

HYPERBRANCHED POLYMERS - UNIQUE DESIGN TOOLS FOR MULTI PROPERTY CONTROL IN RESINS AND COATINGS

Bo Pettersson
Perstorp Polyols - Application Technology
S-284 80 Perstorp SWEDEN

ABSTRACT

A hyperbranched polymer is presented. It is a hydroxyl functional aliphatic polyester and consist of a polyalcohol core from which branches extend, forming a core-shell structure with large number of hydroxyl groups at its peripheral surface. It is polydisperse and consist, apart from the main core/shell fraction, also of a minor fraction with tree-like branches. Hyperbranched polyesters of the presented type have been found to contribute to improved physical, as well as chemical and mechanical properties. Thanks to the unique molecular architecture it is possible to design the hyperbranched polyester in numerous ways to reach desired properties in different applications. This paper will focus on and illuminate how molecular design not only might affect properties in one, but many applications. To illustrate this, examples will be given in the fields of *alkyds*, where presented hyperbranched polymer contributes to low viscosities combined with excellent drying; in *amine cured epoxies*, where a hyperbranched epoxy demonstrates dramatically increased toughening; and in *polyurethanes* and *radcure*, where rapid curing can be obtained by proper molecular design.

1. Introduction

Hyperbranched polymers and dendrimers belong to the same group of polymers with densely branched structures and a large number of reactive groups. They resemble each other in that they are both polymerized from monomers with mixed reactivities, commonly denoted A_2B or A_3B monomers, thus giving branched structures with exponential growth, in both end-group functionalities and molecular weights. However, there are also differences. Dendrimers are defined as monodisperse hyperbranched polymers, while ordinary hyperbranched polymers are polydisperse. The fundamental synthesis approaches differ between the two. Whereas dendrimers require absolute control of all synthesis steps, manufacturing of ordinary hyperbranched polymers is accomplished by a simplified approach similar to conventional resin technology.

Published work^{1,2} on dendrimers and hyperbranched polymers has mainly dealt with basic research on synthesis and characterization. As these polymers are still fairly new to the polymer field, numerous fundamental questions have to be answered, e.g. in the form of new analytical tools for characterization of structures.

A new molecular architecture is, of course, intriguing for many scientific reasons. But from a commercial point of view, what benefits are there to gain from hyperbranched and dendritic technology? What are the properties of hyperbranched polymers and dendrimers? The answers to these questions must be shown to offer sufficient commercial rewards before industry can be expected to act upon the potential.

It is mainly physical properties³, as well as a few examples⁴, that have been reported in the literature. One property often mentioned is the non-Newtonian relationship between viscosities and molecular weight, where hyperbranched and dendritic polymers show *low viscosities at high molecular weights*. For coating applications, this should be highly interesting in terms of the environmental issues, where legislation plays an important role in the future trend towards coatings with lower VOCs than today. However, favorable viscosity is not the only property to which hyperbranched polymers can contribute.

This paper intends to give the reader a broader understanding of how molecular design of an aliphatic hyperbranched polyester can be adapted to several coatings systems, where differences in the shell chemistry give different properties. Enhanced physical as well as mechanical and chemical properties can thus be achieved.

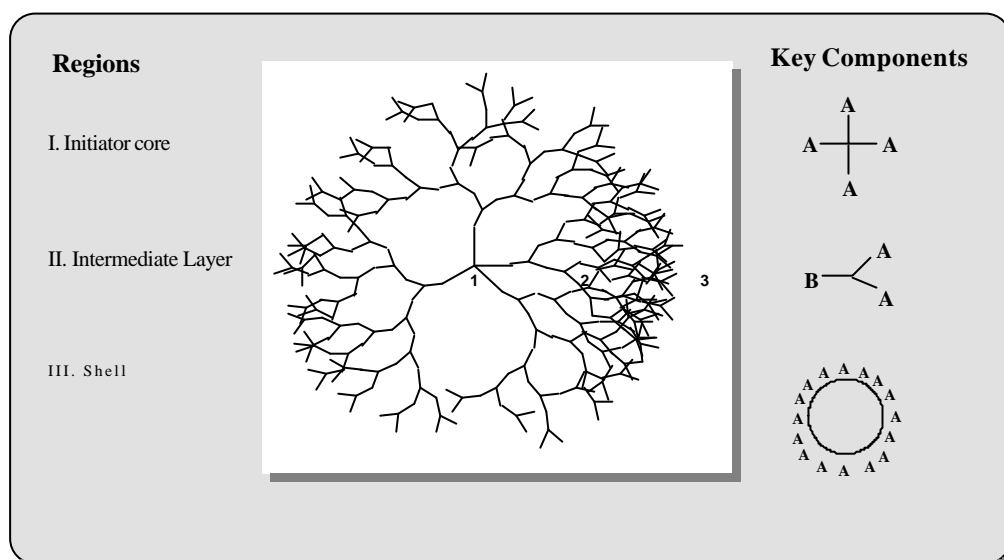
2. Molecular architecture

All hyperbranched polymers, including dendrimers, have tree-like structures. The fact that dendrimers resemble trees is reflected in the name, derived from the Greek word for tree, *dendron*. This paper will begin with a general introduction of dendrimers, as the polydisperse hyperbranched polymers presented here have many structural similarities with dendrimers.

2.1. Structure

Dendrimers typically consist of a core, from which branches extend three dimensionally in space, forming a more or less spherical or rod-shaped structure, depending on the type of core used. Three different regions can be distinguished in a dendritic molecule, as shown in figure 1 below.

Figure 1: A dendritic molecule



The core typically consists of a polyfunctional molecule, where the functionality governs the number of branches that extend from it. The tetrahedral core gives a spherical polymer, whereas linear polymeric cores give rod-shaped dendrimers.

The intermediate layer, or tree-structure, is built from monomers with mixed reactivities denoted as chain extenders. They typically consist of molecules with one reactive group of a certain type, represented by B above, and two or more reactive groups of a different species, here called A. Hence a new branching point is created every time a chain extender reacts with a core or an already-formed hyperbranched structure.

The resulting dendritic polymer will, as shown above, result in a dense spherical structure with a large number of reactive groups at its peripheral surface, represented by groups A in figure 1.

2.2. Dendritic growth

A tree structure begins to form when chain extenders react, either with a core or with other chain extenders. These may or may not have the same type of reactive groups. Dendritic and hyperbranched structures can be produced in three different ways:

- Divergent approach
- Mixed reactivity approach
- Convergent approach

2.2.1. Divergent approach

The tree structure is formed, by reacting a core with an equivalent amount of chain extenders with regard to functional groups on the core and reactive groups B on the chain extender. The resulting molecule will thereby have twice the functionality of the core, provided that the chain extender is of an A_2B -type, and that protective groups are used on the A-groups of the chain extenders. The molecule obtained can then be reacted again with an equivalent amount of chain extenders, which again doubles the functionality. The process is repeated in a similar manner until the desired molecular weight, size and surface functionality is reached. A schematic reaction scheme for divergent growth is shown in figure 2 below.

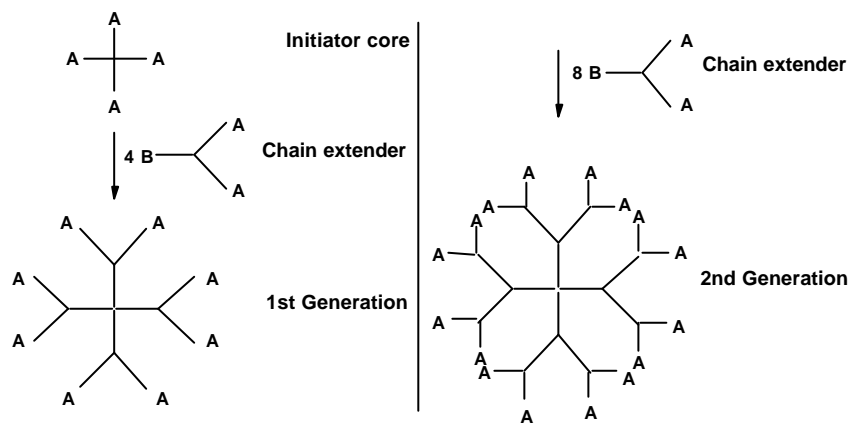


Figure 2: Dendritic growth according to the divergent approach

The term *generation* is often used in dendrimer terminology, and sometimes with hyperbranched polymers, to describe the size of the polymer. Each generation represents one repetitive step when building a dendritic structure of a certain size.

There is also a correlation between the number of generations, n , and the molecular weight of a dendritic or hyperbranched polymers. Some useful expressions are given below.

$$F = f \times 2^n \quad (1)$$

$$N = f(2^n - 1) \quad (2)$$

$$M_{\text{dendrimer}} = N(M_c - M_{R1}) + \mu F(M_t - M_{R2}) + M_i \quad (3)$$

where

n = No. of generations

F = End-group functionality of a dendrimer with n generations

f = Functionality of end-groups A of initiator core

N = Equivalents of chain extender per equivalent initiator in a dendrimer with n generations

$M_{\text{dendrimer}}$ = Molecular weight of an end-group-terminated dendrimer with n generations

M_c = Molecular weight of chain extender

M_{R1} = Molecular weight of product formed in reaction between groups A and B

μ = Degree of end-group termination in dendrimer with n generations

M_t = Molecular weight of terminating group

M_{R2} = Molecular weight of product formed in reaction between terminating group and group A

M_i = Molecular weight of initiator core

Note:All equations are based on reactions with initiator molecules with end-groups A and chain extenders with two end-groups A and one end-group B

Equations (1), (2) and (3) above illustrate the rapid increase in molecular weight and end-group functionality as a function of generation. Consequently, dendrimers with many generations have high molecular weights and a large number of reactive end-groups at their peripheral surfaces.

2.2.2. Mixed reactivity approach

Dendritic structures without defects can also be produced by using different types of chain extenders in each repetitive synthesis step. Hence, protection groups are not necessary, provided that selective chemistry can be adapted. Principles for this approach are that A_2B monomers are reacted onto a C functional core, where B can only react with C and vice versa and A can react with neither B nor C. See figure 3 below. The resulting molecule will have twice the functionality of the core, but be A-functional instead of C-functional. The next generation is produced by adding a C_2D monomer, where D can only react with A, and C can neither react with A nor D.

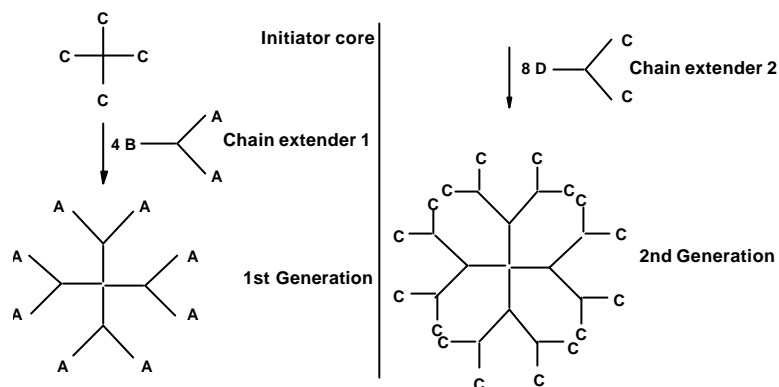


Figure 3: Dendritic growth through mixed reactivity

2.2.3. Convergent approach

A third approach to producing dendritic structures is by first producing branches and then connecting them to a core, hence the name convergent synthesis. In the first step, the branches corresponding to a certain generation are produced according to either of the two methods described above. In a second step, the branches produced are reacted onto a core, and a dendritic structure similar to the one described earlier is obtained. A schematic illustration of the convergent approach is shown in figure 4.

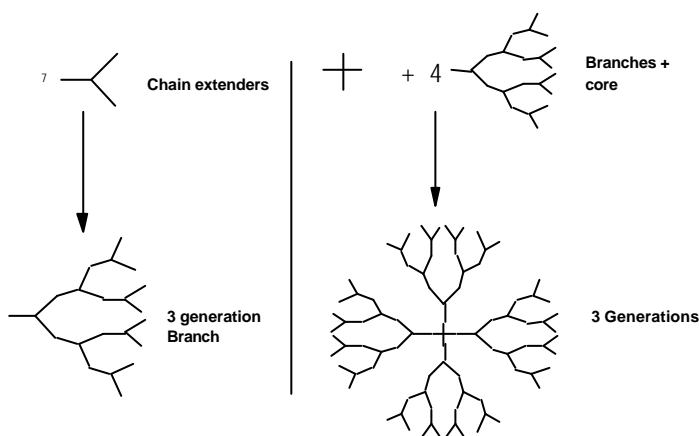


Figure 4: Dendritic growth through the convergent approach

3. Perstorp technology

The hyperbranched polymers developed by Perstorp are aliphatic hyperbranched polyesters with hydroxyl groups at the peripheral surfaces. They are polydisperse polymers, i.e. no protection groups are used to control dendritic growth. Hyperbranched growth is instead controlled by stoichiometric ratios of core-to-chain extenders and carefully chosen processing conditions to avoid side reactions. Perstorp Hyperbranched Polyesters resemble dendrimers in that they consist of a core, from which branches extend, giving a core/shell structure with hydroxyl functional surface (see figure 5 below).

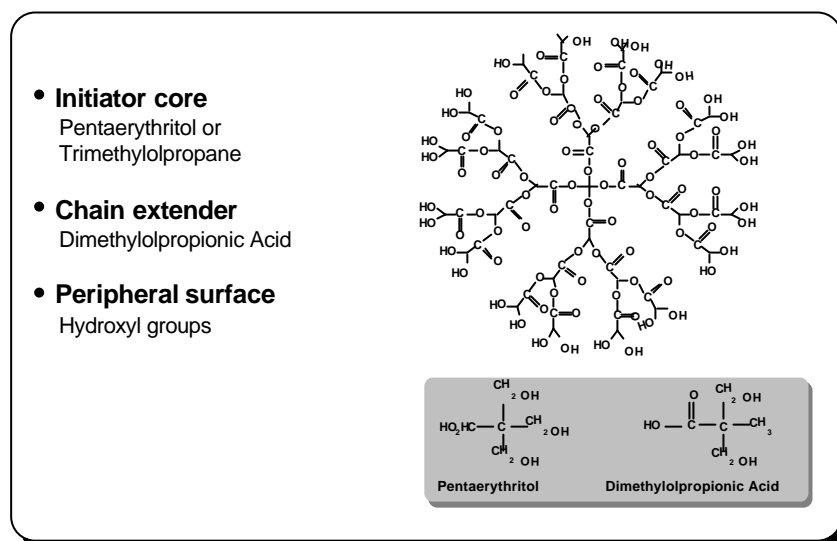


Figure 5: Perstorp technology

The core consists of a polyalcohol, such as Trimethylolpropane (TMP), Pentaerythritol (PE) or derivatives thereof. The type of polyol core used governs the number of branches that will extend from it.

The hyperbranched structure is built from 2,2-Dimethylol propionic acid (Bis-MPA), which has the unique functionality of one COOH-group and two OH-groups.

The shell consists of a large number of OH-groups, where the functionality depends on type of core used and the number of generations.

3.1. Polymer composition

Perstorp Hyperbranched Polymers are primarily produced according to a divergent approach (discussed in section 2.2.1), but also through a convergent approach (section 2.2.3). They are polydisperse as a result of direct esterification of Bis-MPA with a polyol core, or a hyperbranched polymer of a certain generation. The resulting polymer will have a main core/shell fraction and a minor fraction consisting of COOH-functional branches.

The reasons why a core/shell structure is achieved (and not only branches) are illustrated in figure 6 below.

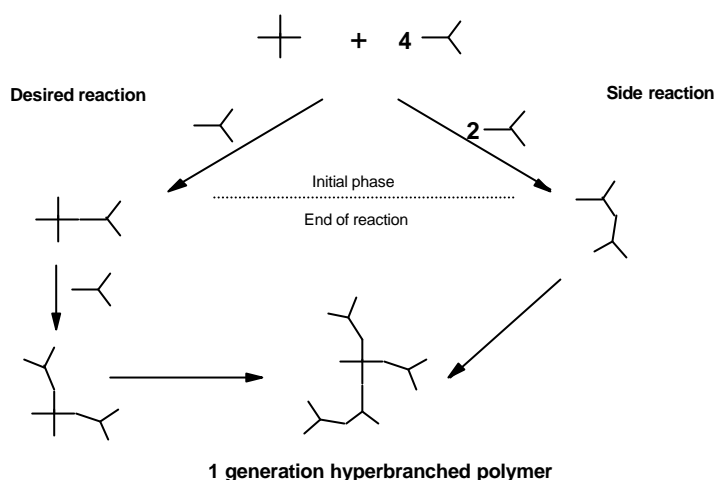


Figure 6: Schematic illustration of hyperbranched growth

When equivalent amounts of core hydroxyl groups and Bis-MPA are mixed and reaction is initiated, two predominant reactions take place:

- Reaction of Bis-MPA with the core (desired reaction)
- Self-condensation of Bis-MPA

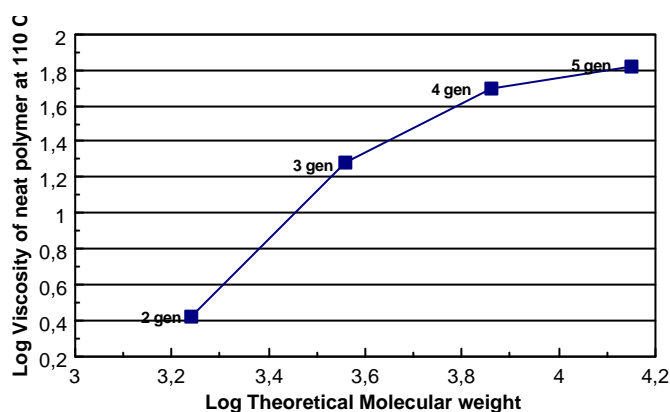
As the reaction starts, it is statistically more probable for two Bis-MPA molecules to react with each other than for a Bis-MPA and a core to react. However, this is in reality not fully true. It is believed that reaction kinetics between a core and Bis-MPA are favored as opposed to self-condensation of Bis-MPA^{ref}. Further, as also shown in fig. 6, even with a statistical approach it is possible to achieve a core/shell structure by pressing the reaction far enough so COOH-functional branches will react onto a core structure. A third observation⁵ shows that core/shell growth is favored by solubility phenomena, where the Bis-MPA is not fully soluble in the polyol core and has the same effect as a continuous feed of small amounts of Bis-MPA on the reaction solution. The resulting polymer will have a main fraction with a core/shell structure and a minor fraction with free branches. The residual acid value in the polymer will originate mainly from these branches.

4. Structure/property relations

This section illuminates the properties of the hyperbranched polyesters presented here and shows how molecular design can be applied to adjust several properties simultaneously. Hence, it might be possible to affect certain properties without impeding others. Examples of properties are given in resin applications to illustrate the versatility of these polymers and the different properties they can give, depending on molecular design.

4.1. Physical properties

Non-linear behavior between viscosity and molecular weight is seen for a neat hyperbranched polyester with a four-functional core and a hydroxy-functional surface as illustrated below.



Graph 1: Viscosity vs. molecular weight of hyperbranched polyester

The graph shows that viscosities of the hyperbranched polyester do not increase linearly as would be expected in a conventional polyester. It will later be shown that such favorable viscosity effects can be obtained in coatings also.

4.2. Reactivities

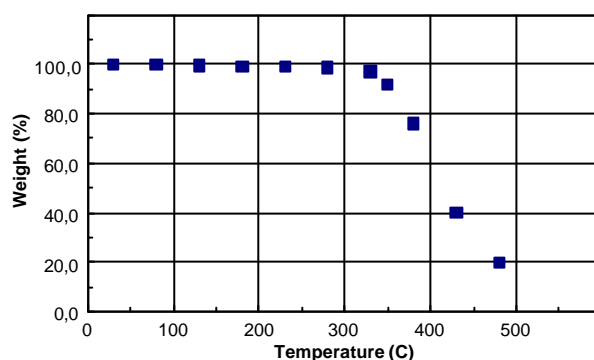
The very structure of hyperbranched polymers indicates that they are likely to be highly reactive. The large number of reactive groups will, upon reaction, rapidly form a network to give a fast cure. This behavior is also seen in the polyesters presented here. It is believed that the rapid cure also contributes to the reactive groups being predominantly at the surface which, in combination with the dense structure, makes them less prone to entanglement and hence more readily accessible for reaction. Further, a narrow polydispersity of the hyperbranched polyester will, upon curing, contribute to a more rapid increase in molecular weight, as high molecular fractions mainly react with each other. Reactivities are, of course, highly dependent on how the molecular surface is adapted for a certain system.

4.3. Chemical resistance

The hyperbranched polyesters presented here are fully aliphatic with tertiary ester bonds. Further, all interior ester links are shielded by the dense tree-structure. It is therefore suggested that a better hydrolytic stability and an improved chemical resistance is obtained compared to a conventional polyester. Initial outdoor durability tests of hyperbranched alkyds have also shown that this is the case.

4.4. Thermal properties

The neat hyperbranched polyesters are amorphous solids at room temperature. They have T_g in the range of 40–45°C with a slight increase in later generations. Melting starts at 70°C and ends at approx. 100°C. The hyperbranched polyesters presented here have good thermal resistance and start to deteriorate at temperatures above 350°C. The thermal resistance is illustrated in graph 2 below.



Graph 2: TGA measurement of a hyperbranched polyester based on a 3-functional core and Bis-MPA

Further, thermo-mechanical properties depend on the shell chemistry. Glass transition temperatures are highly dependent on hydrogen bonds of the surface's hydroxyl groups and decrease dramatically by incorporating aliphatic groups. It is thus possible to go from solid to liquid by simply end-capping the surface with aliphatic groups. Further, the length of the end-capping group will govern the viscosity and glass transition temperature.

4.5. Mechanical properties

The hyperbranched polyesters presented here have been found to contribute to mechanical properties. Epoxy-functional hyperbranched polyesters have been produced and characterized with regard to mechanical properties. Used as additives in conventional epoxy resins, they have been found to give enhanced flexibility and/or dramatically increased toughening without affecting other properties, such as hardness/modulus. Different effects are seen, depending on the type of shell chemistry adapted. Glass transition temperatures can also be affected by proper molecular design. Examples of mechanical properties will be shown in subsequent sections.

It is believed that the mechanical properties observed are not only valid for epoxy resins, but can be applied to other thermosets as well.

4.6. Molecular Design

It has been mentioned several times in the above sections that properties can be affected in various ways, depending on how the shell chemistry is adapted. These chemical adjustments are here referred to as molecular design. The hyperbranched polyesters presented here should be regarded as core/shell polymers with an essentially inert interior and a reactive surface with a larger number of reactive sites. The hyperbranched interior structure basically has a carrier function and the surface determines the final properties, chemical as well as physical. This is, of course, a simplified approach and not fully correct, as properties also can be affected by changing either the core or the hyperbranched structure itself. However, it is an approach that can be utilized to help understand what molecular design is and how it can be applied.

The hyperbranched polyesters presented here have a larger number of reactive hydroxyl groups. One consequence of large number of reactive groups, discussed in section 4.2. and later section 5, is that high reactivities may be achieved. Hence, all reactive sites may not be required to give suitable curing properties, making it possible to use a fraction of the functional surface to incorporate reactive groups. The remaining sites may then be used to control other properties, such as polarities or viscosities. A hyperbranched polymer can thus be designed specifically for a certain application to give multi-property control.

Apart from design, a core/shell system has other consequences. The type of group incorporated on the surface not only governs the design possibilities, but the end use as well. Different types of reactive groups give very different properties. Various design possibilities and end uses are illustrated in figure 6 below.

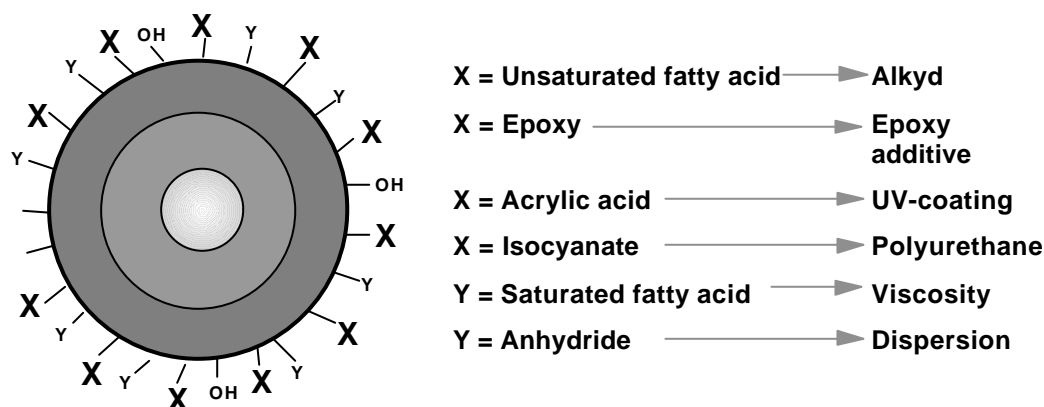


Figure 6: Molecular design of a hyperbranched polymer

5. Applications

Hyperbranched polyesters of the type presented here have been studied in several applications. The purpose has been to evaluate what effects hyperbranched structures have in different applications and how molecular design can be adapted to give enhanced properties. Both coatings and engineering applications have been studied.

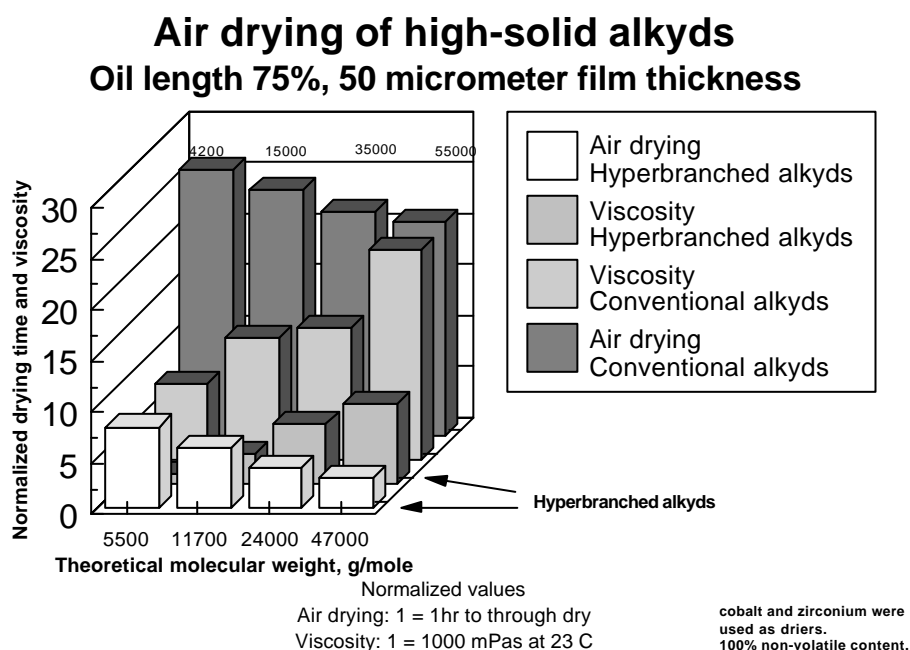
In section 4, structure/property relations were illuminated and examples of some properties of hyperbranched polymers were mentioned. All properties mentioned have been observed in different applications. This section will therefore show some of the results obtained in studies of hyperbranched polyesters in alkyds, radcure, PUR and epoxies.

5.1. High-Solid Alkyds

Hyperbranched alkyds of different generations have been produced from hyperbranched polyesters and tall oil fatty acids. All hyperbranched alkyds were formulated to 75 % oil length, acid values of 10 mg KOH/g and OH values of 7 mg KOH/g. These were then compared with conventional alkyds based on Pentaerythritol, Di-Pentaerythritol, Phthalic anhydride and tall oil fatty acid of similar molecular weights, oil length, acid and OH values. Comparisons were made with regard to:

- Viscosities of solvent-free resins at 23°C
- Through-dry of films with 50 micrometer film thickness as dry film

After recording viscosities, clear coats were formulated with 0.25 wt % Zr and 0.03 wt% Co. Through-dry was thereafter recorded by the thumb test, where 1500 g thumb pressure is applied on the film, followed by a 90 degree twist. Films are regarded as through-dry when no marks remain on the film. The results are shown in graph 2 below.



Graph 2: Air drying of high-solid alkyds

The results shown in graph 2 can be summarized as follows:

- Significantly lower viscosities were obtained with hyperbranched alkyds compared to conventional types. Non-linear behavior of viscosity versus molecular weight is seen in alkyds based on hyperbranched polyesters and agrees with what has previously been reported for both neat hyperbranched polymers and dendrimers.
- Hyperbranched alkyds dried amazingly fast and showed that high reactivities of the hyperbranched polyesters presented here can be obtained.

An initial study on hyperbranched alkyd emulsions has also been made, showing that it was possible to combine good drying with low emulsifier content. The alkyds emulsified were of a similar type to those described above and were not specifically designed for emulsions. There should thus be a possibility for further improvement, e.g. by increasing the hydroxyl number or by incorporating COOH groups on the polymer surface to render more polar hyperbranched alkyds.

Further, initial results on outdoor durability of the above systems indicate that enhanced durability properties are achieved with hyperbranched alkyds compared to conventional high-solid alkyds.

5.2. Hyperbranched epoxies

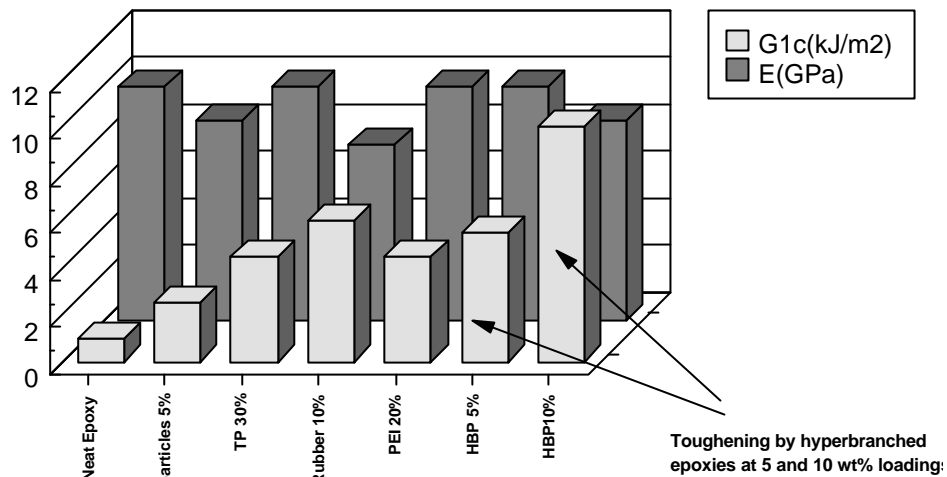
Studies of epoxy-functional hyperbranched polyesters have been performed where the effects of molecular design versus mechanical properties have been investigated. Although hyperbranched epoxies are specially designed for engineering applications, they are included in this paper as it is believed that the properties observed can be applied to coatings as well.

A unique technology has been developed and patented, where hyperbranched epoxies used as additives can act as tougheners without imparting other mechanical properties.

The hyperbranched toughener is designed in such manner as to have proper polarity and reactivity in a conventional epoxy resin. Hence, drastically improved toughening of epoxy resins is achieved through *controlled-phase separation*. Curing proceeds through the following steps:

- Initially, hyperbranched epoxy, conventional epoxy and hardener form a homogenous solution.
- As curing proceeds, resin polarity changes due to formation of OH-groups. Hyperbranched tougheners then start to agglomerate due to lower polarity and reactivity and at a certain point, nucleation occurs.
- Growth of the secondary phase containing hyperbranched toughener thereafter proceeds until the gel point is reached.

If the hyperbranched toughener is properly designed and curing conditions are carefully chosen, a drastic increase in the toughness of the resulting resin can be obtained at low addition levels of hyperbranched toughener. This effect is illustrated in graph 3 below, where a 3-generation hyperbranched epoxy is added to a Ciba Geigy epoxy/hardener system intended for marine and sports applications.



Graph 3: Toughening of epoxy by hyperbranched epoxies

The above results can be summarized as follows:

- Neat resin had a tensile modulus of 3.0 GPa and a fracture energy (G_{1C}) of 110 J/m². Further, a glass transitions temperature of 104°C was recorded
- When adding 5 wt% of hyperbranched epoxy, a drastic increase in toughness was obtained. Toughness, expressed as fracture energy, G_{1C} , increased from 110 to 630 J/m² with hyperbranched modified compared to neat resin. Other mechanical properties such as tensile modulus and glass transition temperature were unaffected by the presence of hyperbranched epoxy.
- Above graph also shows a comparison of toughening performance between hyperbranched epoxies and commercial tougheners of different types. It is seen from the graph that the hyperbranched epoxies clearly outperforms the other types when comparing high fracture energy with high modulus and low loading.
- What is not showed in the above graph is the effect on viscosities of uncured systems. Other types of tougheners, such as rubber particles, give negative effects on resin viscosities, whereas the hyperbranched tougheners virtually not at all affect resin viscosities.

The above results illustrate that specific properties can be achieved by proper molecular design. It is probably also possible to apply the toughener concept to coatings, where similar effects might be obtained. A phase-separated system could be used in coating applications in which opacity is acceptable. If this is not the case, studies of homogenous epoxy systems have also shown toughening and flexibilizing effects, although not as pronounced as those mentioned above.

Hyperbranched polymers as additives to improve mechanical properties should be of interest, e.g. in automotive application where demands on mechanical performance are pronounced.

5.3. Polyurethane dispersions

An initial study has been made where a hyperbranched polyurethane (PUR) dispersion was produced and evaluated. The dispersion was produced in three steps:

- **Step 1** - A 2-generation hyperbranched polyester of the type presented here was partially end-capped with a short saturated fatty acid (C3) to adjust the hydroxyl value to app. 150 mg KOH/g.
- **Step 2** - The product obtained in step 1 was reacted with isophoron diisocyanate (IPDI) in a molar ratio of 5:6 with regard to moles of IPDI and moles of hyperbranched polymer produced according to step 1. Small amounts of Bis-MPA were also added to incorporate carboxylic acid groups.
- **Step 3** - The product obtained in step 2 was neutralized with an amine and dispersed in water.

The resulting PUR dispersion had a viscosity of 16000 mPas and a non-volatile content of 40 %. A cross-linked system was obtained with five theoretically hyperbranched molecules connected by IPDI. Below is a schematic illustration of what the polyurethane dispersion might look like.

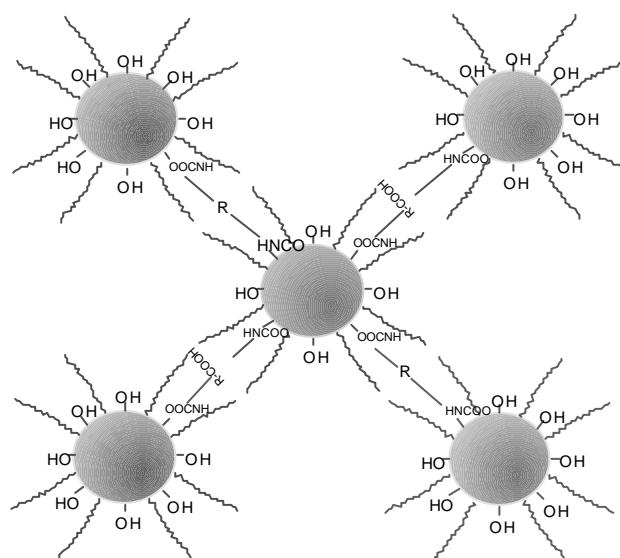
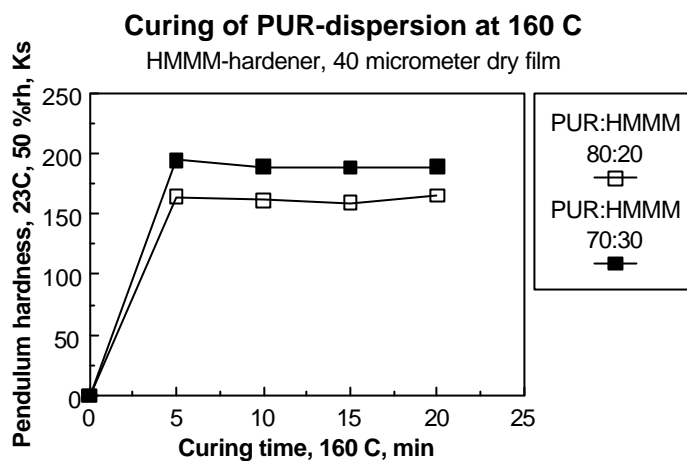


Figure 8: Schematic illustration of hyperbranched PUR dispersion

The above PUR dispersion was then evaluated in a clear coat by curing it with an HMMM resin at 160°C. Film hardness, impact, flexibility, cross-cut and acid etch were thereafter evaluated on the cured films. The results from these test are shown in table 1 and graph 4 below.



Graph 4: Curing behavior of hyperbranched PUR: HMMM clearcoats at 160 C

The above films, with ratios of PUR-dispersion to HMMM resin of 80:20 and 70:30, were then compared with regard to cross-cut and pencil hardness. Results from these tests are shown in table 1 below.

Ratio PUR:HMMM (as solids)	80:20	70:30
Pendulum hardness, Ks	158	194
Curing time, min	5	5
Curing temperature, °C	160	160
Pencil hardness	4H	6H
Cross-cut (0=good adhesion, 5=poor adhesion)	0	0
Film thickness, micometers	30	30

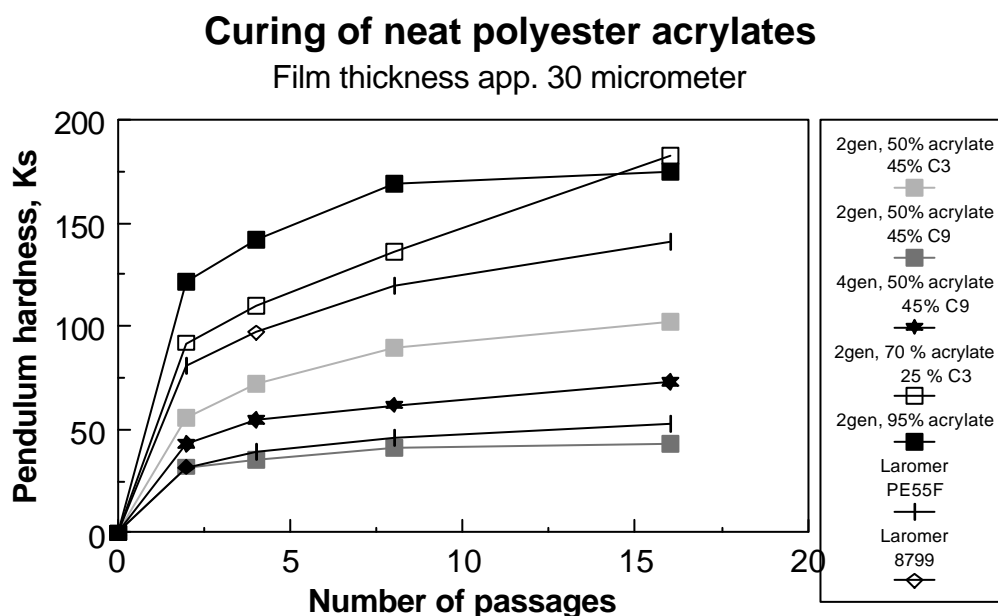
Table 1: Properties of cured PUR dispersion at different cross-linking densities.

The above results can be summarized as follows:

- It is possible to design hyperbranched polymers and produce cross-linked PUR dispersions without gel problems.
- The obtained dispersions gave hard films when cured with HMMM resin at 160 C, 5 minutes.
- In this study, optimal properties with regard to hardness and scratch resistance were obtained at a ratio of 70:30 between hyperbranched PUR dispersion:HMMM resin

5.4. Hyperbranched acrylates

An initial study has also been performed in which acrylate functionality was introduced onto the hyperbranched polymer shell. In this study, the effects of functionality and polarity were investigated with regard to reactivities. Acrylate functionality was varied from 25 to 95 % of accessible OH-groups onto a hyperbranched polymer shell, where the remaining groups would be either propionate esters, C9 esters or hydroxyls. These neat hyperbranched acrylates were then compared with commercial polyester acrylates of different grades. All polyester acrylates were applied on glass and steel plates and cured in a Wallace Knight UV-curing labunit (80W/cm, 20 m/min). Film hardness, Erichsen flexibility and mandrel test were thereafter determined for both the neat hyperbranched acrylates and the commercial polyester acrylates. The in the study obtained results are shown in graph 5 and table 2 below.



Graph 5: UV-curing of neat hyperbranched acrylates

Acrylate type	HBP ¹	HBP ¹	HBP ¹	HBP ¹	HBP ¹	Laromer ² PE55F	Laromer ² 8799
Number of generations	2	2	2	2	4	-	-
Theoretical molecular weight, g/mole	2584	2578	2570	3180	13000	-	-
Tot. surface functionality, eq	16	16	16	16	64	-	-
Acrylate functionality	8	11.2	15.2	8	32	-	-
% of tot. surface	50	70	95	50	50	-	-
Type of fatty acid	C3	C3	-	C9	C9	-	-
Fatty acid funct., eq	7.2	4	-	7.2	28.8	-	-
% of tot. surface	45	25	-	45	45	-	-
Film hardness, 2 pass, Ks	56	92	122	32	43	32	81
Film hardness, 4 pass, Ks	62	110	142	35	55	39	97
Film hardness, 8 pass, Ks	90	136	169	41	62	46	120
Film hardness, 16 pass, Ks	102	183	175	43	73	53	141
Conical mandrel test, 8 pass, mm	<5	8	-	<5	<5	<5	8
Pencil hardness, 8 pass	5B	H	-	6B	6B	5B	F
Film thickness, micro meter	30	30	30	30	30	30	30

¹Hyperbranched polyester with 4 functional core

²BASF AG, Germany

Table 2 : Properties of UV-cured hyperbranched acrylates

The above results may be summarized as follows:

- Hard films with high reactivities can be achieved, provided the shell of the hyperbranched polymer is properly designed.
- Higher acrylate functionality combined with short non reactive fatty acid or no fatty acids at all, give laquers with high reactivities and high film hardness
- Softer films can either be obtained by lowering the functionality and/or partially end-capping with longer saturated fatty acids.
- A higher generation increases the film hardness
- Harder films were obtained with hyperbranched acrylates with high acrylate functionalities compared to the in the study included commercial polyester acrylates

The above performed study quite illustratively shows that a whole range of properties can be obtained from the same hyperbranched polymer by proper molecular design of the reactive surface. Thus properties such as reactivity and film hardness can be tuned to be in a certain range. As also shown in above study, it is possible to make further property adjustments by the use of a different generation

Furthermore, a pre-study of hyperbranched acrylates⁵ has shown that residual unsaturation in cured films as measured by Raman IR is virtually zero, in spite the large number of reactive groups. Hence it is believed that reactive groups at the peripheral surface of a hyperbranched polymer are readily accessible. The pre-study further indicates that cured hyperbranched acrylates shrink less than conventional polyester acrylates. Shrinking was reported to be in the magnitude of 50 % less than with conventional acrylates.

6. Conclusions

This paper has shown the technological feasibility of modifying hyperbranched polyesters to achieve enhanced physical as well as chemical and mechanical properties. Moreover, it has been shown that they can be tailored and further designed to affect several properties simultaneously.

The benefits of the hyperbranched polyesters presented above are illustrated in *alkyds*, where they contribute to low viscosities combined with excellent drying; in *polyurethanes* and *radcure*, where rapid curing can be obtained by proper molecular design ; and in *amine-cured epoxies*, where a hyperbranched epoxy demonstrates dramatically increased toughening without affecting other properties. Toughening effects, for example, are to be expected in a variety of coatings (epoxies, polyurethanes and others) as well as engineering plastics.

The technologically and commercially promising results Perstorp has obtained with hyperbranched polyesters should be seen as clear trends which may be valid for many other applications, where similar effects might be achieved. For instance, low viscosities are not only seen in alkyds, but in epoxies and other resins as well. Viewed in combination with other properties, such as enhanced mechanical properties and reactivities, hyperbranched polyesters may be regarded as versatile tools for multi-property control.

The technology of hyperbranched polymers is still new and largely unexplored. Numerous parameters affect physical as well as mechanical and chemical properties. Today we are beginning to understand some of the possibilities of this unique type of polymer, and are starting to build our bank of knowledge of how molecular design matches technical performance in a number of applications. Given the number of combinations and applications to be explored, the field seems virtually unlimited.

Since most of our scientific endeavours must ultimately win support of interest willing to finance them, it is particularly encouraging to know that hyperbranched polymers are showing signs of significant commercial potential. Knowledge, skill and creativity are the winning ingredients in the

recipe for a bright future for hyperbranched technology. Those who meet the challenge are likely to be highly rewarded in the form of tailor-made products which conform to multi-property specifications, and thus offer outstanding competitive advantages.

7. Acknowledgments

The author would like to thank Dr. Louis Boogh and Prof. Jan-Anders Månson of Ecole Polytechnique Federale de Lausanne (EPFL) for excellent scientific support in defining and optimizing mechanical properties. Dr. Mats Johansson, Eva Malmström and Prof. Anders Hult of the Royal Institute of Technology (KTH) are also acknowledged for a profound work with characterisation and understanding of hyperbranched polymer structures etc.

8. References

1. Newkome, G.R., et al, Aldr. Chim. Acta, 25, No.2, 31-37, 1992
2. Hawker, C.J., Freché, J.M.J., J. Am. Chem. Soc., 112, 7638-7647, 1990
3. Mourey, T.H., Turner, S.R., Robinstein, M., Freché, J.M.J, Hawker, C.J., Wooley, K.L., Macromolecules, 25, 2401-2406, 1992
4. Johansson, M., Malmström, E., Hult, A., Journ. Pol. Sci., 31, 619-624
5. Johansson, M., Malmström, E., Hult, A., Unpublished results, 1994-1995