

1981

## A Comment on the T... Relaxation as Observed in Polymers by Means of Thermally Stimulated Current (TSC) Measurements

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A COMMENT ON THE  $T_{\ell\ell}$  RELAXATION AS OBSERVED IN  
POLYMERS BY MEANS OF THERMALLY STIMULATED CURRENT  
(TSC) MEASUREMENTS

We wish to dispute the claim made by Lacabanne et al.<sup>(1)</sup> that a dispersion observed in anionic polystyrene at a temperature above its glass transition temperature,  $T_g$ , using the thermally stimulated current (TSC) technique is of molecular origin. The dispersion whose location is designated  $T_{\ell\ell}$ , is observed when the depolarization current is plotted versus temperature at a fixed temperature-scanning rate.

In a previous publication<sup>(2)</sup>, we argued that the  $T_{\ell\ell}$  relaxation as observed in torsional braid analysis (TBA)<sup>(3)</sup> is not of molecular origin but is caused solely by the temperature variation of the Newtonian viscosity,  $\eta$ , of the material studied as it is supported on an elastic braid. Here we wish to demonstrate that the  $T_{\ell\ell}$  dispersion observed in TSC can likewise be explained in terms of a simple viscosity effect.

Bui et al.<sup>(4)</sup> have shown that a necessary condition for the occurrence of a relative maximum in the depolarization current versus temperature spectrum is:

$$\left(\frac{d\tau}{dT}\right)_{T_{\max}} = -\left(\frac{dT}{dt}\right)_{T_{\max}} = -\frac{1}{b} \quad (1)$$

where  $T_{\max}$  is the temperature at which the current is a maximum,  $\frac{dT}{dt}$  is the temperature-scanning rate and  $\tau$  is the relaxation time for the dipolar or ionic

species responsible for the polarization. Thus, the occurrence of a peak in a TSC scan means only that Equation 1 is satisfied, i.e. that the rate of change of  $\tau$  with temperature has attained a predetermined value fixed by the scan rate,  $b$ . Whether or not this is related to a molecular transition is in general by no means obvious.

Lacabanne et al.<sup>(1)</sup> have determined  $\tau$  as a function of temperature in the region where  $T_{\ell\ell}$  is observed for three polystyrene samples of differing molecular weights using the method described in reference 4. They have shown that the  $\tau$  versus  $T$  behavior can be described very well by means of the Vogel equation (one form of the well-known Williams-Landel-Ferry [WLF] equation):

$$\tau = \tau_0 \exp \left[ \frac{1}{\alpha(T-T_0)} \right] \quad (2)$$

where  $T_0 = T_g - C_2$ ;  $C_2$  is a universal constant appearing in the WLF equation<sup>(5)</sup>.  $C_2 = 50^\circ\text{K}$ .  $\tau_0$  and  $\alpha$  are constants determined by a fit of the experimental  $\tau$  vs.  $T$  data to Equation 2. Equation 2 also describes the relaxation times above  $T_g$  for many glass-forming liquids, both polymeric as well as simple; glycerol is an example of the latter<sup>(6)</sup>. For a liquid whose  $\tau$  versus  $T$  behavior is described by the WLF equation, the specific condition for a relative maximum in the depolarization current is obtained by inserting Equation 2 into Equation 1:

$$g(T) = \frac{\tau}{(T-T_0)^2} = \frac{\alpha}{b} = \text{constant} \quad (3)$$

Because  $\tau$  decreases monotonically with increasing temperature,  $g(T)$  is a monotonically decreasing function of temperature. Thus, during a TSC scan,  $g(T)$  passes from values greater than  $\alpha/b$  to values less than  $\alpha/b$  producing the dispersion observed by Lacabanne et al.<sup>(1)</sup>.

The WLF equation also describes the temperature dependence of the Newtonian viscosity for these same glass-forming liquids;  $\tau$  and  $\tau_0$  in Equation 2 are replaced by  $\eta$  and  $\eta_0$  respectively<sup>(7)</sup>. Thus,  $\eta$  is proportional to  $\tau$  and the criterion for a maximum can be restated: A relative maximum in the depolarization current will occur at that temperature at which the rate of change of viscosity with temperature is equal to a predetermined constant; the constant depends on the scan rate,  $b$ .

We would encourage the authors to perform "control" experiments on a liquid such as glycerol where, we believe, they would also observe  $T_{\ell\ell}$ -type dispersions whose  $\tau$  versus  $T$  behavior would be described by Equation 2. The work of Lacabanne et al. reinforces our previous contention<sup>(2)</sup> that the  $T_{\ell\ell}$  relaxation is caused solely by the temperature dependence of the Newtonian viscosity of the material being studied above its  $T_g$ . It is interesting to note that the mechanical " $T_{\ell\ell}$ " will be observed only when the sample is supported on a substrate while the TSC " $T_{\ell\ell}$ " will occur whether the sample is supported or not.

#### Acknowledgements

Use of the facilities of the Materials Research Laboratory at the University of Massachusetts is gratefully acknowledged.

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