

Studies of the Molecular Dynamics in Polyurethane Networks with Hyperbranched Crosslinkers of Different Coordination Numbers

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ABSTRACT: Several new polyurethane networks based on hyperbranched polyesters (trade name Boltorn) were synthesized to investigate the influence of the hyperbranched crosslinking agent on the molecular dynamics of the linear segments containing urethane groups. For comparison, linear polyurethanes as well as polyurethanes crosslinked with the classical crosslinker trimethylolpropane were prepared. Broadband dielectric spectroscopy, dynamic mechanical analysis, and differential scanning calorimetry yielded consistent results concerning the molecular relaxation processes; however, dielectric spectroscopy appeared to be more sensitive concerning the secondary relaxation processes. In the temperature range up to 150°C, the molecular relaxations were very similar in all the investigated samples, despite considerable structural differences. The weak influence of the crosslinking on the

molecular properties could be explained by the existence of hydrogen bonds forming a physical network, which was very dense in this temperature range in comparison with the chemical crosslinks and therefore dominated the molecular mobility in all the investigated systems. This hypothesis was confirmed by rheological measurements performed at temperatures above 150°C, when the hydrogen bonds should be thermally destroyed. At these temperatures, the effect of crosslinking was manifested by a strong shift of the flowing point: in the linear polyurethanes, this point occurred at much higher frequencies (and lower temperatures) than in the crosslinked analogues. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 105: 89–98, 2007

Key words: crosslinking; hyperbranched; molecular dynamics; networks; polyurethanes

INTRODUCTION

Dendritic polymers are an intensively investigated class of macromolecular materials. Compared with dendrimers, hyperbranched (HB) polymers are less regular in their molecular structure, but they can be prepared by a single-step process avoiding complicated iterative reaction sequences and difficult purification.

A lot of reviews dealing with the synthesis and properties of dendrimers and HB polymers have been published.^{1–5}

Dendritic polymers show unusual properties, in comparison with their linear analogues, resulting from their specific structure and numerous functional groups. Although HB macromolecules have a branching efficiency usually below 80%, they possess many of the desirable properties for which dendrimers are noted. HB polymers have enormous potential for further reactions to give a wide variety of derivatives with unique properties, especially if alternative one-pot synthetic methods could be developed. Even if their utility value is restricted, they can be used in crosslinking processes or coating applications. A systematic investigation of HB polyesters as curing agents has been developed in Sweden.^{6,7}

Polyurethanes (PUs) are probably the most versatile class of polymers. PU elastomers are usually block copolymers that consist of polyol sequences (soft segments) and diisocyanate/short diol sequences (hard segments). Most publications on this subject show that the composition and conditions of processing are the main factors that influence the

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chemical and morphological structure of the PUs and their properties.^{8–10}

In this work, several PU networks based on HB crosslinkers were synthesized. The concentration of the crosslinking agent in the polymer mass and its coordination number were changed to obtain networks with different structures. The molecular dynamics of the obtained systems were investigated by means of dielectric relaxation spectroscopy (DRS), dynamic mechanical analysis (DMA), differential scanning calorimetry (DSC), and rheological measurements.

EXPERIMENTAL

Materials

Several PU networks crosslinked with HB polymers were synthesized in bulk with polytetrahydrofuran [Terathane 650; number-average molecular weight (M_n) = 650 g/mol] and 4,4'-diisocyanato-diphenylmethane [MDI; weight-average molecular weight (M_w) = 250 g/mol] as monomers and HB polyesters of fourth and third generations (Boltorn H40 and Boltorn H30) and modified Boltorn H40 as crosslinking agents. Additionally, to check the influence of the crosslinking agent on the molecular dynamics, PU systems without a crosslinking agent or crosslinked with trimethylolpropane (TMP) were synthesized. Terathane 650, MDI and TMP were supplied by Sigma-Aldrich Co. (Poznan, Poland and Buchs, Switzerland). The Boltorn samples were produced by Perstorp Sweden Co. (Perstorp, Sweden). The structures of the different crosslinkers used in this study are shown in Figure 1. According to the producer, Boltorn H40 has a molar mass of $M_w = 5100$ g/mol, a polydispersity of $M_w/M_n = 1.8$, and a hydroxyl number of 470–500 mg of KOH/g. These data give on average 44 primary —OH groups in the molecule. Boltorn H30, with a molar mass of $M_w = 3500$ g/mol, a polydispersity of $M_w/M_n = 1.5$, and a hydroxyl number of 480–510 mg of KOH/g has on average 31 primary —OH groups in the molecule. The substrates were used as supplied by the producer without additional purification.

To reduce the number of primary —OH groups in the fourth-generation HB macromolecules, they were modified by *p*-tolylisocyanate (PTI). The schematic outline of the HB aliphatic polyester Boltorn H40 modification reaction is shown in Figure 2. Boltorn H40 was dissolved in tetrahydrofuran (THF) in a weight ratio of about 2:1 in a flask equipped with a magnetic stirrer. An appropriate amount of PTI needed to achieve the desired degree of blocking was added. The mixture was stirred at room temperature for 1 week. The completion of the reaction was determined by Fourier transform infrared (FTIR) spectroscopy, when no peak connected with the

presence of —NCO groups in the material was observed. In the second step, the reaction mixture was placed in a vacuum chamber at 60°C to remove THF. The evaporation was slow and regulated manually to avoid the rapid evacuation of THF and sloshing of the sample bulk. When a large majority of THF was removed, the material was placed in a vacuum drier. The modified Boltorn H40 was dried for 1 week under a high vacuum at 60°C. The residual amount of THF was checked by thermogravimetric analysis and taken into account for further calculations. The degree of modification of Boltorn H40 was calculated in accordance with the following equation:

$$T_m = \frac{\text{Eq(OH)}_{\text{HBnmod}} - \text{Eq(OH)}_{\text{HBmod}}}{\text{Eq(OH)}_{\text{HBnmod}} \cdot [1 + \text{Eq(OH)}_{\text{HBmod}} \cdot M_{\text{PTI}}]} \cdot 100\% \quad (1)$$

where $\text{Eq(OH)}_{\text{HBmod}}$ is the number of —OH group moles per kilogram of modified Boltorn H40, $\text{Eq(OH)}_{\text{HBnmod}}$ is the number of —OH group moles per kilogram of unmodified Boltorn H40, and M_{PTI} is the molar mass of PTI (kg).

The number of moles of —OH groups in modified and unmodified Boltorn materials was determined with pH-metric titration. About 0.5 g of the Boltorn sample was dissolved in 10 mL of THF. Tosyl isocyanate was added in excess to neutralize the —OH groups of Boltorn. Then, the dibutylamine was added in excess to neutralize the rest of the unreacted —NCO groups from tosyl isocyanate. The mixture was titrated by 1N HCl. The end point was indicated when the pH of the solutions reached 3.8. The number of moles of —OH groups per kilogram [Eq(OH)] was calculated with the following equation:

$$\text{Eq(OH)} = \frac{V_{eq} - V_0}{m} \quad (2)$$

where V_{eq} is the number of milliliters of HCl when the pH is 3.8 for a solution containing dissolved Boltorn, V_0 is the number of milliliters of HCl when the pH is 3.8 for a blank test, and m is the mass of dissolved Boltorn.

Eq(OH) for unmodified Boltorn H40 is equal to 8.4 mol of OH/kg and for Boltorn H30 is equal to 8.5 mol of OH/kg. These results confirm data given by the producer.

The main aim of the synthetic work presented in this article is to elaborate networks in which PU linear chains are connected by the HB crosslinkers with different coordination numbers. The number of primary —OH functions present in the HB polymer has to control in fact the number of the linear segments connected to the HB polyester. The linear chains in this network series have a constant length described by the

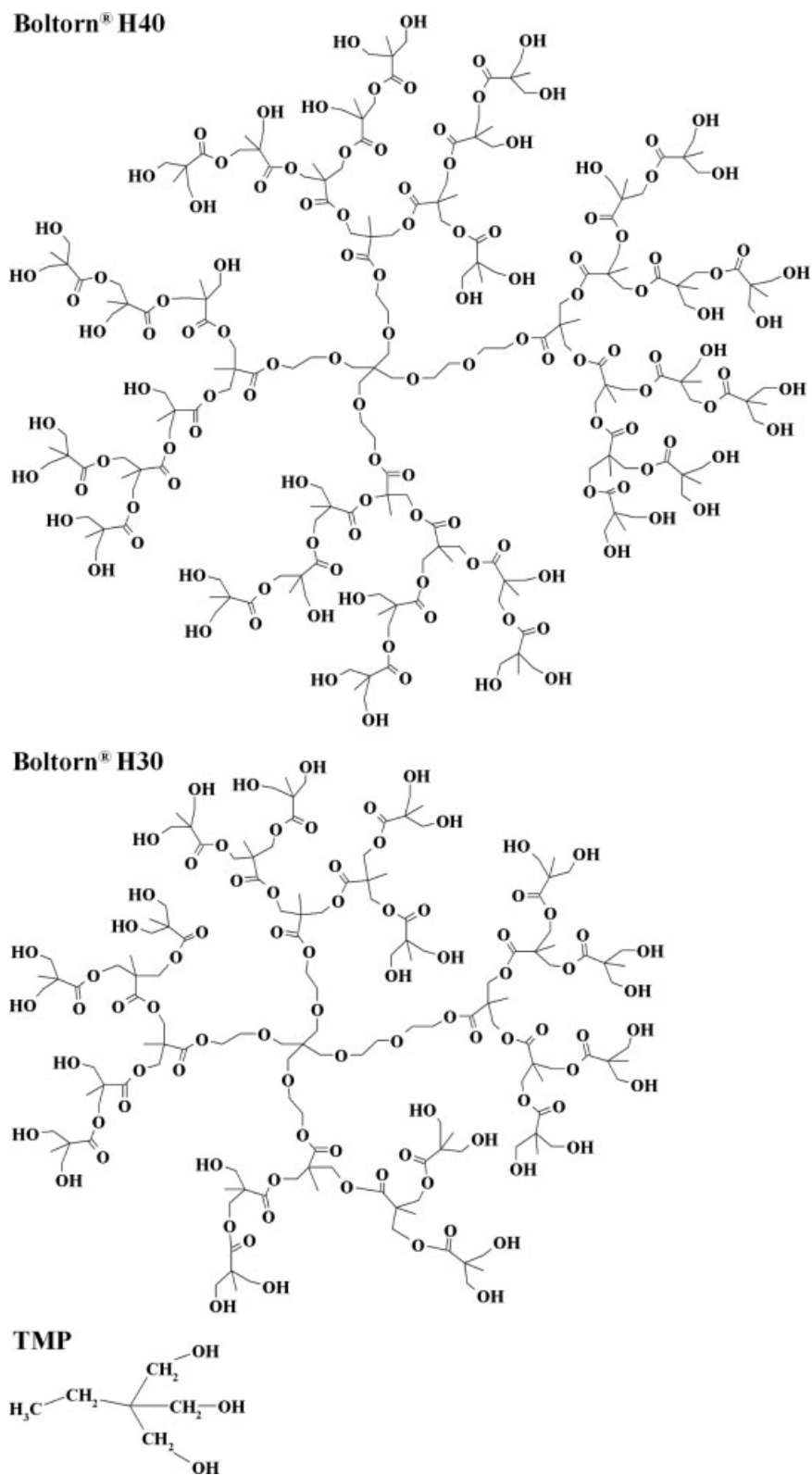


Figure 1 Simplified chemical structures of the crosslinking agents used in the reaction.

number of macrodiol–diisocyanate repeating units (n), which is equal to 4. The synthesis of PUs was carried out in bulk. A schematic route for the synthesis of the PU networks crosslinked with HB centers is shown in

Figure 3. The amounts of the ingredients for the synthesis of the stoichiometric systems were calculated in accordance with the number of —OH groups in the crosslinker and the projected length (in this case, $n = 4$)

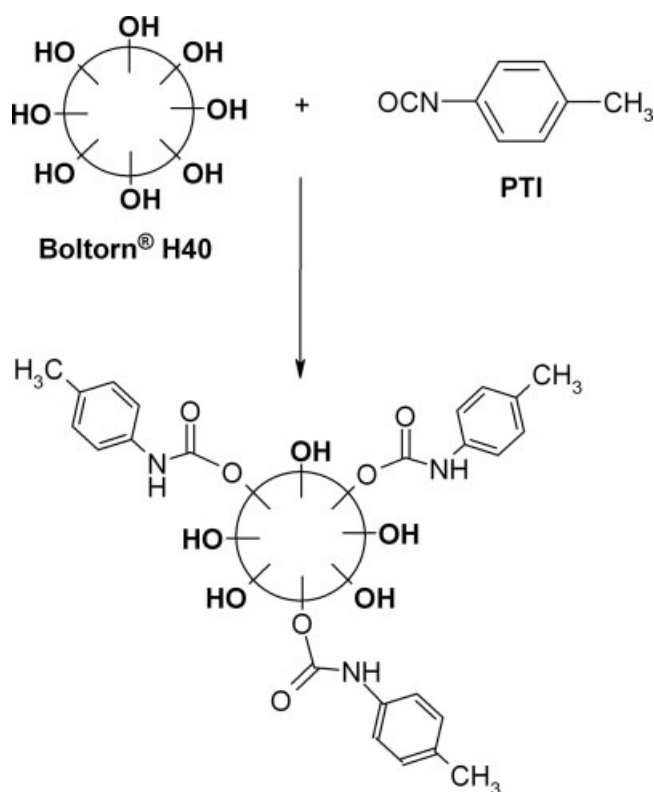


Figure 2 Schematic reaction of the Boltorn H40 modification with the monoisocyanate.

of the linear segments between the crosslinking centers.¹¹ The calculated amount of Terathane was placed in a flask equipped with a magnetic stirrer, heated up to 80°C, and kept there for half an hour *in vacuo*. Then, the crosslinker was added, and the mixture was stirred at about 100°C until the complete dissolution of the reactants. When the solution was clear, it was degassed *in vacuo* at 60°C for half an hour to avoid bubbling during the reaction. In the next step, MDI, preheated up to 60°C, was added. After quick mixing for about 1 min, the reactive solution was cast onto an aluminum pan and again placed *in vacuo* at 60°C for

half an hour. To get the full conversion of the reactive system, the pan was placed in the drying oven at 100°C for 7 h. The polymers were obtained as films with thicknesses ranging from 0.2 to 1 mm. The end of the reaction was determined by FTIR spectroscopy. In the PU networks, the diisocyanate —N=C=O band (2250–2275 cm^{-1}) was absent in the spectra. The bands characteristic of the urethane bonds could be observed at 3320 cm^{-1} for the urethane N—H stretching, at 1731 cm^{-1} for the urethane C=O without hydrogen bonding, at 1710 cm^{-1} for the urethane C=O with hydrogen bonding, and at 1535 cm^{-1} for the urethane C—N—H bonding.

Characterization techniques

The chemical structure of the synthesized materials was verified by FTIR absorption with a Bio-Rad FTS 175 C spectrometer (Krefeld, Germany) in the reflection mode with a Harrick IRS (Krefeld, Germany) attachment.

The glass-transition temperatures (T_g 's) were determined by DSC (DSC 2920, TA Instrument, New Castle, DE) with samples of about 10 mg in sealed aluminum pans. Two runs were performed for each sample in the range from -150 to $+200^\circ\text{C}$ at a heating rate of $10^\circ/\text{min}$ under a nitrogen atmosphere. The cooling scans were performed at an average rate of $25^\circ/\text{min}$. The T_g values were determined as the onset points from the second scan.

Molecular relaxations were characterized in broad temperature and frequency ranges by DMA with a TA Instrument DMA 2980 dynamic mechanical analyzer and by DRS with a Novocontrol (Hundsangen, Germany) broadband dielectric spectrometer. DMA was performed in a film tension mode in the temperature range from -130 up to $+150^\circ\text{C}$ with a temperature ramp of $2^\circ/\text{min}$ on rectangular samples with a length of 25 mm, a width of 5 mm, and a thickness of 1 mm. Three frequencies were applied: 1, 5, and 10

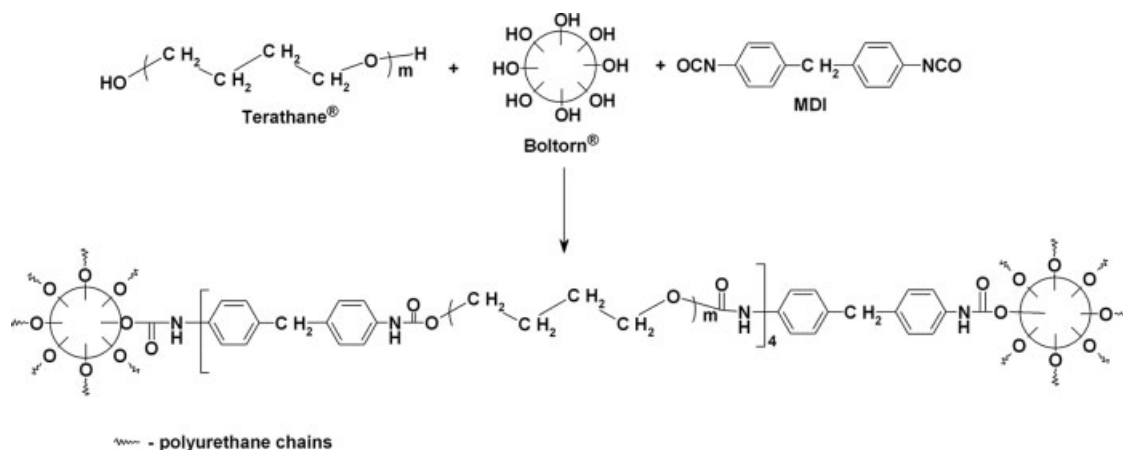


Figure 3 Diagram of the PU network synthesis.

TABLE I
 T_g Values for the PU-Based Systems Determined by DSC

Sample	Crosslinking agent	T_g (°C)
PU	—	-37.3
PU-TMP	TMP	-32.7
PU-HB4-59	Boltorn H40, 59% of -OH blocked	-33.1
PU-HB4-22	Boltorn H40, 22% of -OH blocked	-35.8
PU-HB4-14	Boltorn H40, 14% of -OH blocked	-37.2
PU-HB4-0	Boltorn H40, unmodified	-39.3
PU-HB3-0	Boltorn H30, unmodified	-35.1

Hz. DRS was performed in the frequency range of 0.01 Hz to 1 MHz and in the temperature range from -150 up to +130°C in 5°C steps. For these measurements, circular samples with a diameter of 20 mm and a thickness up to 0.5 mm were used.

Dielectric results were presented in the classical representation of the dielectric permittivity ($\epsilon^* = \epsilon' + i\epsilon''$, where ϵ' and ϵ'' are the real and imaginary parts of the permittivity, respectively) and with the electric modulus ($M^* = M' + iM''$, where M' and M'' are the real and imaginary parts of the electric modulus, respectively) representation defined by Macedo et al.¹² M' and M'' were calculated according to the following equations:

$$M' = \frac{\epsilon'}{\epsilon'^2 + \epsilon''^2} \quad (3)$$

$$M'' = \frac{\epsilon''}{\epsilon'^2 + \epsilon''^2} \quad (4)$$

Although the permittivity representation is easier to interpret, the modulus representation can be very useful when conductivity processes are involved.

The relaxation maps were prepared on the basis of both dielectric and mechanical spectra. The points were taken from the $\epsilon''(f)$ plots with WinFit software (Novocontrol, Hundsangen, Germany) for dielectric relaxations and for conductivity phenomenon manually from the $M''(T)$ plots. For the mechanical relaxations, the points from the loss modulus, $E''(T)$ plots were taken. The relaxation times (τ) were calculated with the following equation: $\tau = 1/(2\pi f)$, where f stands for the frequency.

Linear viscoelastic measurements of the complex shear modulus, where G' is real part and G'' is imaginary part of shear modulus, [$G^*(\omega) = G'(\omega) + G''(\omega)$] were performed with a Rheometrics Instrument RS5 apparatus (Prinstown, USA) in the range of temperatures from +150 to +230°C and for frequencies from 10^{-2} up to 10^2 rad/s. The temperature step was 10°. The samples for these measurements had a diameter of 25 mm and a thickness of about 0.5 mm. Nitrogen was used to prevent thermal oxidation.

RESULTS

The T_g 's of the investigated systems, determined by means of DSC, are collected in Table I. The differences in the T_g 's of the PU networks are not large, but a clear tendency can be observed: T_g increases with the decreasing coordination number of the crosslinker.

Figure 4 shows the three-dimensional frequency and temperature dependence of ϵ'' for the PU network crosslinked by unmodified Boltorn H40 and for the noncrosslinked PU. On the DRS spectra, we can see three relaxation processes, which are named α , β , and γ relaxations in order of decreasing temper-

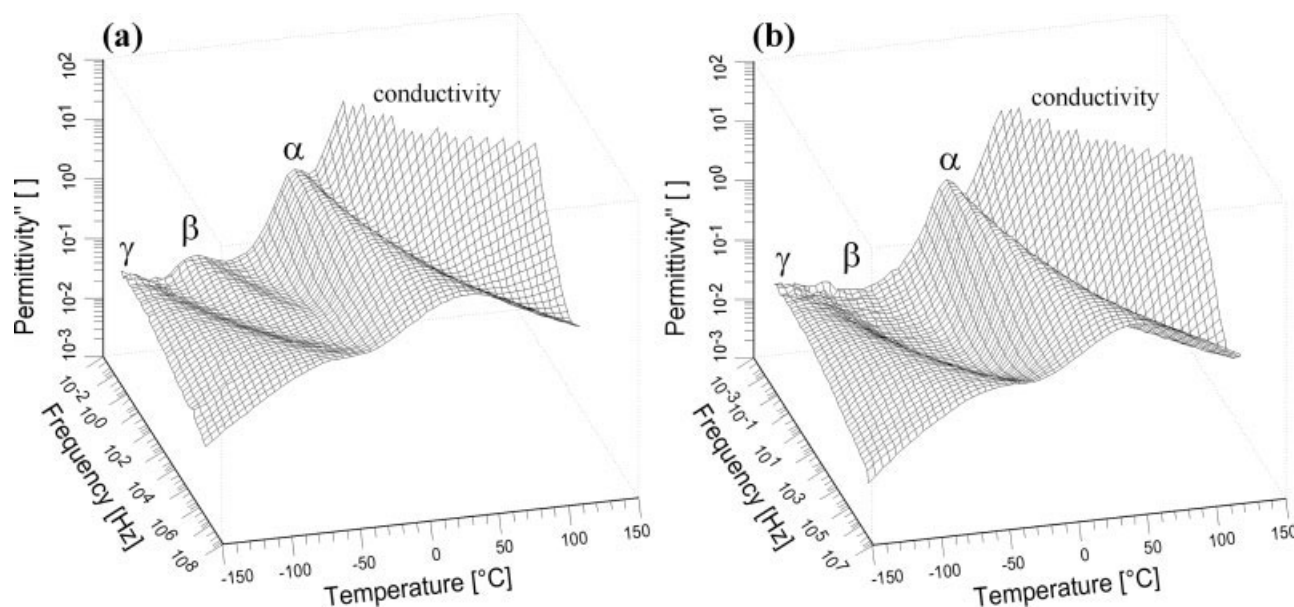


Figure 4 Frequency and temperature dependence of the imaginary part of the permittivity for (a) network PU-HB4-0 and (b) noncrosslinked PU.

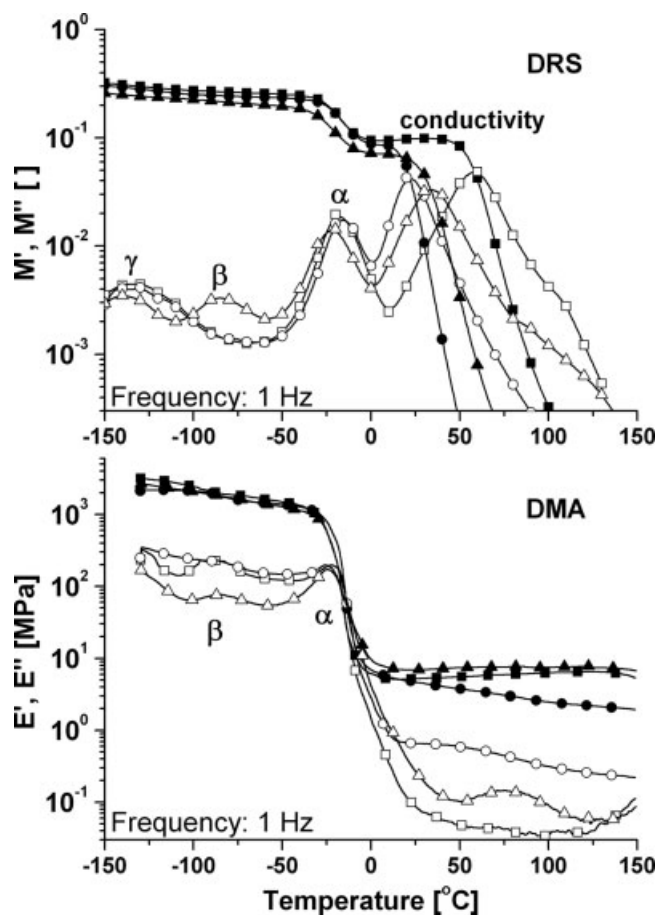


Figure 5 DMA and DRS spectra for (■,□) noncrosslinked PU and networks (●,○) PU-TMP and (▲,△) PU-HB4-0. The full points represent the real part of the moduli, and the open points present the imaginary part.

ature. In the highest temperature range, above the α relaxation, the conductivity phenomenon occurs. The conductivity phenomenon gives on the diagram of the electrical modulus representation (see Fig. 5) one more maximum above the α peak. These relaxation processes can be seen in all the investigated samples, although the β relaxation is well pronounced only in the networks crosslinked by the HB crosslinkers.

Figure 5 shows DRS and DMA spectra for the sample crosslinked by unmodified Boltorn H40 in comparison with the sample crosslinked by the classical crosslinker, TMP, and with the noncrosslinked sample. One can see that the position of the α -relaxation maximum related to T_g depends very weakly only on the kind of crosslinker. At 1 Hz, the maximum of the α -relaxation peak is at about -22°C for the sample crosslinked by Boltorn H40, at -16°C for the sample crosslinked by TMP, and at about -18°C for the noncrosslinked PU. This tendency correlates well with the DSC data shown in Table I. The intensity of these α peaks is almost equal; only for the samples with Boltorn H40, it is slightly lower. As mentioned previously, the β relaxation is well pro-

nounced only for the sample crosslinked with the HB polymer. The temperature position of this peak for a frequency of 1 Hz is about -85°C . The activation energy (E_a) of the β relaxation is about 63 ± 1 kJ/mol. For other samples, this peak is weak, and its exact temperature position was difficult to determine. For all the systems, the γ relaxation is quite visible, and although the differences in its peak position are small, there are noticeable differences in the E_a values. For the noncrosslinked PU, E_a is 38.2 ± 0.2 kJ/mol, whereas E_a is 39.8 ± 0.5 and 44.8 ± 0.5 kJ/mol for the network systems crosslinked by Boltorn H40 and TMP, respectively. The DMA investigations give similar results, but the γ relaxation is beyond the investigation ranges of the frequency and temperature. All points from dielectric and mechanical results are collected on the activation plot shown in Figure 6.

In Figure 7, the results of the rheological measurements at high temperatures for these three samples are shown. As expected, it can be seen that the linear sample differs strongly from the crosslinked samples. The linear sample behaves as a viscoelastic liquid, whereas the crosslinked samples behave as viscoelastic solids. However, this viscoelastic solid behavior is observed only at a high frequency, as the onset of the terminal relaxation zone can be easily seen in this figure. The observation of this relaxation zone, or flowing zone, is rather unexpected for crosslinked systems because an elastic temporary network is pointed out. This can be explained by the fact that the density of the chemical crosslinking is very low; therefore, in these crosslinked systems, it is possible to observe the flowing behavior. In addition, it is also clear from Figure 8, showing the variation of the complex shear modulus versus the frequency for PU-HB4-22 at different temperatures, that the time-

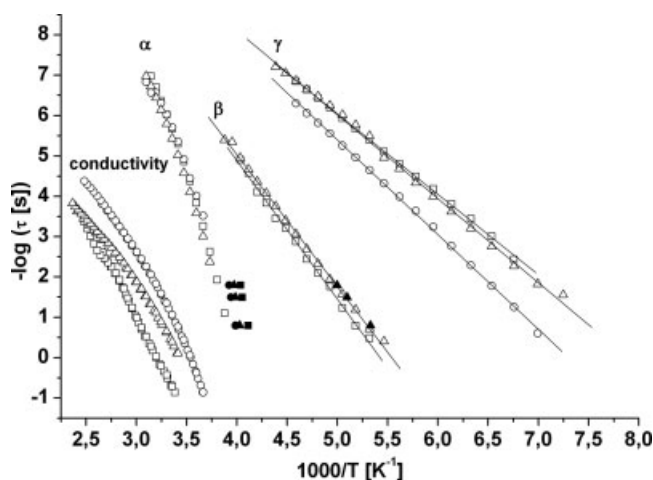


Figure 6 Relaxation map for (■,□) noncrosslinked PU and networks (●,○) PU-TMP and (▲,△) PU-HB4-0. The open points represent DRS, and the full points represent DMA.

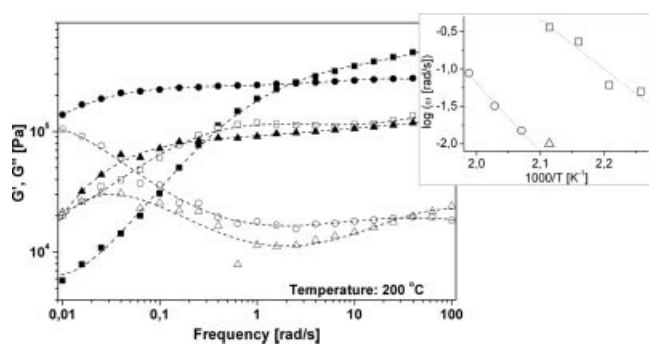


Figure 7 Variation of the complex shear modulus versus the frequency for (■,□) noncrosslinked PU and networks (●,○) PU-TMP and (▲,△) PU-HB4-0. The full points represent the storage modulus, and the open points represent the loss modulus. The inset diagram shows the Arrhenius plot for the flowing points.

temperature superposition cannot be applied in the entire range of investigated temperatures ($150^{\circ}\text{C} < T < 230^{\circ}\text{C}$). Only for temperatures higher than about 180°C can this principle be applied within the experimental error. Actually, this result shows that the nature of the interchain interactions, hydrogen bonding, drastically changes at temperatures close to 180°C . At much higher temperatures, above about 220°C , the time-temperature superposition principle also cannot be applied, presumably because of the beginning of the thermal degradation of the PU.

The onset of the terminal relaxation zone ($\omega_{G'=G''}$) was used to define the onset of the flowing behavior and is named the flowing point in this article. As expected, the flowing points for the noncrosslinked PU are higher than those for the crosslinked samples.

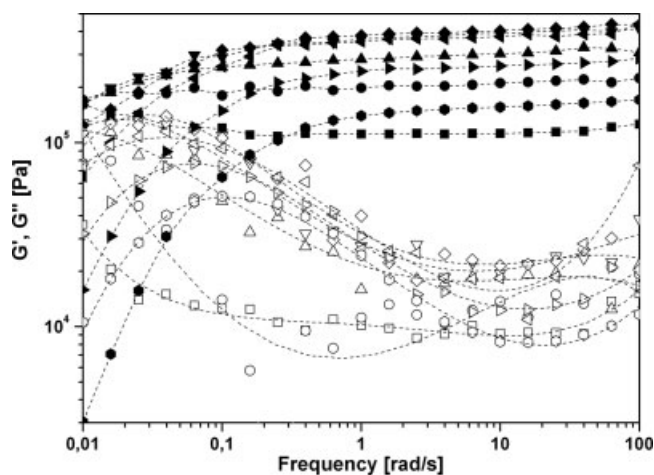


Figure 8 Variation of the complex shear modulus versus the frequency for PU-HB4-22 at different temperatures: (■,□) 150, (●,○) 170, (▲,△) 180, (▼,▽) 190, (◆,◇) 200, (◀,◁) 210, (▶,▷) 220, and (⊙,⊚) 230°C. The full points represent the storage modulus, and the open points represent the loss modulus.

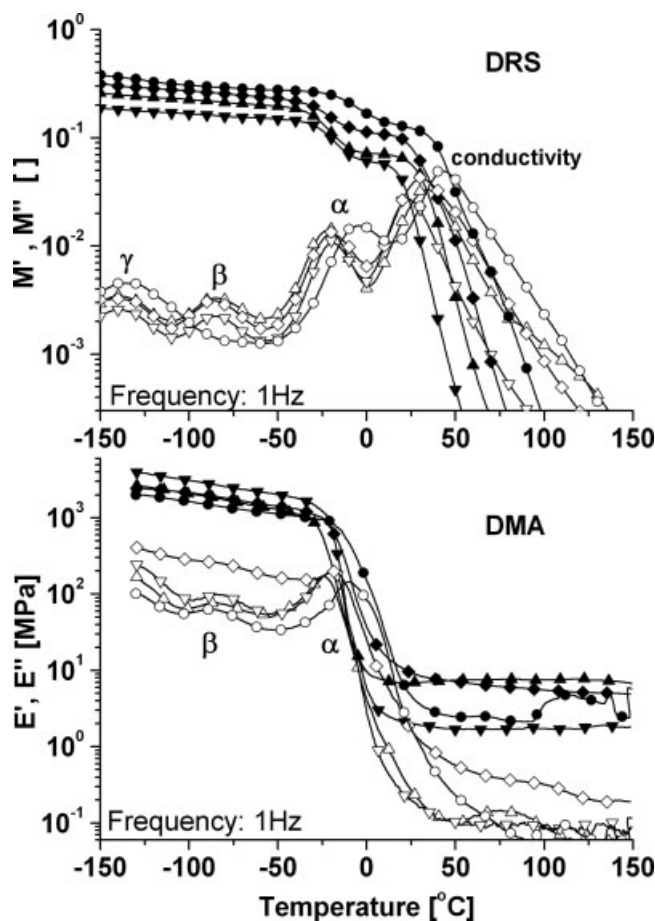


Figure 9 DMA and DRS spectra for the samples crosslinked by Boltorn H40 with different coordination numbers: (▲,△) PU-HB4-0, (▼,▽) PU-HB4-14, (◆,◇) PU-HB4-22, and (●,○) PU-HB4-59. The full points represent the real part of the moduli, and the open points represent the imaginary part.

For usual crosslinked polymers, the flowing point tends to zero (permanent elasticity) above the gel point. Nevertheless, it can be seen from the inset figure in Figure 7 that the results obey the same Arrhenius plot; that is, this phenomenon has the same activation energy. This result means that the hydrogen interactions change with the temperature in the same way for noncrosslinked and crosslinked PUs.

Boltorn H40 was used as a crosslinker in an unmodified form and with partial modification of the terminal $-\text{OH}$ groups. Figure 9 shows the dielectric and mechanical spectra of the PU systems crosslinked by Boltorn H40 crosslinkers with different coordination numbers, and Figure 10 shows the relaxation map collecting all the points from the DRS and DMA maxima. On the dielectric spectra, three relaxation processes and conductivity are visible. The α relaxation connected with T_g depends on the functionality of the HB crosslinker: the more $-\text{OH}$ groups are present in the crosslinking agent, the lower the temperatures are of the α relaxation in

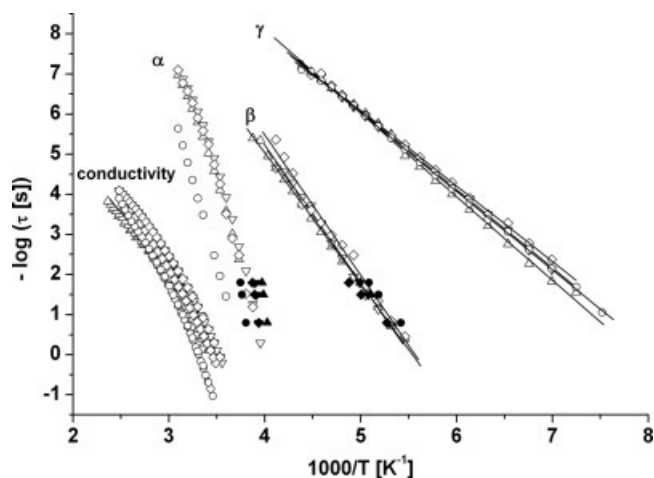


Figure 10 Relaxation map for samples crosslinked by Boltorn H40 with different coordination numbers: (▲,△) PU-HB4-0, (▼,▽) PU-HB4-14, (◆,◇) PU-HB4-22, and (●,○) PU-HB4-59. The open points represent DRS, and the full points represent DMA.

the network. This effect is observed also in the DMA and DSC results. The β relaxation is well pronounced for all the samples, except the one crosslinked by Boltorn with the lowest coordination number (PU-HB4-59). E_a of the β relaxation is similar for all the samples and equals about 62–64 kJ/mol. Also, the γ relaxation does not differ very much with changing crosslinker functionality and appears at about -140°C at 1 Hz. Its E_a is about 36–39 kJ/mol, but the changes are not regular. DMA gives coherent results with the DRS investigations.

The rheological data for the networks based on Boltorn H40 with different modification degrees are shown in Figure 11. One can see that for this series

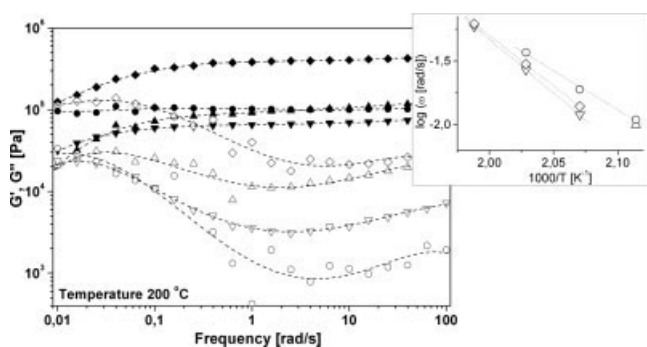


Figure 11 Variation of the complex shear modulus versus the frequency for the samples crosslinked by Boltorn H40 with different coordination numbers: (▲,△) PU-HB4-0, (▼,▽) PU-HB4-14, (◆,◇) PU-HB4-22, and (●,○) PU-HB4-59. The full points represent the storage modulus, and the open points represent the loss modulus. Insert diagram shows the Arrhenius plot for the flowing points.

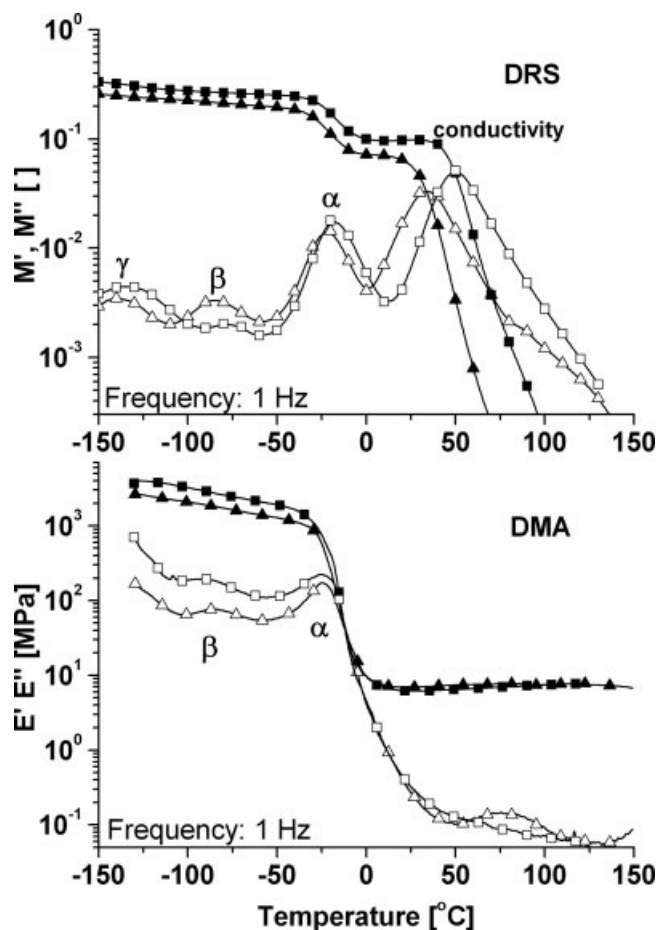


Figure 12 DMA and DRS spectra for the samples crosslinked by Boltorn with different generations: (▲,△) PU-HB4-0 and (■,□) PU-HB3-0. The full points represent the real part of the moduli, and the open points represent the imaginary part.

of samples, the flowing points differ only slightly. This is caused by the fact that the density of the chemical crosslinking in these networks is similar.

Finally, the influence of the crosslinker generation on the molecular dynamics was investigated. In Figure 12(a), a comparison of the DRS and the DMA spectra for the samples crosslinked by Boltorn H40 and Boltorn H30 is shown. Figure 13 shows the activation plot made on the basis of these spectra. Also, for PU-HB3-0, the dielectric spectra show three relaxation processes and the conductivity phenomenon at high temperatures. In DRS, for sample PU-HB3-0, the α relaxation is shifted to lower temperatures in comparison with PU-HB4-0. The β process in the PU-HB3-0 has a higher activation energy, about 81 kJ/mol, whereas for PU-HB4-0, it is only 63 ± 1 kJ/mol. The γ relaxation is practically identical in both samples.

The variation of the complex shear modulus for PU-HB4-0 and PU-HB3-0 is shown in Figure 14 at $T = 200^\circ\text{C}$. It can be observed that the flowing points

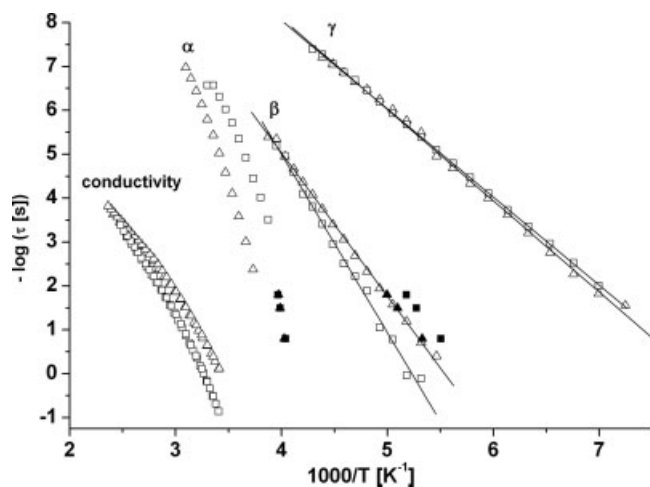


Figure 13 Relaxation map for the samples crosslinked by Boltorn with different generations: (▲,△) PU-HB4-0 and (■,□) PU-HB3-0. The open points represent DRS, and the full points represent DMA.

are nearly the same for these two samples. However, the magnitude of the temporary elastic modulus is quite different. Interestingly, the sample with the fourth-generation crosslinking agent has a lower temporary elastic modulus than the sample with the third generation of the crosslinking agent.

DISCUSSION

In all the investigated systems, three relaxation processes (primary α and secondary β and γ) can be observed with DRS and DMA. In the linear viscoelastic investigations at high temperatures, a characteristic flowing point, $\omega_{G'=G''}$, was determined at lower frequencies. All these molecular processes are more or less sensitive upon the crosslinking of the PU macromolecules.

The primary α relaxation, associated with the glass-transition process, is observed by means of both DRS and DMA. These techniques give coherent results confirmed by the DSC measurements. The introduced crosslinking agent has only a weak influence on the glass transition (T_g shifts by less than 5°C; see Table I). The α relaxation is well pronounced for all the crosslinked systems, and the position of the peak is shifting only slightly to a higher temperature with decreasing crosslinker functionality. Such behavior was expected because the crosslinker concentration in our systems can only slightly influence the flexibility of the linear chains between the crosslinking points, and it is the mobility of the large segments of these chains that determines the position of the α relaxation and the glass transition. Additionally, one can argue that the hydrogen bonds, which are created between ure-

thane groups in the linear chains, form at low temperatures similar physical networks in all these systems. The density of the H bonds is much higher than the density of the chemical crosslinking points in the network, so at temperatures below and near the glass transition, the H bonds play a dominant role. Similar findings of dominating effects of the hydrogen bonds in HB polyurea/urethane systems on their properties are described in an article by Abd Elrehim et al.¹³ Also, Shetha et al.¹⁴ has underlined the role of the distribution of hydrogen bonding in the properties of highly branched, segmented poly(urethane urea) copolymers.¹⁴

The secondary β relaxation is most likely attributable to the local motions of the polar urethane groups.^{10,15,16} Although all the samples show the β relaxation in a similar temperature region, one can see that the β peak is well pronounced only for the samples crosslinked with the HB polymers of a high coordination number. For the rest of the samples, this process is only slightly marked, and its detailed analysis is very difficult, sometimes even impossible. Such differences in the intensity of the β relaxation can be explained by differences in the ease of creation of H bonds between the urethane groups. In the linear systems or systems crosslinked by relatively small TMP molecules, the β relaxation is almost invisible because most of the urethane groups are fixed by hydrogen bonds. The possibility of H-bond creation between urethanes is lower in the samples with Boltorn. The HB molecule has a diameter comparable to the length of the linear segments. Because of such an architecture, one can expect that the linear chains will be more separated and create weaker H bonds. Additionally, the urethane groups connected directly to the HB crosslinkers do not form H bonds at all because of steric hindrance and can move relatively easily. Therefore, more urethane

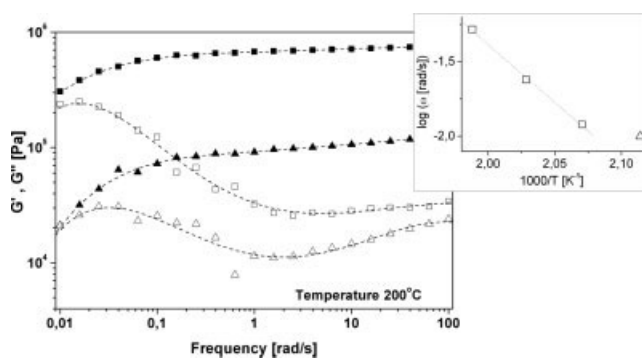


Figure 14 Variation of the complex shear modulus versus the frequency for the samples crosslinked by Boltorn with different generations: (▲,△) PU-HB4-0 and (■,□) PU-HB3-0. The full points represent the storage modulus, and the open points represent the loss modulus. The inset diagram shows the Arrhenius plot for the flowing points.

groups are mobile and can contribute in this case to the β relaxation. In the system crosslinked by Boltorn H30 or Boltorn H40 with a high modification degree, the β -relaxation process is less pronounced because such nonbonded urethane groups are less numerous there.

The γ relaxation visible in all the examined systems is associated with a local motion of the $(\text{CH}_2)_4$ sequences of the soft segments. Because in the investigated systems such sequences are almost identical, no significant differences are observed in the behavior of this relaxation.

To verify the hypothesis that strong H bonds are present in the systems and that the physical network determines the material properties, high-temperature rheological measurements were performed. At temperatures above about 180°C, the hydrogen bonds should be thermally destroyed, and the chemical nature of the networks should be visible. On the rheological plots, one can see that the flowing point for linear PU is detected at a much higher frequency and lower temperature range than for the chemically crosslinked samples, and this results from the higher mobility of the noncrosslinked chains. Surprisingly enough, a nonpermanent elasticity of the crosslinked sample was observed. This strange behavior can be explained by the very low density of the chemical crosslinking. However, all networks show similar flowing behavior in rheological investigations. This is caused by the fact that the density of crosslinking of these networks is the same (the same length of linear chains between crosslinking points).

CONCLUSIONS

It has been found that the molecular dynamics in new PU networks based on HB polyesters are weakly dependent on the network architecture. Unexpected small differences observed between the noncrosslinked and crosslinked samples have been explained by the presence of the physical network. Only at high enough temperatures, when the H bonds can be broken, can the differences in the molecular mobility easily be seen in the rheological properties. An unexpected result has been observed because the crosslinked samples exhibit at a low frequency the onset of a flowing zone (relaxation zone). However, as expected, the flowing point for linear PU is at a much higher frequency (or at a lower temperature) than that for the crosslinked samples.

At lower temperatures, a change in the crosslinking agent nature results in a relatively weak modification of the α relaxations. This is explained by the fact that the dynamics of the PU chains are quite

similar in the different systems as they depend mainly on the physical network created by hydrogen bonds taking place between the urethane groups of the chains, this physical network being nearly the same in all cases. Among the secondary relaxations, only β relaxations show some sensitivity to the presence of the crosslinker. The intensity of the β relaxation depends on the kind of crosslinker, and this process is quite visible only in the samples with the HB crosslinkers. This is because the urethane groups, which are close to the HB crosslinker, have lower probability to create the H bonds between them, so more urethane groups are mobile and can contribute to the β relaxations.

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This paper is dedicated to memory of Professor Marian Kryszewski, founder of Polish school of polymer physics and promoter of Polish-French scientific collaboration.

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