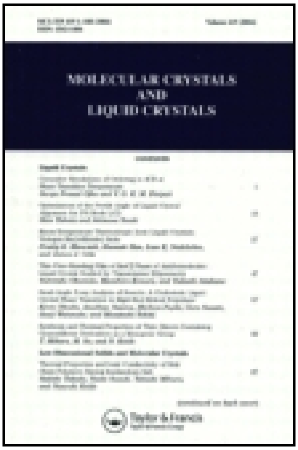

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THE HIDDEN β-RELAXATION OF PENTACHLORONITROBENZENE AS STUDIED BY THERMALLY STIMULATED DEPOLARIZATION CURRENTS

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THE HIDDEN β-RELAXATION OF PENTACHLORONITROBENZENE AS STUDIED BY THERMALLY STIMULATED DEPOLARIZATION CURRENTS

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It was recently reported that an excess wing exists in the higher frequency side of the dielectric loss peak of some glass-forming materials (including pentachloronitrobenzene). A very careful study of the molecular mobility in pentachloronitrobenzene was carried out using the dielectric technique of thermally stimulated depolarization currents (TSDC). The objectives of this study were (1) to look for an eventual TSDC signature of this excess wing; and (2) to contribute to the elucidation of the nature and origin of this relaxation process. The obtained results show that there is a TSDC signature of the excess wing and suggest that it corresponds to the low temperature flank of the β-peak, hidden under the largely dominant α-peak.

Keywords: β-relaxation; excess wing; molecular mobility; TSDC; TSC

INTRODUCTION

A variety of dynamic processes are known in conventional glass formers: the main α-process, and the so-called secondary processes. Among these faster secondary relaxations are the β-relaxations, which arise from intramolecular processes (internal rotations), the β-relaxations without intramolecular contribution (the so-called Johari-Goldstein relaxation), the excess (or high-frequency) wing, and the boson peak. A common feature of these relaxation processes is that their nature and origin are not well understood and are controversially discussed.

It was recently pointed out that, in some glass-forming materials, an excess wing is shown in the higher frequency side of the dielectric loss

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*Corresponding author. E-mail: mouraramos@ist.utl.pt peak of the α-relaxation, some decades above the frequency of the maximum, ω_{max}. The empirical functions used to describe the α-peak fail to describe the high-frequency side in the whole frequency range, and emphasize the existence of the excess wing. The nature of this excess wing is not elucidated. Many authors considered that the excess wing and the Johari-Goldstein relaxations correspond to different processes. Nowadays, however, some indications seem to favor the idea that they are due to the same microscopic process, i.e., that the excess wing is nothing more than the high-frequency flank of the β-peak, hidden under the largely dominant α-peak [1,2].

It was recently shown that the excess wing is observed in the dielectric relaxation spectra of several plastic crystals [2]. In fact, since plastic crystals are often very strong glass formers, the activation energy of the main process is particularly low, so that the secondary and the main relaxations appear in the same temperature region. As a consequence, the β-relaxation can be, in some cases, disguised under the α-process. The technique of thermally stimulated depolarization currents (TSDC) is a dielectric technique that has been widely and successfully used to study the relaxation dynamics in a variety of materials [3–7]. It was used to study motional processes in crystals showing reorientational freedom, i.e., in plastic crystals [8–10]. The objective of the present work is to see if the TSDC technique is able to detect the excess wing observed in dielectric relaxation spectroscopy. If there is a TSDC signature of the excess wing, we will try to see if the TSDC technique is able to provide any clarification to the discussion about the nature and molecular origin of the excess wing. Pentachloronitrobenzene was chosen to pursue these objectives for two reasons. The first is that this substance, which presents rotational freedom in the crystal in a given temperature range, was already studied by TSDC in our laboratory [10]. The other reason is that an extensive study of this plastic crystal by dielectric relaxation spectroscopy in a very wide frequency range (12 decades) was recently published [2], showing an excess wing in the high frequency side of the low temperature dielectric relaxation peaks. To anticipate the conclusions, we will say that there is a signature of the excess wing in the TSDC data, and that the features of this signature suggest that it corresponds to a mobility whose characteristics are very similar to the β-relaxation.

EXPERIMENTAL

Pentachloronitrobenzene (Aldrich product, D 89555 Steinheim, Germany catalogue no. P 220-5, mass fraction > 0.99) was purified by sublimation at

$p \cong 1.3 \times 10^{-3}$ Pa and at $T \cong 70°C$ (343 K). The onset temperature of the melting peak determined by DSC was $T_m = 144.3°C$ (417.5 K).

TSDC experiments were carried out with a TSC/RMA spectrometer (TherMold, Stamford, CT, USA) covering the range from −170 to +400°C. In order to analyze specific regions of the TSDC spectrum, different methods of polarizing the sample can be used, namely the so-called TSDC global experiment and the thermal sampling (TS) experiment (often called thermal windowing or cleaning, or partial polarization). The TS method, where the polarizing field is applied in a narrow temperature interval, allows the polarization of specific segments of a complex global relaxation or, otherwise stated, it enables to resolve a global peak into its individual relaxation modes. The physical background of the TSDC technique is presented elsewhere [11,12]. The basic description of the TSDC experiment, and the discussion of the nature of the information it provides, is presented in detail in recent publications [5,6].

RESULTS AND DISCUSSION

Thermal Sampling Analysis of the TSDC Global Spectrum

The jump in the heat flow, which is the DSC signature of a glass transition, is a very weak signal that appears in the temperature region between −80 and −60°C (193 and 213 K) [10]. The calorimetric glass transition temperature, defined here as the onset temperature, was found to be $\approx -77.5°C$ (196 K), using a heating rate of $10\,K.min^{-1}$. It is to be underlined that very recent adiabatic calorimetry measurements temperatures [13] allowed to detect a step of $\sim 15\,J.K^{-1}.mol^{-1}$ in the heat capacity of pentachloronitrobenzene, around 185 K (−88°C).

The TSDC thermogram shows a global peak with maximum intensity at −87°C (186 K), which is to be attributed to the glass transition relaxation, given that it appears at a temperature close to the calorimetric glass transition signal. This TSDC global peak of pentachloronitrobenzene is shown in Figure 1 (dashed peak), together with some of its partial polarization components, obtained by the usual thermal sampling (TS) procedure.

As shown before [10], this relaxation is dominated by the main (α) relaxation, and the fragility index of this glass-forming liquid calculated from the TSDC data was $m = 15$, in excellent agreement with the $m = 17$ very recently obtained by broadband dielectric relaxation spectroscopy [2]. Figure 2 is similar to Figure 1, but it emphasizes the low temperature side of the TSDC spectrum.

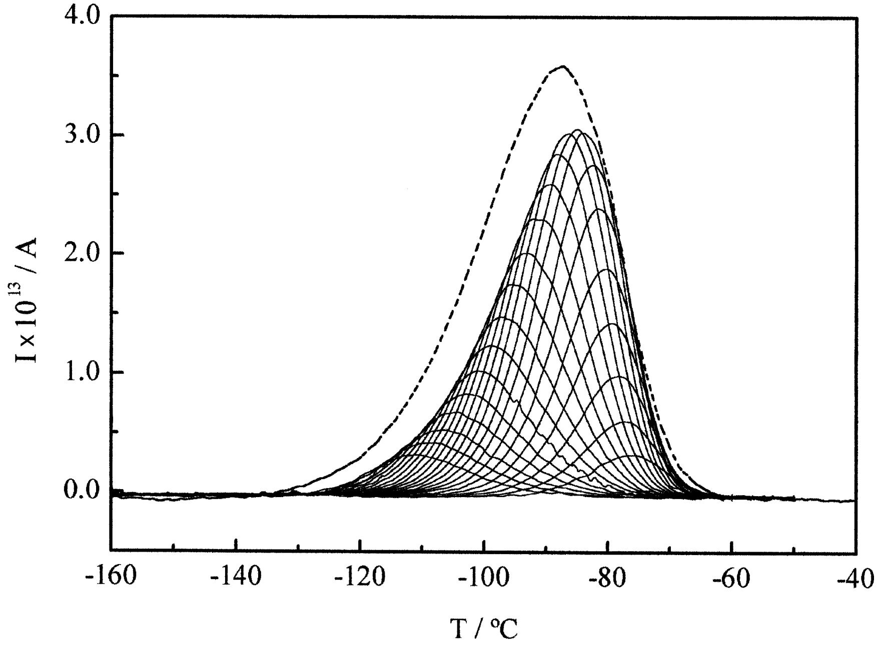

FIGURE 1 Thermal Sampling (TS) components of the relaxation at ~−87°C of pentachloronitrobenzene. The polarization temperatures, T_P, varied between −118 and −74°C (155 and 199 K), with intervals of 2 K. The strength of the polarizing electric field was E = 450 V.mm^{-1}, the polarization time was t_P = 5 min, the width of the polarization window was 2 K, and the heating rate was 4 K.min^{-1}. The dashed peak (arbitrary intensity) is a global TSDC peak obtained with a polarization temperature T_P = −55°C (218 K), and a freezing temperature T_0 = −165°C (108 K). The other experimental conditions are similar to those reported before for the TS experiments.

The TSDC Signature of the Excess Wing

A careful observation of Figure 1 and particularly of Figure 2 shows that the current intensity in the TSDC global peak does not increase sharply in the lower temperature side of the peak. Many thermal sampling peaks with low intensity can be obtained with low polarization temperatures several decades of degrees below the glass transition temperature.

The thermal sampled peaks in the glass transition region often show a modification of the intensity and shape in a narrow temperature interval, such that the steepness and sharpness of the peaks strongly increases as the polarization temperature increases. An example of this behavior was found in a work on *m*-toluidine (see Figure 1 in Correia et al. [4]). Another

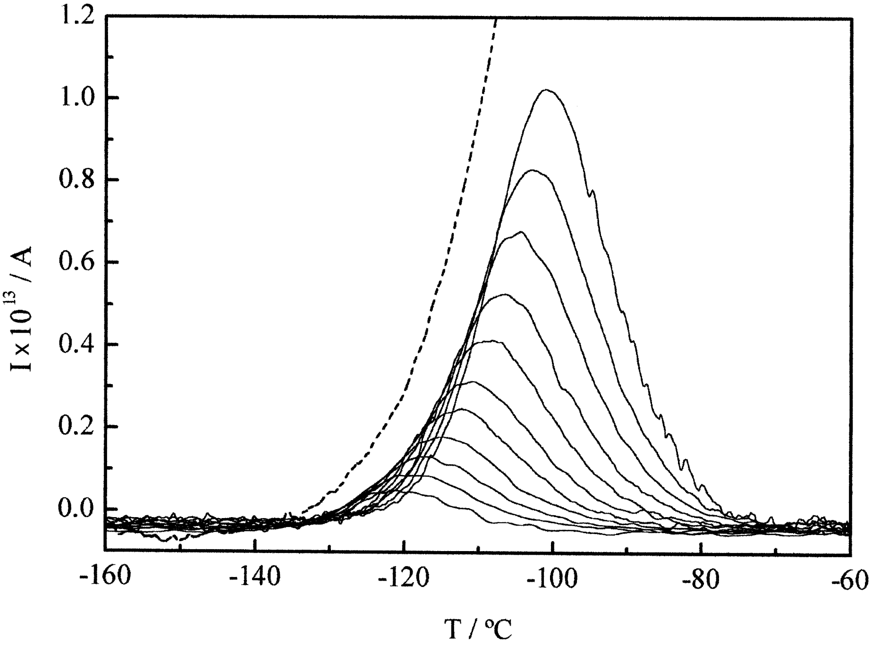

FIGURE 2 Lower temperature thermal sampling (TS) components of the relaxation at ~−87°C of pentachloronitrobenzene. The polarization temperatures, T_P, varied between −128 and −108°C (145 and 165 K), with intervals of 2 K. The strength of the polarizing electric field was E = 450 V.mm^{-1}, the polarization time was $t_P = 5$ min, the width of the polarization window was 2 K, and the heating rate was 4 K.min^{-1}. The dashed line (arbitrary intensity) corresponds to the global TSDC peak shown in Figure 1.

situation is that where a branching between the α- and the β-relaxations is observed in the frequency window of the TSDC technique, so that there is no gap in the TSDC spectrum between the peaks corresponding to those two relaxations. The relaxations overlap, and there is a continuous and slow progress from the TS peaks of the β-relaxation to the TS peaks of the α-relaxation. An example of this behavior was found in a work on sorbitol (see Figure 7 in Correia et al. [5]). In the present case of pentachloronitrobenzene, the situation is somewhat different from the situations previously described: the global peak shows a relatively smooth increase of the current intensity in the low temperature side, something like a tail that drags at lower temperatures, and that is the TSDC signature of the excess wing that is observed in dielectric relaxation spectroscopy. Since this tail exists, one can obtain measurable TS peaks in the temperature region where the tail appears (Figure 2).

Characterization of the Mobility Associated With the Excess Wing

In the present work we carried out a very large number of thermal sampling experiments in a wide temperature interval, from −160°C up to the orientational glass transition temperature that is ∼−87°C, in order to carefully analyze the low temperature side of the glass transition relaxation of pentachloronitrobenzene. The analysis of the obtained TS peaks allows the characterization of the mobility of the corresponding motional processes. Figure 3 shows the representation of the activation enthalpy, $\Delta H^{\neq}$, associated to these TS peaks as a function of the respective temperature location (temperature of maximum intensity, T_m).

First of all, it is clear from Figure 3 that the activation enthalpy of the TS components increases as T_m increases, and that this increase is stronger for the points in the higher temperature side. This increase of the activation enthalpy with increasing temperature is a feature of the glass transition as

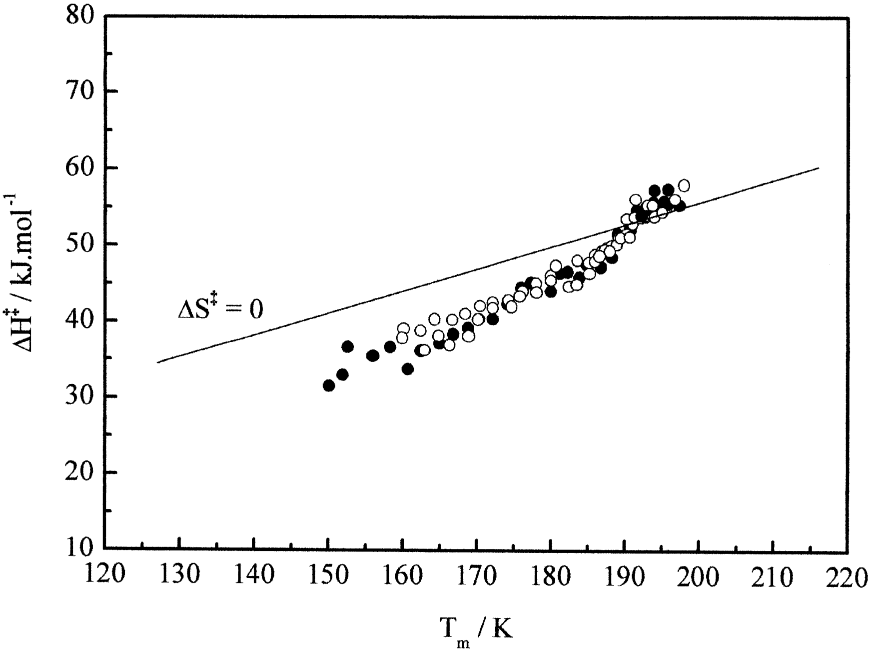

FIGURE 3 Activation enthalpy of the TS components of the relaxation at ∼−87°C of pentachloronitrobenzene as a function of the peak's location, T_m. The continuous line is the zero entropy line. The full circles refer to experiments carried out in the present work (peaks in Figures 1 and 2), while the open circles correspond to TS peaks obtained before and already reported.

studied by TSDC [4,6]. It is very strong in the case of fragile systems, but it is very weak in the present case since we are dealing with a strong glass former (an orientational glass). This increase of the activation enthalpy in a narrow temperature interval arises from the modification of the shape (broadness, steepness) of the peaks in the glass transition region, as will be discussed later.

Figure 3 also shows that many points in the low temperature side lie below the zero entropy line, which indicates that the corresponding molecular motions have negative activation entropies. A negative value of the activation entropy indicates that the transition state of the process is more ordered or more symmetric that the initial state. The physical meaning of this behavior is not easy to understand. However, we must note that we are in the presence of very small deviations from the zero entropy line. Otherwise stated, the motional processes that correspond to the points in the lower temperature side of Figure 3 are characterized by low activation entropies, indicating that they are localized and noncooperative molecular motions.

Figure 4 shows the representation of the temperature of maximum intensity, T_m, of each TS peak as a function of the respective polarization temperature, T_P.

In Figure 4 two different regimes are clearly observed. One of these regimes is at lower temperatures ($T_P < 170\,\mathrm{K}$), roughly corresponding to the TS peaks shown in Figure 2, where the peak position (T_m) shifts continuously and linearly to higher temperatures as the polarization temperature increases. This trend is such that $T_m - T_P$ is nearly constant ($\approx 7\,\mathrm{K}$), indicating that there is no significant modification of the shape of the TS peaks. This behavior is expected for a smooth distribution of relaxation times, which is a feature of the secondary relaxations [14]. The other regime occurs at higher temperatures ($T_P > 170\,\mathrm{K}$), corresponding to the TS peaks shown in Figure 1, where the position of the peaks changes more slightly as T_P increases. In this regime the trend is such that $T_m - T_P$ decreases as T_P increases, giving rise to a curvature in the plot of T_m versus T_P. This behavior, which is characteristic of the glass transition, arises from the modification of the shape (broadness, steepness) of the peaks in the glass transition region [15]. These observations support the idea that the lower temperature TS components of the relaxation at $\sim -87°\mathrm{C}$ of pentachloronitrobenzene (Figure 2) are in fact components of a secondary relaxation disguised by the dominant orientational glass transition relaxation.

CONCLUSIONS

It was shown that the excess wing that is observed in the high frequency side of the dielectric peaks of the α-relaxation appears as a long tail in the

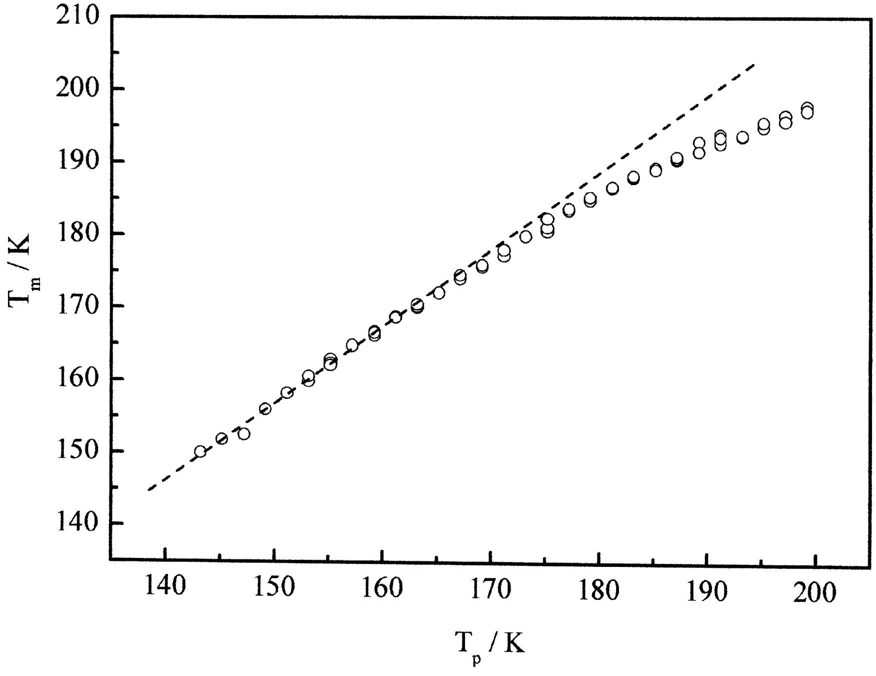

FIGURE 4 Temperature of maximum intensity of the TS peaks, T_m, plotted against the respective polarization temperature, T_P, for all the studied TS components of the relaxation at ~−87°C of pentachloronitrobenzene.

lower temperature side of the TSDC peak. There is thus a signature of the excess wing in the TSDC data. The features of this signature are such that the corresponding activation energies are low and the deviation from the zero entropy line are small. This suggests that it corresponds to a mobility whose characteristics are very similar to the β-relaxation. In this context, the excess wing seems to correspond to a secondary process disguised by the main glass transition relaxation.

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