

A Dielectric Study of the Glass Transition Region in Urethane Elastomers Modified by Ionic Bonds

R. ZIELIŃSKI, *Faculty of Technical Physics and Applied Mathematics, Technical University of Gdańsk, 80-952 Gdańsk, Poland* and M. RUTKOWSKA, *Institute of Organic and Food Chemistry and Technology, Technical University of Gdańsk, 80-952 Gdańsk, Poland*

Synopsis

The urethane elastomers cross-linked by the varying content of triethanolamine and 3-bromo-1,2-propanediol have been investigated by means of dielectric spectroscopy. The complex character of the glass-rubber transition has been determined. It results from different mechanisms of cross-linking (urethane and ionic bonds). The influence of content of cross-linking mixture on the microphase separation has been observed.

INTRODUCTION

The thermomechanical characteristics of urethane elastomers are the result of a submicroscopic phase separation in which hard segments of macrochains form domains in the soft matrix containing flexible chain sections. Both the "hard" and "soft" subphases consist of polar chain segments; therefore the dielectric spectroscopy should enable one to evaluate the characteristics of the molecular motion in each of the phases in connection with their chemical structure and composition. The earlier results of dielectric relaxation studies indicate that, besides an orientation polarization of chain dipoles, an interfacial polarization due to the heterogenous structure and long-range migration of charge carriers and bulk conduction processes take place in these systems.¹⁻⁴

The detailed studies of segmented polyether or polyester urethane by dielectric spectroscopy have demonstrated that the relaxational process in the glass transition region is complicated. North and Reid^{2,3} have published results of the permanent dipole orientation study in segmented polyether urethanes and stated that the spectra for the dielectric loss factor are dominated by a single broad maximum. The authors credit it to the polarization of the ether segments in the frequency regime of the glass transition. For this kind of urethane elastomer, Vallance et al.⁵ observed a modification of the primary dielectric transition in the temperature range corresponding to the glass-rubber transition and the occurrence of a second transition at a somewhat higher temperature. These facts have been related to supercooling of crystallizable polyether segments.

Delides and Pethrick⁶ have studied the glass transition region of segmented polyester urethanes and have also observed that the ϵ'' spectra in the glass transition region show one or two maxima, depending on stoichiometry, ester segment degree of polymerization, and test temperature.

The introduction of the extending and cross-linking mixture capable of forming ionic centers into the structure of urethane elastomers leads to changes of macroscopic properties.^{7,8}

In this work we used the mixture of triethanolamine (TEA), 3-bromine-1,2-propanediol (BPD), and 1,4-butanediol (BD) as chain extenders and cross-linking agents. From the thermomechanical investigations,^{9,10} it results that these modified elastomers are characterized by a higher thermal stability and better tensile strength parameters. We suppose that the factor improving the microscopic properties is the additional cross-linking effect resulting from the formation of ammonium salt between the tertiary nitrogen atom of triethanolamine and the bromine atom from 3-bromine-1,2-propanediol. This leads to the formation of ionic domains formed by the bound nitrogen cations or the macrochains of urethanes and the nonbound bromide ions, which weakly react by coulombic interactions with quaternary ammonium cations. In special conditions, above the glass transition temperature, bromide ions can be mobile and can participate in the electric conductivity of the elastomers.¹¹

Based on the investigations of dielectric relaxation in the glass-rubber transition region, we hoped to obtain information about the influence of the extending and cross-linking mixture and, especially, the additional ionic centers in the structure of urethane elastomers.

EXPERIMENTAL

Materials

The investigated urethane elastomers were prepared by a two-step condensation reaction using a previously described method.¹⁰ from poly(caprolactone) diol, 4,4'-diphenylmethane diisocyanate, and the mixture of 1,4-butanediol, 3-bromine-1,2 propandiol, and triethanolamine at the following molar ratios: first-stage NCO, OH = 4:1, and second-stage NCO, OH = 1.1:1. TEA and BPD were always applied in equimolar quantities, and the contents of TEA + BPD in the mixture amounted to a value in the range 0-25 mol%.

Denoting the contents of TEA + BPD in the mixture by X , the symbol $5X$, for example, describes a sample with a 5 mol% content of TEA, 5 mol% BPD, and 90 mol% BD. Contents of the extending and cross-linking agents are listed in Table I.

Sample Preparation

After synthesis, the urethane elastomers were poured into a mold and heated to the temperature of 393 K for 24 h. The samples were cut into disks of 20×10^{-3} m in diameter from films of thickness of about 10^{-3} m.^{2,3} Silver electrodes were deposited onto cleaned, fat-free surfaces on both sides of the sample using a vacuum evaporation technique. The surface of the collecting electrode was about 10^{-4} m², giving a geometric capacity of 10^{-12} F,³⁻⁵ depending on the thickness of the sample. The electrical leads were connected with the electrodes and the guard ring by an epoxy silver paste.

TABLE I
Chemical Parameters

Polymer Designation	Extending and crosslinking systems (mol%)
0X	100% BC
2X	2% TEA + 2% BPD + 96% BD
5X	5% TEA + 5% BPD + 90% BD
10X	10% TEA + 10% BPD + 80% BD
15X	15% TEA + 15% BPD + 70% BD
20X	20% TEA + 20% BPD + 60% BD
25X	25% TEA + 25% BPD + 50% BD

Instrumentation

Dielectric spectra were measured with a capacitance bridge of the GR 1615A type working within the frequency range of 20 Hz to 100 KHz and a semiautomatic bridge of the BM 484 "Tesla" type for one standard frequency ($f = 1592$ Hz). The measurements were performed between 180 and 400 K, and the sample chamber was filled with nitrogen gas. The automatic temperature regulation system secured a stabilization of temperature with an accuracy of ± 0.01 K and an indication of temperature with an accuracy of ± 0.05 K. The construction of the sample chamber, the bridges used, and the position of electrodes on the samples assured a three-terminal measurement that eliminated the capacity of the leads.

RESULTS AND DISCUSSION

The introduction of the extending and cross-linking mixture X to the structure of urethane elastomers should have an influence on the relaxational process in the glass-rubber transition region.

Figure 1 shows variation of t_g , δ and ϵ' as a function of temperature at one frequency ($f = 1592$ Hz) for two samples: 2X and 25X. All the remaining kinds of the investigated elastomers show an analogous character of dependence t_g , $\delta = f(T)$ and $\epsilon' = f(T)$. The first, low-temperature relaxational maximum β is connected with the sorbed water on NH or CO groups, always present in the systems with hydrogen bonds, particularly in polyamides, cellulose, and polyurethanes^{12,13} and will not be discussed here. The main maximum of t_g , δ seen in Figure 1, defined as α relaxation, is connected with the micro-Brownian motion of kinetic segments of the polyester chains. In segmented urethane elastomers, the glass-rubber transition is determined by properties of soft phases and by the perfection of the phase separation. With increasing content of TEA and BPD in the elastomers, the glass transition temperature T_g and the increment of dielectric permittivity $\Delta\epsilon'$ for this process increase. The further, rapid increasing of t_g , δ in the range of higher temperatures observed for all the samples is connected with direct current (DC) conductivity, but not solely.¹¹

In the range of high temperatures, the next relaxational maximum connected with the hard phase could be expected. It is confirmed by the course of the graph $\epsilon' = f(T)$. After a small decrease of the dielectric permittivity

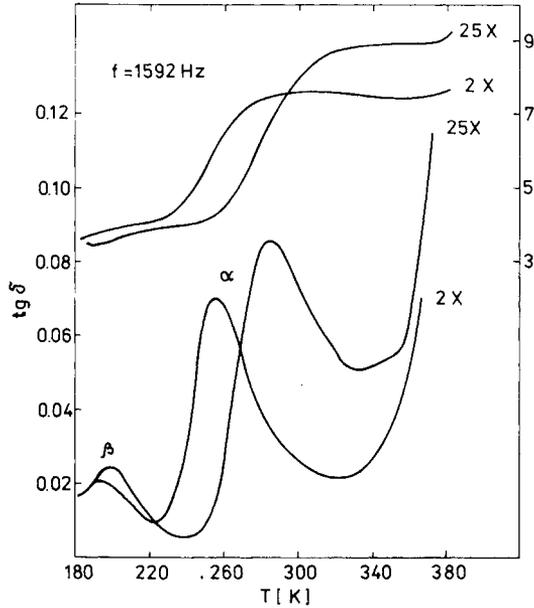


Fig. 1. Dependence of the loss factor and permittivity on temperature for 2X and 25X elastomers.

ϵ' value above T_g for all samples, a further increase of ϵ' with temperature is observed. This problem demands additional studies and will not be analyzed in detail here.

The influence of the extending and cross-linking on the glass transition temperature is seen very clearly in Figure 2, where the dependence of $t_g \delta$ on temperature for all samples at fixed frequency is presented. We can observe very distinctly that $t_g \delta$ maxima shift to higher temperatures with

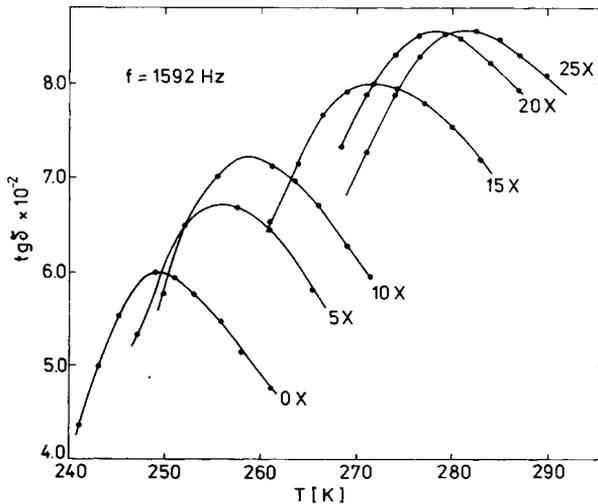


Fig. 2. Variation with temperature of the dielectric loss for a series of urethane elastomers at fixed frequency.

increasing TEA and BPD content. Simultaneously, a systematic increase of $t_g \delta_{\max}$ value is seen. We suppose that both the effects are not only the result of cross-linking of elastomers by TEA and BPD mixture but are also due to the formation of additional ionic centers: the quaternary ammonium cations on the hard segment of urethane elastomers and bromide ions from BPD. The formation of ionic groups in the structure of urethane elastomers causes the growth of polarity, especially of the soft phase. This is confirmed by the increase of dielectric permittivity increment $\Delta\epsilon'$ from the value of 3.5 for the 0X and 2X samples to about 5 for the 25X sample in the glass rubber transition region (see Fig. 1). The data in Figures 1 and 2 explicitly show the increase of cross-linking density (stiffness) of elastomers with increasing TEA and BPD content in the cross-linking mixture.

For all the samples, temperature frequency dependencies of $t_g \delta$ in the range of α relaxation have been measured. It has been found that $t_g \delta$ maxima move toward high temperature with increasing frequency. In Figure 3, the dependences of $t_g \delta$ on temperature at different frequencies for the 10X sample are shown to prove this effect.

All the remaining samples from the range 0 mol% to 25 mol% show an analogous behavior of $t_g \delta = f(T)$ at $f = \text{constant}$. The temperature-frequency shift of $t_g \delta$ for the investigated samples is seen very clearly in Figure 4, where the dependence $\log f_{\max}$ versus reciprocal temperature has been plotted. The course of this dependence, giving two slopes: low-frequency slope of activation energy W_l and high-frequency slope of activation energy W_h , points to the complex mechanism of α relaxation. Moreover, from the plots shown in Figure 4, it follows that the investigated elastomers can be clearly divided into two groups. The first group is made of 0X, 2X, 5X, and 10X elastomers and the second of 15X, 20X, and 25X. This division is seen especially clearly in Figure 5, showing summarized results of our studies: the influence of the chemical composition of the extending cross-linking

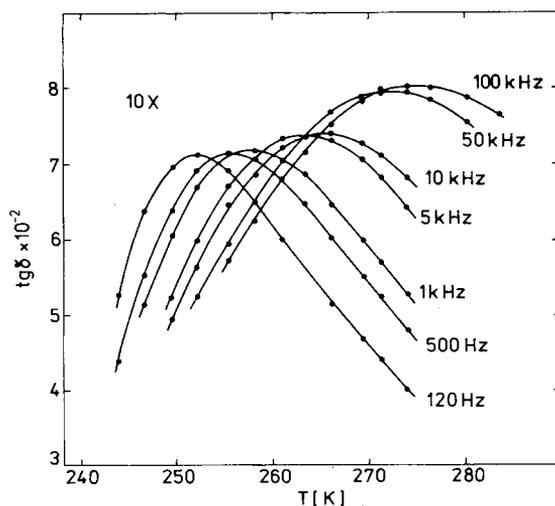


Fig. 3. Temperature dependence of the dielectric loss for 10X elastomer at different frequencies.

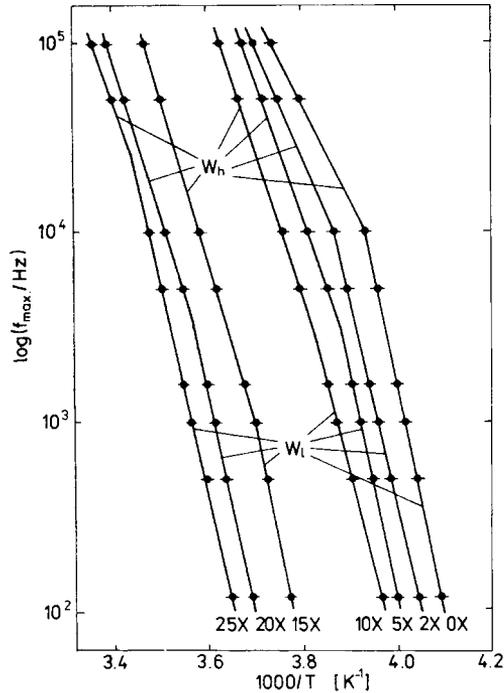


Fig. 4. Activation energy plots in the glass transition region for all investigated elastomers.

mixture on the structure of urethane elastomers. As we can see from the curves in Figure 5, the boundary of division into two groups is at 12–13 mol% of TEA and BPD in the mixture.

The dependence of the glass transition temperature on the content of TEA and BPD in the mixture (Fig. 5) consists of two slopes with different

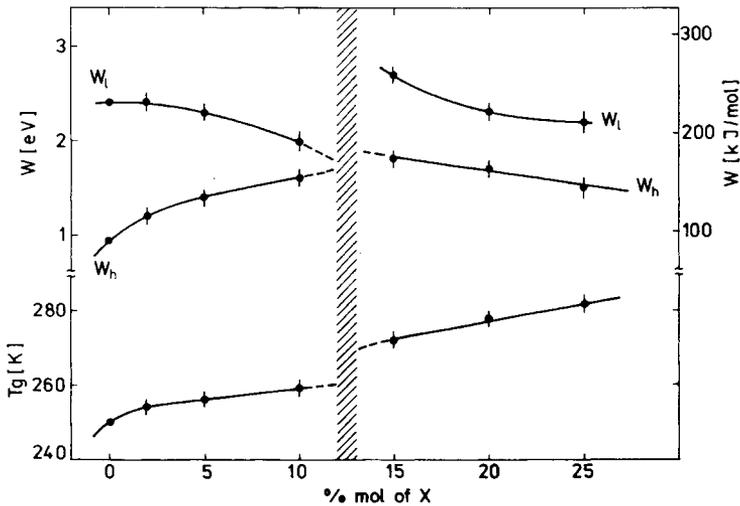


Fig. 5. Variation with TEA and BPD content of the activation energies (W_l and W_h) and the glass-rubber transition temperature.

gradients. It suggests at least two different mechanisms for elastomer cross-linking: the first for the low TEA and BPD content and the second for contents higher than 12–13 mol%. The first mechanism may be the result of the dominating three-functionality of TEA, and the second one may be the effect of an additional formation of ionic centers between the quaternary ammonium cation and bromide ion. Thus, the ammonium salt is an additional cross-linking point in the soft phase of urethane elastomers.

The perfection of phase separation may have an additional influence on changes of the value of glass-rubber transition temperature discussed here. The dependencies of activation energies on the TEA and BPD content in the mixture, observed in Figure 5, seem to be consistent with changes in the structure of urethane elastomers. The 0X, 2X, 5X, and 10X elastomers are characterized by a heterophase structure with gradually disappearing domains of hard segments. This means that the dissolution of the hard domain in the soft matrix takes place along with an increase in cross-linking density. The difference between the low-frequency activation energy and the high-frequency activation energy decreases gradually with the worsening phase separation. We suppose that the urethane elastomers with cross-linking mixture higher than 12–13 mol% (15X, 20X, and 25X) constitute different structural materials in comparison with 0X, 2X, 5X, and 10X elastomers. In these materials, the phase separation disappears; this means that hard segment domains dissolve in an amorphous soft matrix. These elastomers are characterized by a homogeneous structure where hard segments are randomly dispersed in a soft segment matrix. However, both the activation energies low-frequency W_l and high-frequency W_h describe thermofrequency kinetics of the same structure elements in two groups of urethane elastomers ($X < 12\text{--}13$ mol% and $X > 12\text{--}13$ mol%), the character of changes in W_l and W_h in relation to the TEA and BPD content being different because of changes in the structure of elastomers take place.

A similar behavior is demonstrated by the glass-rubber transition temperature dependence on the TEA and BPD content. The noncontinuity of $T_g = f(X)$ at 12–13 mol% of TEA and BPD content and the different character of changes for $X < 12\text{--}13$ mol% and $X > 12\text{--}13$ mol% suggest the structural transformation of the investigated urethane elastomers described above.

CONCLUSIONS

The systematically varied urethane elastomers have been studied using dielectric spectroscopy. The influence of the physical structure and the chemical composition of urethane elastomers on the dielectric relaxation has been determined. The relaxational process of the glass-rubber transition (α relaxation) has been analyzed in detail. The complex character of this process and the influence of the cross-linking mixture on the α relaxation has been stated. The urethane elastomers are heterogeneous when the content of TEA and BPD in the mixture with 1,4-butanediol is less than 12–13 mol%. In the urethane elastomers with more than 12–13 mol%, the large number of the cross-linking bonds does not permit the formation of hard segment domains. In this case, the urethane elastomers are homo-

geneous systems, where the hard segments, joined only by cross-linking bonds, are dissolved in the soft segment matrix. The network of urethane and ionic centers causes a stiffening of the urethane structure and an increase of the glass transition temperature.

References

1. A. M. North, J. C. Reid, and J. B. Shortall, *Europ. Polym. J.*, **5**, 565 (1969).
2. A. M. North and J. C. Reid, *Europ. Polym. J.*, **8**, 1129 (1972).
3. S. B. Dev, A. M. North, and J. C. Reid, in *Dielectric Properties of Polymers*, F. E. Karasz (Ed.), Plenum, New York, 1972.
4. M. A. Vallance and S. L. Cooper, in *Computer Applications in Applied Polymer Science*, T. Provder (Ed.), ACS Symposium Series 197, Washington, D.C., 1982.
5. M. A. Vallance, A. S. Yeung, and S. L. Cooper, *Colloid Polym. Sci.*, **261**, 541 (1983).
6. C. Delides and R. A. Pethrick, *Europ. Polym. J.*, **17**, 675 (1981).
7. D. Dietrich, W. Keberle, and H. Witt, *Angew. Chem. Int. Ed. Engl.*, **9**, 40 (1970).
8. A. Rembaum, *Advan. Urethane Sci. Technol.*, **2**, 109 (1973).
9. M. Rutkowska & R. Zielinski, Proceedings of Macromolecular Conference, Bukareszt, p. 453, 1983.
10. M. Rutkowska, to be published.
11. R. Zielinski and M. Rutkowska, Proceedings of Macromolecular Conference, Bukareszt, p. 448, 1983.
12. P. Hedvig, in *Dielectric Spectroscopy of Polymers*, A. Hilger (Ed.), Techno House, Redcliffe Way, Bristol, England, 1977.
13. D. S. Huh and S. L. Cooper, *Polym. Eng. Sci.*, **11**(5), 369 (1971).

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