

## Determination of the glass transition temperature by means of electrical measurements

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### INTRODUCTION

The determination of the glass transition temperature,  $T_g$ , of polymers, based on electrical measurements, is generally obtained from dielectric data; direct current conductivity measurements are also used but to a lesser extent. In this latter case the experiments are performed recording the current which, at fixed applied voltage, passes through the specimen at temperatures increasing at a constant rate. The measured conductivity,  $\sigma$ , is then plotted versus the temperature and an inflection point can be observed corresponding to a temperature which can be interpreted as the  $T_g$  of the material<sup>1-4</sup>. However, in some cases<sup>5-7</sup>, the possibility of determining the  $T_g$  by plotting the steady state values of the conductivity,  $\sigma_s$ , has been reported.  $\sigma_s$  is obtained after an electrification time sufficient to achieve a stationary value of the current. However for many glassy polymers, this steady value is not reached even after a very long electrification time especially when the electrical conductivity is very low ( $<10^{-13} \Omega^{-1} \text{cm}^{-1}$ ).

### RESULTS AND DISCUSSION

In this Note electrical resistivity data obtained on styrene-acrylonitrile (SAN) (Kostil Montedison) are reported and compared with mechanical experiments performed for detecting the  $T_g$  of the polymer. The resistivity measurements have been carried out by means of a standard three electrode arrangement<sup>9,10</sup> with an applied electrical field of  $1.33 \times 10^3 \text{ V/cm}$ . The data obtained are reported in Figure 1 as  $\log \sigma$  versus  $1/T$  at different electrification times. The data of Figure 1 are well correlated by a straight line in the temperature range in which the maximum electrification time (900 sec) was sufficient to reach the steady state. Using the equation<sup>8</sup>:

$$\sigma_s = \sigma_0 \exp(-E/kT) \quad (1)$$

an activation energy,  $E$ , of 2.68 eV/

molecule is found from the straight line. In Figure 1 the effect of the electrification time is evident. The curves, at each fixed time, deviate from the straight line at temperatures decreasing with increasing time. This result is similar to the specific volume-temperature,  $V-T$ , data normally used for the determination of  $T_g$ <sup>12</sup>. Also in this latter case there is not a discontinuity in the  $V-T$  curve and the  $T_g$  is obtained by extrapolating the straight lines for the liquid and the glass at a fixed time. Clearly,  $T_g$  measured in this way is dependent on the time of the experiment. This feature is common to most of the techniques for  $T_g$  measurement, where the  $T_g$  values are dependent on the time or on the rate of variation of a given physical property [heat capacity (d.t.a., d.s.c.), specific volume (dilatometry), etc.].

Analogously, also using resistivity data, it is possible to detect a phenomenological  $T_g$  which depends on the electrification time. In particular, choosing a time  $t = 30$  sec and defining  $T_g$  as the temperature corresponding to the deviation from linearity of the  $\log \sigma$  vs.  $1/T$  curve, we obtain (Figure 1)  $T_g = 102^\circ\text{C}$  which is comparable with the value of  $100^\circ\text{C}$  reported in the literature<sup>11</sup>.

In some of these experimental techniques the existence of a 'true' transition (obtained for  $t = \infty$ ) is not yet well assessed due to the experimental difficulties. In the case of  $\sigma_s$  measurements, the data shown by Oster<sup>5</sup> on PVC per  $t = \infty$ , are obtained indirectly by subtracting the transient current measured after a sudden elimination of the power supply, from the transient current obtained during the voltage application. Other literature data<sup>6,7</sup> show a break point in the  $\log \sigma - 1/T$  curve but it is not clearly indicated if a sufficient time has been allowed to reach a steady condition, although the conductivity in the range  $10^{-14}$ - $10^{-7} \Omega^{-1} \text{cm}^{-1}$ <sup>7</sup> could imply that the transient state is very short. The change in the slope on the conductivity-temperature curve corresponding to  $T_g$ <sup>5,7</sup> should mean that two distinct conduction mechanisms with two different

activation energies are active below and above  $T_g$ . This difference could be due to two different types of charge carriers. The transient state is a complicating factor arising from the polarization processes<sup>4,5</sup>. The duration of this phenomenon depends on temperature because it is due to molecular motions which are restricted at low temperatures.

The conductivity results can be

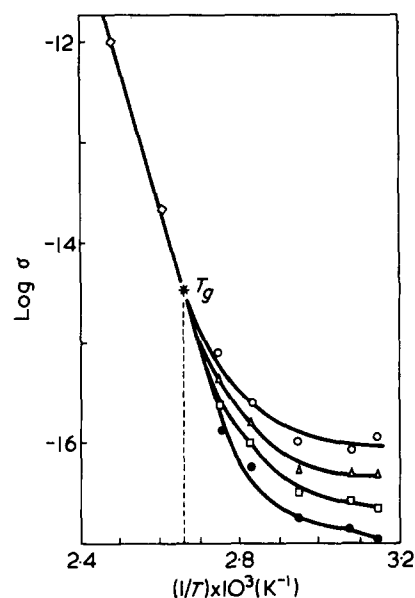


Figure 1 Conductivity,  $\sigma$ , ( $\Omega^{-1} \text{cm}^{-1}$ ) versus  $1/T$  for SAN at different electrification times,  $t$ .  $\circ$ ,  $t = 30$  sec;  $\Delta$ ,  $t = 90$  sec;  $\square$ ,  $t = 300$  sec;  $\bullet$ ,  $t = 900$  sec

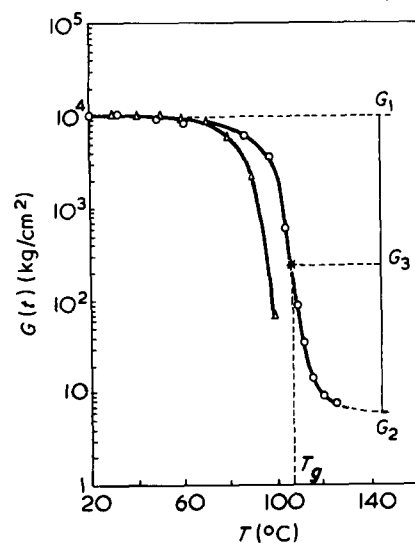


Figure 2 Shear moduli,  $G(t)$  versus  $T$ , at different times of the torque application.  $\circ$ ,  $t = 10$  sec;  $\Delta$ ,  $t = 300$  sec;  $\log G_3 = (\log G_1 + \log G_2)/2$

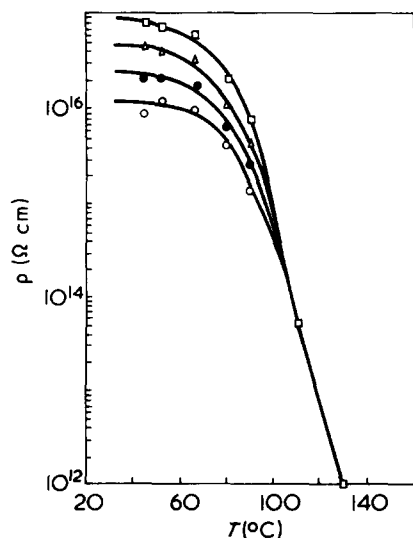


Figure 3 Resistivity,  $\rho$ , ( $\Omega$  cm) versus  $T$  for SAN at different electrification times,  $t$ .  $\square$ ,  $t = 900$  sec;  $\triangle$ ,  $t = 300$  sec;  $\bullet$ ,  $t = 90$  sec;  $\circ$ ,  $t = 30$  sec

compared with the mechanical data shown in Figure 2. In this Figure the shear moduli measured after different times,  $t$ , of application of the torque, are reported, using a Clash-Berg torsional stiffness tester. The isochronal curve obtained for  $t = 10$  sec is generally used for  $T_g$  determination<sup>13</sup> and leads to  $T_g = 106^\circ\text{C}$  for SAN. The curve obtained for  $t = 300$  sec shows a strong dependence of  $T_g$  on the time of the experiment. Mercier and Aklonis<sup>14</sup> discuss the existence of a 'true' transition (for  $t = \infty$ ) for this type of measurement, and correlate these data with those obtained using the dilatometric technique.

To compare electrical and mechanical data more satisfactorily the results shown in Figure 1 are replotted

as resistivity,  $\rho$ , vs. temperature in Figure 3. While the mechanical data are time dependent in the viscoelastic region, the electrical results are affected by the time of the experiment only in the glassy region. In fact the glassy state is a quasi-equilibrium zone for the mechanical response while the viscoelastic region is a transition between a solid and liquid behaviour of the amorphous polymer. With respect to the electrical response, however, the glassy region is affected by the polarization process (i.e. is time dependent) while in the viscoelastic zone only the temperature effect on the stationary current is present.

### CONCLUSIONS

In conclusion, it seems that one should be careful in correlating the discontinuity in the conductivity-temperature curve with the glass transition of the polymer, due to the complexity of the conduction phenomenon. The inflection in these curves can sometimes be an artefact because the data are taken after electrification times not long enough to achieve the steady state condition. In fact, while for poly(vinyl acetate)<sup>1</sup>, the  $\log \sigma$  vs.  $1/T$  curve obtained at steadily increasing temperature shows a break point at  $T_g$ , it does not appear in the  $\log \sigma_s$  vs.  $1/T$  plot.

This fact seems to indicate that, if the polarization process is removed, the  $\log \sigma_s$  vs.  $1/T$  curve presents a break point only if the conduction mechanism is changed during the vitrification

process. The situation is similar to the case of diffusivities of gases in glassy polymers<sup>15</sup>, for which a break in the curve of  $\log$  (diffusivity) vs.  $1/T$  is not always observed at  $T_g$ , depending on the nature of the gas and the polymer.

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## Structure of 3,4-(*cis*-1,4)-*trans*-1,4-polyisoprene by $^{13}\text{C}$ n.m.r.

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### INTRODUCTION

For years  $^1\text{H}$  n.m.r. and infra-red spectroscopic studies have given microstructure information only on content but not on arrangement of the isomeric units of polyisoprene. Little work has been done on polyiso-

prene using  $^{13}\text{C}$  n.m.r. since the work of Duch and Grant<sup>1</sup>. A recent study on the *cis/trans* isomerized 1,4-polyisoprene<sup>2</sup> showed that the distribution of *cis-cis*, *cis-trans* and *trans-trans* linkages can be determined by  $^{13}\text{C}$  n.m.r. Also a detailed account on the sequence structure of a binary

polyisoprene with 3,4 and *cis*-1,4 structural units has recently been published<sup>3</sup>. The purpose of this communication is to report that  $^{13}\text{C}$  n.m.r. spectroscopy gives detailed information on the sequence structure of a ternary polyisoprene with 3,4 and *cis/trans*-1,4 structural units.

### EXPERIMENTAL

The sample was prepared using a sec-butyllithium catalyst in cyclohexane.