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Thermally stimulated depolarization currents in PVDF-α: a dipolar interaction approach to β and γ transitions

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The analysis of the thermally stimulated depolarization current (TSDC) spectrum of the α phase of polyvinilide fluoride (PVDF-α) by means of the thermal sampling technique permits a series of elementary peaks to be obtained. The relaxation associated with γ and β transitions is usually assumed to be due to dipolar motions; however, the relaxation time of these processes when represented as a function of the temperature does not follow an Arrhenius law. The definition of a relaxation time describing the experimental relaxation process requires, in addition to the frequency factor $1/\tau_0$ and the activation energy E, a third parameter, q, which we call the interaction parameter. These considerations lead to defining a relaxation time, which accounts for the dipolar interaction during the relaxation. This relaxation time has successfully described the dipolar relaxation in other materials. The evolution of q, obtained from the elementary peaks of the TSDC spectrum of PVDF-α, leads to the assignment of three relaxation zones, which are in agreement with those reported by other authors, as being associated with the molecular motion in the different phases of PVDF-α.

1. Introduction

The thermal stimulated depolarization current (TSDC) technique was introduced twenty years ago by Bucci and Fieschi [1] for studying the dielectric properties of doped alkali halides. Hitherto, it has been successfully used for determining the dielectric properties of a great variety of materials [2]. The method is characterized by a relative experimental simplicity that however provides a high sensitivity; currents as weak as 10^{-14} A are detected with rather satisfactory signal to noise ratio for a system working in the absence of applied bias.

The TSDC spectra are strongly dependent on the material studied; thus either single peaks of well-defined characteristics or broad bands including several overlapping peaks [3] can be obtained. Among the simplest cases, doped alkali halides have been extensively studied; in these crystals the dipoles are associated with impurities or native defects, which are present in the material in rather low concentration. The plot of the depolarization current against the time fits the Debye equation. Thus the relaxation time can be obtained as a function of the temperature by establishing the relationship between the depolarization current and the remanent polarization at a given temperature. The plot of the logarithm of the relaxation time against the inverse of the temperature fits, for a Debye process, a straight line, which is the well known Arrhenius law describing the non-interacting thermally activated relaxation processes, $\tau = \tau_0 \exp(E/kT)$, where $1/\tau_0$ is a frequency factor, E is the activation energy of the process and k is the Boltzmann constant. This exponential temperature dependence of τ supports the TSDC method, in fact as the temperature increases the relaxation time becomes shorter and therefore the depolarization process is accelerated.

Most of the materials studied do not undergo a Debye relaxation process [4]. In fact, the non-interacting Debye relaxation is only a particular case of the dipolar relaxation processes. Experimental TSDC spectra reported in the literature for different materials account for this assertion.

Thus, it has been claimed that heavily doped alkali halides give TSDC peaks which hardly fit the Arrhenius theoretical plot. This unsatisfactory fitting is mainly observed on the high-temperature side of TSDC peaks [5]. These features have been studied by van Weperen and co-workers [6, 7], who explained it on the basis of the dipolar interaction resulting from the high dipolar density. In these conditions the activation energy associated with the dipoles is not single-valued but it adopts the form of a distribution around a mean value, E_0. The energy distribution function results in a variation of the shape of the corresponding TSDC peak, which undergoes a slight broadening of the high-temperature side.

On the other hand, in recent papers we have studied $Ce_2(SO_4)_3 \cdot 9H_2O$ single crystals, which contain structural dipoles. These crystals yield TSDC peaks whose shape deviates significantly from that reported by Bucci and Fieschi [1] for first-order kinetics in doped alkali halides. In these crystals the dipoles are associated with the hydrogen bonds existing in their structure [8, 9]. The experimentally obtained TSDC peaks for these crystals cannot be fitted by the distribution

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proposed by van Weperen and co-workers [6, 7]. This is not a surprising result, because the dipolar density in these crystals is several orders of magnitude ($\sim 10^5$) higher than the maximum density reported by van Weperen. In fact, the impurity solubility in alkali halides is rather low, the highest possible dipolar densities being $10^{18}\,\text{cm}^{-3}$ [10].

For describing the relaxation in $Ce_2(SO_4)_3 \cdot 9H_2O$ single crystals we have used an empirical relaxation time, which is a function of the dipolar density at each relaxation instant [11]. This relaxation time obeys the relationship

$$\tau = \tau_0 \left(\frac{P_0}{P}\right)^{q-1} \exp\left(\frac{E}{kT}\right) \qquad (1)$$

P_0 is the dipolar density at the initial time ($t = 0$) and P is the remanent dipolar density during the relaxation, $P = P(t)$. q is a parameter related to the dipolar interaction, $q > 1$, which we call the interaction parameter. This mathematical expression has been deduced from the detailed balance equations for general order kinetics [12], and it has been successfully used to account for the non-Debye behaviour of the TSDC peaks in $Ce_2(SO_4)_3 \cdot 9H_2O$ [13].

The pre-exponential factor of Equation 1, τ_0, has time dimensions, but it adopts a very low value in certain cases, which does not permit it to be ascribed to the inverse of a frequency factor in the physical meaning of the double potential well model supporting the Arrhenius law. On the other hand, the activations energy, E, must implicitly include a term accounting for the dipolar interaction; obviously the evaluation of this term is not possible unless we are able to measure the interaction during the relaxation. This presents strong drawbacks; firstly, it is experimentally difficult to reduce the dipolar density to a non-interacting value. Secondly, the dipolar interaction occurs simultaneously with the relaxation process. This dynamical aspect of the interaction has been studied in recent work, where it has been demonstrated that E and q are sensitive to variations of both the heating rate [14] and the relaxing dipolar density [15]. In fact, this dynamical character of the interaction, contrary to the distribution proposed by Van Weperen [7], limits the ability to determine the interactive energetic contribution.

In this paper we will use this empirical procedure for studying the dipolar relaxation of other solids which are expected to have a rather high dipolar density, e.g. polymeric materials. Generally the TSDC spectrum of a polymer exhibits a complex shape. Several peaks are observed in the usual thermal range scanned (100 to 350 K). These peaks extend sometimes to a large thermal range and frequently they look like a broad band enclosing several components [16].

This picture is mathematically described by means of distribution functions, of either the activation energy or the pre-exponential factor [17]. In practice these distributions are hardly justified on the basis of a physical reality [18]. It is obvious that high dipolar densities will induce correlations between dipoles leading the system to behave as non-Debye; with this in mind we have studied PVDF-α (see Section 2) which presents at least two or three relaxation zones, including the γ and β transitions, which have been observed by Leonard *et al.* [19]. The TSDC bands associated with these relaxations can be resolved into several elementary peaks by means of the thermal sampling technique which will be described in the next section.

In the literature on PVDF-α, the relaxation processes associated with these peaks are assumed to be Arrhenius-like [20]. However, as we will see later, values of q significantly higher than unity are required for fitting these peaks to Equation 1. This fact suggests the existence of dipolar interactions during the relaxation, hence a departure from the *a priori* assumed Debye behaviour is expected. On the other hand, the variations observed for the q value allow us to separate the different relaxation modes, which are in agreement with those typically reported as associated with molecular motions in the different transitions of PVDF-α [21].

2. Experimental procedure

Polyvinilidene fluoride (PVDF) is a polymer whose repetitive molecular unity is $CH_2{-}CF_2$. The dipolar moment of this monomer lies around $7.6 \times 10^{-30}\,\text{C m}$ (2.3 Debye). The polymerization of the monomers is organized in the head-to-tail configuration, which allows the existence of a sufficiently high dipolar moment. The crystalline polymer exhibits at least three different configurations depending on the crystallization conditions, all of which are perfectly stable at room temperature. These are referred to as I, II and III forms or β, α and γ phases, respectively, in the current literature on PVDF [22, 23].

The most common polymorphic configuration is the α phase, which is obtained by cooling from the melt. The melting temperature is 170° C. PVDF-α presents a "trans-gauche, trans-gauche′" (TG TG′) configuration [24, 45], packed in an orthorhombic unit cell with antiparallel orientation of molecular links, which results in a null dipolar moment. This phase is usually reported as non-polar or antipolar [26]. The glass transition occurs at 233 K [27]. By means of mechanical treatment under special conditions of crystallization, the polar phases β and γ can be obtained [28, 29]. These phases will not be studied in this paper.

The relaxation modes of this polymer have been largely studied, employing mechanical, dielectric and nuclear magnetic resonance (NMR) techniques [30–33]. All these methods reveal the existence of several transition temperatures which are associated with thermally activated molecular motions in the polymeric structure.

The experimental set-up we have used for measuring TSDC has been described in previous articles [9]. In order to avoid breakdown currents, the experiments are carried out under high vacuum conditions (less than 10^{-5} torr). Silver paste electrodes were painted on the surface of the sample, adopting a parallel plate capacitor configuration. No improvements were detected in the measurements by providing the samples with guard ring [34]. The typical dimensions of the specimens were 5 mm × 5 mm × 0.1 mm.

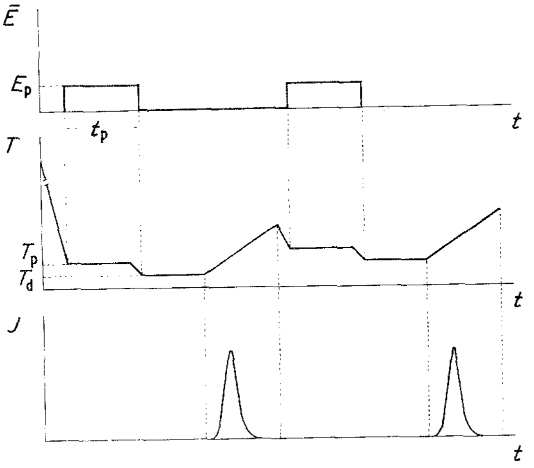

Figure 1 Schematic representation of the thermal sampling technique, showing the polarized bias, $\bar{E}$, at the different temperature stages. The peaks represented are the TSDC peaks corresponding to the thermal margin limited by T_p (polarization temperature) and T_d (depolarization temperature); t is time and J the electrical current density.

The thermal sampling technique used for separating the different dipolar relaxation contributions is schematically depicted in Fig. 1 [35]. The temperature margin of sampling, $T_p - T_d$, is 5 K. A quick temperature scan is possible due to the weak thermal inertia of the cryostat, which allows heating rates as fast as 0.2 K sec^{-1}.

3. Results

A typical TSDC spectrum of PVDF-α is shown in Fig. 2. The dipolar ordering was induced by a 3×10^6 V m^{-1} bias applied at 310 K (the polarization temperature, T_p) for 2 min (polarization time, t_p). The heating rate in the full temperature range scanned was $b = 0.2$ K sec^{-1}. This spectrum is characterized by the existence of three peaks whose maximum temperatures are located at 150, 210 and 320 K, respectively. These data agree with those reported in the literature on this material as obtained by different experimental techniques, e.g. TSDC, dielectric loss and mechanical relaxation (20, 30–33, 36–40). They are related to three different relaxation mechanisms occurring in PVDF-α. By analogy with the terminology used for dielectric losses in this material we will denote them as γ, β and α, respectively. The α peak, which is observed well above the glass transition temperature, is ascribed to molecular motions in the crystalline region [41], which is considered as a prefusion phase. The intensity of this peak increases as the ratio of the crystalline to the amorphous volume increases [27]. The β peak, which is observed in the proximity of the glass transition temperature, is usually related to micro-Brownian motions of molecular links in the amorphous regions [42]. Finally, the γ peak is associated with local molecular motions in the amorphous region [36].

Differential scanning calorimetry (DSC) studies have revealed the existence of two glass transition temperatures, T_g(L) and T_g(U), which are ascribed to two different relaxations [19, 21]. In the same way a resolution of the TSDC spectrum by means of the thermal sampling technique allows us to separate these relaxation modes. The thermal sampling has been done for temperatures ranging from 130 to 320 K, for which 53 experimental TSDC peaks have been obtained; among them 44 correspond to temperatures below 270 K, whereas the remainder can be associated to the relaxation of the α peak.

The relaxation time associated with a TSDC peak can be obtained at a given temperature from the relation between the residual polarization $P(T)$ and the electrical current density $J(T)$ according to the Bucci–Fieschi–Guidi (BFG) relationship [43]:

$$\tau(T) = \frac{P(T)}{J(T)} \qquad (2)$$

In relation to the α peak, it is noteworthy to say that the relaxation time we have obtained fits a Williams–Landel–Ferry (WLF) equation [34, 44, 45], which is in agreement with the results reported elsewhere [20]. The study of this peak is not the aim of this paper; however, it has been reported herein as a check for coincidence between our experimental results and those reported by other authors.

The aim of this paper is the study of the other TSDC peaks. It should be noted that the calculated relaxation time associated with these peaks (Equation 2) does not fit an Arrhenius law. The departures from exponential behaviour are markedly observed on the high-temperature side of the TSDC peaks. Therefore, we have aimed to fit experimental results to the relaxation time defined by Equation 1. As has been stated, this relationship includes a fitting parameter, q, which can be considered as indicative of the dipolar interaction strength. Values of q larger than unity give an increase of the relaxation time, or

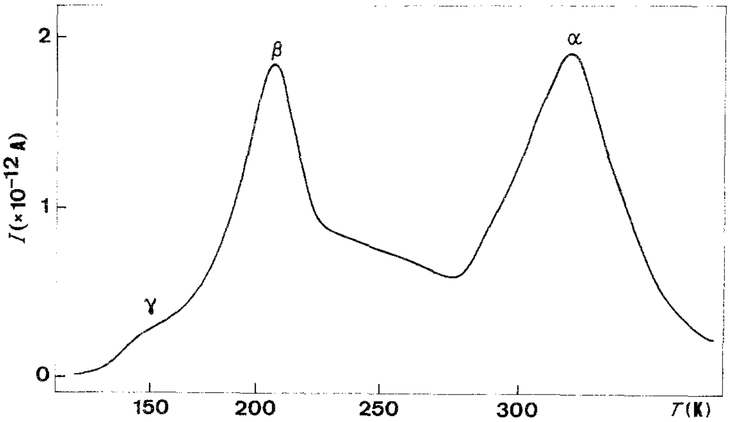

Figure 2 Typical TSDC spectrum of PVDF-α, obtained by polarizing with a bias $\bar{E}_p = 3 \times 10^6$ V m^{-1}, during 2 min at 310 K. The heating rate is 0.2 K sec^{-1}. The TSDC bands have been labelled following the usual nomenclature of TSDC in polymers [16].

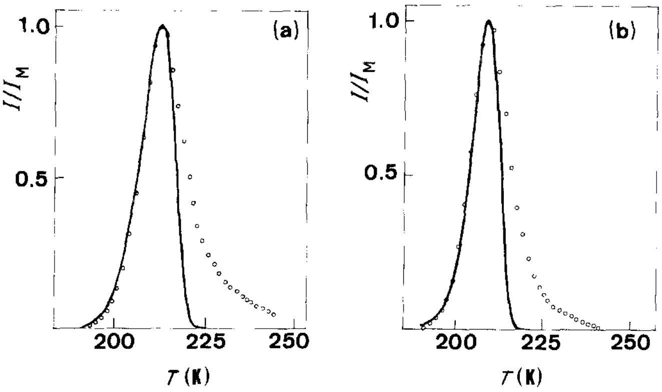

Figure 3 (○) Elementary TSDC peaks as obtained by thermal sampling technique: (a) $T_M = 219$ K, (b) $T_M = 212$ K. The full lines correspond to fitting by the Bucci *et al.* equation [43]. The departure from the experimental curve is noticeable for temperatures higher than T_M. The electric current is normalized to the maximum value I_M.

in other words a delay in the dipolar motion relative to the Debye case. This causes a broadening of the high-temperature side of the TSDC peak. By means of the relaxation time defined by Equation 1, it is possible to deduce the following relationship for the electric current density $J(T)$:

$$J(T) = \frac{P_0}{\tau_0}\exp\left(\frac{-E}{kT}\right) \times \left[1 + \frac{q-1}{\tau_0}\int_{T_0}^{T} f'(T')\exp\left(\frac{-E}{kT'}\right)\mathrm{d}T'\right]^{\frac{q}{1-q}} \qquad (3)$$

where $f'(T')$ is the derivative of the function describing the temperature evolution. In practice it takes a constant value, which is designed as the heating rate [11].

In Figs 3 and 4 a series of TSDC peaks obtained by thermal sampling is shown. Also the theoretical plots corresponding to both the expression of Bucci *et al.* [43] and Equation 3 are presented there. A confident fitting of the experimental peaks can only be obtained with Equation 3. The fitting parameters are three: τ_0, E and q. The study of these parameters, from the 44 experimental TSDC peaks we have resolved, allows us to account for the different dipolar relaxation mechanisms existing in PVDF-α.

4. Discussion

Generally in a broad TSDC band the transition temperature between two different relaxation mechanisms can be deduced from abrupt changes in τ_0 or E. From this and eventually other available experimental data (DSC, NMR, X-rays etc.) it is possible to correlate the experimentally resolved relaxation processes with any particular microscopic mechanism taking place in the material studied. In polymeric materials the glass temperature provides a rough criterium in order to separate different relaxation mechanisms. In fact at temperatures well above this temperature the relaxation processes deal mainly with liquid transitions, which are observed in PVDF-α for temperatures ranging from 300 to 350 K. On the other hand, processes occurring near and below T_g are usually assumed to be produced by dipolar motion.

We have aimed to study only relaxation processes dealing with dipolar orientation, which occurs below 300 K in PVDF-α. The parameters τ_0 and E as obtained by fitting Equation 3 to the experimental TSDC peaks are reported in Figs 5 and 6 as a function of the maximum temperature of each peak. Also, the values of Lacabanne and co-workers [20, 46] have been represented and taken as a comparison. Usually three different relaxation modes are found. Below 190 K the elemental relaxation processes are related to the subglass transition; at the transition temperature there is a sharp change in the relaxation parameters, especially in τ_0. Above this temperature a monotonic increase of the activation energy is observed, reaching a constant value at 245 K. This temperature allows the separation of the two glass transitions, T_g(L) and T_g(U). The existence of two glass transition zones in the glass region is in agreement with the results deduced from dilatometric measurements by Enhs and Simha [21] as well the DSC studied by Leonard *et al.* [19], although other authors [42, 47] disagree with this assignment.

The temperature separating the subglass and glass transitions ($T = 190$ K) coincides with that reported by Lacabanne and co-workers [20, 46]. However, the temperature separating the two glass transition regions, T_g(L) and T_g(U), in our experiment is slightly lower than Lacabanne's value. In spite of this, the evolution

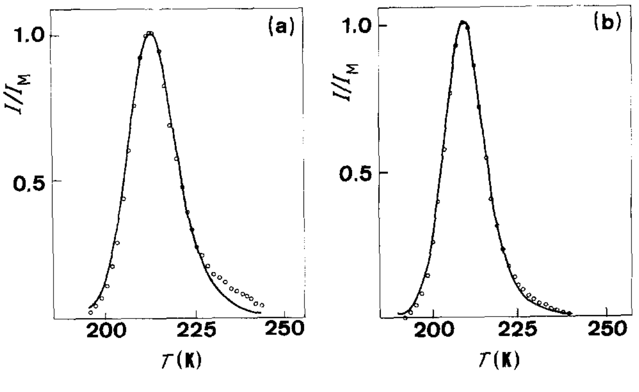

Figure 4 Fitting of (○) experimental TSDC peaks of Fig. 3 by (——) Equation 3. A satisfactory fit can be obtained for (a) $q = 2.8$, (b) $q = 2.5$.

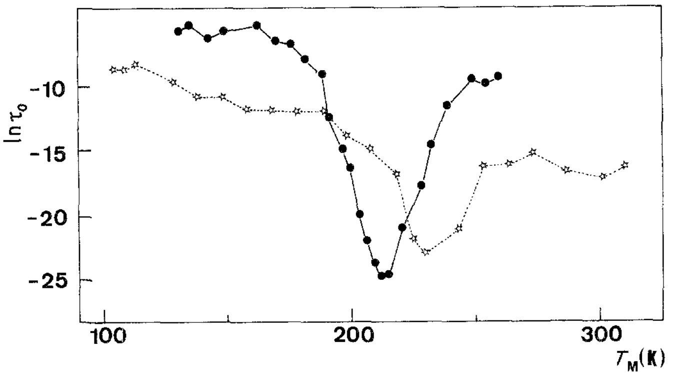

Figure 5 Representation of $\ln \tau_0$ to the temperature of the maximum (T_M) of each peak obtained by (●) thermal sampling; (☆) values obtained by other authors [20, 46].

of the relaxation parameters in our experiments is similar to that observed by these authors. Therefore our analysis of the TSDC data allows us to determine the three transition regions typically observed in PVDF-α. Besides these considerations our analysis provides a third parameter, which is the so-called interaction parameter, q. The values of q as a function of the temperature of the maximum of each peak are represented in Fig. 7. It can be observed that the elementary peaks obtained by thermal sampling are characterized by a value of q greater than unity, hence the corresponding relaxation time deviates from the Arrhenius law proposed in the BFG theory. As we have previously indicated, a value of q higher than unity implies a delay in the relaxation time compared to the non-interacting relaxation time corresponding to the Debye case. So that, for $q > 1$, a TSDC peak undergoes a broadening of its high-temperature side; therefore it presents a more symmetric shape than the classical Debye peak.

Broad peaks are frequently observed in the thermal sampling TSDC peaks of polymeric materials [48]. The problem is then related to the physical interpretation of these peaks. Usual interpretations regard this broadening of a simple peak as a consequence of the coupling between relaxation times belonging to a broad distribution of relaxation times. This coupling is particularly strong for short times (below 100 sec), in fact typical BFG plots show curvature for low relaxation-time values. Generally, this problem is obviated, though not resolved, by considering only relaxation times longer than 100 sec, which would correspond to the low-temperature side of the peak; it is noteworthy that the maximum of the peak corresponds to a relaxation time of approximately 1 sec. This implies that only a fraction of the peak is considered in the classical BFG theory. On the other hand, dielectric loss measurements on polymers have shown departures from the typical Debye behaviour [49]. All this suggests that the relaxation time is not only a function of the pre-exponential factor and the activation energy, but that some dependence inherent in the relaxation process itself must be considered. This implies a departure of the relaxation time from the Arrhenius law. In fact, the delay observed in the relaxation time is associated with the dipolar interaction occurring during the relaxation; this delay is mathematically described in Equation 1 by $P(t)$ and q, which account for the dipolar interaction. In fact, as the density of relaxing dipoles ($\sim P_0 - P$) is thermally enhanced, the delay time of the relaxation increases. This suggests that deviations from the Debye behaviour will begin to appear at temperatures approaching the maximum, and are really noticeable on the high-temperature side of the peak. In fact this idea is in agreement with the strong departures from the BFG theory observed for short relaxation times.

It should be noted that the spurious effects due to neighbouring peaks are rather difficult to avoid; nevertheless an adequate choice of the experimental conditions, reducing as much as possible the margin $T_p - T_d$, allows one to reasonably reduce the influence of neighbouring peaks. Thus, TSDC experiments on $Ce_2(SO_4)_3 \cdot 9H_2O$ under different polarization conditions permit one to obtain almost "clean" TSDC peaks, and it has been demonstrated that the broadening of the high-temperature side persists in these peaks [50].

Once the dipolar interaction has been introduced as a determinant feature in the relaxation mechanism of systems with high dipolar density we will study the influence of this interaction in the TSDC spectrum of PVDF-α.

The evolution of q can be studied for each of the three relaxation regions deduced previously on the basis of the E and τ_0 values. Thus, in the sub-glass transition region, q has a value of 1.2. In the low-temperature glass transition region, $T_g(L)$, q takes an average value of 2.4. Finally in the third region, T_g(U), q is nearly constant ($q \simeq 1.6$) and smaller than the average value for T_g(L). This behaviour of q implies the existence of three different relaxation mechanisms. In the sub-glass transition region the dipolar interaction is really weak, giving a near-Debye relaxation

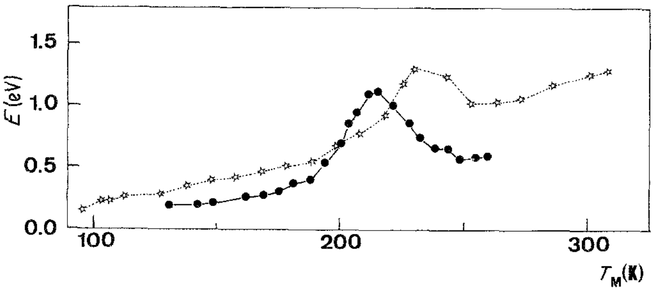

Figure 6 Evolution of the activation energy, E, against maximum temperature, T_M, of (●) the elementary peaks; (☆) values reported by other authors [20, 46].

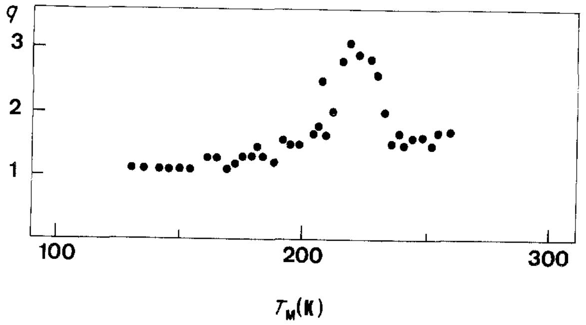

Figure 7 Evolution of the interaction parameter, q, against maximum temperature, T_M. The behaviour of q as a function of T_M permits one to separate three relaxation zones: (i) below 190 K, q is nearly constant and equal to 1.2, (ii) between 190 and 230 K, q is not constant and takes values approximately between 2 and 3; (iii) above 230 K q is nearly constant and takes a value of 1.7. These thermal limits agree with those reported by other authors for defining the transition temperatures.

process. On the other hand the interaction is stronger for the low-temperature glass transition region than for the high-temperature region. It is noteworthy to remark that E and q follow a similar evolution; we have observed this correlation in other materials [13, 14] and we have explained it in terms of a complex activation energy which includes an additive interaction energy component, which is tightly related to the q value.

An important problem to be considered now is how the molecules giving dipolar relaxation in PVDF-α can account for the experimentally observed interactive behaviour. The relaxation modes in the sub-glass transition zone (γ transition) are associated with local molecular motion in the amorphous region, including also some local motion in the crystalline region [36, 46]. In the framework of our analysis the dipolar interaction corresponding to these motions should be rather weak ($q \simeq 1$). This fact implies a strongly localized binding energy, which provides a fast reorientation as the temperature increases, which is in agreement with the fact that the local molecular motion must satisfy this condition.

The relaxation modes of the glass transitions (β transition) are associated with the micro-Brownian motion of the amorphous links [19, 46]. The matrix of the amorphous phase of PVDF-α presents two different structures: (a) a phase of inter-spherules in which one of the edges of the molecular link is free whereas the other edge is in the lamellar region, and (b) a second phase with both edges of the links in the crystalline region. These amorphous phases lie at the origin of the two glass transitions, T_g(L) and T_g(U), respectively [19, 20, 46]. On the basis of the hypothesis of the dipolar interacting analysis it is reasonable to assume that the T_g(L) relaxation region should deal with stronger interaction than the T_g(U) one, due to the weaker binding of the links with a free edge. This assertion would give a higher q for T_g(L) than for the T_g(U) region, which is just the result we obtained (Fig. 7). In conclusion we can state that during a dipolar relaxation with a high concentration of dipolar units the weaker is the dipolar binding, the stronger is the interaction. The relaxation time defined by Equation 1, including the interaction parameter q, seems to be a reliable tool for studying dipolar relaxation in polymeric materials. This assertion is not surprising, because the non-Debye behaviour of the dielectric losses in polymeric materials has been largely demonstrated before [4]. Contrary to the usually assumed non-interacting processes (distribution functions) this behaviour has been explained by Jonscher [4] on the basis of many-body interactions, which account for the experimental departures from the classical Debye equation. This is confirmed by our analysis of the TSDC spectra in PVDF-α.

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