ISTANBUL TECHNICAL UNIVERSITY ★ INSTITUTE OF SCIENCE AND TECHNOLOGY

SYNTHESIS AND CHARACTERIZATION OF HYPERBRANCHED POLYESTER BASED POLYMERS AND THEIR APPLICATION ON UV-CURABLE WOOD COATINGS

Ph.D. Thesis by
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Department : Polymer Science and Technology

Programme : Polymer Science and Technology

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ÇOKDALLANMIŞ POLİESTER ESASLI POLİMERLERİN SENTEZİ, KARAKTERİZASYONU VE AHŞAP KAPLAMA MALZEMESİ OLARAK UYGULAMALARI

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FOREWORD

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ABREVIATIONS

VOC : Volatile Organic Compounds
UV : Ultra Violet
SCVP : Self-condensing Vinyl Polymerization
SCROP : Self-condensing Ring-Opening Polymerization
PTP : Proton-transfer Polymerization
DMM : Double Monomer Methodology
CMM : Couple-Monomer Methodology
MMD : Molar Mass Distribution
PDI : Polydispersity Index
NMR : Nuclear Magnetic Resonance Spectroscopy
TGA : Thermal Gravimetrical Analysis
DSC : Differential Scanning Calorimetry
GPC : Gas Permeation Chromatography
FT-IR : Fourier Transform Infrared Spectrophotometer
UA : Urethane Acrylate
UA/L : Aliphatic Polyurethane Acrylate
UA/HBPE : Hyperbranched Urethane Acrylate
HBPU : Hyperbranched Polyurethane
HBPE : Hyperbranched Polyester
IPDI : Isophorone Diisocyanate
TDI : Toluene Diisocyanate
PPG : Polypropyleneglycol
HEMA : 2-Hydroxy Ethyl Methacrylate
EA : Epoxy Acrylate
DMPA : 2,2-di(methylol)propionic acid
HEPA : 2,2-bis(4-β-hydroxyethoxy) phenyl propane
HEPFA : 2,2-bis(4-β-hydroxyethoxy) phenyl 6F propane
CHDM : 1,4- cyclohexanedimethanol
TPGDA : Tripropyleneglycoldiacrylate
HDDA : 1,6-hexanedioldiacrylate
NVP : N-Vinyl Pyrrolidone
DBTL : Dibutyl Tinlaurate
HEA : Hydroxyethyl Acrylate
HEMA : Hydroxyethyl Methacrylate

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SYNTHESIS AND CHARACTERIZATION OF HYPERBRANCHED POLYESTER BASED POLYMERS AND THEIR APPLICATION ON UV-CURABLE WOOD COATINGS

SUMMARY

Over the past two decades, hyperbranched polymers have attracted wide attention due to interesting physical/chemical properties as a new class polymers of topological structure. Hyperbranched polymers (HBPs) are highly branched macromolecules with a three-dimensional dendritic architecture. Because of their unique features such as highly branched structures, compact molecular shape, presence of large number of end groups, and lack of chain entanglement, the physical and chemical properties of HBPs are quite different from their conventional linear counter-parts. Hyperbranched polymers are relatively inexpensive to produce and, unlike dendrimers, are easy to synthesize in large quantities which encourages their potential use in a variety of important applications, including toughеners for thermosets adhesive agents, rheological additives toughening agents, drug delivery.

Hydroxyl functional aliphatic polyesters based on 2,2-di(methylol)propionic acid (DMPA) are one of the most widely investigated families of hyperbranched polymers. Synthesis of hyperbranched polymers from DMPA with various core molecules such as glycerol, trimethylol propane or pentaerithritol were reported in the literature.

The structural modifications provide a powerful tool for designing the properties of DMPA based hyperbranched polyesters for various application fields, ranging from classical commodity and engineering plastics to advanced and specialty materials, which find use in nanotechnology, nanobiotechnology, nanomedicine, chemical engineering, etc.

Photopolymerization has been the basis of numerous conventional applications in coatings, adhesives, inks, printing plates, optical waveguides, and microelectronics for more than 30 years. The use of photoinitiated polymerization is continuously growing in industry as reflected by the large number of applications in coatings, adhesives, inks, printing plates, optical waveguides, and microelectronics.

UV-Curable coatings offer various advantages such as fast curing, broad formulating range, low volatile organic compound (VOC), reduced energy consumption, coating of heat sensitive substrates. It is well known that polyurethane acrylates are an important class of acrylic oligomers for UV-curable coatings due to the excellent adhesion on substrates, flexibility and impact strength.

Hyperbranched polyesters end-capped with various groups capable of undergoing photopolymerization such as methacrylate, acrylate, thiol-ene, allyl ether groups and fatty acids were employed in UV-curing applications as an oligomer. It was reported that hyperbranched polyesters provide a unique combination of coating properties, such as a high hardness, scratch resistance, and flexibility, whereas at the same time ensuring low viscosity and low shrinkage. Therefore, acrylate functionalized

hyperbanched polyesters containing a large number of terminal groups have great possibility as a new high-performance UV-curing system.

In this study acrylate functionalized hyperbranched polyesters were synthesized and employed as an oligomer in the UV-curable wood coatings to introduce the advantages of hyperbranched polymers into UV-curing technology.

For this purpose, hyperbranched polyesters were synthesized by the polycondensation of 2,2-bis(methylol)propionic acid as AB_2 monomer [contains one carboxyl (A = COOH) and two hydroxyl (B = OH) functional groups] with various B_f core molecules as [2,2-bis(4-β-hydroxyethoxy) phenyl propane] (HEPA), [2,2-bis(4-β-hydroxyethoxy) phenyl 6F propane] (HEPFA) and polyester of 1,4-cyclohexanedimethanol (CHDM). In the second stage these hyperbranched polyesters were acrylated to obtain hyperbranched urethaneacrylates.

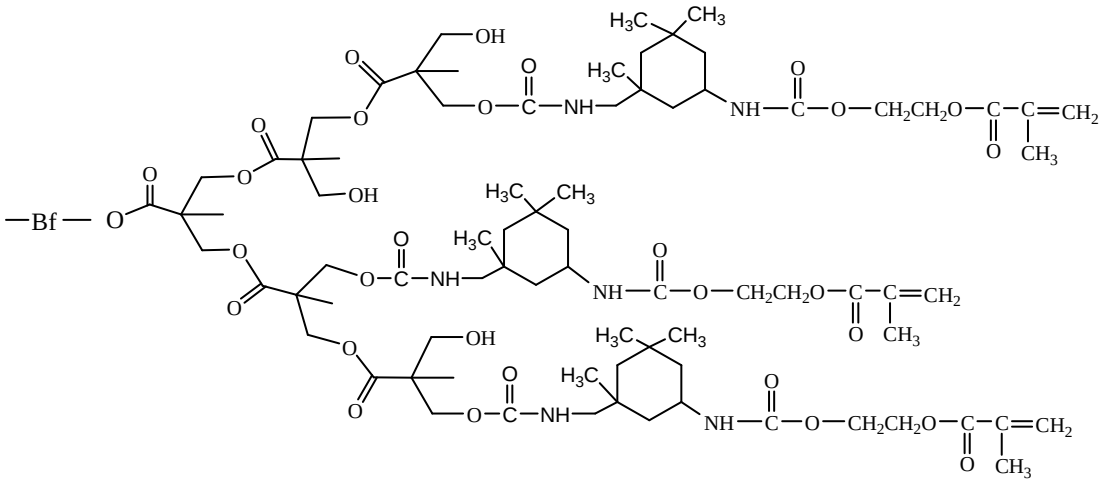


Figure 1: The structure of hyperbranched urethane acrylates.

Hyperbranched urethane acrylates were incorporated into the various types of UV-curable wood coating formulations as new oligomers. The effects of highly branched structure and the large number of functional groups were evaluated by means of coatings properties such as surface, mechanical and physical properties.

ÇOKDALLANMIŞ POLİESTER ESASLI POLİMERLERİN SENTEZİ, KARAKTERİZASYONU VE AHŞAP KAPLAMA MALZEMESİ OLARAK UYGULAMALARI

ÖZET

Son 20 yılda, dikkat çekici fiziksel ve kimyasal özellikleri ve topolojik yapılarından dolayı çokdallanmış polimerler üzerinde yapılan çalışmalar önem kazanmıştır. Üç boyutlu moleküler yapısı ile yeni bir malzeme sınıfı olan Dallanmış (dendritic) polimerler, başlıca dallanmış (dendrimers) ve çok-dallanmış (hyperbranched) polimerler olarak sınıflandırılmaktadır. Çokdallanmış polimerler dallanmış yapıya sahip olmalarının yanı sıra düşük viskozite, iyi çözünürlük ve düz zincirli polimerlere kıyasla çok sayıda reaktif son grup içermeleri gibi benzersiz özellikleriyle de önemli ölçüde dikkat çekmektedir. Düşük maliyet ve yüksek verimle sentezlenebilmesi çokdallanmış polimerlerin darbe dayanımını arttırıcı , akışkanlık düzenleyici, ilaç salınımı sağlayıcı olarak değişik uygulamalarda kullanımını teşvik etmektedir.

2,2-di(methylol)propionic acid (DMPA) esaslı alifatik poliesterlerin sentezi ve karakterizasyonu konusunda çok sayıda çalışma yapılmıştır. Bu tip çokdallanmış polimerler AB_2 monomer özelliğinde olan DMPA veya DMPA ile birlikte gliserol, trimetilol propan, pentaeritritol gibi çeşitli çekirdek molekülleri kullanılarak sentezlenmiştir.

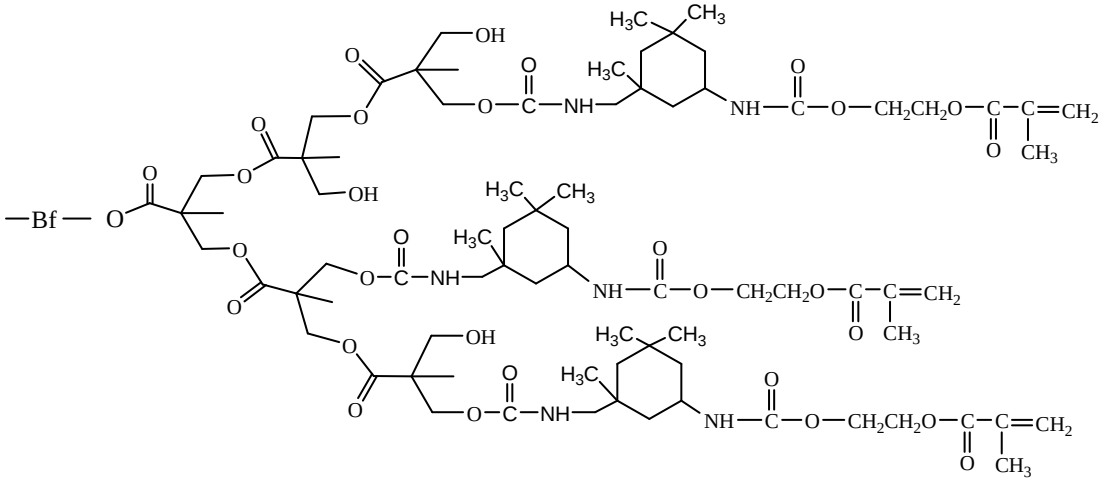
DMPA esaslı çokdallanmış polimerlerin çeşitli uygulamalar için özelliklerinin tasarlamasında yapısal modifikasyonlar çok önemli bir araçtır. Bu tip çokdallanmış polimerler klasik uygulama alanlarının yanı sıra yüksek özellikli plastiklerde, nanoteknoloji, nanobioteknoloji, gibi özel uygulama alanlarında da kendine yer bulmaktadır.

Işıkla polimerizasyon yöntemi kaplama, yapıştırıcı, mürekkep ve mikroelektronik gibi çok çeşitli uygulamalarda kullanılmaktadır. UV-ışınları ile sertleşen kaplamaların hızlı kürlenme, düşük organik uçucu bileşen içerme, düşük enerji tüketimi, geniş formülasyon aralığı, ısıya duyarlı yüzeylerin kaplanması gibi çok çeşitli avantajları mevcuttur. Poliüretan akrilatlarlar yüzeye çok iyi bağlanması, esneklik ve darbe dayanımı gibi özellikleri sayesinde UV-ışınları ile sertleşen kaplama uygulamalarında kullanılan akrilik oligomerler içinde önemli bir yere sahiptir.

Çokdallanmış poliesterler UV-ışınları ile sertleşen kaplamalarda oligomer olarak kullanılmak amacıyla metakrilat, akrilat, tiol-en, allil eter ve yağ asidleri gibi ışıkla polimerleşme özelliği olan çeşitli gruplarla modifiye edilmiştir. Çokdallanmış poliesterler yüksek sertlik, çizilme dayanımı ve esneklik gibi benzersiz kaplama özelliklerinin yanısıra düşük viskozite ve büzülme özelliklerine de sahiptir. Bundan dolayı, çok sayıda uç grup içeren akrilat fonksiyonlu çokdallanmış poliesterler yüksek performanslı UV-ışınları ile sertleşen sistemlere alternatif olarak sunulmaktadır.

Bu tezde, akrilat fonsiyonlu çokdallanmış poliesterler sentezlenmiş ve çokdallanmış polimerlerin sağladığı avantajlardan faydalanmak amacıyla UV-ışınları ile sertleşen ahşap kaplamalarda yeni oligomerler olarak kullanılmıştır.

Bu amaçla, AB_n+B_f polikondenzasyon yöntemi kullanılarak yeni birinci ve ikinci jenerasyon çokdallanmış poliesterler sentezlenmiştir. AB_2 monomeri olarak 2,2-di(methylol)propionic acid ve B_f çekirdek molekülleri olarak [2,2-bis(4-β-hidroksietoksi) fenil propan] (HEPA), [2,2-bis(4-β-hidroksietoksi) fenil 6F propan] (HEPFA) ve 1,4-siklohegzandimetanol (CHDM) esaslı poliester kullanılmıştır. İkinci bölümde çokdallanmış poliesterlerin üretan akrilatları sentezlenmiştir.



Şekil 1: Çokdallanmış üretan akrilatın yapısı.

Çokdallanmış üretan akrilatlar UV-ışınları ile sertleşen çeşitli kaplama formülasyonlarında yeni oligomerler olarak kullanılmıştır. Çokdallanmış ve çok sayıda fonksiyonel grup içeren yapıların yüzey özellikleri, mekanik ve fiziksel özellikler gibi kaplama özellikleri üzerine olan etkileri incelenmiştir.

1. INTRODUCTION

Dendritic polymers, including dendrimers and hyperbranched polymers (HBPs), are the new emerging polymer architectures following the linear, branched, and crosslinking polymers. Dendrimers are well-defined, highly branched macromolecules that radiate from a central core and are synthesized tediously through a stepwise, repetitive reaction sequence that guarantees complete shells for each generation. Dendrimers are thus monodisperse polymers [1]. On the contrary, hyperbranched polymers are more easily made on a large scale in a one pot synthetic step via step-growth polycondensation, self-condensing vinyl or ring-opening polymerization [2]. Hyperbranched polymers are considered irregular analogues of dendrimers since they contain partially reacted linear repeat units in addition to fully reacted (dendritic) and unreacted (terminal) repeat units.

Hyperbranched polymers have less defined structures than dendrimers and have broader molar mass distributions (MMD). The molar mass averages of a hyperbranched polymers can be controlled and polydispersity index (PDI) considerably reduced by the addition of a small amount of multifunctional core molecules, B_f, to the reaction system [3]. This largely prevents the coupling of the polymeric species itself. The most effective procedure is to slowly add AB_n monomers to the core molecules in solution ("core dilution / slow addition technique") [4]. Hult reported a pseudo-one-step reaction where stoichiometric amounts of bis-MPA monomer, corresponding to each generation, were added successively to the core molecules in the bulk under acidic catalysis [5-7].

Hyperbranched polymers have attracted significant interests due to their promising architecture and properties, such as globular structures and a large number of functionalized end groups, low viscosity and high solubility. One major use of commercial interest is as a reactive component in coating and resin formulations. Other potential applications include using these highly branched and highly functional polymers as polymer additives in linear polymers for improving rheology and flow and surface modification. In addition, the excellent thermal stability that

can be designed into a hyperbranched polymer as well as modulus properties qualify these products as interesting polymer additives. The commercial success of hyperbranched polymers are a result of the highly branched and dense but irregular structure that leads to excellent solubility, compared to linear polymers, low solution viscosity, modified melt rheology, and high level of terminal end group functionality [8-11]. Those properties make them attractive in many applications including coatings, additives, catalysts and nonlinear optics [12-14].

UV-curable coatings represent a class of coatings with non-volatile or low-volatile organic compounds, offering many advantages such as fast drying, broad formulating range, reduced energy consumption and low space and capital requirements for curing equipment [15]. UV curable hyperbranched polymers offer interesting possibilities for improving coating properties. The applications of HBPEs in UV-curable coatings have been described in several papers, involving UVcurable oil-based coatings [16], powder coatings [17], waterborne coatings[18-19] and hybrid coatings[20]. Coatings containing HBPEs exhibit very rapid cure rate and lower shrinkage, and UV-cured films have excellent hardness, high chemical resistance, good scratch resistance, small amount of residual unsaturation and low levels of extractables.

The study presented in this thesis is aimed to prepare novel hyperbranched polyester based urethane acrylates and utilise them as oligomers in the UV-curable wood coating systems. Meanwhile, to investigate the effects of unique features of hyperbranched polyester based urethane acrylates on the coating performances.

2. THEORETICAL PART

2.1 Hyperbranched Polymers

It is well known that the shape of organic molecules is one of the important factors which determines their properties. Traditionally, polymer chemistry and technology have been focused on the properties and application of linear polymers. During the last two decades, especially polymer scientists have introduced a new philosophy of 'dendritic macromolecules' and prepared globular and spherical molecules in addition to the more conventional linear ones [21-25] .

Due to the unique properties, dendritic polymers are recognized as a fourth major new architectural class [26] with a young but well established body of interdisciplinary research exploring a remarkable variety of potential applications.

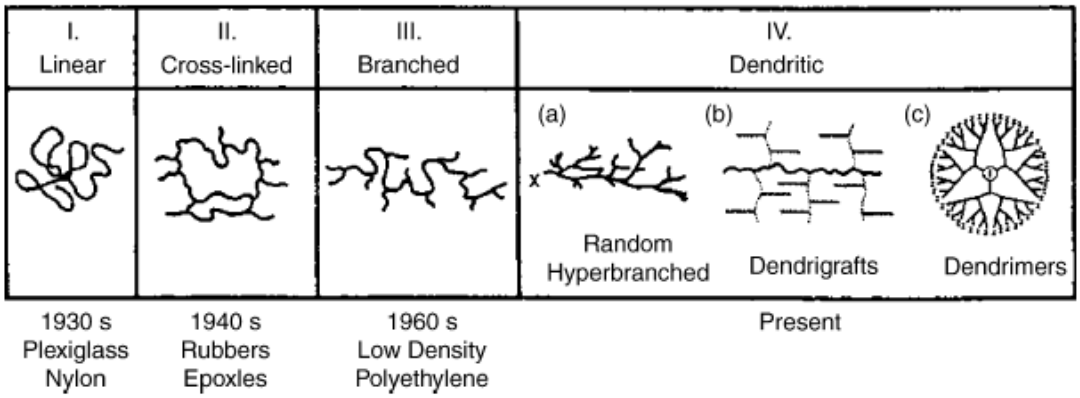


Figure 2.1 : Representation of the four major classes of macromolecular architectures.

As illustrated in Figure 2.1, dendritic polymers can be subdivided according to their degree of structural control into three different categories, namely (a) random hyperbranched polymers, (b) dendrigraft polymers, and (c) dendrimers .

Apart from the dendritic polymers, other important branched topologies in polymer science such as comb and star polymers, networks, and microgels are shown in Figure 2.2 [26].

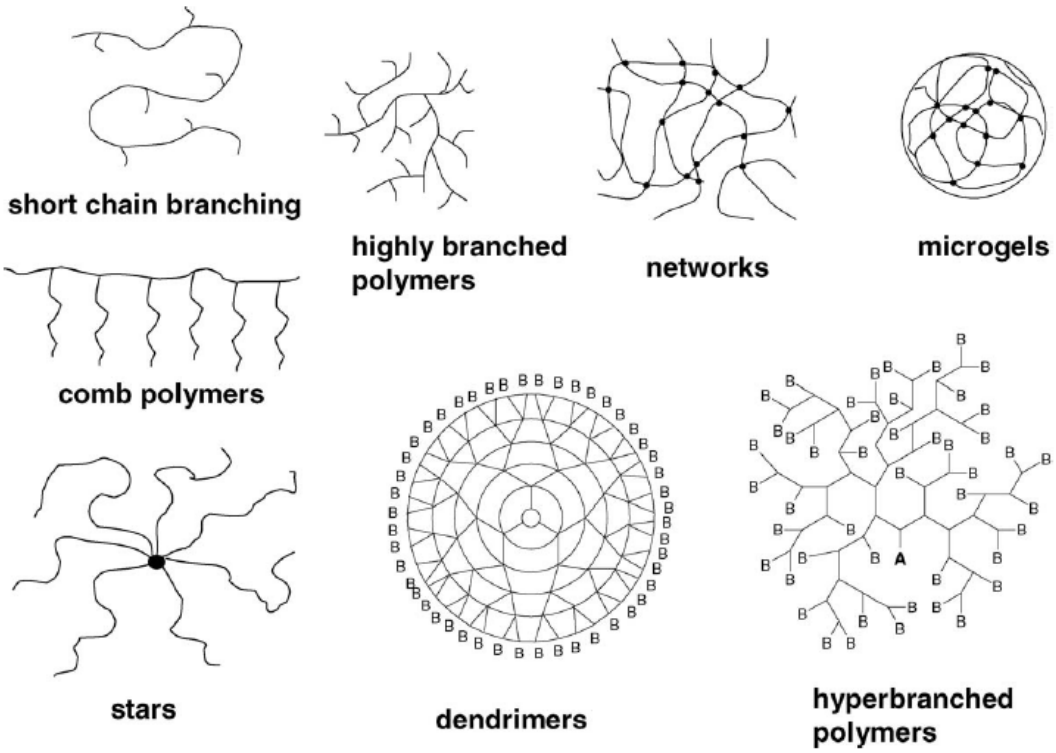


Figure 2.2 : Branched topologies in polymer science.

The term **dendrimer** is derived from the Greekwords dendron (tree) and meros (part). Dendrimers are highly uniform, three dimensional, monodisperse polymers with a tree-like, globular structure and a large number of functional groups. Dendrimers are prepared in a step-wise manner including protection and deprotection strategy from AB_n monomers (where n is 2 or greater) with control over the number of generations and the molecular weight. For the synthesis of dendrimers, two different approaches exist [27]: The divergent approach, starting from a multifunctional core and proceeding radially outward, was developed by Tomalia et al. [28] and by Newkome et al. [29]. A newer approach is the convergent approach proposed by Hawker and Fréchet [30,31], which starts from the periphery, progresses towards the inside, and is followed by coupling of the dendrons to a multifunctional core.

Dendrigrafts were introduced in 1991 as Comb-burst® polymers by Tomalia et al. [32] and as arborescent polymers by Gauthier and Möller [33]. Dendrigraft polymers may be regarded as semi-controlled branched polymer architectures intermediate in terms of structure control between dendrimers and hyperbranched polymers [34]. As described by Teertstra and Gauthier dendrigraft syntheses follow a generation-based growth methodology similar to dendrimers, but use of polymeric chains as building

blocks leading to a rapid increase in molecular weight per generation and therefore, in a few steps, to macromolecules with a high molecular weight (typically one to two orders of magnitude larger than for their dendritic counterparts). In comparison to dendrimers, dendrigraft polymers are less controlled since grafting may occur along the entire length of each generational branch and the exact branching densities are arbitrary and difficult to control [35].

Hyperbranched polymers represent another class of globular, highly branched macromolecules with a large number of functional groups. However, unlike dendrimers, hyperbranched polymers exhibit polydispersity and irregularity in terms of branching and structure. The history of hyperbranched macromolecules can be dated to the end of 19^{th} century, when Berzelius reported the formation of a resin from tartaric acid (A_2B_2 monomer) and glycerol (B_3 monomer) [36]. Following the Watson Smith report of the reaction between phthalic anhydride (latent A_2 monomer) or phthalic acid (A_2 monomer) and glycerol (B_3 monomer) in 1901, Callahan, Arsem, Dawson, Howell, and Kienle, et al. [36-38] studied that reaction further, obtaining results and conclusions still used today. For example, Kienle [37] showed that the specific viscosity of samples made from phthalic anhydride and glycerol was low when compared to numerous specific viscosity values given by Standinger for other synthetic linear polymers, such as polystyrene. In 1909, Baekeland [39] introduced the first commercial synthetic plastics, phenolic polymers, commercialized through his Bakelite Company. The cross-linked phenolic polymers are obtained by the polymerization of soluble resole precursors made from formaldehyde (latent A_2 monomer) and phenol (latent B_3 monomer). Just prior to gelation, these polymers have a so-called random hyperbranched structure.

In the 1940s, Flory et al. [40-44] used statistical mechanics to calculate the molecular weight distribution of three-dimensional polymers with trifunctional and tetrafunctional branching units in the state of gelation, and developed the ‘degree of branching’ and ‘highly branched species’ concepts. However, both the experiments and calculations mentioned above are based on polycondensation of bifunctional A_2 monomer with trifunctional B_3 monomers, so gelation occurs when the degree of polymerization approaches the critical condition.

In 1952, Flory [45] developed the theory that highly branched polymers can be synthesized without the gelation by polycondensation of a monomer containing one

A functional group and two or more B functional ones capable of reacting with A (AB_n monomer, $n \geq 2$).

In 1982, Kricheldorf [46] obtained highly branched polyesters by copolymerization of AB and AB_2 type monomers. Finally, Kim and Webster [47,48] synthesized soluble hyperbranched polyphenylene in 1988. Since then, hyperbranched polymers have attracted increasing attention owing to their unique properties and greater availability as compared with dendrimers.

The tedious step-wise procedure for dendrimers often results in expensive products with limited availability and therefore restricted use for large-scale industrial applications. Unlike dendrimers, hyperbranched polymers are often easy to synthesize on a large-scale [49] and therefore are considered to be alternatives for dendrimers. Companies such as the Perstorp Group (Perstorp, Sweden), DSM Fine Chemicals (Geleen, Netherlands) and BASF AG (Ludwigshafen, Germany) already produce commercially available hyperbranched polymers on a large-scale (Figure 2.3 [50]).

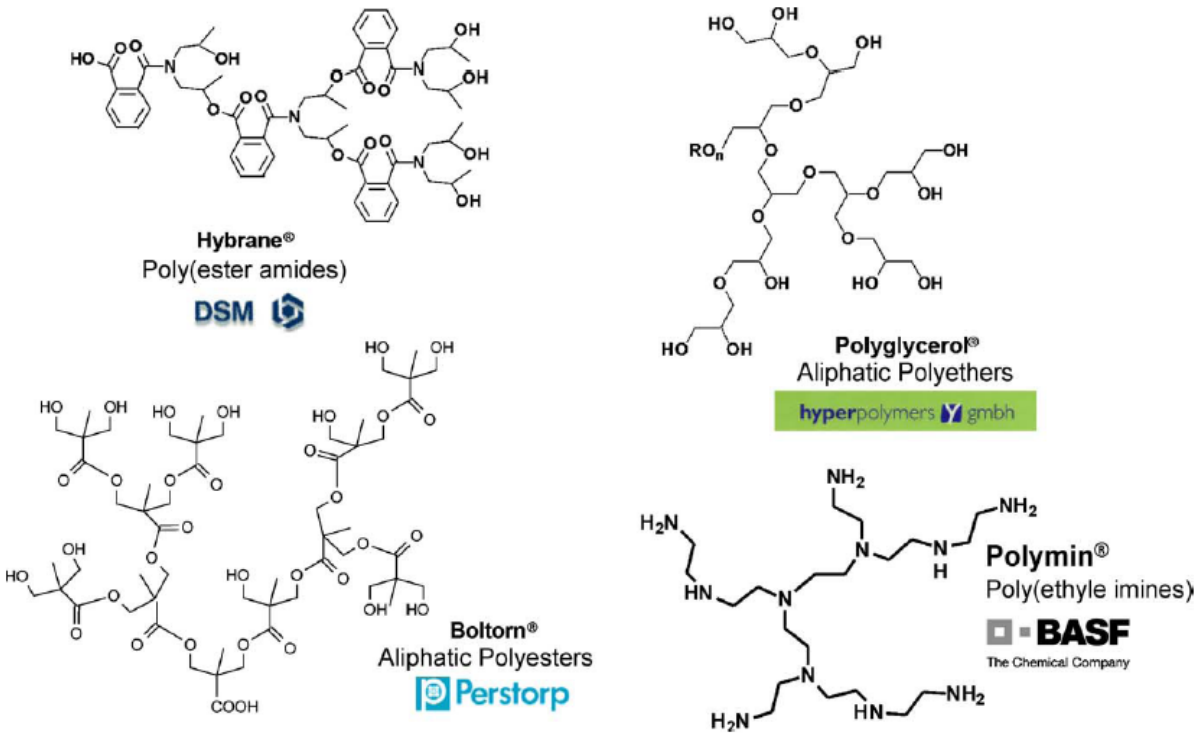


Figure 2.3 : Commercially available hyperbranched polymers.

Most of the applications of hyperbranched polymers are based on the absence of chain entanglements, the globular shape, and the nature and the large number of functional groups within a molecule. Modification of the number and type of

functional groups on hyperbranched polymers is essential to control their solubility, compatibility, reactivity, adhesion to various surfaces, self-assembly, chemical recognition, and electrochemical and luminescence properties. In other words, the large number of functional groups allow for the tailoring of their thermal, rheological, and solution properties and thus provides a powerful tool to design hyperbranched polymers for a wide variety of applications. Figure 2.4 gives an overview of the investigated applications for hyperbranched polymers [50].

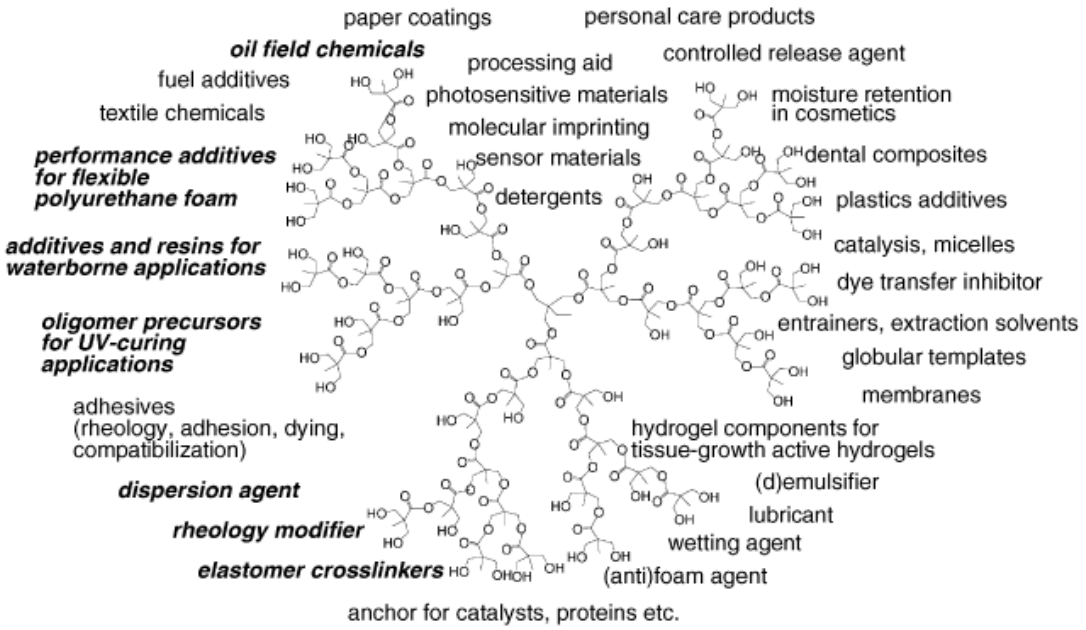


Figure 2.4 : Applications of hyperbranched polymers discussed in literature. Bold italic: commercial applications of hyperbranched polymers.

2.1.1 Synthesis of hyperbranched polymers

Hyperbranched polymers, like dendrimers, are highly branched with a repeating layered structure. Hyperbranched polymers and dendrimers share a few common features such as their preparation from AB_n monomers leading to highly branched macromolecules with a large number of functional end groups. However, the synthetic approaches for hyperbranched polymers and dendrimers differ substantially; hence differences in molecular shape and architectures and sometimes also in properties are observed. Although, hyperbranched polymers contain structural defects and are polydisperse in comparison to dendrimers, they still are believed to possess similar properties including good solubility and low viscosity. Dendrons and dendrimers, having a well-controlled size and shape, are usually prepared by multi-step reactions with tedious isolation and purification procedures [51].

The synthetic techniques for hyperbranched polymers can be divided into two major categories. The first category contains techniques of the single-monomer methodology (SMM), in which hyperbranched macromolecules are synthesized by polymerization of an AB_n, AB* or a latent AB_n monomer.

According to the reaction mechanism, the SMM category includes at least four specific approaches:

1 polycondensation of AB_n monomers

2 self-condensing vinyl polymerization (SCVP)

3 self-condensing ring-opening polymerization and proton-transfer polymerization (ROMBP)

The second category contains examples of the double-monomer methodology (DMM) in which direct polymerization of two types of monomers or a monomer pair generates hyperbranched polymers [52].

- 'A_2 + B_3' methodology has been applied to synthesize three main polymer architectures including polyamides, polycarbonates and polyureas [53].
- Couple-monomer methodology (CMM), which is the combination of the basic SMM and 'A_2 + B_3', is used to prepare many types of hyperbranched polymers such as poly(sulfone amine)s, poly(ester amine)s, poly(urea urethane)s [37].

2.1.1.1 Polycondensation of AB_2 monomers

Polycondensation is the classical way to prepare hyperbranched polymers by AB_n monomers with and without core moieties. The general hyperbanched polymer synthesis involves the self polycondensation of AB_n type monomers, which have one A and *n* B functional groups, where A group of a monomer may react with B group of another monomer, but neither A nor B may react with themselves, so that the hyperbanched polymer will have B end groups.

Almost all classes of condensation polymers have been adopted for hyperbranched polymer synthesis, e.g., polyamides [54-59] (e.g. through 5-1), polyethers [60-64], (e.g. through 5-2, 5-3, 5-4), polyethersulfones and ketones [65-69] (e.g. through 5-5), polyphenylenes [70] (5-6), polyphenylenesulfides [71] (5-7), polyaryleneether [72],

polyphenyleneoxide [73], polycarbonates [74], polyphenyl acetylenes [75], polysiloxanes [76] and various other structures like poly(bis-(alkylene) pyridinium)s [77] (5-8) and poly(arylene oxindole)s [78] (5-9), and were readily synthesized through condensation reactions.

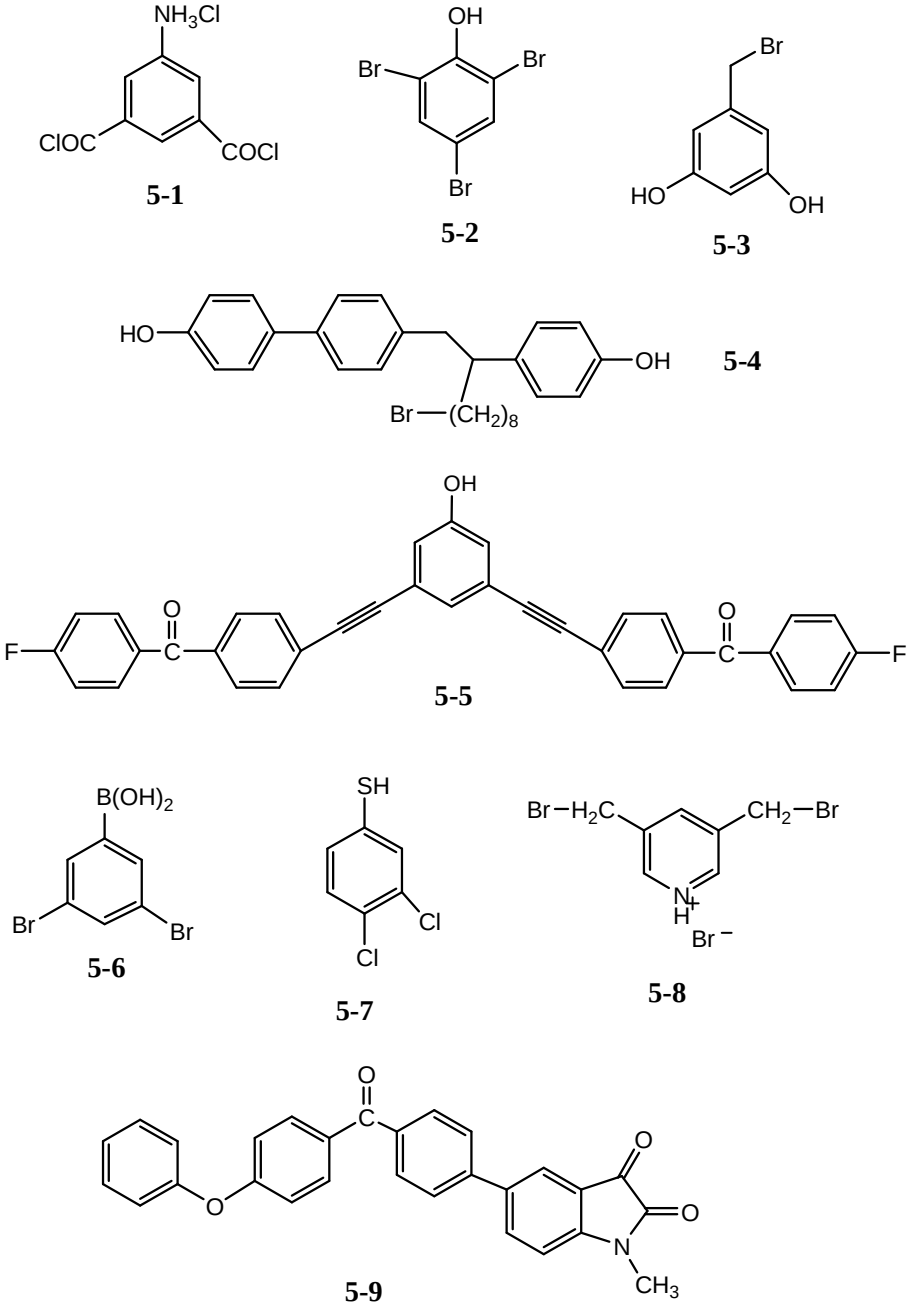


Figure 2.5 : Examples of AB_n monomers for hyperbranched polymers through polycondensation.

Especially hyperbranched polyester structures had been favored by many groups [79-84] and also by industry (Boltorn based on dimethylolpropionic acid) due to the availability of suitable monomers.

Polycondensations are often carried out in bulk, but solution polymerizations are also suitable and often prevent side reactions. As required for all polycondensates, the low molar mass condensation products need to be removed, e.g., by applying vacuum in melt polycondensation in order to drive the reactions to high conversions.

2.1.1.2 Self-condensing vinyl polymerization

Self-condensing vinyl polymerization (SCVP) is based on a vinyl monomer that additionally bears an initiating group ("inimer" = initiator + monomer [85]). These monomers allow propagation through the double bond (=chain growth) and addition of the initiating site to the double bond (=step growth) and thus lead to hyperbranched polymer in a one-pot reaction with possible branching in each repeating unit (Figure 2.6 [86]).

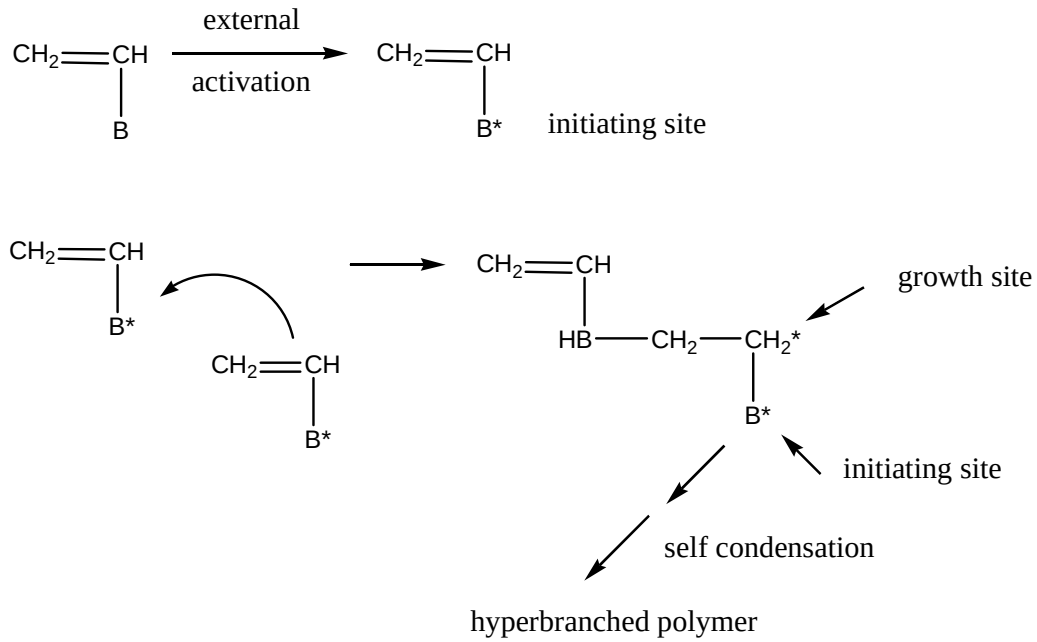


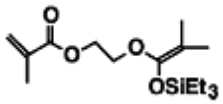
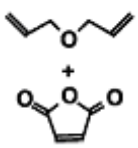
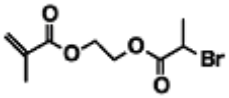
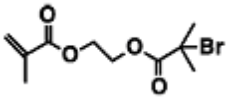
Figure 2.6 : Mechanism of self-condensing vinyl polymerization according to Frechet.

SCVP was invented by Frechet and coworkers in 1995 [87]. This polymerization method is quite versatile, as hyperbranched polymers can be approached via polymerization of AB vinyl monomers. In the reaction, the B groups of the AB monomers are activated to generate the initiating B^* sites. B^* initiates the propagation

of the vinyl group A in the monomer, forming a dimer with a vinyl group, a growth site, and an initiating site. The dimer can function as an AB_2 monomer, and undergo further polymerization to yield the hyperbranched polymer.

In SCVP, the activities of chain propagation of the growth sites and the initiating sites differ, resulting in a lower DB when compared to the DB of the hyperbranched polymer prepared via polycondensation of AB_2 monomers. The theoretical maximum DB of SCVP is 46.5 % [88]. On the other hand, SCVP does exhibit some disadvantages. For example, side reactions may lead to gelation, the molecular weight distribution is usually very broad, and it is difficult to determine DB directly via an NMR analysis. In order to avoid crosslinking, living/controlled polymerizations such as atom transfer radical polymerization (ATRP) and group transfer polymerization (GTP) are combined in SCVP [89-94]. Monomers used in SCVP and polymerization results such as number average molecular weight (M_n) and polydispersity index (PDI, M_w/M_n) are summarized in Table 2.1 [90-95].

Table 2.1: The monomers used in SCVP and polymerization results.

Monomer	Condition	M_n (GPC)	PDI	Reference
	GTP at -50 °C	1630	34	[89,90]
	Copolymerization at 50 °C for 24 h	5980	1.87	[92]
	ATRP (24 °C for 26 h in benzene)	1990	6.6	[95]
	ATRP (24 °C for 26 h in benzene)	650	4.3	[95]

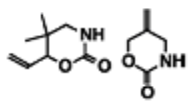
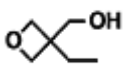
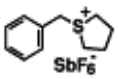
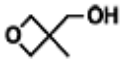
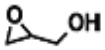
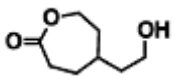
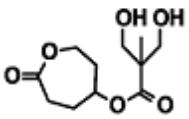
2.1.1.3 Self-condensing ring-opening and proton-transfer polymerizations

Self-condensing ring-opening polymerization (SCROP) or ring-opening multibranching polymerization (ROMBP) differs from SCVP in the fact that instead of a vinyl group a heterocyclic group is used as the monomer part of the inimer. In addition, whereas in SCVP usually irreversible reactions are involved, in ROMBP also reversible preconditions generally have to be considered. The ROMBP approaches have their origin in classical ring-opening reaction mechanism (ROP)

toward linear polymers, especially polyethers and polyesters. Chang and Frechet [96] reacted a diepoxy-substituted phenol involving a proton-transfer mechanism to a hyperbranched polymer.

Hyperbranched polyamines [97,98], polyethers [99-103] and polyesters [104,105] have been prepared through SCROP. Table 2.2 shows some of the monomers employed in SCROP and the polymerization results. Another well-known hyperbranched polymer produced in large scale by ROMBP is polyethyleneimine (PEI), known now under the trade name Lupasol from BASF SE, which was commercialized first under the name Polymin in 1942 [106]. Finally, hyperbranched polyesters with epoxy or hydroxyl end groups [107,108] and hyperbranched polysiloxanes [109] were synthesized through proton transfer polymerization (PTP).

Table 2.2: The monomers employed in SCROP and polymerization results.

Monomer	Condition	Mn (GPC)	PDI	DB	Reference
	Pd (0), 25 °C for 48 h in THF	1800	1.5	0.61	[97]
	 , 120 °C	4170	1.43	0.38	[99]
	BF_3OEt_2, -10 °C to 4 °C for 48 h	1780	1.28	0.33	[102]
	CH_3OK, 95 °C for 12 h	6310	1.47	0.59	[103]
	$Sn(Oct)_2$, 110 °C in bulk	20,300-26,500	3.2	0.5	[104]
	$Sn(Oct)_2$, 110 °C in bulk	3000	2.8	0.5	[105]

2.1.2 Hyperbranched polyester polyols

Polyesters are a dominating class of materials in the field of hyperbranched products. In addition, polyesters have in general a high level of commercial importance, and a variety of well known processing technologies are available. Thus, aliphatic, lower

molar mass polyesters can be used very effectively in coatings and resins, and the combination of the property profile of polyesters with high functionality, low viscosity, and improved miscibility make the hyperbranched products in these fields very attractive [110].

Hyperbanched polyester polyols from AB_n monomers ($n \geq 2$) have been explored, where A and B are hydroxyl and carboxylic acid moieties, respectively. The routes involve thermally driven homo-polymerization or activation of either A or B functionalities. Thermally driven polycondensation of AB_2 monomers is a common method that uses p-toluene sulfonic acid (p-TSA) or an organometallic reagent as a trans-esterification catalyst.

An easily available AB_2 monomer, bis(4-hydroxyphenyl)-pentanoic acid, can be used without any further modification directly in melt [111,112] but also in solution polycondensation [113]. This monomer, in which the phenolic groups are on separated aromatic units, undergoes ideal statistical AB_2 polycondensation with a very low tendency toward any side reaction or cyclizations, and a degree of branching of 50% is achieved [111,114]. Thus, this polymer was used in model studies [114] as well as intensively investigated in various application studies like in coating [114,115] and nanocomposite formulations [116], often by modifying the end groups [117,118].

Ziemer et al. [119] prepared hyperbranched polyester from 4,4-bis(4-hydroxyphenyl) valeric acid in an A_2B approach (Figure 2.7a). The highly activated aromatic AB_2 monomer 3,5-bis(trimethylsiloxy) benzoyl chloride leads in bulk polycondensation to a relatively high degree of branching of about 60%, since the once-reacted monomer activates the second condensation step [120] (Figure 2.8). Also slow monomer addition using 2-ethyl-2-hydroxymethy-1-,3-propanediol (TMP) as B_3 core molecule in combination with 3,5-bis-(trimethylsiloxy)benzoyl chloride (AB_2 monomer) was explored by Frey et al. [121] and led to an even increased degree of branching of 64 %. With a different core moiety, 1,3,5-tris(2-hydroxyethyl) cyanuric acid, was co-condensed with 3,5-dihydroxybenzoic acid in a slow monomer approach, and a degree of branching of the polyesters of 70-80 % was reported [122].

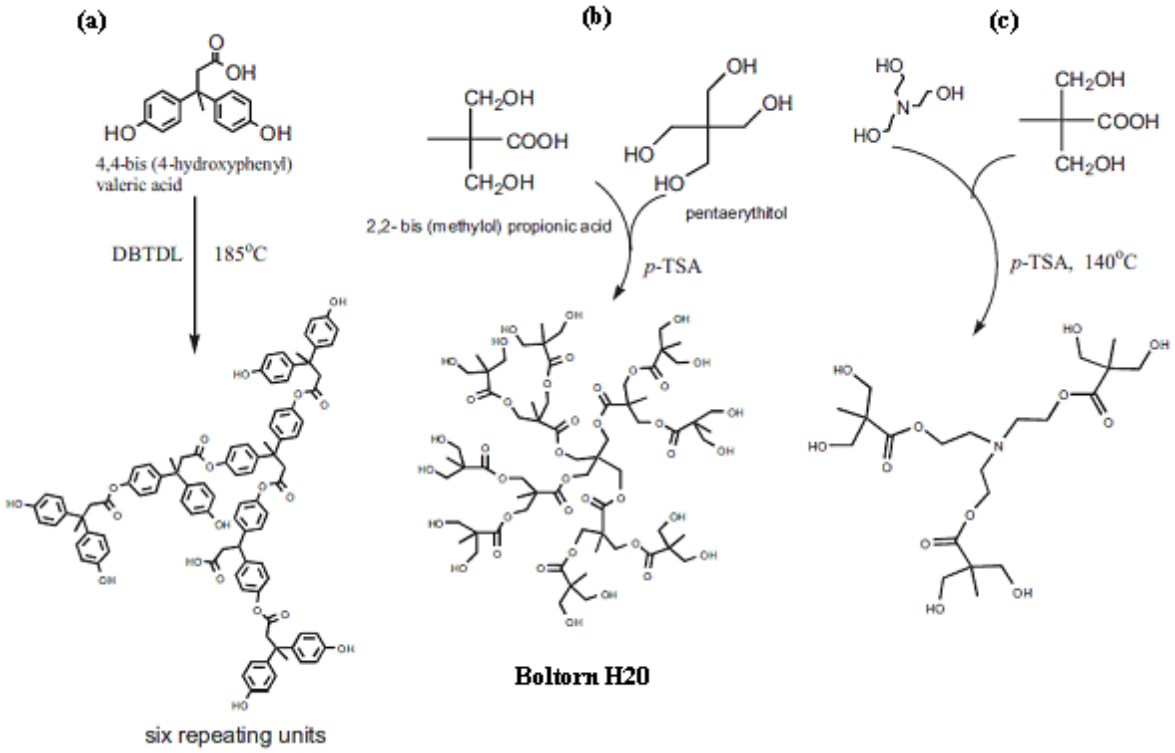


Figure 2.7 : Different synthetic approaches for the preparation of hyperbranched polyols.

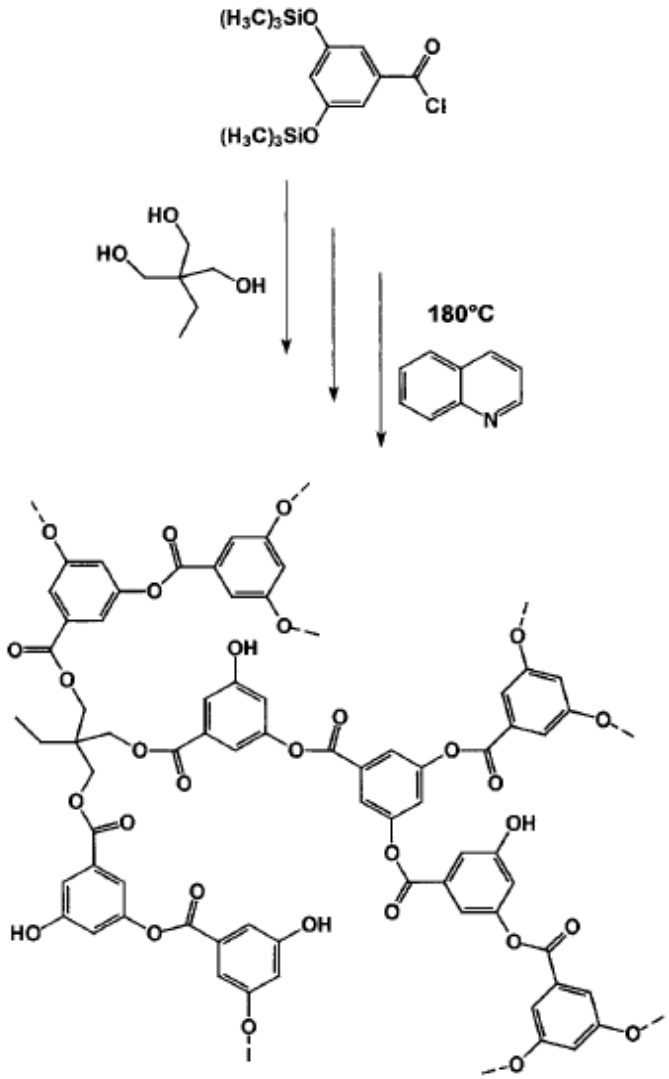


Figure 2.8 : Synthesis of the hyperbranched aromatic homopolyesters.

Theoretical and real systems reveal that the control over molecular mass average (MMA) and molar mass distribution (MMD) of HBPs can be achieved by using multifunctional core molecules as limiting stoichiometric reagent in the reaction system. Malstrom at all synthesized hyperbranched aliphatic polyesters by batch copolymerization of a B_f core molecule with an AB_2 monomer as an improved method to control the polycondensation reaction [123]. Examples of such an AB_2-monomer/B_f-core approach include the preparation of aliphatic hyperbranched polyester synthesized from 2,2-bis(methylol) propionic acid as AB_2 monomer and pentaerythritol [124] (Figure 2.7b), triethanol amine (Figure 2.7c) and trimethylolpropane [125,126] as core molecules. The hyperbranched polyester prepared from 4,4-bis-(4'-hydroxyphenyl)pentanoic acid and trimethylolpropane as core molecule was used by Pavlova et al. [127] for polyurethane coatings

preparation. Several hyperbranched polyester polyols are commercially available from Perstorp Polyols Inc. Perstorp AB, Sweden, with the trade name ‘Boltorn’, and are prepared from 2,2-bis(methylol) propionic acid (AB_2) and ethoxylated pentaerythritol (core) [128].

An A_2+B_3 approach includes the synthesis of hyperbranched aliphatic polyester polyol from adipic acid and glycerol [129]. A number of synthetic routes recently developed that emerge from the combination of the multi-branching polymerization of glycidol with well-established epoxide polymerization techniques, leading to unprecedented polymer architectures is shown by Frey and Haag [130], Sunder et al. [131], Xinling et al. [132] and Xiaoying et al. [133]. The synthesis of hyperbranched polyglycidol involves the cationic ring-opening polymerization of glycidol, by glycerol in the presence of boron trifluoride diethyl etherate catalyst in chloroform and the reaction was carried out in nitrogen atmosphere at 25 °C for more than 3 h (Figure 2.9).

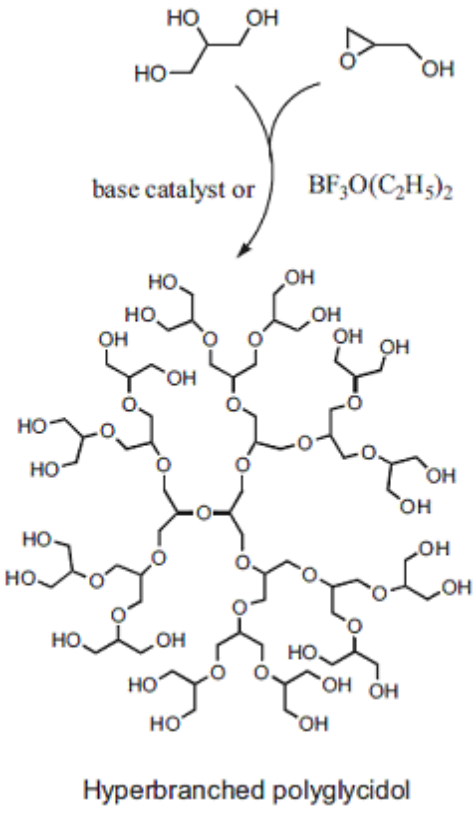


Figure 2.9 : Synthesis of hyperbranched polyglycidol.

2.1.3 Properties of hyperbranched polymers

2.1.3.1 Degree of branching

The synthesis of hyperbranched polymers is less controlled, resulting in a more polydisperse character with structural defects in the polymer backbone. The structure of these subunits contributes to the character of the macromolecule. Dendrimers contain of two different types of monomer units, the “dendritic” and the “terminal”, giving the dendrimer a perfect structure. The “dendritic” monomer units are found in the inner layers and are fully incorporated in the structure. The “terminal” units have unreacted B-groups of AB_n monomer and are found in the outerlayer. In contrast to perfectly branched dendrimers, which possess only dendritic and terminal units, the hyperbranched polymers incorporate additionally linear units. The degree of structural perfection in hyperbranched polymers can be described by the **degree of branching (DB).** DB is one of the most important parameters of hyperbanched polymers, because of the fact that it is directly correlating with the density of the polymer structure and the number and location of the end groups [134].

Hyperbranched polymer obtained by growth of an AB* or AB_2 monomer onto a trifunctional core (“Generations” 0 to 5 Numbered) is shown at Figure 2.10 [135]. The terminal segments, which carry two functional groups were denoted, as **T**, the linear segments, carrying one functional group as **L**, and the branchpoints as **B**.

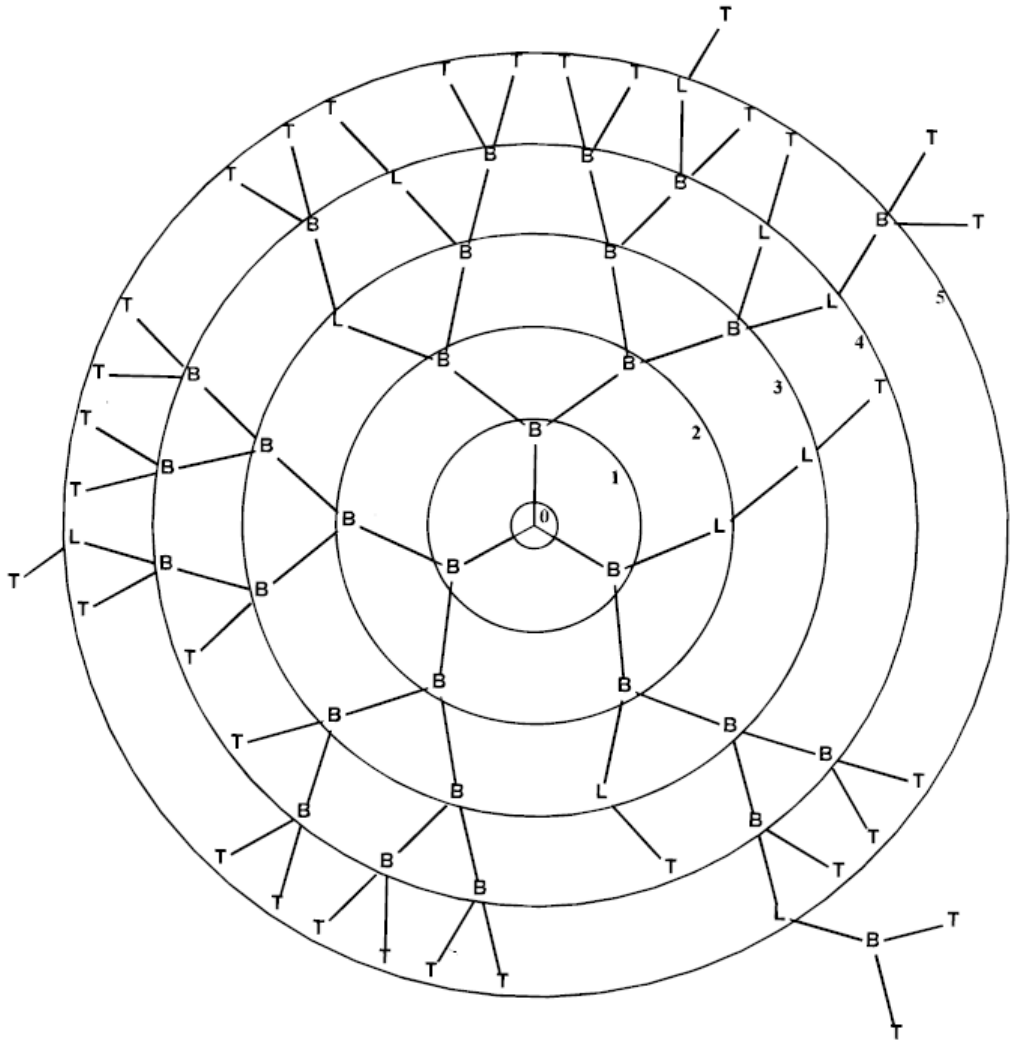


Figure 2.10 : Hyperbranched polymer obtained by growth of an AB* or AB_2 monomer onto a trifunctional core ("Generations" 0 to 5 numbered).

Theoretically [136], in the case of the ideal statistical self-condensation of an AB_2 monomer, which means equal reactivity of all B groups and no side reactions like cyclization, the number of the linear units should occupy 50% and the dendritic units only 25% of all structural units, as shown in Figure 2.11.

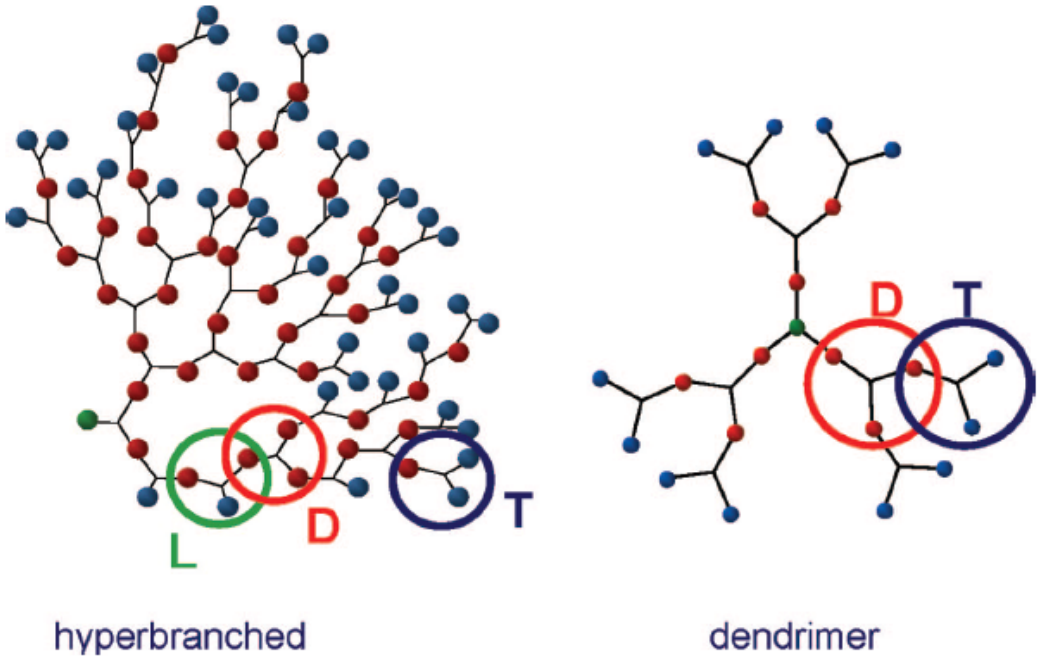


Figure 2.11 : Schematic representation of the different polymer units in hyperbranched polymers compared to dendrimers: L = Linear, D=Dendritic and T = Terminal units.

Where *D*, *L*, *T* are the fraction of dendritic (two reacted hydroxyl groups and one reacted carboxylgroups), linear (one reacted hydroxyl groups and one unreacted hydroxyl groups), and terminal repeat units (two unreacted hydroxyl groups and one reacted carboxyl groups). DB = 1 for a perfect dendrimer, DB = 0 for linear polymer molecules and it is <1 for hyperbranched polymers.

The calculation of the DB for AB_2 type of hyperbanched polymers using the values for **T**, **D**, and **L** was described in the 1990s in the work of Kim and Webster [137] and Fre´chet et al. [138] as a function of the ratio of the dendritic (D), terminal (T), and linear (L) units as

$$DB_{Frechet} = \frac{D + T}{D+L+T} * 100 \qquad \textbf{(2.1)}$$

This definition can indeed accurately describe DB for products with higher polymerization degrees, where the number of the dendritic units is approximating the number of the terminal units, but in the low molar mass region, another equation suggested by Frey et al. [139] and Yan et al. [140] is more suitable for the calculation of the DB:

$$DB_{Frey} = \frac{2D}{2D+L} * 100 \quad \textbf{(2.2)}$$

NMR spectroscopy is a powerful tool to determine the DB of hyperbanched polymers. In addition to ^{1}H NMR, ^{13}C, ^{15}N, ^{19}F and ^{29}Si NMR spectroscopies have all been used to determine the DB for various hyperbanched polymers. When the polymer is composed of degradable linkages such as esters and carbonates, the DB can be calculated by the quantitative analyses for the products after degradation [141,142].

As suggested by Frey, DB of hyperbranched polymers from the one-pot polymerizations of AB_2 monomers tend to be close to 0.5 [143]. There have been several attempts to increase DBs: (1) polymerization of dendrons having prefabricated dendritic units; (2) polymerization of AB_n monomers in the presence of core molecules (B_f); (3) enhancement of the reactivity of linear units formed during the polymerization [144].

The second strategy to increase DB values involves the polymerization of AB_n monomers in the presence of core molecules, B_f. Frey has examined the DB of hyperbranched polymers prepared by the slow monomer addition of an AB_2 monomer to a core molecule B_f or a growing AB_2 type hyperbanched polymer [145].

Some experimental data for the polyemrization of AB_n monomers in the presence of core molecules have already been reported. Hyperbranched aliphatic polyesters with DB more than 0.8 and polydispersities less than 2 have been prepared by the melt polymerization of an AB_2 monomer and a B_3 monomer [146,147].

The addition of core molecules affects not only the DB, but also the polydispersity of the resulting hyperbranched polymers [148,149]. The polydispersity of the polymers from the random polycondensation of AB_2 type monomers statistically becomes extremely large. The major reason for the growth of polydispersity is that the larger propagating molecules have many B functions, and therefore, grow faster than smaller ones and couple each other easily. The coupling of growing molecules can be avoided by slow addition of an AB_2 monomer to a B_f core molecule [150,151].

In the ideal case, PDI is defined by PDI = 1+ (n −1)/f. The most important side reaction in the core dilution/slow addition procedure is a deactivation of the A group

of the AB_n monomer leading to hyperbranched structures without core molecules. This side reaction increases the PDI of the final product.

The control over the MMA and MMD of hyperbranched polymer by the use of a multifunctional core moiety in the polycondensation of AB_2 monomers has been exemplified by the synthesis of hyperbranched aliphatic polyesters from 2,2-bis(methylol)propionic acid (bis-MPA) and various core molecules, either tris(methylol)propane or ethoxylated pentaerythritol [152].

Control over the molar mass and the polydispersity of the hyperbranched aliphatic polyesters has been demonstrated in step by step polycondensation reaction of AB_2 monomers using multifunctional core moieties, where stoichiometric amounts of DMPA monomer, corresponding to the theoretical dendritic composition of each specific generation, were added successively to the core molecules in bulk under acidic catalysis [153-160].

Zagar et all [161] characterized the commercially available Boltorn Hx (x = 20, 30) hyperbranched (HB) polyesters of different theoretical core/monomer ratio (1/12 for H20 and 1/28 for H30) with respect to molar mass, composition, and structure. Boltorn aliphatic polyesters of the 2^{nd}, 3^{rd}, and 4^{th} pseudo-generation synthesized from 2,2-bis(methylol)propionic acid (DMPA) as the tri-functional AB_2 monomer and ethoxylated pentaerythritol (PP50) as the tetrafunctional B_4 core molecule. The term pseudo-generation was suggested by Hult et al. [162] according to the stepwise addition of bis-MPA to PP50 in portions that represent the theoretical dendrimer generations.

With decreasing core/monomer ratio the fraction of dendritic units increases, whereas the fraction of terminal repeat units decreases. The linear repeat units do not show any specific trend. Consequently, the relative amount of hydroxyl groups in linear repeat units increases and the amount in terminal ones decreases in the same order.

Table 2.3: Contents of dendritic (D), linear (L), and terminal (T) repeat units, degree of branching, DB, coefficient of branching.

Parameter	H20	H30	H40
D (%)	10.0	14.0	16.5
L (%)	56.5	57.0	57.0
T (%)	33.5	29.0	26.5
DB_{Frey}	26.1	32.9	36.7
$DB_{Freachet}$	43.5	43.0	43.0

2.1.3.2 Thermal properties

Due to their highly branched structure, dendritic polymers are almost exclusively amorphous materials. Therefore, the glass transition temperature (T_g) is one of the most important thermal property. T_g is an important parameter for a dendritic polymer with respect to potential applications in the field of powder coatings or rheology modifiers. Upon heating, amorphous components convert from a glassy state to a liquid state at T_g, i.e., into a melt for low molar mass substances or a rubbery state for high molar mass compounds. In the melt, thermal energy is sufficiently high for long segments of each polymer chain to move in random micro-Brownian motions. In the amorphous solid state, on the other hand, polymer chains assume their unperturbed dimensions as they do in solution under theta-conditions. Below T_g, all long-range segmental motions cease. Rotations around single bonds become very difficult and the only molecular motions that can occur are short-range motions of several contiguous chain segments and motions of substituent groups [163].

In the case of dendritic polymers the situation is more complex, since segmental motions are also affected by the branching points and the presence of numerous functional groups. The glass transition temperature of a hyperbranched polymer is not only affected by the chain-end composition, but also by the molar mass and the macromolecular composition [164]. According to Schmaljohann et al. it can be understood as a combination of inter- and intramolecular effects. Differences in T_g of hyperbranched polymers with different repeating units but 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 [165].

For dendritic polymer systems T_g increases with generation number to a limit, above which it remains nearly constant [166]. This increase in T_g with generation number is assumed to reflect a decrease in chain mobility due to branching. A number of research groups demonstrated that the chemical nature of the large number of terminal groups strongly affects the glass transition temperature [167-174].

By means of DSC measurements Sunder et al. demonstrated that the flexibility, i.e., T_g, of a modified highly polar hyperbranched polymer with large number of hydroxyl end groups is controlled mainly by two factors: (i) hydrogen bonding of the end groups, increasing the rigidity of the molecules and (ii) tendencies of the substituents to form higher ordered phases (mesophases, crystallization) [175]. It is an important information that the degree of alkyl substitution has hardly any effect on T_m, however there is a pronounced effect on T_g [173].

2.1.3.3 Mechanical and rheological properties

Investigations on new applications of a polymer are often closely related to its material and processing properties. Therefore, the mechanical and rheological properties of hyperbranched polymers are of great importance. Due to the highly branched, globular structure, the configuration of hyperbranched polymers and dendrimers is coined by a lack of chain entanglements. The non-entangled state imposes poor mechanical properties, resulting in brittle dendritic polymers with limited use as thermoplastics [169]. The stress–strain behavior of hyperbranched polymers can be similar to that of ductile metals as observed by Rogunova et al. for hyperbranched polyesters. Like ductile metals, hyperbranched polyesters do not strain harden. This is due to their globular structure, which does not permit the process of chain extension and orientation (the usual mechanisms of strain hardening). However, intermolecular associations, such as hydrogen bonding and possibly intermolecular crystallization of a few linear segments, provide connections between the hyperbranched macromolecules [173].

Apart from the mechanical properties also the viscosity behavior of linear and branched polymers shows remarkable differences. This was already noted by several scientists at the end of the 1960s [177-182].

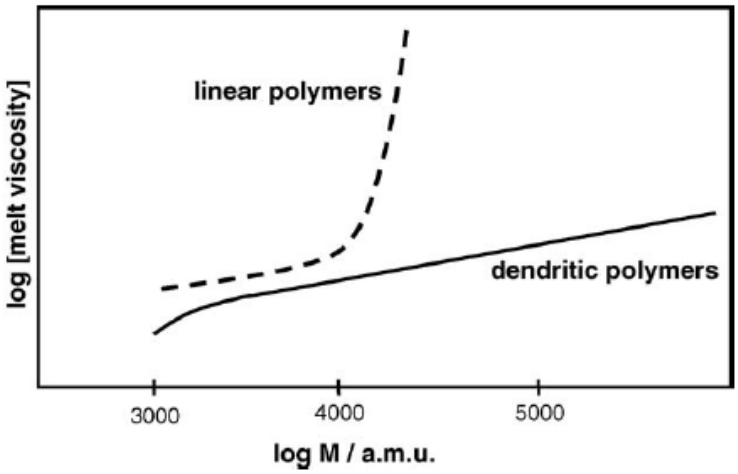


Figure 2.12 : Melt viscosity vs. molar mass of linear and dendritic polymers: a.m.u., atomic mass unit.

Figure 2.12 [176] illustrates the melt viscosity of linear and dendritic polyethers as a function of the molar mass (given in atomic mass units). For linear polymers, above a critical molar mass, a drastic increase in melt viscosity is observed. However, the line for dendritic polymers shows a continuous slope of 1.1 up to 100,000 a.m.u. with no critical mass limit being observed. This behavior can be explained by the different macromolecular structure of linear and dendritic macromolecules. At low molar mass, linear polymers consist of random coil chains which, as the molar mass increases, start to entangle at a critical molecular size, leading to a sharp increase in melt viscosity. Unlike linear polymers, the globular, highly branched architecture of both dendrimers and hyperbranched polymers prevents chain entanglements, resulting in considerably smaller melt viscosities and a continuous slope of the η-function (Figure 2.12). There are a number of studies confirming the strikingly low melt and solution viscosities of dendritic polymers in comparison to linear polymers [169,171,183-186].

2.1.4 Applications of hyperbranched polymers

The main distinguishing features of hyperbranched polymers are the ease of polymerization process when compared to the synthesis of “ideal” dendrimers. A large number of functional groups distributed throughout the polymer structure which impart specific physical and chemical properties, lower intrinsic viscosity than their linear analogues and vastly enhanced solution characteristics due to a low degree of crystallinity and entanglements [187]. Although hyperbranched polymers

are characterized by an irregular structure with high polydispersity, the ease of the synthetic procedures and the globular shape together with the high number of functional groups make those polymers effective candidates for industrial applications.

Based on their unique properties, hyperbranched polymers can be applied as toughenersfor thermosets [188-196], curing, cross-linking or adhesive agents [197-199], dye-receptive additives for polyolefins [200,201], compatibilizers [202], dispersers [203], processing aids, rheology modifiers or blend components [204-211], molecular imprinting [212], catalysis [213], dental composites [214], as macroinitiators [215], in sensors [216,217] and in the encapsulation and to extract guest molecules [218-220]. Hyperbranched polyisocyanates were prepared [221] and used as crosslinkers for the formulation of coatings where they showed better hardness than any other aliphatic isocyanate raw material. Hyperbranched polymers containing labile groups are used as pore forming systems to obtain nanoporous substances for the preparation of low dielectric constant materials for Interlayer Dielectrics [222,223].

2.2 UV Radiation Process

There are two classes of radiation cure coatings; one is UV cure coatings in which the initial step is excitation of a photoinitiator (or photosensitizer) by absorption of photons of UV-visible electromagnetic radiation and the second one is EB (electron beam) cure coatings in which the initial step is ionization and excitation of the coating resins by high energy electrons.

Radiation cure coatings crosslink by reactions initiated by radiation, rather than heat. Such coatings have the potential advantage of being indefinitely stable when stored in the absence of radiation, while after application, cross-linking occurs rapidly at ambient temperature on exposure to radiation. Rapid cure at ambient temperature is particularly significant for heat sensitive substrates, including paper, some plastics, and wood.

UV-radiation curing has become a well accepted technology which has found a large variety of industrial applications because of its distinct advantages. Light-induced polymerization of multifunctional oligomers and monomers is indeed a powerful

method to achieve a quasi-instantaneous transformation of a liquid resin into a solid polymer. The steady development of the UV-curing technology in the past 20 years has opened the way to an increasing number of end uses. The most important ones are to be found in the coating industry for enhanching final properties and surface protection of the product. The vast majority of radiation-curing coatings are based on acrylate chemistry and crosslink via photoinduced radical polymerization.

2.2.1 Basic concepts of UV-curing

Electromagnetic radiation (or light) can be used as the energy source for a variety of processes involving functional monomers, oligomers and polymers. In these processes, it is utilized mainly to effect the formation of new chemical bonds. The light used in polymeric systems typically has wavelengths ranging in the ultraviolet spectral range extending from 200 to 400 nm, although, in some special cases, it may include wavelength in the visible range up to 750 nm (Figure 2.13). Xenon lamps provide significant emissions in the 450 to 550 nm range. Because the energy of radiation increases with increasing frequency (or decreasing wavelength), radiation with short waves contains a large amount of energy. This energy is capable of bringing about certain chemical reactions in a system that is sensitive to light (i.e., the system can absorb light) and the absorbed energy can then generate species that are capable of initiating polymerization or cross-linking reactions.

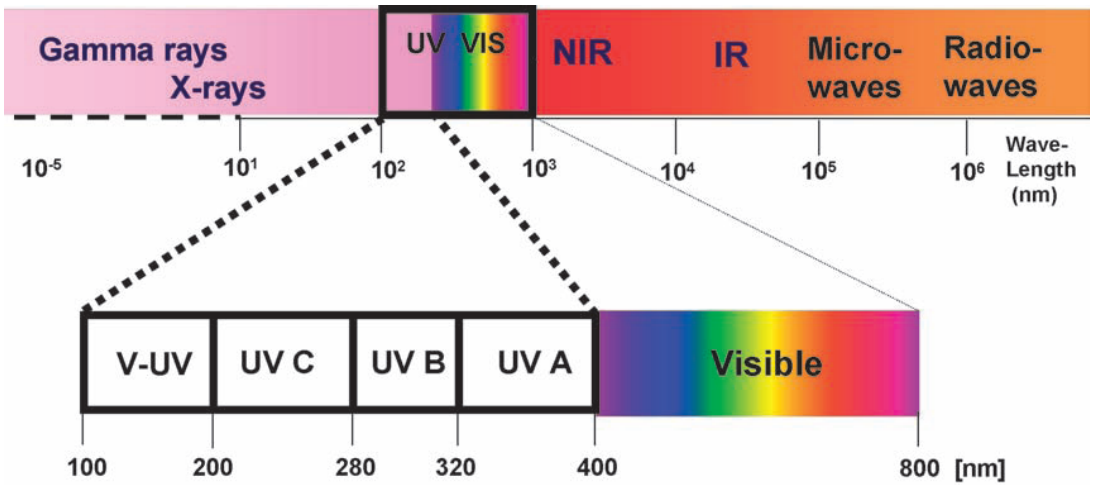


Figure 2.13 : Electromagnetic energy spectrum.

The UV-curing technology is based on the photoinitiated rapid transformation of a reactive liquid formulation into a solid coating film. This process essentially involves polymerization and sometimes polymerization and cross-linking

simultaneously. Monomers and oligomers with the functionality of two form linear polymers, whereas multifunctional polymers (with functionality of more than two) yield three-dimensional cross-linked networks. Cross-linking imparts solvent resistance, increases hardness and improves heat resistance. The main practical utility of these reactions is in curing coatings, inks and in photo-imaging. Cross-linking of already existing polymers is also a viable process and is currently a very active field of research [224].

The processes of photochemistry are the same for polymers and small molecules. The Grotthus-Draper Law states that no photochemical reactions can occur unless a photon of light is absorbed. This means, for example, that many commercial plastics transparent in the near UV can undergo photodegradation only as a result of the absorption of light by impurities.

The intensity of any light absorbed by a light-absorbing species (chromophores) follows Lambert-Beer's Law:

$$I = I_0 \, 10^{-\varepsilon cd} \qquad \textbf{(2.3)}$$

where I_0 is the intensity of the incident light

I is the intensity of transmitted light

ε is the molar extinction coefficient (cm^{-1} mol^{-1})

c is the concentration of absorbing species

d is the optical path length

Absorbance A (or optical density) is defined as $-\log (I/ I_0)$, then $\mathbf{A = \varepsilon cd}$.

Typical chromophoric groups for UV light are C=O, ROOH and aromatic groups. These extend the absorption of monomers, oligomers and polymers into the UV light range. Figure 2.14 shows an energy-level (Jablonski) diagram for a ketone, a common chromophore in polymers. Several intramolecular processes are shown competing with photochemical reactions, including reemission of a photon as fluorescence or phosphorescence, radiationless decay to the ground state and crossing from one excited state to another.

The ground states of almost all organic compounds have all electron spins paired. Absorption of a photon promotes an electron from the singlet state S_0 to a higher

energy singlet state S_1, S_2 … S_n, numbered in the order of increasing energy above the ground state. A change in the spin state of an electronically excited molecule, called intersystem crossing, produces triplet species T_1, T_2 …T_n with two unpaired spins. A triplet state is always lower in energy than the corresponding singlet state.

Singlet states may emit light and return to the ground state. To put it simply:

The absorption of a photon by a chromophore brings about a transition into the excited singlet state.

- Generally, the excited molecule has two possibilities to emit the absorbed energy: It can either return into the ground state by emitting energy by fluorescence or can cross over to the excited triplet state.

- Molecules in the triplet state are biradicals, which can, if the energy is high enough for breaking a bond, form free radicals. The free radicals can then initiate the polymerization and/or cross-linking reaction [225].

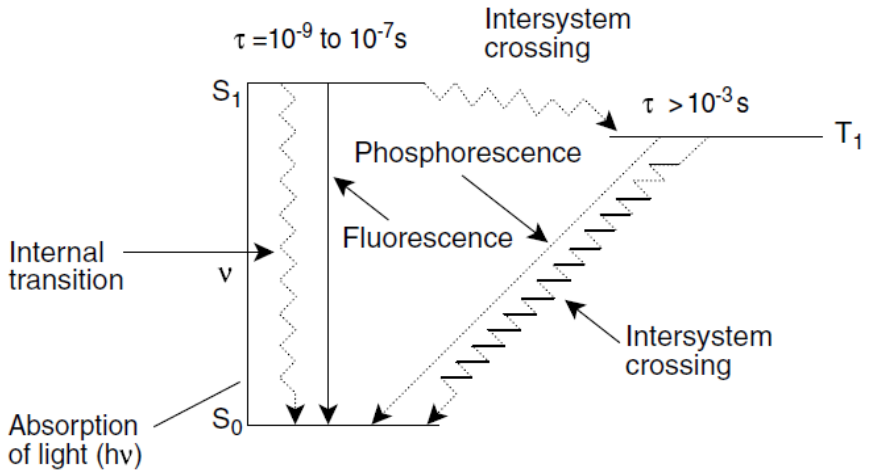


Figure 2.14 : Primary processes occurring in the excited state of a UV radical initiator.

The main decay processes to the ground state shown in Figure 2.14, which is essentially an energy diagram for the different electronic states, are:

- Radiative processes:

- Absorption: $S_0 + h\nu \rightarrow S_1$

- Fluorescence:$S_1 \rightarrow S_0 + h\nu'$

- Phosphorescence: $T_1 \rightarrow S_0 + h\nu''$

where h is the Planck's constant and ν, ν′, and ν″ respective frequencies of the absorbed or emitted light.

- Radiationless processes:
- Internal conversion: $S_1 \rightarrow S_0$ + heat
- Intersystem crossing: $T_1 \rightarrow S_0$ or $S_1 \rightarrow T_1$

The result of a photochemical reaction involving monomers, oligomers and polymers depends on the chemical nature of the material, wavelength of the light and the other components of the system [226].

2.2.2 Principles of photoinduced free radical polymerisation

Photocurable systems are formulations which undergo crosslinking upon irradiation. Two types of photocurable systems are known, namely photosensitive high molecular weight polymers which undergo photocrosslinking reactions and photopolymerisable systems consisting of low molecular weight materials which are cured by a light induced polymerisation reaction. Since the photopolymerisation may be defined as the process whereby light is used to induce an increase in molecular weight, both systems are commonly referred to as photopolymers.

The components of the formulations undergoing polymerisation are not photoreactive, a compound has to be added which can absorb light and subsequently undergo a reaction from its excited state. This reaction finally generates radicals which can initiate the polymerisation process. Molecules or molecular systems capable of forming radicals upon irradiation are termed radical photoinitiators. The initiating radicals can be generated directly by the photochemical reaction or they can be produced by rapid thermal reactions following the primary photochemical reaction.

The initiating radical subsequently adds to a reactive vinyl or acrylate double bond of a monomer, producing a new radical centre on the monomer. This process is the initiation of the polymerisation reaction, which when combined with the previously discussed generation of radical species constitutes the process of photoinitiation.

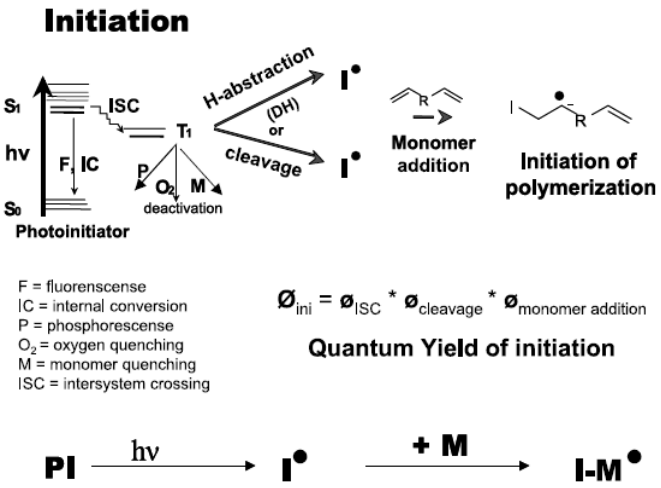


Figure 2.15 : Jablonsky-type diagram for photoinduced radical photoinitiation.

After the initiation step, the classical route of radical polymerisation is valid for the photoinitiated polymerisation process. The following steps are usually distinguished.

i) **Propagation:** Repeated addition of monomeric units in a chain reaction to produce the polymer backbone.

ii) **Chain transfer:** Hydrogen abstraction by the radical on the growing polymer chain to terminate the growing chain with concomitant production of a new radical. If the newly formed radical can start another chain reaction, this is termed a chain transfer process.

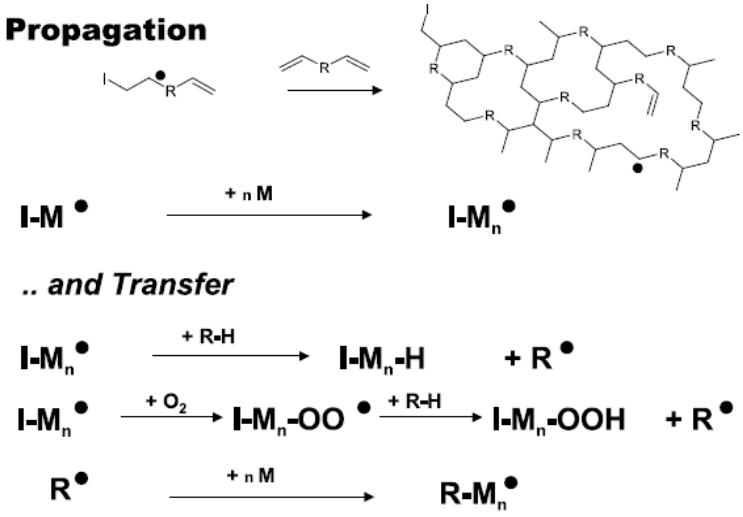


Figure 2.16 : Propagation and transfer.

iii) **Termination:** The chain reaction can be terminated by different processes. Examples are disproportionation or recombination reactions between two growing polymer chains. Termination can also occur upon recombination with any other radical including primary radicals produced by the photoreaction [227].

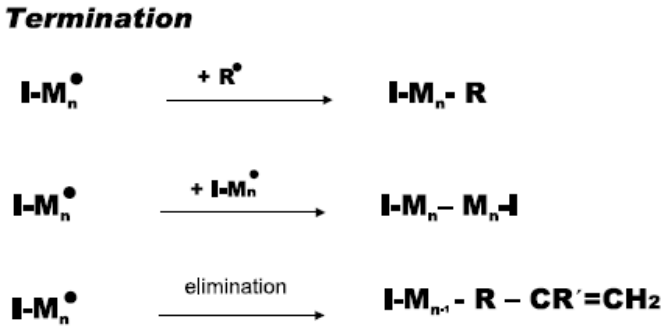


Figure 2.17 : Termination reaction.

2.2.3 Free radical photoinitiators

Photoinitiators are chemicals that form energetic radical species when exposed to UV light. They are essential ingredients in UV-curable coatings in order to obtain polymerization. Depending on factors such as film thickness, UV-light source and particular coating performance requirements, the amount of photoinitiator in a UV coating formulation can range from approximately 0.5 to 15 %.

Photinitiators are generally devided into two classes according to the process by which the initiating radicals are formed. Compounds which undergo unimolecular bond cleavage upon irradiation as shown in Figure 2.18 are named Type I photoinitiators [228] or PI_1- type initiators [229].

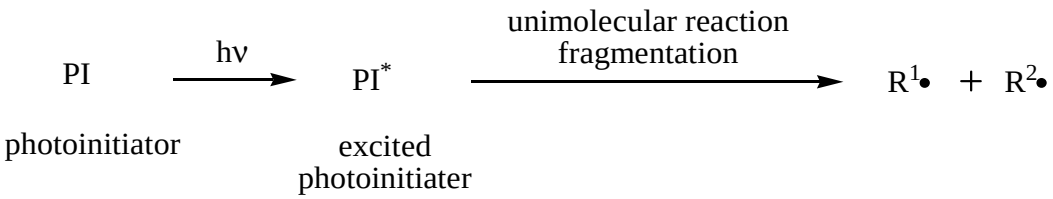


Figure 2.18 : Type I Photoinitiators: Unimolecular fragmentation.

If the excited state photoinitiator interacts with a second molecule (a coinintiator) to generate radicals in a bimolecular reaction as shown in Figure 2.19, the initiating system is termed a Type II photoinititor or PI_2- type initiators.

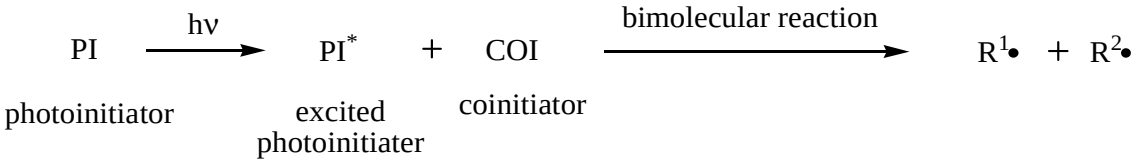


Figure 2.19 : Type II Photoinititor: Bimolecular reaction.

Efficient photoinitiators of both classes are known and find everyday practical usage. Type I photoinitiators are highly reactive UV photoinitiators, but are less frequently used in visible light curing systems. Type II photoinitiators are versatile initiators for UV-curing systems and visible light photoinitiators belong almost exclusively to this class of photoinitiators.

2.2.3.1 Type I photoinitiators

The majority of Type I photoinitiators are aromatic carbonyl compounds containing suitable substituents which facilitate direct photofragmentation, thereby producing radicals. The aromatic carbonyl moiety acts as the chromophore group. An important criteria for a Type I photoinitiator is the presence of a bond with a dissociation enrgy lower than the excitation energy of the reactive excited state, but sufficiently high to provide adequate thermal stability.

Depending on the nature of the functional group and its location in the molecule relative to the carbonyl group the fragmentation can take place at a bond adjacent to the carbonyl group (α-cleavage), at a bond in the β-position (β-cleavage) or, in the case of particularly weak bonds (like C-S bonds or O-O bonds), elsewhere at a remote position. By far the most important fragmentation in photoinitiator molecules is the α-cleavage of the C-C bond between the carbonyl group and the alkyl residue in alkyl aryl ketones which is known as the **Norrish Type I** reaction as shown in Figure 2.20.

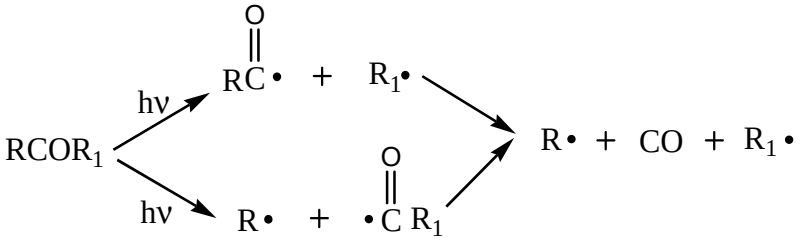


Figure 2.20 : Norrish Type I Reaction.

The Norrish Type II reaction is the abstraction of a hydrogen atom from the γ-position by the carbonyl group, resulting in a 1,4-biradical as the primary photoproduct. Depending on the structure, this will either undergo fragmentation reaction (Type II fragmentation) to give an enol and an alken, or ring closure oxetane as shown in Figure 2.21 [230].

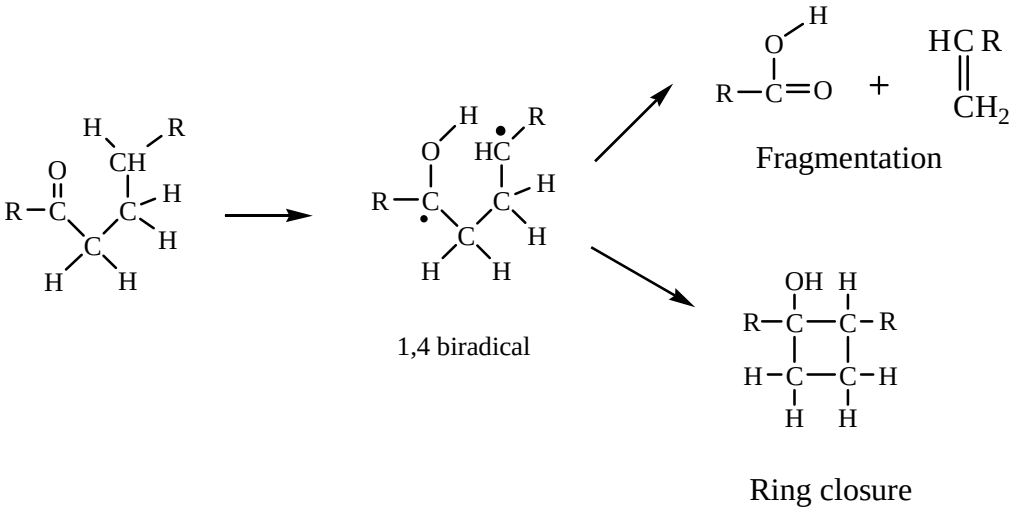
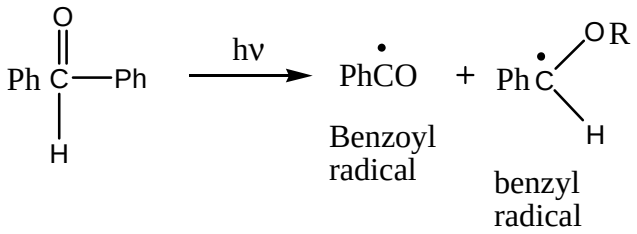


Figure 2.21 : Norrish Type II Reaction.

Benzoin derivatives have long been known to be efficient Type I photoinitiators which have received considerable attention, both in practical applications and photochemical studies. Due to their very fast photochemical reaction, their initiating efficiency is relatively little influenced by interactions with components in the formulation.

α-cleavage of a benzoin ether produces a benzoin radical and α-substituted benzyl radical (Figure 2.22) [231,232]. It has been reported that both types of radicals can initiate the polymerization.



R = H or alkyl

Figure 2.22 : α-cleavage of benzoin ether.

The short excited state life times of many Type I photoinitiators are one of the inherent advantages of unimolecular photoinitiators. Since collision of the excited molecule with another molecule is unnecessary, the excited state does not have to exist for a sufficiently long period of time to allow by molecular reactions to take place as is the case for Type II photoinitiators. A short lived excited state has only limited possibilities to undergo other bimolecular processes, such as quenching reactions by oxygen or monomers which are energy wasting reactions in the photoinitiation process [233].

2.2.3.2 Type II photoinitiators

The short excited state life times of many Type I photoinitiators are one of the inherent advantages of unimolecular photoinitiators. Since collision of the excited molecule with another molecule is unnecessary, the excited state does not have to exist for a sufficiently long period of time to allow by molecular reactions to take place as is the case for Type II photoinitiators. A short lived excited state has only limited possibilities to undergo other bimolecular processes, such as quenching reactions by oxygen or monomers which are energy wasting reactions in the photoinitiation process [233].

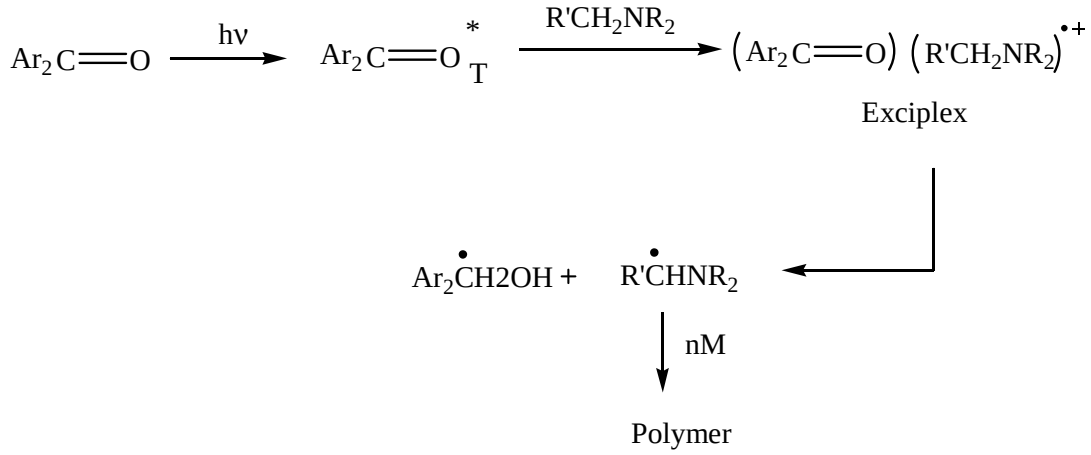


Figure 2.23 : Bimolecular hydrogen abstraction reaction.

The life time of excited state of Type II photoinitiators can not be equally as short, since this would lower the efficiency of the bimolecular initiating reaction to a similar extend as that of the quenching reactions. Bimolecular systems are, therefore, inherently more prone to quenching process. Also, bimolecular reactions are more affected by changes in the environmental parameters (like viscosity) than unimolecular reactions, which is a further advantage of Type I photoinitiators.

2.3 Components of UV Processing

The vast majority of UV curable coatings are based on radical producing photoinitiators. The main components of such formulations based on radical polymerizations are:

- **Reactive resins** containing a plurality of polymerizable double bonds, which govern mainly the desired properties of the final coating;
- **Copolymerizable, monomeric diluents**, which are responsible for the reduction or adjustment of the viscosity of the formulation, a function taken by the solvent in conventional formulations;
- **Photoinitiators** or a photoinitiating system containing photoinitiator and photosensibilizer or coinitiators (described in **Section 2.2.3**);

and, if necessary, **other coating additives**, like surface active additives, slip additives, fillers, pigments, light stabilizers, etc.

2.3.1 Acrylate/Mechacrylate systems

The most widely used UV-curable radical initiated systems are based on acrylate unsaturation, with the general formula H2C=CR-COOR' (if R = H, the monomer is an acrylate, if R = CH_3, it is a methacrylate). Methacrylates are less reactive than acrylates, but are less toxic and cause less skin irritation than acrylates. The curing reaction of acrylates is typical of vinyl monomers. Therefore, the degree of double bond conversion is the measure of the degree of cure. The best results are obtained when using oligomers as binders and monomers as reactive thinners [236].

Monomers, also called **reactive thinners**, are used to reduce viscosity of the prepolymers, but also have an effect on properties of the cured film. They form a high molecular weight network with the prepolymer after curing. To attain an adequate degree of cross-linking, bifunctional and polyfunctional acrylates are principally used. Monofunctional acrylates give a less reactive coating and are less desirable ingredients because of their volatility, odor and skin-irritating effects. Examples of difunctional and polyfunctional acrylates are shown in Table 2.4 [237].

Table 2.4: Examples of difunctional and polyfunctional acrylates used in UV-curing.

Monomer	Type of main chain	Functionality	Abbreviation	Molecular weight	Viscosity, mPa.sec at 25 °C
1,6-hexanediol diacrylate	Linear hydrocarbon	2	HDDA	226	5–10
Tripropyleneglycol diacrylate	Branched ether	2	TPGDA	300	10–20
Dipropyleneglycol diacrylate	Branched ether	2	DPGDA	242	8–12
Trimethylolpropane triacrylate	Branched hydrocarbon	3	TMPTA	296	50–150
Pentaerythritol triacrylate	Branched hydrocarbon	3	PETA	298	350–700
Ditrimethylolpropane tetraacrylate	Branched ether	4	DTMPTA	438	450–900
Dipentaerythritol pentaacrylate	Branched ether	5	DPEPA	525	14000

2.3.2 Urethane Acrylates

Urethane acrylates are used in radiation-curing coatings for industrial applications. The development goal in the area of urethane acrylates is to combine the high performance and many possible applications of polyurethane coating systems with the curing rate and efficiency of photopolymerization. Urethane acrylates are available as solutions in reactive thinners (low viscosity (meth)acrylate esters), as low viscosity oligomers, as solids for powder coating technologies or as urethane acrylate dispersions [238].

Urethane acrylates are manufactured by the addition of hydroxyalkyl acrylates, diisocyanates and polyols, or by the direct addition of hydroxyalkyl acrylates to polyisocyanates. There are two possible methods of preparing the same urethane acrylate when a modifying hydroxyl component is used. In the first method, the diisocyanate and the hydroxy acrylate (or methacrylate) are reacted and the half (or partial) adduct is then reacted with the modifying hydroxy compound. In the second method, the modifying hydroxy compound is reacted with the diisocyanate and the resulting product is then reacted with the hydroxy acrylate. The two processes can be summarised as in Figure 2.24.

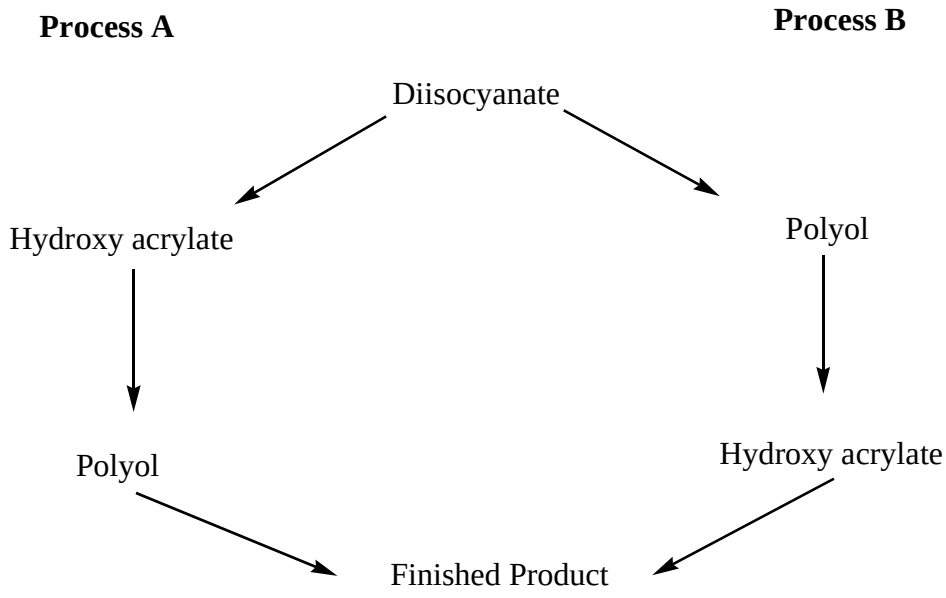


Figure 2.24 : Two alternative processes for preparing a modified urethane acrylate.

The incorporation of non-acrylate (or non-methacrylate) hydroxyl containing components into urethane acrylate structures can vary. The order of addition to the reaction mixture, the type of hydroxyl functionality, the difference in reactivity

between the isocyanate groups, and possible differences in reactivity of the hydroxyl groups, may all have different impacts. For symmetrical diisocyanates, the order of addition is unimportant. For asymmetric diisocyanates (like 2,4 TDI and IPDI) and equivalent amounts of hydroxy acrylate and polyol hydroxyl groups, the order of addition is important. Consider 2,4 TDI for the purposes of illustration. The same argument applies for IPDI. If the hydroxy acrylate is added before a polyol, represented as HO-X-OH (Figure 2.25), then structure [I] is the predominant product, whereas structure [II] predominates if the hydroxy acrylate is added after the polyol.

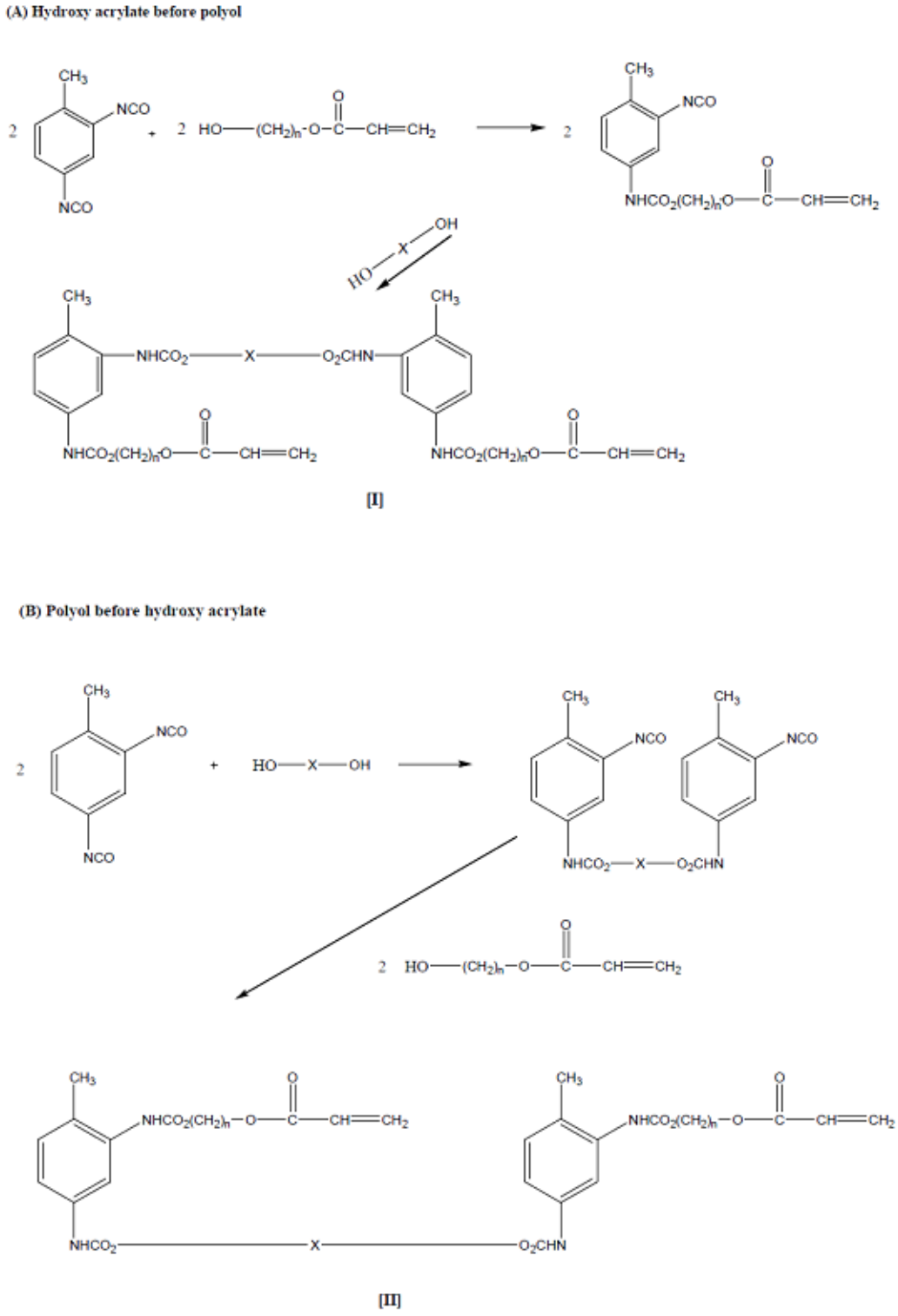


Figure 2.25 : Resulting structures from the reaction of 2,4-TDI, polyol, and hydroxy acrylate, and their order of addition.

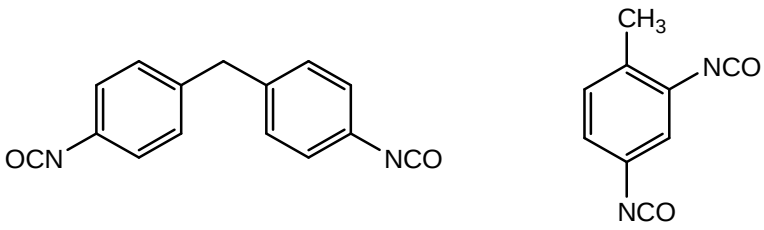
Urethane acrylates can be prepared from a large, diverse range of raw materials. This results in many possible variations in preparation and a very large range of properties of finished products. The diisocyanates which may be acrylated include aromatic and aliphatic isocyanates.

Hydroxy functional monomers include hydroxyethyl acrylate (HEA), hydroxypropyl acrylate (HPA) and hydroxyethyl methacrylate (HEMA). If other hydroxy containing compounds are also present, like polyethers, polyesters or polyols that contain more than one hydroxyl group per molecule, then chain extension is possible. This results in a wide range of prepolymers that vary in functionality and molecular weight with corresponding variations in final film properties. Urethane acrylates offer a far wide range of final film properties of tough, flexible materials that exhibit good abrasion resistance [239].

2.3.2.1 Types of isocyanates and basic reactions

Aromatic isocyanates

The aromatic isocyanates most widely used are based on methylene diphenyl diisocyanate (MDI). MDI is available in several grades: bis(4-isocyanatophenyl)methane, a mixture of 55% of the 2,4' isomer and 45% of the 4,4' isomer; and several oligomeric (frequently called polymeric) MDI with longer chains of methylene phenyl groups. MDI is also used as a prepolymer with polyether polyols. The volatility (particularly of the oligomeric grades) is low enough to reduce toxic hazard, especially as compared to toluene diisocyanate (TDI).



MDI **TDI**

Figure 2.26 : 4,4'-and 2,4'-MDI isomers and an example of an oligomer.

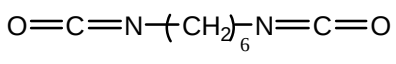
Due to toxic hazards, TDI is not used in final coating formulations. For coatings in which unreacted isocyanate groups are needed, TDI is converted into derivatives of higher molecular weight and higher functionality. Higher molecular weight reduces

the toxic hazard, and the higher functionality yields solvent resistant films more rapidly.

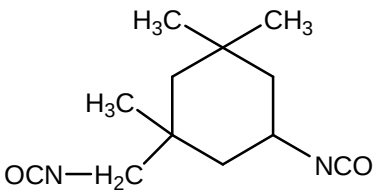
2,4-TDI has the advantage of a differential in reactivity between the ortho- and the para-isocyanate groups with alcohols, which makes possible synthesis of isocyanurates and prepolymers with narrower molecular weight distribution than with diisocyanates, in which the isocyanate groups are equally reactive.

Aliphatic isocyanates

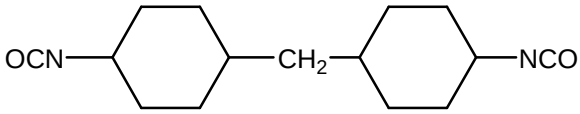
The principal aliphatic isocyanates used are 1,6-hexamethylene diisocyanate (HDI), isophorone diisocyanate (IPDI), bis(4-isocyanatocyclohexyl)methane (H_{12}MDI), 1,3-xylylenediisocyanate (XDI), tetramethyl-m-xylidene diisocyanate (TMXDI) and 2,2,5-trimethylhexane diisocyanate (TMHDI). Diisocyanates are usually converted to derivatives before use in coatings to increase functionality and reduce toxic hazard.



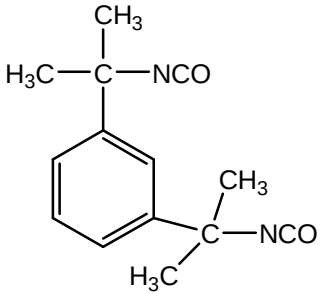
HDI



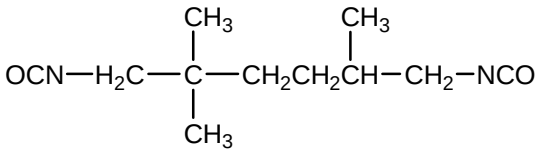
IPDI



H_{12}MDI



TMXDI



TMHDI

Figure 2.27 : Some important aliphatic diisocyanates.

Commercial IPDI is a mixture of Z (cis) and E (trans) isomers in a 75:25 ratio. The isomers are difficult to separate. Isophorone diisocyanate has two different types of NCO groups. Studies performed under different conditions show that with DBTDL catalysis, the secondary NCO group of both Z and E isomers are more reactive than the primary NCO group [240-242]. The selectivity decreases with increasing

temperature, and selectivity is greater with sec-butyl alcohol than with n-butyl alcohol [242]. DABCO promotes selective reaction of the primary isocyanate group of IPDI in contrast to other amines and DBTDL, where selectivity favors reaction with the secondary isocyanate groups. Selectivity decreases with increasing temperature [241,242]. High selectivity is particularly important in making IPDI prepolymers when low molecular weight and narrow distribution of molecular weight are desired. It was concluded that the optimal conditions for prepolymer synthesis based on IPDI are temperatures between 40 - 60°C using DBTDL catalyst. Isocyanurate derivatives of IPDI analogous to the HDI isocyanurates mentioned above are widely used cross-linkers. The rigidity of IPDI affords films with higher T_g. By blending IPDI and HDI isocyanurates, formulators can dial the T_g desired for a particular application.

Basic reactions of isocyanates

Organic isocyanates are manufactured by reacting amines with phosgene.

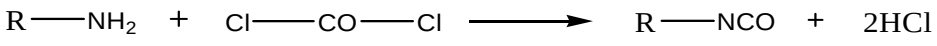


Figure 2.28 : Synthesis of organic isocyanates.

As polyfunctional isocyanates are required for the synthesis of polyurethane resins, poly-amines are used as the base products, preferably diamines. Alternative phosgene-free manufacturing processes have been proven. One example of such an alternative process is the reaction of diamines with urea and alcohols. The diisocyanate is formed via a urethane or diurethane intermediate stage which is then thermally decomposed as shown in Figure 2.29.

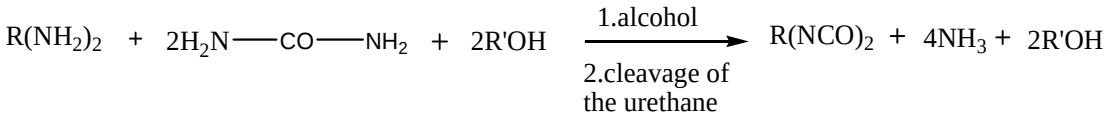


Figure 2.29 : Reaction of diamines with urea and alcohols.

Isocyanates usually react extremely readily by addition with virtually all compounds containing "active" hydrogen. The reactions shown below at Figure 2.30 [243] are of particular interest in the manufacture of polyurethane precursors and for the chemical curing of reactive coatings.

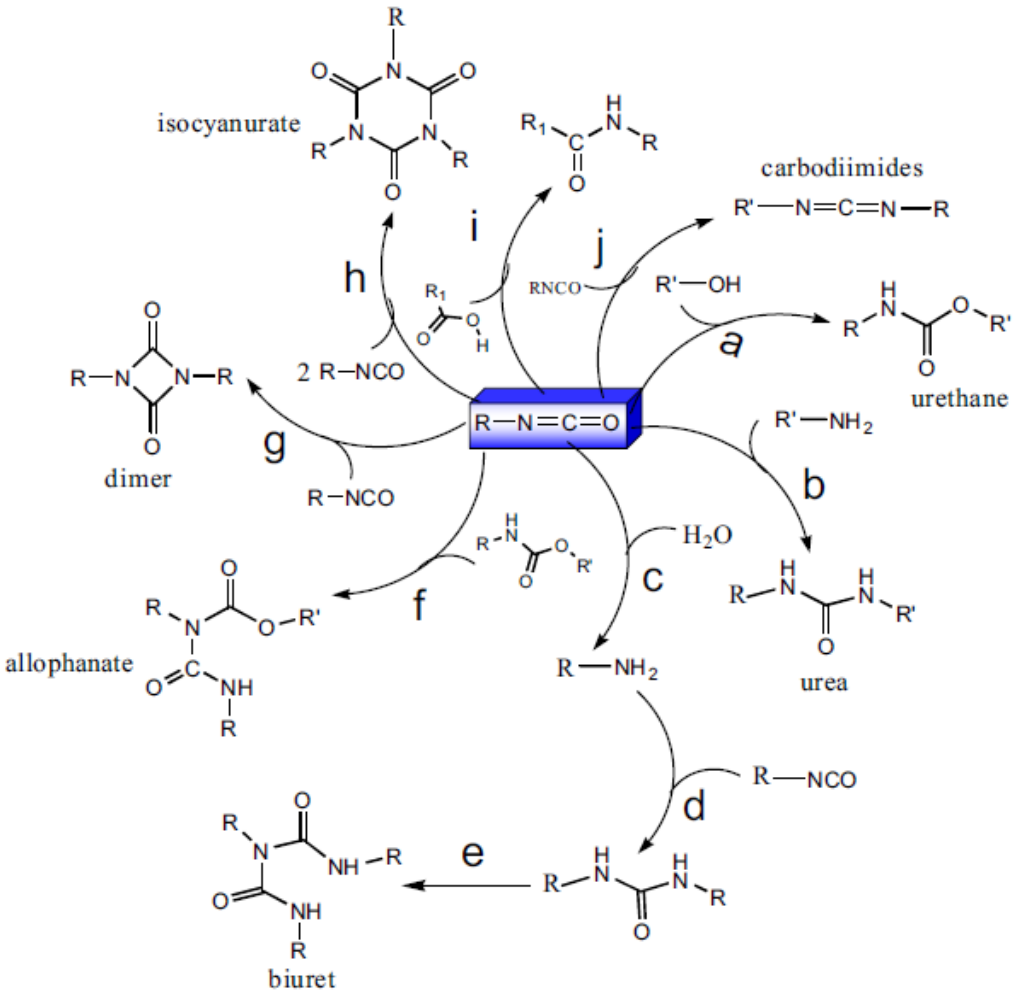


Figure 2.30 : Basic reactions of isocyanate with different reactants.

Formation of urethanes

Isocyanates react with alcohols and phenols to form urethanes which are equivalent in formula to carbamic acid esters.

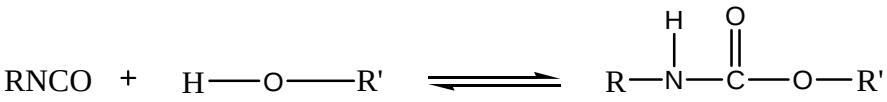


Figure 2.31 : Formation of urethanes.

The reaction is reversible at elevated temperatures. This property is of particular significance in the curing reaction of blocked polyisocyanates. Primary isocyanate groups are more reactive than secondary or tertiary groups. As a rule, the reaction rate with alcohols as the co-reactants follows the same order. Isophorone diisocyanate is the exception.

Formation of amines

Isocyanates react with water via carbamic acids as the intermediate stage to form amines and carbon dioxide. The reaction rate of the water approximates that of secondary alcohols.

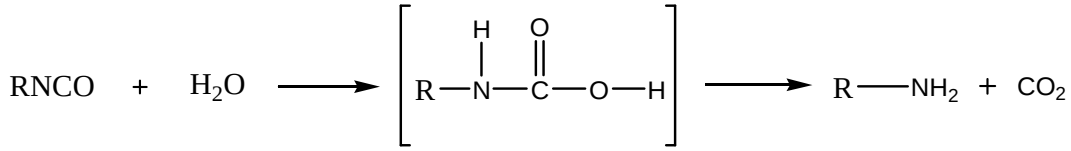


Figure 2.32 : Formation of amines.

The amines formed react with the excess isocyanate to form ureas.

Formation of substituted ureas

Isocyanates react spontaneously with primary and secondary amines to form substituted ureas.

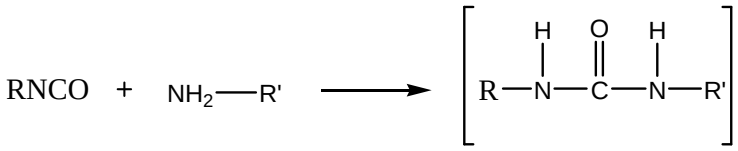


Figure 2.33 : Formation of substituted ureas.

The amines formed react with the excess isocyanate to form ureas.

Formation of biurets

As a rule, isocyanates react with ureas at elevated temperatures to form biurets.

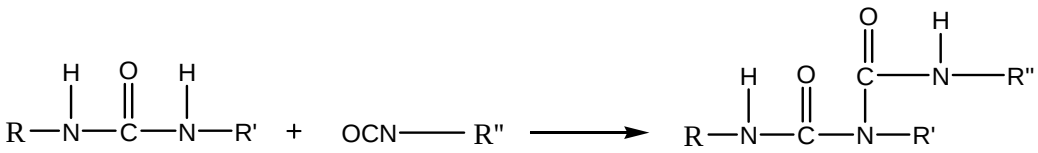


Figure 2.34 : Formation of biurets.

Formation of allophanates

When suitably catalysed or at elevated temperatures, urethanes can be reacted with additional isocyanate groups to form allophanates.

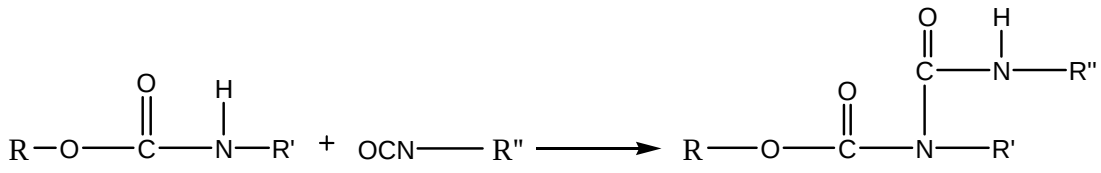


Figure 2.35 : Formation of allophanates.

Formation of uretdiones

Isocyanates can be dimerized under special conditions to form an uretdione ring. This is an equilibrium reaction whose stable state is quickly destroyed at high temperatures, forming a monomer.

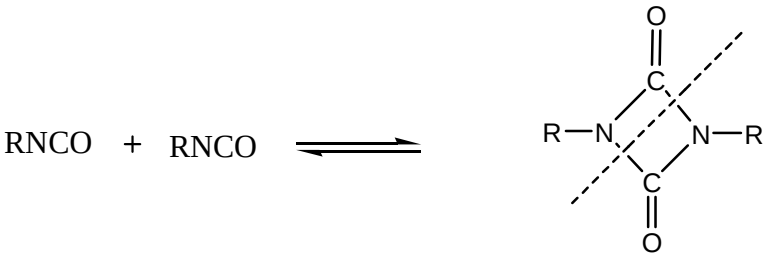


Figure 2.36 : Formation of uretdiones.

Formation of isocyanurates

Trimerization of isocyanates forms an isocyanurate ring which, unlike the uretdione ring, is also stable at high temperatures.

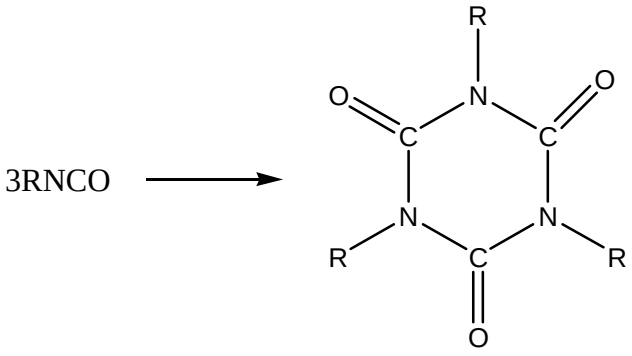


Figure 2.37 : Formation of isocyanurates.

Formation of substituted acid amides

At high temperatures, isocyanates react with carboxylic acids with the intermediate formation of mixed anhydrides. These dissociate to form amide and carbon dioxide.

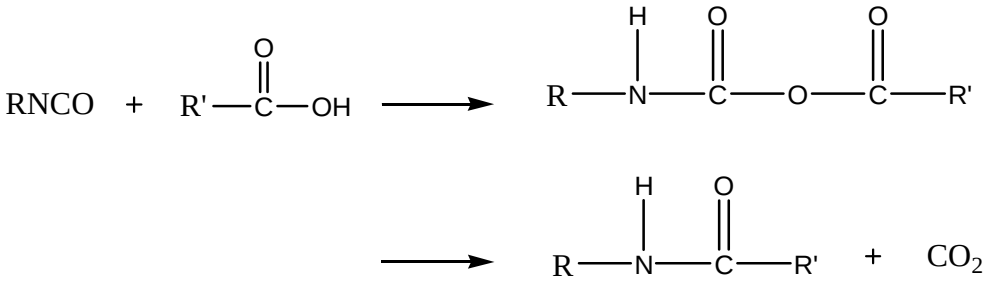


Figure 2.38 : Formation of substituted acid amides.

Formation of carbodiimides

Isocyanates can react with each other, splitting off carbon dioxide [244].

Figure 2.39 : Formation of carbodiimides.

2.3.2.2 Types of Polyols

The properties of polyurethanes are not only affected by the polyisocyanate, but also in large measure by the hydroxyfunctional coreactant, the polyol. Selecting suitable polyols and polyisocyanates makes it possible to control key characteristics of the coating and the resulting paint film. Solids content, drying, gloss, elasticity and hardness, resistance to chemicals and hydrolysis, and cost-effectiveness are just some examples in this respect. Research in the past has therefore concentrated greatly on the development of new and improved resins. The most important coreactants for polyisocyanates are hydroxyl-bearing polymers such as polyester, polyether and polyacrylate polyols.

Polyether polyols

The polyether polyols for elastic polyurethanes are low molecular weight polymers, with terminal hydroxyl groups, characterised by the following general repeating units.

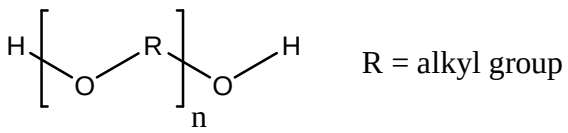


Figure 2.40 : The general formula of polyether polyol.

Polyalkylene oxide polyether polyols are the most important group of polyols for polyurethane, representing around 80% of the total oligo-polyols production. The

polyalkylene oxide polyols are obtained by the polymerisation of alkylene oxides, initiated by different polyols called starters or chain initiators. The most important alkylene oxides (oxiranes or epoxides) used in oligo-polyols synthesis are propylene oxide (PO), ethylene oxide (EO) and butylene oxide (BO). The general formula of a polyalkylene oxide polyether polyol is presented in Figure 2.41.

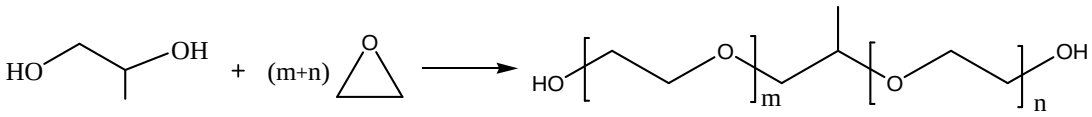


Figure 2.41 : Manufacture of a polyether polyol based on 1,2-propanediol and EO.

Polyvalent alcohols such as ethylene glycol, 1,2-propanediol, glycerol and trimethylolpropane, or amines such as ethylenediamine (which yields tetrafunctional polyether alcohols) are used as the starter molecules. The addition of the aklene oxide is usually performed in an alkaline medium with sodium hydroxide as the base.

Key properties of the polyether such as the melting point, viscosity, hydrophilicity and compatibility can be controlled via the ratio of the ethylene oxide to propylene oxide. Due to their low viscosity, polyether polyols are used mainly in solvent free coating systems. However, because of the poor weather stability of polyethers – a consequence of oxidative polyether chain degradation - their use is restricted to interior applications or to the formulation of primers. On the other hand, these systems are characterized by particularly good resistance to hydrolysis and mechanical stability. For these reasons, they are often used in the construction sector for coatings on mineral substrates such as concrete.

2.3.2.3 Polyester polyols synthesis and applications

Polyester polyols are the second most important group of oligo-polyols for production of polyurethanes after polyether polyols. The superior characteristics of polyester polyol based polyurethanes are explained by a better crystalline structure [245] in the urethane segment, compared to the majority of polyether polyols which are amorphous [except polytetrahydrofuran (PTHF)], due to the superior secondary forces between the polyester chains and also due to a superior thermal and fire resistance, compared to polyether polyol based polyurethanes. Polyester based polyurethanes (flexible foams, coatings), have a superior solvent resistance compared to the polyether-based polyurethanes [246].

Polyester polyols are produced by the polycondensation of di- and polycarboxylic acids with an excess of polyfunctional alcohols (polyols) (Figure 2.42). In addition, polyester polyols are made by the reaction of caprolactone with diols. Poly(caprolactone diols) are used in the manufacture of thermoplastic elastomers with improved hydrolytic stability [247].

The most important polycarboxylic acids and their anhydrides which are available on an industrial scale for the manufacture of polyester polyols include the aromatic acids phthalic acid and isophthalic acid, the aliphatic acids adipic acid and maleic acid, and the cycloaliphatic acids such as tetrahydrophthalic acid and hexahydrophthalic acid.

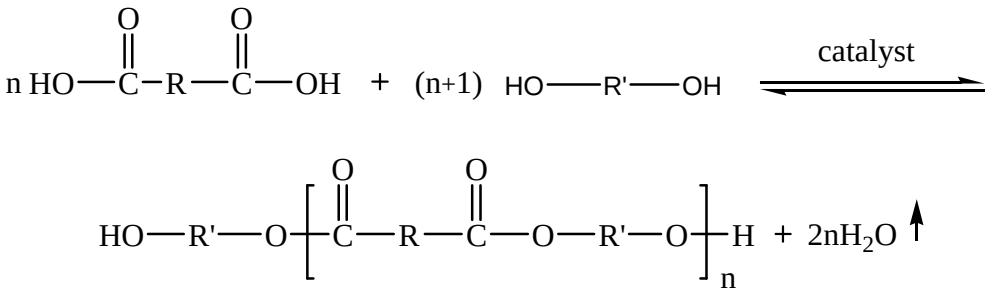


Figure 2.42 : Structure of a linear polyester polyol based on the 1,6-hexanediol/adipic acid.

The polyols used are aliphatic alcohols such as ethane diol, 1,2-propanediol, 1,6-hexanediol, neopentyl glycol, glycerol and trimethylolpropane, and cycloaliphatic alcohols such as 1,4-cyclohexanedimethanol. In addition, monofunctional alcohols or carboxylic acids such as 2-ethyl hexanol or 2-ethyl hexanoic acid can be used as chain terminators [248].

Synthesis of polyester polyols

Polyester polyols are produced by a condensation reaction of polycarboxylic acids with polyols, splitting off water. There are two processes which are used in particular. The first is the melt condensation process in which the coreactants are reacted in the melt at temperatures of approximately 160 to 260 °C. The reaction is performed either in a vacuum or in a stream of inert gas to remove the water. The second process is azeotropic esterification performed in an organic solvent which acts as the carrier to remove the reaction water.

The condensation reaction can be accelerated by increasing the reaction temperature and the amount of inert gas used, by reducing the pressure and/or by the addition of catalysts, which is particularly advantageous towards the end of the esterification process. Suitable catalysts include bases such as lithium hydroxide or tin compounds such as di-n-butyl tin oxide. As a binder for coatings, the polyester polyol is used either solvent-free as a viscous resin or it is dissolved in a solvent. It may also be used in solid form or as a dispersion in water [249].

Properties and applications

The properties of polyester polyols and of the polyurethane coatings in which they are used are determined by the choice of raw materials, the molecular weight, the Tg and the functionality. Generally speaking, saturated polyester polyols have good pigmentability and yield coatings with good weather stability and high gloss. This makes them suitable for a broad range of applications from vehicle finishing (including aircraft) to general industrial coatings (machinery). However, only the non-aromatic products yield good UV stability, since aromatic polyesters tend to yellow on exposure to light. Unsaturated aliphatic/cycloaliphatic polyesters based on maleic acid anhydride represent a special case. Despite the double bond, they have particularly high UV stability [250].

Polycarbonate polyols

Polycarbonate polyols are esterification products formed by the reaction of carbonic acid with polyols. In practice, the carbonate structure is introduced using phosgene or carbonic acid diesters [251]. Because of their poor solubility, aromatic polycarbonates based on bisphenol A are not used in coating applications. In contrast, linear aliphatic polycarbonates are used both as binders in high quality polyurethane coatings and in the production of polyurethane binders, especially polyurethane dispersions [252,253]. Aliphatic polycarbonate polyols are characterized by their low viscosity, and the resulting coatings by good weather stability and very good resistance to hydrolysis.

Polycaprolactone polyols

Polycaprolactone polyols are produced by the ring-opening polymerization of ε-caprolactone. Suitable starter molecules are polyfunctional alcohols such as ethylene

glycol, 1,2-propanediol, glycerol and trimethylolpropane [254]. The ring-opening polymerization takes place at temperatures of approximately 120 to 200 °C and can be accelerated by the addition of catalysts such as organometallic compounds. The process yields low viscosity products with defined functionality. These are used either as sole binders or as reactive thinners in solvent-free or high solid two component polyurethane coatings. Polycaprolactone polyols are also used as polyol building blocks in the manufacture of high molecular weight polyurethanes. A further use of the ring-opening polymerization of ε-caprolactone is in the modification of higher molecular weight polyols, e.g. polyacrylate polyols. The technical advantages of polycaprolactone polyols include their flexibility and weather stability, in addition to their low viscosity. The main applications for these materials are in two-component polyurethane coatings for plastics (automotive sector) and in solvent-free coatings for construction applications. Polycaprolactone diols are also used as soft segment in polyurethane dispersions [255, 256].

Polyacrylate polyols

The term polyacrylate polyols covers copolymers of acrylic and/or methacrylic acid esters - ethyl acrylate, butyl acrylate and methyl methacrylate - which also bear hydroxyl groups. In practice, other comonomers are frequently used together with these, e.g. styrene, vinyl ester or maleates. The hydroxyl groups needed for reaction with isocyanate groups are usually introduced directly via functionalized esters of acrylic and methacrylic acid, e.g. hydroxyethyl acrylate, hydroxyethyl methacrylate or hydroxypropyl methacrylate.

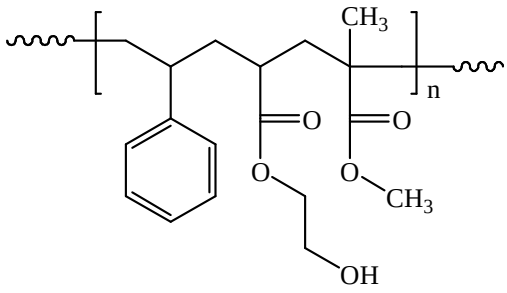


Figure 2.43 : Structure of polyacrylate a polyol.

Another way of generating hydroxyl groups is by polymer-analog reactions on finished polyacrylates [257].

Polyurethane polyols

Polyurethane polyols are produced using the diisocyanate polyaddition process in which diisocyanates are reacted with an excess of diols and/or polyols. On account of their high viscosity, these products are as yet of little importance in the field of solventborne coating systems. By contrast, hydroxyfunctional aqueous polyurethane dispersions are used successfully in one-component and two component systems for wood and plastic coatings, e.g. for producing soft-feel effects, and for glass coatings.

2.3.3 Polyester urethane acrylates

Polyester urethane acrylates or methacrylates can be considered to consist of three major components:

1. Polyester polyol
2. Multifunctional isocyanate
3. Hydroxy compound containing reactive unsaturation which would typically be an acrylate or methacrylate

Preparation

The polyester polyol can be reacted with TDI, followed by hydroxyalkyl acrylate, or a half adduct of a TDI acrylate. The formulation for a half-acrylated product might be as at Table 2.5.

Table 2.5: Polyester urethane acrylate formulation.

Constituent	Composition
Polyester polyol 'D'	1 hydroxyl equivalent
TDI	1 mole (2 hydroxyl equivalents)
Hydroxyalkyl acrylate	1 hydroxyl equivalent

Two possible processing methods can be described in the synthesis of polyester urethane acrylate. In the first method, the polyester polyol, TDI, inhibitor, catalyst, diluent (if necessary) are all charged to the reactor the temperature is held at 30-40°C. The HEA is charged to the reactor when the isocyanate level reaches its theoretical value for complete reaction with the polyester polyol. The reaction is held at 50-60°C until there is less than 1% of -NCO remaining at which time the temperature is raised

to 80-90°C. The reaction is continued until the -NCO level is undetectable and, if necessary, -NCO scavengers are added. The prepolymer is cooled, diluted, if necessary, and discharged.

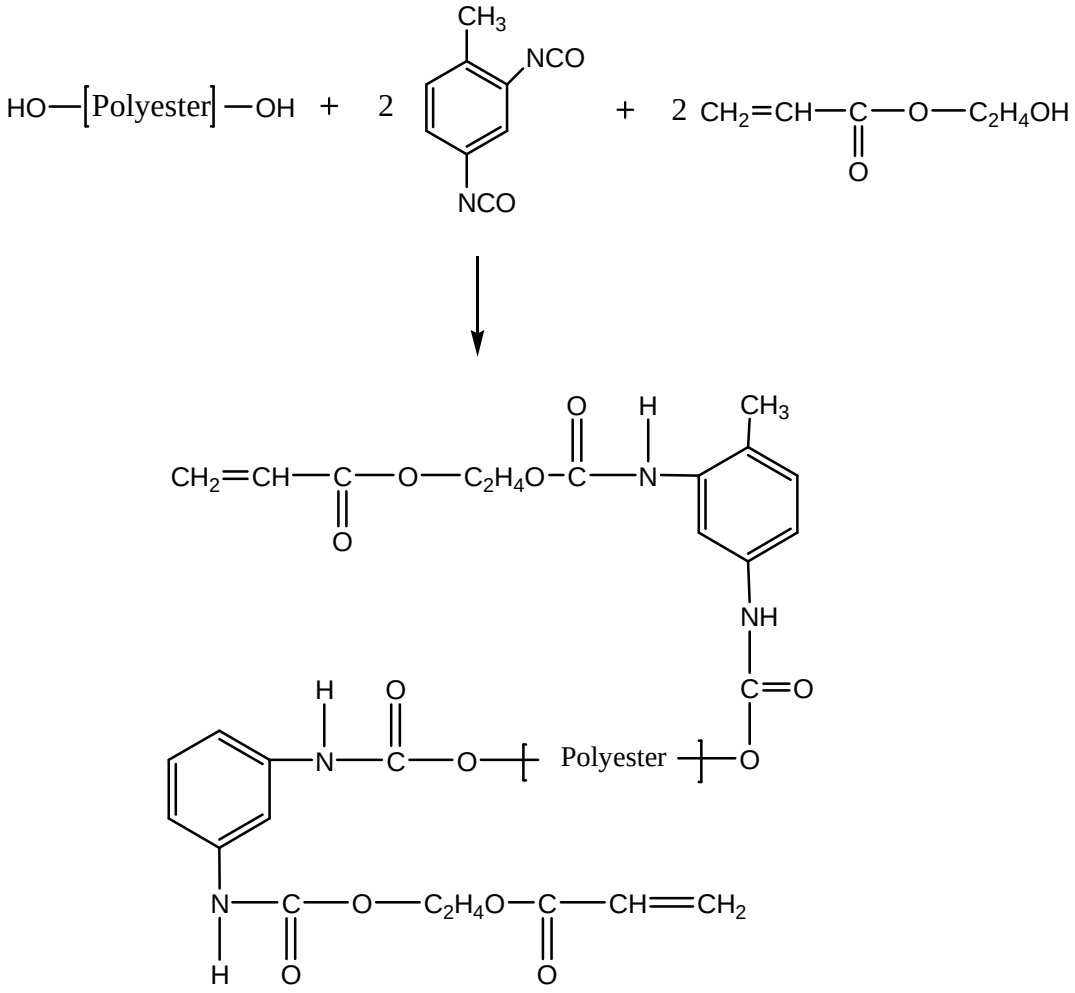


Figure 2.44 : Preparation of Polyester Urethane Acrylate.

In the second method, the TDI, HEA, and inhibitor are charged to the reactor, heated to 30-50°C, and held until the isocyanate level reaches its theoretical value. The polyester, catalyst and diluent are then charged to the reactor and the temperature is held for 1-3 hours at 50-60°C. The process is then continued, as in the first case above. The first method is preferred by some manufacturers because there is less chance of an acrylate gel. The second method is preferred by other manufacturers because the former method results in free HEA. Obviously, TDI can be replaced by other diisocyanates and a variety of commercial polyester polyols can be used [258].

2.3.4 Epoxy acrylate

Epoxy resins are polyether resins containing more than one epoxy group capable of being converted into the thermoset form. These resins, on curing, do not create volatile products in spite of the presence of a volatile solvent. The epoxies may be named as oxides, such as ethylene oxides (epoxy ethane), or 1,2-epoxide. The simplest epoxy resin is prepared by the reaction of bisphenol A with epichlorohydrine. The value of repeat units (*n)* vary from 0 to 25. This determines the end-use applications of the resin [259].

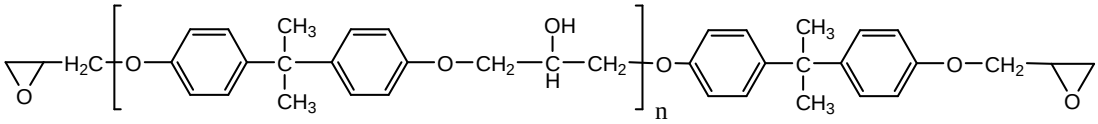


Figure 2.45 : Oligomer of Bisphenol A diglycidyl ether.

The oligomers of bisphenol A diglycidyl ether (DGEBA or BADGE) contain hydroxyl groups. The relationships between n, molecular weight, and physical state are given in Table 2.6.

Table 2.6 Relationship between repeat units and some properties of DGEBA epoxy resins.

Value of n	Molecular weight	Epoxy equivalent	Melting point
0-1	350 - 600	170-310	<40*
1 -2	600 - 900	310-475	40-70
2-4	900- 1400	475-900	70-100
4-9	1400-2900	900-1750	100-130
9- 12	1900-3750	1750-3200	130-150

* usually liquid at ambient temperature

The coatings industry is the biggest consumer of epoxy resins. These resins are used mostly as chemical and special purpose coatings. Epoxy resins provide thin-layer durable coatings having mechanical strength and good adhesion to a variety of substrates. They are resistant to chemicals, corrosion, and solutions. They find applications in washing machines and appliances, ships and bridges, pipelines and

chemical plants, automobiles, farm implements, containers, and floor coatings. Epoxy coating formulations are available as liquid resins, solid resins, high molecular weight thermoplastic resins, multifunctional resins, radiation curable resins, and special purpose resins [260].

Epoxy resins are characterised by the possession of more than one 1,2-epoxy groups per molecules, which are the active centers of the resin [261]. The epoxy group varies in reactivity, depending on whether it is terminal, internal, or ring-situated. In the case of bisphenol A diglycidyl ether and epoxy novolac resins, terminal epoxy groups which react.

The catalysed reaction of an epoxy group with either acrylic or methacrylic acid will result in an epoxy acrylate or methacrylate, respectively [262]. There is a wide range of epoxy acrylates available, including acrylates of bisphenol A diglycidyl ether, epoxy novolacs and epoxidised oils, such as soya or linseed. The wide use of epoxy acrylates based on bisphenol diglycidyl ether and epoxy novolac is due to their versatile chemistry to tailor make products with good adhesion, hardness, and chemical resistance.

The epoxy acrylates prepared by the reaction of epoxides, e.g., Bisphenol-A diglycidylether, with acrylic acid is shown in Figure 2.46. These Bisphenol-A type acrylated epoxides are the dominant products on the market and account for about 70% of all epoxy acrylates used.

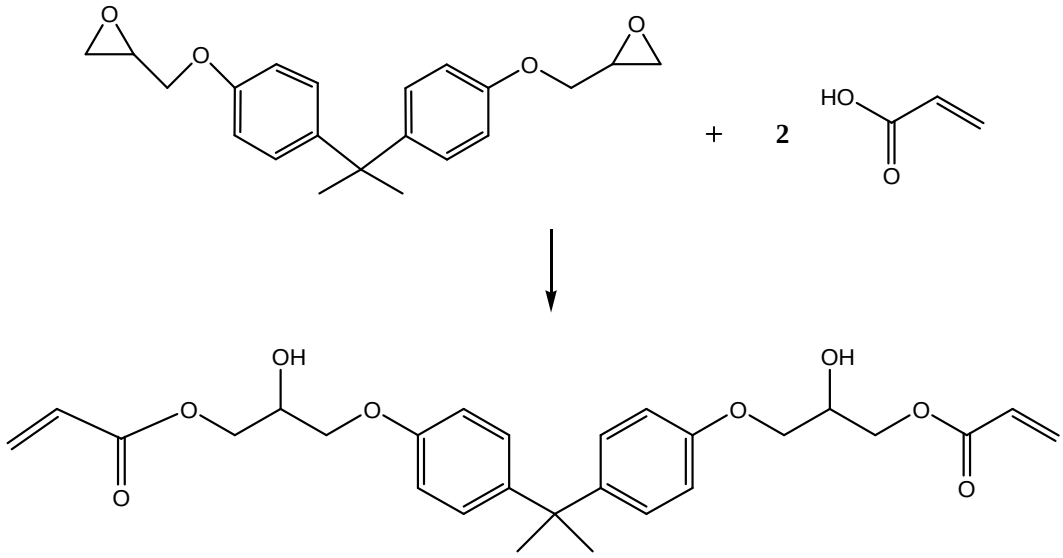


Figure 2.46 : Epoxy acrylate based on Bisphenol-A diglycidylether reaction with acrylic acid.

Due to the high viscosity of especially the Bisphenol-A type epoxy acrylates, they are delivered usually diluted with reactive diluents, like hydroxypropyl acrylate, dipropylene glycol diacrylate, tripropylene glycol diacrylate or hexanediol diacrylate. The epoxy acrylates contributes to adhesion and produce hard and chemically resistant films by high reactivity. Main uses are paper coatings and inks as well as wood coatings [263].

2.3.5 Polyester acrylate

Acrylated polyesters are prepared by reacting the OH group of polyesters with acrylic acid or hydroxy acrylate with acid groups of the polyester structure. Polyester acrylates are often low viscosity resins requiring little or no monomer. They produce coatings and adhesives dominated by the polyester structure used in the oligomer. They are used for pressure-sensitive adhesives and also for strong rigid adhesives for metal-to-metal bonding. Amino-modified polyester acrylates show a high reactivity and low skin irritation.

2.3.6 Polyether acrylate

Polyether acrylates are produced by esterification of polyetherol with acrylic acid. They have a very low viscosity and do not require reactive thinners. Amino-modified polyether acrylates have a higher reactivity and low skin irritance, similar to polyester acrylates. Solid urethane and polyester acrylates can be used as main components of radiation curable powders. Together with suitable unsaturated polyesters, powders are formed that give low film flow temperatures and allow separating of film formation from curing. This technology has been used successfully in powder coating of wood and plastics [264].

2.3.7 Silicone acrylates

Acrylated organopolysiloxanes, which exhibit excellent release properties, are used as release coatings on papers and films. The silicone structure provides flexibility and resistance to heat, moisture, radiation degradation and shear forces.

2.3.8 Structure property relationships

The properties of networks and thus of the coatings depend strongly on the physical state of the materials, being at the application temperature in a glassy state, in a rubber-like soft region or even in the transition between glass and rubber.

In this transition region, the modulus is heavily influenced by temperature and may drop by several orders of magnitude. This transition is defined by the glass transition temperature (T_g). Since almost all crosslinked coatings are amorphous polymer networks, the glass transition temperature has the most prominent influence on the mechanical properties.

The T_g describes the deflection from linearity of the increase or decrease of volume of a polymer during heating, from a glassy to a soft state or during cooling from the soft to a glassy state.

Since the mechanical properties of crosslinked coatings are strongly influenced by the glass transition temperature, the structural influences on the T_g are discussed.

If the T_g of the coating is below the application temperature, the coatings often exhibit some of the following properties:

• Soft and flexible,

• Difficult to sand (rubber-like),

• Exhibiting poor blockability (tacky),

• Low barrier properties (against chemicals, oxygen, water),

• High water uptake and swelling.

If T_g is above the application temperature, the coating can often be characterized as:

• Hard, to some extent brittle,

• Exhibiting low water uptake and swelling,

• High barrier properties against chemicals and water,

• High scratch resistance, and

• High chemical resistance.

Physically, T_g can be explained as the lowest temperature where segments of polymer molecules start moving relative to neighbouring segments and start occupying a larger volume.

The glass transition is not a sharp point, but rather a transition range depending on the thermal history of the sample. With fast heating rates the T_g appears at higher temperatures and if the material was cooled down rapidly, the T_g appears to be lower than with samples that are cooled down more slowly [265].

The main influences of the acrylate (resin) functionalities and resin types on the polymerization process and general properties are exemplarily shown in Figures 2.47 and 2.48.

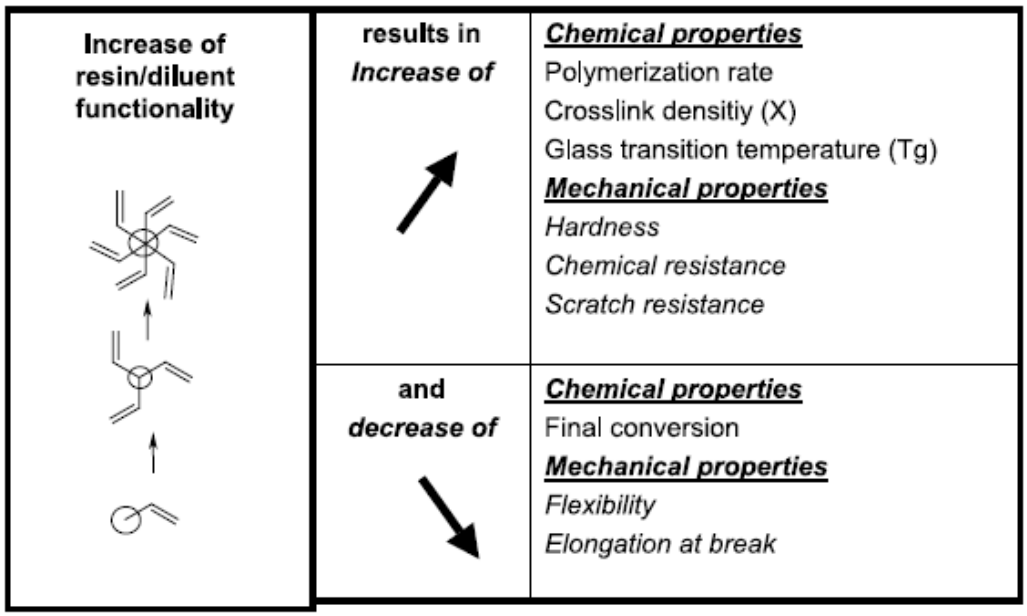


Figure 2.47 : Influence of resin/diluent functionality on the polymerization process and some properties.

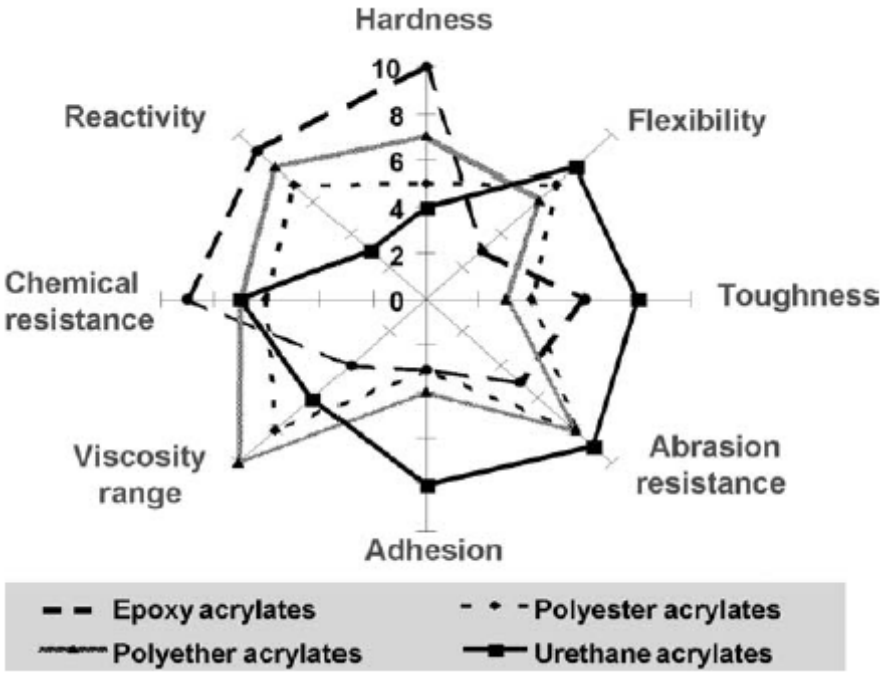


Figure 2.48 : Generalized properties of typical resins of the different UV curable acrylate resin classes (spider diagram: 0, worst; 10, best).

Increasing the monomer (diluent or resin) functionality leads to higher cure speed, higher T_g, higher crosslink density, higher hardness and higher chemical and scratch resistance, but lower flexibility and lower conversion, causing a higher content of uncured residual unsaturated groups. Generalized structure–property relationships of the typical resins used in radiation curable acrylate systems are given in Figure 2.48. The performance criteria shown in the diagram are rated relative to a defined scale, ranging from poor (=0) to excellent (=10).

The (aromatic) epoxy acrylates provide high hardness, reactivity and chemical resistance, whereas urethane acrylates are known for their high flexibility, toughness and abrasion resistance. The polyester acrylates have a well balanced property profile, making them typical all-rounder, and the polyether acrylates are very good reactive diluents due to their low viscosity but also usable as pure resin materials [266].

2.4 Hyperbranched Polymers in UV-curing Systems

As a class of UV-curable oligomers, hyperbranched acrylated systems have attracted increasing attention from a fundamental viewpoint and for the great variety of expected applications. Several groups are working with these materials for use as

oligomers in UV-curable systems [267-269]. The resin could be UV-cured, and the T_g of the cured films can be correlated with the terminal group concentration in the hyperbanched acrylate [270]. Hyperbanched acrylates have low viscosity compared to conventional polyester acrylates of similar molecular weight. Hyperbanched polyester acrylates exhibit rapid cure rate and lower shrinkage than conventional polyester acrylates. The cured films have excellent physical and mechanical properties such as good adhesion, flexibility, impact strength, hardness, chemical resistance, scratch resistance and the presence of small amount of low extractable residual unsaturation. The use of acrylated aliphatic hyperbanched polyesters based on 2,2-bis(methylol) propionic acid in UV-curable application has been described in several papers [271-274] . Resins based on hyperbranched polyurethane acrylates containing phosphorus were found to be flame-retardant or can be used as additives to conventional UV-curable coating systems [275]. Recently, Dzunuzovic et al. [276] and Dunjic et al. [277] described the synthesis and properties of urethane acrylates based on aliphatic hyperbranched polyesters, but the products have rather high viscosity, especially those with higher functionality. In order to reduce the viscosity of the product, urethane acrylates were obtained from an hyperbranched polyester partially modified by a soybean fatty acid, IPDI and 2-HEA. The additional double bonds from the soybean fatty acids enhance its crosslink density [278]. Alkyds based on hyperbranched polyesters and unsaturated fatty acids exhibited a substantially lower viscosity compared to a similar mixture with conventional curing agent. Also they had excellent curing properties with amazingly short curing times, which is beneficial from UV cure point of view [279-281] . Shi and Xu [282] synthesized three UV-curable hyperbranched polyurethane acrylates possessing different double-bond density and partially chain structures, which made the difference in their photopolymerization behaviors and dynamic mechanical and thermal properties.

The synthesis of hyperbranched polyurethane acrylate by Shi and Xu [283] involves a three-step procedure. The authors modified HBPE-OH with succinic anhydride or phthalic anhydride and then further reacted with epoxy propane and TDI-HEA; the photo-polymerization and the dynamic mechanical thermal properties of the resultant materials were studied (Figure 2.49a). In another report from the same group [284], hyperbranched D-1-OH from HBPE-COOH was prepared (Figure 2.49b). D-1-OH is

a translucent viscous liquid and possesses eight double bonds at the periphery. They also prepared dendritic polyester with about 12 and 16 end-double bonds by reacting hydroxyl group of D-1-OH with methacrylic anhydride. Tasic et al. [285] synthesized and evaluated new hyperbanched urethane acrylates having high functionalities and molecular weights, with acceptable viscosities. Their results show that the cured coatings have excellent mechanical properties due to high molecular weights and acrylate functionality.

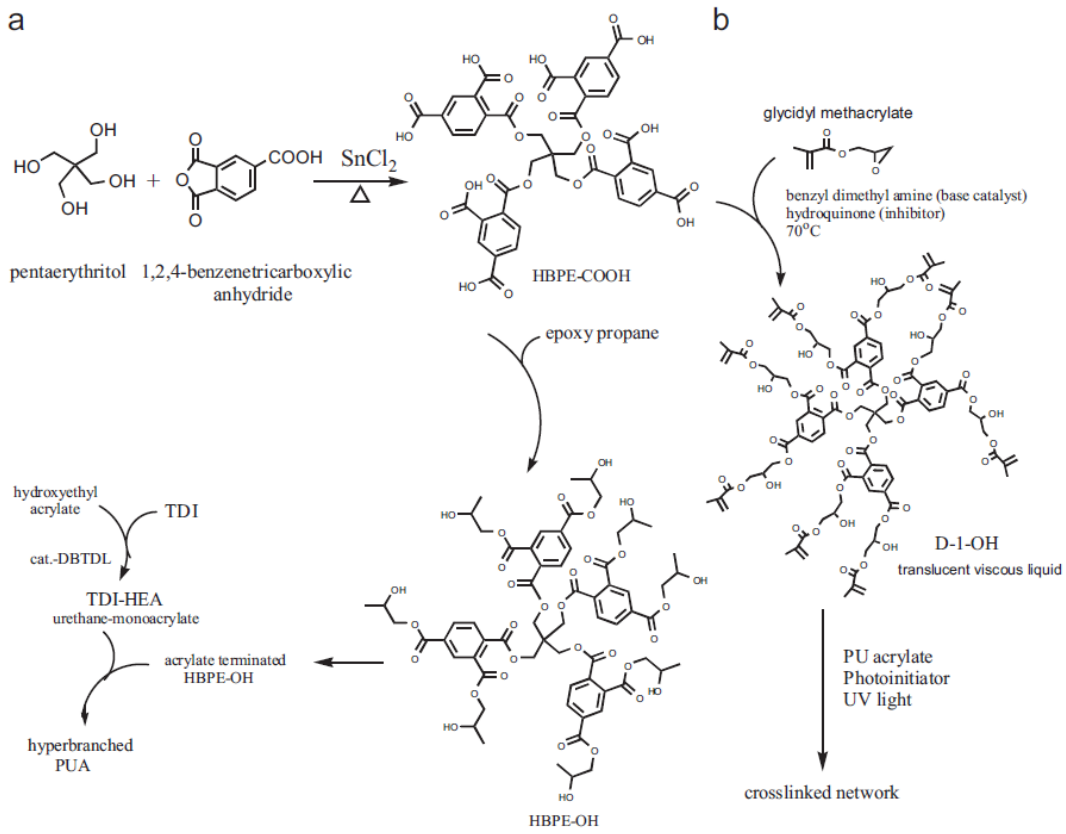


Figure 2.49 : Preparation of UV-cured PU coatings using hyperbranched polymers.

Hyperbanched acrylated aromatic polyester based on 5-hydroxyisophthalic acid as an AB_2 monomer, ethylenediamine tetra-acetic acid (EDTA) as a core molecule, and HEA as an end-group modifier (Figure 2.50) [286] can also be used along with polyurethane acrylated in UV cure coatings. In another report, Wei et al. [287] synthesized an acrylated hyperbanched polyester designated as HBP20-A from Boltorn^{TM} H20. The synthesized HBP20-A was UV-cured with a linear aromatic polyurethane acrylate resin.

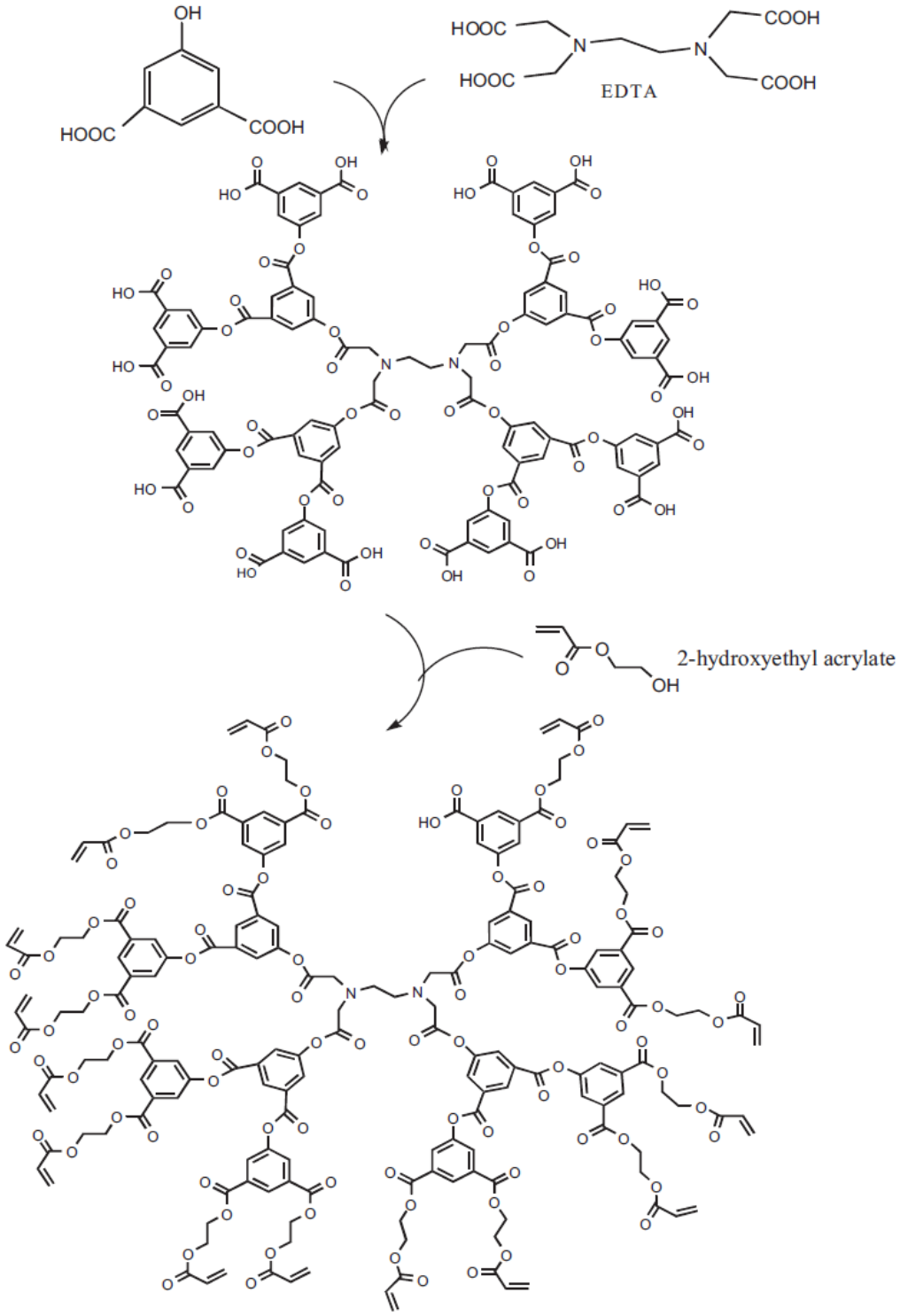


Figure 2.50 : Preparation of acrylate-terminated hyperbranched polymers for UV cure coatings.

2.5 UV-curing Technology and Applications

UV-curing has now been established as an alternative curing mechanism to thermal hardening, contrary to the past, where it was only considered for the curing on temperature sensitive substrates, like wood, paper and plastics. This alternative curing technology uses the energy of photons of radiation sources in the short wavelength region of the electromagnetic spectrum in order to form reactive species, which trigger a fast chain growth curing reaction [288].

From the application point of view, UV-curable coatings are mainly used in such industrial applications where thermal curing is hardly possible, like curing of coatings on temperature sensitive substrates, like wood, paper and plastics, and in imaging applications, where only selected areas should be polymerized, like in polymer printing plates and photoresists.

Specific applications of photocurable coatings are clear coats for parquet, furniture, vinyl flooring, on plastic substrates (skies, boards), compact discs, headlight lenses, overprint varnishes (posters, high gloss packaging), adhesives, protective coatings for optical fibres, electronic parts. Applications of photocurable coatings on metals (automotive, coil coating) and exterior uses are just emerging. These applications cover a large range of properties.

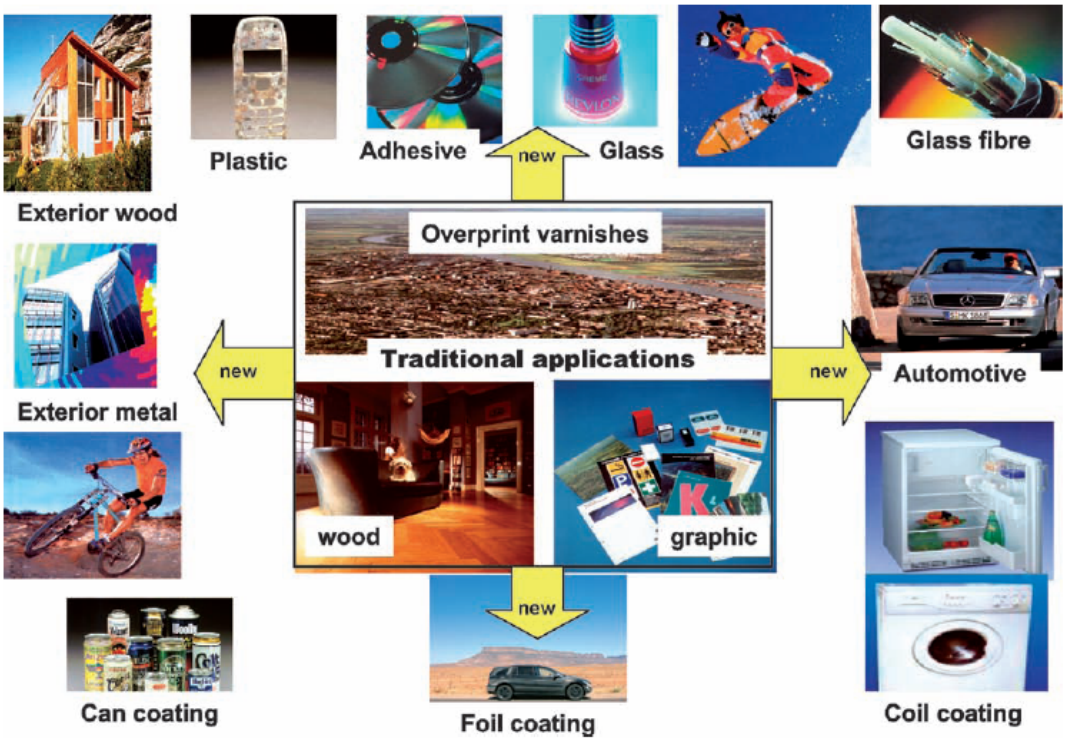


Figure 2.51 : UV coatings from traditional to new applications.

As can be seen from the few application examples shown in Figure 2.51, UV-curable coatings are traditionally used on temperature sensitive substrates, like wood, paper and plastics, for example, clear coats for parquet, furniture, vinyl flooring, on plastic substrates (crash helmet, boards), compact discs, headlight lenses or overprint varnishes (posters, high gloss packaging). However, since coatings are used almost everywhere, the UV-curable coating market is expanding to new applications, where traditionally thermal curing systems have been the workhorses. Applications like UV-curable coatings on metals (automotive, coil coating) and exterior uses on windows, on glass, bikes, on appliances, like refrigerators, washing machines, and most prominently on cars are good examples. A multiplicity of coating applications is often less noticed, such as adhesives and protective coatings for DVD and CD's, protective coating on glass fiber wires, inside and outside of beverage cans, on automotive parts, like headlight mirrors and in multiple functions on electronic parts. This list can easily be extended even further [289].

2.5.1 Wood finising with UV-curable coatings

The usage of wood is very important as it is a natural, renewable raw material. Wood also serves as a beautiful decorative material - a wide scale of decorations can be

created by mixing details from different kinds of wood, coatings and technologies. Furthermore, wood possesses even more remarkable features which in many ways give it a leading position over alternative materials: excellent heat and sound insulation independent of the temperature, as well as the fact that wood does not accumulate electrostatic charges are a few examples [290].

The coating of wooden surfaces serves mainly for surfaces protection and thus increases their utilization properties. Wood coating takes place in different sizes of facilities, from smaller handcraft shops up to large furniture production facilities. In wood processing, furniture production is the largest subsector. A large variety of coatings (conventional solvent-based, high solids, UV-curing, water-based…) is applied by different application techniques (rolling, spraying, curtain coating, brushing, dipping, manual application, etc.) in rather different sizes of facilities [291].

UV-curable coatings are liquid coatings that do not contain any evaporative solvent or water. Their nature is entirely active chemistry that converts directly to a solid finish upon exposure of the applied coating to ultraviolet energy. Since there is no requirement to dry the coating, the wood surface can immediately exit the application section of the finishing line and enter the UV-curing zone or UV "oven." Cure is instantaneous and parts exit the UV oven ready to be handled in the next stage of production. A very significant advantage with 100% UV-curable coatings is the fact that the excess coating may be re-used. UV-curable coatings enable the most rapid of production rates and any application method is possible. It is a proven fact that 100% UV-curable coatings can be and are routinely sprayed on large and small format wood surfaces.

High-build, attractive finishes are easily obtained and are found in custom aircraft interiors, yacht interiors, picture frame mouldings, full-filled floor coatings, tabletops and countertop coatings and other surfaces. Subtle finish appearance is, however, easily achieved by controlling the application rate of both seal coat and topcoat layers. Versatility is the key to 100% UV-curable coatings and a quality coating manufacturer can engineer the system to flow and process well at low-coat weights.

Woods differ in their color, grain, pore structure, density and the type and content of specific constituents. The various wood-based materials such as chipboard, hard-board,

medium-density fiberboard (MDF) and plywood, which are also available with veneer or laminated film finishes, differ widely in their surface structures.

Exact knowledge of a substrate allows selection of a polyurethane system which ensures optimum coating results. In order to achieve special surface effects and qualities, various coatings can be combined in the overall coating system. In contrast to nitrocellulose coatings, unsaturated polyesters or UV-curing systems, polyurethane coatings usually present no problems in terms of compatibility, overcoatability and intercoat adhesion [292].

2.5.1.1 Formulations

Formulations used for radiation curable systems depend on the specific performance requirements of the coatings and have to be adjusted to the application techniques (e.g., viscosity needs). Typically, formulations for UV-curable coatings contain 25–90% oligomeric resins, 15–60% reactive diluents, 0.5–8% photoinitiators, 1–5% additives, like levelling agents, defoamers, and optionally pigments, fillers and matting agents.

The application fields are very wide and therefore the requirements on the coating properties differ very much. From this broad span of applications it is obvious that formulations also differ very much in their chemistry and composition. Classical applications in wood and paper coating often require highly crosslinked coatings for abrasion, scratch and chemical resistant surfaces. Whereas for future applications, such as exterior wood coating, like window frames, or coil coating much more flexible coating properties are needed.

Table 2.5 General composition of wood coatings and function of the components.

Component	**(%)**	**Function**
Oligomer resin	25 – 95	Film formation, basic performance properties
Reactive diluent (monomers)	0 – 60	Film formation, viscosity adjustment
Photoinitiator	1 – 5	Initiation of curing; speed
Fillers / pigments	0 – 50	Increased abrasion resistance, increased scratch resistance, cost reduction (e. g. talc), coloration
Matting agents		Gloss reduction
Additives	0 – 3	Defoaming, wetting, levelling, slip,…

Polyester or epoxy acrylates either alone or in combination in amounts up to 60 %, diluted with 35 % of monomers are mainly used for wood coatings. For parquet and flooring applications the tougher and more abrasion resistant urethane acrylates along with monomers are also employed [293].

2.5.3 Advantages and drawbacks of UV-curable coatings

From the many advantages and disadvantages mentioned in the literature, some of the most importants are listed below [294]:

Economical advantages

• Energy saving (commonly rapid cure at room temperature)

• High production speed

• Small space requirements

• Immediate post cure processing possible

Ecological advantages

• In general solvent free formulations (VOC reduction)

• Possibility of easy recycling (waste reduction)

• Energy saving

Performance advantages

• Low substrate heating

• High product durability

• Application versatility

• High scratch resistance and chemical resistance

• Exceptional abrasion, stain and solvent resistance

• Superior toughness

Drawbacks

• Material costs are higher than, e.g., alkyds, polyesters or epoxies

• 3D curing equipment development is in its infancy

• UV curing in the presence of UV stabilizers decelerated

• Oxygen inhibition at the surface (in many radical curing systems)

• Sensitivity to moisture (cationic curing system)

• Difficult through-cure of pigmented coatings (at thicknesses >5 μm)

Topics to eliminate weaknesses

• Improving adhesion to metal, plastics

• Minimizing skin irritation caused by some reactive diluents

• Reducing odor (of the formulations)

• Reducing extractables of cured coatings

• Improving photoinitiators (cost, migration, volatility)

• Direct food contact packaging approval

The economical and ecological benefits of UV-curable coatings often appear when the question arises “which coating system should be chosen in order to coat a specific surface area” and different coating alternatives may be considered. This is preferably done by comparing the whole process of coating a substrate from cradle to grave with the ecoefficiency method [295].

2.5.4 Driving forces of UV technology

From the discussion of the advantages and drawbacks, the driving forces of the environmentally friendly UV technology for future developments become evident.

In general the main driving forces are listed below:

Performance, exemplarily mentioned are:

• High surface quality

• Chemical and mechanical resistance

• Gloss, scratch and abrasion resistance

Economy, exemplarily mentioned are:

• Energy and material saving process

• Cold cure, no additional heating

Ecology, exemplarily mentioned are:

• Nearly no VOC’s

• Very low emissions after curing

• Very low extractables after curing

These driving forces result in double digit growth rates in classical applications. Due to the high curing speed of UV polymerization other eco compatible coating systems, besides the classical 100% solids UV coatings, such as water-based, powder and dual cure systems, are also being modified in such a way to be curable by UV polymerization. And ultimately, general new exterior applications and especially automotive usage will contribute to further vital growth [296].

3. EXPERIMENTAL WORK

3.1 Materials

Bisphenol A (2,2-bis(4-hydroxyphenyl)propane) is a difunctional organic molecule with molecular weight of 228,29 g/mol and 99% purity supplied from Dow Chemicals.

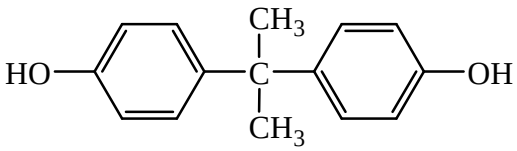


Figure 3.1: Bisphenol A.

6F-Bisphenol A (**[2,2-bis(4-hydroxyphenyl) 6F propane])** is a difunctional organic molecule with molecular weight of 336.29 g/mol and % 99 purity supplied from Aldrich.

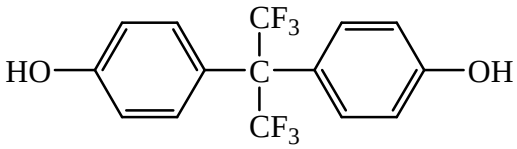


Figure 3.2: 6F-Bisphenol A.

Ethylene Carbonate, 88.06g/mol with % 99.5 purity is supplied from Aldrich and used without purification.

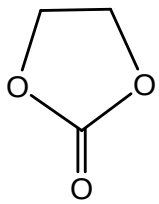


Figure 3.3: Ethylene carbonate.

1,4-Cyclohexyl dimeth anol (CHDM), 144.21 g/mol, % 99,5 is supplied from Eastman and used without purification.

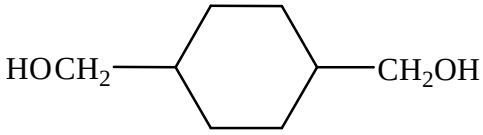


Figure 3.4: CHDM.

Isophorone Diisocyanate is an aliphatic diisocyanate with a molecular weight of 222 g/mol and density of 1.061 g/ml supplied from Perstorp. It is used as a reactant in the synthesis of urethane acrylate.

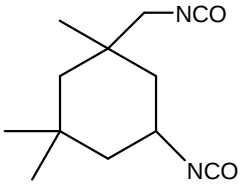


Figure 3.5: IPDI.

Poly(propylene glycol) (PPG) is a polyether polyol that is used in polyurethane synthesis. Its hydroxyl value is 104 mgKOH/g and average molecular weight is 1100 g/mol.

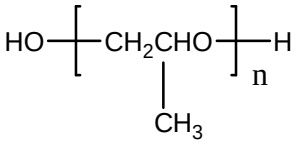


Figure 3.6: PPG.

2-hydroxyethyl methacrylate is a monoacrylate found widespread usage in developments of radiation curing. It has molecular weight of 130.14 g/mol and density of 1.077 g/cm^3.

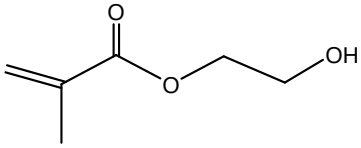


Figure 3.7: HEMA.

Diglycidyl 1,2-cyclohexane dicarboxylate (Epikot Resin 719, epoxy molar mass = 180-190 g) is supplied from Hexion Specialty Chemicals is used in epoxy acrylate synthesis.

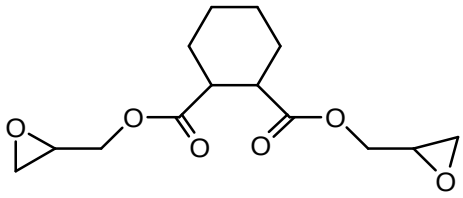


Figure 3.8: Epikot Resin 719.

Adipic acid, is the most important dicarboxylic acid supplied from Merck. It has molecular weight of 146.14 g/mol and density of 1.36 g/cm**.**

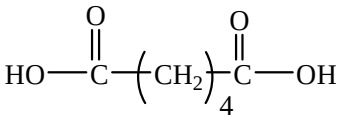


Figure 3.9: Adipic acid.

2,2-Di(methylol)propionic acid (DMPA**),** is a difunctional diol combines two primary hydroxyl groups and one tertiary carboxylic acid group supplied from Perstrorp. Its molecular weight is 134.13 g/mol and purity is % 99.

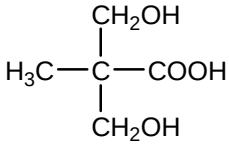


Figure 3.10: DMPA.

Hydroquinone (benzene-1,4-diol) was used as inhibitor. It is white solid and its density is 1,3 g/cm^3.

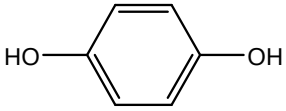


Figure 3.11: Hydroquinone.

Dibutyl tin laurate (DBTL) is an organometallic tin compound that is used as a catalyst in the sytnthesis of polyurethaneacylate. It allows allow the reaction to take place at a rapid rate and at lower temperatures.

Tripropylene glycol diacrylate (TPGDA) is a trifunctional monomer used to increase the gelation stability of UV film formulations at elevated temperatures. It has low viscosity, high Tg, and fast cure speed. It was used as a crosslinking agent in photopolymerization system.

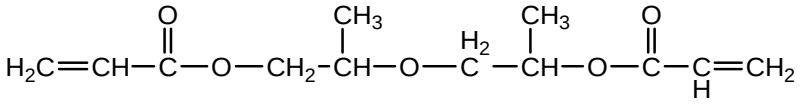


Figure 3.12: TPGDA.

HDDA (1,6-hexanedioldiacrylate) is a low viscosity, fast curing monomer with low volatility, a hydrophobic backbone, and good solvency for use in free radical polymerization. It was used for lower viscosity and crosslinking in polymerization.

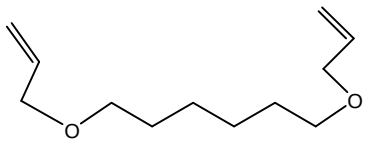


Figure 3.13: HDDA.

NVP (n-vinyl pyrrolidone) has excellent viscosity reducing capabilities with relatively low shrinkage. The flash point (open cup) of NVP (98.4 °C) is substantially higher than any of the preceding non-acrylate monomers. This reduces its fire hazard to make it compatible with the concept of low fire hazard radiation curing.

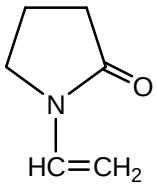


Figure 3.14: NVP.

Irgacure 184 is a versatile photoinitiator for radical polymerisation of unsaturated resins upon UV light exposure.

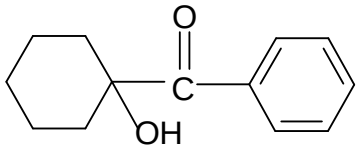


Figure 3.15: Irgacure 184.

p-Toluen Sulfonic Acid (pTSA), is supplied from Fluka has molecular weight of 190,22 g/mol and purity is % 98.

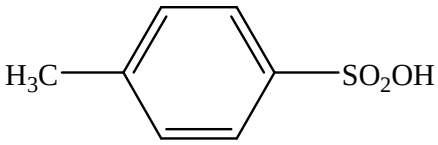


Figure 3.16: pTSA.

3.2 Equipment

3.2.1 Infrared spectroscopy (IR)

Infared analyses were performed with Perkin Elmer Spectrum 100 FTIR spectrometer, equipped with ATR sampling accessory.

3.2.2 Nuclear magnetic resonance spectroscopy (NMR)

(a) ^{1}H NMR and ^{13}C NMR measurements were recorded in $DMSOd_6$ with $Si(CH_3)_4$ as internal standard, using a Varian Inova 500 MHz spectrometer.

3.2.3 Gas permeation chromotography (GPC)

GPC analyses were carried out with a set up consisting of the Agilent pump and refractive-index detector (Model 1100) and four Waters Styragel Columns (HR 5E, HR 4E, HR 3, and HR2). THF was used as the eluent at a flow rate of 0,3 ml/min at 30 °C. The molecular weights of the polymers were calculated with the aid of polystyrene standards.

3.2.4 Thermogravimetric analysis (TGA)

Thermogravimetric analyses were performed with a TA TGA Q50 instrument, under nitrogen atmosphere at a heating rate of 20 °C/min**.**

3.2.5 Differential scanning clorimetry (DSC)

The glass transition temperatures were measured by differential scanning calorimetry, TA DSC Q10, under nitrogen atmosphere at a heating rate of 10 °C/min.

3.2.6 Determination of isocyanate content

The analytical method [297] for isocyanate determination is the reaction of the terminal isocyanate groups with an excess of dibutylamine in toluene (1 mol/L) and allowed to stand at room temperature for 15 min. The reaction mixture is diluted with isopropyl alcohol, and the excess dibutylamine is back-titrated with hydrochloric acid (1 mol/L). The content of isocyanate is calculated from titration volume.

$$\% \text{ NCO} = \frac{(V_2 - V_1) * N * 4202}{m} \qquad \textbf{(3.1)}$$

Where :

V_2 = HCl required for titration of blank, mL,

V_1 = HCl required for titration of sample, mL,

N = normality of HCl, meq/mL,

m = sample used, g

4.202 = constant combining the equivalent weight of NCO (42.02) mg/meq, conversion of g to 1000 mg, and conversion to 100%

3.2.7 Determination of hydroxyl number

The hydroxyl number is defined as the quantitative value of the amount of hydroxyl groups available for the reaction with isocyanates. The hydroxyl number (or hydroxyl index) is expressed as milligrams of potassium hydroxide equivalent for one gram of the sample (mg KOH/g). The most important analytical method for hydroxyl number determination is the reaction of the terminal hydroxyl groups with organic anhydrides (acetic anhydride or phthalic anhydride) [298]. The sample is acetylated with acetic anhydride; the excess acetic anhydride is converted to acetic acid by boiling with water, and then is titrated with aqueous KOH. The acidic carboxyl groups resulting from this reaction are neutralised with the equimolecular quantity of potassium hydroxide.

$$OH = \frac{(V_2 - V_1) * N * 56.1}{m} + AV \qquad \textbf{(3.2)}$$

Where:

OH = hydroxyl value of the sample (as such) in mg KOH / g resin.

V_1 = ml of potassium hydroxide solution needed for the sample.

V_2 = average ml of potassium hydroxide solution needed for the blank.

N = normality of the potassium hydroxide solution.

m = weight of the polymer in g.

AV = acid value of the sample (as such).

3.2.8 Contact angle measurement

The contact angle measurements of the coated wood surfaces were performed with a Krüss Easy Drop DSA16 instrument at room temperature.

3.2.9 Pendulum hardness tester

A Konig Pendulum Hardness (BYK-Gardner) tester was used to measure the film hardness of the urethane acrylate films.

3.2.10 Pencil hardness test

Pencil hardness is the measure of the hardness of pencil leads (made of different proportions of graphite and clay), commonly ranging from 6B (maximum graphite, hence softest) to 6H (least amount of graphite, hence the hardest) with HB (roughly equal amounts of graphite and clay, hence medium soft/hard) in the middle. Pencil hardness is used in indicating the toughness of surface coatings by testing which number pencil-lead can scratch it.

9H 8H 7H 6H 5H 4H 3H 2H H F HB B 2B 3B 4B 5B 6B 7B 8B 9B

Hardest → Medium → Softest

3.2.11 Tensile test

Mechanical properties of the UV-cured free films were determined by Zwick Z010 Universal Tensile Tester under a 500 N load cell and using a crosshead speed of 5

mm/min at room temperature. It was used to determine properties such as modulus, elongation at break and strength.

3.2.12 Cross-cut adhesion test

The adhesion characteristics of the coating are classified with cross-cut adhesion test results accroding to the scale below.

Classification for percentage of area removed:

5B — 0% None

4B — Less than 5%

3B — 5% to 15%

2B — 15% to 35%

1B — 35% to 65%

0B — Greater than 65%

3.2.13 Gel content measurement

Gel content measurements were made against acetone by Soxhlet extraction for 6 h. The cured film samples (m_1) were accurately weighted, and extracted in acetone for 6 h. The extracted films were dried until a constant weight (m_2). Gel content of the cured film was calculated by the following equation:

Gel content (%) = $(m_2/m_1) \times 100$

3.2.14 Water swelling measurement

Water swell was measured by emerging a film in water at room temperature for 24 h. The cured film samples (m_1) were accurately weighted, and swelled in water for 24h. The swelled films were weighted (m_2) and % swell was calculated by the following equation:

Water swelling (%)(Q) = $[(m_2-m_1)/m_1] \times 100$

3.2.15 Solvent resistance measurement

The solvent resistance of the films were made against various solvents by immersing the cured film sample (m_1) in 10 ml solvent for one day. After drying the films until a constant weight those were reweighted (m_2) and weight loss was calculated by the following equation:

Weight loss (%) = $(m_1-m_2)/m_1$ x 100

3.3 Synthesis

3.3.1 Synthesis of [2,2-bis(4-β-hydroxyethoxy) phenyl propane] (HEPA) and [2,2-bis(4-β-hydroxyethoxy) phenyl 6F propane] (HEPFA)

HEPA and HEPFA were synthesized by the reactions of Bisphenol A or 6F Bisphenol A with ethylene carbonate respectively [299]. A spherical flask (500ml), equipped with a reflux condenser, stirrer, thermometer and nitrogen inlet, was charged with Bisphenol A (45.6 g, 0.2 mol), ethylene carbonate (35.2 g, 0.4 mol) and sodium carbonate (0.2 g) as catalyst. The mixture was reacted at 165-170 °C under nitrogen flow for 2 h (Figure 17). The crude product was washed with water several times to remove unreacted ethylene carbonate and recrytallized from methanol. A white crytalline product, mp:105 °C, was obtained in a yield about 90%.

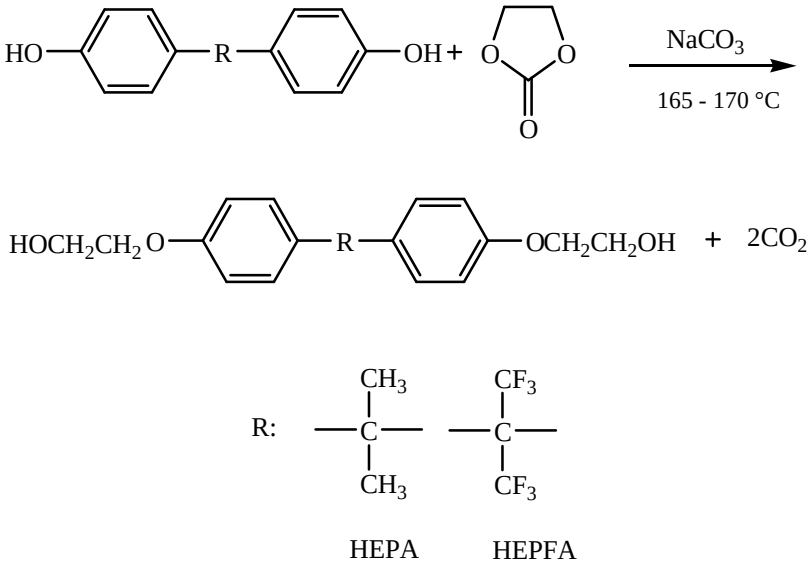


Figure 3.17: The synthesis of HEPA and HEPFA.

3.3.2 Synthesis of 1,4- cyclohexanedimethanol based polyester polyol(PECHDM)

PECHDM was synthesized by the reaction of cyclohexane dimethanol and adipic acid (Figure 18) according to the methods described previously in the literature [300]. The conversion of polyester polyol was monitored by determining the acid value with respect to time until the resin had an acid value under 5 mg KOH/g resin. The acid value and hydroxyl value of polyester were measured according to the

ASTM standards D 1639-89 and D 4274-94, respectively. The acid number of the polyester was 4 and the OH number was 185 mg KOH/g. The molecular weight and polydispersity index (M_w/M_n) were determined from GPC measurement as 1190 g/mol and 1.9 respectively. The T_g of the polyester was determined from DSC measurement as 12 °C.

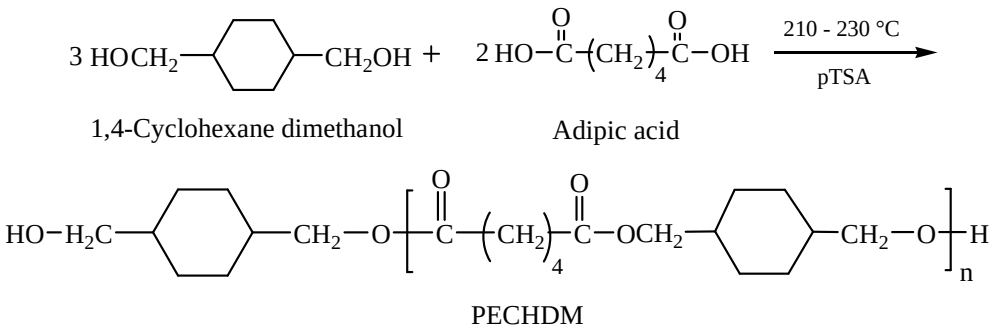


Figure 3.18: The synthesis of PECHDM.

3.3.3 Synthesis of linear urethane acrylate

The linear urethane acrylate was synthesized with a NCO/OH ratio of 2 by the methods described previously in the literature [301]. Isophorone diisocyanate, polypropylene glycol (Mn=1000 g/mol) and 2-hydroxyethyl methacrylate were used as reactive molecules (Figure 19). The completion of the reactions were followed by disappearance of the peak at 2270 cm^{-1} for -NCO group and formation of the characteristic peaks at 3304 cm^{-1} for -NH group, 811 cm^{-1} and 1635 cm^{-1} for acrylate group in FT-IR spectrum.

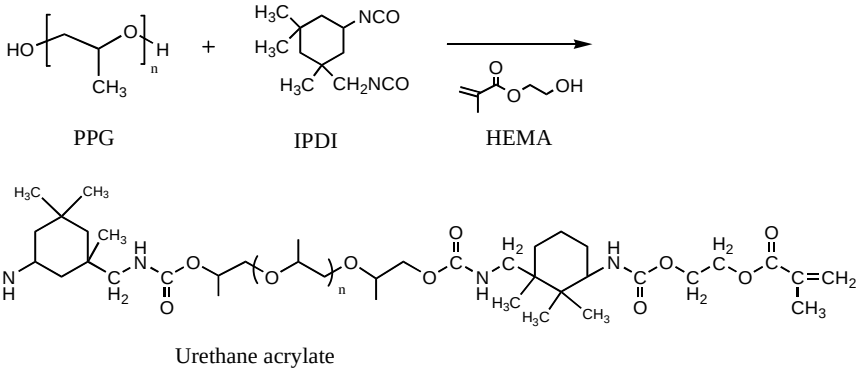


Figure 3.19: The synthesis of urethane acrylate.

3.3.4 Synthesis of epoxy acrylate

The aliphatic epoxy acrylate resin [302] were synthesized by the methods described previously in the literature. Diglycidyl 1,2-cyclohexane dicarboxylate resin and diglycidylether of bisphenol-A type epoxy resin were acrylated with acrylic acid and the reactions were carried out to obtain the products with desired acid value (Figure 20).

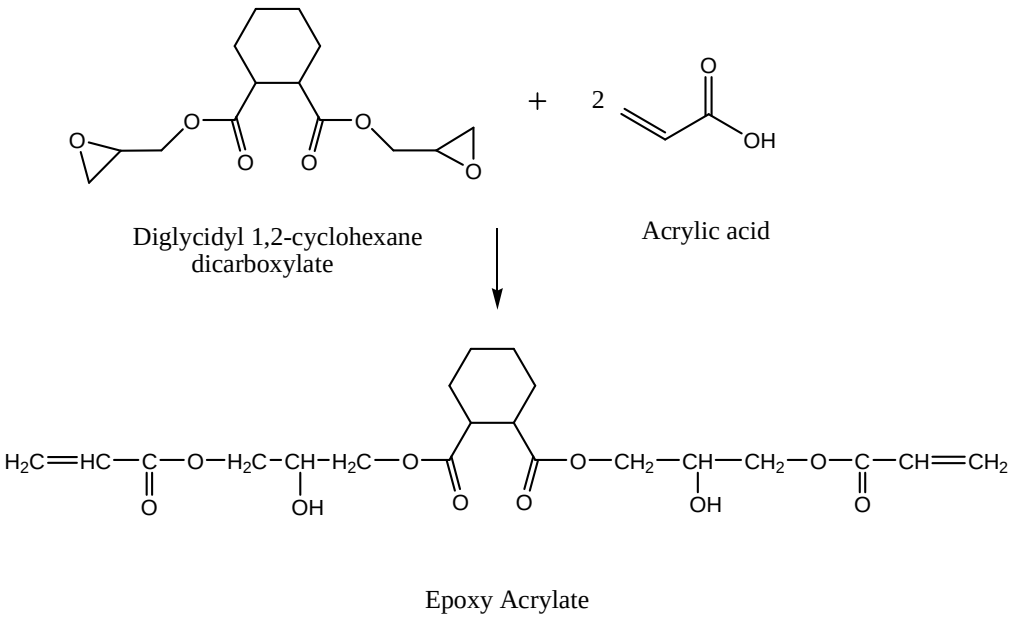


Figure 3.20: The synthesis of epoxy acrylate.

3.3.5 Synthesis of HEPA, HEPFA and CHDM based hyperbranched polyester polyols

First (G1) and second (G2) generation hyperbranched polyester polyols (HB-PEs) were synthesized by melt polycondensation technique. The B_f core molecules were added in a four-necked round-bottomed flask equipped with a thermometer, mechanical stirrer, nitrogen inlet and Dean-Stark apparatus. The required amount of DMPA molecule for first generation was charged to the flask and the reaction mixture was slowly heated to 180 °C. Titanium tetraisopropoxide (TTIP) was used 0.05 wt % as the catalyst for the esterification based on the weight of DMPA. After complete melting of the reactants, the temperature was maintained at 180 °C with a continuous nitrogen flow for about 24 h to follow the course of esterification reaction. The eliminated water was collected from the Dean-Stark apparatus. The

reaction was monitored periodically by checking the acid value through the titration method and stopped when the acid value was below 10.

The second generation hyperbranched polyester polyols were prepared in a stepwise manner from the first generation polyols by adding a stoichiometric amount of DMPA monomer corresponding to the next theoretical second generation. These reactions were also monitored periodically by checking the acid value through the titration method and stopped when the acid value was below 10.

3.3.6 Synthesis of hyperbranched urethane acrylates

The hyperbranched polyester polyols based urethane acrylates were synthesized via a two-step procedure. In the first step urethane monoacrylate was obtained by the reaction of IPDI and HEMA in an equal mole. IPDI (6.0 g, 0.027 mol) and DBTDL (0.23 g) were placed to four-necked flask equipped with mechanical stirrer, a dropping funnel with a water condenser capped with a drying tube, a thermometer and a nitrogen inlet tube. The reaction mixture was dissolved in acetone and stirred at room temperature while HEMA (3.13 g, 0.027 mol) was dropped into the flask. After all amount of HEMA was added to the flask, the reaction maintained at 40 °C until the value of isocyanate reached to the theoretical value.

In the second step, urethane monoacrylate was reacted with hyperbranched polyester polyols with the ratio of 1 : 0.4 at 70 °C until the disappearance of the peak at 2270 cm^{-1} for -NCO group, while the appearance of the peaks at 3304 cm^{-1} for -NH group, at 811 cm^{-1} and 1635 cm^{-1} for acrylate groups in FT-IR spectrum.

After evaporating the solvent and drying the product in vacum slightly yellow to clear, highly viscous hyperbranched uretane acrylates were obtained. All samples of hyperbranched urethane acrylates were synthesized according to the same procedure as described above and characterized by FT-IR, ^{1}H NMR and ^{13}C NMR spectroscopy.

3.4 Wood coating formulations and preparation of free films

UV curable formulations were prepared by mixing hyperbranched polyester based urethane acrylates (UA/HB-PEs), linear urethane acrylate (UA/L) as binder components; n-vinyl pyrrolidone (NVP), hexanediol diacrylate (HDDA) and tripropylene glycol diacrylate (TPGDA) as reactive diluents to adjust the viscosity of

coating formulations and enable the solubilization of the photoinitiator. The composition of UV-curable formulations are given at Table 1. The formulations were stirred to get a homogeneous mixture, then poured on to a teflon mold with 1mm x1cm x 5cm dimensions. UV cured films and wood surfaces were prepared respectively by casting the coating formulations onto a teflon plate (1 mm x1 cm x 5 cm) and wood species (10 mm x 7 mm) at room temperature and cured in a bench type UV processor machine (EMA, 120 W/cm, λmax = 365 nm, medium pressure mercury UV lamps) donated with adjustable conveyor speeds.

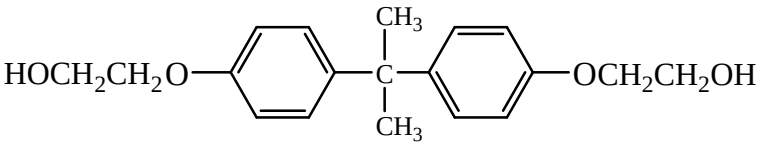
4. RESULTS AND DISCUSSION

In the first part of the study, first (G1) and second (G2) generation novel hyperbranched polyester polyols (HB-PEs) were synthesized by melt polycondensation technique. These hyperbranched polyesters were characterized with GPC, ^{1}H NMR and ^{13}C NMR spectroscopy.

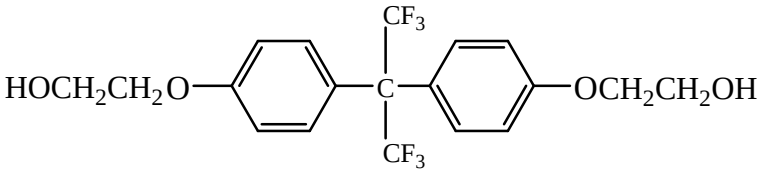
In the second part of the study, hyperbranched polyesters were acrylated to obtain hyperbranched urethaneacrylates. Hyperbranched urethane acrylates were incorporated into the three different series of UV curable wood coating formulations as new oligomers. The effects of core structure and generation number of hyperbranched polyesters (HB-PEs') on the properties of urethane acrylate based UV-curable wood coatings were investigated by means of coatings properties such as surface, mechanical and physical properties.

4.1 The Synthesis of HEPA, HEPFA and CHDM based hyperbranched polyester polyols

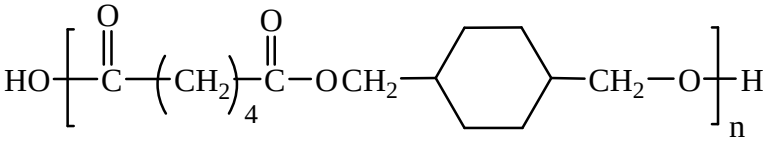
First (G1) and second (G2) generation hyperbranched polyester polyols (HB-PEs) were synthesized by melt polycondensation technique. 2,2-di(methylol)propionic acid (DMPA) was used as AB_2 monomer (contains one carboxyl (A = COOH) and two hydroxyl (B = OH) functional groups) and HEPA, HEPFA and PECHDM were used as B_f (f=2 is the number of core hydroxyl functional groups) core molecules.

B_f Code	B_f structure
1. HEPA	

[2,2-bis(4-β-hydroxyethoxy) phenyl propane]

2. HEPFA	

[2,2-bis(4-β-hydroxyethoxy) phenyl 6F propane]

3. PECHDM	

Cyclohexyl dimethanol-adipic acid polyester polyol

Figure 4.1: The code and structure of B_f core molecules.

Control over the molar mass and the molar-mass distribution of hyperbranched polyesters were achieved by using multifunctional core moiety, B_f, in the polycondensation of AB_2 monomers. The effect of using B_f core molecules in the synthesis of hyperbranched aliphatic polyesters from 2,2-di(methylol)propionic acid (DMPA) have been demonstrated in the previous literature [303-306]. This favors the reaction of monomers with core unit or growing hyperbranched molecules containing the core unit. The undesired reactions between monomers leading to branches were negligible and the polymerization reaction approaches chain growth type kinetics. Hult et al. reported a pseudo-one-step reaction where stoichiometric amounts of DMPA monomer, corresponding to each theoretical dendrimer generation, were added successively to the core molecules in bulk under acidic catalysis. The incremental addition mode of DMPA to core molecules was used for the synthesis of hyperbranched polyester polyols as shown in Figure 3.21.

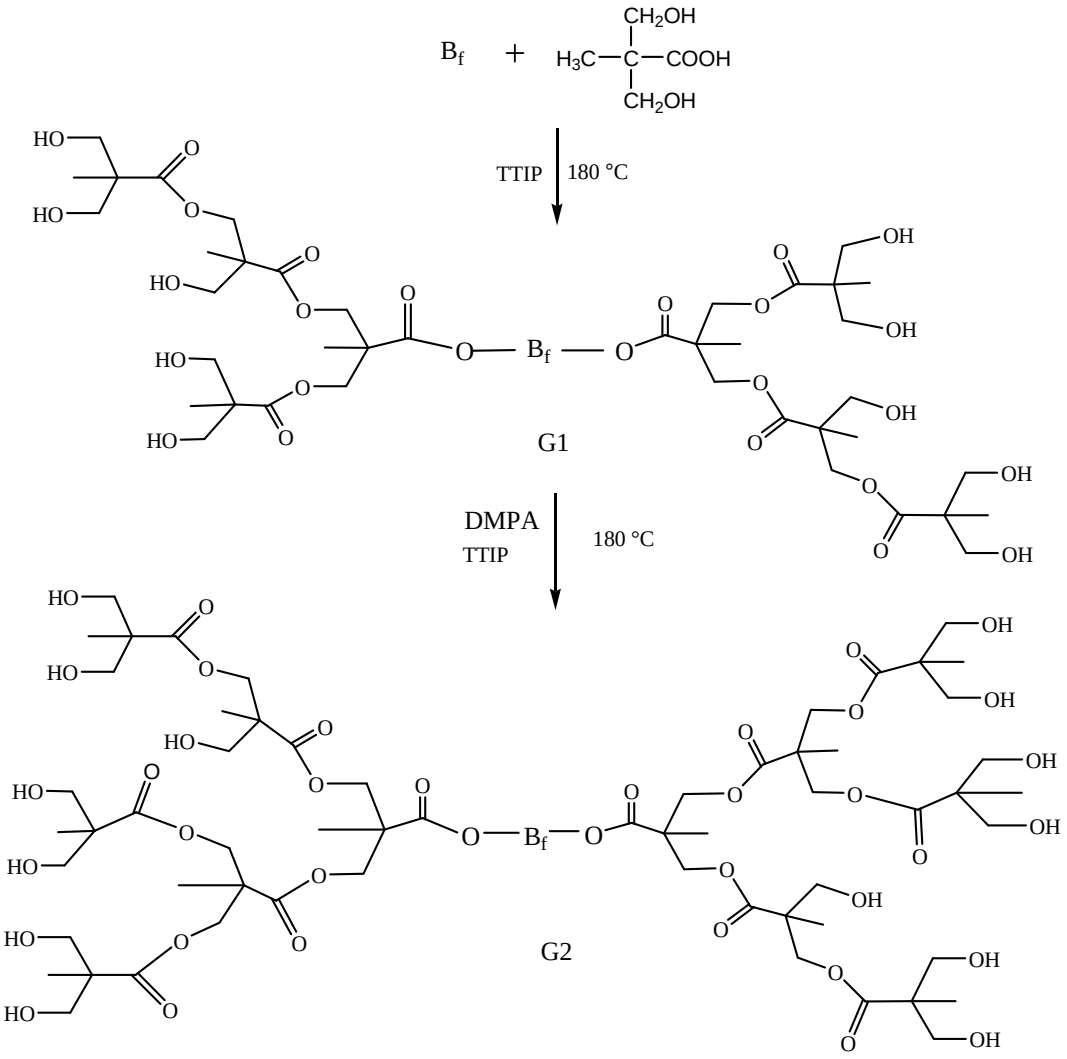


Figure 4.2: Synthesis of hyperbrached polyester polyols.

The characteristics of hyperbranched polyester polyols are given at Table 4.1. The molar mass and molar mass distributions of hyperbranched polyesters were measured by size exclusion chromatography (SEC) calibrated with linear polymer standards. Theoretical values of M_n can be calculated from conversion and stoichiometric considerations. In the case of the reaction of 1 mol AB_n (monomer) and x mol B_f (core molecule), M_n is given by equation (4.1) [307]:

$$\bar{M}_n = \frac{\left(\frac{M_0 - x\,M_C}{1+x}\right) - M_E}{1 - \frac{P_A}{1+x}} + M_E \qquad \textbf{(4.1)}$$

Where, M_n is the weight average molecular weight

P_A is the conversion of A-groups (A ; COOH),

M_0 is the molar mass of AB_2 monomer,

M_C is the molar mass of core molecule, and

M_E is the molar mass of the byproduct, water in the present case.

M_n values of hyperbranched polyesters, experimentally determined by GPC, are slightly different those theoretically calculated ones. This could be explained by the differences between the PSt standarts and hyperbanched polyester structures. It was reported that copolymerization of AB_n monomers with multifunctional B_f cores can reduce the polydispersity of hyperbranched polymers [308-310]; either increment of the reactivity of core or slow addition of AB_n monomers can further make the molecular weight distribution narrower. According to the theoretical calculations at complete conversion of A groups, the polydispersity index of the hyperbranched polymers formed by copolymerization of AB_2 with B_3 can be reduced to be 1.333 and the degree of branching can also be increased to 0.667 [304,311,312]. The polydispersity index (PDI) of hyperbranched polyesters were less than 2.0 and HEPFA based hyperbranched polyesters have the lowest polydispersity index of 1.16 and 1.22. The PDI of HEPA and HEPFA based hyperbranched polyesters slightly increase with increasing core/monomer ratio as mentioned in literature [309].

Table 4.1: Characterization of HB-PEs.

HB-PEs	Theoretical core/monomer ratio	Mn-theo[a] (g/mol)	Mn[b] (g/mol)	M_w/M_n[b]	Hydroxyl number (mgKOH/g)[c]	Acid Number (mgKOH/g)[d]	Tg[e] (°C)
HB-HEPA/G1	1/8	1265	1040	1.35	376	10	21
HB-HEPA/G2	1/12	1650	1295	1.68	380	7	35
HB-HEPFA/G1	1/8	1375	1630	1.16	400	4	21
HB-HEPFA/G2	1/12	1760	1920	1.22	385	5	27
HB-PECHDM/G1	1/8	2140	1945	2.10	258	7	-16
HB-PECHDM/G2	1/12	2720	3250	1.90	251	2	-22

[s]Theoretical molecular weigt is calculated from equation (4.1).
[b] Determined from GPC, based on PSt standarts.
[c] Determined by ASTM standard D 4274 – 94.
[d] Determined by ASTM standard D 1639 – 89.
[e]Determined from DSC under nitrogen at a heating rate of 10 ^oC/min.

Owing to their globular shape and their highly branched structures, hyperbranched polymers are expected to be amorphous. The thermograms obtained from DSC measurements confirmed that all hyperbranched polyesters are amorphous. Due to the increase in the molar mass of HB-PEs the Tg values were slightly increased from first to second generation for HEPA and HEPFA. In analogy with their solution properties, the thermal properties of hyperbranched structures and their T_g values also depend on the nature of their end groups, as well as factors that are specific to the inner part such as the backbone rigidity, the degree of branching, etc. The decrease in T_g values of PECHDM based hyperbanched polyester can be ascribed to the decrease in backbone rigidity. In the case of linear polyester, PECHDM, core structure causes plasticiser effect lowering T_g values.

The chemical structure of hyperbranched polyester polyols were characterized by ^1H and ^{13}C NMR spectroscopy. The ^1H NMR spectrum of HEPA based first and second generation polyesters display signals at 1.0 - 1.4 ppm for –(C<u>H</u>$_3$) protons of DMPA, at 1.6 ppm for –(C<u>H</u>$_3$) protons of Bis A, at 3.4 – 3.6 ppm for –(OCOC<u>H</u>$_2$) and –(OC<u>H</u>$_2$) protons, at 4.0 – 4.4 ppm protons of –(C<u>H</u>$_2$OH) protons, at 4.6 – 4.7 ppm protons of –(O<u>H</u>) on therminal unit, 4.8 – 5.0 ppm protons of –(O<u>H</u>) on linear unit and 6.8 – 7.2 ppm for –Ph protons of Bis A as shown in Figure 4.3 and 4.4, respectively.

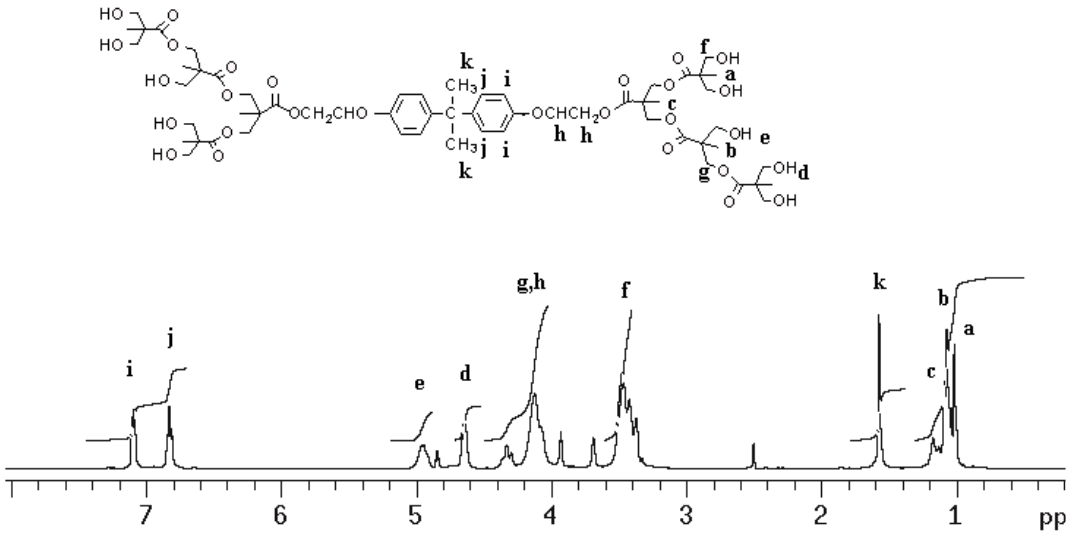


Figure 4.3: ^1H NMR spectrum of HB-HEPA/G1 in DMSO d_6.

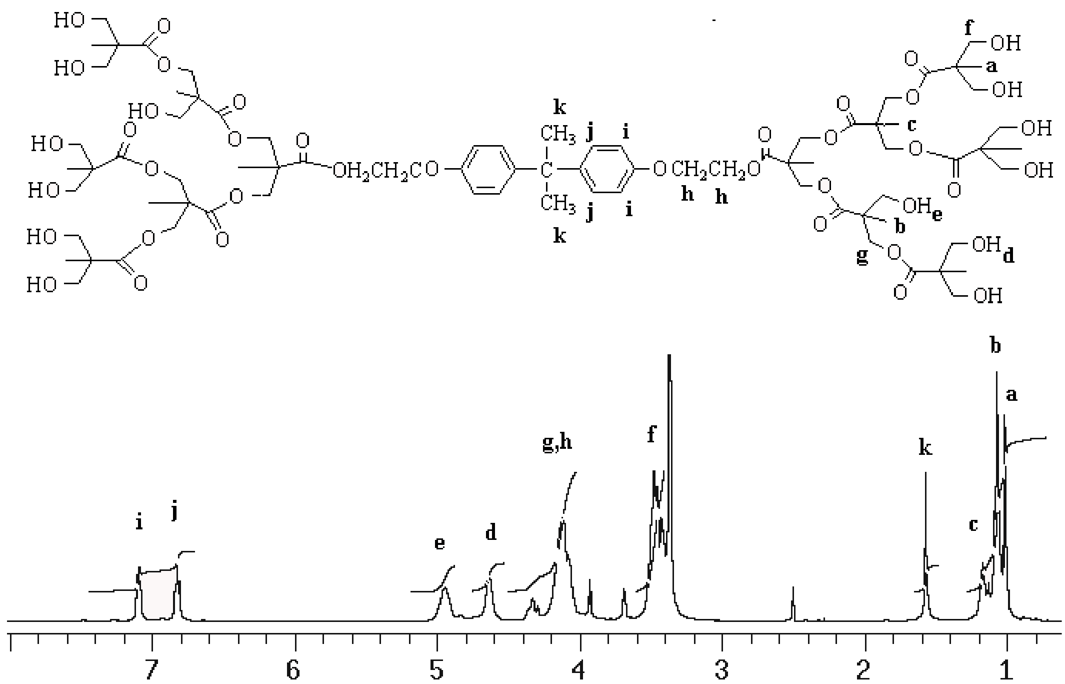


Figure 4.4: ^{1}H NMR spectrum of HB-HEPA/G2 in DMSO d_6.

The ^{1}H NMR spectrum of HEPFA based first and second generation polyesters displays signals at 1.0 – 1.4 ppm for –(C$\underline{H}_3$) protons of DMPA, at 3.4 – 3.6 ppm for –(OCOC$\underline{H}_2$) and –(OC$\underline{H}_2$) protons, at 4.0 – 4.4 ppm protons of –(C$\underline{H}_2$OH) protons, at 4.6 – 4.8 ppm protons of –(O$\underline{H}$) on therminal unit, 4.8 – 5.0 ppm protons of –(O$\underline{H}$) on linear unit and 6.8 – 7.4 ppm for –Ph protons of 6F-Bis A as shown in Figure 4.5 and 4.6, respectively.

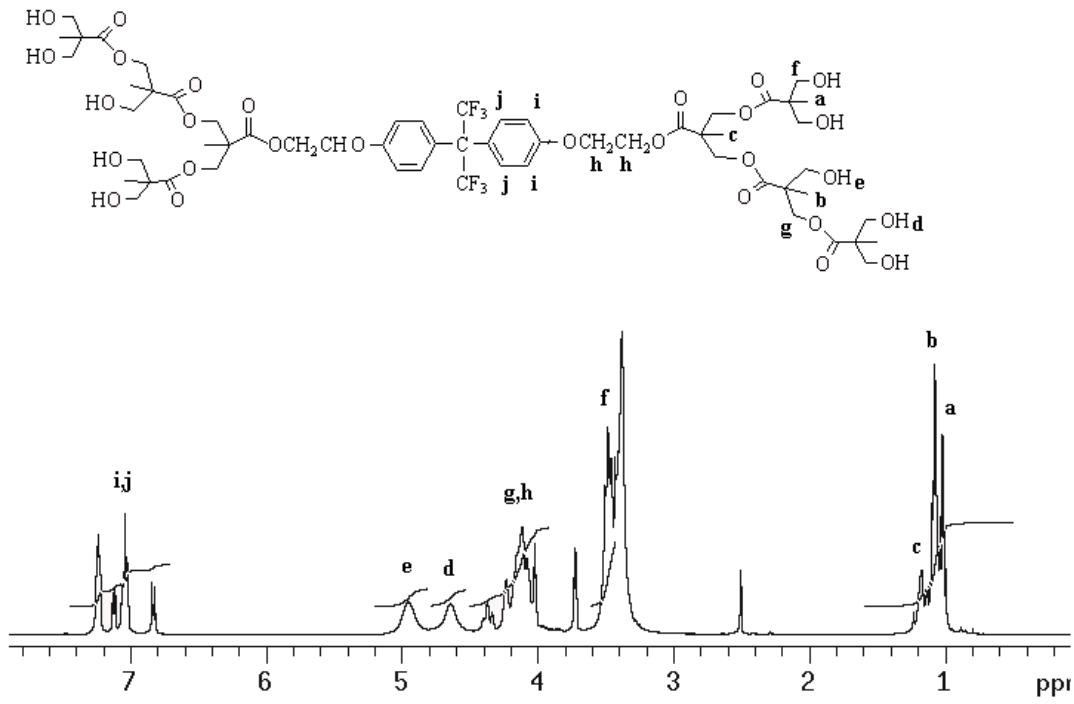


Figure 4.5: ^{1}H NMR spectrum of HB-HEPFA/G1 in DMSO d_6.

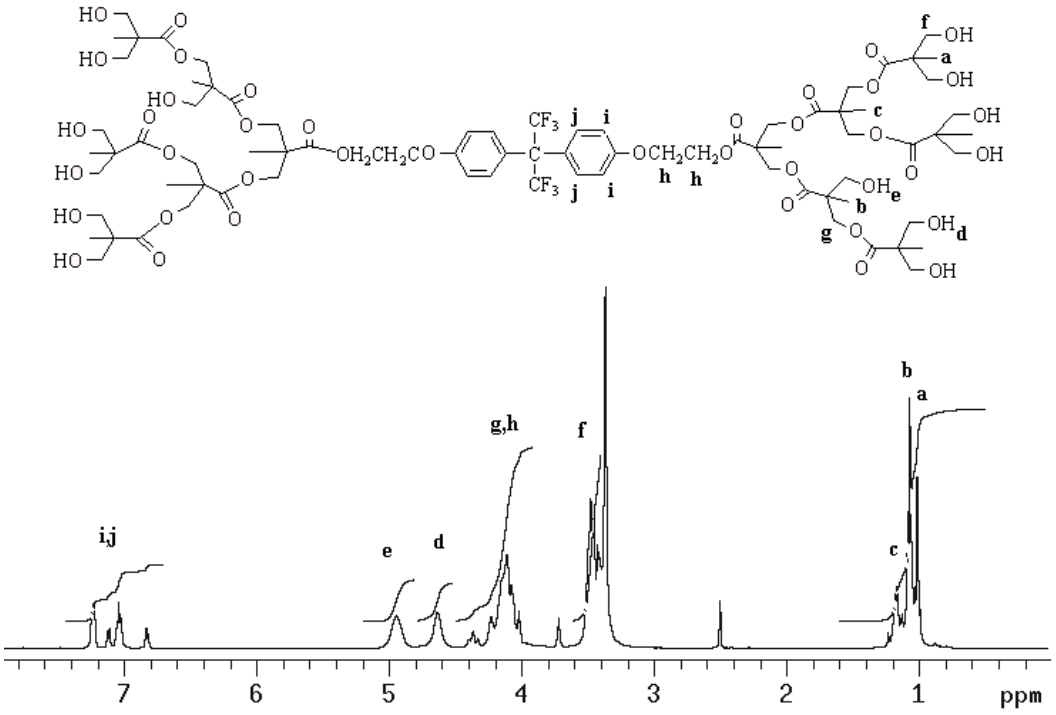


Figure 4.6: ^{1}H NMR spectrum of HB-HEPFA/G2 in DMSO d_6.

The 1H NMR spectrum of PECHDM based first and second generation polyesters displays signals at 1.0 - 1.4 ppm for –(CH3) protons of DMPA, at 1.4 - 1.6 ppm for –(CH2) and –(CH) protons of CHDM, at 1.6 - 1.8 ppm for –(CH2) protons, at 2.2 - 2.4 ppm for –(OOCCH2) protons, at 3.4 – 3.6 ppm for –(OCOCH2) protons

of DMPA, at 3.8 – 4.0 ppm for -(OCOC$\underline{H}_2$) protons attached to the CHDM, at 4.0 – 4.2 ppm protons of –(C$\underline{H}_2$OH) protons, at 4.6 – 4.8 ppm protons of –(O$\underline{H}$) on therminal unit, 4.8 – 5.0 ppm protons of –(O$\underline{H}$) on linear unit as shown in Figure 4.7 and 4.8, respectively.

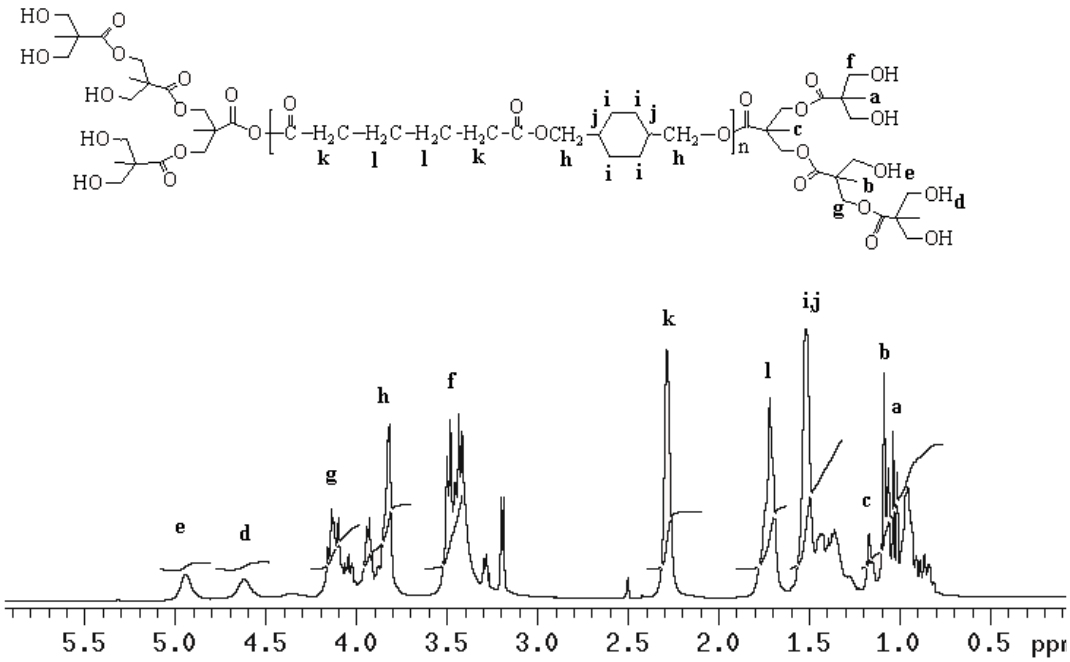


Figure 4.7: ^{1}H NMR spectrum of HB-PECHDM/G1 in DMSO d_6.

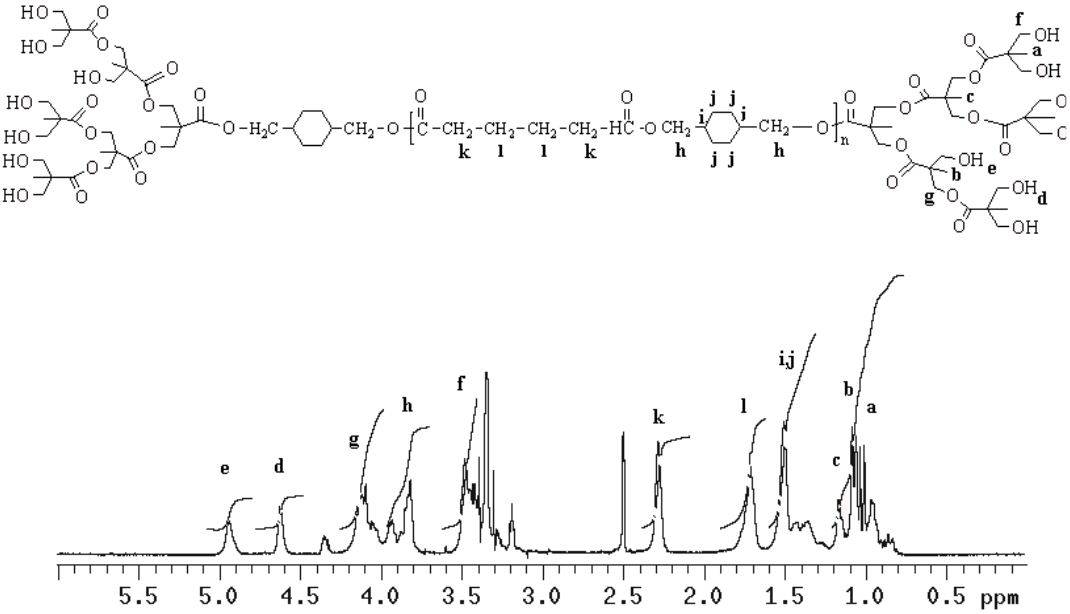


Figure 4.8: ^{1}H NMR spectrum of HB-PECHDM/G2 in DMSO d_6.

Hyperbranched polymers prepared from AB_n monomers have highly, but not perfectly, branched structures. They are composed of terminal (T), linear (L), and dendritic (D) units, which were distinguished by the number of unreacted functional groups in the molecule. The fractions of D-, L- and T- repeating units and degree of branching were usually determined by NMR spectroscopy [313]. ^{13}C NMR spectra of novel hyperbranched polyester polyols are shown in Figures 4.9 - 4.13. The ^{13}C NMR spectrum of HEPA based hyperbranched polyesters display signals at 18.5 ppm for methyl carbon of DMPA, 44 – 52 ppm for quaternary carbons including 46.6 ppm for dendritic, 48.6 ppm for linear and 50.6 ppm for terminal repeating units, 62 – 68 ppm for methylene carbons and 173-178 ppm for carbonyl carbons as shown in Figure 4.9.

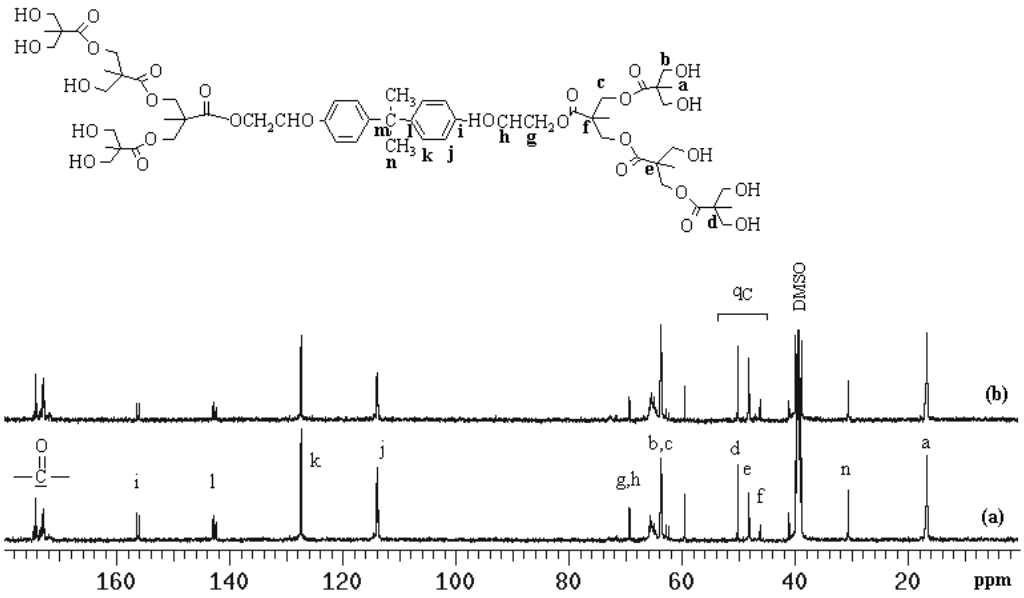


Figure 4.9: ^{13}C NMR spectra of (a) HB-HEPA-G1 and (b) HB-HEPA-G2 in DMSO-d_6.

The ^{13}C NMR spectrum of HEPFA based hyperbranched polyesters display signals at 18.5 ppm for methyl carbon of DMPA, 44 – 52 ppm for quaternary carbons including 46.6 ppm for dendritic, 48.6 ppm for linear and 50.6 ppm for terminal repeating units, 62 – 68 ppm for methylene carbons and 173 – 178 ppm for carbonyl carbons as shown in Figure 4.10 - 4.11.

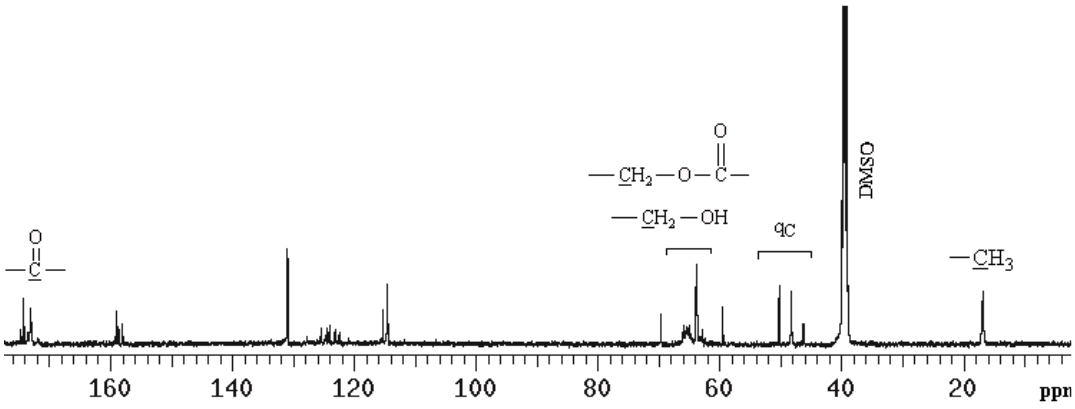


Figure 4.10: ^{13}C NMR spectrum of HB-HEPFA-G1 in DMSO-d_6.

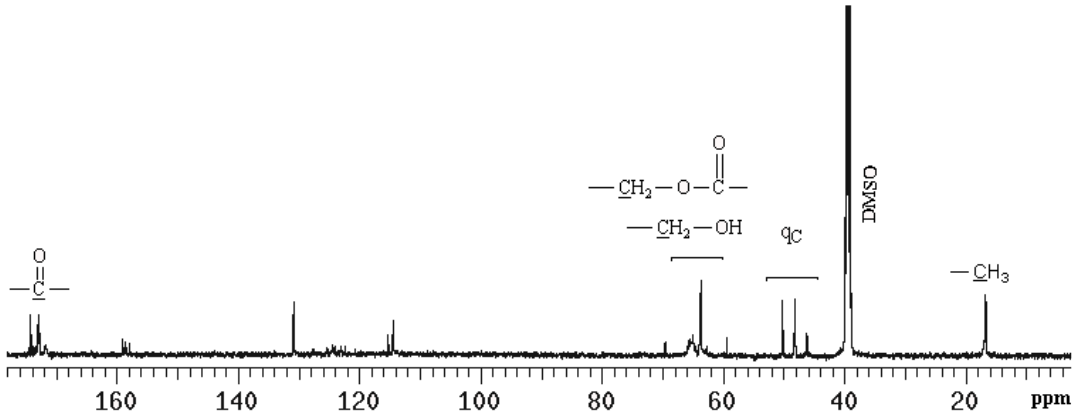


Figure 4.11: ^{13}C NMR spectrum of HB-HEPFA/G2 in DMSO-d_6.

The ^{13}C NMR spectrum of PECHDM based hyperbranched polyesters display signals at 18.5 ppm for methyl carbon of DMPA, 44 – 52 ppm for quaternary carbons including 46.6 ppm for dendritic, 48.6 ppm for linear and 50.6 ppm for terminal repeating units, 62 – 68 ppm for methylene carbons and 173 – 178 ppm for carbonyl carbons as shown in Figure 4.12 - 4.13.

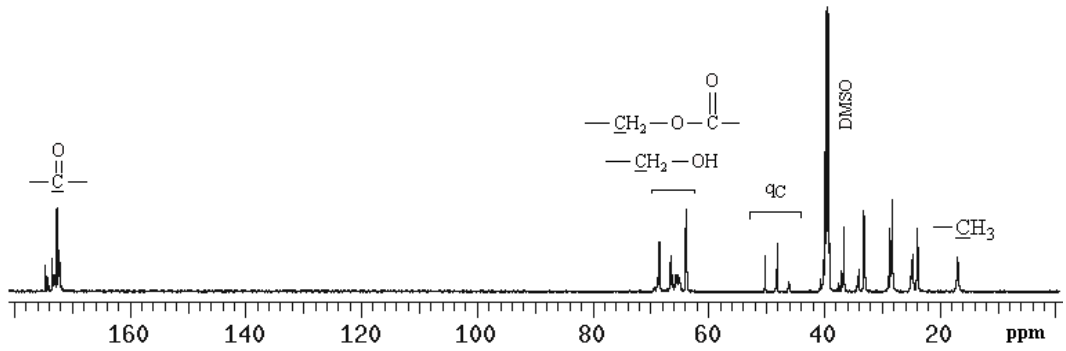


Figure 4.12: ^{13}C NMR spectrum of HB-PECHDM-G1 in DMSO-d_6.

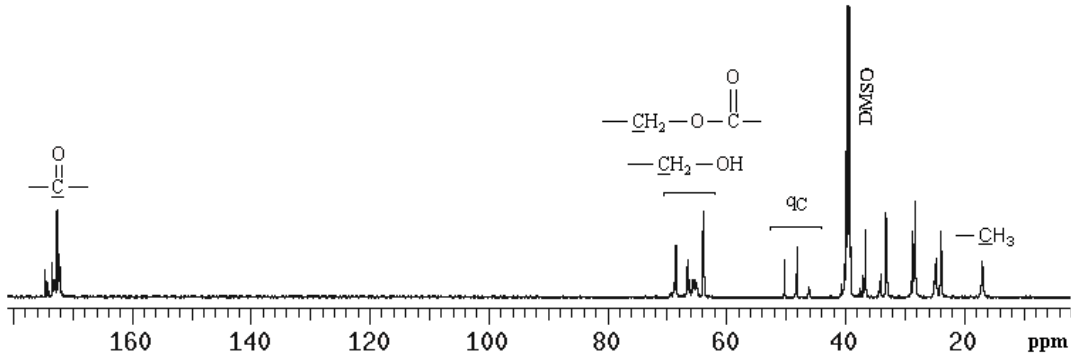


Figure 4.13: ^{13}C NMR spectrum of HB-PECHDM-G2 in DMSO-d_6.

The degree of branching (DB) of the hyperbranched polyesters were calculated according to the Frechet [314] and Frey [315] from quaternary carbon zone (q_C) of ^{13}C NMR data and the results are shown in Table 4.2. Frey reported that one-pot polymerization of AB_2-type monomers statistically gives a DB of 0.5 when the reactivities of functional groups in each unit are identical [316]. Here, average values of $DB_{Frechet}$ ~ 0.45 (DB_{Frey} ~ 0.40) of hyperbranched polyesters are found quite consistent with the results obtained by Zagar et al ($DB_{Frechet}$ ~ 0.43 and DB_{Frey} ~ 0.30) [317]. A value of DB = 0.5 would have been expected if all OH groups were equireactive in the DMPA polyesterification reaction. A lower DB suggests that the terminal hydroxyls might have a higher reactivity in the original polyesterification.

Table 4.2: Degree of branching of first and second generation hyperbranched polyester polyols.

	Quaternary carbon zone (q_C)			Degree of Branching	
HBPEs	**D (%)**	**L (%)**	**T (%)**	**Frechet (%)**	**Frey (%)**
HB-HEPA-G1	12	56	32	44	30
HB-HEPA-G2	15	57	28	43	36
HB-HEPFA-G1	17	54	29	46	39
HB-HEPFA-G2	18	57	25	43	39
HB-PECHDM-G1	18	56	26	44	39
HB-PECHDM-G2	19	54	27	46	41

4.2 Synthesis and Characterization of Hyperbranched Urethane Acrylates

In the second part of the work, three different series of hyperbranched polyester based urethane acrylates (UA/HB-PEs) were synthesized. The effects of generation and core molecule of HB-PEs' on the properties of urethane acrylate based UV-curable wood coatings were investigated. For this purpose, theoretically 40 % of OH groups of hyperbranched polyesters were end-capped with urethane acrylate via a two step reaction as shown in Figure 4.14. In the first step, secondary cycloaliphatic NCO group of IPDI was reacted [318] with an equimolar amount of HEMA and in the second step -NCO bearing adduct, urethane monoacrylate, was reacted with hydroxyl functional HB-PEs respectively. The reaction was monitored with IR spectroscopy.

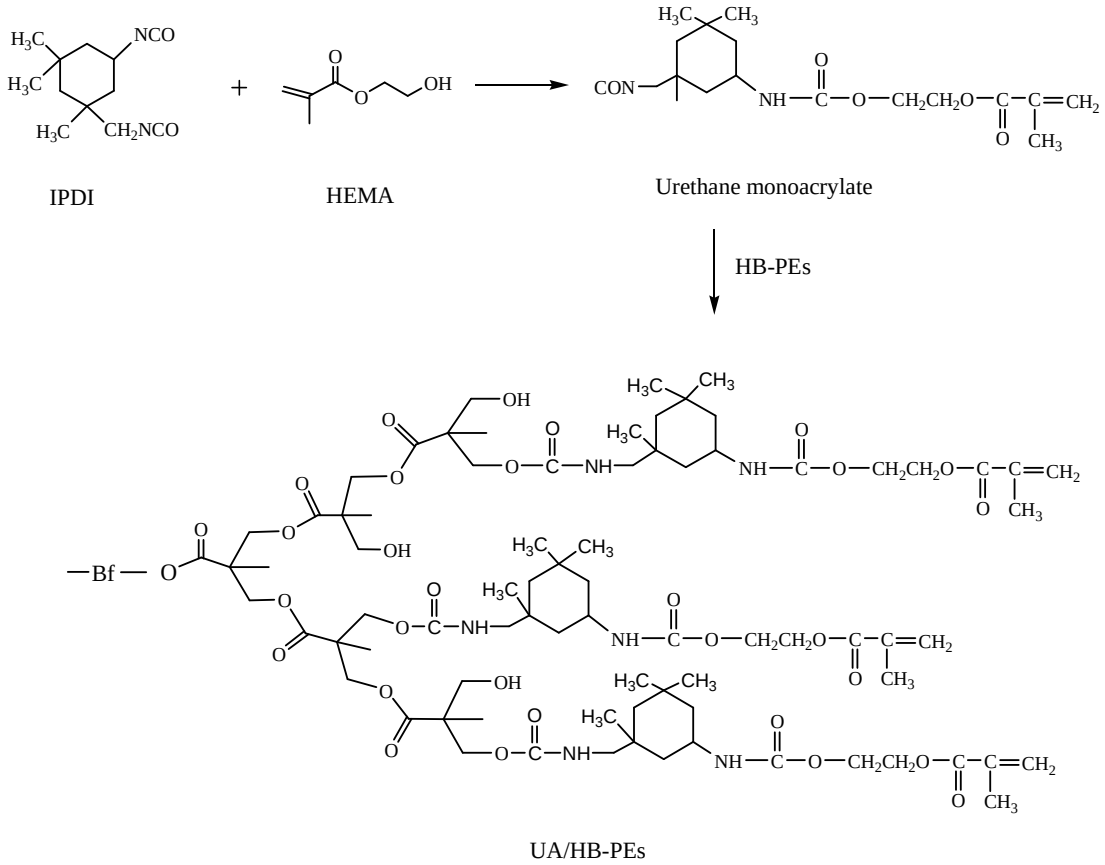


Figure 4.14: Synthesis of hyperbranched urethane acrylates.

According FT-IR spectra of UA/HB-PEs show characteristic peaks of N-H stretching vibrations at 3300–3360 cm^{-1}, C-H aliphatic stretching vibrations at 2945, 2858 cm^{-1}, amide I stretching of the ester C=O bond at 1700-1730 cm^{-1}, amide II stretching vibration of C-N bond at 1520–1570 cm^{-1} and amide III stretching vibration of N-H bending and CN stretching at 1230-1250 cm^{-1}. The spectra of UA/HB-PEs showed the absorption peaks for C=C bending at 1638 cm^{-1} and =C-H bending at 810 cm^{-1} which illustrated that the acrylate C=C bond had been incorporated in the structure (Figure 15-18).

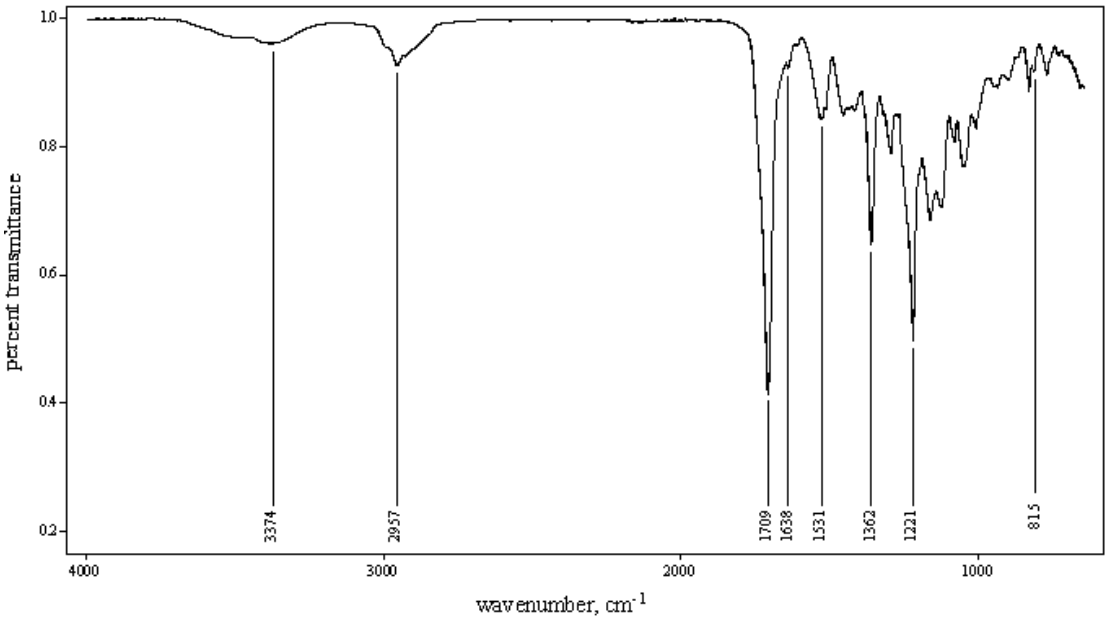


Figure 4.15: FT-IR spectrum of UA/HB-HEPA/G1.

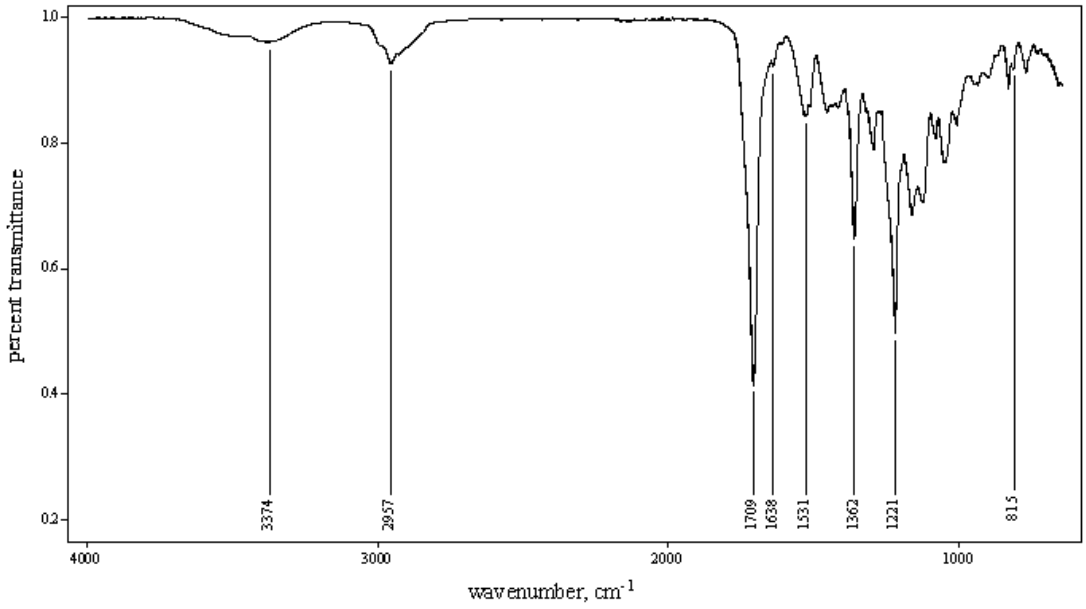


Figure 4.16: FT-IR spectrum of UA/HB-HEPA/G2.

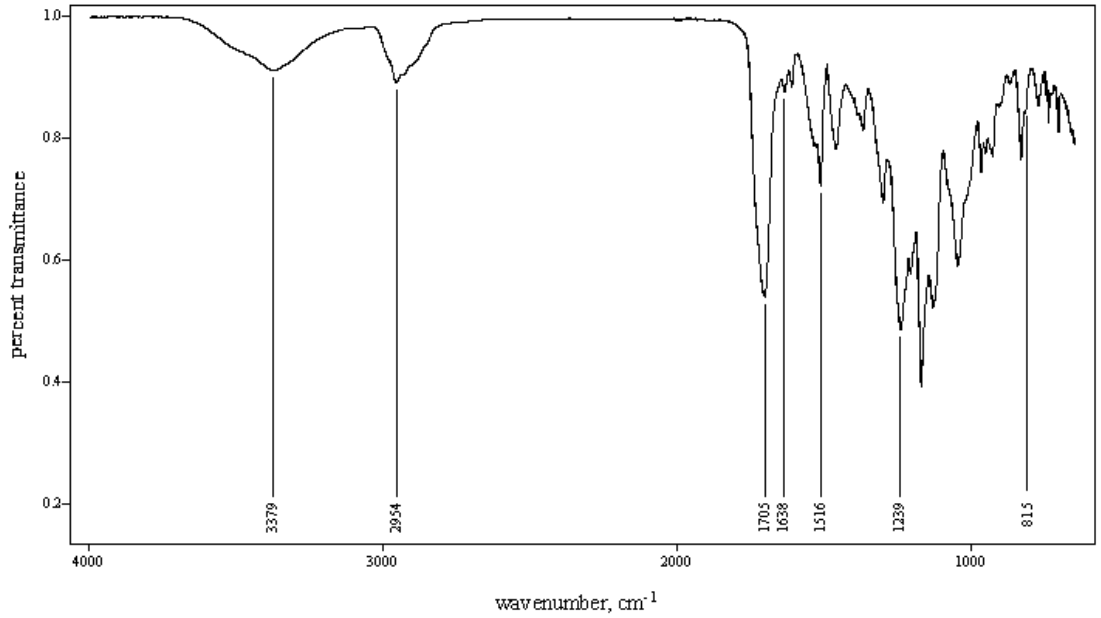


Figure 4.17: FT-IR spectrum of UA/HB-HEPFA/G1.

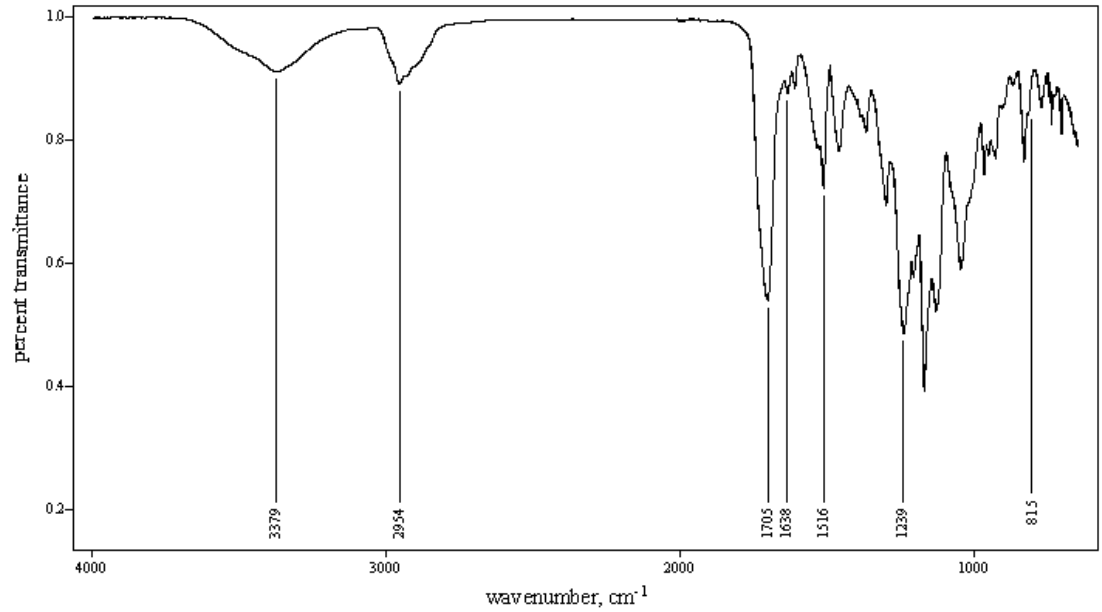


Figure 4.18: FT-IR spectrum of UA/HB-HEPFA/G2.

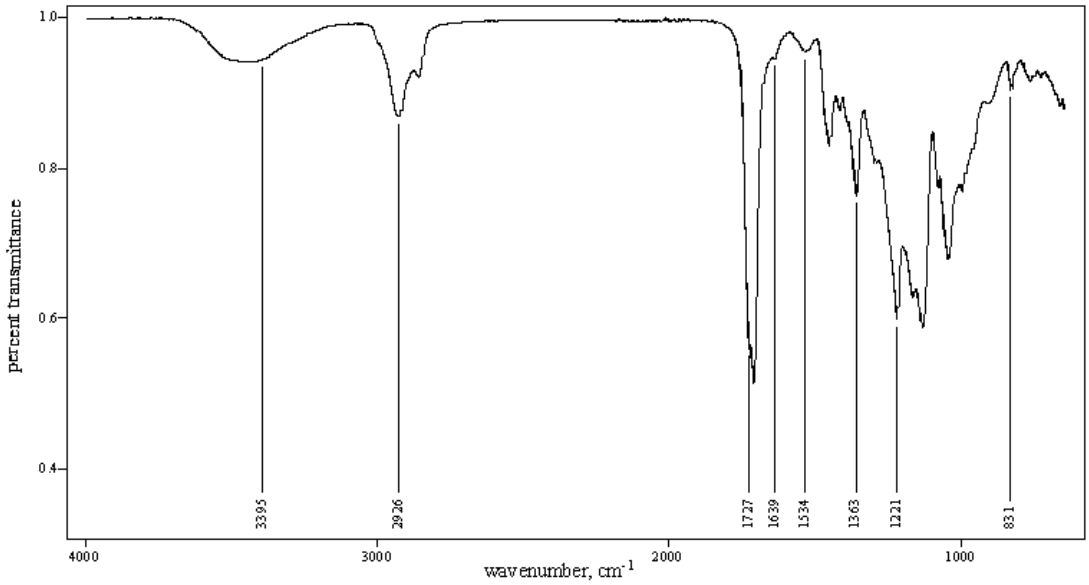


Figure 4.19: FT-IR spectrum of UA/HB-PECHDM/G1.

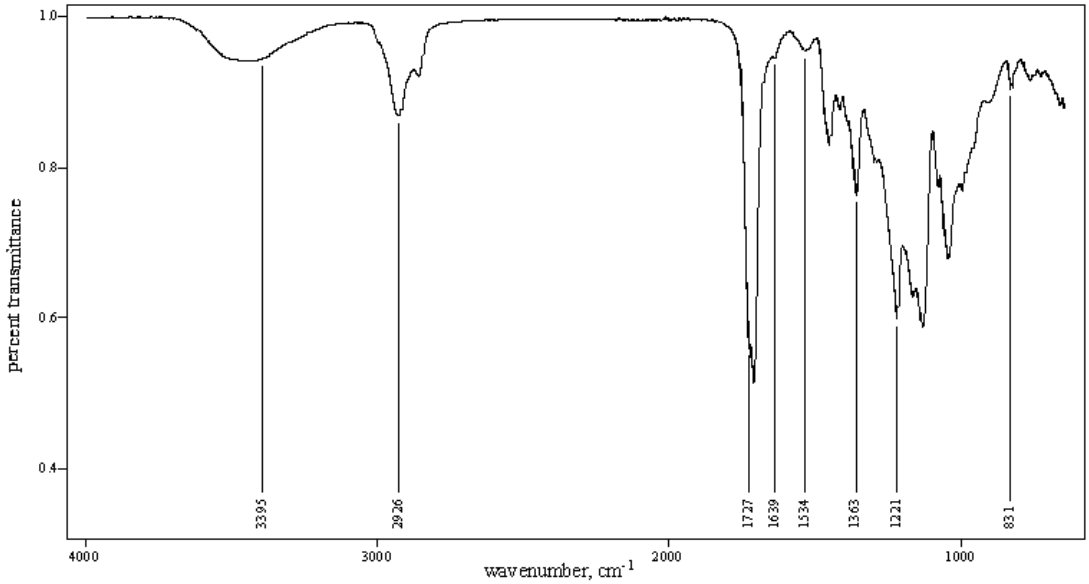


Figure 4.20: FT-IR spectrum of UA/HB-PECHDM/G2.

The chemical structure of hyperbranched polyester based urethane acrylates are also characterized by ^{1}H NMR spectroscopy. The peaks at 5.7 and 6.1 ppm prove the existence of acrylate groups in UA/HB-PEs molecular structure. The degree of acrylation was calculated by comparing the signal intensities of the protons of the methylene groups adjacent to the hydroxyl end groups, the protons next to the ester groups and the protons of acrylic groups. The degree of acrylation, calculated as 40 % for HB-HEPA and HB-HEPFA based urethane acrylates and 30 %, 35 % for HB-PECHDM/G1, G2 based urethane acrylates, were in good agreement with the

theoretical acrylation degree of 40 %. The ^{1}H NMR spectra of hyperbranched polyesters based urethane acrylates are shown in Figure 4.21 - 4.26.

The ^{1}H NMR spectrum of HB-HEPA/G1,G2 based hyperbranched urethane acrylates display signals at 1.0 - 1.4 ppm for –(C<u>H</u>$_3$) protons of DMPA and IPDI, at 2.7 ppm for –(C<u>H</u>$_2$NHCO) of IPDI, at 3.4 – 3.6 ppm for –(OCOC<u>H</u>$_2$) and –(OC<u>H</u>$_2$) protons, at 4.0 – 4.4 ppm protons of –(C<u>H</u>$_2$OH) protons, at 4.6 – 4.8 ppm protons of –(O<u>H</u>) on therminal unit, 4.8 – 5.0 ppm protons of –(O<u>H</u>) on linear unit, at 5.7 and 6.1 ppm for –(C=C<u>H</u>$_2$) and 6.8 – 7.4 ppm for –Ph protons of HEPA as shown in Figure 4.21 and 4.22, respectively.

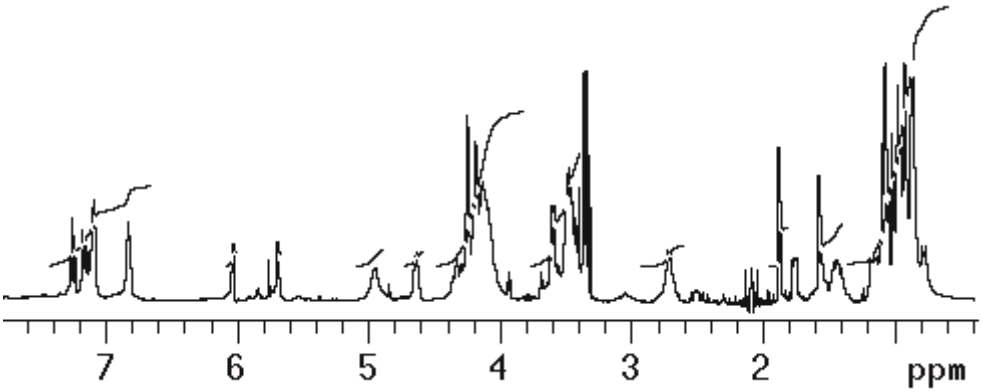


Figure 4.21: ^{1}H NMR spectrum of UA/HB-HEPA/G1 in DMSO-d$_6$.

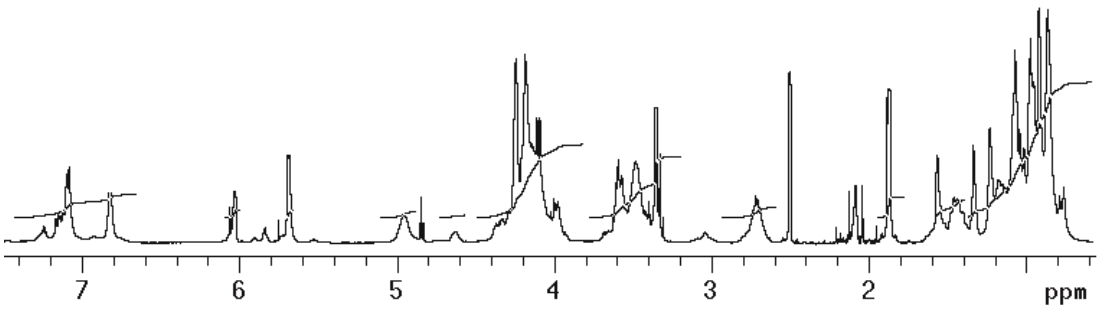


Figure 4.22: ^{1}H NMR spectrum of UA/HB-HEPA/G2 in DMSO-d$_6$.

The ^{1}H NMR spectrum of HB-HEPFA/G1,G2 based hyperbranched urethane acrylates display signals at 1.0 - 1.4 ppm for –(C<u>H</u>$_3$) protons of DMPA and IPDI, at 2.7 ppm for –(C<u>H</u>$_2$NHCO) of IPDI, at 3.4 – 3.6 ppm for –(OCOC<u>H</u>$_2$) and –(OC<u>H</u>$_2$) protons, at 4.0 – 4.4 ppm protons of –(C<u>H</u>$_2$OH) protons, at 4.6 – 4.8 ppm protons of –(O<u>H</u>) on therminal unit, 4.8 – 5.0 ppm protons of –(O<u>H</u>) on linear unit, at 5.7 and

6.1 ppm for –(C=C$\underline{H}_2$) and 6.8 – 7.4 ppm for –Ph protons of HEPFA as shown in Figure 4.23 and 4.24, respectively.

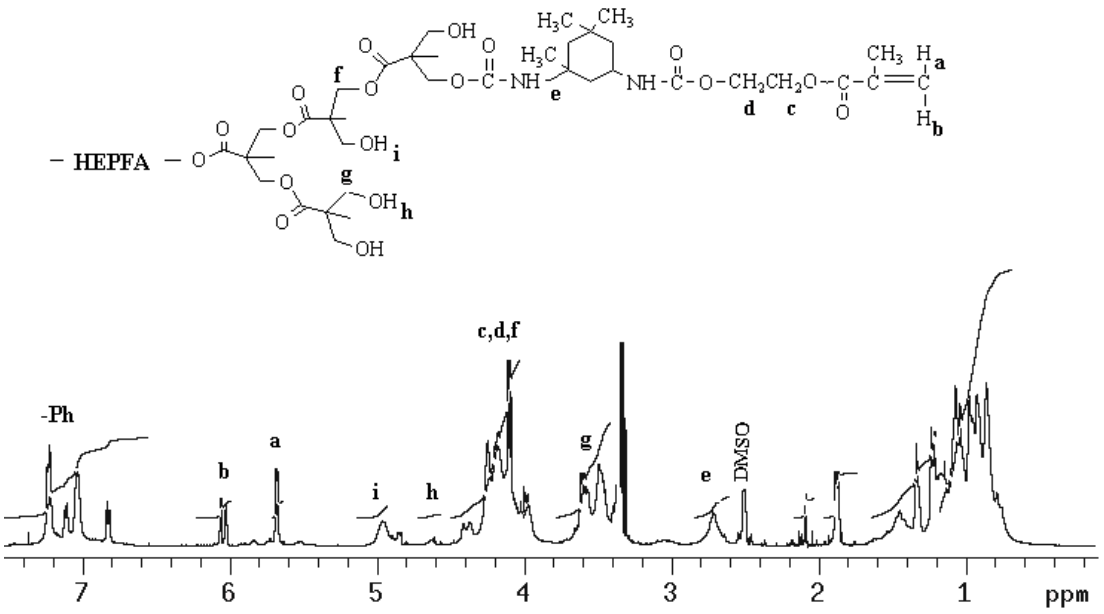


Figure 4.23: ^{1}H NMR spectrum of UA/HB-HEPFA/G1 in DMSO-d_6.

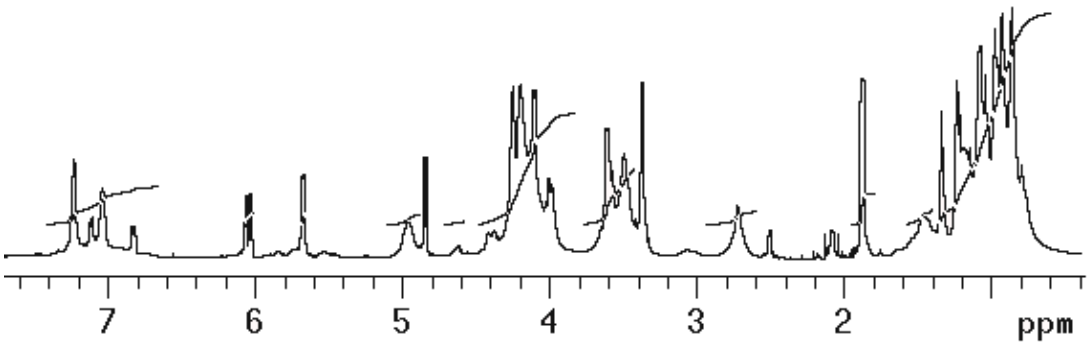


Figure 4.24: ^{1}H NMR spectrum of UA/HB-HEPFA/G2 in DMSO-d_6.

The ^{1}H NMR spectrum of HB-PECHDM/G1,G2 based hyperbranched urethane acrylates display signals at 1.0 - 1.4 ppm for –(C$\underline{H}_3$) protons of DMPA and IPDI, at 2.7 ppm for –(C$\underline{H}_2$NHCO) of IPDI, at 3.4 – 3.6 ppm for –(OCOC$\underline{H}_2$) and –(OC$\underline{H}_2$) protons, at 4.0 – 4.4 ppm protons of –(C$\underline{H}_2$OH) protons, at 4.6 – 4.8 ppm protons of –(O$\underline{H}$) on therminal unit, 4.8 – 5.0 ppm protons of –(O$\underline{H}$) on linear unit, at 5.7 and 6.1 ppm for –(C=C$\underline{H}_2$) as shown in Figure 4.25 and 4.26, respectively.

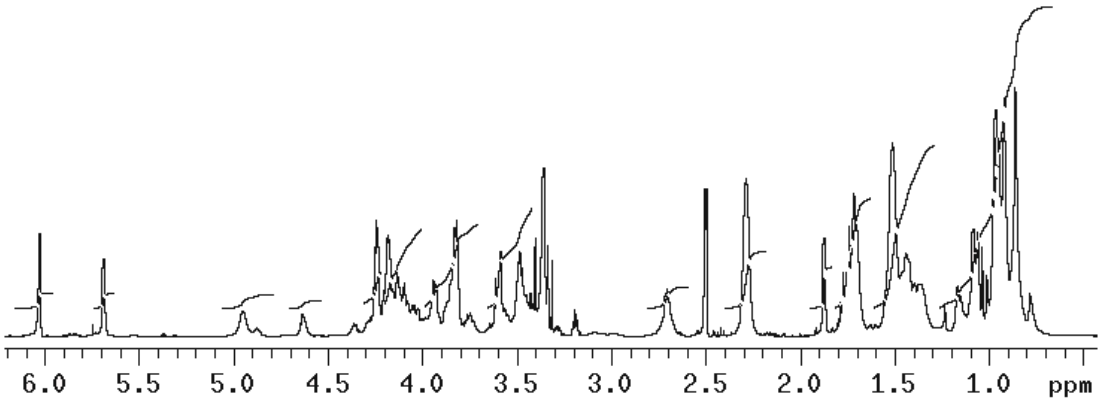


Figure 4.25: ^{1}H NMR spectrum of UA/HB-PECHDM/G1 in DMSO-d_6.

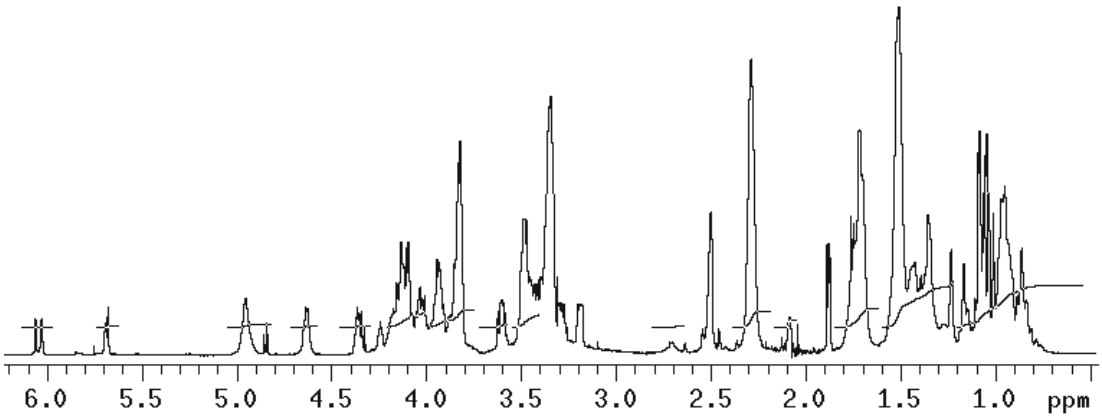


Figure 4.26: ^{1}H NMR spectrum of UA/HB-PECHDM/G2 in DMSO-d_6.

4.3 Application of UV-Curable Hyperbranched Urethane Acrylates on Wood and Determination of Coating Performance

Hyperbranched urethane acrylates were used as new oligomers in three types of UV-Curable wood coating formulations. In the first type of coating formulations, new hyperbranched urethane acrylates were used as main oligomer and named as neat formulations. The effects of generation number, core structure and number of functional groups were discussed by means of coating and free film properties.

In the second type of coating formulations, aliphatic polyurethane acrylate was modified with new hyperbranched urethane acrylate oligomers. The contributions of hyperbranched structure on the coating and free film properties were evaluated.

In the third type of coating formulations, aliphatic epoxy acrylate was modified with new hyperbranched urethane acrylates. The efficiency of modified formulations were

compared with high durable character of epoxy acrylate based formulations. The compatibility of epoxy acrylate and hyperbranched polyester based urethane acrylates were evaluated by means of the coating and free film properties.

The surface properties of wood coatings were investigated by contact angle (θ°), gloss (20°-60°), pencil hardness (H – 7H), pendulum hardness (könig) and cross-cut adhesion (0-5B) test results. The mechanical, thermal and physical properties were also investigated. The resulting performances are discussed in detail under the following topics.

4.3.1 Characterization of hyperbranched urethane acrylate based neat formulations

UV curable compositions were prepared by mixing hyperbranched polyesters based urethane acrylates (UA/HB-PEs), linear urethane acrylates (UA/L) as oligomers; n-vinyl pyrrolidone (NVP), hexanediol diacrylate (HDDA) and tripropylene glycol diacrylate (TPGDA) as reactive diluents to adjust the viscosity of coating formulations and enable the solubilization of the photoinitiator. The composition of UV-curable formulation are given at Table 4.3.

Table 4.3: The composition of UV-curable formulations.

Formulation (F)	F-UA/HB-PEs	F-UA/L
UA/HB-PEs	55 %	-
UA/L	-	55 %
NVP	15 %	15 %
HDDA	15 %	15 %
TPGDA	12 %	12 %
IRGACURE 184	3 %	3 %

4.3.1.1 Contact angle, gloss, pendulum hardness, pencil hardness, and cross-cut adhesion test results

The hardness of a coating depends mainly on chain flexibility of the molecules and crosslink density [319]. Due to the increasing crosslink density of HB-HEPA and HB-HEPFA based urethane acrylates higher pendulum hardness values were achieved with the increasing generation number. Also, high scratch resistance surfaces were obtained compared to the UA/L and the pencil hardness values were increased from H to 7H. Second generation HB-PECHDM based hyperbranched uerthane acrylate gave lower pendulum (75) and pencil hardness (2H) values thus

indicating the formation of a flexible coating. The contact angle, gloss, pencil hardness, pendulum hardness and cross-cut values are given at Table 4.4.

Table 4.4: Contact Angle, gloss, pencil hardness, pendulum hardness and cross-cut adhesion results of aliphatic and hyperbranched urethane acrylates coated wood surfaces.

	Contact Angle	**Gloss**				
Formulation	**θ°**	**20°**	**60°**	**Pendulum Hardness**	**Pencil Hardness**	**Cross-cut**
F-UA/L	75	145	146	65	H	5B
F-UA/HB-HEPA/G1	80	155	152	85	7H	4B
F-UA/HB-HEPA/G2	85	158	152	88	7H	5B
F-UA/HB-HEPFA/G1	88	153	150	88	7H	5B
F-UA/HB-HEPFA/G2	82	153	150	94	7H	5B
F-UA/HB-PECHDM/G1	80	149	146	85	7H	5B
F-UA/HB-PECHDM/G2	92	153	150	75	2H	5B

As can be seen from Table 4.4 shiny films were obtained with UA/HB-PE oligomers and slightly higher gloss values were provided compared to the linear oligomer. High adhesion characteristics of the UA/HB-PEs to the wood surfaces were proved with 5B cross-cut test results. In general, coating properties of wood surfaces were improved by utilizing hyperbranched polyester based urethane acrylates.

4.3.1.2 Mechanical tests

Mechanical properties were seriously effected by the crosslink density and chemical structure of the polymeric film. Due to the increased number of OH functional groups in the second generation hyperbranched polyester based urethane acrylates the crosslinking density of UV cured films were increased and higher tensile strength values were obtained. The increase in molecular weight of second generation hyperbranched PECHDM caused formation of more flexible urethane acrylate than first generation one. This emphasizes the rubbery behavior of second generation hyperbranched PECHDM based urethane acrylate and improves the elongation at break values while decreasing the tensile strength. The mechanical properties of UV-cured films are given at Table 4.5.

Table 4.5: Mechanical properties of aliphatic and hyperbranched urethane acrylate based UV-cured films.

Formulation	Modulus (N/mm^2)	Tensile strength (Mpa)	Elongation at break (%)
F-UA/L	127	11	13
F-UA/HB-HEPA/G1	595	36	10
F-UA/HB-HEPA/G2	625	42	12
F-UA/HB-HEPFA/G1	600	22	4
F-UA/HB-HEPFA/G2	645	38	6
F-UA/HB-PECHDM/G1	285	16	12
F-UA/HB-PECHDM/G2	120	11	18

4.3.1.3 Thermal properties

The thermal properties of coatings were investigated by thermogravimetric analysis under nitrogen atmosphere. The thermograms are shown in Figure 4.27 and the results are collected at Table 4.6, respectively. All samples exhibited a 5% weight loss at around 285 °C followed by a rapid loss over the temperature range of 400 °C (Figure 4.27). Increase in the OH content of the HEPA and HEPFA based hyperbranched polyester drastically increased char yield. Thermal stabilities of UA/HB-HEPA and UA/HB-HEPFA based films were slightly increased from first to second generation.

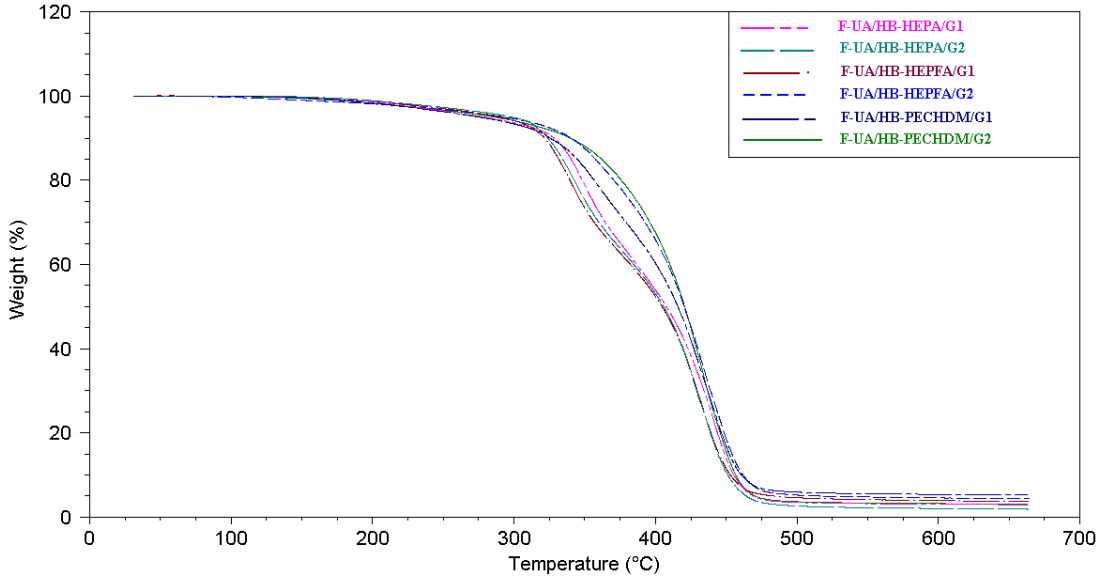


Figure 4.27: TGA curves of the hyperbranched urethane acrylate based UV-cured films.

Table 4.6: Thermal characteristics of aliphatic and hyperbranched urethane acrylates based UV-cured films.

Formulation	5% weight loss (°C)	First max-weight loss (°C)	Char yield (%)
F-UA/L	290	395	1.20
F-UA/HB-HEPA/G1	275	410	2.95
F-UA/HB-HEPA/G2	285	410	4.00
F-UA/HB-HEPFA/G1	290	405	3.65
F-UA/HB-HEPFA/G2	295	405	4.95
F-UA/HB-PECHDM/G1	275	415	5.25
F-UA/HB-PECHDM/G2	265	380	1.00

DSC analysis were also performed to investigate the thermal properties of UV-cured urethane acrylates. The thermograms are shown in Figure 27-30 and T_g values are given at Table 4.7, respectively.

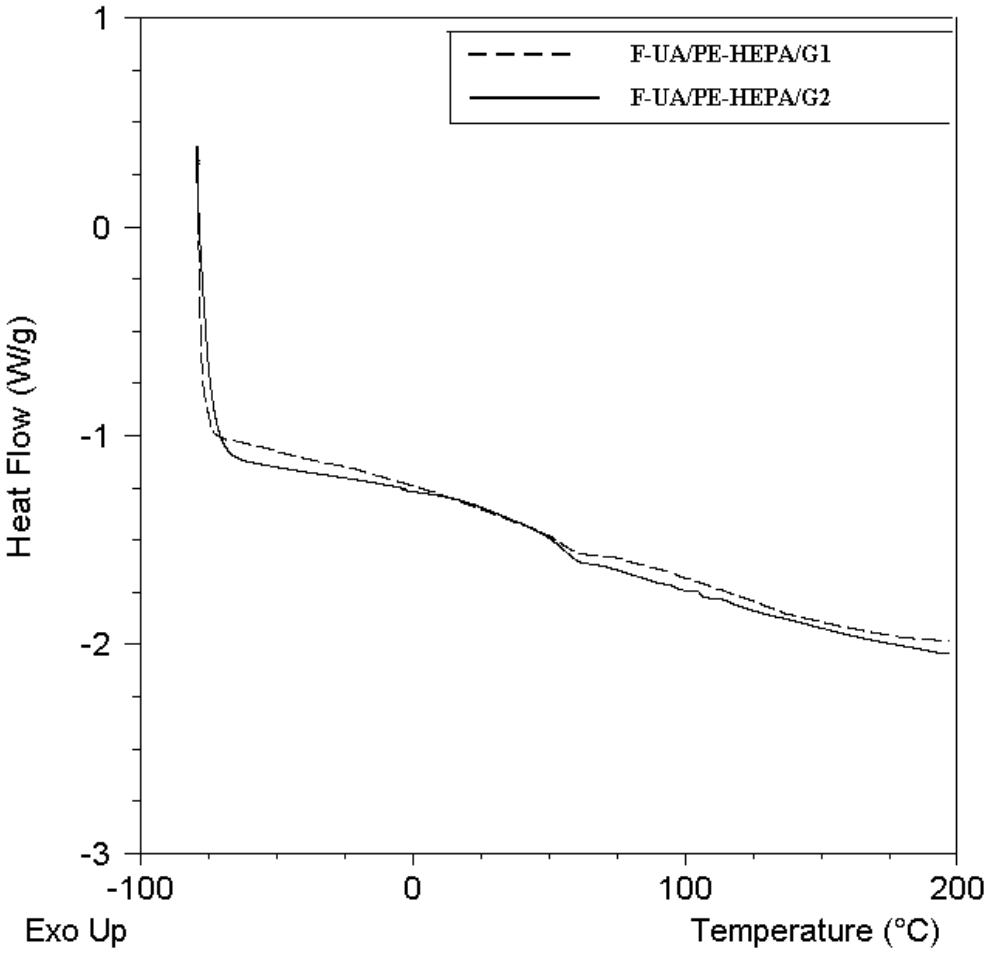


Figure 4.28: DSC curves of F-UA/HB-HEPA/G1, F-UA/HB-HEPA/G2.

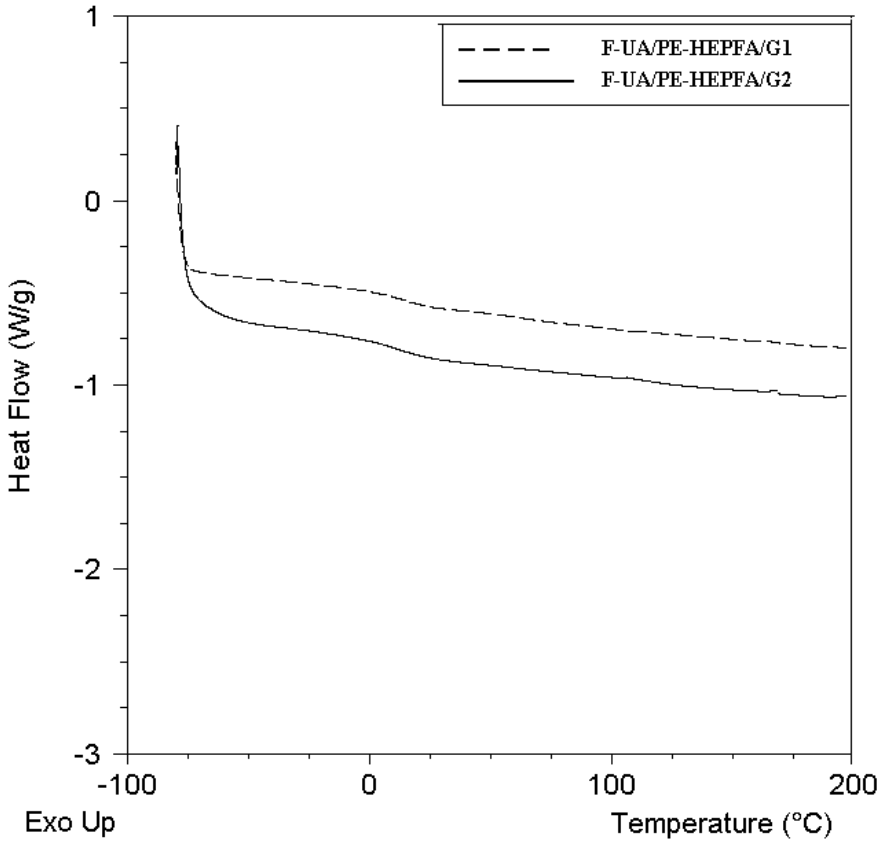


Figure 4.29: DSC curves of F-UA/HB-HEPFA/G1, F-UA/HB-HEPFA/G2.

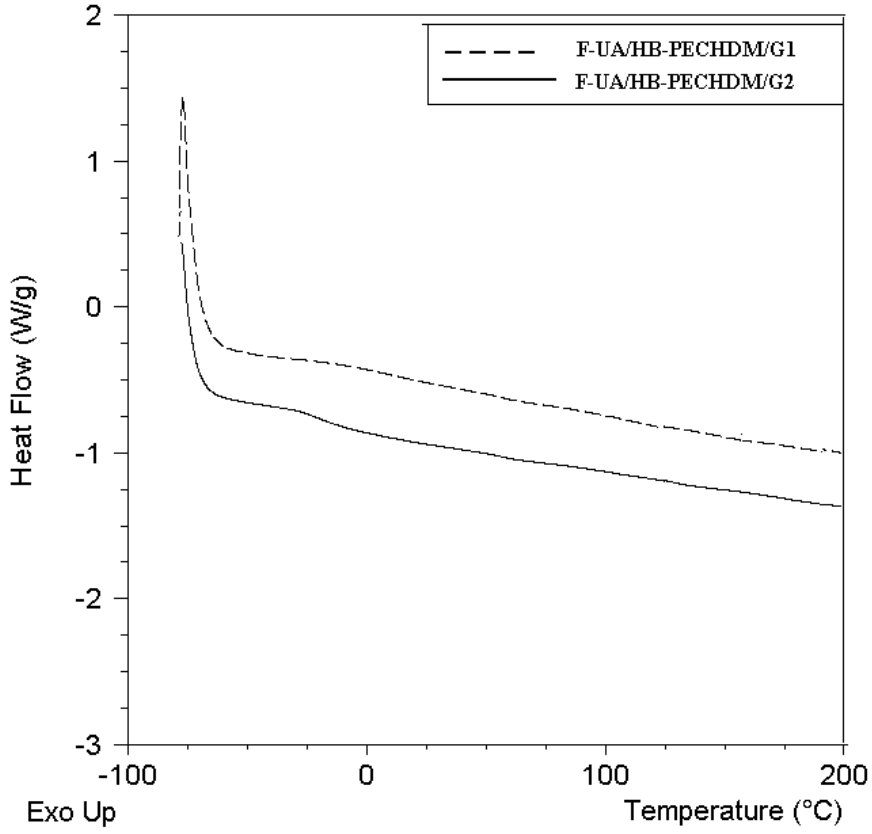


Figure 4.30: DSC curves of F-UA/HB-PECHDM/G1, F-UA/HB-PECHDM/G2.

Table 4.7: T_g of hyperbranched and aliphatic urethane acrylate based UV-cured films.

Formulation	Tg (°C)
F-UA/L	-10
F-UA/HB-HEPA/G1	53
F-UA/HB-HEPA/G2	57
F-UA/HB-HEPFA/G1	60
F-UA/HB-HEPFA/G2	62
F-UA/HB-PECHDM/G1	10
F-UA/HB-PECHDM/G2	-20

UA/HB-HEPA and UA/HB-HEPFA based coating formulations gave higher T_g values compared to linear urethane acrylates. Also, T_g values of UA/HB-HEPA and UA/HB-HEPFA based formulations showed a linear increase from first to second generation.

The hardness of coating and the T_g are known to be related. They both depend on the crosslink density of the cured films and also on the structure of the UV-curable resin [320]. An almost linear relationship was found between the modulus and T_g values of first and second generation HB-HEPA or HB-HEPFA based urethane acrylates.

4.3.1.4 Gel content and swelling results

The gel content and swelling properties are important parameters for evaluation of the polymerization degree of UV cured films. Higher crosslinking density and polymerization degree in hyperbranched polyester based urethane acrylates result with high gel content and swelling values. As shown in Table 4.8, the maximum gel content values of hyperbranched HEPFA based urethane acrylates indicate the highest crosslink density formation in these structures. Also, UA/HB-HEPA/G1-G2 and UA/HB-PECHDM/G1 based coating formulations provided high gel content values. The only exception in the trend was observed for UA/HB-PECHDM/G2 which shows lower gel content. The swelling results proved that the water resistance of the hyperbranched urethane acrylates were higher than that of the linear urethane acrylates.

Table 4.8: Gel Content and swelling (Q) results of aliphatic and hyperbranched urethane acrylate based UV-cured films.

Formulation	Gel content	% Q (water)
F-UA/L	94	10.00
F-UA/HB-HEPA/G1	96	6.50
F-UA/HB-HEPA/G2	96	7.00
F-UA/HB-HEPFA/G1	99	6.50
F-UA/HB-HEPFA/G2	99	7.50
F-UA/HB-PECHDM/G1	97	7.00
F-UA/HB-PECHDM/G2	70	9.00

4.3.1.5 Chemical and solvent resistance results

The chemical resistances of the free films were tested in 10 % solutions of sulfuric acid, sodium hydroxide and acetic acid, while solvent resistances were tested against xylene and methanol (Table 4.9). The films maintained the transparent and glossy appearances without any breaks after they treated to chemicals and solvents. UA/HB-PEs based films were found much resistant than corresponding linear urethane acrylates.

Table 4.9: The chemical and solvent resistances of aliphatic and hyperbranched urethane acrylate based UV-cured films.

	Chemicals			Solvents	
	Acetic acid (10%)	H_2SO_4 (10%)	NaOH (10%)	Xylene	Methanol
Formulation	Weight Loss %	Weight Loss %	Weight Loss %	Weight Loss %	Weight Loss %
F-UA/L	1.0	2.0	1.0	1.5	4.0
F-UA/HB-HEPA/G1	1.0	1.0	1.0	0.1	3.0
F-UA/HB-HEPA/G2	0.2	0.5	0.2	1.0	3.0
F-UA/HB-HEPFA/G1	0.2	1.0	0.2	0.1	5.0
F-UA/HB-HEPFA/G2	0.5	1.0	0.2	0.5	5.0
F-UA/HB-PECHDM/G1	1.0	1.0	0.5	0.5	7.0
F-UA/HB-PECHDM/G2	2.0	2.0	12	3.0	30

4.3.1.6 Results

Hyperbranched urethane acrylates were used as the main oligomer in UV-Curable wood coating formulations. Better surface and mechanical properties were obtained with the hyperbranched HEPA and HEPFA based urethane acrylates. The increase in number of hydroxyl functional groups in the second generation hyperbranched

urethane acrylates of HB-HEPA and HB-HEPFA enhanced the crosslink density in the coating resulting higher gel content and modulus values.

PECHDM core structure provides shiny and hydrophobic surfaces with high adhesion characteristics. Higher molecular weight of second generation PECHDM based urethane acrylate provides rubbery behavior and causes higher elongation values. As a consequence HEPA and HEPFA based hyperbranched urethane acrylates contribute a significant improvement on the coating properties of UV curable wood coatings.

4.3.2 Characterization of Hyperbranched Urethane Acrylate Modified Aliphatic Polyurethane Acrylate Based Formulations

In this part, aliphatic polyurethane acrylate is modified by incorporation of hyperbranched urethane acrylates into the coating formulations as a second oligomer. The objective was to focus on the influence of number of functional groups and core structure of hyperbranched urethane acrylates on coating properties of linear urethane acrylate. Also, it was the goal to achieve improved surface and mechanical properties compared to the linear urethane acrylate.

UV curable formulations were prepared by mixing hyperbranched urethane acrylates (UA/HB-PEs), aliphatic polyurethane acrylate (UA/L) as oligomers; n-vinyl pyrrolidone (NVP), hexanediol diacrylate (HDDA) and tripropylene glycol diacrylate (TPGDA) as reactive diluents to adjust the viscosity of coating formulations and enable the solubilization of the photoinitiator. The composition of UV-curable formulation are given at Table 4.10.

Table 4.10: The composition of UV-curable formulations.

Formulation (F)	F-UA/L	F- UA/L-UA/HB-PEs
UA/HB-PEs	-	27.5 %
UA/L	55 %	27.5 %
NVP	15 %	15 %
HDDA	15 %	15 %
TPGDA	12 %	12 %
IRGACURE 184	4 %	5 %

4.3.2.1 Contact angle, gloss, pendulum hardness, pencil hardness, and cross-cut adhesion test results

The wetting characteristics of wood surfaces were tested by measuring the contact angles against water. The maximum contact angle value was obtained by addition of UA/HB-PECHDM/G2. The gloss value of coatings were slightly increased by incorporation of hyperbranched urethane acrylates into the formulations.

Due to the enhancement of crosslink density especially by incorporation of HB-HEPA and HB-HEPFA based hyperbranched urethane acrylates sharp increase obtained in pendulum hardness values of linear urethane. Paralel to the high pendulum hardness values the pencil hardness values were also improved and high scratch resistance surfaces were obtained compared to the UA/L. Improved hardness of the coating were supported with high adhesion characteristic of the coatings and no area were removed after the cross-cut tests. All of the results are illustrated in Table 11.

Table 4.11: Contact angle, gloss, pencil hardness and cross-cut adhesion results of hyperbranched urethane acrylate modified aliphatic polyurethane acrylate coated wood surfaces.

	Contact Angle	Gloss				
Formulation	**θ°**	**20°**	**60°**	**Pendulum Hardness**	**Pencil Hardness**	**Cross-cut**
F-UA/L	75	145	146	65	H	5B
F-UA/L-UA/HB-HEPA/G1	70	145	146	94	5H	5B
F-UA/L-UA/HB-HEPA/G2	72	155	151	96	5H	5B
F-UA/L-UA/HB-HEPFA/G1	72	158	151	92	4H	5B
F-UA/L-UA/HB-HEPFA/G2	75	140	141	98	5H	5B
F-UA/L-UA/HB-PECHDM/G1	70	155	151	90	2H	5B
F-UA/L-UA/HB-PECHDM/G2	80	140	147	73	H	5B

4.3.2.2 Mechanical tests

The modulus, tensile strength and elongation at break values are used to characterize the mechanical properties of UV-cured films. A significant increase in modulus and tensile strength values were observed by incorporation of hyperbranched urethane acrylates in aliphatic polyurethane acrylate (Table 4.12). Due to the increased number of OH functional groups in the second generation HB-HEPA and HB-HEPFA based urethane acrylates the crosslink density of UV cured films were increased and higher modulus values were obtained.

Table 4.12: Mechanical properties of hyperbranched urethane acrylates modified aliphatic polyurethane acrylate based UV-cured films.

Formulation	Modulus (N/mm^2)	Tensile strength (Mpa)	Elongation at break (%)
F-UA/L	127	11	13
F-UA/L-UA/HB-HEPA/G1	265	23	23
F-UA/L-UA/HB-HEPA/G2	340	23	11
F-UA/L-UA/HB-HEPFA/G1	360	24	10
F-UA/L-UA/HB-HEPFA/G2	430	27	11
F-UA/L-UA/HB-PECHDM/G1	240	16	12
F-UA/L-UA/HB-PECHDM/G2	65	7	12

4.3.2.3 Thermal properties

The thermal properties of coatings were investigated by thermogravimetric analysis under nitrogen atmosphere. The thermograms are shown in Figure 4.31 and the results are collected at Table 4.13.

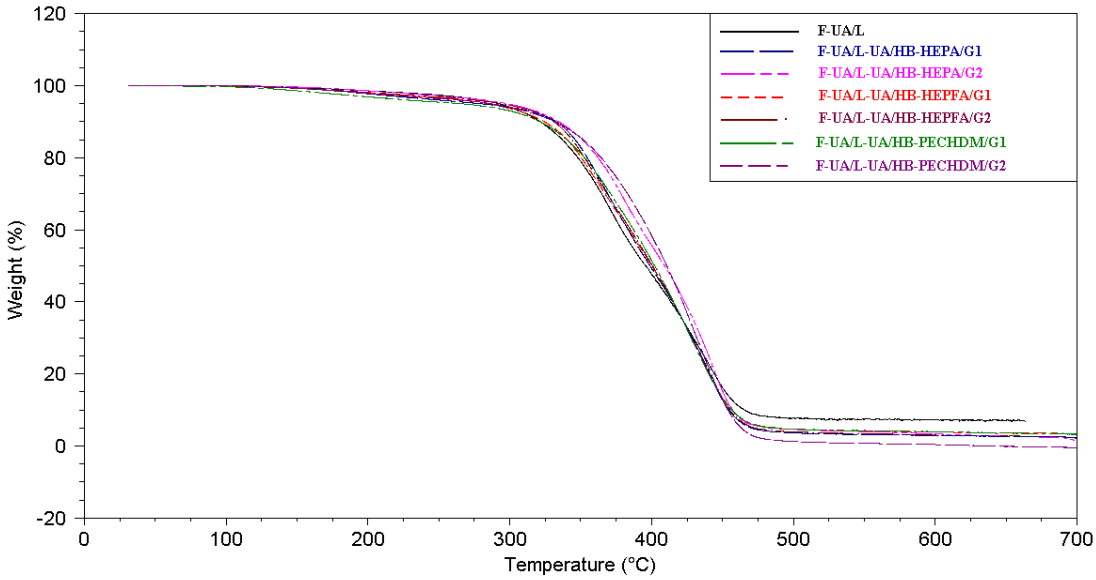


Figure 4.31: TGA curves of hyperbranched urethane acrylates modified aliphatic polyurethane acrylate based UV-cured films.

All samples exhibited a 5% weight loss at around 290 °C followed by a rapid loss over the temperature range of 400 °C.

Table 4.13: Thermal characteristics of of hyperbranched urethane acrylates modified aliphatic polyurethane acrylate based UV-cured films.

Formulation	5 % weight loss (°C)	First max-weight loss (°C)	Char yield (%)
F-UA/L	290	395	1.20
F-UA/L-UA/HB-HEPA/G1	280	400	2.95
F-UA/L-UA/HB-HEPA/G2	300	400	1.55
F-UA/L-UA/HB-HEPFA/G1	285	400	3.30
F-UA/L-UA/HB-HEPFA/G2	295	400	4.30
F-UA/L-UA/HB-PECHDM/G1	260	400	3.35
F-UA/L-UA/HB-PECHDM/G2	290	410	1.00

Thermal stabilities of UA/HB-HEPA and UA/HB-HEPFA based films were slightly increased from first to second generation.

4.3.2.4 Gel content and swelling results

As shown in Table 4.14, higher gel content values obtained by hyperbranched urethane acrylate modified formulations. The swelling values in water remained about the same as that of the aliphatic polyurethane acrylate. The only exception was observed for UA/HB-PECHDM/G2 modified linear urethane acrylate which shows lower gel content and swelling values.

Table 4.14: Gel content and swelling (q) results of hyperbranched urethane acrylates modified aliphatic polyurethane acrylate based UV-cured films.

Formulation	Gel content	% Q (water)
F-UA/L	94	10.00
F-UA/L-UA/HB-HEPA/G1	96	10.00
F-UA/L-UA/HB-HEPA/G2	96	9.00
F-UA/L-UA/HB-HEPFA/G1	96	10.00
F-UA/L-UA/HB-HEPFA/G2	96	10.00
F-UA/L-UA/HB-PECHDM/G1	96	9.00
F-UA/L-UA/HB-PECHDM/G2	82	20.00

4.3.2.5 Chemical and solvent resistance results

The chemical resistances of the free films were tested in 10 % solutions of sulfuric acid, sodium hydroxide and acetic acid, while solvent resistances were tested against xylene and methanol (Table 4.15). The chemical and solvent resistances of hyperbranched urethane acrylates modified formulations were as high as aliphatic

polyurethane acrylate. However, the UA/HB-PECHDM/G2 modified films were broken and gave higher weight loss values after they treated to methanol.

Table 4.15: The chemical and solvent resistances of hyperbranched urethane acrylates modified aliphatic polyurethane acrylate based UV-cured films.

	Chemicals			Solvents	
	Acetic acid (10%)	H_2SO_4 (10%)	NaOH (10%)	Xylene	Methanol
Formulation	Weight Loss %	Weight Loss %	Weight Loss %	Weight Loss %	Weight Loss %
F-UA/L	0.1	2.0	1.0	1.5	4.0
F-UA/L-UA/HB-HEPA/G1	none	2.5	1.0	1.0	4.0
F-UA/L-UA/HB-HEPA/G2	none	1.5	1.0	1.2	4.0
F-UA/L-UA/HB-HEPFA/G1	none	2.0	1.0	1.2	11
F-UA/L-UA/HB-HEPFA/G2	none	2.0	1.0	1.5	11
F-UA/L-UA/HB-PECHDM/G1	0.1	3.0	1.0	1.0	5.0
F-UA/L-UA/HB-PECHDM/G2	1.0	2.0	1.5	1.5	40

4.3.2.6 Results

The hyperbrached urethane acrylates were incorporated into the linear urethane acrylate based formulations successfully. High gloss values of formulations can be an indication of the compatibility of hyperbanched urethane acrylates with aliphatic polyurethane acrylate. Incorporation of HB-HEPA and HB-HEPFA based hyperbranched urethane acrylates into the UV-curable wood coating formulations improved surface and mechanical properties of coatings by increasing the crosslink density of the system. Higher gel content values also proved the higher polymerization degree of HB-HEPA and HB-HEPFA based urethane acrylates in the formulations.

4.3.3 Characterization of hyperbranched urethane acrylates modified aliphatic epoxy acrylate based formulations

Epoxy acrylates are extensively used as oligomers in UV-curable systems to produce hard and chemically resistant films. To improve their impact performance, urethane acrylates or polyester acrylates are generally incorporated into epoxy acrylate formulations [321]. Also, hyperbranched polyesters were added without modification into the UV-Curable epoxy systems for increasing the toughness of the cured polymeric films [322,323].

In this part, aliphatic epoxy acrylate is modified by incorporation of hyperbranched urethane acrylates into the coating formulations. The goal is to investigate the effects of multifunctional acrylated oligomers to the epoxy acrylate by means of surface and mechanical properties.

UV curable compositions were prepared by mixing hyperbranched urethane acrylates (UA/HB-PEs), epoxy acrylate (EA) as oligomers; n-vinyl pyrrolidone (NVP), hexanediol diacrylate (HDDA) and tripropylene glycol diacrylate (TPGDA) as reactive diluents to adjust the viscosity of coating formulations and enable the solubilization of the photoinitiator. The composition of UV-curable formulation are given at Table 4.16.

Table 4.16: The composition of UV-curable formulations.

Formulation (F)	F-EA	F- EA-UA/HB-PEs
UA/HB-PEs	-	27.5 %
EA	55 %	27.5 %
NVP	15 %	15 %
HDDA	15 %	15 %
TPGDA	12 %	12 %
IRGACURE 184	3. %	4. %

4.3.3.1 Contact angle, gloss, pendulum hardness, pencil hardness and cross-cut adhesion results

The wetting characteristics of wood surfaces were tested by measuring the contact angles against water. The contact angle values of wood surfaces were increased proportionally with increasing generation number of hyperbranched urethane acrylates. The maximum contact angle value was observed with UA/HB-PECHDM/G2 modified coating. The high gloss value of coatings were maintained with incorporation of hyperbranched polyester based urethane acrylates into the formulations. The hardness of the coatings increased with incorporation of HB-HEPA and HB-HEPFA based urethane acrylates into the formulations. Also, high scratch resistance character of epoxy coating is supplied by hyperbranched urethane acrylates. Cross-cut test results were 4B to 5B that were proved the high adhesion characteristics of the coating formulations onto the wood surfaces. The results are illustrated at Table 4.1.

Table 4.17: Contact angle, gloss, pendulum hardness, pencil hardness and cross-cut adhesion results of hyperbranched urethane acrylates modified epoxy acrylate coated wood surfaces.

	Contact Angle	Gloss				
Formulation	**θ º**	**20 º**	**60 º**	**Pendulum Hardness**	**Pencil Hardness**	**Cross-cut**
F-EA	75	152	148	95	6H	5B
F-EA-UA/HB-HEPA/G1	68	155	151	100	5H	5B
F-EA-UA/HB-HEPA/G2	78	156	151	110	5H	5B
F-EA-UA/HB-HEPFA/G1	80	152	152	105	5H	5B
F-EA-UA/HB-HEPFA/G2	82	150	148	110	5H	5B
F-EA-UA/HB-PECHDM/G1	75	149	153	90	5H	4B
F-EA-UA/HB-PECHDM/G2	82	146	148	70	3H	4B

4.3.3.2 Mechanical tests

The modulus, tensile strength and elongation at break values are used to characterize the mechanical properties of UV cured films. As listed in the Table 4.18 tensile strength and modulus values are increased by the addition of HB-HEPA and HB-HEPFA based hyperbranched urethane acrylates into the formulations. On the contrary the addition of HB-PECHDM based hyperbranched urethane acrylate would decrease the tensile strength and increase the percent elongation. It can be attributed to the lower crosslink density due to the long flexible core structure of the molecule.

Table 4.18: Mechanical properties of hyperbranched urethane acrylates modified epoxy acrylate based UV-cured films.

Formulation	**Modulus (N/mm^2)**	**Tensile strength (Mpa)**	**Elongation at break (%)**
F-EA	540	32	7
F-EA-UA/HB-HEPA/G1	565	42	12
F-EA-UA/HB-HEPA/G2	580	50	12
F-EA-UA/HB-HEPFA/G1	655	43	8
F-EA-UA/HB-HEPFA/G2	665	44	8
F-EA-UA/HB-PECHDM/G1	475	30	11
F-EA-UA/HB-PECHDM/G2	353	22	13

4.3.3.3 Thermal properties

The thermal properties of coatings were investigated by thermogravimetric analysis under nitrogen atmosphere. The thermograms are shown in Figure 4.32 and the results are collected at Table 4.19.

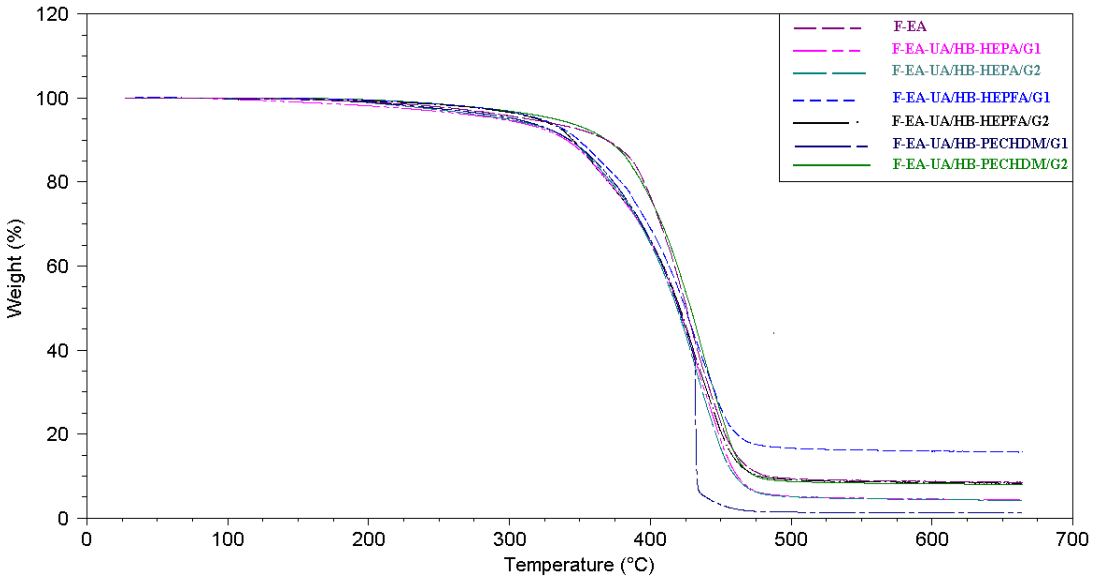


Figure 4.32: TGA curves of hyperbranched urethane acrylates modified epoxy acrylate based UV-cured films.

The modification with second generation hyperbranched urethane acrylates slightly increased the thermal stability.

Table 4.19: Thermal characteristics of hyperbranched urethane acrylates modified epoxy acrylate based UV-cured films.

Formulation	5 % weight loss (°C)	First max-weight loss (°C)	Char yield (%)
F-EA	312	425	8.50
F-EA-UA/HB-HEPA/G1	295	420	4.30
F-EA-UA/HB-HEPA/G2	300	420	4.20
F-EA-UA/HB-HEPFA/G1	320	425	15.80
F-EA-UA/HB-HEPFA/G2	320	420	8.25
F-EA-UA/HB-PECHDM/G1	305	420	1.20
F-EA-UA/HB-PECHDM/G2	335	430	8.00

The glass transition temperature (T_g) values of the formulations were obtained from DSC measurements. The thermograms are shown in Figure 4.33-4.35 and the results are collected at Table 4.20, respectively.

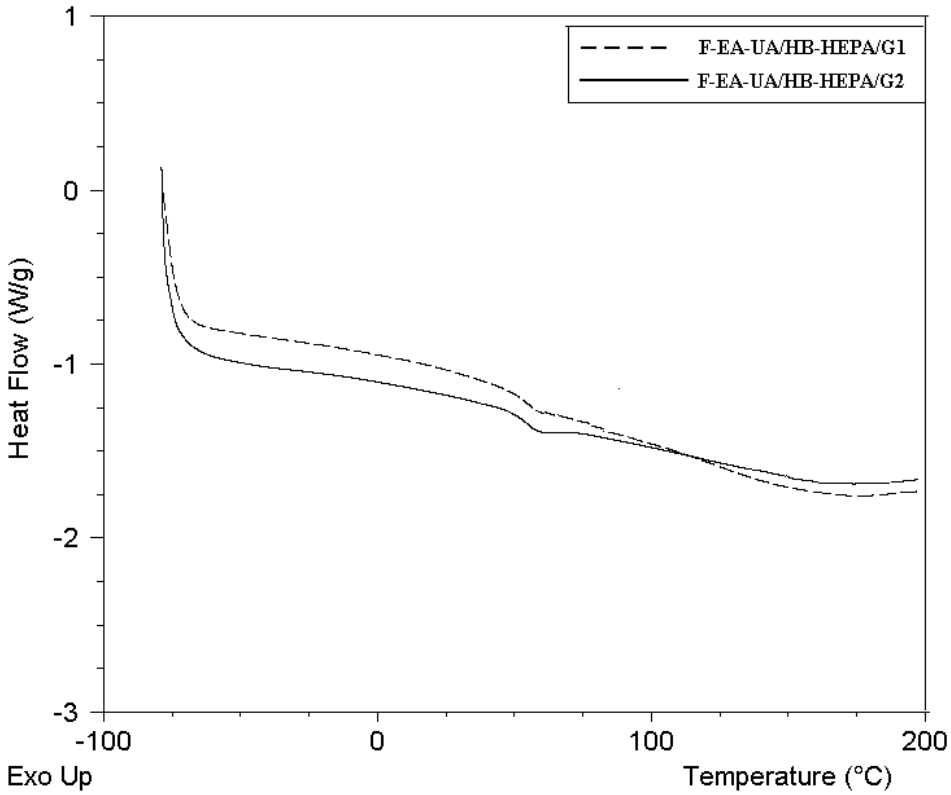


Figure 4.33: DSC curves of F-EA-UA/HB-HEPA/ G1 and F-EA-UA/HB-HEPA/G2.

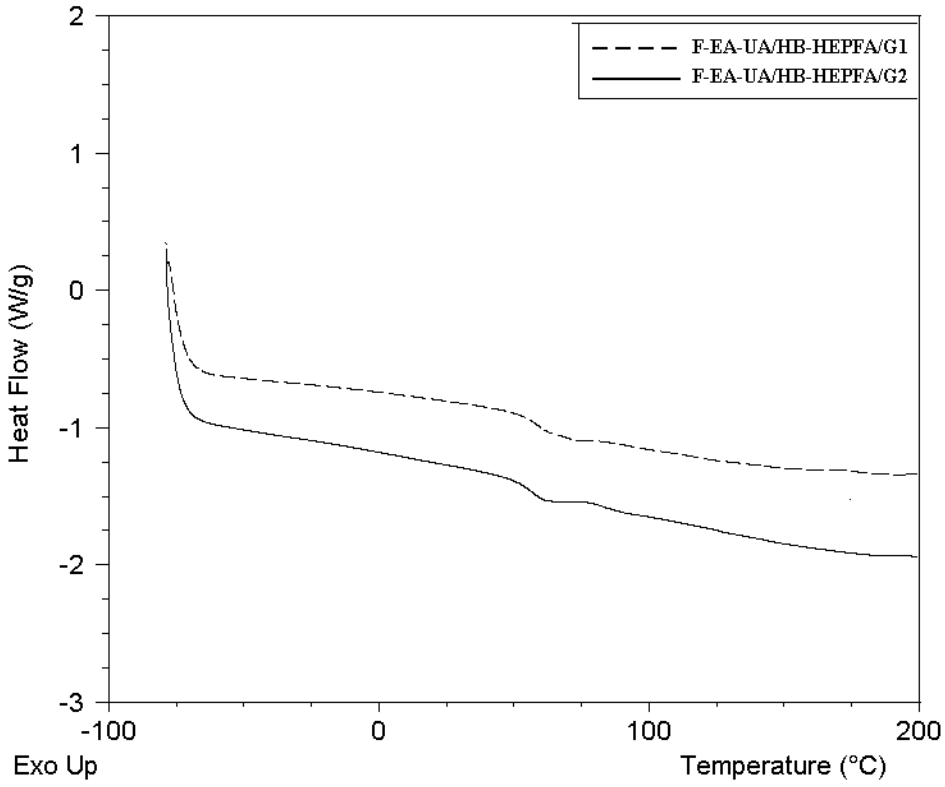


Figure 4.34: DSC curves of F-EA-UA/HB-HEPFA/ G1 and F-EA-UA/HB-HEPFA/G2.

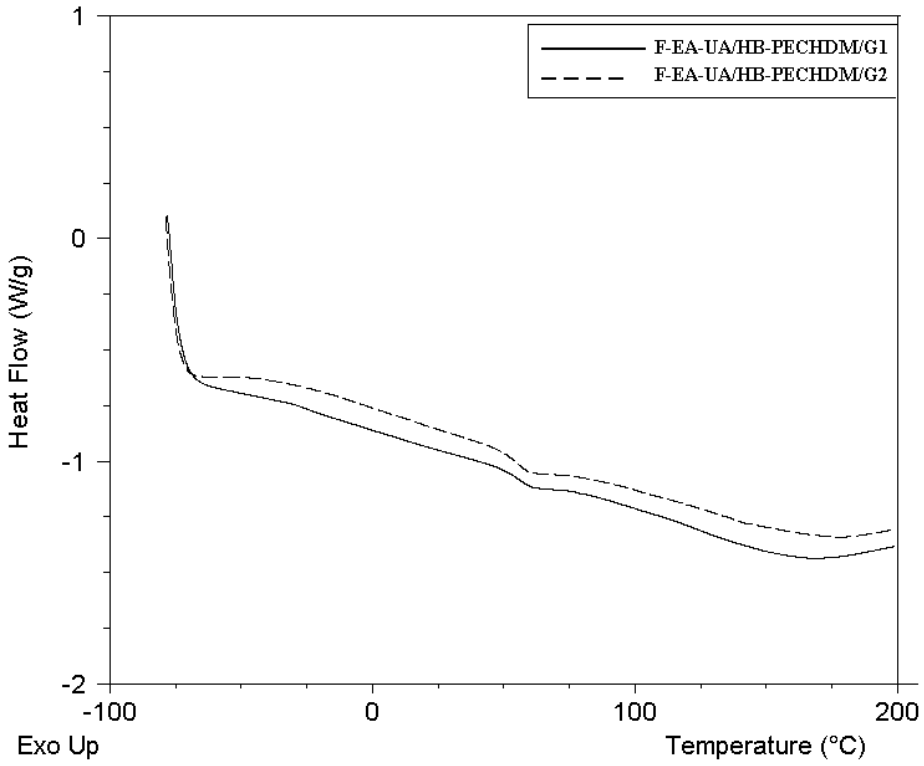


Figure 4.35: DSC curves of F-EA-UA/HB-PECHDM/ G1 and F-EA-UA/HB-PECHDM/G2.

As can be seen from the Table 4.20 the hyperbranched urethane acrylates modified films showed a glass transition temperature that are so similiar to the neat film.

Table 4.20: T_g of hyperbranched urethane acrylates modified epoxy acrylate based UV-cured films.

Formulation	Tg (°C)
F-EA	56
F-EA-UA/HB-HEPA/G1	54
F-EA-UA/HB-HEPA/G2	55
F-EA-UA/HB-HEPFA/G1	58
F-EA-UA/HB-HEPFA/G2	57
F-EA-UA/HB-PECHDM/G1	55
F-EA-UA/HB-PECHDM/G2	57

4.3.3.4 Gel content and swelling results

The gel content and swelling values are increased by incorporation of HB-HEPA and HB-HEPFA hyperbranched urethane acrylates into the epoxy acrylate due to the improved crosslink density as shown in Table 4.21.

Table 4.21: Gel content and swelling (Q) results of hyperbranched urethane acrylates modified epoxy acrylate based UV-cured films.

Formulation	Gel content	% Q (water)
F-EA	96.5	10
F-EA-UA/HB-HEPA/G1	99.5	8.3
F-EA-UA/HB-HEPA/G2	99	8.0
F-EA-UA/HB-HEPFA/G1	99	9.0
F-EA-UA/HB-HEPFA/G2	99	9.3
F-EA-UA/HB-PECHDM/G1	95	6.5
F-EA-UA/HB-PECHDM/G2	82	9.0

4.3.3.5 Chemical and solvent resistance results

The chemical resistances of the free films were tested in 10 % solutions of sulfuric acid, sodium hydroxide and acetic acid, while solvent resistances were tested against xylene and methanol (Table 4.22). The chemical and solvent resistances of UA/HB-PEs containing films were as high as epoxy acrylate based film. Especially alcohol resistances were effectively enhanced by incorporation of hyperbranched urethane acrylates into the formulations.

Table 4.22: The chemical and solvent resistances of hyperbranched urethane acrylates modified epoxy acrylate based UV-cured films.

	Chemicals			Solvents	
	Acetic acid (10%)	H_2SO_4 (10%)	NaOH (10%)	Xylene	Methanol
Formulation	Weight Loss %	Weight Loss %	Weight Loss %	Weight Loss %	Weight Loss %
F-EA	0.5	1	none	none	15
F-EA-UA/HB-HEPA/G1	none	7	7	0.2	6
F-EA-UA/HB-HEPA/G2	0.5	1	5	0.5	2
F-EA-UA/HB-HEPFA/G1	none	7	7	none	6
F-EA-UA/HB-HEPFA/G2	none	1	1	none	4
F-EA-UA/HB-PECHDM/G1	4	4	4	0.1	6
F-EA-UA/HB-PECHDM/G2	none	5	5	0.5	18

4.3.3.6 Results

It can be seen that incorporation of hyperbranched urethane acrylates into the epoxy acrylate formulations significantly improved the coating properties. High compatibility of epoxy acrylate and hyperbranched urethane acrylates provided shiny surfaces. Compatible feature of both types of oligomers was also observed by DSC

studies. The hyperbranched urethane acrylate modified films gave high gel content values with superior mechanical properties due to the high degree of polymerization and crosslink density.

5. CONCLUSION

In the first part of the thesis, first and second generation hyperbranched polyester polyols were synthesized with AB_2 and B_2 molecules by melt polycondensation technique and characterized successfully with GPC, ^{1}H NMR and ^{13}C NMR spectroscopy. Control over the molar mass and the molar-mass distribution of hyperbranched polyesters were achieved by using multifunctional core moieties, B_f, in the polycondensation of AB_2 monomers. The polycondensation of AB_2 monomers with B_2 cores resulting with the molecular weight distribution narrower. The polydispersity index (PDI) of hyperbranched polyesters were less than 2.0 and HEPFA based hyperbranched polyesters have the lowest polydispersity index of 1.16 and 1.22. The PDI of HEPA and HEPFA based hyperbranched polyesters slightly increase with increasing core/monomer ratio as mentioned in literature.

The thermograms obtained from DSC measurements confirmed that all hyperbranched polyesters are amorphous. Due to the increase in the molar mass of HB-PEs the Tg values were slightly increased from first to second generation for HEPA and HEPFA. The decrease in T_g values of PECHDM based hyperbanched polyester can be ascribed to the decrease in backbone rigidity. In the case of linear polyester, PECHDM, core structure causes plasticiser effect lowering T_g values.

The fractions of D-, L- and T- repeating units and degree of branching were usually determined by ^{13}C NMR spectroscopy. Here, average values of $DB_{Frechet} \sim 0.45$ ($DB_{Frey} \sim 0.40$) of hyperbranched polyesters are found quite consistently with the results obtained by Zagar et al ($DB_{Frechet} \sim 0.43$ and $DB_{Frey} \sim 0.30$)[317].

In the second part of the thesis, hyperbranched polyester based urethane acrylates were synthesized and characterized with FT-IR, ^{1}H NMR and ^{13}C NMR spectroscopy. The hyperbranched urethane acrylates were utilized in three types of UV-curable wood coating formulations as new oligomers. The mechanical, thermal and physical properties were investigated to characterize the structure property relationships.

HB-HEPA and HB-HEPFA based urethane acrylates provided better surface and mechanical properties. The increase in OH functional groups in the second generation hyperbranched urethane acrylates of HB-HEPA and HB-HEPFA enhanced the crosslink density in the coating resulting with higher gel content and modulus values. PECHDM core structure based hyperbranched urethane acrylates provided high gloss values and hydrophobic surfaces with high adhesion characteristics. Higher molecular weight of second generation PECHDM based urethane acrylate provides rubbery behavior and causes higher elongation values.

The hyperbrached urethane acrylates modified aliphatic polyurethane acrylate based formulations provided high gloss values due to the formation of a homogeneous blend. Incorporation of HB-HEPA and HB-HEPFA based hyperbranched urethane acrylates into the UV curable wood coating formulations improved surface and mechanical properties of coatings by increasing the crosslink density of the system. Higher gel content values also proved the higher polymerization degree of HB-HEPA and HB-HEPFA based urethane acrylates in the formulations.

The hyperbrached urethane acrylates modified epoxy acrylate based formulations provided high gloss values that can be an indication of the compatibility of both types of oligomers. It can be seen that incorporation of hyperbranched urethane acrylates into the epoxy acrylate formulations significantly improved the coating properties. Compatible feature of both types of oligomers was also observed by DSC studies. The hyperbranched urethane acrylate modified films gave high gel content values with superior mechanical properties due to the high degree of polymerization and crosslink density.

The hyperbranched urethane acrylates modified epoxy acrylate coatings provided higher coating performances compared to the hyperbranched urethane acrylate based neat coatings. The mechanical properties and thermo-oxidative stability of neat formulations improved especially by incorporation of HB-HEPA and HB-HEPFA based urethane acrylates into the epoxy acrylate coatings.

As a consequence hyperbranched urethane acrylate structures contribute a significant improvement on the coating performances and free film properties of the coatings.

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