

# Study of Some Polyurethane Elastomers Using Electrical Methods

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## SYNOPSIS

A study of some poly ether/ester urethanes has been carried out using electrical methods, viz. dielectric spectroscopy (400–10<sup>5</sup> Hz), dc conductivity, and dc step-response techniques. X-ray diffraction and thermal analysis also are used for characterization of the samples. The studies indicate a hard-segment glass transition  $T_{gh}$  around 318–322 K in addition to a soft-segment glass transition around 233–270 K. The breakage of hydrogen bonding mainly starts above  $T_{gh}$ . The studies also show a hard-segment melting around 1.5–1.8  $T_{gh}$ , but do not reveal any soft-segment melting except in the case of the polyetherurethane sample. © 1994 John Wiley & Sons, Inc.

## INTRODUCTION

Polyurethane block polymers are a family of elastomeric materials whose chains are composed of alternating low glass transition (soft) segments and more rigid, polar urethane (hard) segments that soften much above room temperature. This property makes them very useful industrial materials. The soft segments are generally polyethers or polyesters, and the hard segments are formed from the extension of a diisocyanate (often aromatic) with a low-molecular-weight diol. The existence of microphase separation, caused by clustering of at least some of the hard and soft segments into separate domains, has been well established.<sup>1–5</sup> The typical polyurethane is extensively hydrogen (H—) bonded, the donor being the —NH group of the urethane linkage. The H-bond acceptor may be in either the hard urethane segment (the carbonyl of the urethane group) or the soft segment (an ester carbonyl or ether oxygen). The breakage of H bonding and its connection to the phase separation has been the subject of much discussion in a number of studies.<sup>1–9</sup> In the present communication, we report our experimental findings on the above subject for some

polyurethane block polymers that have been prepared by the reaction of bis (chloromethyl) compounds with potassium cyanate in dimethylformamide (DMF) in the presence of ether-glycols.

## EXPERIMENTAL

The samples used in this study were prepared and characterized using infrared spectroscopy, viscometry, and dilatometry, as described by Ibrahim et al.<sup>10,11</sup> and some of the relevant details are given in Table I along with the molecular formulae. The molecular weight estimated from the viscosity data using the Mark–Houwink relation<sup>12</sup> is found to be around a few tens of thousands. All the samples were characterized further using X-ray spectroscopy, differential Thermal analysis (DTA), and thermogravimetric analysis (TGA) and were studied in detail using dielectric spectroscopy and dc conductivity.

The X-ray diffractograms were obtained at room temperature with a Phillips unit (Phillips X-ray Generator PW1140), which has a vertical goniometer attachment. Nickel-filtered Cu-K<sub>α</sub> radiation was used for the X-ray studies. The DTA and TGA were taken on a Simultaneous Thermal Analyser Model No. STA 780 series (Stanton Redcroft, UK).

All the samples were studied in detail using dielectric spectroscopy and dc step-response tech-

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**Table I** Details of the Samples under Study

Sample Code	Chemical Structure	Viscosity ( $\eta$ ), dl/g
S1		0.14
S2		0.58
S3		0.61
S4		0.48

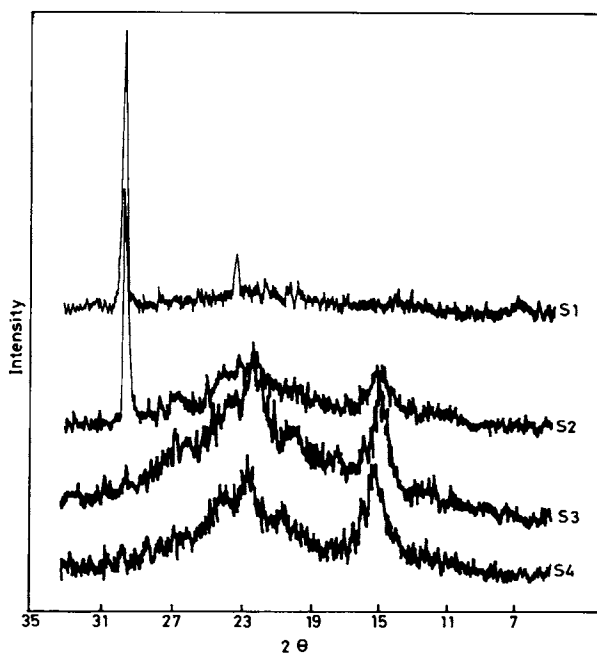
nique. Dielectric relaxation data were taken in the temperature range 298–403 K and in the frequency range 200 Hz–100 KHz. A three-terminal electrode assembly, with a guard ring arrangement, was used for this purpose, and the temperature was controlled with the help of an electronic controller. The highest temperature covered in these experiments is 403 K due to onset of degradation of the samples. As all the samples are in powder form, pellets of 1.3 cm<sup>2</sup> and 0.1–0.2 cm in thickness were prepared with a vacuum die at a pressure of 3 Kbar. Electrical contacts were made with the help of evaporated electrodes on both faces of the sample.

The dc step-response technique was used to measure the absorption (charging and discharging) currents, which incorporate a Keithley 610 Electrometer and a dc power supply. The system was capable of measuring currents down to 10<sup>-15</sup> A. The maximum temperature of measurement was limited to 373 K due to considerable ionic conduction and visible decomposition of the samples. For further details of this experimental setup and dc conductivity measurements, the reader may consult Ref. 13.

## RESULTS

The X-ray diffractograms taken at room temperature (Fig. 1) indicate that the first two samples, viz.

S1 and S2 (see Table I), are partially crystalline and show an intense peak in the vicinity of 29°–30°. However, samples S3 and S4 are found to be more or less amorphous with some less intense crystalline peaks in the region of 23°–25° and 14°–16°.



**Figure 1** X-ray diffractograms for the samples.

**Table II** Details of Various Transition Temperatures

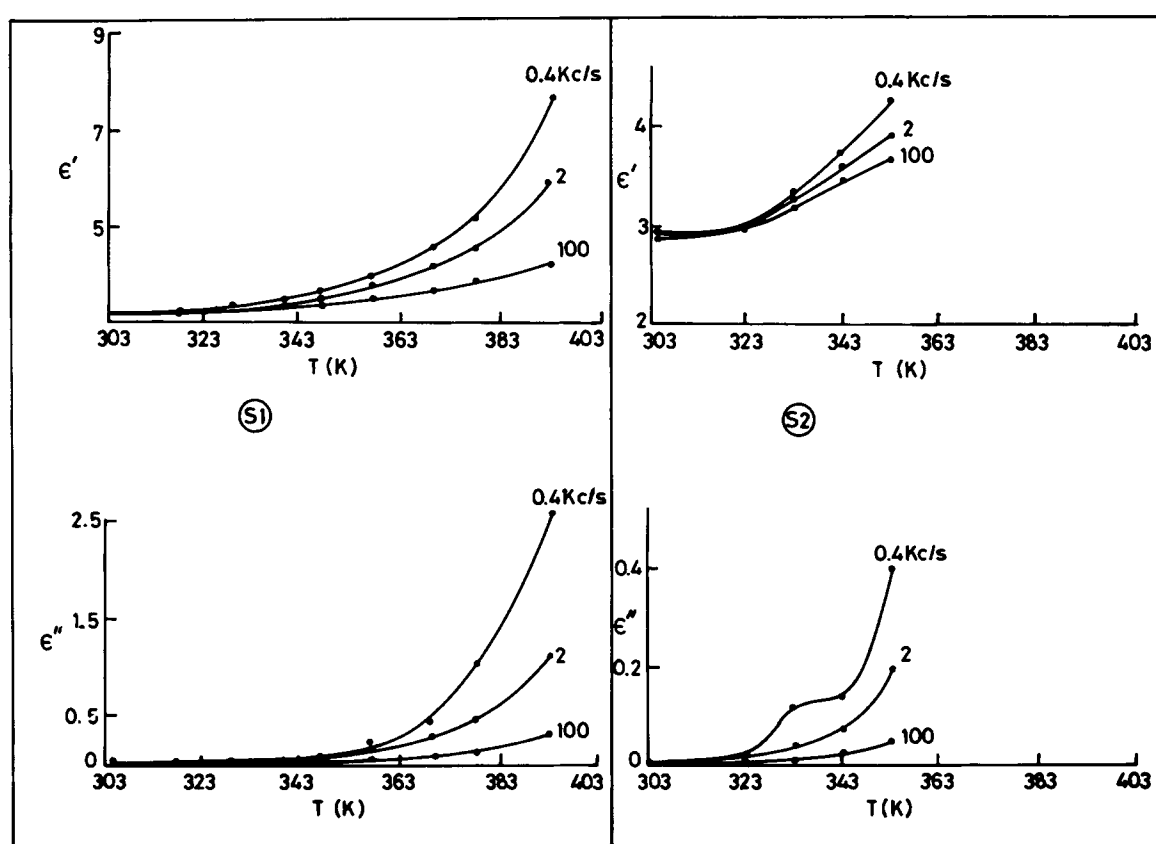
Experimental Method	Transition Temperature (K)			
	S1	S2	S3	S4
Dilatometry <sup>a</sup>	262 <sup>b</sup>	244 <sup>b</sup>	247 <sup>b</sup>	232 <sup>b</sup>
DTA	321, <sup>b</sup> 552	325 <sup>b</sup>	326, <sup>b</sup> 527	309, <sup>b</sup> 487.5
Conductivity	323, <sup>b</sup> 351	330.5 <sup>b</sup>	319.5 <sup>b</sup>	303 <sup>b</sup>
Discharge currents	322, <sup>b</sup> 363	322.5 <sup>b</sup>	322 <sup>b</sup>	300 <sup>b</sup>
Dielectric relaxation (400 Hz)	358	338	—	325

<sup>a</sup> Taken from Refs. 10 and 11.

<sup>b</sup> Corresponds to glass transition.

The thermogravimetric data reveal that all the samples are stable up to 473–523 K (2% weight loss). The DTA curves do not reveal the melting as a sharp and pronounced event due to low crystallinity and also, perhaps, due to polydispersity. Hence the peak temperature of the endotherm is taken as the melting temperature. In general all the samples reveal a small steplike change in the DTA baseline around 303–328 K, characteristic of a glass transition event (see Table II).

In Figures 2 and 3, we show the variations of the dielectric constant and loss with temperature, which show a shoulder at the lower frequency side indicative of the onset of a relaxation process. The case of S1 is shown separately in Figure 4, in the form of  $\log \epsilon''$  vs.  $1/T$  to enable us to see a small steplike change in the curves in the vicinity of 353 K at all frequencies, indicative of a small melting event. We show the relaxation behavior of the samples at all temperatures in Figure 5 in the form of Cole-Cole


**Figure 2** Variation of  $\epsilon'$  and  $\epsilon''$  with temperature in S1 and S2.

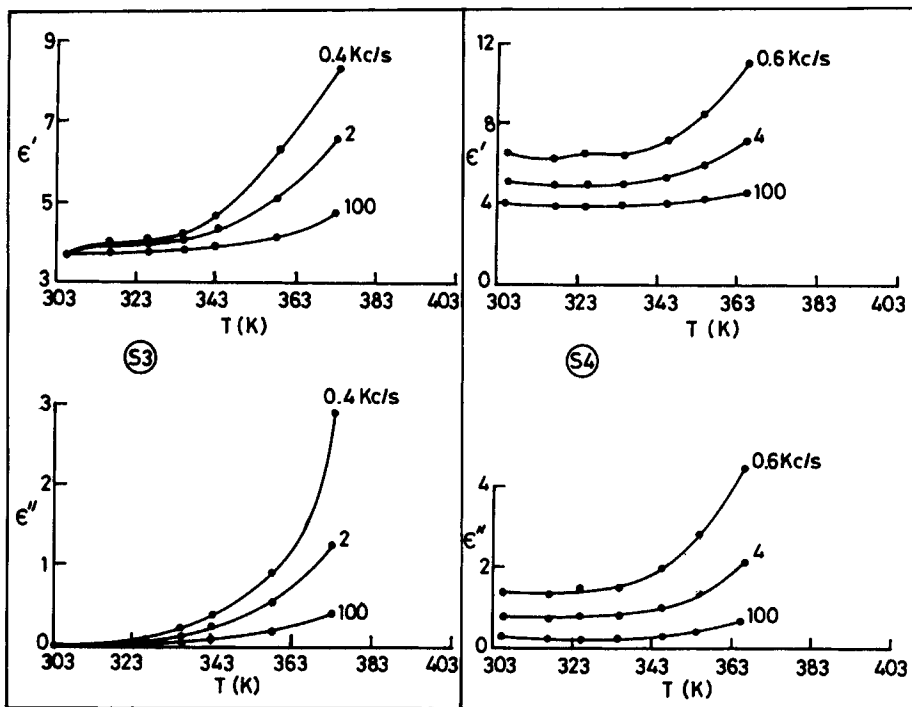


Figure 3 Variation of  $\epsilon'$  and  $\epsilon''$  with temperature in S3 and S4.

diagrams (i.e., the dielectric constant  $\epsilon'$  is plotted against the dielectric loss  $\epsilon''$ ), which can be described by a Hevriliak-Negami equation<sup>14</sup>:

$$\frac{\epsilon^* - \epsilon_\infty}{\epsilon_0 - \epsilon_\infty} = \frac{1}{[1 + (i\omega\tau_0)^{1-\alpha}]^\beta} \quad (1)$$

where  $\tau_0$  is the relaxation time,  $\epsilon_0, \epsilon_\infty$  are the limiting dielectric constants, and  $\alpha, \beta$  are the distribution parameters.

In Figure 6, we show the temperature variation of the isochronal discharging current for samples S1 and S3 as representative of the samples. In Figure

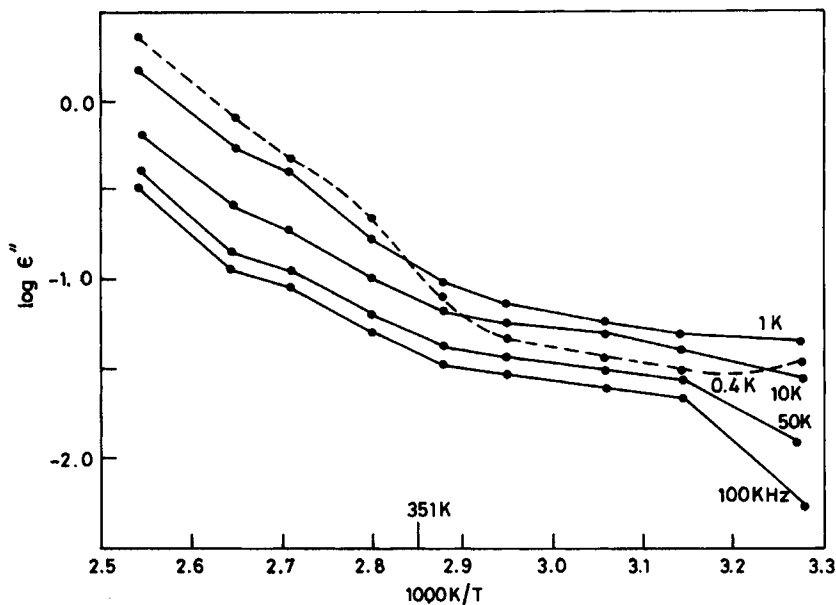


Figure 4 Variation of  $\epsilon''$  in S1 with  $10^3/T$ . Note that around 351 K, there is a small steplike change in  $\epsilon''$  values at all frequencies.

7, we show the Arrhenius plot of the dc conductivity. For the other details of the measurements the reader may consult Ref. 13.

All the samples, in the high-temperature region, exhibit ionic conductivity that appears as a power law behavior of the form<sup>15,16</sup>:

$$(\epsilon' - \epsilon_\infty) \propto \epsilon'' \propto f^{n-1} \quad (2)$$

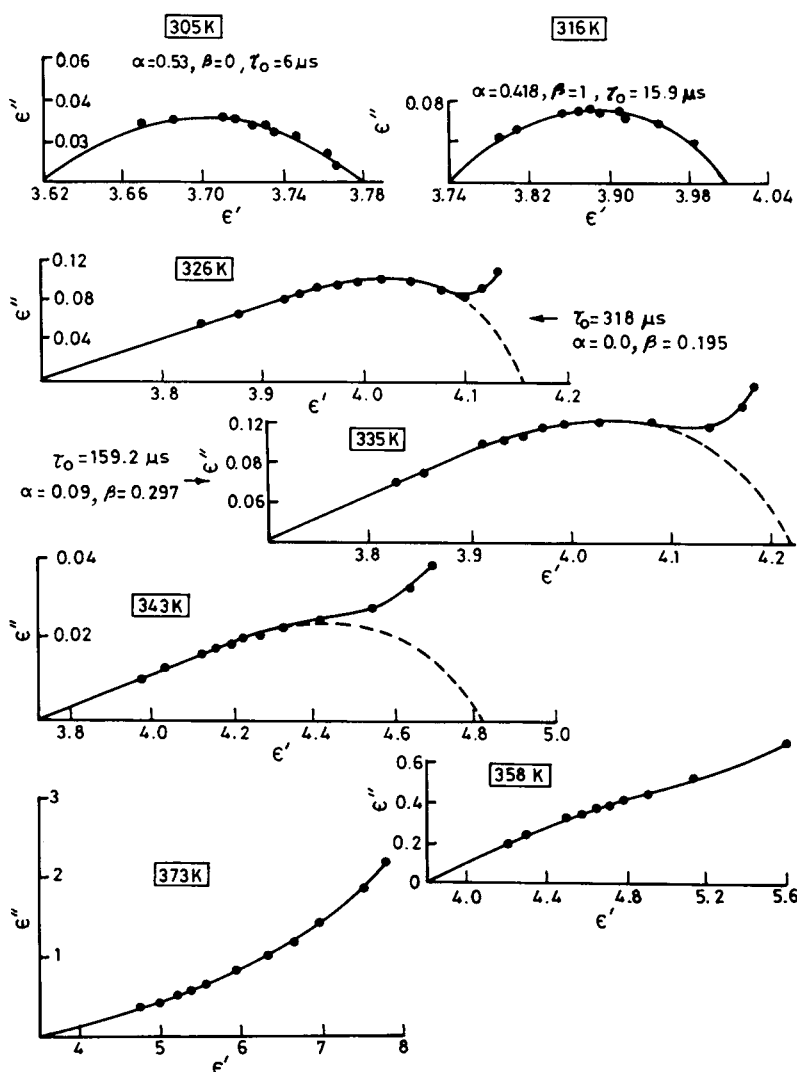
$$\frac{\epsilon''}{\epsilon' - \epsilon_\infty} = \cot \frac{n\pi}{2} \quad (3)$$

for the real and imaginary parts of the complex dielectric constant. In the above equations the parameter  $n$  may be described as a short-range order parameter. In Figure 8 we show this situation for the

case of two of the samples, where the curves are normalized as described in Ref. 15. It is noticeable that the samples decompose at much lower temperatures in the presence of an electric field due to the large ionic conduction that dissipates lots of energy in the medium.<sup>17</sup>

## DISCUSSION

The X-ray diffractograms of these polymers (Fig. 1) show that overall they are amorphous in nature. One possible reason for this may be the presence of methyl groups in the side chain (see Table I), which can cause steric hindrance for close packing of the molecules and thereby reduce their crystallinity. The



**Figure 5** C—C plot of S3 at different temperatures. The parameters of Eq. (1) are also given.

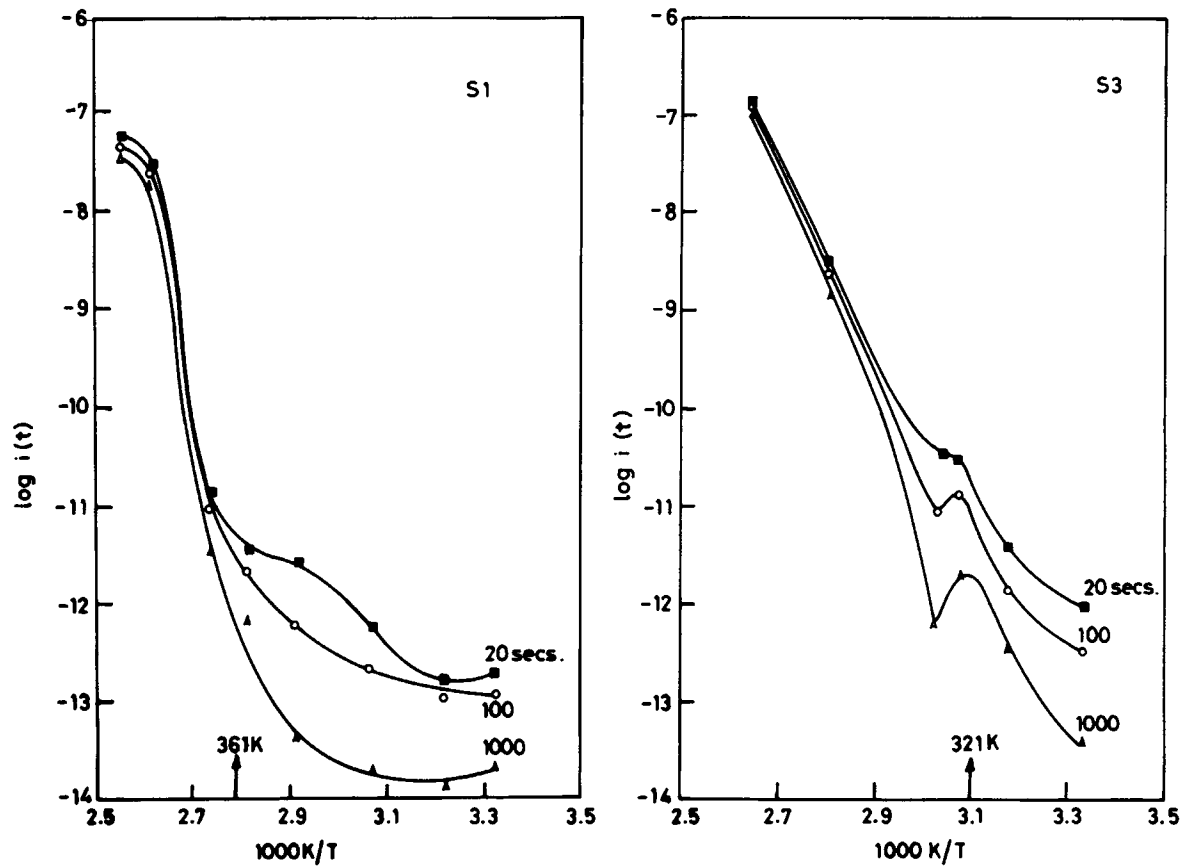


Figure 6 Variation of isochronal discharge currents in S1 and S3 with  $10^3/T$ .

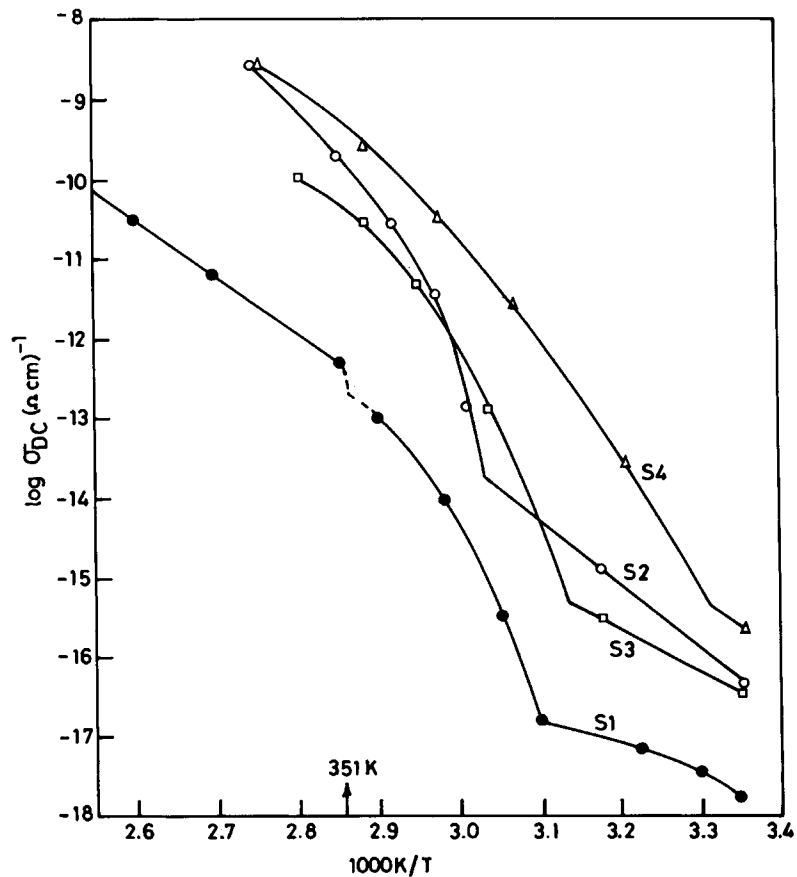
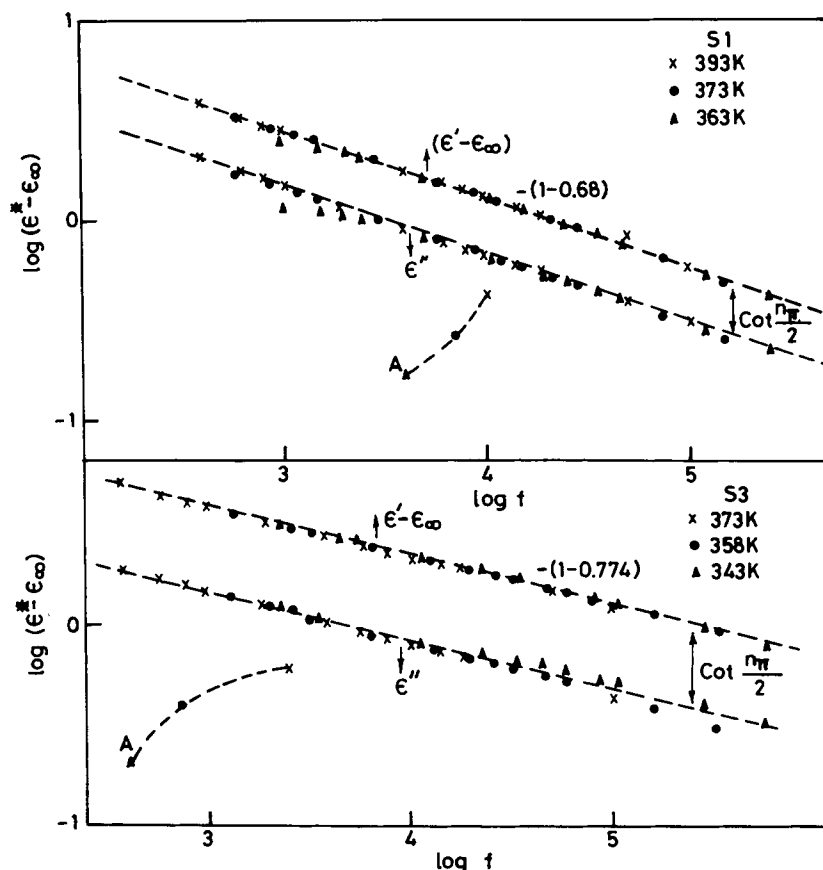


Figure 7 Arrhenius diagram of the dc conductivity in the samples. Note that all the curves show a discontinuity of the slope around 318–323 K and in addition the curve corresponding to S1 shows a small steplike change in the vicinity of 351 K.



**Figure 8** Variation of  $\epsilon''$  and  $(\epsilon' - \epsilon_\infty)$  with frequency in S1 and S3. Point A is the reference point for normalization<sup>15,16</sup> of the curves. Note that both  $\epsilon''$  and  $(\epsilon' - \epsilon_\infty)$  follow Eq. (2). The value shown above the curves is the slope, which is equal to  $-(1 - n)$ .

para-linked polymers S1 and S2, however, showed partially crystalline patterns (in the vicinity of  $29^\circ$ – $31^\circ$ ), whereas the meta-linked polymer showed a typical amorphous pattern. This tendency has also been noticed in the other polymers, viz. polyether urethanes synthesized by Ibrahim et al.<sup>10,11</sup> The DTA of the samples show clearly two transition temperatures (Table II). The one around 318–323 K, which is seen as a small steplike change in the baseline, probably corresponds to the hard-segment glass transition ( $T_{gh}$ ). The second transition, which is seen as a small endotherm in samples that have some amount of crystallinity, is clearly due to the melting of the crystallites. The ratio of this temperature to  $T_{gh}$  is around 1.5–1.7, which is similar to the case of other polymers.<sup>18</sup> This observation tempts us to attribute the melting in these polymer to the hard segment ( $T_{mh}$ ). In Figure 7 the corresponding dc conductivity curves clearly reveal a sharp break around  $T_{gh}$ , above which the variation of the dc conductivity is William–Landel–Ferry (WLF) type as in nylons,

etc.<sup>13</sup> Note that below  $T_{gh}$ , the dc conductivity is very small. These observations clearly show that the transition  $T_{gh}$  can be considered as the actual glass transition for all practical purposes.

The dielectric relaxation data of these samples clearly show that there is some molecular mobility even at room temperature, which is probably due to the soft segments. But if one looks at the magnitude of the dielectric strength ( $\epsilon_0 - \epsilon_\infty$ ) (see Fig. 5, for example), it gives the impression that the movement of the soft segment is highly hindered. The variation of the real and imaginary parts of the dielectric constant with temperature (Figs. 2 and 3) indicate a small shoulder on the low-frequency (400 Hz) side around 345 K, which is probably due to the large-scale mobility of the hard segments above  $T_{gh}$ . However, the peaks in dielectric loss are masked by the large ionic losses (see Fig. 5) at higher temperatures. One may also notice some change in the shape of the C—C diagrams above  $T_{gh}$  in Figure 5. The relaxation time obtained by force fitting the data to

Eq. (1) appears to increase with temperature, which is probably due to the overlapping of the primary relaxations corresponding to soft and hard segments and a low-frequency ionic polarization mechanism.

The isochronal discharge current data on these polymers clearly indicate peaks with temperature as shown in Figure 6, the locations of which coincide approximately with  $T_{gh}$  values. Also, significant ionic conductivity is seen above  $T_{gh}$ , which varies in a WLF fashion with temperature.<sup>13</sup>

In S1 there is no clear evidence of  $T_{gh}$  either in the dielectric data or in the discharge current data (see Figs. 2 and 6). However, these measurements indicate a sharp steplike change in the dielectric loss (Fig. 4) and dc conductivity (Fig. 7) and discharge current data (Fig. 6) around 353 K, which may perhaps be due to soft-segment melting ( $T_{ms}$ ). However, there is no indication of such a change in the DTA data.

## CONCLUSIONS

We have studied some polyurethane elastomers using X-ray, thermal analysis, dc conductivity, dielectric spectroscopy, and dc step-response techniques:

1. These polymers exhibit a hard-segment glass transition ( $T_{gh}$ ) in the region 318–323 K above which the H-bonding breakage and hence ionic conductivity starts.
2. All the polymers exhibit hard-segment melting ( $T_{mh}$ ) around 1.5–1.7  $T_{gh}$ .
3. There is no evidence of any soft-segment melting in the samples except for the polyether urethane sample.

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