Hyperbranched polyesters for polyurethane coatings: their preparation, structure and crosslinking with polyisocyanates

PHD THESIS

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Contents

Abbreviations Used

1 Introduction

1.1 Hyperbranched and similar functional polymers

1.1.1 Types of highly branched polymers

1.1.2 Synthesis and history of hyperbranched polymers

1.1.2.1 History

1.1.2.2 Synthetic approaches to hyperbranched polymers

1.1.2.2.1 Polycondensation of AB\textsubscript{1} monomers

1.1.2.2.2 Self-condensing vinyl polymerization

1.1.2.2.3 Self-condensing ring-opening polymerization

1.1.2.2.4 Addition reactions

1.1.2.2.5 Off-stoichiometric reactions of A\textsubscript{3} and B\textsubscript{2} monomers

1.1.3 Hyperbranched polyesters based on BHPPA

1.1.4 Commercially available dendritic OH-functional polymers

1.1.5 Application of HBP’s

1.1.5.1 HBP’s in Biomaterials

1.1.5.2 HBP’s in Blends

1.1.5.3 HBP’s as Additives

1.1.5.4 HBP’s in Polymer films

1.1.5.5 HBP’s in Coatings

1.1.5.6 Other HBP’s applications

1.2 Crosslinking of hyperbranched precursors

1.2.1 Multifunctional precursors of polymer networks

1.2.1.1 Polymer network formation

1.2.1.2 Network precursors

1.2.2 Use of hyperbranched polymers in polyurethane coatings

1.2.3 Intramolecular cyclizations during network formation

1.2.4 Reactivity of functional groups used for coating preparation

1.2.4.1 Catalyzed vs. non-catalyzed system

1.2.4.2 Possible side reactions

2 The aim of this work

3 Experimental part

3.1 Chemicals used

3.1.1 Solvents

3.1.2 Auxiliary chemicals and catalysts

3.1.3 OH-functional monomers for HBP polyesters synthesis

3.1.4 Isocyanates

3.1.5 The characterization of Desmodur N 3300

3.2 Syntheses

3.2.1 Preparation of hyperbranched polyesters (poly-BHPPA)
3.3 Molecular weight determination ......................................................... 44
3.4 Determination of reactive groups in (poly-BHPPA) .............................. 45
  3.4.1 Determination of COOH groups ..................................................... 45
  3.4.2 Determination of OH groups .......................................................... 47
3.5 Preparation of thin poly-BHPPA layers (coating films) ......................... 50
3.6 Determination of the glass transition temperature via DSC ..................... 50
3.7 Content of -NCO groups in Desmodur N 3300 ......................................... 51
3.8 Reaction of OH and NCO groups, kinetics followed by FTIR .................. 52
3.9 Crosslinking of Poly-BHPPA to Polyurethanes ........................................ 54
  3.9.1 Preparation of polyurethane formulations ........................................ 54
  3.9.2 Determination of the gel point conversion ....................................... 55
  3.9.3 Preparation of rectangular polyurethane plates ................................ 55
  3.9.4 Preparation of thin polyurethane coatings ....................................... 55
3.10 Properties of networks synthesized from HBP ...................................... 56
  3.10.1 Determination of equilibrium swelling ........................................... 56
  3.10.2 Sol content in the polyurethane networks ....................................... 57
  3.10.3 Determination of the concentration of Elastically Active Network Chains 57
  3.10.4 Investigation of cyclization reactions ............................................. 58
  3.10.5 Determination of the glass transition temperature via DMTA .......... 60
  3.10.6 TGA ................................ ............................................................... 60
  3.10.7 Contact angle measurement ....................................................... 60
  3.10.8 Topography of the surface ......................................................... 61
  3.10.9 Shore D hardness - ISO 868 ....................................................... 61
4 Results and discussion ................................................................................ 63
4.1 Synthesis and characterization of poly-BHPPA ..................................... 63
  4.1.1 Conditions of the poly-BHPPA synthesis ........................................ 63
    4.1.1.1 Condensation Temperature ..................................................... 64
    4.1.1.2 Incorporation of core monomers ............................................. 64
    4.1.1.3 Water content ................................................................. 65
    4.1.1.4 Reduction of the poly-BHPPA functionality ............................ 66
  4.1.2 Molecular weights of the poly-BHPPA prepared ............................... 67
    4.1.2.1 Determination of the number average molecular weight (Mn) ... 67
    4.1.2.2 Determination of the weight average of the molecular weight (Mw) 71
  4.1.3 Functionality of the poly-BHPPA prepared ..................................... 76
  4.1.4 Microstructure of poly-BHPPA prepared (degree of branching) ......... 78
    4.1.4.1 1H-NMR Spectroscopy: Determination of Mn .......................... 78
    4.1.4.2 13C-NMR Spectroscopy: Detailed microstructure .................... 80
      4.1.4.2.1 Degree of branching .................................................... 80
      4.1.4.2.2 Carboxyl groups signals in poly-BHPPA ......................... 85
      4.1.4.2.3 Determination of core monomer conversion ....................... 87
      4.1.4.2.4 Amounts of free monomer and of the side products ............ 88
      4.1.4.2.5 Mn determination from 13C-NMR ................................. 89
  4.1.5 Glass transition temperatures ....................................................... 91
  4.1.6 Thermal stability ........................................................................... 94
4.2 Kinetics investigations of polyurethane formation .................................. 96
  4.2.1 Model experiments: Reactions of low-molecular-weight compounds ...... 96
Abbreviations Used

AB$_f$  Monomer with two types of functional group (f = 2-6)
AG  Core monomer with one type of functional groups (g = 2,3,4 or 6)
AN  Acid Number
BHPPA  4,4-bis- (4’-hydroxyphenyl) pentanoic acid
BuI  Butyl Isocyanate
C  Molar concentration
$^{13}$C NMR  Carbon ($^{13}$C) Nuclear Magnetic Resonance
CRM  Critical Molar Ratio of functional group
D  Dendritic units of hyperbranched polymer
DB  Degree of Branching
DMTA  Dynamic Mechanical Thermal Analysis
DSA  Drop Shape Analysis
DSC  Differential Scanning Calorimetry
DBTDL  Dibutyltin Dilaureate
EAC  Elastically Active Crosslink
EANC = $\nu_c$  Concentration of Elastically Active Network Chains
EINC  Concentration of Elastically Inactive Network Chains
EPH  4-ethylphenol
$<f_{\lambda}>_1$  First moment of functionality distribution of OH group
$<f_{\lambda}>_2$  Second moment of functionality distribution of OH group
FT-IR  Fourier-Transformed Infrared Spectroscopy
GPC  Gel Permeation Chromatography
HBP  Hyperbranched Polymer
$^1$H NMR  Proton ($^1$H) Nuclear Magnetic Resonance
HN  Hydroxyl Number
L  Linear units of hyperbranched polymer
$M_n$  Number average of molecular weight
MPK  Methyl Propyl Ketone
$M_w$  Weight average of molecular weight
mp  Melting point
n  Mol
PEG  Poly (ethylene glycol)
### Abbreviations

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>$P_n$</td>
<td>Polymerization degree</td>
</tr>
<tr>
<td>Poly-BHPPA</td>
<td>Hyperbranched polyester based on 4,4-bis-(4’-hydroxyphenyl) pentanoic acid</td>
</tr>
<tr>
<td>PU</td>
<td>Polyurethane</td>
</tr>
<tr>
<td>T</td>
<td>Terminal units of hyperbranched polymer</td>
</tr>
<tr>
<td>Tg</td>
<td>Glass transition temperature</td>
</tr>
<tr>
<td>TGA</td>
<td>Thermo Gravimetric Analysis</td>
</tr>
<tr>
<td>THF</td>
<td>Tetrahydrofuran</td>
</tr>
<tr>
<td>Tri-HDI</td>
<td>Trimer of 1,6-diisocyanatohexane = Desmodur N3300</td>
</tr>
<tr>
<td>VPO</td>
<td>Vapour Pressure Osmometry</td>
</tr>
<tr>
<td>$w_g$</td>
<td>Weight fraction of gel</td>
</tr>
<tr>
<td>$\alpha$</td>
<td>Conversion of functional groups</td>
</tr>
<tr>
<td>$\alpha_{c,t}$</td>
<td>Theoretical critical conversion of functional groups at the gel point</td>
</tr>
<tr>
<td>$\alpha_{c, \text{exp}}$</td>
<td>Experimental critical conversion of functional groups at the gel point</td>
</tr>
<tr>
<td>$\varphi_2$</td>
<td>Volume fraction of the polymer in a swollen sample</td>
</tr>
<tr>
<td>$\varphi_2^0$</td>
<td>Volume fraction of the polymer in the solution during network formation</td>
</tr>
<tr>
<td>$\chi$</td>
<td>Polymer-solvent interaction parameter</td>
</tr>
</tbody>
</table>
1 Introduction

1.1 Hyperbranched and similar functional polymers

1.1.1 Types of highly branched polymers

Hyperbranched polymers

Hyperbranched polymers (HBP) are defined as polymer systems containing a large number of branch points connected by relatively short chains in their molecular structure. Their structure is not uniform (as in the case of dendritic polymers) and the individual molecules can have different molecular weight and degrees of branching (cf., Part 4.1.4). HBP’s can be prepared in one-step or in several steps. Due to a usually broad molecular weight distribution and to occasionally occurring side reactions during the synthesis, such polymers are complex product mixtures. On the other hand, they exhibit a lower solution viscosity compared to their linear analogues with similar molecular weight (a property typical also for dendrimers). In some applications, the HBP’s replace dendrimers, because of their similar properties combined with a much lower price. The large number of functional groups offers the possibility for further modifications of HBP’s and for special applications.

Fig. 1-1: Basic scheme of hyperbranched, dendritic, and highly-branched polymers
1 Introduction

Dendrimers

Dendrimers (Fig.1, centre) are similar to hyperbranched polymers, but possess a strictly regular branched structure, so that they are sometimes referred to as structurally perfect hyperbranched polymers. Dendrimers have a high concentration of functional groups on the surface for a given molecular weight and volume. They are often prepared step by step in reactions during which subsequent monomer layers, called generations, are attached to the surface functional groups, often using the protection-deprotection technique. The core molecule (cf., Part 1.1.3) is referred to as “generation 0”. Each successive repeating unit along all branches forms the next generations until the terminating generation.

Highly branched functional polymers

A third type of branched polymers similar to both described earlier, are highly-branched functional polymers. They are formed from $A_{fA}$ and $B_{fB}$ monomers where $f_A$ and $f_B$ denote the functionalities. For alternating reaction ($A+B\rightarrow AB$) in $A_{fA} + B_{fB}$ systems, the reaction under stoichiometric or somewhat off-stoichiometric conditions leads to gelation [1]. To avoid gelation it is possible to stop the polymerization by precipitation or to deactivate one of the two types of functional groups before reaching the critical point of gelation. Alternatively, off-stoichiometric systems can be used. For this type of reactions, the critical molar ratio (CMR) should be calculated or determined experimentaly for avoidance of gelation. The value of CMR depends mostly on the functionality of the components, but also on the reactivity of functional groups, which are involved in bond formation. Comparing this synthesis with the classical polycondensation of an $AB_f$ monomer, it was found that the structure of hyperbranched polymers prepared by both methods are basically the same. The advantage of the $A_3 + B_2$ reactions is a lower price of input materials and the wide range of variation of architecture of the end groups.
The basic differences between the functional dendrimers, classical hyperbranched polymers (from AB\textsubscript{r} monomers), and highly branched off-stoichiometric polymers are the following:

1) Functional dendrimers have a spherically symmetric structure with all functional groups at the branch extremities.

2) Classical hyperbranched polymers (HBP’s) are characterized by a distribution of polymerization degrees and of numbers of functional groups per molecule, as well as of branching degrees. If no core monomer is used, and in the absence of cyclization, each HBP molecule has one focal group “A”. If cyclization occurs, each molecule can have only one cycle. Without cyclization and without core monomer, both the number (M\textsubscript{n}) and the weight-average (M\textsubscript{w}) molecular weights diverge strongly at full conversion of functional groups.

3) Highly-branched off-stoichiometric polymers are characterized by a distribution of degrees of polymerization, of functional groups numbers per molecule and of degrees of branching. At full conversion of “A” groups, each molecule contains only “B” functions. If cyclization occurs, the molecules can contain more than one cycle. While M\textsubscript{w} diverges, M\textsubscript{n} is always finite.

1.1.2 Synthesis and history of hyperbranched polymers

1.1.2.1 History

The synthesis, structure characterization and crosslinking of hyperbranched polymers formed from AB\textsubscript{2} monomers are the basic tasks of this thesis. The first mentioning of highly branched molecules can be dated to the end of 19\textsuperscript{th} century, when Berzelius reported the formation of resins from tartaric acid and glycerol [2]. Later, Watson and Smith reported the reaction between phthalic anhydride (latent A\textsubscript{2}) and glycerol (B\textsubscript{3} monomer) [2, 3]. Kienle showed [4] that the specific viscosity of samples made from phthalic anhydride and glycerol was low when compared to numerous synthetic linear polymers, such as polystyrene, whose specific viscosity values were measured by Staudinger. In the 1940’s, Flory [5] used the probability theory to calculate the molecular weight distribution of linear polymers and extended later his calculation to branching systems containing tri- or tetrafunctional monomers, which gelled at a certain critical conversion of functional groups. In 1952 Flory [6] extended his theoretical approach to the polycondensation of BA\textsubscript{r} monomers (alternating reaction A+B\rightarrow AB), which
yields hyperbranched polymers, and showed that the polyaddition of these monomers can never lead to gelation. The interest in hyperbranched polymers arose again at the beginning of the 1990’s, following the discovery of dendrimer synthesis (starburst polymers) by Tomalia, and was stimulated by DeGennes, who was expecting a special behavior of dendrimers in comparison to the well known branched polymers. The name “Hyperbranched Polymers” was given to AB$_f$ polymers by Kim and Webster [7], indicating clearly that there is only a limited analogy to dendrimers but a close relation to the classical randomly branched polymers. Over the past 15 years, the interest in hyperbranched polymers increased extremely. In this time, the dendrimers were unusually popular because of their specific properties. The interest in hyperbranched polymers (with irregular structures but similar properties like the dendrimers) came from the industry, as it was obvious from the beginning on, that the step-by-step synthesis of dendrimers will restrict their large-scale industrial application. The introduction of random branching on the other hand, for example into polycondensation, was a well-established technique, which can be combined with known technical processes.

1.1.2.2 Synthetic approaches to hyperbranched polymers

Synthetic techniques used for preparing the hyperbranched polymers (HBP) can be divided into two groups:

The first group includes the **single monomer reactions**, i.e.: the polycondensation of AB$_f$ monomer or of AB$_f$ monomer plus core monomer; self-condensing vinyl polymerizations; ring opening reactions and addition reactions.

The second group includes the **two monomers reactions**. This category of reactions includes the classical reaction of A$_{\text{fa}}$ and B$_{\text{fb}}$, which in the case of an extreme difference in the group reactivities (eg. AA’ and BB’) leads to the *in situ* formation of an AB$_2$ intermediate which further polymerizes to form a hyperbranched polymer. In that special case, the classical hyperbranched polymers “cross” with highly-branched off-stoichiometric polymers, however, with some distinct differences in structure development during the formation process.

1.1.2.2.1 Polycondensation of AB$_f$ monomers

The polycondensation of AB$_f$ monomers involves the typical features of a step growth reaction of multifunctional monomers and of the formed oligomers but without the possibility of crosslinking (and hence gelation). As result, hyperbranched molecules are obtained, which
contain one focal group (A group), and dendritic, linear and terminal units (depending on the reactivity of the “A” group) (Fig. 1-1).

Through polycondensation of the AB monomers, hyperbranched polyesters, polyureas, polycarbonates, polyamides, and polyethers have been successfully synthesized [8, 9]. AB, AB₃ [10] [e.g., poly(carbosilane) (Scheme 1-1)], AB₄, AB₅, and even AB₆ [11] monomers were used to synthesize hyperbranched polymers. AB₂ monomers predominate in the synthetic approaches to hyperbranched products and the structural variety of these polymers is very broad.

![Scheme 1-1: AB₃ monomer for polycondensation](image)

Among the AB₂ based polymers, the polyester structures were favoured by many authors due to the availability of suitable monomers. (Fig. 1-2)

![Fig. 1-2: AB₂ monomers for synthesis of hyperbranched polyesters](image)

- a) 4,4-bis (4'-hydroxyphenyl) pentanoic acid
- b) 2,2-bis (hydroxymethyl) propionic acid
- c) 3,5-bis (trimethylsiloxy) benzoyl chloride
- d) 2,2-bis (hydroxymethyl) butanoic acid

Also poly(ethersulfone)s and poly(etherketones), polycarbonates, polyamides, poly(phenylacetylene)s, polysiloxane- or polycarbosilanes were synthesized [12,13, 14, 15, 16, 17, and 18].
During syntheses of HBP’s, side reactions and intramolecular reactions (cyclization) are often observed. It was found [19], that cyclization reactions occur and strongly depend of the monomer structure. For instance, the fully aliphatic polyester based on 2,2 (dihydroxymethyl) propionic acid is obtained as a hyperbranched polymer with up to 92% cycles instead of the focal “A” units, as verified by KIDS and Electrospray FTMS measurements. In the aliphatic-aromatic system based on 4,4-bis(4’-hydroxyphenyl)pentanoic acid, only up to 5% of focal groups were transformed into cycles [20]. The cyclization reduces the molecular weight of the polymers and their polydispersity.

1.1.2.2.2 Self-condensing vinyl polymerization

This type of reaction was described first by Frechêt [21] in 1995. This polymerization method is quite versatile, as hyperbranched polymers can be approached via AB vinyl monomers. In the reaction, the B groups of the AB monomers (here A and B are unsaturated groups) are activated to generate the initiating B* sites. B* initiates the polymerization of the vinyl groups A of the monomer, forming a dimer with a vinyl group, a growth site, and an initiating site. The dimer can function as an AB₂ monomer, and undergoes further polymerization to yield the hyperbranched polymer. This method has some disadvantages. A side reaction can lead to gelation or very broad molecular weight distribution [22]. In order to avoid these problems, controlled living polymerizations such as atom transfer radical polymerization or group transfer polymerization, are combined to carry out the self condensing vinyl polymerization. The highly branched polymethacrylates, obtained by self condensing group transfer copolymerization of the initiator-monomer 2-(2-methyl-1-triethylsiloxy-1-propenlyoxy) ethyl methacrylate (general structure AB*, where A stands for a double bond and B* represents an initiating group) with methyl methacrylate [23] (Scheme 1-2) have molecular weight up to $M_w = 240 000$ and a polydispersity of 3.
1.1.2.2.3 Self-condensing ring-opening polymerization

The self-condensing ring-opening polymerization was first reported in 1992 [24]. The reaction yields a dendritic polyamine from the monomer 5, 5-dimethyl-6-ethenylperhydro-1,3-oxazin-2-one under CO$_2$ evolution (Scheme 1-3) and is carried out at room temperature in THF, using a Pd-based catalyst.

A nucleophilic ring opening reaction was used for the preparation of hyperbranched poly(etheramides) based on monomer 2-(3,5-dihydroxyphenyl)-1,3-oxazoline [25]. The obtained polymer bears a large number of functional groups and exhibits excellent solubility and low solution viscosities.

Also hyperbranched polyethers and polyesters were synthesized in classical ring opening reactions. The cationic ring opening polymerization as a path to HBP’s was preliminarily investigated by Kim [26], but success was achieved one year later, in 1999 [27, 28]: the
polymerization of 3-ethyl-3-(hydroxymethyl)oxetane yielded branched soluble molecules with multiple glycolic end groups. The $M_n$ of the polymers was between 2 000-5 000 and the degree of branching was 41%.

An interesting example of the preparation of hyperbranched polymers by ring opening polymerization was described by Frechét [29]: The 4-(2-hydroxyethyl)-ε-caprolactone is a monomer, which contains an ε-caprolactone ring, which is well known to polymerize by ring opening polymerization, and a primary alcohol group that may initiate the ring opening polymerization of ε-caprolactone, under specific conditions. The polymerization is initiated by the ring opening of one AB monomer with one initiating alcohol group of another monomer. The obtained dimer has an ε-caprolactone group and two primary alcohol groups, so it can act as an AB$_2$ type monomer, thus leading to hyperbranched macromolecules (Scheme 1-4).

Scheme 1-5: Ring opening polymerization
1 Introduction

1.1.2.2.4 Addition reactions

AB₂ monomers are often used for the synthesis of hyperbranched polymers by addition reactions, for example for the preparation of polyurethanes and polycarbosilanes. Very interesting is the Diels-Alder cycloaddition reaction shown in Fig. 1-3 leading to hyperbranched polymers.

![Monomers used in addition reaction](image)

Fig. 1-3: Monomers used in addition reaction

The monomer shown in Fig. 1-3 (c) is much more complex and was used as AB₂ –type monomer in a “criss- cross” cycloaddition with the maleimide group as A-function and the azine as two B-group [30]. This polymerization leads to HBP’s with degree of branching (DB) equal 100%.

1.1.2.2.5 Off-stoichiometric reactions of A₃ and B₂ monomers

Alternative synthesis routes towards the highly branched polymers are reactions between A₅₆₅₆ and B₇₉ monomers. The most important reaction in this group is the off-stoichiometric reaction of A₃ and B₂ monomers leading to highly branched structures [1] (Fig. 1-4).
In this type of polymer syntheses an important characteristic can be a different reactivity of the same type of functional groups (e.g. reaction of $A_2$ and $BB'B''$ monomers). In such cases the off-stoichiometry needed to obtain highly branched but not gelating products does not need to be so pronounced.

1.1.3 Hyperbranched polyesters based on BHPPA

This work is focused on the hyperbranched polyesters obtained by polycondensation of 4, 4-bis (4’-hydroxyphenyl)pentanoic acid [31]. The polycondensation reaction of this monomer was well described using the $^1$H-NMR and $^{13}$C-NMR [32] spectroscopy. Via combination of both NMR methods it was possible to quantify the amounts of all six reaction states of a monomeric structural unit (1T, 2T, 1L, 2L, 1D and 2D, see Fig. 1-5) as a function of conversion.
Introdaction

Fig. 1-5: Reaction states of units of a monomer of type $AB_2$

Also, it was found that the polycondensation of 4, 4-bis (4’-hydroxyphenyl) pentanoic acid is an example for an ideal hyperbranched $AB_2$ polycondensation with equal reactivity of both phenolic groups ("B"-groups, $k_T = k_L$, based on group concentration, see Scheme 1-6).

Scheme 1-6: $k_T = k_L$

In order to receive a narrower molecular weight distribution and a smaller amount of carboxylic groups in the product mixture, the 2-, 3-, 4-, and 6-functional core monomers (see Fig. 1-6) containing equivalent aliphatic hydroxyl groups can be added [33].
### 1.1.4 Commercially available dendritic OH-functional polymers

Since some time, hyperbranched polymers with OH groups are also **commercially available**. The Perstorp Polyols, Inc. company [34] produces several commercial grade dendritic polymers, suitable for many applications, named "Boltorn® Dendritic Polymers". Mostly they are based on the monomer 2,2-bis(hydroxymethyl)propionic acid and contain different types of core monomers. These products also differ in molecular weight. Some examples are shown in Tab. 1-1. Similar, products from 2,2-bis(hydroxymethyl)butanoic acid are commercially available in Japan.

**Tab. 1-1:** Commercially available hyperbranched polymers Boltorn® from Perstorp Polyols, Inc.

<table>
<thead>
<tr>
<th>Product</th>
<th>Molecular weight</th>
<th>Functionality</th>
<th>State / Appearance</th>
</tr>
</thead>
<tbody>
<tr>
<td>Boltorn H20</td>
<td>1750</td>
<td>16</td>
<td>solid / yellowish</td>
</tr>
<tr>
<td>Boltorn H30</td>
<td>3570</td>
<td>32</td>
<td>solid / yellowish</td>
</tr>
<tr>
<td>Boltorn H40</td>
<td>7250</td>
<td>64</td>
<td>solid / yellowish</td>
</tr>
<tr>
<td>Boltorn H311</td>
<td>5700</td>
<td>23</td>
<td>liquid / light brown</td>
</tr>
</tbody>
</table>

Another commercially available hyperbranched product with –OH groups is the Hybrane® [35], a hyperbranched poly(ester amide) from DSM. This product is obtained by polycondensation of a monomer prepared by the reaction of a cyclic anhydride with diisopropanol amine.
1.1.5 Application of HBP's

Hyperbranched polymers were considered for many applications because of the low viscosity of their solutions and melts, in many cases also for their good solubility, the large number of functional groups and their good processability. The high functionality could be sometimes a disadvantage, because it leads to fast gelation during crosslinked product synthesis. The HBP’s are a cheap alternative to dendrimers for applications that necessitate high functionality, but do not require the high structural precision of dendrimers. The HBP’s polarity and functionality can be modified by partial substitution of reactive groups. The most common applications in which hyperbranched polymers have been used are shown in Fig. 1-7, and some of them will be described below.

![Applications of hyperbranched polymers](image)

**Fig. 1-7:** Applications of hyperbranched polymers

1.1.5.1 HBP’s in Biomaterials:

The perfectly branched dendrimers were applied in medicine as drug carrier molecules. Now, they are partly replaced by well-defined hyperbranched polymers with multifunctional terminal groups. As carriers, hyperbranched macromolecules can offer their interior or peripheral functional groups to covalently fix bio-objects. Hyperbranched aromatic polyamides, synthesized by self condensation of AB$_2$ monomers or by polycondensation of reactant pairs are used as enzyme-supporting materials and have the potential to serve as supports for protein immobilization [36]. Suitable hyperbranched polymers can also be applied in medicine as biodegradable materials [37].
1.1.5.2 **HBP’s in Blends:**

Hyperbranched polyphenylene blended with linear polystyrene reduces the latter its viscosity at higher temperatures and improves its thermal stability [38]. Another effect observed was a change in the mechanical properties of polystyrene after blending - the increase of initial modulus - was attributed to weak physical cross-linking of the polystyrene through aryl–aryl interactions. HBP can act as a reology control agent for polymers. Blends of hyperbranched polyesters with linear polymers such as polyesters, polyamides and polycarbonates were investigated [39], using a variety of functional hyperbranched polymers bearing hydroxy and acetoxy (protected hydroxy) terminal groups. For comparative purposes, blends involving poly(vinylphenol) and poly(acetoxystyrene) instead of the hydroxyl and acetoxy functionalized HBP’s were also studied. The results obtained for both the thermal and the phase behavior of these blends revealed, that the hydroxy-terminated hyperbranched polyesters exhibited similar characteristics like poly(vinylphenol) if blended with linear polymers, such as bisphenol A polycarbonate and poly(butylene adipate). These results infer that hydrogen bonding is a more important factor in blends of this type rather than the polymer architecture of the additive.

1.1.5.3 **HBP’s as Additives:**

Hyperbranched polyesters or polyethers modified by alkyl chain termination of functional groups show an amphiphilic character and can be used as carrier molecules for physically enclosed organic molecules. For example, a modified hyperbranched polyester was used as dye carrier in polyolefine blends [40]. The addition of HBP causes a homogenous distribution of the dye in the matrix and also a reduction of melt viscosity.

1.1.5.4 **HBP’s in Polymer films:**

Hyperbranched polymers carry many functional groups and moieties with interesting optical, electrochemical or mechanical properties and can be incorporated into HBP polymer films without any crosslinking. Various techniques including template-based approach and photolithography have been developed on such systems by Ghosh and co-workers. The templates consist of self-assembled monolayers fabricated by micro-compact printing (μCP), while photolithographic patterning relies on a photomask [41, 42, and 43].
1.1.5.5 **HBP’s in Coatings:**

**Powder coatings**

A hyperbranched polyesteramide can be synthesized from the cyclic carboxylic anhydride and diisopropanolamine [44] (see Scheme 1-7), which first react to form in situ an AB$_2$ monomer shown in Scheme 1-7, right.

![Scheme 1-7: Synthesis of AB$_2$ monomer applicable for synthesis of hyperbranched polyesteramide](image)

The AB$_2$ monomer polycondensates under the synthesis conditions, yielding the final product, the hyperbranched polyesteramide Hybrane™. This product is commercially available as component for powder coating from the company DSM.

Also the hyperbranched polyester based on 2, 2-bis (methylol)propionic acid was used to prepare powder coatings [45]. The above mention polymers were modified with long aliphatic chain before they were used in coatings.

In both cases, the HBP are used as components in a powder-binder system. They are mixed with the other component, such as additives and degassing agents. The binder systems are in the glassy state at normal conditions and they are applied on a substrate’s surface as an extruded powder. Subsequently, the temperature is raised to 170-200°C. At this temperature the binder system melts and also starts to crosslink.

**High solids coatings:**

HBP-based high solids coatings are also studied. For example, they can be prepared by UV curing [46, 47, 48]. For this type of reaction, the functional groups of the hyperbranched polymers are usually end-capped with methacrylate, acrylate or vinyl groups. Aliphatic-aromatic hyperbranched polyesters were modified by vinyl ether or oxetane and cured in a photoinitiated cationic process. The resulting products were obtained as stable, sufficiently highly crosslinked films with good mechanical properties [49].
1.1.5.6 Other HBP’s applications:

During the last four years, experiments with hyperbranched polymers as **optical components** have been described in the literature. Another area of intense investigation is the use of hyperbranched polymers as a new class of **ion-conducting materials**. At first Hawker and co-workers synthesized hyperbranched poly (ether-esters) containing linear ethylene glycol units and tested them as novel electrolytes or ion-conducting elastomers. Hyperbranched polymers have also been studied as templating agents for nanoporosities in organosilicates. The investigated polymers were hyperbranched polyesters synthesised via the ring-opening polymerisation of a -caprolactone derivative [50]. Hyperbranched polythiophenes [51] were described as **light–harvesting** molecules. A gradient of conjugation lengths exists in a single conjugated hyperbranched macromolecule, resulting in a light harvesting effect, and thus in enhanced light emission or in an intramolecular energy transfer from the less conjugated units to the longest conjugated fragment. The conjugation lengths increase on increasing the molecular weight of the polymer. A modified hydroxyl-functional hyperbranched polyester resin crosslinked by UV light was used as barrier against oxygen and water [52]. The above examples show the potential for a broad use of hyperbranched polymers in all areas of life.
1 Introduction

1.2 Crosslinking of hyperbranched precursors

1.2.1 Multifunctional precursors of polymer networks

Covalent polymer networks or crosslinked polymers rank among the largest molecules known. Their molecular weight is given by the macroscopic size of the object made of such a polymer. Polymer networks in contrast to non-crosslinked polymers display attractive properties like dimensional stability (memory of shape; ability to store information), increased thermal and chemical resistance, etc.

1.2.1.1 Polymer network formation

Polymer networks are formed by crosslinking reactions from monomeric or polymeric network precursors [53]. As the crosslinking reaction proceeds, the molecular weight averages of the products formed and their polydispersity increase. At the gel point, the weight-average molecular weight and the polydispersity diverge and the first “infinite” molecule is formed (definition of gel point). This first gel molecule is no more dissolved in the reaction mixture (neither soluble nor extractable), but swollen. When the gel point is surpassed, the mass fraction of the infinite structure increases at the expense of the still soluble product fraction (sol). Also, the connectivity of the gel structure increases and more and more unit sequences (chains) within the gel become active in elastic response when objects made from the reaction mixture are deformed mechanically. This gradual development of network structure characteristics is a universal feature, but the position of the gel point on the group conversion axis can vary widely, ranging from 0.01 % (crosslinking of polyfunctional primary chains) to almost 100% (low-functionality polycondensation or step polyaddition systems).

The differences in the gel-point-conversion arise from differences in:
- network formation mechanism: stepwise vs. chain-wise and initiated reactions
- kinetic consecutiveness of the formation of bonds of different types
- reactivity control or diffusion control of the bond formation
- functionality of the components

For the formation of a polymer network, the starting components must have a number of functional groups per molecule higher than two. This is a necessary but often not sufficient condition. In order that an infinite path of bonds may exist, infinite repetitions of certain sequences of units connected by bonds should be possible [54].
1 Introduction

In step-wise reactions, all functional groups take part in bond formation. In many cases, their reactivity can be considered independent of the size and shape of the molecules or substructures they are bonded to (Flory principle). If such dependence nevertheless exists, it is mainly due to steric hindrance.

1.2.1.2 Network precursors

Polymer networks are synthesized from functional precursors with various architectures, various numbers and kinds of functional groups. Syntheses of precursors for the use in network build-up have been motivated by the following needs:
- adjustment of viscosity of curing systems before gelation,
- control of the critical gel conversion or critical time,
- lowering of shrinkage by making some bonds in the liquid state,
- incorporation into the network structure of specific groupings which affect network properties (mainly thermomechanical properties),
- incorporation into the network of specific substructures determining the network functions.

The most frequently used types of precursors for network preparation are:
Telechelic polymers (usually two monofunctional groups at their extremities), functional stars, functional copolymers (statistical, block, alternating), cyclopolymer and comb polymers, functional ladders and cage precursors, reactive microgels and micronetworks (prepared by suspension, emulsion or microemulsion polymerization), dendrimers with terminal functional groups and highly-branched precursors. Some examples are shown schematically in Fig. 1-8. In this work, hyperbranched polymers were investigated as polyurethane network precursors.

![Different types of precursors](image)

**Fig. 1-8:** Different types of precursors
1 Introduction

Hyperbranched polymers prepared from AB\textsubscript{f} (f ≥ 2) type are less spherical, but also less expensive if compared with dendritic molecules. Moreover, they show a low viscosity and often a good solubility, which are advantages for any applications.

For the application of hyperbranched polymers as precursors of polymer networks including organic binders (for coatings), the following structural features are important:

- Chemical microstructure – groups and bonds introduced into the network structure can change its thermal or mechanical properties,
- Average values of molecular weight and functionality of the hyperbranched polymer,
- Polydispersity and functionality distribution

The contribution of the hyperbranched architecture to the network structure can be changed by the modification of its functional end groups or by the incorporation of a core monomer in the HBP structure. By increasing the size of the hyperbranched precursors, a domain structure of the network, in which they are incorporated, is achieved.

High functionality of network precursors and polydispersity of their functional distribution cause early gelation (lower gel-point conversion).

The architecture of polymer precursors influences the elastic properties of the network, into which they are incorporated (namely the concentration of Elastically Active Network Chains (EANC)). The concentration of EANC is calculated from the number of elastically active cross-links (EAC), which already exist in the precursors. Each bond with an infinite continuation issuing from an EAC contributes by \( \frac{1}{2} \) to the number of EANC’s.

Hyperbranched polymers prepared from AB\textsubscript{2} monomers contain many branching points, as well as many functional groups. HBP are known as polymers with a broad molecular weight distribution. It would be difficult and unpractical to sum contributions to the concentration of EANC’s by active branching points in all the different fractions. An alternative for the calculation of EANC concentration is to employ the calculation of the probability generating function and to use it in the mathematic description of the crosslinking process [55].

1.2.2 Use of hyperbranched polymers in polyurethane coatings

The main goal of this work was to prepare polyurethane networks based on hyperbranched polyesters for low VOC coatings. In the literature, only a few examples of preparation of such a kind of coatings have been described. One interesting contribution was published by Huybrechts and Dušek and was concerned with the preparation of polyurethane coatings from star polymers and polyisocyanates [56]. Star polymers are a special class of the first generation type dendrimers. They are practically monodisperse. The star polymers used in the
above mentioned coating recipe were synthesized using subsequent reactions of a hydroxyl-functionalized cyclic anhydride with a carboxyl-epoxide. These precursors were crosslinked with polyisocyanates to form networks. The rate of polyurethane formation, the increase of viscosity, gelation as well as changes of structure and of some properties beyond the gel point were studied. The hydroxy-star based systems were compared with polyurethane film formed from linear hydroxy-functional acrylate copolymers crosslinked with the same polyisocyanates.

The synthesis of polyurethanes from a hyperbranched aliphatic polyester based on the dihydroxymethylpropionic acid and crosslinked with 4,4’-diisocyanato-diphenylmethane (MDI) was also preliminary studied. The same hyperbranched polyester was also chosen for coating preparation in a reaction with the trimer of hexamethylene diisocyanate (Desmodur N 3300).

Hyperbranched polyamidoamines were used for the partial replacement (1-2%) of the polyol in polyisocyanate-polyol formulations. This addition of HBP improved the mechanical properties and increased the crosslinking density of the polyurethanes obtained [57].

Generally, polyurethane coatings based on hyperbranched polymers with terminal -OH groups appear to be promising materials and were - till now - investigated only superficially. In this work polyurethane coatings were prepared based on hyperbranched esters and two types of polyisocyanates: 1,6-diisocyanatoohexane and its trimer (Desmodur N 3300.). Some preliminary results were already published [58, 59, 60].

1.2.3 Intramolecular cyclizations during network formation

Generally, ring structures formed during network build-up by intramolecular reactions postpone gelation, because they reduce the probability of chains to continue to infinity. Some of the pre-gel and post-gel intramolecular reactions lead to the formation of inelastic loops in the final network. A first treatment and basic characterization of such intramolecular cyclizations, which occur during random polymerization, was described by Jacobson and Stockmayer [61].

These intramolecular reactions are important for the discussion of the network syntheses done in this work. These reactions lead to a decrease of average molecular weight of reaction
products (if compared at a same conversion of functional groups), to the displacement of the gel point to higher conversions, to an increase of sol content and to lower equilibrium shear modulus in the rubbery state.

The definition of the cyclization is simple before the gel point, but the situation becomes complicated in the post-gel state, where uncorrelated cycles (circuits) are formed in any case. The cycles are specified as elastically inactive, it means that they must not contain any unit issuing more than two independent paths to infinity. The inactive cycles may become activated during the curing reaction if one of their segments becomes attached to the gel.

For example the critical molar ratio of reactive groups in an epoxy-amine non-stoichiometric system depends on the dilution that influences cyclization. This was already investigated and compared with the results calculated from the theory of branching processes, which was modified by including cyclization into the calculations [62]. Stepto found, that the properties of polyurethane networks prepared from poly(oxypropylene) triol and tetrol and diisocyanates are strongly dependent on the extent of the pre-gel intramolecular reactions. The presence of solvent during network formation can increase the fraction of cycles, leading to the formation of inhomogeneities.

1.2.4 Reactivity of functional groups used for coating preparation.

Polyurethane networks are synthesized from two principal components: polyols and polyisocyanates.

The rate of reaction between the isocyanate and alcohol groups depends of several factors. The most important are: the initial concentrations of the NCO and OH groups, the nature of the NCO and OH reagents, the temperature, the type of solvent or its absence and the presence and type of catalyst.

It is well known, that the reactivity of NCO groups strongly depends of the structure of the molecule. The NCO reactivity increases if substituents X in X-NCO increase the positive partial charge on the isocyanate groups’ carbon atom. This is why aliphatic isocyanates are less reactive than aromatic ones. The reactivity of isocyanates groups decreases in the following order: aromatic isocyanates > aliphatic isocyanates > cycloaliphatic isocyanates. Naturally, steric hindrance on either the isocyanate or the hydroxyl compound slows down the urethane formation. For example the tertiary alcohol triphenylcarbinol (Ph₃C-OH) is so hindered sterically, that it is completely unreactive towards isocyanates [63]. The specificity of catalysts also depends on the reactivity of the various isocyanate and hydroxyl components.
In contrast to typical polyurethanes, networks prepared with poly BHPPA as hydroxyl component contain aromatic OH groups. It is known that the reactivity of phenolic OH groups is considerably lower than that of primary aliphatic hydroxyls. Also the stability of urethane units containing arylxy substructures is lower than of urethanes with alkylxy substructures. For this reason, phenols are often used in reactions with isocyanates as blocking agents. Alternative blocking agents are tertiary alcohols, \(\varepsilon\)-caprolactam, malonic acid esters, ketoximes or 3,5-dimethylpyrazole. The blocked isocyanate groups can be handled and processed without concern about their further reactions or gelation, since no reactive isocyanate remains. When the processing is complete, heat is applied to decompose the phenolic urethanes, regenerating the isocyanate functions, and allowing the polyurethane to fully cure. The unblocking temperatures are typically between 90\(^\circ\)C and 180\(^\circ\)C, depending on the isocyanate and on the blocking agent. Blocked aromatic isocyanates are unblocked at lower temperatures than blocked aliphatic isocyanates. The dissociation temperature decreases in the following order: alcohols > lactams > ketoxims > active methylene groups compounds. Products like methyl ethyl ketoxime (MEKO), diethyl malonate (DEM) and 3,5-dimethylpyrazole (DMP) are used most frequently as blocking agents. DEM-blocked isocyanate crosslinkers have an enormous potential in powder and liquid coatings applications.

Very stable are aliphatic polyurethanes based on aliphatic isocyanates (e.g. HDI) and polyesters with aliphatic –OH groups or acrylic polyols. Aliphatic polyurethanes are more expensive than aromatic, but are UV resistant and color stable. Therefore, they are often used for exterior and any other applications, where color stability is important.

In order to understand well the crosslinking reactions in polyurethanes, model reactions with low molecular weight components should be studied first. The kinetics of polyurethane formation was investigated since 1949 in the fundamental work of Backer [64, 65]. From the beginning on, many authors applied the second order kinetics treatment to the isocyanate-hydroxyl-reaction. For a stoichiometric reaction ([OH] = [NCO]), the following simple expression is used to fit the urethane formation kinetic data:

\[
\frac{d[NCO]}{dt} = -k[NCO][OH] = -k[NCO]^2
\]
1 Introduction

For a reaction with alcohol in large excess to isocyanate, a pseudo-first order kinetics in respect to isocyanate is obtained [66].

As mentioned earlier, there are many aspects, which can change the kinetics of polyurethane formation. In this work, we will consider only some of them, which are listed below.

1. Catalyzed vs. non-catalyzed systems
2. Effect of weak acids
3. Solvent effects
4. Possible side reactions

If polyfunctional components are involved and crosslinked polyurethanes are formed, the kinetics becomes more complicated.

1.2.4.1 Catalyzed vs. non-catalyzed system

The majority of authors presume that the uncatalyzed urethane formation occurs apparently by a bimolecular mechanism, even if some particularities should be considered [67 and 68]. It was early discovered however [69], that the hydroxyl function of an alcohol has a catalytic effect on the urethane formation. In the second reaction step (Scheme 1-8 bottom), the free alcohol molecule mediates the proton transfer from O to N.

\[
\begin{align*}
\text{R—NCO} & + \text{R’—OH} \ \overset{k_1}{\underset{k_2}{\rightleftharpoons}} \text{R—N—C—O}^- \\
\text{R—N—C—O}^- & + \text{R’—OH} \ \overset{k_3}{\rightarrow} \text{R—N—C—O} \quad \text{H—O—R'} \ + \text{R’—OH}
\end{align*}
\]

\textbf{Scheme 1-8:} Steps of non-catalyzed NCO+OH reactions postulated by Baker and co-workers.

Based on the above mechanism (Scheme 1-8), the reaction rate can be expressed as follows [70]:

\[
- \frac{d[NCO]}{dt} = k_1[NCO][OH] \frac{k_3[OH]}{k_2 + k_3[OH]}
\]

According to this equation, if [OH] is large enough so that \( k_2 \) is substantially smaller than \( k_3[OH] \) (and can be omitted) - which implies early reaction stages - the reaction will follow the simple second-order kinetics mentioned further above (with \( k = k_1 \)).
An often used catalyst for the polyurethane synthesis is dibutyltin dilaurate (DBTDL). The mechanism of the catalyzed polyurethane formation differs from that of the non-catalyzed reaction. Organotin-catalyzed isocyanate - alcohol reactions in solution were described many times, and there were attempts to explain the mechanism involving the catalyst. Urban investigated reactions of polyisocyanates with acrylic polyols with and without catalyst [70]. He examined the reaction mechanism and the effect of the catalyst (DBTDL) on the reaction rate. Bloodworth and co-workers [71], who used trialkyltin methoxide as catalyst, proposed that the reaction between isocyanate and alcohol, in the presence of tin catalyst, proceeds through an intermediate formation of tin alkoxide from the alcohol and the tin compound. For the acrylic-OH/NCO/DBTDL systems, the following reaction steps are proposed (see Scheme 1-9):

The first reaction step is a reaction between catalyst and alcohol resulting in an anionic complex and a proton. The complex anion reacts with NCO (insertion of NCO into the R”O-Sn bond via nucleophilic attack of the R’O⁻-Ligand on the isocyanate carbonyl) and forms another complex anion (step 2), which will rapidly react (protonation of the N(R’”')COOR” ligand by R’OH) with another alcohol to form free urethane and the regenerated catalyzing complex anion.

**Scheme 1-9:** Catalytic cycle of the dibutyltin dilaurate catalyzed polyurethane formation
1.2.4.2 Possible side reactions

In humid environment, the isocyanate groups react with water as shown in the equations given below, in Scheme 1-10. The isocyanate group first adds one water molecule to form the carbamic acid intermediate.

\[
R{-}NCO + H_2O \rightarrow [RHN{-}C{-}OH]
\]

\[
[RHN{-}C{-}OH] \rightarrow R{-}NH_2 + CO_2
\]

\[
R{-}NCO + R{-}NH_2 \rightarrow [RHN{-}C{-}NHR]
\]

Scheme 1-10: Side reaction of isocyanate with humidity

The carbamic acid is unstable and spontaneously decarboxylates to an amine, releasing carbon dioxide, which leaves the reaction system (or sometimes the CO$_2$ bubbles become entrapped in the viscous forming resin in the form of undesired bubbles). The amine can react with intact isocyanate groups, rapidly producing urea. The investigation of the moisture-curing process of aliphatic hexyl isocyanate reacted with water showed that this reaction follows second order kinetics in analogy to the non-catalyzed reaction of isocyanate with alcohol. For the tin catalyzed systems cured by water, different reaction pathways were proposed [72] in analogy to the isocyanate-alcohol reaction [73]. In this case tin also provides free coordinating sites for water and isocyanate molecules.
Other known side reactions are the reactions of urethane and urea with free isocyanate groups to form allophanates or biurets (Scheme 1-11).

**Scheme 1-11:** Formation of biurets (top) and allophanates (bottom)
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The aim of this work was to prepare and characterize hyperbranched oligomers of 4,4-bis-(4’-hydroxyphenyl)pentanoic acid (BHPPA) as OH-polyfunctional precursors of polyurethane networks via BHPPA polycondensation. Products of different molecular masses and also such containing multifunctional polyols as core monomers had to be prepared.

The reactivity of the poly-BHPPA products towards isocyanates had to be investigated and suitable conditions for the crosslinking of these products with 1,6-diisocyanatohexane (HDI) and with the HDI-trimer (Desmodur N 3300) had to be found.

Finally, networks synthesized from the different types of poly-BHPPA and from HDI and Desmodur N3300 had to be characterized and their suitability as coating films had to be investigated.
3 Experimental part

3.1 Chemicals used

3.1.1 Solvents

- 2-Pentanone, Aldrich
- Diethylene glycol dimethyl ether, 99 % (GC) (Diglyme), Aldrich
- N,N–dimethylformamide, 99, 8%, Aldrich
- Acetone p.a., Lachema Neratovice, s.r.o.
- THF p.a., Lachema Neratovice, s.r.o.

All solvents were dried using molecular sieve (4 Å) and the amount of the residual water was determined by the Karl Fisher method.

3.1.2 Auxiliary chemicals and catalysts

- 4-Ethylphenol, 99%, Aldrich
- 1-Hexanol, Fluka, puriss. p.a., standard for GC, ≥ 99.9% (GC)
- Dibutylamine, Fluka
- Acetanhydride p.a., Lachema a.s.
- Hydrochloric acid 35% aqueous solution, Lachema a.s.
- Potassium hydroxide p.a., Lachema a.s.
- Dibutyltin diacetate, Aldrich
- Dibutyltin dilaurate, Aldrich
- 1-Methylimidazole, Fluka, puriss >99% (GC)
- Pyridine p.a., Lachema a.s.
3.1.3 OH-functional monomers for HBP polyesters synthesis

4,4-bis (4-hydroxyphenyl)valeric acid, 95 %, Lancaster,
White to light pink powder, $M_n = 286.33$ g/mol,
mp = 167-172°C, free phenol: 0.5% max.

Poly (ethylene glycol) - (PEG), Aldrich
Liquid, $M_n = 190-200$ g/mol
(ca. tetramer)

2-Ethyl-2-(hydroxymethyl)-1,3-propanediol, > 99%
Merck
Solid, $M_n = 134.17$ g/mol, mp = 56-58°C

Pentaerythritol, > 98% Merck
Solid, $M_n = 136.15$ g/mol, mp = 253-258°C

Dipentaerythritol, Aldrich
Solid, $M_n = 254.28$ g/mol, mp = 215-218°C
3.1.4 Isocyanates

1,6-Diisocyanatohexane (HDI), 98%, Aldrich, Liquid, \(M_n = 168.19\) g/mol,

\[
\text{ONC}-(\text{CH}_2)_6-\text{NCO}
\]

Desmodur N 3300, Bayer Corporation, Aliphatic triisocyanate (Trimer of HDI), liquid, solvent-free Equivalent weight - approx. 193 g/mol

\[
\text{OCN}-(\text{CH}_3)_6-\text{NCO}
\]

Butyl isocyanate, 98 %, Aldrich Liquid, \(M_n = 99.13\) g/mol, bp. = 115 °C

\[
\text{H}_2\text{C}-\text{C}-\text{C}-\text{C}-\text{NCO}
\]

3.1.5 The characterization of Desmodur N 3300

Desmodur N 3300 was obtained from the Bayer Company. It was known, that this product displays a functionality distribution. Due to the high reactivity of its NCO groups, it is not possible to determine the composition of Desmodur N 3300 by standard techniques such as liquid chromatography or mass spectroscopy and it is necessary to deactivate the NCO groups prior to analysis [1]. The deactivation can be done by the reaction with a monofunctional reagent, such as a secondary amine or a monoalcohol. In this experiment, benzyl alcohol was used in slight excess (10%) over the NCO groups to assure their complete conversion. The advantage of this deactivating reagent is the presence of an aromatic ring, which offers the possibility to apply UV detection. The NCO-deactivated product was analyzed by mass spectrometry (Electrospray Fourier Transform Mass Spectrometry, ES-Ft-MS, Dupont, Marshall Lab) and, for comparison, also by Gel Permeation Chromatography (GPC) in form of a solution in THF. The ES-Ft-MS gave the following semi quantitative results shown in Fig. 3-1.
Fig. 3-1: Expansion plots of the ES-FT-MS spectrum of Desmodur 3300 deactivated with benzyl alcohol
The main signals were interpreted, and following products were discovered:

<table>
<thead>
<tr>
<th>m/z [Daltons]</th>
<th>composition</th>
<th>rel. intensity</th>
<th>assumed structure</th>
<th>NCO functions</th>
</tr>
</thead>
<tbody>
<tr>
<td>549</td>
<td>2HDI + 2BzOH – CO₂ + H₂O</td>
<td>&gt; 5</td>
<td><img src="image1.png" alt="Structure 1" /></td>
<td>2</td>
</tr>
<tr>
<td>851</td>
<td>3HDI + 3BzOH + Na</td>
<td>100</td>
<td><img src="image2.png" alt="Structure 2" /></td>
<td>3</td>
</tr>
<tr>
<td>1274</td>
<td>5HDI + 4BzOH + Na + H⁺ - (Na – H⁺)</td>
<td>40</td>
<td><img src="image3.png" alt="Structure 3" /></td>
<td>4</td>
</tr>
<tr>
<td>1296</td>
<td>5HDI + 4BzOH + Na + H⁺</td>
<td>22</td>
<td><img src="image4.png" alt="Structure 4" /></td>
<td>4</td>
</tr>
<tr>
<td>1412</td>
<td>6HDI + 4BzOH + Na + H⁺ - 2CO₂ + 2H₂O</td>
<td>4</td>
<td><img src="image5.png" alt="Structure 5" /></td>
<td>4</td>
</tr>
<tr>
<td>1438</td>
<td>6HDI + 4BzOH + Na + H⁺ - CO₂ – H₂O</td>
<td>50</td>
<td><img src="image6.png" alt="Structure 6" /></td>
<td>4</td>
</tr>
</tbody>
</table>
The MS results discussed above were compared with the of GPC analyses. It was proven that both methods give similar results.

The values of functionality averages are the following:

\[ <f_A>_1 = 3.50 \]
\[ <f_A>_2 = 3.60 \]

where:

\[ <f_A>_1 \text{ is the first moment of functionality distribution (number average functionality)} \]
\[ \langle f_A \rangle_1 = \sum f_{A_i} n_{A_i} \]
\[ <f_A>_2 \text{ is the second moment of functionality distribution} \]
\[ \langle f_A \rangle_2 = \frac{\sum f_{A_i}^2 n_{A_i}}{\sum f_{A_i} n_{A_i}} \]

These averages were found to be higher than the ideal functionality of 3.
3 Experimental part

3.2 Syntheses

3.2.1 Preparation of hyperbranched polyesters (poly-BHPPA)

The hyperbranched poly-BHPPA polyesters were synthesized from the 4,4-bis-(4’-hydroxyphenyl) pentanoic acid (BHPPA) and in some cases a polyol was also added as core monomer (low molecular weight component with one type of functional groups (A) used sometimes in polycondensations of BA monomers). The polymers were prepared by melt polycondensation using dibutyltin diacetate as catalyst. The details for all the samples prepared are given in Tab. 3-1.

**Tab. 3-1: Set of poly-BHPPA polymers**

<table>
<thead>
<tr>
<th>Product Name</th>
<th>BHPPA [g]</th>
<th>Polyol - Core</th>
<th>Core [g]</th>
<th>Dibutyltin diacetate [g]</th>
</tr>
</thead>
<tbody>
<tr>
<td>EP₀₁</td>
<td>80</td>
<td>No core</td>
<td></td>
<td>0.01</td>
</tr>
<tr>
<td>EP₀₂</td>
<td>80</td>
<td>No core</td>
<td></td>
<td>0.01</td>
</tr>
<tr>
<td>EP₀₃</td>
<td>80</td>
<td>No core</td>
<td></td>
<td>0.01</td>
</tr>
<tr>
<td>EP₁₂ (15%)</td>
<td>80</td>
<td>Tetra (ethylene glycol), techn. grade</td>
<td>4.20</td>
<td>0.01</td>
</tr>
<tr>
<td>EP₁₃ (5%)</td>
<td>60</td>
<td>2- Ethyl-2- (hydroxymethyl) -1,3- propanediol</td>
<td>0.47</td>
<td>0.01</td>
</tr>
<tr>
<td>EP₁₃ (10%)</td>
<td>80</td>
<td>2- Ethyl-2- (hydroxymethyl) -1,3- propanediol</td>
<td>1.25</td>
<td>0.01</td>
</tr>
<tr>
<td>EP₁₃ (15%)</td>
<td>80</td>
<td>2- Ethyl-2- (hydroxymethyl) -1,3- propanediol</td>
<td>1.87</td>
<td>0.01</td>
</tr>
<tr>
<td>EP₁₄ (15%)</td>
<td>80</td>
<td>Pentaerythritol</td>
<td>1.43</td>
<td>0.01</td>
</tr>
<tr>
<td>EP₁₆ (15%)</td>
<td>80</td>
<td>Dipentaerythritol</td>
<td>1.78</td>
<td>0.01</td>
</tr>
</tbody>
</table>

**Synthesis procedure, sample EP₁₄ (15%):**

80 g (279.4 mmol) of 4,4-bis-(4’-hydroxyphenyl)pentanoic acid (BHPPA) and 1.43 g (10.5 mmol) of pentaerythritol (“core monomer”, polyol) were placed in a flask equipped with gas inlet and outlet and put under nitrogen atmosphere. Subsequently, this mixture was molten (m.p.(BHPPA) = 167-172 °C), warmed to 185-190°C and stirred. To this mixture 0.01 g (0.0285 mmol, 4 drops) of dibutyltin diacetate (catalyst) were added and well stirred. The first reaction stage, 2 h, was performed at 185-190°C under a steady N₂ stream in order to remove the forming water. Afterwards, the temperature was raised to 230°C and the reaction mixture was put under vacuum in order to further increase the conversion. This final polycondensation stage was carried out for 6 - 8 h. Thereafter the product mixture was cooled, crushed in liquid N₂, and the so obtained powder was used without any purification.
The core content was denoted in % of COOH groups of the BHPPA monomer, which had to be esterified with the aliphatic core polyol (assuming the full conversion of latter), e.g. in EP\textsubscript{C2(15%)} with a difunctional core: \( n(\text{tetraethyleneglycol OH groups}) = 15\% \times n(\text{BHPPA monomer}) \Rightarrow n(\text{tetraethyleneglycol}) = 7.5\% \times n(\text{BHPPA}) \).

For samples, which did not contain core monomer, the synthesis procedure was fully analogous.

The products were characterized by NMR spectroscopy, showing very similar spectra with the following typical signals:

\textbf{\textsuperscript{1}H-NMR} signals, in d\textsubscript{6}-DMSO (\( \delta(\text{H}) = 2.50 \text{ ppm} \)): \( \delta \) (ppm) = 1.46, 1.52, 1.57, and 1.62 (CH\textsubscript{3}); 1.94 (CH\textsubscript{2}COOH); 2.21, 2.28, 2.35, and 2.41 (CH\textsubscript{2}); 6.66, 6.97, 7.18 (aromatic protons); 9.14, 9.17, 9.20, 9.23, 9.41 (OH); 11.97 (COOH)

\textbf{\textsuperscript{13}C-NMR} signals, in d\textsubscript{6}-DMSO (\( \delta(\text{C}) = 39.6 \text{ ppm} \)): \( \delta \) (ppm) = 44.18, 44.30, 44.67, 44.78, 45.15, 45.25 (quaternary C), 172.04, 172.2, 172.34, 172.34 (aromatic ester COOR); 174.77, 174.91, 175.08 (focal group); 176.52, 176.72 (side product).

In the case of products containing core monomers the following new \textsuperscript{13}C signals from aliphatic ester groups appear: \( \delta = 172.8, 172.93, \) and 173.1 ppm (COOR’, where R’=aliphatic group).

The NMR analyses were carried out on a Bruker DRX 500 NMR spectrometer operating at 500.13 MHz for \textsuperscript{1}H and at125.75 MHz for \textsuperscript{13}C NMRspectra. DMSO-d\textsubscript{6} was used as solvent, lock, and internal standard (\( \delta(\text{H}) = 2.5 \text{ ppm}, \delta(\text{C}) = 39.60 \text{ ppm} \)).
3.3 Molecular weight determination

The molecular weights of synthesized polymers were determined as follows:

**Gel permeation chromatography (GPC)** investigations were carried out with refraction-index- and UV-detectors. The experiments were performed at room temperature, N,N-dimethylacetamide containing 2 vol % of water and 3 g/L of LiCl was used as mobile phase. A combination of Zorbax PSM 60 and 300 columns (from Rockland Technologies) was employed. The molecular weights were calculated using poly (2-vinylpyridine) standards.

**Vapour pressure osmometry (VPO)** measurements were performed on the Vapour Pressure Osmometer K-7000 from Knauer (solvent: THF; cell temperature: 45° C; measurement time: 1 min.; calibration: PS standards).

The molecular weights were also calculated from **acid (AN) and hydroxyl (HN) numbers** and also from **$^1$H NMR** and **$^{13}$C NMR spectra**.
3.4 Determination of reactive groups in (poly-BHPPA)

3.4.1 Determination of COOH groups.

The acid number of a sample is a technical magnitude defined as mg of KOH needed to neutralize 1 g of the sample ( mg(KOH) / g(sample) ).

The acid numbers were determined via the neutralization of samples with potassium hydroxide (KOH) (see Scheme 3-1) according to ISO 2554-1974.

\[
\text{RCOO}^- + \text{K}^+ + \text{OH}^- \rightarrow \text{RCOO}^- + \text{K}^+ + \text{OH}_2
\]

Scheme 3-1: Neutralization of carboxylic group

The chemical amount of the acidic protons is equal to the chemical amount of KOH needed for the titration till equilibrium. The equivalent molecular weight per COOH group (in g / mol (COOH)) can be calculated from the chemical amount of acidic protons and the sample’s mass.

Hydroxyl and acid numbers of the synthesized polymers were determined using the potentiometric titrator L50 from Mettler Toledo.

Analysis procedure (in accordance with ISO 2554-1974)

About 0.4 - 0.6 g (the exact weight was noted) of polymer were dissolved in 5 ml of pyridine. Thereafter, 10 ml of toluene and 2 ml of water were added. The mixture was heated for 10 min at its boiling point under reflux. After cooling the mixture to room temperature, the condenser was rinsed with 5 ml of ethanol (in order to prevent water loss in form of drops on the condenser). Finally, the analysis mixture was titrated with a 0.5 mol/l ethanolic KOH solution, using a potentiometric titrator (Mettler Toledo L 50) to determine the equivalence point. The acid number (AN) was calculated from the results of the titration using the formula:
$AN = \frac{V_1 \times C \times M_{KOH}}{m}$

Eq. 3-1

where:

$V_1$ - the volume of potassium hydroxide (ml) used for the sample titration

$C$ - concentration of KOH [mol/l]

$M_{KOH}$ - molecular weight of potassium hydroxide

$m$ - the mass of the polymer sample
### 3.4.2 Determination of OH groups

The hydroxyl number of a polymer is a technical magnitude defined as mg of KOH needed to neutralize 1 g of polymer (mg (KOH) / g (Sample)) in the hypothetical reaction shown in Scheme 3-2. This hypothetical reaction is not suited for an experimental determination of OH-groups, because the basicity of OH⁻ and RO⁻ groups is similar, thus leading to an equilibrium reaction instead of full conversion.

\[
\text{R-O}^- + \text{K}^+ + \text{OH}^- \rightarrow \text{R-O}^- + \text{K}^+ + \text{H}_2\text{O}
\]

**Scheme 3-2:** Hypothetical neutralization reaction of poly-BHPPA by KOH

For the above reason, hydroxyl numbers are determined via an indirect titration according to ISO 2554-1974. The three-step analysis procedure is shown in Scheme 3-3.

In the first step of the analysis, the hydroxyl groups are treated with an excess of acetic anhydride (reaction (1) in Scheme 3-3). One mol acetylation reacts with the one mol hydroxyl groups, yielding one mol acetoxy groups and one mol acetic acid. The remaining acetylation stays unchanged during reaction (1) (Scheme 3-3). In the second step of the analysis (reaction (2) in Scheme 3-3), the remaining acetic anhydride is hydrolysed to acetic acid. The total amount of the acetic acid formed in steps (1) to (2) is determined through titration by KOH in step (3). The difference between the chemical amount of acetic acid, which would form by hydrolysis of all acetic anhydride used (n(CH\text{\textsubscript{3}}\text{COOH\textsubscript{theoretic}})) and the amount really formed (n(CH\text{\textsubscript{3}}\text{COOH\textsubscript{REAL}})) is equal to the chemical amount of hydroxyl
groups (n(OH)). From the chemical amount of the hydroxyl groups and the sample mass, the equivalent molar mass of the sample per OH-group can be calculated. The hydroxyl number (HN) according to the above definition for a sample without acidic groups can be calculated from the formula:

\[ HN = \frac{n(OH) \times M_{KOH}}{m(Polymer)} \]

where:
- \( n(OH) \) - amount of the OH-groups [mol]
- \( M_{KOH} \) – molecular weight of potassium hydroxide [g/mol]
- \( m \) – the mass of polymer sample [g]

If the analyzed sample also contains acidic protons besides the OH groups, they influence the result of the above analysis, because they behave like an additional amount of acetic acid which is formed by hydrolysis of acetic anhydride. The real chemical amount of OH groups is equal to:

\[ n(OH) = n(CH_3COOH_{theoretic}) - \{ n(CH_3COOH_{REAL}) - n(\text{Acidic Protons}) \} \]

\[ = n(CH_3COOH_{theoretic}) - n(CH_3COOH_{REAL}) + n(\text{Acidic Protons}) \]

The corrected hydroxyl number for the general case is:

\[ HN = \frac{n(OH) \times M_{KOH}}{m(Polymer)} + AN \]

**Analysis procedure (in accordance with ISO 2554-1974)**

An acetylating solution was prepared by dissolving 11.8 ml of acetic anhydride in 100 ml of toluene. About 0.4 – 0.6 g of the polymer sample were dissolved in 4 ml N,N-dimethylformamide and 4 ml of 1-methylimidazole (catalyst) were added. Subsequently, 2 ml of the acetylating solution were added. The analysis mixture was stirred for 20 min at room temperature. Thereafter 2 ml of water were added in order to hydrolyze the excess acetic anhydride. Finally, the analysis mixture was titrated with a 0.5 mol/l ethanolic KOH solution, using a potentiometric titrator (Metler Toledo L 50) to determine the equivalence point.

A fully analogous “blank experiment” was performed without the polymer sample with exactly the same amount of the acetylating mixture.
The hydroxyl number (HN) was calculated from the results of both titrations using the formula:

\[
HN = \frac{(V_0 - V_1) \times C \times M_{\text{KOH}}}{m} + AN
\]

where:

- \( V_0, V_1 \) – equivalence titration volume of potassium hydroxide in ml from the blank experiment and from the sample titration, respectively
- \( C \) – concentration of KOH [mol/l]
- \( M_{\text{KOH}} \) – molecular weight of potassium hydroxide, [g/mol]
- \( m \) – the mass of polymer sample [g]
3.5 Preparation of thin poly-BHPPA layers (coating films)

Preparing the Glass Substrates

Glass substrates (Clear–White Glass, ISO Standard 8037/I) were used to prepare HBP coatings. Before their use, these substrates were immersed in acetone at room temperature and treated for 20 min with ultrasound. Thereafter the glasses were washed with distilled water and subsequently immersed in a 70°C warm “Piranha solution” (H$_2$O$_2$ (30 %, Merck) + H$_2$SO$_4$ (98 % Merck), volume ratio 1:3) for 20 min. After this treatment, the substrates were washed three times with distilled water, dried in an oven at 100°C and were ready for use after cooling down to room temperature.

Coatings Preparation

Poly-BHPPA coatings in the thickness range from 0.05 - 0.2 mm (not crosslinked) were prepared by casting a 50 % (w/w) solution of the poly-BHPPA sample in THF, MPK or ethyl acetate, on a previously prepared glass plate using the doctor blade technique. The films were left to evaporate freely for 24 h at room temperature and were subsequently dried for 5 h in a vacuum oven at 90°C.

3.6 Determination of the glass transition temperature via DSC

The glass transition temperature of the HBP polyesters prepared was determined by DSC. It was an ideal method for these samples, as they were too brittle and too difficult to handle for DMTA measurements. It was measured on the differential scanning calorimeter DSC.7 from Perkin Elmer, which was calibrated according to standard procedures. The experiments were carried out in the temperature range from 70 to 200°C, using the heating / cooling rate of 10 K/min. The Tg values of the samples were determined as the inflection points of the 2$^{nd}$ heating curves.
3.7 Content of - NCO groups in Desmodur N 3300

The content of isocyanate (NCO) groups in Desmodur N 3300 was determined in accordance with the ISO/FDIS 9369:1996 (E) standard by reacting the isocyanate groups with excess dibutylamine (Scheme 3-4 (1)) and by determining subsequently the amount of the remaining unreacted amine through titration with hydrochloric acid (Scheme 3-4 (2)).

\[
\begin{align*}
\text{R-N=C=O} + (\text{C}_4\text{H}_9)_2\text{NH} & \rightarrow \text{R} - \text{N} - \text{C} - \text{N}(\text{C}_4\text{H}_9)_2 \\
\text{(C}_4\text{H}_9)_2\text{NH} + \text{H-Cl} & \rightarrow (\text{C}_4\text{H}_9)_2\text{NH}^+\text{Cl}^- 
\end{align*}
\]

Scheme 3-4: Determination of NCO groups

Analysis procedure

5 ml (1 mmol) of a 0.2 mol/l solution of di-n-butylamine in dry THF were put in an Erlenmeyer flask and diluted by 10 ml of THF. A small amount of the isocyanate (Desmodur sample), typically 0.05g, was dissolved in 10 ml of THF and added to the amine solution. The reaction mixture was stirred at room temperature for ca. 10 min in order to reach full conversion of the NCO groups. Thereafter 3-4 drops of a 1 g / l solution of bromophenol blue (indicator) in ethanol were added and the reaction mixture was titrated by a 0.1 mol / l aqueous hydrochloric acid solution (typical titration volume was ca. 6-7 ml). As reference measurement, a fully analogous “blank experiment” was carried out with exactly the same amount of dibutylamine but without isocyanate. The isocyanate equivalent \( I_{\text{Eq}} \) (corresponding to the number of moles of isocyanate groups per kilogram of sample) was calculated using the formula:

\[
I_{\text{Eq}} = \frac{(V_0 - V_1) \times C}{m}
\]

where:

\( V_0, V_1 \) - volume of hydrochloric acid (ml) used for the blank experiment and for the experiment with isocyanate sample, respectively

\( C \) - concentration of hydrochloric acid [mol/l]

\( m \) - mass of the test portion taken [g].
3.8 Reaction of OH and NCO groups, kinetics followed by FTIR

In order to study the crosslinking reaction of phenol-functional polymers with polyisocyanates, model experiments were performed with low molecular weight compounds: 4-ethylphenol and 1-hexanol with monofunctional butyl isocyanate and with the polyfunctional trimer of 1,6-hexamethylene diisocyanate (Desmodur N3300). FT-IR analyses (kinetics of NCO conversion) were performed on a Perkin Elmer PARAGON 1000.

The reaction kinetics of the same isocyanates with an exemplary Poly-BHPPA product was also followed (Fig. 3-2)

\[ 	ext{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{OH} \]

1-Hexanol

\[ \text{CH}_2\text{CH}_3\text{O} \]

4-Ethylphenol (EPH)

\[ \text{H}_3\text{C} - \text{C} - \text{C} - \text{NCO} \]

Butyl isocyanate (BuI)

\[ \text{OCN} - \left(\text{CH}_2\right)_6 - \text{NCO} \]

Desmodur N 3300 (idealized structure)

\[ \text{Tri-HDI} \]

Poly-BHPPA

Fig. 3-2: Components used in kinetic reactions
Preparation of the reacting mixtures

The reaction mixtures for the kinetics were prepared as follows: The OH-component was dissolved in the calculated amount of diglyme, thereafter the calculated amount of a 2% DBTDL (catalyst) solution in diglyme was added under stirring. Finally, the calculated amount of the isocyanate was added and the reaction mixture was stirred well. The amounts of the components were calculated so, that the NCO groups concentration was always 1.42 mol / kg, the catalyst concentration was always $2.7 \times 10^{-3}$ mol / kg and the initial molar ratio $[OH]:[NCO]$ was kept equal to 1. These concentrations corresponded to the conditions in network formulations with 60% of “solids“. The reaction mixtures were kept at 25 °C. Samples for NCO analyses were taken from the reaction vessels and analyzed by means of IR spectroscopy.

The kinetics investigated are listed in Tab. 3-2.

**Tab. 3-2 : List of kinetic reactions**

1. 1-hexanol + butyl isocyanate
2. 1-hexanol + tri-HDI (Desmodur N 3300)
3. 4-ethylphenol + butyl isocyanate
4. 4-ethylphenol + tri-HDI (Desmodur N 3300)
5. poly-BHPPA (EP$_{02}$) + butyl isocyanate
6. poly-BHPPA (EP$_{02}$) + tri-HDI (Desmodur N 3300)

The kinetics measurements

The NCO concentration changes during polyurethane formation were followed by measuring the intensities of the NCO stretching band at 2273 cm$^{-1}$. As internal standard signal, the absorption band at 2930 cm$^{-1}$ (C-H stretching) was used, which remains practically unaffected throughout the reaction. The actual relative NCO concentrations were calculated as ratios of the signal intensities $I(\text{NCO}) / I(\text{C-H})$, thus ensuring that the quantitative results were independent of the thickness of the thin sample film in the infrared transmission cell.
3 Experimental part

3.9 Crosslinking of Poly-BHPPA to Polyurethanes

3.9.1 Preparation of polyurethane formulations

The polyurethane formulations for the samples synthesized in this work were prepared as follows: Solid Poly-BHPPA was dissolved in the calculated amount of the solvent (usually methyl n-propyl ketone (MPK) or diglyme), thereafter the 1% DBTDL (catalyst) solution in the same solvent was added (the mass of this solution was similar to the main solvents mass) and the solution was stirred well. Finally, the calculated amount of the isocyanate was added. The amounts of the components were calculated so that the mass fraction of the reactants (poly-BHPPA and isocyanate, also referred to as “solids”) was either 50 (wt-%) or 60 (wt-%), respectively, the amount of the catalyst was 2000 ppm per mass unit of the “solids” and the initial molar ratio [OH]:[NCO] was kept equal to 1.

The details for the important polyurethane network samples discussed in this work are given in Tab. 3-3.

**Tab. 3-3** : Set of polyurethane network prepared

<table>
<thead>
<tr>
<th>Poly-BHPPA [g]</th>
<th>Poly-BHPPA used</th>
<th>Solvent [g]</th>
<th>Main Solvent</th>
<th>DBTDL-solution [g]</th>
<th>Isocyanate [g]</th>
<th>Isocyanate</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>EP$_{03}$</td>
<td>2</td>
<td>diglyme</td>
<td>0.35</td>
<td>1.52</td>
<td>Tri-HDI</td>
</tr>
<tr>
<td>2</td>
<td>EP$_{03}$</td>
<td>1.51</td>
<td>diglyme</td>
<td>0.27</td>
<td>0.66</td>
<td>HDI</td>
</tr>
<tr>
<td>2</td>
<td>EP$_{C2(15%)}$</td>
<td>2.07</td>
<td>diglyme</td>
<td>0.35</td>
<td>1.56</td>
<td>Tri-HDI</td>
</tr>
<tr>
<td>2</td>
<td>EP$_{C2(15%)}$</td>
<td>1.52</td>
<td>diglyme</td>
<td>0.27</td>
<td>0.68</td>
<td>HDI</td>
</tr>
<tr>
<td>4</td>
<td>EP$_{C3(15%)}$</td>
<td>4.19</td>
<td>diglyme</td>
<td>0.73</td>
<td>3.38</td>
<td>Tri-HDI</td>
</tr>
<tr>
<td>4</td>
<td>EP$_{C3(15%)}$</td>
<td>3.12</td>
<td>diglyme</td>
<td>0.54</td>
<td>1.47</td>
<td>HDI</td>
</tr>
<tr>
<td>3</td>
<td>EP$_{C4(15%)}$</td>
<td>3.18</td>
<td>diglyme</td>
<td>0.56</td>
<td>2.61</td>
<td>Tri-HDI</td>
</tr>
<tr>
<td>4</td>
<td>EP$_{C4(15%)}$</td>
<td>3.13</td>
<td>diglyme</td>
<td>0.55</td>
<td>1.51</td>
<td>HDI</td>
</tr>
<tr>
<td>3</td>
<td>EP$_{C6(15%)}$</td>
<td>3.11</td>
<td>diglyme</td>
<td>0.55</td>
<td>2.49</td>
<td>Tri-HDI</td>
</tr>
<tr>
<td>4</td>
<td>EP$_{C6(15%)}$</td>
<td>3.08</td>
<td>diglyme</td>
<td>0.54</td>
<td>1.45</td>
<td>HDI</td>
</tr>
</tbody>
</table>
3.9.2 Determination of the gel point conversion

In order to determine the gel point conversion, samples were taken from the investigated reaction mixture in suitable time intervals and their NCO conversion was determined via FT-IR as described above (FT-IR kinetics). Furthermore the solubility in acetone (good solvent) of the samples taken was tested. The NCO conversion of the first sample, which did not dissolve, was taken as the gel point conversion.

3.9.3 Preparation of rectangular polyurethane plates

Polyurethane plates were prepared from the above described formulations by pouring them into glass moulds. Typical size: 1 – 2 mm thickness, 80 mm height, 60 mm width. The reaction mixtures were left to react in the moulds for 2 days at room temperature. Finally, the samples were removed from the mold and heated for 5 h in a vacuum oven at 90°C.

3.9.4 Preparation of thin polyurethane coatings

Polyurethane coatings in the thickness range from 0.05 - 0.4 mm were prepared as freely evaporating films by casting the prepared formulation on a previously prepared glass plate (see p. 50) using the doctor blade technique. The films were left to react and evaporate freely for 24 h at room temperature. Thereafter the film samples were investigated in the contact angle experiments.
3 Experimental part

3.10 Properties of networks synthesized from HBP

3.10.1 Determination of equilibrium swelling

Specimens of the polyurethane networks prepared, typically 0.1 – 0.2 g, were put in a sufficient amount (about 50 times larger than the sample volume) of the solvent examined. The solvent was allowed to penetrate freely in the sample until equilibrium was reached (till the weight of the samples remained constant). After the equilibrium was reached, the solvent was exchanged 5 times in order to extract the sol fraction. The changes of swollen samples weights with time were recorded. Finally, the original solvent was replaced by the more volatile dichloromethane, and the samples were dried at 90-110 °C, under reduced pressure to constant weight. In this way the gel fraction was determined. The described swelling experiments were performed with diglyme, MPK and acetone.

The volume fraction of polymer in the swollen sample (\( \phi_2 \)) was calculated using the balance relation (Eq. 3-2.)

\[
\phi_2 = \frac{m_d}{\rho_p} \left( \frac{m_d}{m_{sw}} + \frac{m_{sw} - m_d}{\rho_s} \right)
\]

where:

- \( m_d \) - mass of dry sample after swelling experiment
- \( m_{sw} \) - mass of the swollen sample in equilibrium
- \( \rho_s \) - density of solvent
- \( \rho_p \) - density of polymer

Also kinetics of swelling was measured.
3 Experimental part

3.10.2 Sol content in the polyurethane networks

In order to determine their sol content, samples of the prepared polymer networks were cut into small pieces and dried to constant weight ($m_{s1}$). Thereafter, the dry pieces were swollen in the good solvent acetone. To promote sol extraction, the solvent was replaced 5 times. Each extraction step was carried out for 24 h. In order to determine the fraction of gel and sol in the samples, the gel was dried to a constant weight ($m_{s2}$) again. The weight fraction of sol in the polyurethane sample was calculated using the formula:

$$w_{sol} = \frac{m_{s1} - m_{s2}}{m_{s1}}$$

3.10.3 Determination of the concentration of Elastically Active Network Chains (EANC).

The concentration of elastically active network chains was determined by means of tensile deformation experiments on swollen samples. The samples of the typical size of 0.1×1×4cm were swollen to equilibrium in diglyme. The specimens were fastened between the clamps of a tensile instrument in such a way that they were not deformed or anyhow distorted. The instrument was equipped with an environmental chamber, allowing the sample to be fully immersed in the solvent (diglyme) during the whole experiment. The samples length was increased in small deformation steps ($\Delta l$), and the force necessary for these deformations was measured.

The theoretical dependence of the stress from the sample deformation for ideal elastic chains can be expressed as:

$$\frac{F}{A_S} = \nu_e A_f RT (\phi_2^0)^{2/3}(\phi_2)^{1/3}(\lambda - \lambda^{-2})$$

The concentration of the elastically active chains is obtained as:

$$\nu_e = \frac{(F / A_S)}{A_f RT (\phi_2^0)^{2/3}(\phi_2)^{1/3}(\lambda - \lambda^{-2})} \quad \text{Eq. 3-3}$$

where:

- $F$ - force applied to the sample
- $A_S$ – cross-section area of the swollen sample
- $\lambda$ - deformation expressed as $l/l_0$
3 Experimental part

\(l_0\) - initial length of the sample

\(l\) - length of the deformed sample

\(\varphi_0^2\) is the volume fraction of the polymer during network formation,

\(\varphi_2\) is the volume fraction of the polymer in the swollen network,

\(R\) is the universal gas constant,

\(T\) is the temperature in K,

\(A_f\) is the front factor (\(A_f = 1\) was assumed).

3.10.4 Investigation of cyclization reactions

In order to investigate cyclization reactions, which occur during the formation of the polyurethane networks prepared in this work, the dependence of the critical conversion at the gel point on the dilution of the reacting system was examined. Different types of Poly-BHPPA precursors (with and without core monomer, namely EP\(_{03}\), EP\(_{C3(15\%)}\), EP\(_{C4(15\%)}\), EP\(_{C6(15\%)}\)) were crosslinked with Desmodur N 3300 at 25°C in equimolar ratio of NCO : OH groups. Reaction mixtures with 70, 60, 50 and 40\% of the diglyme solvent were prepared. The molar ratio \([\text{OH}] / [\text{NCO}]\) was kept equal to one. The change of the NCO concentration with time was followed by FTIR spectroscopy. Samples were taken directly from reaction mixture until the gel point was reached. The gel point was recognized by solubility tests.

The dependence of the experimental gel point conversion, \(\alpha_{c,\text{exp}}(x)\) (\(x\) is the dilution of the system), on the reciprocal concentration of functional groups in the initial system, \(c_0\), can be extrapolated to the hypothetical “infinite” concentration of functional groups (\(1/c_0 = 0\), see Fig. 3-3).
The extrapolated value $\alpha_{c,\text{ext}}$ should be equal to $\alpha_{c,t} (1/c_0 = 0)$ obtained by calculation from the ring-free theory. The ring-free-theory calculation of $\alpha_{c,t}$ operates with the functionality distributions of the network components, using the Stockmayer equation:

$$\alpha^2_{\text{crit}} = \frac{1}{(\langle f_A \rangle_2 - 1)(\langle f_B \rangle_2 - 1)}$$

Where: $\langle f_A \rangle_2$ and $\langle f_B \rangle_2$ are the second moment averages of functionality distribution of network components.

The fraction of the bonds wasted in cycles is calculated as follows:

$$\text{Bond in cycles} = \alpha_{c,\text{exp}(x)} - \alpha_{c,t}$$
3.10.5 Determination of the glass transition temperature via DMTA

The glass transition temperature of the polyurethane networks was determined by DMTA analysis. In difference to the hyperbranched precursor polymers, the DSC was not sensitive enough to detect the glass transition in the polyurethane networks. The DMTA spectra were measured on an ARES apparatus from Rheometric Scientific. The samples were investigated by oscillatory shear deformation at a constant frequency of 1Hz and the rate of heating was 3 °C/min. Temperature dependences of storage and loss shear moduli (G’ and G’’, respectively) were obtained in the range from 25°C to 130°C. The glass temperatures (Tg) of the networks were determined as temperatures of loss factor (tan δ = G’’/ G’) maxima.

3.10.6 TGA

Thermogravimetric analyses were performed for the samples without core monomer and for such with a 3-functional core crosslinked by di- and tri-functional polyisocyanates. The measurements were performed on a TGA.7 instrument from Perkin-Elmer in an inert atmosphere in the temperature range from 40 to 700°C. The rate of heating was 10K / min.

3.10.7 Contact angle measurement

The surface properties of the polymer networks and polymer coatings were investigated by means of contact angle measurements, based on the Drop Shape Analysis (DSA). The measurements were performed on a G2 instrument from Krüss GmbH, establishing the tangent 1 of a liquid drop with a solid surface at the base. The advancing contact angles were measured with the error ±1°.
3.10.8 Topography of the surface

Sample Preparation:
The polyurethane coatings to be investigated were prepared from poly-BHPPA and isocyanate crosslinker in 50 % w/w solution in MPK or diglyme as freely evaporating films of 0.05-0.4 mm thickness, by casting the solution on a glass plate using the doctor blade technique. The films were dried for a few hours in a vacuum oven at 90°C, in order to reach full conversion.

The topography of the polyurethane coatings on glass substrate was examined using Microglider® FTR (roughness contour topography) from Company Fries Research & Technology.

3.10.9 Shore D hardness - ISO 868

Sample Preparation:
The polyurethane coatings to be investigated were prepared from poly-BHPPA and Desmodur N3300 crosslinker in 60 % solution in MEK and dried to remove all solvent. The thickness of the film was about 4.0 mm.

The Shore hardness was measured with an apparatus known as Durometer. The hardness value was determined by the penetration of the Durometer indenter foot into the sample (2.0 and 3.8 mm deep). The indenter has a sharp end for the measurement of the Shore D hardness. Because of the possible resilience of the material, the indentation’s evolution in time was followed. In the measurements done, this indentation time was 15s. For each sample, 8 measurements were done, and the average value was calculated [2].
3 Experimental part

Literature, Experimental Part

1 P. Vlasak, M. Dušková-Smrčková, W. J. Simonsick, Jr., and K. Dušek, Polymers for Advanced Technology 2003 Conference, Ft. Lauderda

2 Hardness - shore D ISO 868
4 Results and discussion

4.1 Synthesis and characterization of poly-BHPPA

4.1.1 Conditions of the poly-BHPPA synthesis

Functional hyperbranched polymers are interesting precursors for polymer networks, particularly for coating applications. The synthesis of hyperbranched polyesters by melt polycondensation of the 4,4-bis(4'-hydroxyphenyl)-pentanoic acid (BHPPA) with or without the addition of a polyol “core monomer” was already investigated in previously and published [1, 2].

Scheme 4-1: Polycondensation of BHPPA, schematically (top) and as full structures (bottom)
4.1 Results: Poly-BHPPA Synthesis and Characterization

The poly-BHPPA products are similar to those obtained from 2,2-bis-(hydroxymethyl)propanoic acid [3, 4], but the poly-BHPPA display a higher $T_g$, and thus they can be expected to be attractive polyol precursors for two-component high-solids polyurethane coatings. Another advantage of the poly-BHPPA products is their better solubility in organic solvents.

The potential of poly-BHPPA as network precursor is also seen in the possible tuning of film-forming and surface properties of polyurethane formulations cured at ambient as well as at elevated temperature (baked systems). However, the phenolic OH groups of BHPPA are less reactive than aliphatic ones, and also the polyurethanes formed from poly-BHPPA are less stable than polyurethanes formed from precursors with aliphatic OH groups.

4.1.1.1 Condensation Temperature

The polycondensation of BHPPA without a core monomer is schematically shown in Scheme 4-1. The final stage of the reaction was conducted at 220-230°C, which is a higher temperature than originally used for poly-BHPPA synthesis [1]. This change was taken because of the low reactivity of the functional groups.

4.1.1.2 Incorporation of core monomers

The incorporation of core monomers containing OH groups during the polycondensation of hydroxy-acids like BHPPA [5, 6] can cause a decrease of the amount of carboxyl end groups in the product mixtures and a narrower molecular weight distribution. Under suitable conditions, the core monomers can bind together several poly-BHPPA molecules of different sizes and, for statistic reasons, this would cause a lower polydispersity. Core monomers with functionalities equal to 2 (technical grade tetraethylene glycol), 3 (bis-2,2-(hydroxymethyl)-propanol), 4 (pentaerythritol) and 6 (dipentaerythritol) were used in poly-BHPPA syntheses in this work.

The core monomers were present in the reaction mixtures from the beginning of the polycondensation, as they could be easily dispersed at the initial stage of the reaction. The characterization of the products obtained shows only a moderate effect of the core monomers on the polydispersity, as illustrated by results shown in Tab. 4-3.
4.1 Results: Poly-BHPPA Synthesis and Characterization

4.1.1.3 Water content

Originally, a typical purification method for poly-BHPPA was the polymer precipitation by water from a solution in THF and subsequent drying in vacuum. The products, which were worked up in this way, contained up to 10 wt-% of solvents, including water, which were difficult to remove. Especially the water content was unacceptable for the planned use of the poly-BHPPA as OH-component in polyurethanes. Because the water removal was too difficult and problematic (due to hydrogen bonding to the product), the precipitation step was skipped from the standard poly-BHPPA preparation procedure used in this work. After the polycondensation step was finished, the reaction mixture was simply cooled down and subsequently frozen by liquid nitrogen. The product was crushed and powdered. The poly-BHPPA prepared in this way was then used without any further purification. It was shown by NMR analysis that even without the purification by precipitation, the content of monomeric BHPPA was fairly low. The presence of dibutyltin diacetate (condensation catalyst) in the products did not present a problem for the reaction of poly-BHPPA with isocyanates, as this reaction was catalyzed by a nearly identical reagent, the dibutyl tin dilaurate. The water content in the polymers prepared was determined by the Karl Fisher method. The products were found to contain no more than 0.5% (wt.) of water.
4.1 Results: Poly-BHPPA Synthesis and Characterization

4.1.1.4 Reduction of the poly-BHPPA functionality

The hyperbranched polymers prepared were found to have functionalities in the range $<f>_1 = 7-14$ (see Tab. 4-3 further below), what classifies them as high functionality precursors. As mentioned in the Introduction chapter, a high functionality of precursors can cause an undesirably fast gelation of resin formulations. One method to slow down the gelation process as well as to change properties of precursors like Tg is a reduction of functionality by chemical blocking of a part of the functional groups. The modification of poly-BHPPA sample named “EP\textsubscript{02}” (core-free) by blocking 30\% of OH groups was tested using two different monoisocyanates: cyclohexyl isocyanate (CHI) and phenyl isocyanate (PhI) (Scheme 4-2). The modification progress was followed via IR spectroscopy. It was observed that the reaction with phenyl isocyanate proceeded till completion, while in the case of the modification with cyclohexyl isocyanate, a crystallization of cyclohexyl isocyanate started before the end of the reaction, thus preventing its completion (Fig. 4-2). Both products (modified with cyclohexyl- and with phenyl isocyanate) show thermal stability till 130°C, at which point the release of the blocking agent starts, setting the polymers’ OH groups free again (see Fig. 4-13 in the chapter about thermal stability). This means that the curing of such modified products has to be carried out at temperatures below 130°C and that a subsequent modification by freeing the OH groups above 130°C is possible.

Scheme 4-2: Modification reaction (reduction of poly-BHPPA functionality), where R’ is a cyclohexyl- or a phenyl- group.

Fig. 4-2: NCO peak region in the IR spectrum after modification of poly-BHPPA (EP\textsubscript{02}) with monoisocyanates
4.1.2 Molecular weights of the poly-BHPPA prepared

The poly-BHPPA products prepared were oligomeric product mixtures with polymerization degree ranging from 7 to 20. The direct determination of \( M_w \) is very difficult for products of such a low molecular mass. \( M_n \) can be usually directly determined via GPC, VPO, NMR or functional group analysis. The GPC method is well suited for linear polymers, which display a coil-like structure in solution. Hyperbranched polymers or dendrimers do not belong to this group and their molar masses can not be correctly determined via GPC. The VPO method is well suited for products of lower molar masses, but is not very precise and is very sensitive to low molecular mass impurities. \(^1\)H- and \(^{13}\)C-NMR spectroscopy as well as the functional group analysis can yield relatively precise results for poly-BHPPA of low molecular masses, which do not contain core monomers. The results obtained by these three methods were in reasonable agreement in such cases. The functional group analysis, namely the determined acid and hydroxyl numbers can be used for the calculation (indirect determination) of \( M_n \) and \( M_w \) even for core containing hyperbranched polymers. [7].

4.1.2.1 Determination of the number average molecular weight (\( M_n \))

The number average of the poly-BHPPA molecular mass was determined by calculation from the acid (\( AN \)) and hydroxyl (\( HN \)) numbers as shown in Eq. 4-1-Eq. 4-9. \( AN \) and \( HN \) were determined by titration in accordance with the ISO 2554-1974 standard, as explained in experimental part (cf., Part 3.4.1, 3.4.2) and are defined as follows:

\[
AN = \frac{n(COOH) \times M_{KOH}}{m(\text{Polymer})}
\]

\[
HN = \frac{n(OH) \times M_{KOH}}{m(\text{Polymer})}
\]

From the AN and HN values, the conversions of carboxylic (\( \alpha_B \)) and of hydroxyl groups (\( \alpha_A \)), respectively, were calculated, using Eq. 4-1 - Eq. 4-5.
4.1 Results: Poly-BHPPA Synthesis and Characterization

\[
AN = \frac{(1 - \alpha_b) n_M \times M_{\text{KOH}}}{M - M_{\text{H,O}} \times \alpha_b n_M} \times 10^3 \quad \text{Eq. 4-1}
\]

\[
\alpha_b = \frac{n_M \times M_{\text{KOH}} \times 10^3 - AN \times M}{n_M \times (M_{\text{KOH}} \times 10^3 - M_{\text{H,O}} \times AN)} \quad \text{Eq. 4-2}
\]

\[
HN = \frac{(1 - \alpha_a)(f n_M + g n_C) \times M_{\text{KOH}} \times 10^3}{M - M_{\text{H,O}} \times \alpha_a (f n_M + g n_C)} \quad \text{Eq. 4-3}
\]

\[
\alpha_a = \frac{(f n_M + g n_C) \times M_{\text{KOH}} \times 10^3 - M \times HN}{(f n_M + g n_C)(M_{\text{KOH}} \times 10^3 - M_{\text{H,O}} \times HN)} \quad \text{Eq. 4-4}
\]

\[
\bar{M} = n_M M_M + n_C M_C \quad \text{Eq. 4-5}
\]

where:

- \( n_M \) is the molar fraction of the BA\(_f\) monomer
- \( n_C \) the molar fraction of A\(_g\)
- \( M_M \) the molecular weight of BA\(_f\)
- \( M_C \) the molecular weight of A\(_g\)
- \( f \) is the A-functionality of the BA\(_f\) monomer
- \( g \) is the A-functionality of A\(_g\)

The number average of the molecular weight \( M_n \) can be calculated from the conversion of COOH or of OH groups according to Eq. 4-6 or Eq. 4-7, respectively. Both results should be equal, according to the balance equation (Eq. 4-8). A difference between both values of number average molecular weight can be due to experimental error, but on the other hand it can testify that the product contains intramolecular cycles.
4.1 Results: Poly-BHPPA Synthesis and Characterization

\[ M_n(AN) = \frac{\bar{M}}{1 - n_M\alpha_B} \]  
**Eq. 4-6**

\[ M_n(HN) = \frac{\bar{M}}{1 - (f_M\alpha_A + gn_c\alpha_A)} \]  
**Eq. 4-7**

\[ n_M\alpha_B = f_M\alpha_A + gn_c\alpha_A \]  
**Eq. 4-8**

For further evaluation, number average molecular weights \( M_n \) calculated according to Eq. 4-9 were used. These \( M_n \) values depend of both the conversion of carboxylic (\( \alpha_B \)) and of hydroxyl groups (\( \alpha_A \)).

\[ M_n = \frac{\bar{M}}{1 - (n_M f\alpha_A + n_M\alpha_B + n_c g\alpha_A)/2} \]  
**Eq. 4-9**

The number average molecular weights (\( M_n(AN) \), \( M_n(HN) \) and \( M_n(AN, HN) \)) of the polymers prepared, which were calculated from their hydroxyl (\( HN \)) and acid numbers (\( AN \)), are shown in Tab. 4-1. The \( M_n \) values of the samples vary between 1.1\( \times \)10\(^3\) and 3.4\( \times \)10\(^3\) g/mol (Tab. 4-1). The results obtained by GPC, VPO, and by \(^1\)H-NMR spectroscopy are also shown in the table. As it was observed earlier [1] the GPC results overestimate the molecular weights of HBP in the low molar mass region. Therefore, this method was used only for example in two cases. The \(^1\)H-NMR determination of \( M_n \) based on the determination of the percentage of unreacted COOH groups (usable only for core-free products, see further below, p.78 ) and the \( M_n \) calculation from acid and hydroxyl number gave consistent results and are therefore trustworthy.
### Tab. 4-1: Number average molecular weight ($M_n$) of poly-BHPPA prepared, and conversion ($\alpha$) of functional groups.

<table>
<thead>
<tr>
<th>Sample code</th>
<th>AN [mgKOH/g]</th>
<th>$\alpha_A$</th>
<th>HN [mgKOH/g]</th>
<th>$\alpha_B$</th>
<th>$M_n$ (AN) [g/mol]</th>
<th>$M_n$ (HN) [g/mol]</th>
<th>$M_n$ (AN,HN) [g/mol]</th>
<th>$M_n$ (GPC) [g/mol]</th>
<th>$M_n$ ($^1$H NMR) [g/mol]</th>
<th>$M_n$ (VPO) [g/mol]</th>
</tr>
</thead>
<tbody>
<tr>
<td>EP01</td>
<td>30</td>
<td>0.42</td>
<td>232</td>
<td>0.85</td>
<td>1980</td>
<td>1850</td>
<td>1910</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>EP02</td>
<td>27</td>
<td>0.43</td>
<td>229</td>
<td>0.87</td>
<td>2190</td>
<td>2060</td>
<td>2120</td>
<td>4200</td>
<td>2200</td>
<td>1300</td>
</tr>
<tr>
<td>EP03</td>
<td>19</td>
<td>0.45</td>
<td>220</td>
<td>0.91</td>
<td>3130</td>
<td>3090</td>
<td>3110</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>EP$_{c2}$ (15%)</td>
<td>16</td>
<td>0.44</td>
<td>232</td>
<td>0.92</td>
<td>1930</td>
<td>2180</td>
<td>2050</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>EP$_{c3}$ (5%)</td>
<td>14</td>
<td>0.45</td>
<td>224</td>
<td>0.93</td>
<td>3420</td>
<td>3300</td>
<td>3470</td>
<td>5100</td>
<td>2080</td>
<td></td>
</tr>
<tr>
<td>EP$_{c3}$ (10%)</td>
<td>27</td>
<td>0.41</td>
<td>244</td>
<td>0.87</td>
<td>1750</td>
<td>1740</td>
<td>1750</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>EP$_{c4}$ (15%)</td>
<td>22</td>
<td>0.42</td>
<td>247</td>
<td>0.89</td>
<td>1820</td>
<td>1860</td>
<td>1840</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>EP$_{c6}$ (15%)</td>
<td>25</td>
<td>0.41</td>
<td>251</td>
<td>0.87</td>
<td>1780</td>
<td>1780</td>
<td>1780</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>EP$_{c6}$ (15%)</td>
<td>13</td>
<td>0.43</td>
<td>239</td>
<td>0.94</td>
<td>3290</td>
<td>3260</td>
<td>3280</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

where:
- AN - acid number of poly- BHPPA
- HN - hydroxyl number of poly- BHPPA
- $\alpha_A$ is conversion of OH groups (calculated from HN)
- $\alpha_B$ is conversion of COOH groups (calculated from AN)
- $M_n$ (AN) – number average molecular weight calculated from acid number
- $M_n$ (HN) – number average molecular weight calculated from acid number
- $M_n$ (AN, HN) – number average molecular weight calculated from both: acid and hydroxyl number
- $M_n$ (GPC) – number average molecular weight determined by GPC
- $M_n$ ($^1$H NMR) – number average molecular weight calculated from proton NMR
- $M_n$ (VPO) – number average molecular weight determined by VPO
4.1.2.2 Determination of the weight average of the molecular weight ($M_w$)

The weight average molecular weight for $\text{BA}_f + \text{A}_g$ (core) monomers can be calculated using the theory of branching processes and formalism of generation functions [7]. These calculations can be done with the assumption that all A groups from the main monomer and A groups from the core have the same reactivity, that no cyclization and no side reaction occur. For such systems the basic number fraction - probability generating function (pgf) is given by Eq. 4-10.

All calculation were done using the data presented in Tab. 4-1 and Tab. 4-2.

**Tab. 4-2: Characterization of main and core monomers.**

<table>
<thead>
<tr>
<th>Sample code</th>
<th>$g$</th>
<th>$f$</th>
<th>$\psi_M$</th>
<th>$\psi_C$</th>
<th>$n_M$</th>
<th>$n_C$</th>
<th>$m_M$</th>
<th>$m_C$</th>
<th>$M_M$</th>
<th>$M_C$</th>
</tr>
</thead>
<tbody>
<tr>
<td>EP$_{01}$</td>
<td>-</td>
<td>2</td>
<td>1</td>
<td>0</td>
<td>1</td>
<td>-</td>
<td>1</td>
<td>-</td>
<td>286.33</td>
<td>-</td>
</tr>
<tr>
<td>EP$_{02}$</td>
<td>-</td>
<td>2</td>
<td>1</td>
<td>0</td>
<td>1</td>
<td>-</td>
<td>1</td>
<td>-</td>
<td>286.33</td>
<td>-</td>
</tr>
<tr>
<td>EP$_{03}$</td>
<td>-</td>
<td>2</td>
<td>1</td>
<td>0</td>
<td>1</td>
<td>-</td>
<td>1</td>
<td>-</td>
<td>286.33</td>
<td>-</td>
</tr>
<tr>
<td>EP$_{C2}$ (15%)</td>
<td>2</td>
<td>2</td>
<td>0.93</td>
<td>0.07</td>
<td>0.93</td>
<td>0.07</td>
<td>79.89</td>
<td>-</td>
<td>286.33</td>
<td>200</td>
</tr>
<tr>
<td>EP$_{C3}$ (5%)</td>
<td>3</td>
<td>2</td>
<td>0.975</td>
<td>0.025</td>
<td>0.986</td>
<td>0.014</td>
<td>0.992</td>
<td>0.08</td>
<td>286.33</td>
<td>134.17</td>
</tr>
<tr>
<td>EP$_{C3}$ (10%)</td>
<td>3</td>
<td>2</td>
<td>0.953</td>
<td>0.047</td>
<td>0.968</td>
<td>0.032</td>
<td>0.984</td>
<td>0.016</td>
<td>286.33</td>
<td>134.17</td>
</tr>
<tr>
<td>EP$_{C3}$ (15%)</td>
<td>3</td>
<td>2</td>
<td>0.93</td>
<td>0.07</td>
<td>0.952</td>
<td>0.048</td>
<td>0.977</td>
<td>0.023</td>
<td>286.33</td>
<td>134.17</td>
</tr>
<tr>
<td>EP$_{C4}$ (15%)</td>
<td>4</td>
<td>2</td>
<td>0.93</td>
<td>0.07</td>
<td>0.966</td>
<td>0.034</td>
<td>0.983</td>
<td>0.017</td>
<td>286.33</td>
<td>136.15</td>
</tr>
<tr>
<td>EP$_{C6}$ (15%)</td>
<td>6</td>
<td>2</td>
<td>0.93</td>
<td>0.07</td>
<td>0.976</td>
<td>0.024</td>
<td>0.987</td>
<td>0.022</td>
<td>286.33</td>
<td>254.28</td>
</tr>
</tbody>
</table>

where:

$g$ is the A-functionality of $A_g(C)$

$f$ is the A-functionality of the $\text{BA}_f$ monomer

$\psi_M$, $\psi_C$ are molar fractions of A groups in “M” ($\text{AB}_f$) monomer and “C” (core monomer), respectively

$n_M$ is the molar fraction of the

$n_C$ the molar fraction of $A_g$

$m_M$ is the weight fraction of the $\text{BA}_f$ monomer

$m_C$ the weight fraction of $A_g$

$M_M$ the molecular weight of $\text{BA}_f$

$M_C$ the molecular weight of $A_g$
4.1 Results: Poly-BHPPA Synthesis and Characterization

\[ F_{0n} = (Z_{M}, Z_{C}, Z_{A}, Z_{B}, z_{BM}, z_{AM}, z_{AC}) = \]
\[ n_{B} Z_{M}^{M'} [(1 - \alpha_{A}) Z_{A} + \alpha_{A} z_{BM}]^{f} [(1 - \alpha_{B}) Z_{B} + \alpha_{B} (\psi_{M} Z_{AM} + \psi_{C} z_{AC})] + n_{C} Z_{C}^{M'} [(1 - \alpha_{A}) Z_{A} + \alpha_{A} z_{BM}]^{e} \]

Eq. 4-10

Where \( Z, z \) are auxiliary variables of the generating function:

- \( F_{0n} \) is the number fraction generating function
- \( Z_{M} \) refers to the monomer unit \( BA_{f} \) (denoted as M)
- \( Z_{C} \) refers to the core unit \( A_{g} \) (denoted as C)
- \( Z_{A} \) refers to unreacted groups A; \((1 - \alpha_{A})\) calculated from HN
- \( Z_{B} \) refers to unreacted groups B; \((1 - \alpha_{B})\) calculated from AN
- \( z_{BM} \) refers to bonds from A groups of monomer or core to B groups of monomer
- \( z_{AM} \) refers to bonds from B groups of monomer to A groups of monomer
- \( z_{AC} \) refers to bonds from B groups of monomer to A groups of core

\( \psi_{M}, \psi_{C} (= 1 - \psi_{M}) \) – are molar fractions of A groups in “M” (ABf) monomer and “C” (core monomer), respectively. They are calculated from Eq. 4-11

\[ \psi_{M} = \frac{f_{n_{M}}}{f_{n_{M}} + g_{n_{C}}} \]

Eq. 4-11

The pgf’s for units already bonded to preceding generations by bond involving one of its reacted functional groups correspond to the variable \( z \) and read:

\[ F_{BM}(Z, z) = Z_{M}^{M'} [(1 - \alpha_{A}) Z_{A} + \alpha_{A} z_{BM}]^{f} \]

Eq. 4-12

\[ F_{AM}(Z, z) = Z_{M}^{M'} [(1 - \alpha_{A}) Z_{A} + \alpha_{A} z_{BM}]^{f-1} [(1 - \alpha_{B}) Z_{B} + \alpha_{B} (\psi_{M} z_{AM} + \psi_{C} z_{AC})] \]

Eq. 4-13

\[ F_{AC}(Z, z) = Z_{C}^{M'} [(1 - \alpha_{A}) Z_{A} + \alpha_{A} z_{BM}]^{e-1} \]

Eq. 4-14

\( F_{BM}, F_{AM}, F_{AC} \) are probability generating functions respectively, for unit M rooted by its A group (bond \( A \rightarrow AM \) loading into the unit), its B group (bond \( AM \rightarrow BM \)) and core unit C (bond \( BM \rightarrow AC \)).
4.1 Results: Poly-BHPPA Synthesis and Characterization

The relevant identifiers are $Z_M$ and $Z_C$, and $Z_A=Z_B=1$. The long range correlations are obtained by cascade substitution by which $z\rightarrow u$.

The weight fraction generating function, $W(Z)$ reads:

$$W(Z, u) = m_M Z_M^{M_M} [1 - \alpha_A + \alpha_A u_{BM}] [1 - \alpha_B + \alpha_B (\psi_M u_{AM} + \psi_C u_{AC})] + m_C Z_C^{M_C} [1 - \alpha_A + \alpha_A u_{BM}]$$  \hspace{1cm} \text{Eq. 4-15}

where:

- $W(Z, u)$ is probability generating function
- $m_M$ is weight fraction of $B_A$ monomer
- $m_C$ is weight fraction of $A_B$ monomer (core)

$$u_{AM} = Z_M^{M_M} [1 - \alpha_A + \alpha_A u_{BM}] [1 - \alpha_B + \alpha_B (\psi_M u_{AM} + \psi_C u_{AC})]$$  \hspace{1cm} \text{Eq. 4-16}

$$u_{BM} = Z_M^{M_M} [1 - \alpha_A + \alpha_A u_{BM}]$$  \hspace{1cm} \text{Eq. 4-17}

$$u_{AC} = Z_C^{M_C} [1 - \alpha_A + \alpha_A u_{BM}]$$  \hspace{1cm} \text{Eq. 4-18}

The (Eq. 4-16-Eq. 4-18.) equations were differentiated with respect to $Z_M$ and $Z_C$. ($Z_M=Z_C=1$)

The weight-average molecular weights ($M_w$) were calculated using the formula:

$$u_{BM}^M = \left[ \frac{\partial u_{BM}}{\partial Z_M} \right]_{Z=1}$$

$$u_{AC}^M = \left( \frac{g-1}{1-f\alpha_A} \right) M_M$$

$$u_{AC}^M = \left( \frac{g-1}{1-f\alpha_A} \right) M_M$$

$$u_{BM}^C = 0$$

$$u_{AM}^M = \frac{M_M}{(1-f\alpha_A)(1-\varphi_M \alpha_B)} [1 - \alpha_A + \alpha_A \varphi_C (g-1)]$$

$$u_{AM}^C = \frac{\varphi_C \alpha_B M_C}{1-f\alpha_B \varphi_M}$$

$$u_{AM}^C = M_C$$
4.1 Results: Poly-BHPPA Synthesis and Characterization

\[ M_w = \left[ \frac{\partial W(Z, u(Z))}{\partial Z_M} + \frac{\partial W(Z, u(Z))}{\partial Z_C} \right]_{Z=1} \]

where:

\[ u_{AM} \] means the value of derivation of \( u_{AM} \) with respect to \( Z_C \) for all \( Z \) equal to one.

The \( M_w \) values calculated using the probability generation functions are presented in Tab. 4-3, together with the previously determined \( M_n \) values and polydispersity indices (\( M_w/M_n \)).

Tab. 4-3: Calculated molecular weight, polydispersity, and the first and second moment of functionality of the products prepared

<table>
<thead>
<tr>
<th>Sample code</th>
<th>( M_n ) (AN, HN) [g/mol]</th>
<th>( M_w ) (AN, HN) [g/mol]</th>
<th>( M_n ) (GPC) [g/mol]</th>
<th>( M_w ) (GPC) [g/mol]</th>
<th>( M_n/M_w ) (AN, HN)</th>
<th>( M_n/M_w ) (GPC)</th>
<th>( &lt;f_{\alpha}&gt;_1 )</th>
<th>( &lt;f_{\alpha}&gt;_2 )</th>
<th>( &lt;f_{\alpha}&gt;<em>2/ &lt;f</em>{\alpha}&gt;_1 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>EP(_01)</td>
<td>1910</td>
<td>8150</td>
<td>4.27</td>
<td>7.9</td>
<td>29.5</td>
<td>3.73</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>EP(_02)</td>
<td>2120</td>
<td>9880</td>
<td>4.65</td>
<td>8.7</td>
<td>35.5</td>
<td>4.08</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>EP(_03)</td>
<td>3110</td>
<td>19850</td>
<td>18200</td>
<td>6.38</td>
<td>4.3</td>
<td>11.9</td>
<td>70.3</td>
<td>5.91</td>
<td></td>
</tr>
<tr>
<td>EP(_C2) (15%)</td>
<td>2050</td>
<td>9770</td>
<td>4.77</td>
<td>7.8</td>
<td>34.6</td>
<td>4.44</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>EP(_C3) (9%)</td>
<td>3470</td>
<td>5100</td>
<td>20540</td>
<td>23000</td>
<td>5.92</td>
<td>4.51</td>
<td>13.7</td>
<td>72</td>
<td>5.26</td>
</tr>
<tr>
<td>EP(_C3) (10%)</td>
<td>1750</td>
<td>6540</td>
<td>3.74</td>
<td>7.4</td>
<td>23.6</td>
<td>3.19</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>EP(_C3) (15%)</td>
<td>1840</td>
<td>6910</td>
<td>3.75</td>
<td>7.8</td>
<td>24.8</td>
<td>3.18</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>EP(_C4) (15%)</td>
<td>1780</td>
<td>6170</td>
<td>3.47</td>
<td>7.8</td>
<td>22.6</td>
<td>2.90</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>EP(_C6) (15%)</td>
<td>3280</td>
<td>13130</td>
<td>4.00</td>
<td>13.7</td>
<td>47.4</td>
<td>3.46</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

As mentioned before, the addition of a polyfunctional core monomer to the reaction mixture should cause a decrease of polydispersity. The results shown in Tab. 4-3 indeed show a moderate decrease in polydispersity in the case of samples containing core monomers, if products with similar molecular weight are compared (e.g. EP\(_03\) with EP\(_C6\)(15%), or of EP\(_01\), EP\(_02\) with EP\(_C3\)(15%)).

However, at this point we did not consider difference in reactivity of aromatic and aliphatic OH groups. If the reactivity difference were taken into account, the effect on polydispersity would be even stronger.
The dependences of the polydispersity ($M_w/M_n$) on the acid number (AN) for polymers with different cores (core OH amount = 15% of COOH amount from monomer, referred to as “15%” core) are graphically illustrated on Fig. 4-3, left. Fig. 4-3 right shows this dependence for poly-BHPPA with varying amount of the trifunctional core comonomer.

**Fig. 4-3**: Dependence of polydispersity ($M_w/M_n$) on the acid number (AN)
4.1.3 Functionality of the poly-BHPPA prepared

The average functionality is an important characteristic of hyperbranched polymers, especially for their application as network precursors.

The first moment functionality average is calculated from the functional groups conversion (obtained in turn from AN and HN) according to Eq. 4-20:

$$
\langle f_A \rangle_1 = \frac{\sum f_A n_f}{\sum f_A n_f} \frac{(n_M f + n_C g)(1 - \alpha_A)}{1 - [n_M f + n_M \alpha_B + n_C g \alpha_A]/2}
$$

Eq. 4-20

The second-moment-functionality average $<f_A>_2$ is defined as:

$$
\langle f_A \rangle_2 = \frac{\sum f_{A}^{2} n_f}{\sum f_A n_f}
$$

Eq. 4-21

where: $n_f$ is a number fraction of molecules bearing $f_A$ functional groups of type A.

$<f_A>_2$ can be calculated using the theory of branching processes (TBP) similarly as the mass average molecular weight ($M_w$) by using Eq. 4-22-Eq. 4-26.

$$
\Phi(Z_A, u(Z_A)) = \psi_M [(1 - \alpha_A)Z_A + \alpha_A u_{BM}] [1 - \alpha_B + \alpha_B (\psi_M u_{AM} + \psi_C u_{AC})] + \psi_C [(1 - \alpha_A)Z_A + \alpha_A u_{BM}]^\psi
$$

Eq. 4-22

where:

- $\Phi$ is the probability generating function for distribution of unreacted functional groups.
- $Z_A$ and $Z_B$ are the relevant identifiers and $Z_M = Z_C = 1$. We are interested only in groups A
- $\psi_M, \psi_C$ ($= 1 - \psi_M$) – are molar fractions of A groups in “M” (ABr) monomer and “C”

$$
u_{BM} = [(1 - \alpha_A)Z_A + \alpha_A u_{BM}]^{f'}
$$

Eq. 4-23

$$
u_{AM} = [(1 - \alpha_A)Z_A + \alpha_A u_{BM}]^{f'-1} [1 - \alpha_B + \alpha_B (\psi_M u_{AM} + \psi_C u_{AC})]
$$

Eq. 4-24

$$
u_{AC} = [(1 - \alpha_A)Z_A + \alpha_A u_{BM}]^{f'-1}
$$

Eq. 4-25
4.1 Results: Poly-BHPPA Synthesis and Characterization

By differentiation of the function $\Phi$ (and of its components $u$ with respect to $Z_A$ and by putting $Z_A=1$, the second moment of functionality average, is equal to:

$$\langle f_A \rangle_2 = \psi_M (\{f(1-\alpha_A + \alpha_A u_{BM}^A) + (\alpha_B \psi_M u_{AM}^A + \alpha_B \psi_C u_{AC}^A)\} + \psi_C g[1-\alpha_A + \alpha_A u_{BM}^A]$$  \hspace{1cm} \text{Eq. 4-26}

Where:

$$u_{BM}^A = \frac{f(1-\alpha_A)}{1-f\alpha_A}$$

$$u_{AC}^A = \frac{(g-1)(1-\alpha_A)}{1-f\alpha_A}$$

$$u_{AM}^A = \frac{(1-\alpha_A)[f-1+\alpha_b (g-1)\varphi_C]}{(1-f\alpha_A)(1-\alpha_B \varphi_M)}$$

The above calculations are valid, if the reactivity of OH groups from both AB$_f$ monomer and A$_g$ core are equal and if no cyclization and no side reaction occur. From earlier investigations it follows, however, that during the BHPPA polycondensation, a side product is formed. The first and second moment of functionality for the products prepared are given in Tab. 4-3. The ratio

$$\frac{<f_A>_{2}}{<f_A>_{1}}$$

was found to be similar but somewhat lower than the polydispersity of the polymers ($M_w/M_n$).
4.1.4 Microstructure of poly-BHPPA prepared (degree of branching)

4.1.4.1 $^1$H-NMR Spectroscopy: Determination of $M_n$

The molecular weight $M_n$ of core-free products can be determined using $^1$H NMR. The ratio of the signal integral of the $-\text{CH}_2\text{-COOH}$ protons (signal at 1.97 ppm, labelled “a” in Fig. 4-4) to the integral of a suitable reference signal, like that of the aromatic protons (labeled “D”) or that of the methyl groups (labeled “c”) leads to the polymerization degree $P_n$:

$$P_n = \frac{\int \text{"a"}(\text{monomer})}{\int \text{"reference"}(\text{monomer})} \frac{\int \text{"a"}(\text{prod.})}{\int \text{"reference"}(\text{prod.})}$$

where “reference” is either integral of the signal “D” or “c” ($\int \text{"a"}(\text{monomer})/\int \text{"D"}(\text{monomer}) = 0.25$, and $\int \text{"a"}(\text{monomer})/\int \text{"c"}(\text{monomer}) = 2/3$) as shown (Fig. 4-4).

**Fig. 4-4:** $^1$H-NMR spectrum of a hyperbranched polyester based on 4, 4-bis-(4'-hydroxyphenyl) pentanoic acid (EP$_{02}$)
The above calculation is based on the assumption, that each polymer molecule contains exactly one focal carboxyl group \(-\text{CH}_2\text{-COOH}\), which means that no significant cyclization or side reactions occur. The knowledge of \(P_n\) yields (under the above assumptions) the exact value of the number average molecular weight:

\[
M_n = P_n \times M_W(\text{dendritic repeat unit}) + (P_n + 1) \times M_W(H) + M_W(\text{OH})
\]

where \(M_W\) are molecular masses of a dendritic repeat unit (267.3 g/mol), of hydrogen (1.01 g/mol) and of an OH group (17.01 g/mol).

One sample, the product named EP\(_{02}\), was analyzed using \(^1\text{H}\) NMR (see Fig. 4-4) yielding \(P_n = 8.62\) (with “D” as reference signal) and \(P_n = 7.84\) (with “c” as reference), in average \(P_n = 8.23\) and \(M_n = 2225\) g/mol (rounded as 2200 g/mol). For comparison, \(M_n\) based on the AN and HN was calculated to be 2120 g/mol (see Tab. 4-3) which is an excellent agreement allowing the conclusion that the fraction of side product and internal cycles is very low.

The average number of hydroxyl groups per repeat unit was found to be ca. 0.91 based on the integration of the phenol signal (Fig. 4-4).

The above \(^1\text{H}\) NMR spectroscopic analysis can not be used for BHPPA polymers containing core monomer units, because the focal groups \(-\text{CH}_2\text{-COOH}\) of the poly-BHPPA segments are to a large part esterified (ideally 100% esterification) by the core and thus difficult to resolve from the “internal” \(-\text{CH}_2\text{-COO}\)- groups which are esterified with phenolic OH groups. Moreover, the \(^1\text{H}\)-NMR spectroscopy of the given resolution did not yield any exact information about the degree of branching in the products prepared. For the above reasons, the microstructure of all the samples was analysed by means of \(^{13}\text{C}\)-NMR spectroscopy, which yielded more detailed informations.
4.1.4.2 $^{13}$C-NMR Spectroscopy: Detailed microstructure

The $^{13}$C-NMR spectroscopy is an excellent method for the quantitative determination of the microstructure (e.g. degree of branching) of the BHPPA polymers prepared. Fig. 4-5 shows the assignment [1] of the $^{13}$CNMR signals for a typical BHPPA repeat unit in a polymer.

The error of the signal integration is in the range of 2 to 5%.

![Fig. 4-5: $^{13}$C NMR spectrum of hyperbranched polyester EP$_{02}$](image)

4.1.4.2.1 Degree of branching

Fig. 4-6 illustrates the different binding situations of BHPPA repeat units in poly-BHPPA: dendritic (D), linear (L) and terminal (T). The D, L and T units are either “internal” units (D2, L2, T2), bonded through both OH and COOH groups into the polymer, or so-called “focal” groups, bonded through OH groups only, standing on the “tip” of the branched structure (D1, L1, T1). The unit T1 is in fact free monomer, as it combines both 2 unreacted phenolic OH groups.
4.1 Results: Poly-BHPPA Synthesis and Characterization

groups of a terminal unit with the focal unreacted COOH group. In copolymers with core polyols, there are core bound focal BHPPA units, which stand on the tip of the poly BHPPA structure and are at the same time bonded to the core through their carboxylic groups (D1c, L1c and T1c).

![Chemical structures](image)

**Fig. 4-6**: D, L, T units in poly-BHPPA.
The distribution of the above described D, L ant T repeat units characterizes the microstructure of the BHPPA polymers prepared, which can be quantitatively described by the degree of branching (see further below).

The $^{13}$C-signals of the BHPPA units, shown and assigned in Fig. 4-5, present additional splitting due to different bonding situations of different repeating units. Especially interesting for the microstructure analysis are two signal regions: The signals of quaternary C atoms (“C5” in Fig. 4-5) and the signals of the carboxyl C atoms (“C9” in Fig. 4-5).

The signals of the quaternary C atoms (“C5”) at 43-45 ppm are very useful: As shown in Fig. 4-8, the signals of D2, D1, L2, L1, and T2, T1 are always well separated and easily integratable, allowing quantitative determination. In the case of polymers containing aliphatic polyols as core, the signals of the D1c, L1c and T1c BHPPA repeat units can be often but not always resolved from the D1, L1 and T1 signals (Fig. 4-8). The determined distributions of D, L and T units in the polymers prepared are presented in Tab. 4-4.

**Fig. 4-7:** Signals from quaternary carbon (C5) for polymers without core (EP$_{02}$)

**Fig. 4-8:** Signals from quaternary carbon (C5) for polymers with core (EP$_{C4(15\%)}$)
4.1 Results: Poly-BHPPA Synthesis and Characterization

<table>
<thead>
<tr>
<th>Sample</th>
<th>D2 (mol%)</th>
<th>D1 (mol%)</th>
<th>D1c (mol%)</th>
<th>L2 (mol%)</th>
<th>L1 (mol%)</th>
<th>L1c (mol%)</th>
<th>T2 (mol%)</th>
<th>T1 (mol%)</th>
<th>T1c (mol%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>EP01</td>
<td>13.53</td>
<td>3.76</td>
<td>0.00</td>
<td>37.59</td>
<td>10.15</td>
<td>0.00</td>
<td>27.82</td>
<td>7.14</td>
<td>0.00</td>
</tr>
<tr>
<td>EP02</td>
<td>14.05</td>
<td>3.31</td>
<td>0.00</td>
<td>41.32</td>
<td>7.44</td>
<td>0.00</td>
<td>28.51</td>
<td>5.37</td>
<td>0.00</td>
</tr>
<tr>
<td>EP03</td>
<td>17.08</td>
<td>2.50</td>
<td>0.00</td>
<td>41.67</td>
<td>5.00</td>
<td>0.00</td>
<td>28.75</td>
<td>5.00</td>
<td>0.00</td>
</tr>
<tr>
<td>EPC2(15%)</td>
<td>13.98</td>
<td>1.22</td>
<td>-</td>
<td>30.40</td>
<td>13.98</td>
<td>-</td>
<td>28.57</td>
<td>11.85</td>
<td>-</td>
</tr>
<tr>
<td>EPC3(5%)</td>
<td>13.36</td>
<td>3.02</td>
<td>0.86</td>
<td>43.10</td>
<td>7.33</td>
<td>0.86</td>
<td>26.29</td>
<td>4.74</td>
<td>0.43</td>
</tr>
<tr>
<td>EPC3(10%)</td>
<td>9.15</td>
<td>3.05</td>
<td>-</td>
<td>33.90</td>
<td>12.20</td>
<td>-</td>
<td>30.17</td>
<td>11.53</td>
<td>-</td>
</tr>
<tr>
<td>EPC3(15%)</td>
<td>9.00</td>
<td>4.00</td>
<td>-</td>
<td>33.33</td>
<td>12.67</td>
<td>-</td>
<td>30.00</td>
<td>11.00</td>
<td>-</td>
</tr>
<tr>
<td>EPC4(15%)</td>
<td>8.18</td>
<td>1.89</td>
<td>2.52</td>
<td>31.45</td>
<td>5.35</td>
<td>8.49</td>
<td>30.19</td>
<td>4.72</td>
<td>7.23</td>
</tr>
<tr>
<td>EPC6(15%)</td>
<td>10.04</td>
<td>2.60</td>
<td>2.97</td>
<td>37.17</td>
<td>2.23</td>
<td>8.18</td>
<td>30.11</td>
<td>1.49</td>
<td>5.20</td>
</tr>
</tbody>
</table>

From the content of dendritic, linear and terminal units, the degree of branching ($DB$) of the materials prepared can be calculated. The degree of branching is an important material characteristic, as it has a determining influence on the products physical properties, especially on their viscosity in melt or solution. Kim, Webster and Fréchet [8, 9] defined $DB$ as a function of the amounts of the three structural units types (T, L and D) in polymers made from AB$_2$ monomers as given in Eq. 4-27. Generally, $T = D + 1$ in all products ($T$ and $D$ mean here the amounts). The Fréchet definition is suitable for products of higher molecular mass, in which small oligomers and unreacted monomer can be neglected. In the case of small oligomer this definition leads to unrealistically high degrees of branching (e.g. (linear) dimer: $DB = 0.5$). Frey presents a different definition of $DB$ [5], which is well suited for oligomers as well as for larger molecules, given in Eq. 4-28.

$$DB_{Fréchet} = \frac{T + D}{T + D + L}$$ \hspace{1cm} \text{Eq. 4-27}

$$DB_{Frey} = \frac{2D}{2D + L}$$ \hspace{1cm} \text{Eq. 4-28}

The hyperbranched polyesters presented in this work do not have a high molecular weight, so their degrees of branching were should be determined according to the Frey definition (Tab. 4-5). In the case of polymers containing aliphatic core units a degree of branching was also calculated for the BHPPA part of their structure. The products obtained had all a similar degree of branching of 0.34 – 0.45 with a relatively good match for calculations based on C5 and C9, respectively. For comparison, the $DB$ values calculated according to Fréchet are also given in the table.
Tab. 4-5: Degree of branching ($DB$) according to Frey calculated from the quaternary C signals; for comparison $DB$ according to Fréchet and $DB_{Frey}$ calculated (see below) from carboxyl signals.

<table>
<thead>
<tr>
<th>Sample</th>
<th>DB(Frey)</th>
<th>DB(Fréchet)</th>
<th>DB(Frey) from COO groups</th>
</tr>
</thead>
<tbody>
<tr>
<td>EP₀₁</td>
<td>0.42</td>
<td>0.52</td>
<td>0.41</td>
</tr>
<tr>
<td>EP₀₂</td>
<td>0.42</td>
<td>0.51</td>
<td>0.47</td>
</tr>
<tr>
<td>EP₀₃</td>
<td>0.46</td>
<td>0.53</td>
<td>0.46</td>
</tr>
<tr>
<td>EP₂(15%)</td>
<td>0.41</td>
<td>0.56</td>
<td>0.45</td>
</tr>
<tr>
<td>EP₃(5%)</td>
<td>0.40</td>
<td>0.49</td>
<td>0.46</td>
</tr>
<tr>
<td>EP₃(10%)</td>
<td>0.35</td>
<td>0.54</td>
<td>0.33</td>
</tr>
<tr>
<td>EP₃(15%)</td>
<td>0.36</td>
<td>0.54</td>
<td>0.37</td>
</tr>
<tr>
<td>EP₄(15%)</td>
<td>0.36</td>
<td>0.55</td>
<td>0.37</td>
</tr>
<tr>
<td>EP₆(15%)</td>
<td>0.40</td>
<td>0.52</td>
<td>0.47</td>
</tr>
</tbody>
</table>
4.1.4.2.2 Carboxyl groups signals in poly-BHPPA

An analytically interesting region of the $^{13}$C spectra are the well-separated signals of carboxyl-C atoms (see Fig. 4-9).

Fig. 4-9: Carbonyl-carbon signals for EP$_{C4(15\%)}$

In the carboxyl region, the following signals can be recognized: The signals of aromatic esters (R-C(O)-O-Ar), which are part of the “normal” poly-BHPPA structure, appear at $\delta = 171.6$-$172.5$ ppm. Aliphatic ester carboxyls (R-C(O)-O-R'$_{core}$), which are part of focal BHPPA units attached to the aliphatic core monomers, show signals at $\delta = 173.2$-$172.6$ ppm. The unreacted focal COOH groups display signals at $\delta = 174.5$-$175.2$ ppm. The BHPPA polymers usually contain a small but visible amount of an elimination-side-product, a lactone with one phenol OH group, which is known to be formed from the monomer via phenol elimination during the polycondensation (see Scheme 4-3). This side product shows its characteristic signals in the region of $\delta = 176.2$-$177.0$ ppm [5]. The identity of this compound was proven in literature work [5] using mass spectroscopy.
4.1 Results: Poly-BHPPA Synthesis and Characterization

The carboxyl signals of the above described BHPPA units are further split due to their bonding situation: D, L, T units (with all 2, 1, or no phenolic OH groups reacted) can be distinguished. Also in the case of the side product, the free side product, as well as its polymer bound analogue (with its only phenolic OH esterified) can be recognized. The information about the D, L, T units is less detailed and precise if compared with the quaternary C signals, but as far the carboxyl signals are intense enough, their splitting exactly reproduces the information about the degree of branching obtained from the quaternary C signals (see Tab. 4-5). The determined distributions of the above described carboxyl groups in the polymers prepared are presented in Tab. 4-6.

**Scheme 4-3:** Side product formed during polycondensation

The carboxyl signals of the above described BHPPA units are further split due to their bonding situation: D, L, T units (with all 2, 1, or no phenolic OH groups reacted) can be distinguished. Also in the case of the side product, the free side product, as well as its polymer bound analogue (with its only phenolic OH esterified) can be recognized. The information about the D, L, T units is less detailed and precise if compared with the quaternary C signals, but as far the carboxyl signals are intense enough, their splitting exactly reproduces the information about the degree of branching obtained from the quaternary C signals (see Tab. 4-5). The determined distributions of the above described carboxyl groups in the polymers prepared are presented in Tab. 4-6.

**Tab. 4-6:** Signal intensities of the different COO groups in the poly-BHPPA prepared, given as % of all COO groups.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Ar-Es T (mol%)</th>
<th>Ar-Es L (mol%)</th>
<th>Ar-Es D (mol%)</th>
<th>Aliph-Es T (mol%)</th>
<th>Aliph-Es D (mol%)</th>
<th>Foc-Gr T (mol%)</th>
<th>Foc-Gr L (mol%)</th>
<th>Foc-Gr D (mol%)</th>
<th>free Side Prod (mol%)</th>
<th>focal Side Prod (mol%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>EP01</td>
<td>29.12</td>
<td>38.46</td>
<td>13.74</td>
<td>0.00</td>
<td>0.00</td>
<td>3.30</td>
<td>6.59</td>
<td>2.20</td>
<td>4.40</td>
<td>2.20</td>
</tr>
<tr>
<td>EP02</td>
<td>28.22</td>
<td>38.65</td>
<td>17.79</td>
<td>0.00</td>
<td>0.00</td>
<td>3.68</td>
<td>6.13</td>
<td>1.84</td>
<td>2.45</td>
<td>1.23</td>
</tr>
<tr>
<td>EP03</td>
<td>29.57</td>
<td>35.48</td>
<td>16.67</td>
<td>0.00</td>
<td>0.00</td>
<td>2.69</td>
<td>11.83</td>
<td>3.76</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>EP C2(15%)</td>
<td>28.44</td>
<td>25.33</td>
<td>10.67</td>
<td>7.56</td>
<td>11.56</td>
<td>0.89</td>
<td>1.78</td>
<td>3.56</td>
<td>5.33</td>
<td>4.00</td>
</tr>
<tr>
<td>EP C2(5%)</td>
<td>28.57</td>
<td>44.72</td>
<td>19.25</td>
<td>-</td>
<td>2.48</td>
<td>0.62</td>
<td>4.35</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>EP C2(10%)</td>
<td>27.31</td>
<td>34.26</td>
<td>9.26</td>
<td>4.63</td>
<td>5.56</td>
<td>0.93</td>
<td>3.70</td>
<td>6.48</td>
<td>1.39</td>
<td>4.63</td>
</tr>
<tr>
<td>EP C2(15%)</td>
<td>28.32</td>
<td>31.86</td>
<td>10.18</td>
<td>5.31</td>
<td>7.96</td>
<td>2.21</td>
<td>4.42</td>
<td>3.98</td>
<td>0.44</td>
<td>3.10</td>
</tr>
<tr>
<td>EP C3(15%)</td>
<td>33.86</td>
<td>29.13</td>
<td>9.45</td>
<td>5.12</td>
<td>6.69</td>
<td>1.97</td>
<td>3.94</td>
<td>5.51</td>
<td>0.79</td>
<td>2.36</td>
</tr>
<tr>
<td>EP C3(15%)</td>
<td>27.27</td>
<td>38.07</td>
<td>17.61</td>
<td>4.55</td>
<td>6.82</td>
<td>2.27</td>
<td>2.84</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

**Table 4-6:** Signal intensities of the different COO groups in the poly-BHPPA prepared, given as % of all COO groups.
4.1.4.2.3 Determination of core monomer conversion

The carboxyl signals yield an important information about the degree of incorporation of the core monomer, which can be given as the percentage of esterified aliphatic OH groups of the core monomer: From the percentage of BHPPA units linked to the core units and from the known chemical amount of the BHPPA monomer used in the synthesis, the chemical amount of the reacted aliphatic OH groups can be calculated. From the also known chemical amount of the OH groups of the aliphatic core monomer, its degree of conversion (describing its incorporation) can be calculated (see also Tab. 4-7):

\[
\text{Conversion} = \frac{n(\text{Core OH reacted})}{n(\text{Core OH})}
\]

\[
\text{Number of OH reacted per core molecule} = \frac{\text{Conversion}}{\text{Func(Core)}}
\]

where:

fr(Aliph_ES) is the fraction of carboxyl groups, which are part of aliphatic ester units, what means that they are attached to core monomer units,

n are chemical amounts of compounds or functional groups,

Func(Core) is the core functionality.

The degree of conversion of the core OH groups is ca. 100% for the cores “C2” (tetraethylene glycol; bifunctional) and “C3” (tris(hydroxymethyl)propane; trifunctional). In the case of the higher functional cores “C4” (pentaerythritol) and “C6” (dipentaerythritol), the OH conversion is around 89% (see Tab. 4-7), meaning, that in average, every second of these cores has one unreacted OH group. In the case of the C2(5%) polymer with a very low core content the carboxyl signals are very weak and the determination of the core conversion was not very precise.
### 4.1 Results: Poly-BHPPA Synthesis and Characterization

#### 4.1.4.2.4 Amounts of free monomer and of the side products

The amounts of free monomer and of side products in the polymers prepared are given in Tab. 4-8. The free (monomeric) side product (Scheme 4-3 (I)) content in the polymers synthesized was found to be 0.6 - 4.4% of monomer units, or 0.07 - 0.36 side product molecules per number average polymer molecule. The content of side product bound as focal group in the polymers was 0.89 – 2.2% of monomer units, or 0.08 - 0.18 focal side product molecules per number average polymer molecule. The content of free monomer was between 1.5 and 12% of monomer units, meaning 0.18 – 1.0 monomer molecules per number average polymer molecule.

#### Tab. 4-8: Content of side products and of free monomer in molar % of monomer units and as molecules (or structure unit) per polymer ($P_n$, calc. from AN and HN) molecule.

<table>
<thead>
<tr>
<th>Sample</th>
<th>free side product</th>
<th>focal side product</th>
<th>free monomer from quaternary C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Mon%</td>
<td>n/Molec($P_n$)</td>
<td>Mon%</td>
</tr>
<tr>
<td>EP_{01}</td>
<td>4.40</td>
<td>0.35</td>
<td>2.20</td>
</tr>
<tr>
<td>EP_{02}</td>
<td>2.45</td>
<td>0.21</td>
<td>1.23</td>
</tr>
<tr>
<td>EP_{03}</td>
<td>0.00</td>
<td>0</td>
<td>0.00</td>
</tr>
<tr>
<td>EP_{C2(15%)}</td>
<td>4.00</td>
<td>0.35</td>
<td>0.89</td>
</tr>
<tr>
<td>EP_{C3(10%)}</td>
<td>4.63</td>
<td>0.36</td>
<td>1.85</td>
</tr>
<tr>
<td>EP_{C3(15%)}</td>
<td>3.10</td>
<td>0.24</td>
<td>2.21</td>
</tr>
<tr>
<td>EP_{C4(15%)}</td>
<td>2.36</td>
<td>0.17</td>
<td>1.18</td>
</tr>
<tr>
<td>EP_{C6(15%)}</td>
<td>0.57</td>
<td>0.07</td>
<td>0.00</td>
</tr>
</tbody>
</table>

*) “n/ Molec($P_n$)” is the amount of BHPPA monomers or of side product, respectively, per number average ($P_n$) polymer molecule.
4.1.4.2.5 $M_n$ determination from $^{13}$C-NMR

The $^{13}$C-NMR spectra can also be used to determine the numeric average molar masses of the prepared products. The results are given in Tab. 4-9.

**Tab. 4-9:** Molar masses ($M_n$) calculated from the signal intensities of quaternary C-atoms. In the case of core-containing polymers, the simplifying assumption was made, that both the free and the core-bound poly-BHPPA structures have the same average degree of polymerization. The $M_n$ values calculated from $AN$ and $HN$ are given for comparison.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Mon / Core (recapture)</th>
<th>Pn (BHPPA Segment)</th>
<th>BHPPA Segments per Core</th>
<th>Eff. core functionality</th>
<th>Core-Free / Core-Cont. Polym</th>
<th>Pn (whole average molecule) $^{13}$C</th>
<th>$M_n$ (Polymer) $^{13}$C</th>
<th>$M_n$ (AN / HN)</th>
<th>$M_n^{(13)}$ / $M_n$(AN-HN)</th>
</tr>
</thead>
<tbody>
<tr>
<td>EP01</td>
<td>$\infty$</td>
<td>4.75</td>
<td>$\infty$</td>
<td>$\infty$</td>
<td>$\infty$</td>
<td>4.75</td>
<td>1293</td>
<td>1910</td>
<td>0.68</td>
</tr>
<tr>
<td>EP02</td>
<td>$\infty$</td>
<td>6.21</td>
<td>$\infty$</td>
<td>$\infty$</td>
<td>$\infty$</td>
<td>6.21</td>
<td>1683</td>
<td>2120</td>
<td>0.79</td>
</tr>
<tr>
<td>EP03</td>
<td>$\infty$</td>
<td>8.00</td>
<td>$\infty$</td>
<td>$\infty$</td>
<td>8.00</td>
<td>2165</td>
<td>3110</td>
<td>0.70</td>
<td></td>
</tr>
<tr>
<td>EP$_{C2}(15%)$</td>
<td>13.30</td>
<td>3.70</td>
<td>3.60</td>
<td>2</td>
<td>1.60</td>
<td>5.12</td>
<td>1462</td>
<td>2050</td>
<td>0.71</td>
</tr>
<tr>
<td>EP$_{C3}(5%)$</td>
<td>58.66</td>
<td>5.80</td>
<td>10.11</td>
<td>3</td>
<td>7.11</td>
<td>7.23</td>
<td>1972</td>
<td>3470</td>
<td>0.57</td>
</tr>
<tr>
<td>EP$_{C3}(10%)$</td>
<td>29.31</td>
<td>3.73</td>
<td>7.85</td>
<td>3</td>
<td>4.85</td>
<td>5.01</td>
<td>1382</td>
<td>1750</td>
<td>0.79</td>
</tr>
<tr>
<td>EP$_{C3}(15%)$</td>
<td>19.51</td>
<td>3.61</td>
<td>5.40</td>
<td>3</td>
<td>2.40</td>
<td>5.74</td>
<td>1592</td>
<td>1840</td>
<td>0.87</td>
</tr>
<tr>
<td>EP$_{C4}(15%)$</td>
<td>25.85</td>
<td>3.31</td>
<td>7.80</td>
<td>3.56</td>
<td>4.24</td>
<td>4.93</td>
<td>1363</td>
<td>1780</td>
<td>0.77</td>
</tr>
<tr>
<td>EP$_{C6}(15%)$</td>
<td>39.05</td>
<td>4.41</td>
<td>8.86</td>
<td>5.32</td>
<td>3.53</td>
<td>8.62</td>
<td>2382</td>
<td>3280</td>
<td>0.73</td>
</tr>
</tbody>
</table>

The $^{13}$C-NMR spectra yield easily the information about the numeric average polymerization degree of the core-free poly-BHPPA structures:

$$P_n(BHPPA) = \frac{\text{all } D \_ L \_ T \_ units}{\text{focal } D \_ L \_ T \_ units} = 1 + \frac{D2 + L2 + T2}{D1 + D1c + L1 + L1c + T1 + T1c}$$

where $D2$, $D1$, $D1c$, $L2$, $L1$, $L1c$, $T2$, $T1$ are $T1c$ are the respective amounts of the above described dendritic, linear and terminal repeat units. In the case of core free polymers the above defined $P_n(BHPPA) = P_n$(product).
In the case of the polymers with core, the cores incorporation has to be taken into account. If the simplifying assumption is made, that both the free and the core-bound poly-BHPPA structures have the same average degree of polymerization, the calculation of $M_n$ is easy and proceeds as follows:

The monomer to core ratios are known from the synthesis recipe and from them and $P_n$(BHPPA), the ratio of polyBHPPA segments to core molecules can be calculated as:

$$\text{polyBHPPA segments / cores} = (\text{monomer / core})*(1/ P_n(\text{BHPPA}))$$.

From the knowledge of the ratio polyBHPPA segments / cores and of the average effective core functionality (which was determined in the carboxyl signals analysis), the ratio of average core free to the average core containing polymer molecules can be calculated and is given in the Tab. 4-9. The molar masses of these both components can be calculated from $P_n$(BHPPA) and the effective core functionality. From these average masses of both components of the product mixture and from their ratio, the average molecular mass $M_n$ of the product was calculated (see Tab. 4-9).

The $M_n$ values obtained from $^{13}$C-NMR spectra are direct experimental values only in the case of the core-free polymers. Nevertheless, the $M_n$ values obtained via $^{13}$C-NMR and from the acid and hydroxyl numbers are relatively similar in the case of all products, the $M_n(^{13}\text{C})$ values being always somewhat smaller: $M_n(^{13}\text{C}) = (0.7-0.8)* M_n(\text{AN, HN})$. (The somewhat lower than expected $M_n(^{13}\text{C})$ value for EP$_{C3(5\%)}$ is due to the low signal intensity of the core related signals and to their unprecise integration).
4.1.5 Glass transition temperatures

The poly-BHPPA prepared show Tg values listed in Tab. 4-10, ranging near near 105°C. This high Tg values are due to the interaction of the aromatic rings and of numerous OH groups.

Tab. 4-10: Tg values of the synthesized BHPPA polymers, as determined by DSC

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Tg [°C]</th>
<th>M_n(AN, HN)</th>
</tr>
</thead>
<tbody>
<tr>
<td>EP₀₁</td>
<td>108</td>
<td>1980</td>
</tr>
<tr>
<td>EP₀₂</td>
<td>105.9</td>
<td>2190</td>
</tr>
<tr>
<td>EP₀₃</td>
<td>109.4</td>
<td>3130</td>
</tr>
<tr>
<td>EP₇₂(15%)</td>
<td>84.2</td>
<td>1928</td>
</tr>
<tr>
<td>EP₇₃(5%)</td>
<td>113.8</td>
<td>3419</td>
</tr>
<tr>
<td>EP₇₃(10%)</td>
<td>102.2</td>
<td>1750</td>
</tr>
<tr>
<td>EP₇₃(15%)</td>
<td>108.2</td>
<td>1824</td>
</tr>
<tr>
<td>EP₇₄(15%)</td>
<td>106.4</td>
<td>1780</td>
</tr>
<tr>
<td>EP₇₆(15%)</td>
<td>126.3</td>
<td>3290</td>
</tr>
</tbody>
</table>

Tg was determined by DSC, at a scanning rate of 10°C/min. A typical DSC scan is shown in Fig. 4-10 (sample EP₀₂). The Tg values of the samples were determined as the inflection points of the 2nd heating curves.
The correlation between the molecular mass $M_n$ and $T_g$ and also between the functionality $<f_A>$ and $T_g$ is shown in Fig. 4-11. Both correlations are similar (as the functionality increases with increasing molecular mass) and show a mild increase of $T_g$ with increasing polymerization degree. The properties of the core molecule incorporated in the product can influence $T_g$, as can be seen on the example of the difunctional core (tetraethylene glycol, 13-atom linear chain, see Fig. 4-12), which lowers $T_g$ by at least 20°C (Tab. 4-10) if compared to core free polymers of nearly the same molecular mass. In case of the higher functional cores, the structure of the cores as well as of the whole polymer becomes more compact, the $T_g$-lowering effect disappears. Polymers with high functional cores display higher $T_g$ values than core-free products of similar $M_n$ (Tab. 4-10).
4.1 Results: Poly-BHPPA Synthesis and Characterization

Fig. 4-11: Dependence of the glass transition temperature on molecular weight and functionality $<f_A>$ for different type of hyperbranched polyesters.

Fig. 4-12: Example of the somewhat larger core-containing EP$_{C2(15\%)}$ molecule
4.1.6 Thermal stability

The poly-BHPPA prepared show similar thermal stability. The decomposition in air starts near 300°C and is fastest near 350°C, a second degradation step, probably oxidation of the carbonized remains starts at ca 470°C, leading to quantitative (100%) weight loss (see Fig. 4-13).

![Graph showing thermal stability](image)

**Fig. 4-13:** Thermogravimetry analysis of poly-BHPPA (EP$_{02}$) and of its derivatives modified by deactivation of 30% of OH groups by phenyl- and cyclohexyl isocyanate

Fig. 4-13 also shows the stability characteristics of the products with 30% of the OH groups deactivated by addition of phenyl- and cyclohexyl isocyanate. The modified products behave very similarly: at first the elimination of phenyl- or cyclohexyl isocyanate, respectively, starts at ca. 130°C, setting the blocked OH groups free; the decomposition of the polymer itself shows the same characteristic decomposition steps as in case of the non-modified product.
4.1 Results: Poly-BHPPA Synthesis and Characterization

Literature, Poly-BHPPA characterization

2. H. R. Kricheldorf, R. Hobzova, G. Schwarz; Polymer; 2003, 44, 7361
5. A. Ziemer; PhD thesis; 2003
7. K. Dušek; unpublished results
8. Y. H. Kim, O. W. Webster; Macromolecules; 1992, 25, 5561
4.2 Kinetics investigations of polyurethane formation

4.2.1 Model experiments: Reactions of low-molecular-weight compounds

In order to better understand the reactivity of poly-BHPPA, an aliphatic-aromatic hyperbranched polyester-polyphenol, towards isocyanates, model experiments were performed with the low molecular weight 4-ethylphenol (EPH) 4-I. For comparison, the reactivity of an aliphatic alcohol, 1-hexanol (4-II), was also investigated.

\[
\text{CH}_2\text{CH}_3\text{-OH} \quad \text{HO-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH} = \text{NCO}
\]

4-I: 4-ethylphenol (EPH; a monofunctional phenol).

4-II: 1-hexanol (a monofunctional alcohol):

\[
\text{H}_3\text{C-CH}_2\text{-CH}_2\text{-CH}_2\text{-NCO}
\]

4-III: Butyl isocyanate (BuI; a monofunctional isocyanate)

The above monofunctional –OH components were reacted with the monofunctional butyl isocyanate (BuI) (4-III), and with the trifunctional trimer of 1,6-diisocyanatohexane, called „Tri-HDI“ or Desmodur N 3300; see 4-IV

\[
\begin{array}{c}
\text{OCN-CH}_2\text{NOCN} \\
\text{O-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-NCO}
\end{array}
\]

4-IV: Tri-HDI (idealized structure), commercial product: Desmodur N 3300.

The model reactions were always carried out at 25° C, in solution, at the concentrations \( C_{\text{NCO}} = C_{\text{OH}} = 1.42 \times 10^{-3} \text{ mol/g} \) (stoichiometric ratio), at the same molar concentration that was used in poly-BHPPA - isocyanate crosslinking mixtures, which had to be prepared mostly as 60 wt% of solids (meaning 60% of both -OH and -NCO). The studied reactions were catalyzed by dibutyltin dilaurate (DBTDL), \( C_{\text{DBTDL}} = 2.7 \times 10^{-6} \text{ mol/g} \). The catalyst concentration was chosen so that crosslinking systems reached the gel point in approximately 3h after mixing the components. DBTDL itself was selected from the wide range of polyurethane catalysts because it slows down the possible undesired reactions with moisture. 1,2-Dimethoxy-ethylenediglycol (diglyme) was used as solvent for all the reactions.
investigated, because it was found to be a good and nonvolatile solvent, boiling point = 162°C (clear solutions of products with $M_n = 1500$ to $3500$ g/mol), for poly-BHPPA; almost no solvent evaporated during preparation and measurement of kinetics samples).

The progress of the isocyanate reaction with the OH-compounds was monitored by decreasing of the infrared absorption peak of the NCO groups at $2270$ cm$^{-1}$ with time (see example in Fig. 4-14).

![Absorbance vs. Time](image)

**Fig. 4-14:** The decrease of the NCO absorption band with reaction time during the reaction of poly-BHPPA (EP$_03$) with Tri-HDI.

The kinetics results for the reactions of 1-hexanol and 4-ethyl-phenol with BuI and Tri-HDI are plotted in Fig. 4-15 and Fig. 4-16. The half times of these reactions were determined and are listed in Tab. 4-11.

As expected, the the reaction between EPH with BuI and Tri-HDI is about 25 times slower as that of the aliphatic OH component (1-hexanol).

Interestingly, the reaction of aliphatic and phenolic OH group with Tri-HDI is a little faster than their reaction with the monofunctional BuI. This can be due to a substitution effect and can be investigated separately. The substitution effect can hardly be caused by conjugation or induction effect, but can be rather a consequence of the change of microenviroment when the rather unpolar NCO group is exchanged by more polar urethane group.
**4.2 Results: Kinetics**

**Fig. 4-15:** NCO conversion as function of reaction time for the systems 1-hexanol + BuI and 1-hexanol + Tri-HDI. T = 25°C, $C_{NCO} = C_{OH} = 1.42 \times 10^{-3}$ mol/g, $C_{DBTDL} = 2.7 \times 10^{-6}$ mol/g. Solvent: diglyme.

**Fig. 4-16:** NCO conversion as function of reaction time for the systems EPH + BuI and EPH + Tri-HDI. T = 25°C, $C_{NCO} = C_{OH} = 1.42 \times 10^{-3}$ mol/g, $C_{DBTDL} = 2.7 \times 10^{-6}$ mol/g. Solvent: diglyme.

The rate constants for the above described model reactions were determined by the linearization of experimental data according to the second order reaction $y = 1/C_{NCO}$ vs. time.

In the case of the reaction of 1-hexanol with BuI and Tri-HDI, the linearity of the second-order plots was good till the end of the reactions (90% NCO conversion, see Fig. 4-17).

The experimental data of the reactions of EPH with BuI and Tri-HDI could be linearized up to 74 % and 65 % conversion of NCO groups, respectively. At higher conversions a deviation from ideal second order kinetics were observed.

**Fig. 4-17:** Second-order-kinetics linearization of the experimental data for the reaction of 1-hexanol with BuI and Tri-HDI.

**Tab. 4-11:** Half times and rate constants for the reactions investigated.
The y or the graphs is equal to: \[ y = \frac{C_{0(NCO)} - C_{NCO}}{C_{0(NCO)} \times C_{NCO}} \]

where: \( C_{0(NCO)} \) is the initial concentration of NCO groups,

\( C_{NCO} \) is a concentration of NCO groups, which changes in time.
4.2.2 Reactivity of highly functional poly-BHPPA

The poly-BHPPA EP\textsubscript{03} (core-free, \(M_n = 3100\) g/mol, \(<f>_1 = 12\)) synthesized in this work was chosen for kinetics investigations of the reaction of poly-BHPPA products with the same isocyanate components as used in the above described model reactions, Bul and Tri-HDI. The reaction conditions (concentrations, temperature and solvent) were the same as in the case of the above model reaction.

4-1: The possible structure of an exemplary EP\textsubscript{03} (poly-BHPPA) molecule.

The reaction between EP03 and Tri-HDI is an example of a crosslinking reaction, where the gel point was reached at about 25% conversion of the NCO groups. It was expected that this network-build-up-reaction will be slower than the reaction of EP\textsubscript{03} with Bul, because of the increasing viscosity of the reaction mixture. Surprisingly, the same effect as in the case of the model reactions was observed: The polyisocyanate Tri-HDI reacts faster with the hyperbranched polymer than Bul (see Fig. 4-18 and Tab. 4-11) at the same concentration of NCO and OH groups. Rather an acceleration can be observed due to increasing cyclization or change of microenvironment.
4.2 Results: Kinetics

Fig. 4-18: NCO conversion as function of time for the system poly-BHPPA (EP03) + Bul and + Tri-HDI. T = 25°C, \( C_{\text{NCO}} = C_{\text{OH}} = 1.42 \times 10^{-3} \, \text{mol/g} \), \( C_{\text{DBTDL}} = 2.7 \times 10^{-6} \, \text{mol/g} \). Solvent: diglyme.

Fig. 4-19: Second-order-kinetics linearization of the experimental data for the reaction of poly-BHPPA (EP03) with Bul and Tri HDI using the least square fit.

Linearity of the second order plots for the reaction of poly-BHPPA (EP03) with Bul and Tri-HDI was observed till 60% (Bul) and 55% (Tri-HDI) conversion of NCO groups, respectively (Fig. 4-19). The observed deviation from linearity for the crosslinking system can be explained with the above mentioned possible cyclic reaction which, according to the literature, represents a 1st order reaction.

4.2.3 Different reactivity of phenolic OH groups of 4-ethylphenol and poly-BHPPA

An important point in this part of the work was to describe the reactivity of poly-BHPPA in comparison with other OH compounds and the explanation of this behaviour. As expected, the isocyanates react slower with phenolic than with aliphatic, OH groups, which can be clearly seen if comparing the reactions of EPH and 1-Hexanol with Bul and Tri-HDI (Fig. 4-20 and Fig. 4-21). The polymer EP03 contains phenolic groups like EPH, but its reactivity is about three times lower than that of EPH. The structure of poly(4,4-bis-(4’-hydroxyphenyl) pentanoic acid) is hyperbranched, some of the OH groups can be screened and therefore their reactivity can be lower. Besides the sterical hindrance of OH groups, possible hydrogen-bonding within the poly-BHPPA molecule may play a role in the lower reactivity of the phenolic groups. A lower rate of urethane formation can be observed in the presence of weak acids (1), which block the tin catalyst by complex formation, even if their concentration is
4.2 Results: Kinetics

much smaller than the concentration of the catalyst. This could also be an explanation of the lower reactivity of poly-BHPPA. The reaction mixture contains carboxylic groups of the focal units of poly-BHPPA and also some free monomer, the presence of which was determined by $^{13}$C NMR measurements. In the literature (1) it is suggested, that the inhibiting effect of carboxylic groups is due to the formation of Sn-RCOOH complexes.

**Fig. 4-20:** NCO conversion as a function of time for the systems Bul + 1-hexanol, + EPH and + poly-BHPPA (EP03). $T = 25^\circ C$, $C_{NCO} = C_{OH} = 1.42 \times 10^{-3}$ mol/g, $C_{DBTDL} = 2.7 \times 10^{-6}$ mol / g. Solvent: diglyme.

**Fig. 4-21:** NCO conversion as a function of time for the systems Tri-HDI + 1-hexanol, + EPH and + poly-BHPPA (EP03). $T = 25^\circ C$, $C_{NCO} = C_{OH} = 1.42 \times 10^{-3}$ mol/g, $C_{DBTDL} = 2.7 \times 10^{-6}$ mol / g. Solvent: diglyme.

4.2.4 Catalyzed vs. non-catalyzed reactions of phenols with isocyanates

Our study of OH groups’ reactivity was limited to DBTDL-catalyzed systems, for which it is characteristic that the reaction of NCO groups with traces of water present in the reaction mixture becomes important only after the organic hydroxyl groups have been consumed. Comparative experiments with non catalyzed phenol + isocyanate model systems (EPH + Bul and EPH + Tri-HDI) showed that even after 24 hours there was no measurable NCO conversion.
4.2.5 Conclusions from the kinetics experiments

(1) The reactivity of aliphatic OH groups under DBTDL catalysis was found to be ca. 25 times higher (ratio of rate constants) than that of phenolic groups.

(2) The phenolic OH groups of poly-BHPPA display a 2-3 times lower reactivity than those of ethylphenol.

(3) The reactivity of the NCO groups in the triisocyanate Tri-HDI is somewhat higher than in butyl isocyanate (by the factor of 1.5). This may be due to several factors, such as the substitution effect. In the case of crosslinking systems cyclization reactions may also contribute to the higher reactivity of Tri-HDI.

(4) The use of DBTDL as catalyst is useful not only for reaching reasonable reaction times but also for lowering the negative effect of the presence of moisture.

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1 A. C. Draye, J. J. Tonder; Journal of Molecular Catalysis A: Chemical; 1999, 138, 135
4.3 Polyurethane networks from poly-BHPPA

4.3.1 Crosslinking of poly-BHPPA polyesters

Polyurethanes (PU) can be prepared as linear polymers from diols and difunctional isocyanates. Polyurethane networks possess more practical importance and are prepared from components of higher functionality. The effect of the polyurethane network structure on its physical properties was studied intensely in the group of Dušek [1,2,3]. The use of hyperbranched polymers as network precursors was described in the literature by Johansson and Hult [4,5]. This part of work focuses on the use of the prepared hyperbranched polyesters (poly-BHPPA), which contain a high amount of phenolic OH end groups, as precursors for polyurethane networks.

Fig. 4-22: Polyurethane networks

Polyurethane networks were prepared from poly-BHPPA products with no core (EP01, EP03) and from such containing 2-, 3-, 4- and 6-functional core monomers (EP_{C2(15%)}, EP_{C3(15%)}, EP_{C4(15%)}, and EP_{C6(15%)}, respectively). The poly-BHPPAs were crosslinked with the difunctional hexamethylene diisocyanate (HDI) and also with its trimer, the ca. trifunctional Desmodur N3300 (Tri-HDI). The reactions were carried out in mild dilution, usually as “60% solids” (meaning 60 wt% of the OH and NCO components together in the mixture) using diglyme as solvent. DBTDL was used as catalyst. The polyurethane networks were prepared either as 1 – 2 mm thick sheets (plates), by pouring the reaction mixtures into a glass mold (Fig. 4-22 (a)), or as free-standing coating films of 0.05 – 0.4 mm thickness, by down-
drawing the solution on a glass plate using the doctor blade technique (Fig. 4-22 (b)) and putting off the film from the substrate after drying.

The curing of the PU resins was illustrated on Scheme 4-4 and followed using FTIR spectroscopy.

\[
\begin{align*}
\text{Scheme 4-4: Crosslinking reaction between EP} & \text{ and Tri-HDI} \\
\end{align*}
\]

The Fig. 4-23 shows the achieved conversion \( \alpha_{NCO} \), calculated from the NCO peak intensity, for different curing conditions. In order to reach a full conversion of the isocyanate groups, it was necessary to heat the PU samples (here films) for 5 hours at 100°C as final synthesis step. The 1 mm thick samples were prepared in the same way as the films.
Fig. 4-23: Conversion of NCO ($\alpha_{\text{NCO}}$) during polyurethane film formation. Film thickness prepared from (EP01 + Tri-HDI) was 100 µm.
4.3 Results: Polyurethane networks from poly-BHPPA

4.3.2 Swelling Experiments

The swelling behavior at 25°C of the PU networks prepared (EP<sub>C4(15%)</sub> + HDI and Tri-HDI; thickness of samples were 1 mm) was investigated for five solvents, methylpropyl ketone (MPK), diglyme, acetone, toluene and benzene. A preliminary study of swelling kinetics showed a different behavior of the networks prepared in these solvents (see Fig. 4-24 and Fig. 4-25). The polyurethane samples achieved very fast (in ca. 1 day) the equilibrium swelling in acetone and diglyme, while the swelling in MPK till equilibrium took about 10 days. The highest swelling degree was achieved in diglyme, followed by acetone and MPK. The aromatic solvents, toluene and benzene, did not swell the prepared PU samples significantly. Diglyme was chosen as the best swelling solvent for the PU networks prepared, and used for the equilibrium shear modulus measurements.

![Swelling kinetics of the network EP<sub>C4(15%)</sub>-Tri-HDI in Acetone, Diglyme, and MPK at 25°C](image1)

![Swelling kinetics of the network EP<sub>C4(15%)</sub>-HDI in Acetone, Diglyme, and MPK at 25°C](image2)

The swelling experiments yielded the parameter \( \phi_2 \) (see ref. 3.10.1), the volume fraction of polymer in a swollen sample, which is needed for the calculation of the concentration of elastically active network chains in the networks prepared. The parameters \( \phi_2 \) and also the \( \phi_2^0 \), the volume fraction of the polymer in the solvent during network formation, are listed in the Tab. 4-12 for the networks investigated.
4.3 Results: Polyurethane networks from poly-BHPPA

**Tab. 4-12:** Volume fraction of polymer during network formation ($\varphi_2^0$), volume fraction of polymer in the swollen sample ($\varphi_2$) and the swelling degree for the samples swollen in diglyme.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>$\varphi_2^0$</th>
<th>$\varphi_2$</th>
<th>HDI</th>
<th>Tri-HDI</th>
<th>HDI</th>
<th>Tri-HDI</th>
<th>Swelling degree [%]*</th>
</tr>
</thead>
<tbody>
<tr>
<td>EP$_{03}$</td>
<td>0.49</td>
<td>0.61</td>
<td>0.56</td>
<td></td>
<td>0.56</td>
<td></td>
<td>60</td>
</tr>
<tr>
<td>EP$_{C2 (15%)}$</td>
<td>0.50</td>
<td>0.58</td>
<td>0.54</td>
<td></td>
<td>0.56</td>
<td></td>
<td>52</td>
</tr>
<tr>
<td>EP$_{C4 (15%)}$</td>
<td>0.50</td>
<td>0.63</td>
<td>0.59</td>
<td></td>
<td>0.59</td>
<td></td>
<td>48</td>
</tr>
</tbody>
</table>

*) swelling degree % = \( \frac{m_{\text{swelling}} - m_{\text{dried}}}{m_{\text{dried}}} \times 100 \)

### 4.3.3 Concentration of Elastically Active Network Chains

The equilibrium elasticity of polymer networks is known to be determined by the number of Elastically Active Network Chains (EANC). The EANC concentration ($\nu_e$) describes the crosslink density and depends on the internal structure of the network precursors; $\nu_e$ is calculated from the number of elastically active cross-links (EAC), which already exist in the precursors. Each bond with infinite continuation issuing from an EAC contributes by $\frac{1}{2}$ to the number of EANC’s [3]. Hyperbranched polymers (HBP) prepared from AB$_2$ monomers contain many branching points as well as many functional groups. Unfortunately, the HBP’s are known as polymers with a broad molecular weight distribution. It would be too difficult and unpractical to sum the contributions to $\nu_e$ by the active branch points of the different HBP fractions. Another possibility for the theoretical calculation of $\nu_e$ is to employ the theory of branching processes in the description of the crosslinking process.

#### 4.3.3.1 Calculation of the theoretical concentration of EANC

In an ideal poly-BHPPA-isocyanate network, it is assumed that all OH and COOH groups have reacted intermolecularly, either by esterification reaction when the hyperbranched poly-BHPPA precursor was formed, or subsequently during the crosslinking of the OH groups with the NCO groups of HDI or Tri-HDI. It is assumed that the conversion of COOH groups during the poly-BHPPA formation is close to 100% and that the reaction of the few remaining percent of COOH groups with NCO groups can be neglected (if the concentration...
of residual COOH groups and their reaction with NCO cannot be neglected, the described calculation can be modified). The calculation of \( \nu_e \) as a function of conversion of NCO groups can be performed by considering a gradual activation of branch points as described in ref. [6]. These procedures can be adapted for the case discussed here. However, for the sake of simplicity we will consider here only the final state when all OH groups of poly BHPPA have reacted with isocyanates groups.

The number of moles of OH groups per mass unit of a poly-BHPPA with core, A, can be expressed as:

\[
A \left[ \frac{mol \ OH}{g \ HBP} \right] = \frac{(1-\alpha_A)(f_{n_M} + g_{n_C})}{n_M M_M + n_C M_C - 18\alpha_A(f_{n_M} + g_{n_C})}
\]

For a stoichiometric network, 1 g of the hyperbranched polyester is required for \( x \) g of polyisocyanate. The value of \( x \) is given by the relation:

\[
A = \frac{xf_i}{M_i}; \quad x = \frac{AM_i}{f_i}
\]

The amount of polyisocyanate in moles per gram poly-BHPPA is equal to: \( x / M_i = A / f_i \), where:

\( M_i \) – molar mass of the polyisocyanate
\( f_i \) - the number of NCO groups per isocyanate molecule (functionality)

The concentration of EANC’s per unit mass (\( \nu_{enm} \)), then reads:

\[
\nu_{enm} = \frac{(f+1)n_M + g_{n_C}}{n_M M_M + n_C M_C - 18\alpha_A(f_{n_M} + g_{n_C}) + \frac{xf_i}{2M_i} + A} = \frac{(f+1)n_M + g_{n_C}}{M - 18\alpha_A(f_{n_M} + g_{n_C}) + \frac{A}{2}} = \frac{A}{2} \left[ \frac{(f+1)n_M + g_{n_C} + 1}{1 + x} \right]
\]

and the concentration of EANC’s in unit volume (\( \nu_e \)) is equal:

\[
\nu_{e} = \frac{A}{2} \left[ \frac{(f+1)n_M + g_{n_C} + 1}{1 + x} \right] \rho
\]

Eq. 4-29

where \( \rho \) is density of the polymer sample.
4.3 Results: Polyurethane networks from poly-BHPPA

4.3.3.2 Experimental determination of the EANC concentration

The experimental concentrations of EANC \( (v_e) \) were determined for the PU networks prepared using the experimental data for \( \varphi_2 \) and \( \varphi_2^0 \) (calculated from the solvent content of 40% during the synthesis). The samples investigated were swollen to equilibrium in diglyme, at 25°C. During swelling, the sol fraction was extracted from the networks. Series of tensile stress-strain experiments were carried out and the average concentrations of elastic chains were calculated using Eq. 4-30 (see also exp. part 3.10.3)

\[
V_e = \frac{(F / A_f)}{A_f R T (\varphi_2^0)^{2/3} (\varphi_2)^{1/3} (\lambda - \lambda^{-2})}
\]

where: \( \varphi_2^0 \) is the volume fraction of polymer during network formation, \( \varphi_2 \) is the volume fraction of polymer in the swollen network, \( R \) is the universal gas constant, \( T \) is the temperature in K, and \( A_f \) is the front factor (\( A_f = 1 \) was assumed).

The experimentally determined, together with the theoretically calculated (ideal) concentrations of EANC’s for the networks prepared are shown in Tab. 4-13.

**Tab. 4-13:** Experimentally determined and theoretically calculated (ideal) concentrations of EANC \( (v_e) \) for the PU networks prepared.

<table>
<thead>
<tr>
<th></th>
<th>Concentration of EANC in reaction with HDI</th>
<th>Concentration of EANC in reaction with Tri-HDI</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ideal [mol/cm(^3)]</td>
<td>Experimental [mol/cm(^3)]</td>
</tr>
<tr>
<td>EP(_{03})</td>
<td>4.31×10(^{-3})</td>
<td>2.29×10(^{-3})</td>
</tr>
<tr>
<td>EP(_{C2(15%)})</td>
<td>4.04×10(^{-3})</td>
<td>1.85×10(^{-3})</td>
</tr>
<tr>
<td>EP(_{C4(15%)})</td>
<td>4.27×10(^{-3})</td>
<td>2.17×10(^{-3})</td>
</tr>
<tr>
<td>EP(_{C6(15%)})</td>
<td>4.33×10(^{-3})</td>
<td>3.40×10(^{-3})</td>
</tr>
</tbody>
</table>

The ideal concentrations of EANC are about twice higher compared to the experimental ones. The deviation can have several reasons. Cyclization is one of them.
4.3 Results: Polyurethane networks from poly-BHPPA

4.3.4 Polymer-solvent interaction: determination of the interaction parameters

The importance of the polymer/solvent interaction parameter $\chi$ in the thermodynamic behavior of polymer solutions has been established by numerous studies. A convenient experimental technique for the determination of the $\chi$ parameter is the measurement of the equilibrium swelling of networks.

The interaction parameters for the networks prepared were calculated using the formula:

$$\chi = \frac{-(\log(1 - \varphi_z) + V_c V_{mol} (A_f (\varphi_z^0)^{2/3} \varphi_z^{1/3} - B \frac{\varphi_z^2}{2}))}{(\varphi_z)^2}$$

Eq. 4-31

As expected, the interaction parameters for the networks studied have high values (see Tab. 4-14). Crosslinked polyurethanes generally do not swell much, because of their compact structure, but the networks prepared from poly-BHPPA and HDI or Tri-HDI show good swelling properties, especially in diglyme.

**Tab. 4-14**: Experimental data of interaction parameters calculated for polyurethane networks and three type of solvents: diglyme, MPK, and acetone

<table>
<thead>
<tr>
<th></th>
<th>Interaction parameter $\chi$ for diglyme</th>
<th>Interaction parameter $\chi$ for MPK</th>
<th>Interaction parameter $\chi$ for acetone</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>HDI</td>
<td>Tri-HDI</td>
<td>HDI</td>
</tr>
<tr>
<td>EP$_{C03}$</td>
<td>0.48</td>
<td>0.52</td>
<td>0.71</td>
</tr>
<tr>
<td>EP$_{C2(15%) }$</td>
<td>0.61</td>
<td>0.64</td>
<td>0.84</td>
</tr>
<tr>
<td>EP$_{C4(15%) }$</td>
<td>0.53</td>
<td>0.56</td>
<td>0.78</td>
</tr>
<tr>
<td>EP$_{C6(15%) }$</td>
<td>0.65</td>
<td>0.69</td>
<td>0.84</td>
</tr>
</tbody>
</table>
4.3.5 Cyclization

Intramolecular cyclization reactions during a real network formation process cause the gelation to be delayed, because the cycles reduce the probability of chains continuing to infinity. The Fig. 4-26 shows schematically an intramolecular cyclization -in a poly-BHPPA-Ti-HDI system. The experimental determination of the amount of cyclization is based on the known fact that the extent of cyclization increases with increasing dilution. In order to quantify the cyclizations, the gel point conversion of NCO groups was determined (by FT-IR spectroscopy, as described earlier) for series of samples with varying amounts of diluting solvent. The point of gelation was determined by solubility tests.

![Intramolecular reaction between a poly-BHPPA polyester and Tri-HDI.](image)

**Fig. 4-26:** Intramolecular reaction between a poly-BHPPA polyester and Tri-HDI.

Four series of experiments were done: Poly-BHPPA without, with 3-, 4- and 6-functional core monomer were crosslinked with Tri-HDI (Desmodur N 3300) under stoichiometric conditions. In each series, reactions were carried out for the concentrations 40, 50, 60 and 70% of “solids” in diglyme, which was found to be a good solvent for the systems investigated. The reaction temperature was 25°C. The results are shown in Fig. 4-27
4.3 Results: Polyurethane networks from poly-BHPPA

Fig. 4-27: Gel point conversion as a function of dilution (40, 50, 60 and 70 %) for the system poly-BHPPA - Tri-HDI.

From the results obtained (plots of gel point conversion against reciprocal concentration), the experimental gel point conversion at infinite concentration, $\alpha_{c, \text{ext}}$, was extrapolated (reciprocal concentration equal to zero: see Fig. 4-27).

The theoretical value of the gel point conversion at infinite concentration ($\alpha_{c,t}$) for systems with no cyclization (ring-free theory) is defined as follows:

$$\alpha_{c}^{2} = \frac{1}{(<f_{A}>_{2} - 1)(<f_{B}>_{2} - 1)}$$

Eq. 4-32

Where: $<f_{A}>_{2}$ and $<f_{B}>_{2}$ are the second moment averages of functionality distribution.

The extrapolated experimental values $\alpha_{c,\text{ext}}$ (shown in Fig. 4-27) are very similar to the $\alpha_{c,t}$ values calculated according to the ring-free theory (Eq. 4-32), see Tab. 4-15.
4.3 Results: Polyurethane networks from poly-BHPPA

Tab. 4-15: Theoretical and extrapolated values of critical conversion ($\alpha_c$) for the systems shown on Fig. 4-27

<table>
<thead>
<tr>
<th></th>
<th>$\alpha_{c, t}$</th>
<th>$\alpha_{c, ext}$</th>
<th>$\alpha_{c, exp (40% \text{ dilution})}$</th>
<th>$\alpha_{c, exp (50% \text{ dilution})}$</th>
<th>$\alpha_{c, exp (60% \text{ dilution})}$</th>
<th>$\alpha_{c, exp (70% \text{ dilution})}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>EP$_03$ (no core)</td>
<td>0.074</td>
<td>0.8</td>
<td>0.118</td>
<td>0.133</td>
<td>0.135</td>
<td>-</td>
</tr>
<tr>
<td>EP$_C3$ (15%) (3 functional core)</td>
<td>0.127</td>
<td>0.13</td>
<td>0.248</td>
<td>0.274</td>
<td>0.316</td>
<td>0.379</td>
</tr>
<tr>
<td>EP$_C4$ (15%) (4 functional core)</td>
<td>0.133</td>
<td>0.12</td>
<td>0.22</td>
<td>0.250</td>
<td>0.284</td>
<td>0.360</td>
</tr>
<tr>
<td>EP$_C6$ (15%) (6 functional core)</td>
<td>0.091</td>
<td>0.076</td>
<td>0.12</td>
<td>0.135</td>
<td>0.158</td>
<td>0.2</td>
</tr>
</tbody>
</table>

In a real diluted system, the percentage of bonds lost in cycles is calculated using Eq. 4-33, where $\alpha_{c, t}$ and $\alpha_{c, exp}$ are the ring-free-theoretical and the experimental gel point conversions, respectively.

$$\text{Cyclic Bonds (EINC)}\%_{at \_ gel \_ point} = \frac{\alpha_{c, exp(x)} - \alpha_{c, t}}{\alpha_{c, exp(x)}} \times 100$$

Eq. 4-33

where x is dilution of the system

The percentage of cyclization reactions as function of the concentration of the reacting system was calculated for the experiment series investigated and the results are depicted in Fig. 4-28.
4.3 Results: Polyurethane networks from poly-BHPPA

![Graph showing bond cyclic percentage dependence on dilution for poly-BHPPA crosslinked with Desmodur N 3300.](image)

**Fig. 4-28:** The ring-closing bond dependence on dilution for poly-BHPPA crosslinked with Desmodur N 3300

The theoretical values of $\alpha_{c,1}$ are significantly lower for the systems investigated if compared with polyurethanes prepared from Tri-HDI and di-, tri-, and even tetra functional OH precursors in dilution of 40, 50, 60 and 70 % [7]. As expected, the higher functional systems show a steeper shift of gel points to higher conversion with increasing dilution [8]. Therefore, the amount of cyclization at the gel point in the “standard” poly-BHPPA-Tri-HDI networks prepared in this work (at 60% of solids) is relatively high due to the high functionality of the OH precursors and due to short distances between the functional groups. As the functionality of the OH precursors linearly depends of their mass, the dependence of the percentage of cyclization at gel point from the poly-BHPPA functionality can also be expressed as dependence on the molecular weight of the poly-BHPPA precursors, as shown in Fig. 4-29.
4.3 Results: Polyurethane networks from poly-BHPPA

The differences between theoretical and experimental values of EANC’s concentrations (which were determined earlier, see Tab. 4-13 on p. 110) give the concentration of elastically inactive network chains (EINC) in the case of fully reacted samples. These results could be presented also as percentage of EINC according Eq. 4-34 and are shown in Tab. 4-16 and in Fig. 4-30.

\[
\% \text{EINC}_{\text{post-gel state}} = 100 - \% \text{EANC} \quad *)
\]

*) % EANC are presented in Tab. 4-13

For comparison also the amount of cyclic bonds at the gel point was calculated according to Eq. 4-33 and is presented in the Tab. 4-16. The amount of bonds wasted in cycles at the post gel state is higher than at the gel point.

**Tab. 4-16**: Amount of cyclic (elastically inactive) structures for different networks prepared in the post-gel state. The samples were prepared in 60 % of solution.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>% of EINC at gel point</th>
<th>% of EINC at post-gel state</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>HDI</td>
<td>Tri-HDI</td>
</tr>
<tr>
<td>( \text{EP}_{C03} )</td>
<td>-</td>
<td>29.2</td>
</tr>
<tr>
<td>( \text{EP}_{C2 (15%)} )</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>( \text{EP}_{C4 (15%)} )</td>
<td>-</td>
<td>39.54</td>
</tr>
<tr>
<td>( \text{EP}_{C8 (15%)} )</td>
<td>-</td>
<td>25.2</td>
</tr>
</tbody>
</table>
In all cases the fraction of bonds wasted in cycles is higher for the systems, where Tri-HDI (Desmodur N 3300) was used as isocyanate crosslinker in comparison to systems crosslinked with the difunctional HDI. This finding could be explained by the higher functionality of Desmodur N 3300.

**Fig. 4-30:** Fractions of elastically inactive network chains in polyurethane network in postgel state. Dilution of prepared systems was 40% of diglyme.
4.3 Results: Polyurethane networks from poly-BHPPA

4.3.6 Sol fraction

The sol content in polymer networks has a substantial impact on product properties. A higher sol content can indicate an incomplete conversion, an inexact stoichiometry of the network components, or a strong tendency to cyclization or other side reactions.

The sol contents of the most important polymer networks prepared in this work are listed in Tab. 4-17. The sol contents of the products prepared are small, in the range of 1 to 4%.

**Tab. 4-17**: Sol fraction for networks prepared from poly-BHPPA and polyisocyanates

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Network with HDI</th>
<th>Network with Tri HDI</th>
</tr>
</thead>
<tbody>
<tr>
<td>EP&lt;sub&gt;03&lt;/sub&gt;</td>
<td>1.6%</td>
<td>3.8%</td>
</tr>
<tr>
<td>EP&lt;sub&gt;C2(15%)&lt;/sub&gt;</td>
<td>3.8%</td>
<td>4.0%</td>
</tr>
<tr>
<td>EP&lt;sub&gt;C4(15%)&lt;/sub&gt;</td>
<td>1.4%</td>
<td>1.2%</td>
</tr>
<tr>
<td>EP&lt;sub&gt;C6(15%)&lt;/sub&gt;</td>
<td>2.6%</td>
<td>2.2%</td>
</tr>
</tbody>
</table>
4.3.7 Glass transition temperatures of the polyurethane networks prepared

The glass transition temperatures of the polyurethane networks prepared were determined (see Tab. 4-18) by dynamic mechanical thermal analysis (DMTA), as maxima of the loss factor \( (\tan \delta) \). The polyurethane networks prepared from the above described poly-BHBPA’s and HDI or Tri-HDI show similar DMTA spectra (see example, Fig. 4-31). The use of different poly-BHPPA’s as precursors shifts the values of the glass transition temperature \( (T_g) \), see Fig. 4-32) of the products prepared using the same isocyanate component. The structure of the isocyanate crosslinker also has a considerable influence on \( T_g \), as can be shown by comparing products prepared from the same poly-BHPPA and crosslinked by HDI or Tri-HDI (see Fig. 4-36 and Fig. 4-37).

![Graph showing DMTA spectrum of EP C4(15%) + HDI](image)

**Fig. 4-31:** DMTA spectrum of the network \( \text{EP}_{\text{C4(15%)}} + \text{HDI} \)
4.3 Results: Polyurethane networks from poly-BHPPA

4.3.7.1 Effect of the poly-BHPPA precursors on PU networks Tg

The effect of the choice of the poly-BHPPA precursor on the PU networks $T_g$ is more distinct for the products crosslinked with hexamethylene diisocyanate (HDI; see $G' = f(T)$ in Fig. 4-33).

![Fig. 4-32: $G' = f(T)$ for networks made from different types of poly-BHPPA and crosslinked by HDI](image1)

![Fig. 4-33: $\tan \delta = f(T)$ for networks made from different types of poly-BHPPA and crosslinked by HDI](image2)

The $T_g$ values of the networks crosslinked by HDI are in the range from +68°C to +102°C, thus shifting by 46°C, depending of the poly-BHPPA precursor used. If the networks prepared from HDI and poly-BHPPA containing core monomer are compared, the $T_g$ value increases with the increasing core monomer functionality (core functionality = 2 to 6). The network made from core-free poly-BHPPA shows a $T_g$ value and a $G' = f(T)$ curve, which lay between the networks prepared from the tetrafunctional and hexafunctional cores.

The above results should be considered in view of the molar masses and functionality of the poly-BHPPA’s. The polyphenols with the core functionality from 2 to 4 have all practically the same number of OH groups per molecule (~8) and have also very similar molar masses (1780 to 2050 g/mol, see Tab. 4-18). In the case of these products, the differences in the $T_g$ values and the DMTA curves should be predominantly due to the microstructure of the poly-BHPPA precursors containing different cores. The poly-BHPPA with “core 6” shows approximately a twice as high molar mass and functionality as the poly-BHPPA precursors with core functionality 2 to 4 and hence the difference between the $T_g$ values of the networks EP$_{C4(15\%)}$-HDI and EP$_{C6(15\%)}$-HDI is larger than expected. The molecular mass and
functionality of the core free poly-BHPPA lay between those for poly-BHPPA’s with “core 6” and “core 4”, being closer to the poly-BHPPA with “core 6”. The network EP\textsubscript{03}-HDI containing the core-free poly-BHPPA EP\textsubscript{03} shows a $T_g$ value and a DMTA curve between the networks with the 4-functional and 6-functional core monomers. Here both, the microstructure and the molar mass and functionality of the poly-BHPPA component play an important role.

The networks made from poly-BHPPA and Tri-HDI (Desmodur N3300) show generally a similar but less pronounced dependence of their $T_g$ values from the type of poly-BHPPA used (Fig. 4-34 and Fig. 4-35). The largest difference between two $T_g$ values is only +14°C. Here the network with poly-BHPPA containing “core 4” shows a slightly lower $T_g$ than that with the poly-BHPPA containing “core 3”. The latter polyphenol has a somewhat higher molar mass.

![Graph](image)

**Fig. 4-34:** $G' = f(T)$ for networks made from different types of poly-BHPPA and crosslinked by Desmodur (Tri-HDI)

![Graph](image)

**Fig. 4-35:** $\tan \delta = f(T)$ for networks made from different types of poly-BHPPA and crosslinked by Desmodur (Tri-HDI)
4.3 Results: Polyurethane networks from poly-BHPPA

4.3.7.2 The isocyanate effect on the $T_g$ of the PU networks prepared

If analogous networks, synthesized from the same poly-BHPPA and crosslinked by HDI or Tri-HDI, respectively, are compared, a general trend concerning the influence of the isocyanate also can be observed: The networks prepared from HDI generally show a higher $T_g$ and a broader glass transition region. This “isocyanate” effect is increasingly pronounced with increasing core functionality or increasing molar mass and OH number per poly-BHPPA molecule (see comparison in Fig. 4-36 and Fig. 4-37) and could be explained by better ordering possibilities in the HDI-based networks.

1) $T_g$ of PU networks < $T_g$ of precursors because aromatics are enriched by aliphatic units.
2) $T_g$ of the same poly-BHPPA crosslinked with Tri-HDI is lower because more aliphatic per NCO are incorporated.

Fig. 4-36: $G' = f(T)$ for networks made from EP$_{C3(15\%)}$ and crosslinked with HDI and Tri-HDI, respectively

Fig. 4-37: $G' = f(T)$ for networks made from EP$_{C4(15\%)}$ and crosslinked with HDI and Tri-HDI, respectively

The $T_g$ values of the PU networks prepared are listed in Tab. 4-18 together with the $T_g$ values and number average molecular weight ($M_n$) of the poly-BHPPA precursors used.
4.3 Results: Polyurethane networks from poly-BHPPA

4.3.8 Thermal stability of the prepared polyurethane networks

The thermal stability of the polyurethane networks prepared from poly-BHPPA and HDI or Tri-HDI was investigated by thermogravimetric analysis. The experiments were carried out under N\textsubscript{2}, at a heating rate of 10 K/min, in the range of 40°C to 700°C. All the samples exhibited similar profiles (see Fig. 4-38). The first loss of weight was observed near 200°C, leading to a loss of ca 10% of weight (start: 1% loss at 140°C). This was assigned to the decomposition of the phenolic urethane bonds. In the case of the sample EP\textsubscript{03}-HDI, prepared in diglyme, this process begins somewhat earlier, at 116°C (1% loss; maximum speed at 180°C), possibly due to the presence of some solvent remnants. In the range 340-360°C, the first large weight loss is observed caused by the destruction of the hyperbranched polymers. The second large decomposition step is observed in the range 440-460°C, except for the sample EP\textsubscript{03}-HDI (in diglyme), where it is small or not present at all. The samples prepared from the core-free poly-BHPPA EP\textsubscript{03} show a final decomposition step in the range 530-570°C and loose all weight in this step. The samples containing core monomer do not show such a step, completing their pyrolysis in the above mentioned range 440-460°C. These samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>Tg of network</th>
<th>Tg of poly-BHPPA</th>
<th>M\textsubscript{w} of poly-BHPPA</th>
</tr>
</thead>
<tbody>
<tr>
<td>EP\textsubscript{03} +HDI</td>
<td>95</td>
<td>109</td>
<td>3130</td>
</tr>
<tr>
<td>EP\textsubscript{03} +Tri-HDI</td>
<td>82</td>
<td>109</td>
<td>3130</td>
</tr>
<tr>
<td>EP\textsubscript{C2(15%)} +HDI</td>
<td>68</td>
<td>84</td>
<td>1928</td>
</tr>
<tr>
<td>EP\textsubscript{C2(15%)}+ Tri HDI</td>
<td>72</td>
<td>84</td>
<td>1928</td>
</tr>
<tr>
<td>EP\textsubscript{C3(15%)} +HDI</td>
<td>90</td>
<td>108</td>
<td>1824</td>
</tr>
<tr>
<td>EP\textsubscript{C3(15%)}+ Tri HDI</td>
<td>70</td>
<td>108</td>
<td>1824</td>
</tr>
<tr>
<td>EP\textsubscript{C4(15%)} +HDI</td>
<td>94</td>
<td>106</td>
<td>1780</td>
</tr>
<tr>
<td>EP\textsubscript{C4(15%)}+ Tri HDI</td>
<td>81</td>
<td>106</td>
<td>1780</td>
</tr>
<tr>
<td>EP\textsubscript{C6(15%)} +HDI</td>
<td>102</td>
<td>126</td>
<td>3280</td>
</tr>
<tr>
<td>EP\textsubscript{C6(15%)}+ Tri HDI</td>
<td>86</td>
<td>126</td>
<td>3280</td>
</tr>
</tbody>
</table>
show a constant weight from 500°C on, corresponding to ca. 8% of the original weight and do not show any further weight loss until the experiment end at 700°C. The TGA results are summed up in Tab. 4-19.

**Tab. 4-19: TGA results**

<table>
<thead>
<tr>
<th>Sample</th>
<th>( T ) at 1% weight loss [°C]</th>
<th>( T ) at 10% weight loss [°C]</th>
<th>Weight loss at 700°C [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{EP}_\text{C3(15%)} + \text{HDI, prepared in MPK} )</td>
<td>143</td>
<td>261</td>
<td>91.8</td>
</tr>
<tr>
<td>( \text{EP}_\text{C3(15%)} - \text{Tri-HDI, prepared in MPK} )</td>
<td>143</td>
<td>282</td>
<td>91.8</td>
</tr>
<tr>
<td>( \text{EP}_\text{03(HDI, prepared in diglyme} )</td>
<td>116</td>
<td>235</td>
<td>100</td>
</tr>
<tr>
<td>( \text{EP}_{03(\text{Tri-HDI, prepared in MPK})} )</td>
<td>140</td>
<td>280</td>
<td>100</td>
</tr>
</tbody>
</table>
Fig. 4-38: TGA for some representative PU networks prepared.
4.3 Results: Polyurethane networks from poly-BHPPA

4.3.9 Surface properties

4.3.9.1 Surface roughness of the PU networks prepared

The surface roughness is an important property for the possible application of the PU networks prepared in coatings. For this reason freely evaporating films of 0.05 mm thickness were prepared on glass substrates from pure poly-BHPPA (EP₀₃ in different solvents) and from three poly-BHPPA(EP₀₃, EP₃₃(15%) and EP₃₄(15%))-Tri-HDI networks. The polyurethane networks were prepared as 50% solids mixture in MPK and cured as described in the experimental part. The topography (roughness, contour topography) of the film surfaces prepared was examined with the Microglider FTR 180, an instrument designed for optical surface measurements by scanning the sample in the 3D imaging mode.

**Fig. 4-39:** Topography of a coating prepared from EP₀₃ (evaporation of a 50% solution in MPK), Thickness (0.05 mm): Roughness 14 nm

**Fig. 4-40:** Topography of a coating prepared from EP₀₃-Tri-HDI (from a 50% solution in MPK), Thickness (0.05 mm): Roughness 20 nm

The results of the surface roughness measurements are presented in Tab. 4-20. The surface of the pure poly-BHPPA (Fig. 4-39) seems to be smoother than that of the polyurethane film (Fig. 4-40), however both surfaces have good properties. The small roughness value of the polyurethane networks supports the idea that they form homogeneous films.

**Tab. 4-20:** Values of surface roughness for films prepared from poly-BHPPA and from polyurethanes.

<table>
<thead>
<tr>
<th>Sample</th>
<th>EP₀₃ (50% solution in MPK)</th>
<th>EP₀₃ (50% solution in THF)</th>
<th>EP₀₃ (50% solution in Ethyl Acetate)</th>
<th>EP₀₃ + Tri-HDI</th>
<th>EP₃₃(15%) + Tri-HDI</th>
<th>EP₃₄(15%) + Tri-HDI</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Rq [nm]</strong></td>
<td>14</td>
<td>14</td>
<td>16</td>
<td>20</td>
<td>19</td>
<td>26</td>
</tr>
</tbody>
</table>
4.3 Results: Polyurethane networks from poly-BHPPA

4.3.9.2 Contact angle with water

Polyurethane surface can be also characterized by measuring the contact angle with water, thus obtaining information about the surface energy. Contact angles are often used as empirical parameters describing the wettability of materials (Fig. 4-41).

Fig. 4-41: Schematic sessile-drop contact angle measurement.

The surface properties of several samples of the network EP_{03+}Tri-HDI were characterized by measurement of contact angle with water, based on Drop Shape Analysis (DSA). These experiments required a smooth surface, which was already proven by the previously discussed roughness measurements (with Microglider).

The Young’s equation (Eq. 4-35) interrelates measurable quantities, the liquid-vapor interfacial tension \( \gamma_l \) and the contact angle \( \theta \) to the non measurable interfacial tensions \( \gamma_{sv} \) and \( \gamma_{sl} \) of the solid-vapor and solid-liquid interfaces.

\[
\gamma_l \cos \Theta = \gamma_{sv} - \gamma_{sl}
\]

Eq. 4-35

In order to determine \( \gamma_{sv} \) and \( \gamma_{sl} \), an additional equation relating these quantities is required [9].

The advancing contact angles were averaged to yield a mean contact angle with an error of \( \pm 1^\circ \). The results are summarized in (Tab. 4-21).

<table>
<thead>
<tr>
<th>Tab. 4-21: Contact angles of the polyurethane network EP_{03-Tri-HDI} with water after curing at different temperatures</th>
</tr>
</thead>
<tbody>
<tr>
<td>50% solids MPK 0.1 mm</td>
</tr>
<tr>
<td>------------------------</td>
</tr>
<tr>
<td>60°C – 6h</td>
</tr>
<tr>
<td>90°C – 3h</td>
</tr>
<tr>
<td>90°C – 18h</td>
</tr>
<tr>
<td>110°C – 6h</td>
</tr>
</tbody>
</table>
The measured contact angles of the polyurethanes networks with water are relatively small, taking into account that they contain (hydrophobic) aromatic rings. The results show, that polyurethane films prepared exhibit hydrophilic surface properties. With increasing curing temperature, the contact angle increases, this is in accordance with the expected higher conversion of OH groups.

Comparing the contact angle of the prepared polyurethane networks with other polymers [10] presented in Tab. 4-22, it can be confirmed, that the contact angle is similar to that of other polyurethane polymers (poly(ether urethane)).

**Tab. 4-22:** Contact angle of the different type of polymers with water as liquid phase.

<table>
<thead>
<tr>
<th>Polymers</th>
<th>Liquid phase</th>
<th>Contact Angle[°]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Poly (butyl cyanoacrylate)</td>
<td>Water</td>
<td>69</td>
</tr>
<tr>
<td>Poly (ether urethane)</td>
<td>Water</td>
<td>80</td>
</tr>
<tr>
<td>Poly (ethyl cyanoacrylate)</td>
<td>Water</td>
<td>65</td>
</tr>
<tr>
<td>Poly (methoxyethyl methacrylate)</td>
<td>Water</td>
<td>46</td>
</tr>
<tr>
<td>Poly (methyl cyanoacrylate)</td>
<td>Water</td>
<td>57</td>
</tr>
<tr>
<td>Poly (methyl methacrylate)</td>
<td>Water</td>
<td>62-73</td>
</tr>
<tr>
<td>Polystyrene</td>
<td>Water</td>
<td>66</td>
</tr>
<tr>
<td>Polytetrafluoroethylene</td>
<td>Water</td>
<td>110</td>
</tr>
<tr>
<td>Teflon</td>
<td>Water</td>
<td>110</td>
</tr>
<tr>
<td>Poly (vinyl chloride)</td>
<td>Water</td>
<td>69</td>
</tr>
<tr>
<td>Silicone</td>
<td>Water</td>
<td>110</td>
</tr>
</tbody>
</table>

### 4.3.10 Shore hardness of the polyurethane networks

The hardness of representative polyurethane networks was determined by the Shore D Durometer test, which is a standard test for measuring the hardness of plastics.

Two samples prepared from the core-free poly-BHPPA EP\textsubscript{03} and crosslinked with HDI and Tri-HDI were investigated. Both products were found to possess Shore hardness around 70.
4.3 Results: Polyurethane networks from poly-BHPPA

References: Results: Polyurethane networks

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6. K. Dušek, M. Dušková-Smrčková; Macromolecules; 2003, 36, 2915
7. A. Duračková, H. Valentová, M. Dušková-Smrčková, K. Dušek; Polymer Buletin; 2006, in press
9. D. Y. Kwok, A. W. Neumann; Advances in Colloid and Interface Science; 1999, 81, 167
5 Conclusions

In this work, hyperbranched aromatic polyesters-polyphenols based on 4,4-bis(4’-hydroxyphenyl)pentanoic acid (BHPPA) were prepared and, according to the authors’ knowledge, for the first time tested as precursors for polyurethane bulk resins and coatings.

Comparison of poly-BHPPA with competing products

The materials prepared in this work show better properties than their aliphatic polyester-polyol analogs based on 2,2-bis-(hydroxymethyl)propanoic acid (BHMPA). Especially, the solubility of poly-BHPPA in organic solvents is better and poly-BHPPAs also do not tend to microphase separation during their reaction with isocyanates, in contrast to poly-BHMPAs. The poly-BHPPA and the polyurethane networks made from them display higher Tg values than analogous poly-BHMPA compounds. Because of the high Tg of the reacting and final systems, curing must occur at elevated temperatures (90°C) in order to avoid undercure. The lower reactivity of phenolic OH groups prevents the reaction from being too fast at that temperature. A drawback of the polyurethanes based on the aromatic polyesters-polyols prepared is the lower thermal stability of their urethane bonds, if compared to aliphatic urethanes.

An interesting possibility for future investigations would be the modification of the BHPPA monomer in order to change the OH functionality from phenolic to aliphatic OH, e.g. by replacement of the phenolic OH by hydroxymethyl or hydroxyethyl groups (requires a strong modification of the monomer synthesis) or simpler by reacting the phenolic OH of BHPPA with a suitable reagent like oxirane, which would lead to groups like O-CH₂-CH₂-OH in the place of the phenolic OH. Such a BHPPA modification should in turn yield modified “poly-BHPPA” polycondensates, which would combine the advantages of poly-BHPPA with those of aliphatic OH precursors of polyurethanes.

Poly-BHPPA synthesis

Hyperbranched polymers of the 4,4-bis-(4’-hydroxyphenyl)pentanoic acid (BHPPA) were synthesized successfully by the catalyzed (by dibutyltin diacetate) polycondensation of BHPPA. The products obtained were oligomers with number average molecular weight ranging from 1800 to 3400 g/mol (polymerization degree of ca. 6 to 12), displaying a first moment of functionality in the range 7 to 14. Such products were good OH precursors for the preparation of polyurethane coatings, because higher functional polymers would gel at low conversions. The analysis of the functional groups (determination of acid and hydroxyl
5 Conclusions

numbers) and the $^1$H-NMR and the $^{13}$C-NMR spectroscopy were found to be good methods for the determination of molecular weights. The polydispersity of the poly-BHPPA products was in the range 3.5 to 6. Their degree of branching was found to be in the range 0.36 to 0.47.

Poly-BHPPA containing aliphatic polyols as core monomers were also prepared successfully. Difunctional and trifunctional core monomers usually reached a full conversion of their OH groups, while the tetra- and hexafunctional core monomers were converted only to 89%. In all these products however, a considerable amount, usually even a majority, of the polymer molecules were core free.

The poly-BHPPA products prepared displayed relatively high glass transition temperatures, in the range of 84°C to 114°C, obviously due to interactions between the phenol groups and to hydrogen bridging. The thermal stability of these products was also high, with decomposition occurring near 350°C (at a heating rate of 10°C / min)

Kinetics investigations of the poly-BHPPA reactivity towards isocyanates

The poly-BHPPA are polyphenols and were expectedly found to react significantly slower with isocyanates than aliphatic alcohols. The reactivity of poly-BHPPA was also found to be somewhat lower than that of the monofunctional, low molar-mass 4-ethylphenol. Hexamethylene diisocyanate trimer, Desmodur N3300, was found to be more reactive than hexamethylene diisocyanate (HDI) or butyl isocyanate in all experiments, possibly due to a substitution effect. The substitution effect can be explained by a change of microenvironment caused by conversion of isocyanate group and OH group into urethane groups. The reactions of low-molecular-mass alcohols or phenols with low molecular weight isocyanates followed well the 2$^{\text{nd}}$ order kinetics, while the reactions of poly-BHPPA with isocyanates show deviations from ideal 2$^{\text{nd}}$ order kinetics at higher conversions. All the kinetics experiments were carried out under catalysis by dibutyltin dilaurate. This catalyst inhibits the undesired reaction of isocyanate groups with moisture. It was also found that the catalysis was necessary to reach reasonable curing times for poly-BHPPA based polyurethane networks. The uncatalyzed systems reacted extremely slowly.
Preparation of polyurethane networks from poly-BHPPA

The poly-BHPPA products prepared were used successfully as OH functional precursors of polyurethane networks. The networks prepared contained only very low sol fractions. Acetone and also ethylene diglycol dimethylether (diglyme) were found to be good swelling solvents for the networks prepared, while methyl propyl ketone was a much poorer solvent and aromatic compounds like toluene or xylene practically did not swell the poly-BHPPA based polyurethanes.

The networks prepared contain a relatively high amount of cyclic bonds, 40 to 50% in the finally cured state, which is an expected result for systems with precursors of high functionality and with small distances between the functional groups.

The temperature of glass transition ($T_g$) of the networks prepared (ranging from 68°C to 126°C) depends of the poly-BHPPA precursor used: it increases with increasing molecular mass and with increasing core functionality. The choice of the isocyanate crosslinker also influences $T_g$: the networks made from HDI show higher $T_g$ values, than networks made from the same poly-BHPPA but crosslinked with Desmodur N3300 (Tri-HDI).

The urethane bonds in the networks prepared start to decompose near 140°C. The easier degradation of PU with aromatic urethane bonds is a disadvantage in comparison with aliphatic polyurethanes, whose decomposition starts at 200°C.

The surfaces of polyurethane coatings prepared are smooth, displaying a roughness of ca. 20-25 nm, and relatively hydrophilic: the contact angle with water was found to be near 80°. The prepared networks are also relatively hard, possessing the Shore D hardness of 70.