# Hyperbranched Polyesteramides for Imaging Applications

***Anindya Mukherjee and Peter E. Froehling***
***DSM New Business Development / DSM Research***
***Saddle Brook, New Jersey, USA / Geleen, the Netherlands***

## Abstract

Hyperbranched polymer are highly branched molecules with properties which are very different from conventional linear polymers. A compact, flexible shape and a large number of reactive end groups lead to special rheological and interfacial behavior. Structure and properties of DSM's HYBRANE hyperbranched polyesteramides can be tailored for many applications in the imaging area, as is illustrated by a number of examples.

## Introduction: Polymer Architectures

Polymers play a role in many phases and components of printing processes. Virtually all types of inks and toners contain a number of polymeric components, which can act as rheology (viscosity) control agent, binder, pigment dispersant or film former. Also in the production or modification of printing substrates (e.g. paper), polymers can contribute significantly to the properties of the material, such as printability or drying speed.

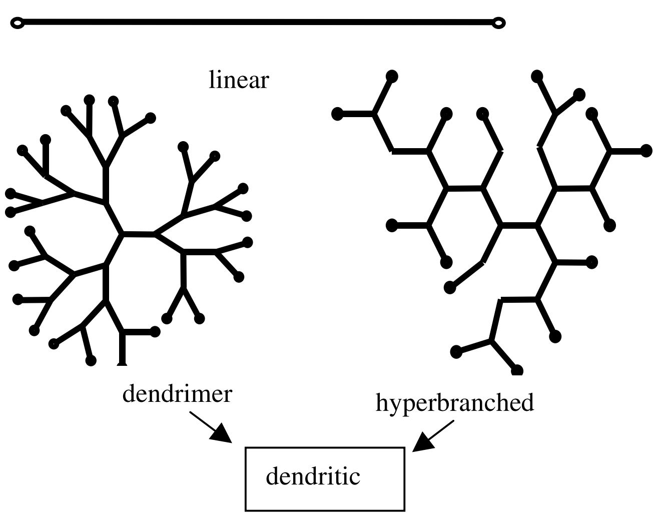



*Figure 1. Polymer architectures*

Most synthetic and naturally occurring polymer molecules have a simple linear structure. They consist of a covalently linked chain of repeating monomer building blocks, with one end group at each end of the chain. These two end groups rarely play a part in the properties of the polymeric material. However, polymer chemistry has created a number of non-linear variations on this simple structure over the past twenty years. These variations are commonly denoted as "macromolecular architectures". One of these new architectures arises from the introduction of a large number of branches during the synthesis of the polymer, which leads to a molecule with many end groups.

Two classes of highly branched polymers (or "dendritic" polymers, from "dendron", the Greek word for tree) are represented in *Fig. 1*: dendrimers, with a perfectly branched uniform structure, and hyperbranched polymers, where the (still very high) degree of branching is more randomly occurring. In this paper we will first introduce the chemistry and properties of DSM's HYBRANE™ hyperbranched polyesteramide resins, followed by discussion of a number of possible applications of these polymers for imaging-related applications.

## General Properties of Dendritic Polymers

Characteristic for dendritic polymers is the presence of a large number of end groups, which often are reactive, and many branching points. Many of the properties of dendritic polymers are closely related to the nature of the end groups. Thus it is possible to tailor properties such as solubility, compatibility or surface activity by appropriate chemical modification of the end groups. The large number of branches leads to a very compact spherical shape of the molecule, which contrasts with the highly flexible random chain of linear polymers. This compact shape has important implications for the rheological behavior of dendritic polymers both in bulk and in solution. Due to the reduced intermolecular interactions compared to linear polymers, melt and solution viscosities of dendritic polymers are generally low. At interfaces, the spherical shape generally will flatten out due to interactions with e.g. solid substrates as e.g. paper or pigments.

Finally, by making use of specific interactions, guest molecules such as dyes can be absorbed into the interior of the molecule.

## HYBRANE™ Polyesteramides[1,2]

Hyperbranched polyesters are generally prepared by an $AB_2$ polycondensation reaction, starting from a monomer with e.g. one carboxylic (COOH) and two hydroxy (OH) groups. DSM's development of the HYBRANE™ polyesteramides is also based on this principle (*Fig.2*). The $AB_2$ monomer is prepared by reaction of a cyclic anhydride with diisopropanol amine, after which the reaction product is converted into the hyperbranched polymer. This polycondensation is carried out without a catalyst at relatively low temperatures, and is now succesfully produced on mulit-ton scale.

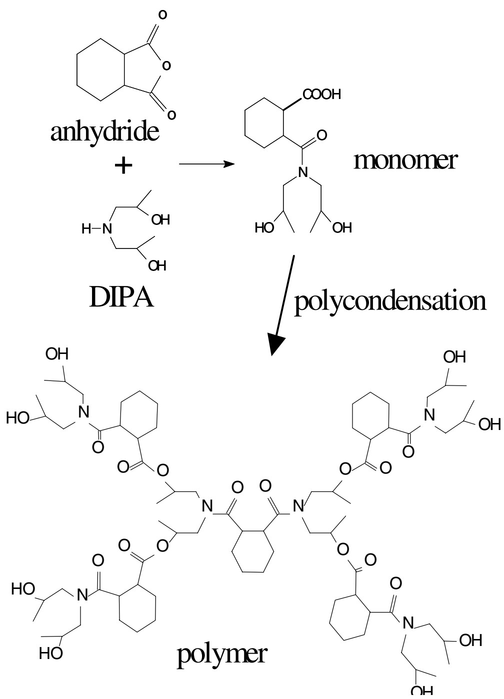
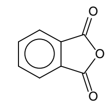
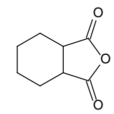
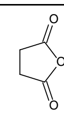
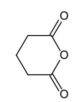



*Figure 2. Two-step route to HYBRANE hyperbranched polymers*

The two-step route makes it possible to vary the structure of the anhydride building block (or even to use mixtures of anhydrides) in order to tailor the properties of the final polymer. An example of the effect of anhydrides on the glass transition temperature of the polymer is given in Table 1. Details of the chemistry can be found in the literature.[1,2]

A second way to control the properties of the HYBRANE™ polymer is by modfication of the end groups. In a standard polymerization a polymer with only hydroxy end groups is produced. These groups can e.g. be esterified by fatty acids, introducing hydrophobic entities into the molecule which improves the solublity in e.g. aliphatic or aromatic hydrocarbons. By partial modification, an amphiphilic molecule is obtained which possess surface activity. Other end groups, e.g. tertiary amines, carboxylic groups or polyethylene oxide chains, each again leading to specific properties, can be introduced in different ways.

**Table 1. Glass transition temperature ($T_g$) of HYBRANE polymers as a function of the anhydride building block.**

| cyclic anhydride | | $T_g$ (°C) |
|---|---|---|
| phthalic |  | 95 |
| hexahydrophtalic |  | 70 |
| succinic |  | 41 |
| glutaric |  | 19 |

The large scala of possible end groups and combinations of end groups within one molecule, combined with the use of different cyclic anhydride building blocks, enables us to vary the properties of the polymer into many directions for many types of applications.[3]

## Some Imaging-Related Applications of HYBRANE

The low viscosity and high drying speed of hyperbranched polymers make them interesting for application in ink jet printing. By an appropriate choice of building blocks and end groups properties such as solubility, substrate wetting / adhesion and water fastness all can be tailored. This of course also applies to many other solvent-based printing technologies.

Another important aspect is the tailoring of surface interactions of hyperbranched polyesteramides. By choosing the right combination of apolar and polar groups the surface and interfacial properties of the polymer can be varied at will. HYBRANE™-based amphiphilic molecules can e.g. be used as pigment dispersants in a variety of solvents by balancing the differences in polarity between the pigment surface and the solvent **(Fig. 3)**. It should therefore also be possible to develop water-borne pigmented inks by using the appropriate building blocks and end groups.

A very different type of application is in the toner area. Because of the possibility to control rheological and thermal behavior, film formation and interfacial properties simultaneously, hyperbranched polyesteramides are good candidates for use as binder resins, pigment dispersants or wax additives in toner systems.

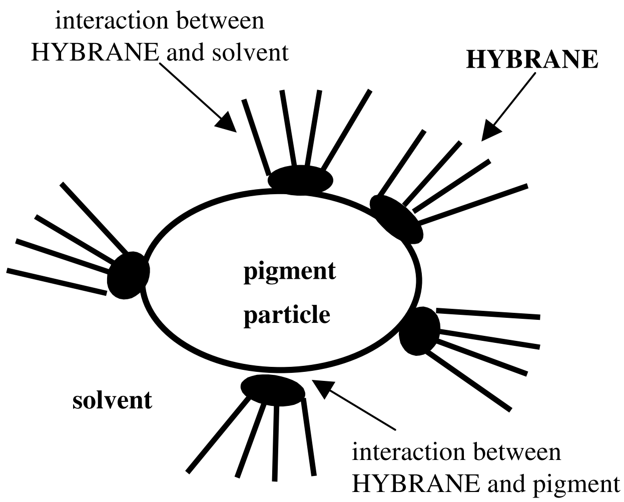



*Figure 3. Modified HYBRANE as pigment dispersant.*

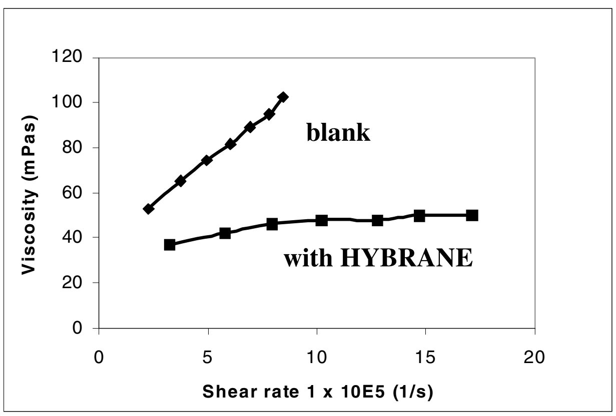



*Figure 4. Effect of HYBRANE on rheological behavior of a high-solids paper coating.*

Finally we have achieved a breakthrough in the formulation of paper coatings for e.g. offset and inkjet papers by means of water soluble HYBRANE™ polymers. Addition of small quantities of HYBRANE™ to high-solids coating dispersions (based on e.g. calcium carbonate and latex binders) does not only lead to a drastic improvement of the rheological behavior of those dispersions (lower and les shear-dependent viscosity), but also improves the printability of the coated paper. It is again a combination of low viscosity, film formation and controlled surface properties which has lead to this development.

## Conclusions

HYBRANE™ hyperbranched polyesteramides can be prepared in a straightforward polycondensation reaction, which is scaled up to industrial size without problems. The versatility of the chemistry allows the production of a wide variety of structures and a close control and fine-tuning of many properties such as solubility and compatibility, rheological, thermal and interfacial behavior. All of these are of relevance in printing-related applications such as ink-jet and other inks, toners and paper coatings.

## Acknowledgements

The close cooperation with the HYBRANE team at DSM, Geleen, the Netherlands is gratefully acknowledged.

## References

1. D. Muscat, R.A.T.M. van Benthem, *Topics in Current Chem.*, **212**, 41 (2001)
2. R.A.T.M. van Benthem *et al., Macromolecules*, **34**, 3559 (2001)
3. P.E. Froehling, *Dyes and Pigments*, **48,** 187 (2001)

## Biography

Anindya Mukherjee has an MS in Polymer Science from The University of Akron, Akron, Ohio and an MBA from Vanderbilt University, Nashville, Tennessee. Since 1989 Anindya has worked in the thermoplastic compounding industry, developing and leading the development of materials based on polyamides, polyolefins, polyesters and thermoplastic elastomers. Most recently he has been involved in business development in the area of functional chemicals and polymers with potential in several markets including the imaging sciences area.