rho$ . In the last stage of this crystallization, in which growth is dominant,  $\alpha_c$  and  $\rho_c$  are formed, at first being overlapped with  $\rho$  relaxation, and at the end being the only relaxations of crystalline PET.

#### ACKNOWLEDGEMENT

This work is a part of Research Projects no. 0743/81 and no. 935/85 supported by the Comisión Asesora de Investigación Científica y Técnica (CAICYT), Spain.

#### REFERENCES

- 1 Van Turnhout, J. 'Thermally Stimulated Discharge of Polymer Electrets', Elsevier, Amsterdam, 1975
- 2 Vanderschueren, J. and Gasiot, J. 'Thermally stimulated relaxation in solids', 'Topics in Applied Physics', Vol. 37 (Ed. P. Braünlich), Springer-Verlag, Berlin, 1979
- 3 Van Turnhout, J. 'Electrets', 'Topics in Applied Physics', Vol. 33 (Ed. G. M. Sessler), Springer-Verlag, Berlin, 1980
- 4 Belana, J. Doctoral Thesis, University of Barcelona, Spain, 1978
- 5 Creswell, A. R. and Perlman, M. M. *J. Appl. Phys.* 1970, **41**, 2363
- 6 Miyairi, K. and Ieda, M. 'Charge Storage, Charge Transport and Electrostatics with their Applications' (Ed. Y. Wada, M. M. Perlman and H. Kokado), Elsevier, Amsterdam, 1979, p. 327
- 7 Lilly, A. C., Stewart, L. L. and Henderson, R. M. *J. Appl. Phys.* 1970, **41**, 2001
- 8 Sacher, E. *J. Macromol. Sci. Phys.* 1970, **B4**, 449
- 9 Sacher, E. *J. Macromol. Sci. Phys.* 1972, **B6**, 151
- 10 Sacher, E. *J. Macromol. Sci. Phys.* 1972, **B6**, 365
- 11 Sacher, E. *J. Macromol. Sci. Phys.* 1972, **B6**, 377
- 12 Sacher, E. *J. Macromol. Sci. Phys.* 1981, **B19**, 131
- 13 Asano, Y. and Suzuki, T. *Jap. J. Appl. Phys.* 1972, **11**, 1139
- 14 Asano, Y. and Suzuki, T. *J. Appl. Phys.* 1973, **44**, 1378
- 15 Hino, T. *Jap. J. Appl. Phys.* 1973, **12**, 611
- 16 Hino, T. *J. Appl. Phys.* 1975, **46**, 1956
- 17 Miyairi, K. and Yanagisawa, I. *Jap. J. Appl. Phys.* 1978, **17**, 593
- 18 Kojima, K., Maeda, A., Takai, Y. and Ieda, M. *Jap. J. Appl. Phys.* 1978, **17**, 1735
- 19 Belana, J., Colomer, P., Montserrat, S. and Pujal, M. *Anal. Fis. B* 1982, **78**, 8
- 20 Belana, J., Colomer, P., Montserrat, S. and Pujal, M. *Anal. Fis. B* 1982, **78**, 142
- 21 Belana, J., Colomer, P., Pujal, M. and Montserrat, S. *J. Macromol. Sci. Phys.* 1984-85, **B23**, 467
- 22 Schneider, W. A. and Wendorff, J. H. *Colloid Polymer Sci.* 1984, **262**, 761
- 23 McCrum, N. G., Read, B. E. and Williams, G. 'Anelastic and Dielectric Effects in Polymeric Solids', Wiley, New York, 1967
- 24 Murayama, T. 'Dynamic Mechanical Analysis of Polymer Materials', Elsevier, Amsterdam, 1978
- 25 Illers, K. H. and Breuer, H. *J. Colloid Sci.* 1963, **18**, 1
- 26 Takayanagi, M., Yoshino, M. and Minami, S. *J. Polym. Sci.* 1962, **61**, 173
- 27 Dumbleton, J. H. and Murayama, T. *Kolloid Z. Z. Polymer* 1967, **220**, 41
- 28 Groeninckx, G., Berghmans, H. and Smets, G. *J. Polym. Sci. Polym. Phys. Edn* 1976, **14**, 591
- 29 Saito, S. *Kolloid Z. Z. Polymer* 1963, **189**, 116
- 30 Reddish, W. *Trans. Faraday Soc.* 1950, **46**, 459
- 31 Hedvig, P. 'Dielectric Spectroscopy of Polymers', Adam Hilger, Bristol, 1977

- 32 Coburn, J. C. and Boyd, R. H. *Macromolecules* 1986, **19**, 2238  
33 Boyd, R. H. *Polymer* 1985, **26**, 323, 1123  
34 Vanderschueren, J. L'effet thermoélectret et les phénomènes de relaxation dans les polymères à l'état solide, Thesis Doctoral, Université de Liege, 1974  
35 Yeh, G. S. Y. and Geil, P. H. *J. Macromol. Sci. Phys.* 1967, **B1**, 235, 251  
36 Klement, J. J. and Geil, P. H. *J. Macromol. Sci. Phys.* 1971, **B5**, 505, 535  
37 Stuart, H. A. *Angew. Chem.* 1967, **6**, 844  
38 Allen, G. and Petrie, S. E. B. (Eds) 'Physical Structure of the Amorphous State', Marcel Dekker, New York, 1976  
39 Illers, K. H. and Breuer, H. *J. Colloid Sci.* 1963, **18**, 1  
40 Lawton, E. L. and Cates, D. M. 'Analytical Calorimetry', Vol. 1 (Eds R. S. Porter and J. F. Johnson), Plenum Press, New York, 1969, p. 89  
41 Kilian, H. G., Halboth, H. and Jenckel, E. *Kolloid Z. Z. Polymer* 1960, **172**, 166  
42 Mayhan, H. G., James, W. J. and Bosch, W. J. *Appl. Polym. Sci.* 1965, **9**, 3617  
43 Schönherr, F. *Faserforsch. Textiltech.* 1970, **21**, 246  
44 Danz, R., Deshant, J. and Ruscher, G. *Faserforsch. Textiltech.* 1970, **21**, 251  
45 Illers, K. H. *Kolloid Z. Z. Polymer* 1971, **245**, 393  
46 Deblase, F. J., McKelvy, M. L., Lewin, M., Bulkin, B. J. *J. Polym. Sci., Polym. Lett. Edn* 1983, **23**, 109  
47 Wunderlich, B. *J. Chem. Phys.* 1958, **29**, 1395  
48 Dole, M. *Kolloid Z. Z. Polymer* 1959, **165**, 40  
49 Ke, B. J. *Appl. Polym. Sci.* 1962, **6**, 624  
50 Busico, V., Corradini, P., Riva, F., Seves, A. and Vicini, L. *Makromol. Chem. Rapid Comm.* 1980, **1**, 423  
51 Turnbull, D. and Cohen, M. H. 'Modern Aspects of the Vitreous States' (Ed. J. D. Mackenzie), Butterworth, London, 1960, p. 38-62  
52 Fielding-Russell, G. S. and Pillai, P. S. *Die Makromol. Chem.* 1970, **135**, 263  
53 Matusita, K., Maki, T. and Tashiro, M. *Phys. Chem. Glasses* 1974, **15**, 106  
54 Matusita, K. and Tashiro, M. *Phys. Chem. Glasses* 1973, **14**, 77  
55 Matusita, K. and Sakka, S. *Bull. Inst. Chem. Res. (Kyoto Univ.)* 1981, **59**, 159  
56 Matusita, K., Komatsu, T. and Yokota, R. *J. Mater. Sci.* 1984, **19**, 291  
57 Wissler, G. E. and Crist, B. J. *Polym. Sci., Polym. Phys. Edn* 1980, **18**, 1257  
58 Boyer, R. F. *J. Polym. Sci. Symp.* 1975, no. 50, 189  
59 Hellvege, K. H., Hennig, Y. and Knappe, W. *Kolloid Z. Z. Polymer* 1962, **186**, 29