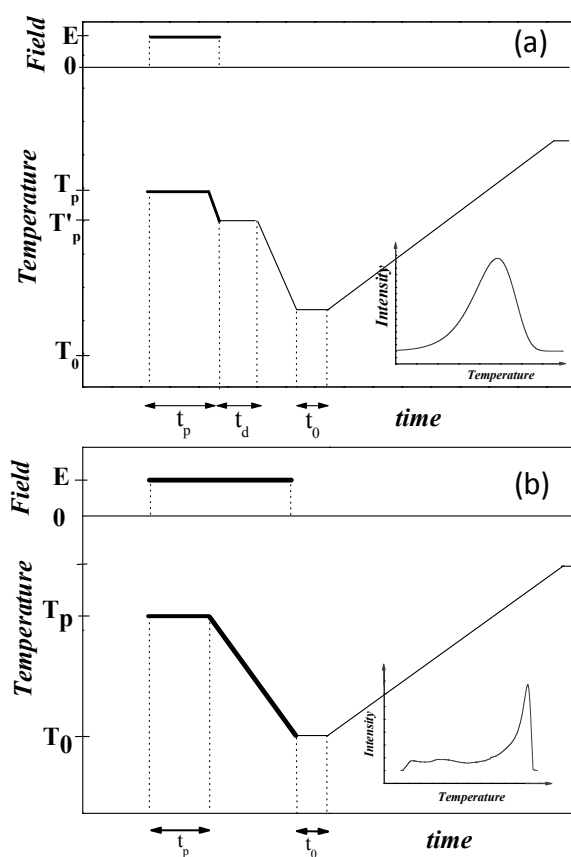


Appendix 1: Experimental procedure

In a TSDC experiment, the sample under study is placed between the electrodes of a parallel plane capacitor. When a dc electric field is applied, at a given temperature (T_P) for a given period of time (t_p), a polarization is induced in the sample as result of the preferential orientation of permanent dipoles. In order to retain the polarization originated at this T_P , the sample is cooled down to a temperature $T_P' = T_P - \Delta T$ in the presence of the electric field and only when the sample attains this T_P' the electric field is removed. Depending of the width of the temperature interval, ΔT , over which the sample is cooled under the effect of the electric field, more or less variety of dipolar motions will be frozen. Finally, the polarized sample is submitted to a constant rate heating process up to T_P in such a way that the different dipolar motions previously hindered recover progressively their mobility and the sample returns to the equilibrium state. This depolarization process gives rise to a measurable current intensity, I , the depolarization current, which is recorded as a function of temperature.

The difference between global (Scheme 1.a) or partial (Scheme 1.b) TSDC experiments makes references to the width of the polarization window (ΔT) where the electric field is applied. In the limit of a narrow temperature interval, the retained polarization at the beginning of the constant heating rate step would correspond to a single motional process.



Scheme 1: Experimental protocol in the form of a temperature-time diagram for a (a) wide polarization window experiment, and a (b) narrow polarization window, or partial polarization (PP), experiment. Bold lines indicate the temperature window ($\Delta T = T_p - T_p'$) where the electric field is applied. In the inserts are representative peaks obtained for the depolarization current.

Appendix 2: The zero-entropy approximation

When it is assumed that for a single motional process, the decay of polarization with time follows a first order rate process, the next relation is verified: $J(T) = P(T)/\tau(T)$ (Equation 1 in the manuscript). When the derivative in function of the temperature is applied, results that:

$$\frac{dJ(T)}{dT} = \left[\frac{dP(T)}{dT} \frac{1}{\tau(T)} - \frac{P(T)}{\tau^2(T)} \frac{d\tau(T)}{dT} \right] \quad \text{Equation 1}$$

This equation can be combined with **Error! Reference source not found.** (in the manuscript), which described the remaining polarization at a temperature T when a constant heating rate was applied over the polarized sample, given place to:

$$\frac{dJ(T)}{dT} = \left[-\frac{1}{r} - \frac{d\tau(T)}{dT} \right] \frac{P(T)}{\tau^2(T)} \quad \text{Equation 2}$$

When the depolarization current is evaluated at the maximum (at T_m), *i.e.* $[dJ(T)/dT]_{T=T_m} = 0$, this relation lead us to:

$$\left[\frac{d\tau(T)}{dT} \right]_{T=T_m} = -\frac{1}{r} \quad \text{Equation 3}$$

where r is the heating rate of the TSDC experiment ($r = dT/dt$); this equation is a very important feature of the formalism of the TSDC technique. This relation means that at the temperature of the maximum of a partial polarization peak obtained by TSDC, there is a crossing between the time scale of the relaxation process, defined by the temperature derivative of the relaxation time, and the time scale of the thermal sampling experiment, defined by the reciprocal of the heating rate.

As alternative to the Arrhenius equation for describing the temperature dependence of the relaxation time of a single reorientational motion, it is used the Eyring's equation¹ that reads:

$$\tau(T) = \frac{h}{kT} \exp\left(-\frac{\Delta S^\ddagger}{R}\right) \exp\left(\frac{\Delta H^\ddagger}{RT}\right) \quad \text{Equation 4}$$

where h and k are respectively the Planck and the Boltzmann constant, R is the gas constant, and ΔH^\ddagger and ΔS^\ddagger are the molar enthalpy and the molar entropy of activation of the molecular motion respectively. When the Eyring's formalism is then applied to solve the Equation 3, the resulting expression is:

$$\tau(T_m) = \frac{RT_m^2}{r(\Delta H^\ddagger + RT_m)}$$

For local motions, *i.e.* molecular motions that do not involve changes in the activation entropy ($\Delta S^\ddagger = 0$), the latter relation can be reduced to:

$$\frac{RT_m^2}{r(\Delta H^\ddagger + RT_m)} = \frac{h}{kT_m} \exp\left(\frac{\Delta H^\ddagger}{RT_m}\right)$$

which can be used to graphically construct the zero entropy line. From this relationship, it can be concluded that, for a given rate of temperature scan, the temperature location of the maximum, T_m , of the PP components of a non-cooperative relaxation only depends on the corresponding activation enthalpy.

Reference List

- (1) Eyring, H. *The Journal of Chemical Physics* **1936**, *4*, 283-291.