On the high temperature TSDC peak in poly(ε-caprolactone)

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Abstract

The high temperature dielectric relaxation process, observed above the glass transition temperature in poly(ε-caprolactone) is studied by Thermally Stimulated Depolarization Currents experiments. The characterization is made by using the windowing polarization technique, decomposing the complex high temperature relaxation into Debye-like peaks. The profile of each peak is then analyzed by using a general kinetic order model, and the origin of the complex relaxation is discussed through the analysis of the parameters obtained from the best fit to the model. The distribution of the trap depths is obtained and their activation energies is found to vary from 0.8 to 1.2 eV. The space charge accumulation is mainly responsible for this relaxation mode in poly(ε-caprolactone). © 2000 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Thermally stimulated depolarization current (TSDC) techniques have been extensively used to study the dielectric properties of polymeric materials, due to the relative simplicity of the experimental setup and the high resolution of the method. The low equivalent frequency associated with these techniques is clearly an advantage over the conventional dielectric spectroscopy in order to study secondary β relaxations as well as the α relaxation associated to the glass–rubber transition in glass forming liquids with molecular groups that present a dipolar moment. These dipolar orientations have different relaxation times and the corresponding current peaks occur at different temperatures in the TSDC spectrum [1,2]. The advantage of TSDC experiments in addition to its high resolving power associated to its very low equivalent frequency, $f_{eq} \approx 10^{-3}$ Hz, resides in the possibility to isolate a single relaxation peak by a proper choice of the polarization temperature T_p, the polarization time, t_p, the external applied electric field, E_p, and the temperature sequence used in the experiment. As the recorded complex (or global) peaks are always too broad to be interpreted as originated by a single relaxation mode, many attempts have been done to extract the relaxation times distribution from the experimental profiles. The ther-

mal sampling (TS) also called the windowing polarization, WP, technique [3–7] consists in removing the electric field at some point, T_f, during the rapid cooling of the sample after the polarization isothermal step. The width of the polarization window is determined by the temperature interval, $\Delta T = T_p - T_f$, where the sample is polarized and usually varies from 0 to 10 K. The polarization window is then shifted in order to sweep the temperature range where the complex current peak occurs. The resulting curves are supposed to be elementary processes, each of them characterized by a single relaxation time. This experimental decomposition of the complex TSDC peak leads to the determination of one relaxation time per curve by using the conventional fractional integration to measure the relaxation times from the rise of the current peak. Other approaches have been proposed to determine the relaxation times distribution from the complex TSDC peak. One can assume a profile for this distribution, e.g. a Gaussian function for the reorientation energies, and adjust the experimental complex curve to the new expression of the depolarization current. The best parameters that characterize the assumed distribution are then determined. This method has been successfully applied to the case of the observed broadening in inorganic single crystals such as the fluorites [8]. In the case of polymeric materials the variation of the pre-exponential relaxation time factor has also to be considered due to the variations in shape of the potential barriers that are surrounding the reorienting dipoles of a same kind. A new computer method has been

proposed to access the distribution of relaxation times by decomposing the complex profile in true Debye modes, either by using a conventional non-linear least squares algorithm [9], or a simulated annealing Monte Carlo procedure [10].

In addition to the above-mentioned dipolar reorientations, there are other physical mechanisms responsible for dielectric relaxations generally observed at temperatures above the glass transition, $T > T_g$, and labeled ρ peaks. Such mechanisms commonly known as free charge relaxations, to distinguish them from the bound dipoles reorientation, are caused by a variety of microscopic processes. One can mention Maxwell–Wagner–Sillars (MWS) processes (accumulation of charges in the interfaces of a multiphase material, e.g. a semicrystalline homopolymer or a segregated block copolymer), or ions migration and subsequent trapping, electrons or holes drift and trapping and charge injection from the electrodes [11,12]. Additionally, a polymeric material may exhibit a dipolar electric moment with perpendicular and parallel components to the chain contour. In such systems, the perpendicular dipolar moment is responsible for the local and segmental relaxations. The parallel dipolar moment is active for the slowest modes occurring at temperatures above the glass transition, and it is usually labeled as the normal mode relaxation. These modes are related with the longest relaxation times; the cumulative dipole moment for any chain conformation is proportional to the end-to-end distance and its relaxation depends strongly on the chain length. For molecular weights lower than a certain critical value (M_c), the whole chain mobility has been described by Rouse and others by using a normal-coordinate analysis of an ideally Gaussian chain. In the dielectric relaxation spectra, the parallel dipole relaxation is dominated by the first normal mode, which corresponds to the variation of the end-to-end distance. For molecular weights higher than M_c, the chain relaxation is extremely retarded by molecular entanglements and the topological constraints hinder the ideal Rouse behavior. In this molecular weight range, reptation behavior starts to better describe the whole chain mobility.

Recently, several studies on these high temperature relaxations have been published on heterogeneous materials by dielectrical characterization, using predictions of the MWS approach and related models [13–15]. In order to elucidate the physical mechanisms responsible for a high temperature TSDC peak, it is useful to study the behavior of the peak as a function of the polarization parameters such as the polarization temperature and polarization field.

Due to the structure of the poly(ϵ-caprolactone) [16], the total electric dipole moment in such a material has both components (type-A2 polymer) and it is expected that the dipolar moment parallel to the main chain produces a normal mode relaxation which might be detected dielectrically above the glass transition temperature. Moreover, these materials are semi-crystalline and present a heterogeneous structure, where accumulation of free charges at the interfaces should occur and may originate relaxation modes at sufficiently high temperatures. Recently, Mudarra et al. [3–5] have applied a general kinetic model to the study of the space charge relaxation in PMMA. They performed WP experiments on the ρ peak and concluded to a distribution of trapping levels. In this model, the polarization as a function of time does not present an exponential decay and it is written as:

$$\frac{\mathrm{d}P(t)}{\mathrm{d}t} = -\frac{P_0}{\tau}\left(\frac{P(t)}{P_0}\right)^{\beta} \tag{1}$$

where P_0 is the initial frozen-in polarization, $P(t)$ is the polarization at time t, τ is the characteristic time and β represents the kinetic order. The exponent β may take values of 1 or 2, the first corresponding to a slow retrapping case [17] and the second one, to a strong retrapping probability [18]. However, in real systems these models do not describe the complex phenomena observed, and a general kinetic model is used in order to consider all the possible phenomena with intermediate values allowed for β between 1 and 2. In order to use the general kinetic model to interpret the TSDC spectra, Eq. (1) has to be written in the temperature domain. The linear relationship between time and temperature imposed experimentally by a constant heating rate b_h, allows us to write the current density $J(T)$ as:

$$J(T) = -b_h\frac{\mathrm{d}P(T)}{\mathrm{d}T} = +\frac{P_0}{\tau(T)}\left(\frac{P(T)}{P_0}\right)^{\beta} \tag{2}$$

which gives after integration:

$$J(T) = \frac{P_0}{\tau(T)}\left[1 + \frac{\beta-1}{b_h}\int_{T_0}^{T}\frac{\mathrm{d}T'}{\tau(T')}\right]^{\frac{\beta}{1-\beta}} \tag{3}$$

However, it is less time consuming to solve numerically the differential equation for $P(T)$ (Eq. (2)) to calculate the current density. The temperature dependence of the relaxation time of each elementary curve is assumed to follow an Arrhenius behavior:

$$\tau(T) = \tau_0\exp\left(\frac{E_a}{kT}\right) \tag{4}$$

here τ_0 is the pre-exponential factor and E_a the activation energy for the reorientation process.

In this article, we analyze quantitatively the elementary TSDC peaks obtained from windowing polarization by using a general kinetic order model, in order to study the characteristics of the processes involved in the high temperature relaxation in poly(ϵ-caprolactone).

2. Experimental

The poly(ϵ-caprolactone) samples, PCL, are compression molded films from pellets obtained from Aldrich Chemicals. Its weight-average molecular mass is $M_w = 155,000$ g/mol measured by Gel Permeation Chromatography and the
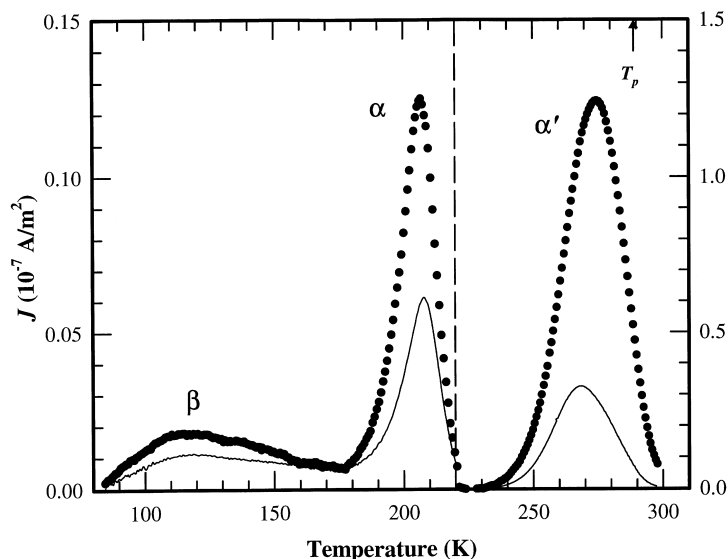
Fig. 1. TSDC complex spectrum of poly(ϵ-caprolactone). ($\bullet$) stainless steel electrodes; (—) sapphire disks intercalated. $T_p = 289$ K, $E_P = 836$ kV/m.

polydispersity is 1.56. The crystallinity of the sample used here is 60%, measured by DSC from the melting peak at a heating rate of 10°C/min. A value of 65% is obtained from the WAXS experiment for the crystallinity degree at room temperature. The sample for TSDC is disk shaped with a diameter of 20 mm and a thickness of 359 μm. The melting and crystallization peaks recorded by differential scanning calorimetry have maxima at 325 and 303 K, respectively, and these peaks are quite narrow in temperature. There is also some evidence of a recrystallization process slightly below room temperature.

The experimental setup designed and built in our laboratory, consists of a high vacuum cell and an automatic measuring system [19]. The sample is located between two metallic disks used as the plates of a capacitor. The cell is previously evacuated (2×10^{-6} Torr) for a prudential time (typically 24 h) before starting the TSDC measurements, in order to eliminate any sample contamination or humidity in the cell atmosphere. During the polarization and cooling steps, the cell is filled with nitrogen gas at a pressure of 600 Torr, and for the depolarization step, dry helium at a pressure of 100 Torr is used as an interchange gas. An electric polarization field E_p is applied to the sample at a constant temperature T_p during a time t_p, typically 3 min, long enough to reach a new equilibrium state of ordered electric dipoles partially aligned with the applied field at the chosen polarization temperature, provided that the dipoles under study are sufficiently mobile at T_p. At this point there are two possibilities: to maintain the applied field during the cooling step down to T_0, or to turn off the electric field before starting the cooling of the sample. The first procedure guarantees the polarization of all the thermally activated processes occurring between T_p and the final cooling temperature T_0 (in our case liquid nitrogen temperature). The second one is a particular case of the windowing polarization technique or thermal sampling, in which the

width of the temperature window is null. This 0 K window is used here to ensure the selection of the narrowest part of the complex curve. Once the final temperature T_0 is reached, usually liquid nitrogen temperature, a Keithley 642 electrometer is connected in series to the sample in order to measure the depolarization current induced by the loss of the frozen-in polarization which occurs as temperature is increased. The sample is then heated at a constant rate, $b_h = 0.07$ K/s for all the spectra measured here. The analog output of the electrometer, as well as temperature and time, are collected with a voltmeter-scanner and stored in a computer file for subsequent analysis. All the spectra shown are polarized with an electric field $E_p = 836$ kV/m, a polarization time $t_p = 3$ min, and a cooling rate $b_c = 3.3$ K/min is used after the polarization stage in WP experiments. This slow cooling rate instead of the usual quenching, is an additional precaution to guarantee the activation of the processes that only relax within a narrow energy window. The highest temperature used in this series of experiments is 300 K in order to minimize the effect of the changes in morphology due to fusion or crystallization.

3. Results

In Fig. 1 the TSDC spectrum between 80 and 300 K is represented with filled symbols for the bare sample in contact with the metallic electrodes. The complex spectrum shows a broad low temperature peak between 80 and 170 K, the secondary β relaxation which is associated to localized motions of the polar groups. The α peak related with the glass transition temperature appears at 207 K, and at higher temperature an intense peak labeled α' is present at 275 K. The secondary β relaxation consists of a broad peak with at least two complex relaxation processes, related with short-range motions of the polar groups. The α relaxation which is
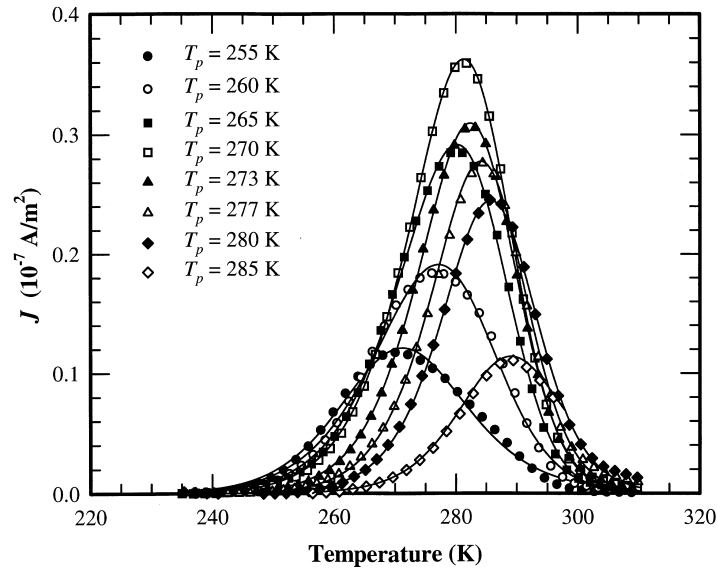
Fig. 2. Windowing polarization of the α' peak of poly(ε-caprolactone) at different polarization temperatures: (symbols) experimental data; (—) fitting results. $\Delta T = 0$ K.

the dielectric manifestation of the molecular motions at the glass transition, is associated with the segmental cooperative motions that involve important segments of the main chain. The high temperature α' peak might be the result of the relaxation of free charges accumulation, dipolar relaxations due to the existence of a parallel dipolar moment or a complicated mixture of both mechanisms. The variation of the total frozen-in polarization (area under the $J(T)$ α' peak divided by the heating rate) as a function of the polarizing field is linear up to 2.2 MV/m and for higher voltages almost saturates with a further decrease from this saturation value of about 10% for $E_p = 5$ MV/m. One criterium to decide upon the dipolar character of a peak is its intensity linear variation with the applied field. The non-linearity seems to characterize relaxation of trapped charges at the crystal/amorphous interfaces in MWS modes [12]. Sauer et al. [7] report for the ρ peak in PEKK, a break in the linearity of the intensity vs. E_p below 1 MV/m. For PCL, the onset of this observed non-linearity occurs at higher fields. The intensity, position and profile of the β and α peaks are reproducible when the sample is replaced, whereas the α' peak intensity varies with the nature of the electrodes and the quality of the contacts. When blocking electrodes are used, i.e. sapphire disks ($\phi = 20$ mm, 127 μm thick) intercalated between the sample and the metallic electrodes, some changes are observed on Fig.1 (continuous line). If the ratio of the areas of the α' peak to the α peak, $A_{\alpha'}/A_\alpha$, are compared, there is a decrease by a factor of 0.52 resulting from the presence of the blocking electrodes. This decrease suggests that there is some charge injection from the metallic electrodes, which is prevented in the second trace taken with sapphire disks. The remaining trapped charge is due to internal polarization effects. Also the ratio $A_{\alpha'}/A_\alpha$ decreases with the metal used for the electrodes around the bare sample on

going from aluminum to stainless steel (83%) and from stainless steel to copper (56%). The changes are similar to those obtained in PMMA [12]. Traces of humidity increase the intensity (2%) of this high temperature peak slightly and shift it by an amount of −3 K.

In order to study this relaxation, windowing polarization experiments on this peak are made and the results are presented on Fig. 2 as symbols. The idea of the WP experiments is to discriminate the energies involved in a quasi-Debye process as compared to the complex spectrum, which is related to a wide polarization window, i.e. a wide range of activation energies. The polarization temperature is varied between 255 and 285 K, with a window $\Delta T = 0$ K. Each peak resulting from this decomposition is analyzed by fitting the experimental results to Eqs. (2) and (4) by using a Levenberg–Marquardt minimization algorithm with P_0, τ_0, E_a and β as adjustable parameters. The continuous lines in Fig. 2 correspond to these fitting results. The model fits well the experimental curves for the six most intense peaks; for the less intense peaks located on the low and high temperature tails, the agreement is worse and is quantified by a Sum of Square Residuals (SSR) larger than that of the most intense peak. This cannot be attributed to noisy signals as the recorded curves are remarkably noise-free. The deviation of the extreme curves can be due to the effect of overlapping processes, which contradicts the assumption of a single relaxation time involved in each elementary curve. This is often the case in WP experiments where the consideration of the high temperature tail of the peaks is often omitted in the analysis [20]. The advantage of the WP technique is that the charge released in one of these elementary relaxations, when they are not overlapped by neighboring modes, is associated to the charge trapped within the narrowest temperature range available ($\Delta T = 0$ K), and
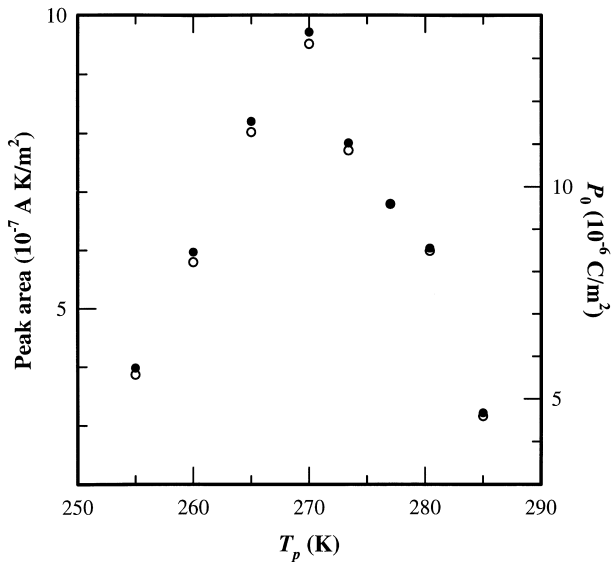
Fig. 3. WP experiments on poly(ϵ-caprolactone). Variation of: ($\bigcirc$) the area under each experimental elementary peak (left vertical axis); ($\bullet$) the initial polarization, P_0, resulting from the curve fitting (right vertical axis) as a function of the polarization temperature.

the parameters found in each curve fit to the general kinetic order model (P_0, τ_0, β and E_a) are thus related to a narrow range of trap depths.

First, the variation of the area of each elementary peak with the polarization temperature is plotted in Fig. 3, open circles, left vertical scale. The area shows a maximum value for $T_p = 270$ K, corresponding to the peak located at the same temperature as the maximum current of the complex peak. This result indicates that the maximum of the frozen-in global polarization occurs at the same temperature as the initial trapped charge for the elementary relaxation at this
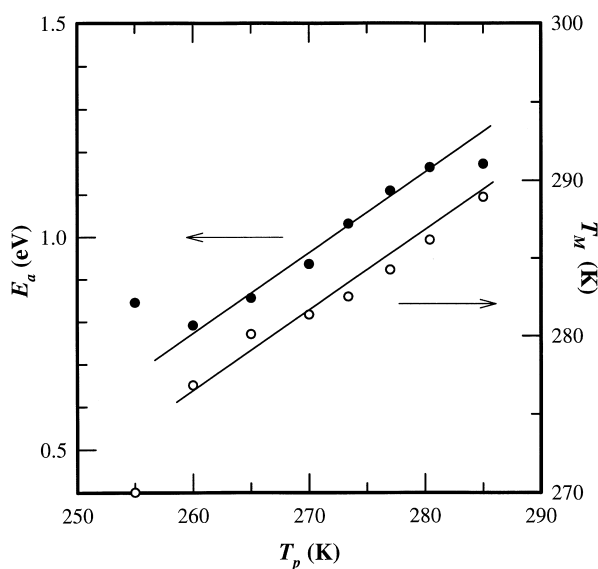

Fig. 4. WP experiments on poly(ϵ-caprolactone): Variation of the activation energy E_a ($\bullet$) and temperature of the maximum ($\bigcirc$), as a function of the polarization temperature. The lines are drawn as guides to the eye.

same temperature. The resulting fitted P_0 values follow closely this same behavior and are reported on Fig. 3 by filled symbols, right vertical scale. An excellent agreement between P_0, resulting from the fitting, and the value measured from the area under the experimental curve, $J(T)$, is noted on the results plotted in Fig. 3. These curves show the evolution of the charge trapping process as a function of temperature. The low value found for the peak corresponding to the higher polarization temperature could be due to a decrease in the amount of the amorphous regions in the material due to the recrystallization process which may occur during the polarization step at 285 K.

The almost linear variation of the temperature of the maximum for each peak (empty circles) as a function of T_p is shown in Fig. 4. Again the lowest temperature elementary curve does not follow the general trend of the curves taken at higher polarization temperatures.

The variation of the activation energies resulting from the fit of each peak as a function of the polarization temperature is also shown in Fig. 4 (filled circles). The energy is found to be an increasing function (if the lowest curve and highest curve are not included the variation is linear) of the polarization temperature and ranges from 0.8 to 1.2 eV. The somewhat high values obtained here result from the assumption of Arrhenius dependence for the characteristic time for relaxation modes at $T > T_g$. However, the energy values found here are less than half of those found by Mudarra and Belana [3] for the space charge relaxation in PMMA. This is clearly due to the difference in the temperature ranges where these relaxations occur. The temperature of the peak is 280 K for PCL vs. 393 K for PMMA. This activation energy variation allows us to deduce the profile of the reorientation energies distribution in the material as each elementary curve recorded with a 0 K width window selects a narrow interval for the energy of trapping levels to be detected at each temperature. The charge carriers that may be trapped in deeper levels are not activated as the corresponding relaxation times are too large at the polarization temperatures; additionally, as the field is switched off after a time t_p at the polarization temperature and the temperature is lowered at a slow rate, the carriers trapped in shallow levels are freed and the charge released in the cooling step is not present in the record of the corresponding elementary peak. Thus, the charge trapped in each of the elementary peaks corresponding to a thermal sampling should represent a group of traps with a narrow energy range. The profile of the distribution of the trapping levels energy may then be approximated by plotting P_0 (or the area under each curve) as a function of E_a as shown in Fig. 5. It is readily seen that the number of trapping levels is maximum for 0.94 eV and that the distribution of these energy levels is asymmetric with a longer tail towards high energies. The most abundant trapping levels correspond to depths 0.94 eV which is much lower than the 2.35 eV value found by Mudarra and Belana [3] for the space charge process in PMMA. At higher energies the number of traps decreases
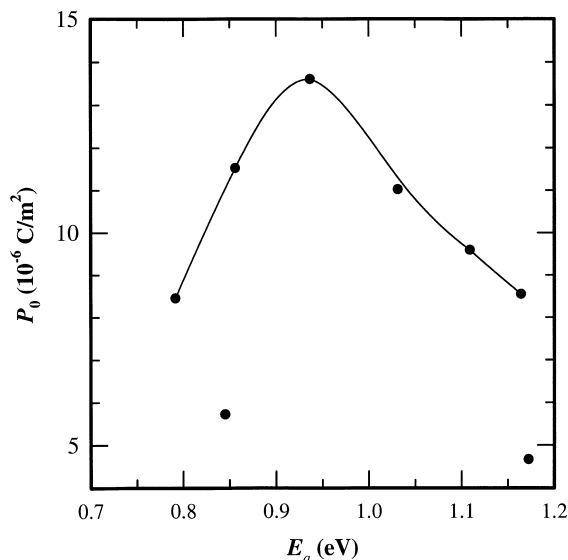
Fig. 5. WP experiments on poly(ε-caprolactone): Variation of the initial polarization (obtained from the fitting) as a function of the activation energy. The line is drawn as a guide to the eye.

Fig. 7. WP experiments on poly(ε-caprolactone): Variation of the pre-exponential time, τ_0, as a function of the activation energy. The line corresponds to the compensation law with $\tau_c = 11.9$ s, $T_c = 297.6$ K.

sharply and for trapping depths higher than 1.2 eV reaches the third of the maximum value. These results also show that for a polarization temperature of 270 K the charge carriers are trapped with the maximum efficiency.

Another parameter to be considered is the kinetic order β in order to decide if the charge trapping mechanisms that lead to the formation of space charges in the semi-crystalline material follow the model as its value may give an indication of the trapping processes that occur within the material [17,18]. Values near 1 or 2 show the predominance of a weak or a strong retrapping probability, respectively. The variation of this parameter obtained from the fittings shown in Fig. 2 is plotted on Fig. 6. It is observed that if the
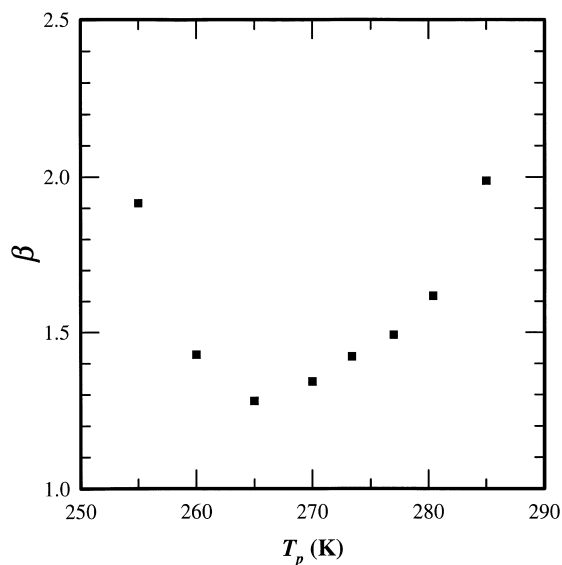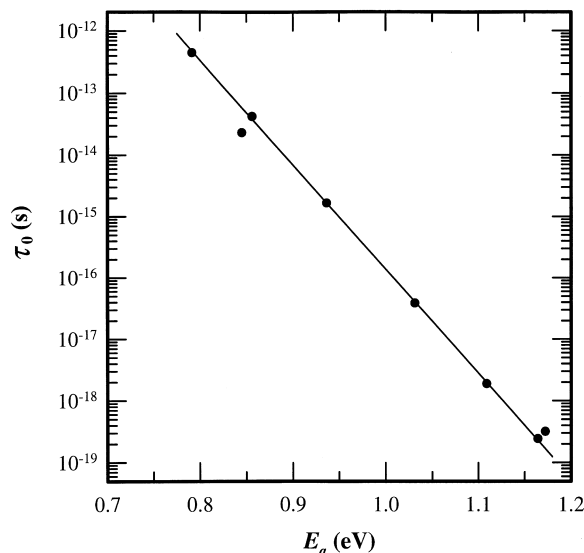

Fig. 6. WP experiments on poly(ε-caprolactone): Variation of the kinetic order β as a function of the polarization temperature.

two extreme points are omitted β has a value of 1.4 ± 0.2, which is comparable to that of the ρ peak in other polymers. The last parameter obtained from the best fit of the data to the model is the pre-exponential factor, τ_0, which also varies widely for the elementary curves recorded here. A semilog plot of τ_0 vs E_a, Fig. 7, shows a linear variation and the values found for τ_0 range between 10^{-12} and 10^{-19} s which, as usual in the WP results, are real low but not as small as the values reported for PMMA [3]. This linear dependence is interpreted as the existence of a compensation law [20] (compensation time $\tau_c = 11.9$ s and a compensation temperature, $T_c = 297.6$ K), which has been attributed to the manifestation of a cooperative character when found in the WP in the α relaxation region. The common origin for the processes involved in the compensation law is thus shown here. If this is accepted, the importance of the cooperative molecular motions which happen at $T > T_g$ in the trapping processes of carriers which originate the space charge accumulation is demonstrated here. However, it is to be noted that the compensation law has been associated with experimental errors propagation and it could be a statistical effect due to the strong correlation among the uncertainties of the activation energies and pre-exponential times [21].

In order to compare our results with previous determinations of the relaxation parameters of the high temperature peak involved in the general kinetic order model, one has to refer to the determinations in PMMA space charge relaxation [3–5] as well as in polymers with a semicrystalline structure such as poly(ethylene-2,6-naphthalene dicarboxalate), PEN [22]. In both cases, as expected, the kinetic order was found to be approximately constant, $\beta = 1.25$ with a spread of 9% for temperatures going from 383 to 403 K in PMMA and $\beta = 1.3 \pm 0.2$ for temperatures
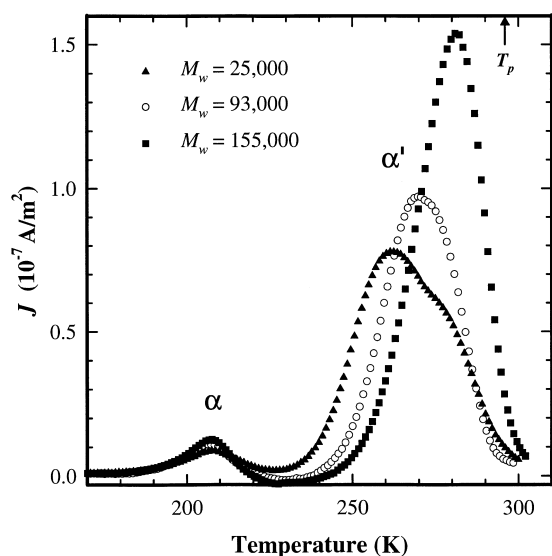
Fig. 8. High temperature TSDC spectra of poly(ε-caprolactone) with different molecular weights with the same polarization conditions.

going from 418 to 431 K in PEN. In our case if we also use a temperature interval of 20 K for the analysis, i.e. we exclude the results corresponding to 255 and 285 K, the estimated value is 1.4 ± 0.2. The exclusion of these extreme points seems justified as in reviewing Figs. 3–6 it is clearly seen that the parameters extracted from these two curves do not follow the general trend of the more intense elementary peaks. Moreover, it is to be noted that the profile fittings realized here are not the usual procedure to adjust experimental curves in order to obtain the relaxation parameters. Usually one uses the rise of the current to temperatures near the maximum of the elementary peak and for estimating the remaining polarization at each temperature, an approximate form of the integral on the right-hand side of the peaks, not the entire experimental trace, is used [20]. Following Mudarra and Belana [3] no approximation of the experimental trace is performed and the whole profile of the elementary curve obtained after a WP experiment is analyzed here.

There are few previous studies on dielectric characterization of bulk PCL. In the pioneering work of Vanderschueren et al. [23] the homopolymer, PCL, and diblock copolymers with polystyrene in the segregated phase were studied. In this work, the high temperature peak, labeled ρ, is observed in the homopolymer, and in the block copolymers poly(ε-caprolactone-*b*-styrene). The authors attributed the ρ(relaxation observed in the TSDC complex spectrum to an ionic process of the MWS type due to the marked effect of doping and water sorption. As the peak is still present in the fully amorphous copolymer poly(styrene-*b*-ε-caprolactone), $S_{74}CL_{26}$, it is concluded that there is a pile up of charge carriers at polymer–polymer interfaces, relaxation of which causes the ρ peak rather than an accumulation of charges at the interfaces of the crystalline and amorphous regions. In our case, a careful study has been performed on the water sorption by PCL. The main changes observed on

the TSDC spectrum given by the wet material are located on the high temperature tail of the low temperature β relaxation where a new relaxation grows with the degree of humidity. The effect of water sorption is not observed on the α or α' mode beyond a 2 K shift to lower temperatures; also the intensity of these modes is not significantly affected, i.e. there is no significant plasticization effect.

Recent broad band dielectric relaxation studies of poly(ε-caprolactone) in dilute solutions [16,24,25] demonstrate the existence of a dielectric response associated with a normal mode relaxation in dilute and semi-dilute solutions, and measure the molecular weight, M_w, dependence of the relaxation time. In agreement with the Rouse–Zimm normal mode predictions, these studies show that the relaxation strength is an increasing function of M_w in dilute solutions, and the frequency of the imaginary part of the dielectric constant, ϵ'' peak, shifts to lower values indicating an increase in the relaxation time of the normal mode with M_w with the power of 1.63 ± 0.03 [25]. In bulk PCL the existence of a normal mode has not been reported to the best of our knowledge. Even though it is not possible to relate our complex α' spectra recorded in temperature domain, with the predictions valid for a pure normal mode, the comparison between samples of different molecular weight is indicative of the effect of an increasing M_w. In Fig. 8 the TSDC high temperature spectrum for three samples of PCL with different molecular weights are presented. It is clearly seen that with the same polarization conditions, the α' mode is more intense and shifts to higher temperatures as the molecular weight increases. Also its multicomponent character is observed in this same figure. Dielectric broad band spectroscopy experiments are being performed on these same materials to quantify the relaxation time variation with M_w. However, a difficulty is present in this semi-crystalline materials where the effective molecular weight of the chains which motion originates this mode is not known due to the variable length of the chains in the amorphous zones. The nominal molecular weights are much larger than the length of the amorphous segments between crystalline lamellas, which additionally must have a wide distribution. The reported variation of this α' peak can also be attributed to the change in morphology of these materials where the degree of crystallinity as determined by WAXS decreases from 79% for the lowest molecular weight to 65% for the other two samples. As the crystallinity increases the peak shifts to lower temperatures which means more shallow traps than for the high molecular weights.

4. Conclusions

The windowing polarization technique is used to study the high temperature peak of PCL. In order to analyze the experimental results the general order kinetic model is used and the entire profiles of each of the elementary peaks obtained from WP at different temperatures are fitted to

the model. The parameters extracted from these fittings are not entirely satisfactory in the whole temperature range swept here, but gives reasonable results in a 20 K interval which is the same or larger than the range previously used on PMMA and PEN. In this way, the profile of the distribution of depth traps present in the sample is obtained, together with the variation of the kinetic order, which is intermediate between a weak and strong retrapping probability. The numerical results derived from this model seem to indicate that the observed complex peak is mainly originated by free charges release and trapping. If a mixture of charges release and dipolar disorientation is present, due to the end-to-end distance variation, as PCL belongs to the type-A2 polymers (type-A/non-type-A-alternating polymers) according to Urakawa et al. [25] classification, these results show that the major contribution has to be attributed to the space charge accumulation at the phase boundaries. The semi-crystalline character of this polymer with crystallinities ranging from 79 to 65% as the molecular weight increases also makes difficult any estimate of the molecular weight of the chains whose motions are at the origin of the normal mode, if any, and introduces another important parameter which is the variation in the morphologies of the materials which could be at the origin of the important shift in temperature as the nominal molecular weight increases. If the phenomena leading to the α' peak takes place at the interphases of the material, the changes in the morphology, e.g. the lamellar thicknesses distribution variation with the molecular weight, could explain the change in profile and the observed temperature shift of the high temperature peak.

Acknowledgements

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