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Compensation laws and β-relaxation in poly(vinyl chloride)

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ABSTRACT

Thermally Stimulated Depolarization Current measurements have been carried out in a temperature range between -180ºC and 20ºC on different Poly(Vynil Chloride) samples characterized by different molecular weights and tacticities. Dielectric relaxation times involved in the β-relaxation were obtained by the fractional polarization procedure. The distribution of the Arrhenius-like kinetic parameters deduced from the relaxation times, has been interpreted in terms of compensation laws. Two different compensation laws, which are likely associated to two kinds of thermally activated molecular motions, were obtained. This compensation behaviour does not result to be significantly affected by both tacticity and molecular weight. The two compensation laws obtained in the β-region have been compared with the compensation behaviour in the α-relaxation range of PVC previously studied. Results obtained are discussed in the frame of the correlation between β and α relaxations of Poly(Vinyl Chloride) frequently assumed in the literature.

INTRODUCTION

As is well known, Poly(Vinyl Chloride) (PVC) shows a secondary β-relaxation which extends to a wide range of temperature around some 200 K. This process, detected by different mechanical and dielectric techniques, has been commonly related with the local motions of short elements of the chain backbone (1-3). The mean activation energy for these motions has been found to be about 0.5 eV (1-3).

On the other hand, different works reported in the literature (4-6) have shown that the main features of the β-relaxation in PVC are not strongly affected by crystallinity, microstructure, tacticity, molecular weight and the thermal history of the samples. In spite of these results the precise nature of the β-relaxation is a question which still remains open to controversy. In this way, we have recently shown (7) by thermally stimulated techniques that the elementary processes involved in the β-relaxation of a commercial PVC can be grouped into two different relaxation modes, each of them being characterized by a different compensation law. In this work, going into these questions, we have investigated to see if this behaviour is a common feature of the β-relaxation in PVC. For this, we have performed a careful study of the β-relaxation in different PVC samples with different tacticity and molecular weight. To perform this study we have used Thermally Stimulated Depolarization Current technique (TSDC). This has been proved to be more accurate than the classical mechanical and dielectric spectroscopies in the detection and the study of the different molecular motions involved in a given relaxation process. This

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is a consequence of the power of separation of neighbouring processes owing to the low equivalent frequency ($\sim 10^{-3}$ Hz) of this technique and to the use of the fractional polarization procedure.

EXPERIMENTAL

Three different PVC samples were used. They were polymerized at -50 ºC, 0 ºC and 90 ºC resulting syndiotactic, atactic and isotactic respectively (8). Their average number molecular weight ranged from 10^4 to $2x10^5$

Samples for TSDC experiments were prepared as circular pellets with 8 mm diameter and 0.4 mm thickness.

Experimental equipment used in this work has been widely described in other papers (7,8)

The operating principle has been described in other works (7,8) and we will briefly recall it (see Figure 1):

The sample is subjected to an electric field Ep at a temperature Tp for a time which allows the complete orientation of the mobile units that one wishes to consider.

The temperature is then lowered to T<Tp where any molecular motion is completely hindered; then the field is removed.

The sample is subsequently warmed at a constant rate so that the mobile units can randomize. The polarization P, its time derivative (J = dP/dt) and the temperature T are obtained versus time t. The J(T) curve is known as the global TSDC spectrum.

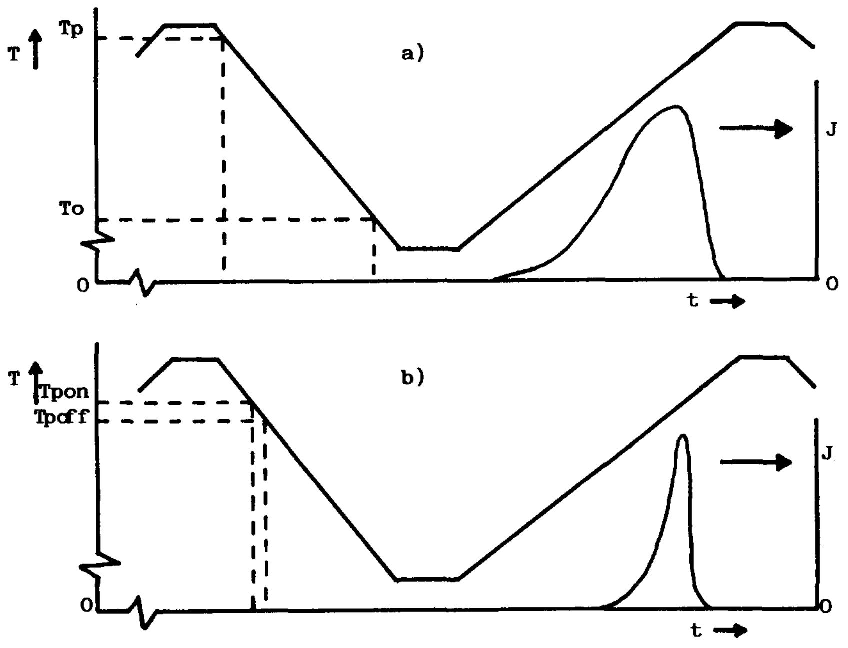

Figure 1.- Sample temperature during polarization and depolarization processes. a) Global polarization; b) Fractional polarization.

In this work, the samples were polarized with a field of 1 MV/m during cooling at 20K/min and heated at a rate of 10 K/min.

If the relaxation process is governed by a single relaxation time, τ, the $\tau(T)$ behaviour can be obtained, in the temperature range where the J signal is recorded, from the relationship (9):

$$\tau(T) = P(T)/|J(T)| \qquad /1/$$

However, a broad distribution of relaxation times is commonly observed in amorphous polymers like PVC (1,2,9) and the spectra obtained by the above mentioned procedure cannot generally be described by a single relaxation time (9). In that case, the technique allows us to resolve the complex spectra into elementary processes. This possibility arises from the use of the fractional polarization procedure (9) which allows a whole spectrum to be resolved into elementary spectra, each of them well approximated by a single relaxation time.

The fractional polarizations procedure was applied in the present work as follows (see Figure 1):

The electric field is applied at a temperature Tpon during cooling in order to allow the mobile units with a retardation time lower than the experimental one to orient. This experimental time is defined by the inverse of the cooling rate.

When the sample reaches the temperature Tpoff = Tpon - 10 K, the electric field is cut off, so that units of retardation times lower than the experimental one return to equilibrium.

By varying the values of Tpon by steps of 10 K in the temperature range where the global curve appears, the elementary processes of a given relaxation are separated and the relaxation time can be obtained at each temperature by using relationship /1/.

Usually the temperature evolution of the relaxation times can be well approximated by the Arrhenius equation:

$$\tau(T) = \tau_o \exp(E/KT) \qquad /2/$$

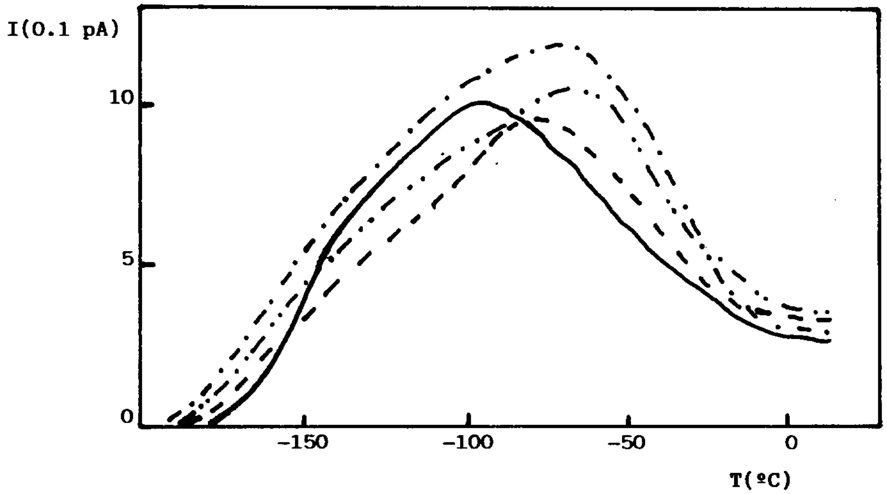

Figure 2.- Global TSDC spectra corresponding to the β-relaxation of PVC polymerized at 90ºC (---), 0ºC (-·-) and -50ºC (-··-) and commercial PVC (——)

where τ_o is a preexponential factor, K the Boltzmann's constant and E the apparent activation energy for the process.

If the logarithm of the preexponential factor τ_o varies linearly with the activation energy E, as is often experimentally found in polymeric solids, one observes a compensation law (10, 11):

$$\tau_o = \tau_c \exp(-E/KT_c) \qquad /3/$$

Then, expression /2/ becomes:

$$\tau(T) = \tau_c \exp[E/K\ (1/T - 1/T_c)] \qquad /4/$$

where τ_c and Tc are phenomenological parameters, respectively known as compensation time and compensation temperature. The physical significance of these parameters is not yet clear, but the most general interpretation consists of considering them as characteristic of processes arising from the same molecular mechanism (11,12).

RESULTS AND DISCUSSION

Figure 2 shows the global TSDC spectra corresponding to the β-relaxation temperature region of the different PVC samples investigated in this work. A global TSDC peak obtained in the same experimental conditions in the β-relaxation range of a commercial PVC (7) is also shown for comparison. As can be seen, all the curves are widely extended and each of them presents a broad maximum located around 180 K. Although small differences among the different curves can be observed, we cannot conclude a systematic influence of molecular parameters characterizing the different samples (tacticity and molecular weight) in both the position and width of the peaks.

Each whole TSDC spectrum was decomposed in Debye-like elementary peaks by using the fractional polarization procedure described in the experimental section. Assuming a single relaxation time $\tau(T)$ for each of the elementary TSDC peaks obtained, the Arrhenius-like kinetic parameters, E and τ_o, were calculated from experimental points through equations /1/ and /2/. The values of E obtained range between 0.2 and 0.9 eV for all the samples studied and are very close to those obtained for the commercial PVC not only by TSDC but also by Thermally Stimulated Creep (TSC) technique (7). These values of E, as well as the corresponding values of τ_o (ranging between 10^{-6} and 10^{-18} sec.) are in good agreement with the well assumed local character of the molecular motions in the β-relaxation of polymers.

The values of kinetic data obtained (E , τ_o) have been interpreted in terms of compensation laws. Figure 3 shows the compensation plot, ln τ_o vs. E, obtained. As can be seen, the couples of values (ln τ_o , E) can be grouped in only two different compensation lines, which are characterized by two sets of compensation parameters for all the PVC samples investigated. The values of the compensation parameters obtained are:

$$\begin{aligned} T_{c1} &= 200\text{K} & \tau_{c1} &= 0.13\ \text{s} \\ T_{c2} &= 245\text{K} & \tau_{c2} &= 10\ \text{s} \end{aligned} \qquad /5/$$

Moreover, these two compensation laws are the same as those previously obtained for a commercial PVC (7). These results confirm that neither tacticity nor molecular weight seem to affect the β-relaxation behaviour in PVC.

On the other hand, the two compensation laws obtained suggest, in the framework of the general interpretation of compensation laws (11,12), that two different microscopical mechanisms could be involved in the β-relaxation in PVC. However, althiugh the microscopical origin of β-relaxation in PVC remains unclear, one of the most extended assumptions (1,3) is to relate the β-relaxation with the local motions of short elements of the chain backbone, i.e. only one mechanism being involved on the molecular level. This interpretation implies that the structural units involved in both β and α (glass transition) relaxations should be the same. In the case of α-relaxation the motion of these units becomes coupled by a high degree of cooperativity. Taking into account these ideas, both β and α relaxations result to be correlated and β-relaxation could be viewed as a kind of precursor of the α-relaxation. However, such a picture would imply that kinetic data, E and τ_o, corresponding to elementary processes in both β and α relaxations, should fit the same compensation law. In order to go into these ideas, Arrhenius-like kinetic data obtained in previous works (7,8) from TSDC and TSC measurements, which were performed in the glass transition region on different PVC samples, have also been drawn in Figure 3. As can be seen, these E and τ_o values fit a compensation law, different from the two compensation laws obtained in the β-relaxation region, with compensation parameters:

$T_c = 356.5$ K $\qquad \tau_c = 21.9$ s $\qquad$ /6/

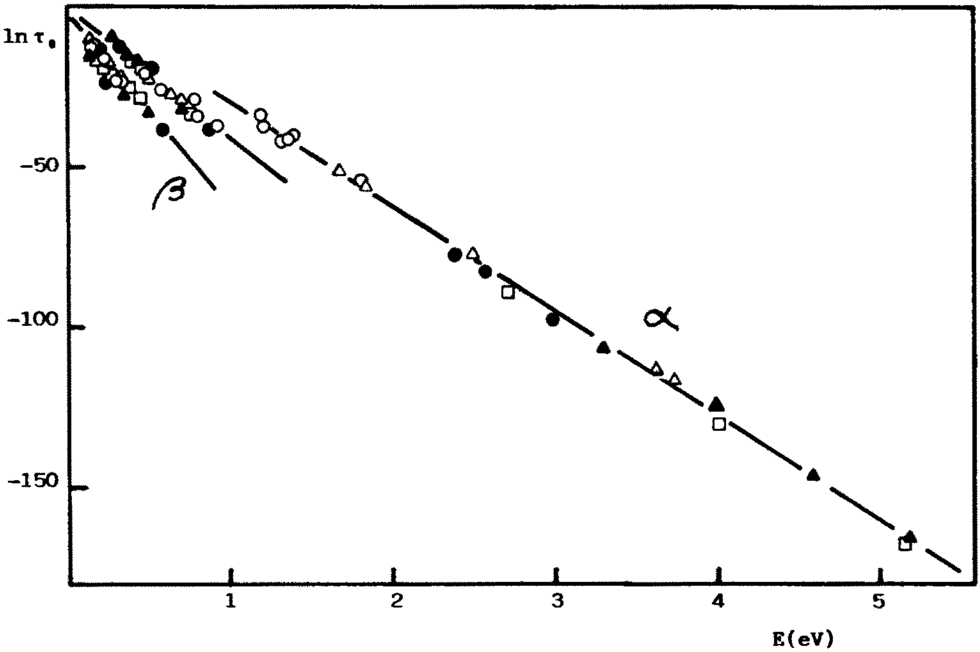

Figure 3.- Compensation plot of the β and α processes obtained by TSDC on PVC polymerized at -50ºC (O), 0ºC (Δ) and 90ºC (□) and on commercial PVC by TSDC (●) and TSC (▲).

From this compensation analysis, we can conclude that, against the ideas stablished up to now (1,3), the microscopical origin of the β and α relaxations in PVC seems to be different. Therefore, it is difficult to view the β-relaxation as a precursor of the α-relaxation, as has been above commented.present in the β-relaxation range. In this sense, there is no clear evidence in the literature about these two different molecular mechanisms from both dynamic and thermostimulated measurements. Kakutani and Asahima (13) have already described two possible relaxation mechanisms in the β-relaxation range of PVC from mechanical and dielectric dynamic measurements. They assign them to different local motions corresponding to crystalline and amourphous regions respectively. However, it is well known that tacticity affects the amount of crystallinity in PVC samples (14). Therefore, syndiotactic samples would show a different compensation behaviour to the isotactic one because of their different crystallinity. This has not been observed by us as shown in Figures 2 and 3. However, this possibility cannot be discarded and, in order to clarify this point, a future TSDC work performed on a serie of PVC samples with different well characterized amount of crystallinity would be necessary.

Finally, although a fine compensation analysis of the β-relaxation in PVC has been proved to be adequate to apport new ideas, a correct molecular assignment of the different compensation mechanisms involved would need the use of microscopic techniques as, for example, solid state Nuclear Magnetic Resonance (NMR). This kind of study will be the subject of a future work.

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