

**HIGHLY BRANCHED, SEGMENTED POLYUREA and  
POLYURETHANE ELASTOMERS THROUGH OLIGOMERIC  
 $A_2 + B_3$  APPROACH**

by

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## ABSTRACT

Oligomeric  $A_2 + B_3$  approach was used for the preparation of highly branched, elastomeric, segmented polyurea, polyurethane and poly(urethane urea) copolymers where  $A_2$  was a difunctional monomer or oligomer and  $B_3$  was a trifunctional monomer or oligomer. In most cases, oligomeric  $A_2$  had isocyanate functional ends, whereas  $B_3$  was a triamine or triol. Three different synthetic methods were investigated; where (i)  $A_2$  was slowly added over  $B_3$ , (ii)  $B_3$  was slowly added over  $A_2$  or (iii) both reactants were mixed together at the beginning and reacted.  $A_2$  type oligomeric soft segments included PTMO, PEO, PPO and PDMS with number average molecular weights between 1000 and 10800 g/mol. A PPO based  $B_3$  oligomer with average branch length of 1000 g/mol and low molecular weight triamines with different structures were also used. The diisocyanates utilized were bis(4-isocyanatocyclohexyl)methane (HMDI), 1,6-hexamethylene diisocyanate (HDI) and trans-1,4-cyclohexyl diisocyanate (CHDI). Gel points were determined experimentally and with Monte Carlo simulations, for reactions where  $A_2$  was slowly added onto  $B_3$  or vice versa at different solution concentrations. When  $B_3$  was added onto  $A_2$  gelation took place at lower conversions when compared with the reaction where  $A_2$  was added on  $B_3$ . A number of highly branched polymers with different compositions were synthesized. Materials obtained were characterized by FTIR spectroscopy and thermal and mechanical tests. DMA and stress-strain tests indicated that for polymers with similar chemical compositions those prepared by the addition of  $A_2$  over  $B_3$  possessed better mechanical properties than those prepared by  $B_3$  over  $A_2$  addition. As expected the end capped polymers showed better mechanical strength than their uncapped counterparts like the chain-extended ones. Modeling studies were also done to determine the influence of reaction procedure on

polymer topology for; (i)  $A_2$  over  $B_3$  addition, (ii)  $B_3$  over  $A_2$  addition, and (iii) mixing  $A_2$  and  $B_3$  together at the beginning. Structures formed by the addition of  $B_3$  over  $A_2$  displayed different topologies and possessed much higher degree of branching than other two polymerization methods, which interestingly displayed very similar topologies.

## ÖZET

Bu çalışmada, oligomerik  $A_2+B_3$  yöntemi kullanılarak çok dallı, elastomerik poliüre, poliüretan ve poli(üretan üre) kopolimerler sentezlendi. Bu yöntemde  $A_2$  olarak iki fonksiyonlu bir monomer veya oligomer,  $B_3$  olarak ise üç fonksiyonlu bir monomer veya oligomer kullanıldı. Çoğunlukla oligomerik  $A_2$  izosiyanat uç gruplarına sahipken,  $B_3$  amin veya hidroksil grupları içermekte idi. Bu çalışmada üç farklı polimer sentez yöntemi incelendi: (i)  $A_2$ 'nin  $B_3$ 'ün üzerine yavaşça eklenmesi, (ii)  $B_3$ 'ün  $A_2$ 'nin üzerine yavaşça eklenmesi, (iii)  $A_2$  ve  $B_3$ 'ün karıştırılıp reaksiyona sokulması.  $A_2$  tipindeki oligomerler olarak molekül ağırlığı 1000 ve 10800 g/mol arasında değişen PTMO, PEO, PPO ve PDMS kullanıldı. Ayrıca, ortalama zincir uzunluğu 1000 g/mol olan PPO bazlı  $B_3$  oligomeri ve farklı yapılarda düşük molekül ağırlıklı triaminler de kullanıldı. Diizosiyanat olarak Bis(4-izosiyanatosikloheksil)metan (HMDI), 1,6-hekzametilen diizosiyanat (HDI) ve trans-1,4-sikloheksil diizosiyanat (CHDI) kullanıldı. Jelleşme noktaları, deneysel çalışmalarla ve Monte Carlo simülasyonlarıyla  $A_2$ 'nin  $B_3$ 'ün üzerine yavaşça eklenmesi ve  $B_3$ 'ün  $A_2$ 'nin üzerine yavaşça eklenmesi durumları için farklı çözelti konsantrasyonlarında belirlendi.  $B_3$ 'ün  $A_2$ 'nin üzerine yavaşça eklenmesi yöntemi izlendiğinde jelleşmenin diğer sentez yöntemine kıyasla daha az  $A_2$  harcandığında gerçekleştiği gözlemlendi. Farklı kompozisyonlarda pek çok sayıda çok dallı polimer sentezi yapıldı. Oluşan malzemeler FTIR spektroskopisi ve termal, mekanik testlerle karakterize edildi. DMA ve çekme-koparma testleri, benzer kompozisyona sahip olsalar da genellikle  $A_2$ 'nin  $B_3$ 'ün üzerine eklenmesi yöntemi izlenerek oluşan polimerlerin  $B_3$ 'ün  $A_2$ 'nin üzerine eklenmesi ile oluşan polimerlerden daha üstün mekanik özelliklere sahip olduğunu gösterdi. Beklendiği gibi, uçları tek fonksiyonlu monomerlerle kapatılan polimerler zincir uzatıcı kullanılarak sert

kısım oranı arttırılan polimerlerde olduđu gibi daha iyi mekanik özellikler gösterdiler. Bunların dışında, uygulanan reaksiyon yönteminin polimerlerin topolojisine etkileri de incelendi. Modelleme çalışmaları sonunda, B<sub>3</sub>'ün A<sub>2</sub>'nin üzerine eklenmesi yöntemi kullanılarak hazırlanan polimerlerin aynı polimer topolojisiyle sonuçlanan diđer iki yönteme göre çok daha fazla dallanma derecesine sahip olduđu gösterdi.

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## NOMENCLATURE

$\alpha$	constant in Mark–Houwink–Sakurada equation
$\alpha$	branching coefficient
$\alpha_c$	critical branching coefficient for gel formation
$\rho$	ratio of B groups on branch units to all B groups in the reaction mixture
$\eta$	viscosity
$\Delta H$	change in enthalpy
$\Delta S$	change in entropy
A <sub>2</sub>	difunctional monomer or oligomer
B <sub>3</sub>	trifunctional monomer or oligomer
CHDI	trans-1,4-cyclohexyl diisocyanate
CHI	cyclohexyl isocyanate
D	dendritic units
DB	degree of branching
DMA	dynamic mechanical analysis
DMF	dimethylformamide
DYTEK	2-Methyl-1,5-diaminopentane
E'	storage modulus
EDA	ethylene diamine
$f$	functionality of the branched units
FTIR	Fourier transform infrared spectroscopy
HB	hyperbranched
HDI	1,6-hexamethylene diisocyanate
HMDI	bis(4-isocyanatocyclohexyl)methane
HS	hard segment



IPA	isopropyl alcohol
k	constant in Mark–Houwink–Sakurada equation
L	linear units
M	molecular weight
MC	Monte Carlo simulation
M <sub>n</sub>	number average molecular weight
MPa	mega pascal
M <sub>w</sub>	weight average molecular weight
NBA	N-butylamine
NMR	Nuclear Magnetic Resonance
p	extent of reaction
PAMAM	polyamidoamine
PDMS	poly(dimethyl siloxane)
PEO	poly(ethylene oxide)
PPO	poly(propylene oxide)
PTMO	poly(tetramethylene oxide)
PUU	poly(urethane urea)
<i>r</i>	ratio of the A groups to the B groups
ROMBP	ring-opening multibranching polymerization
SCVP	self condensing vinyl polymerization
T	terminal units
T	temperature
T-12	dibutyltin dilaurate
Tan δ	storage modulus over loss modulus
T-3000	trifunctional PPO (XTJ-509)
T <sub>g</sub>	glass transition temperature

THF	tetrahydrofuran
TMP	trimethylolpropane
TPE	thermoplastic elastomer
TRI	polyoxyalkylenetriamine (Jeffamine T-403)
TRIS	tris(2-aminoethyl)amine

## Chapter 1

### AN INTRODUCTION TO HIGHLY BRANCHED POLYMERS

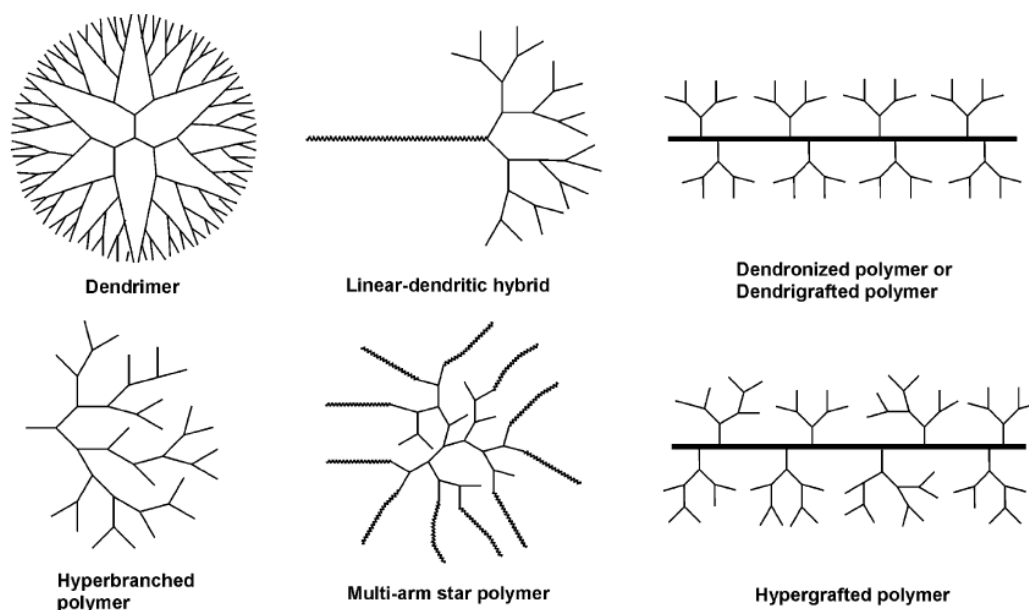
#### 1.1. Introduction

Synthetic polymers have contributed significantly to our everyday lives for the last 100 years or so. Especially during and after the Second World War there have been dramatic discoveries in polymer science and technology that have affected many disciplines, such as; aerospace and civil engineering, medicine, electronics, energy, transportation and material science. Scientists have been successfully fulfilling the needs for society in traditional polymer science during the last century by developing and commercializing novel linear (thermoplastic) polymers or crosslinked (thermoset) polymers.

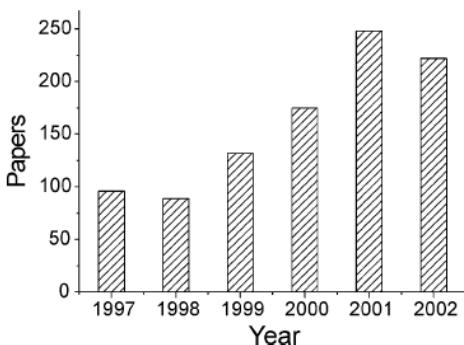
For the last two decades a new type or class of polymeric materials has attracted the attention of the polymer community. These thermoplastic materials had tree-like or highly branched structures. Depending on the regularity of the arms, these materials are called as “dendritic” or “hyperbranched” polymers.

Dendritic architecture is common in nature such as; snow crystals, lightning, branches and roots of a tree, neurons, polysaccharides, etc. Researchers have tried to mimic these structures because of their unique combination of properties when compared to their linear analogs. Dendritic polymers (dendron meaning “tree” and meros meaning “part” in Greek) are highly branched macromolecules and include 6 subclasses: (a) dendrimers, (b) linear-dendritic hybrids, (c) dendronized or dendrigrafts, (d) hyperbranched polymers, (e) multi-

arm star polymers, (f) hypergrafts or hypergrafted polymers. Schematic descriptions of each of these structures are shown in Figure 1.1. [1] The first three subclasses have well-defined structures while the latter three exhibit random branching. The most important subclasses in these polymers are dendrimers and hyperbranched polymers. Dendrimers are synthesized in a step-wise manner by following tedious isolation and purification procedures, whereas hyperbranched polymers are irregularly branched and usually prepared through a one-step polymerization method. That is why it is easier and cheaper to produce hyperbranched polymers that have properties similar to those of dendrimers. Interest in hyperbranched polymers is increasing rapidly. This can be seen in the increase in the number of publications between 1997 and 2002 as shown in Figure 1.2. However, hyperbranched polymers are polydisperse systems both in terms of molecular weight and branching, whereas dendrimers have highly regular chemical structures, controlled molecular weights and narrow molecular weight distributions.



**Figure 1.1.** Schematic description of dendritic polymers [1]

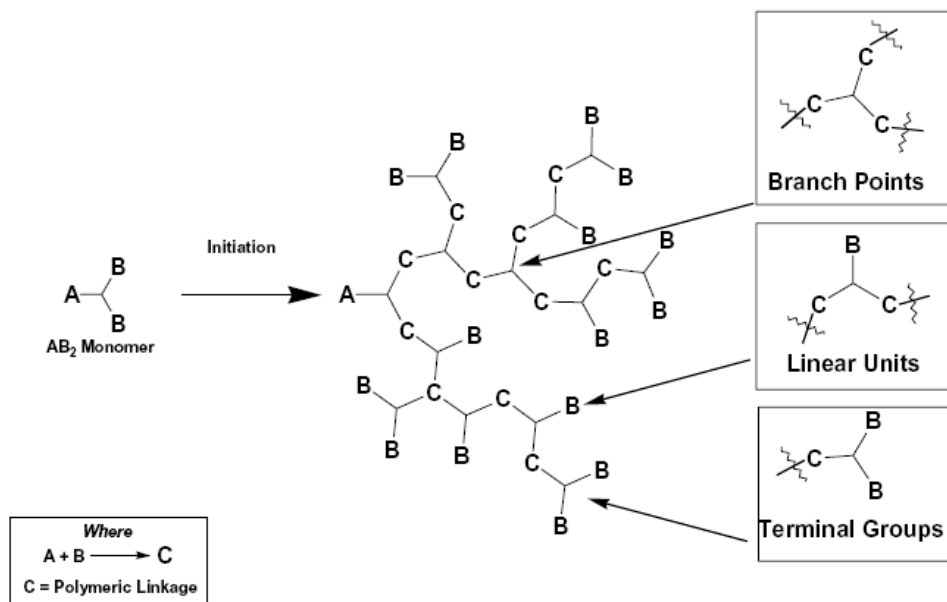


**Figure 1.2.** Scientific publications as a function of publication year searched by SCIE (ISI web of science) between 1997 and 2002 with “hyperbranched” as the topic.[1]

The properties of hyperbranched polymers which make them attractive can be listed as the presence of large number of functional end groups, high solubilities, low melt and solution viscosities and their globular structure. On the other hand, a major drawback is the lack of chain entanglements which results in the lack of mechanical strength and toughness, which makes them unsuitable in structural applications. Other factors affecting the properties are isomerism and degree of branching. All of these concepts will be discussed in the following sections.

Hyperbranched polymers can be synthesized by a variety of polymerization techniques, such as; addition, condensation, self-condensing vinyl polymerization and ring-opening reactions. The conventional method of synthesis consists of one-step polymerizations of  $AB_x$  type monomers to generate highly branched and soluble polymers. Typical growth in polymer structure and branching in the polymerization of an  $AB_2$  type monomer is schematically shown in Figure 1.3. This approach leads to branched polymers with

uncontrolled or statistical growth. Consequently, the resulting structures are imperfect and polydisperse.



**Figure 1. 3.** Formation of a hyperbranched polymer by the polymerization of  $AB_2$  monomers. [2]

The final properties of hyperbranched polymers are determined firstly, by the structure of the repeating unit, and secondly, by the nature of the resulting end groups, or vice-versa. When those two effects are well understood, one can look for the effect of degree of branching, molecular weight and molecular weight distribution. [3] Large number of functional end groups on the linear and terminal units of hyperbranched polymers can be conveniently end-capped with small organic molecules. End groups are easily accessible for chemical modifications and the nature of the end groups determine the thermal and physical properties to a great extent.

## 1.2. Degree of branching

A hyperbranched architecture consists of branch points called as dendritic units, which are fully incorporated  $AB_x$  monomers; linear units (L) which have one B group unreacted; and terminal units (T), which have two B groups unreacted as shown in Figure 1.3. In 1991 Frechet defined the term “degree of branching” (DB) to better explain the structure of hyperbranched polymers as described in Eq. (1): [4]

$$\text{Degree of branching (DB)} = (D+T) / (D+T+L) \quad (1)$$

where D represents the number of dendritic units, T the number of terminal units and L the number of linear units. Frey et al. [5] also made a modified description of DB:

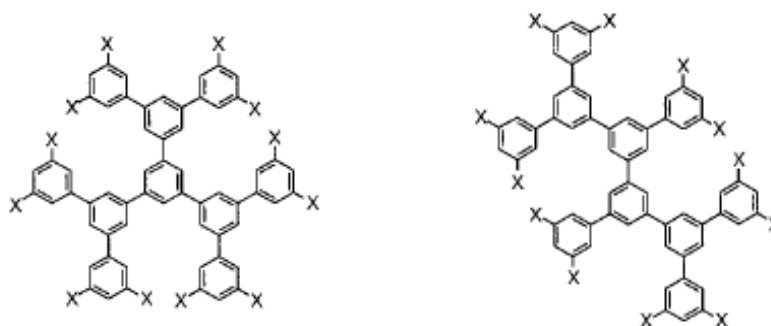
$$\text{Degree of branching (DB)} = (2D) / (2D+L) \quad (2)$$

Frechet’s approach involves the synthesis of low molecular weight model compounds resembling the repeat units to be found in the hyperbranched skeleton. The model compounds are characterized with  $^{13}\text{C}$ -NMR to assign the different peaks in the spectra of the hyperbranched polymers. The degree of branching is calculated from the integrals of the corresponding peaks in the spectrum of the polymer. In Frey’s expression for the degree of branching, the degree of polymerization is also taken into consideration which leads to more accurate results at low molecular weight polymers.

In  $AB_2$  polymerizations, DB of hyperbranched polymers statistically approaches to 0.5 as pointed by Frey. On the other hand DB is 1.0 for a perfect dendrimer and 0 for a linear polymer. NMR spectroscopy is a powerful tool to determine the DB of hyperbranched polymers. It is important to understand the effect of DB on polymer properties. The degree

of branching indicates the flexibility of the branching components contained within the architecture as well as the intrinsic viscosity of the polymer. The higher the degree of branching the lower the viscosity of the hyperbranched polymer, which in turn has an effect on the relative solubility of polymer in various media. Hawker and Chu found that polymers with higher DBs have higher solubilities. [6]

Isomerism is one of the most important distinctions between hyperbranched polymers and linear polymers. Because the addition of each monomer takes place randomly, a large number of geometrical isomers can be formed even for a given molecular weight and DB. Isomerism causes further polydispersity in the aspect ratio of the polymer molecule. Figure 1.4 shows two polyphenylenes that have the same molecular weight and DB, but they differ in geometry or isomerism. This variation of geometry has an important effect on the solution as well as solid-state packing structure of the polymer and as a result on polymer properties. For example, the packing order influences not only the relaxation process but it also affects the solubility of the polymer. [7] Large number of isomers increases the state of entropy for the system, and is expected to lower the transition temperature as indicated by:

$$T = \Delta H / \Delta S$$


**Figure 1. 4.** Two isomers of HB polyphenylenes [7]



### 1.3. Thermal properties of highly branched polymers

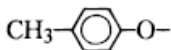
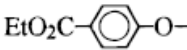
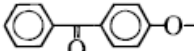
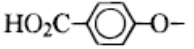
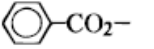
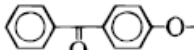
Since hyperbranched polymers are generally amorphous materials, the analysis of glass transition temperature ( $T_g$ ) is important. The glass transition temperature of a hyperbranched polymer is not only affected by the chain-end composition, but also by the molar mass, the macromolecular composition and the degree of branching. [6,8]. Chemical structure has a similar effect as in the case of linear polymers; for example, an aliphatic backbone has a lower  $T_g$  than its aromatic counterpart. According to Schmaljohann et al. [9]  $T_g$  can be understood as a combination of inter- and intramolecular effects. Differences in  $T_g$  of hyperbranched polymers with different repeating units but with the same end groups demonstrate the intramolecular effect of segmental motion, whereas the change of  $T_g$  through variation of the end groups (their polarity in particular) can be assigned to translational motion and an intermolecular effect. [9] Since there are several factors affecting  $T_g$ , it is quite hard to make a complete model to predict the  $T_g$  of a hyperbranched polymer.

A study by Chu and Hawker shows how functional groups affect the  $T_g$ 's of highly branched polymers. In comparing the  $T_g$ 's of hyperbranched poly(ether ketones) with modified functional end groups, shown as R on Table 1.1, authors have observed dramatic effect of the end-group type and structure on the glass-transition temperatures of the polymers. [6]

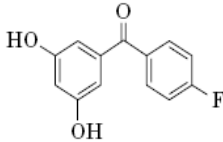
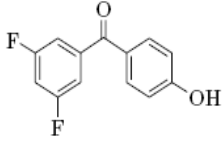
Same authors in a different publication have prepared  $AB_2$ -type monomers, which should give poly(ether ketone) with an identical backbone structure, but with different terminal groups. A large difference in the  $T_g$  of these two iso-structural polymers also suggests the importance of the terminal groups on the polymer properties. [10] Due to large differences in the polarity of the connecting groups and terminal groups, the physical properties,

including the  $T_g$ , would be affected by the nature of the backbone as well as the terminal groups (Table 1.2).

**Table 1.1.**  $T_g$  values of hyperbranched poly(ether ketone) derivatives [6]

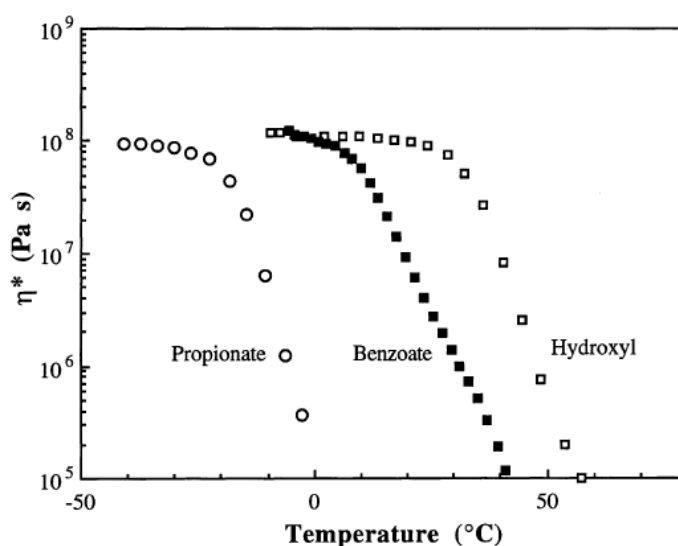
R	$T_g(^{\circ}\text{C})$
F-	162
HO-	127
	139
	154
	117
$\text{CH}_3(\text{CH}_2)_7\text{-O-}$	97
	290
	147
$\text{CH}_3\text{-CO}_2\text{-}$	118
	119

**Table 1.2.** Properties of iso-structure hyperbranched poly(ether ketone) [10]

Monomer	$M_n$ (D)	End Group	$T_g$	Solubility
	95000 (2.2)	OH	127	Soluble in DMF, KOH solution
	20000 (1.8)	F	162	Soluble in DMF, KOH solution

#### 1.4. Mechanical and rheological properties

It is essential for a material to have the suitable mechanical and rheological properties for an appropriate use when commercially introducing it to the market. This is especially important for load bearing or structural applications. Due to the lack of entanglements caused by the highly branched, globular structure, hyperbranched polymers have poor mechanical properties resulting in poor film forming and brittle materials.

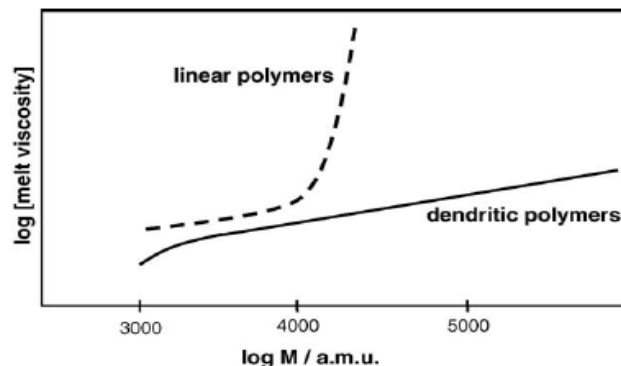


**Figure 1.5.** Complex dynamic viscosity as function of temperature for three different aliphatic hyperbranched polyesters based on bismethylol propionic acid and having different end group structure. [12]

Viscosity behaviors of HB and linear polymers show remarkable differences. The rheological properties for hyperbranched polymers are characterized by a Newtonian behavior in the molten state; i.e., no shear thinning or thickening is observed [11], indicating lack of entanglements for these polymers. This has limited the use of these polymers as thermoplastics to applications where the mechanical strength is extremely

important. Hence, these polymers are mainly suitable as additives or as thermosets when high mechanical strength is required for a certain application. The melt behavior has been shown to be greatly affected by the structure of the end-groups where an increase in the polarity of the end-groups can raise the viscosity by several orders of magnitude as shown in Figure 1.5 [12]. This is of great importance in applications where low viscosity is essential for the processing of the material.

Another very special feature of these (highly branched) polymers is the relationship between molecular weight and melt viscosity. For linear polymers, the increase in melt viscosity with molecular weight is linear with a transition to a 3.4 power law when the molecular weight reaches the critical mass for entanglements,  $M_c$ . However, the line for dendritic polymers shows a continuous slope of 1.1 up to 100,000 a.m.u with no critical mass [13]. At low molar mass, linear polymers consist of random chains which, as the molar mass increases, start to entangle at a critical molecular size, leading to a sharp increase in the melt viscosity. Unlike linear polymers, the globular or highly branched architecture of both dendrimers and hyperbranched polymers prevents chain entanglements, resulting in considerably lower melt viscosities and a continuous slope of the  $\eta$ -function, which is depicted in Figure 1.6.



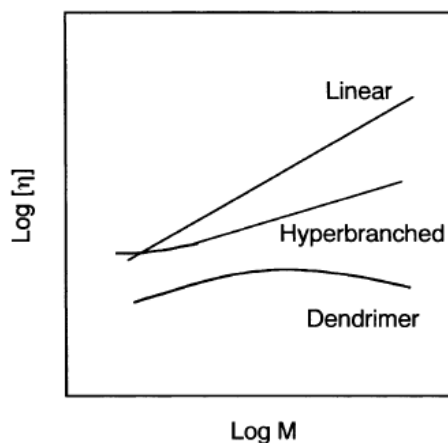
**Figure 1.6.** Melt viscosity vs. molar mass of linear and dendritic polymers [13]

### 1.5. Solution behavior

HB polymers have higher solubilities and lower solution viscosities than their linear analogs. The viscosity of a dilute polymer solution can be related to its molar mass,  $M$ , by the Mark–Houwink–Sakurada equation (Eq. (3)), where  $(k)$  and  $(\alpha)$  are constants specific to a certain solvent-polymer combination at a certain temperature.

$$[\eta] = kM^\alpha \quad (3)$$

The relationship between the intrinsic (solution) viscosity and the molecular weight for different polymer architectures is outlined graphically in Figure 1.7. From the plot, it can clearly be observed that dendrimers and hyperbranched polymers do not obey the Mark–Houwink–Sakurada relationship. Dendrimers display an unusual bell-shaped relationship that results from their globular structures. For hyperbranched polymers, the slope is smaller than that for linear polymers although the intrinsic viscosities do increase with increasing molecular weight.



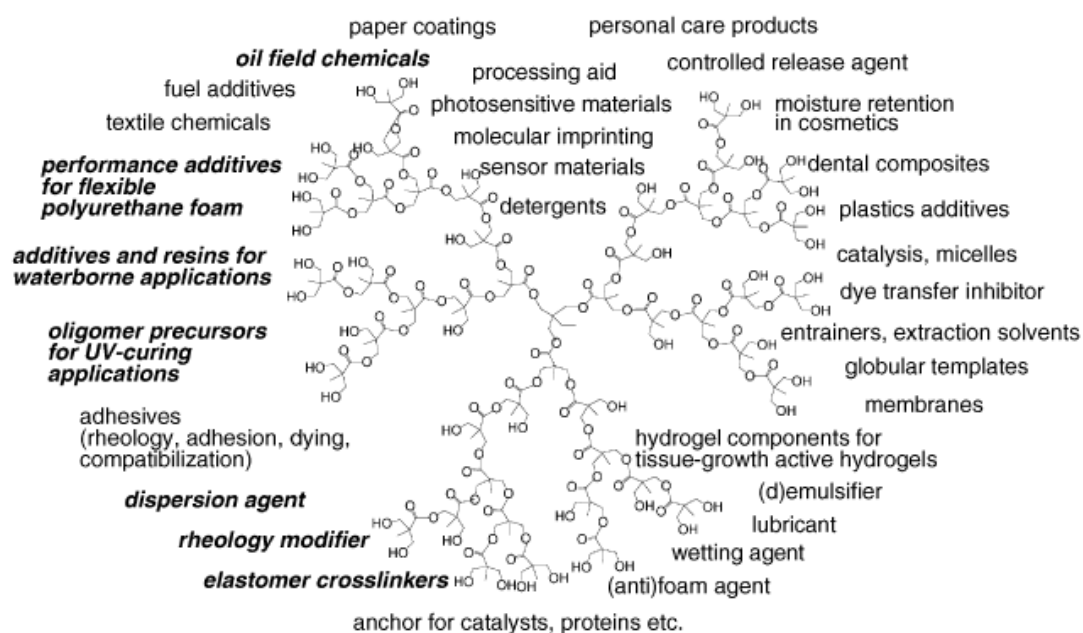
**Figure 1.7.** Plots for the relationship between  $\log M$  and  $\log [\eta]$  for polymers [14]

Generally,  $\alpha$  lies between 0.5 and 1.0 for randomly coiled linear polymers, and less than 0.5 for hyperbranched polymers, which suggests that they exhibit a spherical shape in solution. These hyperbranched macromolecules when in solution reach a maximum intrinsic viscosity where their shape changes from an extended to a more compact globular structure, especially at high molecular weights. [2]

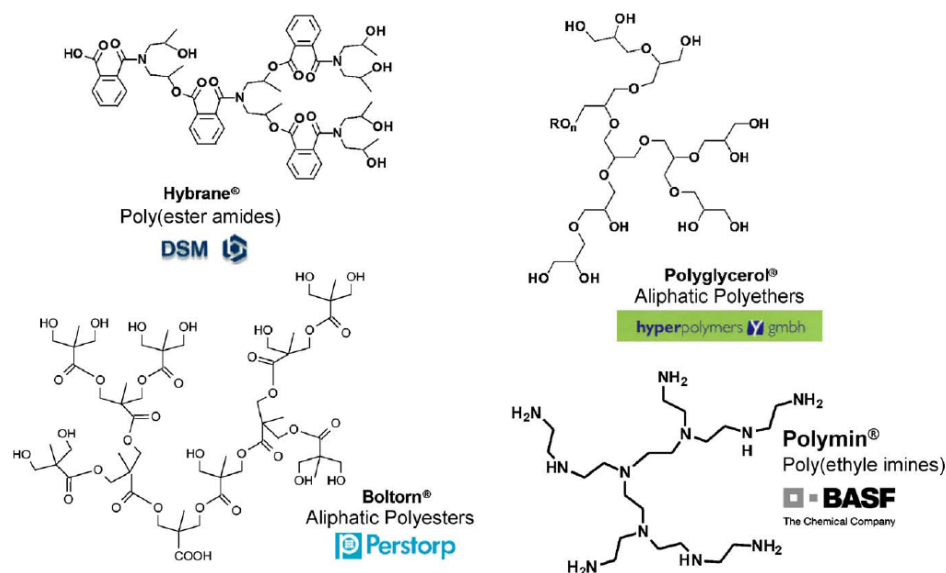
### 1.6. Applications

HB polymers are promising new materials that can possibly find applications in many different areas where low viscosity and large number of functional groups are of advantage. Figure 1.8 shows possible applications for HB polymers. There are several companies such as DSM Fine Chemicals (Geleen, Netherlands), BASF AG (Ludwigshafen, Germany), the Perstorp Group (Perstorp, Sweden), and Hyperpolymers GmbH (Freiburg, Germany) that already commercially produce hyperbranched polymers on a large-scale. Structures of these polymers together with their trade names and producers are provided in Figure 1.9. [15]

HB polymers draw attention primarily as blend components, additives and coatings. HB polymers may function as crosslinkers in coatings and thermosets. Blends of HB and linear polymers result in reduced viscosity at high temperatures and display improved thermal stability compared to their linear analogs, without loss of mechanical properties. HB polymers can also be used as carriers for organic molecules (for example organic dyes). There is also an interest in the preparation of nanoporous polymers as low dielectric constant materials for use as novel interlayer dielectric materials. Other studies for the applications of HB polymers include serving as surface modifiers, tougheners, drug-delivery systems and optical modifiers. [11,16]



**Figure 1.8.** Possible applications of HB polymers. Bold italic: present commercial applications, others: potential application areas. [15]



**Figure 1.9.** Chemical structures of some commercial hyperbranched polymers [15]

### 1.7. Thermoplastic polyurethanes and polyureas

Segmented copolymers consisting of alternating hard and soft segments along their macromolecular backbone have the ability to develop microphase separation which provides many useful properties. In the segmented copolymers, the hard blocks account for the mechanical stability of the material, since they give rise to reversible crosslinks, which are embedded in a continuous amorphous phase with a low glass transition temperature. This continuous amorphous phase is mainly composed of the soft segment, and gives the material its flexibility. In many thermoplastic elastomers (TPEs), the reversible crosslinks are formed by crystalline or glassy hard domains. Above the melting point or glass transition temperature of these domains, a viscous polymer melt is obtained, that can be processed easily. Next to reversible crosslinks, the hard blocks also act as reinforcing fillers, causing the material to be stiffer at higher hard block content. [17]



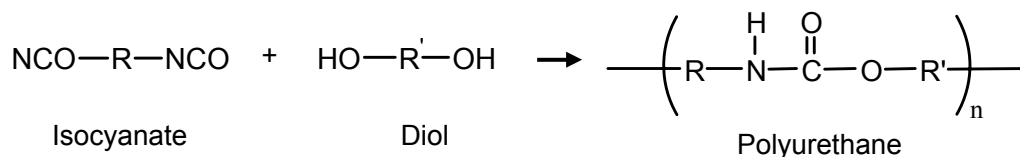
**Figure 1.10.** Microphase separation in TPEs

Segmented thermoplastic polyurethanes (TPU) and polyureas are versatile materials that find applications in many areas as coatings, adhesives, elastomers, fibers, foams, artificial organs, etc. These polymers are synthesized by the step-growth addition reactions between isocyanates and alcohols or amines, respectively, which is shown in Figure 1.11. Segmented polyurethanes, polyureas and poly(urethane urea)s comprise a morphology with

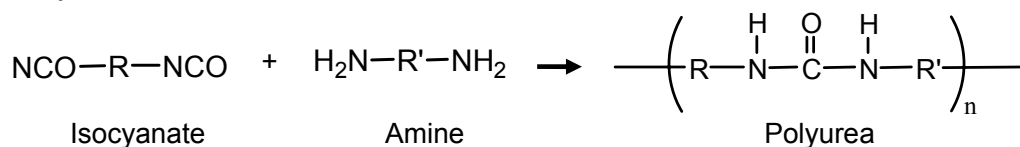


a continuous soft segment matrix in which hard segments phase separate into domains. This conventional morphology is shown in Figure 1.10. At room temperature, the low melting soft segments are incompatible with the polar and high melting point hard segments, which leads to phase separation. These soft segments act as a spring giving the material its elastic properties, while the hard segment works as physical cross-links through either crystalline domains and/or through hydrogen bonding. Intermolecular hydrogen bonding between urethane and urea groups is schematically shown in Figure 1.12. The degree of phase separation is highly dependent on the formation of hydrogen bonds between urea/urethane groups, miscibility of the starting compounds, average segment molecular weights, hard segment content and possible formation of hydrogen bonding with soft segments. The mechanical properties also depend on chemical compositions of soft and hard segments, hard segment content and the degree of phase separation. [18,19]

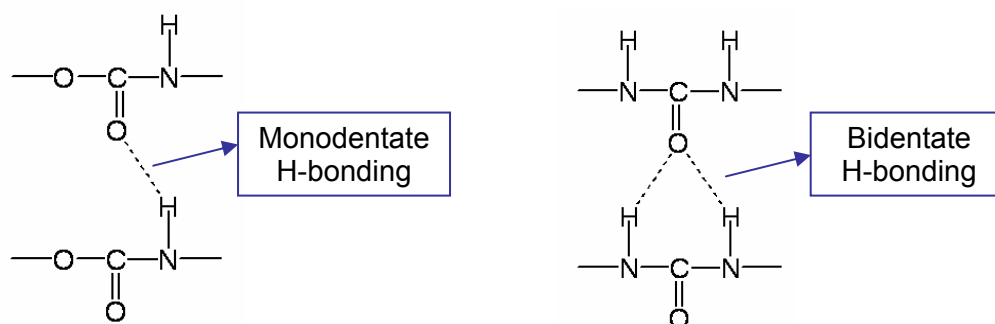
**Polyurethane formation reaction:**



**Polyurea formation reaction:**



**Figure 1.11.** Polyurethane and polyurea chemistry



**Figure 1.12.** H-bonding in polyurethanes and polyureas

In this study; highly branched, segmented polyurethane and polyurea copolymers were synthesized by applying a technique that is slightly different than the conventional procedures, which generally use low molecular weight monomers. In this approach, which can be termed as oligomeric  $A_2+B_3$  approach,  $A_2$  represents a difunctional monomer or oligomer and  $B_3$  a trifunctional monomer or oligomer. Properties of these HB polymers are quite different than the classical HB polymers explained in the above sections. Oligomeric  $A_2+B_3$  approach results in polymers with mechanical properties comparable to their linear analogs due to strong H-bonding and chain lengths above critical molecular weight. [47,49]

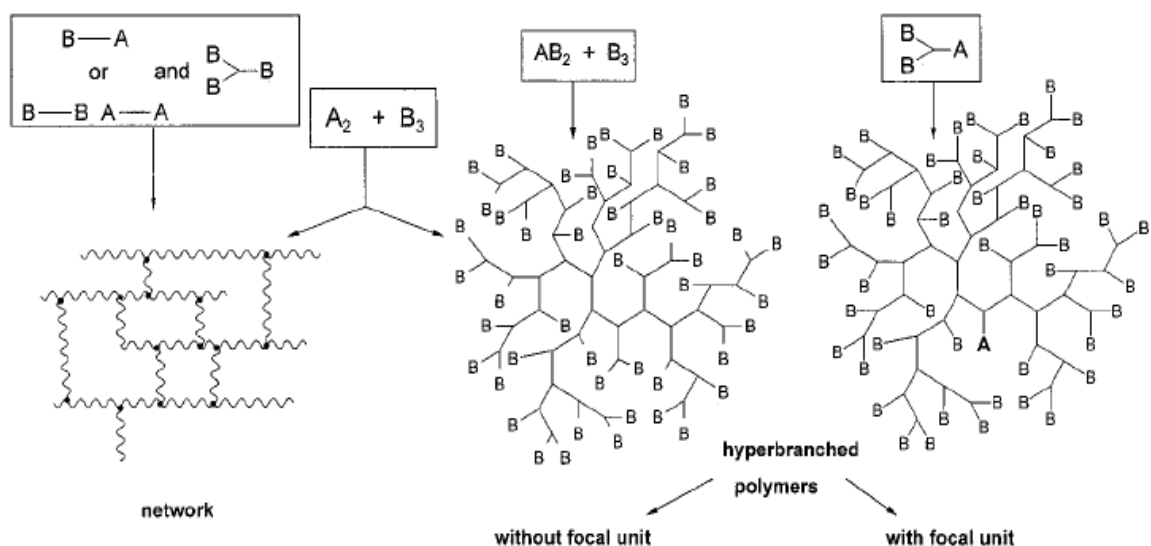
In addition to the use of oligomers as starting materials, in this study slow addition of reactants was applied during the polymer synthesis, which leads to more controllable branching and molecular weight growth. Monomers and oligomers with various molecular weights and structures were used and the influence of chemical structure and molecular weights of hard and soft segments on polymer structure and property were investigated. Influence of the procedure followed ( $A_2$  and  $B_3$  reacted together,  $A_2$  over  $B_3$  or  $B_3$  over  $A_2$ ),

end-capping and use of chain-extenders were also investigated. Modeling studies were also performed to investigate the influence of reaction procedure on the topology, molecular weight and molecular weight distribution of the polymers formed at different cyclization ratios. The structures and physical properties of the polymers are identified by spectroscopic studies, dynamic mechanical analysis and stress-strain tests.

## Chapter 2

### HIGHLY BRANCHED POLYMERS: A COMPREHENSIVE REVIEW

Flory was the first polymer scientist who described the formation of branched polymers from multifunctional monomers, typically used in thermosetting polymers. He provided the basic definitions and performed theoretical calculations using the condensation polymerization from multifunctional monomers and developed the “degree of branching” and “highly branched species” concepts during 1940s and 1950s. [20-22] In his studies he demonstrated that the analysis of highly branched systems are much more complicated than linear systems as a result of their branched structure. For the analysis of these highly branched structures he concluded that first of all the “crosslinking” and “gelation” terms had to be clarified. Crosslinking means that a branch or branches from one polymer molecule is attached to other molecules in the system. As Odian explains [23], crosslinking is distinguished by the occurrence of gelation at some point in the polymerization. At this “gel point” an insoluble polymer is formed in which different polymer molecules have been chemically linked (crosslinked) to each other to form a macroscopic molecule. The non-gel portion in the system still remains soluble and is called as the “sol”.



**Figure 2.1.** Synthetic strategies towards networks and hyperbranched polymers based on the classic branched polycondensation theory of Flory. [16]

Assuming that all A and B groups have equal reactivity and there is no reaction between A and B groups (or no internal cyclization) on the same molecule, Flory found important results for the formation of highly branched structures. Concerning the gelation, for the polymerization of  $A_2$  (difunctional A type monomer),  $B_2$  (difunctional B type monomer) and  $A_3$  (trifunctional A type monomer) monomers, he showed that reaction will always gel after a critical conversion whereas in the polymerization from  $AB_2$  monomers it will never gel. Theoretical study behind these results will be discussed in the experimental part. Figure 2.1 schematically represents the highly branched polymer structures obtained by different synthetic methods.

Despite the pioneering work of Flory, highly branched polymers did not draw much attention for many years until the end of 1970s. The concept of repetitive growth with branching was first reported in 1978 by Vögtle and coworkers [24] where low molecular weight amines were synthesized. Then, Tomalia and co-workers at Dow Chemicals synthesized polyamidoamine dendrimers (PAMAM). This was the first article where the term “dendrimer” was used. [25] In the same year Newkome et al. [26] also presented a paper dealing with dendrimers. During that time studies on randomly branched structures also started as a result of the need for easier synthetic methods leading to the formation of hyperbranched polymers.

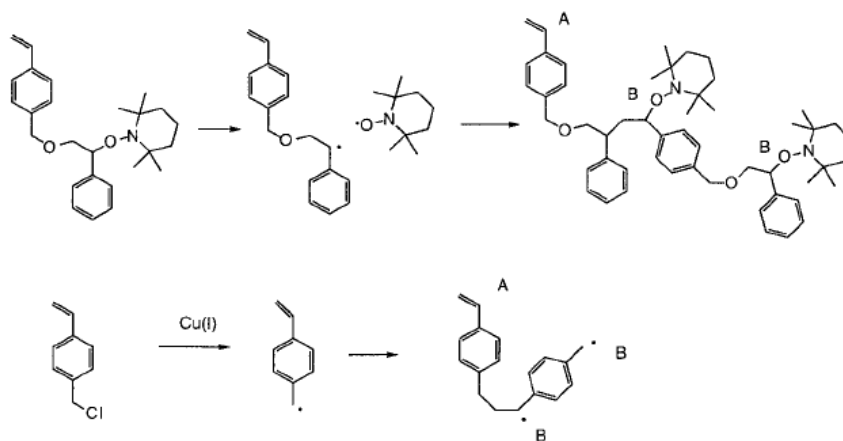
In 1982, Kricheldorf reported first synthesis of hyperbranched polymers. [27] The name “hyperbranched polymer” was first used by Kim and Webster in 1988 for the polyphenylene polymers synthesized by the polymerization of  $AB_2$  type monomers at DuPont laboratories. [28,29] First patent on hyperbranched systems was warranted again by the same co-workers in 1987. [7] Research on dendrimers increased rapidly, however there were only a few papers on hyperbranched systems in 1980s. [30] After the beginning of 1990s the research based on the hyperbranched polymers started to increase rapidly.

Hyperbranched polymers are classically synthesized by four main categories: condensation reactions, addition reactions, self condensing vinyl polymerization (SCVP) and ring-opening multibranching polymerizations (ROMBP).

Many kinds of hyperbranched polymers can be synthesized by  $AB_x$  polymerization where one-step self-polycondensation procedure is followed.  $AB_2$  monomers are generally used as the starting materials while monomers where  $x > 2$  can also be used. For successful synthesis of hyperbranched polymers from  $AB_x$  monomers, certain requirements have to be fulfilled, as the absence of side reactions, equal reactivity of the two B functionalities, and

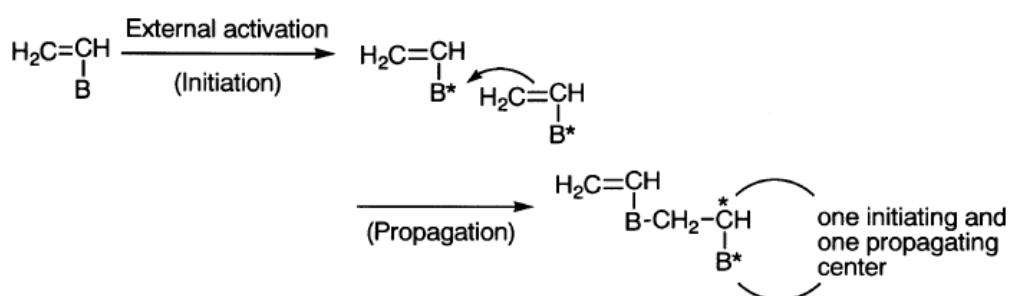
no internal cyclization reactions. Although Flory demonstrated that gelation is statistically impossible with  $AB_x$  monomers, gelation may be observed due to undesired side reactions. Strong intermolecular interactions like H-bonding can also cause physical and (reversible) gel formation. Preparation of  $AB_x$  monomers prior to polymerization is another drawback of these reactions. Polymers like polyphenylenes, polyesters, polyethers, polyamides, polyurethanes and many others have been successfully synthesized by this method. [2,3,14]

Addition polymerization of monomers that contain an initiating function and a propagating function in the same molecule has been shown to give hyperbranched polymers. In addition polymerization, multiple reactive sites are formed in the propagating species which are generated as a result of vinyl addition reaction as well as already existing initiating function. A number of vinyl monomers containing an initiating moiety were self-polymerized. [7]



**Figure 2.2.** Schematic representation for the preparation of hyperbranched polymers by addition polymerization [7]

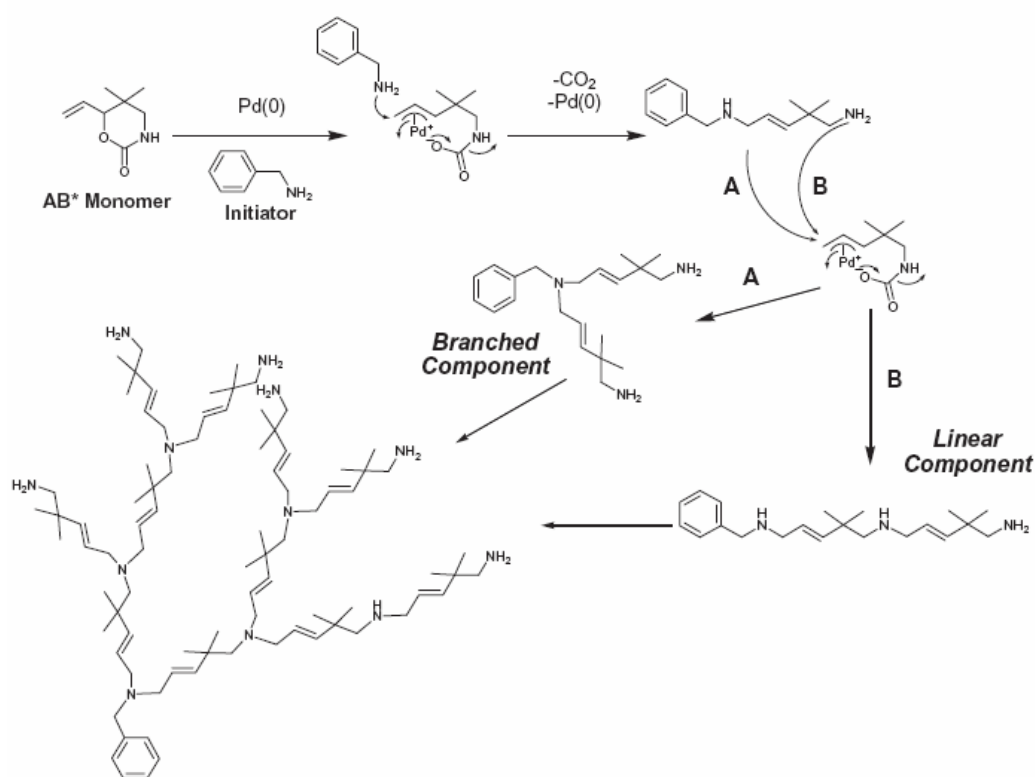
Self condensing vinyl polymerization (SCVP), which is shown in Figure 2.3., was first described by Frechet in 1995. [31] In this procedure, AB\* monomers containing one vinyl group, one initiating moiety and a double bond are used to form highly branched systems. Activated species can be a living free radical, a cation or a carbanion. Polystyrenes, polymethacrylates and polyacrylates have been synthesized by applying this method so far. [2]



**Figure 2.3.** Schematic representation of Self condensing vinyl polymerization (SCVP) leading to the formation of hyperbranched polymers [14]

The third method is ring-opening multibranching polymerizations (ROMBP) which was reported by Suzuki et al. in 1992, shown in Figure 2.4. [32] This method involves the generation of the branching units during the ring-opening reaction, while the starting AB monomers do not contain branching units. Active sites are generated by the addition of proper initiators which may allow for control over molecular weight and polydispersity of the resulting polymers. ROMBP polymerizations of cyclic carbamates, epoxides, oxetanes and lactones have been reported in literature. [14]

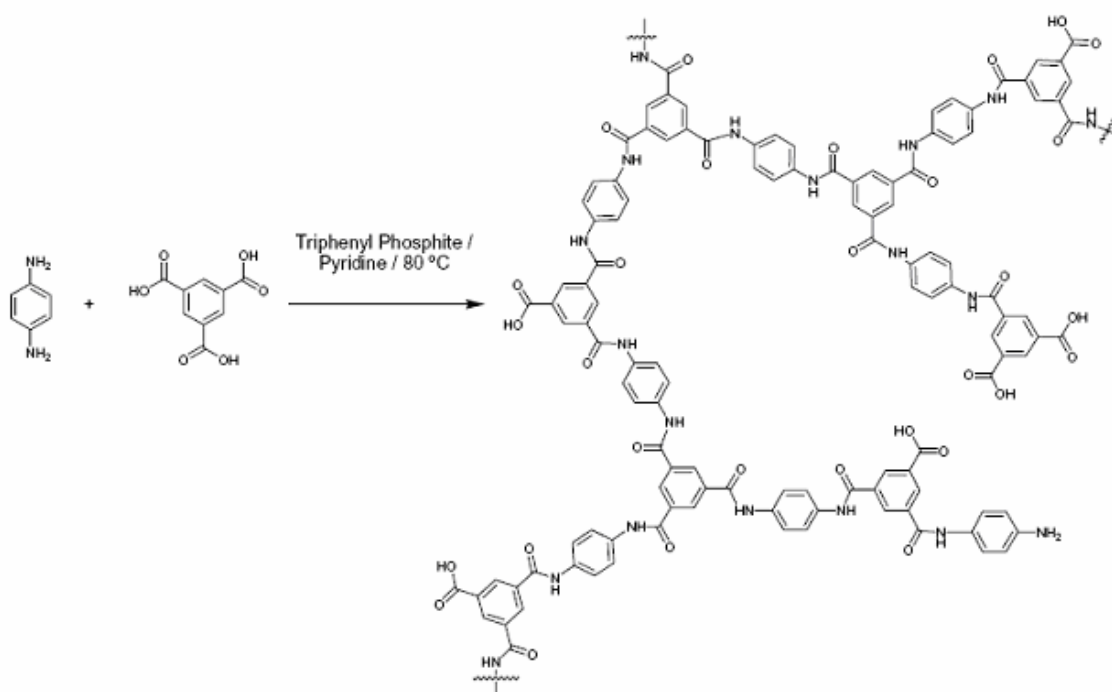




**Figure 2.4.** Synthesis of hyperbranched polyamine via ring-opening multibranching polymerizations (ROMBP) in Suzuki's method. [2,32]

Since the commercial availability of  $AB_2$  monomers are limited, new synthetic strategies are studied to overcome this disadvantage. That is why a new methodology for the synthesis of hyperbranched polymers is found:  $A_2 + B_3$  approach. Although these monomers have been used for network formation, preparation of hyperbranched polymers by this technique is a new approach. First hyperbranched polymer synthesis by  $A_2 + B_3$  approach was reported by Kakimoto [33] and Frechet [34] where the first one involved aromatic polyamide synthesis and the second one aliphatic polyethers containing chain end epoxy substituents. In the polymerization of  $A_2$  monomer with  $B_3$  monomer, reaction will

gel at a critical point, thus crucial problem is to avoid gelation and obtain soluble polymers. This can be done by one of several different approaches, which include; stopping the reaction through precipitation, end-capping prior to gel point, slow addition of monomers, using special catalysts or determining the stoichiometry at the beginning of the reaction accordingly. The success of this approach is also dependent upon many other factors including the ratio of functionalities, solvent and reagent purity, concentration of reaction medium, reaction time and temperature. Main polymer architectures studied by this method are polyamides, polycarbonates and polyureas. Several more recent works where hyperbranched polymers are synthesized by  $A_2 + B_3$  approach involves the preparation of hyperbranched aliphatic polyethers [35], poly(arylene ether phosphine oxide)s [36] and poly(arylene ether)s [37].



**Figure 2.5.** Synthesis of hyperbranched polyamide using  $A_2 + B_3$  approach as proposed by Kakimoto et al. [2,33]

In 1993, Spindler and Frechet were the first to demonstrate the synthesis of hyperbranched polyurethanes by using  $AB_2$  monomers where A was a hydroxyl group and  $B_2$  were protected isocyanate groups. [38] Polymerization was conducted in refluxing THF in the presence of dibutyltin dilaurate as the catalyst. End-capped and soluble polymer was isolated from the system. Later Kumar and Ramakrishnan synthesized aromatic hyperbranched polyurethanes by the self-polycondensation of  $AB_2$  and  $A_2B$  monomers. [39, 40] Tang and co-workers also reported the synthesis of hyperbranched polyurethanes where they used 3,5-dihydroxybenzoic acid as the  $AB_2$  monomer. [41]

In these methods, where polymerization is started by using  $AB_2$  type monomers, it is hard to obtain an  $AB_2$  monomer which contains both a hydroxyl and an isocyanate group due to their high reactivities with each other. For that reason, generally an  $AB_2$  monomer containing a functional group such as a carbonyl azide that can be transferred in situ into the isocyanate group. There are other studies where hyperbranched polyurethanes are produced using  $AB_2$  type monomers [42-44].

After 10 years from the first polyurethane synthesis, Bruchmann and Schrepp [45] synthesized hyperbranched poly(urethane urea)s in a one step process using commercially available monomers where they applied  $AA^* + B^*B_2$  approach.  $AA^*$  monomer is a difunctional isocyanate with intramolecular reactivity difference and  $B^*B_2$  monomer is a trifunctional alkanolamine where  $B^*$  part is a NH functional group and  $B_2$  part is a difunctional OH group.

Another approach is  $A_2 + CB_n$  method described by Gao and Yan [42,46] for the synthesis of hyperbranched poly(urea urethane)s with alternating ureido and urethane units where  $A_2$

is again the difunctional isocyanate and  $CB_n$  is a multi-hydroxyl amine, NH group being represented by “C” and n number of OH groups being represented by “ $B_n$ ”.

Recently Yilgor et. al. [47-49] reported the synthesis and investigation of hyperbranched poly(urea urethane) polymers by oligomeric  $A_2 + B_3$  approach. This approach is a new technique for the preparation of hyperbranched polyurethanes and ureas which have mechanical strength similar to linear polymers that entangle. [49] In this method, a polyether based oligomer that is end-capped with isocyanate groups is used as  $A_2$  and a trifunctional amine is used as  $B_3$ . Polymerization is carried out by the slow addition of  $A_2$  oligomer onto  $B_3$ , unlike other examples that are synthesized in bulk, where both monomers are mixed at the beginning of the reaction. Mechanical and other tests showed that these polymers are micro-phase separated like their linear analogs and they have comparable, thermal and mechanical properties. [47-49]

In this study we continued our efforts on understanding the effect of reaction procedure used on the structure and properties of the highly branched polymers formed. As will be discussed later in detail, we have demonstrated both by modeling studies and experiments that slow addition of  $A_2$  on  $B_3$  or slow addition of  $B_3$  on  $A_2$  generate completely different polymer topologies. Structure-property behavior of a wide range of highly branched polyurethanes and polyureas by using oligomeric  $A_2 + B_3$  approach and different experimental procedures, such as;

- (i)  $A_2$  over  $B_3$  - slow addition of  $A_2$  type monomers/oligomers onto  $B_3$
- (ii)  $B_3$  over  $A_2$  - slow addition of  $B_3$  type monomers/oligomers onto  $A_2$
- (iii)  $A_2 + B_3$  - mixing both  $A_2$  and  $B_3$  at the beginning of the reaction

will be explained.

Modeling studies were also performed to determine the influence of reaction procedure on the polymer topology and other properties. Studies were performed by using three different synthetic procedures, similar to the experiments.

## Chapter 3

### EXPERIMENTAL

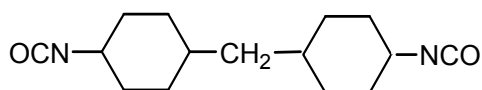
#### 3.1. Materials used

Bis(4-isocyanatocyclohexyl)methane (HMDI) and 1,6-hexamethylene diisocyanate (HDI) were kindly provided by Bayer, Germany. Trans-1,4-cyclohexyl diisocyanate (CHDI) was purchased from DuPont and cyclohexyl isocyanate (CHI) from Aldrich. Purities of isocyanates were greater than 99.5% as determined by dibutylamine back titration method. Tris(2-aminoethyl)amine (TRIS) and  $\alpha,\omega$ -aminopropyl terminated poly(tetramethylene oxide) (PTMO) ( $M_n = 1080$  g/mol) were purchased from Aldrich.  $\alpha,\omega$ -Aminopropyl (PDMS-NH<sub>2</sub>) oligomers with molecular weights of 3200 and 10800 g/mol were obtained from Wacker-Chemie, Germany. Di and trifunctional, amine terminated polyethers; Jeffamine T-3000 (PPO with  $M_n = 3060$  g/mol), Jeffamine D-2000 (PPO with  $M_n = 2000$  g/mol), Jeffamine ED-900 (amine terminated PEO with  $M_n = 1000$  g/mol) and polyoxyalkylenetriamine (Jeffamine T-403) (TRI) ( $M_n = 440$  g/mol) were kindly supplied by Hunstman. 2-Methyl-1,5-diaminopentane (Dytek A) (DuPont), Poly(tetramethylene oxide) glycol (PTMO) with  $\langle M_n \rangle = 975$  g/mol and  $\langle M_n \rangle = 2000$  g/mol (DuPont), N-butylamine (NBA) (Aldrich), ethylene diamine (EDA) (Aldrich), dibutylamine (DBA) (Merck) HPLC grade isopropyl alcohol (IPA) (Merck), tetrahydrofuran (THF) (Merck), dimethylformamide (DMF) (LaChema) were also used. Dibutyltin dilaurate (T-12) was obtained from Air Products. 1-Butanol was purchased from LaChema (74.12 g/mol). Trimethylolpropane (TMP) (134.2 g/mol) was commercially available.

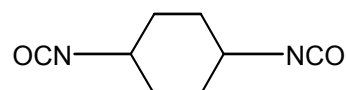
Chemical structures of the reactive A<sub>2</sub> and B<sub>3</sub> type monomers and oligomers and end-blockers are provided on Table 3.1.

**Table 3.1.** Chemical structures of reactive A<sub>2</sub> and B<sub>3</sub> type monomers and oligomers and end-blockers

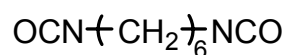
**Isocyanates:**



Bis(4-isocyanatocyclohexyl)methane  
(HMDI)

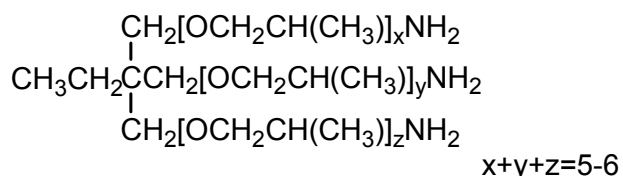


Cyclohexyl diisocyanate  
(CHDI)

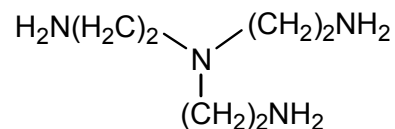


1,6-hexamethylene diisocyanate  
(HDI)

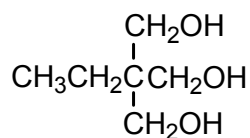
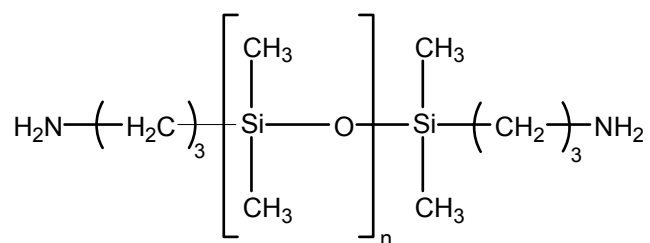
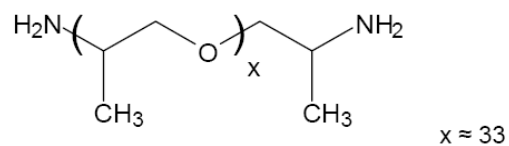
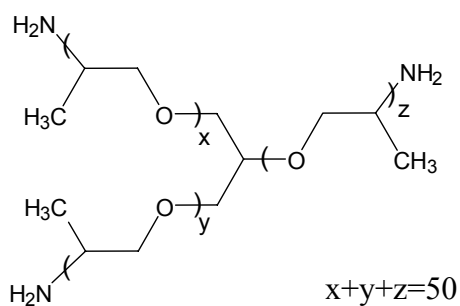
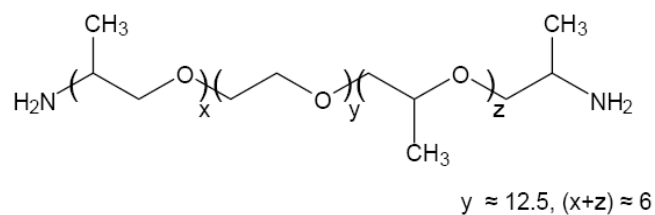
**Triamines:**



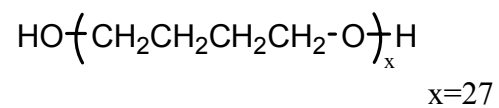
Polyoxyalkylenetriamine (Jeffamine T-403)  
(x+y+z=5-6) (Mn=440g/mol) (TRI)



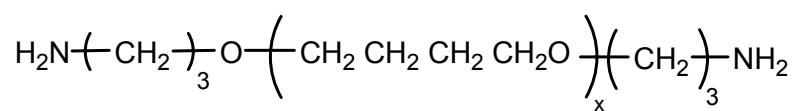
Tris(2-aminoethyl)amine  
(TRIS)

**Table 3.1. (continued)****Triol:**Trimethylolpropane  
(TMP)**Oligomers:** $\alpha,\omega$ -Aminopropyl terminated  
polydimethylsiloxane oligomer (PDMS-NH<sub>2</sub>)Jeffamine D-2000  
(PPO) Mn=2000 g/molJeffamine T-3000 (XTJ-509)  
(T-3000) (Mn=3060 g/mol)Jeffamine ED-900 (XTJ-501)  
(ED-900) (Mn=1000 g/mol)

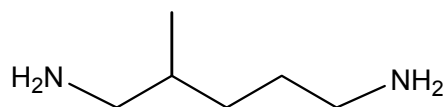


**Table 3.1. (continued)**

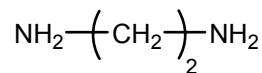
poly(tetramethylene oxide) glycol  
(PTMO)



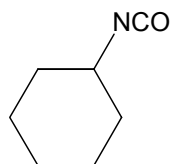
$\alpha,\omega$ -aminopropyl terminated poly(tetramethylene oxide)  
(PTMO-NH<sub>2</sub>)

**Chain extenders:**

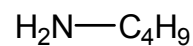
2-Methyl-1,5-diaminopentane  
(Dytek)



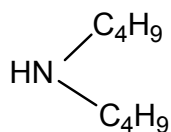
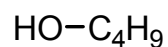
Ethylene diamine  
(EDA)

**End-blockers:**

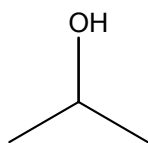
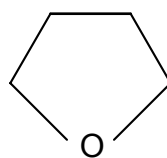
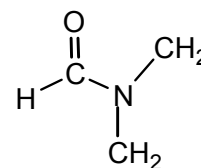
Cyclohexyl isocyanate  
(CHI)



N-butylamine  
(NBA)

**Table 3.1. (continued)****End-blockers: (continued)**dibutylamine  
(DBA)

1-butanol

**Solvents:**Isopropyl alcohol  
(IPA)Tetrahydrofuran  
(THF)Dimethylformamide  
(DMF)**3.2. Instrumentation**

Reactions were followed by FTIR spectroscopy on a Nicolet Impact 400D FTIR spectrometer, using thin films cast on KBr disks.

Stress-strain tests were conducted on an Instron 4411 using dog-bone-shaped samples (ASTM D 1708) at room temperature with a 25 mm/min cross-head speed. At least three

different samples were tested for each polymer and the average values of Young's modulus, ultimate tensile strength and elongation at break values from these three runs are reported.

TA model Q 800 instrument was used for dynamic mechanical analysis (DMA). The film samples were quenched from room temperature to  $-100^{\circ}\text{C}$  using liquid nitrogen and immediately thereafter subjected to a  $3^{\circ}\text{C}/\text{min}$  heating scan under a dry nitrogen atmosphere.  $\tan \delta$  and storage modulus,  $E'$ , data were obtained at a frequency of 1 Hz under tension.

### **3.3. Reaction procedures**

All reactions leading to the formation of highly branched polymers were carried out in 250 mL, 3-neck, round bottom flasks equipped with an overhead stirrer and addition funnel. Urea formation reactions were conducted at room temperature. Solution concentrations were about 10-12% solids, unless otherwise noted. Reactions were conducted by dropwise addition of one reactant over the other, under strong agitation. Completion of the reactions was determined by FTIR spectroscopy following the disappearance of strong isocyanate peak at  $2260\text{-}2270\text{ cm}^{-1}$ .

#### **3.3.1. Gel point determination**

All reactions were performed in 100 mL, 3-neck, round bottom flasks equipped with an overhead stirrer and addition funnel. For the determination of the effect of solution concentration and cyclization on gelation bis(4-isocyanatocyclohexyl)methane (HMDI) (MW=262.35 g/mol) was used as  $A_2$  and polyoxyalkylenetriamine (Jeffamine T-403) (TRI) (Mn=440 g/mol) as  $B_3$ . Reactions were carried out at room temperature under strong agitation. Reactants were dissolved separately in IPA at specific concentrations (varying

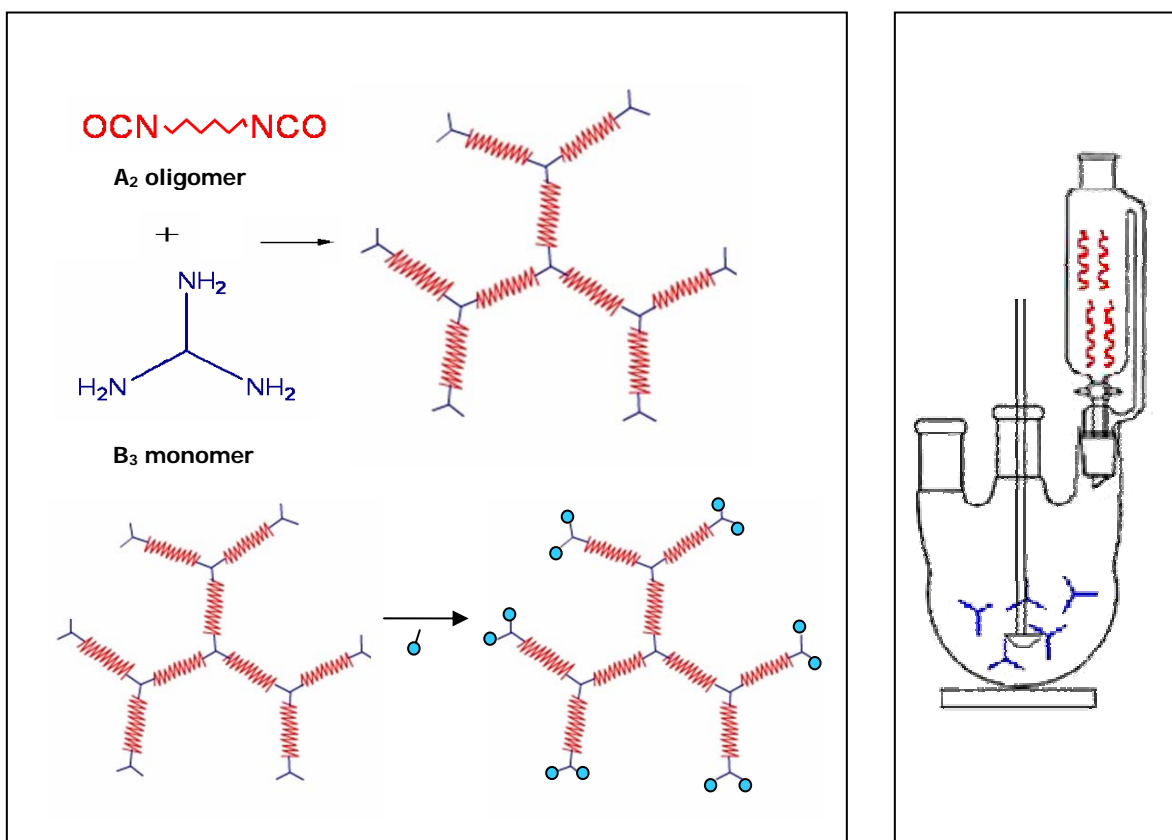
between 5 to 25% by weight of solids). Depending on the procedure to be followed ( $A_2$  over  $B_3$  or  $B_3$  over  $A_2$ ) one of the reactant solutions was introduced into the addition funnel and the other into the reaction flask. The reactant in addition funnel was then added dropwise into the reactor until the observation of gelation. Gel point was determined upon a sudden increase in the solution viscosity that was also confirmed by the formation of insoluble species in the reaction mixture. When  $A_2$  was added over  $B_3$ , TRI was placed in the reactor and HMDI into the additional funnel. Reverse was performed in the case of  $B_3$  addition over  $A_2$ .

### 3.3.2. Preparation of polydimethylsiloxane containing highly branched polymers

All reactions were conducted at room temperature. In the first step isocyanate terminated PDMS prepolymer (oligomeric  $A_2$ ) was formed. For this purpose HMDI was dissolved in IPA in the reactor. PDMS oligomer was dissolved in IPA separately and introduced into the addition funnel, and added dropwise into the reactor. Molar ratio of  $[HMDI]:[PDMS]=2.0$  was used to prepare the prepolymer. Hyperbranched polymers based on PDMS were synthesized in IPA under strong agitation where the total solid content of reaction solutions was 10, 12 or 15% by weight. During the reactions oligomeric  $A_2$  solution was added over TRIS ( $B_3$ ) solution (in the reactor) dropwise from an addition funnel ( $A_2$  over  $B_3$  addition). In some reactions  $B_3$  was added over  $A_2$  using the same set-up. A schematic representation of the  $A_2+B_3$  reaction leading to highly branched polymers and a sketch of the polymerization set-up used during the preparation of highly branched polymers is given in Figure 3.1.

Since equimolar amounts of  $A_2$  and  $B_3$  ( $[A]/[B]=2/3=0.67$ ) were used, in the case of  $A_2$  over  $B_3$  addition,  $[B]$  was always in excess and gelation was not observed during the reactions. In the case of  $B_3$  over  $A_2$  addition,  $[B_3]/[A_2]=0.55/1.0$  and  $[A]$  was always

excess. Gelation was again not observed. In  $A_2$  over  $B_3$  addition, completion of the reactions was determined by FTIR spectroscopy following the disappearance of strong isocyanate peak at  $2260\text{ cm}^{-1}$ . Then, end groups of the hyperbranched macromolecule were capped with CHI. In  $B_3$  over  $A_2$  addition, excess isocyanate end groups were capped with NBA or DBA.



**Figure 3.1.** A schematic representation of the  $A_2+B_3$  reaction and a sketch of the polymerization set-up used during the preparation of highly branched polymers.

### 3.3.3. Preparation of poly(propylene oxide) containing highly branched polymers

All reactions were performed at room temperature. First, amine-terminated trifunctional PPO oligomer (T-3000) was weighed into a reactor. Depending on the hard segment content of the polymer, different amounts of ethylene diamine (EDA) chain extender was also added and the mixture was dissolved in IPA. Diisocyanate (HMDI, CHDI or HDI), which was dissolved separately in IPA, was slowly added over this solution through an addition funnel. Equimolar amounts of A<sub>2</sub> and B<sub>3</sub> were used. End groups were capped with CHI.

### 3.3.4. Preparation of poly(ethylene oxide) containing highly branched polymers

ED-900 oligomer was dissolved in IPA and slowly added over HMDI in the reactor, which was dissolved in THF by using different stoichiometric ratios. If the polymer was chain-extended, EDA was added into the system after the completion of the prepolymer reaction. Preparation of the hyperbranched polymer was obtained by the addition of this prepolymer (A<sub>2</sub>) over TRIS (B<sub>3</sub>). TRIS was put into a new reactor and dissolved in IPA. Equimolar amounts of A<sub>2</sub> and B<sub>3</sub> were used. End-capping was obtained by the addition of CHI.

### 3.3.5. Preparation of hydroxyl terminated poly(tetramethylene oxide) (PTMO-2000) containing highly branched poly(urethane-ureas)

Isocyanate end-capped PTMO was prepared at 80°C under the catalytic action of dibutyltin dilaurate (T-12) by the bulk reaction of PTMO and HMDI. During the reactions [HMDI]/[PTMO] ratio was always 2.0. After the completion of the reactions, prepolymer (oligomeric A<sub>2</sub>) was dissolved in IPA+THF. To prepare the highly branched polymer TRIS was weighed into a clean reactor, oligomeric A<sub>2</sub> solution was introduced into the addition funnel and added dropwise into the reactor. In these systems when A<sub>2</sub> is added over B<sub>3</sub> equimolar amounts were used. However, for polymers obtained by B<sub>3</sub> (TRIS) over A<sub>2</sub>

addition  $[B_3]/[A_2]$  was 0.55/1.0. CHI was used for end-capping in the case of  $A_2$  addition over  $B_3$ , whereas NBA was used as the end-capping reagent in the case of  $B_3$  addition over  $A_2$  or ends were left uncapped.

### **3.3.6. Preparation of highly branched polyureas based on amine terminated poly(tetramethylene oxide) and TRIS or TRI**

#### **3.3.6.1. Reactions with TRIS**

For the preparation of isocyanate end capped  $A_2$  oligomers, HMDI was dissolved in IPA in the reactor. PTMO was separately dissolved in THF, introduced into the addition funnel and added dropwise into the reactor. During the reactions  $[HMDI]/[PTMO]$  ratio was always 2.0. For the preparation of hyperbranched polymers, oligomeric  $A_2$  solution was introduced into the addition funnel and slowly added over TRIS ( $B_3$ ) which was dissolved in IPA or vice versa. When  $A_2$  over  $B_3$  addition method was used equimolar amounts of  $A_2$  and  $B_3$  were reacted whereas in the addition of  $B_3$  over  $A_2$   $[B_3]/[A_2]= 0.55/1.0$ . CHI was used for end-capping in the case of  $A_2$  addition over  $B_3$ , whereas NBA was used as the end-capping reagent in the case of  $B_3$  addition over  $A_2$  or ends were left uncapped.

#### **3.3.6.2. Reactions with TRI**

In this study we first formed a urea based triisocyanate in-situ by reacting TRI with 3-fold excess HMDI. HMDI and TRI were separately dissolved in IPA. TRI solution was introduced into the addition funnel and slowly added over HMDI solution. For the preparation of hyperbranched polymers based on TRI, PTMO (oligomeric  $A_2$ ) solution that was dissolved in IPA+THF mixture was added over the triisocyanate ( $B_3$ ) solution dropwise or  $B_3$  was added over  $A_2$ . When  $A_2$  over  $B_3$  addition method was used equimolar amounts of  $A_2$  and  $B_3$  were reacted whereas in the addition of  $B_3$  over  $A_2$   $[B_3]/[A_2]=$

0.55/1.0. CHI was used as the end-blocker in the case of B<sub>3</sub> addition over A<sub>2</sub> whereas NBA was used in the case of A<sub>2</sub> addition over B<sub>3</sub> or ends were left uncapped.

### **3.3.7. Preparation of trimethylolpropane (TMP) containing highly branched polyurethanes**

To investigate the influence of B<sub>3</sub> structure and its hydrogen bonding capacity on polymer properties, homologous highly branched polyurethanes were also prepared by using TMP and compared with those polymers based on TRIS and TRI. Isocyanate end-capped PTMO (oligomeric A<sub>2</sub>) was prepared at 80°C under the catalytic action of dibutyltin dilaurate (T-12) by the bulk reaction of PTMO and HDI. During the reactions [HDI]/[PTMO] ratio was always 2.0. Prepolymer was dissolved in DMF. For the preparation of hyperbranched polymers based on TMP, prepolymer (oligomeric A<sub>2</sub>) solution was slowly added over TMP solution (B<sub>3</sub>) which was also dissolved in DMF. When A<sub>2</sub> over B<sub>3</sub> addition method was used equimolar amounts of A<sub>2</sub> and B<sub>3</sub> were reacted whereas in the addition of B<sub>3</sub> over A<sub>2</sub> [B<sub>3</sub>]/[A<sub>2</sub>]= 0.55/1.0. A<sub>2</sub>+B<sub>3</sub> method was also used where prepolymer solution was mixed with TMP solution at the beginning of the reaction. Here, either equimolar amounts of A<sub>2</sub> and B<sub>3</sub> or equimolar amounts of A and B were used. All reactions were performed at 80°C under strong agitation where the total solid percentages were 10, 15, 20, 25 and 30. No end-capping was done except one reaction, where 1-butanol was used as the end-capper.



## Chapter 4

### RESULTS AND DISCUSSION

Earlier reports have demonstrated that hyperbranched polyureas prepared by oligomeric  $A_2+B_3$  method have produced interesting materials with very good elastomeric properties. [47-49] In order to extend this technique further, and prepare novel materials with interesting properties we undertook this study, to investigate;

- (i) the influence of different polymerization procedures ( $A_2$  over  $B_3$ ;  $B_3$  over  $A_2$  or  $A_2+B_3$ ),
- (ii) influence of oligomeric soft segments with different chemical structures, such as polydimethylsiloxane, poly(ethylene oxide), poly(propylene oxide) and poly(tetramethylene oxide),
- (iii) influence of chain extension with low molecular weight organic diamines, and
- (iv) effect of using an oligomeric  $B_3$ , instead of oligomeric  $A_2$

on the structure-property behavior of segmented, highly branched polyurethanes, polyureas and polyurethaneureas.

Experimental studies started with gel point determination reactions and investigation of solution concentration on gel point. As discussed in the literature review, hyperbranched polymers prepared by  $A_2 + B_3$  method form a gel at a critical conversion, which can be determined by theoretical calculations. In order to obtain soluble, thermoplastic highly

branched polymers, it is important to determine this gel conversion and stop the reaction before gel formation. Gel point determination was performed by using HMDI and TRI in IPA, similar to the literature. [48]

After determining the percent conversions at gel points for different synthetic procedures ( $A_2$  addition over  $B_3$  and  $B_3$  addition over  $A_2$ ) and at different solution concentrations of reaction medium, from 5 to 25% solids by weight, I started working on the preparation and characterization of highly branched polymers. During the synthesis a variety of  $A_2$  and  $B_3$  type starting materials and different synthetic methods were used.

#### 4.1. Gel point determination

As discussed earlier, Flory [20-22] developed the theory for the formation of hyperbranched or crosslinked polymers depending on the monomer functionality, stoichiometry of the monomers and extent of reaction. He also compared his results with experimental studies and showed that calculated and observed values of conversions at gel point were in very good agreement. For the polymerization of  $A_2$  monomers with  $B_3$  in bulk, he calculated the theoretical gel point conversions assuming all A and B functional groups are chemically equivalent in reactivity and no cyclization or side reactions occurred during the reactions. He demonstrated that;

$$\alpha_c = \frac{1}{f-1} \quad (1)$$

$$\alpha_c = \frac{r p_A^2 \rho}{1 - r p_A^2 (1 - \rho)} \quad (2)$$

where ( $\alpha$ ) is the branching coefficient (probability that a functional group of a branch unit at the end of a polymer chain segment leads to another branch unit), ( $\alpha_c$ ) is the critical branching coefficient for gel formation, ( $f$ ) is the functionality of the branched units, ( $p_A$  and  $p_B$ ) are the extent of reaction for A and B type reactive groups, ( $\rho$ ) is the ratio of B groups on branch units to all B groups in the reaction mixture, and ( $r$ ) is the ratio of the A groups to that of B groups. As Flory showed in his studies, when  $\alpha < \alpha_c$ , gel formation is impossible, but it may be possible when  $\alpha > \alpha_c$  [20].

For an  $A_2+B_3$  system, where equimolar amounts of  $A_2$  and  $B_3$  are initially present in the reaction mixture;  $f=3$ ,  $\alpha_c=1/2$  and  $r=2/3$ . Since all A groups are on branching units ( $B_3$ )  $\rho=1$ . Then Eq. (2) becomes:

$$\alpha_c = r p_A^2 = \frac{p_B^2}{r} \quad (3)$$

As demonstrated in a previous study by Yilgör and co-workers [48], substituting the values of  $\alpha_c=1/2$  and  $r=2/3$  in Eq. (3),  $p_A$  and  $p_B$  are calculated as 0.866 and 0.577, respectively. This shows that in an  $A_2+B_3$  system, where equimolar amounts of  $A_2$  and  $B_3$  are initially present in the reaction mixture, the gelation will take place when 57.7% of the  $B_3$  monomer or 86.6% of the  $A_2$  monomer has reacted. If however, the stoichiometry of A groups and B groups are equal ( $r=1$ ), then theoretically,  $p_A=p_B=0.707$  at the gel point.

It is possible to apply this theoretical work to slow addition of  $A_2$  monomer onto a large excess of  $B_3$ . In this case, each B group would be found in one of two possible states: (1) the B group is on an unreacted  $B_3$  monomer, or (2) the B group has reacted with an  $A_2$ , which has also reacted with another  $B_3$ . Then, the branching coefficient  $\alpha$  will be the conversion of  $B_3$ , which is denoted as  $p_B$ . For the limit of slow  $A_2$  addition, conversion of

$A_2$  can be defined as  $p_A=3/2p_B$ , which is the molar percent of  $A_2$  added into the reactor when compared with the number of moles of  $B_3$  present in the reactor. Since the critical branching coefficient at gel formation is 0.50,  $p_B$  will be 0.50 and  $p_A$  will be 0.75 at this point. In the same manner, when  $B_3$  is added slowly onto  $A_2$  monomer  $p_B$  will be 0.75 and  $p_A$  will be 0.50.

**Table 4.1.** Theoretical conversion of  $A_2$  monomer for different polymerization methods

Method of polymerization	$p_A$
$A_2+B_3$	0.86
$A_2$ over $B_3$	0.75
$B_3$ over $A_2$	0.50

Experimental results on the determination of the gel point in the preparation of hyperbranched poly(urethane urea)s for slow addition of  $A_2$  over  $B_3$  have been reported [48]. In this study HMDI ( $A_2$ ) was slowly added over TRI ( $B_3$ ) at different solution concentrations varying from 5% to 25% solids, where IPA was the reaction solvent. It is important to understand the influence of solvent concentration on gelation and cyclization during the polymerization. In this project, reactions performed in the previous study [48] were repeated. In addition, gel points were also determined for the slow addition of  $B_3$  over  $A_2$ . Gel points were identified by a sudden increase in the solution viscosity that was also confirmed by the formation of insoluble species in the reaction mixture.

Theoretically, in a bulk reaction gel formation is expected to take place at 75% conversion of  $A_2$  according to the calculations of Flory for  $A_2$  over  $B_3$  reactions. However, when solution reactions are performed Flory's theory cannot be used. As shown in Table 4.2., at highest solution concentration of 25% solids that we have tried, when  $A_2$  is added over  $B_3$ , the gelation took place at 82.3% of  $A_2$  addition, which is much higher than 75% predicted

by Flory. As tabulated on Table 4.2., in the second column, as the concentration of the reaction medium was decreased higher differences between the theoretical and experimental results were observed. These differences indicate substantial amount of cyclization during the reactions, which was also reported by others [48]. At 5% solution concentration no gelation was observed. These results are comparable to those published by others [48]. In the case of slow addition of B<sub>3</sub> over A<sub>2</sub>, gel point conversions were quite different than that of A<sub>2</sub> over B<sub>3</sub>. When reaction medium had a concentration of 25% solids, gelation took place at 67.2% conversion, much lower than that of Flory's prediction (75%) and also much lower than that of A<sub>2</sub> over B<sub>3</sub> addition (82.3%). Similar to A<sub>2</sub> addition over B<sub>3</sub> procedure, in B<sub>3</sub> over A<sub>2</sub> addition also when the solution concentration decreased, conversion at gel point increased due to cyclization reactions. At 5% solution concentration no gel formation was observed in B<sub>3</sub> over A<sub>2</sub> addition reactions, either. For reactions carried out at identical solution concentrations, gel points obtained for slow addition of B<sub>3</sub> over A<sub>2</sub> was always much smaller than that of slow addition of A<sub>2</sub> over B<sub>3</sub> as clearly shown on Table 4.2. This prompted us to perform modeling studies, in order to better understand this phenomenon.

**Table 4.2.** Influence of the concentration of reaction medium on gel point in HB polyureas formed by the slow addition of HMDI over TRI in IPA and vice versa at room temperature.

<b>Solution concentration by weight(%)</b>	<b>(A<sub>2</sub> over B<sub>3</sub>) A<sub>2</sub> added at gel point(%)</b>	<b>(B<sub>3</sub> over A<sub>2</sub>) A<sub>2</sub> consumed at gel point(%)</b>
5	no gel	no gel
7.5	120.5	102.6
10	109.4	86.5
15	97.2	84.8
20	89.9	81.3
25	82.3	67.2

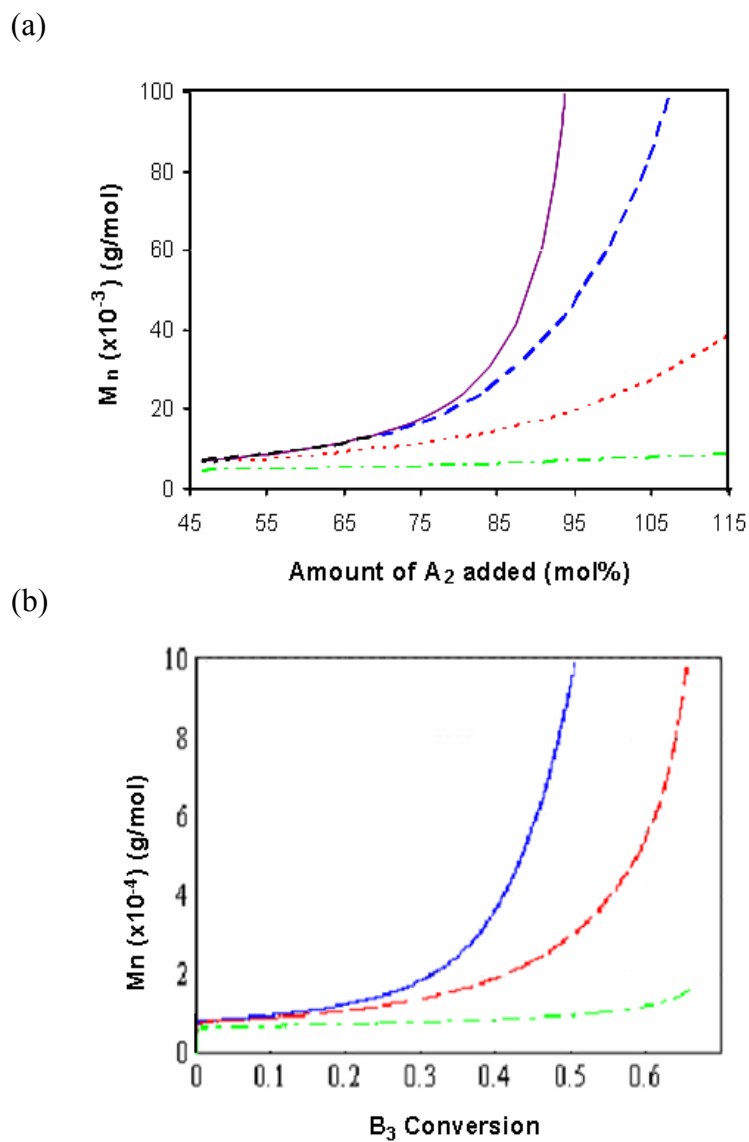
Flory's calculations are applied under the assumption that no cyclization occurs which is not realistic especially in solution polymerizations. For that reason, Monte-Carlo (MC) simulations were done at Georgia Tech by Martha Gallivan and Cihan Oguz as an alternative to the theoretical results of Flory. In this simulation slow  $A_2$  addition onto a large excess of  $B_3$  or vice versa were applied and molecular weight evolution was examined taking into account cyclization effect. By this way a better understanding of the influence of reaction conditions on the development of the molecular structure and molecular weight as well as the determination of the gel point during the preparation of hyperbranched poly(urethane urea) copolymers through  $A_2+B_3$  approach can be achieved.

Simulations were carried out assuming different cyclization ratios of 0 (no cyclization), 0.01, 0.1 and 1 (complete cyclization). Simulations started with the addition of an  $A_2$  monomer to the system. An unreacted B group is then selected, and is reacted with one of the two A groups. Each unreacted B group in the system has an equal probability of being selected, independent of molecular structure. In the third step, the remaining A group is selected with another B group. If there is no cyclization then the A group and the B group must be selected from different molecules where each B group has the same probability of selection.

In case where cyclization is taken into account; an A group and a B group in the same molecule may react, but the selection probability for each B group is not equal. Instead, there is one selection probability for each B group in the same molecule as the A group, and a different probability for each B group not in that molecule. Selection probabilities are calculated from rates, using the Kinetic Monte Carlo simulation algorithm. Calculations were done for a 1000X1000 ( $A_2XB_3$ ) system.

Fig 4.1 shows the Monte Carlo simulation results on the development of number average molecular weights as a function of  $A_2$  addition on  $B_3$  (a) and  $B_3$  addition on  $A_2$  (b). In these calculations average molecular weights of  $A_2$  and  $B_3$  were taken as 2500 and 440 g/mol, respectively. From these figures, it can clearly be observed that gelation takes place at lower conversions in the case of  $B_3$  over  $A_2$  addition. The growth in the number average molecular weight is limited when there is high level of cyclization, which is expected. When there is 100% cyclization very low molecular weight products are obtained. However, at moderate and low level of cyclization ratios, there is still substantial growth of molecular weight in the highly branched polymers formed. Thus, cyclization effects both the conversion at the gel point and also the average molecular weight of the intermediates and polymers formed.

The results of theoretical calculations, Monte Carlo simulations and experimental studies all suggest that an optimum solution concentration and conversion can be found to prepare highly branched polymers with low levels of cyclization and relatively high molecular weights without gelation. For that reason in our studies we selected 10-12% solid concentration to the right solution concentration to meet these requirements. When Table 4.2 is closely examined it will be seen that at 10% solution concentration gelation takes place at 109.4%  $A_2$  addition or 57.7%  $B_3$  addition (86.5%  $A_2$  consumption). Based on these experimental studies on gel point determination, all reactions were performed at 1:1 ( $A_2:B_3$ ) ratio when  $A_2$  is added over  $B_3$  and 0.55:1.0 ( $B_3:A_2$ ) ratio when  $B_3$  is added over  $A_2$ .



**Figure 4.1.** Development of number average molecular weight as a function of  
(a) amount of  $A_2$  added for the addition of  $A_2$  over  $B_3$  and  
(b)  $B_3$  conversion for the addition of  $B_3$  over  $A_2$   
(—) no cyclization (---) 1% cyclization, (---) 10% cyclization, (-.-) 100% cyclization.



#### 4.2. Polydimethylsiloxane (PDMS) containing highly branched polyureas

There are no reports in the literature that describes the preparation of highly branched segmented polyureas that are based on PDMS soft segments. Our interest in PDMS has been its unique combination of properties, such as its; (i) extremely low glass transition temperature and chain flexibility, (ii) very low surface energy and surface activity, (iii) excellent gas permeability, (iv) good UV and thermal stability, and (v) commercial availability of functionally terminated oligomers. Highly branched polymers based on PDMS could be used directly or can be blended with other systems and used as surface modifiers, in applications such as specialty paints and coatings, biomaterials and membranes.

Table 4.3 gives a detailed list of PDMS containing highly branched polyureas prepared by using A<sub>2</sub> over B<sub>3</sub> or B<sub>3</sub> over A<sub>2</sub> method. As shown in Table 4.3 in the preparation of highly branched polyureas two different PDMS oligomers with number average molecular weights of 3200 and 10800 g/mol were used together with TRIS as (B<sub>3</sub>). Polymers prepared by A<sub>2</sub> over B<sub>3</sub> method were end capped with CHI whereas those prepared by B<sub>3</sub> over A<sub>2</sub> method were end capped by DBA, to increase their hydrogen bond content and to improve their mechanical properties. In one case (SC-55) a short diamine (2-methyl-1,5-diaminopentane or DYTEK) was also used as a chain extender and in another case (SC-122), an amine terminated PPO oligomer (2000 g/mol) was used in addition to PDMS oligomers to prepare a polyether-PDMS-polyurea terpolymer with improved properties. Both reactions were performed in IPA as the reaction solvent at a solid content of 10-15% by weight.

**Table 4.3.** Chemical compositions and various properties of PDMS based HB polyureas

Name	PDMS	End cap.	% Hard sgm.	% Solids	Remarks	Method
SC-26	PDMS-3200	DBA	20.1	10	Low strength film	B <sub>3</sub> over A <sub>2</sub>
SC-29C	PDMS-3200	CHI	20.6	10	Low strength film	A <sub>2</sub> over B <sub>3</sub>
SC-30	PDMS-10800	-	-	15	Gelation	A <sub>2</sub> over B <sub>3</sub>
SC-31	PDMS-10800	CHI	7.2	10	Low strength film	A <sub>2</sub> over B <sub>3</sub>
SC-55	PDMS-10800 +DYTEK	CHI	10.0	12	Rigid and opaque film	A <sub>2</sub> over B <sub>3</sub>
SC-120B	PDMS-3200	NBA	16.6	10	Low strength film	B <sub>3</sub> over A <sub>2</sub>
SC-122	PDMS-3200 +PPO-2000	CHI	23.4	10	Low strength film	A <sub>2</sub> over B <sub>3</sub>
SC-124	PDMS-3200	CHI	20	10	Low strength film	A <sub>2</sub> over B <sub>3</sub>
SC-129	PDMS-3200	DBA	17.2	10	Low strength film	B <sub>3</sub> over A <sub>2</sub>

All hyperbranched polymers synthesized by using PDMS oligomer had fairly low tear strengths, which is typical for PDMS polymers. SC-30 was synthesized with 15% concentration where PDMS-10800 is used. Gelation occurred in this reaction and then same reaction was performed at 10% concentration, without gelation where a nice film was obtained. Film of SC-55 where DYTEK was used was very rigid and opaque, clearly displaying the influence of chain extension. *We believe, this is the first attempt, where a chain extender is used during the preparation of highly branched polymers.* Since they displayed poor tear strengths, no mechanical tests were done on the polymers listed in Table 4.3. However as we examine the films it is easily seen that they have fairly low mechanical strengths. For linear polymer containing silicones, it was shown that very nice microphase separation occurs due to very non-polar nature of PDMS oligomers and polar

isocyanates. [50, 51]. We believe poor mechanical properties in highly branched PDMS-ureas may be due to incomplete microphase separation, when compared with their linear analogs. Synthetic variables and compositions of these interesting systems need to be optimized in order to obtain good physicochemical properties. They may be used as surface modifying additives for polyurethanes.

### 4.3. Poly(propylene oxide) containing highly branched polyureas

So far, as the name implies, in oligomeric  $A_2+B_3$  approach, the oligomeric component was always  $A_2$ . In this study, for the first time an oligomeric  $B_3$ , a trifunctional, amine terminated polyether oligomer (Jeffamine T-3000), with an average arm length of 1000 g/mol was reacted with difunctional HMDI, HDI or CHDI and EDA (chain extender) for the investigation of the effect of the chain extender in mechanical properties of the hyperbranched polyureas. Chemical compositions of these polymers are provided on Table 4.4. IPA was used as the solvent, where solution concentrations were kept 10% in all reactions. DMF was used as the reaction solvent where CHDI was used as the diisocyanate. All reactions were performed by the slow addition of  $A_2$  over  $B_3$  and the amine chain ends were capped with CHI in every case.

**Table 4.4.** Compositions, hard segment contents and appearance of a trifunctional oligomeric PPO Jeffamine T-3000 based HB polyureas

Name	$A_2$	% Hard sgm.	Remarks
SC-37B	HMDI+EDA	17.9	Nice film
SC-37	HMDI+EDA	25.4	Nice film
SC-38	HDI+EDA	14.8	Inhomogenous film
SC-39A	HDI+EDA	11.9	Very brittle film
SC-39B	HDI+EDA	10.5	Very brittle film
SC-43	CHDI	8.7	Brittle film

When HDI and CHDI were used as the diisocyanates, we had some solubility problems during the reactions and as a result, films obtained were either inhomogeneous or brittle. However nice, elastomeric films were obtained when HMDI was used. Table 4.5 shows the chemical compositions and Table 4.6 shows the tensile properties of these polymers with code names SC-37B and SC-37, which had different amount of chain extenders in their backbones.

**Table 4.5.** Chemical compositions of T-3000 based chain-extended HB polymers

Name	Method	T-3000 (g)	HMDI (g)	EDA (g)	CHI (g)	HS (%)
SC-37B	A <sub>2</sub> over B <sub>3</sub>	6.121	1.067	0.131	0.137	17.9
SC-37	A <sub>2</sub> over B <sub>3</sub>	6.121	1.585	0.242	0.262	25.4

**Table 4.6.** Tensile properties of T-3000 based chain-extended HB polymers

Name	Method	Urea hard segment (%)	Tensile stress (MPa)	Elastic modulus (MPa)	Elongation (%)
SC-37B	A <sub>2</sub> over B <sub>3</sub>	17.9	1.45	2.0	105
SC-37	A <sub>2</sub> over B <sub>3</sub>	25.4	3.50	8.2	190

As the amount of hard segment in the polymer increases from 17.9% to 25.4% by weight, with the incorporation of the chain extender (SC-37B versus SC-37), the elastic modulus and the tensile strengths also increase, as expected. Ultimate tensile strength for SC-37B, which contained 17.9% urea hard segment, was 1.45 MPa, more than twice of the tensile stress of the other polymer that contained 25.4% hard segment by weight. Modulus increased from 2.0 MPa to 8.2 MPa, and very interestingly elongation at break also increased from 105% to 190% for polyurea containing higher amount of hard segment. In

spite of fairly high urea contents, tensile strengths of these HB polymers were not very high. This we believe is mainly due to branched PPO structure giving rise to fairly high extent of phase mixing between PPO and the urea groups.

#### 4.4. Poly(ethylene oxide) containing highly branched polymers

PEO (polyethylene oxide) is a water soluble oligomer, which yields fairly hydrophilic polyurea copolymers. During the synthesis ED-900 oligomer was end-capped with HMDI which was followed by the addition of this prepolymer onto TRIS. EDA (chain extender) was also added in one case. Chemical compositions of PEO based HB polymers are provided on Table 4.7. All reactions were performed by slow addition of oligomeric A<sub>2</sub> over B<sub>3</sub> and in one case reactive amine ends were capped with CHI. Although they had fairly high urea hard segment contents of 40 to 50% by weight, unfortunately, all ED-900 based HB polyureas resulted in sticky films. This we believe is due incomplete phase separation between PEO and urea groups in these HB architectures.

**Table 4.7.** Chemical compositions of PEO (Jeffamine ED-900) based HB polyureas

Name	Method	HMDI (g)	ED-900 (g)	EDA (g)	TRIS (g)	CHI (g)	HS (%)	Remarks
SC-44	A <sub>2</sub> over B <sub>3</sub>	2.105	4.014	-	0.590	-	40.2	Sticky film
SC-50	A <sub>2</sub> over B <sub>3</sub>	2.101	4.015	-	0.600	0.511	44.4	Sticky film
SC-52	A <sub>2</sub> over B <sub>3</sub>	2.392	3.018	0.194	0.453	-	50.2	Sticky film

#### 4.5. Hydroxyl terminated poly(tetramethylene oxide) (PTMO) containing highly branched poly(urethane ureas) (PUU)

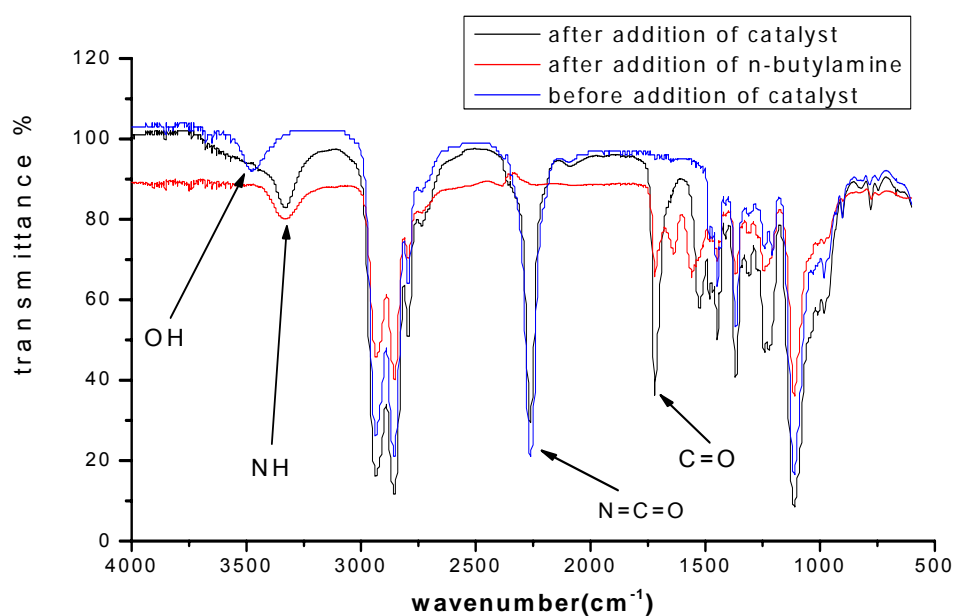
In this part of the study two different hyperbranched poly(urethane ureas) were synthesized by reacting isocyanate (HMDI) end-capped PTMO oligomers with a molecular weight of 2000g/mol with TRIS (B<sub>3</sub>) by using two different procedures as shown in Table 4.8. Both reactions were carried out in IPA and THF mixture at 10% solids and both polymers were properly end-capped.

**Table 4.8.** Chemical compositions of PTMO-2K based HB poly(urethane ureas) synthesized by A<sub>2</sub> over B<sub>3</sub> and B<sub>3</sub> over A<sub>2</sub> method

Method	PTMO 2K (g)	HMDI (g)	TRIS (g)	NBA (g)	CHI (g)	HS (%)	Remarks
A <sub>2</sub> over B <sub>3</sub> (SC-34)	7.088	1.711	0.408	--	0.285	25.3	Good film
B <sub>3</sub> over A <sub>2</sub> (SC-33)	7.012	1.889	0.262	0.251	--	25.5	Good film

FTIR spectra taken at different stages of the reaction during the preparation of SC-33 (B<sub>3</sub> over A<sub>2</sub> addition) are given in Fig 4.2. Blue spectrum was taken after mixing HMDI and PTMO in the reactor and heating to 80°C, for the prepolymer reaction, but before the catalyst addition, where a broad O—H peak centered at 3500 cm<sup>-1</sup> due to PTMO and strong NCO peak at 2270 cm<sup>-1</sup> due to HMDI can be clearly seen. Since the reaction of alcohols with aliphatic isocyanates are fairly slow and need to be run under the action of a catalyst, 1 drop of 1% T-12 (dibutyltin dilaurate) catalyst solution was added into the reaction mixture. After about 10 minutes black spectra was observed which shows the complete disappearance of O—H peak and formation of strong N—H (3350 cm<sup>-1</sup>) and C=O (1730 cm<sup>-1</sup>) absorption peaks, clearly showing the formation of the urethane linkages and

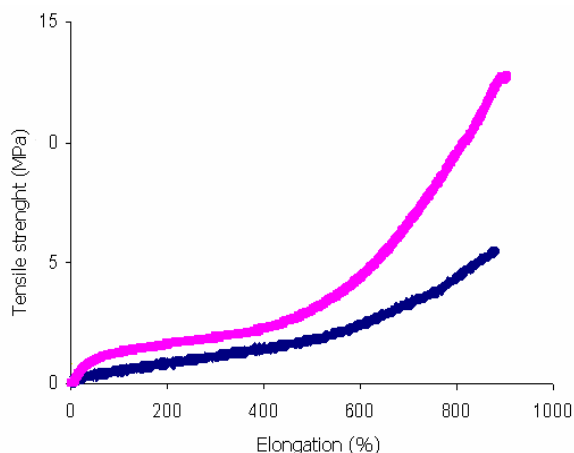
completion of prepolymer reaction. Then, the TRIS solution was added over the prepolymer solution and the HB polymer produced was end-capped with NBA. When red spectra is investigated, it is clearly seen that all isocyanate functional groups were reacted, indicating the completion of the reaction and the formation of hyperbranched poly(urethane urea) (PUU) polymer.



**Figure 4.2.** FTIR spectra of PTMO2K based HB PUU synthesis at various stages of the reaction.

Tensile behaviors of these polymers were investigated by stress-strain analysis. Fig 4.3 shows the tensile behavior of polymers SC-33 and SC-34 which had the same chemistry and same hard segment content but prepared by two different reaction procedures. In the first reaction (SC-33) TRIS was added over the isocyanate end-capped prepolymer whereas

in the second one prepolymer was added over TRIS. Table 4.9 provides a summary of the tensile results.



**Figure 4.3.** Tensile behavior of HMDI end capped PTMO2K and TRIS based HB PUUs synthesized by different polymerization methods. (—) SC-34 (A<sub>2</sub> over B<sub>3</sub> addition), (—) SC-33 (B<sub>3</sub> over A<sub>2</sub> addition)

It is very interesting to observe the strong effect of the reaction procedure on the tensile properties of the polymers formed, which have almost identical chemical compositions. *This we believe is the first report of such an effect in the literature.* While HB PUU prepared by the addition of A<sub>2</sub> over B<sub>3</sub> method (SC-34) displayed nice elastomeric properties, with a tensile strength of 12.7 MPa, Young's modulus of 5.0 MPa and elongation of 905%, HB PUU polymer with the same chemical composition but formed by the addition B<sub>3</sub> over A<sub>2</sub> (SC-33) displayed much lower mechanical properties. Ultimate tensile strength of SC-33 was only 5.5 MPa, compared to 12.7 MPa for SC-34. Its modulus was also lower than that of SC-34, however, its elongation at break value of 880% was very similar to that of SC-34. These results clearly show that HB PUU synthesized by A<sub>2</sub>



over B<sub>3</sub> addition displays better tensile properties than the one prepared by the opposite method.

**Table 4.9.** Tensile properties of HMDI end capped PTMO2K and TRIS based HB PUUs synthesized by different polymerization methods.

Method	Hard segment (%)	Tensile strength (MPa)	Elastic Modulus (MPa)	Elongation (%)
A <sub>2</sub> over B <sub>3</sub> SC-34	25.3	12.7	5.0	905
B <sub>3</sub> over A <sub>2</sub> SC-33	25.5	5.5	4.0	880

These results were fairly puzzling for us initially. However, as we will discuss in detail later, when we started modeling the topologies of the polymers formed by these two different methods, we were able to correlate this difference in properties to the topology and more importantly to the degree of branching (DB) values of the polymers formed.

#### **4.6. Amine terminated poly(tetramethylene oxide) (PTMO) containing highly branched polyureas (PUr)**

To compare the effect of differences in hydrogen bond strength of hard segments on the structure-property behavior of hyperbranched polymers PTMO based polyureas were also prepared. These polymers were based on amine terminated PTMO1K and was formed by reacting HMDI end-capped PTMO oligomers with a molecular weight of 1080g/mol with TRIS (B<sub>3</sub>), by using both A<sub>2</sub> over B<sub>3</sub> and B<sub>3</sub> over A<sub>2</sub> procedures. To understand the end-group effect on properties, some polymers were end-capped while some were not. All

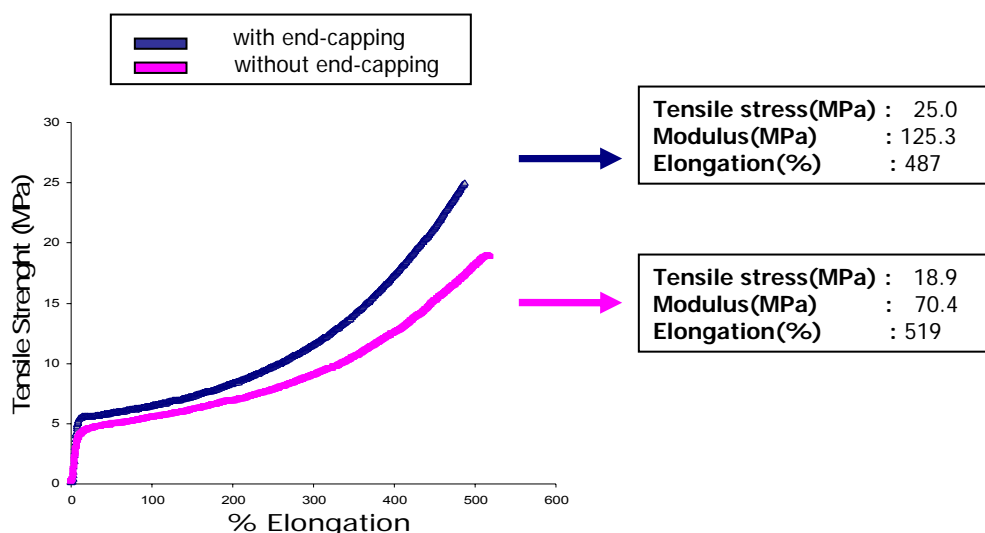
reactions were conducted in IPA+THF which contained 10% solid. A<sub>2</sub> was HMDI+PTMO1K and B<sub>3</sub> was TRIS all the time. Chemical compositions and hard segment contents of the polymers are provided on Table 4.10. All polymers were film forming.

**Table 4.10.** Chemical compositions of amine terminated PTMO1K based HB polyureas synthesized by A<sub>2</sub> over B<sub>3</sub> and B<sub>3</sub> over A<sub>2</sub> methods

Name	Method	PTMO 1K-NH <sub>2</sub> (g)	HMDI (g)	TRIS (g)	CHI (g)	NBA (g)	HS (%)
SC-49	A <sub>2</sub> over B <sub>3</sub>	3.264	1.571	0.458	0.376	-	42.5
SC-54	A <sub>2</sub> over B <sub>3</sub>	2.240	1.099	0.321	-	-	38.7
SC-71	B <sub>3</sub> over A <sub>2</sub>	3.242	1.578	0.225	-	0.137	37.4
SC-80B	B <sub>3</sub> over A <sub>2</sub>	3.240	1.574	0.222	-	-	35.7

Some of these reactions were repeated because gelation occurred due to strong H-bonding [52] after the addition of TRIS or the prepolymer. That is why these reactions were performed with very slow addition and under very strong agitation. All films formed were strong and transparent.

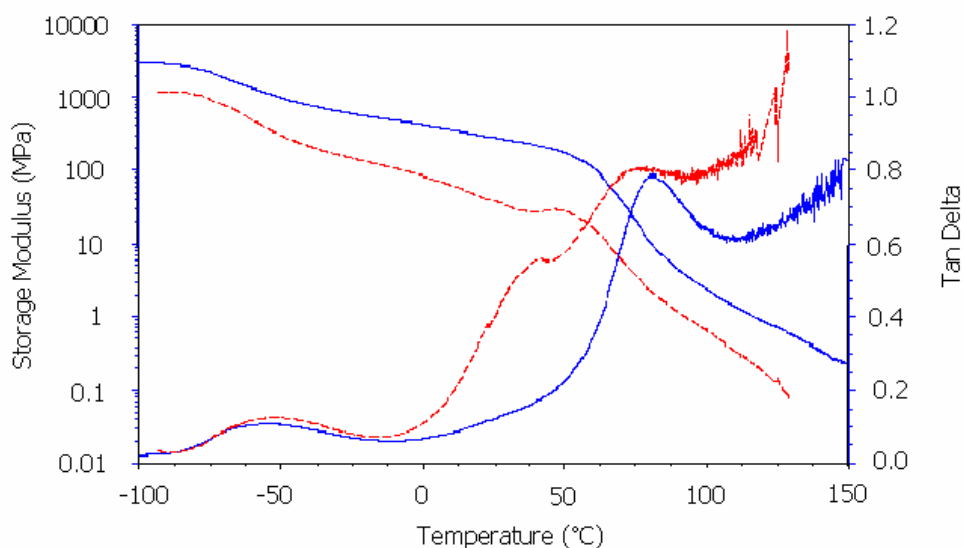
Fig. 4.4 shows the tensile behavior of SC-49 and SC-54 films, where former one was end-capped but the latter one was not. Ultimate tensile strength of the end-capped polyurea was 25.0 MPa, whereas for the uncapped polymer it was measured as 18.9 MPa. Additionally, modulus of the capped one was 125.3 MPa but it was only 70.4 MPa for the uncapped one. From these results, it can clearly be seen that end-capping strongly improves the mechanical properties in HB polyureas also, similar to poly(urethane ureas), which was discussed in the previous section.



**Figure 4.4.** Tensile behavior of PTMO1K based HB polyureas with or without end-capping. (—) SC-54, (—) SC-49.

To better understand the effect of polymerization method on the polymer morphology, dynamic mechanical behavior (DMA) of PTMO1K-NH<sub>2</sub> based HB polyureas prepared by A<sub>2</sub> over B<sub>3</sub> (SC-49) and B<sub>3</sub> over A<sub>2</sub> (SC-71) method (where both were end-capped) were investigated. Modulus-temperature and tanδ-temperature curves for these polymers are provided in Figure 4.5., from -100 to +150 °C. Interestingly, SC-49 prepared by A<sub>2</sub> over B<sub>3</sub> method, displays a much higher glassy modulus than SC-71, prepared by A<sub>2</sub> over B<sub>3</sub> method. Both polymers show a very broad glass transition region between -75 and -25 °C. Broad tanδ-temperature curves peak at -55 °C indicating the T<sub>g</sub> for the PTMO soft segment. Such broad soft segment glass transition indicates appreciable amount of mixing between soft and hard segments (i. e. ether and urea groups). Interestingly there is only a very small decrease in the storage modulus during soft segment glass transition for HB

polyureas, unlike those of HB poly(urethane ureas) reported earlier [47,48]. Rubbery plateau extends from about  $-50^{\circ}\text{C}$  to  $+50^{\circ}\text{C}$  for SC-71 and to slightly higher temperature for SC-49. This narrow rubbery plateau may be due to lower number entanglements per chain in oligomeric hyperbranched systems and difficulty in hydrogen bonding due to branching as described by Yilgor et al. [47,49], which seems to also depend on the polymerization method used (or the polymer topology produced). Rubbery plateau is followed by flow for both polymers. This is due to breaking up of the fairly weak H-bonding in the system. These DMA curves clearly indicate that these materials are melt processible, which is important for commercial applications. Linear segmented polyureas with high urea contents are not melt processible.



**Figure 4.5.** Dynamic mechanical analysis of PTMO1K-NH<sub>2</sub> based HB polymers synthesized by different polymerization methods (Blue curves=SC-49; Red curves SC-71).

Yilgor et al. [49] showed that HB poly(urethane urea) copolymers having comparable properties to their linear analogs can be synthesized where in both cases nice phase

separation is observed. In that study PTMO 2000 was used which leads to better phase mixing whereas PTMO 1K-NH<sub>2</sub> is used here.

#### 4.7. Amine terminated poly(tetramethylene oxide) (PTMO) and poly(oxyalkylene triamine) (TRI) containing highly branched polyureas

In this part of the work, we employed yet a slightly different approach during the synthesis of HB polyureas. Here we first prepared a urea based triisocyanate in-situ, by the addition of TRI into three-fold excess of HMDI, in IPA, under strong agitation, at room temperature. Later on HB polyureas were synthesized by using HMDI end-capped TRI as B<sub>3</sub> and amine terminated PTMO1K as A<sub>2</sub>. All polymers were prepared in 10% THF+IPA and were end-capped. A list of these polymers and their compositions and synthetic methods used are provided on Table 4.11. As can clearly be seen from Table 4.11, we were able to prepare soluble, HB polyureas with extremely high urea contents of 55 to 60% by weight, which is almost impossible for linear polyureas due to solubility problems. All of the polymers gave very strong films. In one case we also used a small amount of DYTEK as the chain extender, which resulted in a fairly rigid material, due to strong H-bonding.

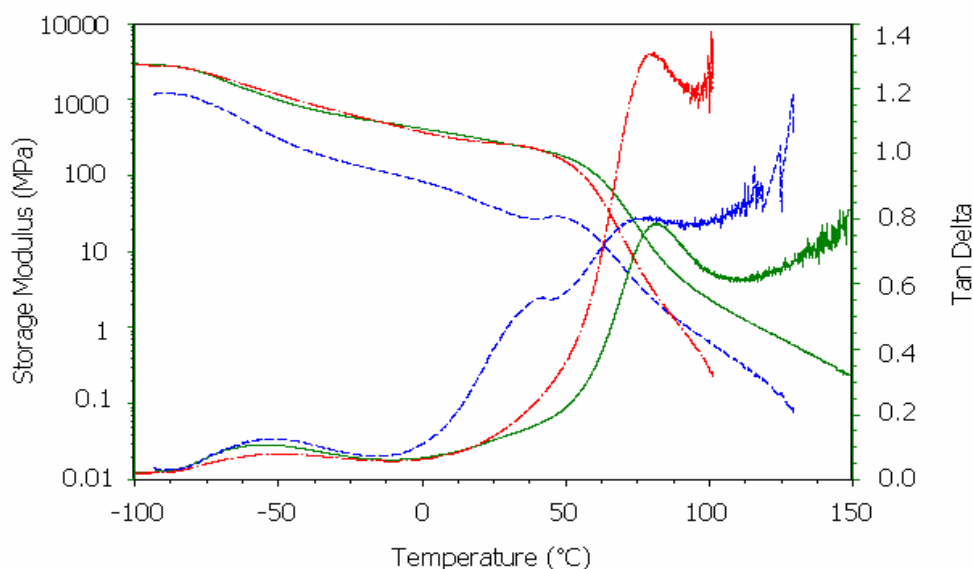
**Table 4.11.** Chemical compositions of amine terminated PTMO1K based HB polyureas prepared by using an in-situ formed triisocyanate from HMDI and TRI

Name	Method	A <sub>2</sub>	End cap.	% HS	Remarks
SC-75B	A <sub>2</sub> over B <sub>3</sub>	PTMO 1K-NH <sub>2</sub>	NBA	55.5	Strong film
SC-77	A <sub>2</sub> over B <sub>3</sub>	PTMO 1K-NH <sub>2</sub> + DYTEK	NBA	59.7	Very rigid film
SC-79	B <sub>3</sub> over A <sub>2</sub>	PTMO 1K-NH <sub>2</sub>	CHI	37.1	Strong film
SC-87	A <sub>2</sub> over B <sub>3</sub>	PTMO 1K-NH <sub>2</sub>	NBA	55.4	Strong film

**Table 4.12.** Chemical compositions of PTMO 1K-NH<sub>2</sub> based HB polymers containing TRIS and TRI which are synthesized by A<sub>2</sub> over B<sub>3</sub> and B<sub>3</sub> over A<sub>2</sub> methods

Name	Method	PTMO 1K-NH <sub>2</sub> (g)	HMDI (g)	TRI (g)	TRIS (g)	CHI (g)	NBA (g)	HS (%)
SC-49	A <sub>2</sub> over B <sub>3</sub>	3.264	1.571	--	0.458	0.382	--	42.5
SC-87	A <sub>2</sub> over B <sub>3</sub>	2.165	1.574	0.885	--	--	0.232	55.4
SC-71	B <sub>3</sub> over A <sub>2</sub>	3.242	1.578	--	0.225	--	0.031	37.4

DMA behavior of SC-87, which has 55.4% HS, was compared with those of SC-49 (42.5% HS) and SC-71 (37.4% HS) in Figure 4.6. DMA behaviors of SC-49 and SC-71 have already been discussed in the previous section. As can be seen in Figure 4.6, the modulus-temperature behavior of SC-87 is very similar to that of SC-49. The soft segment (PTMO 1K-NH<sub>2</sub>) and the diisocyanate (HMDI) are the same for both polymers. The only difference is in the structure of the triamine. Interestingly, SC-87 and SC-49 have almost identical modulus-temperature curves, although SC-87 has much higher urea content than SC-49. This is due to TRI, which is ether based and more flexible triamine compared to TRIS. Presence of ether groups also may give rise to phase mixing with the urea hard segments [50]. As a result TRI based HB polyureas needs much higher urea content (55.4%) to have similar properties as TRIS based copolymer, which has 42.5 % urea content.



**Figure 4.6.** Comparison of DMA responses of PTMO1K-NH<sub>2</sub> based HB polymers synthesized by using different triamines and different polymerization methods. (Red curves=SC-87, green curves= SC-49, blue curves=SC-71)

#### 4.8. Trimethylolpropane (TMP) containing highly branched polyurethanes

So far we have always used triamines in the preparation of HB polymers. For comparison a triol, trimethylolpropane (TMP) was also used as (B<sub>3</sub>) for the preparation of HB polyurethane copolymers. In these reactions HDI was used as the diisocyanate and hydroxyl terminated PTMO-1000 as the soft segment. During the reactions, first HDI end-capped PTMO1K was prepared as (A<sub>2</sub>). All reactions were conducted at 80°C under the action of T-12 catalyst and in DMF solutions. End-capping was only done in SC-100 with 1-butanol. MDI was also tried but it did not dissolve well so HDI was used as the diisocyanate. In one case HMDI was also used but despite the addition of high amount of catalyst and heating, reaction was very slow and no film was formed at the end of the

reaction. Polymerizations were conducted for  $A_2$  over  $B_3$  addition,  $B_3$  over  $A_2$  addition and  $(A_2 + B_3)$  - mixing both  $A_2$  and  $B_3$  at the beginning. Reactions were performed at  $A_2:B_3$  ratios of 1:1 as well as 3:2. Tables 4.13 and 4.14 provide detailed compositional data, polymerization method used, percent solids, and quality of the films formed during these HB polyurethane formation reactions, where TMP was the  $B_3$ .

**Table 4.13.** Compositional data and polymerization procedure used in the preparation of HDI, PTMO1K and TMP based HB polyurethanes.

Name	% Hard sgm.	% Solids	Remarks	Method
SC-91	29.6	10	Sticky film	$B_3$ over $A_2$
SC-93	32.7	10	Sticky film	$A_2$ over $B_3$
SC-95	32.6	10	No film formed	$A_2+B_3$
SC-96	32.6	15	Sticky film	$A_2+B_3$
SC-97	32.5	20	No film formed	$A_2+B_3$
SC-98	32.5	25	Sticky film	$A_2+B_3$
SC-99	32.5	30	Gelation	$A_2+B_3$
SC-100	31.7	10	Sticky film	$B_3$ over $A_2$
SC-104	32.6	20	Sticky film	$A_2+B_3$
SC-107	29.6	20	No film formed	$B_3$ over $A_2$
SC-109	32.6	20	No film formed	$A_2$ over $B_3$
SC-112	29.3	25	Sticky film	$B_3$ over $A_2$
SC-114	30.5	10	No film formed ( $A_2/B_3$ - 3:2)	$A_2+B_3$
SC-115	30.4	20	No film formed ( $A_2/B_3$ - 3:2)	$A_2+B_3$
SC-117	30.3	25	No film formed ( $A_2/B_3$ - 3:2)	$A_2+B_3$
SC-118	30.2	30	Sticky film ( $A_2/B_3$ - 3:2)	$A_2+B_3$
SC-125	32.6	25	No film formed	$A_2$ over $B_3$



These reactions had a different behavior than usual; no gelation occurred as the percent solid amount was increased despite using the same stoichiometry used for 10% solid concentration. In B<sub>3</sub> over A<sub>2</sub> addition and A<sub>2</sub>+B<sub>3</sub> polymerization, film was formed up to 25% solid concentration. When A<sub>2</sub>:B<sub>3</sub> ratio was 3:2, film was even formed at 30% solid concentration but not at 10%, 20% and 25%. However, when A<sub>2</sub> was added over B<sub>3</sub> film was only formed at 10% solid concentration, others gelled. All of the films formed were very weak and sticky, clearly indicating the influence of weaker hydrogen bonding between urethane hard segments as compared with urea hard segments in former HB polymers and very poor, if any microphase separation.

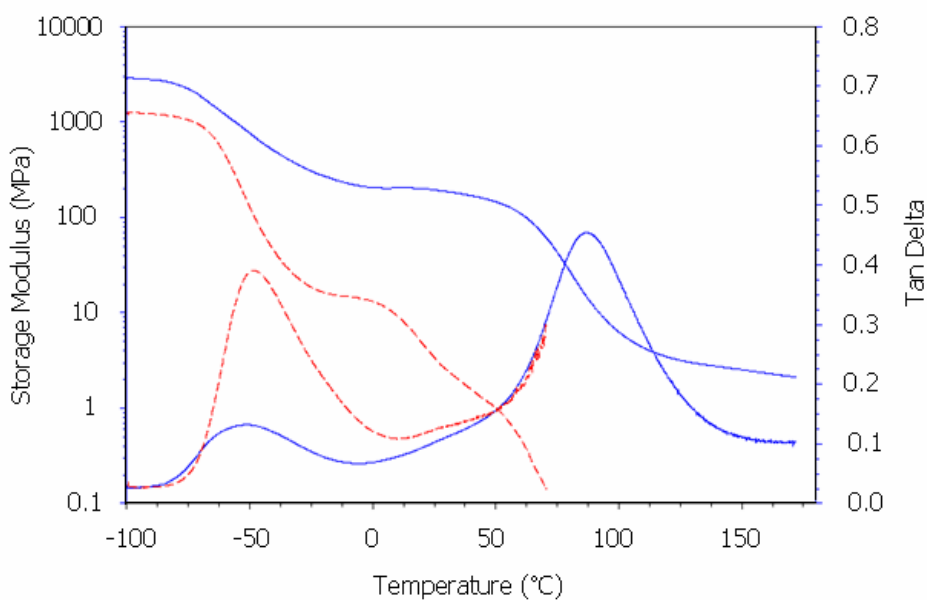
**Table 4.14.** List of all TMP based HB reactions according to polymerization method used and solid concentration. Influence of the reaction procedure.

A <sub>2</sub> over B <sub>3</sub> (1:1)	B <sub>3</sub> over A <sub>2</sub> (0.55:1.0)	A <sub>2</sub> +B <sub>3</sub> (1:1)	A <sub>2</sub> +B <sub>3</sub> (3:2)
10% no film formed	10% film	10% no film	10% no film
10% film (done slower)	10% (end-capped with but.) film	15% film	20% no film
20% no film	10% (with HMDI) no film	20% no film	25% no film
25% no film	10% film	20% film	30% film
	20% no film	25% film	
	25% film	30% gelled	

Comparison of the dynamic mechanical properties of PTMO 1K-NH<sub>2</sub> and TRIS based HB polyureas with PTMO1K-OH and TMP based polyurethanes were also performed to see the influence of hydrogen bond strength on the modulus-temperature behavior. Detailed chemical compositions of these HB polymers are provided on Table 4.15. They were both prepared by B<sub>3</sub> over A<sub>2</sub> addition method. HB urethane is based on HDI and had 29.3% hard segment content, whereas HB urea was based on HMDI and had a urea content of 35.7% by weight.

**Table 4.15.** Chemical compositions of TMP and TRIS based HB polymers

Method	PTMO1 K-NH <sub>2</sub> (g)	PTMO 1K (g)	HMDI (g)	HDI (g)	TRIS (g)	TMP (g)	HS (%)	Soln. Conc. (%)
<b>B<sub>3</sub> over A<sub>2</sub></b> (SC-80B)	3.240	--	1.574	--	0.222	--	35.7	10
<b>B<sub>3</sub> over A<sub>2</sub></b> (SC-112)	--	11.715	--	4.042	--	0.888	29.3	25



**Figure 4.7.** Comparison of DMA responses of PTMO1K-NH<sub>2</sub> + TRIS based HB polyurea (SC-80B blue curves) with PTMO1K-OH + TMP based HB polyurethane (SC-112 red curves)

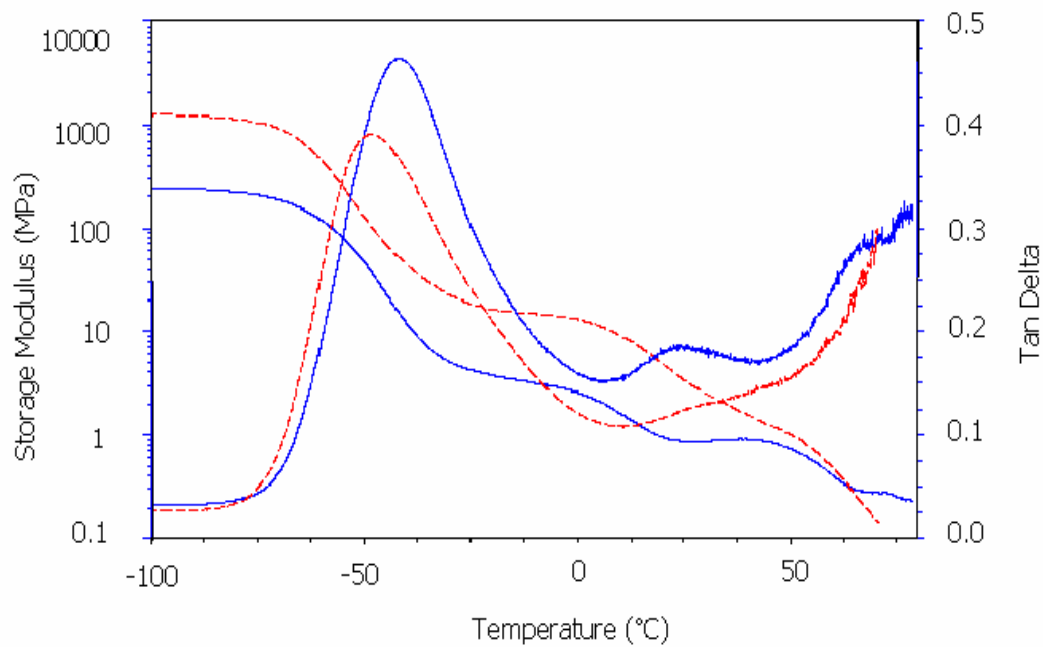
Modulus-temperature and  $\tan\delta$ -temperature curves for SC-80B (urea) and SC-112 (urethane) are reproduced in Figure 4.7. SC-80B which made a strong film starts with a higher storage modulus than SC-112 which made a sticky film. Both polymers show fairly

well defined and broad soft segment glass transitions, with fairly symmetrical  $\tan\delta$  peaks between  $-75^{\circ}\text{C}$  and  $-25^{\circ}\text{C}$ . This is followed by a short rubbery plateau, where SC-80B displays a much higher modulus than SC-112 and by the flow region, which starts around room temperature.

Influence of the reaction procedure on the DMA behavior of HB polyurethanes was also investigated. (Fig 4.8) Chemical compositions of these HB polyurethanes and their method of synthesis are provided on Table 4.16. They have comparable hard segment contents of around 30% by weight. Interestingly SC-112 displays almost an order of magnitude higher storage modulus than SC-93. SC-112 synthesized by  $B_3$  over  $A_2$  method seems to also display slightly better modulus-temperature behavior than SC-93. Since the concentration of reaction media for SC-112 was 25% solids compared to 10% for SC-93, this may be due to much less cyclization and much higher overall molecular weight of SC-112. These polymers have very short, almost no rubbery plateaus due to weaker H-bonding between polyurethanes and higher degree of phase mixing between hard and soft segments.

**Table 4.16.** Chemical compositions of TMP based HB polymers prepared by different methods

Name	Method	PTMO 1K (g)	HDI (g)	TMP (g)	HS (%)	Soln. Conc. (%)
SC-93	$A_2$ over $B_3$	3.908	1.355	0.540	32.7	10
SC-112	$B_3$ over $A_2$	11.715	4.042	0.888	29.3	25



**Figure 4.8.** Comparison of DMA responses of TMP based HB polyurethanes synthesized by different polymerization methods. (Blue curves=SC-93; Red curves SC-112).

## Chapter 5

### MODELING STUDIES

#### 5.1. Introduction

Modeling studies were performed to understand the influence of polymerization procedure on the topology, degree of branching, number and weight average molecular weight and polydispersity index of the highly branched polymers. Conventionally branched polymers are prepared by mixing and reacting desired amounts of  $A_2$  and  $B_3$  type monomers together. Recently a new method was reported, where  $A_2$  type monomer was slowly added over  $B_3$  to obtain high molecular weight HB polymers without gelation (47). During these studies, as discussed before, we also prepared polymers by the slow addition of  $B_3$  on  $A_2$ , which in some cases, produced polymers with quite different properties than the former method.

In order to better understand the differences in the topologies of polymers produced, we undertook modeling studies on three different synthetic methods for the preparation of HB polymers, which are:

- (i) slow addition of  $A_2$  over  $B_3$  denoted as  $A_2$  over  $B_3$ ,
- (ii) slow addition of  $B_3$  over  $A_2$  denoted as  $B_3$  over  $A_2$  and
- (iii) mixing  $A_2$  and  $B_3$  at the beginning of the reaction similar to the conventional approaches, which is denoted as  $A_2 + B_3$  method.

During our modeling studies no steric, size and cyclization effects were taken into account. Reactivities of A and B groups on any molecule were assumed to be exactly the same. Modeling studies on the topology development during polymerization reactions were performed by using 30  $A_2$  and 30  $B_3$  molecules, in bulk. Two-dimensional structures were formed using just a probabilistic approach. By this way, small number of molecules allowed us to easily present the distinct differences between the topologies of the polymers formed by different polymerization methods.

It is well known that in linear step-growth or condensation polymerization reactions there is cyclization, together with the formation of linear species. Amount of cyclization is higher if polymerization reactions are conducted in solution [48,53]. Cyclization may have a strong effect on the overall molecular weights of the polymers formed and as a result on their physicochemical properties.

Modeling studies were also performed by using 10  $A_2$  and 10  $B_3$ , 20  $A_2$  and 20  $B_3$  and 50  $A_2$  and 50  $B_3$  molecules. However, only those results obtained with 30+30 molecules, which we believe provides a very good representation of the polymerization process, will be given here.

In the following sections, structures formed by reacting;

- (i) 30  $A_2$  molecules with 30  $B_3$  together,
- (ii) by slowly adding 30  $A_2$  molecules over 30  $B_3$  molecules, and
- (iii) by slowly adding 30  $B_3$  molecules over 30  $A_2$  molecules will be discussed.

For the representation of the topology development, structures formed both for the addition of  $A_2$  molecules over  $B_3$  molecules and the addition of  $B_3$  molecules over  $A_2$  molecules will

be shown at various levels of  $A_2$  addition during the reactions. For number average and weight average molecular weight calculations mass of one difunctional monomer was taken as 1000 g/mol and mass of one trifunctional monomer was taken as 300 g/mol.

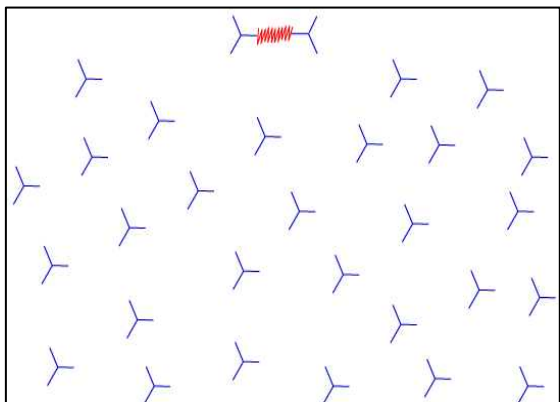
## **5.2. Stepwise topology development in slow addition of $A_2$ over $B_3$ and slow addition of $B_3$ over $A_2$ methods (30+30)**

Modeling studies were performed for the slow addition of 30  $A_2$  monomers over 30  $B_3$  monomers and 30  $B_3$  over 30  $A_2$  where final topology of the resulting structure was obtained in 30 steps. In each step one monomer was added into the system. For the representation of the topology developments not all the steps but some of them are reproduced.

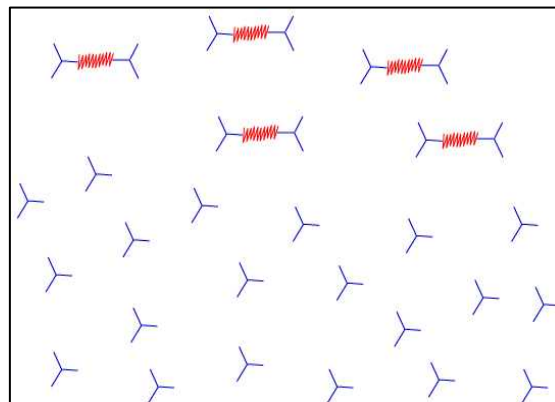
### **5.2.1. Modeling studies on topology development in HB polymers obtained by slow addition of $A_2$ over $B_3$ (30 $A_2$ + 30 $B_3$ )**

At the beginning (Step 1), there are 30  $B_3$  molecules inside the reactor. In the first step one  $A_2$  monomer is added into the system. Then, one B group is selected and reacted with one of the two A groups. Each unreacted B group in the system has an equal probability of being selected. After that, the remaining A group is reacted with another B group. Since there is no cyclization, the A group and the B group are selected from different molecules. In step 5, structures formed after the addition of 4 more  $A_2$  monomers are shown. Since there are still excess of unreacted  $B_3$  monomers, A groups are all reacted with any of the 8 B groups in the system. Since there is no cyclization each reacted B group belongs to a different  $B_3$  monomer.

Step 1:

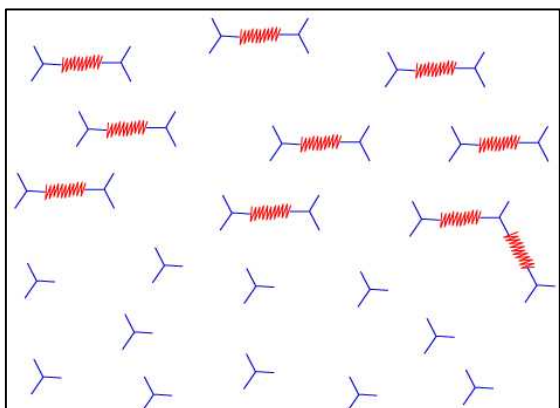


Step 5:

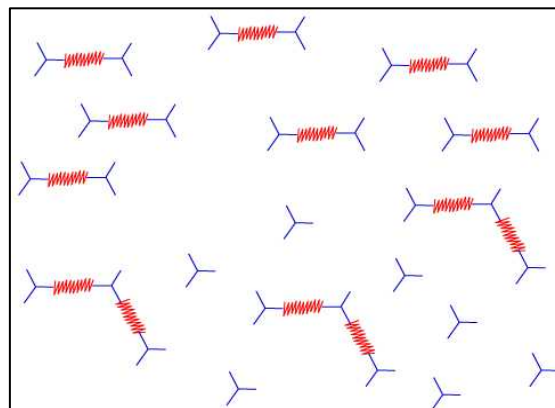


When we come to step 10, formation of  $B_3$  capped  $A_2$  molecules are continued until the number of their end groups were larger than the number of B groups belonging to  $B_3$  monomers. After the addition of 10<sup>th</sup>  $A_2$  monomer it is reacted with one  $B_3$  capped  $A_2$  and one unreacted  $B_3$  monomer. In step 13, formation of 2 more structures that formed at the end of step 10 are continued. There are 13  $A_2$  molecules added into the system and 26 A groups are reacted so far. 7  $B_3$  monomers still remain unreacted.

Step 10:



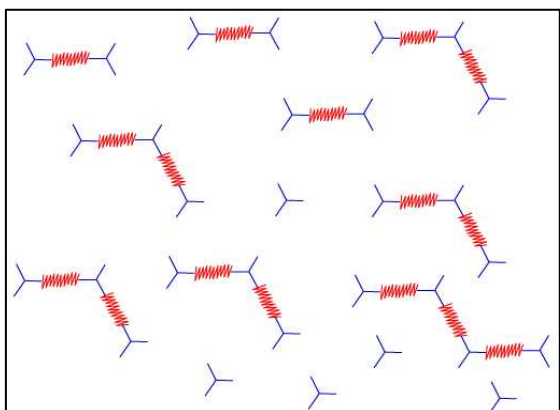
Step 13:



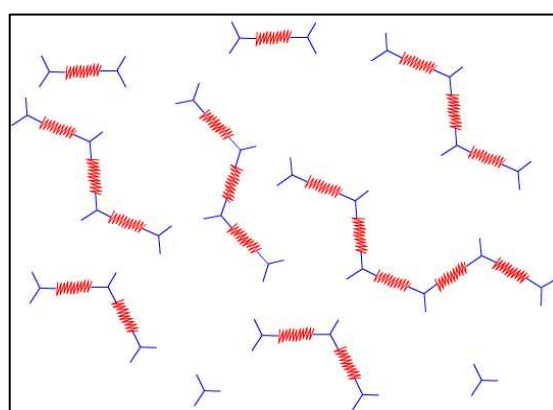


In step 16,  $B_3$  capped  $A_2$  molecules start to react with each other since the number of B groups belonging to  $B_3$  groups with one end reacted are larger than the number of B groups belonging to  $B_3$  monomers with all ends unreacted. In the same manner, longer chains are formed when we pass to step 20. Only 2  $B_3$  molecules are left unreacted and totally 20  $A_2$  molecules are reacted so far.

Step 16:

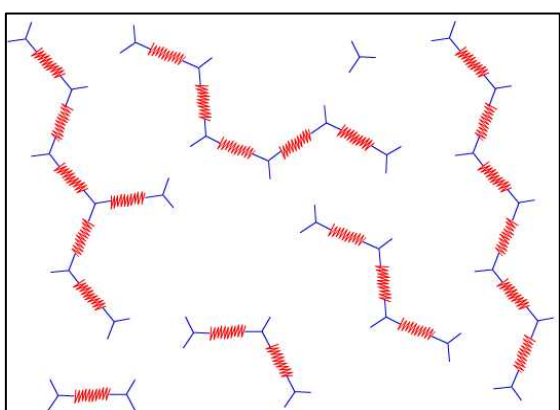


Step 20:

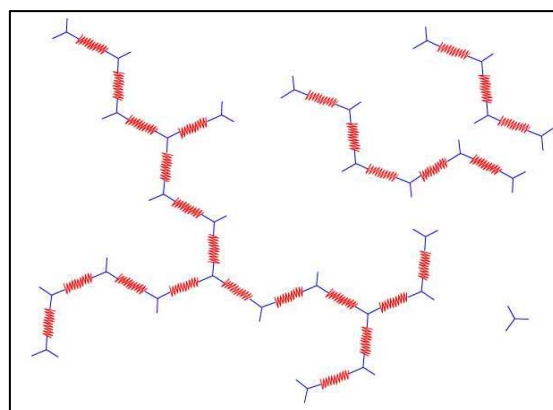


Chains having the higher statistical probability to chemically react continue linking to each other in step 23. In this step first dendritic unit is formed and one  $B_3$  molecule is left totally unreacted. In step 26 more dendritic units are formed.

Step 23:

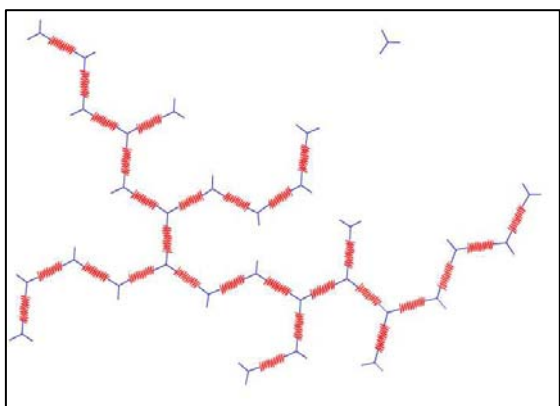


Step 26:

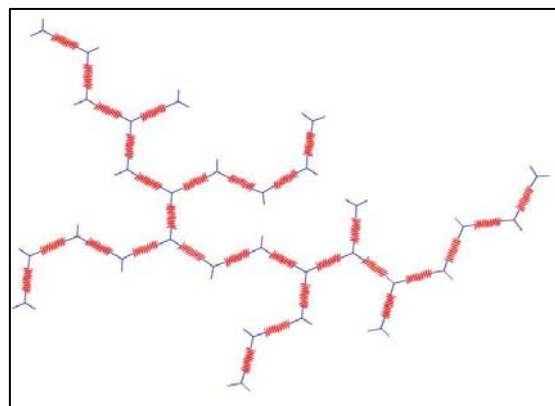


In step 28 one large molecule is formed by the reaction of three structures presented in step 26. In step 29 one more  $A_2$  monomer is added and its unreacted end is reacted with  $B_3$  monomer. Totally 29  $A_2$  monomers (58 A groups) and 30  $B_3$  monomers (58 B groups) are reacted.

Step 28:

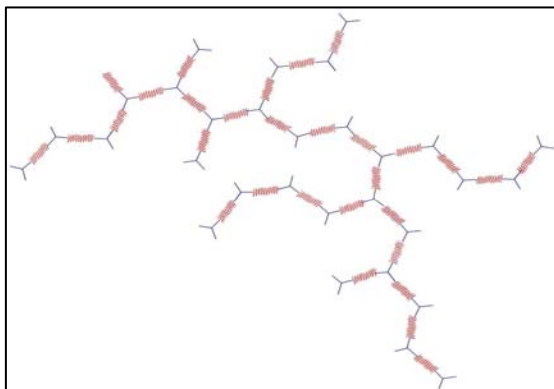


Step 29:



In the last step, last  $A_2$  monomer is added and its one end is left unreacted since there are no  $B_3$  groups left and we assumed no cyclization. At the end of the model reaction one hyperbranched polymer molecule with 7 dendritic units, 15 linear units and 8 terminal units is formed.

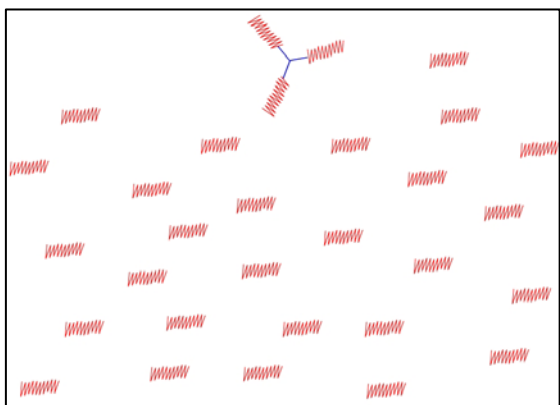
Step 30:



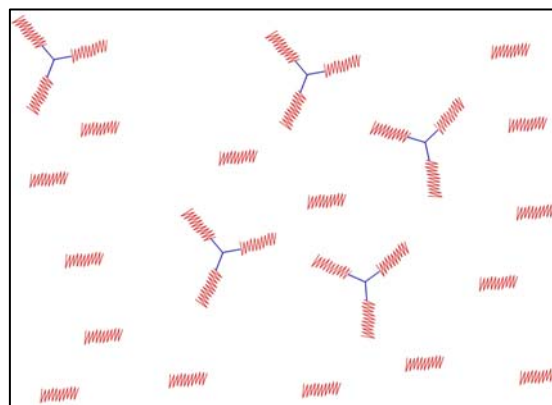
### 5.2.2. Modeling studies on topology development in HB polymers obtained by slow addition of $B_3$ on $A_2$ ( $30 B_3 + 30 A_2$ )

In the first step, one  $B_3$  is added onto 30  $A_2$  molecules that are originally present in the reactor. As soon as this first monomer is introduced into the system its functional ends groups are capped with 3 A groups in the reactor, each one belonging to a different  $A_2$  molecule. Each unreacted A group in the system has an equal probability of being selected. Since there is no cyclization, the A groups and the B groups are selected from different molecules. In step 5, totally 5  $B_3$  molecules are added and all ends of all  $B_3$  molecules are capped with A groups since still there is an excess of A molecules in the system.

Step 1:

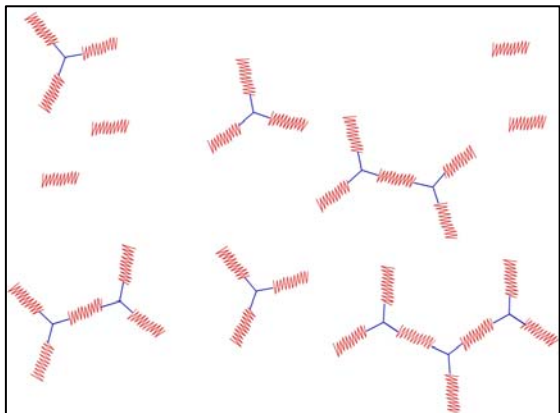


Step 5:

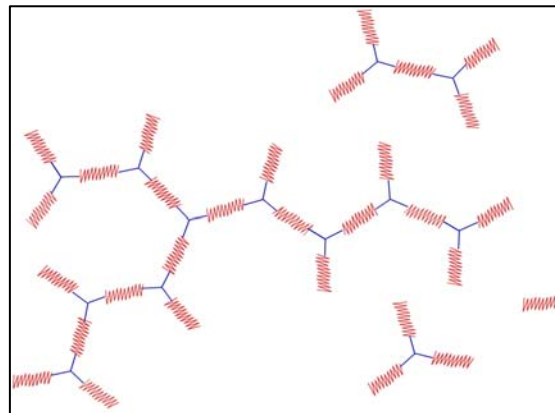


Formation of  $B_3$  molecules of which all ends are capped with  $A_2$  molecules continues until the number of A groups on these molecules are larger than the number of A groups on  $A_2$  molecules. Beginning in Step 8,  $B_3$  molecules added connects to other growing oligomer molecules inside the reactor. In step 10, statistically there are only 4  $A_2$  molecules that are left unreacted. However in the case of  $A_2$  over  $B_3$  addition, there were 11 unreacted molecules in the system. In step 13, there are totally 4 structures in the reactor where only one  $A_2$  is left.

Step 10:

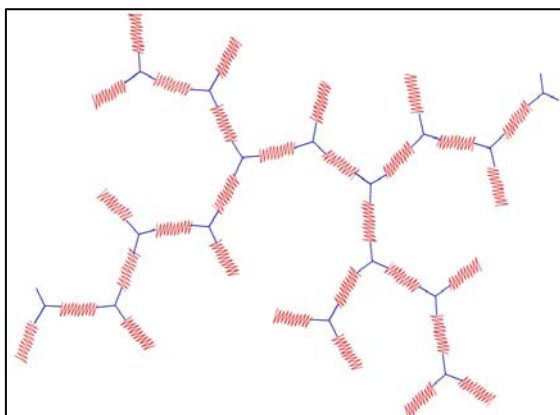


Step 13:

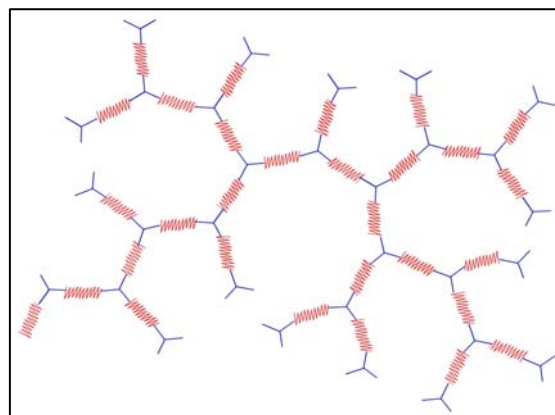


In step 15, all  $A_2$  monomers are reacted forming one large structure where all B groups are reacted with A groups. There is only one B group in this structure which is left unreacted. Starting from the addition of 16<sup>th</sup>  $B_3$  (step 16), each  $B_3$  added into the system reacts with one of the unreacted A groups on the HB molecule. When the addition of 30  $B_3$  molecules is finished a structure where all ends except one have terminal B groups is formed.

Step 16:

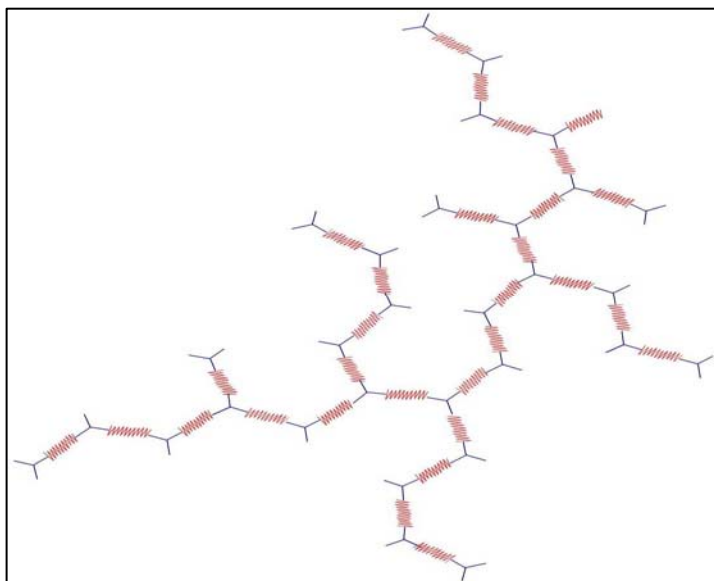


Step 30:



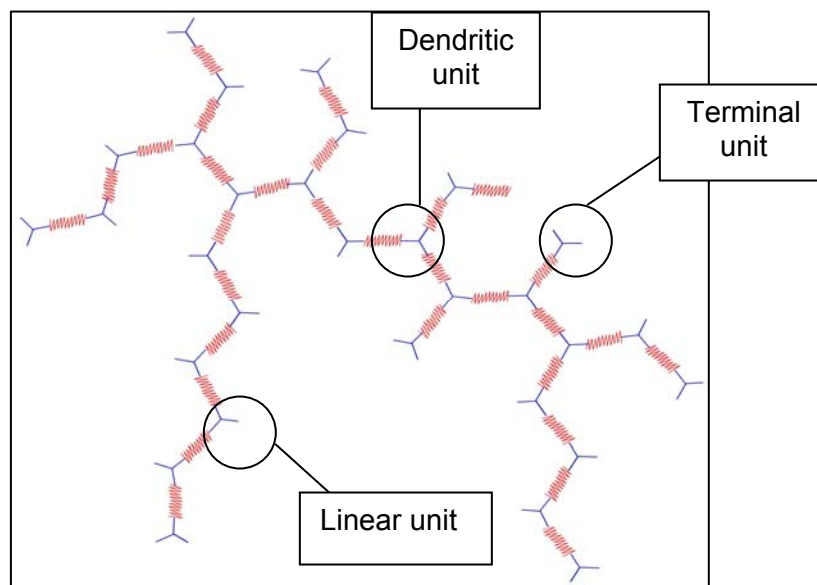
### 5.3. HB structures formed in modeling studies by using three different polymerization methods and comparison of their degree of branching

There are 7 dendritic units, 15 linear unit and 8 terminal units in the structure formed by slow addition of  $A_2$  over  $B_3$  method, in the HB polymer described above in Step 30, which is also reproduced in Figure 5.1.

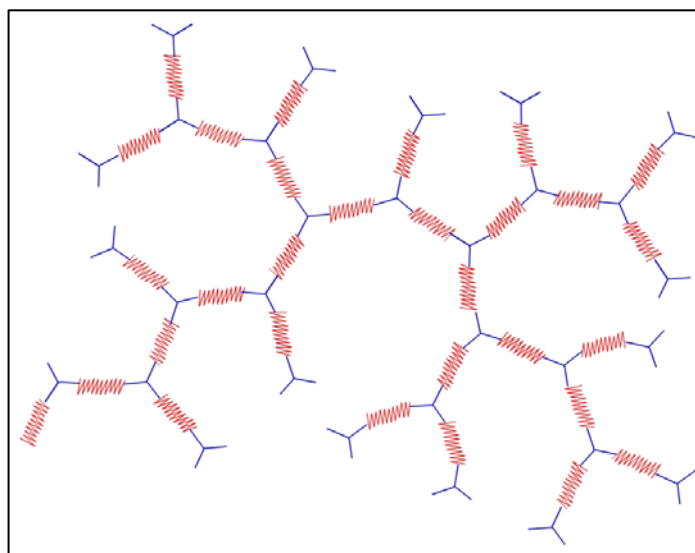


**Figure 5.1.** Topology development in slow addition of  $A_2$  over  $B_3$  method (30+30)

Interestingly, for the model reaction where  $A_2$  and  $B_3$  are both added together ( $A_2+B_3$ ) simulations gave exactly the same distribution of dendritic, linear and terminal unit distribution of 7, 15 and 8 respectively as the  $A_2$  addition over  $B_3$ . This structure is given on Figure 5.2.



**Figure 5.2.** Topology development in  $A_2 + B_3$  method (30+30)



**Figure 5.3.** Topology development in slow addition of  $B_3$  over  $A_2$  method (30+30)

When similar modeling studies were performed for the reaction system where B<sub>3</sub> is slowly added on A<sub>2</sub> the resulting highly branched polymer had 14 dendritic units, 1 linear unit and 8 terminal units, quite different that other two polymers obtained by different methods. Topology of this polymer is provided on Figure 5.3.

Degree of branching calculations were performed according to the definitions of both Frechet and Frey where,

$$DB_{\text{Frechet}} = (D+T)/(D+L+T)$$

$$DB_{\text{Frey}} = (2D)/(2D+L)$$

Degree of branching is found to be 0.97 (both by Frechet and Frey definition) when B<sub>3</sub> is added over A<sub>2</sub>, whereas it was found to be 0.50 (Frechet's definition) and 0.48 (Frey's definition) when they are mixed together or A<sub>2</sub> is added over B<sub>3</sub>. These results are provided on Table 5.1.

**Table 5.1.** Degree of branching values according to Frechet and Frey for three different polymerization methods

Method	DB (Frechet)	DB (Frey)
A <sub>2</sub> +B <sub>3</sub>	0.5	0.48
A <sub>2</sub> over B <sub>3</sub>	0.5	0.48
B <sub>3</sub> over A <sub>2</sub>	0.97	0.97

These results clearly indicate that polymerization procedure has a great effect on the topology of the resulting polymer. If  $B_3$  over  $A_2$  method is used, much higher branching ( $DB_{\text{Frechet}} = 0.97$ ,  $DB_{\text{Frey}} = 0.97$ ) is observed in the polymers formed when compared to the other methods. However, same DB results ( $DB_{\text{Frechet}} = 0.50$ ,  $DB_{\text{Frey}} = 0.48$ ) are found for  $A_2$  over  $B_3$  addition and  $A_2+B_3$  methods. In these two methods structures obtained are highly linear. Less branching may be the reason for better mechanical properties in these materials when compared to those produced by  $B_3$  over  $A_2$  method. Since there is less branching and longer linear segments, probability of making entanglements also increases. In the case of  $B_3$  over  $A_2$  addition, there will be large amount of cyclization in reality, which was not taken into account here. But still it is obvious than very different topologies are formed when different polymerization methods are utilized.

Finally, since we used very small number of monomers and assumed complete reaction, percent conversion of A functional groups was 98.3% and B functional groups was 65.6% in all three cases. Number and weight average molecular weights of all structures formed were 39,000 g/mol since only one molecule is formed (perfectly unimodal molecular weight polymer!).



## Chapter 6

### CONCLUSIONS

Gel point determination studies showed that conversion of  $A_2$  at gel point is lower in the case of  $B_3$  over  $A_2$  addition when compared to  $A_2$  over  $B_3$  addition. In polymerizations performed by  $A_2$  over  $B_3$  addition which were conducted at a solution concentration of 25% by weight gelation took place at the stoichiometric ratio  $[A_2]/[B_3]=0.823$  whereas this ratio was 0.672 in the case of  $B_3$  over  $A_2$  addition. At 5% solution concentration neither addition methods resulted in gelation, however gelation is delayed as the concentration of reaction medium decreases. Gel points found at 25% solution concentration were somewhat higher than the theoretical ratios which are probably due to increased internal cyclization. Monte-Carlo simulations also showed that as the cyclization is increased molecular weight development is decreased.

Polymers were prepared based on PDMS, PTMO, PEO, PPO soft segments with molecular weights ranging from 1000-10800 g/mol where various isocyanate and amine chemistry were used and their structure-property relationships were investigated. It was observed both by stress-strain and dynamic mechanical analysis that in general polymers prepared by the addition of  $A_2$  over  $B_3$  display better mechanical properties than those prepared by  $B_3$  over  $A_2$  addition. Urea end capped polymers show better mechanical strength than their uncapped counterparts due to stronger hydrogen bonding in the capped systems. Increasing the amount of chain extender increases the tensile strength of the branched polymer

obtained. In the same manner polyurea samples show better dynamic mechanical properties than polyurethane samples.

Modeling studies which were done to determine the influence of reaction procedure on polymer topology for three different synthetic approaches: (i)  $A_2$  over  $B_3$  addition, (ii)  $B_3$  over  $A_2$  addition, (iii) mixing  $A_2$  and  $B_3$  together at the beginning, showed that structures formed by the addition of  $B_3$  over  $A_2$  possessed a higher degree of branching than other two polymerization methods resulting in different properties.

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