Development of DSM's Hybrane® Hyperbranched Polyesteramides

PEER FROEHLING
R&D Department, DSM Hybrane BV, PO Box 18, Geleen 6160 MD, the Netherlands

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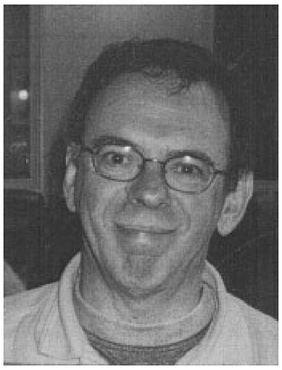
ABSTRACT: The development of DSM's Hybrane® hyperbranched poly(ester amides) is described. The monomer (1) for the hyperbranched polyester is obtained from the reaction of a cyclic anhydride with diisopropanol amine, yielding a tertiairy amide with one COOH and two OH groups. Polycondensation takes place via an oxazolinium intermediate in bulk at relatively mild conditions in the absence of catalyst. The reaction has been scaled up to ton scale. By varying and combining anhydrides, and modification with several types of end groups, a large variety of structures with concomitant properties and industrial applications has been realized. J Polym Sci Part A: Polym Chem 42: 3110–3115, 2004

Keywords: hyperbranched; dendrimers; polycondensation; polyesters



PEER FROEHLING

Peter E. ("Peer") Froehling, born 1949, works as Application Development Manager for DSM Hybrane, a startup daughter company of DSM Venturing and Business Development. He studied chemistry at the Technical University of Eindhoven, and obtained a Ph.D. in biomedical materials science at the University of Twente. In 1977, he joined DSM's research laboratories in Geleen, the Netherlands, where he has been involved in a broad variety of polymer-related research activities such as thermosets, morphology, molecular imprinting, preceramic and conductive polymers, and (since 1995) application development of dendrimers and hyperbranched polymers. He is (co)author of about 35 scientific papers and 15 patent applications. His extracurricular interests include hiking (on relatively horizontal surfaces), opera, genealogy, and playing the viola.

Correspondence to: P. Froehling (E-mail: peer.froehling@dsm.com)

INTRODUCTION

Dendritic macromolecules (i.e., dendrimers and hyperbranched polymers) have already been the subject of many of these Highlights. Some earlier authors are Kim[1] (research activities at DuPont), Voit[2] (a broad overview of the chemistry of hyperbranched systems), and Tomalia and Fréchet[3] (history of dendrimers). In this Highlight, I want to show how the development of Hybrane® hyperbranched polyesteramides was first inspired by the success of our Astramol poly(propylene imine) dendrimers,[4] and how it evolved into the realization of a large variety of new structures and properties. This has ultimately led to a series of industrial applications that make use of the unique properties of dendritic structures such as the lack of entanglements, the large number of reactive end groups, and the possibility to interact with guest molecules.

FIRST STEPS AND BREAKTHROUGH

Within DSM, dendritic molecules had from the beginning a special attraction for researchers in the coating resins area. Their high functionality, combined with their low viscosity due to the absence of entanglements, should make dendrimers or dendrimer-like molecules a very useful new type of crosslinker in, for example, powder coatings. However, the production of dendrimers would always be relatively costly because of the required large number of consecutive steps needed either in convergent or divergent syntheses. In an application field that is largely cost-driven, the use of dendrimers seemed therefore prohibitively expensive, and an alternative in the form of hyperbranched macromolecules would be much more attractive. Therefore, the hunt for hyperbranched polymers was opened in 1994 by Ton Loontjens, then manager of DSM's coatings research department in Geleen. The practical development of hyperbranched polymers based on Flory's AB_2 concept[5] (Fig. 1) had started only a few years earlier. What still was missing, however, was an AB_2 monomer based on low-cost chemistry and technology, a *conditio sine qua non* for coatings applications.

Ton and his coworker Dirk Stanssens rapidly came up with a list of ideas for commercially attractive AB_2 chemistries. Dirk had already done fundamental work on β-hydoxyalkyl-amides,[6] a class of compounds that possesses a highly increased esterification rate with carboxylic acids whereby the formation of an oxazolinium intermediate has a key role (Fig. 2).

It seemed logical to use this type of reactant, already known in coatings chemistry, to make hyperbranched polyesters. Dirk's idea was to make an AB_2 monomer by the reaction between a cyclic (e.g., phthalic) anhydride and diethanolamine (DEA), which both are economically very attractive starting materials. The polycondensation of this product via an oxazolinium intermediate would then lead to a hyperbranched polyesteramide without the need of catalysts or high temperatures (Fig. 3). Moreover, for the intended coating resins application, it was necessary to have a solvent-free product, which logically led to the idea to conduct the monomer synthesis and the subsequent polymerization to a hyperbranched polymer in a one-pot solventless reaction system.

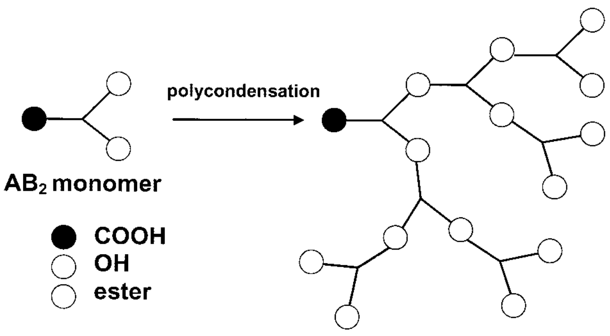


Figure 1. AB_2 polycondensation as described by Flory[5] leads to a hyperbranched macromolecule.

Unfortunately, the first experiments with phthalic anhydride and DEA only led to strongly discolored, partially crosslinked, or even gelled products, not at all what eventually might become an acceptable material for coating applications. Another problem was the inherent lack of molecular weight control in the AB_2 polymerization.

The breakthrough that made it eventually possible to develop an industrially viable route to hyperbranched poly(ester amides) came in 1996. It was accomplished by Rolf van Benthem, who had recently joined DSM's coating research team at Geleen. He found that the cause of the gelation was an undesired side product from the reaction of the OH group of the DEA instead of the amine group. The remaining secondary amine in the formed ester would not only lead to extensive discoloration, it could also react with the cyclic anhydride yielding a A_2B reactant that would rapidly lead to an undesired crosslinking of the whole system. Rolf first proposed to replace DEA by diisopropanolamine (DiPA), which through the diminished reactivity of its secondary hydroxyl group would suppress the side reaction in favor of the reaction of its amine with the anhydride (Fig. 3). Next, he also introduced the use of an excess of DiPA to control the molecular weight of the formed polymer. Another idea was to make modified polymers by esterification of the OH end groups by (partial) esterification with added monofunctional carboxylic acids. This gave an additional control of the molecular weight (typically

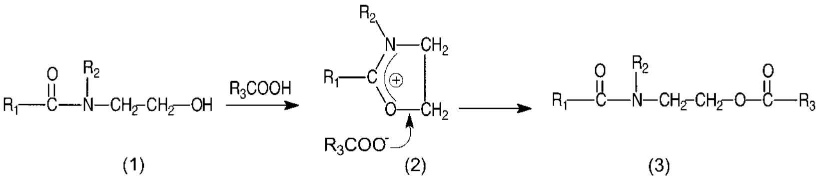


Figure 2. Reaction of a β-hydroxyalkylamide (1) with a carboxylic acid leads to esters (3) via an oxazolinium ion intermediate (2) without the use of catalysts, as discovered by Stanssens.[6] R_1, R_2, R_3 = alkyl or aryl.

in the range 1000–10,000), and also yielded products with an improved flow and (by using, e.g., oleic acid) air-drying properties for use in combination with alkyd resins. Soon it turned out that these modifications of the original concept indeed made it possible to have full control over the system, and to make reproducible products even at a much larger scale[7] (Fig. 4).

STRUCTURES AND PROPERTIES

Very soon we became aware of the fact that the chemistry described above could yield a much broader variety of products. Not only choosing different cyclic anhydrides or end groups, but especially also combining different elements in one molecule should lead to a virtually endless list of structures. This principle would give us the possibility to fine-tune the product's properties toward all kinds of applications, certainly also outside the coating resins area.

One of the properties we could control by choosing the appropriate combination of anhydrides and end groups was solubility. Initially, we found that most hydroxy-terminated base resins were soluble in a large variety of solvents, with water and hydrocarbons as notable exceptions on the edges of the polarity spectrum. Only resins made with succinic anhydride turned out to be water soluble (Fig. 5).

Next, it was found that succinic-based resins could tolerate reasonable amounts of other anhydride building blocks or end groups such as acetate, benzoate, or even fatty acid esters, and still remain soluble in water. Hydrocarbon solubility could easily be achieved by esterification with larger amounts of fatty acids. Another possibility was the use of alkenylsuccinic anhydride building blocks, which puts hydrocarbon chains in the molecule's core, leaving the end groups free for other modifying entities. These different approaches proved that is was possible to fine-tune the properties of the resins, which should open the way to a broad area of applications.

A different type of end group modification was introduced by replacing part of the DiPA reactant by other secondary amines.[8] This made it possible, for example, to introduce tertiary amine end groups leading to cationic water-soluble resins. Carboxylic-terminated polymers were also made, thanks to a clever change in the stoichiometry.[9] Another type of end group modification was realized by Dirk Muscat, who coupled monofunctional alcohols and, for example, poly(ethylene glycol) to the hyperbranched core, which further extended the spectrum of attainable structures and properties.[10]

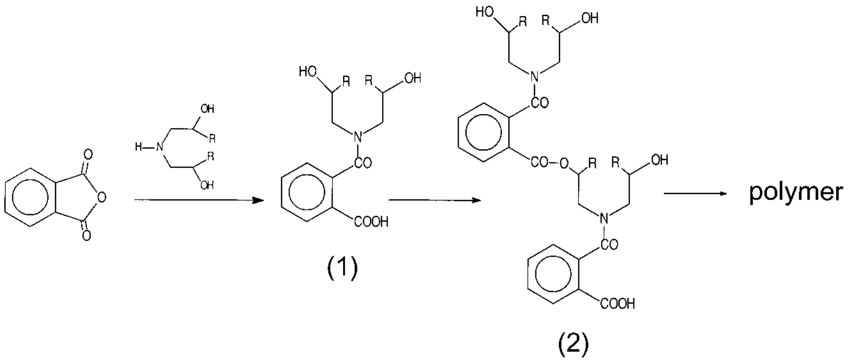


Figure 3. First reaction steps to a Hybrane® hyperbranched poly(ester amide): reaction of a cyclic anhydride (here phthalic anhydride) with a dialkanolamine leads to an AB_2 monomer (1), which subsequently polymerizes to a hyperbranched structure. When R = H (diethanol amine), side reactions lead to crosslinking; when R = CH_3 (diisopropanol amine), the side reaction is suppressed.

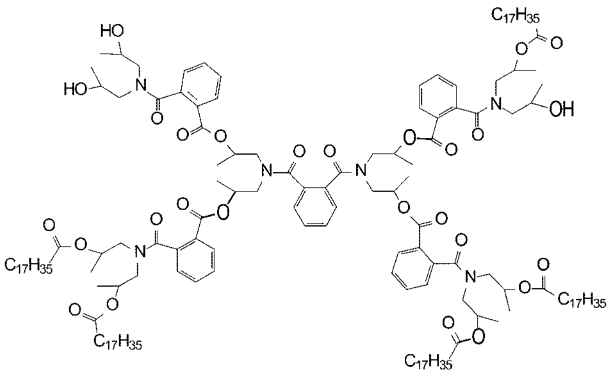


Figure 4. A typical structure of a Hybrane® macromolecule, built up from phthalic anhydride and an excess of diisopropanol amine; the OH end groups are partly esterified with stearic acid. This product is being tested for plastics additives applications.

While all these application-oriented activities were continuing, a more fundamental project was set up to give more insight in size, shape, and composition of the structures that we were making. Size exclusion chromatography, mass spectrometric techniques (matrix-assisted laser desorption/ionization time-of-flight and electrospray/mass spectrometry), and small-angle neutron scattering were all put to work to characterize a series of products made under carefully controlled conditions. Combined with the application of mathematical models, the results of the analytical work confirmed that the ideas of the chemists indeed gave full control over the structures as described above. We published the work in the form of two extensive articles,[11,12] which unexpectedly also yielded us the annual DSM Publication Award (Fig. 6).

TO THE MARKET

From the previous paragraph, one can conclude that already in an early stage we had been thinking of applications outside of the coatings area. This took a more solid form by transfer of the noncoatings part of the project in 1999 to DSM Venturing and Business Development.[13] Dirk Stanssens, who was already responsible for the commercialization of the DSM dendrimers, became business manager for hyperbranched polymers, whereas I got the task to match potential applications with the many types of structures and properties that could be realized. The newborn baby had to be given a name, which became "HYBRANE," derived from "highly branched."

In developing commercially viable applications, we have subsequently been working in close cooperation with very diverse industries, and I will give a number of examples of applications in which Hybrane® has proven successful thanks to the efforts of many people both inside and outside DSM.

Dyeable Poly(propylene) (PP) Fibers

PP is a very attractive fiber material both in price and properties, and only the lack of dyeability (caused by the polymer's extreme apolarity) has always prevented the use of PP fibers in large parts of the textile world. The idea to incorporate a dye-binding polymeric additive to PP dates back to the 1960s, and using either dendrimers or hyperbranched polymers for this purpose should in our view give a new impulse to the development of a dyeable PP fiber. Because of their compact structure, it was expected that the addition of small quantities of dendritic polymers would hardly influence the fiber's mechanical properties. The presence of a large number of polar groups inside the molecule, the chemical nature of which could be chosen more or less at will, would create an ideal receptor site for all sorts of dye molecules. Finally, the outside of dendrimers or hyperbranched molecules could be modified by reacting the end groups with long-chain fatty acids, thus making the additive highly compatible with the PP matrix.

Together with several textile companies and institutions (especially the University of Leeds[14]), the effect of adding Hybrane® to PP was investigated, and indeed it was found that the dyeability of PP fibers is highly improved without affecting other properties of the material.

Oil Field Chemicals

When I was working on dendrimer applications in the mid-1990s, I had discovered that highly branched mac-

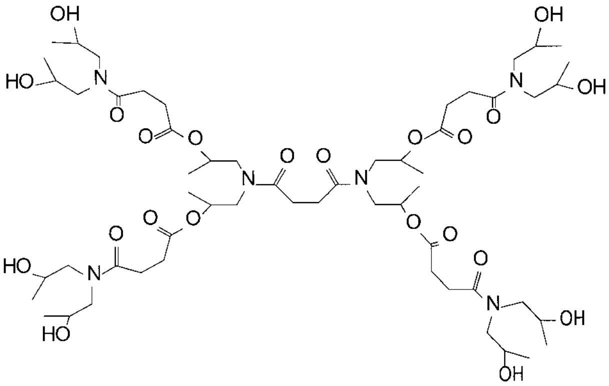


Figure 5. Based on succinic anhydride and diisopropanol amine, this Hybrane® is water soluble, and has been tested, for example, for paper coating applications.

Figure 6. The two articles on fundamental aspects of Hybrane®[11,12] unexpectedly yielded the annual DSM Publication Award. Left to right: Theo Zwartkruis, Carlo Vermeulen, Peer Froehling, Patrick Hendriks, Eric Geladé, Rolf van Benthem, and Dirk Muscat.

romolecules could have a profound effect on the crystallization of inorganic or organic compounds from solution, an effect that since then has been corroborated by several other research groups. This led to our contact with Shell Global Solutions in Amsterdam, where a research team led by Ulfert Klomp soon found that appropriate versions of Hybrane® were able to suppress the crystallization of gas hydrates from water–hydrocarbon mixtures.[15] Gas hydrate formation can be very disruptive in the production and transport of gas or oil at low temperatures or high pressures, and Shell's results have been the start of a fruitful cooperation with the oil field chemicals industry.

Paper Coatings

Printing paper is often coated with a thin coating of inorganic pigments (clay, $CaCO_3$) and binders (latex, starch) to improve its appearance and printability. This coating is applied from a high-solids aqueous dispersion of the pigment to a moving paper "web," which has a width of 5–10 m and runs at a speed of more than 1500 m/min. The rheological properties of the coating dispersion at these high speeds are often limiting the rate at which the coating can be applied.

In cooperation with an innovative paper chemicals manufacturer, it was found that the addition of small quantities of water-soluble Hybrane® to the paper coating would give an improved control over the rheology of the dispersion at high speeds,[16] which means in practice that the paper-coating machines can run at higher speeds without problems. This surprising application of Hybrane® is now fully commercial, and is finding its place in an increasing number of paper plants.

Breaking of Azeotropes

A very different kind of Hybrane® application was developed at the Technical University of Berlin by Professor Arlt's team. The presence of a minimum azeotropic boiling point in the ethanol–water system prevents the complete separation of both components by fractional distillation. The use of azeotrope-breaking additives such as ethylene glycol which compete with the ethanol–water interactions is well known. Low-molecular-weight additives such as glycol tend to leave undesirable residues in the distillate, and the use of polymeric additives should overcome this disadvantage. However, the high viscosity of linear polymers in such a system leads to problems in heat and mass transfer, and therefore the attention of the Berlin group was directed to highly branched polymers which inherently have a low solution viscosity.[17] Indeed, it was found that hydroxy-terminated Hybrane® was very effective in breaking several types of water-containing azeotropes, that is, with ethanol and with dioxane. The work by the Berlin group is continuing.

Scale-Up of Hybrane® Production

For the commercialization of Hybrane®, it was of course necessary to make products on an industrial scale. Fortunately, the Hybrane® chemistry as explained above is determined by thermodynamics rather than by kinetics, which means that upscaling should not be too difficult. This was already proven in an early stage of the project, when 100-kg batches turned out to be fully identical to lab-scale products. The next step was of course the production of ton-sized batches. In the past years, we have successfully realized this for a variety of products without encountering essential problems. Standard melt polycondensation equipment, that is, a powerful stirrer, heating capacity up to 160–180 °C, and a reasonable vacuum to drive of the produced water, is sufficient for the reproducible production of 5–25 ton lots for various industrial applications as described above.

CONCLUSIONS

In mid-2003, the DSM Hybrane company was founded as a separate legal entity. This certainly shows the confidence of DSM's management in the commercial potential of the hyperbranched poly(ester amides). Over the past years, we have proven that Hybrane® is a concept that exploits all special aspects of dendritic macromolecules to a maximum degree. The chemical flexibility of the product has made it possible to produce tailor-made performance additives for an ever-expanding multitude of industrial applications, the end of which is not in sight. It is only through the dedicated efforts of many people, colleagues in DSM Research and in DSM's business units, and many industrial and academic partners, that this success could be realized.

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