Structure and molecular dynamics of hyperbranched polymeric systems with urethane and urea linkages

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ABSTRACT

Two series of hyperbranched polymers (HP), polyurethanes and polyureas, with aromatic and aliphatic structures, are synthesized in one-pot method using commercially available monomers. The obtained HP samples were characterized by [1]H Nuclear Magnetic Resonance (NMR) spectroscopy, Gel Permeation Chromatography (GPC), Differential Scanning Calorimetry (DSC) and Thermal Gravimetric Analysis (TGA) measurements. Molecular dynamics in these systems were investigated by combining Thermally Stimulated Depolarization Currents (TSDC) and broadband Dielectric Relaxation Spectroscopy (DRS) techniques. High conductivity contribution in dielectric loss does not allow the study of the segmental α relaxation associated with the glass transition. In the glassy state two secondary relaxation mechanisms have been investigated, the γ and the β mechanism. The γ relaxation mechanism, at low temperatures/high frequencies, is attributed to motions of the end groups (–OH for polyurethanes and –NH$_2$ for polyureas), and has been found faster in the hyperbranched polyureas. In addition, our results reveal that γ relaxation mechanism in both series depends on the chemical structure, being faster for aliphatic structures. The β relaxation mechanism, at higher temperatures/lower frequencies, is attributed to the motions of branched ends with polar groups. Our study suggests that this mechanism may be a typical relaxation process for hyperbranched polyurethanes structures, not existed in the linear counterparts. All the systems exhibit dc conductivity at temperatures higher than T_g which shows Arrhenius-like temperature dependence and is characterized by rather high activation energies (in the order of 200 kJ/mol). At temperatures lower than T_g all the systems studied exhibit remarkably high charge mobility. In particular, aliphatic hyperbranched polyureas exhibit dc conductivity which has been found to be of VTF type concerning the temperature dependence. This result implies that the conduction mechanism is coupled with molecular motions in the glassy state of the polymer.

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1. Introduction

Dendritic polymers are nanoscopic globular macromolecules whose architecture consists of three domains: 1) Core, which can be a single atom or a group of atoms, 2) Branch units, which divide radially grown concentric layers termed generations, and 3) Functional surface groups which play a key role in determining their properties [1]. Dendritic polymers can be either dendrimers or hyperbranched polymers. Dendrimers are characteristic by their perfect monodisperse structure and molar mass. In contrast, hyperbranched polymers, HPs, have a less defined structure with incorporated linear units and are therefore polydisperse in structure and molar mass [2,3]. The properties of dendritic polymers differ from their linear equivalents of the same molar mass, e.g. dendritic polymers exhibit lower viscosities, are non-entangled globular structures, and have higher solubilities in various solvents [4–8].

Dendritic and hyperbranched structures have been synthesized for almost all class of polymers, for example, polyalkylenes, polyacrylenes, polyamines, polyethers, polyesters, polycarbonates, polysiloxanes and polycarbosilanes [2,9–11]. First reports on the successful preparation of dendritic polyurethanes appeared in 1993 [12,13]. The majority of the reported synthesis of either aliphatic or aromatic hyperbranched polyurethane was done via polycondensation reaction of AB$_2$ or A$_2$B monomers [14–16]. Novel hyperbranched polyurethanes and polyureas, can be used to form nano-domain structured networks which can be viewed as three dimensional, cross-linked materials comprising covalently bonded

nanoscopic, hyperbranched domains which may be of the same or different chemical composition of the rest of the network [16,17]. These materials can be formed into clear, highly transparent films, sheets, membranes, coatings or other objects and may exhibit different glass transition temperatures that may rank them among either elastomers or plastomers.

But despite a considerable amount of research on hyperbranched polymers a few reports have been published about their chain dynamics. The first paper on this subject has been reported by Malmström et al. [18] on the hyperbranched polyester terminated by hydroxyl units. Employing dielectric relaxation spectroscopy they found two relaxations, γ and β, below the glass transition temperature and one associated to the glass transition called α-relaxation for the fifth generation. The conductivity contribution was found to mask out that relaxation in all other generations. This is now considered as a common feature in the hyperbranched polymers. Dielectric relaxation studies on a similar system carried out by Zhu et al. confirmed these results [19]. In addition, this work revealed that the secondary γ relaxation, attributed to the motions of polar hydroxyl end groups, is somehow coupled with the motion of the arms and thus glass transition relaxation.

Dielectric relaxation spectroscopy, DRS, techniques have been used for the investigation of the molecular dynamics of dendritic (dendrimers [20–27] and hyperbranched [28–32]) polymers. The main goal of these studies was the characterization of the recorded relaxation mechanisms and the investigation of the underlying molecular motions. Usually, the relaxation phenomena are divided to phenomena connected with the center of the globular macromolecules and to phenomena occurred in the periphery of the macromolecules (mainly related with the mobility of the end groups).

For hyperbranched polyurethane systems a few studies on the structure and chain dynamics have been published. The structure–property behavior has been studied by means of Small Angle X-ray Scattering (SAXS) [33,34], Atomic Force Microscopy (AFM) and Dynamic Mechanical Analysis (DMA) [33] experimental methods and by kinetic Monte-Carlo simulations [35]. A few dielectric relaxation studies of hyperbranched polyurethane systems have also been reported in the literature [36,37]. In most of those works the comparative study of hyperbranched polyurethanes and their linear analogues provide valuable information with respect to structure and dynamics of the hyperbranched macromolecules. Okrasa et al. [36] have studied comparatively hyperbranched polyurethanes and blends of hyperbranched polyurethanes with their linear counterparts. They showed that molecular relaxations are much more sensitive to the changes of the chemical character of polyurethane linear links between the hyperbranched centers, than to crosslinking density. In the blends, the molecular dynamics is dominated by the linear component. A significant influence of hyperbranched polyurethane in the blends is observed only in case of the primary relaxation connected with the high-temperature glass transition.

The principle objective of this study is to conduct an investigation of two series of hyperbranched polymers, the first being hyperbranched polyurethane aromatic, Ar-HPUreth, and aliphatic, Al-HPUreth, and the second series is hyperbranched polyurea aromatic, Ar-HPUrea, and aliphatic, Al-HPUrea, and to quantify the effect of presence of different structural units on their dynamics.

2. Experimental section

2.1. Materials and synthesis

Toluene 2,4-diisocyanate and isophorone diisocyanate were products of Fluka. Diethylene triamine, glycerol and tetrahydrofurane

(THF) were obtained from Aldrich chemical company. All chemicals are used as received and the solvent was dried over molecular sieve A4.

2.1.1. Synthesis of hyperbranched polyurethanes (HPUreth)

Two samples are prepared through the reaction of either 2,4-toluene diisocyanate (TDI) with glycerol for the aromatic polymer, or isophorone diisocyanate (IPDI) with glycerol to give aliphatic structure (Scheme 1). The method or preparation is identical in both cases and it is as follows:

In three-neck round bottom flask filled with Argon, 5.55 g (0.025 g/mol) IPDI is dissolved in THF (10 ml) and 0.01 g of DABCO (a catalyst) is added. The temperature is raised to 50 °C, then 3.35 g (0.0375 g/mol) glycerol dissolved in 23 ml THF, is added drop by drop to IPDI solution. The reaction proceeded for 22 h. The formed polymer was precipitated from H_2O drop by drop addition to a big amount of water with fast stirring. White polymer is obtained which is soluble in THF, dimethylacetamide (DMAc) and dimethylsulphoxide (DMSO) which is a good evidence that hyperbranched polymer and not cross linked structure is obtained.

Hyperbranched polyurethanes were characterized by ^{1}H NMR spectroscopy and the representative NMR spectrum of aromatic polyurethanes, Ar-HPUreth, is shown in Fig. 1. The ^{1}H NMR spectra of hyperbranched polymers were recorded on a ^{1}H NMR. JEOL ECA500 or Field Gradient NMR spectrometer were used, it operated at 500 MHz. DMSO-d_6 was used as solvent and internal standard. The spectra were measured at 303 K using 5 mm sample tubes.

Al-HPUreth: [1]$H NMR$-DMSO-d_6 (δ ppm): 0.9 (CH$_3$), 1.4 (Cyclohexyl ring), 2.7 (CH$_2$–NH), 3.4 (CH$_2$–OH), 3.6 (CH$_2$–O–CO), 3.9 (CH–OCO), 4.5: 5.0 OH, 6.9: 7.2 (NH ureth).

Ar-HPUreth: [1]$H NMR$-DMSO-d_6 (δ ppm): 2.1 (CH$_3$), 3.4 (CH$_2$–NH), 3.7 (CH$_2$–OH), 3.9 (CH$_2$–O–CO), 4.1 (CH–OCO), 4.5: 5.2 OH, 7.0: 8.1 (Aromatic ring), 8.7 NH (O-ureth), 9.5 NH (P-ureth).

We employed gel permeation chromatography (GPC) through Zorbax PSM 60 + 300 column coupled with differential refractometer (RI). As eluent, mixture of dimethyl acetamide, 2 vol% H_2O and 3 g/L LiCl was used with flow rate of 0.5 ml min^{-1}. Linear polyvinylpyridine (PVP) standards were used to calibrate the column. GPC/RI molar mass for aliphatic structure was estimated at 4200 g/mol (PDI = 2.1) whereas a value of 4800 g/mol (PDI = 2.3) was estimated for the aromatic structure. Although this method is considered as relative one to determine the molar mass for hyperbranched polymers it gives an idea about the M_n values.

A Degree of Branching (DB) = 82% was estimated for the aromatic structure (calculated according to Fréchet equation, (DB) = $(d+t)/(d+t+l)$ where (t) stands for terminal, (l) for linear, and (d) for dendritic units) whereas for Al-HPUreth a value of DB could not be calculated due to presence of different isomers for IPDI.

2.1.2. Synthesis of hyperbranched urea (HPUrea)

Two samples are prepared through the reaction of either 2,4-toluene diisocyanate (TDI) with diethylene triamine for the aromatic polymer, or isophorone diisocyanate (IPDI) with diethylene triamine to give aliphatic structure. The method of preparation is identical in both cases:

Two neck round bottom flask is evacuated and filled with Ar gas. Diethylene triamine (DETA) 0.05 g/mol was dissolved in 150 ml THF and the temperature was lowered till −70 °C through immersing the flask in liquid N$_2$. IPDI in case of aliphatic polymer or TDI 0.075 g/mol in case of aromatic one, was dissolved in THF and added dropwise to the monomer DETA, the addition lasted 2 h. After complete addition, the temperature is raised to room temperature during this stage of the reaction the polymer is

Al - HB Urethane

Al - HB Urea

Ar - HB Urethane

Ar - HB Urea
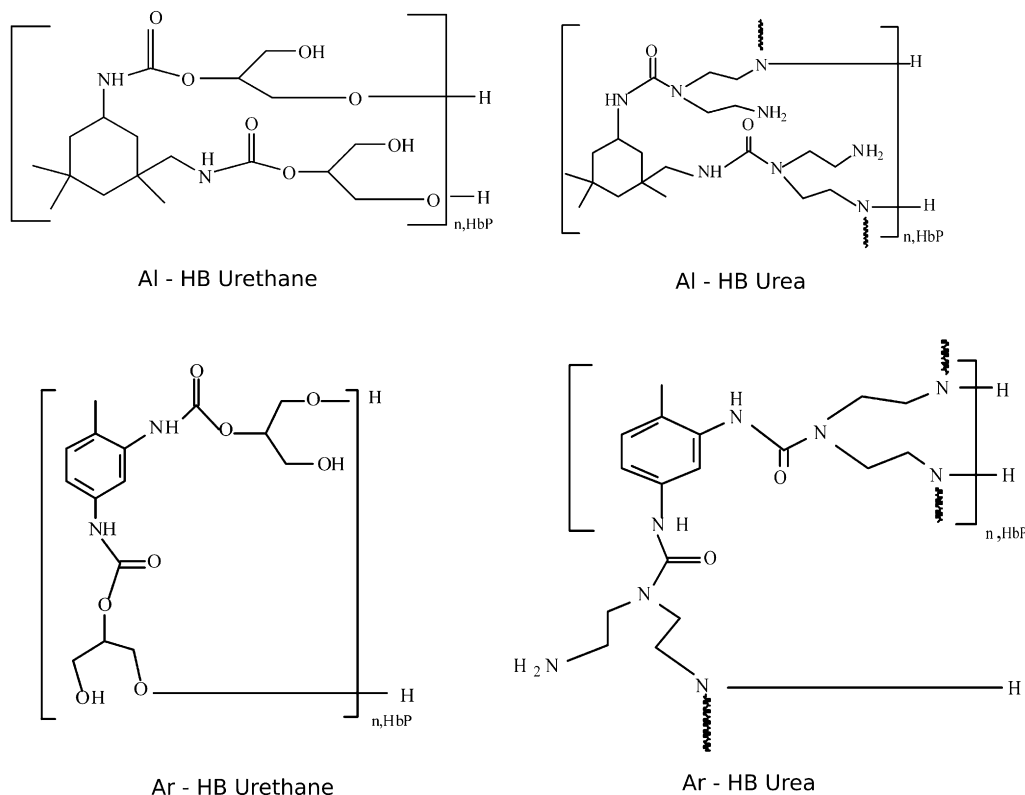
Scheme 1. Chemical structure of hyperbranched polyurethanes and polyureas.

precipitated by time; the reaction proceeded for 20 h. THF is removed by rotary evaporator; white polymer is obtained, washed with diethyl ether and dried under vacuum at 50 °C. The obtained polymers are soluble in high polar solvents.

The chemical shifts of protons in Al-HPUrea and Ar-HPUrea respectively are as follows:

^{1}H NMR-DMSO-d_6 (δ ppm): 0.8:1.1 (CH$_3$), 1.5 (Cyclohexyl ring), 2.4 (NH$_2$), 2.6 (CH$_2$–NH$_2$), 2.7 (CH$_2$ linked to cyclohexyl ring–NH–CON), 3.3 (CH from the ring–NHCON), 5.7:6.5 (NH urea).

^{1}H NMR-DMSO-d_6 (δ ppm): 2.10 (CH$_3$), 2.4 (NH$_2$), 2.69 (NH$_2$–CH$_2$), 3.43 (N–CH$_2$), 6.9–7.65 (aromatic protons), 7.87 (NH urea).
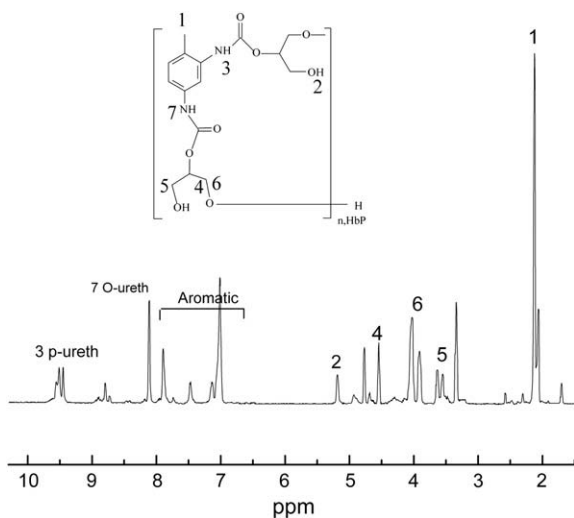

Fig. 1. ^{1}H NMR spectrum of Ar-HPUreth in DMSO-d_6.

Due to bad solubility of the polymers, the polymer sample did not give reproduce-bare peaks in GPC/RI. So the molar mass of the polymers could not be determined.

A Degree of Branching (DB) = 65% was estimated for the aromatic structure (calculated according to Fréchet equation) whereas for Al-HPUrea could not be estimated.

2.2. Measurements and instruments

Differential Scanning Calorimetry (DSC) measurements were carried out in the temperature range 0 to 160 °C using a Perkin-Elmer Pyris 6 calorimeter. Any previous thermal history of the samples had been erased by performing a first heating run up to 150 °C and cooling down to room temperature with a cooling rate of 10 °C/min. The second heating scan is then recorded.

The dielectric measurements were carried out on films which have been prepared by pressurizing polymer powder at about 5–10 degrees above T_g under a pressure of 6–7 tonnes. The powder was pressurized between Teflon sheets and thus flat films with thickness of about 0.1 mm have been prepared. The film samples were inserted between the brass plates of a capacitor, with the thickness changing slightly during the measurements due to changes in the temperature. This fact induces a remarkable uncertainty (in the order of 5%) in the estimated values of dielectric permittivity.

Thermally stimulated depolarization current (TSDC) is a dielectric technique in the temperature domain [38]. TSDC corresponds to measuring dielectric loss at a constant low frequency in the range 10^{-4} to 10^{-2} Hz (equivalent frequency) [38]. TSDC measurements were carried out using a Keithley 617 electrometer in combination with a Novocontrol sample cell for TSDC measurements. The temperature was controlled to better than 0.1 K with a Novocontrol Quatro system. The measuring capacitor was heated to polarization temperature T_P, and polarized by the

application of an electric field, E_P, of about 5 kV/cm, for a time, t_P, of 5 min. The polarization temperature for each sample was chosen properly (T_P close to glass transition temperature T_g) in order to separate glass transition peak from a steep increase of current at higher temperatures associated with conductivity effects, which seem to be inherent characteristics of hyperbranched polymers [39]. Then, with the electric field still applied, the sample was cooled to $-150\,°C$, short-circuited and reheated; the cooling and heating rates were 10 K/min and 3 K/min, respectively. A discharge current was measured as a function of temperature.

Dielectric Relaxation Spectroscopy (DRS) measurements in the frequency range 10^{-1} to 10^6 Hz has been carried out by means of a Novocontrol Alpha analyzer. The temperature was controlled by using the Novocontrol Quatro system.

Dielectric permittivity, $\varepsilon^*(f)$, data were obtained by admittance measurements $Y^*(f)$

$$\varepsilon^*(f) = \frac{Y^*(f)}{i\,2\pi f C_o} = \frac{\sigma'(f) + i\sigma''(f)}{i\,2\pi f \varepsilon_o} \qquad (1)$$

where $\sigma^*(f)$ is the conductivity, C_o is the vacuum capacitance of the measuring cell, ε_o the permittivity of free space and f the frequency.

3. Results and discussion

3.1. DSC measurements

In Fig. 2 we show DSC heating thermograms of all the samples investigated in this work, obtained at a heating rate of 10 °C/min. We observe that all samples exhibit the endothermic step associated with the glass transition. The glass transition temperature, T_g, is estimated as the temperature of half C_p increase. The values determined for the glass transition temperature and the related heat capacity jump ΔC_p for each sample are given in Table 1. Lower T_g values have been estimated for the polyureas. For polyurethanes Al-HPUreth and Ar-HPUreth (in particular) an overshot effect can be observed, indicating an enthalpy recovering during the heating process. It is known that this effect is related with the structural relaxation of the polymeric chains in the super cooled regime [40]. The finding that hyperbranched polyureas do not show the overshoot effect and the fact that the heat capacity jump ΔC_p at T_g for polyureas is almost half of the values for polyurethanes indicate remarkable differences in the structural relaxations of the two systems in the super cooled regime. This may originate in the
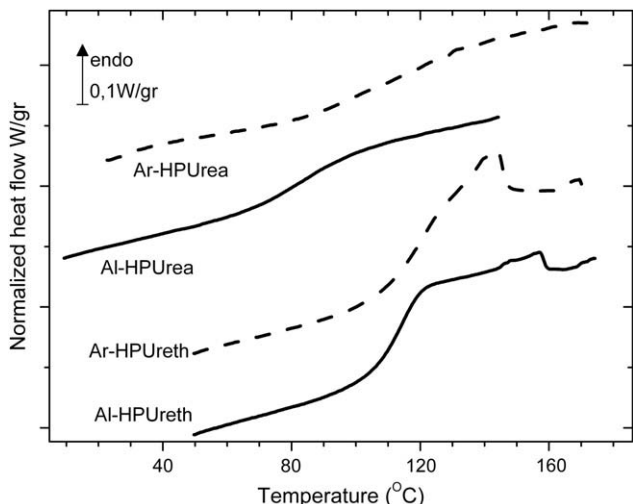
Table 1
Glass transition temperature, T_g, and heat capacity jump, ΔC_p, at T_g determined by DSC heating thermograms.

Sample	T_g (°C)	ΔC_p (W/K gr)
Al-HPUreth	112	0.44
Ar-HPUreth	120	0.53
Al-HPUrea	84	0.21
Ar-HPUrea	107	0.22

existence of different hydrogen bond network in the two classes of materials. The latter may be the result of different end groups existing in the materials (–OH in hyperbranched polyurethane instead of –NH$_2$ in hyperbranched polyurea) and of the different strength of urethane and urea bonds. This interpretation is supported also by the lower T_g measured for the hyperbranched polyurea.

3.2. TSDC measurements

In Fig. 3 we show a TSDC spectrum obtained with Ar-HPUreth sample (as a representative TSDC spectrum for the samples studied). The electric field is applied 10–15 K higher than the T_g determined by DSC for each sample. The depolarization current is recorded during heating from approximately $-150\,°C$ up to $+150\,°C$. In Fig. 3 we observe that the spectrum consists of several depolarization peaks: at low temperatures a relaxation peak, called β relaxation peak, appears at about $-80\,°C$ (this peak appears in all the measured TSDC spectra, though at slightly different temperature regions). The location of this peak in TSDC thermograms has been taken into account in the construction of the Arrhenius plots for the local molecular mobility of these hyperbranched systems (Fig. 7). At even lower temperatures the spectrum provides indication for the existence of a second local relaxation mechanism. However, the corresponding temperature region coincides with the low temperature limit of our experimental setup and consequently the temperature of the maximum is characterized by significant uncertainty. Therefore, we do not further analyze this peak.

In the temperature region of the glass transition (at about 120 °C in the case of Ar-HPUreth in Fig. 3) the TSDC spectra show a depolarization current with the contribution of the segmental (α) relaxation appearing usually as a shoulder in the low temperature side of the recorded dispersion. This finding indicates that
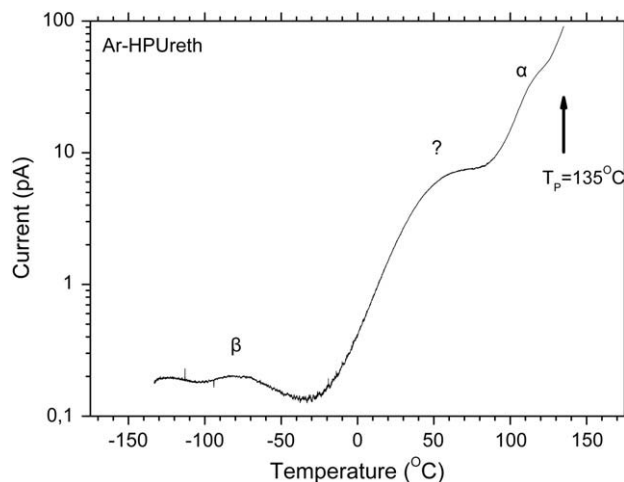
Fig. 2. DSC heating thermograms obtained with all samples studied.

Fig. 3. Global TSDC spectrum obtained with Ar-HPUreth sample. The polarization temperature is indicated on the plot.

enhanced conductivity is related with the glass transition temperature giving rise to depolarization currents due to space charge polarizations. TSDC spectra although providing evidence for the location of segmental relaxation (shoulder in TSDC high temperature peak) do not provide quantitative information for the depolarization peak attributed to dipolar α relaxation (e.g. temperature and maximum current of the peak).

At a few decades of degrees lower than T_g the TSDC spectrum in Fig. 3 shows an almost separated depolarization peak (labeled by a question mark) at the very low temperature side of the depolarization peak related with the glass transition. We note here that for the other samples this contribution is not similarly discerned appearing usually as a shoulder in the low temperature side of the high temperature depolarization peak. The origin of this contribution is not clear at the moment. The characteristics of the peak, i.e. temperature of maximum a few decades lower than T_g and rather high intensity of the peak, could suggest that it originates in the relatively high charge mobility occurred at the glassy state and accumulation of charges at interfaces between regions of different molecular mobility (interfacial polarization effect). Further experimental studies are needed, however, for the clarification of this contribution.

3.3. DRS measurements

DRS measurements have been carried out in the temperature region of −150 to +150 °C. In Fig. 4 we present, as a representative case, the frequency dependence of the imaginary part of dielectric permittivity, ε'', obtained in isothermal conditions for the Al-HPUreth sample (at 4 selected temperatures). We observe that with increasing temperature two secondary relaxation mechanisms enter in our frequency window, the relaxation mechanisms called γ and β. We notice that relaxation mechanism γ appears to be very broad at −100 °C. At the temperature region of the glass transition (about 107 °C for Al-HPUreth) the conductivity contribution in dielectric losses is rather high and masks any features of the loss spectra at relatively low frequencies. Thus, our measured dielectric loss spectra do not allow the study of the segmental relaxation α of the hyperbranched systems.

The values of $\varepsilon''(f)$ for all the samples measured at the frequency of 10 Hz under isothermal conditions have been plotted as a function of temperature and are shown in Fig. 5. We observe the
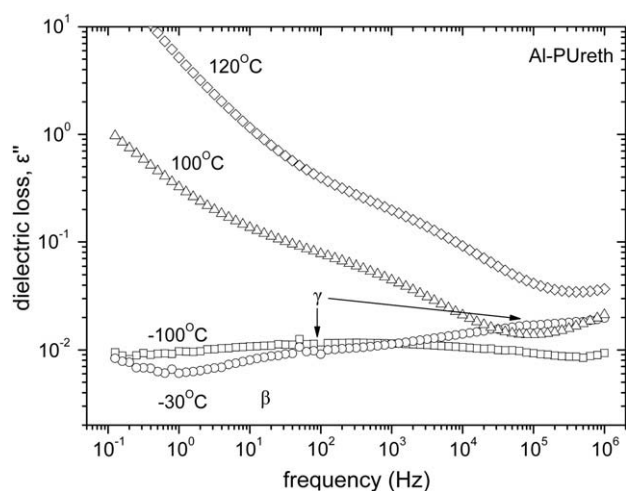
secondary relaxation mechanisms γ and β at low temperatures and, in addition, indications of a relaxation mechanism activated at the temperature region of a few decades below the glass transition temperature (in the temperature region between 30 and 90 °C). We speculate that this polarization mechanism may be related with the polarization mechanism observed in TSDC spectra and labeled by a question mark (Fig. 3). No further investigation of this mechanism will be presented here since this paper focus on the secondary relaxation mechanisms and on the dc conductivity of the systems.

For Al-HPUrea we observe that dielectric loss (at 10 Hz) exhibits remarkably high values at temperatures lower that T_g (even 80 degrees lower than T_g) implying the existence of remarkably high conductivity at the glassy state of the polymeric system.

In the following we will focus on the secondary relaxation mechanisms and the dc conductivity mechanism of the hyperbranched polymeric systems under investigation.

3.3.1. Secondary relaxations

In Fig. 6 we show the dielectric loss spectra of all the samples at the temperature of −100 °C (Fig. 6(a)) and −50 °C (Fig. 6(b)). At −100 °C we observe the loss peak related with the γ relaxation mechanism. We could mention that for polyurethanes (Al- and Ar-HPUreth) the maximum of loss peak is located at lower frequencies compared to polyureas, i.e. the γ relaxation mechanism is slower in polyurethanes. In addition, for Al-HPUrea we observe that the contribution of the β secondary relaxation mechanism at the low frequency side of the spectrum is remarkably high. This indicates that for Al-HPUrea the β relaxation mechanism is faster than that of the other systems since it is observed in our frequency window already at −100 °C. This observation is confirmed by the loss spectra at −50 °C given in Fig. 6(b). The maximum of the relaxation peak of β mechanism for Al-HPUrea is located at higher frequencies compared to other three systems.

The imaginary part of the obtained dielectric permittivity was analyzed by fitting the symmetric Cole–Cole model function to the experimental data [41].

$$\varepsilon^*(f) = \varepsilon_\infty + \frac{\Delta\varepsilon}{\left(1 + if/f_{\max}\right)^\alpha} - i\frac{\sigma_o}{\varepsilon_o f^s} \tag{2}$$

In Eq. (2) ε_∞ is the high frequency value of the dielectric permittivity, $\Delta\varepsilon$ is the dielectric strength, $f_{\max}$ is the frequency of
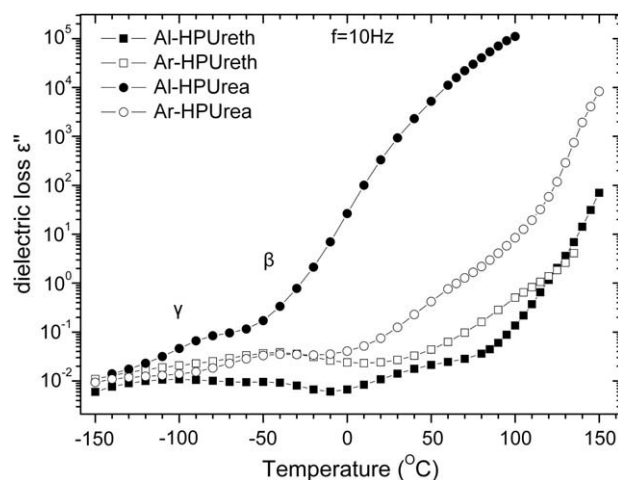

Fig. 4. The imaginary part of the dielectric permittivity, ε'', vs frequency for Al-HPUreth at 4 selected temperatures. The secondary γ and β relaxations are indicated on the plot.

Fig. 5. The imaginary part of the dielectric permittivity, ε'', measured at the frequency of 10 Hz, as a function of temperature for all the samples studied. The secondary γ and β relaxation mechanisms are indicated on the plot.
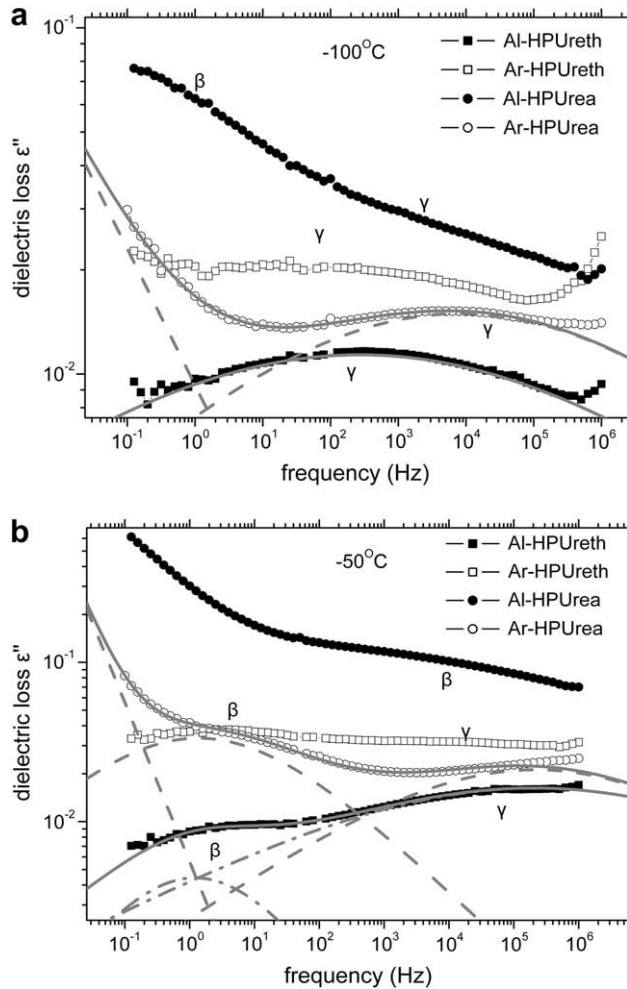
Fig. 6. The frequency dependence of the imaginary part of the dielectric permittivity, ε'', for all the samples at $-100\,^{\circ}$C (a) and $-50\,^{\circ}$C (b).

Table 2
Fitting parameters for the local relaxation mechanisms of all the samples at 2 selected temperatures: $-100\,^{\circ}$C and $-50\,^{\circ}$C.

Sample	γ relaxation			β relaxation		
	f_{max}	$\Delta\varepsilon$	α	f_{max}	$\Delta\varepsilon$	α
($-100\,^{\circ}$C)				–	–	–
Al-HPUreth	2.7×10^2	0.18	0.16	–	–	–
Ar-HPUreth	1.9×10^2	0.32	0.15	–	–	–
Al-HPUrea	3.4×10^4	0.13	0.30	–	–	–
Ar-HPUrea	8.2×10^3	0.20	0.19	–	–	–
($-50\,^{\circ}$C)						
Al-HPUreth	2.1×10^5	0.19	0.21	1.2×10^0	0.04	0.51
Ar-HPUreth	3.0×10^4	0.41	0.18	8.0×10^{-1}	0.15	0.38
Al-HPUrea	–	–	–	3.7×10^2	1.40	0.20
Ar-HPUrea	–	–	–	1.4×10^0	0.21	0.39

$$\tau(T) = \tau_o \exp\left(E_{act}/kT \right) \qquad (3)$$

have been estimated by fitting Eq. (3) to the experimental data. The obtained E_{act} and τ_o values are given in Table 3.

With respect to γ relaxation mechanism the plots in Fig. 7 show clearly that the mechanism is faster in polyureas compared to polyurethanes. In addition, the plots reveal a dependence of γ relaxation mobility on the structure of the hyperbranched polymers: in aliphatic structures the mechanism is slightly faster than in aromatic structures (for both, hyperbranched polyureas and hyperbranched polyurethanes).

With respect to β relaxation mechanism the plots in Fig. 7 confirm that this secondary mechanism is remarkably faster in aliphatic polyureas. For the other three samples the β relaxation process is characterized by comparable mobility at relatively high temperatures (the mechanism being slightly faster in aromatic polyurea sample). At lower temperatures and at the frequency range of the TSDC data the β relaxation mechanisms in polyurea are located at lower temperatures than in polyurethanes indicating that this mechanism becomes faster in hyperbranched polyurea at low temperatures. On the other hand, the data in Table 3 show no systematic dependence of activation energies on the structure of the systems.
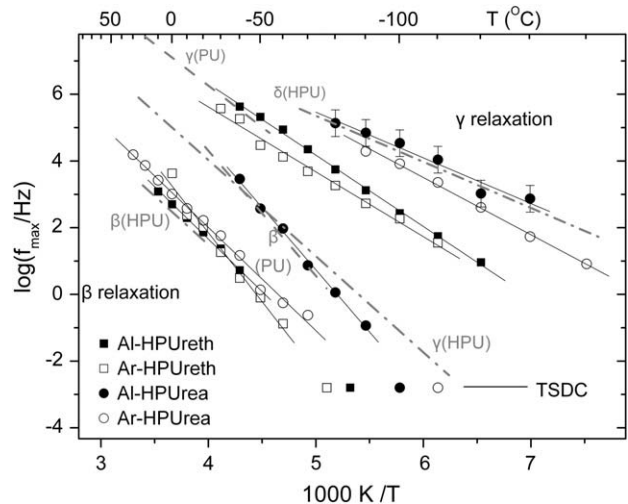
maximum and α is a shape parameter. In some cases a term representing the conductivity contribution to the loss spectrum is also used the last term in the right-hand side of Eq. (2) whereas in the case of more than one overlapping mechanisms a proper sum of Cole–Cole expressions is used. Applying this fitting procedure we were able to obtain dynamic characteristics of the underlying relaxation mechanisms, i.e. time scale, intensity of the mechanisms, shape parameters related with the distribution of relaxation times. In Fig. 6(a) and (b) we show the components contributing to measured dielectric loss spectra of Ar-HPUrea and of Al-HPUreth at $-100\,^{\circ}$C and $-50\,^{\circ}$C, respectively. In Table 2 we give, as indicative values, the fitting parameters obtained by applying this procedure to the spectra measured at $-100\,^{\circ}$C and $-50\,^{\circ}$C for all the samples.

In Fig. 7 we show the corresponding Arrhenius plots for the secondary relaxation mechanisms γ and β. Data obtained by the TSDC method for the β local relaxation mechanism are also included. (As a usual convention an equivalent frequency of about 10^{-3} Hz has been taken into account for the TSDC method [38]). We observe that, as expected, the temperature dependence of the frequency of maximum loss for the secondary relaxation mechanisms is of Arrhenius type and the points obtained by TSDC are in agreement with the DRS data (the Ar-HPUrea system being an exception). The activation energies, E_{act}, and the pre-exponential factors, τ_o, for the secondary relaxation processes obeying the Arrhenius equation

Fig. 7. Arrhenius plots for the secondary γ and β relaxations of all the samples. TSDC data, corresponding to β relaxation, are included (details in text). In the figure are also included molecular mobility data obtained with linear segmental polyurethanes, PU, [41,36] (dashed lines) and with hyperbranched polyurethanes, HPU, [36] (dash dot lines).

Table 3
Arrhenius parameters, activation energies, E_{act}, and pre-exponential factors, log τ_o, for secondary γ and β relaxation mechanisms.

Sample	γ relaxation		β relaxation	
	E_{act} (kJ/mol)	$\log\tau_o$	E_{act} (kJ/mol)	$\log\tau_o$
Al-HPUreth	41.3 ± 0.7	15.0 ± 0.2	60.2 ± 1.2	14.3 ± 0.3
Ar-HPUreth	33.4 ± 0.8	12.3 ± 0.2	71.4 ± 2.5	16.6 ± 0.6
Al-HPUrea	26.2 ± 2.6	12.3 ± 0.8	71.8 ± 2.7	19.5 ± 0.7
Ar-HPUrea	32.8 ± 0.8	13.8 ± 0.3	62.6 ± 2.0	15.1 ± 0.4

Concerning the γ relaxation mechanism our experimental findings (very fast mechanism, clearly different mobility for hyperbranched polyurethane and polyurea) support the interpretation that this mechanism is related with the relaxation process of terminal groups (–OH for urethanes and –NH$_2$ for ureas). Stronger hydrogen bonding interactions formed by –OH groups result in slower γ relaxation mechanism for hyperbranched polyurethanes compared to hyperbranched polyureas. On the other hand the fact that γ process mobility depends on the chemical structure (being faster for aliphatic structures) may originate in the fact that the structure of hyperbranched macromolecules deviates from the ideal structure of a dendrimer (having terminal groups only on the outer surface of the globular macromolecule). The terminal groups in hyperbranched structures located within the globular-like macromolecule and on the outer surface, as well, might participate in a hydrogen bond network which is affected by the structure of the macromolecule. The γ relaxation is thus coupled with the motions of the end groups not isolated or independent of the motions of the arms [19].

The mobility of γ relaxation mechanism found in our study is consistent with the mobility of terminal groups estimated for other dendritic and hyperbranched structures [26,30,31,36]. Moreover, the activation energies related with the γ relaxation mechanism, as estimated in these publications are in agreement with the values estimated in this work (Table 3). More specifically, Mijović et al. [26] have estimated a value of 23.4 kJ/mol for the activation energy of the local process associated with the motions of the terminal amino groups on the outer surface of poly(amidoamine) (PAMAM) dedrimers, Hakme et al. [30] have found a value of about 31 kJ/mol for the process associated with the motions of amino end groups hyperbranched aromatic polyamides, Garcia-Bernabé et al. [31] have estimated a value of about 40 kJ/mol for the process associated with the motions of terminal hydroxyl groups in hyperbranched polyglycerols and Okrasa et al. [36] estimated a value of 28 kJ/mol for the activation energy of the process associated with the motions of carboxyl end groups in hyperbranched polyurethanes. This range of published activation energies and molecular mobility imply that the relaxation mechanism associated with the terminal groups in hyperbranched polymers is sensitive on the structure of the globular macromolecule and the existent inter- and intramolecular interactions.

With respect to β relaxation mechanism our results do not show systematic differences between hyperbranched polyurethanes and polyureas (contrary to what occurs for the γ mechanism). It is obvious that only Al-HPUrea exhibits remarkably faster β mechanism. On the basis of this comparison, we conclude that this mechanism may originate in relaxation process which exists in all systems and is activated exhibiting similar dynamics.

Exploring the hypothesis that β relaxation mechanism in such hyperbranched systems may be a common characteristic for hyperbranched polyurethanes and polyureas we included in the Arrhenius plots presented in Fig. 7 data from the literature concerning dielectric studies on other polyurethane systems. More specifically we included data on average relaxation times of molecular processes on hyperbranched polyurethanes, HPU [36],

and on linear segmental polyurethanes as well, PU [42,36]. Comparison of the data leads to the following conclusions: Linear segmental PU systems exhibit two relaxation processes, called γ and β mechanism, associated with crankshaft motions of the (CH$_2$)$_n$ sequence in the soft domains (γ process) and with the motions of the polar carbonyl group (β process, sensitive on adsorbed water traces). The HPUrethane system studied by Okrasa et al. (actually polyurethane system without soft segment) exhibits three relaxation mechanisms: a fast δ relaxation mechanism (attributed to processes on the surface of the globular molecules, i.e. to the terminal –OH groups), a relaxation mechanism called γ and a new one called β relaxation mechanism (slower than the β mechanism observed in linear PU systems). Interestingly, the mobility of this relaxation mechanism coincides with the β relaxation mechanism observed in the systems studied in this work. In addition, the activation energy of this relaxation process is determined in [36] about 56 kJ/mol, comparable with the values presented in Table 3 for the β relaxation mechanism of our systems. This mechanism is not observed in the linear counterparts, thus, it may be associated with molecular motions which are dielectrically active solely in hyperbranched systems. We could suggest that, in agreement with interpretations of similar relaxation mechanisms observed in dendrimers [20,26] and other hyperbranched polymers [31], this mechanism is associated with relaxation processes of branch ends with polar groups. A network of hydrogen bonding interactions may control this process shifting the relaxation process to longer average relaxation times than the β process appeared in linear PU. In Al-HPUrea sample studied here, however, weaker hydrogen bonding interactions may exist and, consequently, there is not shift of this process to longer average relaxation times. It is worth pointing out here that Al-HPUrea is, additionally, the only system which exhibits dc conductivity in the glassy state (see next Section 3.3.2).

3.3.2. dc conductivity

We turn now our attention to the conduction mechanism related with the dc conductivity that appeared in our systems. In Fig. 8 we show the frequency dependence of the real part of conductivity, σ', for all the samples, at temperatures close to the calorimetric T_g of each sample. It is obvious that Al-HPUrea exhibits remarkably higher values of conductivity at the temperature region of T_g, compared to other three systems. All the systems show the characteristic dc conductivity plateau at temperatures slightly higher than T_g ($\sigma'(f)$ plots in Fig. 8 approach constant values at relatively low frequencies, the σ_{dc} value).

It is well known that for conductive systems the conduction mechanism can be studied also in the formalism of electric modulus [43,44]. In Fig. 8 we show also the corresponding data in the formalism of the electrical modulus (imaginary part). We observe that, as is expected, $M''(f)$ curves exhibit low frequency peaks with frequencies of maximum at the frequency region (crossover frequency) where $\sigma'(f)$ curves start to change from the plateau values at lower frequencies to the power law dependence on frequency at higher frequencies (the manifestation of the so called conductivity relaxation). We note, however, that for Ar-HPUrea the maximum of $M''(f)$ curve is located at higher frequencies, reflected actually the existence of a polarization mechanism at frequencies higher than the crossover frequency. This polarization mechanism exists, actually, in all the systems and appears in both $\sigma'(f)$ and $M''(f)$ curves at frequencies higher than the crossover frequency for all the samples. However, only for Ar-HPUrea this polarization mechanism dominates in $M''(f)$ plots with the consequence that the peak related with the conductivity relaxation appears as a shoulder in the low frequency side of the $M''(f)$ curve. Based on the plots shown in Fig. 8 we conclude that a fitting procedure is necessary for the investigation of the conductivity
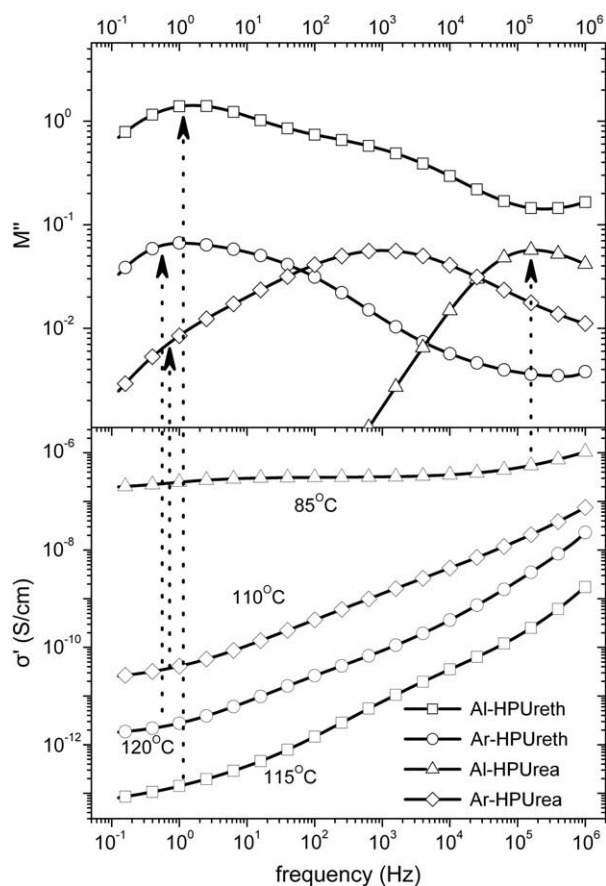
Fig. 8. Real part of conductivity, σ', and imaginary part of electric modulus, M'', vs frequency for all the samples studied. For each sample the selected temperature (indicated on the plot) is close to the calorimetric T_g. The vertical arrows indicate the relationship between $M''(f)$ peak and changing in slope of $\sigma'(f)$ curve (conductivity relaxation). Details in text.

relaxation process within the modulus formalism. Since the scope of this paper is restricted to the investigation of the dc conduction mechanism, we decided not to go into such details using that formalism.

Instead, we estimated the dc values of the conductivity from plots like those in Fig. 8 (where the extrapolation at very low frequencies provides the σ_{dc} values) and then constructed the
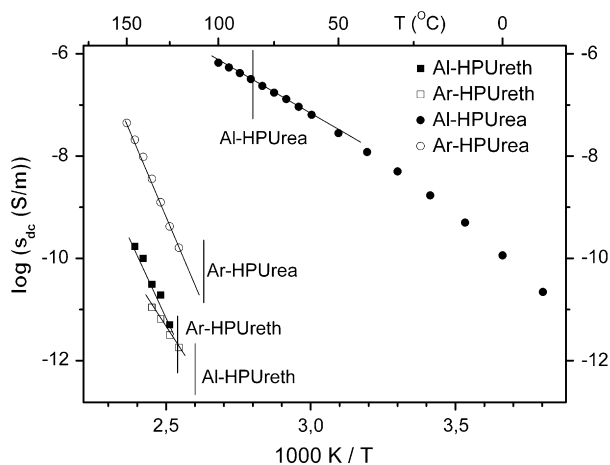

Fig. 9. Arrhenius plots of dc conductivity values for all the samples studied. The vertical lines indicate the glass transition temperature of each sample.

Table 4
Activation energies of the dc conduction mechanism, E_{act}, obtained by fitting Eq. (3) to the σ_{dc} data shown in Fig. 9.

Sample	E_{act} (kJ/mol)
Al-HPUreth	250 ± 19
Ar-HPUreth	163 ± 10
Al-HPUrea	60 ± 2
Ar-HPUrea	262 ± 6

Arrhenius plots of σ_{dc} vs 1000/T. In Fig. 9 we show the obtained Arrhenius plots with an indication of the calorimetric T_g of each sample. Such plots allow the study of the temperature dependence of the dc conductivity.

We observe that Al-HPUrea exhibits enhanced conductivity in a wide temperature range and it is the only system which shows dc conductivity mechanism at temperatures significantly lower than the T_g. The temperature dependence of this conductivity is of Vogel–Tamman–Fulcher (VTF) type, i.e. non-Arrhenius like, implying that the conduction mechanism is coupled with "cooperative" molecular motions which are activated in the glassy state of the polymer. This finding supports the claim that hyperbranched polymers are special systems, particularly with respect to conduction mechanisms and the molecular dynamics associated with the glass transition [19,25,31].

On the other hand, for all the systems studied in this work the plots in Fig. 9 reveal that the dc conduction mechanism at temperatures higher than T_g is of Arrhenius type, i.e. the temperature dependence of σ_{dc} can be described by the Arrhenius equation

$$\sigma_{dc}(T) = \sigma_o \exp\left(-\frac{E_{act}}{kT}\right) \qquad (4)$$

where E_{act} is the apparent activation energy of the dc conduction mechanism. The values of E_{act} obtained by least-square fittings of Eq. (4) to the data (lines in Fig. 9) are given in Table 4. Although the limited number of data in some systems affects the precision of these values, it is worth mentioning the relative high values of activation energies, E_{act}, for the conduction mechanism of these systems with the Al-HPUrea being an exception. Aliphatic hyperbranched polyurea seems to have a structure that facilitates charge motions with relatively low barriers for the transport of the charged particles. Further experimental studies are now in progress in order to investigate the relationship between structure of hyperbranched polymers and remarkably high charge mobility in the glassy state.

4. Conclusion

In this work we investigated the molecular dynamics and the dc conduction mechanism in two series of hyperbranched polymers: hyperbranched polyurethanes, aromatic, Ar-HPUreth, and aliphatic, Al-HPUreth, and hyperbranched polyureas, aromatic, Ar-HPUrea, and aliphatic, Al-HPUrea. The dielectric methods of Thermally Stimulated Depolarization Currents (TSDC) and broadband Dielectric Relaxation Spectroscopy (DRS) were used as the experimental techniques of investigation.

At the temperature region of the glass transition the enhanced conductivity contribution to the dielectric losses masks any features of the loss spectra at relatively low frequencies and thus we were not able to study the segmental relaxation which is associated with the glass transition. Therefore, we focus on the two secondary relaxation mechanisms observed in all the samples, the γ at low temperatures/high frequencies and the β at higher temperatures/lower frequencies.

The γ relaxation mechanism is attributed to motions of the end groups (–OH for urethanes and –NH$_2$ for ureas) and has been found faster in the hyperbranched polyureas probably due to weaker hydrogen bonding interactions formed by –NH$_2$ groups. In addition, our results reveal that γ relaxation mechanism in both series depends on the chemical structure, being faster for aliphatic structures, the activation energy, however, exhibiting not such structure dependence. This coupling of the local γ relaxation mechanism with the structure and the motion of the arms may exist due to the fact that in hyperbranched structures the terminal groups are located in both places, within the globular macromolecules and on the outer surface, participating, thus, in a hydrogen bond network which is affected by the structure of the macromolecule.

Regarding the β local relaxation mechanism we attribute this process to the motions of branched ends with polar groups. Based on comparison with data on hyperbranched polyurethanes that appeared in the literature we suggest that this mechanism may be a typical relaxation process for hyperbranched polyurethane structures, at least, which is not dielectrically active in the linear counterparts. The inter- and intramolecular interactions may control the mobility of this process. Further investigation is needed, however, for any quantification of this claim.

With respect to dc conduction mechanism, two interesting features are disclosed from this study. First, at temperatures higher than T_g the dc conductivity shows Arrhenius-like temperature dependence with rather high activation energies (in the order of 200 kJ/mol). This finding implies strong decoupling between charge mobility and polymeric chain mobility. Second, at temperatures lower than T_g, i.e. in the glassy state, all the systems studied exhibit remarkably high charge mobility. In particular, Al-HPUrea system exhibits long range conductivity (dc plateau) in a broad temperature interval below T_g. The temperature dependence of this conductivity is of VTF type implying that the conduction mechanism is coupled with "cooperative" molecular motions in the glassy state of the polymer. Aliphatic hyperbranched polyureas, thus, seems to have a structure that facilitates charge motions with relatively low barriers for the transport of the charged particles.

Acknowledgements

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