Synthesis and characterization of hyperbranched poly(urea-urethane)s

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ABSTRACT

The present thesis aims to synthesize hyperbranched poly(urea-urethane) polymers (HPU) in one-pot method using commercially available monomers. The monomers used to achieve our goal are 2,4-toluylene diisocyanate (TDI) as aromatic diisocyanate and isophorone diisocyanate (IPDI) and 2(3-isocyanatopropyl) cyclohexylisocyanate (IPCI) as aliphatic diisocyanates. Those proposed diisocyanates were reacted with diethanolamine (DEA) or diisopropanolamine (DIPA). Conditions of polymerization reactions were optimized that the reactions were stopped before gelation. Complete structural analysis using ^{1}H and ^{13}C NMR for the obtained aromatic polymers was carried out. The degree of branching was determined for polymers based on TDI and was found to be $>$ 60% for TDI/DEA and 45-48% for TDI/DIPA. Aliphatic polymers have spectra with overlapped signals therefore, no full structural analysis was possible. Molar masses were determined using SEC/RI detector which shows that the prepared polymers have M_w values between 1600 g/mol and 106000 g/mol. Thermal analysis for different polymer systems showed that aliphatic HPU are more thermally stable and have values of glass transition temperature higher than aromatic ones.

Modification of the end groups in the prepared hyperbranched polymers was carried out using three different modifiers and degree of modification up to 100% was reached depending on type of modifier. The modified polymers have good solubility in different organic solvents. Their molar masses are influenced by reaction conditions and side reactions.

Aromatic and aliphatic linear poly(urea-urethane)s based on the same diisocyanate monomers were prepared to compare the properties of hyperbranched systems with their linear analogs. Measurements of solution viscosity showed that HPU have lower solution viscosity values than their linear analogs of comparable molar masses. Rheological measurement of some polymer samples of different systems were carried out and showed that our hyperbranched systems exhibit a more elastic behavior than the linear polymers.

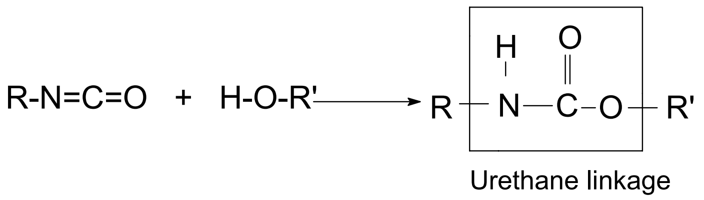
Surface studies for thin films prepared from different polymer systems (hyperbranched, linear and modified) were carried out and the obtained thin films were characterized using light microscope, microglider, GC-MS, and AFM. Contact angle measurements showed that HPU have a relatively hydrophilic character. The modified polymers have higher contact angle values than the unmodified ones due to the lack of OH end groups.

Networks based on aliphatic and aromatic HPU were prepared through the reaction of HPU with trimer of 1,6-diisocyanatohexane in DMF. The obtained networks were characterized by DSC, GC-MS, DMA and AFM which showed that the domain size in aromatic networks is larger than in aliphatic networks. Tensile test was carried out and it was found that aliphatic network is more elastic than aromatic one.

1- INTRODUCTION

Polyurethanes are extremely large and complex molecules produced by combining a large number of simpler molecules called monomers. Monomers are compounds whose properties (molecular weight, boiling point, melting point, crystallinity, etc.) are discrete. Polyurethanes, like other polymers on the other hand, typically do not have discrete properties but have average properties that represent a range of molecules with differing molecular weight and often slightly differing structure. The molecular weight of polyurethanes can greatly affect the physical properties of a polymer[1]. Molecular weight distribution can also have a significant effect upon polyurethane characteristics, especially processing and rheoligical characteristics.

The chemistry of urethanes makes use of the reactions of organic isocyanates with compounds containing hydroxyl groups, as shown in Figure 1.1. When polyfunctional isocyanates and intermediates containing at least two active hydrogens per mole are reacted at proper ratios, a polymer results that can produce rigid or flexible foams, elastomers, coating, adhesives, and sealants. An isocyanate group reacts with the hydroxyl groups of a polyol to form the repeating urethane linkage.



$$R{-}N{=}C{=}O \; + \; H{-}O{-}R' \longrightarrow R-\boxed{\overset{H}{\overset{|}{N}}-\overset{O}{\overset{\|}{C}}-O}-R'$$

Figure 1.1: Classical urethane linkage reaction.

The polymer chains, in general, have a special architecture. They may be linear, branched, or network. Polyurethanes display stereo microstructure and can exist as homopolymers and copolymers. Copolymers may be random, alternating, segmented, block, or graft types. Polyurethanes can be crystalline solids, segmented solids, amorphous glasses, or viscoelastic solids. With respect to mechanical properties, polyurethanes are nonideal solids. The mechanical properties of the polymers are time dependent. For every excitation, there are two responses: a viscous response and an elastic response, i.e. a time dependent and a non-time dependent response. There is also inverse relationship between modulus of elasticity and frequency in a typical polyurethane.

Polyurethanes are used in surprising array of commercial applications. Figure 1.2 presents the universe of polyurethane applications which can be divided into seven major groups: flexible slab, flexible molded foams, rigid foams, solid elastomers, RIM, carpet backing, and two component formulations. The fabrication and application of slab stock foam is easier and faster than the use of animal hair, bird feathers or other filling materials. Improved molding techniques of flexible foam are responsible for its acceptance in furniture with unusual shapes. Molded rigid foam has made great inroads into the furniture industry. One of the major uses of rigid polyurethane foam is in home refrigerators. Most major manufacturers are currently using rigid urethane foam as insulation in their lines, because of the superior insulating characteristics of the fluorocarbon-blown foams. Large ships have used rigid polyurethane foam as void fillers and also in lifeboats and refrigerator ships.

The major benefits offered by polyurethane are that it retains its high impact strength at low temperatures, it is readily foamable, and it is resistant to abrasion, tear propagation, ozon, oxidation, fungus, and humidity. Although thermoplastic polyurethane is attacked by steam, fuels, ketones, esters, and strong acids and bases, it is resistant to aliphatic hydrocarbons and dilute acids and bases. The highest recommended use temperature of thermoplastic polyurethane is approximately 104 °C. Aromatic thermoplastic polyurethane has poor weatherability stemming from its poor resistance to UV degradation. Since polyurethane can be painted with flexible polyurethane paints without pretreatment, it has found use in many automotive exterior parts.

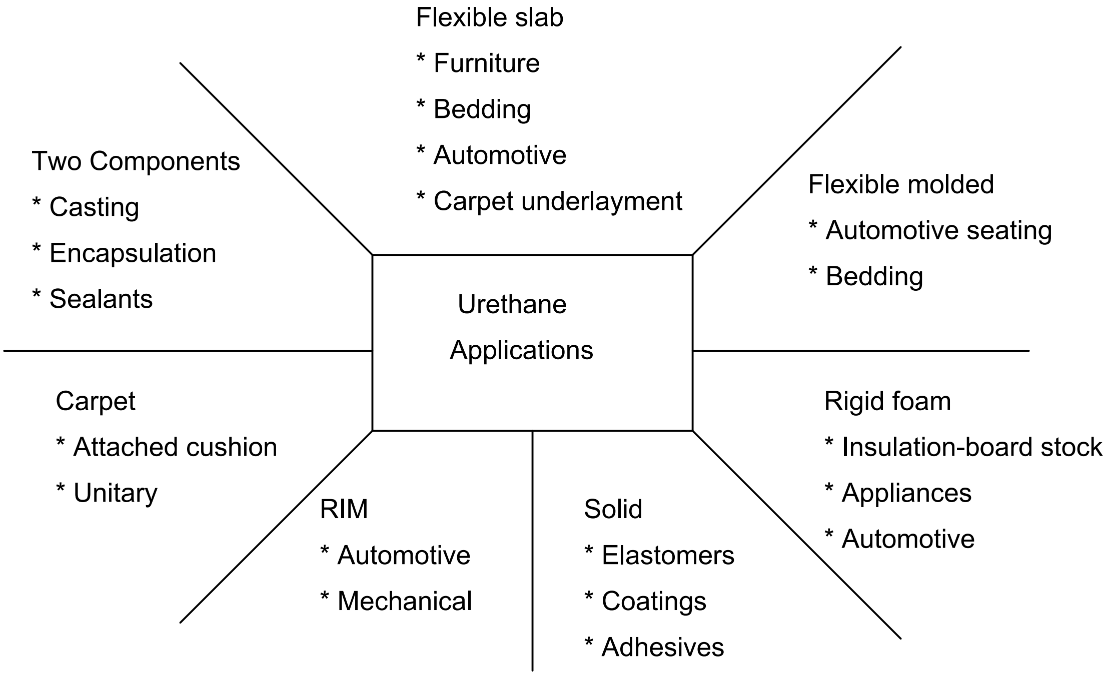


Figure 1.2: Applications of polyurethane.

At the end of World War II, synthetic polymers started to be utilized for commercial products. The most common techniques have been either simply to develop a new monomer and synthesize a new polymer, or to modify an existing polymer by some chemical route. Highly branched polymers have so far mainly been used as oligomers in thermosets for high solid coating binders, alkyds, and in resins for composites. Flory[2] in his book, Principles of Polymer Chemistry, theorized about synthesizing condensation polymers from multifunctional monomers of A_xB type. The polymers produced are non-crystalline and have highly branched structure. After a little more than 30 years first papers on the synthesis of dendritic polymers emerged[3,4].

Dendritic polymers synthesized from A_xB monomers comprise monodisperse dendrimers with exact branching and irregularly branched, polydisperse, hyperbranched polymers. Dendritic polymers, in contrast to linear polymers, behave more like molecular micelles[5]. Many dendrimers have been prepared and presented in the literature such as polyamidoamine[6,7] poly(propylene imine)[8,9], aromatic polyethers[10-12] and polyesters[13,14], aliphatic polyethers[15] and polyesters[16], polyalkane[17,18], polyphenylene[19], polysilane[20] and phosphorous[21]. Kim and Webster were the first who developed a route for one step synthesis of dendritic polyphenylenes[22-24]. These polymers were polydisperse and highly branched, they were called hyperbranched polymers. Ever since, a wide variety of hyperbranched polymers were prepared using polycondensation reactions of AB_2 or even AB_3 monomers (mostly of equal reactivity of B functionalities). The variety of reported structures is huge such as hyperbranched polyesters, polyamides, polyethers, polyesteramides, polysulphones, polyetherketones, also polyaddition reactions were used to prepare polycarbosilanes, polyurethanes, polyarylenes and polythioethers.[25] The A_2+B_3 approach is also used to prepare hyperbranched polymers which opens pathways to tailor the properties of the formed polymer under technical conditions. Although hyperbranched polymers consist of a large amount of different isomeric macromolecules beside their polydispersity, they are characterized by their low solution viscosity and good solubility compared to linear analogues due to the branches. The presence of large amount of end groups in the hyperbranched polymer facilitate, through modification, optimizing their properties for special applications such as in the classical field of coatings and blends[26,27], microelectronics, information technology, optics and medicine. One limitation of the A_2+B_3 technique is the possibility of crosslinking which could be overcome by optimizing reaction conditions and stopping the reaction before gelation.

2- THEORETICAL PART

Polyurethanes are produced by the condensation reaction of isocyanate and a compound with a hydroxyl functionality, such as polyol. In fact, often the majority of the linkages found in polyurethanes are derived from the polyol compound such as ether or ester linkages. One of the most important applications of polyurethanes formed through the reaction of isocyanate and polyol, beside foams, is the polyurethane coatings. These formulations require the use of a catalyst to complete the reaction in a timely manner and appropriate temperatures. The unique combination of the properties of toughness, flexibility, abrasion resistance and solvent resistance has led to widespread and continually increase of polyurethane coatings in many uses. Typical uses include leather coatings, fabric coating corrosion-resistant finishes, floor varnishes, marine finishes, magnet wire coating, and concrete sealing. Polyurethanes are closely related to polyurea which are formed through the reaction of isocyanate with amine-terminated resins producing a polymer contains urea linkages. Polyurea is generally used as an industrial coating in severe environments with good chemical resistance to hydrocarbons and hydrogen sulfide gas immersed sewage applications.

Polyurea/polyurethane hybrid formulations can be defined as the result of a chemical reaction between an isocyanate and a mixture of polyol and amine reactants. These formulations provide an “intermediate” polyurea that displays many of the same properties of a polyurea. However, hybrid formulations can also display some of the problems associated with polyurethane chemistry. In coating formulation, hybrids generally contain a polyether/ polyester polyol and a primary amine resulting in a chemical backbone comprised of amine and hydroxyl functionality. Polyurea/polyurethane hybrids are normally associated with use on “non-critical” items that generally do not require immersion or extreme temperature conditions for application.

2.1 Polyurethane chemistry

The basis of polyurethane chemistry is the high reactivity of isocyanates. They react under mild conditions with all compounds that contain “active” hydrogen atoms. These are mainly alcohols (OH group) but also amines. When the isocyanate group (NCO) reacts with alcohols, amines, carboxylic acids and water, urethane, urea and amide linkages are formed. The reaction of isocyanate with water is important for the production of foams because during this reaction, gaseous CO_2 is formed and acts as a ”chemical” blowing agent. The reactions involved in the preparation of polyurethane are shown in Figure 2.1. Those reactions proceed, for number of applications, through the reaction of the so-called prepolymers with diisocyanates. Prepolymers with terminal NCO groups are obtained by reacting a polyetherol or polyesterol (polyol) with an excess of diisocyanate. There are two important advantages associated with this procedure: First, because of the high molecular weight of the prepolymers, they have a lower vapor pressure which helps to improve the workplace environment. Secondly, processing can be better controlled so that properties of the polyurethane-part being produced can adjusted more easily.

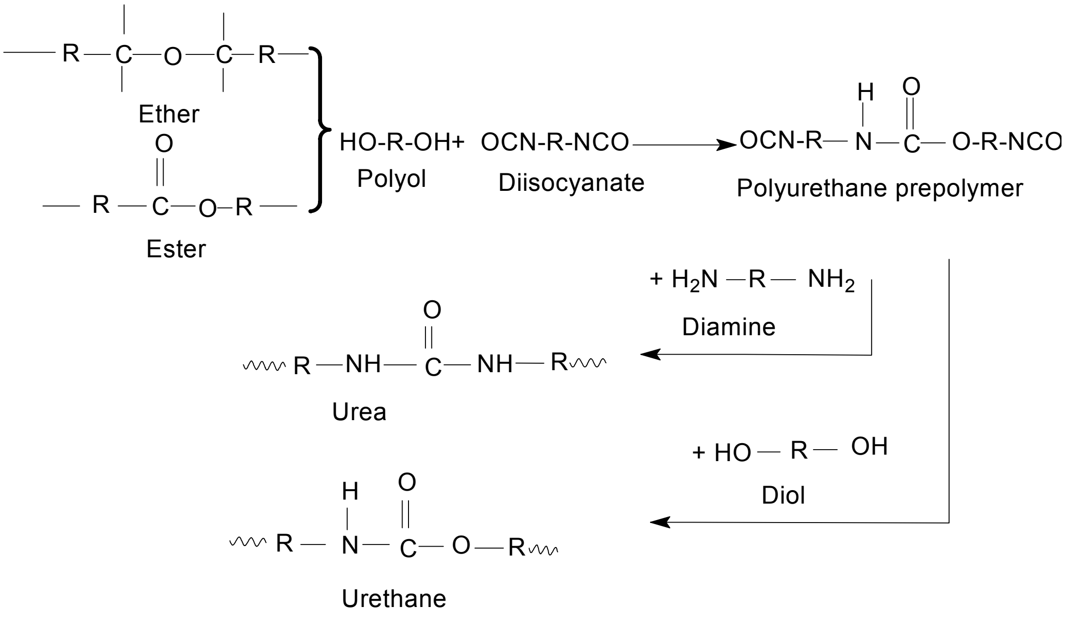


Figure 2.1: Chemical reactions involved in polyurethane preparation.

2.1.1 Polyols

The predominant reaction partners of the isocyanate are polyhydroxyl compounds (polyols). These are characterized by the hydroxyl number which is inversely proportional to molecular weight. Polyols have a profound effect on the properties of the finished polyurethane. While associating the properties of the polymers with the urethane linkage, the structure of the polyol has a direct bearing on both processing and finished properties of the polyurethane polymer. The two main classes of polyols are polyesterols and polyetherols. 80 to 90% of the used polyols today are polyetherols. Polyetherols are produced by the alkali-catalyzed polymerization of ethylene oxide and propylene oxide. Low molecular weight di- and polyfunctional alcohols or amines are used as initiators (Figure 2.2). The structure of the polyols and hence the processing and property profile of the polyurethane can be controlled within wide limits by the selection of the length and composition of the polyether chains and the functionality of the starter molecules. For flexible foams, polyetherols based on trifunctional initiators such as glycerol or trimethylolpropane with molecular weights of around

6000 g/mol are generally used. Polyols for rigid foams are characterized by higher functionality and shorter polyether chains. Polyurethane products based on polyetherols are more stable to hydrolysis but more sensitive to oxidation. Polyetherols can be produced in low-viscosity variations.

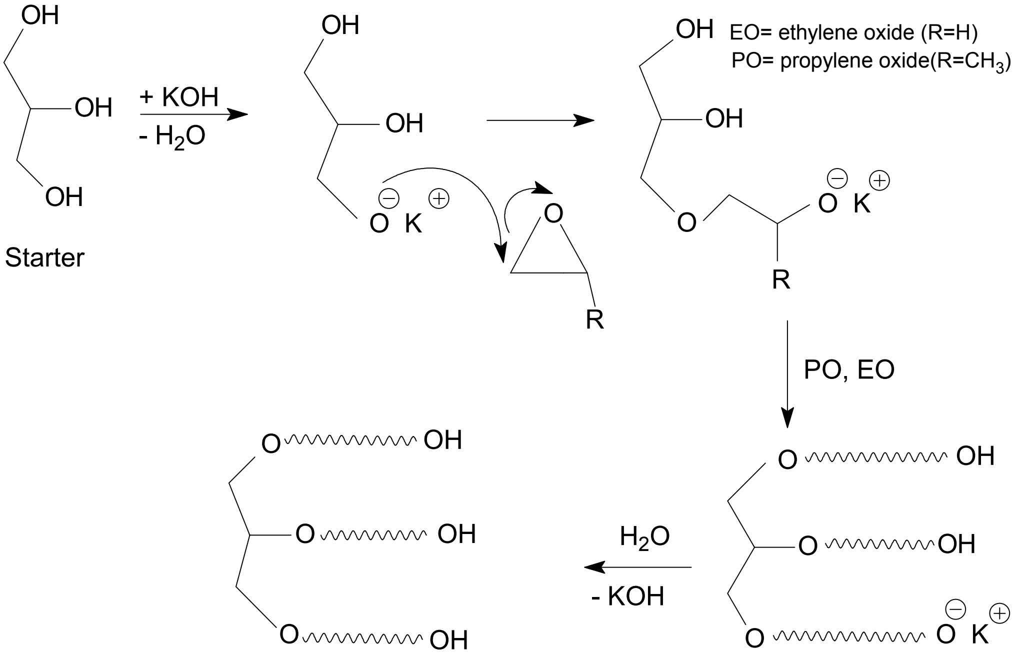


Figure 2.2: Synthesis of polyetherols.

Polyesterols are produced by polycondensation of di- or polycarboxylic acids or their anhydrides with di- or polyalcohols (Figure 2.3). The most important polyesterols are reaction products of adipic acid or phthalic anhydride with aliphatic diols containing 2 to 6 carbon atoms, oligoether diols or triols. An important application is the use as soft segments in thermoplastic elastomers.

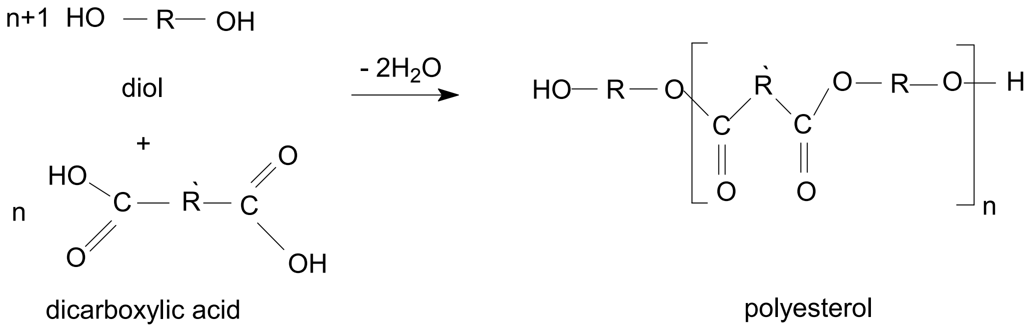
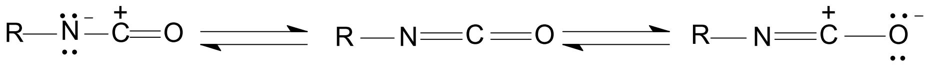


Figure 2.3: Polyesterol via polycondensation.

2.1.2 Industrially important isocyanates

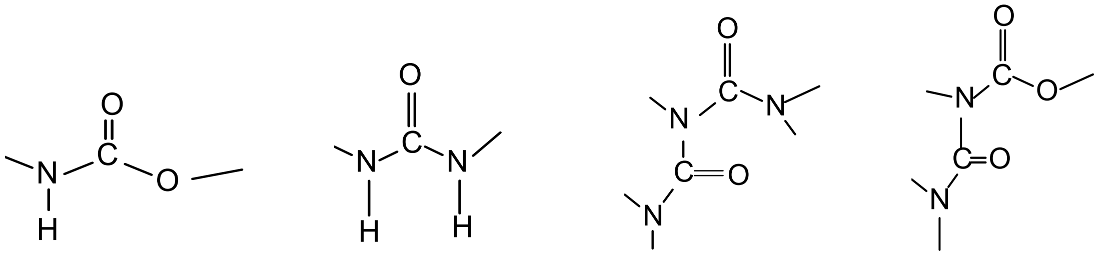
Isocyanates are liquids or solids that are highly reactive and undergo addition reaction across the C=N double bond of the NCO group. Reactions with alcohols, carboxylic acids, and amines have been widely exploited in developing a variety of commercial products. The basis of high reactivity of the isocyanates is the low electron density of the central carbon, as indicated by the resonance structures of Figure 2.4. Electron-withdrawing or –donating substituents alter the electrophilic nature of the isocyanate. Thus, whereas p-N,N-dimethylaminophenyl isocyanate is a rather slow-reacting material, sulphonyl or acyl isocyanates are noted to be extremely reactive. The reactivity of isocyanates is also manifested in their tendency to react with themselves to form dimers, trimers, or higher oligomers and polymers. Analytically, isocyanates are readily identified through derivatization (urea formation) or via IR spectroscopy using the strong absorbance between 2300 and 2200 cm^{-1}.



$$R-\ddot{\underset{\cdot\cdot}{N}}^{-}-\overset{+}{C}=O \rightleftharpoons R-N=C=O \rightleftharpoons R-N=\overset{+}{C}-\ddot{\underset{\cdot\cdot}{O}}^{-}$$

Figure 2.4: Resonance structures of isocyanates.

Urethane linkage which is formed through the reaction of isocyanate with hydroxyl group is shown in structure (1). The isocyanates also react with amines to form substituted urea linkages, structure (2); they will react with water to form carbamic acid, which is an unstable intermediate, and it decomposes readily to evolve carbon dioxide and an amine. This amine, in turn, reacts with additional isocyanate to form disubstituted urea. In addition, a number of cross-linking reactions may take place, depending on the reaction conditions such as temperature, the presence of catalysts, the structure of the isocyanate, alcohols, and amines involved. These reactions form linkages of biuret [reaction between substituted urea and isocyanate, structure (3)], allophanate [reaction between urethane-isocyanate, structure (4)]. Chemical structures of different isocyanate linkages are shown in Figure 2.5.



(1) (2) (3) (4)

Figure 2.5: Chemical structures of different isocyanate linkages.

Industrially, isocyanates have become large-volume raw material for addition polymers such as polyurethanes, polyureas and polyisocyanurates. By varying the reactants (isocyanates, polyols, polyamines, and others) for polymer formation, a lot of products have been developed, ranging from flexible and rigid insulation foams, to high-modulus automotive exterior parts, high- quality coatings and abrasion-resistant elastomers.

The most important aromatic isocyanates are: 2,4-toluene diisocyanate (2,4-TDI), 2,6-toluene diisocyanate (2,6-TDI), 4,4'-methylene diphenyl diisocyanate (MDI), p-phenylene diisocyanate (PDI) and naphthalene-1,5-diisocyanate (NDI). While the most important aliphatic diisocyanates are 1,6-hexamethylene diisocyanate (HDI), isophorone diisocyanate (IPDI), and 1,4-cyclohexane diisocyanate (CHDI). What concern us from all types of isocyantes are TDI as an example for aromatic diisocyanate and IPDI as an example for aliphatic diisocyanates.

-TDI

The most important technical mixture of TDI is the 80:20 mixture of 2,4-TDI and 2,6-TDI. The classical manufacturing process for the production of TDI depends on the nitration of toluene in the presence of sulfuric acid. The nitrotoluene is then hydrogenated to the corresponding diamine, and finally the diamine is phosgenated to the corresponding diisocyanates.

-IPDI

A popular non-discoloring isocyanate is 3-isocyanatomethyl-3,5,5-trimethylcyclohexyl isocyanate, commonly known as isophorone diisocyanate. IPDI is extensively used in the preparation of polyurethane-based, light- stable coatings. Its desirable pot life and cure rate are due to two isocyanate groups with different reactivities, one hindered and the other unhindered. IPDI is prepared from isophorone by converting it into isophorone diamine which is then phosgenated to IPDI.

2.1.3 Catalysis of the isocyanate-hydroxyl reaction

The catalysis of the isocyanate-hydroxyl reaction has been studied by many authors[28] who found that the reaction of aliphatic isocyanates with hydroxyl groups is catalyzed by many metal carboxylates and organo-tin compounds. t-Amine catalysis of the reaction of aromatic isocyanates with hydroxyl groups has been practiced for some time and is common for the preparation of flexible polyurethane foams[29]. The reaction of IPDI with alcohols was studied[30,31] in the absence and in presence of dibutyltin dilaurate (DBTL) and 1,4-diazobicyclo[2,2,2]-octane (DABCO). In the presence of DBTL, the reaction of the secondary isocyanate group was favored, while in the presence of DABCO the reaction of the primary isocyanate group was preferred. The relative reactivity of the isocyanate group depends on the mode of catalysis and steric hindrance.

Dibutyltin compounds are generally recognized to function as Lewis acid catalysts by complexing with the isocyanate[32]. The mechanism of catalysis of amines has been related to Lewis base catalysis, the amine complexing the alcohol. It has been observed that the rate of the reactions between aromatic diisocyanates and primary alcohols was much faster than that of aliphatic diisocyanates and alcohols under the same reaction conditions. Another important observation was the difference in the reactivity of the second NCO group on the same molecule after the first one has reacted. Measurements and modeling have shown that the presence of one urethane group on the tolylene molecule quenches the reaction rate of the remaining isocyanate as much as ten fold[33]. The effect of catalyst on the synthesis of polyurethane prepolymer was investigated[34] and it was found that this effect extends beyond a simple increasing of the reaction rate. The catalysts serve to promote the slower reactions more than the faster ones. This would imply that for the preparation of polyurethane prepolymers, a catalyst might serve to equalize the reaction rates between the first and the second isocyanate groups to react in a diisocyanate. This rate equalization will serve to produce a greater relative amount of the multisegment molecules. Yilgör et al[35] studied the effect of using various catalysts such as $Hg(CH_3COO)_2$, $Zn(CH_3COO)_2 .2H_2O$, and $SnCl_4. 5H_2O$ on the reaction of HMDI with n-butanol and found that the inorganic salts are effective catalysts for these reactions. It is also possible to have preferential catalysis of primary reaction between NCO and OH over side reactions, depending on the stoichiometric ratio of NCO/ OH and also the concentration of the catalyst used.

In the preparation process of poly(urethane-urea)s, urethane and urea groups form almost simultaneously, so the information about the effect of urea groups on reaction kinetics of polyurethane formation are necessary for thoroughly understanding the poly(urethane-urea) polymerization. Luo et al[36] studied the effect of urea groups on polyurethane formation and confirmed the catalytic effect of urea groups on polyurethane polymerization. The suggested mechanism to explain this effect is based on the hydrogen bonding between the urea carbonyl groups and the hydroxyl groups.

2.1.4 Depolymerization of polyurethane

All polymers can be depolymerized, polyurethanes are no exception. There are several ways polyurethanes can be depolymerized chemically, among them: hydrolysis, thermolysis, photolysis, pyrolysis and solvolysis. Hydrolysis is defined as a chemical reaction in which water reacts with another molecule to form two or more substances. Thermolysis reactions are those that occur due to heat. Oxidation is the reaction in which oxygen combines chemically with another substance. Oxidation can be initiated with heat (thermooxidation) or by light (photooxidation). Photolysis is the decomposition of a chemical compound into smaller molecular weight units caused by the interaction with light. Pyrolysis is the transformation of a substance into other by heat alone i.e. without oxidation. Attack on polyurethanes by solvents, for example alcohols, can cause a surface degradation referred to as solvolysis.

The three bonds most susceptible to hydrolytic degradation are the ester, urea, and urethane (Figure 2.6). The ester reverts to the precursor acid and alcohol, the urea bond can hydrolyze to form a carbamic acid and an amine. The carbamic acid normally is instable and typically undergoes further reaction. The urethane linkage, although somewhat less susceptible, may undergo hydrolysis to yield a carbamic acid and the precursor alcohol.

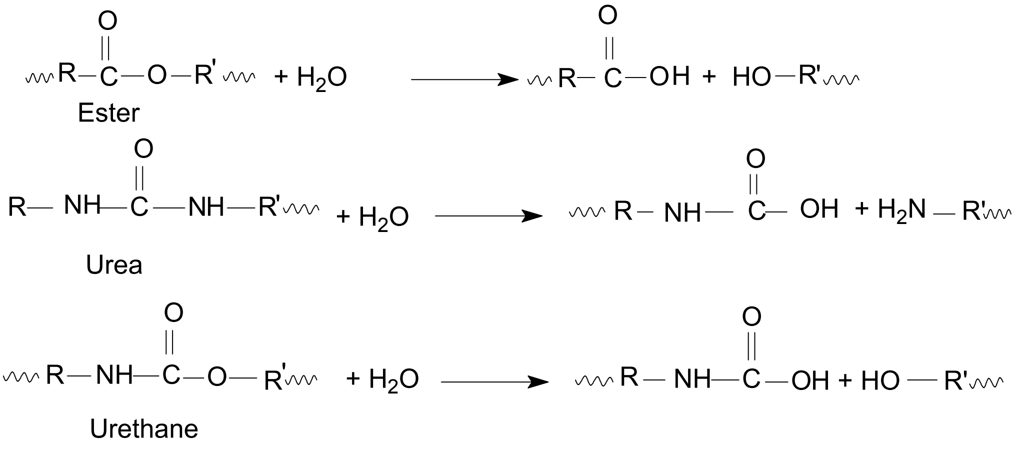


Figure 2.6: Bonds susceptible to hydrolytic attack.

Heat can cause the degradation of polyurethanes. The onset of allophanate dissociation is around 100 to 120°C. The dissociation temperature of the biuret linkage is around 115 to 125°C. These reactions are dissociations and somewhat reversible which revert to the urethane or urea from what they were formed. The aromatic-based urethane bond begins its thermal disassociation around 180°C, which is prior to the urea linkage which is about 160 to 200°C. Urethane linkage may undergo three separate types of thermal degradation: (1) the formation of the precursor isocyanate and the precursor alcohol; (2) cleavage of the oxygen of the alpha CH_2 group and association of one hydrogen on the second CH_2 group would lead to the carbamic acid and olefin with subsequent carbamic acid decomposition to give a primary amine and CO_2 as depicted in Figure 2.7; (3) the formation of a secondary amine and CO_2.

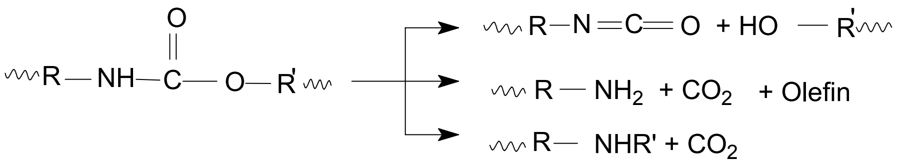


Figure 2.7: Thermal degradation of urethane linkages.

It was demonstrated that esters are weak bonds in hydrolysis. For thermooxidation the ether is the weak link. Thermooxidation proceeds via a free radical mechanism. Heat causes a hydrogen elimination from a carbon alpha to the ether linkage. This radical is subjected to oxygen addition forming a peroxide radical. The peroxide radical then extracts another hydrogen from the backbone to form a hydroperoxide. The hydroperoxide radical then decomposes to form an oxide radical and the hydroxide free radical. The order of thermooxidation stability is ester > urea > urethane >> ether. The oxide radical will cleave at either two places (Figure 2.8), at the carbon bond adjacent to the oxide radical forming formats or at the carbon-oxygen bond forming aldehydes.

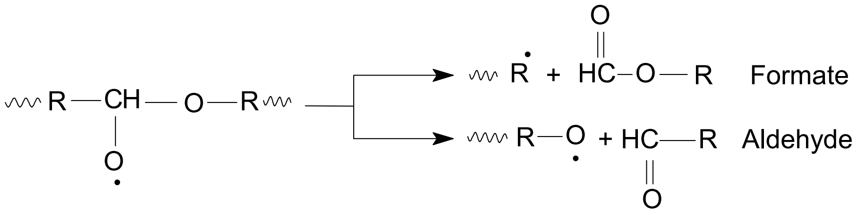


Figure 2.8: Thermooxidation-oxide cleavage.

2.1.5 Molecular forces and chemical bonding

Polyurethanes are characterized by the forces at work within and between the molecules. Of these, covalent bonds are the strongest and most significant. To gain a fuller understanding of the nature of polyurethane, we must account for secondary bonding forces that act between individual polyurethane molecules. Although much weaker than covalent bonds, they nevertheless, directly affect the material’s physical properties, such as viscosity, surface tension, frictional forces, miscibility, volatility and solubility. In order of increasing strength, these secondary forces are classified as van der Waals forces, dipole interaction, hydrogen bonding.

Van der Waals forces are responsible for the short-range natural attraction of similar molecules. When they are overcome by heating, softening and melting follows. Hydrogen bonding, often considered a strong form of dipole interaction, is a third category of secondary bonding forces. Hydrogen bonding is associated with the group in backbones and the –OH or

NH_2 groups in the side chains found in polyurethane or polyurea. As in dipole interacton, oxygen and nitrogen atoms attract positively charged hydrogens of othr molecules. Polymers with hydrogen bonding usually are compatible with small molecules such as those constituting plasticizers, solvents, and water. Secondary bonds usually yield before covalent bonds under heat. The polymers with strong secondary forces exhibit high viscosities and are more difficult to process.

2.1.6 Segmented polyurethane

One reason for the excellent physical properties of polyurethane elastomers is their tendency to pack themselves into tight, stereoregular molecular chains a phenomenon referred to as crystallinity. However, it is known that polyurethane consist of a mixture of crystalline and amorphous domains, a state described as *segmentation*. Polyurethane as thermoplastic elastomer contains physical netpoints forming a two-phase structure, where the hard segments separate to form discrete domains in a matrix of soft segments. The rigid segments act as bridges and as filler particles, reinforcing the soft segment matrix. The hard segments are considered held together in discrete domains through the action of van der Waals forces and hydrogen bonding interactions. Interchain attractive forces between rigid segments are greater than those present in the soft segments, due to the high concentration of polar groups and the possibility of extensive hydrogen bonding. Hard segments significantly affect mechanical properties, particularly modulus, hardness, and tear strength. The performance of elastomers at elevated temperatures is very dependent on the structure of the rigid segments and their ability to remain associated at these temperatures. Rigid segments are considered to result from contribution of the diisocyanate and chain extender components. Hydrogen bonding occurs between the individual hard blocks giving rise to a three-dimensional molecular domain structure. These domains may themselves be in a larger, ordered arrangement including both soft and hard blocks. The hard blocks being built up in a transverse orientation to their molecular axis leading, in cases, to the appearance of spherulites in the polymer. The morphology is unstable with respect to temperature and thus, thermoplastic elastomers can be processed from the melt but act like networks at application temperature.

2.2 Dendritic Polymers

From a historical perspective, progress towards the deliberate construction of macromolecules possessing branched architectures can be considered to have occurred during three different eras. The first period occurred roughly from the late 1860's to the early 1940's, when branched structures were considered as being responsible for insoluble and intractable materials formed in polymerization reactions. Synthetic control, mechanical separations, and physical characterization were primitive at best as judged by current standards; isolation and proof of structure were simply not feasible. The early 1940's to the late 1970's defines the second period, in which branched structures were considered primarily from a theoretical vantage point with initial attempts at preparation via classical, or single-pot, polymerization of functionally differentiated monomers.

During 1941 and 1942, Flory[37-40] disseminated theoretical and experimental evidence for the appearance of branched-chain, three dimensional macromolecules. He discussed a feature of polymerization reactions called "gelation". Descriptive terminology used by Flory to categorize differing polymeric fractions included the terms "gel" and "sol" referring to polymers that were insoluble or soluble, respectively. Flory showed statistically that branched polymeric products begin to appear after polymerization had progressed to a definite extent. Molecular size distributions, the number average degree of polymerization, as well as derivations relating tri- and tetra-functional branching units (monomers) were also addressed. Polymer architecture represented by Flory is shown in Figure 2.9 which resulted from polymerization of AB_2 monomers.

The modern era of cascade or dendrimer chemistry came to life when Vögtle[41] published in 1987 his paper entitled "Cascade and Nonskid-chain-like Synthesis of Molecular Cavity Topologies".

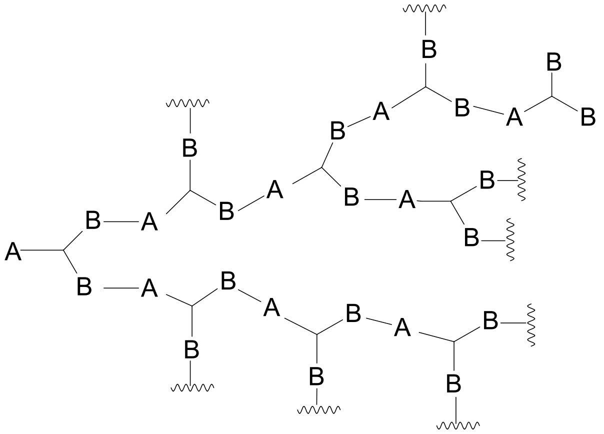


Figure 2.9: Branched polymer architecture as demonstrated by Flory[40] by the assembly of AB_2-type monomers.

Repetitive and multiple reactions were employed for the generation of new, branched molecular assemblies. Most notable about these synthesis is that for the first time, “generational” molecules were prepared and characterized at each stage of the construction process. Denkewalter, Kolc, and his coworkers[42] presented a method for the synthesis of polylysine-based dendrimers. Interesting features of these dendritic polymers include 1→2 asymmetric branching pattern and the incorporation of multiple chiral centers at each tier. Aharoni, Crosby, and Walsh[43] studied these lysine dendrimers and reported that each member of the series was monodisperse.

Tomalia et al.[44] reported the divergent preparation of an entire series of dendrimers possessing trigonal, 1→2 N-based, branching centers. The first convergent preparation of dendrimers resulted in poly(aryl ether) architecture as reported by Fréchet and Hawker[11]. Innovative use of their pivotal phenoxide-based, benzylic bromide displacement sequence has led to many creative and novel macromolecular assemblies. Miller and Neenan[45] used the convergent method to prepare aromatic-based, all-hydrocarbone dendrimers. High rigidity was inherent in this series.

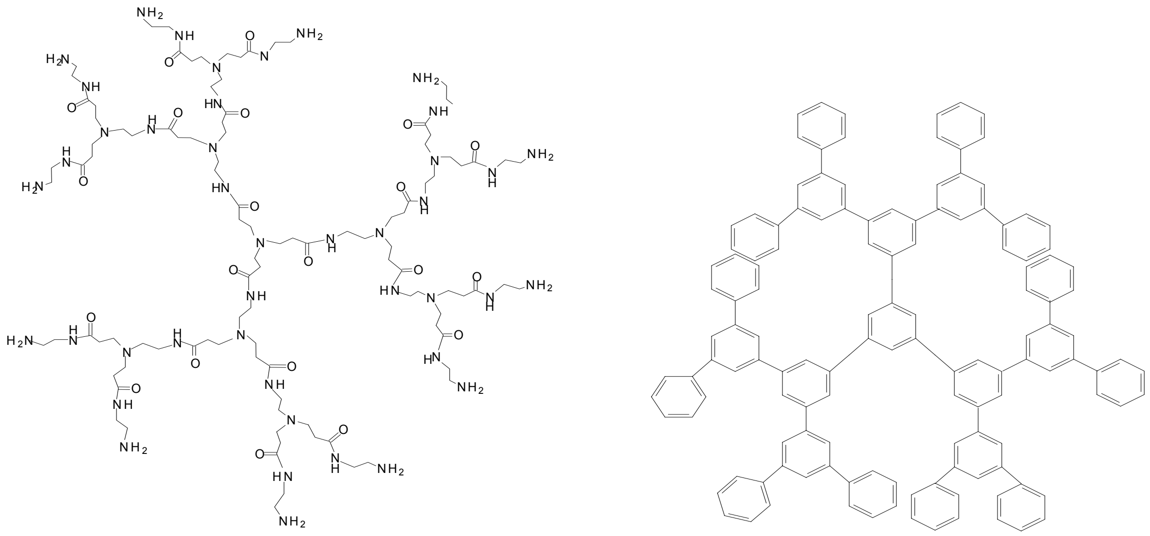


Figure 2.10: Illustration of different dendritic architectures

2.2.1 Methods of synthesis: Divergent procedures

Divergent dendritic construction results from sequential monomer addition beginning from a core and proceeding outward toward the macromolecular surface. To a respective core representing the zeroth generation and possessing one or more reactive site(s), a generation or monomeric building blocks is covalently connected. Branching is dependent on the building block valency. Thus, a core possessing one reactive moiety, such as a primary amine, is divalent and will accommodate two monomers. Newkome et al.[4] and Tomalia et al.[44] published different divergent routes to branching arborols and dendrimers. These authors described the construction of polyfunctional molecules that possessed multiple branching centers and offered spectral characterization supporting the structural assignments. Wörner und Mülhaupt[45] improved Vögtle[46] procedure and used Raney nickel[47] at ambient temperature to prepare a dendrimer extended to the fifth generation. ^{15}N NMR spectra of these dendrimers confirm their highly branched and well-defined structures[48]. Tomalia et al.[6] described the preparation of polyamidoamine “starburst polymers”, or “dendrimers”, which were generated from a three-directional core. For the first time, an iterative synthesis as well as structural, computer simulated was reported[49]. Comparative and electron microscopy[50] , and physical characterization[51,52] of these macromolecules were carried out. Standard spectroscopic methods, e. g. ^{1}H and ^{13}C NMR[53,54], IR as well as mass spectrometry (electrospray)[55], HPLC, GPC, DSC, TGA and intrinsic viscosity[56] for these dendrimers have been evaluated. Haddleton et al[57] reported the determination of molecular masses of two series of dendritic aryl esters by matrix- assisted laser desorption ionization (MALDI-TOF) mass spectrometry. Three tiers were constructed and characterized by MALDI mass spectral studies which showed no evidence for dimer or trimer formation either during the synthesis or within the mass spectrometer.

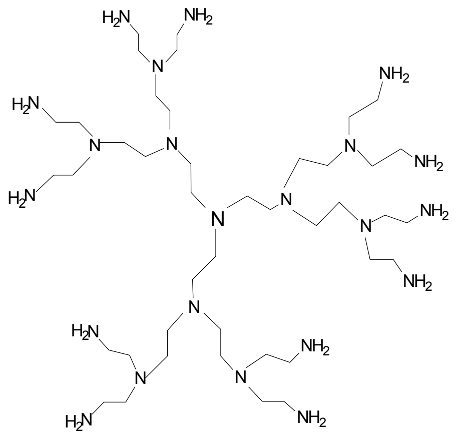


Figure 2.11: “Starburst” poly(ethyleneimine) dendrimer prepared by divergent method.

2.2.2 Methods of synthesis: Convergent procedures

The “convergent” mode of dendritic construction is another strategy whereby branched arms (dendrons) are synthesized from the “outside-in”. This concept was initially described by Fréchet and his coworkers[11,58], at about the same time Miller and Neenan reported[59] the synthesis of monodisperse molecular spheres based on 1,3,5-trisubstituted benzene. The synthesis starts at the periphery of the final dendron and proceeds inwards. Polymer segments (“wedges” or “monodendrons”), synthesized stepwise via a protection-deprotection mechanism, are connected to a multifunctional core in the final step. There are no limitations in size for the core molecules[60] and complexing agents[61] or metal atoms[62] can be used for the final connection of special monodendrons. Furthermore only three functionalities have to react in each step and the number of reaction sites does not increase with the number of generations (Figure 2.12). Therefore, more monodisperse products can be obtained, purification and characterization is facilitated.

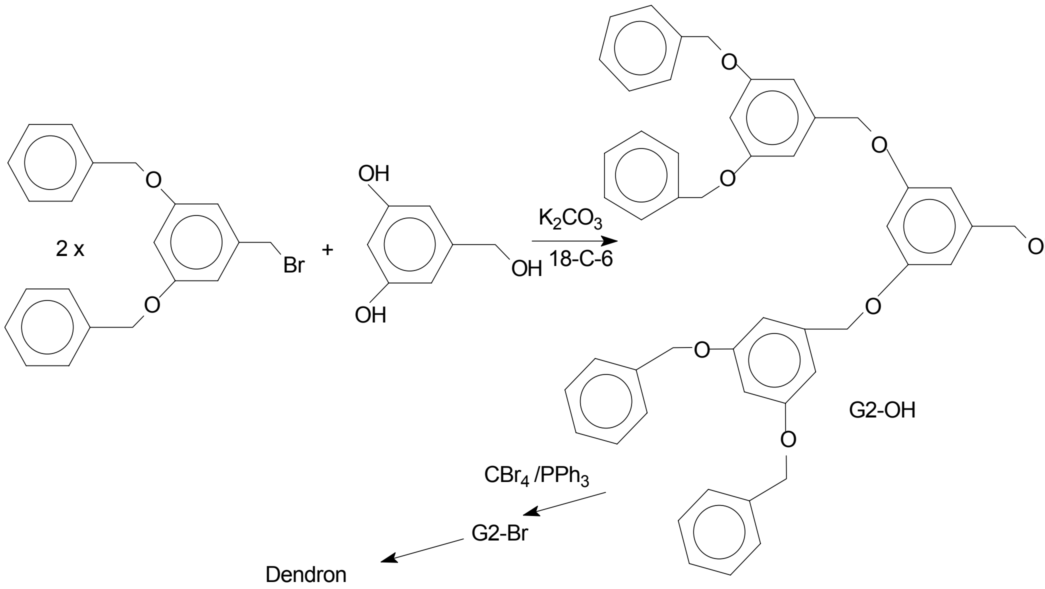


Figure 2.12: Synthesis of polyether monodendrons[10].

2.2.3 Methods of synthesis: One- step hyperbranched polymers.

Hyperbranched polymers are synthesized by means of a direct, one-step polycondensation of AB_x monomers, where $X \geqslant 2$. Such one-step polycondensation afford products possessing a high degree of branching, but are not as idealized as the stepwise constructed dendrimers. Due to the special arrangement of the functional groups on one molecule and the excess of A functionalities no gel point can be reached in this system. The characteristic features for a hyperbranched polymer derived from AB_x monomers are one unreacted A functionality, a high number of unreacted B functionalities, distributed randomly throughout the polymer, and a degree of branching usually between 50% and 75% (Figure 2.13). Each macromolecule will have a high density of B functional groups, which due to the statistical growth, can also be inside and not only on the outside surface. The number of these groups can be directly connected with the degree of polymerization (DP). If the reaction is performed with an AB_2 monomer, each molecule will have exactly one functional group more than the number of repetition units (DP + 1)[63].

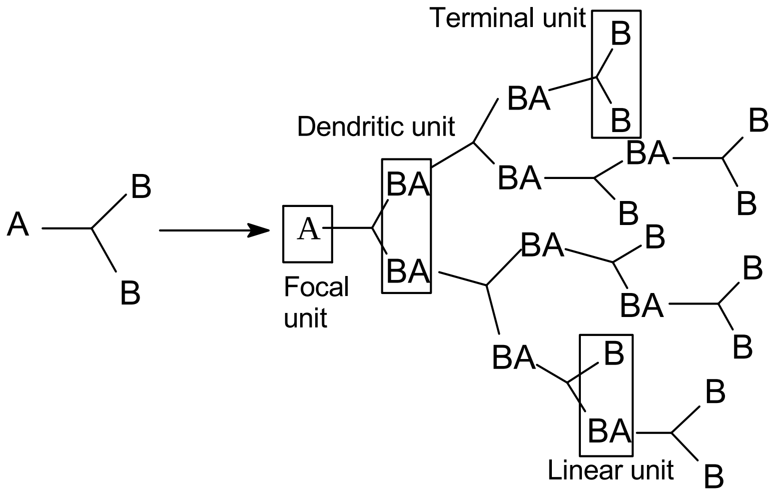


Figure 2.13: Hyperbranched polymer formed from an AB_2 monomer.

Hyperbranched polymers exhibit typical polymer features, as a broad molar mass distribution, isomerism, and an irregular growth with a statistical distribution of functional groups throughout the structure. They are even considered as having close resemblance with networks just before the gel point[64-66]. On the other hand, they show a higher solubility and a linear solution viscosity compared to linear analogues[67,68]. A strategy to overcome the disadvantage of polydispersity and broad molar masses is to add a B_y-functional core molecule, where $y \geq 3$. This limits the polydispersity and also provides a tool to control the molecular weight of the final polymer. One of the most important aspects of hyperbranched polymer characterization is the determination of its structure, namely the evaluation of the concentration of terminal (t), linear (l), and dendritic (d) units. The above values allow to calculate the degree of branching (DB). The degree of branching is generally calculated[69,70] according to the following equation;

$$DB = (d+t) / (d+t+l)$$

Equation 2.1: Calculation of DB according to Fréchet [69].

From the definition, DB 100% for perfect dendrimers, 50% for statistically grown hyperbranched polymers and 0% for linear chains. DB depends on the different parameters that can influence the path of the reaction[64-75].

The main distinguishing features of hyperbranched polymers are the ease of polymerization process when compared to the synthesis of “ideal” dendrimers, a large number of functional groups distributed throughout the polymer structure which impart specific physical and chemical properties, lower intrinsic viscosity than their linear analogues and vastly enhanced solution characteristics due to a low degree of crystallinity and entanglements[76]. Although hyperbranched polymers are characterized by an irregular structure with high polydispersity, the ease of the synthetic procedures and the globular shape together with the high number of functional groups make those polymers effective candidates for industrial applications. Hyperbranched aliphatic polyesters are commercially produced[77,78] and at the moment five different product grades are available[79] depending on the average number of –OH groups and on the water content of the samples. Those polymers are successfully employed as additives for polymer matrix composites[80] as UV-curable coatings[81], and as macroinitiators[82]. Many other applications for hyperbranched polymers are also reported, for example due to their good miscibility and melt viscosity they find application as melt modifiers[23,83], additives and as blend components[84,85] in processing procedures. Hyperbranched polymers, specially poly(ether)s[86] and poly(ester)s[87,88] have amphiphilic properties and therefore can be employed as carriers for small molecules. Modification of functional groups give the chance for hyperbranched polymers to be used as cross-linkers[89,90] in high solid or powder coatings and in thermosets[91]. Hyperbranched poly(ester)s were modified using long chain alkyl chains to increase the compatibility with polyolefins and enable the even distribution of dyes in poly(propylene)[92]. Hyperbranched polymers containing labile groups are used as pore forming systems to obtain nanoporous substances for the preparation of low dielectric constant materials for ILDs (Interlayer Dielectrics)[93,94]. Other applications for hyperbranched polymers were also reported for example in molecular imprinting[95], catalysis[96], dental composites[97], as macroinitiators[98], in sensors[99,100] and in the encapsulation and to extract guest molecules[101-103].

The use of AB_2 monomers predominates the synthetic approaches leading to a hyperbranched polymer. Polyester structures were favored by many researchers[104-113] due to the availability of monomers. Many other hyperbranched polymers were synthesized[114-120]. For successful statistical polymerization process, equal reactivity of two B functionalities is required and no internal cyclization reactions limiting the growth of the hyperbranched polymer. Other non-desired side reactions during the polycondensation reaction may lead to intermolecular reactions and finally crosslinking[121]. DB of about 60% was achieved[122] by plain AB_2 polycondensation by slight activation of the formed intermediate through estrification, whereas using “criss-cross’” cycloaddition gave rise to a hyperbranched polymer consisting exclusively of branched and terminal repeating units and therefore which has a DB of 100%[123].

The synthesis of hyperbranched polymers through the reaction of A_2 monomers with B_3 monomers is also reported[124-128]. The resulting products are soluble hyperbranched polymers when the reaction is stopped before reaching the gel point. However the critical conversion in these condensations depends on the ratio of A and B functionalities (optimum seems to be

2:3) purity of the solvent, reaction time, and temperature[129]. The products of A_2+B_3 are distinguished by the presence of several A functions in a single hyperbranched macromolecule that might cause the crosslinking. Hyperbranched polymers prepared from direct polymerization of A_2 and B^*B_2 type monomers are reported[130-134]. A dominant AB^*_2 intermediate is generated from the reaction between an A group of A_2 an a B group of B^*B_2 during the initial period of the reaction. The use of commercially available, of different reactivity, AA* and B^*B_2 monomers has been developed. The idea is to use the selectivity of higher reactivity of one A functions and one B function to produce $A(A^*+B^*)B_2$ intermediate. This new strategy is characterized by the formation of the intermediate in-situ i.e. there is no border line between the generation of $A(A^*+B^*)B_2$ and its polymerization. Also the propagation reaction generally occurs as soon as the formation of an $A(A^*+B^*)B_2$ molecule so, it hardly can be separated.

Surface modification reactions have been carried out with dendritic and hyperbranched polymers due to presence of great number of functional groups. In dendrimers the end groups are all located in the periphery and also can be found in the dendrimer interior[135,136].The modification reactions for hyperbranched polymers are very similar. The uncontrolled structures show no crystalline packing and cavities in the structure allow the penetration of solvent. Therefore the accessibility of the functional groups is quite good for small reagent. However, conversion decreases for polymers of high molecular weight and for large reagent molecules. Solubility and thermal behavior change dramatically by introducing new functional groups for example the T_g of hyperbranched polyesters with identical internal structure but different end groups can vary more than 250°C[137]. The functional groups also influence polarity and in some cases the dimension and the shape of the dendritic polymer in solution[138].

2.3 Hyperbranched polyurethanes

Dendritic and hyperbranched structures based on amide linkages[139-145] have received considerable attention due to the fact that polyamides are commercially important. Dendritic polyurethanes are much less studied and most of the reported synthesis of either aliphatic or aromatic [115,146-148] hyperbranched polyurethane was done via polycondensation reaction of AB_2 or A_2B monomers (Figure 2.14). However, due to the high reactivity of isocyanate group, yielding either dimers, via self condensation or a carbamate via the reaction with water, the monomers have to be produced in-situ. A degree of branching was determined as being close to 60% using NMR spectroscopy[115] for a hyperbranched polyurethane prepared through in-situ generation of a dihydroxphenyl isocyanate monomer, by the thermal decomposition of the corresponding carbonyl azide. The formed hyperbranched polyurethane showed complete solubility in common organic solvents like tetrahydrofurane (THF), acetone, and dimethylsulfoxide (DMSO). Surprisingly there are only few reports[149,150] on the synthesis of hyperbranched or dendritic polymers based on urea linkages. This could be because of the inherent difficulties in the synthesis and purification of monomers containing both amine and isocyanate groups, necessary to obtain urea.

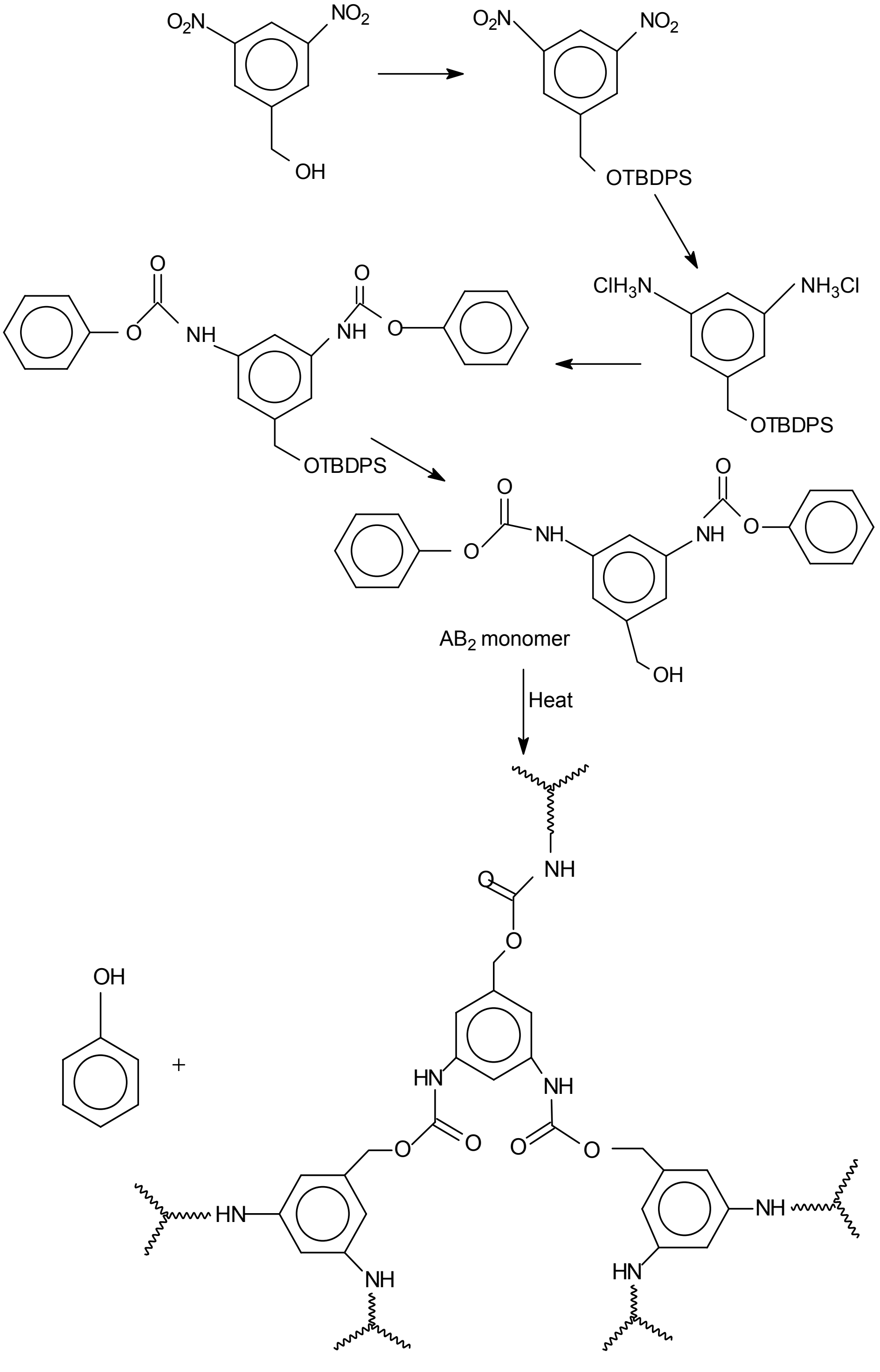


Figure 2.14: Hyperbranched polyurethane based on AB_2[148].

Lately[151-154] a novel route for the preparation of hyperbranched poly (urea-urethane) is reported, using AA* and B_2B^* monomers depending on the selectivity of the highly reactive functional groups. This strategy is working due to selective reactions between specific functional groups giving rise to a defined construction of hyperbranched polymers. The polymerization reactions take place without any specific protection of specific functional groups. The produced hyperbranched structures contain urea and urethane groups in the polymer chain. This method opens flexibility in synthesis and variability in structure/property relationships and allows to choose aliphatic as well as aromatic monomers, this reaction will be further studied in the present work.

2.4 Applications

Novel Hyperbranched polyurethanes and polyureas[151] 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. These materials may 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. They can also offer new ways of preparing specialty membranes, protective coatings, novel composites and controlled porosity materials. Other applications can be found in biomedical areas and medical engineering. The use of hyperbranched polymers as the base for various coating resins has been described in the literature[155-157]. Different resin types are obtained depending on the reactive end-group structure which is attached to the hyperbranched polymer. Several thermoset resin materials have been described where the hyperbranched polymer exhibit a low resin viscosity, thereby reducing the need for solvents to reach the application viscosity. At the same time, rapid curing (high reactivity) and good film properties (high molecular weight of the resin) are obtained. Resins based on hyperbranched polyurethane acrylates containing phosphorus were found to be flame-retardant or can be used as additives to conventional UV curable coating systems[158]. Hyperbranched polyisocyanates were prepared[153] and used as crosslinkers for the formulation of coatings where they showed better hardness than any other aliphatic isocyanate raw material.

3- AIM

The combination of the concept of dendritic macromolecules with urethane chemistry might offer a new, very versatile approach for the synthesis of new polyurethane materials. Hyperbranched polymers are phenomenologically different from linear polymers of the same molecular weight since they can be simply prepared in one step synthesis, also they are unique in their properties and easily tailored by changing the nature of the end groups. In general, hyperbranched polymers are synthesized by self-condensation of AB_n type monomers which have one "A" functional group and *n* "B" functional ones. However, most of the AB_n molecules are not commercially available and the preparation of such designed monomer takes a longer time in comparison with the following polymerization. On the other hand, many difunctional monomers (A_2) are commercially available as monomers for linear condensation polymers. Furthermore, some trifunctional monomers (B_3) used for branching or cross-linking agents are also available. If the first polymerization of A_2 and B_3 molecules is faster than the following propagation, an AB_2 type molecule would be formed as an intermediate molecule and accumulated in solution. In the last two decades several hyperbranched polymers were prepared through intermediate AB_2 molecules formed from A_2 and B_3 monomers.

Hyperbranched polyurethanes (HPUs) should be synthesized from commercially available materials, using the same idea as for linear polyurethanes, through the polycondensation of monomers containing diisocanate groups with trifunctional monomers which contain active hydrogens. They can be considered as new raw materials for polyurethane coating systems with improved product properties. The use of A_2+B_3 in the preparation of HPUs approach yields hyperbranched polymers with several A functions in one macromolecule which might cause crosslinking. Due to this reason a new strategy was developed for the synthesis of hyperbranched polyurethanes using commercially available AA* and B*B_2 monomers. Making use of the different reactivity of the functional groups and the selectivity of the monomers, one can obtain AB_2 monomer in-situ as represented in Figure 3.1.

Thus, synthesizing hyperbranched polyurethanes in one step using commercially available monomers and exploring their properties is the main aim of this work. Using the advantage of intramolecular reactivity differences of isocyanate groups in the diisocyanates and the reactivity differences of OH and NH groups in the dihydroxylamine, it is possible to generate AB_2 intermediate which polymerizes forming hyperbranched polymer. 2,4-Toluylene diisocyanat (TDI) as aromatic diisocyanate, and isophorone diisocyanate (IPDI) and 2(3-isocyanatopropyl) cyclohexylisocyanate (IPCI) as aliphatic diisocyanates, were proposed as diisocyanate monomers which react with diethanolamine (DEA) or diisopropanolamine

(DIPA) in order to prepare HPUs. Actually, the reaction of diisocyanate can be with either amino or hydroxyl groups present in the dihydroxyl amine. So, the obtained polymers are named hyperbranched poly(urea-urethane)s.

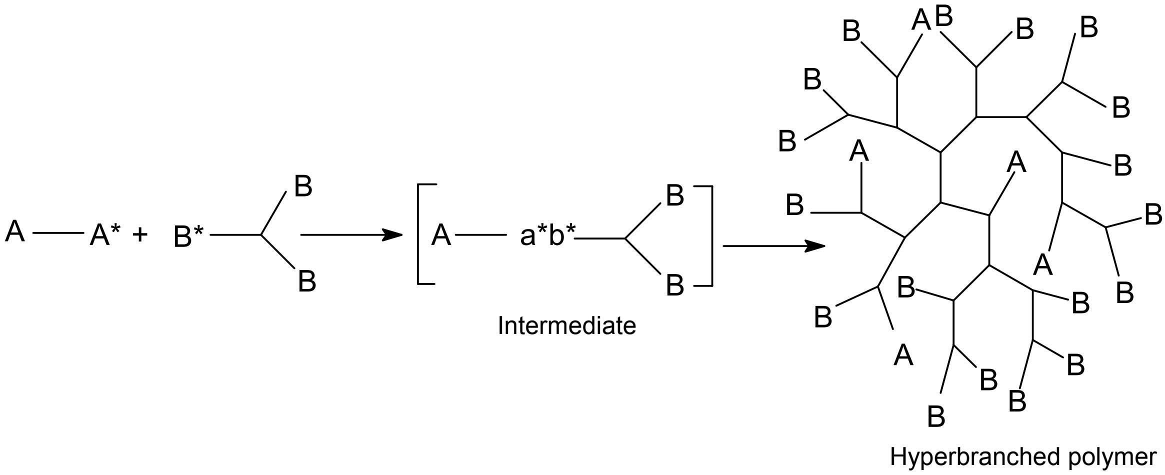


Figure 3.1: Schematic representation for hyperbranched polymer formation from AA* and B^*B_2 monomers.

The aim of this work is achieved through the following investigations:

- Synthesis of different model compounds and model structures that would help firstly, in the elucidation of the structure of the hyperbranched polymers. And secondly, proving that the reaction of AA* monomer with B^*B_2 monomer goes through the formation of in-situ AB_2 intermediate.
- Synthesis of aromatic and aliphatic hyperbranched poly(urea-urethane)s and optimizing the polymerization reaction conditions.
- Complete structural analysis for the prepared polymers using NMR with the help of model compounds and model reactions
- Synthesis of aromatic and aliphatic linear PU for comparison.
- Modification of the end groups in the polymers using different modifiers and study of the properties of the modified polymers.
- Preparation of thin films from the HPUs and investigation of their surface properties.
- Using of hyperbranched polymers as dendritic polyols in network preparation and study of the mechanical properties of these materials.

4- RESULTS AND DISCUSSION

The main aim of this work is the synthesis and characterization of hyperbranched poly(urea-urethane)s through AA*+ B*B_2 polycondensation reaction. The “in-situ” formation of an AB_2 intermediate is postulated before the hyperbranched macromolecules was found (Figure 4.1).

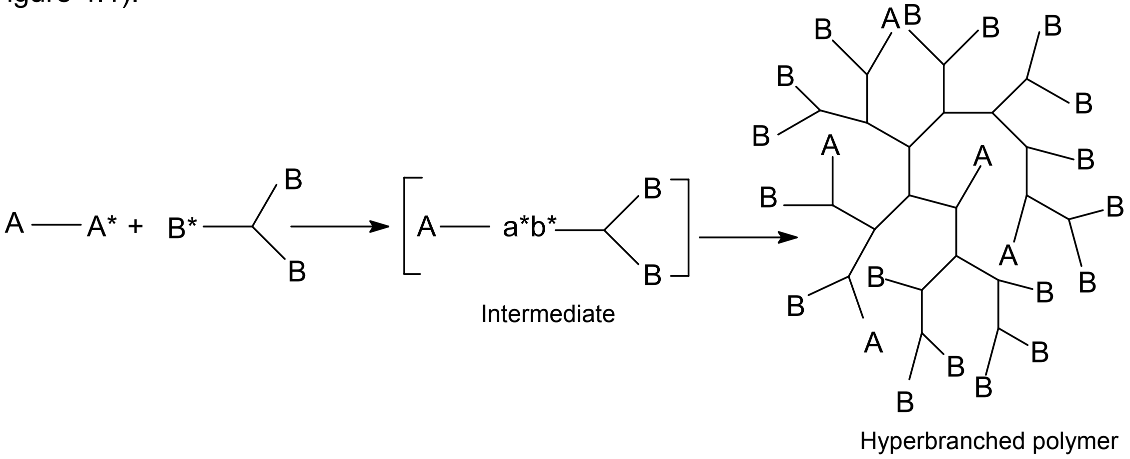
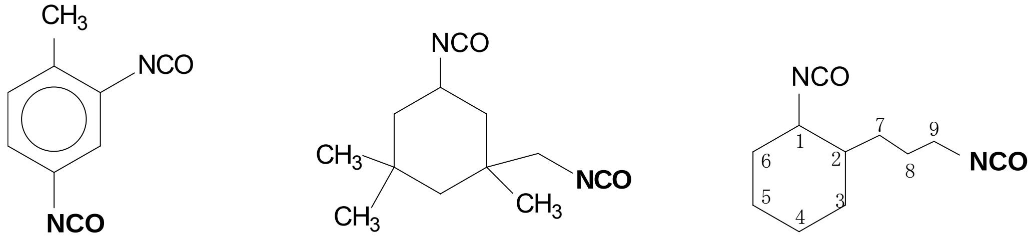


Figure 4.1: Hyperbranched polymer formation from AA* and B*B_2 monomers.

In this work, commercially available 2,4-toluene diisocyanate (TDI), isophorone diisocyanate (IPDI) and 2(3-isocyanatopropyl)cyclohexyl isocyanate (IPCI) were chosen as AA* monomers and diethanol amine (DEA) and diisopropanol amine (DIPA) as B*B_2 monomers. The structures of the used monomers are given in Figure 4.2.



25% trans 41% trans

75% cis 59% cis

TDI IPDI IPCI

AA*

DEA DIPA

B*B_2

Figure 4.2: Chemical structures of the used monomers.

It is known that the reactivity of NH and OH groups toward isocyanate addition differ drastically[159] however, usually not supported with numbers. Only recently, ratios of reactivity constants for urea and urethane formation have been calculated theoretically to about 150 in case of IPDI and about 15000 in case of TDI in favor of the NH / NCO reaction.[154] Thus, ideally, the isocyanate group reacts preferentially with the amino group of the dihydroxy amine at low temperatures. For what concerns TDI as monomer, it was reported[160,161]that the reactivity of the NCO group in p-position is about 70 times higher than the reactivity of NCO group in o-position when reacted with alcohol functions. For IPDI and IPCI, there are two types of NCO groups in the molecule, a primary one, CH_2-NCO, and a secondary one, CH-NCO. Thus, the chosen monomers seemed to be suitable for the concept of in-situ AB_2 intermediate formation when the more reactive NCO group in the diisocyanates reacts primarily at low temperature with the amino group of the B^*B_2 monomer. Moreover, it was approved by NMR spectroscopy that both monomers consist of a mixture of two isomers according to whether the -NCO and CH_2-NCO are cis or trans to each other on the cyclohexane ring. For IPDI it was shown that the isomer ratio has a value of 75% for the cis isomer and 25% for the trans isomer[162]. NMR investigation were carried out to determine this ratio for IPCI and it was found to be 59/41 cis/ trans. In both isomers the 2-substituent is in the equatorial position as indicated by the J_{HH} coupling constants of H_1 and by the chemical shifts of H_1 and H_2 for both isomers. The presence of isomers makes full structure assignment of the obtained polymer more difficult.

4.1 Synthesis of linear poly (urea-urethane)s

It was important to prepare linear polymers to recognize the general features of polyurethane and also to use them in order to compare their properties with the hyperbranched poly(urea-urethane)s under investigation. Linear aliphatic and aromatic poly(urea-urethane)s were prepared through the reaction of AA* monomer with 2-ethanolamine (2-EA) under the polymerization conditions which will be used to prepare hyperbranched poly (urea-urethane).

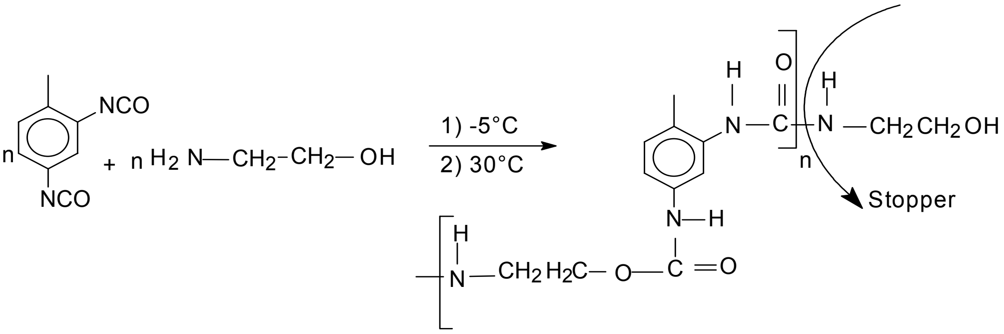


Figure 4.3: Reaction of TDI as AA* monomer with 2-EA to prepare linear poly(urea-urethane).

The reaction starts at low temperature (-5°C) through, most likely, the NCO group in the p- position that reacts either with the amino group (preferentially) to form urea or with the hydroxyl group of the amino alcohol to form urethane. 2-EA was added drop by drop in order to firstly, control the molar mass of the formed polymer and secondly, since the reaction of the NCO with NH_2 group is fast and exothermic, it was important to use the slow addition method to favor urea formation at low temperature. The reaction temperature was increased in the second step. The reaction of isocyanate with amino or hydroxyl groups depends on the electron density around the carbon atom of the NCO- so that in case of aromatic AA* monomers the reaction proceeds fast due to the high reactivity of NCO attached to the aromatic ring which is not the case with aliphatic AA* monomer. Increasing the temperature in the second step needs to be accompanied by the addition of catalyst in case of aliphatic monomers. The conversion is followed by determination of the isocyanate concentration present in the reaction medium that is equivalent to the monomer conversion and this to the obtained molar mass. The method used can be summarized as follows: samples of definite weights were withdrawn from the reaction mixture at certain time intervals, 20 ml of 0.1M dibutylamine/ chlorobenzene was added to quench the unreacted isocyanate. The excess amine is determined by back-titration with 0.1M HCl. The end point was determined potentiometrically. At the required NCO% which is equivalent to a definite degree of polymerization, the reaction was stopped. The amount of stopper added, which is the same ethanol amine, is calculated according to the remaining NCO. Thus all remaining NCO groups are capped and converted into OH end groups.

Table 1 gives the reaction conditions and polymer characteristics for both aromatic linear polymers (Ar-LPU) and aliphatic linear polymers (Al-LPU). Sample Ar-LPU (1) was prepared through the reaction of TDI and N-methyl diethanol amine in order to study the effect of the hydrogen atom present at the urea group on the inter/ intra-molecular interactions. Although DABCO was used as catalyst during the preparation of the aliphatic polymers, higher temperatures and longer reaction time were required in order to get significant increase in the molar mass.

Table 1: Reaction conditions of some prepared aromatic and aliphatic linear polymers.

Polymer	Catalyst	Time/min.	Temp./°C	NCO%	M_n (g/mol)	M_w (g/mol)	T_g /°C
Ar-LPU(1)*	---------	140	40	0.54	3500	6900	90
Ar-LPU(2)	---------	110	30	0.40	9000	16400	152
Ar-LPU(3)	---------	45	30	0.89	3600	6300	132
Ar-LPU(4)	---------	65	30	0.55	4400	8500	139
Ar-LPU(5)	---------	90	30	0.52	5500	10000	145
Al-LPU (6)	DABCO	130	40	0.61	2700	5000	141
Al-LPU (7)	DABCO	125	60	0.30	3500	6700	157
Al-LPU (8)	DABCO	220	65	0.18	5600	10200	170
Al-LPU (9)	DABCO	200	60	0.17	4500	7700	165

* TDI + N-methyl diethanol amine, Ar-LPU=TDI+2-EA, Al-LPU= IPDI+2-EA.

The most important characterization for polymers is the determination of their molecular weight and their polydispersity. There are several methods for the determination of polymers molar mass among them is the *size exclusion chromatography* (SEC). SEC is the most common method for determination of molecular weights and polydispersity of polymers[163.] The polymer sample eluted through a column separated in fractions. Those fractions are separated according to their hydrodynamic volumes in the used solvent and finally detected by *refractive index* detector (RI). In the conventional SEC, the column should be calibrated before measurement mostly using linear standards. Normally linear polystyrene is the common standard, in our case poly(2-vinyl pyridine) is used as linear standard. Molar masses of linear aromatic and aliphatic polymers were measured using SEC/ RI detector and a mixture of DMAc and LiCl/H_2O as eluting solvent. The values obtained for molecular weight showed that they became higher with increasing reaction time in case of aromatic linear polymers at constant temperature.

Glass transition temperature (T_g) which is an important property for a polymer was determined by *Differential Scanning Calorimetry* (DSC). A heating program is used for the measurements (-60 to 200°C) with heating rate 20 K/min under N_2 atmosphere. Values of T_g obtained for the aliphatic linear polymers, as shown in the table above, are generally higher than those obtained for aromatic polymers. This is due to the rigidity and bulkiness of the cyclohexyl ring. Also it was noticed, as expected, that T_g increases with increasing molar masses. When N-methyl ethanol amine instead of 2-EA is used, the T_g is reduced significantly since the hydrogen bonding in the polymer is reduced.

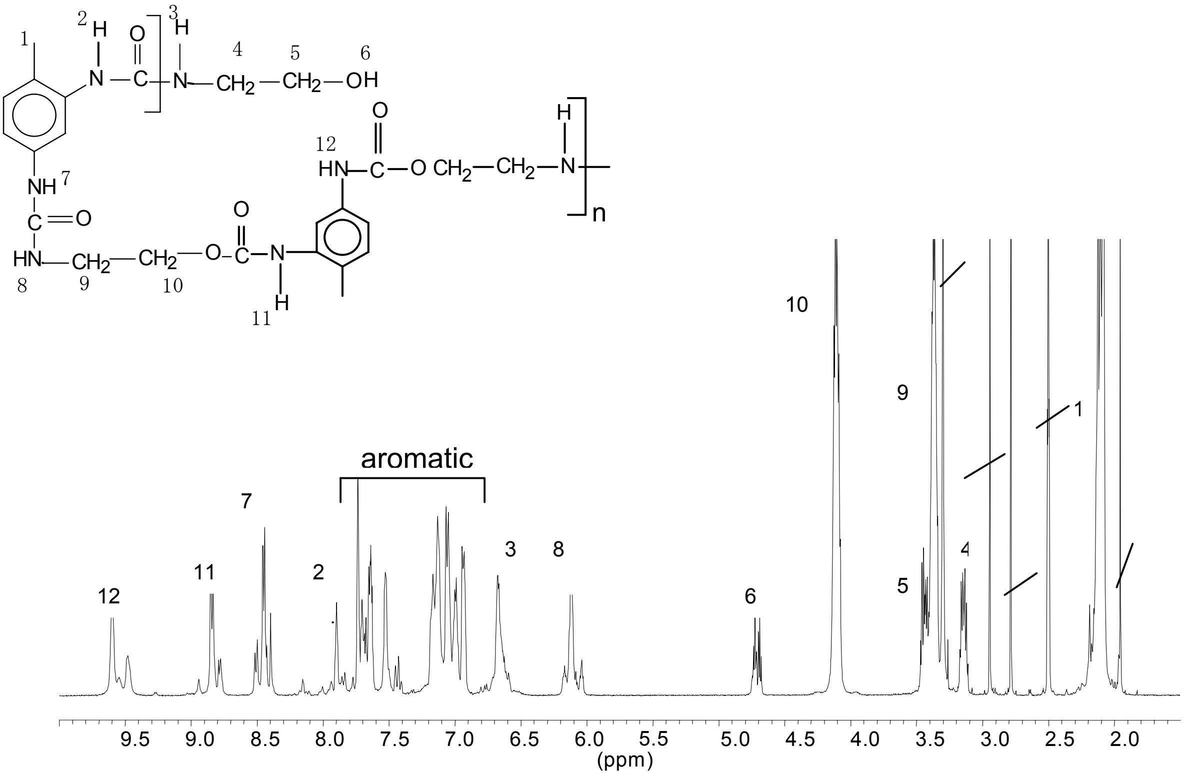


Figure 4.4: ^{1}H NMR spectrum for sample Ar-LPU(2) (DMSO-d_6).

The prepared linear polymers were characterized by ^{1}H NMR, the spectrum of sample Ar-LPU(2) is shown in Figure 4.4. The spectrum shows clearly the signals of protons present at different positions. It can be noticed the signals of o- and p-urea groups at 7.9 and 8.5 ppm, respectively. The protons of o- and p-urethane groups can be found at 8.85 and 9.5 ppm. Good separation is observed between not only the signals of the urea and urethane groups but also between the o- and p-groups as well. The protons of the groups formed as a result of the reaction of OH-group with NCO-group, $C\underline{H}_2OCO$ are seen clearly at 4.11 ppm while protons of the end group $C\underline{H}_2OH$ are found at 3.45 ppm. Signal of protons of methyl group at the phenyl ring can be found at 2.1 ppm. While protons of the phenyl ring itself have overlapped signals in the range of 7.0 to 7.7 ppm.

Although the linear polymers prepared are structurally not identical to our hyperbranched ones, they can give us good information about solubility and viscosity/ molecular weight relationship in comparison with the hyperbranched polymers under investigation since they have the same ratio of urea and urethane linkages as well as the same isocyanate structure. The main difference to the hyperbranched polymers is the number of end groups. Whereas the linear polymers should have 2 OH end groups independent on the molar mass, the hyperbranched polymers have DP+ 1 end groups.

4.2 Synthesis of aromatic hyperbranched poly(urea-urethane)s

The synthesis of aromatic hyperbranched polymer starts through the reaction of one of the isocyanate groups of AA* monomer with amine or hydroxyl groups at B^*B_2 monomer. Since there is a difference in the reactivity of amine and hydroxyl groups toward isocyanate at low temperatures (see p.25), the reaction was started at low temperatures (-5°C) to be sure that the attempted AB_2 intermediate is formed. The temperature was raised after the complete addition of the B^*B_2 monomer and the conversion was followed by titration of the rest NCO until the aimed molar mass is reached, then the reaction was stopped through the addition of calculated amount of stopper (usually the same bishydroxyl amine). The reaction of TDI was fast and did not require the use of catalysts, although it was slower in case of its reaction with DIPA mostly because of the resonance effect of the CH_3 group in DIPA and steric hindrance. The need for model studies arose to reveal that the assumed intermediate is formed and to study the reactivity difference of the two isocyanate groups present in the chosen aromatic AA* monomer. Also it was necessary to make model reactions which enables us to make complete structural analysis for the prepared hyperbranched polymers.

4.3 Synthesis of model compounds and model reactions

Model compounds were prepared through the reaction of tolyl monoisocyanate isomers with B^*B_2 monomers in order to be able to interpret NMR spectra of the hyperbranched polymers. The ratio of the reactants was kept as 2:1 tolyl monoisocyanate: bishydroxy amine. The completion of the reaction was followed by IR spectroscopy (peak of NCO- at 2270 cm^{-1}) and the excess solvent was removed by vacuum distillation. The formed product mixture was investigated by NMR spectroscopy without further purification. The reaction of o- tolyl monoisocyanate with DEA and the formed in-situ terminal t, linear l, and dendritic d model structures is shown in Figure 4.5.

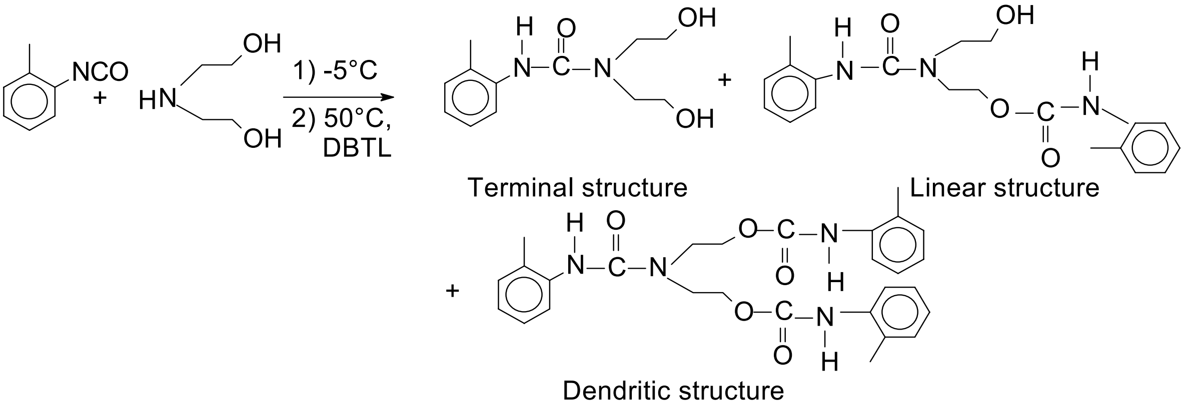


Figure 4.5: Reaction of o- tolyl monoisocyanate with DEA to prepare model compounds.

Considering the structures shown in the above figure through the model compounds, we know that the macromolecule contains three different types of subunits as shown in Figure 4.6. Since the degree of branching DB according to Fréchet[69] is defined as shown in equation (2.1).

$$DB = (d+t) / (d+t+l)$$

so, both the dendritic and terminal units d, t contribute to the perfect hyperbranched structure of the molecule while the linear units l reduce the degree of branching.

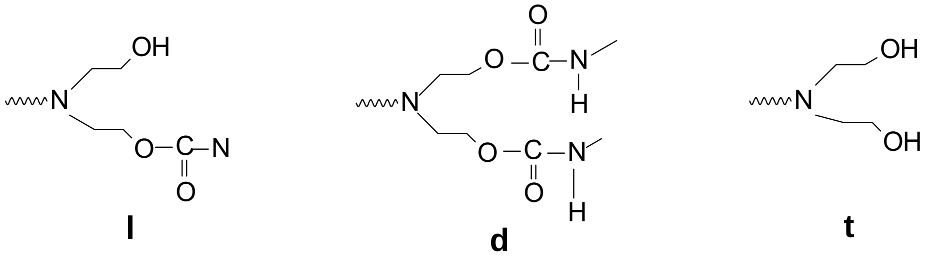


Figure 4.6: Three possible substructures which can be found in a hyperbranched poly (urea-urethane).

The resulting model compounds, as reaction mixture were analyzed by ^{1}H, ^{13}C NMR spectroscopy and the signal assignment is shown in Figure 4.7.

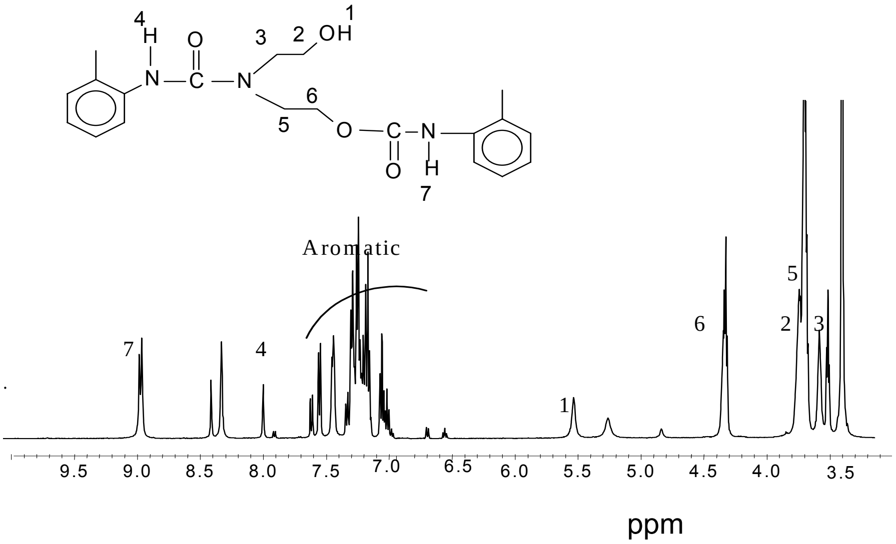


Figure 4.7: ^{1}H NMR spectrum of mixture of all three of the reaction products of o- tolyl monoisocyanate with DEA, only linear structure is assigned (DMSO-d_6).

4.4 Model reaction for substitution pattern

A model reaction was carried out in order to study the reactivity of o- and p-NCO groups towards both amino and OH groups. TDI was reacted with N,N-diethyl amine mixed with ethanol (1:1:2) (Figure 4.8). The presence of NCO groups was followed by IR. After completion of the reaction, the excess solvent was removed under high vacuum and the product was analyzed by NMR without further purification. Depending on the exact stoichiometry and the reaction conditions, it was found that only about 17 to 28% of the desired compound which is Ureth 2/Urea 4 were formed beside the other three isomers. From different experiments it was found that the percentage of formation of different isomers depends on the sequence of addition of N,N-diethyl amine and ethanol that means if they were added together or amine at first then the alcohol. The same reaction was made but stopped at low temperature (-5°C) by adding dibutylamine to examine the reactivity of NCO group toward OH at low temperature. It was found that the isomer Ureth2/ Ureth4 is not formed while all the other three isomers were identified. The quantities for the different isomers were found to be 51% for Urea2/ Urea4, 36% for Urea2/ Ureth 4, and 13% for the isomer Ureth2/ Urea4. This means that in this reaction the reactivity of both o-NCO and p-NCO groups are identical. It could be confirmed however, that amino group is more reactive toward isocyanate than hydroxyl group. Furthermore, in case of TDI it is also possible that the reactivity of one isocyanate group changes depending on whether the other group is isocyanate or has reacted to form urethane or urea group[159].

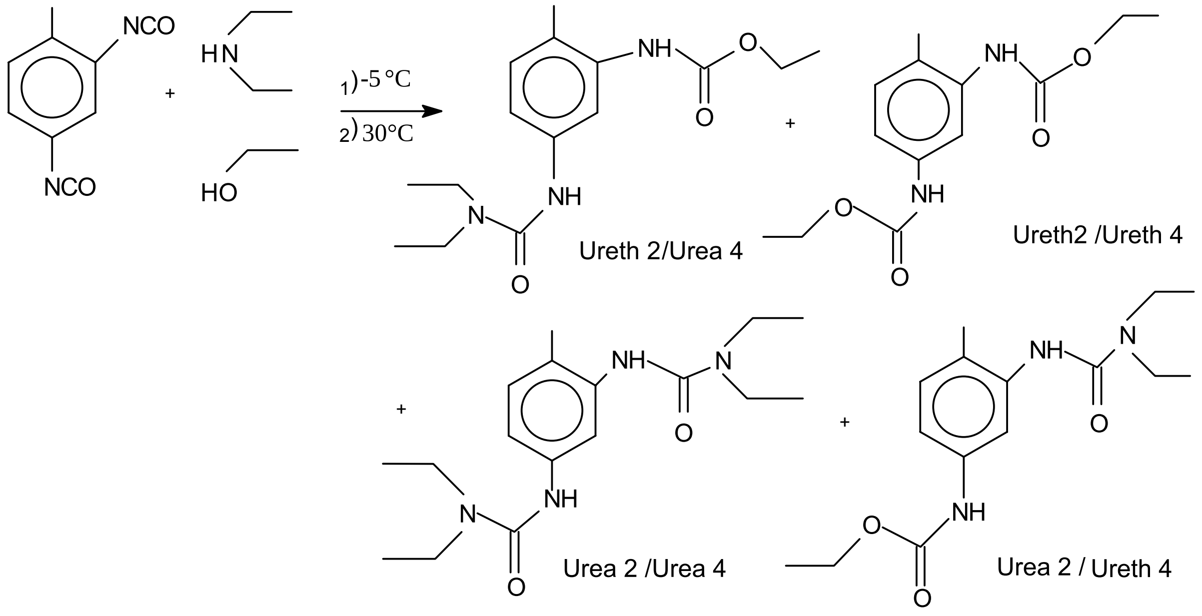


Figure 4.8: Model reaction to study the reactivity of ortho and para- isocyanates and the formed 4 isomers.

4.5 Preparation of aromatic hyperbranched polymers and variation of reaction conditions

In principle, the synthesis of a hyperbranched poly(urea-urethane) was described in the literature when this work started, however, it was necessary to optimize the reaction conditions to avoid the gel point. It was reported[164] that, while preparing similar systems, no gelation occurred when a 10 wt% concentration was used and ratio of functional groups reached 1:1. Gelation was observed on using feed ratio 3:2 of monomer AA* to monomer B^*B_2 and high temperature (60-80°C), also it was not sure whether cross-linking would occur or not, which depends on the reaction temperature and concentration. However, It is found that[154] limiting reaction time and temperature avoid side reactions and the probability of crosslinking and network formation. So, the need for optimum polymerization reaction conditions arises in order to control the formation of the hyperbranched polymer, its molar mass and avoid gelation.

Aromatic hyperbranched poly(urea-urethane)s (Ar-hpu)-OH was prepared using different reaction conditions until it was optimized in order not to reach the gel point. This system involved the formation of a large number of different structural units within one single branched molecule and thus, an easy description is not possible. A try of a schematic picture is given in Figure 4.9. Usually the reaction was started at –5°C when the monomer B^*B_2 was added slowly to AA*. After about 30 min at this low temperature the temperature was raised above room temperature and was kept there 0.5 to 7 hours until a certain NCO conversion was reached, then stopper was added to convert remaining NCO groups into OH as unreactive end groups. Due to the higher reactivity of the aromatic isocyanate groups the reactions occurred fast and did not need any catalyst. As can be seen from the reaction pathway, the formed hyperbranched polymers contain not only urea and urethane groups, but also dendritic, linear, and terminal groups, and hydroxyl groups as end groups which give the polymers a hydrophilic character. Therefore, the resulting polymers were fully soluble in polar solvents like DMSO and DMAc (Table 2 is showing reaction conditions). During the reaction, usually, a molar ratio 1:1 diisocyanate to bishydroxyamine is used, which means a ratio of functional groups A:B of 2:3. However, in this case the ratio of isocyanate to amine is 2:1 and assuming a full reaction of all amines first, then the ratio remaining isocyanate towards alcohol is 1:2. Samples (Ar-hpu)-OH-1 and (Ar-hpu)-OH-2 were prepared in the ratio of 1:1.1 (TDI:DEA) which means a somewhat higher amount of B* units which should allow to better control the molar masses of the final polymer and to overcome the problem of gel formation. As mentioned before, due to the reactivity difference between the two isocyanate groups at the phenyl ring, an AB_2 intermediate is assumed to be formed (Figure 4.9). This intermediate can not be isolated and no clear borderline can be determined between the formation of AB_2 and its polymerization. The propagation reaction generally occurs as soon as AB_2 is formed until the whole complete conversion or definite amount of stopper is added to stop the reaction at the required molar mass and before gelation.

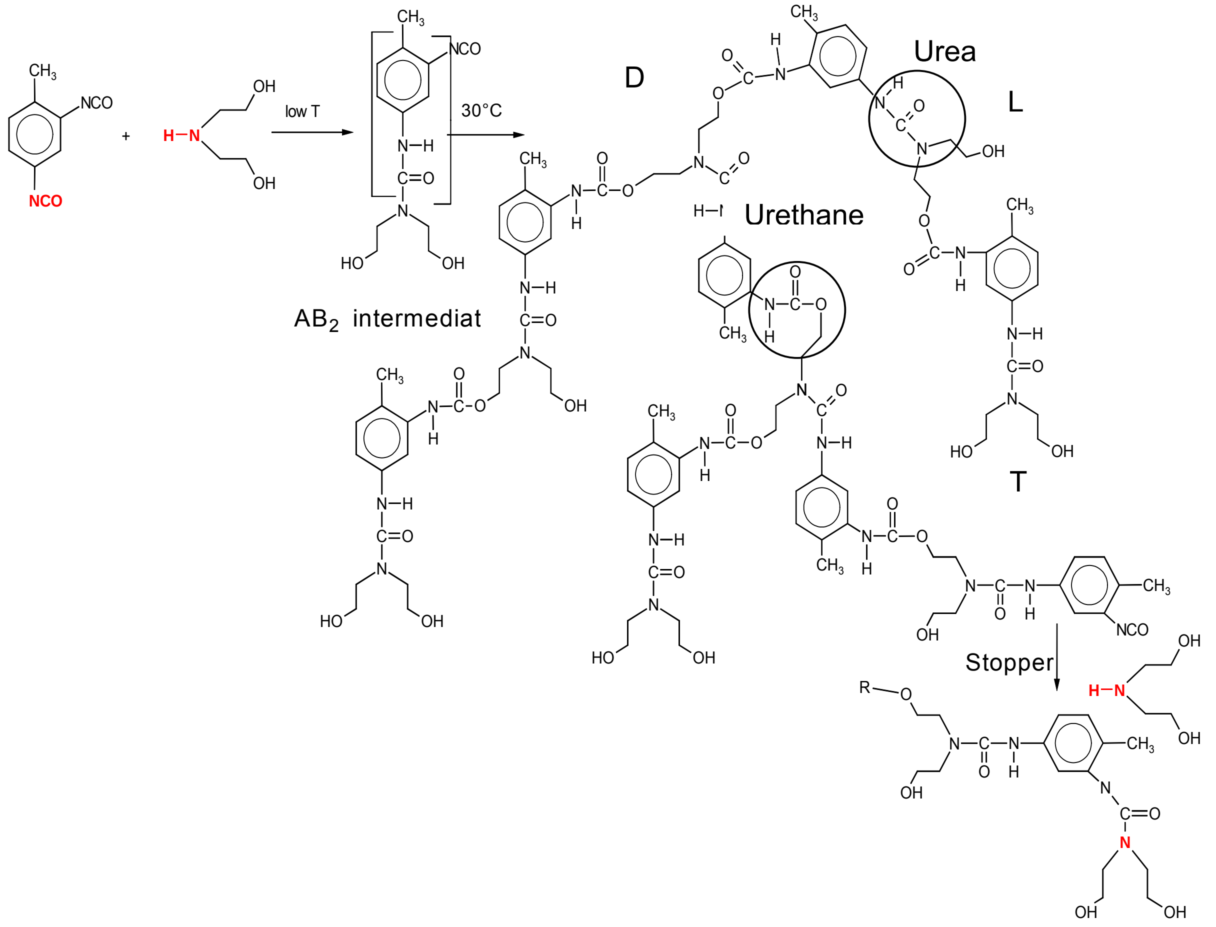


Figure 4.9: Examples of some structural units present in (Ar-hpu1)-OH4.

Table 2: Reaction conditions for the preparation of (Ar-hpu)-OH.

Polymer	Conc.(wt.%)	Temp./°C	Time/min.	NCO %[a)]
(Ar-hpu1)-OH1[b)]	30	30	40	0.13
(Ar-hpu1)-OH2[b),c)]	30	30	50	0.13
(Ar-hpu1)-OH3[c)]	30	30	30	0.47
(Ar-hpu1)-OH4	30	30	30	0.27
(Ar-hpu1)-OH5	30	20	15	0.34
(Ar-hpu1)-OH6[d)]	30	30	30	0.37
(Ar-hpu1)-OH7	20	50	40	0.14
(Ar-hpu1)-OH8	10	40	45	0.16
(Ar-hpu2)-OH1	30	10	420	0.63
(Ar-hpu2)-OH2	30	30	235	0.53
(Ar-hpu2)-OH3	30	50	90	0.42

(Ar-hpu1)-OH = TDI+ DEA, (Ar-hpu2)-OH = TDI+ DIPA

a) unreacted isocyanate content (as determined by titration) before adding the stopper

b) molar ratio AA* to B^*B_2 = 1:1.1

c) stopped by DBA

d) used for further investigations without precipitation

The yield obtained lies between 60 and 75% of the total amount of reactants. Although we used polycondensation reaction i.e. no weight loss should be observed. Due to precipitation of the prepared polymers and filtration processes, a considerable amount of the formed low molecular weight oligomers present in the filtrate which is the main reason for weight loss.

4.5.1 Determination of molar masses

There are several methods for the determination of polymers molar masses and their polydispersity. SEC is the one used to characterize our prepared hyperbranched systems. For the investigation of hyperbranched polymers several problems arises; first: the branched, globular structure of the hyperbranched polymers which have different hydrodynamic volumes in comparison with the linear polystyrene molecules used as standard of the same molar masses. So the measured molar mass of the hyperbranched polymer is only relative and one can assume a large deviation from the real molar masses. Second problem is the large number of polar groups as end groups, which may lead to aggregation of the polymer molecules or adsorption of the polymer on the material of the column. The aggregation apparently increases the molecular weight of the polymer while adsorption leads to larger elution times and this preventing lower molar masses. To avoid the problem of aggregation, modification of polar groups should be carried out although the disadvantage of this method is that the hydrodynamic volume of the polymer molecules will be changed due to the change in the chemical structure and molar mass.

Table 3: Values of molar masses of (Ar-hpu)-OH (SEC/RI).

Polymer	M_n (g/mol)	M_w (g/mol)	PDI
(Ar-hpu1)-OH1[b)]	6100	16100	2.64
(Ar-hpu1)-OH2[b),c)]	6700	19500	2.91
(Ar-hpu1)-OH3[c)]	9700	40500	4.18
(Ar-hpu1)-OH4	9100	56800	6.24
(Ar-hpu1)-OH5	3100	10600	3.36
(Ar-hpu1)-OH6[d)]	2600	6300	2.42
(Ar-hpu1)-OH7	11100	77700	7.00
(Ar-hpu1)-OH8	6100	11700	1.92
(Ar-hpu2)-OH1	1200	3500	2.91
(Ar-hpu2)-OH2	4100	8200	2.00
(Ar-hpu2)-OH3	5300	12000	2.26

(Ar-hpu1)-OH = TDI+ DEA, (Ar-hpu2)-OH = TDI+ DIPA

a) unreacted isocyanate content (as determined by titration) before adding the stopper

b) molar ratio AA* to B^*B_2 = 1:1.1

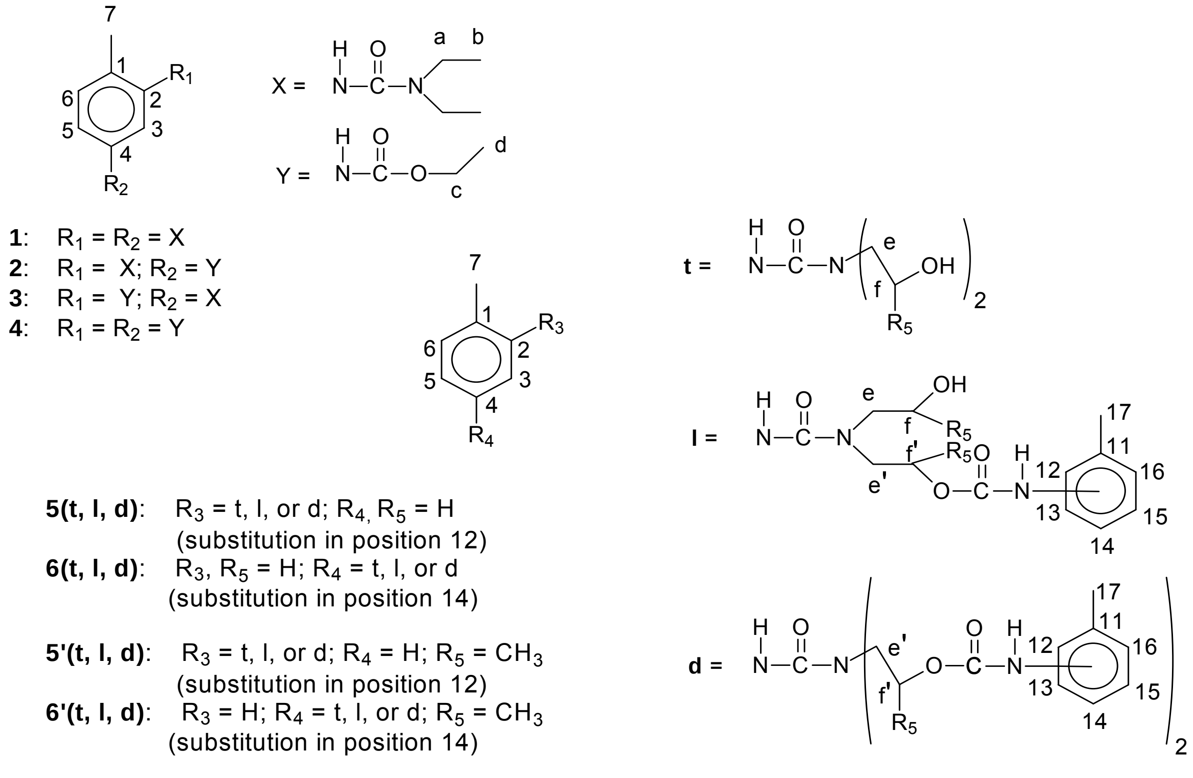
c) stopped by DBA

d) used for further investigations without precipitation

The molar masses and polydispersity of the prepared aromatic hyperbranched polymers were determined using SEC-RI method in which the polymer samples were dissolved in mixture of DMAc and LiCl/ H_2O and measured at room temperature. As mentioned before the molar masses reported by this method are not absolute and may contain a large error due to calibration with linear standards. Nevertheless, it is believed that SEC allows us to compare the different hyperbranched polymers and to draw some conclusions regarding the effect of the reaction conditions. As can be seen from Table 4, the molar masses of samples (Ar-hpu)-OH-1 and (Ar-hpu)-OH-2 which are prepared using the molar ratio 1:1.1 (TDI: DEA) to overcome the problem of gelation, are lower compared to (Ar-hpu)-OH-3 and (Ar-hpu)-OH-4 and consequently the molar mass distribution is more narrow (PDI = 2-3). The effect of temperature was studied in the polymerization reactions of (Ar-hpu2)-OH1 to (Ar-hpu2)-OH3, carried out at 10, 30, and 50°C, respectively. We noticed that the reaction rate was affected (increased) to a great extent with the raise of temperature from 10 to 50°C. At 10°C only an oligomer was obtained (M_n = 1200 g/mol). The molar mass of the formed polymer at 50°C is with M_n values around 5300 g/mol. In general, the reaction times were kept below 7 hours and molar masses with M_w values between 3500 g/mol and 77000 g/mol is achieved. In our chosen concentration regime (30-50 wt%) no gelation occurred under the used conditions allowing technical relevant reaction conditions for the preparation of HPU.

4.5.2 NMR structural analysis

A detailed structural analysis of hyperbranched poly(urea-urethane)s made from several AA* / B*B_2 monomers is carried out. The system TDI / DEA (Ar-hpu1)-OH seems to be suited for a detailed structural analysis by ^{1}H and ^{13}C NMR spectroscopy. It was shown for several hyperbranched polymers[122,164-166] that the combination of 1D and 2D NMR can allow a complete structural analysis without using model compounds. Unfortunately, intense overlap of the signals of aromatic protons of the different substructures prevented unequivocal signal assignments for the (Ar-hpu1)-OH by 2D techniques. For that reason several model compounds were synthesized (Figure 4.10, see also 4.3, 4.4), whereas 1 – 4 describe the different substitution pattern of the reacted TDI unit with respect to urea and urethane moieties in 2- and 4-position, 5 (6) t/l/d describe the influence of both the position of methyl and reacted NCO group (5 vs. 6) and the substitution of the DEA unit (t, l, d) on the chemical shifts. A superposition of all these effects gives a rough picture to analyze the NMR spectra of the system TDI / DEA.



1: $R_1 = R_2 = X$
2: $R_1 = X; R_2 = Y$
3: $R_1 = Y; R_2 = X$
4: $R_1 = R_2 = Y$

5(t, l, d): R_3 = t, l, or d; R_4, R_5 = H
(substitution in position 12)
6(t, l, d): R_3, R_5 = H; R_4 = t, l, or d
(substitution in position 14)

5'(t, l, d): R_3 = t, l, or d; R_4 = H; $R_5 = CH_3$
(substitution in position 12)
6'(t, l, d): R_3 = H; R_4 = t, l, or d; $R_5 = CH_3$
(substitution in position 14)

Figure 4.10: Model reaction and model compound used for structural analysis of (Ar-hpu)-OH polymers.

It had to be realized that ^{1}H and ^{13}C signals of the tolyl moieties are not appropriated for a detailed quantification of structural units due to extensive signal overlap. However, the signals of the OH protons differ in their chemical shifts both with respect to the ring position (o or p) of the urea moiety and to t and l structures (Figure 4.11a and 4.11b). Despite the overlap of these signals for the HPU (Fig. 4.11c), their integrals and so the content of t and l units can be determined. The signal of the –C<u>H</u>$_2$O-C(O)NH protons is due to l and d units. Corrected by the content of l units (from OH integration) the d content and, finally, the degree of branching can be calculated. Fortunately, the OH proton signals allow to apply this procedure also to determine DB for the system TDI/DIPA (Figure 4.11d). Here, model compounds 5't/l/d and 6't/l/d were used for signal assignment.

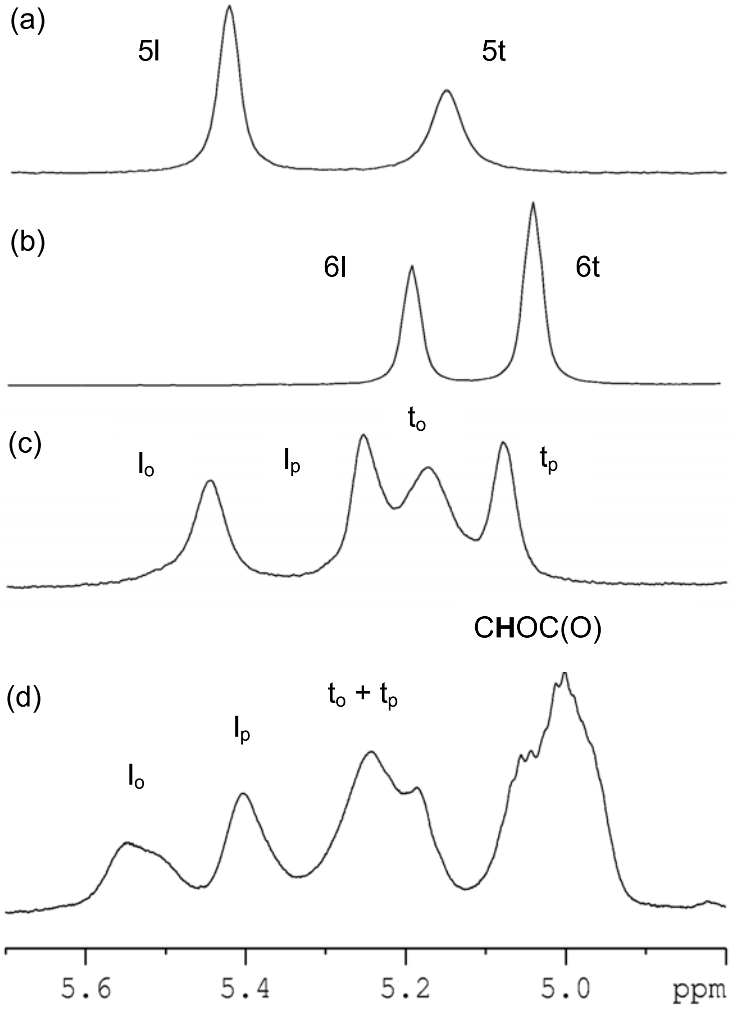


Figure 4.11: ^{1}H NMR spectra (regions) showing the OH signals of model compounds 5(t,l) (a), 6(t,l) (b), (Ar-hpu1)-OH (c), and (Ar-hpu2)-OH (d).

It was reported[164] that DB for the TDI with DEA and DIPA can be determined from ^{13}C NMR signal intensities of the carbons in α-position to non-reacted (l, t) hydroxyl groups. They should show a splitting in signals due to t and l moieties. This was illustrated for a B^*B_2 monomer where these carbons are two bonds away[164]. However, they are separated by four bonds for DEA and DIPA what reduces the shift effects and, in addition, DIPA results in diastereomeric structures. Therefore, we can confirm this procedure only for TDI/DEA but not for TDI/DIPA. In the TDI/DIPA system two signal regions are observed in fact for the CH-OH methine carbon (Figure 4.12c) but the high field region is due to t and l structures as can be concluded from model compounds (Figure 4.12a,b). However, because both diastereomers are equally populated $(l_p + l_o) = (l_p^* + l_o^*)$ and so the intensity of t units can be calculated from the high-field region, finally DB, also using the intensity of CHO-C(O)NH carbons (d and l), can be derived. DBs calculated in this way and from the ^1H NMR data as described above are in good agreement (Table 4).

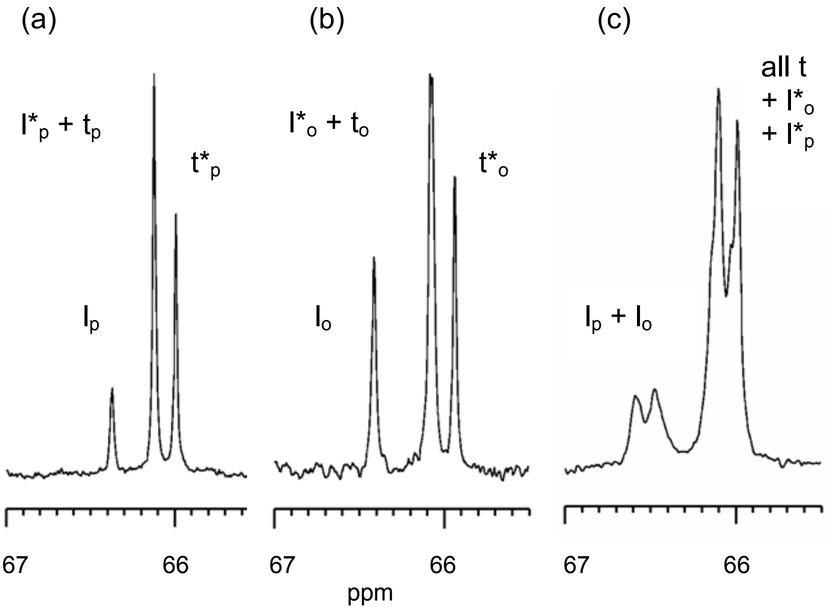


Figure 4.12: ^{13}C NMR spectra (regions) showing the *C*HOH signals of model compounds 5'(t,l) (a) 6'(t,l) (b), and of (Ar-hpu2)-OH (TDI/DIPA) (c) (* signal of the second diastereomer).

Table 4: Structural characteristics of hyperbranched polymers from TDI and DEA (Ar-hpu1)-OH and DIPA (Ar-hpu2)-OH respectively, determined by ^{1}H and ^{13}C NMR.

Polymer	DB[a)] %		% of t, l and d		Urea : Urethane[b)]		%
	^{1}H	^{13}C	^{1}H[d)]	^{13}C[e)]	^{1}H	^{13}C	side reactn.[c)]
(Ar-hpu1)-OH1	69	71	44,31,25	46,29,25	1.25	1.25	0
(Ar-hpu1)OH2[f)]	59	59	35,41,24	35,41,24	1.16	1.21	2
(Ar-hpu1)OH3[f)]	61	62	31,39,30	33,38,29	1.20	1.24	1
(Ar-hpu1)-OH4	64	64	37,36,27	37,36,27	1.05	1.07	1
(Ar-hpu2)-OH1	46	48	30,54,16	29,52,19	-	1.17	3
(Ar-hpu2)-OH2	47	45	34,53,13	35,55,10	-	1.22	6
(Ar-hpu2)-OH3	48	47	31,52,17	33,53,14	-	1.18	4

a) DB = (t + d) / (t + l + d)

b) determined from the NH and C=O signal region, resp., according Figures 4.13 and 4.14

c) N,N'-p-tolylurea units as side product for the TDI system; quantification using the C=O signal at 152.55 ppm relative to all C=O signals

d) determined from the OH signal region according Figure 4.11

e) determined from the ^{13}C signal intensities of $CH_{(2)}OH$ (l), $CH_{(2)}OH$ (t), and $CH_{(2)}OC(O)NH$ (l + d).

f) % of total NCO groups end-capped with N,N-dibutyl amine: 4 for (Ar-hpu1)OH2 and 13 for (Ar-hpu1)3.

Besides the DB also the substitution pattern of the tolyl ring according structures 1 – 4 is of interest. It is influenced by the different reactivity of the A and A* functionalities towards the B and B* functionalities under experimental conditions. Figure 4.13 depicts the NH protons region in the ^{1}H NMR spectra of the model compounds and a TDI/DEA polymer. The signals of urea and urethane NH protons appear in well separated regions and are very sensitive to the ring position (ortho or para) but also to the second substituent (Figure 4.13c). The substitution pattern of the DEA unit (t, l, or d) affects the urea NH in a characteristic way (Figure 4.13a,b). The signal assignment for the polymer given in (Figure 4.13d) is based on these. The assignments for the d unit signals were proved in addition by converting the t and l units in “pseudo” dendritic units by reaction with phenyl isocyanate. The increase in line width going from t to d units signals is well known from other systems[162,167]. From the NH region information about the urea/urethane and about the o-urethane/p-urethane ratios can be obtained (Table 5).

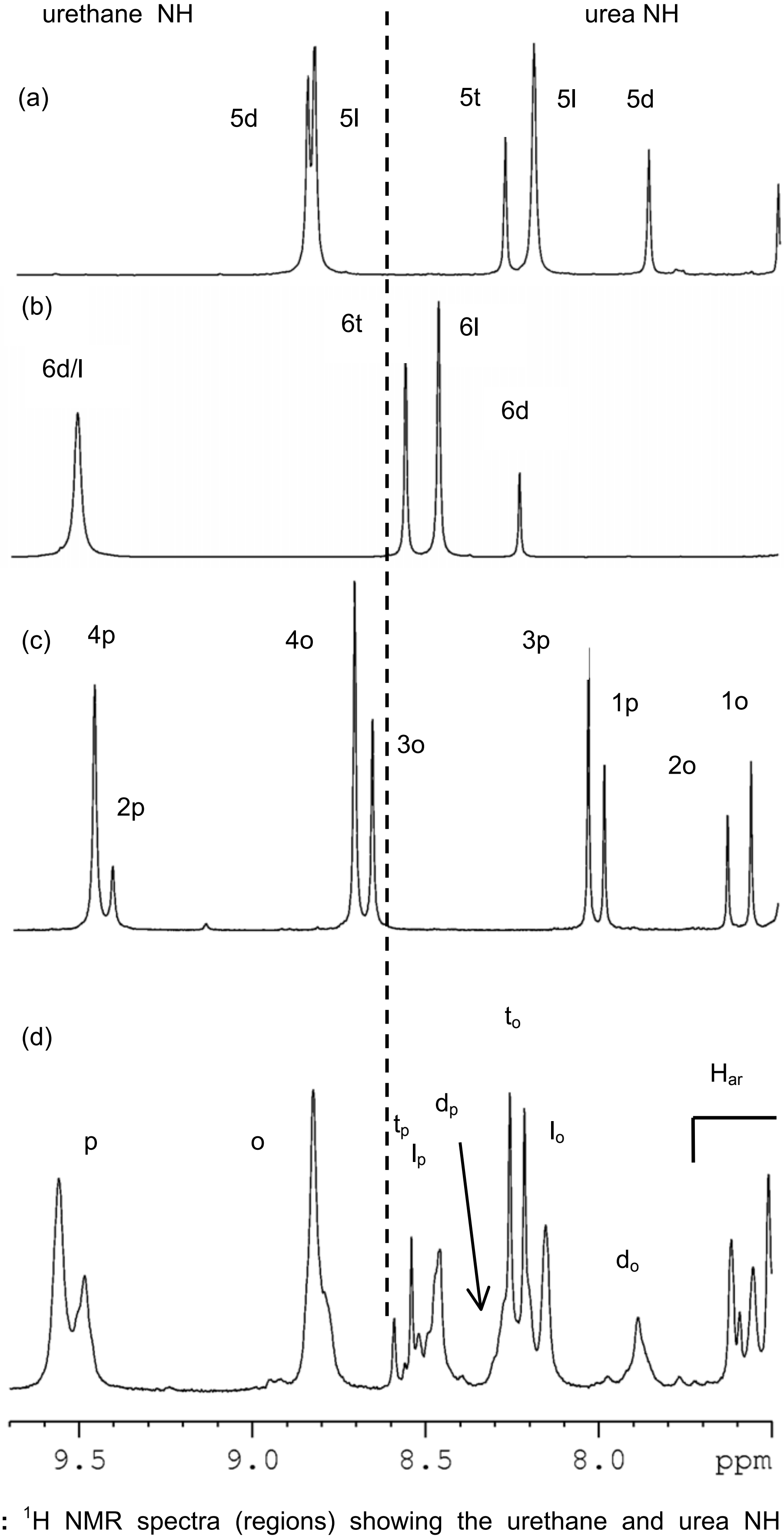


Figure 4.13: ^{1}H NMR spectra (regions) showing the urethane and urea NH signals of model compounds 5(t,l,d) (a), 6(t,l,d) (b), 1 - 4 (c), and (Ar-hpu1)-OH (TDI/DEA) (d).

In case of TDI/DIPA the signal group of o-urethane moieties overlaps with the p-urea signals. Furthermore, most urea signals split of in two signals due to the two diasteromers of t, l, and d structures. Finally, the carbonyl carbons region in the ^{13}C NMR spectra of TDI/DEA was analyzed, Figure 4.14 based on the model compounds. A similar picture as for the NH protons region is observed. Urethane and urea regions are separated and the urea carbonyl carbon is sensitive to the substitution of the DEA unit. Urethane groups in o- and p-position can be well distinguished but chemical shift effects due to the second substituent are too low to distinguish between urea and urethane substitution. These effects are larger for the urea carbonyl carbons. Therefore, the signals of t and l units clearly split up in two signals. The broadening, observed for l and d unit signals, may be due to restricted motion (relaxation time effects) and/or due to long-range substituent effects - the two urethane groups of a d-unit can be of p/p, p/o, or o/o type. The $^2J_{CH}$ correlation between N$\underline{H}$ and $\underline{C}$=O of the different urea groups obtained from a HMBC spectrum are in full agreement with the assignments given in Figures 4.13d and 4.14d. The quantification of different structures is given in Table 5.

Table 5: Substitution pattern for TDI / DEA polymers determined by NMR spectroscopy from the carbonyl carbon region (comp. Figure 4.14) and the NH proton region (comp. Figure 4.13) compared with data obtained from a model reaction $^{a)}$.

Polymer	%p-urea (^{13}C) (t, l, d)	%o-urea (^{13}C) (t, l, d)	%p-urethane (^{13}C) / %p-urethane (^{1}H)	%o-urethane(^{13}C) / %o-urethane (^{1}H)
(Ar-hpu1)-OH1	21 (29, 29, 42)	34 (55, 25, 20)	28 / 28	17 / 17
(Ar-hpu1)-OH2	22 (25, 37, 38)	33 (43, 34, 23)	27 / 26	18 / 20
(Ar-hpu1)-OH3	21 (25, 34, 41)	34 (35, 28, 37)	28 / 27	17 / 18
(Ar-hpu1)-OH4	22 (24, 33, 43)	32 (47, 31, 22)	28 / 30	18 / 19
Model reaction$^{a)}$	25	28	25	22

a) TDI + diethyl amine + ethanol (1:1:2).

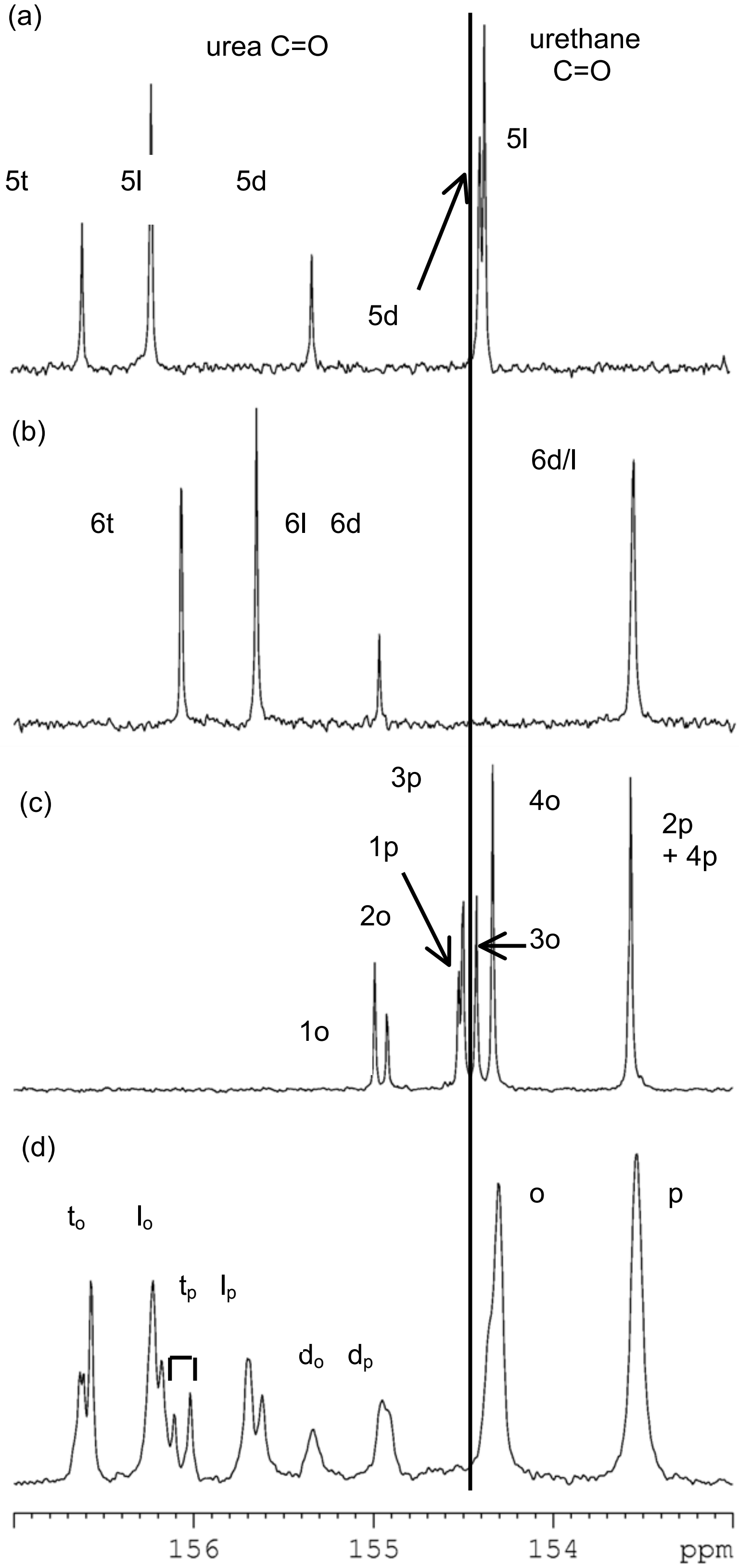


Figure 4.14: ^{13}C NMR spectra (regions) showing the urethane and urea carbonyl signals of model compounds 5 (t,l,d) (a), 6(t,l,d) (b), 1-4 (c), and (Ar-hpu1)-OH (d).

Through the detailed NMR analysis, it was verified that the most important side reaction is the hydrolysis of isocyanate to amine and its reaction with excess of isocyanate to N,N'-diaryl urea but no other structures e.g. biuret or allophanate could be detected in the HPUs since at the given reaction temperatures those side reactions seem to be successfully suppressed. N,N'-p-tolyl-, N,N'-o-tolyl- and N-p-tolyl-N'-o-tolyl-urea were synthesized as model compounds to assign the NH and C=O signals of corresponding structures in the ^{1}H and ^{13}C spectra of TDI systems. Whereas their carbonyl carbons resonate outside the signal region of the hyperbranched polymers (152.68, 153.03, and 152.75 ppm, respectively) there is a signal overlap in the NH protons region (8.46, 8.21, and 8.87/7.84 ppm, respectively). However, only signals of the N,N'-p-tolyl-urea group (152.55 and 8.43 ppm) were observed for some samples, Table 5 indicating that the p-isocyanate group is the more reactive one in TDI.

Summarizing, the quantification of t, l, and d units and so the calculation of DB is possible for the TDI systems (Table 4). The TDI/DEA system can also be analyzed with respect to the substitution pattern on the tolyl moiety (Table 5). The NMR analysis and the results given in Tables 4 and 5 allow now to discuss differences in the structure of the hyperbranched polymers depending on the used monomers and the applied reaction conditions. Firstly, it was found that (Ar-hpu)-OH based on TDI and DEA have significant higher DB in comparison with those prepared through the reaction of TDI and DIPA. In the series of (Ar-hpu2)-OH all DB values are below 50%. This might be due to the lower reactivity of OH group in the secondary hydroxylamine (also indicated by the much longer reaction time needed) causing a lower tendency to form dendritic units. The primary OH group in DEA is more reactive towards NCO and in absence of a sterically hindering group, like CH_3 as present in DIPA, the formation of dendritic units seems to be favored and hence an increase of the degree of branching is observed. The lower reactivity of the DIPA compared to DEA gives also rise to a slight increase in the amount of side reaction (3-6 % compared to 0-2% for DEA).

Regarding the first polymer system (Ar-hpu1)-OH, we notice that all samples have DB> 65%, but by looking at the values of t, l, and d subunits we notice that they are highly affected by two factors: (a) monomer molar ratio, (b) type of stopper. Sample (Ar-hpu1)-OH1 has higher number of t units than sample (Ar-hpu1)-OH2 although they were prepared using the same monomer ratio. However, since DBA is used as stopper for the polymerization reaction of the second polymer, the amount of t-subunits is lowered since the dibutylurea units are not counted as terminal units. The same trend can be noticed by comparing the values of t units for samples (Ar-hpu1)-OH3 and (Ar-hpu1)-OH4 (again the same monomer molar ratio but different stoppers).

It can be concluded that a significant amount of the terminal units is introduced in the last step of the reaction when a stopper molecule is added. On using an excess of B^*B_2 compared to AA*, also a higher fraction of terminal groups is introduced (compare (Ar-hpu1)-OH1 and (Ar-hpu1)-OH4. One should state that it was reported by another group[164] DB values for the TDI/DEA system of only 45% using similar evaluation of the ^{13}C NMR signals. However, it is assumed that the amount of terminal units equals that of dendritic units and thus, a simplified equation was used for calculation of DB. As one can see in this study, in an A_2+B_3 system, the assumption of d=t, which derives form the statistical AB_2 reaction, does not apply and full quantitative analysis of all structural units becomes very important. Earlier studies on A_2+B_3 system confirm this conclusion[167]. Very interesting are also the results which could be obtained for the substitution pattern in the TDI/DEA system (Table 5). In general, for all TDI polymers a slight excess of urea compared to urethane units could be detected in the polymer structure (Table 4). The analysis of the substitution pattern shows that the excess urea is mainly caused by an excess of ortho substituted units which are probably introduced by the stopper reaction. Otherwise it looks like the substitution pattern is nearly random which is in accordance with earlier observations that no clear preference in the reaction of o- and p-isocyanate groups in TDI towards amines can be confirmed experimentally. An additional model reaction, where TDI was reacted with diethyl amine and ethanol under identical reaction conditions as those of the polyreaction giving enough time to reach full conversion (which means: no stopper molecule) verified a nearly statistical ratio of the four possible reaction compounds (Table 5). Therefore, we have to conclude that in the TDI/DEA system, and probably also in the TDI/DIPA system, we are dealing more with an A_2 + B^*B_2 than a AA* + B^*B_2 situation.

4.6 Synthesis of aliphatic hyperbranched poly(urea-urethane)s

Preparation of aliphatic hyperbranched poly(urea-urethane)s (Al-hpu)-OH was achieved through the reaction of isophorone diisocyanate (IPDI) or 2(3-isocyanatopropyl) cyclohexylisocyanate (IPCI) as AA* monomers with diethanol amine (DEA) or diisopropyl amine (DIPA) as B*B_2 monomers. The reaction of one of the isocyanate groups with either amino or hydroxyl groups yields the intermediate AB_2. Through using low temperature and slow addition of the B*B_2 monomer we can control the reaction path toward the formation of intermediate of the type shown in Figure 4.15.

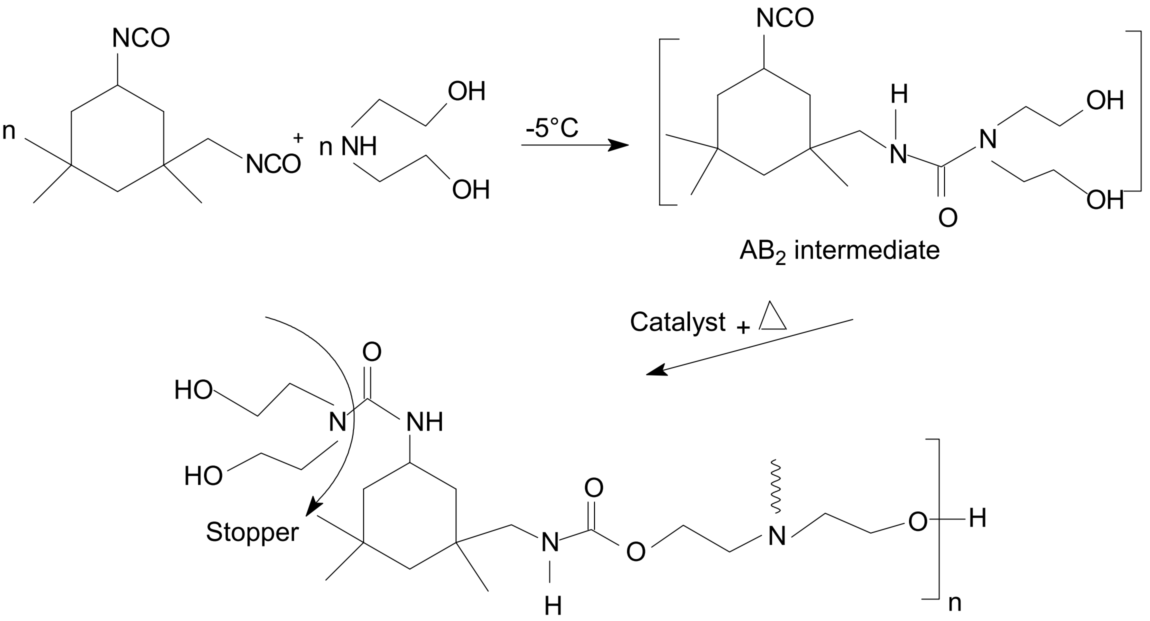
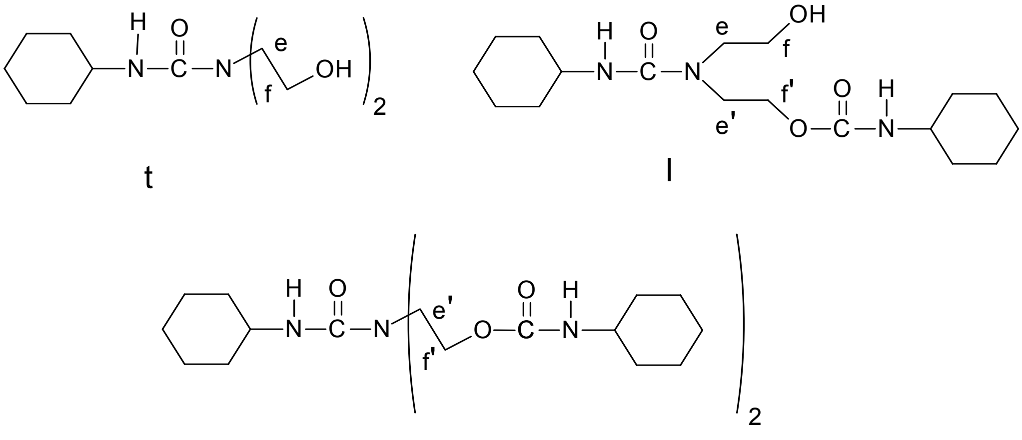


Figure 4.15: Reaction of IPDI as AA* monomer with DEA as B*B_2 monomer which yields aliphatic hyperbranched poly(urea-urethane) polymer (Al-hpu1)-OH.

4.7 Synthesis of model compounds

Similar as for the aromatic systems, model compounds had to prepared to facilitate the structural characterization of the complex hyperbranched molecule. Cyclohexyl monoisocyanate was reacted with B*B_2 monomers to prepare model compounds. The method is the same as that used in case of aromatic model compounds. The structures of the possible formed products are shown in Figure 4.16 which represent the terminal (t), linear (l) and dendritic (d).



t

l

d

Figure 4.16: Structures of the formed model compounds:

4.8 Model reaction for substitution pattern

The reactivity of the primary and secondary isocyanate groups in the AA* monomers towards amino and hydroxyl groups, is studied through model reactions between an AA* monomer and diethyl amine and ethanol respectively. The concentration of the AA* monomer to the other reaction molecule was 1:2. It was noticed that the reaction of AA* monomer with diethyl amine is fast and does not need activation using catalyst while in case of using ethanol the reaction was very slow and DBTL as catalyst was used as well as high temperature. This is maybe due to the fact that the presence of urea groups in the reaction mixture facilitate the urethane formation[36].

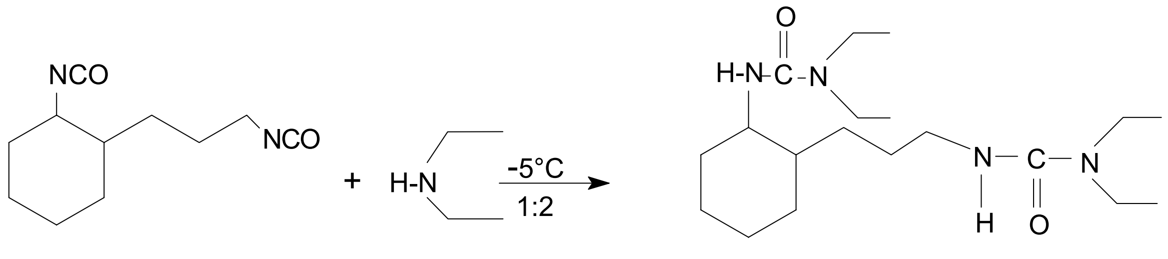
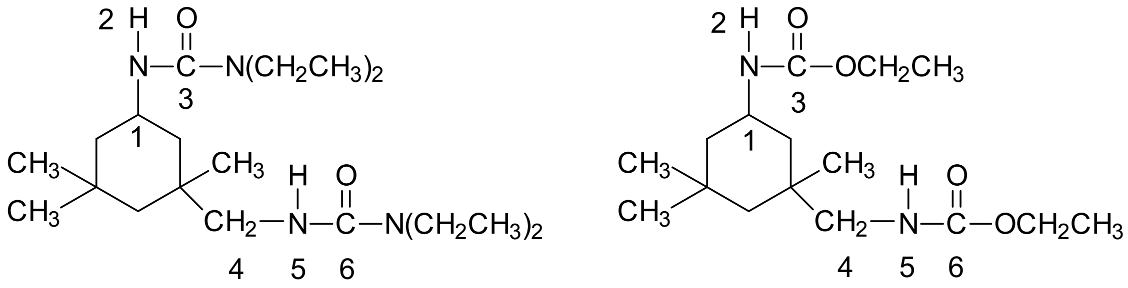


Figure 4.17: Preparation of a model compound based on IPCI and diethyl amine.

Model compounds based on IPDI were prepared by reacting the monomer with diethyl amine or ethanol. The reaction was started at low temperature until complete addition of diethyl amine in the first experiment or ethanol in the second one (in contrast to aromatic model compounds, the aliphatic ones were prepared separately). No mixture attempted because we shall obtain very complicated NMR spectra. The temperature was raised and the catalyst was added till complete conversion, Figure 4.18 shows the chemical structures of the products.



(1) (2)

Figure 4.18: Products of the chemical reactions between IPDI and diethyl amine (1) and ethanol (2).

4.9 Preparation of aliphatic hyperbranched polymers and variation of reaction conditions

Aliphatic hyperbranched polymers (Al-hpu)-OH were synthesized using different reaction conditions (Table 6). In the polymerization reactions of aliphatic monomers it was essential to use a catalyst to activate the reaction, DBTL and DABCO were chosen for this purpose. The catalyst was added in the second step of the polymerization reaction i.e. when the reaction temperature was raised above room temperature. It is known that each catalyst has its mechanism and preferable site to catalyse the isocyanate containing compound. In case of DBTL, the reaction with alcohol is favoured more on the secondary NCO while DABCO increases the selectivity of the primary NCO. However, since we added the catalyst after the first stage of the reaction where the intermediate is formed, no major effect was expected for the catalyst regarding the final polymer structure. Regarding the reaction time shown in Table 6, we notice that the polymerization reactions involving DIPA needed more time than those of DEA although using catalyst. This is due to the lower reactivity of the secondary alcohol group and the steric effect. On the other hand we can notice that the increase of temperature has more effect on the rate of the reaction than the type of the catalyst used. This can be observed by comparing the reaction time of samples (Al-hpu3)-OH2 which was prepared using DBTL as catalyst and needed 90 min at 30°C to achieve 0.49 NCO%, with sample (Al-hpu3)-OH3 which was prepared using DABCO. There, a NCO% value of 0.23 was reached after 30 min of the beginning of the reaction by raising the temperature by 10°C.

Table 6: Reaction conditions for preparation of (Al-hpu)-OH.

Polymer	Catalyst	Conc. (wt %)	Temp /°C	Time/min	NCO %
(Al-hpu1)-OH1	DBTL	25	50	115	0.34
(Al-hpu1)-OH2	DBTL	50	50	87	1.10
(Al-hpu1)-OH3	DBTL	50	50	15	0.41
(Al-hpu1)-OH4	DABCO	50	50	90	0.45
(Al-hpu1)-OH5	DABCO	30	30	205	0.40
(Al-hpu2)-OH1	DBTL	30	30	1070	0.42
(Al-hpu2)-OH2	DABCO	30	30	1630	0.99
(Al-hpu3)-OH1	DABCO	30	30	90	0.55
(Al-hpu3)-OH2	DBTL	30	40	90	0.49
(Al-hpu3)-OH3	DABCO	30	50	30	0.23
(Al-hpu4)-OH1	DABCO	30	30	1080	0.91
(Al-hpu4)-OH2	DBTL	30	40	1050	0.55
(Al-hpu4)-OH3	DABCO	30	70	1300	0.49

(Al-hpu1)-OH= IPDI+DEA, (Al-hpu2)-OH=IPDI+DIPA, (Al-hpu3)-OH=IPCI+DEA, (Al-hpu4)-OH=IPCI+DIPA.

Polymers (Al-hpu1)-OH3 and (Al-hpu1)-OH4 were prepared by using different catalyst (DBTL for the first and DABCO for the latter). Regarding the resulting values of molar masses for these polymers (Table 7). It can be noticed that using DBTL gave polymers of significantly higher molar mass than in case of using DABCO, but as expected the polydispersity increased, too. The polymerization reaction involving IPCI is a good example for the effect of temperature not only on the resulting molar mass but also on the appearance of the polymer. Increasing M_n from 1000 g/mol to 1600 g/mol changed the polymer appearance from sticky rubber to white powder. In general, the reactivity of IPCI is significantly lower than that of IPDI and only products (Al-hpu3)-OH3 and (Al-hpu4)-OH3 with relatively low molar masses could be isolated so far even when we raised the temperature to 70°C. The yield obtained for the final polymer lies between 55 to 73%, mostly because of the precipitation and filtration processes to isolate the polymer.

Table 7: Values of molar masses of (Al-hpu)-OH as measured using SEC/RI.

Polymer	M_n (g/mol)	M_w (g/mol)	PDI
(Al-hpu1)-OH1	3700	8500	2.29
(Al-hpu1)-OH2	2800	8900	3.18
(Al-hpu1)-OH3	9200	107100	11.64
(Al-hpu1)-OH4	5800	17000	2.93
(Al-hpu1)-OH5	4100	8200	2.00
(Al-hpu2)-OH1	4900	14700	3.00
(Al-hpu2)-OH2	2000	2800	1.40
(Al-hpu3)-OH1	1600	2800	1.75
(Al-hpu3)-OH2	1200	2200	1.83
(Al-hpu3)-OH3	2200	3700	1.68
(Al-hpu4)-OH1	1000	1400	1.40
(Al-hpu4)-OH2	1000	1600	1.60
(Al-hpu4)-OH3	1600	2200	1.37

(Al-hpu1)-OH= IPDI+DEA, (Al-hpu2)-OH=IPDI+DIPA, (Al-hpu3)-OH=IPCI+DEA, (Al-hpu4)-OH=IPCI+DIPA.

- NMR Structural analysis

The analysis of chemical structure of the synthesized aliphatic hyperbranched poly(urea-urethane)s is not an easy task since the used AA* monomers, as mentioned before, is composed of different isomers which are the cis and trans isomers. Moreover there are two types of isocyanate groups either primary or secondary. This makes the picture very complicated. The ^{1}H NMR spectrum of an aliphatic hyperbranched polymer based on IPDI and DEA is shown in Figure 4.19. Generally, we can describe the spectrum as follows: the signals of protons in the cyclohexyl ring (H2:H7) can be found in the chemical shift range of 0.7 to 1.7 ppm. The urethane signals are found at 6.9 to 7.1 ppm while urea groups can be found in the area of 6.25 to 6.35 ppm. The signal at 5.0 is for t_{cis} subunit and the peak at 4.9 ppm is assumed to be for t_{trans} while at 4.8 ppm the signal of $l_{cis+\ trans}$ can be found, the signal for the proton of the d group can be found at 4.0 ppm. The signals of hydroxyl protons of t and l units are not separated.

For the IPCI/DEA system it can be differentiated between (t + l) units bonded to CH_{cis}, CH_{trans}, and CH_2 at 5.08, 5.02, and 4.79 ppm, respectively (Figure 4.20). Obviously, the propyl spacer between ring and reacted NCO group simplifies the spectrum. Such a signal assignment failed for IPDI / DEA due to the great variety of combinations. Structural conclusions with respect to the quantitative content of structural units and so DB are not possible for these systems. For the IPDI and also for the IPCI systems several signals were observed for the CH_2OH and CHOH carbons (depending on the B^*B_2 monomer) and a doubtless separation in signals due to t and l units seems to be impossible from our investigations. Therefore, no degrees of branching were calculated for systems with IPDI and IPCI as AA* monomers, even though, the observed signal splitting clearly confirms the branched structure.

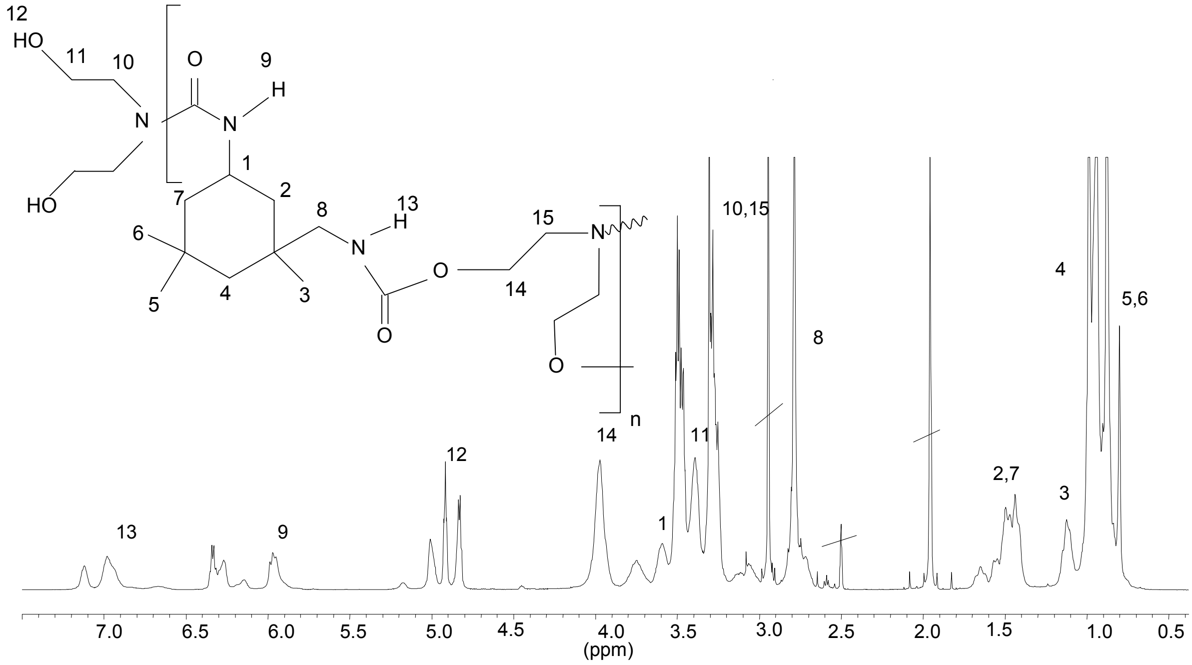


Figure 4.19: ^{1}H NMR spectrum of (Al-hpu1)-OH1 based on IPDI and DEA in DMSO-d_6.

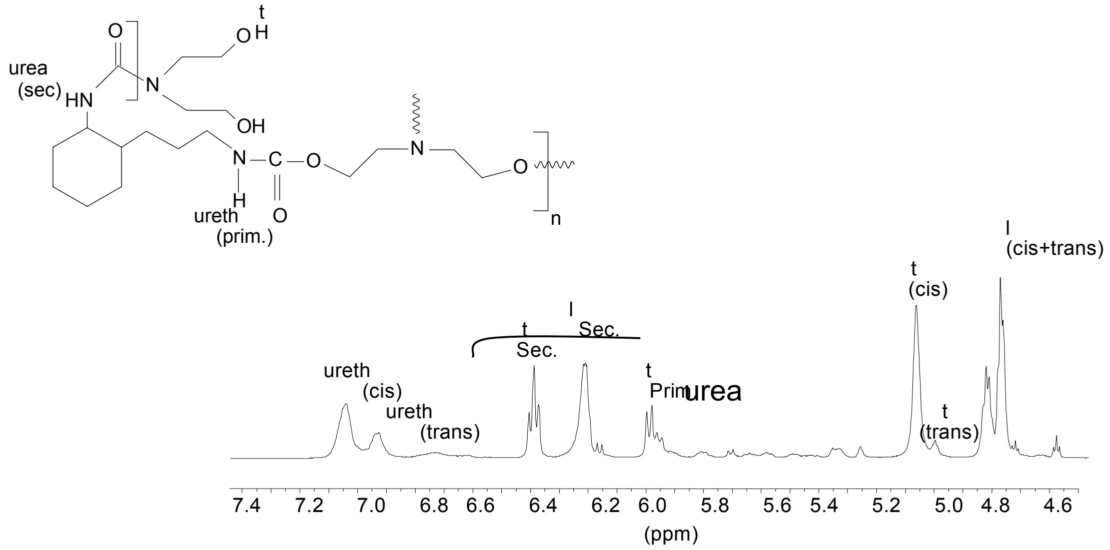


Figure 4.20: ^{1}H NMR spectrum of hyperbranched polymer (Al-hpu3)-OH2, (selected section) in DMSO-d_6.

The urethane to urea ratio for IPDI and IPCI/DEA system can be determined from the integrals over 7.2 - 6.5 ppm (urethane) and 6.5 - 5.8 ppm (urea). Similar as for the aromatic systems, also for (AL-hpu1)-OH and (AL-hpu3)-OH a urea/urethane ratio slightly above 1.0 was found (1.03-1.22). Measurements at 353 K provide a better signal separation but doubtless signal assignment similar to TDI/DEA system was not possible.

Model compounds synthesized from IPDI and N,N-diethyl amine or ethanol (1 and 2, Figure 4.16) show that the carbonyl carbons of urethane and urea from sec. and prim. isocyanate units are well separated showing an additional splitting due to the cis and trans isomers. Unfortunately, the urea and urethane regions overlap in the hyperbranched polymers.

Model compounds from cyclohexyl isocyanate and DEA (Figure 4.21) proved the sensitivity of the urea carbonyl to the conversion of the B_2 groups. Although 2D NMR techniques allowed to assign some signals, a complete assignment as described for TDI/DEA can not be given for IPDI and IPCI systems.

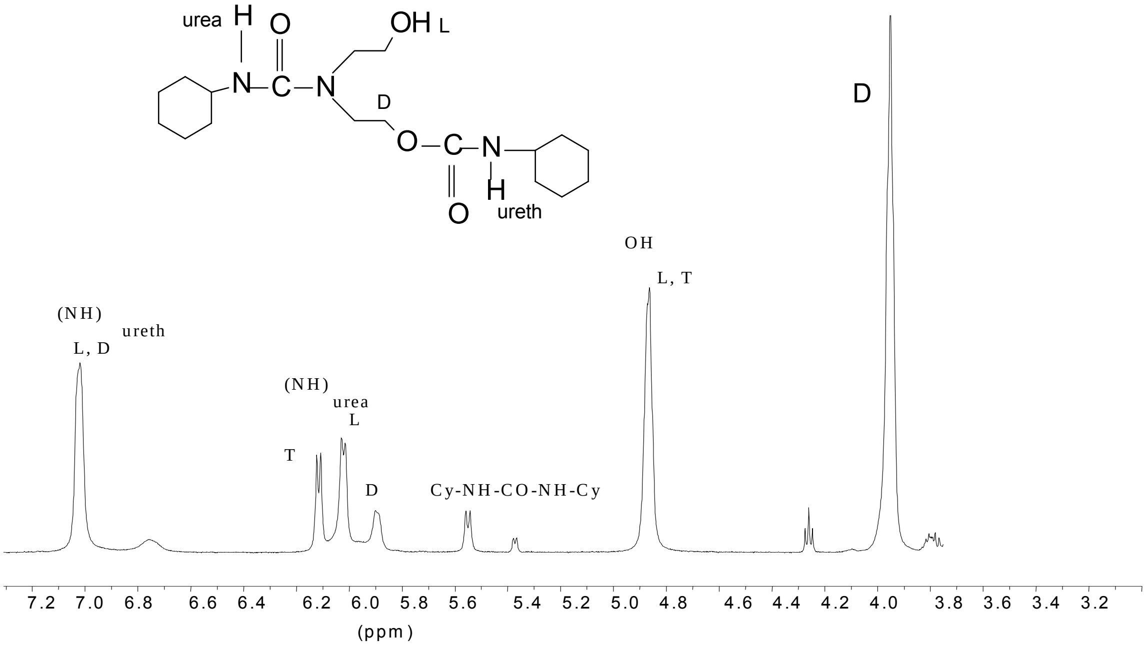


Figure 4.21: ^{1}H NMR spectrum of reaction product of cyclohexyl isocyanate and DEA in DMSO-*d*$_6$.

4.10 Fractionation of aromatic hyperbranched polymers

Since hyperbranched polymers are characterized by their broad molar mass distribution, the determination of the molar mass dependent parameters is difficult. So far, there was neither a synonymous picture of the structure of hyperbranched molecules nor is the relation of this structure to the macroscopic properties known. Furthermore, the special molecular structure and conformation exert a further difficulty on the determination of the exact molar mass. Routine measurements with (SEC), as mentioned before, does not give accurate values since it is relative method which is commonly calibrated with linear standards[168,169]. It is useful to know the form of the molar mass distribution in a polymer sample, as this can have a significant bearing on the physical properties. It is also advantageous to be able to prepare sample fractions, whose homogeneity is considerably better than the parent polymer. Using controlled conditions, could allow a given molecular species to precipitate, while leaving larger or smaller molecules in solution. This process is known as fractionation. Experimentally, a polymer sample can be fractionated in a variety of ways and three in common use are: (1) addition of a non-solvent to a polymer solution; (2) lowering the temperature of the solution; and (3) column chromatography. In the first method, a non-solvent is added to the polymer solution which causes precipitation of the longest chains first and these can be separated from the shorter chains which remain in solution. In practice the polymer solution is held at a constant temperature while precipitant is added to the stirred solution. When the solution becomes turbid the mixture is warmed until the precipitate dissolves. The solution is then returned to the original temperature and the precipitate which reforms is allowed to settle and then separated. This ensures that the precipitated fraction is not broadened by local precipitation during the addition of the non-solvent. Successive additions of small quantities of non-solvent to the solution allow a series of fractions of steadily decreasing molar mass to be separated. The mass and molar mass of the fractions are recorded an a distribution curve for the sample can be constructed from the results. We used the previously described method for preparative fractionation of hyperbranched polymer samples with broad molar masses in order to get more reliable information about the molar mass and its distribution. Two samples were chosen for this purpose (Ar-hpu1)-OH7 which has M_n value of 11100 g/mol and PDI of 7.0, and sample (Ar-hpu1)-OH4 with M_n of 9100 g/mol and PDI value of 6.07. In our fractionation solvent gradient was used but at ambient temperature as described in the literature[170]. THF was used as non-solvent for the chosen polymers and DMAc is picked as good solvent. During the procedures, a glass column filled with Ballotini (glass beads of 0.1-0.2 mm diameter) coated by the hyperbranched polymer is used. The coating of the surface

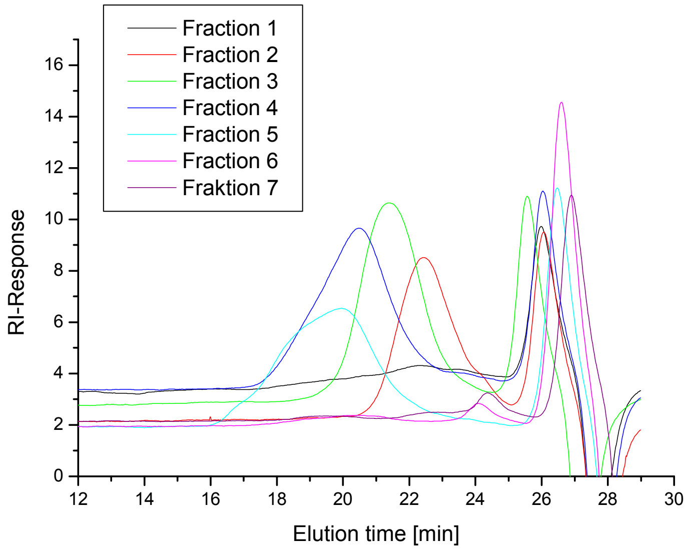


Figure 4.22: GPC results of small fractionation from sample (Ar-hpu1)-OH7 (number of fractions 7).

of the glass beads was carried out by exposing the glass material to the polymer solution followed by vacuum evaporation. First fractionation is made for a small quantity of the sample (70 mg) to optimize the procedures, then fractionation of a larger amount can be done. In both samples the fractionation of small quantities was successful. The separated fractions were measured with GPC coupled with RI- detector. The flow rate was 0.5 ml/ min and PVP (polyvinyl pyridine) was used as linear standard. The results of fractionation process for sample (Ar-hpu1)-OH7 is shown in Figure 4.22. The molar masses and polydispersities of the individual fractions are represented in Table 8.

Table 8: Molar masses of fractions obtained from sample (Ar-hpu1)-OH7 (GPC/RI detector).

Fraction	M_n (g/mol)	M_w (g/mol)	PDI
1*	0	0	0
2	3330	5875	1.76
3	6104	12200	1.99
4	26002	64772	2.49
5	55049	220611	4.01
6*	0	0	0
7*	0	0	0

*No signals observed.

The results given in the above table shows the molar masses and polydispersity for only 4 of 7 separated fractions. Fractions 2 and 3 have relatively low polydispersity but fractions 4 and 5 are broad which indicates that, up to now the fractionation conditions are not ideal. Actually, again the use of linear standards for calibration is not successful due to the difference in the molecular density for both linear and hyperbranched polymers.

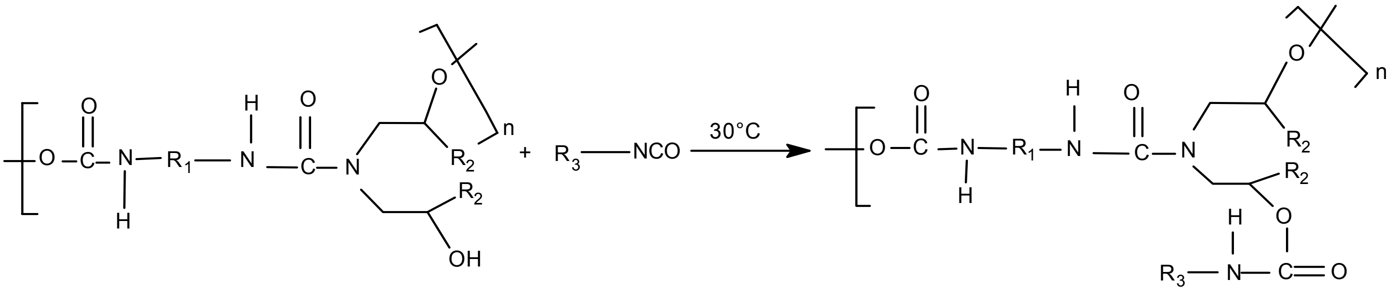
In the second fractionation process of a larger amount not all of the sample completely dissolved in DMAc/ LiCl/ H_2O mixture, only up to fraction 6 the solubility was good, Nevertheless, test measurements were made (the dissolved part of the samples were injected in GPC). It was noticed that starting from fraction 11 no further signals could be observed. The presence of insoluble part in the prepared samples suggests that side reactions occurred during the preparative procedures. Characterization of the fractionated samples using ^{1}H NMR was carried out and it was found that there are changes in the chemical structure up fraction 9. It can be concluded that the conditions for preparative fractionation of hyperbranched polymers need to be optimized to obtain successful fractionation.

4.11 Modification of end groups

The influence of the end groups on the properties of a linear polymer is, at a sufficiently high molecular weight, negligible. However, irrespective of what synthetic procedure is used to obtain the hyperbranched polymers, the resulting macromolecules have a large number of end groups. The end groups have been demonstrated to be easily accessible for chemical modifications and the nature of the end groups has been found to determine the thermal and physical properties of the hyperbranched polymers to a great extent. So, modification of the functional groups of hyperbranched polymers was of high interest to optimize material properties[24,136-138]. This is primarily achieved by polymer analogous reactions on performed hyperbranched polymer, for example as demonstrated in the alkyl modification of aliphatic[87] polyesters.

Aromatic and aliphatic hyperbranched poly(urea-urethane)s were reacted with different mono-isocyanates to modify their end groups as shown in Figure 4.23. End groups modification was carried out using phenyl monoisocyanate (Ph-NCO) as aromatic modifier, butyl monoisocyanate (Bu-NCO) as aliphatic modifier, and stearyl monoisocyanate (St-NCO) as long alkyl chain aliphatic modifier. The amount of OH groups present in the hyperbranched polymer was determined through integration of OH signals in the ^{1}H NMR spectrum. Accordingly, the equivalent amount of monoisocyante is used for modification reaction. At first, the ratio used for OH: NCO was 1: 1; then it was found that some of the monoisocyanat used for modification is consumed in side reactions. Different ratios of OH:

NCO was tried in order to obtain 100% modification. It was found that lower reaction times is needed in case of using Ph-NCO for complete modification of end groups than in case of using aliphatic modifiers. Using a catalyst instead of increasing reaction time in case of using Bu-NCO as modifier was successful and 100% modification was obtained. In case of using St-NCO as modifier not only catalyst was used but the reaction time was increased to 24 hours, which increase side reactions and affect the molar mass of the obtained modified polymer. Mostly, the hydrolysis of some of the used monoisocyanate to the corresponding amine occur as side reaction. The amine can further react with more monoisocyanate forming aromatic or aliphatic urea. Temperature of the modification reactions was kept at 30°C and DBTL was used to catalyse the reaction, especially in case of modification of aliphatic hyperbranched polymers.



R_1 = aryl of TDI or cyclhexyl of IPDI.
R_2 = H or CH_3 from DEA or DIPA
R_3 = Ph-, Bu- or Stearyl-isocyanate.

Figure 4.23: Modification reaction of aromatic hyperbranched polymer.

4.11.1 Characterization of modified polymers

Hyperbranched polymers prepared using different systems, were modified as mentioned before using Ph-NCO as aromatic modifier and Bu-NCO and St-NCO as aliphatic ones. Different reaction conditions were used in order to obtain high modification percentage. For the aliphatic hyperbranched polymers the percentage of modification is 100 in all cases (i.e. on using aliphatic or aromatic modifier) but of course the reaction needed catalysis. The obtained modified polymers showed good solubility in organic solvents except those modified with St-NCO due to non-polar long alkyl chain.

The molecular weight of the modified polymers is higher than that of the starting polymer also the polydispersity became higher. The modified polymer M(Ar-hpu1)-1 was prepared from sample (Ar-hpu1)-OH9, using ratio of 1:1 for OH: NCO. The sample was found to have a broad molar mass distribution like the parent polymer, but the molar mass is a little lower (Table 9). The given molar mass contains only the lower molar mass fractions since the GPC curve was so broad that the high molar mass fractions exceeded the elution volume of the column thus, it could not be evaluated. One also has to consider that the modification of the polymer sample results in a change in the hydrodynamic radius of the polymer in the GPC solvent due to different solvent interactions. It was found that the molar mass of the formed modified polymers depends to great extent on the reaction time. By noticing the value for molar mass and polydisperity for samples M(Ar-hpu1)-2 and M(Ar-hpu1)-3 which were prepared by modifying the polymer (Ar-hpu2)-OH2 using Ph-NCO. The first sample was prepared using ratio of polymer : modifier 1:2, reaction time was 5 hours and the obtained modified polymer had 100% modification. While, sample M(Ar-hpu1)-3 was prepared using ratio of 1:1 and the reaction proceeded 24 hours also 100% modification was obtained. Comparing molecular weights of the two samples we notice that sample M(Ar-hpu1)-2 has molar mass 4400 g/mol and low polydispersity while the second one M(Ar-hpu2)-3 has lower molar mass (1700 g/mol). So, increasing reaction time allows side reactions especially in presence of reactive isocyanate. In case of using Bu-NCO as modifier it took about 24 hours to obtain a polymer with 100% modification by using ratio of 1:2 [polymer: modifier, sample M(Ar-hpu1)-4]. On using St- NCO as modifier M(Ar-hpu1)-5 we could obtain only 70% modification due to steric hindrance and shielding effect.

Table 9: Characteristics of some of the prepared modified polymers.

Polymer	M_n g/mol	PDI
(Ar-hpu1)-OH9	14900	17.19
(Ar-hpu2)-OH2	4100	2.00
(Al-hpu1)-OH2	2800	3.18
M(Ar-hpu1)-1 [(Ar-hpu1)-OH8+PH-NCO]	13800	8.26
M(Ar-hpu2)-2 [(Ar-hpu2)-OH2+PH-NCO]	4400	1.57
M(Ar-hpu2)-3 [(Ar-hpu2)-OH2+PH-NCO]	1700	3.18
M(Ar-hpu2)-4 [(Ar-hpu2)-OH2+Bu-NCO]	3200	1.94
M(Ar-hpu2)-5 [(Ar-hpu2)-OH2+St-NCO]	----*	----
M(Al-hpu1)-1 [(Al-hpu1)-OH2+Ph-NCO]	3500	3.9
M(Al-hpu1)-2 [(Al-hpu1)-OH2+Bu-NCO]	2600	4.19
M(Al-hpu1)-3 [(Al-hpu1)-OH2+St-NCO]	----*	----

(Ar-hpu1)-OH9= TDI+DEA, (Ar-hpu2)-OH2= TDI+DIPA, (Al-hpu1)-OH2= IPDI+DEA.

* Solubility not enough for GPC analysis.

- ^{1}H NMR Characterization

Characterization of the modified polymers by ^{1}H NMR showed that 100% modification can be achieved on using phenyl isocyanate and butyl isocyanate as end groups modifiers. In case of St-isocyanate, a mixture of DMSO and $CHCl_3$ (1:1) was used to dissolve the long aliphatic chains of the modifier and 70% modification is obtained. From the ^{1}H NMR spectra shown in Figure 4.24 a-c we see that hydroxyl groups peaks present in the subunits I and t are found which are normally in the range of 5.4 to 5.04 ppm, respectively are disappeared completely due to the formation of new urethane groups as a result of the reaction of OH with NCO of the Ph-NCO and Bu-NCO respectively. Figure 4.24-d also shows ^{1}H NMR spectrum which belongs to the modification reaction of aromatic polymer with St-monoisocyanate, two small peaks at 5.1 and 5.4 ppm suggesting that the OH groups found in the terminal subunits are more susceptible for the modification reaction with monoisocyanate completely or partially forming new linear groups found at 5.4 ppm. Side reactions can also occur during modification with isocyanate due to its high reactivity. As mentioned before, some of the isocyanato-modifier is hydrolysed forming amine which may further react with another isocyanate group forming aromatic or aliphatic urea. In the second and third ^{1}H NMR spectra we see a peak at 5.7 and 5.55 ppm respectively, for aliphatic urea. The extent of the formation of side products depends on the reaction time and the amount of modifier.

Modified with Ph-NCO
100% modification

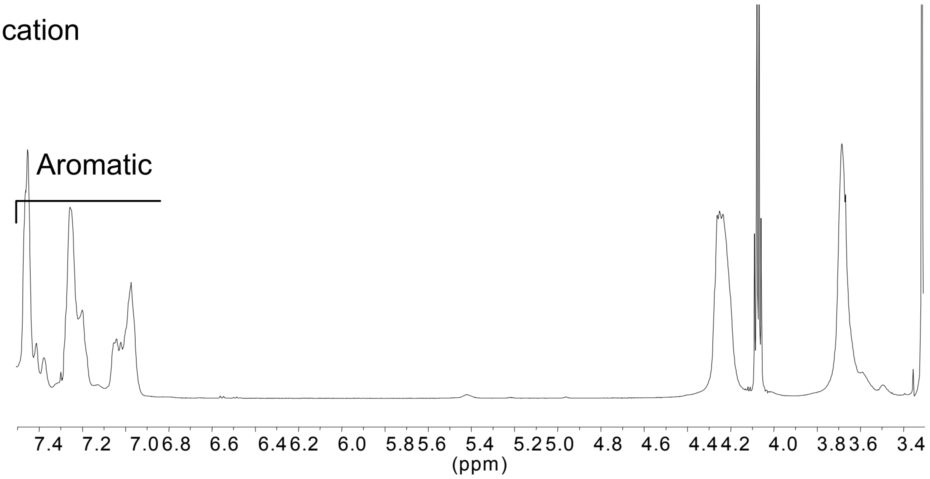


Figure 4.24-a: ^{1}H NMR spectra of hyperbranched polymers (Ar-hpu2)-OH2 modified with Ph-NCO in DMSO-d_6.

Modified with Bu-NCO

100% modification

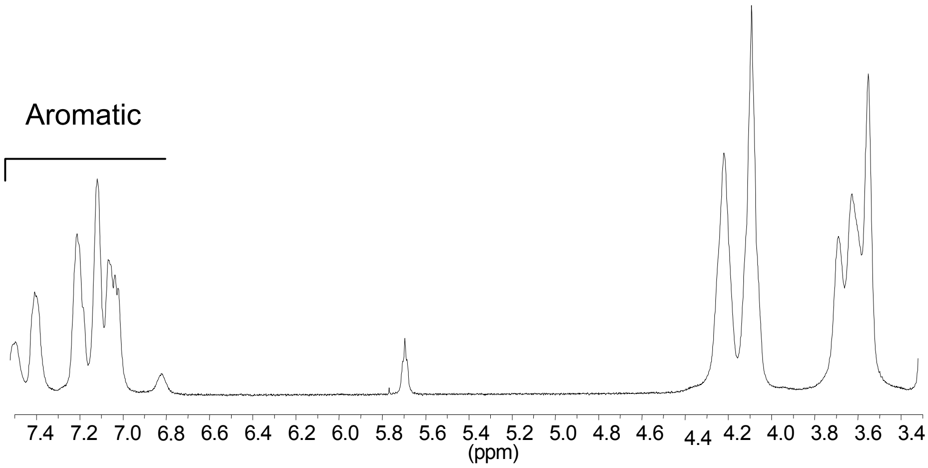


Figure 4.24-b: ^{1}H NMR spectra of modified hyperbranched polymers M(Ar-hpu2)-4 (DMSO-*d*$_6$).

Modified with St-NCO

70% modification

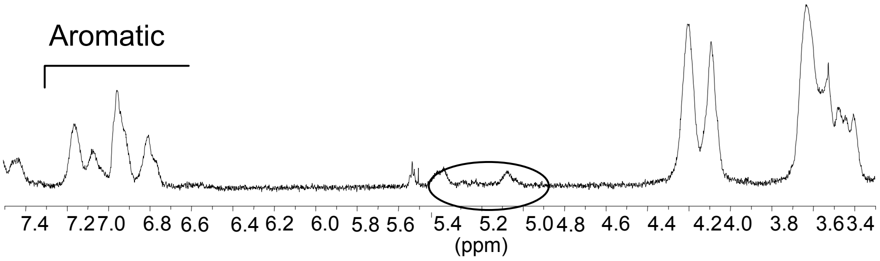


Figure 4.24-c: ^{1}H NMR spectra of modified hyperbranched polymers M(Ar-hpu2)-5 (DMSO-*d*$_6$/ CDCl$_3$).

- Fractionation of modified aromatic polymer

Fractionation of a modified hyperbranched polymer was performed in order to help in structural analysis. The same preparative fractionation procedures as mentioned before were used for the modified polymer M(Ar-hpu1)-1. There were no solubility problems during the fractionation process as the fractions obtained were all completely soluble. Due to the fact that the end groups are modified to urethane linkages, and there is a lower chance for side reactions. THF was used as good solvent and hexane as non-solvent, 20 fractions were obtained as shown in Figure 4.25. Fractions 1- 8 do not contain anything of the polymer since they represent higher concentrations of non-solvent and lower concentration of good-solvent. From fraction 10 (ratio of hexane: THF 50% : 50%) polymer fractions starts to be separated. The molar masses of the fractions were determined using GPC/RI and PVP as linear standard. The values of molecular weight distribution showed that the fractions have low polydispersity except fractions 19 and 20 (Table 10).

Table 10: M_n and PDI for some Fractions, GPC/RI.

Fraction no.	M_n (g/mol)	PDI
15	2200	1.73
16	2500	1.70
17	3000	1.69
18	5200	1.32
19	13400	4.83
20	20000	6.20

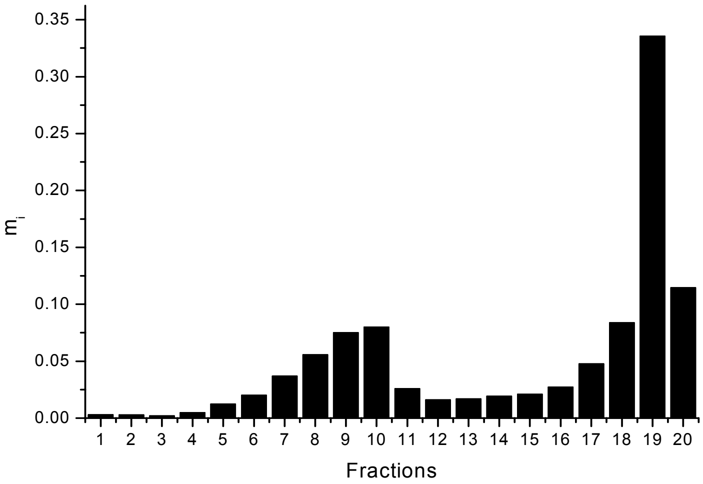


Figure 4.25: Fractionation of modified polymer M(Ar-hpu1)-1.

Succeeding in the fractionation process gives the opportunity to use one of the fractions as standards for calibration of the GPC column coupled with light scattering detector (LS) during molar mass determination of hyperbranched polymers[170] which would give more reliable values for molecular weight of hyperbranched materials under investigation.

^{1}H NMR was used to characterize the obtained fractions. Fraction 9 is identified as the low molecular weight by-product formed through the side reaction of hydrolysed isocyanat with a new molecule of monoisocyanate (Figure 4.26). The amount of the diphenyl urea as by-product was determined to be 42% of the polymer while the rest (58%) is the macromolecule itself. This means that about 40% of the monoisocyanate is consumed through side reactions, which should be taken into account during modification reactions. The other fractions were found to have the same structural units as the hyperbranched macromolecule (as an example Figure 4.27).

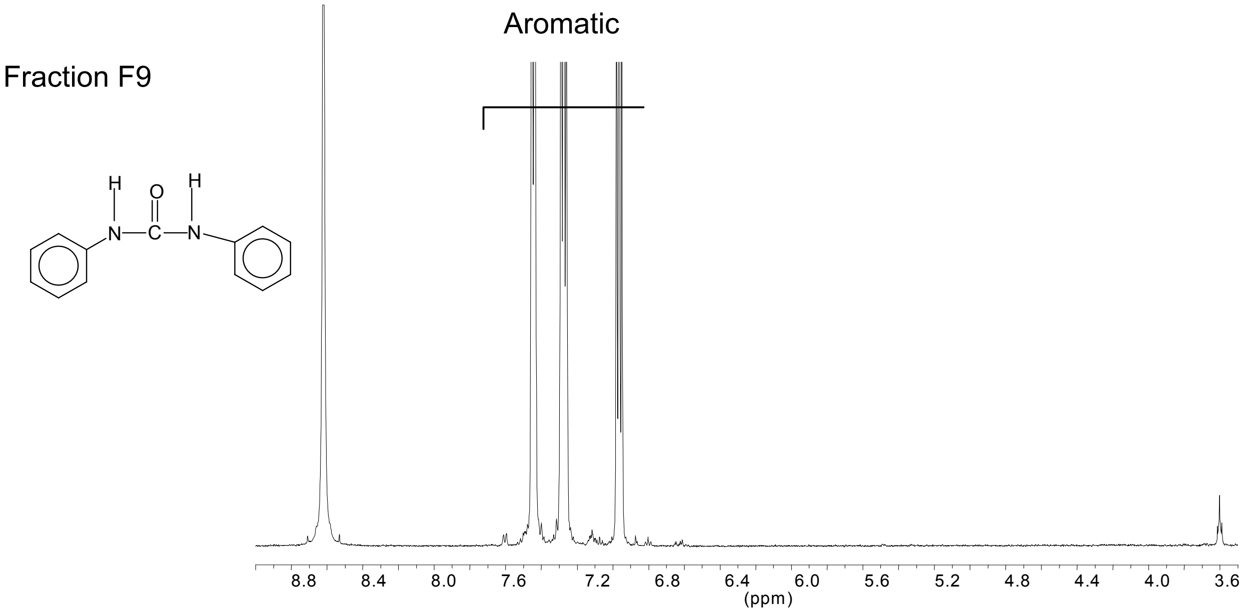


Figure 4.26: ^{1}H NMR spectrum of a fraction product identified as diphenylamine in DMSO-d_6.

F20 high molecular weight fraction
M_n = 20000 g/ mol

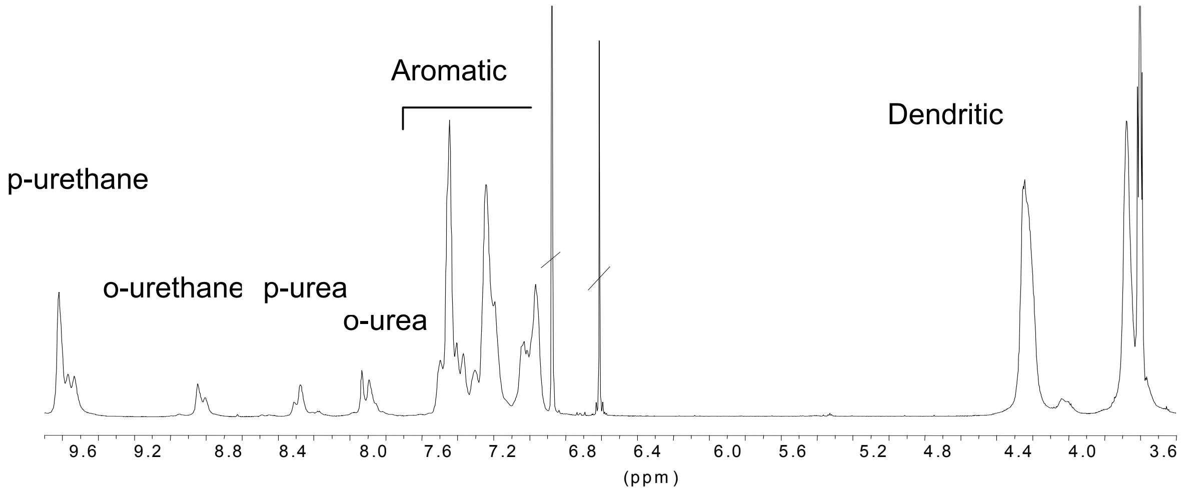


Figure 4.27: ^{1}H NMR spectrum of a fraction product showing the different subunits of M(Ar-hpu1)-1 polymer in DMSO-d_6.

4.11.2 Following the modification reaction using in-situ FT-IR spectroscopy

The use of IR spectroscopy as a tool to follow chemical reactions and processes in real time becomes a practical reality when modern FTIR instrumentation and software are combined with fiber-optic probes. Spectroscopic data can be obtained directly from reactors and used to derive kinetic and mechanistic information, and to monitor processes and determine end-points, even in cases where the detailed chemistry of a system is not fully understood. The instrument we used is based on mid-infrared Fourier transform infrared (FTIR) spectroscopy. During the modification reaction we faced the problem of the hydrolysis of part of the monoisocyanate modifier and formation of diphenyl- or dialkyl urea. Consequently, some of the modifier was consumed in this side reaction. For optimisation of the reaction in-situ FT-IR measurements were carried out during the modification of an TDI/EDA sample with Ph-NCO. This allows to identify the ideal reaction time and amount of modifying agent. The decrease of the modifier amount (Ph-NCO) through the reaction with OH end groups could be followed through the decrease in the NCO group (peak at 2261 and 2281 cm^{-1}) and formation of the new urethane group (peak at 1709 cm^{-1}) as can be seen in Figure 4.28.

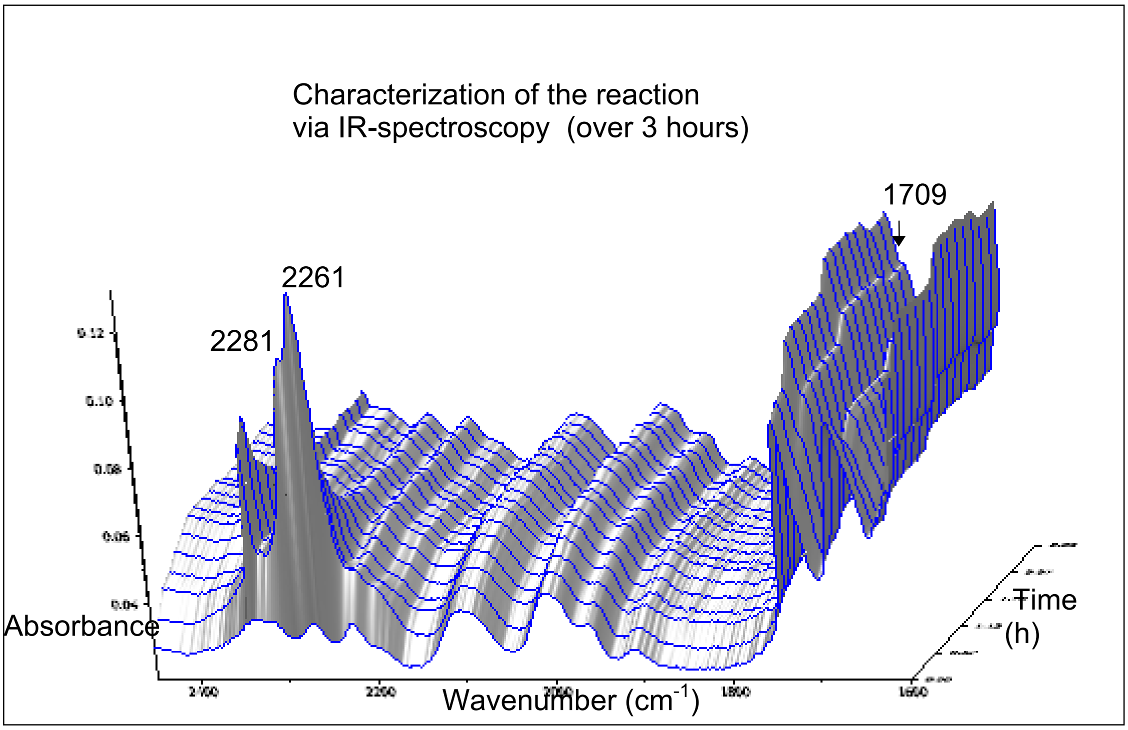


Figure 4.28: In-situ FT-IR for modification reaction of aromatic hyperbranched polymer.

Solvent used in this experiment was DMSO which unlike DMAc has no amide groups that can overlap with the urethane peaks. Since the new urethane vibration band appears as shoulder to the urethane groups of the polymer (peak at 1721 cm^{-1}), it was difficult to integrate the area under peak and make complete kinetic investigations. Using this method quantitatively is possible when a calibration curve is constructed between absorbance and concentration of isocyanate group. Such curve needs time and many specific experiments are necessary to be carried out. With the help of such curve, we can also determine the exact time required to complete the modification reaction. In our system this kind of calibration was not an easy task since the decrease of intensity of NCO bands is not only a result of the reaction with OH end groups. The difficulty of calibration arises also from two reasons. First, part of the used isocyanate was consumed through the side reaction which should be taken into account during calculation. Second, CO_2 is evolved as a result of hydrolysis of isocyanate in presence of traces of water (which was used to precipitate the polymer). For the mentioned reasons complete quantitative measurement could not be done. More work is necessary in order to avoid moisture in the which might hydrolyze the used monoisocyanate and hence affect the results.

4.12 Interactions between polymer molecules

Intramolecular interactions are interactions within the same molecule while intermolecular ones are the interactions between the polymer chains. Hyperbranched polymers which have OH end groups, such as hyperbranched polyesters, show hydrogen bonding interactions within the molecule and between the chains. Hydrogen bonding can affect the chain length, chain packing, rigidity, and molecular order. Infrared spectroscopy was extensively employed to study the hydrogen bonding and was demonstrated as a powerful tool in identifying the characteristics of hydrogen bonding[171-174]. The hydrogen bonding is characterized by a frequency shift to values lower than those corresponding to the free groups (i.e. no hydrogen bonding). Meanwhile, the extent of the frequency shift is usually used to estimate the H-bonding strength. Particularly polyether-based thermoplastic polyurethanes, several studies have attempted to elucidate the relationships between structure and properties within it using FTIR[173]. In case of hyperbranched poly(urea-urethane)s, due to high polarity of the OH end groups and the presence of both urea and urethane groups as functional groups in the polymer backbone, hydrogen bonding appear to be the main cause for inter- and intramolecular interactions. Hydrogen bonding can be formed between nitrogen in an urea linkage with hydrogen of amino group [structure (1)], between oxygen atom of urethane group and hydrogen of hydroxyl group [structure (2)], or between oxygen of urea linkage and hydrogen of hydroxyl group [structure (3)], or H-bonding can be between oxygen of urethane group and hydrogen of amino group [structure (4]). The different possibilities for hydrogen bonding in poly(urea-urethane)s are shown in Figure 4.29. FT-IR was used to study the effect of temperature on the hydrogen bonds present in aromatic and aliphatic hyperbranched polymers as well linear analogs for comparison. The polymer samples were heated from 30°C up to 160°C and cooled. The polymers show absorption bands at wavenumbers 3270, 1618 and 1526 cm^{-1} which are attributed to νNH+νOH, νC=O of urea amide I, and νC-N + δN-H amid II of urea and urethane, respectively. It was confirmed by several analysis that the sample used (Ar-hpu1)-OH5 showed no degradation in the used temperature regime (heating up to 160°C and cooling again). From the FT-IR measurements (Figure 4.30) we found that there is no change in wavenumber with increase of temperature for stretching vibration of groups C=O urethane amide I at 1707cm^{-1} and νC–C aromatic at 1602cm^{-1}. Due to the changes observed in case of νNH+ νOH (3270 cm^{-1}), νC=O urea amide I (1618cm^{-1}) and ν(C–N)+ δ(N–H) amide II of urea, it is suggested that hydrogen bonds are mainly formed between hydroxyl groups and amide groups of urethane or urea groups (Figure 4.29). It was noticed that all the changes are fully reversible i.e. the broken hydrogen bonds due to heating are reformed through cooling.

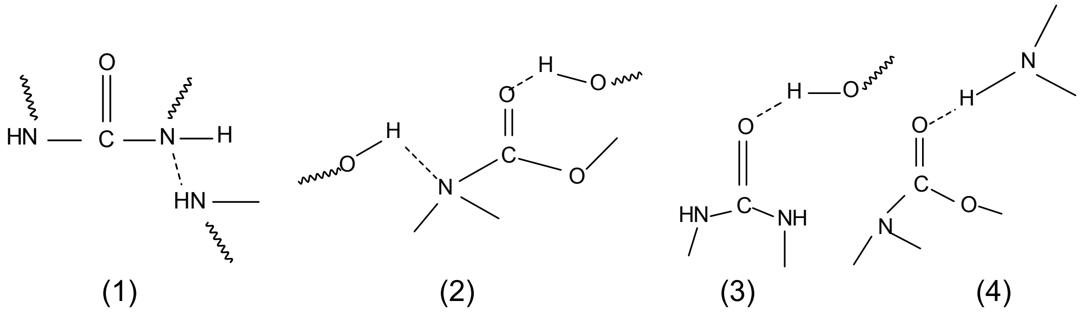


Figure 4.29: The different possibilities for hydrogen bonding.

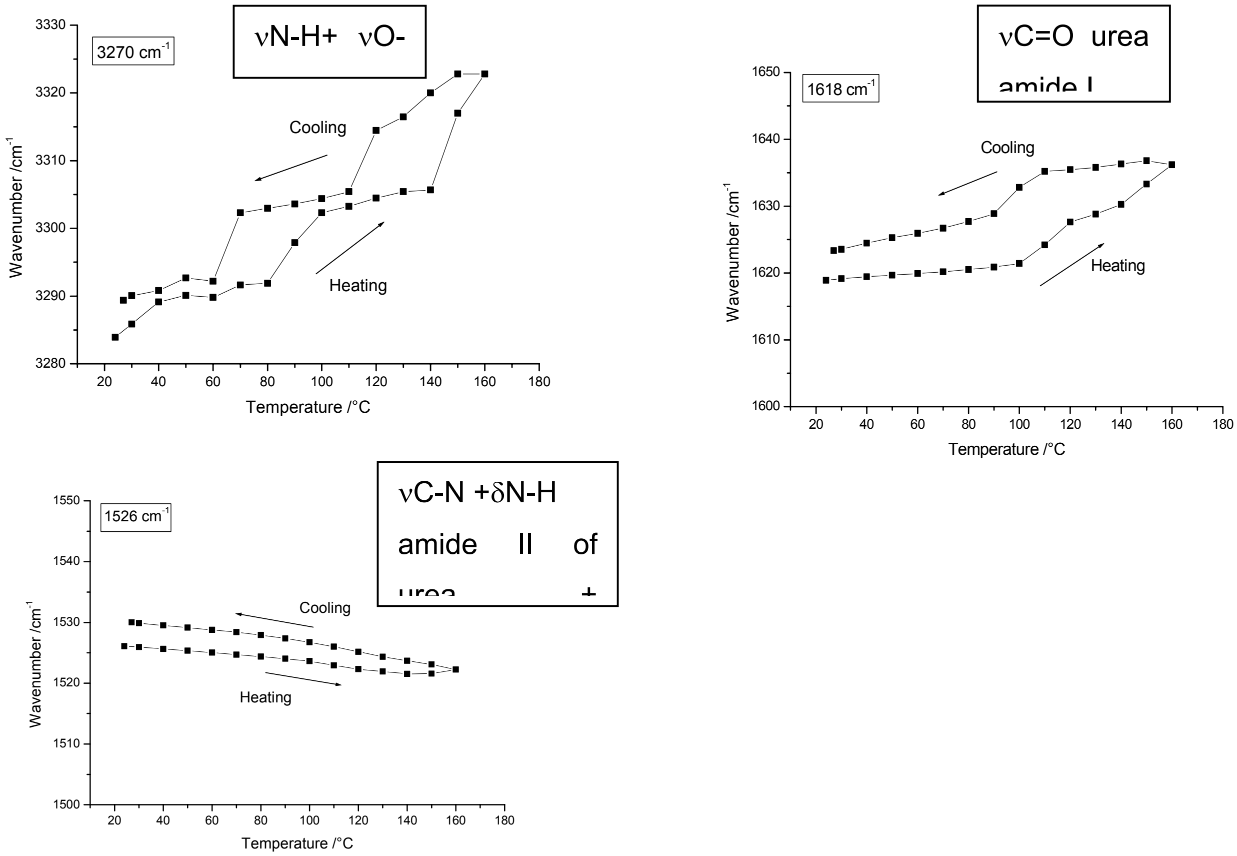


Figure 4.30: Wavenumber-temperature dependence of IR-spectra (different sections) for aromatic hyperbranched polymer.

The effect of H-bonding interactions in case of aliphatic hyperbranched polymers was studied and it was found that there is no change in the wavenumber with the increase of temperature for the stretching vibration of the carbonyl group of urethane amide I at 1700 cm^{-1} and νC=O urea amide I at 1624 cm^{-1}. The effect is more significant for the stretching vibration of the groups ν NH+ νOH at 3324 cm^{-1} and combination vibration of C–N stretching and N-H bending (amide II) (Figure 4.31). These intramolecular interactions in the polymer are fully reversible i.e. the hydrogen bonds which breaks at high temperatures are formed again on cooling. Also, as in case of aromatic hyperbranched polymers, no degradation was observed during investigations.

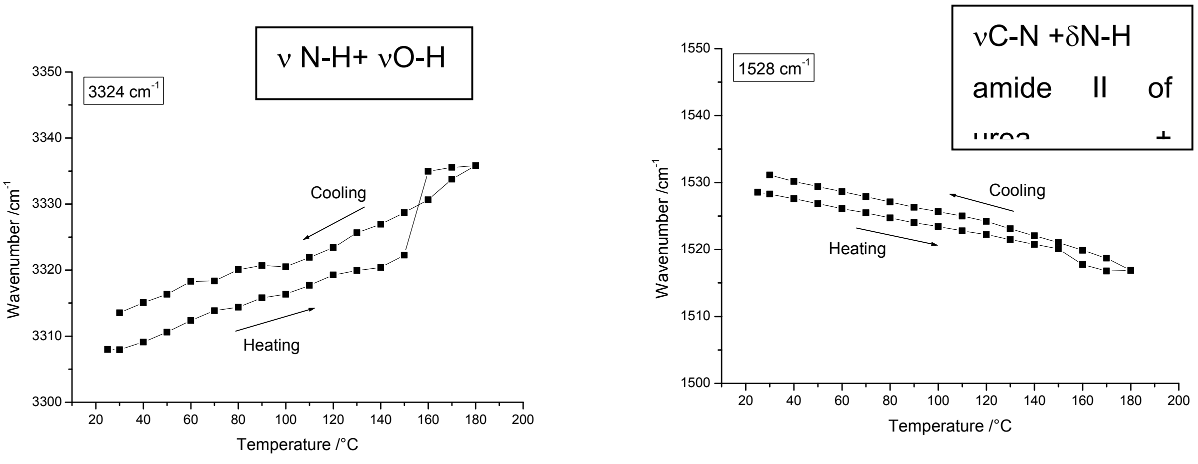
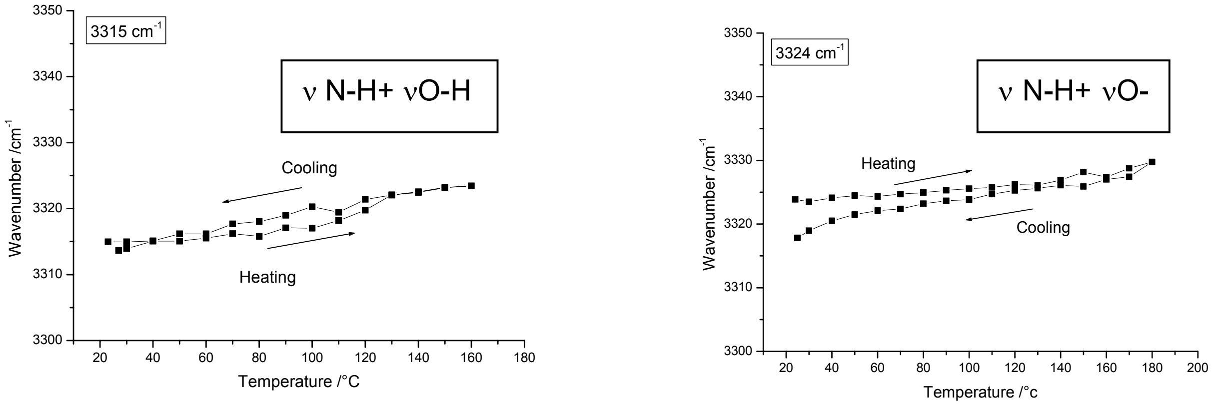


Figure 4.31: Wavenumber-temperature dependence of IR-spectra (different sections) for aliphatic hyperbranched polymer.

For linear aromatic and aliphatic polymer analogs it was found that there is no change in the wavenumber-temperature curves for the absorption bands of νC=O urethane amide I at 1705 cm^{-1}, νC=O urea amide I at 1650 cm^{-1} and νC–C aromatic at 1600 cm^{-1}. There is a slight change in case of the band found at 3315 cm^{-1} (Figure 4.32) which is equivalent to stretching vibration of both NH and OH groups. On comparison of the change in the absorption-temperature dependence curves in case of hyperbranched and linear aromatic polymers we notice that it is more obvious in case of hyperbranched polymers due to the fact that they contain higher number of OH groups than the linear analogs.



(a) (b)

Figure 4.32: Wavenumber-temperature dependence of IR-spectra (different sections) for aromatic (a) and aliphatic (b) linear polymers, respectively.

4.13 Thermal Analysis

4.13.1 Differential Scanning Calorimatry (DSC)

Glass transition temperature (T_g) was determined by DSC using heat program up to 160 ^{o}C and only in some cases up to 200°C verifying first that no major degradation occurred (Table 11). The second heating curve was used for T_g evaluation. As it is known, the glass transition temperature depends on number of factors which affect rotation of chain links, mobility, and chain-chain interaction. These factors include molecular structure, molar mass, degree of branching, nature of end groups, and interactions like hydrogen bonding within the polymer structure. The studied hyperbranched polymers did not show any melting in the observed temperature regime. However, as a first surprise, in general our aromatic hyperbranched polymers gave T_g in the range of 100°C. Furthermore, the T_g values are affected by the molar mass of the polymer and the amount of OH groups present as end groups whereas differences in degree of branching DB had no major effect. Thus (Ar-hpu1)OH1 shows a T_g of 118^{o}C and (Ar-hpu1)OH3 of 117^{o}C, even though the DB differed by 10%. In general, the T_g leveled of when a certain molar mass in the range of about 4000 g/mol was reached. Therefore, especially for the polymer (Ar-hpu1)-OH6, which has T_g value of 12°C since it has low M_n value and large solvent content which affect the value of T_g. An increase in molar mass of less than 1000 g/mol raised the T_g to about 65^{o}C. A second surprise was that the incorporation of DIPA instead of DEA had nearly no effect at all. That confirms the assumption that mainly polar interactions within the polymer chain determine the T_g and not the sterical features of the monomer structure.

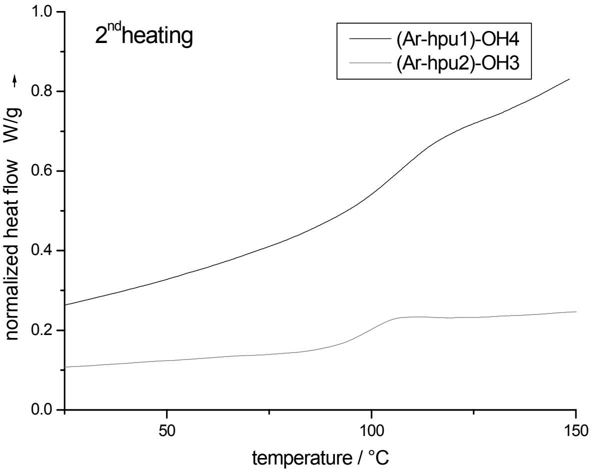


Figure 4.33: DSC of two samples prepared from the systems (Ar-hpu1)-OH4 and (Ar-hpu2)-OH3.

Table 11: T_g values as measured by half step point

Polymer	M_n (g/mol)	T_g /°C
(Ar-hpu1)OH1	6100	118
(Ar-hpu1)OH2	6700	116
(Ar-hpu1)-OH3	9700	117
(Ar-hpu1)-OH4	9100	107
(Ar-hpu1)-OH5	3100	85
(Ar-hpu1)-OH6	2600	12
(Ar-hpu2)-OH1	1200	97
(Ar-hpu2)-OH2	4100	128
(Ar-hpu2)-OH3	5300	110

Aliphatic hyperbranched polymers showed higher T_g values in comparison to those obtained for aromatic hyperbranched polymers. A possible explanation might be the bulky and rather rigid structure of IPDI cyclohexyl ring but also the existence of hydrogen bonding between urea and urethane groups and the hydroxyl end groups. The effect of molar mass on the value of T_g is obvious in the lower molar mass products of the aliphatic isocyanate IPCI in which the molar mass effect was very dramatic: the oligomers had T_g values below 0^oC (-22 and 29^oC) and an increase in molar mass of less than 1000 g/mol raised the T_g to about 65^oC Table (12). One can assume that the T_g plateau level is not yet reached for (AL-hpu3)-OH and (AL-hpu4)-OH and finally values comparable to the products from IPDI might be achieved.

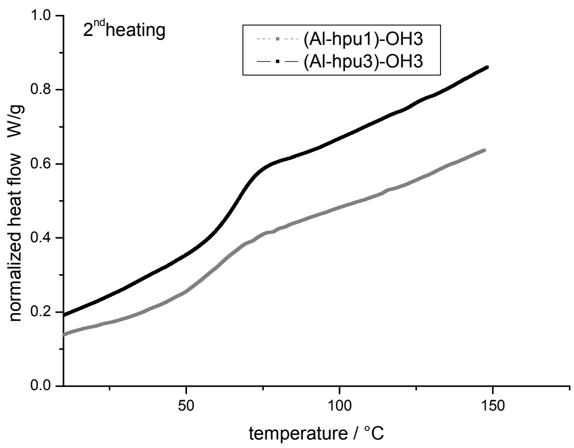


Figure 4.34: DSC of two samples prepared from the systems (Al-hpu1)-OH3 and (Al-hpu3)-OH3.

Table 12: T_g values of some (Al-hpu)-OH.

Polymer	M_n (g/mol)	T_g /°C
(AL-hpu1)-OH3	9200	130
(AL-hpu1)-OH4	5800	133
(AL-hpu2)-OH1	4900	124
(AL-hpu2)-OH2	2000	99
(AL-hpu3)-OH1	1600	-23
(AL-hpu3)-OH3	2200	66
(AL-hpu4)-OH1	1000	-30
(AL-hpu4)-OH3	1600	65

Differential scanning calorimetry was also used to measure the glass transition temperature for the modified hyperbranched polymers of both types aromatic and aliphatic. As mentioned before the modification was carried out using Ph-NCO as aromatic modifier and Bu-NCO and St-NCO as aliphatic modifier. The effect of modification and inserting of a new end group in the polymer chains is very obvious on T_g (Table 13). Generally, the modified polymers have T_g values lower than the pure polymers. The reason for that is the presence of polar end groups in the polymer chain increases their glass transition temperature due to the intra and intermolecular interactions. Noticing the values depicted in Table 13, we find that samples 1 and 2 modified with Ph-NCO have nearly the same T_g while sample 3 has lower value due to the decrease in the polymer molecular weight. Inserting an aromatic ring increases T_g value more than in case of inserting alkyl group since the bulky phenyl groups hinders the chain motions. On using modifiers with long alkyl chains like St-

NCO (CH_3-$(CH_2)_{17}$-NCO), glass transition disappears and melting transition of the long alkyl chain can be observed (Figure 4.35).

Table 13: Values of T_g for some modified aromatic and aliphatic hyperbranched polymers.

Polymer	M_n (g/mol)	T_g /°C
M(Ar-hpu1)-1 [(Ar-hpu1)-OH8+PH-NCO]	13800	113
M(Ar-hpu2)-2 [(Ar-hpu2)-OH2+PH-NCO]	4400	114
M(Ar-hpu2)-3 [(Ar-hpu2)-OH2+PH-NCO]	1700	102
M(Ar-hpu2)-4 [(Ar-hpu2)-OH2+Bu-NCO]	3200	80
M(Ar-hpu2)-5 [(Ar-hpu2)-OH2+St-NCO]	----	T_m= 117
M(AL-hpu1)-1 [(AL-hpu1)-OH2+Ph-NCO]	3500	92
M(AL-hpu1)-2 [(AL-hpu1)-OH2+Bu-NCO]	2600	73
M(AL-hpu1)-3 [(AL-hpu1)-OH2+St-NCO]	----	T_m= 114

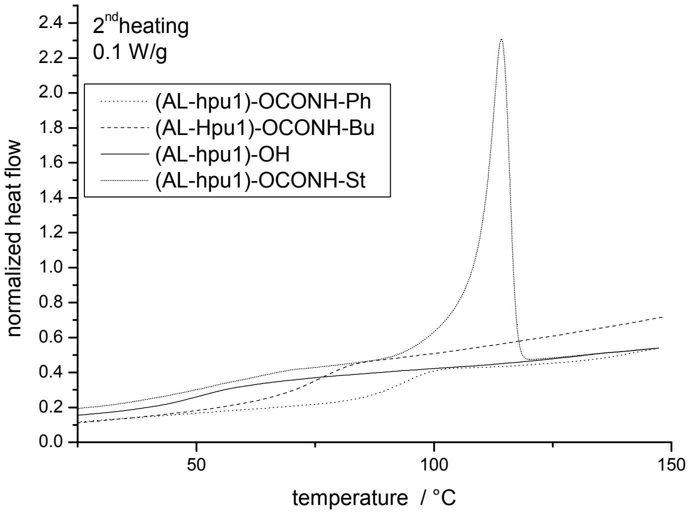


Figure 4.35: DSC traces of pure (Al-hpu1)-OH and its modified forms.

Glass transition temperatures were measured for linear polymers and are shown in Table 1. It was found that T_g for hyperbranched polymers is lower than that obtained for linear polymers either aliphatic or aromatic. As mentioned before there are many factors affecting T_g among these factors branching and chain flexibility. The flexibility of the chain is undoubtedly the most important factor influencing T_g. It is a measure of the ability of a chain to rotate about the constituent chain bonds, hence flexible chain has a low T_g whereas rigid chain has a high T_g. In our case the presence of branches in the hyperbranched polymer increase chain flexibility and hence lower T_g. For aliphatic hyperbranched polymers due to the rigid cyclohexyl ring, the polymers have relatively higher T_g than that of aromatic ones and the same trend can be noticed for the linear analogs.

4.13.2 Thermo Gravimetric Analysis (TGA)

Thermal stability of all polymer series was studied by thermal gravimetric analysis (TGA) in a temperature program 50-700 °C with heating rate 10 K/min and using N_2 gas as inert atmosphere. TGA showed that hyperbranched polymers have relatively good thermal stability up to 160°C then the degradation starts till maximum at about 200 °C. Of course the temperature for maximum degradation depends on the polymer structure whether the polymer is linear or hyperbranched[23]. It was noticed that (Al-hpu)-OH polymers have higher thermal stability than (Ar-hpu)-OH polymers, but linear aromatic polymers are the most stable ones. Figure 4.36 shows thermogram of some different polymer systems. From the following thermogram we notice that the aromatic hyperbranched polymer has sharp degradation slope. Which means that they suffer degradation more quickly than the aliphatic ones due to the presence of the aromatic ring which facilitate the ease of degradation. Temperatures at which 10% weight loss is achieved for some selected polymer are given in Table 14.

Table 14: $T_{10\%}$ for some selected polymers.

Polymer	T /°C (10% wt. loss)
(Ar-hpu1)-OH4	207
(Al-hpu1)-OH4	234
(Al-hpu3)-OH3	226
Ar-LPU (2)	237
Al-LPU (8)	253
M(Ar-hpu1)-2	200
M(Ar-hpu2)-4	210
M(Ar-hpu2)-5	230

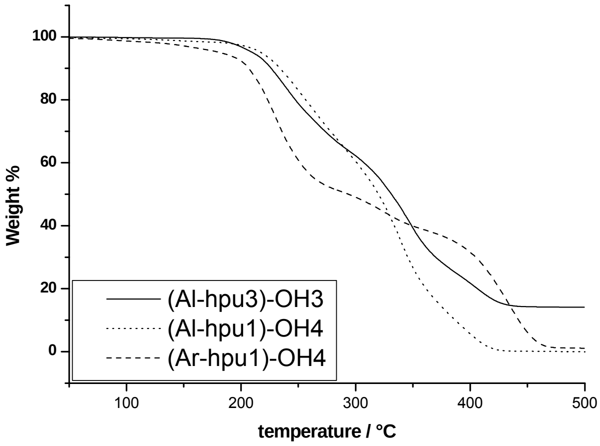


Figure 4.36. TGA traces for three different polymers systems.

Incorporation of phenyl group at the end of the polymer chains through modification may decreases polymer stability due to the reactivity of aromatic ring (compare samples (Ar-hpu1)-OH4 and M(Ar-hpu1)-2, table 14). The effect of change of end groups on the stability of the polymer appears more obvious when we compare the degradation temperatures of the polymer modified by Bu- or St- groups. From the temperature values of 10% wt. loss for samples M(Ar-hpu2)-4 (modified with Bu-NCO) and M(Ar-hpu2)-5 (modified with St-NCO) we notice that increase of the length of alkyl chain as end group increases thermal stability of the polymer.

4.14 Viscosity measurements

When a polymer dissolves in a liquid, the interaction of the two components stimulates an increase in polymer dimensions over that in the unsolvated state. Because the vast difference in the size between solvent and solute, the frictional properties of the solvent in the mixture are drastically altered, and an increase in viscosity occurs which should reflect the size and shape of the dissolved solute, even in dilute solutions. One of the first properties of hyperbranched polymers is that their solution behavior differs from the linear polymers. It is known that they have lower solution viscosity in comparison with their linear analog and this is consistent with highly branched and compact structure. Relative viscosities are usually determined indirectly by performing separate measurements on the pure solvent and the polymer solutions using the same viscometer. Capillary viscometers have many advantages when compared to other types of viscometers. They are of relatively simple construction and require only small volumes of polymer solution whose viscosity is to be measured. Temperature is controlled by placing the viscometer in a thermostated water bath. Two general classes of capillaries have found use, namely U-tube viscometer and suspended level viscometers. In this study an Ubbelohde viscometer is used. Viscosity measurements of hyperbranched aromatic and aliphatic polymers and their linear analogs were made to compare the relative viscosity of hyperbranched polymers with the linear ones, the determined values are given in Table 15. Polymer solutions were prepared by dissolving the polymer in DMAc at 25°C with concentration of 0.2 g/dl. The polymer solutions were filtered before the measurements. By noticing the values of samples Ar-LPU5 and (Ar-hpu1)-OH8 which have M_w values comparable to each other, we notice that $\eta_{rel.}$ for the linear polymer is higher than the hyperbranched one. The same trend we can see on comparing η_{rel} for samples Ar-LPU2 and (Ar-hpu1)-OH1. Although the difference in solution viscosity values for hyperbranched polymers and linear polymers is not high specially in case of aliphatic polymers, but the trend is maintained in favor of hyperbranched polymers. In general, one can conclude that our hyperbranched systems have solution viscosity values lower than that of the linear polymers of compared values of weight average molecular weight.

Table 15: Relative viscosity data for both hyperbranched and linear polymers.

Ar-polymer	M_w (g/mol)	η_{rel}	Al-polymer	M_w (g/mol)	η_{rel}
(Ar-hpu1)-OH8	11700	1.253	(Al-hpu1)-OH6	5000	1.172
(Ar-hpu1)-OH1	16100	1.272	(Al-hpu1)-OH1	8400	1.193
(Ar-hpu1)-OH4	55250	1.416	(Al-hpu1)-OH5	8200	1.201
(Ar-hpu1)-OH7	77700	1.768	(Al-hpu2)-OH1	14500	1.233
Ar-Lpu2	16400	1.342	Al-hpu6	5000	1.234
Ar-Lpu3	6300	1.299	Al-hpu7	6700	1.250
Ar-Lpu4	8500	1.265	Al-hpu9	7600	1.283
Ar-Lpu5	10000	1.308	Al-hpu8	10900	1.316

Of course, one have to discuss these results carefully since we know that at least the M_w values of hyperbranched polymers might have a high error (determined by SEC). However, in general, one can assume that the real M_w of HPU are even higher than the given ones which leads to an even stronger reduction in solution viscosity.

4.15 Rheological properties

Rheology is the science of deformation and flow. Because the close relationship between rheology and processing properties, characterization of the rheological flow behavior of dendritic polymers is important. Such studies can provide insights into the intermolecular interactions and the effects that molecular variables such as nature of end groups and degree of branching have on the bulk properties. It was reported[175] that the rheological behavior of poly(ether-imide) and aliphatic polyester hyperbranched polymers ranges from Newtonian to viscoelastic. This behavior is affected by molecular variables such as DB and M_w, however, the molecular architecture appears to be the most important factor determining the nature of the intermolecular interactions and consequently the rheological behavior. For a system such as hyperbranched aliphatic polyesters based on bismethyl propionic acid[176], it was found that it is characterized by a Newtonian behavior in the molten state i. e. no shear thinning is observed, indicating a lack of entanglements for these polymers. Hyperbranched poly(ether amide)s with OH end groups and their modified ones were examined also rheologicaly[177]. It was found that the unmodified polymers have rather high complex viscosity at low frequencies with no leveling out. Therefore, no reliable zero shear viscosity data could be determined. The acetate modified polymers showed melt viscosity values significantly lower than the unmodified ones. A similar effect was observed for hyperbranched polyesters with phenol and alkoxy end groups[178]. Whereas the products with phenolic end groups showed a frequency dependency of the complex melt viscosity, the products with alkyl end groups exhibited Newtonian behavior at low stress. This means that melt viscosity of hyperbranched polmers might be strongly affected by polar interactions of functional groups, and in this case hyperbranched polymers with polar end groups exhibited elastic behavior in the melt.

In this part we investigated the rheological parameters, storage modulus (G') and complex viscosity (η^*) of some hyperbranched and linear poly(urea-urethane) samples (Table 16), and studied the effect of end group modification on the melt behavior of the polymers

.

Table 16: Polymer systems used for rheological properties measurements.

Polymer	M_w (g/mol)	PDI
Ar-LPU(2)	16400	1.80
(Ar-hpu1)-OH4 (TDI+ DEA)	56800	6.24
M(Ar-hpu2)-2 (modified with Ph-NCO)	6900	1.57
Al-LPU(7)	6700	1.90
(Al-hpu2)-OH1 (IPDI+ DIPA)	14700	2.29
M(Al-hpu2)-2 (modified with Bu-NCO)	10890	4.19

Storage modulus G' and η* of (Ar-hpu1)-OH4 and M(Ar-hpu2)-2 (modified with Ph-NCO) were determined at temperature 30°C above T_g for each sample and are plotted in Figure 4.37 and, Figure 4.38. It can be noticed that the dynamic mechanical modulus of (Ar-hpu1)-OH4 is increased by the incorporation of (Ph-NCO) due to increase of the bulkiness of the chains even though molar mass is decreased.

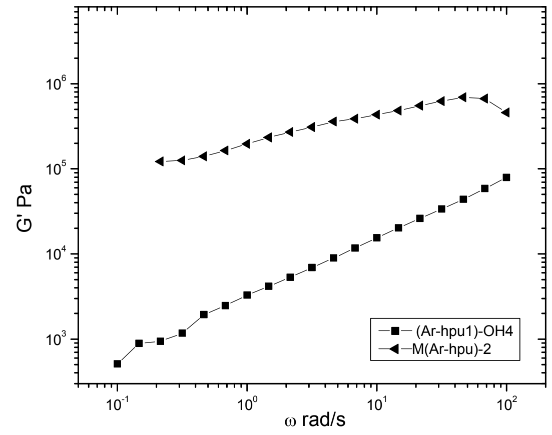


Figure 4.37: G' of (Ar-hpu1)-OH4 and M(Ar-hpu2)-2

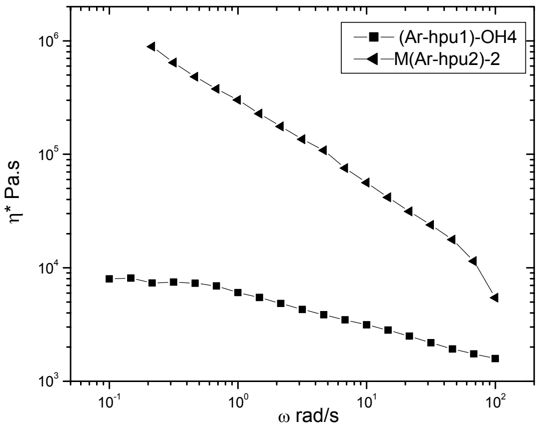


Figure 4.38: η* for both (Ar-hpu1)-OH4 and M(Ar-hpu2)-2

In addition, η* of M(Ar-hpu2)-2 is higher than this of (Ar-hpu1)-OH4 and η* of M(Ar-hpu2)-2 deviates strongly from the Newtonian plateau at low frequency. This must be owing to a lowering in the mobility of the modified aromatic hyperbranched chains. Previous melt rheologhy studies for hyperbranched polyester with OH end groups and those modified with alkyl long chains showed[178] that the complex viscosity of the modified polymers is lower than that of the unmodified polymers. Clearly, this in contrast to our results which means that the effect of OH end groups in our polymer systems is not pronounced and the melt viscosity is more affected by polar interactions within the polymer chains and the structural units.

The storage modulus G' and complex viscosity η*of linear aromatic polymer Ar-LPU(2) and (Ar-hpu1)-OH4 are plotted in Figure 4.39 and Figure 4.40. In these Figures the storage modulus of the hyperbranched polymer is higher than the linear one due to the effect of the branches. This effect is seen also in η* of (Ar-hpu1)-OH4 as compared to η* of Ar-LPU(2). As shown in Figure 4.40, η* of (Ar-hpu1)-OH4 is 2 order of magnitudes higher than Ar-LPU(2) over the entire frequency range.

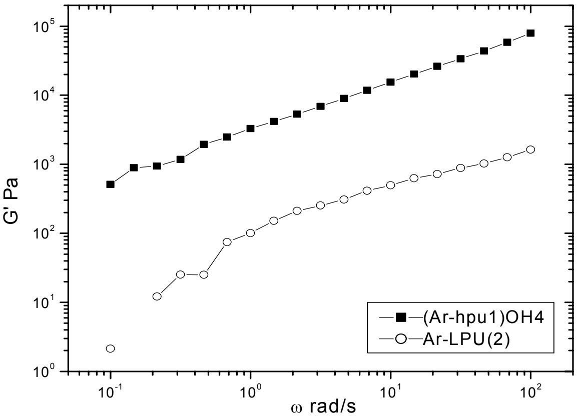


Figure 4.39: G' of (Ar-hpu1)-OH4 and Ar-LPU (2)

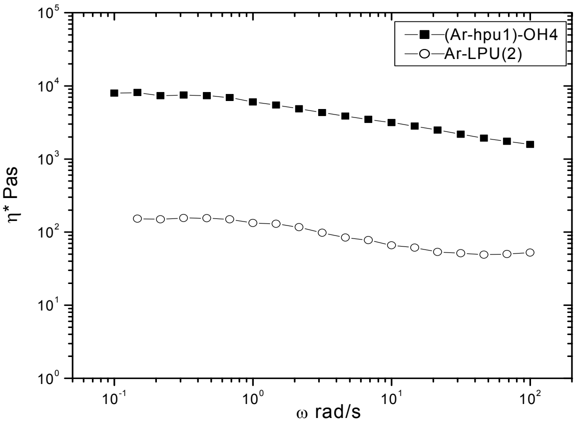


Figure 4.40: η* vs. frequency for both (Ar-hpu1)-OH4 and Ar-LPU (2).

Again this behavior is in contrast to expectations; the melt viscosity of hyperbranched polymers should be lower than that of the linear analogue. However, in our case the molar mass of (Ar-hpu1)-OH4 [M_w = 56800 g/mol] is much higher than that of the linear polymer [M_w = 16400 g/mol] which might explain the higher melt viscosity. Also higher η* values for hyperbranched polymers are often found when stronger polar interactions exists than in the linear polymers. Our hyperbranched polymer systems showed significant inter and intramolecular interactions as investigated with FT-IR (see section 4.12). Those interactions are probably also responsible for the found higher complex viscosity.

The storage modulus, G' of aliphatic (Al-hpu2)-OH1 and modified polymer M(Al-hpu2)-2 (modified by Bu-NCO) is presented in Figure 4.41. It shows clearly the effect of the aliphatic modifier (Bu-NCO) since the dynamic mechanical modulus of the M(Al-hpu2)-2 is again higher than that of (Al-hpu2)-OH1 over the entire frequency range. Figure 4.42 presents η* of M(Al-hpu2)-2 and (Al-hpu2)-OH1 as a function of frequency. For both samples η* decreases monotonically with increasing ω and drops by many orders of magnitude but some leveling off at low frequency is found.

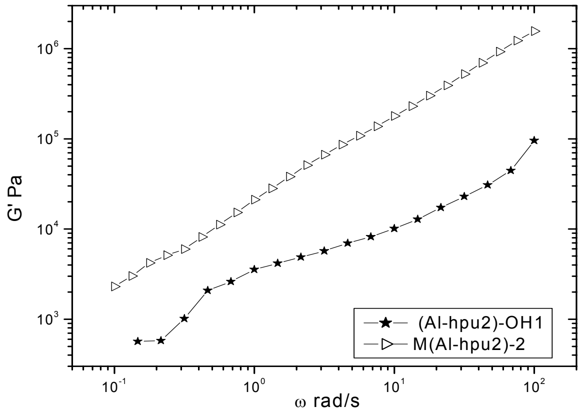


Figure 4.41: G' vs. ω for (Al-hpu2)-OH1 and M(Al-hpu2)-2.

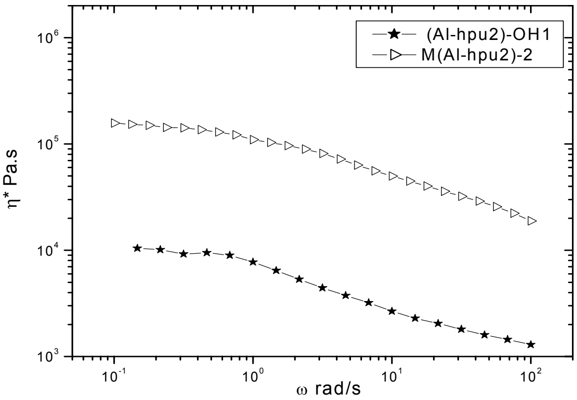


Figure 4.42: η* vs. ω for (Al-hpu2)-OH1 and M(Al-hpu2)-2.

Again, significant increase in η* of M(Al-hpu2)-2 compared to (Al-hpu2)-OH1 is found also over entire ω range. This indicates again, that for these hyperbranched polymer systems, the melt viscosity behavior is not governed by polar end groups.

The storage modulus of aliphatic (Al-hpu2)-OH1 and the linear analog Al-LPU(7) is shown in Figure 4.43. This Figure shows that at low frequency, the value of G' of (AL-hpu2)-OH1 is also higher than this of Al-LPU(7). That has to be owing to the higher elasticity of the hyperbranched chains. The complex viscosity, η* (Figure 4.44) of (Al-hpu2)-OH1 is lower as compared to Al-LPU(7) at high frequency, while at low frequency η* of (Al-hpu2)-OH1 increases. It looks like in the flow regime (at low frequency) the Al-LPU(7) chains melt rapidly unlike the hyperbranched chains. Aromatic and aliphatic hyperbranched polymers behave differently in this case (compare Figures 4.44 and 4.40).

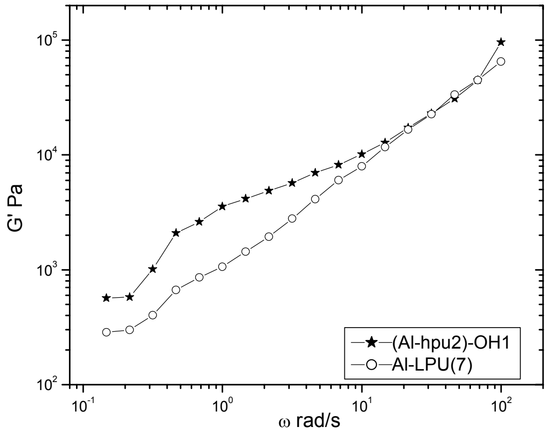


Figure 4.43: G' vs. ω for both (Al-hpu2)-OH1 and Al-LPU(7).

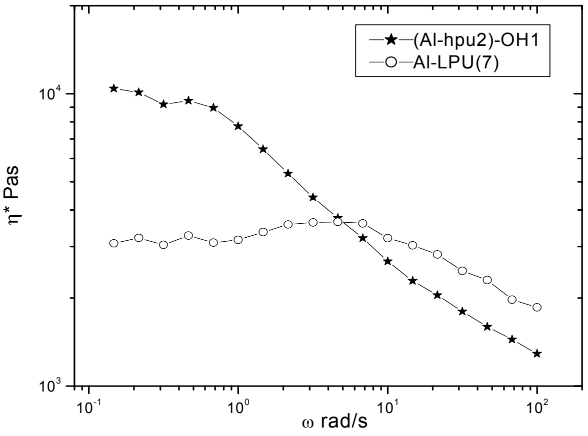


Figure 4.44: η* vs. ω for (Al-hpu2)-OH1 and Al-LPU(7).

The melt viscosity of hyperbranched polymers is affected by several factors, such as type of end groups, molecular weight of the polymers and chemical structure of the polymer. It was found that polypropylene/ hyperbranched polyesters blends have lower melt viscosity than that of pure polypropylene and higher than that of polyester[92]. Usually, the melt viscosity of hyperbranched polymers is lower than that of the linear analogue. In our case, since the studied HPU samples have higher M_w than the linear ones they showed η^* values higher than that of the linear polymers. For other systems the polarity of end groups can raise the viscosity by several orders of magnitude[92,177,178]. For our systems, it was shown previously (section 4.12) that strong interactions are found due to the urea and urethane groups within the polymer backbone. Those interactions increase the melt viscosity significantly even if the polymer end groups are modified. In our modified systems we found out that both modified aromatic and aliphatic hyperbranched poly(urea-urethane)s have higher G' than the unmodified polymers i.e. they are more elastic.

Since rheological properties for hyperbranched polymers depend mainly on the molecular weight of the polymer and its chemical structure, it is difficult to set a rule for all hyperbranched systems. One should deal with every system as individual one and take into consideration functional groups within the polymer chains, interactions between the chains and values of weight average molecular weight and polydispersity of the polymer under investigation.

4.16 Surface properties of thin films

Investigation of surface properties of polymers is of considerable interest regarding the prediction of their adhesion, wetting properties and surface polarity. Different modification techniques can be applied to alter the wetting and adhesion behavior of polymer material. The surface properties become of more importance when the prepared polymeric material is intended to be used for coating applications. So, thin films of different polymer samples were prepared in order to study the characteristics of hyperbranched films like adhesion, effect of end groups on surface energy and zeta-potential. At first thin films were prepared using spin coating technique on silicon wafers. Si-wafers were cleaned before use with a mixture of concentrated sulfuric acid and hydrogen peroxide in ratio 3:1 for twenty minutes at 40°C in an ultrasonic bath, washing with Millipore water for several times and finally drying them in vacuum with a stream of N_2 gas. Examining the film surface of different polymer samples prepared by spin coating by light microscope (LM) showed that the films are not homogeneous with big holes. They also have high roughness but they showed no cracks as shown in Figure 4.45.

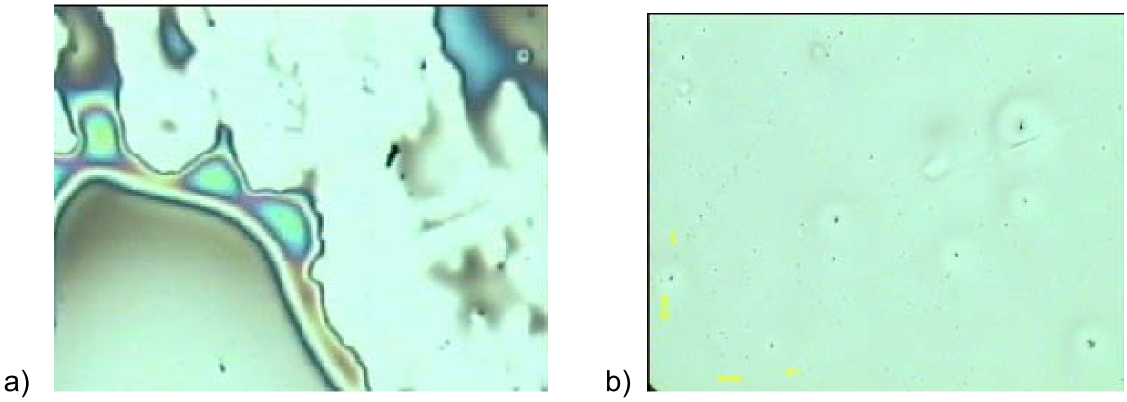

a)
b)

Figure 4.45: Pictures obtained for spin coated polymer (2 wt% DMAc solutions) of a) aromatic hyperbranched polymer and b) aliphatic hyperbranched polymer in DMAc.

Although the films prepared by spin coating are thin (film thickness about 50 nm as measured by atomic force microscopy[179] AFM), the quality of the films was not good enough to make further surface studies, since the homogeneity of the film is very important in order to get reliable results for contact angle. So, we used another technique to prepare our films which is “doctor blade technique” on glass substrates. The glass was cleaned before use with acetone, washed with water and dried. Polymer solutions of 25 or 20 wt% in DMAc were prepared and applied on the glass after filtration with a syringe. 50, 100, and 200 μm gap sizes were used to obtain different film thickness. The samples were dried in vacuum at 70°C over night, then analyzed. It was found that the polymer films are more homogeneous and smoother by using smaller gap size. (LM) pictures of thin film prepared from M(Ar-hpu3)-3 are shown in Figure 4.46. It is obvious that the film prepared using 50 μm gap size is the most homogeneous one with nearly no porous or holes.

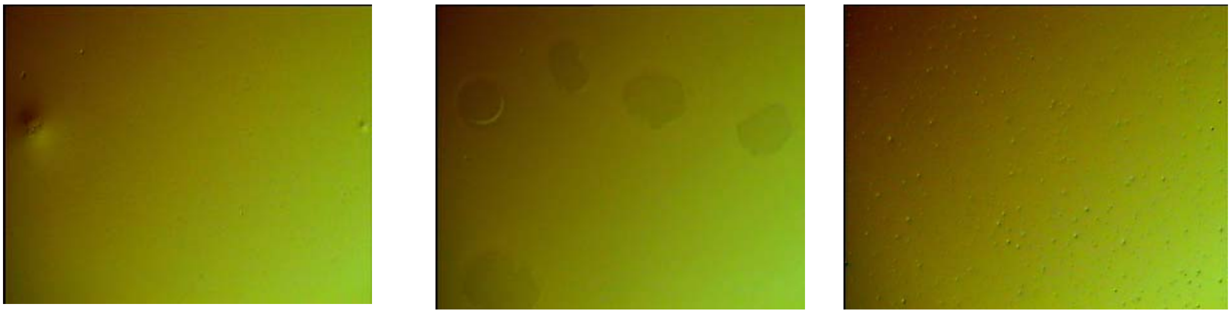

(a) (b) (c)

Figure 4.46: Light microscope pictures of films prepared from modified aromatic hyperbranched polymer M(Ar-hpu3)-3 of (a) 50 μm, (b) 100 μm, and (c) 200 μm.

It is important to have information about the solvent content of the prepared thin films since presence of solvent can not be avoided due to the polarity of our polymer systems. But the amount of solvent should not be so high that it may influence the adhesion of the polymer or affect the values of contact angle. In order to determine the amount of solvent present in the thin films GC-MS was used. It is a combination of gas chromatograph and mass spectrometer. The glass object should be weighed before film application, the polymer film is dried thoroughly in vacuum at 70°C till constant weight. The glass object with the applied polymer film is then crashed and analyzed to quantify the amount of solvent by weight, the values are given in Table 17. It was found that solvent content increases by increasing film thickness this can be noticed for different polymer samples either hyperbranched or linear polymers. In case of film samples prepared from modified hyperbranched polymers, only traces of solvent were found, obviously due to the lack of OH-end groups which form hydrogen bonding with the solvent. Film thickness was determined using AFM and is depicted in Table 17. As mentioned the films were bladed on glass objects using different gap sizes, also the concentration of the polymer solution is an important parameter which affect the film thickness. When concentrated solution of 20 wt% of polymer in DMAc were used normally thicker films are obtained by increasing gap size. Also film thickness increases by increasing concentration of polymer solution e.g. by using polymer solution of 25 wt% [see Table 17, Ar-LPU(1)].

Table 17: Values of film thickness and solvent content for some film samples.

Polymer	(Al-hpu1)-OH4	(Ar-hpu1)-OH5	(Ar-hpu1)-OH2	Ar-LPU(1)	M(Ar-hpu2)-2
Gap thickness μm	200	50, 200	50	200	50, 200
Film thickness μm	2.71	2.14, 2.65	0.8	3.21	2.23, 2.87
Solvent content wt%	1.0	1.8, 0.8	1.45	3.35	Both 0.001

Surface roughness is an important property for polymer films which can find applications as coatings or adhesives. Microglider[180] (MG) was used to determine the value of surface roughness for different film samples. It is an instrument for the precise optical topography measuring of surfaces. MG works as an optical profilometer (2D) as well as an imaging measuring instrument (3D) by means of a scanning process. Roughness and waviness can be determined in 2D or 3D according to DIN/ISO standards. The sample is illuminated by focused white light. Evaluating the reflected light the sensor investigates at a working distance of 5 mm the strictures of the sample.

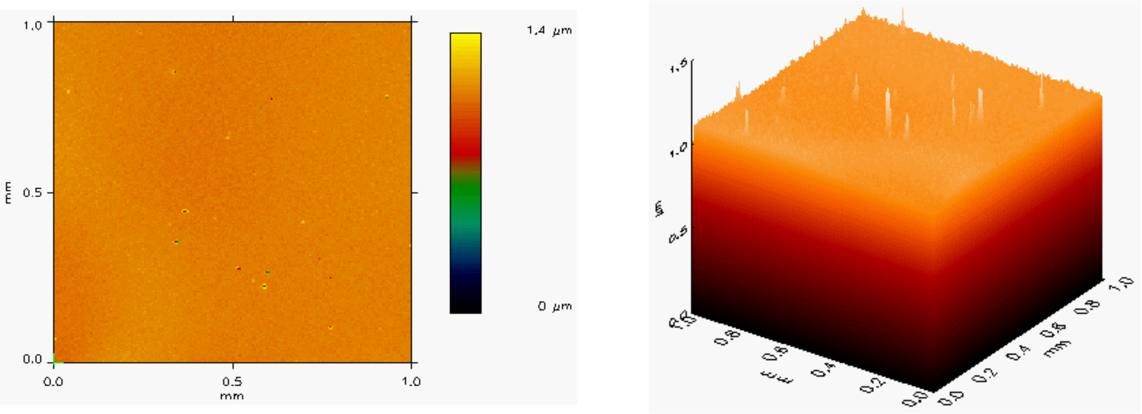


Figure 4.47: Microglider (MG) pictures for film 2.14 μm thick prepared from (Al-hpu1)-OH5; 50 mm gap size, surface roughness of 18 nm., the scanned area is 1 mm^2.

The values of surface roughness as obtained from MG are given in Table 18. We notice that the values of surface roughness for the prepared polymer films are low between 9 and 18 nm in comparison with 2 or 3 μm film thickness. This reflects an idea about how smooth and homogeneous our polymer films are. However, we can not get a relation of surface roughness of the film either with the structure of the polymer or with the gap size. After obtaining good information about the quality of our prepared films, we can start measuring contact angle, to get information about surface energy, since the values of contact angle is influenced to a great extent by the homogeneity and roughness of the investigated surfaces.

Table 18: Values of surface roughness for different films as measured by MG.

Polymer	M(Ar-hpu3)-3	Al-LPU(6)	(Ar-hpu1)-OH5	(Al-hpu1)-OH5	(Al-hpu3)-OH3
Gap size μm	50,100,200	100	50,100	50,100	50
R_Q nm	9,13,13	19	13,14	18,13	13

4.17 Contact angle measurements

Wetting phenomena are of considerable technical interest. Many processes in polymer production, processing and modification include wetting of solids with liquids. Examples of such technological processes are polymer blending, coating and the production of polymer composites by reinforcement with fibers or inorganic fillers. Contact angles measured on the solid /liquid systems are often used as empirical parameters to quantify wettability.

Young's equation (2) interrelates the measurable quantities, liquid-vapor interfacial tension γ_{lv} and the contact angle Θ, to the non-measurable interfacial tensions γ_{sv} and γ_{sl} of the solid-vapor and solid-liquid interfaces:

$$\gamma_{lv} \cos \Theta = \gamma_{sv} - \gamma_{sl} \qquad (2)$$

Equation (2): Young's relation used to measure contact angle on the solid/ liquid systems.

Since only γ_{lv} and Θ are directly measurable, one requires an additional information about the interfacial tension to determine γ_{sv} and $\gamma_{sl.}$ At present, approaches[181-183] to determine solid surface tension from contact angles were largely inspired by this idea. The calculated γ_{sv} and γ_{sl} values are used to interpret and predict the wetting and adhesion properties in technically relevant systems.

Contact angles of water were measured by sessile drop method [drop shape analysis (DSA)] using conventional goniometer device (Krüss GmbH). The liquid drop deposited on the given solid surface and a tangent is drawn at the three-phase contact line of the drop at its base. To produce advancing and receding angles, a manually controlled micrometer syringe was used to push liquid into the drop from above or to withdraw the liquid from the drop. The advancing angle measurements reflect the hydrophobic character of the material while the receding angle is more characteristic of the roughness of the surface. Advancing and receding angles were measured statically immediately after increasing the radius of the three-phase contact angle line. Five advancing and receding contact angles were measured for each drop. The accuracy of the technique is in the order ± 2°. The water used for contact angle measurements was distilled, deionized, and filtered through a Millipore-Q system. Contact angle measurements were carried out for different polymer systems, hyperbranched, linear and modified polymers. At first thin films were prepared by spin coating on silicon wafer as mentioned before. Since not all the films were smooth and homogeneous we decided to use doctor blade technique. The measurements showed that there is no big difference in the values of contact angle between both films on glass or on silicon wafer. Table 19 gives the values for advancing contact angle Θ_a and interfacial surface tension between solid and vapor γ_{sv}. Aromatic hyperbranched polymers showed contact angle values relatively low since the polymers have hydroxyl end groups this means that they have hydrophilic character. On comparing the values of contact angle obtained for the hyperbranched aliphatic polymer with those for the aromatic ones we notice that the former have higher values than in case of aromatic hyperbranched polymers although they contain also OH- end groups. The reason might be that the rigid cyclohexyl rings orient themselves toward the surface of the film giving a more hydrophobic nature to it.

Table 19: Values of advanced contact angle Θ_a and surface tension γ_{sv} obtained by DSA for films of different polymer systems.

Film Sample	Θ_a	γ_{sv}
(Al-hpu1)-OH4	72.0	39.9
(Al-hpu2)-OH1	71.8	40.0
(Al-hpu3)-OH3	65.3	44.0
(Ar-hpu2)-OH	62.0	46.0
(Ar-hpu1)-OH5	63.8	44.9
(Ar-hpu1)-OH2*	65.6	43.8
(Ar-hpu1)-OH1	57.3	48.8
Ar-Lpu2	66.9	43.0
Ar-Lpu3	67.0	43.0
Al-Lpu6	71.6	40.1
M(Ar-hpu)-4	73.4	39.0
M(Ar-hpu)-1	76.9	36.8

*DBA used as stopper in the polymerization reaction of the hyperbranched polymer

The effect of using different stoppers during the polymerization reaction is obvious when we compare the results of samples (Ar-hpu1)-OH1 which was prepared from a polymer stopped with DEA, and sample (Ar-hpu1)-OH2 which was prepared using a polymer stopped with DBA. The latter sample has value of Θ_a lower than the former one; this is because of the decrease in the number of terminal OH groups which are replaced by the hydrophobic DBA groups. Linear polymers did not show much difference in the values of contact angle in comparison with the hyperbranched polymers. We should take into account that contact angle as property is influenced not only by the end groups at the surface but also, for a great extent, by the surface roughness of the films. However, we assume that in our case our films are smooth enough to show the effect of polar structural groups in the polymer backbone. Regarding the values obtained for the modified aromatic hyperbranched polymers, we find that films obtained from modified polymers are more hydrophobic than the unmodified ones due to the lack of hydrophilic end groups through modification. Also, the film prepared from sample M(Ar-hpu2)-4 which was modified by Bu-NCO has lower value for Θ_a than in case of M(Ar-hpu1)-1 that was obtained through using Ph-NCO as modifier due to the presence of aromatic ring in the modifier. Surface tension γ_{sv} is a measure for the surface energy of the solid, however it can be seen that the unmodified polymer systems indicate the highest γ_{sv} values whereas the modified polymers have lower γ_{sv} i.e. a less hydrophilic surface. Nevertheless, the surface properties are mainly governed by the poly(urea-urethane) backbone. Thin films were prepared from modified aliphatic hyperbranched polymers M(Al-hpu1)-I (Modified using Ph-NCO), M(Al-hpu1)-2 (Bu-NCO as modifier), the films are transparent but completely inhomogeneous and many cracks appear on the surface. It seems that the presence of OH end groups in the aliphatic hyperbranched polymer improves the quality of the film through hydrogen bonding with the surface of the glass substrate. Introduction of phenyl or butyl groups through modification reactions, decrease the adhesion of the film on the substrate. As a result, shrinkage and consequent fracture of the film take place. However, the values of contact angle obtained for such polymer films are not reliable and hence could not be added to the Table.

4.18 Zeta potential measurements

One of the significant surface properties is the surface charge. This is an important factor in determining the interactions between particles, and hence dispersion characteristics such as dispersion stability, flocculation, viscosity, and film forming characteristics. The surface charge cannot be measured directly. Instead the charge at a distance from the particle, called the zeta potential is measured. This potential is usually of more interest because particles interact according to the magnitude of this value, rather than the potential at the surface of the particle. The zeta potential (ζ) is a consequence of the existence of surface charge, and can give information on the electrical interaction forces between the dispersed particles. Surface charges on suspended particles can be caused by a variety of phenomena. Dissociation of functional surface groups and/or adsorption of ions are the most important processes. The zeta potential is the controlling parameter for particle interactions and to modify it a knowledge of the potential of the surface and its chemistry is required. Investigation of the interaction of ions with the surface, and their effect on zeta potential is assisted by the determination of zeta potential as a function of a number of parameters such as pH, conductivity and the concentration of any specifically adsorbed ions or polymers in the system.

So, we can see that zeta potential measurements is a very sensitive method to get indirect information about the functional groups at the outermost surface of the polymer. To perform this kind of measurements sedimentation method was used in which the polymer particles are suspended in an electrolyte solution (3×10^{-3} mol/l KCl). From the zeta potential vs. pH of the electrolyte solution, information about the acid-base character of the solid surface is obtained[184]. Samples of the prepared poly (urea-urethane)s systems either unmodified, modified or linear systems were measured in the powder shape. Figure 4.48 shows zeta potential illustrated graphically versus pH. If the dissociation of functional groups is the predominant mechanism of double layer formation, the isoelectric point (IEP) is a measure of the acidic or basic character of the solid surface. In the case of low IEP values, the solid surface possesses acidic functional groups, whereas IEP's in the alkaline pH range are an indication for basic functional groups at the outermost surface.

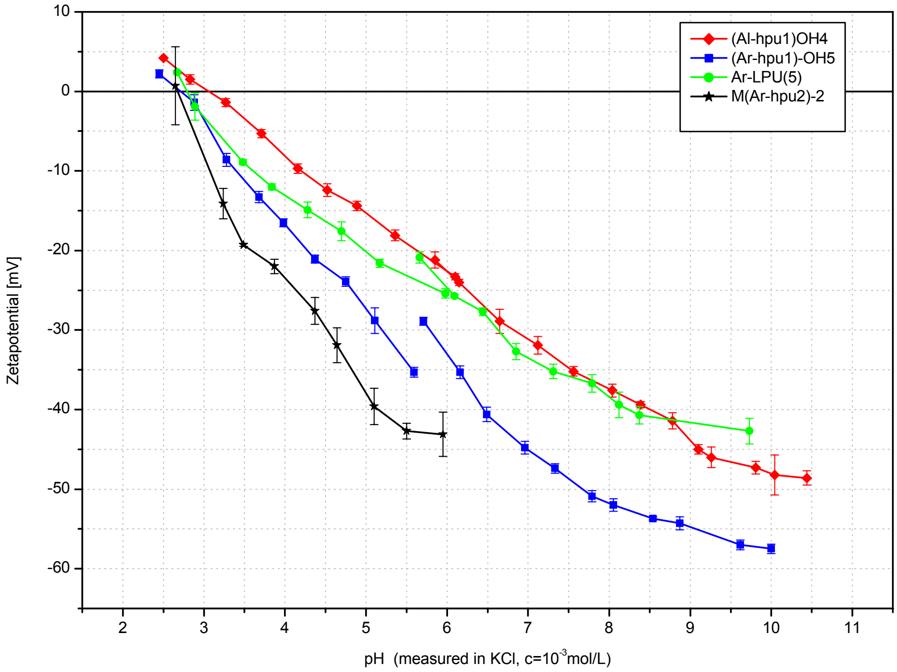


Figure 4.48: Zeta potential of different poly(urea-urethane)s systems as a function of the pH of the electrolyte solution.

As can be seen from Figure 4.48, the isoelectric point obtained has nearly the same value for all systems and is unexpectedly very low (ζ at pH = 2.6) although the measured systems have different end groups. It was reported that the surface properties of hyperbranched polyesters with OH end groups have higher IEP in comparison to those contain COOH groups in the outermost surface[185]. In case of our system a low IEP value is obtained which is valid not only for the unmodified hyperbranched or linear polymers but the same value is obtained for the modified hyperbranched polymer as well. This means that the acidic character of the polymers is not determined by the end groups in the outermost surface but another groups in the polymer structure. Since it was verified that the urea/urethane ratio in the polymer backbone is slightly above 1.0, it is assumed that the urea groups are responsible for the acidic character of the polymer.

4.19 Cross-linked polymers

Polyurethanes are often linear copolymers of difunctional polyols reacted with difunctional isocyanates. In many cases, however, trifunctional polyols or trifunctional isocyanates are added to result in a cross-linked polymer with a network structure. A traditional approach to study network properties would involve blending a trifunctioal polyol at various levels into a formulation with a difunctional polyol and a diisocyanate. From this, one could study the effect of network structure on physical properties. Several applications of hyperbranched polymers as precursors for synthesis of crosslinked materials have been reported[186-188]. The main advantage of technical applications of hyperbranched structures rests in rheology and in some cases, an added value in properties (e.g. hardness). In this part of work, the fact that hyperbranched polymers contain high amount of OH end groups was used to prepare networks through the reaction of aliphatic (Al-hpu1)-OH2 (M_n = 2800) or aromatic (Ar-hpu1)-OH6 (M_n =2600 g/mol) hyperbranched polymers with polyisocanate. The polymers used for this purpose were prepared without precipitation from water but by directly removing the solvent in high vacuum to avoid the risk of isocyanate hydrolysis. The samples were prepared by reacting aromatic or aliphatic hyperbranched polymer with polyisocyanate (BASONAT HI 100), chemical structure is shown in (Figure 4.49), 50 wt% solid content in Dimethyl formamide (DMF), and traces of DBTL are used to catalyze the reaction. Amount of polyisocyanate used is calculated to be equivalent to number of OH-groups present in the polymer as determined from ^{1}H NMR. The prepared networks (when the reaction mixture was viscous enough) were bladed on glass using 600 μm gap size. The free standing films were left till complete drying first for 24 hours at room temperature, then in vacuum oven at 80°C. The thickness of the sheets were measured using micrometer and found to be 250 μm.

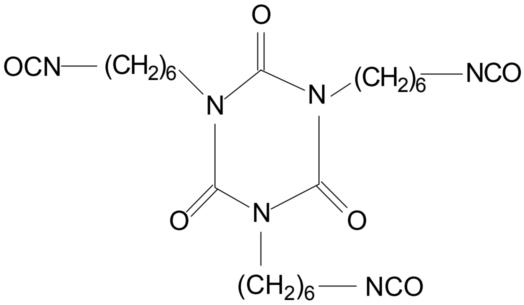


Figure 4.49: Chemical structure of (BASONAT HI 100).

4.19.1 Determination of glass transition temperature

Glass transition temperature (T_g) measurements were made using DSC with heating rate 20 K/min in N_2 atmosphere and temperature range –60 to 150°C. The weight of the samples was 4.7 mg for aliphatic network (Al-Network) and 5.0 mg for aromatic network (Ar-Network), Figure 4.50 shows the DSC traces for the networks.

DSC showed that T_g for (Al-Network) is 51°C which is a low value in comparison with the value of pure aliphatic hyperbranched polymer (Al-hpu1)-OH2 (T_g =66°C). This could be due to the lack of OH end groups which increase the value T_g through inter- and intramolecular interactions.

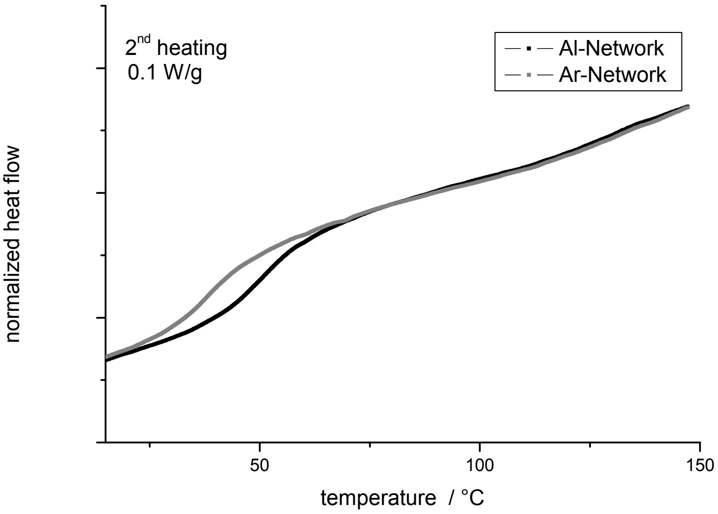


Figure 4.51: DSC curves for aliphatic and aromatic networks.

The hyperbranched polymer (Ar-hpu1)-OH6 we used for network formation had a T_g of 12°C which is very low value in comparison with the whole prepared series of aromatic hyperbranched polymers. Which is probably due to remaining solvent (sample not precipitated, see Table 11). The formed network based on this polymer has T_g of 41°C. This increase of T_g might be due to the increase of molecular weight of the crosslinked matrix. Both networks showed only a single T_g and thus, no phase separation.

4.19.2 Solvent content

GC-MS was used to determine the amount of solvent trapped inside the network matrix which was found to be very low about 0.004% in case of (Ar-Network) and 0.005% for (Al-Network) by weight.

4.19.3 Determination of sol fraction

Sol fractions were measured from samples of definite weight (0.05 g) which were immersed in DMF for 2 days, dried and weighed, immersed again in fresh solvent. This process is repeated until constant weight. The percentage of sol part for (Al-Network) was found to be 15% while for (Ar-Network) was 10.7% by weight. The higher sol content in the aliphatic network is consistent with the lower reactivity of this system which leads to incomplete reaction. For full conversion of functional groups no sol fraction should be present. The values obtained for sol fractions indicated that imperfection occurred during polymerization. These could be due to incomplete conversion, inexact stoichiometry of the polyols to isocyanate, cyclization or other side reactions[189]. Incomplete conversion together with the inexact stoichiometry of OH: NCO are the main reasons for the formation of imperfect structures in the networks called “dangling chains”[190]. The dangling chains are linear or branched sequences of units which are only singly connected at one end with the gel structure. Their motion is expected to be intermediate between faster relaxing elastically active network chains and slowly relaxing sol molecules.

4.19.4 Dynamic mechanical analysis (DMA)

Dynamic mechanical analysis (DMA) measures the modulus (stiffness) and damping (energy dissipation) of materials under periodic stress. Such measurements provide quantitative and qualitative information about the performance of the material. DMA can be used to evaluate a wide variety of materials particularly those polymeric materials, which exhibit time, frequency, and temperature effects on mechanical properties because of their viscoelastic nature.

Sample networks were analyzed by DMA at frequency 1 Hz temperature range from –60 to 250°C, heating rate 2 K/min. The sample size was 9.4 mm length, 12.89 mm width and 0.25 mm thickness. From the measurements, temperature dependence storage modulus and loss modulus could be obtained as shown in Figures 4.51, 4.52.

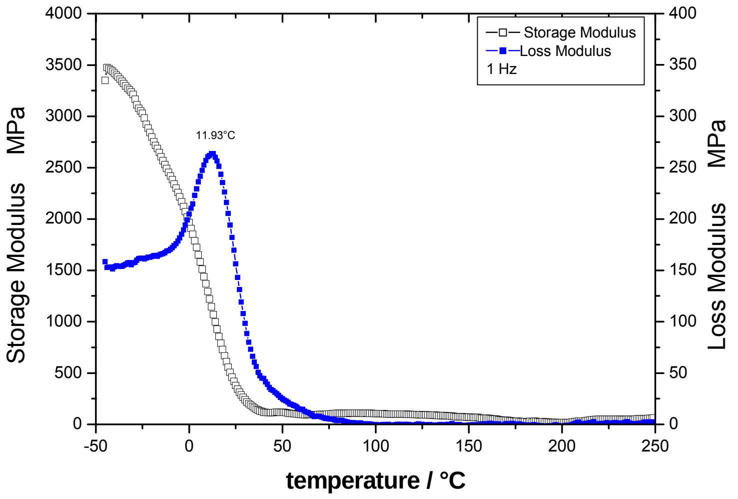


Figure 4.51: Storage modulus and loss factor vs. temperature for (Ar-Network).

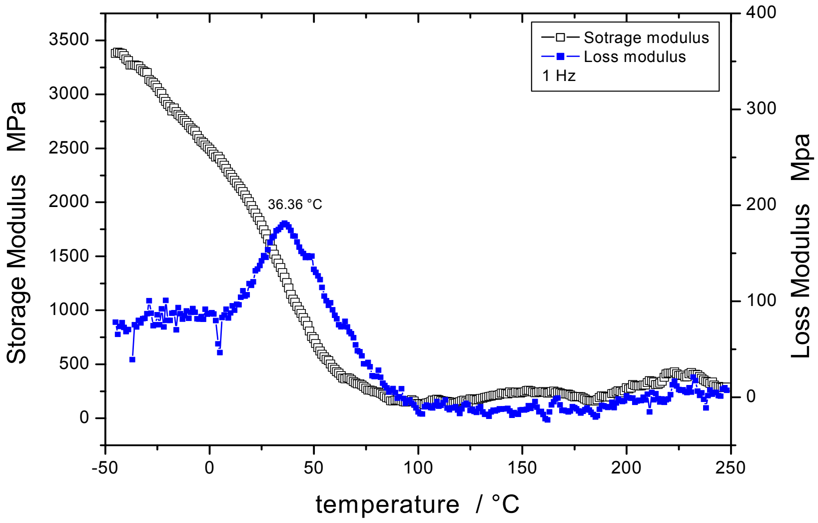
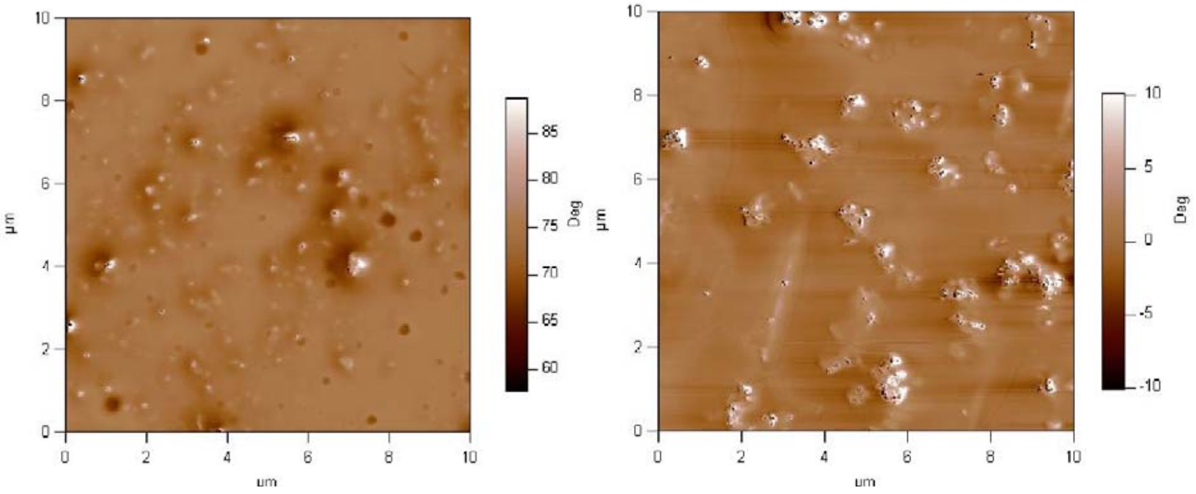


Figure 4.52: Storage and loss moduli vs. temperature for (Al-Network).

From the dynamic mechanical data a number of observations can be considered. The position of loss peak in case of (Ar-Network) fall in very tight temperature range in comparison with the aliphatic network with higher loss of energy. On the other hand, the loss peak is more broad in case of aliphatic network this might be due to the high molecular weight of the dangling chains and sol[191]. The transition, that is observed in the dynamic mechanical data, is due to the glass transition. Therefore the position of the loss peak correlates with the glass transition temperature. The aromatic network has higher loss factor (250 Mpa) while its value is lower (200 Mpa) for aliphatic network. The relationship between storage modulus and temperature can be observed from the Figures. It can be noticed that the slope of the storage modulus for (Ar-Network) is more sharp in comparison with the aliphatic network. This is an evidence for fast deformation of the material in a small temperature range also the resistance for deformation is small at low temperatures.

4.19.5 Atomic Force Microscopy (AFM)

AFM proved to be a valuable tool for evaluating the surface features of the cross-linked materials and to ascertain the roles of the preparation conditions and coating compositions in the surface topography. Figure 4.53 shows AFM images for (Al-network) and (Ar-Network) respectively. The surface roughness of both samples is measured and found to be 12 nm for (Al-Network) and 68 nm for (Ar-Network). By phase images analysis one can conclude that the matrix is composed of domains of soft segments containing the polyol (hyperbranched polymer) inside the network and hard segments containing the polyisocyanate on the surface. The domains size is 80 to 150 nm and 500 to 1200 nm for (Al-Network) and (Ar-Network), respectively. This means that the domains in (Ar-Network) are larger than that of the aliphatic one. No major phase separation on the μ-scale was observed from the AFM pictures and as also indicated by the existence of a single T_g.



(a) (b)

Figure 4.53: AFM phase images for (a) aliphatic and (b) aromatic networks, respectively.

4.19.6 Tensile strength

The data derived from stress-strain measurements for polymers are important from the practical viewpoint, since they provide information on the modulus, the brittleness, and the ultimate and yield strengths of the polymer.

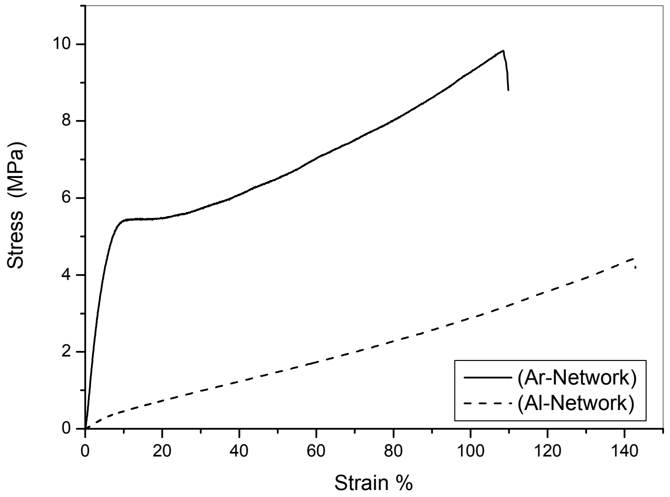


Figure 4.54: stress-strain dependence of aromatic and aliphatic networks.

By subjecting the specimen to a tensile force applied at a uniform rate and measuring the resulting deformation, a stress-strain curve can be constructed. Tensile test was performed on the two prepared networks to study their mechanical properties, (Figure 4.54) shows the stress-strain curve for the two aliphatic and aromatic networks.

From the shape of the curve related to (Ar-Network) we notice that the initial portion of the curve, from which tensile modulus *E* is obtained from its slope, is linear which is not the case for the aliphatic network. The value of Young’s modulus for (Ar-Network) is 10 folds greater than the value obtained for (Al-Network) which suggests an elastic and strong behavior of the sample representing (Al-Network). The point which represents the stress beyond which a brittle material will fracture (stress at break) can be distinguished only for (Ar-Network). The curve also shows higher yield point for the network based on aromatic hyperbranched polymer than for the aliphatic one. Table 19 gives the mechanical properties for both networks.

Table 20: Mechanical data for aromatic and aliphatic networks.

Network	E_t (Mpa)	σ_B (Mpa)	ε_B (%)
Ar-Network	71.4	9.9	114.5
Al-Network	7.9	3.8	128.8

E_t : Young’s modulus (initial slope of the stress-strain curve).

σ_B : Stress at break

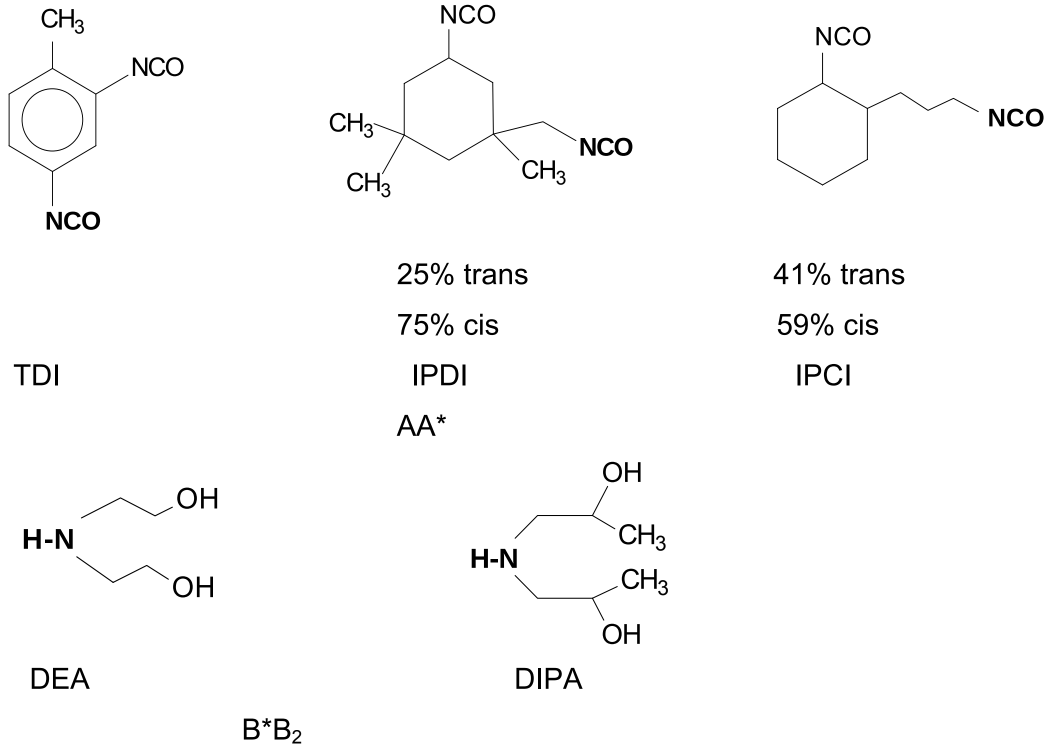
ε_B : Elongation at break.

In summery, several investigations were made for the aromatic and aliphatic networks based on our synthesized hyperbranched polymers. The results show that the prepared formulations give us what we need from a coating system such as lightweight, waterproof, chemical resistance high transparency and flexibility.

5- CONCLUSION AND OUTLOOK

By modifying the chemical approach, a new synthetic strategy toward hyperbranched poly(urea-urethane) polymers in a one-step method, was introduced. Commercially available AA* and B*B_2 monomers were used for the preparation of the polymers taking advantage from the reactivity differences of the functional groups present in the monomer. The prepared hyperbranched poly(urea-urethane) polymers can be inserted as polyol in a cross-linked formulation which can find applications for coating systems.

Three different diisocyanate monomers were reacted as AA* monomers with two bishydroxy amines as B*B_2 monomers in order to prepare hyperbranched poly(urea-urethane)s. The monomers used to achieve our goal were 2,4-toluylene diisocyanate (TDI) as aromatic diisocyanate and isophorone diisocyanate (IPDI) and 2(3-isocyanatopropyl) cyclohexylisocyanate (IPCI) as aliphatic diisocyanate. Those proposed diisocyanates were reacted with diethanolamine (DEA) or diisopropanolamine (DIPA) to prepare HPU (see Figure 5.1). The main strategy of the work was to use the advantage of intramolecular reactivity differences of isocyanate groups in the diisocyanate and the reactivity differences of OH and NH groups in the dihydroxyamine. By this, it was possible to generate AB_2 intermediate which polymerizes forming hyperbranched polymer (Figure 5.3).



25% trans
75% cis

41% trans
59% cis

TDI IPDI IPCI

AA*

DEA DIPA

B*B_2

Figure 5.1: Chemical structure of the used monomers.

First of all, I had to prepare linear aromatic and aliphatic polymers of nearly the same structure and molecular weights as our hyperbranched polymers for comparison of the solution properties and other characteristics. For this purpose TDI or IPDI were reacted with 2-ethanolamine in the same reaction conditions that would be used to synthesis HPU (Figure 5.2). The obtained polymers were characterized using NMR and their molar masses were determined by GPC.

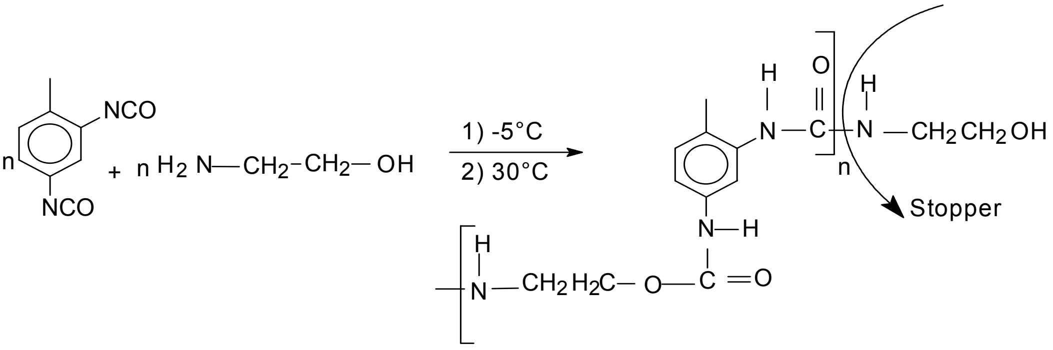


Figure 5.2: Reaction of TDI as AA* monomer with 2-EA to prepare linear poly (urea-urethane)s.

Reaction conditions for the preparation of aromatic and aliphatic hyperbranched poly(urea-ureathane)s, such as type of solvent, temperature, monomers, concentration, and catalysts, were optimized. The polymerization reaction was carried out and stopped before reaching gel point. Stopping of the reaction was made using excess of the dihydroxyamine monomer or dibutylamine (DBA) and the polymerization reaction was followed by titration of the NCO.

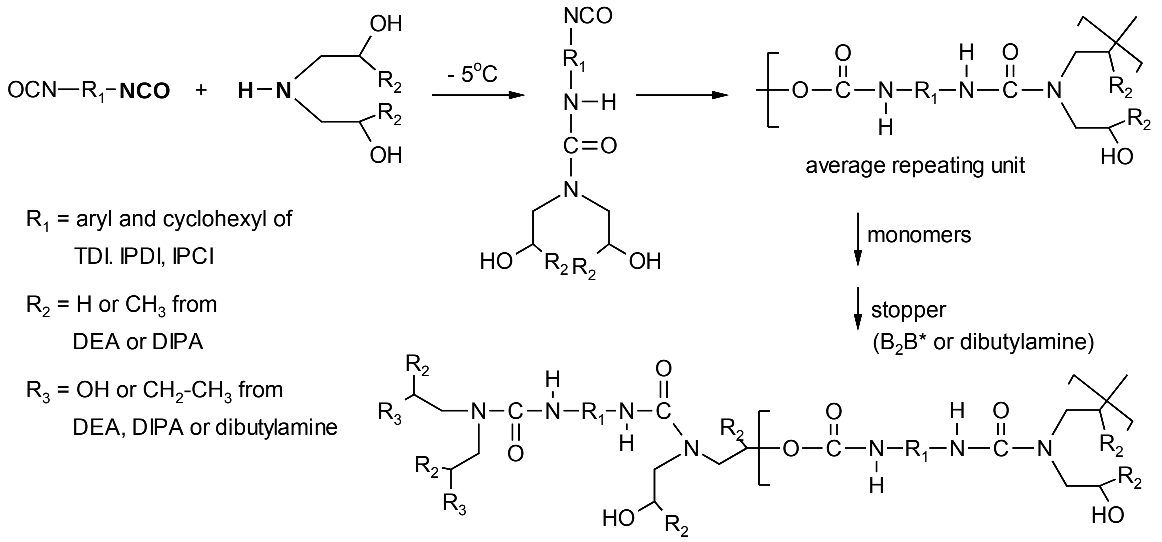


Figure 5.3: The reaction path of AA* with B^*B_2 monomers to prepare hyperbranched poly(urea-urethane)s.

In general, the reaction times were below 7 hours and still M_w values were achieved between 1400 g/mol and 107000 g/mol. In our chosen concentration regime (30-50 wt%) no gelation occurred allowing technical relevant reaction conditions for the preparation of hyperbranched polymers. The resulting products show good thermal stability up to 160°C and relatively high T_g values up to 133°C. Aliphatic hyperbranched polymers based on IPDI have higher T_g values than those obtained using TDI. The values of T_g are more influenced by the intra- and intermolecular interactions (H-bonding) than by changes in monomer structure. Furthermore, a very strong dependence of T_g on molar mass was found for samples with $M_n < 3000$ g/mol.

Complete structural analysis could be carried out using ^1H and ^{13}C NMR in case of aromatic polymers based on TDI. The content of t, l, and d subunits were calculated which were found to be affected significantly by monomer structure, monomer feed ratio, type of stopper, and reaction temperature. Thus, DB could be calculated and was found to be $>$ 60% for TDI/DEA and 45-48% for TDI/DIPA. Aliphatic polymers have spectra with overlapped signals due to the presence of 4 different isomers and therefore, no full structural analysis was possible. For all hyperbranched polymers it was also verified that the urea/urethane ratio in the polymer backbone is slightly above 1.0. We assume that the excess of urea units is introduced by the stopper reaction.

The reactivity difference of the two isocyanate groups was studied through model reactions, and analyzing the substitution pattern in the TDI/DEA polymer. It is known that p-NCO in TDI is more reactive than o-NCO towards hydroxyl groups. However, it looks like that the substitution pattern in the polymer is nearly random. Therefore, no clear preference in the reaction of o- and p-NCO groups towards amines could be confirmed experimentally. An additional model reaction, led to a nearly statistical ratio of the four possible reaction compounds. However, the higher reactivity of the amine group compared to the alcohol toward isocyanate could be fully verified leading to an A_2+ B^*B_2 systems for aromatic hyperbranched polymers. In contrast, the higher reactivity of primary isocyanate groups in the aliphatic diisocyanates towards amines could be confirmed which allows to call this system a real AA^*+ B^*B_2 situation.

Modification of the end groups in the prepared hyperbranched polymers was carried out using three different modifiers which were phenyl isocyanate, butyl isocyanate and stearyl isocyanate. Percentage of modification up to 100 % was achieved in case of using phenyl isocyanate and butyl isocyanate while in case of stearyl isocyanate only 70% modified polymer was obtained. The modified polymers have good solubility (except those obtained using stearyl isocyanate) and could be fully characterized. The side reaction product (aromatic urea) was separated by fractionation.

Inter- and intramolecular interactions were studied by FT-IR spectra. The measurements showed that hydrogen bonding in hyperbranched polymers are more pronounced than in case of linear polymers since they are favored by the presence of OH end groups.

Solution viscosity of hyperbranched polymers was measured and compared with that of the linear polymers of comparable molar mass. The measurements were made in DMAc at 25°C and the results showed that HPUs have lower solution viscosity values than those obtained for linear polymers with comparable M_w values.

Rheological measurement of some polymer samples of different systems were carried out and showed that our hyperbranched systems behave more elastic than the linear polymers exhibiting higher G' and η^*. Also, the modified hyperbranched polymers have, unusually, melt viscosity values higher than the unmodified polymers and their melt viscosity decrease linearly with the frequency. On the other hand, the hyperbranched systems showed a Newtonian plateau with zero-shear viscosity. We have to assume that not the OH end groups determine the melt rheological behavior but the presence of polar groups within the polymer chains.

Thin films for different polymer types (hyperbranched, linear and modified) were prepared using both spin coating and doctor blade techniques. Films made using the second method are more homogenous as was proved by light microscope and microglider. Surface roughness only up to 20 nm were obtained for a dry film thickness up to 3.26 μm depending on gap size and concentration of polymer solution. Solvent content in the films was determined using GC-MS and found to be about 1.5 mass% for hyperbranched polymers with polar end groups while films prepared from modified polymers contain only 0.001 mass%. Measurements of contact angle showed that aromatic hyperbranched poly(urea-urethane)s are more hydrophilic than those of the other types. Also, modified polymers gave higher values of contact angle (lower hydrophilicity) than the parent polymer.

(a) (b) (c)

Figure 5.4: LM pictures of films prepared from modified aromatic hyperbranched polymer M(Ar-hpu2)-3 of (a) 50 μm, (b) 100 μm, and (c) 200 μm.

Effect of using different stopper during polymerization reaction is obvious in the values of contact angle i.e. those films prepared from polymers which were stopped by dibutyl amine (DBA) have higher contact angle than those were stopped using diethanol amine. Obviously, the samples stopped by the polar diethanol amine have a higher number of terminal OH groups.

Measurement of Zeta-potential for different polymeric samples, hyperbranched , linear, and modified, was carried out using sedimentation technique. From the value obtained for isoelectric point (at pH= 2.6) we can conclude that not the end groups but the urea groups in the polymer backbone are responsible for the charge on the outermost surface.

Networks based on aliphatic and aromatic hyperbranched polymers were prepared through the reaction of HPU with trimer of 1,6-diisocyanatohexane in DMF. Sheets of 250 μm were prepared by blading the cross-linked polymers on glass. It was found that the aliphatic networks contain more sol part than the aromatic one which is in consistent with the lower reactivity of the aliphatic isocyanate. Thermal transitions of the networks were measured using DSC and DMA. Only one transition was found in both methods that was due to the glass transition (Figure 5.5) and no major phase separation occurred..

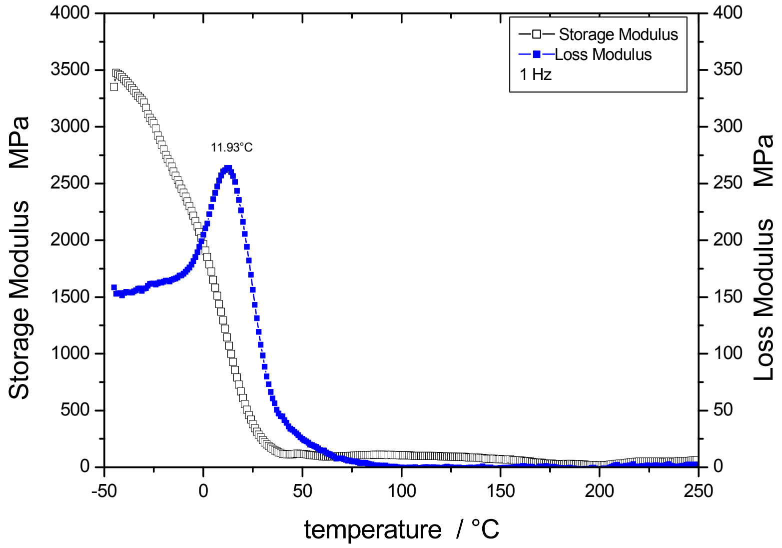


Figure 5.5: Storage modulus and loss factor vs. temperature for (Ar-Network).

AFM was used to study the morphology of the prepared networks which showed that surface roughness of the aliphatic network is lower than that of the aromatic network but generally the prepared samples have relatively homogeneous and smooth surfaces. It was found that the matrix was composed of domains of soft segments containing the polyol (hyperbranched polymer) inside the network and hard segments containing the polyisocyanate on the surface. The domain size was measured and found to be in the range of 80 to 150 nm for aliphatic network and 500 to1200 nm for the aromatic one. The data derived from stress-strain measurements (Figure 5.6), showed that the aromatic network has a higher yield point than the aliphatic network, whereas the aliphatic sample is more elastic than the aromatic based network.

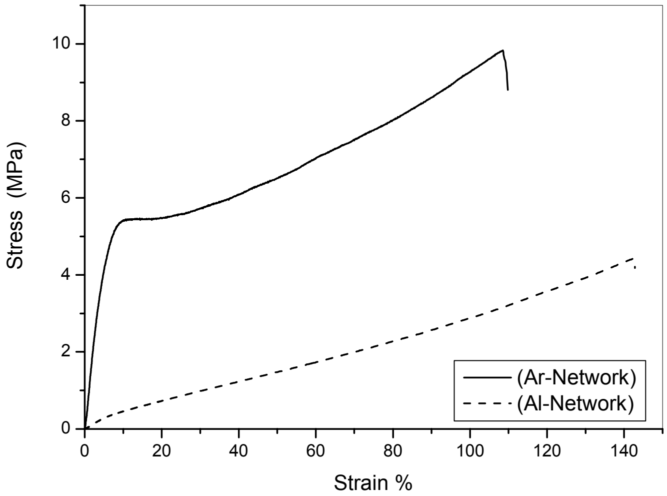


Figure 5.6: Stress-strain dependence of aromatic and aliphatic networks.

Hyperbranched poly(urea-urethane)s are a versatile class of new hyperbranched material. The simplicity of synthesis, combined with the possibility to chose readily available polyurethane raw material as monomer source, makes this polymer class highly attractive for commercial applications, e.g. as additives in printing inks or as crosslinkers in industrial coating systems. The presented study allowed to obtain a deeper understanding of the parameters which influence the reaction and the resulting branched structure. Furthermore, the effect of branching and end groups on material and surface properties were elucidated. The behavior of macromolecules near the surfaces and interfaces of organic coatings has a significant effect on the numerous properties of the coatings and plays a vital role in their applications. Therefore, an understanding of the interfaces responsible for durability, adhesion, and mechanical properties is important for development of new organic coatings. More work can be done on the properties of interface for developing and optimizing this improved coating materials

6- EXPERIMENTAL PART

6.1 Materials and methods

6.1.1 Materials

The monomers 2,4-toluylene diisocyanate (TDI), isophorone diisocyanate (IPDI), 2(3-isocyanatopropyl) cyclohexyl isocyanate (IPCI), diethanol amine (DEA), diisopropanol amine (DIPA) and the catalyst dibutyltin dilaurate (DBTL) were obtained from BASF AG and used as received; the catalyst 1,4-diazabicyclo[2.2.2]octane (DABCO) was obtained from Fluka. Tetrahydrofurane (THF) was dried over sodium and stored over molecular sieve while dimethylacetamide (DMAc) was dried over CaH_2, both of them and Phenyl monoisocyanate, Butyl monoisocyanate, Stearyl monoisocyanate, and trans 1,4- Cyclahexylene diisocyanate were purchased from Fluka as well. o-, p-tolyl monoisocyanate, N,N-diethyl amine, N-Methyl diethanol amine and dibutylamine were products from Aldrich. Ethanol was purchased from Merck.

6.1.2 Instruments

- Nuclear Magnetic Resonance (NMR)

The samples were analyzed by NMR using a Bruker DRX 500 spectrometer operating at 500.13 MHz for ^{1}H and 125.75 MHz for ^{13}C. DMSO-d_6 was used as solvent, lock, and internal standard ($\delta(^1H) = 2.50$ ppm, $\delta(^{13}C) = 39.60$ ppm). The spectra were measured at 303 K using 5 mm o. d. sample tubes. Quantitative ^{13}C NMR spectra were obtained using inverse gated decoupling, 30° ^{13}C pulses and a pulse delay of 6 s. The 1D NMR measurements were completed by ^{1}H-^{1}H correlated (COSY) and ^{1}H-^{13}C one and multibond shift correlated (HMQC, HMBC) spectra. The quantification of different structural units was done by integration and signal deconvolution of the corresponding signal regions in the NMR spectra. The error in determining the fractions of the different units depends on the NMR signal region used and is estimated to $\leq 2\%$.

- NCO% Titration

The determination of NCO% was carried out through titration with the instrument DL70 from Mettler. The method used can be summarized as follows: samples of definite weights were withdrawn from the reaction mixture at certain time intervals, 20 ml of 0.1M dibutylamine/ chlorobenzene was added to quench the unreacted isocyanate. The excess amine is determined by back-titration with 0.1M HCl. The end point was determined potentiometrically.

- Size Exclusion Chromatography (SEC)

The instrument is from Knauer, Berlin, with RI detector and a Zorbax PSM 60+300 column. Calibration was performed with linear polyvinylpyridine (PVP) standards, DMAc + 3 g/L LiCl + 2 vol% H_2O was used as eluent with a flow rate 0.5 ml/min.

- FT-IR spectroscopy

The IR spectra were obtained using FTIR-Spectrometer IFS 66v (Bruker) with MCT detector. The range of measurements is 600-4000 cm^{-1} with 100 scans/ measurement. Samples were measured in the solid form.

- Differential Scanning Calorimetry (DSC)

A Perkin Elmer DSC7 (heating rate 20 K/min; temperature range usually -60°C to 150°C or -60° to 200°C) was used for the DSC analysis

- Thermal Gravimetric Analysis (TGA)

TGA measurements were carried out by a Perkin Elmer TGA7 under N_2 atmosphere (temperature program from 30°C to 700°C and heating rate 10 K/min).

- Viscosity measurements

The measurements were performed in a Ubbelohde viscometer from Schott, with a capillary of thickness ‘I’ and a correction constant k = 0.01007. The samples were dissolved in dried DMAc. The viscometer filled with polymer solution was immersed in a thermostatic water bath model CT 1450 from Schott at 25°C. The measurements were repeated for every solution 5 times with a Schott AVS 310 instrument.

- Headspace GC/MS

Headspace sampler HP 7694 from HP (Hawlett Packard) at 200°C (15 min equilibrium) GC temperature: 2 min at 50°C then heating rate 12° /min till 250°C. Column 5MS from HP, 25m x 0.2mm internal diameter. Transporting gas is helium with the rate 1 ml/min.

- Melt Reology

ARES-Rheometer (Rheometric Scientific). The rheometer was operated in the dynamic mode on the plate-plate geometry of 25 mm diameter and about 1 mm gap. The gap size changes with the temperatures and is read electronically and allows absolute moduli to be determined. The measurements were performed under nitrogen atmosphere, strain amplitude 5%, at 30°C above the glass transition temperature of each sample over angular frequency (ω) varied from 100 to 0.3 radian/s.

- Dynamic contact angle

(Krüss GmbH G2) instrument for drop shape analysis (DSA) includes video measuring system to record drop image, Matrox pulser video framegrabber board and computer with measuring program.

- Mechanical properties

ISO Zwicki instrument i.A. (GMbH), dimensions of measured part 0.25 mm X 2.00 mm, thickness of sample is 0.25 mm. Strength= 100 N, start of determination of E-module at 0.05% and finish at 0.25%. Speed of E-module is 5 mm/min.

- Dynamic mechanical analyser (DMA)

Instrument 2980 DMA, Module DMA Multi - Frequency–single Cantilever. Sample networks were analysed by DMA at frequency 1 Hz, temperature range from –60 to 250°C, heating rate 2 K/min. The sample size was 9.4 mm length, 12.89 mm width and 0.25 mm thickness. From the measurements, temperature dependence storage modulus and loss modulus could be obtained.

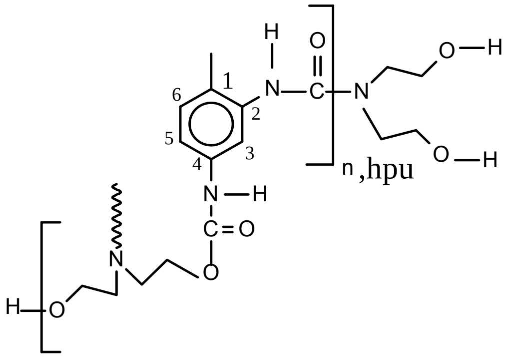
- Other equipments

Light Microscope	ZS 100 Carl Zeiss GmbH
Microglider	From the company Fries Research & Technology
AFM	Nanoscope IIIa, Multimode, D3100, Digital Instruments
Zeta potential	Electrokinetic Analyzer EKA of Anton Paar KG, Austria

6.2 Synthesis of hyperbranched polymers

6.2.1 Synthesis of aromatic hyperbranched polymers (Ar-hpu1)-OH1

8.69 g of TDI (50 mmol) was dissolved in DMAc in a three-necked round bottom flask fitted with thermometer, dropping funnel, and gas-inlet pipe. Dry N_2 was bubbled in the flask during the reaction and the solution was cooled down to -5°C. The second monomer DEA (5.25 g-50 mmol) dissolved in DMAc was added at this low temperature dropwise until the whole amount of the bishydroxyamine was charged into the flask. The ice bath was removed and the reaction proceeded until the required temperature was reached. The amount of NCO present in the solution was followed by titration. The method can be summarized as follows: samples of definite weights were taken from the reaction mixture at certain time intervals, 20 ml of 0.1M dibutylamine/ chlorobenzene was added; the mixture was titrated against 0.1M HCl. The end point was determined potentiometrically. At the required NCO% which is equivalent to a definite degree of polymerization the reaction was stopped by addition of the calculated amount (based on remaining NCO) of stopper molecule which was usually the used bishydroxyamine (B^*B_2). The amount added of DEA as stopper is 0.645 g. The polymer was precipitated in water, filtered, and dried in vacuum over P_2O_5.



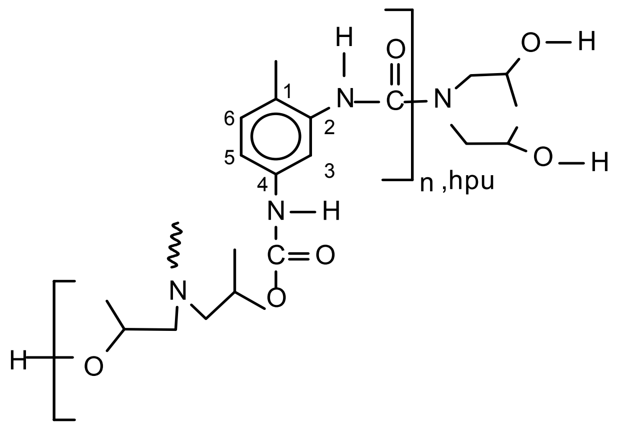
Yield: 62.8%, white powder

^1H NMR (DMSO-d_6): δ ppm = 9.57 and 9.49 (NH, urethane, *para* to CH_3) 8.83 and 8.80 (NH, urethane, *ortho* to CH_3), 8.58 and 8.53 (t_p), 8.51 and 8.45 (l_p), 8.28 (d_p), 8.25 and 8.20 (t_o), 8.20 and 8.15 (l_o), 7.87 (d_o) (NH, urea), 7.65 - 7.35 (H_3), 7.35 - 6.9 (H_5 ,H_6), 5.44 (l_o), 5.25 (l_p), 5.17 (t_o), 5.08 (t_p) (OH), 4.19 (CH_2-OC(O), l and d), 3.7 - 3.5 (CH_2-OH and N-CH_2, l and d), 3.43 (N-CH_2, l), 3.43 (N-CH_2, t), 2.10 and 2.07 (CH_3).

^{13}C NMR (DMSO-d_6): δ ppm = 156.62 and 156.57 (t_o), 156.23 and 156.18 (l_o), 156.11 and 156.02 (t_p), 155.71 and 155.62 (l_p), 155.33 (d_o), 154.95 (d_p) (C=O, urea), 154.35 and 154.31 (C=O, urethane, ortho to CH_3), 153.54 (C=O, urethane, para to CH_3), 139 - 136 (C_2 , C_4), 130.5 - 129.5 (C_6), 126 - 122 (C_1), 117 - 113 (C_3, C_5), 62.68 (CH_2-OC(O), l and d), 60.58, 60.45 (CH_2-OH, l), 60.26 (CH_2-OH, t), 50.92, 50.49 (N-CH_2, l), 50.54 (N-CH_2, t), 46.71 (N-CH_2, l and d), 17.43, 17.46, 17.32, 17.19 (CH_3).

6.2.2 Synthesis of aromatic hyperbranched polymers (Ar-hpu2)-OH2

8.69 g of TDI (50 mmol) was dissolved in DMAc in a three-necked round bottom flask fitted with thermometer, dropping funnel, and gas-inlet pipe. Dry N_2 was bubbled in the flask during the reaction and the solution was cooled down to -5°C. The second monomer DIPA (6.65 g-50 mmol) dissolved in DMAc was added at this low temperature dropwise until the whole amount of the bishydroxyamine was charged into the flask, the whole amount of solvent is 51 g (30 wt%). The same steps as shown above were performed used and the amount of used stopper (DIPA) is 1.04 g. The formed polymer was precipitated in water, filtered, and dried in vacuum over P_2O_5.



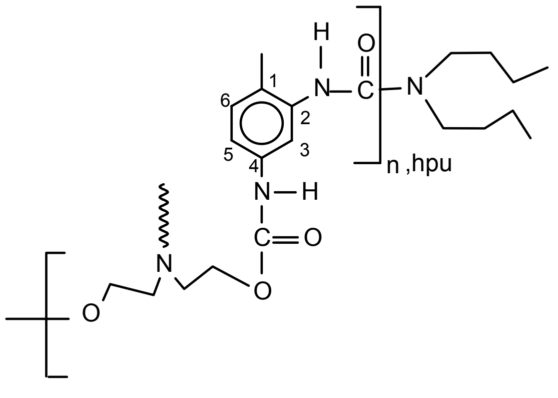
Yield: 59.8%, white powder

^{1}H NMR (DMSO-d_6): δ ppm = 9.46 and 9.37 (NH, urethane, para to CH_3), 9.4 - 8.6 (NH, urethane, ortho to CH_3 and NH, urea), 8.6 - 8.1 (NH, urea), 7.85 (NH, urea, d_o), 7.65 - 7.35 (H_3), 7.35 - 6.9 (H_5 ,H_6), 5.55 (l_o), 5.40 (l_p), 5.25 and 5.18 (t_o and t_p), 5.05 and 5.00 (CH-OC(O), l and d), 3.93 (C*H*-OH, t and l), 3.8 - 3.2 (N-CH_2), 2.11, 2.08 (Ar-CH_3), 1.21 (CH(OC(O))-CH_3), 1.06 (CH(OH)-CH_3).

^{13}C NMR (DMSO-d_6): δ ppm = 157.22, 156.96, 156.94, 156.71, 156.58, 156.53, 156.43, 156.11, 155.97 (C=O, urea, t and l), 155.46, 155.15, 154.92 (C=O, urea, d), 154.01 (C=O, urethane, ortho to Ar-CH_3), 153.23 (C=O, urethane, para to Ar-CH_3), 139 - 136 (C_2 , C_4), 130.5-129.5 (C_6), 126-122 (C_1), 117-113 (C_3, C_5), 70.5 - 69 (*C*H-OC(O), l and d), 66.59, 66.48, 66.10, 65.99 (CH-OH, t and l), 56.3 - 55.6 (N-CH_2, t and l), 52.62. 52.05, 51.89, 51.73 (N-CH_2, l and d), 21.43, 21.33, 21.21, 21.14 (CH(OH)-*C*H_3), 18.06 (CH(OC(O))-*C*H_3), 17.56, 17.19 (Ar-CH_3).

6.2.3 Synthesis of aromatic hyperbranched polymers (Ar-hpu1)-OH2

12.17 g of TDI (70 mmol) was dissolved in DMAc in a three-necked round bottom flask fitted with thermometer, dropping funnel, and gas-inlet pipe. Dry N_2 was bubbled in the flask during the reaction and the solution was cooled down to -5°C. The second monomer DEA (8.085 g-70 mmol) dissolved in DMAc was added at this low temperature dropwise until the whole amount of the bishydroxyamine was charged into the flask, total amount of solvent is 67 g (30 wt%). The ice bath was removed and the reaction proceeded until the required temperature was reached. The amount of NCO present in the solution was followed by titration. The method can be summarized as follows: samples of definite weights were taken from the reaction mixture at certain time intervals, 20 ml of 0.1M dibutylamine/ chlorobenzene was added; the mixture was titrated against 0.1M HCl. The end point was determined potentiometrically. At the required NCO% which is equivalent to a definite degree of polymerization the reaction was stopped by addition of the calculated amount (based on remaining NCO) of stopper molecule which was usually the used bishydroxyamine (B^*B_2). The amount added of DBA as stopper is 0.28 g. The polymer was precipitated in water, filtered, and dried in vacuum over P_2O_5.



Yield: 68.4%, white powder

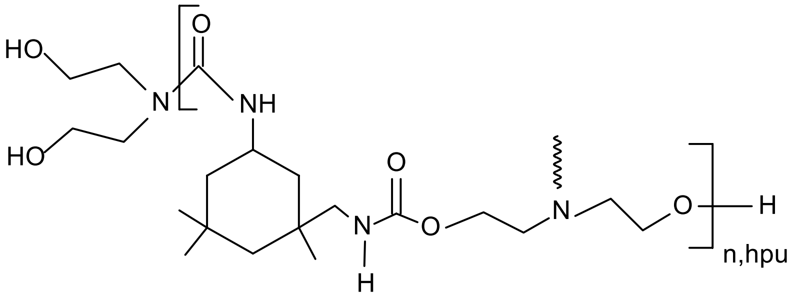
^1H NMR (DMSO-d_6): δ ppm = 9.57 and 9.49 (NH, urethane, para to CH_3) 8.83 and 8.80 (NH, urethane, *ortho* to CH_3), 8.58 and 8.53 (t_p), 8.51 and 8.45 (l_p), 8.28 (d_p), 8.25 and 8.20 (t_o), 8.20 and 8.15 (l_o), 7.87 (d_o) (NH, urea), 7.65 -7.35 (H_3), 7.35 -6.9 (H_5 ,H_6), 5.44 (l_o), 5.25 (l_p), 5.17 (t_o), 5.08 (t_p) (OH), 4.19 (CH_2-OC(O), l and d), 3.7- 3.5 (CH_2-OH and N-CH_2, l and d), 3.43 (N-CH_2, l), 3.43 (N-CH_2, t), 2.10 and 2.07 (CH_3), 3.25 (NCH_2), 1.50 (NCH_2CH_2), 1.28 (CH_2CH_3), 0.90 (CH_3).

^{13}C NMR (DMSO-d_6): δ ppm = 156.62 and 156.57 (t_o), 156.23 and 156.18 (l_o), 156.11 and 156.02 (t_p), 155.71 and 155.62 (l_p), 155.33 (d_o), 154.95 (d_p) (C=O, urea), 154.35 and 154.31

(C=O, urethane, *ortho* to CH_3), 153.54 (C=O, urethane, *para* to CH_3), 139 -136 (C_2 , C_4), 130.5 -129.5 (C_6), 126 -122 (C_1), 117 -113 (C_3, C_5), 62.68 (CH_2-OC(O), l and d), 60.58, 60.45 (CH_2-OH, l), 60.26 (CH_2-OH, t), 50.92, 50.49 (N-CH_2, l), 50.54 (N-CH_2, t), 46.71 (N-CH_2, l and d), 17.43, 17.46, 17.32, 17.19 (CH_3), 46.20 (NCH_2), 30.46 (NCH_2CH_2), 19.67 (CH_2CH_3), 13.97 (CH_3).

6.2.4 Synthesis of aliphatic hyperbranched polymers (Al-hpu1)-OH3

15.57 g of IPDI (70 mmol) was dissolved in DMAc in a three-necked round bottom flask fitted with thermometer, dropping funnel, and gas-inlet pipe. Dry N_2 was bubbled in the flask during the reaction and the solution was cooled down to -5°C. The second monomer DEA (7.35 g-70 mmol) dissolved in DMAc was added at this low temperature dropwise until the whole amount of the bishydroxyamine was charged into the flask, total amount of solvent is 45.8 g (50 wt%). The ice bath was removed and the reaction proceeded until the temperature is 30°C then DBTL is added (0.01 g). The amount of NCO present in the solution was followed by titration as mentioned before. The amount added DEA as stopper is 0.48 g. The polymer was precipitated in water, filtered, and dried in vacuum over P_2O_5.



Yield: 84.45%, white powder

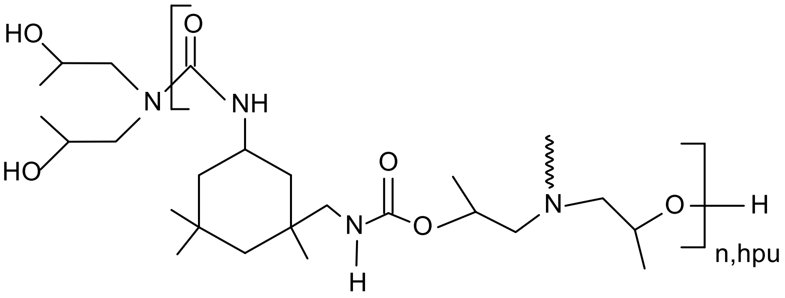
^{1}H NMR (DMSO-d_6) (353 K): δ ppm = 6.73 (NH, CH_2-urethane, cis), 6.58 (br, NH, CH_2-urethane, trans and CH-urethane, cis / trans), 6.17 (t_c), 6.07 (t_t, l_c, l_t), 5.90 (d_t, d_c) (NH, CH_2-urea), 5.80, 5.76, 5.67 (NH, CH-urea), 4.84, 4.73, 4.66, 4.58 (OH), 4.03 (CH_2-OC(O)), 3.8 (CHN, urea), 3.63 (CHN, urethane), 3.53 (CH_2-OH), 3.42 (N-CH_2-CH_2-OC(O)), 3.32 and 3.30 (N-CH_2-CH_2-OH), 3.2-3.1 (trans-CH_2N, urea and urethane), 2.95 -2.70 (cis-CH_2N, urea and urethane), 1.8 - 0.8 (remaining CH_2 and CH_3 of aliphatic ring system).

Selected regions at 303 K: 7.25-6.5 (NH, urethane), 6.4 - 5.8 (NH, urea), 5.16, 5.01, 4.91, 4.82 (OH).

^{13}C NMR (DMSO-d_6): δ ppm = 159.35, 159.12, 158.55, 158.34, 158.07, 157.97, 157.40, 157.23, 156.88, 156.73, 155.47 (C=O, urea and urethane), 62.43, 62.15 (*C*H$_2$-OC(O)), 60.61, 60.53, 60.44, 60.31 (*C*H$_2$-OH), 54.4 - 54.0 (CH$_2$-NH, cis), 50.70, 50.54, 50.28, 50.12 (N-CH$_2$-CH$_2$-OH), 47.5 - 45.5 (N-CH$_2$-CH$_2$-OC(O); CH$_2$-NH, trans; CH$_2$, ring), 44.08 (CHN, urethane), 43.43 (CHN, urea), 42.22 and 41.58 (CH$_2$, ring), 36.8 -35.5 (C, ring), 35.13, 35.24 (CH$_3$, ring), 31.62, 31.49 (C, ring), 30.23, 27.66, 27.56, 27.01, 26.88, 23.40 (CH$_3$, ring).

6.2.5 Synthesis of aliphatic hyperbranched polymers (Al-hpu2)-OH1

11.1 g of IPDI (50 mmol) was dissolved in DMAc in a three-necked round bottom flask fitted with thermometer, dropping funnel, and gas-inlet pipe. Dry N$_2$ was bubbled in the flask during the reaction and the solution was cooled down to -5°C. The second monomer DIPA (6.65 g-50 mmol) dissolved in DMAc was added at this low temperature dropwise until the whole amount of the bishydroxyamine was charged into the flask, total amount of solvent is 59.2 g (30 wt%). The ice bath was removed and the reaction proceeded until the temperature is 30°C then DBTL is added (0.01 g). The amount of NCO present in the solution was followed by titration as mentioned before. The amount added DIPA as stopper is 0.74 g. The polymer was precipitated in water, filtered, and dried in vacuum over P$_2$O$_5$.



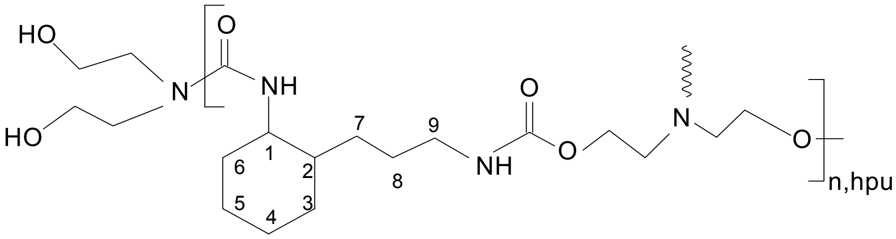
Yield: 45.63%, white powder

^{1}H NMR (DMSO-d_6): δ ppm = 7.02, 6.88, 6.57, 6.48, 6.42, 6.20, 6.05 (br, NH, urethane and urea), 5.25 - 4.85 (OH), 4.75 (C*H*-OC(O)), 3.9-3.7 (C*H*-OH, CHN, urea), 3.58 (CHN, urethane), 3.4 - 2.95 (N-CH$_2$, C*H*$_2$NH, *trans*), 2.9 - 2.65 (C*H*$_2$NH, *cis*), 1.7-0.7 (remaining CH$_2$ and CH$_3$ of aliphatic ring system and CH$_3$ of reacted DIPA).

^{13}C NMR (DMSO-d_6): δ ppm = 160.19, 159.96, 159.69, 159-158.4, 157.9 - 157.4, 156.8-156.3, 155.3-154.8 (C=O, urea and urethane), 70 - 69 (*C*H-OC(O)), 65.8 – 66.5 (*C*H-OH), 56.5-55 (N-*C*H$_2$-CHOH), 55 - 53.5 (CH$_2$-NH, cis), 53-51.5 (N-*C*H$_2$-CHOC(O)), 48-45.5 (CH$_2$-NH, trans; CH$_2$, ring), 43.95 (CHN, urethane), 43.41 (CHN, urea), 42.08 and 41.45 (CH$_2$, ring), 36.8 - 35.5 (C, ring), 35.20, 35.08 (CH_3, ring), 31.57, 31.44 (C, ring), 30.25, 27.61, 27.56, 27.01, 26.88, 23.40 (CH_3, ring), 21.40, 21.25 (CH(OH)-*C*H_3), 18.15 (CH(OC(O))-*C*H_3).

6.2.6 Synthesis of aliphatic hyperbranched polymers (Al-hpu3)-OH3

10.4 g of IPCI (50 mmol) was dissolved in DMAc in a three-necked round bottom flask fitted with thermometer, dropping funnel, and gas-inlet pipe. Dry N_2 was bubbled in the flask during the reaction and the solution was cooled down to -5°C. The second monomer DEA (5.25 g-50 mmol) dissolved in DMAc was added at this low temperature dropwise until the whole amount of the bishydroxyamine was charged into the flask, total amount of solvent is 52 g (30 wt%). The ice bath was removed and the reaction proceeded until the temperature is 50°C then DABCO is added (0.01 g). The amount of NCO present in the solution was followed by titration as mentioned before. The amount added DEA as stopper is 0.26 g. The polymer was precipitated in water, filtered, and dried under high vacuum.



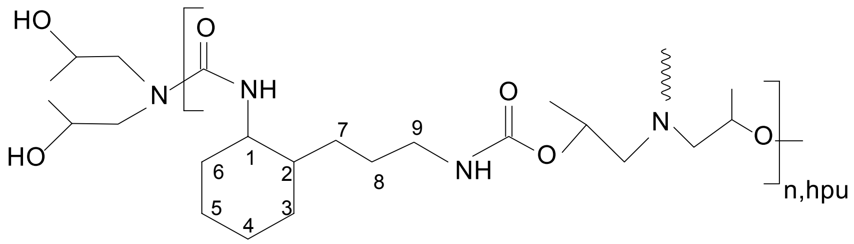
Yield: 57.82%, white particles

^{1}H NMR (DMSO-d_6): δ ppm = 7.06, 6.94, 6.75, 6.68 (NH, urethane), 6.40, 6.23, 5.99 (NH, urea), 5.08 (t + l, OH related to CH_{cis}-urea), 4.84 (t + l, OH related to CH_{trans}-urea), 4.79 (t + l, OH related to CH_2-urea), 3.95 (C*H_2*-OC(O)), 3.77 (H_1, cis, urea), 3.67 (H_1, cis, urethane), 3.5 - 3.2 (C*H_2*-OH; N-CH_2; H_1, trans, urea), 3.05 - 2.85 (H_1, trans, urethane; H_9), 2.0 - 0.8 (H_2-H_6, H_7, H_8).

^{13}C NMR (DMSO-d_6): δ ppm = 159.05, 159.02, 158.81, 158.42, 158.21, 157.76, 157.46 (C=O, urea), 156.15, 155.95, 155.79 (C=O, urethane), 62.5 – 62 (*C*H_2-OC(O)), 60.76 (t + l, CH_2-OH related to CH_{cis}-urea), 60.35 (t + l, CH_2-OH related to CH_{trans}-urea), 60.19 and 60.16 (t + l, CH_2-OH related to CH_2-urea), 53.94, 53.38, 53.18, 53.07, 52.97 (C_1, trans), 50.75, 50.29, 50.24, 50.08 (N-*C*H_2-CH_2-OH), 49.46, 48.36, 48.16, 48.02 (C_1, cis), 47-46 (N-*C*H_2-CH_2-OC(O), 42-41.4 (C_2, trans), 40.81, 40.76, 40.61, 40.56 (C_9), 39.35, 38.82, (C_2, cis), 33.8, 33.5, 31-24 (large number of signals, C_3-C_6, C_7, C_8).

6.2.7 Synthesis of aliphatic hyperbranched polymers (Al-hpu4)-OH3

10.4 g of IPCI (50 mmol) was dissolved in DMAc in a three-necked round bottom flask fitted with thermometer, dropping funnel, and gas-inlet pipe. Dry N_2 was bubbled in the flask during the reaction and the solution was cooled down to -5°C. The second monomer DIPA (6.65 g-50 mmol) dissolved in DMAc was added at this low temperature dropwise until the whole amount of the bishydroxyamine was charged into the flask, total amount of solvent is 56 g (30 wt%). The ice bath was removed and the reaction proceeded until the temperature is 30°C then DABCO is added (0.01 g), The reaction temperature is raised till 70°C and it was proceeded for about 21 hours. The amount of NCO present in the solution was followed by titration as mentioned before. The amount added DEA as stopper is 0.83 g then the polymer is precipitated from water and dried under high vacuum till constant weight.



Yield: 52.78%, white powder

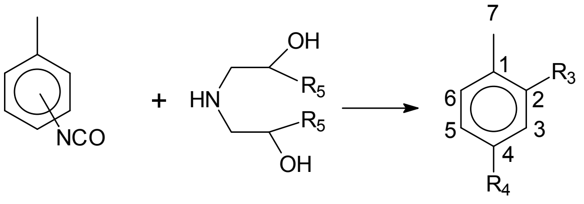
^{1}H NMR (DMSO-d_6): δ ppm = 6.96, 6.83, 6.72, 6.63, 6.36, 6.3, 6.15, 6.09 (NH), 5.29, 5.15, 5.04, 5.00, 4.95, 4.9 (OH), 4.76 (C*H*-OC(O)), 3.9 - 3.7 (C*H*-OH, H_1, cis, urea), 3.67 (H_1, cis, urethane), 3.5 - 3.05 (N-CH_2, H_1, trans, urea), 3.05 - 2.85 (H_1, trans, urethane; H_9), 2.0 - 0.8 (H_2-H_6, H_7, H_8 and CH_3 of reacted DIPA).

^{13}C NMR (DMSO-d_6): δ ppm = 160.03, 159.89, 159.64, 159.38, 159.13, 158.93, 158.35, 158.28, 157.93, 155.91, 155.68, 155.57 (C=O), 69.6 - 69 (*C*H-OC(O)), 66.48, 66.37, 66.18, 66.02, 65.88 (*C*H-OH), 56.46, 56.06, 55.89, 55.36 (N-*C*H_2-CHOH), 53.88, 53.06, 54-1.5 (C_1, trans, N-*C*H_2-CHOC(O)), 49.5, 48.1, 46.9 (C_1, cis), 42-41.4 (C_2, trans), 40.89, 40.57 (C_9), 39.5, 38.8, (C_2, cis), 34.1, 33.6, 31.5 - 24 (large number of signals, C_3-C_6, C_7, C_8); 21.4, 21.3, 21.2, 21.1 (CH(OH)-*C*H_3), 18.1 (CH(OC(O))-*C*H_3).

6.3 Synthesis of model compounds

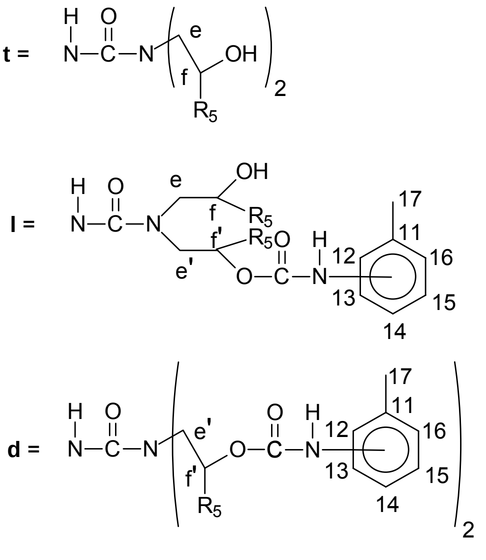
6.3.1 Synthesis of model compounds based on o- and p- tolyl monoisocyanate

Model compounds were prepared through the reaction of tolyl monoisocyanate isomers with B_2B^* monomers in order to interpret NMR spectra of the hyperbranched polymers. The method is nearly the same as in case of preparing the polymer but the ratio of the reactants is 2:1 tolyl monoisocyanate : bishydroxyamine. The amount of tolyl monoisocyanate was dissolved in THF and cooled down to -5°C; the slow addition of B^*B_2 was started at this low temperature. After complete addition the temperature was raised up to 50°C and DBTL was added as a catalyst. The presence of NCO in the reaction mixture was followed by IR (peak of NCO- at 2270 cm^{-1}). After complete reaction the excess THF was removed by vacuum distillation and the formed product mixture was investigated by NMR spectroscopy without further purification. As an example for the amounts used, 3.33 g (25 mmol) of p-tolyl monoisocyanate was reacted with 5.25 g (50 mmol) diethyamine in presence of 171.56 g of THF (5 wt%) 0.01% DBTL was added.



5(t, l, d): R_3 = t, l, or d; R_4, R_5 = H
(substitution in position 12)
6(t, l, d): R_3, R_5 = H; R_4 = t, l, or d
(substitution in position 14)

5'(t, l, d): R_3 = t, l, or d; R_4 = H; R_5 = CH_3
(substitution in position 12)
6'(t, l, d): R_3 = H; R_4 = t, l, or d; R_5 = CH_3
(substitution in position 14)



Yield: not determined

Model compounds prepared from o-tolyl isocyanate and p-tolyl isocyanate, resp., and DEA 5(t, l, d) and 6(t, l, d) or DIPA 5’(t, l, d) and 6’(t, l, d):

1,1-Bis-(2-hydroxy-ethyl)-3-o-tolyl-urea (5t):

^1H NMR (DMSO-d_6): δ ppm = 8.29 (NH), 7.50 (H_3), 7.11 (H_6), 7.08 (H_4), 6.90 (H_5), 5.15 (OH), 3.61 (H_f), 3.41 (H_e), 2.18 (H_7).

^{13}C NMR (DMSO-d_6): δ ppm = 156.60 (C=O), 138.66 (C_2), 130.1 (C_6), 128.57 (C_1), 125.88 (C_4), 122.50 (C_5), 122.07 (C_3), 60.26 (C_f), 50.55 (C_e), 18.06 (C_7).

o-Tolyl-carbamic acid 2-[1-(2-hydroxy-ethyl)-3-o-tolyl-ureido]-ethyl ester (5l):

^{1}H NMR (DMSO-d_6): δ ppm = 8.84 (NH, urethane), 8.21 (NH, urea), 7.43 (H_3), 7.34 (H_{13}), 7.17 (H_{16}), 7.13 (H_{14}), 7.12 (H_6), 7.08 (H_4), 7.03 (H_{15}), 6.94 (H_5), 5.42 (OH), 4.22 (H_h), 3.64 (H_f), 3.59 (H_g), 3.48 (H_e), 2.20 (H_{17}), 2.17 (H_7).

^{13}C NMR (DMSO-d_6): δ ppm = 156.22 (C=O, urea), 154.37 (C=O, urethane), 138.41 (C_2), 136.39 (C_{12}), 131.8 (C_{11}), 130.3 (C_{16}), 130.1 (C_6), 129.75 (C_1), 126.0 (C_{14}), 125.84 (C_4), 124.9 (C_{13}, C_{15}), 123.15 (C_3), 123.10 (C_5), 62.58 (C_h), 60.55 (C_f), 50.75 (C_e), 46.63 (C_g), 18.03 (C_7), 17.78 (C_{17}).

1,1-Bis-(2-o-tolylcarbamoyloxy-ethyl)-3-o-tolyl-urea (5d):

^{1}H NMR (DMSO-d_6): δ ppm = 8.86 (NH, urethane), 7.88 (NH, urea), 7.33 (H_{13}), 7.22 (H_3), 7.17 (H_{16}), 7.13 (H_{14}), 7.12 (H_6), 7.09 (H_4), 7.03 (H_{15}), 7.02 (H_5), 4.24 (H_h), 3.66 (H_g), 2.19 (H_{17}), 2.16 (H_7).

^{13}C NMR (DMSO-d_6): δ ppm = 155.33 (C=O, urea), 154.39 (C=O, urethane), 137.85 (C_2), 136.32 (C_{12}), 133.31 (C_1), 131.8 (C_{11}), 130.3 (C_{16}), 130.1 (C_6), 126.33 (C_3), 126.0 (C_{14}), 125.74 (C_4), 124.9 (C_{13}, C_{15}), 124.74 (C_5), 62.64 (C_h), 46.82 (C_g), 17.94 (C_7), 17.75 (C_{17}).

1,1-Bis-(2-hydroxy-ethyl)-3-p-tolyl-urea (6t):

^{1}H NMR (DMSO-d_6): δ ppm = 8.52 (NH), 7.23 ($H_{3/5}$), 7.02 ($H_{2/6}$), 5.04 (OH), 3.58 (H_f), 3.40 (H_e), 2.23 (H_7).

^{13}C NMR (DMSO-d_6): δ ppm = 156.60 (C=O), 138.10 (C_4), 130.23 (C_1), 128.83 ($C_{2/6}$), 119.22 ($C_{3/5}$), 60.25 (C_f), 50.48 (C_e), 20.35 (C_7).

p-Tolyl-carbamic acid 2-[1-(2-hydroxy-ethyl)-3-p-tolyl-ureido]-ethyl ester (6l):

^{1}H NMR (DMSO-d_6): δ ppm = 9.51 (NH, urethane), 8.48 (NH, urea), 7.33 ($H_{13/15}$), 7.27 ($H_{3/5}$), 7.07 ($H_{12/16}$), 7.02 ($H_{2/6}$), 5.20 (OH), 4.19 (H_h), 3.61 (H_f, H_g), 3.47 (H_e), 2.23 (H_7, H_{17}).

^{13}C NMR (DMSO-d_6): δ ppm = 155.66 (C=O, urea), 153.56 (C=O, urethane), 137.93 (C_4), 136.60 (C_{14}), 131.31 (C_{11}), 130.49 (C_1), 129.12 ($C_{12/16}$), 128.78 ($C_{2/6}$), 119.64 ($C_{3/5}$), 118.47 ($C_{13/15}$), 62.44 (C_h), 60.41 (C_f), 50.38 (C_e), 46.64 (C_g), 20.35 (C_7, C_{17}).

1,1-Bis-(2-p-tolylcarbamoyloxy-ethyl)-3-p-tolyl-urea (6d):

^{1}H NMR (DMSO-d_6): δ ppm = 9.51 (NH, urethane), 8.24 (NH, urea), 7.33 ($H_{13/15}$), 7.33 ($H_{3/5}$), 7.07 ($H_{12/16}$), 7.02 ($H_{2/6}$), 4.22 (H_h), 3.69 (H_g), 2.23 (H_7, H_{17}).

^{13}C NMR (DMSO-d_6): δ ppm = 154.97 (C=O, urea), 153.56 (C=O, urethane), 137.68 (C_4), 136.51 (C_{14}), 131.38 (C_{11}), 130.90 (C_1), 129.12 ($C_{12/16}$), 128.66 ($C_{2/6}$), 120.48 ($C_{3/5}$), 118.47 ($C_{13/15}$), 62.44 (C_h), 46.55 (C_g), 20.35 (C_7, C_{17}).

Selected ^{1}H and ^{13}C NMR signal assignments for 5’(t, l, d) and 6’(t, l, d):

5’t: ^{1}H NMR (DMSO-d_6): δ ppm = 8.54 and 8.48 (NH), 5.26 (OH), 3.95 (C*H*-OH).

^{13}C NMR (DMSO-d_6): δ ppm = 157.27 and 156.99 (C=O), 66.08 and 65.93 (CH-OH), 56.18 and 55.86 (N-CH$_2$), 21.29 and 21.18 (CH-*C*H$_3$).

5’l: ^{1}H NMR (DMSO-d_6): δ ppm = 8.74 (NH, urethane), 8.36 and 8.35 (NH, urea), 5.57 and 5.53 (OH), 5.09 (CH-OC(O)), 3.95 (C*H*-OH).

^{13}C NMR (DMSO-d_6): δ ppm = 156.55 and 156.46 (C=O, urea), 154.09 and 154.05 (C=O, urethane), 69.87 and 69.79 (*C*H-OC(O)), 66.42 and 66.08 (CH-OH), 55.84 (N-CH$_2$, e), 52.54 and 52.02 (N-CH$_2$, e’), 21.24 and 21.10 (CH(OH)-*C*H$_3$).

5’d: ^{1}H NMR (DMSO-d_6): δ ppm = 8.74 (NH, urethane), 7.82 (NH, urea), 5.09 (CH-OC(O)).

^{13}C NMR (DMSO-d_6): δ ppm = 155.46 and 155.27 (C=O, urea), 154.14 and 154.11 (C=O, urethane), 69.79 and 69.45 (*C*H-OC(O)), 52.29 and 51.88 (N-CH$_2$).

6’t: ^{1}H NMR (DMSO-d_6): δ ppm = 8.86 and 8.79 (NH), 5.20 and 5.18 (OH), 3.91 (C*H*-OH).

^{13}C NMR (DMSO-d_6): δ ppm = 156.69 and 156.58 (C=O), 66.12 and 65.99 (C*H*-OH), 56.11 and 55.86 (N-CH$_2$), 21.25 and 21.16 (CH-*C*H$_3$).

6’l: ^{1}H NMR (DMSO-d_6): δ ppm = 9.43 (NH, urethane), 8.65 (NH, urea), 5.36 (OH), 5.03 (CH-OC(O)), 3.91 (C*H*-OH).

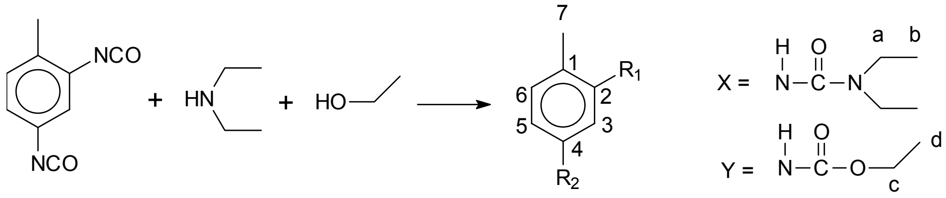
^{13}C NMR (DMSO-d_6): δ ppm = 156.04 and 155.93 (C=O, urea), 153.31 and 153.26 (C=O, urethane), 69.79 and 69.50 (*C*H-OC(O)), 66.37 and 66.12 (CH-OH), 55.66 and 55.45 (N-CH$_2$, e), 52.57 and 52.00 (N-CH$_2$, e’), 21.25 and 21.09 (CH(OH)-*C*H$_3$), 18.08 and 18.05 (CH(OC(O))-*C*H$_3$).

6’d: ^{1}H NMR (DMSO-d_6): δ ppm = 9.43 (NH, urethane), 8.22 and 8.20 (NH, urea), 5.03 (CH-OC(O)).

^{13}C NMR (DMSO-d_6): δ ppm = 155.14 and 155.04 (C=O, urea), 153.31 and 153.29 (C=O, urethane), 69.50 and 69.33 (*C*H-OC(O)), 51.96 and 51.73 (N-CH$_2$), 17.98 and 17.97 (CH-*C*H$_3$).

6.3.2 Synthesis of model compounds for substitution pattern

A model reaction was prepared in order to study the reactivity of *ortho* and *para* NCO groups towards both amino and OH groups. 10 mmol of TDI was dissolved in THF and charged in three-necked flask under N_2 gas and cooled down to –5°C. N,N-diethylamine (10 mmol) was mixed with ethanol (20 mmol) and dissolved in THF. The mixture was dropped over TDI in the period of 30 min. The overall concentration of the solution was 30 wt-%. The temperature was raised up to 30°C and the solution was stirred with a magnetic stirrer and left until the reaction of TDI with both N,N-diethylamine and ethanol was completed. The presence of NCO groups was followed by IR. After completion of the reaction, the excess THF was removed under high vacuum and the product was analyzed by NMR without further purification.



1: $R_1 = R_2 = X$
2: $R_1 = X; R_2 = Y$
3: $R_1 = Y; R_2 = X$
4: $R_1 = R_2 = Y$

Yield:	not determined

^1H and ^{13}C NMR signal assignments for model compounds 1 - 4 prepared from TDI, ethanol and N,N-diethyl amine:

3-[5-(3,3-Diethyl-ureido)-2-methyl-phenyl]-1,1-diethyl-urea (1; $R_1 = R_2$ = urea):

^1H NMR (DMSO-*d*$_6$): δ ppm = 8.00 (NH; R_2), 7.58 (NH; R_1), 7.35 (H_3), 7.19 (H_5), 6.98 (H_6), 3.32 (H_a; R_1/R_2), 2.085 (H_7), 1.10, 1.08 (H_b; R_1/R_2).

^{13}C NMR (DMSO-*d*$_6$): δ ppm = 154.97 (C=O; R_1), 154.50 (C=O; R_2), 138.52 (C_4), 137.87 (C_2), 129.22 (C_6), 126.40 (C_1), 118.45 (C_3), 116.47 (C_5), 40.55, 40.51 (C_a; R_1/R_2), 17.28 (C_7), 13.95 (C_b; R_1/R_2).

[3-(3,3-Diethyl-ureido)-4-methyl-phenyl]-carbamic acid ethyl ester (2; R_1 = urea, R_2 = urethane):

^1H NMR (DMSO-*d*$_6$): δ ppm = 9.41 (NH; R_2), 7.65 (NH; R_1), 7.34 (H_3), 7.13 (H_5), 7.03 (H_6), 4.10 (H_c), 3.32 (H_a), 2.08 (H_7), 1.23 (H_d), 1.08 (H_b).

^{13}C NMR (DMSO-d_6): δ ppm = 154.93 (C=O; R_1), 153.57 (C=O; R_2), 138.43 (C_2), 137.01 (C_4), 129.81 (C_6), 127.26 (C_1), 116.60 (C_3), 114.72 (C_5), 60.13 (C_c), 40.60 (C_a), 17.33 (C_7), 14.58 (C_d), 13.93 (C_b).

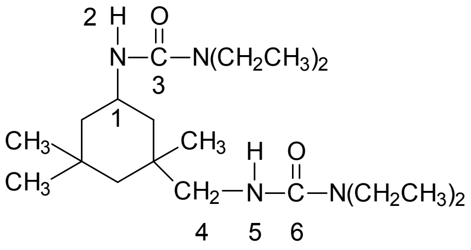
[5-(3,3-Diethyl-ureido)-2-methyl-phenyl]-carbamic acid ethyl ester (3; R_1 = urethane, R_2 = urea):
^{1}H NMR (DMSO-d_6): δ ppm = 8.67 (NH; R_1), 8.05 (NH; R_2), 7.48 (H_3), 7.20 (H_5), 7.00 (H_6), 4.10 (H_c), 3.32 (H_a), 2.105 (H_7), 1.23 (H_d), 1.08 (H_b).
^{13}C NMR (DMSO-d_6): δ ppm = 154.50 (C=O; R_2), 154.43 (C=O; R_1), 138.82 (C_4), 136.04 (C_2), 129.59 (C_6), 124.92 (C_1), 116.96 (C_3), 116.90 (C_5), 60.04 (C_c), 40.53 (C_a), 17.11 (C_7), 14.67 (C_d), 13.93 (C_b).

(5-Ethoxycarbonylamino-2-methyl-phenyl)-carbamic acid ethyl ester (4; R_1 = R_2 = urethane):
^{1}H NMR (DMSO-d_6): δ ppm = 9.47 (NH; R_2), 8.72 (NH; R_1), 7.49 (H_3), 7.15 (H_5), 7.05 (H_6), 4.10 (H_c; R_1/R_2), 2.11 (H_7), 1.23 (H_d; R_1/R_2).
^{13}C NMR (DMSO-d_6): δ ppm = 154.34 (C=O; R_1), 153.58 (C=O; R_2), 137.29 (C_4), 136.55 (C_2), 130.21 (C_6), 125.62 (C_1), 115.05, 115.00 (C_3 / C_5), 60.15, 60.05 (C_c; R_1/R_2), 17.15 (C_7), 14.63, 14.58 (C_d; R_1/R_2).

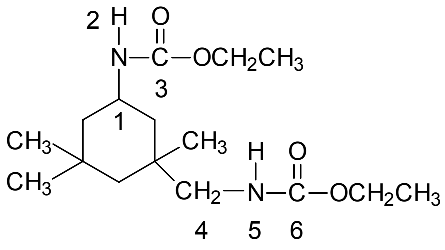
6.3.3 Synthesis of model compounds based on the reaction of IPDI with N,N-diethylamine and ethanol

A model reaction was prepared in order to study the reactivity of both primary and secondary isocyanate groups toward amino and hydroxyl groups through the reaction of IPDI with N,N.diethylamine and ethanol. 5 mmol of AA* aliphatic monomer was dissolved in THF and charged in three-necked flask under N_2 gas and cooled down to -5°C. N,N-diethyl amine (10 mmol) was dropped over AA*monomer solution in the period of 30 min. The overall concentration of the solution was 30 wt%. The temperature was raised up to 30°C and 3 drops of DBTL as catalyst was added. The solution was stirred with a magnetic stirrer and left until the reaction of AA* with N,N-diethyl amine was completed. The presence of NCO groups was followed by IR. After completion of the reaction, the excess THF was removed under high vacuum. The same procedure was made but by using methanol solution (10 mmol) instead of N,N-diethyl amine. The reaction products in each case were analyzed by NMR without further purification.

Selected ^{1}H and ^{13}C NMR signal assignments for model compounds 1 and 2 prepared from IPDI and N,N-diethyl amine and ethanol, respectively.



1



2

1: ^{1}H NMR (DMSO-d_6): δ ppm = 5.93 (t, 5_{cis}), 5.65 (d, 2_{cis}), 5.63 (d, 2_{trans}), 5.58 (t, 5_{trans}), 3.79 (1_{cis}), 3.73 (1_{trans}), 3.17 (4_{trans}), 2.81 (4_{cis}).

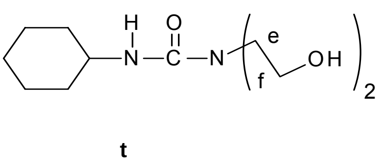
^{13}C NMR (DMSO-d_6): δ ppm = 156.93 (6_{cis}), 156.77 (6_{trans}), 155.50 ($3c_{is}$), 155.42 (3_{trans}), 53.68 (4_{cis}), 46.11 (4_{trans}), 43.44 (1_{trans}), 43.30 (1_{cis}).

2: ^{1}H NMR (DMSO-d_6): δ ppm = ^{1}H: 7.03 (t, 5_{cis}), 6.90 (d, 2_{cis}), 6.87 (t, 5_{trans}), 6.85 (d, 2_{trans}) (major rotamers), 6.8-6.4 (broad signals due to the minor rotamers of 2 and 5), 3.57 (1_{cis}), 3.55 (1_{trans}), 3.10 and 2.99 (4_{trans}), 2.71 (4_{cis}).

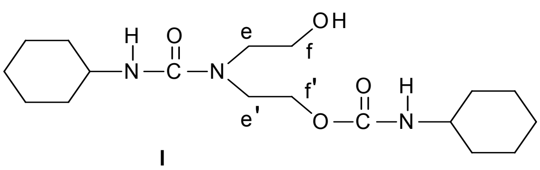
^{13}C NMR (DMSO-d_6): δ ppm = 157.08 (6_{cis}), 156.99 (6_{trans}), 156.33 (3_{trans}), 156.10 (3_{cis}), 54.26 (4_{cis}), 47.53 (4_{trans}), 43.85 (1_{trans} and 1_{cis}).

6.3.4 Synthesis of model compounds based on cyclohexylisocyanate and DEA

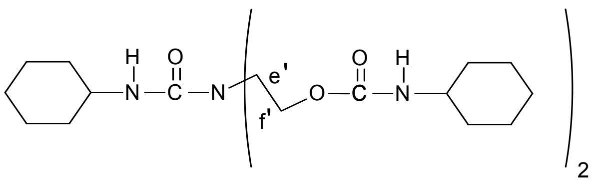
3.75 g cyclohexylisocyanate (0.03 mmol) was dissolved in THF and cooled down to -5°C; the slow addition of 1.57 g DEA (0.015 mmol) dissolved in THF was started at this low temperature, the whole amount of solvent is 53 g. After complete addition the temperature was raised up to 50°C and 0.01% of DBTL was added as a catalyst. The presence of NCO in the reaction mixture was followed by IR (peak of NCO- at 2270 cm^{-1}). After complete reaction the excess THF was removed by vacuum distillation and the formed product mixture was investigated by NMR spectroscopy without further purification.



t



l



d

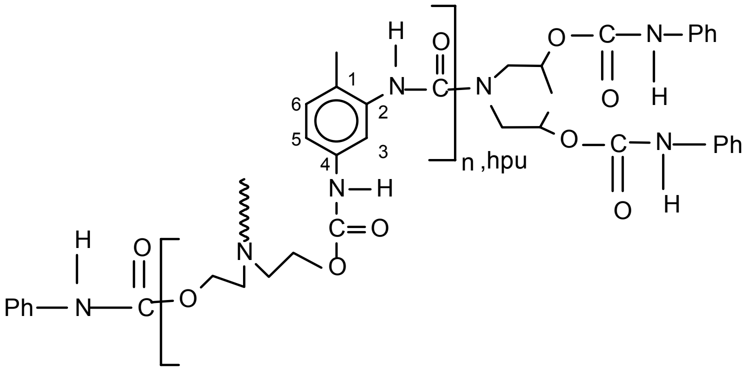
Selected ^{1}H and ^{13}C NMR signal assignments for model compounds (t, l, d) prepared from cyclohexylisocyanate and DEA..

t: ^{1}H NMR (DMSO-d_6): δ ppm = 6.12 (d, NH), 4.87 (OH), 3.47 (f), 3.39 (CH), 3.25 (e).
^{13}C NMR (DMSO-d_6): δ ppm = 158.00 (C=O), 60.31 (f), 50.27 (e), 48.65 (CH).
l: ^{1}H NMR (DMSO-d_6): δ ppm = 7.02 and 6.76 (NH, urethane, major and minor rotamer), 6.02 (d, NH, urea), 4.87 (OH), 3.95 (f'), 3.47 (f), 3.40 (CH, urea), 3.38 (e'), 3.25 (e; CH, urethane).
^{13}C NMR (DMSO-d_6): δ ppm = 157.20 (C=O, urea), 155.34 (C=O, urethane), 62.04 (f'), 60.31 (f), 50.17 (e), 49.46 (CH, urethane), 48.87 (CH, urea), 46.54 (e').
d: ^{1}H NMR (DMSO-d_6): δ ppm = 7.02 and 6.76 (NH, urethane, major and minor rotamer), 5.89 (d, NH, urea), 3.95 (f'), 3.40 (CH, urea), 3.38 (e'), 3.25 (CH, urethane).
^{13}C NMR (DMSO-d_6): δ ppm = 156.30 (C=O, urea), 155.34 (C=O, urethane), 62.04 (f'), 49.46 (CH, urethane), 49.20 (CH, urea), 46.54 (e').

6.4 modification of hyperbranched polymers

6.4.1 Modification of (Ar-hpu1)-OH2 with Ph-NCO

2 g of polymer (Ar-hpu1)-OH2 (5.6 mmol OH) was dried carefully and dissolved in DMAc and reacted with 2.04 g of Ph-NCO (5.6 mmol) for 3 hours at room temperature. The reaction was followed through noticing the vanishing of the NCO-group using IR. The modified polymer is precipitated from water, filtered and dried under high vacuum.

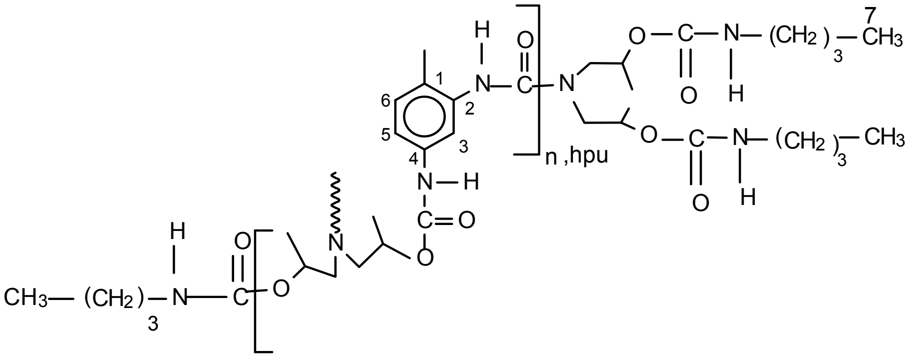


Yield: 60.4%, white powder

^{1}H NMR (DMSO-d_6): δ ppm = 9.46 and 9.37 (NH, urethane, para to CH_3), 9.4-8.6 (NH, urethane, ortho to CH_3 and NH, urea), 8.65 (NH, diphenyl urea by-product), 8.6-8.1 (NH, urea), 7.85 (NH, urea, d_o), 7.65-7.35 (H_3), 7.35-6.9 (H_5 ,H_6), 4.2 (CH-OC(O)), 3.8 - 3.2 (N-CH_2), 2.11, 2.08 (Ar-CH_3), 1.21 (CH(OC(O))-CH_3).

6.4.2 Modification of (Ar-hpu1)-OH2 with Bu-NCO

1 g of polymer (Ar-hpu1)-OH2 (2.85 mmol OH) was dried carefully and dissolved in DMAc and reacted with 0.56 g of Bu-NCO (5.7 mmol) in presence of DABCO as catalyst (0.01%) for 3 hours at room temperature. The reaction was followed through noticing the vanishing of the NCO-group using IR. The modified polymer is precipitated from water, filtered and dried under high vacuum.

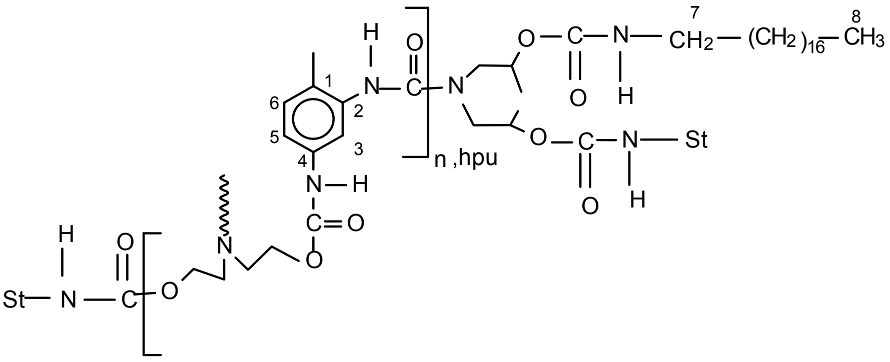


Yield: 74.35%, white powder

^{1}H NMR (DMSO-d_6): δ ppm = 9.46 and 9.37 (NH, urethane, para to CH_3), 9.4-8.6 (NH, urethane, ortho to CH_3 and NH, urea), 8.6-8.1 (NH, urea), 7.85 (NH, urea, d_o), 7.65-7.35 (H_3), 7.35-6.9 (H_5 ,H_6), 5.6 (aliphatic amine; by-product), 4.2 (CH-OC(O)), 2.1 (CH_3 aromatic), 0.8 (H_7).

6.4.3 Modification of (Ar-hpu1)-OH2 with St-NCO

1 g of polymer (Ar-hpu1)-OH2 (2.85 mmol OH) was dried carefully and dissolved in DMAc and reacted with 1.68 g of St-NCO (2.85 mmol) in presence of DABCO as catalyst (0.01%) for 24 hours at room temperature. The solution was turbid white after 3 hours of the reaction. The reaction was followed through noticing the vanishing of the NCO-group using IR spectroscopy. The precipitated modified polymer was filtered and dried under high vacuum.

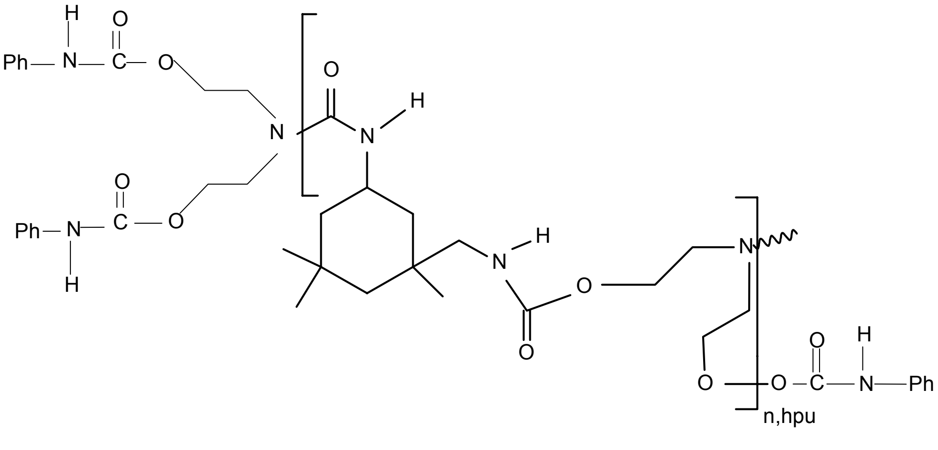


Yield: 75.37%, white powder

^{1}H NMR (mixture of CD_3Cl and DMSO-d_6): δ ppm = 9.46 and 9.37 (NH, urethane, para to CH_3), 9.4-8.6 (NH, urethane, ortho to CH_3 and NH, urea), 8.6-8.1 (NH, urea), 7.85 (NH, urea, d_o), 7.65-7.35 (H_3), 7.35-6.9 (H_5 ,H_6), 5.6 (aliphatic amine; by-product), 4.4 (CH-OC(O)), 3.5 (H_7), 2.95 (aliphatic urea; by-product), 2.1 (CH_3 aromatic), 1.8: 0.8 (H_8 and alky protons)

6.4.4 Modification of (Al-hpu1)-OH2 with Ph-NCO

2.015 g of polymer (Al-hpu1)-OH2 (8.8 mmol OH) was dried carefully and dissolved in DMAc and reacted with 1.048 g of Ph-NCO (8.8 mmol), in presence of 0.01% DBTL, for 3 hours at 40°C. The reaction was followed through noticing the vanishing of the NCO-group using IR. The modified polymer is precipitated from water, filtered and dried under high vacuum.



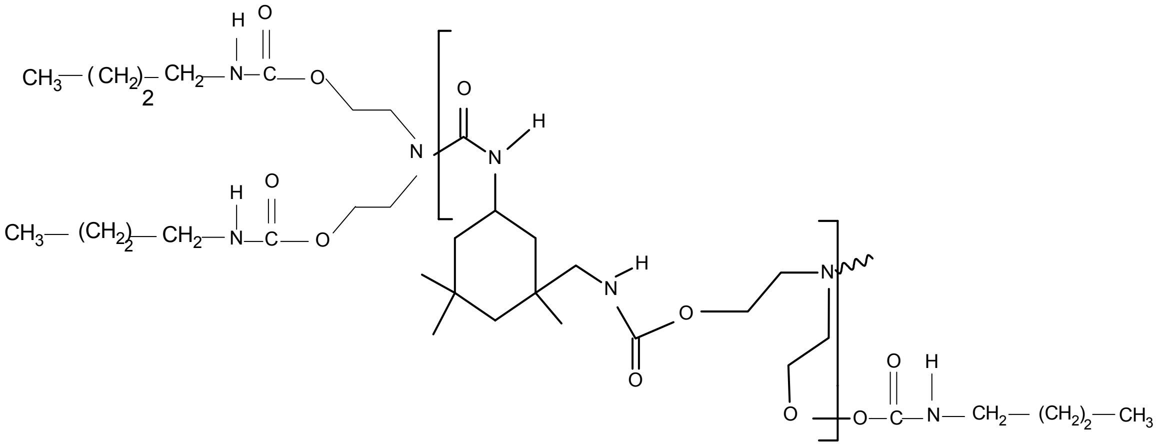
Yield: 2.48 g (80.96%, white powder)

^{1}H NMR (DMSO-d_6): δ ppm= 6.73 (NH, CH_2-urethane, *cis*), 6.58 (br, NH, CH_2-urethane, *trans* and CH-urethane, *cis* / *trans*), 6.17 (t_c), 6.07 (t_t, l_c, l_t), 5.90 (d_t, d_c) (NH, CH_2-urea), 5.80, 5.76, 5.67 (NH, CH-urea), 4.15 (CH_2-O(CO)NH-Ph), 4.03 (CH_2-OC(O)), 3.8 (CHN, urea), 3.63

(CHN, urethane), 3.42 (N-C*H*$_2$-CH$_2$-OC(O)), 3.2-3.1 (*trans*-CH$_2$N, urea and urethane), 2.95 - 2.70 (*cis*-CH$_2$N, urea and urethane), 1.8-0.8 (remaining CH$_2$ and CH$_3$ of aliphatic ring system).

6.4.5 Modification of (Al-hpu1)-OH2 with Bu-NCO

2.77 g of polymer (Al-hpu1)-OH2 (8.8 mmol OH) was dried carefully and dissolved in DMAc and reacted with 0.89 g of Ph-NCO (9.0 mmol), in presence of 0.01% DBTL, for 3 hours at 40°C. The reaction was followed through noticing the vanishing of the NCO-group using IR. The modified polymer is precipitated from water, filtered and dried under high vacuum.

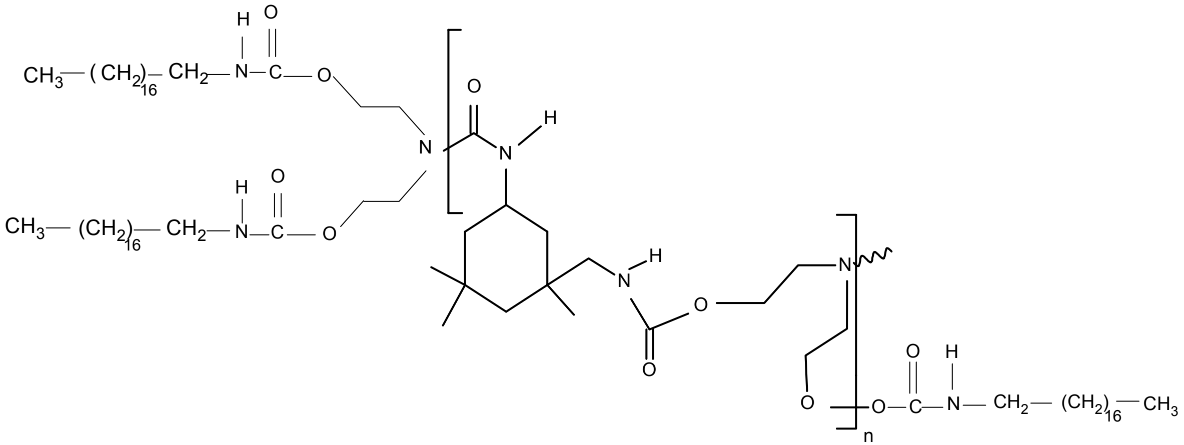


Yield: 72.4%, white powder

^{1}H NMR (DMSO-d_6): δ ppm= 6.73 (NH, CH$_2$-urethane, cis), 6.58 (br, NH, CH$_2$-urethane, trans and CH-urethane, cis / trans), 6.17 (t$_c$), 6.07 (t$_t$, l$_c$, l$_t$), 5.90 (d$_t$, d$_c$) (NH, CH$_2$-urea), 5.80, 5.76, 5.67 (NH, CH-urea), 4.03 (C*H*$_2$-OC(O)), 3.8 (CHN, urea), 3.63 (CHN, urethane),.4.2 (N-C*H*$_2$-CH$_2$-OC(O)), 3.2 - 3.1 (trans-CH$_2$N, urea and urethane), 2.95 - 2.70 (cis-CH$_2$N, urea and urethane), 1.8 - 0.8 (remaining CH$_2$ and CH$_3$ of aliphatic ring system and aliphatic groups of the modifier).

6.4.6 Modification of (Al-hpu1)-OH2 with St-NCO

2.038 g of polymer (Al-hpu1)-OH2 (8.9 mmol OH) was dried carefully and dissolved in DMAc and reacted with 2.64 g of St-NCO (9.0 mmol), in presence of 0.01% DBTL, after 1 hour a white precipitate is formed. The reaction proceeded for 3 hours at 40°C and was followed through noticing the vanishing of the NCO-group using IR. The modified polymer is precipitated from water, filtered and dried under high vacuum



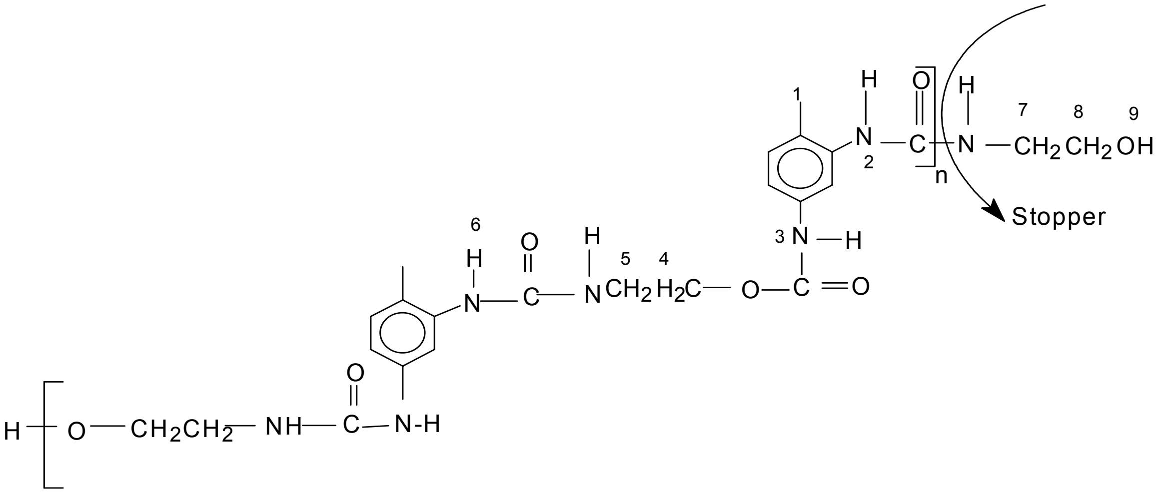
Yield: 56.64%, white powder

^{1}H NMR (DMSO-*d*$_6$ +$CDCl_3$): δ ppm= 6.73 (NH, CH_2-urethane, cis), 6.58 (br, NH, CH_2-urethane, trans and CH-urethane, cis / trans), 6.17 (t_c), 6.07 (t_t, l_c, l_t), 5.90 (d_t, d_c) (NH, CH_2-urea), 5.80, 5.76, 5.67 (NH, CH-urea), 4.03 (CH_2-OC(O)), 3.8 (CHN, urea), 3.63 (CHN, urethane), 3.53 (CH_2-OH), 3.42 (N-CH_2-CH_2-OC(O)), 3.2-3.1 (trans-CH_2N, urea and urethane), 2.95 -2.70 (cis-CH_2N, urea and urethane), 1.8-0.8 (remaining CH_2 and CH_3 of aliphatic ring system and alkyl chain).

6.5. Synthesis of linear polymers

6.5.1 Synthesis of aromatic linear polymer based on TDI and 2-ethanol mine.

Linear aromatic polymers were prepared using TDI and 2-EA by weighing 4.35 g (25 mmol) TDI with 1.53 g (25 mmol) 2-EA under inert atmosphere at -5°C. The amount of solvent used is 19.59 g (30 wt%) The hydroxyl amine was added to the diisocyanate dropwise in time period of about one hour until the whole amount is finished. The temperature was raised to 30°C in second step. The reaction proceeded under stirring under inert gas. The amount of NCO was followed by titration. The linear polymer was precipitated from water giving white powder, dried carefully in vacuum and finally characterized.

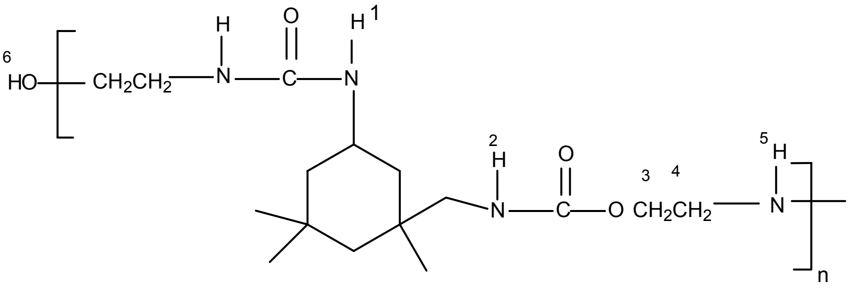


Yield: 55.8%, white powder

^{1}H NMR (DMSO-d_6): δ ppm= 2.1 (H1), 3.14 (H7), 3.45 (H8), 4.11 (H4), 4.69, 4.72 (H9), 6.12 (N*H* CH$_2$, o-position), 6.68 (N*H*-CH$_2$, p-position), 6.9: 7.7 (H aromatic ring), 8.2 (H2), 8.5(H6), 9.51 (H3).

6.5.2 Synthesis of aromatic linear polymer based on IPDI and 2-ethanol mine.

11.1 g of IPDI (50 mmol) was reacted with 3.05 g 2-EA (50 mmol) under inert atmosphere at -5°C. The amount of solvent used is 47 g (30 wt%) The hydroxyl amine was added to the diisocyanate dropwise in time period of about one hour until the whole amount is finished. The temperature was raised to 30°C in second step. The reaction proceeded under stirring under inert gas. The amount of NCO was followed by titration. The linear polymer was precipitated from water giving white powder, dried carefully in vacuum and finally characterized.



Yield: 65.2%, white powder

^{1}H NMR (DMSO-d_6): δ ppm= 0.8-1.8 (remaining CH_2 and CH_3 of aliphatic ring system and alkyl chain), 3.19 (H4), 3.36 (CH_2 OH), 3.89 (H3), 4.62 (H6), 5.84 (H1), 7.0 (H2).

6.6 Preparation of cross-linked polymer.

Preparation of cross-linked polymer (aliphatic network) was carried out through the reaction of 2.1 g (11 mol) BASONAT HI 100 (NCO content of 22 wt%), obtained from BASF, with 3 g (Al hpu1)-OH3 (11 mol). 50 wt% solid content was used as concentration in DMF. 0.01% DBTL catalyst was added. The reaction was stirred for 30 min before blading on glass using gap size 600 μm. The formed network was dried in vacuum oven at 70°C, then it was characterized.

7- LIST OF SYMBOLS AND ABBREVIATIONS

AFM	Atomic Force Microscopy
COSY	Correlation spectroscopy
°C	temperature in degrees Celsius
d	dendritic subunit
DB	Degree of branching
DEA	Diethanol amine
DBA	Dibutyl amine
DIPA	Diisopropanol amine
DMA	dynamic mechanical analysis
DMAc	Dimethylacetamide
DMF	Dimethylforamide
DMSO	Dimethylsulfoxide
DSC	Differential Scanning Calorimetry
EA	Ethanol amine
FT-IR	Fourier Transform Infrared Spectroscopy
g	gram
G’	storage modulus
GC-MS	Gas Chromatography-Mass Spectroscopy
GPC	Gel Permeation Chrromatography
h	hour
HMBC	Hydroneuclear Multiple Bond Correlation
HPU	Hyperbranched poly(urea-urethane)
Hz	Herz
i.e.	that is (Latin: id est)
IR	Infrared Spectroscopy
IPCI	2(3-isocyanatopropyl) cyclohexylisocyanate
IPDI	isophorone diisocyanate
J	coupling constant
l	linear subunit
LiCl	Lithium chloride
LM	Light Microscope
LS	Light Scattering
MG	Micro Glider
min	minute

mmol	millimole
ml	milliliter
M_n	number average molecular weight
mol	mole
Mpa	megapascale
M_w	weight average molecular weight
M_w/M_n	polydispersity
nm	nanometer
NMR	Neuclear Magnatic Resonance
PDI	polydispersity index
ppm	part per million
R_Q	surface roughness
RI	Refractive Index
RIM	Reaction Injection Molding
SEC	Size Exclusion Chromatography
sec	second
T	Temperature
t	terminal subunit
TDI	2,4 toluylene diisocyanate
TGA	Thermo Gravimetric Analysis
T_g	glass transition
wt%	weight per cent
η	relative viscosity
ω	frequency
Θ	Contact angle
Θ_a	advanced contact angle
γ_{sv}	interfacial tension of solid-vapour interface
η^*	complex viscosity
ζ	isoelectric point
μm	micrometer
E	tensile modulus
σ_B	stress at break
ε_B	elongation at break

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