

Dielectric Properties of Segmented Polytetramethyleneoxide-Based Polyurethanes

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Synopsis

Three series of segmented polyurethanes, based on polytetramethylene oxide (PTMO) soft segments, having molecular weights of 650, 1000, and 2000 and MDI/butane diol hard segments, were synthesized and their dielectric properties examined. The effect of the soft segment length, soft segment concentration (ssc) as structural variables, and frequency and temperature as experimental variables, on relative permittivity and $\tan \delta$, were examined. The results were discussed in terms of the structural parameters such as the degree of phase separation and soft segment phase state. It was found that both soft segment length and ssc strongly affect dielectric behavior.

INTRODUCTION

Segmented polyurethanes are a class of block copolymers, consisting of alternating "hard" and "soft" blocks.¹⁻⁵ Due to the immiscibility of the blocks, phase separation takes place. The morphology of these two-phase systems varies with soft segment concentration (ssc) from a continuous hard phase with a dispersed soft phase (at low ssc) to a continuous soft phase with dispersed hard domains (at high ssc).⁶ Intermediate morphology, with both phases continuous, is found at about equal concentrations of the two phases.⁷ Soft segments are usually made of polyether or polyester chains having molecular weights between 1000 and 3000, while the hard segment usually consists of a diisocyanate and short chain diol or diamine, called "chain extender." The properties of segmented polyurethanes can be varied across a wide range, by varying soft segment length, ssc, and chemical structure of both segments. One of the important features of these polymers is that their mechanical behavior can be varied from the nylonlike, at low ssc, to the soft rubberlike, at high ssc.

Hard domains in the soft phase play the role of physical crosslinks, allowing high elastic (reversible) deformations. Polyurethane elastomers are advanced materials with many applications in various fields. Thus, the study of property-structure relationships is of great scientific and practical importance. It has been found, however, that the degree of phase separation is determined

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not only by the chemical structure of both phases, but also by the previous thermal and mechanical history.^{8,9} Very often, investigations on these polymers are carried out on nonequilibrium structures, thus producing contradictory results. The structure of these systems is also chemically heterogeneous, depending on the method of synthesis.¹⁰ The most regular structures are obtained by the two-step solution polymerization process, while synthesis in bulk tends to give a wider distribution of chemical structures, i.e., soft segment concentrations, differing from the average ssc.

The mechanical properties of these systems have been widely studied, but very few references deal with dielectric properties. Since both the hard and the soft phases of these polymers can be either crystalline or amorphous complex dielectric spectra are to be expected. Also, the existence of an interphase layer would make the picture even more complicated. The hard phase behavior can be compared with that of either the linear polyurethanes or the polyamides. The close similarity of mechanical and dielectric transitions in various polyamides and polyurethanes suggests that the main factor in determining the transitions is the structure due to hydrogen bonds and not the structure of the main polymer chains.¹¹ The α -transition at about 50°C is ascribed to the glass transition of the amorphous part of the polymer. The transition at about -60°C takes place when water is present and is consequently weak in dry polymers. At still lower temperatures of -120°C local motions of groups between hydrogen bonds take place. Kajiyama and MacKnight¹² studied the γ -transition in a series of polyurethanes with different number of CH₂ groups between urethane groups and were able to resolve three types of γ -relaxations, all coming from relaxations of the sequence of CH₂ groups from various parts of the molecules. The δ -relaxation at about -160°C was assigned to the rotation of the methyl group. On the other hand, the high molecular weight polytetramethylene oxide polymer has its melting point at about 35°C, and displays a glass transition at about -50°C while the β -transition takes place at about -120°C. The dielectric and mechanical α -relaxations occur in the same frequency-temperature locations, and the same is true for the β -regions.¹³

Thus, a combination of pure urethane (hard segment) and PTMO relaxation spectra are to be expected in segmented polyurethanes, but specific effects may be expected from the various lengths of both soft and hard segments as well as from their interactions. North and co-workers¹⁴⁻¹⁶ studied dielectric relaxation in poly(ethylene glycol) (PEG) and poly(propylene glycol) (PPG)-based polyurethanes at low frequencies. They found several dielectric processes in order of increasing frequencies: (1) polarization of sample-electrode interfaces (10^{-5} - 10^{-1} Hz); (2) polarization of domain boundaries (Maxwell-Wagner-Sillars polarization), which was found to depend on the impurity level and thermal history but independent of charging voltage and electrode material; (3) ac conduction; and (4) orientation polarization of the polyether segment.

Delides and Pethrick¹⁷ carried out ultrasonic and dielectric studies on polyester-segmented polyurethanes. They found that an increase of the segment length produced an increase in the activation energy for the glass transition. A dielectric study of filled segmented polyurethanes based on polyacetal polyether and PPG soft segments revealed an α' transition in the

region of 85–120°C, related to the hard domain T_g , an α transition at 0–16°C, related to the soft segment T_g , and a high temperature transition at about 150–180°C, related to melting of hard domains.¹⁸ Vallance et al.¹⁹ studied the glass transition region in segmented PTMO-based polyurethanes. They varied molecular weight of PTMO from 977 to 5430 but also the soft segment concentration in a narrow range from 56 to 73% at the same time. The emphasis in their study was on the effect of crystallinity of the soft segment on dielectric behavior. Generally, crystallinity restricts motion of the chains suppressing their orientation in the direction of the electric field. As a consequence, relative permittivity and $\tan \delta$ remain low.

In this study, the effect of soft segment length *and* concentration on dielectric properties was studied. At molecular weights lower than 2000, the soft segments do not crystallize and the full contribution to segment-dipole orientation is obtained. Three series of polyurethanes based on polytetramethyleneoxide (PTMO) glycols of different length were synthesized. Series A was based on PTMO having MW = 650, series B on PTMO having MW = 1000, and series C on soft segment MW = 2000. The concentration of the soft segment in each series was varied in regular intervals from 0 to 60% or higher, where it was possible.

The hard segment was based on diphenylmethane diisocyanate (MDI) and butane diol as chain extender. The chemical structure of the polymers is given on Figure 1, and the composition in Table I.

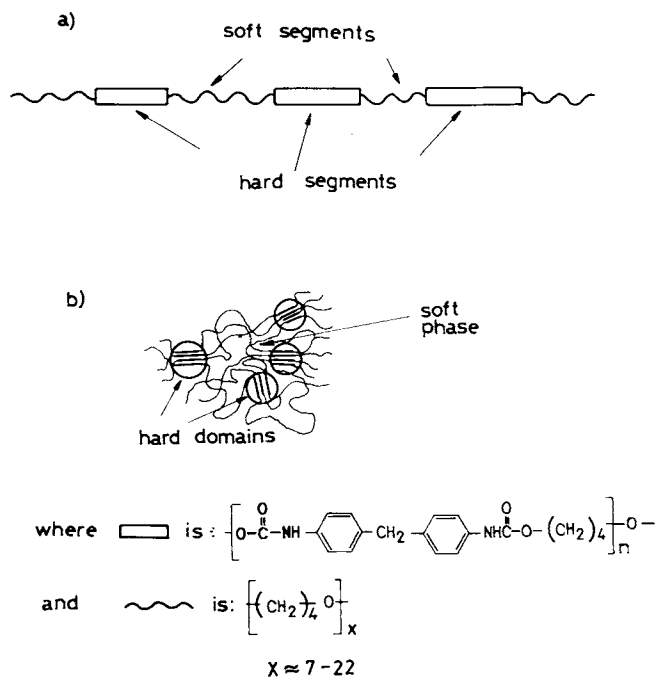


Fig. 1. Schematic representation of segmented structure of the polyurethane molecule (a) and the two-phase structure of the bulk polymer (b).

TABLE I
Designation and Composition of Polyurethane Samples

ssc (%)	20	40	50	60	68.3	77.5	80	87
A series (PTMO 650)	A1	A2	A3	A4	A5			
B series (PTMO 1000)	B1	B2	B3	B4		B5		
C series (PTMO 2000)	C1	C2	C3	C4			C5	C6

EXPERIMENTAL

Materials

A detailed description of the synthesis and properties of all three series of polyurethanes is given in Refs. 20 and 21. The polymers were tested in the form of films, cast from DMF, roughly 0.2 mm thick.

Methods

The measurement of permittivity and conductivity was carried out using a bridge method with an ac current, by measuring the capacity and the conductivity of the measuring condenser. This measuring setup allows simultaneous and continuous monitoring of the dependence of permittivity and conductivity on temperature and frequency. The temperature range used was from -80 to 180°C and the frequency from 0.6 to 200 kHz. The layout of the measuring set up is given on Figure 2. The error of measurement of absolute permittivity was generally caused by the uncertainty of thickness measurement and was assessed to be about 5%, while the error of the permittivity change was much smaller, about 0.2%.

RESULTS AND DISCUSSION

Figures 3 and 4 show the dependence of relative permittivity and $\tan \delta$ on temperature and frequency for sample A_2 . The relative permittivity was

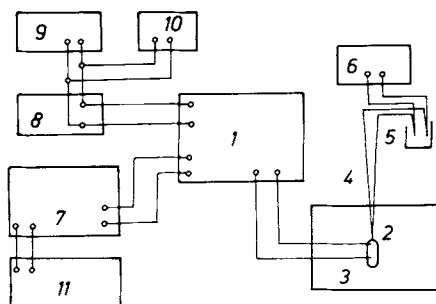


Fig. 2. The layout of the measuring setup: (1) measuring bridge; (2) measuring condenser; (3) thermostatic chamber; (4) thermocouple; (5) reference bath for the thermocouple; (6, 10) digital multimeter; (7) ortholoc; (8) frequency meter; (9) function generator; (11) x , y_1 , y_2 plotter.

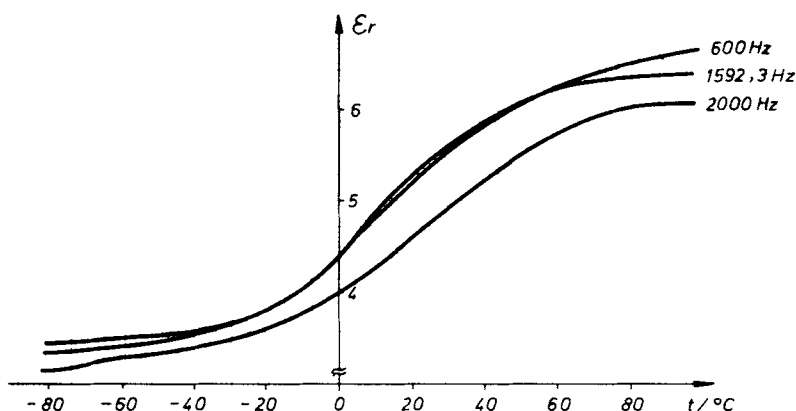


Fig. 3. Dependence of relative permittivity on temperature with sample A2, at 600, 1952.3, and 20,000 Hz.

found to increase from about 3 to about 6 in a broad temperature region from -20 to 60°C , indicating a major transition such as T_g . T_g values assessed by DSC and dynamic mechanical methods were about -40° and -4°C , respectively. The so-called α transition is related to the glass transition of the soft segment and is dependent on frequency. When frequency is increased from 0.6 to 20 kHz, dielectric $\tan \delta$ maxima occur at about 5 and 15°C . Careful inspection of the $\tan \delta$ curves reveals upward trends, leading to additional maxima below -80°C and above 80°C . Testing above 80°C was limited by the change of sample thickness under the load of electrodes due to softening. Dynamic mechanical analysis (DMA) reveals a peak at about -120°C , which is expected to shift to higher temperatures in dielectric measurements due to the higher frequencies used. The increase in $\tan \delta$ above 80°C is related to the hard segment T_g , which was found at about 80°C . It is interesting that $\tan \delta$ in this region is strongly frequency-dependent, indicating considerable conduction losses at lower frequencies. The effect of ssc on the position of the glass transition in series A is illustrated in Figures 5 and 6.

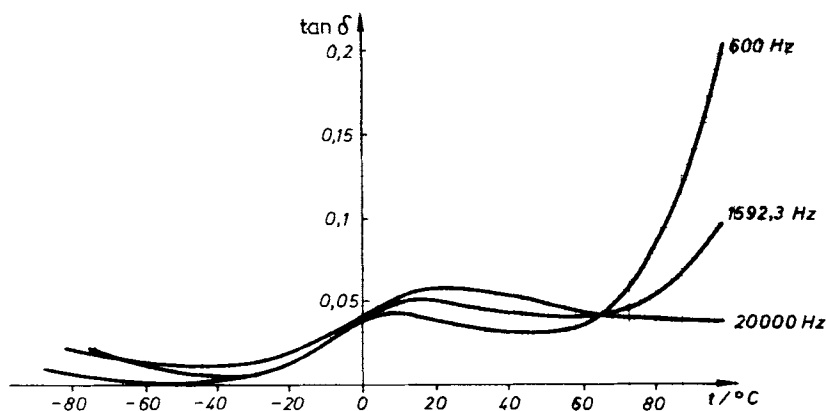


Fig. 4. Dependence of $\tan \delta$ on temperature with sample A2, at 600, 1952.3, and 20,000 Hz.

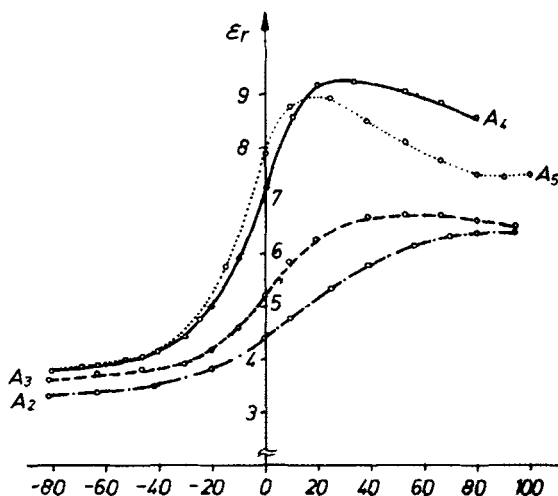


Fig. 5. Dependence of relative permittivity on temperature at 1592.3 Hz for samples in A series.

Figure 5 displays the change of relative permittivity with temperature, at 1592.3 Hz, which is higher, the higher the soft segment content. However, this jump is especially high between A_3 and A_4 , i.e., between 50 and 60% ssc where phase inversion (change from two continuous phases to one single continuous soft phase) is expected. If the magnitude of the $\tan \delta$ peak correlates with the freedom of segmental rotation, then this freedom should be greater at higher ssc. This can be judged from the magnitude of $\tan \delta$ per unit ssc (Table II).

Another feature of the dependence of the peak temperatures on ssc is that they shift to lower temperatures with increase in ssc. The same behavior is observed with the B series (Figs. 7 and 8), except that $\tan \delta$ maxima appear at lower temperatures. Table III shows temperatures of α peaks at two frequen-

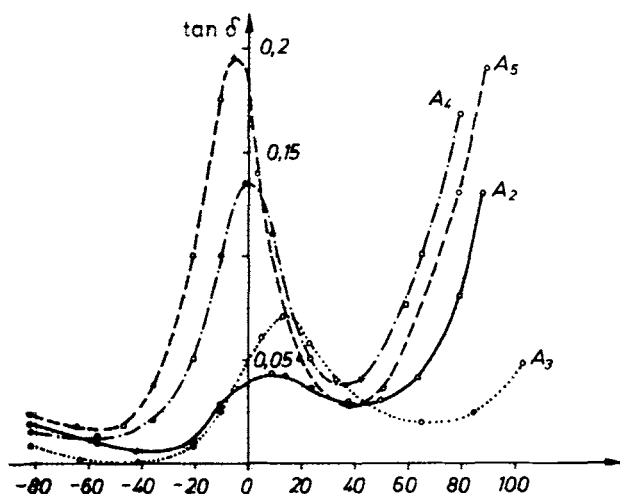


Fig. 6. Dependence of $\tan \delta$ on temperature at 1592.3 Hz for samples in A series.

TABLE II
Change of Relative Magnitude of $\tan \delta$ per Unit Mass of Soft Segment

Polymer	ssc (%)	$\tan \delta$	$10^4 \times \tan \delta / \text{ssc}$
A ₂	40	0.043	11
A ₃	50	0.072	14
A ₄	60	0.135	23
A ₅	68.3	0.196	29

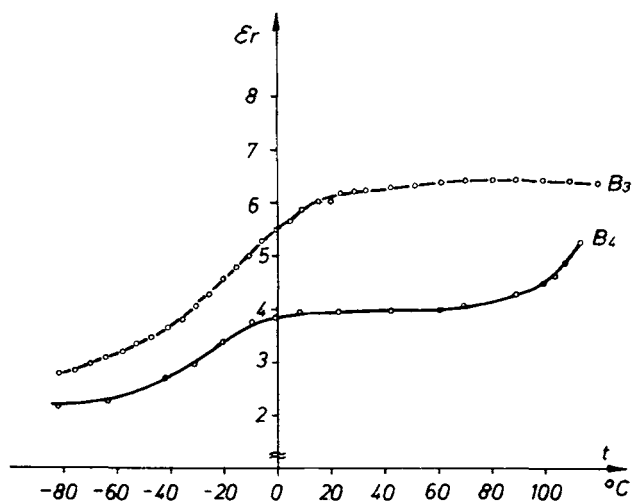


Fig. 7. Dependence of relative permittivity on temperature, at 1592.3 Hz for B3 and B4.

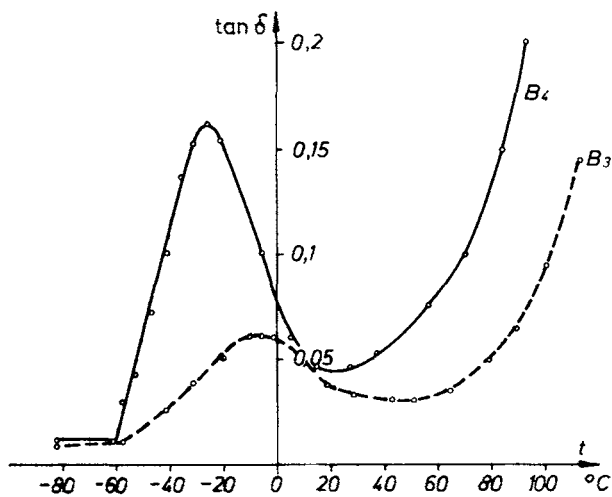


Fig. 8. Dependence of $\tan \delta$ on temperature, at 1592.3 Hz for B3 and B4.

TABLE III
Glass Transitions of the Soft Segment in A and B Series at 1952.3
and 20,000 Hz and Corresponding Activation Energies E_a

Polymer	T_g (°C) at 1592.3 Hz	T_g (°C) at 20 kHz	E_a (kJ/mol)
A ₂	13	22	197
A ₃	15	23	224
A ₄	0	20	84
A ₅	-5	5	157
B ₃	-7	7	112
B ₄	-26	-10	85

cies and the corresponding activation energies for both A and B series polymers.

C series polymers displayed completely different behavior (Figs. 9 and 10). Relative permittivity did not show the characteristic S-shaped transition between -80 and 120°C . In addition, low temperature $\tan\delta$ maxima were observed at about -30°C and two additional maxima were seen at about 40 and 80°C , with sample C₅. This behavior can be attributed to crystallization of the soft segment which does not occur with the other two series. Thus, the

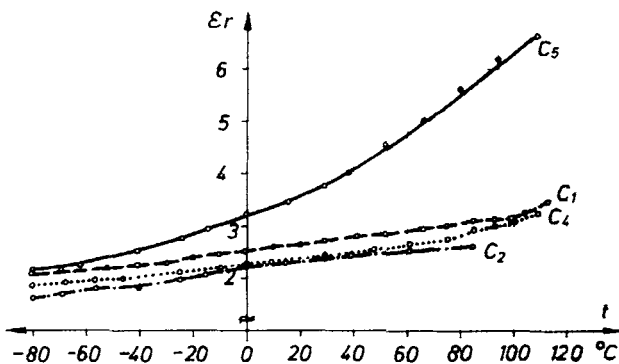


Fig. 9. Dependence of relative permittivity on temperature at 1592.3 Hz for samples in C series.

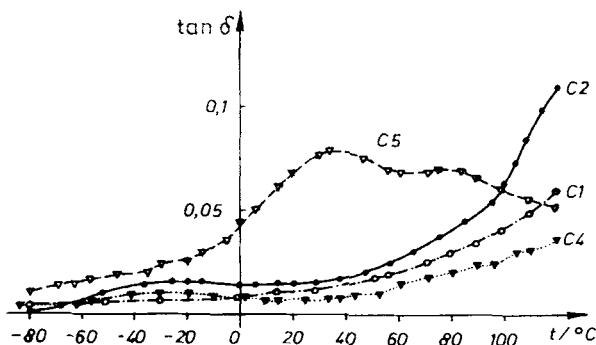


Fig. 10. Dependence of $\tan\delta$ on temperature, at 1592.3 Hz for samples in C series.

fraction of molecules taking part in the amorphous glass transition (at -30°C) is very small. It should be emphasized that all polymers were tested at least 1 year after synthesis; thus, enough time was available to reach equilibrium morphology and maximal degree of crystallization. It has been shown earlier that the PTMO soft segment in polyurethanes crystallizes when its molecular weight is 2000 or higher.^{20,21} Melting of the soft phase crystallites in series C takes place at about $15\text{--}20^{\circ}\text{C}$. At high frequency, this shifts to about 30 or 40°C in C_5 . Interestingly enough, this peak should be expected also in other samples in the series, in particular in C_4 (60% sec), but it was not observed. By increasing soft segment length and decreasing ssc, the length of the hard segment is increased.²⁰ Longer hard segments tend to form larger domains so that phase inversion is shifted to higher ssc. Phase inversion of similar polymers was reported⁶ to be at about 65% ssc, which suggests that dielectric behavior might be controlled by morphology.

If C series samples were cooled relatively quickly (in 2 h from 150 to -80°C), then the curves for C_5 were more like those for the other polymers in the series (Fig. 11). Repeated measurements on quickly cooled C_4 gave practically the same curve with slightly more pronounced maximum at about -30°C and a shoulder starting at about 60°C . All this demonstrates the importance of thermal treatment or morphology of the sample. Activation energies of the glass transition process tends to decrease with increase of the ssc, but there were no clear indications as to how soft segment length would affect them. Higher E_a values suggest a lower mobility of the chains or higher restrictions imposed by the hard phase. However, the reported activation energy for dielectric relaxation at glass transition of PTMO homopolymer is 154 kJ/mol (37 kcal/mol).²² The behavior of the PTMO soft segment in thermoplastic polyesters is not expected to be much different from that in polyurethanes except that hydrogen bonding is absent. Thus, the data of Lilaonitkul and Cooper could be used for comparison.²² They found that activation energy of the PTMO block (MW = 1000) glass transition increases from 154 to 249 kJ/mol as the hard segment concentration increases from 34 to 84 wt %. They also found that annealing decreases and absorbed water increases the activation energy of the β transition. In our case activation energy also decreases with ssc, except for the very low values for A_4 and B_4 of about 85 kJ/mol.

Our general conclusion is that $\tan \delta$ peaks shift to lower temperatures with increase of soft segment length but also with increase in ssc. While the first finding is to be expected, the second differs from DSC data which shows rather little change of T_g with ssc. However, it does agree with dynamic mechanical results. Variation of T_g with soft segment length can be explained by the "network effect," where T_g is dependent on the molecular weight between junctions, which means here, between hard domains which function as crosslinks.²¹ The change of T_g with ssc may be explained by phase mixing, which is expected to be higher in polymers with a higher hard segment content. One must be careful, however, since DSC and partly thermomechanical T_g values do not change with ssc. Increase of the transition temperature in composites by dynamic mechanical tests may only be the consequence of the presence of the high modulus second phase. It is not clear, however, what would cause this shift in dielectric measurements.

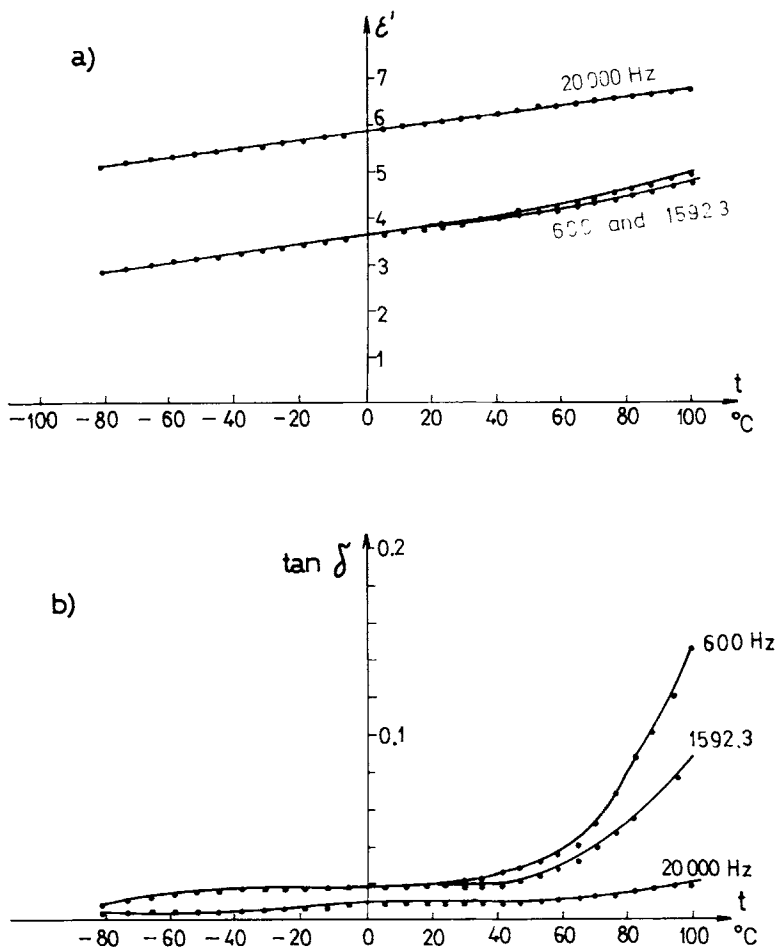


Fig. 11. Dependence of ϵ' and $\tan \delta$ on temperature, at three frequencies, for quickly cooled sample C5.

Dependence of conductivity, κ , on temperature for sample B_3 is shown in Figure 12, and for sample C_2 in Figure 13. At temperatures above the soft segment glass transition region for C_2 ($10^{-3}/T < 3.3$), as shown in Figure 13, $\log \kappa$ decreases almost linearly with the increase of $1/T$, indicating that dc conductivity dominates in this region. Linearity is also observed in the region of the hard segment glass transition ($10^{-3}/T = 2.3-2.7$). In the linearity region (from 37 to 125 $^{\circ}\text{C}$), there is a change of slope, which indicates a change of activation energy. In the region from 35 to 85 $^{\circ}\text{C}$, activation energy is 21 kJ/mol, while, above 85 $^{\circ}\text{C}$, it assumes a value of 36 kJ/mol. In the region of the soft segment glass transition $\log \kappa$ tends to increase or at least does not change with the increase of $1/T$, because dc conductivity is superimposed with the dielectric losses coming from the soft segment glass transition. The sample C_2 is characterized by the continuous hard phase and longer hard segments than those in B_3 , which is reflected in the conductivity-temperature differences.

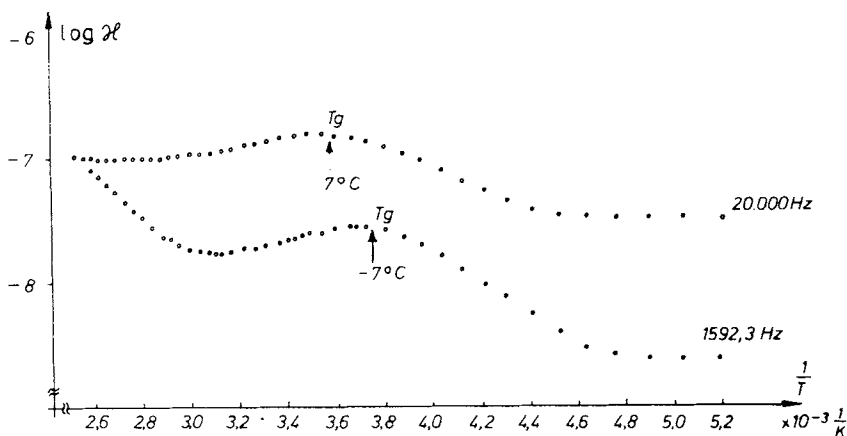


Fig. 12. Dependence of conductivity on temperature, at 1592.3 and 2000 Hz for B3.

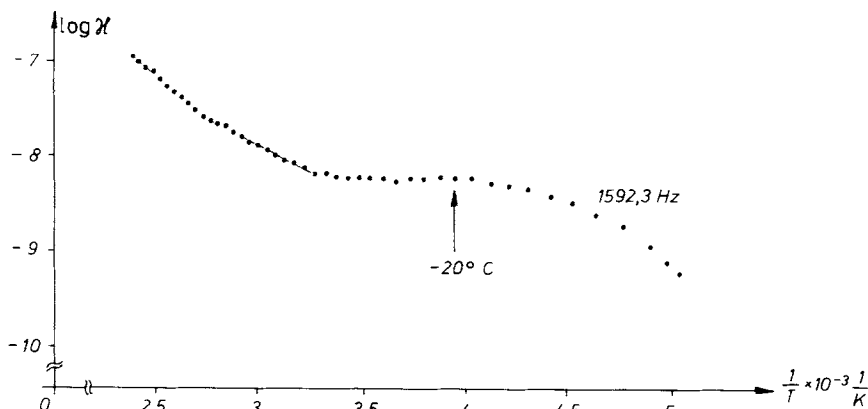


Fig. 13. Dependence of conductivity on temperature at 1592.3 Hz for C2.

Below soft segment T_g , $\log \kappa$ decreases linearly with the increase of $1/T$, but the gradient is less. This fact could be explained by the decrease in the number of charge carriers in the glassy state.

CONCLUSIONS

Three series of segmented polyurethanes based on a PTMO soft segment with molecular weights of 650, 1000, and 2000 were synthesized and the effect of soft segment length and concentration on dielectric behavior, in the region between -80 and 120°C , has been examined. Generally, two relaxation transitions were observed, soft segment glass transition in the region between -30 and 20°C , depending on the soft segment length, ssc, and the frequency of the test, and the hard segment glass transition in the region of 80°C , manifested as the increased loss due to conduction. Also, an indication of the third transition, below -80°C , was observed.

Relative permittivities above the soft segment glass transition were generally higher in samples with shorter soft segments, which was ascribed to the higher contribution to polarization of noncrystalline soft phase in the two series based on lower molecular weights of soft segments. Increasing soft segment concentration within the series brought about an increase in relative permittivity below the hard segment glass transition.

Tan δ values were strongly affected by frequency above 80°C, where high conduction losses were emphasized at lower frequencies. Tan δ maxima, corresponding to the soft segment glass transition, shifted to lower temperatures with increase of the ssc, which could be interpreted as the higher degree of phase mixing at lower ssc. The relative magnitude of tan δ per ssc unit, at the maximum, increased with increase of the soft segment concentration, suggesting a higher mobility of the PTMO chains in samples with higher ssc. Samples in the C series (based on PTMO 2000) displayed completely different relaxation spectra. Tan δ values at the maximum were lower than in the other two series due to the crystallization of the soft segments. The length of the hard segment for the same ssc increased as the soft segment grew longer. Consequently, onset of the conduction region was shifted to higher temperatures.

Activation energies of the soft segment glass transition process were found to decrease with the increase of soft segment length and ssc, demonstrating the higher chain mobility in the longer soft segments and in the continuous soft phase.

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