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Polyurethane Networks Based on Hyperbranched Polyesters: Synthesis and Molecular Relaxations

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ABSTRACT

Several polyurethane networks based on hyperbranched polyesters (trade name Boltorn[®]H40) were synthesised. Molecular dynamics in these systems were investigated by means of broadband dielectric spectroscopy and comparatively by dynamic mechanical analysis. Glass transition temperatures were determined by differential scanning calorimetry. It was found that these techniques yield consistent results concerning molecular relaxation processes, however the dielectric spectroscopy appears to be the most sensitive to evidence the secondary relaxation processes. The molecular relaxations are much more sensitive to the changes of the chemical character of polyurethane linear links between the hyperbranched centres, than to crosslinking density changed by the length of linear PU chains. The weak influence of the PU chain length on the molecular properties can be explained by the existence of hydrogen bonds forming a physical network, which is more dense and consequently, much stronger than the chemical network in the investigated temperature range.

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Keywords: polyurethane networks, hyperbranched polymers, molecular dynamics, dielectric spectroscopy, dynamic mechanical analysis

1. INTRODUCTION

One of the most recently intensively investigated groups of polymers with complex architecture is a class of dendritic macromolecules. It consists mainly in dendrimers [1] and hyperbranched (HB) polymers [2,3]. Over the last few years syntheses of a large number of dendritic polymers have been reported in the literature [4,5]. They have potential applications in a variety of fields, such as biomedical applications, catalysis and commercial coatings [6,7]. However because the synthesis of dendrimers is tedious, expensive and time consuming, they are not used for large scale applications. The alternative solution is the use of hyperbranched polymers, which show properties similar to the dendrimers, but they can be synthesised in a one step polymerization process. It has been recognized that the architecture of macromolecules was an important tool to obtain polymers with desired properties. For example the introduction of a large amount of branching units into a polymer chain dramatically changes its physical properties such as viscosity and solubility [8,9].

Polyurethanes (PU) have been intensively studied since many years and have found wide applications [10,11]. One of the powerful techniques to investigate the dynamic material properties is dielectric relaxation spectroscopy. This technique can be applied to polar materials and seems to be ideal for studies of PU materials. Several dielectric relaxation studies of the linear and branched PU systems have been reported in the literature [12-14], in particular on the molecular dynamics under pressure dependence [15] or the effect of the interfacial interactions [16]. Roussos et al. investigated novel linear/low-branched polyurethanes by means of dielectric techniques [17]. They examined the microphase separation in a PU consisting of hard and soft segments. Recently new polyurethane systems with hyperbranched polymers, incorporated in a PU matrix as blends [18] or

introduced in the network as a crosslinker, attracted an increasing attention. They offer an opportunity of modification of the structure of the synthesized materials in a controlled way.

In this paper the synthesis of different PU networks based on HB polyester is described. The calculation of the monomer amounts needed for the reaction is also reported. Then DSC experiments have been performed to determine the thermodynamical transitions of the different investigated systems. The molecular relaxations were investigated by dynamic mechanical analysis (DMA) and broadband dielectric relaxation spectroscopy (DRS).

2. EXPERIMENTAL

2.1. Materials

Several PU networks crosslinked by hyperbranched polymer were synthesized in bulk using hydroxy-terminated polyoxytetramethylene (Terathane[®]650 with number average molar mass $M_n = 650$ g/mole or Terathane[®]2900 with $M_n = 2900$ g/mole) and 4,4'-diisocyanatodiphenylmethane (MDI with $M = 250$ g/mole) as monomers and HB polyester of fourth generation (Boltorn[®]H40) as a crosslinking agent. The purpose of this work was to describe new systems containing polyurethane chains connected to the crosslinking center. The distance between the crosslinking points was changed by two parameters: the number n of the repeating units (the hard-soft segments) in the PU chain or by different length of the macrodiol used for the reaction.

The weight average molar mass (M_w) of Boltorn[®]H40 given by the producer is 5100 g/mole with polydispersity $M_w/M_n = 1.8$ and the hydroxyl number equals 470-500 mg KOH/g. The exact value of the hydroxyl number, necessary to adjust stoichiometry in the coming syntheses, was confirmed by a pH-metric titration (471 ± 11 mg KOH/g). Functionality of Boltorn[®]H40 calculated from data given by the producer is about 42. However due to the difficulties with estimation of the molecular weight of the hyperbranched polymers different researchers obtain different results, i.e. Zagar et al. [19] have obtained the molar mass of Boltorn[®]H40 $M_n=2625$ g/mole and in

consequence functionality equal about $f_n=22$ or Thomasson et al [20] found the $M_n=2930$ g/mole and the functionality $f_n=24.6$

Additionally some systems were synthesised with a polycaprolactone diol (Capa[®]200, $M_n = 550$ g/mole). Structures of the used macrodiols are shown in Fig.1. The composition of the investigated systems is reported in Table 1.

PU systems were synthesized at stoichiometric ratio of hydroxyl and isocyanate groups, taking into account the number of –OH groups in Boltorn[®]H40 and the total number of macrodiol units used to build the length of the PU chain between the crosslinking centers. The amount of Terathane[®] (resp. Capa[®]) was calculated using the following equation:

$$m_{Ter} = n_{OH} \cdot M_{Ter} \cdot \frac{n}{2}, \quad (1)$$

where: m_{Ter} – mass of Terathane[®] used for the reaction, M_{Ter} – molar mass of Terathane[®], n – expected number of Terathane[®] segments in the PU chain. The assumption that Terathane[®] has a functionality equal to 2 was made for calculation. The number of moles of –OH groups present in HB polyester n_{OH} was calculated from equation:

$$n_{OH} = m_{HB} \cdot Eq(OH), \quad (2)$$

where: m_{HB} – mass of HB polyester used for reaction (in kilograms), $Eq(OH)$ – number of moles of –OH groups per kilogram of the HB polyester.

The amount of MDI was calculated using the following equation:

$$m_{MDI} = n_{OH} \cdot M_{MDI} \cdot \frac{n+1}{2} \quad (3)$$

where: m_{MDI} – mass of MDI used for the reaction, M_{MDI} – molar mass of MDI.

The monomers were used as supplied by the producer without additional purification. The adequate Terathane[®] was placed in a flask equipped with magnetic stirrer and heated up to 80°C and kept during half an hour under vacuum. Then the calculated amount of Boltorn[®]H40 was added and the solution was mixed at about 100°C until the HB polyester was dissolved. When the solution was

clear, it was placed under vacuum at 60°C for half an hour in order to remove air and water, which can be present in HB polyester (this compound is strongly hygroscopic). In the next step MDI, heated up to 60°C, was added. After quick stirring the reaction mixture was cast in an aluminium pan and placed under vacuum at 60°C for half an hour in order to take off air inclusion and consequently to avoid bubbles in the obtained materials. The next step was heating of the reaction mixture at 100°C during 7 h. The polymers were obtained as films with a thickness from 0.2 to 1 mm. The schematic synthesis reaction of PU networks crosslinked with HB centres is shown in Fig. 2.

In the PU networks the diisocyanate -N=C=O band ($2250\text{-}2275\text{cm}^{-1}$) was absent in the IR spectra, meaning that all was well reacted. The bands characteristic for polyurethane bonds formation appear at: 3320cm^{-1} - urethane N-H stretching; 1731cm^{-1} - urethane C=O free from hydrogen bonding; 1710cm^{-1} - urethane C=O with hydrogen bonding; 1535cm^{-1} - urethane C-N-H bonding.

2.2. Characterization techniques.

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

The glass transition (T_g) temperatures were determined using Differential Scanning Calorimetry (TA Instrument DSC 2920). Two runs were performed under nitrogen atmosphere for each sample in the range: -150 to 200°C with heating rate $10^\circ/\text{min}$ and cooling scan with the maximal speed about $-25^\circ/\text{min}$. Although both heating scans were the same, the T_g was determined as the onset point from the second scan. No difference between the first and the second heating scans indicates that there was no water departure between the scans.

Molecular relaxations were characterized in broad temperature (T) and frequency (f) ranges by dynamic mechanical analysis using TA Instrument DMA 2980 Dynamic Mechanical Analyser, and dielectric relaxation spectroscopy using Novocontrol Broadband Dielectric Spectrometer. DMA

was performed in tension film mode in the temperature range from -130 up to 150°C with a temperature ramp of $2^{\circ}/\text{min}$. Three frequencies were applied: 1, 5 and 10 Hz. The rectangular samples with the average geometry: length 25mm; width 5mm and thickness 1mm were tested. DRS was performed in the frequency range 0.01Hz – 1MHz and in the temperature range from -150 up to 130°C with the step 5°C . The circular shape samples with a thickness about 0.2 mm and diameter 20 mm were placed between two electrodes without metallization. Before measurement, the samples were dried at 100°C under vacuum during 2 h.

Dielectric results were presented in the classical representation of dielectric relaxations, i.e. permittivity vs. temperature and vs. frequency, as well as in the electric modulus representation defined by Macedo et al. [21]. The real M' and imaginary M'' parts of the electric modulus were calculated according to the equations 4 and 5:

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

$$M'' = \frac{\varepsilon''}{\varepsilon'^2 + \varepsilon''^2} \quad (5)$$

where: ε' and ε'' are, respectively, real and imaginary part of permittivity.

Although the permittivity representation is easier in an interpretation, modulus representation can be very useful, where conductivity processes are involved.

The activation maps were prepared on a base of both dielectric as well as mechanical spectra. The data points were calculated from $\varepsilon''(f)$ plots using WinFit software for dielectric relaxations, or manually from $M''(T)$ for conductivity phenomenon. For mechanical relaxations, the data were calculated from $E''(T)$ plots.

3. RESULTS

The glass transition temperatures for the investigated systems are collected in Table 1. The samples are representing three categories focussing on the differences in the structure: different number of repeating units in linear PU linkage between crosslinking centres, different lengths and chemical nature of the macrodiol.

Fig. 3. shows the DMA and DRS spectra for one series of the materials, which have different concentrations of the crosslinking agent. In the dielectric spectra three relaxation processes and a high temperature dielectric conductivity (DC) peak are present. The relaxations were named α , β and γ in an order of decreasing temperature. The α -relaxation maximum is visible at 1Hz in the region from -30 to -22°C depending on n . For each sample the subglass relaxation processes β at about -85°C (1 Hz) and γ at about -135°C (1 Hz) can be seen. These two processes are practically independent on n . Activation energies for β - and γ -processes are given in Table 2. In the DMA spectra of the loss modulus E'' versus temperature (Fig. 3) two relaxation processes are seen at 1Hz: the α -process around $T = -25^\circ\text{C}$ and the β -process at about $T = -85^\circ\text{C}$. The γ -relaxation is visible only at higher frequencies. The activation map collecting all data of DRS and DMA investigations for these samples is shown in Fig. 4.

Dielectric spectra and activation map for the samples with different lengths of macrodiol are shown in Fig. 5. The sample based on T2900 reveals at 1Hz three relaxational processes shifted to the lower temperatures as compared with the 10-T650 sample: α -relaxation around -60°C, β -relaxation at about -95°C and γ -relaxation at about -140°C. Additionally at high temperatures the conductivity phenomenon is present.

The last parameter under investigation was the nature of the macrodiol. For this purpose polycaprolactone was used instead of polyether in the reaction (Fig. 1). Both of them have similar molar masses. As shown in Fig. 6, from the DRS measurements three relaxation processes and a

dielectric conductivity phenomenon are visible for the samples with both polyethers (Terathane[®] 650) and polycaprolactone (Capa[®]200). For the system with Capa[®]200 at 1 Hz the α -relaxation occurs at about 0°C, and the β - and γ -relaxations at -85 and -130°C, respectively. The relaxations visible in the DMA spectra (Fig. 6.) are in reasonable agreement with those seen in DRS. Again the γ -relaxation was visible in the DMA spectra only at high frequencies. The activation map for these systems is shown in Fig. 7.

4. DISCUSSION

One could expect that the changes of the crosslinking density should affect significantly the molecular dynamics of the PU systems. Such effect occurs indeed, but it is rather weak.

Density of chemical crosslinking was changed by increasing the length of the linear PU chains between the HB centres. The DSC results show that with increasing number of the repeating (soft and hard) segments (n) the T_g slightly decreases. The results of the DMA and DRS investigations confirm this effect. One can see in Fig. 3. that with increasing n the temperature position of the α -relaxation peaks shifts to lower temperatures. This effect can be expected, because with increasing length of the PU chains the polymer becomes softer and its T_g should be lower. The question is why these changes are so small. The weak dependence of the α -relaxation temperature position on the PU chain length can be caused by a presence of hydrogen bonds, which can be created between the PU linear chains [22]. In our case the effect of the physical crosslinking seems to be more important than the effect of chemical crosslinking by the HB centres, which are much less numerous than the hydrogen bonding points. Additionally it is visible from the mechanical and dielectric spectra that the change of the PU chain length has practically no influence on the β - and γ -relaxations. The β -relaxation process is most probably connected with movements of a chain part containing the urethane group attached to crosslinker, and γ -relaxations are connected with movements of the

$(\text{CH}_2)_x$ groups of the macrodiol. Also the activation energy (calculated from the DRS) for these relaxations are similar for all the samples and no clear tendency can be found, as one can see in Table 2. Only for the highest $n = 20$ some increase of the activation energy occurs. It can be caused by the fact that the chemical structure of the PU linear chain is practically not changed. Additionally in the mechanical spectra one can observe that the storage modulus for the investigated samples in the rubbery region have the same value for all samples with Terathane[®]650 and is independent on the increase of the PU chain length in contrast to our expectation that with increasing the number of repeating units in the chain the value of the storage modulus should decrease. However increasing n not only increases the average length between the crosslinking points but also the amount of possible hydrogen bonds between these chains by creating numerous new rigid aromatic urethane groups. The constant and relatively high value of the storage modulus supports our hypothesis of dominating role of the hydrogen bonds, which would compensate the increase in length and would make the polymer stiffer also above the T_g .

The length of the macrodiol (different molecular weight) has much stronger effect on the α -relaxation than the number of macrodiol segments in PU chain. This influence is well visible in Fig. 5. In the case of the macrodiol with molecular weight 2900g/mole the value of the maximum of α relaxation at 1 Hz is about -80°C , i.e. lower by about 40°C in comparison to the system with T650. This seems sound since the increase in the macrodiol length results in an increase in the total length between the crosslinking points, without creation of new hydrogen bonds. This effect is confirmed also by the DSC measurements.

The influence of the macrodiol length on the secondary relaxations is also visible – however, it is not so spectacular effect. One can see that the temperature position of the β -relaxation peak in the dielectric spectra for the sample 10-T2900 is shifted to lower temperature in comparison with the sample 10-T650. On the other hand the activation energy of the β -relaxation for 10-T2900 is

slightly higher. Such effect of increasing activation energy of β -relaxation is similar to the effect observed when the length of PU chain was changed by increasing n from $n=10$ to $n=20$ (see Table 1). The γ -relaxation is less sensitive to the changes of the molecular weight of macrodiol used for the reaction.

The last study performed in this work was an analysis of the influence of the macrodiol chemical structure on the properties of the obtained networks. As seen in Fig. 6 the influence of the macrodiol chemical structure on the α -relaxation is observable, both in DMA and DRS spectra: the use of Capa[®]200 instead of Terathane[®]650 results in a higher T_g by about 30°C (note that the difference between the T_g temperatures of the initial macrodiols is about the same, namely $T_g = -95^\circ\text{C}$ for Terathane[®]650 [23] and $T_g = -78^\circ\text{C}$ for Capa[®]200 [24]). In contrast to the α -process, the β -relaxation seems to be independent on the chemical character of the macrodiol - the dielectric as well as the mechanical measurements show that the temperature positions of the β peaks are not changing. Calculated activation energies are also not much different for both samples. It confirms our presumption that this relaxation process is connected with movements of the chain part containing the urethane group attached to the crosslinker. The change of macrodiol from Terathane[®]650 to Capa[®]200 results in a shift of the γ -relaxations by about 10°C to higher temperatures, but the activation energies of these processes are the same.

Similarly to the samples with Terathane[®]650 the networks based on Capa[®]200 have a high value of storage modulus in the rubbery region. In the case of polycaprolactone this value is slightly lower than the one for the polyether based samples, and equals about 6 MPa. This behaviour indicates that also in the systems with polycaprolactone the hydrogen bonds are present.

5. CONCLUSIONS

Investigations of the mechanical and dielectric relaxations in different PU networks crosslinked by hyperbranched agents show that the α -relaxation (related to the glass transition of the polymer) is sensitive to changes of the structure of the PU systems. It was found that the strongest effect on the α -relaxations is observed when the chemical nature, or molecular weight of the macrodiol is changed. An increase of the macrodiol length also results in changes of the secondary relaxations (β and γ). On the other hand, increasing length of the PU chains in the network, without changing their chemical structure, results only in very weak changes of T_g and has practically no influence on the secondary relaxations. Such weak influence of the PU chain length on the molecular dynamics can be explained by the prevailing influence of the hydrogen bonds between the polyurethane chains playing the role of physical crosslinkages. Larger differences between the systems with different PU chain lengths should be observed at high temperatures, at which the physical hydrogen bonds crosslinking will be destroyed. Preliminary high temperature rheological measurements for the investigated systems show that at enough high temperatures the hydrogen bonds can be (reversibly) broken. These results showing more clearly the dependence of the molecular relaxation on the network architecture will be published when the rheological studies will be completed.

6. ACKNOWLEDGEMENTS

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Figure captions

Fig. 1. Structure of macrodiols used in syntheses of PU ($R = -\text{CH}_2-\text{CH}_2-\text{O}-\text{CH}_2-\text{CH}_2-$).

Fig.2. Schematic description of the synthesis of PU Terathane-based network.

Fig. 3. DMA and DRS plots for the n -T650 systems with different n

Fig. 4. Activation map for the n -T650 systems with different n .

Fig. 5. DRS spectra and activation map for the systems with different molecular weights of macrodiol.

Fig. 6. DMA and DRS plots for the systems $n=6$ with different kinds of macrodiol.

Fig. 7. Activation map for the systems with different kinds of macrodiol.

Table 1. Values of the T_g for the investigated PU systems

Sample	Type of macrodiol	n	T_g [°C]
4-T650	Terathane [®] 650	4	-39
6-T650	Terathane [®] 650	6	-40
8-T650	Terathane [®] 650	8	-42
10-T650	Terathane [®] 650	10	-43
20-T650	Terathane [®] 650	20	-45
10-T2900	Terathane [®] 2900	10	-81
6-C550	Capa [®] 200	6	-7

Table 2. Activation energies of the β and γ relaxations for the investigated systems (Calculated from DRS).

	Activation energies [kJ/mole]						
Sample	4-T650	6-T650	8-T650	10-T650	20-T650	10-T2900	6-C550
β -relaxation	62.5 \pm 0.7	64.4 \pm 0.9	60.6 \pm 0.4	58.5 \pm 0.7	67.7 \pm 0.6	73.7 \pm 3.8	59.1 \pm 0.8
γ -relaxation	39.9 \pm 0.5	35.8 \pm 0.3	37.2 \pm 0.1	35.9 \pm 0.2	36.1 \pm 0.4	33.2 \pm 0.8	36.8 \pm 0.3

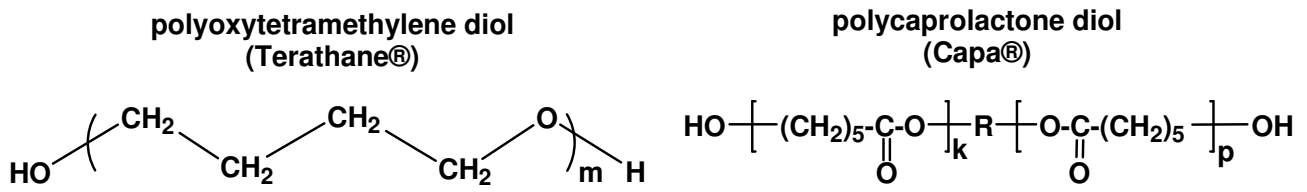


Fig. 1. Structure of macrodiols used in syntheses of PU (R = -CH₂-CH₂-O-CH₂-CH₂-).

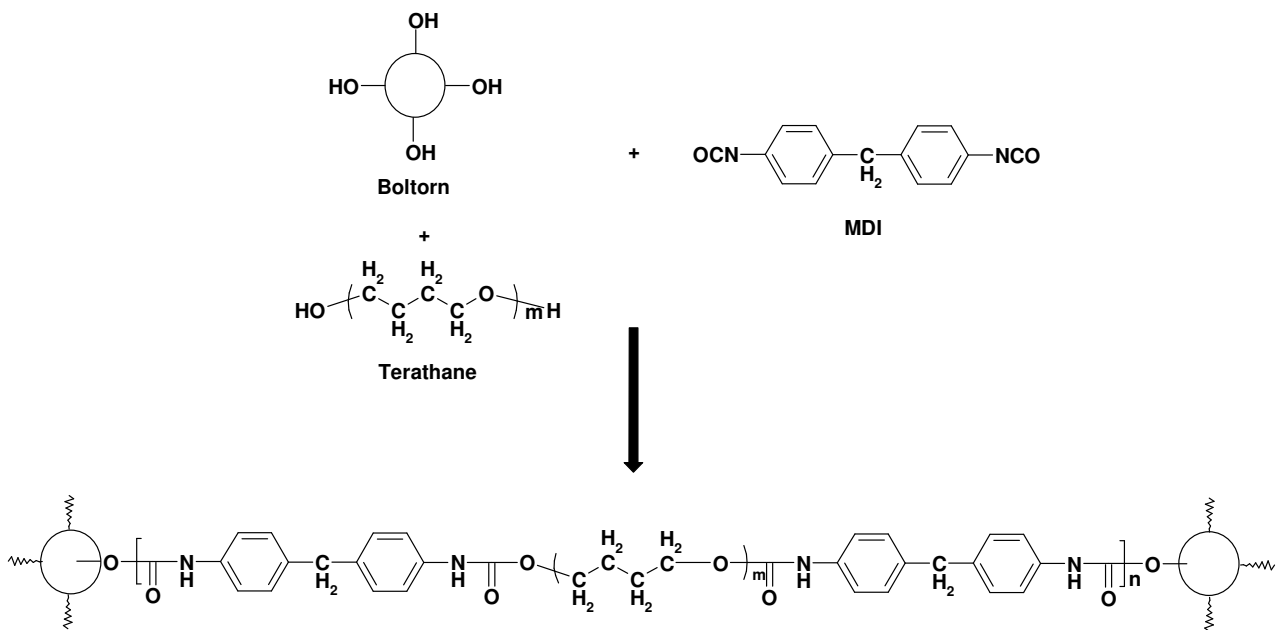


Fig.2. Schematic description of the synthesis of PU Terathane-based network.

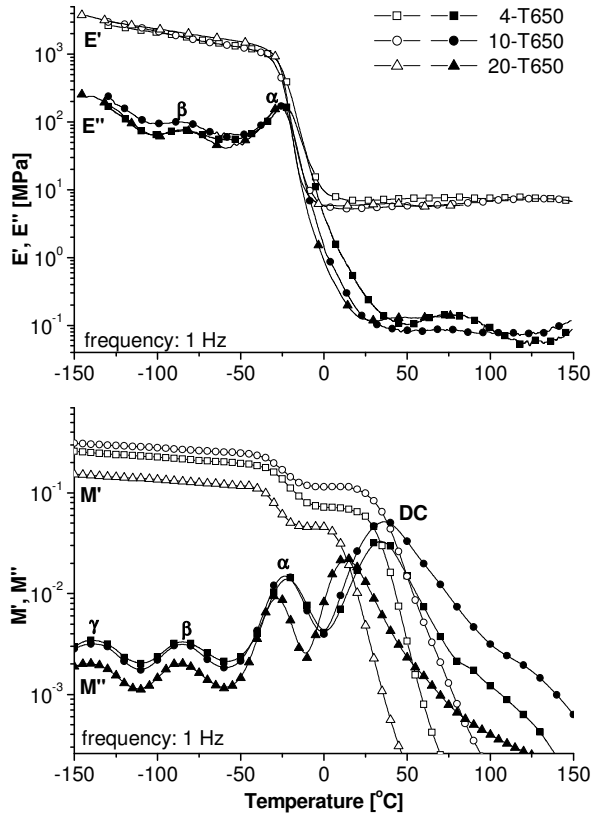


Fig. 3. DMA and DRS plots for the n-T650 systems with different n

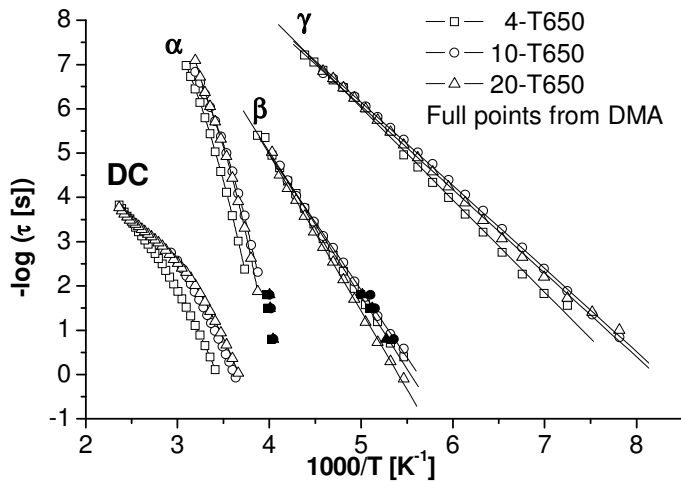


Fig. 4. Activation map for the n-T650 systems with different n

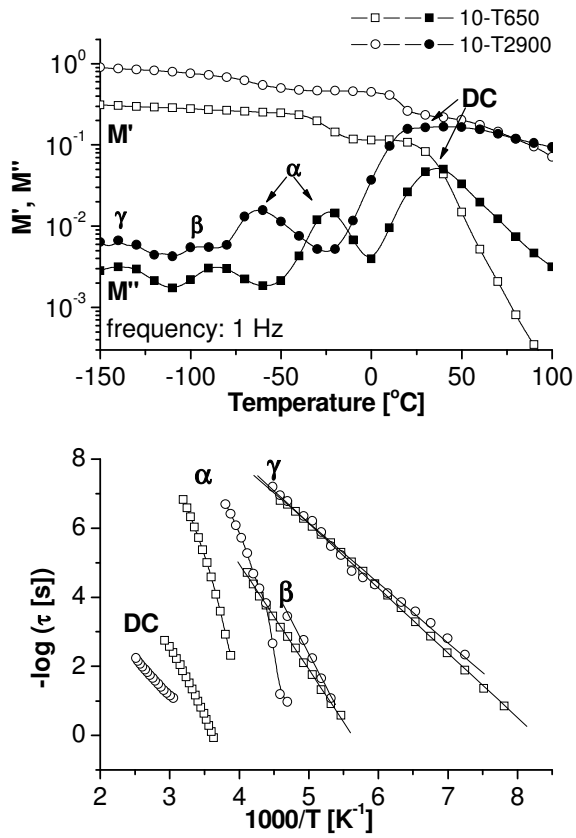


Fig. 5. DRS spectra and activation map for the systems with different weights of macrodiol

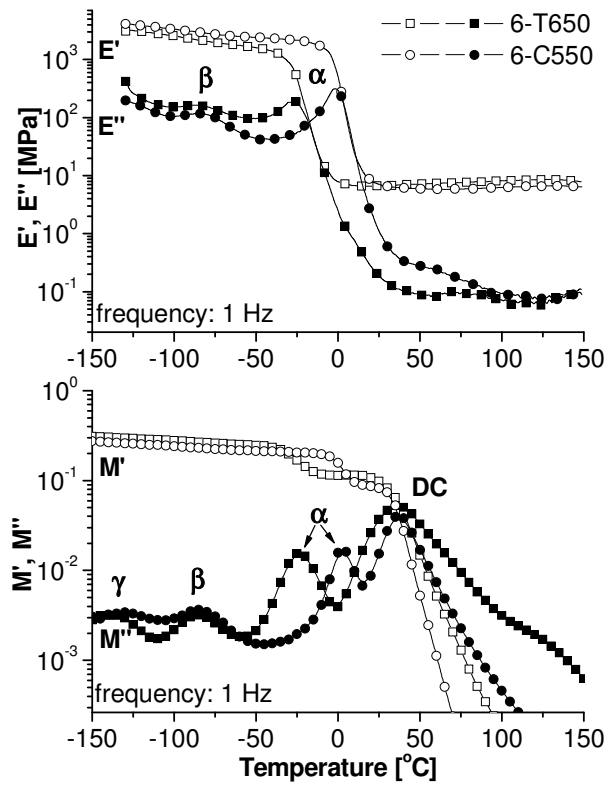


Fig. 6. DMA and DRS plots for the systems $n=6$ with different kinds of macrodiol

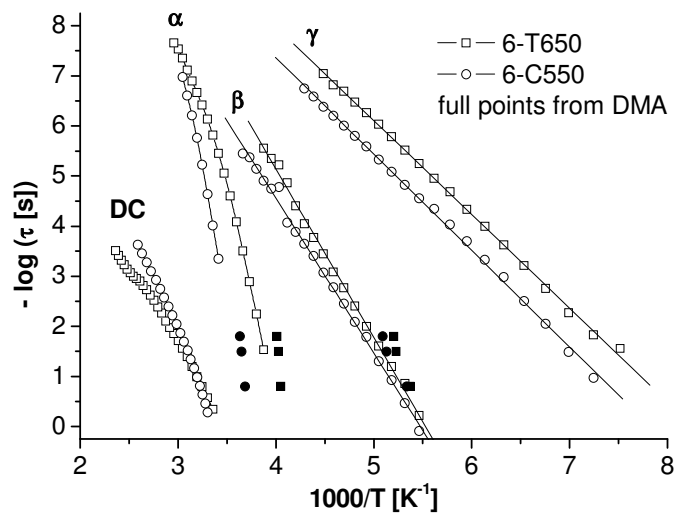


Fig. 7. Activation map for the systems with different kinds of macrodiol