



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 ¹H 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_2B 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

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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 tetrahydrofuran

(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 H₂O 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 ¹H NMR spectroscopy and the representative NMR spectrum of aromatic polyurethanes, Ar-HPUreth, is shown in Fig. 1. The ¹H NMR spectra of hyperbranched polymers were recorded on a ¹H 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: ¹H NMR-DMSO-*d*₆ (δ ppm): 0.9 (CH₃), 1.4 (Cyclohexyl ring), 2.7 (CH₂-NH), 3.4 (CH₂-OH), 3.6 (CH₂-O-CO), 3.9 (CH-OCO), 4.5: 5.0 OH, 6.9: 7.2 (NH ureth).

Ar-HPUreth: ¹H NMR-DMSO-*d*₆ (δ ppm): 2.1 (CH₃), 3.4 (CH₂-NH), 3.7 (CH₂-OH), 3.9 (CH₂-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% H₂O and 3 g/L LiCl was used with flow rate of 0.5 ml min⁻¹. Linear polynylpyridine (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 N₂. 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

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