



Molecular dynamics in polyester- or polyether-urethane networks based on different diisocyanates

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ABSTRACT

Different non-conventional polyurethane networks crosslinked with a hyperbranched polyester (Boltorn[®]H40) were synthesised with an aim to determine the influence of the polyurethane chemical structure as well as of the length of the linear chains between crosslinking centres on molecular relaxations in such systems. For that purpose, both polyether- and polyester-type macrodiols as well as two different diisocyanates were used to synthesise the connecting polyurethane chains between crosslinks. Molecular dynamics were investigated by dielectric spectroscopy and by dynamic mechanical analysis. It was found that the changes of the repeating macrodiol-diisocyanate unit number (*i.e.* length of the polyurethane linear chains) practically did not affect the molecular relaxations. This effect was explained by the formation by hydrogen bonds between urethane groups of similar, independent of the polyurethane linear chain length, physical networks, which control the molecular mobility. By contrast, the chemical nature of the precursors strongly influences the molecular relaxation associated with glass transition, and to some extent also the sub-glass secondary relaxation processes occurring in the investigated networks.

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1. Introduction

Polyurethanes (PUs) are unique polymeric materials with a wide range of physical and chemical properties [1]. PUs can be tailored to meet the highly diversified demands of modern technologies such as coatings, adhesives, fibres, foams and thermoplastic elastomers. Linear segmented PU elastomers can be considered as block copolymers, which consist of soft segments formed by polymer glycol and hard segments based on diisocyanate and chain extender. The properties of these PU elastomers are strongly dependent on the molar mass and polymolecularity of the soft segment component [2], as well as on the chemical structure of all the components [3–6].

As far as the PU networks are concerned, one of the important factors used for changing their properties is the type of crosslinking agent. In such systems two kinds of networks can be present: physical and chemical. The physical network results from the H-bonds linking the carbonyl and amine groups of adjacent chains [7]. The physical network density influences strongly the material properties up to *ca.* 150 °C [2]. Chemical network parameters depend on the crosslinker's nature. Recently some papers dealing

with the use of dendritic molecules as crosslinking agents were published [8]. Especially random hyperbranched (HB) macromolecules, which can be easily obtained by one-pot synthetic methods, are very promising crosslinking agents [2,9,10].

In this work several PU networks based on a hyperbranched polyester of the fourth pseudo-generation were investigated by means of dielectric spectroscopy and dynamic mechanical analysis, which give complementary information about the molecular dynamics of these materials. More precisely, these networks were based on a macrodiol of adjustable chemical nature and length, a diisocyanate used in varying excess, and finally a multifunctional hydroxylated hyperbranched crosslinking agent. In previous papers the influence of several network parameters such as the average length of the PU chains between crosslinks (regulated either by the length of the starting macrodiol or by the number of repeating macrodiol-diisocyanate units) [2], the coordination number (regulated by a partial chemical modification of the hydroxyl chain ends) [11], and the pseudo-generation [12] of the crosslinking agent was investigated. These works showed that in such polyurethane networks, the parameters strictly affecting the global chemical network architecture (namely the coordination number and generation of the crosslinker, and the length of the connecting PU chains) had only a very weak influence on molecular dynamics, as long as the physical network formed by hydrogen bonds was not affected itself. Only the β sub-glass relaxation seemed to show

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some sensitivity to the coordination number of the used crosslinker [11]. In contrast when the overall H-bond “concentration” was varied in a significant way, *i.e.* by varying the PU connecting chains through changing the length of the starting macrodiol, strong effects were indeed observed both on the α -relaxation and on the overall material behaviour [2]. This suggests that the modification of the physical network can be the most efficient way of tailoring the properties of these materials.

In the present work, the architecture of the polyurethane networks was modified at the smallest possible molecular scale by changing the chemical nature of the diisocyanate and of the starting hydroxy-terminated oligomer (polyester- or polyether-type macrodiols). Additionally the samples with varying length of the PU chains between the crosslinks (regulated by changing the number of the repeating macrodiol–diisocyanate units in the chain) were also synthesised and investigated to check the possible influence of this parameter in the particular case of chemically different precursors, as complementary studies to those previously reported [2].

2. Experimental details

2.1. Materials

Several PU networks were synthesised using polytetrahydrofuran (Terathane[®]650, abbreviated as T₆₅₀, with $M_n = 650$ g/mol) or polycaprolactone (Capa[®]550, abbreviated as C₅₅₀, with $M_w = 550$ g/mol) macrodiols and pure difunctional 4,4'-diisocyanatodiphenylmethane (MDI with $M_w = 250$ g/mol) or 4,4'-diisocyanatodicyclohexylmethane (H₁₂MDI with $M_w = 262$ g/mol) as monomers. The chemical structures of these four monomers are shown in Table 1. As a crosslinking agent the non-modified hyperbranched polyester of the fourth pseudo-generation (Boltorn[®]H40, Perstorp AB, abbreviated as HB4-0) was used [10]. According to the producer Boltorn[®]H40 has a molar mass $M_w = 5100$ g/mol with polymolecularity $M_w/M_n = 1.8$ and hydroxyl number 470–500 mg KOH/g.

The aim of the synthesis presented in this work and in our previous papers was to obtain new series of networks, in which polyurethane linear chains are connected by the HB crosslinker

[2,10–12]. The PU linear chains in these series have different chemical structures and/or different lengths, controlled by the average number (n varying from 4 to 20) of the repeating macrodiol–diisocyanate units. On the other hand, the number of primary –OH functions present in the HB polymer (that controls the number of PU chains connected to the hyperbranched polyester) was kept constant throughout this work. A schematic representation of the synthesis of the PU networks crosslinked with HB centres is displayed in Fig. 1, and a short guide to the sample designation is given in Table 1.

The synthesis of polyurethane was carried out in bulk at 100 °C for 7 h [2]. Amounts of ingredients for the synthesis of stoichiometric systems were calculated in accordance with the average numbers of –OH groups in the macrodiol and HB crosslinker and with the projected length of the PU chains (related to the parameter n) between the crosslinking centres [10,11]. The end of reaction was determined by FTIR spectroscopy, when the band at 2250–2275 cm⁻¹ characteristic of the free diisocyanate –N=C=O groups completely disappeared.

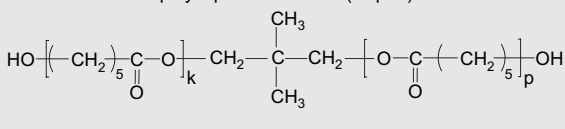
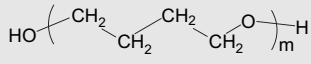
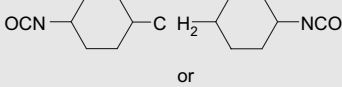
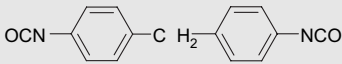
2.2. Measurements

The chemical structure of the synthesised materials was verified by FTIR spectra using Bio-Rad FTS 175C spectrometer in the reflection mode with the Harrick IRS attachment.

Differential scanning calorimetry (DSC) measurements were carried out using a 2920 TA Instrument. Samples of approximately 10 mg were sealed in aluminium pans and measured with a heating rate of 10 °C/min in the temperature range: –150 °C to 200 °C under nitrogen atmosphere. The glass transition temperatures (T_g s) were determined at the midpoint of the step.

Molecular relaxations were characterised in broad temperature range by dynamic mechanical analysis (DMA) using TA Instrument DMA 2980 Dynamic Mechanical Analyser, and by dielectric relaxation spectroscopy (DRS) using Novocontrol Broadband Dielectric Spectrometer. DMA was performed in film tension mode in the temperature range from –130 °C up to 150 °C with a temperature ramp of 2 deg/min using rectangular samples with the length 25 mm, width 5 mm and thickness 1 mm. Three frequencies were

Table 1
Specification of the monomers used in the synthesis of PU networks

Name of PU sample	n^a	Macrodiol:	Diisocyanate:
		polycaprolactone diol (Capa [®])  or polyoxytetramethylene diol (Terathane [®]) 	4,4'-diisocyanatodicyclohexylmethane (H ₁₂ MDI)  or 4,4'-diisocyanatodiphenylmethane (MDI) 
6-C ₅₅₀ -H ₁₂ MDI-HB4-0	6	Capa [®] 550 ^b	H ₁₂ MDI
4-C ₅₅₀ -MDI-HB4-0	4	Capa [®] 550 ^b	MDI
6-C ₅₅₀ -MDI-HB4-0	6	Capa [®] 550 ^b	MDI
10-C ₅₅₀ -MDI-HB4-0	10	Capa [®] 550 ^b	MDI
20-C ₅₅₀ -MDI-HB4-0	20	Capa [®] 550 ^b	MDI
4-T ₆₅₀ -H ₁₂ MDI-HB4-0	4	Terathane [®] 650 ^c	H ₁₂ MDI
10-T ₆₅₀ -H ₁₂ MDI-HB4-0	10	Terathane [®] 650 ^c	H ₁₂ MDI
20-T ₆₅₀ -H ₁₂ MDI-HB4-0	20	Terathane [®] 650 ^c	H ₁₂ MDI
10-T ₆₅₀ -MDI-HB4-0	10	Terathane [®] 650 ^c	MDI

All the samples were crosslinked using non-modified HB Boltorn[®]H40 (HB4-0).

^a See Fig. 1.

^b $p + k = 4$.

^c $m = 9$.

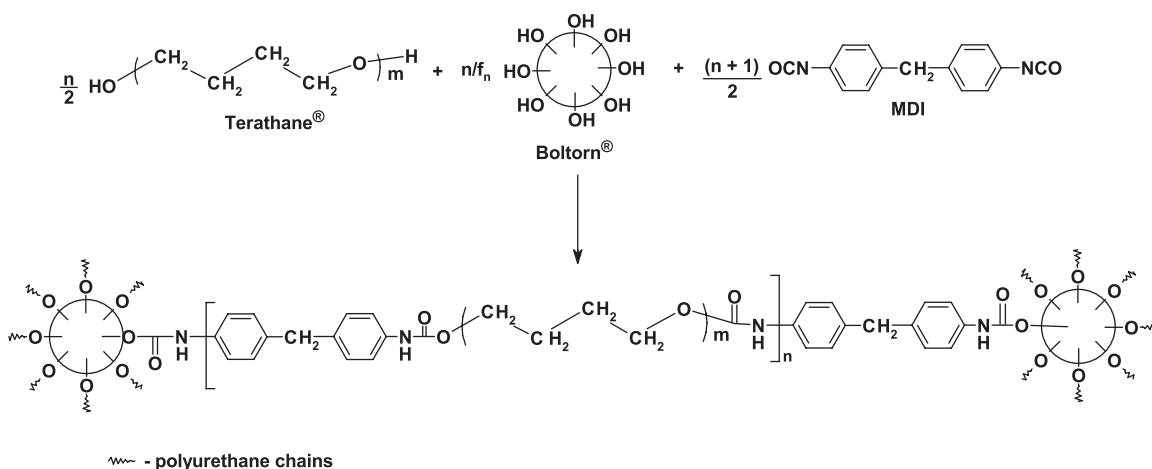


Fig. 1. Idealized scheme of the PU network synthesis; $n = 4, 6, 10$ or 20 .

applied: 1, 5 and 10 Hz. DRS was performed in the frequency range 0.01 Hz–1 MHz and in the temperature range from -150 °C up to 130 °C with the step of 5 °C. For the DRS measurements circular shaped samples with diameter 20 mm and thickness up to 0.5 mm were used.

Analysis of the dielectric results was performed using both the classical representation of dielectric relaxations, *i.e.* dielectric permittivity, as well as using the electric modulus representation defined by Macedo et al. [13]. The real M' and imaginary M'' parts of the electric modulus were calculated according to the Eqs. (1) and (2):

$$M' = \frac{\epsilon'}{\epsilon'^2 + \epsilon''^2} \quad (1)$$

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

where ϵ' and ϵ'' are the real and imaginary parts of permittivity, respectively, which implement the following equation $\epsilon^* = \epsilon' + i\epsilon''$.

The points used for the activation maps were determined from positions of the maxima of the $\epsilon''(f)$ curves using WinFIT software or manually from $M''(T)$ dependence for conductivity phenomena and from the $E''(T)$ dependence for mechanic spectra. The relaxation times (τ) were calculated from the equation: $\tau = 1/(2\pi f_{\max})$, where f_{\max} is the frequency of the relaxation peak at a given temperature T .

3. Results

Fig. 2 shows the three-dimensional frequency and temperature dependencies of the electric modulus imaginary part (M'') for the exemplary PU networks with different chemical structures of linear linkage. The corresponding activation maps are shown in Fig. 3.

The effect of the diisocyanate nature can be deduced from a comparison between Fig. 2(a) and (b), or between Fig. 2(c) and (d); while the effect of the macrodiol chain nature, polyester or polyether, can be studied by comparing Fig. 2(a) or (b) with their counterparts Fig. 2(c) or (d). All these samples have rather comparable lengths of the macrodiol units, and even of the PU chains: n is slightly higher for the samples (c) and (d), but it was shown before for polyester-based networks [2] that changing the macrodiol length much more affected their properties than varying the parameter n , even from 4 to 20, while keeping this macrodiol length constant; therefore, 6-C₅₅₀ networks have almost the same behaviour as 10-C₅₅₀ networks and can definitely be compared with 10-T₆₅₀ networks. For the same reason, the length distribution

of the PU chains between the crosslinker molecules (due to the polyaddition reaction) should not have a big effect as compared to a theoretical, “perfect” network, with monodisperse connecting chains. In the DRS spectra one can distinguish three regions. In the highest temperature range the conductivity phenomenon occurs, manifested by an additional maximum above the T_g . At lower temperatures, in the glass temperature range, the primary α -relaxation appears. As seen in Fig. 3 both of these phenomena show non-Arrhenius type behaviour. In the glassy state the secondary relaxations, connected with local movements, are visible. From the activation maps seen in Fig. 3 the activation energies were determined and collected in Table 2.

Fig. 4 shows the comparison of the relaxation spectra obtained from dielectric and the dynamic mechanical experiments. The chemical nature of the monomers used for the synthesis has obviously an influence on relaxation phenomena in the obtained PU networks. At first, one can see that the kind of used diisocyanate has a noticeable influence on the molecular dynamics of the networks, especially on the primary α -relaxation. It appears that the α -relaxation in the samples based on H₁₂MDI occurs at lower temperature than in the samples based on MDI (this effect is well seen in Fig. 4(a)). The same tendency is also observed in the DMA results shown in Fig. 4(b). The results of DRS and DMA are in good agreement with the DSC measurements collected in Fig. 5 showing that the difference in T_g s is about 8 °C. In the glassy state, in all the investigated samples at the lowest temperature range the secondary γ -relaxation is visible. This relaxation is slightly dependent on the kind of diisocyanate employed – the temperature positions of this relaxation for the systems with MDI are a few degrees higher in comparison to the systems with H₁₂MDI (see Figs. 3 and 4). The activation energies for both the systems are similar (see Table 2). Next, with increasing temperature, another secondary relaxation, the so called β -relaxation, is also not very much sensitive on the diisocyanate kind used in the synthesis (see Fig. 4). This relaxation phenomenon appears at slightly higher temperatures in the samples based on MDI than in analogues based on H₁₂MDI. However, in the n -T₆₅₀-H₁₂MDI-HB4-0 samples the β -relaxation is not visible at all (*cf.* Fig. 2(c)). On the other hand in all the samples based on H₁₂MDI a new β' -relaxation occurs (see Fig. 4 and Table 2). This relaxation appears in a higher temperature range than the β -relaxation (the difference is *ca.* 25 °C). The activation energies of the β' -relaxation, collected in Table 2, seem to be also slightly higher than the activation energies of the β -relaxation, however, a direct comparison for the most samples is not possible because the β -relaxation in the n -T₆₅₀-H₁₂MDI-HB4-0 series is not visible in the spectra (*cf.* Fig. 2(c)). The results of the DMA measurements confirm

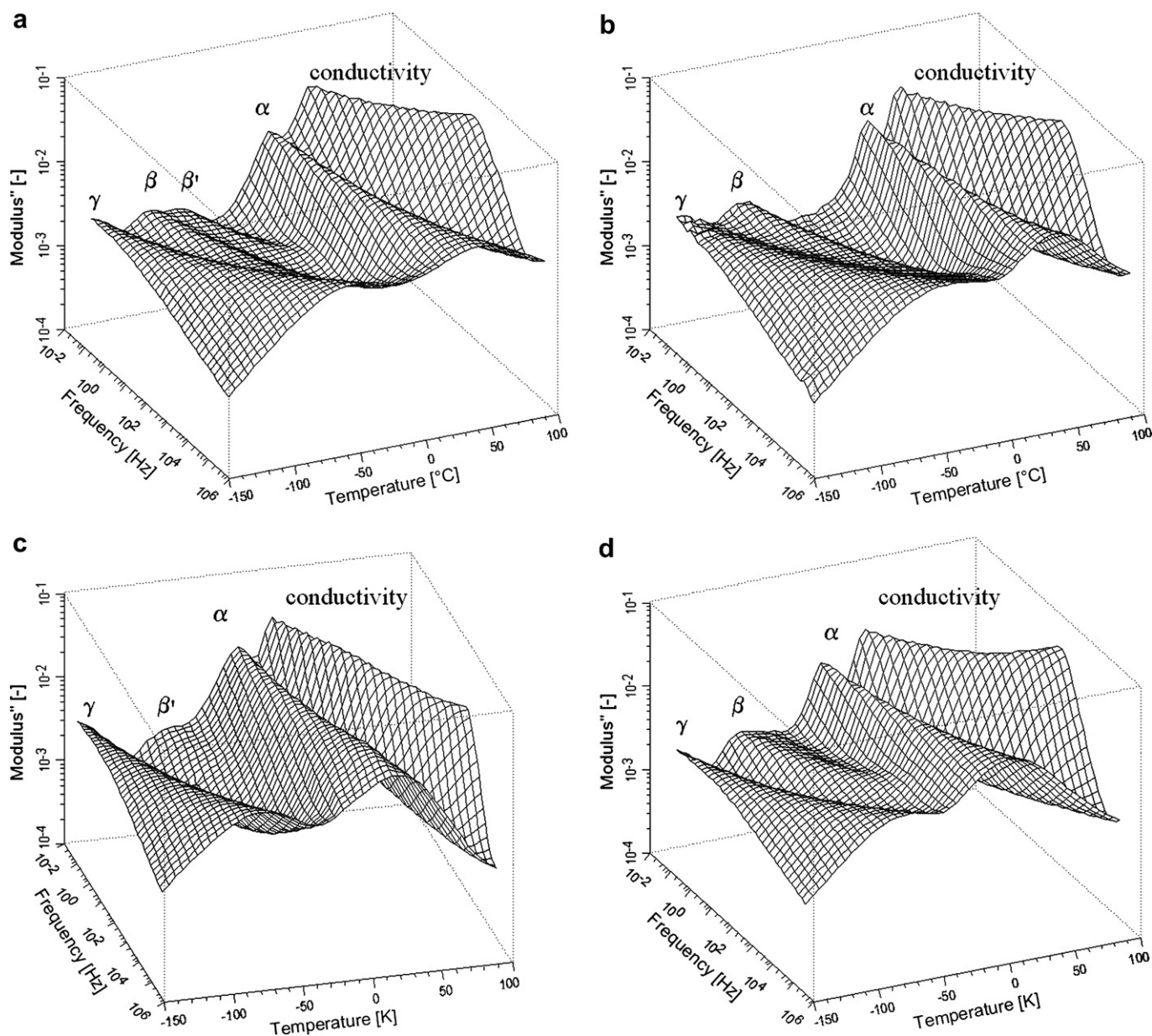


Fig. 2. Frequency and temperature dependencies of the imaginary part of electric modulus for exemplary PU networks: (a) 6-C₅₅₀-H₁₂MDI-HB4-0; (b) 6-C₅₅₀-MDI-HB4-0; (c) 10-T₆₅₀-H₁₂MDI-HB4-0 and (d) 10-T₆₅₀-MDI-HB4-0.

the DRS results, which is well seen in Figs. 3 and 4. Please note the expanded β - and β' -relaxation region shown as an inset in Fig. 4(b). Moreover, the DMA spectra show that the kind of diisocyanate used in the synthesis also changes the PU network properties above the glass transition. The residual storage modulus for the materials based on MDI is about 7 MPa, and only about 0.7 MPa for the samples based on H₁₂MDI.

Also the kind of macrodiol used in the synthesis of the PU networks influences the molecular dynamics of these materials. Similarly, as before, the most sensitive phenomenon is the glass transition and the associated α -relaxation, but differences are much more spectacular. The samples based on the polyester Capa[®] always show the α -relaxation at much higher temperatures than their analogues based on the polyether Terathane[®] (compare e.g. the M'' plots in Fig. 4(a) – dot and dash lines). As one can see in Fig. 5 the difference in the T_g s is higher than 30 °C. The β -relaxation is very similar in all the systems (however, as already indicated before, in the n-T₆₅₀-H₁₂MDI-HB4-0 series the β -relaxation is not visible). The

β' -relaxation is also not sensitive to the change of the macrodiol. As one can see in Table 2 the activation energies of both relaxations are similar in both kinds of materials – based on polycaprolactone and on polytetrahydrofuran. In contrast to the β - and β' -relaxations, the γ -relaxation is sensitive to the change of macrodiol. In the samples based on polycaprolactone Capa[®] the γ -relaxation appears at higher temperature range and has a slightly lower activation energy than the samples based on polyether Terathane[®] (see Table 2).

Besides the polyurethane chemical structure, also the linkage length was changed. The polyurethane chain length was regulated by changing the number (n) of the repeating macrodiol–diisocyanate units. Fig. 6 shows the activation plots for two series of PU systems with different lengths of PU chains. One can see that the secondary relaxation processes are practically independent of PU chain length changed by increasing the number n (cf. also Table 2). The α -relaxation is more sensitive to the PU linkage length – the positions of the corresponding maxima shift towards lower temperatures with increasing n . This effect corresponds to changes of

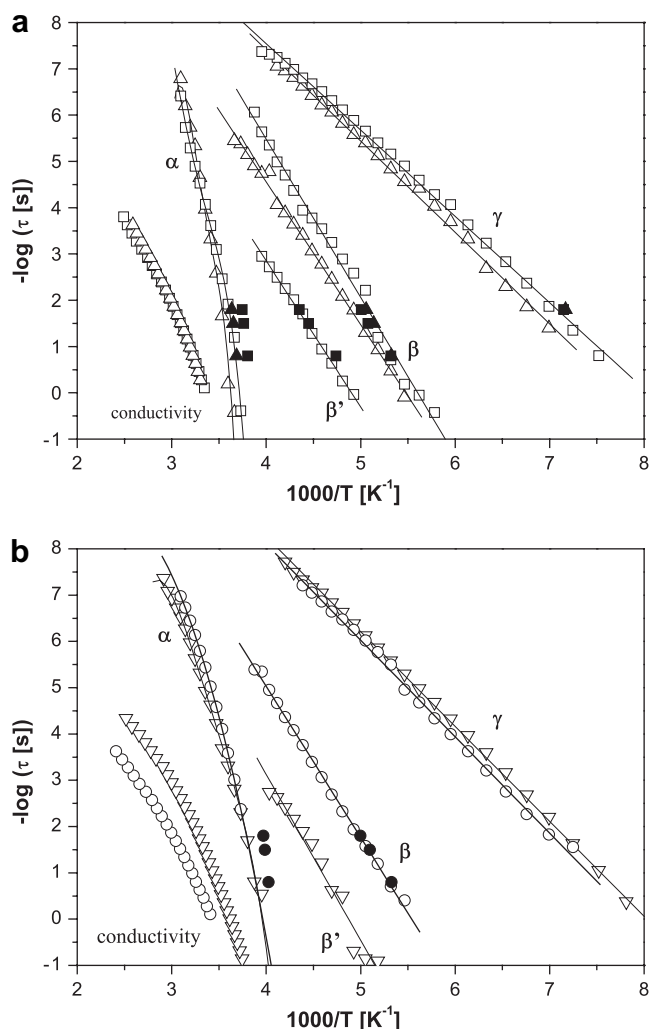


Fig. 3. Activation maps of relaxation phenomena (where τ – relaxation time) in PU networks based on (a) Capa[®]550 and (b) on Terathane[®]650: (\square) 6-C₅₅₀-H₁₂MDI-HB4-0; (Δ) 6-C₅₅₀-MDI-HB4-0; (∇) 10-T₆₅₀-H₁₂MDI-HB4-0; (\circ) 10-T₆₅₀-MDI-HB4-0. Open points from DRS, full points from DMA.

the T_g values as determined by DSC (see Fig. 5). One can notice that the samples based on polycaprolactone are more sensitive to changes of n than the samples based on polytetrahydrofuran.

4. Discussion

The chemical structure of the linear PU chains between the crosslinking points affects significantly the molecular dynamics.

Table 2

Activation energies of the secondary relaxations in the PU systems calculated from DRS data

Name of sample	Activation energy [kJ/mol]		
	β' -Relaxation	β -Relaxation	γ -Relaxation
6-C ₅₅₀ -H ₁₂ MDI-HB4-0	61 ± 1	60 ± 3	35.7 ± 0.5
4-C ₅₅₀ -MDI-HB4-0	–	56.7 ± 0.5	35.5 ± 0.2
6-C ₅₅₀ -MDI-HB4-0	–	59.0 ± 0.9	35.9 ± 0.6
10-C ₅₅₀ -MDI-HB4-0	–	57.6 ± 0.7	35.6 ± 0.4
20-C ₅₅₀ -MDI-HB4-0	–	59.0 ± 0.5	35.3 ± 0.3
4-T ₆₅₀ -H ₁₂ MDI-HB4-0	60 ± 6	–	38.3 ± 0.4
10-T ₆₅₀ -H ₁₂ MDI-HB4-0	69 ± 5	–	37.5 ± 0.5
20-T ₆₅₀ -H ₁₂ MDI-HB4-0	68 ± 7	–	38.0 ± 0.9
10-T ₆₅₀ -MDI-HB4-0	–	59 ± 1	38.9 ± 0.5

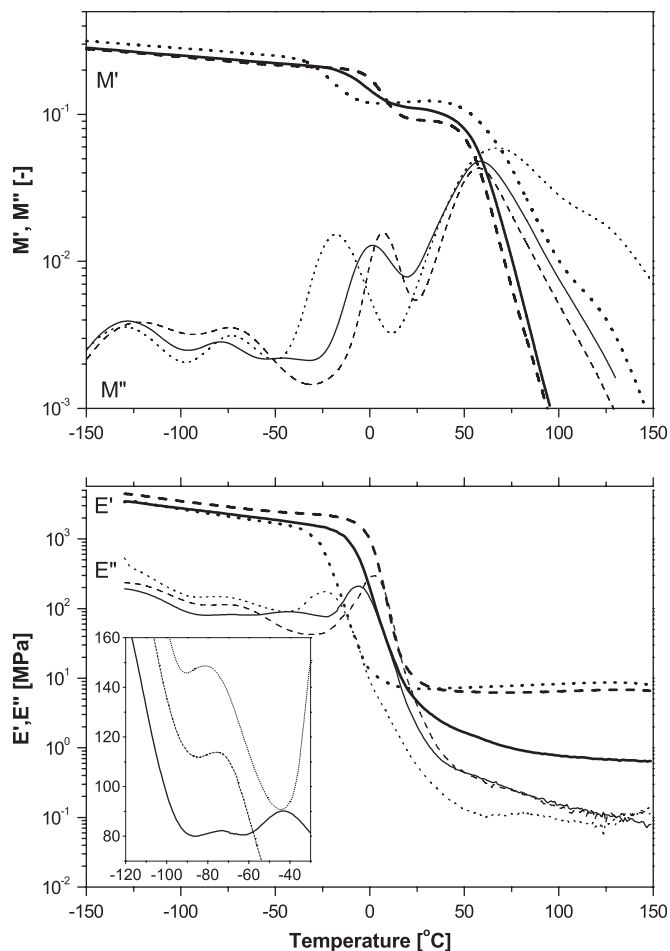


Fig. 4. (a) DRS (real and imaginary parts of electric moduli) and (b) DMA (storage and loss moduli) spectra at 10 Hz for the PU samples with different structures: 6-C₅₅₀-H₁₂MDI-HB4-0 (solid line), 6-C₅₅₀-MDI-HB4-0 (dash line), 6-T₆₅₀-MDI-HB4-0 (dot line). Inset shows the β -relaxation region.

However, the sensitivity of the different relaxation processes on various structure parameters is different.

The γ -relaxation is assigned to the movements of the $(CH_2)_x$ sequences in the soft segments of PU chains [14–16]. For this reason the γ -relaxation activation energy is similar in all the systems based on the same macrodiol because in these materials such sequences are identical. Slight shifts in the temperature scale can result from the differences in the environment of the $(CH_2)_x$ sequences. Stronger differences can be observed in the samples based on different macrodiols: in the samples based on polycaprolactone Capa[®] the γ -relaxation has a slightly lower activation energy than in the samples based on polyether Terathane[®] (see Table 2). It results from the difference in the chemical structure of the sequence responsible for this relaxation. In Capa[®] $(CH_2)_5$ segments are present whereas in Terathane[®] only $(CH_2)_4$ groups occur. This additional CH_2 group in Capa[®] facilitates the local movements of the $(CH_2)_x$ sequences.

The secondary β -relaxation can be most probably attributed to the local motions of the polar urethane groups, as proposed by several authors [2,15–17]. It is, however, not clear why this relaxation is not visible in the systems based on both the macrodiol Terathane[®]650 and the diisocyanate H₁₂MDI. In all others samples (also those based on Terathane[®]650 but without H₁₂MDI, and vice versa) this relaxation is well visible and its parameters are very similar.

In all the samples based on H₁₂MDI another, so called β' , secondary relaxation occurs. This relaxation was assigned to

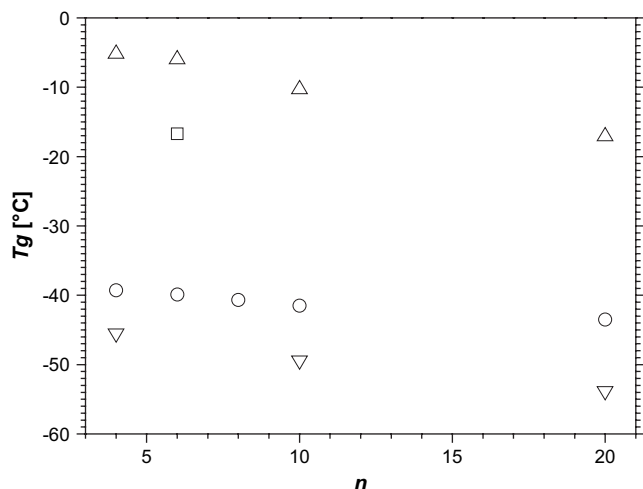


Fig. 5. DSC glass transition temperature values for samples based on Capa[®]550 or Terathane[®]650 as starting macrodiol and based on MDI or H₁₂MDI as starting diisocyanate vs. number of repeating macrodiol–diisocyanate units n : (□) n -C₅₅₀-H₁₂MDI-HB4-0; (Δ) n -C₅₅₀-MDI-HB4-0; (▽) n -T₆₅₀-H₁₂MDI-HB4-0; (○) n -T₆₅₀-MDI-HB4-0.

movements of the cyclohexyl ring [14]. This relaxation is similar in all the relevant samples and seems to be weakly sensitive to changes of the soft segment structure.

The α -relaxation, associated with the glass transition, shifts considerably to higher temperatures with the change of the macrodiol from polytetrahydrofuran to polycaprolactone. Capa[®] possesses ester groups, which make the macrodiol stiffer than the polyether, and this can be a reason for the shift of the α -relaxation and of the T_g to higher temperature (in homopolymers with high molar masses, the $T_g = -60$ °C for polycaprolactone and $T_g = -84$ °C for polytetrahydrofuran [18], and for our short macrodiols the glass transition temperatures measured by us show a similar difference: $T_g = -78$ °C for C550 and -95 °C for T650). Also the presence of the phenyl group from MDI, instead of cyclohexyl ring from H₁₂MDI, results in the stiffening of the PU chain, that shifts the T_g and associated α -relaxation to higher temperatures by about 8 °C. The influence of the diisocyanate moieties is, however, much weaker than that of the macrodiol because their overall concentration in the material is much smaller.

Because the investigated samples are crosslinked, they reveal above T_g the residual storage modulus. In the MDI-based samples this residual modulus is higher than in the samples based on the hydrogenated analogue again probably due to stiffer phenyl groups as compared with cyclohexyl groups. In the literature most of the reported comparisons between both the diisocyanates are related to linear polyurethanes and show contradictory results, the rubber modulus observed with H₁₂MDI being either higher [19] or lower [20,21] than with MDI for otherwise similar samples. However, in these works the discrepancy can be probably related to a varying degree of microphase separation between soft and hard domains in both the types of samples; microphase separation was sometimes shown to be higher with H₁₂MDI than with MDI [17]. By contrast in our systems strong microphase separation can be excluded, since the materials display only one T_g and a flat rubbery modulus above the α -mechanical transition (see Fig. 4b). Moreover no crystallization can occur in the samples studied in the present work: first, the connecting PU chains based on soft macrodiol segments are much too short (in a previous work on polyester-based samples this crystallization was detected only for macrodiols with a molar mass above 2000 g/mol), and their crystallization would obviously be detected between room temperature and 50–60 °C. As for

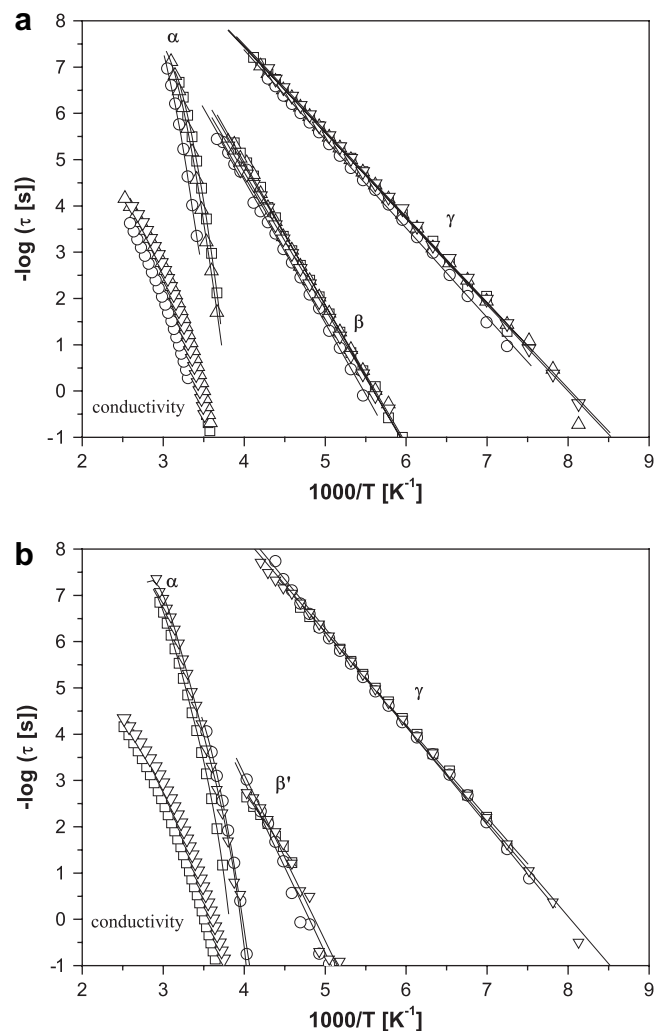


Fig. 6. Activation maps of relaxation phenomena (data from DRS) in PU networks (a) n -C₅₅₀-MDI-HB4-0 and (b) n -T₆₅₀-H₁₂MDI-HB4-0 with different n : (□) $n=4$; (Δ) $n=6$; (▽) $n=10$; (○) $n=20$.

a possible crystallization of the crosslinked diisocyanate-hyperbranched polyester units, which could maybe lead to melting phenomena above 180 °C (by analogy with the same hyperbranched polyester modified with paratolyliisocyanate [22]), *i.e.* indeed out of the presently studied temperature window, it should (if it exists) nevertheless occur in about the same proportions for MDI- and H₁₂MDI-based samples, and therefore should not account for a big difference in the rubbery moduli.

One could expect that the changes of the length of the PU linear chain between the crosslinking centres would affect significantly the molecular dynamics. Such effect indeed occurs, but is very weak. The DSC results show that with increasing number of repeating macrodiol–diisocyanate segments (n) the T_g only slightly decreases. The α -relaxation seen in the DMA and DRS spectra shows similar tendency. Such weak sensitivity of the α -relaxation on the PU chain elongation can be explained by the presence of numerous hydrogen bonds, which can be created between the PU linear chains, as it was previously observed on a series of polytetrahydrofuran-based PU networks [2]. In that case the T_g and the α -relaxation were shown to be mainly dependent on the concentration of urethane groups in the material. Also in the presently discussed PU systems the density of the physical network does not change significantly with the number n changing in both macrodiol series.

5. Conclusions

The chemical nature of the PU linear chains between the crosslinking centres influences, more or less significantly, the molecular dynamics of the PU networks crosslinked by the hyperbranched polyester. The strongest effects were observed for the α -relaxation, what was documented by coherent results obtained from all used measurement techniques: DRS, DMA and DSC. These changes in α -relaxation and T_g were rationalised by analysing an influence of the modification of the chemical structure on the stiffness of the PU chains and on intermolecular interactions. An influence of the chemical structure of the linear linkage on the secondary relaxations in the glassy state is less significant, nevertheless some changes are clearly connected with chemical structure, for example, an appearance of a new β' -relaxation in all the samples based on H₁₂MDI, or a decrease in activation energy of the γ -relaxation if polyether Terathane[®] was used instead of polycaprolactone Capa[®].

Taking into account the results presented by us in this and in previous papers [2,10–12] we could formulate the following general rules for designing of new PU networks with hyperbranched crosslinkers:

- the coordination number of the hyperbranched crosslinkers has a minor influence on the properties of the PU networks;
- the length of the PU chains may influence the properties of PU networks at high temperatures (T_g , flowing point, crystallization), but not the properties and molecular relaxations in the glassy state;
- chemical modification of the PU chains between the crosslinking points is the most effective method of changing the properties of the PU networks, since in this way one can change the stiffness of the linear PU chains, structure of the groups involved in molecular relaxation and distribution of the hydrogen bonds.

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