

Effect of the Hard-Segment Structure on the Dielectric Relaxation of Crosslinked Polyurethanes

Stefan Oprea

Petru Poni Institute of Macromolecular Chemistry, Aleea Grigore Ghica Voda 41-A, Iasi 700487, Romania

Received 30 March 2010; accepted 10 June 2010

DOI 10.1002/app.32958

Published online 27 August 2010 in Wiley Online Library (wileyonlinelibrary.com).

ABSTRACT: Two series of crosslinked polyurethanes based on poly(tetramethylene ether) glycol soft segments and hexamethylene diisocyanate/1,4-butane diol and glycerin or castor oil as a hard segments were synthesized, and their dielectric properties were examined. We examined the influence of the structural heterogeneity of the copolymers (as a function of the quantity and structure of the hard segments and crosslinking density, as measured by comonomer composition), frequency, and temperature as experimental variables by observing changes in the dielectric behavior. Two relaxation peaks were observed in

the temperature range of -30 to 40°C for polyurethanes with various hard-segment contents. The dangling chains of the castor oil presented a plasticizing effect that was exerted during the relaxation processes, an effect that was studied. It was found that both the amount and the structure of the hard segment strongly affected the dielectric behavior. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 119: 2196–2204, 2011

Key words: crosslinking; dielectric properties; polyurethanes

INTRODUCTION

Polymeric materials are used in the fields of electronics, optoelectronics, batteries, and insulators; these fields require the study of the electrical and dielectric properties of the materials.

Dielectric spectroscopy is a noninvasive method, particularly applicable to heterogeneous systems, which can be used in many fields, including chemistry, biology, and materials.^{1–4}

Polyurethanes (PUs) have a wide range of applications, including coatings, adhesives, sealants, and composites, because they possess excellent mechanical properties, good biocompatibility, design flexibility, light weight, and low cost.^{5,6} The properties of segmented polyurethanes can be influenced by many factors, such as the volume fractions of the soft and hard segments, the chemical compositions of these segments, and their degree of crosslinking. The versatile physical properties of PUs are attributed to their microphase-separated structure, which result from the thermodynamic incompatibility between the hard and soft segments.^{7,8}

Vegetable oils are an abundant biological source that can be used as a starting material for the synthesis of biobased polyurethanes because they present advantages such as a low toxicity, inherent bio-

degradability, and high purity.^{9–12} The elastically inactive regions of the resulting oil–polyurethane networks (dangling chains) represent imperfections in the network structure and act as plasticizers that reduce polymer rigidity and improve polymer flexibility.^{13–18}

The mechanical properties of polyurethane systems have been widely studied, but few studies have dealt with their dielectric properties. Segmented polyurethanes are block copolymers that generally exhibit a phase-segregated morphology made up of soft rubbery segments and hard glassy or semicrystalline segments. These systems can obtain complex dielectric spectra by molecular and interfacial polarization in heterogeneous systems.¹ The dielectric transitions in various polyurethane elastomers suggest that the main factor in determining the transitions is the structure generated by the hydrogen bonds and crosslinking density. If the transition was to be analyzed in a series of polyurethanes with various numbers of CH_2 groups between urethane groups, one would find three types of relaxations, determined by the sequence of CH_2 groups from various parts of the molecules.¹⁹ From the Maxwell stress equation,²⁰ elastomers are expected to generate higher dielectric constants when a lower voltage is applied.²¹ Most polymers used in various actuator devices have dielectric constants between 2 and 10.²²

In this study, two series of polyurethanes based on poly(tetramethylene ether)glycol (Terathane 1400) and hard segments of different structures and

Correspondence to: S. Oprea (stefop@icmpp.ro).

TABLE I
Formulations and T_g Values of the
Crosslinked Polyurethanes

Sample	Polyether/HDI/ chain extender molar ratio	Chain extenders	T_g by DSC (°C)
PU1	1 : 2 : 1	CO and BD	-70.3
PU2	1 : 3 : 2	CO and BD	-66
PU3	1 : 4 : 3	CO and BD	-62.8
PU4	1 : 2 : 1	Gly and BD	-57.3
PU5	1 : 3 : 2	Gly and BD	-54.7
PU6	1 : 4 : 3	Gly and BD	-49.8

crosslinking densities were synthesized. The hard segment was based on 1,6-hexamethylene diisocyanate (HDI)/1,4-butane diol (BD) and glycerin (Gly) or castor oil (CO) as a chain extender. For both sample series, the relaxations were observed in the temperature range of -100 to 100°C and at a frequency of 1 to 10^6 Hz. The dielectric spectra were analyzed with the purpose of obtaining the distribution parameters as a function of the composition of the copolymer.

EXPERIMENTAL

Materials

All chemicals used in this study were used as received from the suppliers unless otherwise stated. Polyether and the chain extenders were checked for the content of moisture and, if necessary, dried *in vacuo*. HDI was obtained from Fluka (Fluka Chemie AG, Buchs, Switzerland). The polyether diol was poly(tetramethylene ether) glycol (Terathane 1400); it had an average molecular weight of 1400 g/mol and was obtained from Fluka. The chain extenders (BD, Gly, and CO) were obtained from Aldrich (Sigma-Aldrich Chemie GmbH, Taufkirchen, Germany) and were used as received.

Synthesis of the polyurethane elastomers

The polymers were prepared in a two-step polymerization process under a nitrogen atmosphere, as previously described.^{23,24} The average hard-segment composition was controlled by the variation of the poly(ether diol)/HDI/diol and triol molar ratios used in the synthesis. Three different molar ratios of the polyether to the diisocyanate and chain extenders (which were varied from $1/2/1$ to $1/3/2$ to $1/4/3$) were chosen for the formulations. The OH diol/OH triol ratio used was $1/1$ in each of the synthesized polyurethane samples.

Typically, the synthesis of PUs was done by the following procedure, and the compositions of the polyurethane samples are shown in Table I.

The synthesis of the PUs was performed in a 1-L glass reactor at normal pressure under a nitrogen

blanket and with vigorous agitation. The NCO/OH_{polyether} ratio of all of the formulations was 1.03 – 1.05 . In the case of the prepolymer procedure, polyether diol was reacted with a diisocyanate at 80°C for 2 h to yield a prepolymer that was mixed in the second step with the chain extenders at 80°C for 10 min. The reaction end point was determined by the disappearance of the NCO stretching peak (2270 cm^{-1}), which was observable through IR spectroscopy. The resulting material was cured at 80°C for 20 h. Under these conditions, the addition of catalysts was not necessary. Polyurethane films thus prepared were used for the determination of the dielectric properties.

Measurements

Measurements of the complex dielectric properties were made by broad-band dielectric spectroscopy equipment with a NOVOCONTROL Concept 40 dielectric analyzer (NOVOCONTROL Technologies GmbH, Hundsbang, Germany). Frequency sweeps were performed isothermally from 1 to 10^6 Hz in the temperature range -100 to 100°C .

A PerkinElmer DSC-7 differential scanning calorimeter (Corporate Headquarters, Massachusetts) was used for thermal analysis and was operated at a heating rate of $10^\circ\text{C}/\text{min}$. The thermal transition behavior was studied in the temperature range -100 to 60°C . Tests were conducted on samples of about 10 mg, which were gradually heated for observation of the glass-transition temperature (T_g).

RESULTS AND DISCUSSION

The polarization of materials can be due to several mechanisms: electronic, ionic (molecular), atomic, dipolar (orientational), and interfacial polarizations.²⁵

The technique used to study the dielectric properties of materials is dielectric spectroscopy. Dielectric spectroscopy investigates different molecular motions and relaxation processes. The dielectric properties are closely correlated with the constituent materials and their structures in each phase of a heterogeneous system.

For a heterogeneous system comprised of crosslinked copolymers, the dielectric behavior can be readily understood from the viewpoint of Maxwell-Wagner interfacial polarization theory.²⁶ The Maxwell-Wagner model²⁰ assumes the dependence of the dielectric constant on the frequency:

$$\epsilon' = \epsilon_\infty + \frac{\epsilon_s - \epsilon_\infty}{1 + \omega^2\tau^2} \quad (1)$$

where ϵ' is the dielectric constant, ϵ_∞ is the dielectric constant at an infinitely high frequency, ϵ_s is the

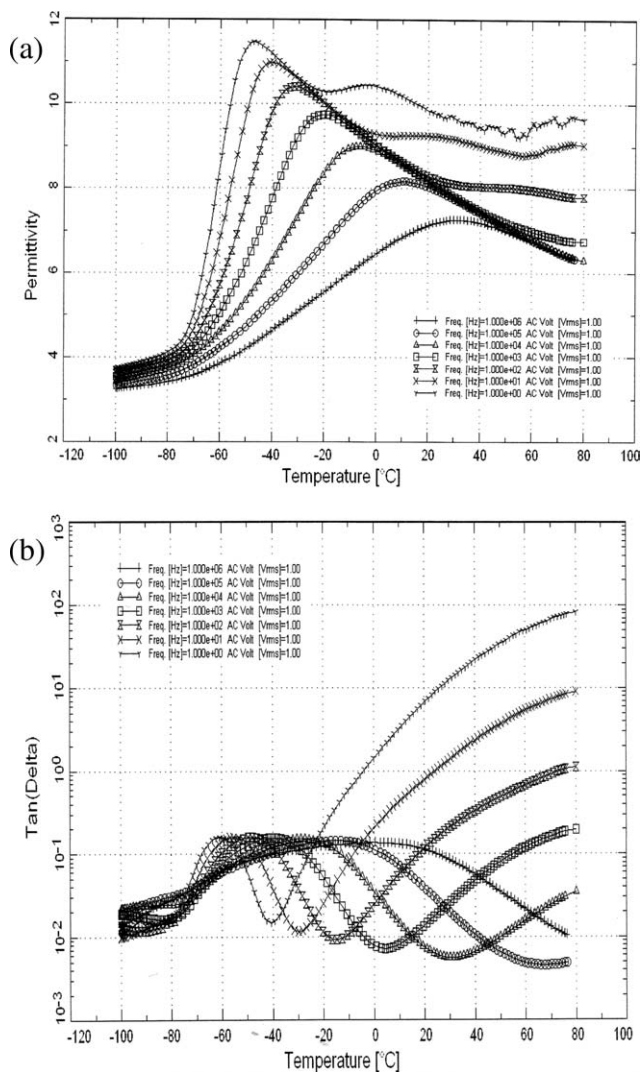


Figure 1 Dependence of the (a) permittivity and (b) $\tan \delta$ on the temperature and frequency of the PU1 samples in the CO series.

dielectric constant at a low frequency, ω is the angular frequency, and τ is the relaxation time. In the case of this model, the interfacial polarization decreases at high frequency, and the dielectric constant is expected to be lower at a higher frequency.^{22,27}

The dielectric properties of the polyurethanes with CO or Gly crosslinker were relevant for the potential application in electrical insulation, with a special focus in the relaxation processes of these materials. The dielectric spectroscopy of polyurethanes was carried out in the temperature range from -100 to approximately 100°C and at six frequencies from 1 to 10^6 Hz.

Figures 1–3 show the dependence of relative permittivity and $\tan \delta$ on the temperature and frequency of the samples of castor-oil-based polyurethane.

The relative permittivity was found to increase from about 3.5 to about 11 for PU1 (1/2/1), from about 3.5 to about 10 for PU2 (1/3/2), and from

about 3.5 to about 9 for PU3 (1/4/3) in the broad temperature region from -80 to -20°C . The T_g values assessed by differential scanning calorimetry (DSC) were approximately -70 and -60°C . When the frequency was increased from 1 to 10^6 Hz, a dielectric permittivity maxima occurred from about -55°C (1 Hz) to about 25°C (10^6 Hz). The permittivity values for PU1 decreased with increasing frequency from 11 (1 Hz) to 7 (10^6 Hz).

In all cases, a dispersion of permittivity was observed in the low-frequency regions, and the decrease in permittivity with increasing frequency may have been due to the electrical relaxation processes.

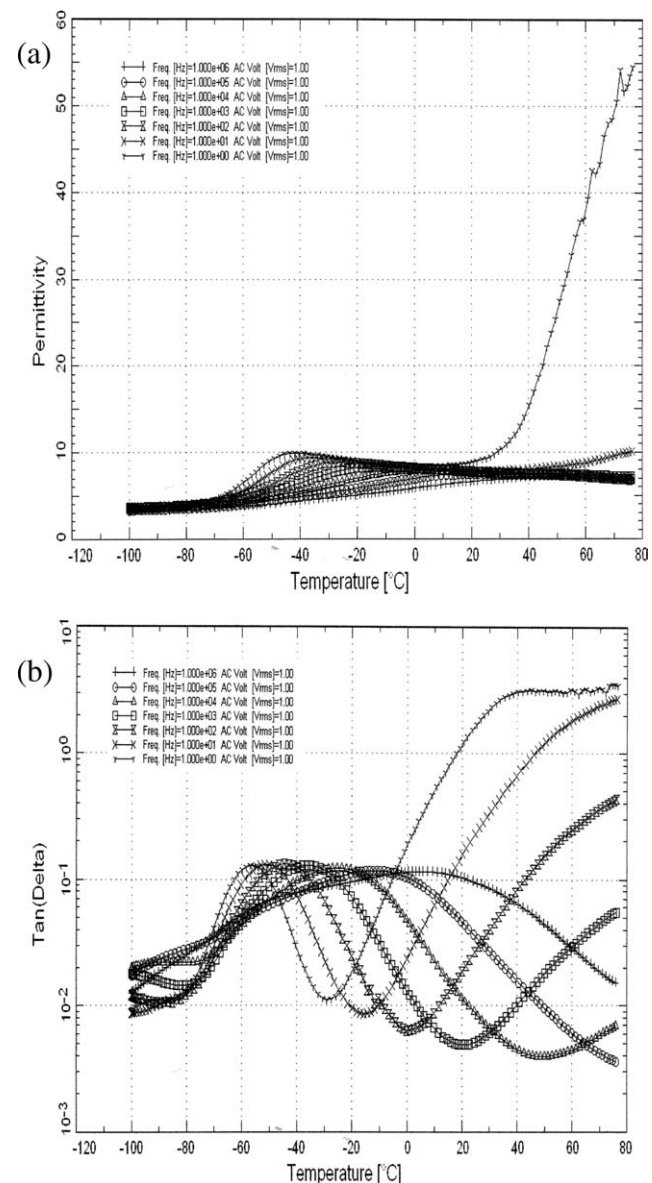


Figure 2 Dependence of the (a) permittivity and (b) $\tan \delta$ on the temperature and frequency of the PU2 samples in the CO series.

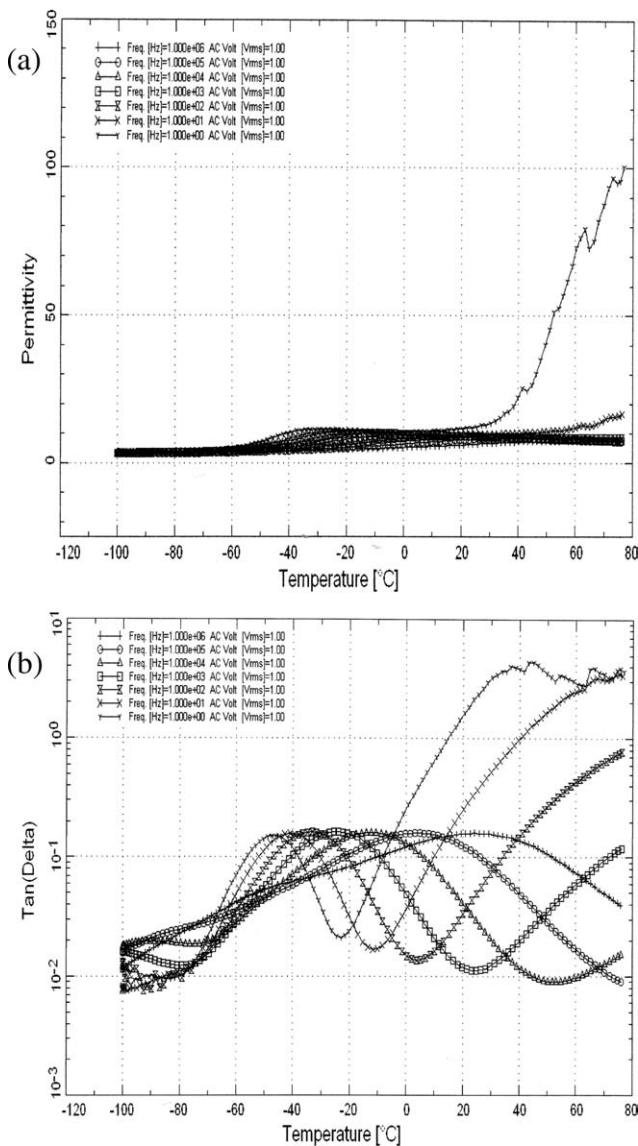


Figure 3 Dependence of the (a) permittivity and (b) $\tan \delta$ on the temperature and frequency of the PU3 samples in the CO series.

The polarization of microdomains resulting from the separation of the hard and soft segments of PU chains can cause the accumulation of charges, a process that can be attributed to the different conductivities between soft and hard microdomains.²⁸ Nonlinear behavior showed that relaxations were due to induced dipoles, but the possibility that the charge migration was blocked at the interfaces between the soft and hard microdomains of the sample may have also contributed to this behavior. A greater number of hard domain increased the interfacial polarization because of the uneven distribution of the hard microdomains in the continuous soft phase.

When the frequency was increased from 1 to 10⁶ Hz, the dielectric $\tan \delta$ maxima occurred from about -60°C (1 Hz) to about 5°C. The $\tan \delta$ curves revealed upward trends, which led to additional

maxima below -60°C and above 80°C. $\tan \delta$ peaks occurred at higher temperatures with increasing hard-segment content but also with increasing cross-linking density. Testing above 80°C was limited by the modification of the sample under the load of electrodes.

Figures 2 and 3 show the change of relative permittivity as a function of temperature. At various frequencies, permittivity became higher with increasing hard-segment content and crosslinking. This jump was especially high between PU2 (1/3/2) and PU3 (1/4/3), with their permittivity values being 55 and 100, respectively. The magnitude of the $\tan \delta$

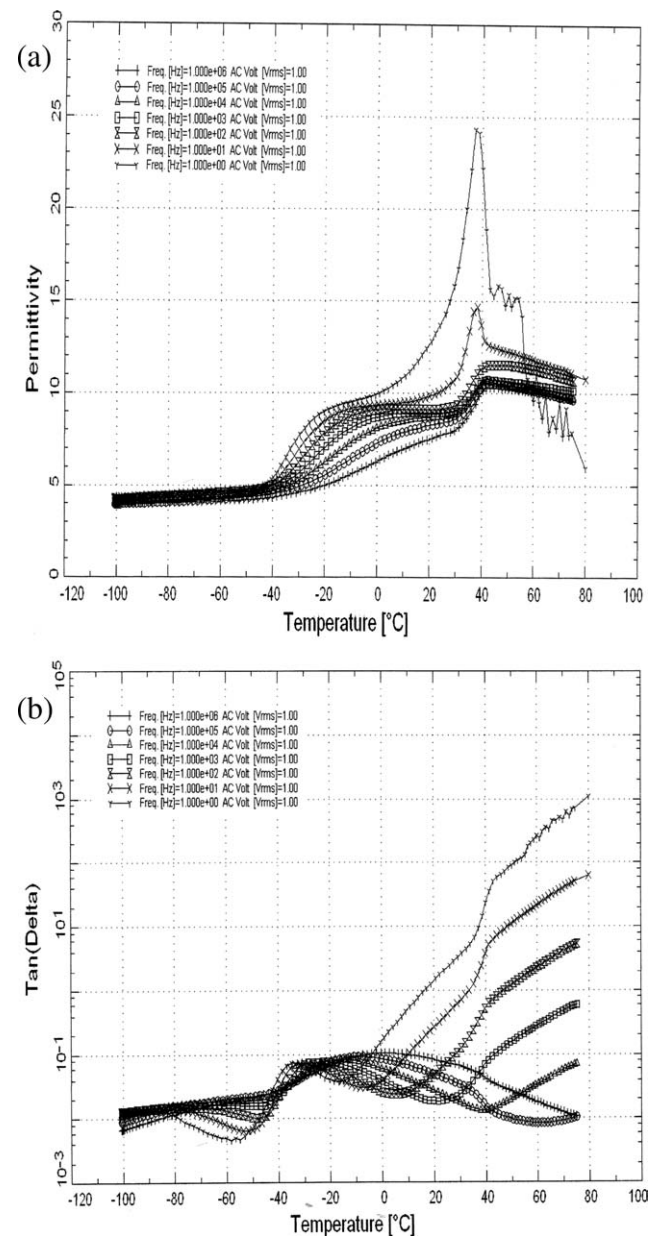


Figure 4 Dependence of the (a) permittivity and (b) $\tan \delta$ on the temperature and frequency of the PU4 samples in the Gly series.

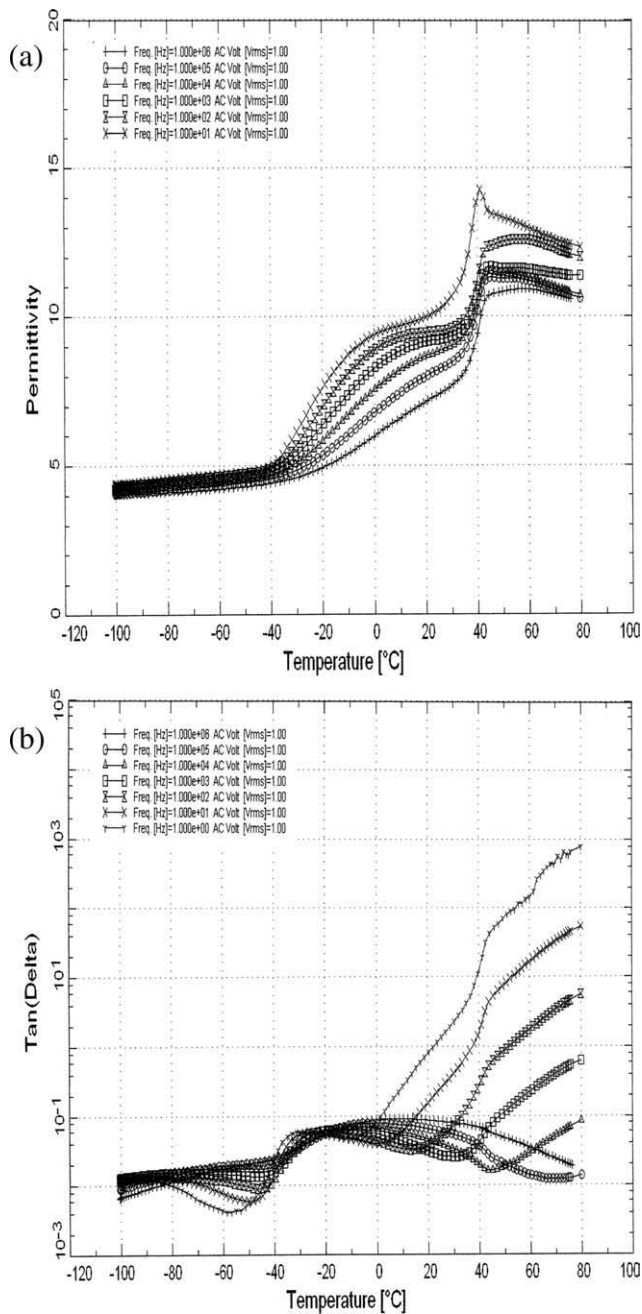


Figure 5 Dependence of the (a) permittivity and (b) $\tan \delta$ on the temperature and frequency of the PU5 samples in the Gly series.

peak was correlated with the freedom of segmental rotation being restricted by large crosslinks.

A different behavior was observed in the Gly series (Figs. 4–6), where the permittivity and $\tan \delta$ maxima appeared at higher temperatures.

The relative permittivity did not show the characteristic S-shaped transition between -80 and 80°C . In addition, the temperature $\tan \delta$ maxima were observed from about -40 to -30°C , and additional maxima were seen at about 40 and 80°C . This behavior was attributed to the crystallization of the hard

segment, which did not occur with the CO series. PU elastomers with a CO crosslinker had different properties as a result of a higher network structure with a large amount of dangling chains. Dangling chains represent the imperfections in the network structure.^{29,30}

Figures 7 and 8 show the variation of the imaginary part of the permittivity [i.e., the dielectric loss (ϵ'')] as a function of the temperature for a variety of frequencies.

All of the materials exhibited a frequency-dependent permittivity at all temperatures, with ϵ'' appearing toward higher temperatures with increasing

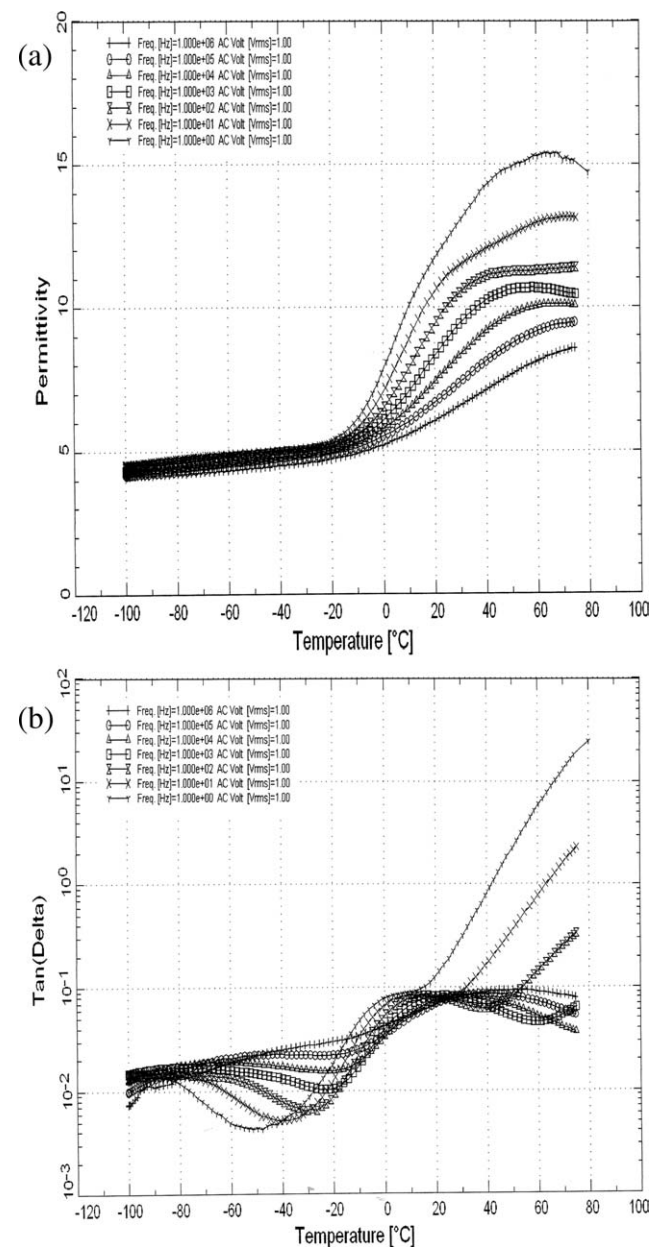


Figure 6 Dependence of the (a) permittivity and (b) $\tan \delta$ on the temperature and frequency of the PU6 samples in the Gly series.

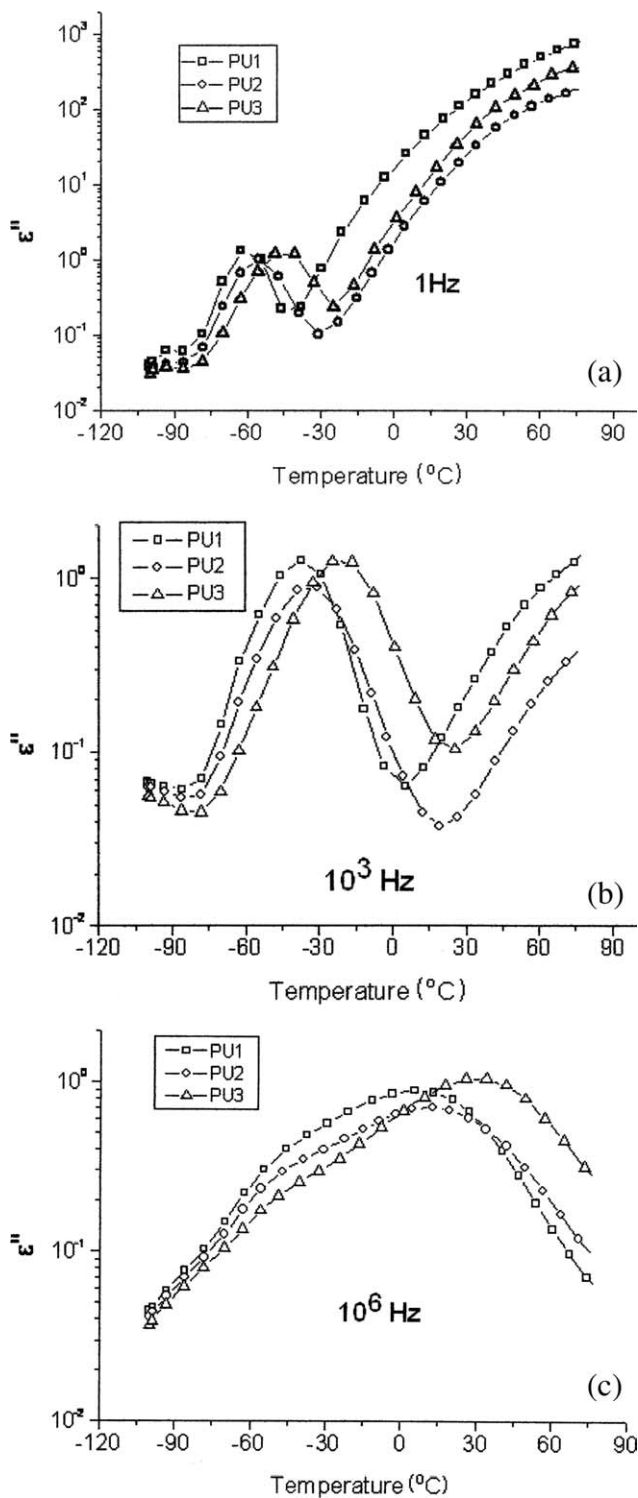


Figure 7 Variation of ϵ'' as a function of the temperature for polyurethane elastomers based on CO at different frequencies: (a) 1, (b) 10^3 , and (c) 10^6 Hz.

frequency. Also, as the crosslinking density of the copolymer increased (with increasing concentration of the crosslinker in the copolymer), the heterogeneity of the network increased. Thus, with increasing amount of hard segment and crosslinking density, ϵ''

was obtained at higher temperatures. Increases in the hard-segment content and density of crosslinks led to the formation of larger domains containing phase inversion; this suggests that the dielectric behavior might have been controlled through morphology.

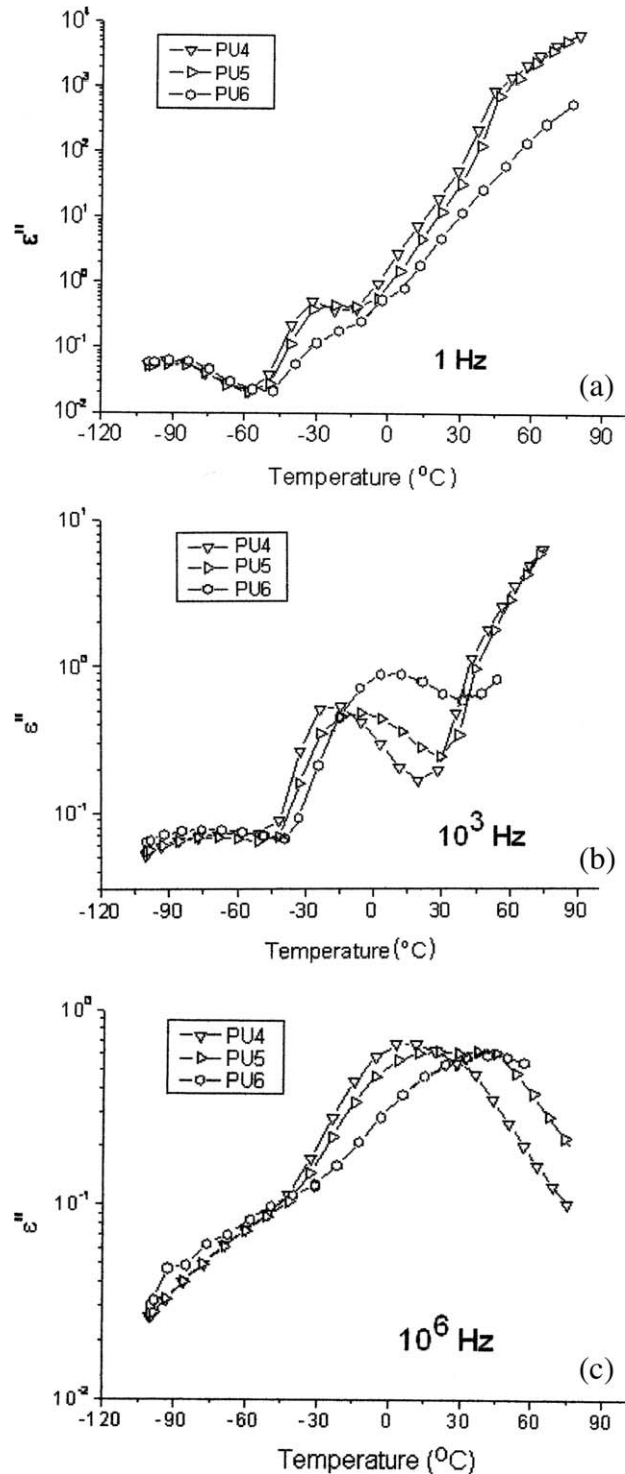


Figure 8 Variation of ϵ'' as a function of the temperature for polyurethane elastomers based on Gly at different frequencies: (a) 1, (b) 10^3 , and (c) 10^6 Hz.

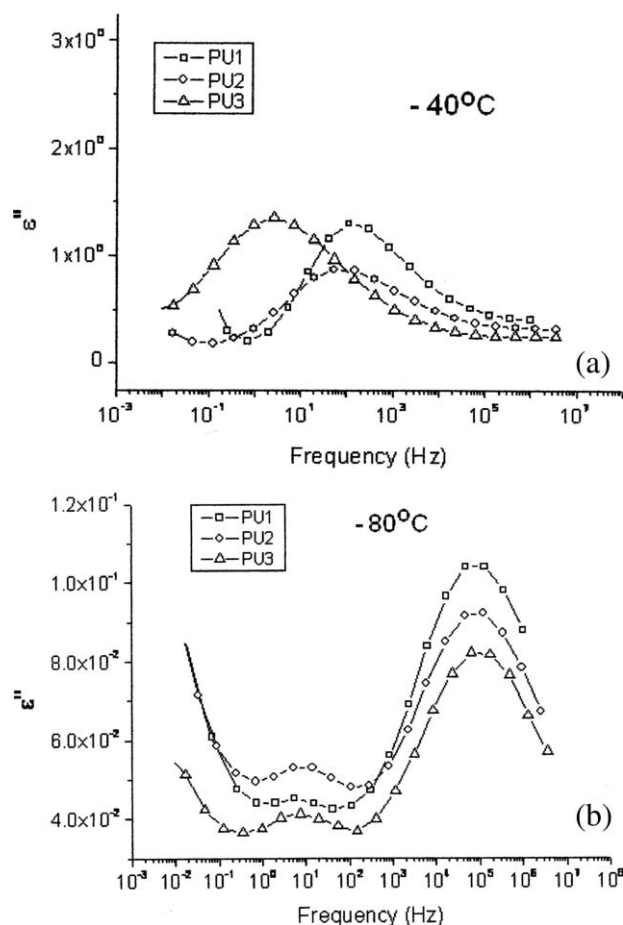


Figure 9 Variation of ϵ'' as a function of the frequency for polyurethane elastomers based on CO at different temperatures: (a) -40 and (b) -80°C .

At high frequencies, the dielectric constant was very low because the polar groups in the polymer were not mobile during short time frames and did not orient enough to provide a discernible change in the polarization. As the frequency decreased, the timescales increased and the most mobile groups began to orient; this induced a polarization, which was measured.

Figures 9 and 10 show ϵ'' of the crosslinked polyurethane elastomers as a function of the frequency at two temperatures (-40 and -80°C).

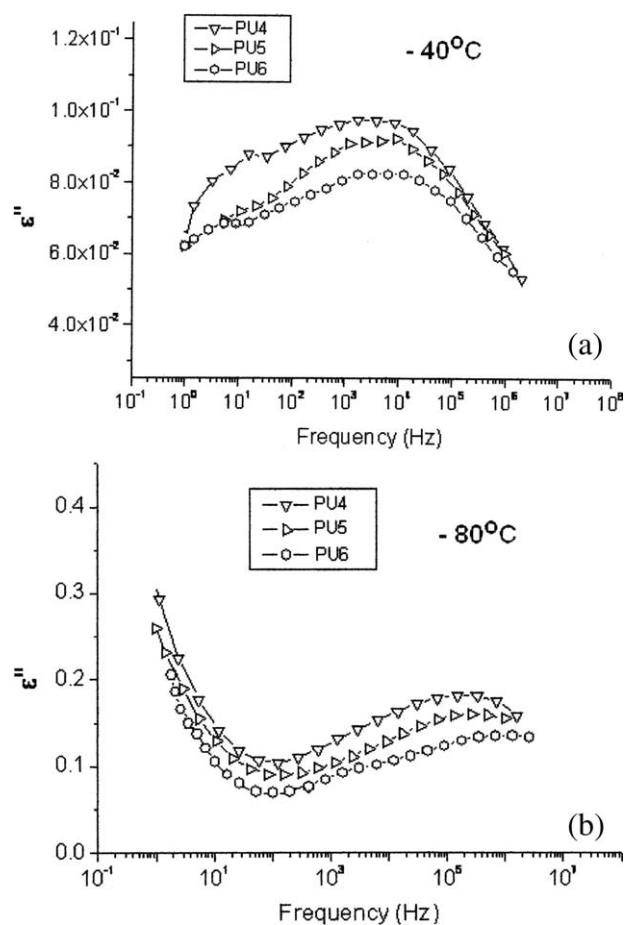


Figure 10 Variation of ϵ'' as a function of the frequency for polyurethane elastomers based on Gly at different temperatures: (a) -40 and (b) -80°C .

A large peak was observed at low frequencies in each curve. This peak was the glass-transition peak of the sample and moved toward higher frequencies with increasing amount of hard segments in the polyurethane formulations.

The second peak was observed around 10^5 Hz [in the case of polyurethanes based on CO; Fig. 9(b)] and was the secondary transition peak; this may have been caused by the dangling chains from CO, which are found in several mobile environments.

TABLE II
Fitting Parameters for the Polyurethane Elastomers Obtained with CO

Sample	τ maximum (s)		$\Delta\epsilon$	
	-80°C (β and γ relaxations)	-40°C (α relaxation)	-80°C	-40°C
PU1	2.167×10^{-2} 1.655×10^{-6}	1.235×10^{-3}	6.7870×10^{-2} 6.9580×10^{-1}	6.9910
PU2	1.794×10^{-2} 1.555×10^{-6}	2.105×10^{-3}	1.2640×10^{-1} 6.3020×10^{-1}	5.5360
PU3	2.413×10^{-2} 1.393×10^{-6}	6.295×10^{-2}	1.0610×10^{-1} 5.5810×10^{-1}	8.5210

$\Delta\epsilon$, represent the intensity of relaxation.

TABLE III
Fitting Parameters for the Polyurethane Elastomers Obtained with Gly

Sample	τ maximum (s)		$\Delta\epsilon$	
	-80°C (β and γ relaxations)	-40°C (β and γ relaxations)	-80°C	-40°C
PU4	3.831×10^{-2}	7.892×10^{-5}	3.1990×10^{-1}	2.2470×10^{-1}
	1.519×10^{-5}	4.627×10^{-7}	7.5990×10^{-1}	1.1470
PU5	5.945×10^{-2}	8.462×10^{-5}	1.2120×10^{-1}	8.2760×10^{-2}
	2.703×10^{-5}	4.182×10^{-7}	8.8160×10^{-1}	1.1160
PU6	1.059×10^{-1}	2.778×10^{-4}	1.8660×10^{-1}	5.1130×10^{-2}
	2.551×10^{-5}	4.339×10^{-7}	6.9840×10^{-1}	8.7960×10^{-1}

$\Delta\epsilon$, represent the intensity of relaxation.

The presence of a secondary transition at a much higher frequency implied a very high degree of structural heterogeneity in the copolymer networks examined. The fact that a second peak was observed implied that the network had distinct, high-mobility regions.

The rearrangement of the side chains together with the cooperative motions reoriented the segments of the polymer network toward higher temperatures (when the segments of the network had a higher mobility because of the increased thermal energy).

The individual relaxations could be described with the Havriliak–Negami modification of the single-relaxation-time Debye expression³¹:

$$\epsilon^* = \epsilon' - i\epsilon'' = \epsilon_U - \frac{\epsilon_R - \epsilon_U}{[1 + (i\omega\tau_{HN})^a]^b} \quad (2)$$

where $\omega = 2\pi f$ is the angular frequency (f is the ordinary frequency); ϵ_R and ϵ_U represent the relaxed ($\omega \rightarrow 0$) and unrelaxed ($\omega \rightarrow \infty$) values of the dielectric constant for each relaxation, respectively; τ_{HN} is the relaxation time for each process; and a and b represent the broadening and skewing parameters, respectively. The WINFIT software package provided with the Novocontrol spectrometer was used to obtain Havriliak–Negami best fits for the ϵ'' versus frequency data for each temperature.

The fit of ϵ'' of the complex dielectric constant is shown in Tables II and III.

In this way, because of the constraints imposed on the fitting procedure, a reliable estimate of the parameters of the dispersion was obtained. This procedure gave a set of parameters that described the distribution of mobilities and the relatively low conductivity of the samples investigated.

When the temperature was low and the sample was glassy, the parameter values were low, especially for samples with a high content of hard domains. As the temperature was increased beyond the glass-transition temperature of the sample ($T_g = -40^\circ\text{C}$), the value of this parameter increased. This observation suggested that the dis-

tribution of polymer segmental mobilities became increasingly homogeneous.

The increase in the temperature led to an increase in the mobility of molecules. The motion of molecules, in turn, induced dipole moments; this led to increases in the dielectric constants.³²

The variation of dielectric properties with hard-segment content could be explained by the network effect, which was dependent on the molecular weight between junctions, which here means between the hard-domain crosslinks.

CONCLUSIONS

Two series of crosslinked polyurethanes based on a poly(tetramethylene ether) glycol soft segment with a molecular weight of 1400 were synthesized, and the effects of the amount and structure of the hard segments on the dielectric behavior in the region between -100 and 100°C was examined. In all of the cases, a dispersion of permittivity was observed in the low-frequency region, and the decrease in permittivity with increasing frequency was attributed to electrical relaxation processes. Increasing hard-segment concentration within the series brought about a decrease in the relative permittivity.

Tan δ peaks occurred at higher temperatures with increasing hard-segment content but also with increasing crosslinking density. The relative magnitude of tan δ at its maximum decreased with increasing hard-segment concentration. With increasing amount of hard segments and crosslinking density, ϵ'' was obtained at higher temperatures. The samples from the CO series displayed different relaxation spectra because of the effects of the dangling chains. The dependence of the peak temperatures on the hard segments was that they occurred at higher temperatures with increasing hard segments and crosslinking.

The authors are thankful to Valentina Musteata for her assistance with the dielectric measurements.

References

1. Asami, K. *Prog Polym Sci* 2002, 27, 1617.
2. Chen, Z.; Zhao, K. S. *J Colloid Interface Sci* 2004, 276, 85.
3. Sancho, M.; Martinez, G.; Martin, C. *J Electrostat* 2003, 57, 143.
4. Oleinikova, A.; Sasisanker, P.; Weingartner, H. *J Phys Chem B* 2004, 108, 8467.
5. Petrovic, Z. S.; Ferguson, J. J. *Prog Polym Sci* 1991, 16, 695.
6. Chen, G.; Hu, J. W.; Zhang, M. Q.; Rong, M. Z. *Sens Actuators B* 2005, 105, 187.
7. Georgoussis, G.; Kyritsis, A.; Pissis, P.; Savelyev, Y. V.; Akhranovich, E. R.; Privalko, E. G. *Eur Polym J* 1999, 35, 2007.
8. Kanda, D. H. F.; Nagashima, H. N.; Malmonge, J. A.; Sakamoto, W. K.; Chierice, G. O. *J Mater Sci* 2008, 43, 5436.
9. Biermann, U.; Friedt, W.; Lang, S.; Luhs, W.; Machmuller, G.; Metzger, J. O.; Klaas, M. R.; Schafer, H. J.; Schneiderusch, M. P. *Angew Chem Int Ed* 2000, 39, 2206.
10. Andjelkovic, D. D.; Larock, R. C. *Biomacromolecules* 2006, 7, 927.
11. Tsujimoto, T.; Uyama, H.; Kobayashi, S. *Macromolecules* 2004, 37, 1777.
12. Guner, F. S.; Yagci, Y.; Erciyes, T. *Prog Polym Sci* 2006, 31, 633.
13. Guo, A.; Javni, I.; Petrovic, Z. *J Appl Polym Sci* 2000, 77, 467.
14. Malmonge, J. A.; dos Santos, M. A.; Sakamoto, W. K. *J Mater Sci* 2005, 40, 4557.
15. Dusek, K.; Ilavsky, M. *Prog Colloid Polym Sci* 1989, 80, 26.
16. Sakamoto, W. K.; Kanda, D. H. F.; Andrade, F. A.; Das-Gupta, D. K. *J Mater Sci* 2003, 38, 1465.
17. Fedderly, J. J.; Lee, G. F.; Lee, J. D.; Hartmann, B.; Dusek, K.; Duskova-Smrckova, M.; Syomvarsky, J. *J Rheol* 2000, 44, 961.
18. Lee, Y. L.; Sung, P. H.; Liu, H. T.; Chou, L. C.; Ku, W. H. *J Appl Polym Sci* 1993, 49, 1013.
19. Kajiyama, T.; MacKnight, W. J. *Macromolecules* 1969, 2, 254.
20. Raju, G. G. *Dielectrics in Electric Fields*; Marcel Dekker: New York, 2003.
21. Pelrine, R. E.; Kornbluh, R. D.; Joseph, J. P. *Sens Actuators A* 1998, 64, 77.
22. Soares, B. G.; Leyva, M. E.; Barra, G. M.; Khastgir, D. *Eur Polym J* 2006, 42, 676.
23. Oprea, S. *Adv Polym Technol* 2009, 28, 165.
24. Oprea, S. *J Am Oil Chem Soc* 2010, 87, 313.
25. Scaife, B. K. P. *Principles of Dielectrics*; Oxford Science: Oxford, 1998.
26. Maxwell, J. C. *A Treatise on Electricity and Magnetism*, 3rd ed.; Clarendon: Oxford, 1891; Vol. 1.
27. Ku, C. C.; Liepins, R. *Electrical Properties of Polymers*; Hanser: New York, 1987.
28. Tsonos, C.; Apekis, L.; Zois, C.; Tsonos, G. *Acta Mater* 2004, 52, 1319.
29. Zlatanovic, A.; Lava, C.; Zhang, W.; Petrovic, Z. S. *J Polym Sci Part B: Polym Phys* 2004, 42, 809.
30. Lee, Y. L.; Sung, P. H.; Liu, H. T.; Chou, L. C.; Ku, W. H. *J Appl Polym Sci* 1993, 49, 1013.
31. Havriliak, S.; Negami, S. *J Polym Sci Part C: Polym Symp* 1966, 14, 99.
32. Riad, A. J.; Korayem, M. T.; AbdulMalik, T. G. *Physica B* 1999, 270, 140.