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Influence of chain extenders and chain end groups on properties of segmented polyurethanes. II. Dielectric study

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Thermally stimulated depolarization currents (TSDC) measurements (temperature range 77–300 K) and broadband a.c. dielectric relaxation spectroscopy (frequency range 10 mHz–2 GHz) were employed to investigate molecular mobility and microphase separation in model segmented polyurethanes (SPUs) from oligotetramethylene glycol 1000, 4,4′-diphenylmethane diisocyanate and different chain extenders. The magnitude of the interfacial Maxwell–Wagner–Sillars (MWS) polarization TSDC peak and of d.c. conductivity have proved to sensitively reflect changes of the degree of microphase separation (DMS). The dielectric strength of both the primary and the secondary transition of the soft segments rich microphase are highest for the SPU with the highest DMS, whereas frequency (temperature) position and shape of the response are not significantly affected by DMS.

(Keywords: segmented polyurethanes; degree of microphase separation; primary and secondary transitions)

INTRODUCTION

Microphase separation between soft and stiff segments (SFT and STF, respectively) may be regarded as the most prominent feature of segmented polyurethanes (SPUs) manifesting itself by the occurrence of two temperature intervals of softening of SFT and STF (T_{g1} and T_{g2}), respectively. The location of these two temperature intervals gives an idea on the degree of microphase separation (DMS); the latter is higher the closer the T_{g1} and T_{g2} are to the softening temperatures of SFT and STF homopolymers, and is lower otherwise.

In the first paper of the present series[1], phase morphology and DMS of two series of model SPUs were shown to depend on the chemical nature and relative content of chain extenders and chain end-groups. This second paper describes the effect of chemical composition on dielectric behavior of samples of the second series of these SPUs in a wide range of frequencies and in a broad temperature interval.

EXPERIMENTAL

Materials used

Details on synthesis and sample preparation are given in the previous paper[1]. Sample coding and chemical composition of materials under investigation are given in *Table 1*.

Thermally stimulated depolarization current (TSDC) measurements

The principle of TSDC is based on the strong dependence of dielectric relaxation time, τ, on temperature T. A brief description of the technique is given below[2]. The sample is inserted between the plates of a capacitor and is polarized by the application of a field, E_p, at a temperature, T_p, for a time, t_p (which is longer than the relaxation time at T_p of the dielectric dispersion under consideration). With the electric field still applied, the sample is cooled down to a temperature, T_o, sufficiently low to prevent depolarization by thermal agitation. Next it is short-circuited and reheated at a constant rate b. A discharge current is generated as a function of temperature which is meassured with a sensitive electrometer. The resultant TSDC spectrum often consists of several peaks whose shape and location are characteristic of the relaxation mechanisms of the sample.

We used a common experimental apparatus for TSDC measurements in the range 77–300 K[3]. The samples, cut from sheets, were cylinders of 13 mm diameter and 0.10–0.50 mm thickness. Typical experimental conditions were $V_p = 300$ V for the polarizing voltage, $T_p = 295$ K for the polarization temperature, $t_p = 5$ min for the polarization time, 6 K min^{-1} for the coooling rate down to T_0, and 3 K min^{-1} for the heating rate.

Table 1 Sample coding and chemical composition of chain extenders and chain ends of SPUs. For details we refer to paper I of this series ([1])

Sample coding	Chain extender, chain end (mol)				
	DIPA	DDDC	OOMQ	MHBC	ABST
355	5	–	1	–	–
357	6	–	1	–	0.8
358	1	0.01	0.1	0.1	–

(All SPU samples have similar soft segments content $x \cong 0.6$)

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A.c. dielectric measurements

Broadband a.c. dielectric relaxation spectroscopy measurements were taken using two different experimental set-ups. In the frequency range of 5 Hz to 2 × 10^9 Hz and the temperature range of 173 to 363 K, two Hewlett-Packard Network Analysers (HP 3755B and HP8510B) were used. The samples were placed in a shielded capacitor-like measurements cell inserted into a transmission line, in a home-made thermostatic oven and the transmission coefficient was measured. The dielectric parameters can be determined via these impedance measurements[4]. A Schlumberger frequency response analyser (FRA 1260) supplemented by a buffer amplifier of variable gain was used for measurements in the frequency region 10^{-2}–10^6 Hz. We performed complex admittance measurements with a two-terminal electrode configuration. For both set-ups the samples were in the form of discs of 13 mm diameter and of 0.10–0.50 mm thickness.

RESULTS AND DISCUSSION

TSDC studies

Figure 1 shows the TSDC thermogram measured on the 355 sample. The TSDC spectra from all the samples exhibit a structure similar to that shown in *Figure 1*.

Four dispersions are well discerned: β_2, β_1, α, and a fourth one above T_g in the order of increasing temperature. The β_2 peak is located at 113 K and the β_1 peak at 163 K. These secondary relaxations have been associated with local motions of chain segments[5,6]. Measurements with different polarizing fields and mesurements with blocking electrodes (thin insulating foils between the sample and the capacitor plates) indicate[2,3] that both the α peak and the fourth peak above T_g are due to bulk (volume) polarization. These results suggest, in particular, that the fourth peak above T_g is due to Maxwell–Wagner–Sillars (MWS) interfacial polarization rather than to space-charge polarization, which is in agreement with results obtained with other polyurethane systems[7,9]. The α peak is dipolar and is located near to the calorimetric glass transition temperature[7], whereas the MWS peak is related with morphology changes at glass transition[6,8]. For the polyurethanes under investigation the α peak located at 223 K arises from the reorientation of the polar soft segments of the chain during the glass transition of the soft (SFT)-rich microphase. DSC measurements confirm this result[1]. The MWS peak located in the temperature range 248–254 K is due to dielectric polarization between the SFT-rich and the stiff (STF)-rich microphases[8,9].

The normalized current maximum I_n of the α peak and of the MWS peak in *Table 2* is the current maximum (current at peak temperature, T_m) divided by heating rate, surface area of the sample and polarizing field. It is a measure of the contribution of a peak to the static dielectric constant, $\Delta\varepsilon$, i.e. a measure of the number of relaxing units contributing to the peak[2].

Table 2 Temperatures T and normalized current maxima I_n of the α and MWS peaks for the samples under investigation

	α Peak		MWS peak	
SPU	I_n (a.u.)	T_α (K)	I_n (a.u)	T_{MWS} (K)
355	0.22	223	0.16	248
357	0.20	222	0.24	254
358	0.33	223	0.73	253

a.u., arbitrary units

Within experimental error for I_n (± 10%), no systematic changes were observed in the magnitude of the α peak for samples 355 and 357, whereas the highest values of I_n were observed for sample 358. We note that all three SPU samples have similar soft segment contents, $x \cong 0.6$. The highest I_n value for sample 358 may be explained by an increased degree of microphase separation (DMS) caused by a dilution of DIPA with crown-ether containing DDDC

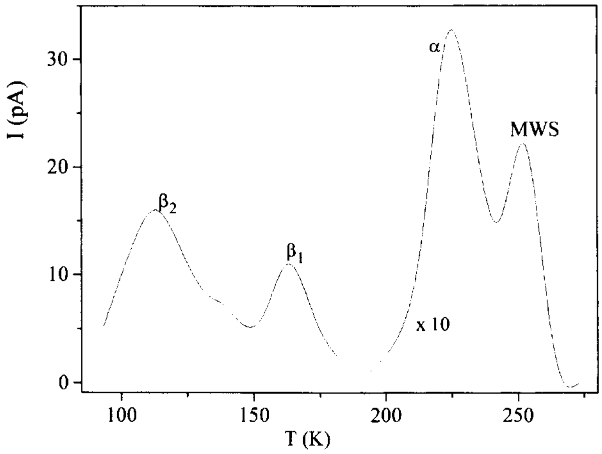

Figure 1 TSDC thermogram for sample 355

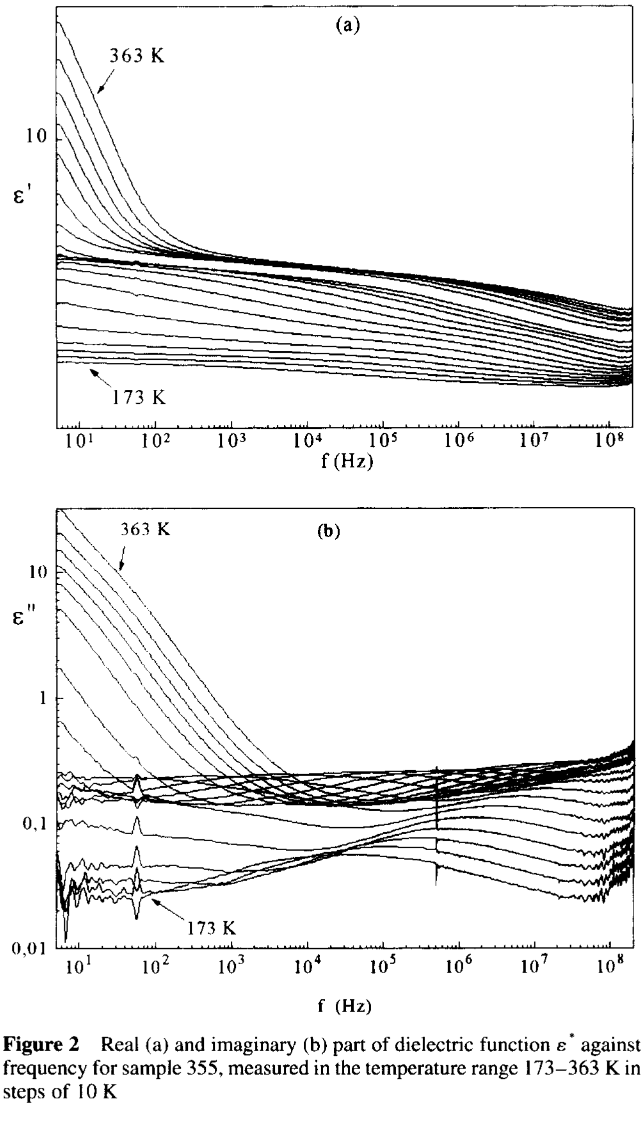

Figure 2 Real (a) and imaginary (b) part of dielectric function ε^* against frequency for sample 355, measured in the temperature range 173–363 K in steps of 10 K

and MHBC, which is in agreement with the results of SAXS measurements on the same samples[1]. From the methodological point of view it is interesting to note that higher DMS results in higher I_n (TSDC) and lower Δc_p at glass transition (DSC)[1].

The MWS peak in the polyurethanes studied is related to the ionic polarization of MWS type (interfacial polarization) in the diffuse interphase boundary region between STF and SFT-rich microphases[8]. The higher value of I_n of the MWS peak for sample 358 (*Table 2*) suggests that the total surface area of the interphase boundary region between hard and soft segment phases is larger for sample 358, i.e. the polyurethane containing crown-ether fragments into hard block segments. This result is consistent with the higher DMS for sample 358 (I_n for α peak and Ref. [1]).

We now turn our attention to the temperature position of the α and the MWS peaks. A.c. dielectric measurements and a.c. DSC measurements of the dynamics of the glass transition in the glass-forming liquid salol (phenyl salicylate) have shown that the corresponding Arrhenius plots practically coincide in the common frequency range of the two techniques[10]. These results suggest that although the phenomena measured are physically different, both techniques probe the mobility at glass transition of units of similar size. This justifies the use of dielectric techniques to measure glass transition temperatures[11]. In addition, TSDC measurements are carried out at heating rates similar to those used in DSC (a few K min^{-1}), i.e. TSDC and DSC are characterized by similar time scales. For these reasons, the temperature of current maximum of the TSDC α peak (peak temperature, T_α) is a good measure of the calorimetric glass transition T_g as confirmed by measurements on several systems[3,7–9]. T_α for all three samples was found to be about 223 K, within experimental errors (± 2 K), which is in agreement with the results of DSC measurements on the same samples[1]. This result suggests in particular that the molecular mobility of the soft segments in the SFT-rich microphase is not affected by the incorporation of crown-ether (DDDC) into the rigid chain blocks (STF). Also the temperature position of MWS peak for all three samples shows no systematic variation.

A.c. studies

The dielectric behavior of a material is usually described by using the dielectric function, $\varepsilon^*(\omega,T)=\varepsilon' - i\varepsilon''$. In *Figure 2* we show in log–log plots the real and the imaginary parts of ε^* against frequency f, for sample 355 in wide ranges of temperatures (T = 173–363 K) and frequencies (f = 5 Hz–2 × 10^9Hz). Similar results were obtained with samples 357 and 358. Due to the wide ranges of frequencies and temperatures, the dielectric spectra of *Figure 2* include practically all the relaxations present in the material under investigation.

At low temperatures *Figure 2b* shows the secondary mechanism which shifts to higher frequencies with increasing temperature. We assign this mechanism to overlapping of the β_1 and β_2 mechanisms in TSDC measurements (*Figure 1*). At higher temperatures ($T > 243$ K) the α peak associated to the glass–rubber transition of the SFT-rich microphase enters our frequency window and shifts to higher frequencies with increasing temperature.

The high values of ε' and ε'' at low frequencies and high temperatures do not refer to the bulk of the material. They indicate the existance of space-charge polarization and free-charge motion within the material (related to the conductivity current relaxation)[12].

Figure 3 shows for comparison $\varepsilon''(f)$ for 355, 357, 358 samples at $T = 253$ K. The α peak dominates the spectra in the KHz frequency range. At higher frequencies we observe the secondary β relaxation. In agreement with the TSDC results, the frequency position of the α peak is practically the same for all three samples, whereas the magnitude of the peak is higher for sample 358. The same is also true for the secondary β relaxation. Measurements at several temperatures provided results similar to those in *Figure 3*. Thus, it appears that higher DMS results in the increased intensity of not only the main α transition for segmental motion, but also for the smaller scale mobility responsible for the secondary β transition.

The shape of the isothermal a.c. responce is often described quantitatively by the Havriliak–Negami (HN) equation[13]:

$$\varepsilon^*(\omega)=\varepsilon_\infty+\frac{\Delta\varepsilon}{[1+(i\omega\tau)^{1-\alpha}]^{\beta}} \qquad (1)$$

where $\Delta\varepsilon=\varepsilon_s-\varepsilon_\infty$ the relaxation strength, and α, β shape parameters describing the shape of the $\varepsilon''(\omega)$ peak below and above the frequency of the peak, ($0 \le \alpha < 1$, $0 < \beta \le 1$). The relaxation time ($\tau = 1/2\pi f_{HN}$) is closely related to the peak frequency. A sum of two HN terms was fitted to the experimental data similar to those shown in *Figure 3*, and the results of the fitting procedure applied in the whole frequency range of the spectra for samples 355, 357, 358 at 243 K are listed in *Table 3*. These results confirm that for both relaxations, $\Delta\varepsilon$ is larger for sample 358 whereas the position (τ) and the shape (α, β) of the peaks do not change systematically from sample to sample. The latter is confirmed also by scaling plots (not shown here).

Using susceptibility measurements we can estimate energy parameters associated with a mechanism (loss peak in $\varepsilon''(f)$ plots) through the so-called Arrhenius plots. The temperature-dependence of the relaxation time τ of the

Table 3 Parameters of the HN equation (equation (1))

	355		357		358	
	α-Relax	β-Relax	α-Relax	β-Relax	α-Relax	β-Relax
$\Delta\varepsilon$	2.57	1.32	3.2	1.5	3.8	2.0
$1-\alpha$	0.80	0.61	0.75	0.70	0.73	0.60
β	0.84	0.80	0.80	0.80	0.72	0.64
f_{HN}(Hz)	270	8×10^6	212	7×10^6	212	4×10^6

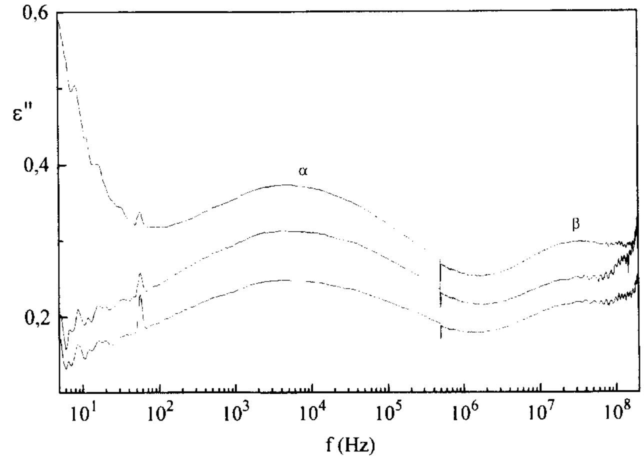

Figure 3 Dielectric losses, ε'', against frequency, f, for samples 355, 357, 358, from bottom upwards, measured at $T = 253$ K.

molecular motions responsible for the secondary mechanism is usually described by the Arrhenius equation

$$\tau = \tau_0 \cdot \exp(E/kT) \qquad (2)$$

where τ_0 is the pre-exponential parameter, k is Boltzmann's constant, and E is the apparent activation energy[5]. For the cooperative α-relaxation, the temperature dependence of τ is often described by the Vogel–Tammann–Fulcher (VTF) equation[14]:

$$\tau = A \cdot \exp[B/(T - T_0)] \qquad (3)$$

where A is the pre exponential parameter B is an activation parameter and T_0 is the ideal glass transition temperature ($T_0 \approx T_g - 50$)[5].

Figure 4 shows the Arrhenius plots ($f = 1/(2\pi\tau)$ against reciprocal temperature) for $\varepsilon''(f)$ data for samples 355, 358 and 357. The lines are fits of equations (2) and (3) to the β and α data respectively. TSDC points are also included in the plots. They correspond to the frequency at which a.c. experiments should be performed in order to obtain a loss peak having the same peak temperature as the TSDC peak and should have been deduced from the fitting parameters[15].

The results of the fitting procedure are listed in *Tables 4* and *5*. The β relaxation is described by practically the same E and τ_0 parameters for all three samples. For the α relaxation, it is striking that the VTF parameters are different for sample 358 compared with the other two samples and that T_0 is unsusually small for sample 358. At this stage we can only speculate about the significance of these results, which may be indicative of the fact that the cooperative primary α process is more sensitive to morphology changes than the local secondary β process. It should be noted that the lowest frequency of measurements in *Figure 4* is 5 Hz and there is some ambiguity with the VTF fits.

Figure 5 shows the a.c. conductivity for samples 355, 357, 358 measured at 343 K. Again, samples 355 and 357 show similar overall behavior, whereas sample 358 is characterized by values at low frequencies which are two orders of magnitude higher. D.c. conductivity values for all three samples were obtained at several temperatures from extrapolations to low frequencies of plots similar to those shown in *Figure 5* [16]. The corresponding Arrhenius plot is shown in *Figure 6*. For samples 355 and 357 $\sigma_{dc}(T)$ is described by

$$\sigma_{dc} = \sigma_0 \exp[-E'/kT] \qquad (4)$$

with the parameters listed in *Table 6*, whereas the VTF equation

$$\sigma_{dc} = A' \exp[-B'/(T - T'_0)] \qquad (5)$$

describes the data for sample 358 with parameters $A' = 2.5$

Table 4 Parameters of the Arrhenius equation (equation (2)) for the α relaxation

	355	357	358
E_{act} (eV)	0.32	0.29	0.36
τ_0 (s)	3.1×10^{-15}	1.3×10^{-15}	3×10^{-16}

Table 5 Parameters of VTF equation (equation (3)) for the α relaxation

α-Relax	355	357	358
A (s)	2.9×10^{-13}	2.5×10^{-12}	6.3×10^{-16}
B (K)	439	362	763
T_0 (K)	147	157	119

Table 6 Parameters of equation (4) for the d.c. conductivity

SPU	E (eV)	σ_0 (S/m)
355	0.34	9.5×10^{-5}
357	0.30	2.5×10^{-7}

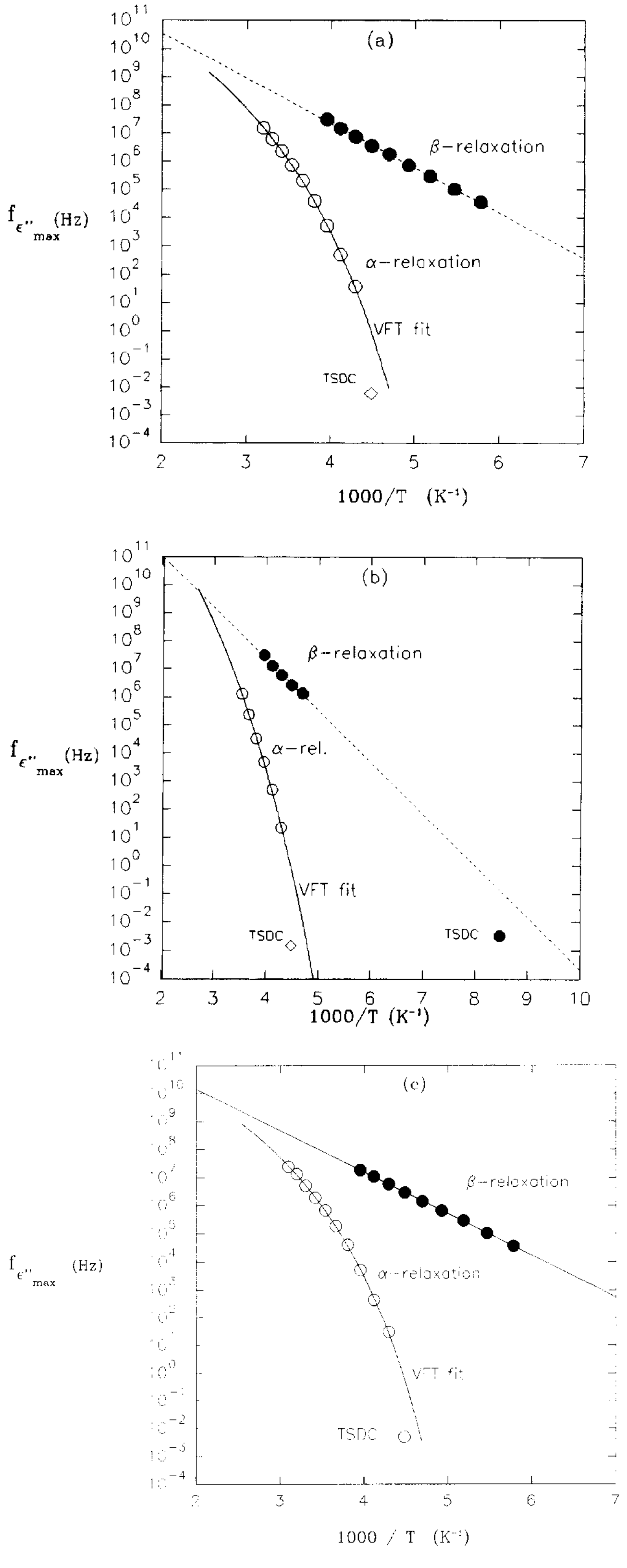

Figure 4 Arrhenius plots for samples 355 (a), 358 (b), and 357 (c)

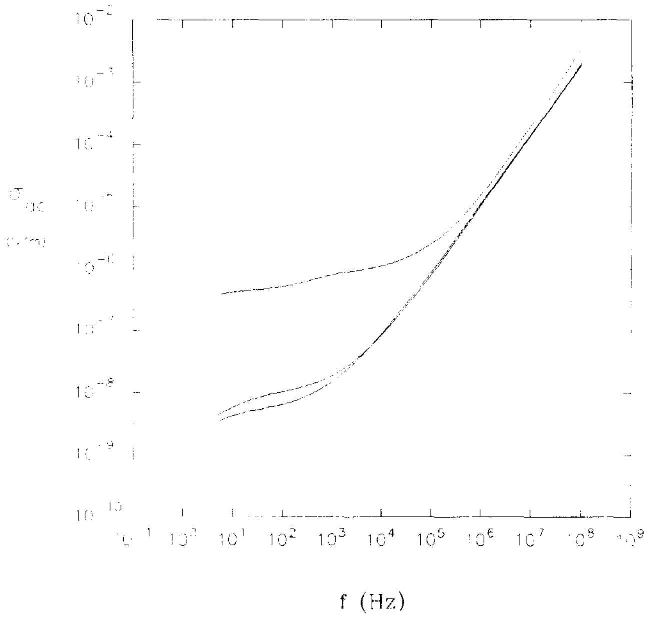

Figure 5 A.c. conductivity, σ_{ac}, against frequency, *f*, for samples 355, 357, 358, from bottom upwards, measured at $T = 343$ K

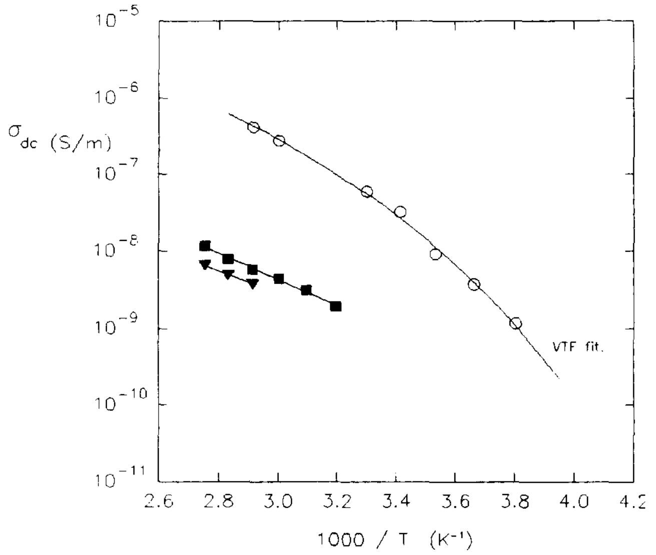

Figure 6 Arrhenius plot of the d.c. conductivity values for samples 355 (■), 357 (▼) and 358 (O)

$\times 10^{-4}$ (S/m), $B' = 201$ K and $T'_0 = 178$ K. The results are consistent with a conductivity mechanism governed by the cooperative motion of polymer chain segments (similar to polymer electrolytes[17]) in the case of sample 358 and with a charge carrier diffusion-controlled conductivity mechanism in the case of samples 355 and 357.

The different behavior of sample 358 compared with samples 355 and 357 with respect to d.c. conductivity may suggest long-range connectivity of the more conductive SFT-rich microphases in the case of sample 358, which is characterized by larger DMS, or alternatively, conductivity through the diffuse boundary region between SFT and STF-rich microphases. Measurements on samples from series 1 [1] should help to clarify whether the increased d.c. conductivity is related to the addition of MHBC to the polyurethanes.

CONCLUSIONS

1. Judging by the normalized intensities of MWS peaks of TSDC thermograms, the DMS of studied SPUs changes in the order: 358 > 357 ≅ 355.

2. The higher DMS of sample 358 compared with samples 355 and 357 results in higher values of strength of both the primary and the secondary relaxation mechanisms, whereas frequency and shape of the response are not significantly affected.

3. The higher d.c. conductivity of sample 358 compared with 355 and 357 may be explained by the stronger tendency of STF for self-association due to long-range electrostatic interactions between negatively-charged cavities of crown ethers, and proton-donating sites of SFT fragments.

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