Macromol. Symp. ***151,*** *581–589 (2000)*

Properties and applications of poly(propylene imine) dendrimers and poly(esteramide) hyperbranched polymers

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SUMMARY: Synthesis, structure and properties of ASTRAMOL poly(propylene imine) dendrimers and HYBRANE hyperbranched poly(esteramides) are reviewed. Many chemical and physical properties of these dendritic macromolecules can be tailored to specific applications by appropriate chemical modifications. A concise overview is given of commercially relevant applications of dendrimers and hyperbranched polymers.

Introduction

Since the pioneering work by Tomalia(1) the synthesis of a wide structural variety of dendritic macromolecules has been undertaken by an increasing number of researchers(2). The total current literature on dendrimers consists of more than 1200 articles. The fact that in many places serious thought is given to commercial applications of dendrimers and hyperbranched polymers follows from the fact that up to now more than 150 patents have been filed.

The construction of dendritic macromolecules is a challenge to the organic and polymer chemistry field. Many structural elements for building up the regular, highly branched dendrimers and the less regular hyperbranched polymers have been proposed(3). Besides common organic building blocks based on carbon, hydrogen, nitrogen and oxygen, an increasing interest is given to dendrimers containing less common elements(4) such as silicon, phosphorus and various metals.

The availability of dendrimers of varying chemical structure and size has lead to an increasing insight into the relation between their structure and physicochemical properties, and to the development of numerous interesting applications. From a commercial point of view the application of dendrimers will only be feasible in high-end applications as e.g. in devices and in the biomedical field. In contrast, hyperbranched macromolecules(5) retain many of the

CCC 1022-1360/00/$ 17.50+.50/0

dendrimers' structure (high degree of branching, approximately spherical shape, large number of end groups) and related properties (rheology, ability to take up guest molecules), which are attained via a much simpler and therefore economically much more attractive synthetic pathway.

In this paper we will review synthesis, structure and properties of both dendritic polymers from DSM, viz. the ASTRAMOL poly(propylene imine) dendrimers and the recently introduced HYBRANE hyperbranched poly(esteramides), together with a number of commercially relevant applications.

Poly(propylene imine) dendrimers: synthesis, structure and properties

Currently, DSM is producing poly(propylene imine) dendrimers from the first up to the fifth generation by a divergent synthesis$^{6,7)}$. The first two steps of the synthetic route are depicted in Figure 1. By a Michael addition of two molecules of acrylonitrile to a primary amine, followed by a catalytic reduction of nitrile to amine, the number of amine groups is doubled for each subsequent dendrimer generation. The starting molecule for the dendrimer construction is 1,4-diaminobutane.

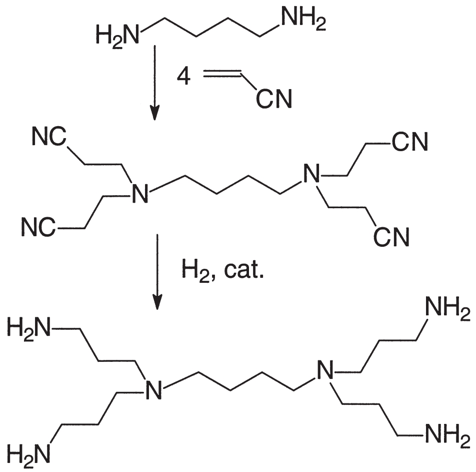

Fig. 1. Synthesis of the first generation of ASTRAMOL poly(propylene imine) dendrimers.

By repeating the depicted steps on the formed tetra-amine, the dendrimer structure is built up. An overview of some general characteristic of the amine-terminated ASTRAMOL dendrimers is given in Table 1.

Table 1. Some basic parameters of ASTRAMOL amine-terminated poly(propylene imine) dendrimers.

generation	molecular weight	primary amines per molecule	tertiary amines per molecule	radius of gyration (SANS), nm
1	317	4	2	0.44
2	773	8	6	0.69
3	1687	16	14	0.93
4	3514	32	30	1.16
5	7168	64	32	1.39

The large number of amine groups makes the poly(propylene imine) dendrimer a polyelectrolyte with interesting fundamental properties. Titration behavior(8) and complex formation with oppositely charged polyelectrolytes(9) have been studied extensively.

Through the large number of reactive end groups, the amine-terminated poly(propylene imine) dendrimers are very amenable to chemical modification. As the physical properties of dendrimers are largely determined by the nature of the end groups, chemical modification forms a precision tool to tailor the properties towards a desired application. A modification we have been using for a variety of applications is the conversion of amine to alkyl amide. This can be realized on an industrial scale by direct amidation with fatty acids at temperatures of about 150 °C, assisted by vacuum or by xylene (via azeotropic distillation) to remove the liberated water.

We have found that the partial amidation of amine-terminated dendrimers with e.g. 50 % of the stoechiometric quantity of stearic acid gives rise to molecules with interesting application potential, as will follow from the next paragraph. The partial modification of dendrimers is in itself a relevant study object, as it can give rise to a number of interesting structural varieties(10). We have investigated both the compositional and positional heterogeneity of partially amidated dendrimers using several methods. The composition follows the expected binomial distribution. However, the positional distribution pattern (expressed as the substitution pattern of dyadic end groups, i.e. non-, single- or double-substituted pairs of end groups) deviates from a random pattern for higher generations.

Poly(propylene imine) dendrimers: applications

The fatty acid modified dendrimers are readily soluble in apolar solvents. We found that they are able to act as polybases in extraction experiments where acid dyes were extracted from aqueous solutions(11). It appears that all amine groups in the dendrimer are able to act as proton receptor sites for the acid dye molecules. The fifth generation of modified dendrimer can thus act as a host for 62 dye anion molecules. The extraction behavior is pH and pK dependent. Higher generations of dendrimer show a markedly higher extraction efficiency. A number of physicochemical aspects of the extraction process are currently under investigation.

A closely related commercial application of dye extraction is the acid dyeing of poly(propylene fibers), to which small quantities of modified dendrimers are added(12). The alkyl chains make the dendrimer compatible with the polyolefin matrix, while the dendrimer's interior acts as a receptor site for the dye molecules. With neutron scattering experiments we have found that that the dendrimers aggregate in the polymer matrix into micelle-like particles(13). Currently, commercial PP fibers are not dyeable, while the market is strongly interested in a dyeable PP system. We are developing this application further in cooperation with several other companies and institutions.

Monolayer and aggregate formation of fatty acid modified dendrimers have been studied extensively(14). It is to be expected that these amphiphilic dendrimers have special properties as surface active agents. They resemble the recently described "gemini surfactants"(15) which possess two polar heads and two apolar tails. Dendrimers can be converted into "multiplet surfactants", with any number of heads and tails dependent on the dendrimer's generation and substitution pattern.

The surfactant action of fatty acid modified dendrimers has been put into practical use for the dispersion of silica into rubbers, a subject of environmental importance through the development of the "green tire"[16)]. The rolling resistance of cars is greatly reduced when silica is used as a reinforcing filler in the tires, which results in a substantial reduction of fuel consumption. However, the mixing of silica with rubbers is a tedious process, which currently is assisted by the addition of large quantities of reactive silanes. We have found that small quantitites of stearamide-modified dendrimers can act as dispersion agents for silica in natural rubber[17)]. The special effect of dendrimers on the dispersion of silica is supported by model experiments in heptane; see Figure 2.

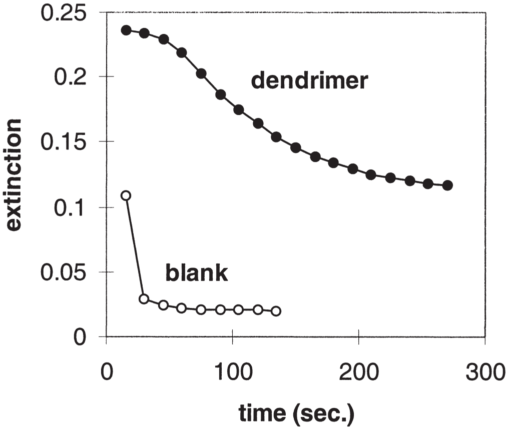

Figure 2. Stabilization of a silica dispersion in heptane by fatty acid modified dendrimer.
To a dispersion of 25 mg of silica in 10 ml of heptane, 2.5 mg of stearamide-modified first generation of poly(propylene imine) dendrimer were added. The settling of the silica was followed in time by measuring the extinction at 446 nm. In a blank experiment, the silica settled rapidly and completely. When dendrimer was added, a stable dispersion resulted.

Synthesis, properties and application of hyperbranched poly(ester amides)

The synthesis of DSM's recently introduced HYBRANE hyperbranched poly(ester amides) is based on readily available starting materials, viz. cyclic anhydrides (e.g. succinic, hexahydrophthalic or phthalic anhydride) and diisopropanol amine[18)]. In a single step, a hyperbranched structure is built up from these compounds under relatively mild conditions. The first step is the reaction of the aminodiol with the anhydride (Figure 3), while the hyperbranched structure is formed in a subsequent reaction (Figure 4).

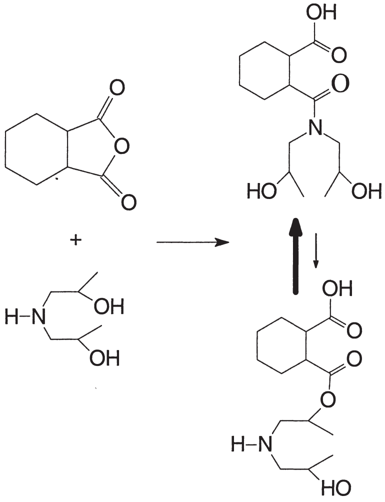

Figure 3. Primary step to hyperbranched poly(ester amide) is the reaction of cyclic anhydride with diisopropanol amine.

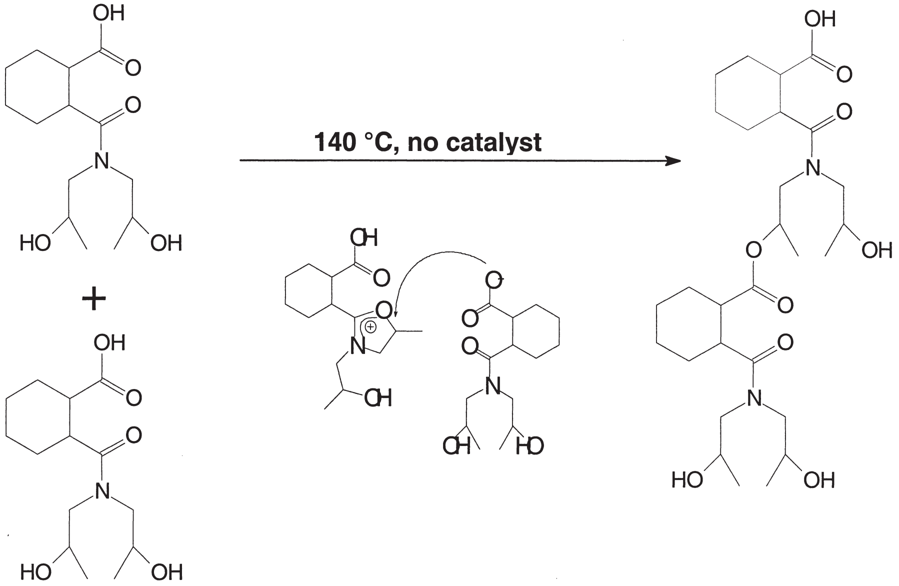

Figure 4. Via a reactive oxazolinium intermediate[19)], the hyperbranched structure is formed at relatively low temperatures and without catalyst.

By careful control of the reaction conditions, the molecular weight and the number of end groups can be set to predetermined values. For a hexahydrophthalic anhydride based polymer, the number-average molecular weight can be tuned between 670 and 2700, with a corresponding number of hydroxy end groups between 5 and 13. Contrary to dendrimers, hyperbranched polymers produced along this route have a broad molecular weight distribution, with a polydispersity varying between 3 and 4.

Figure 5 gives an impression of the hyperbranched poly(ester amide) structure.

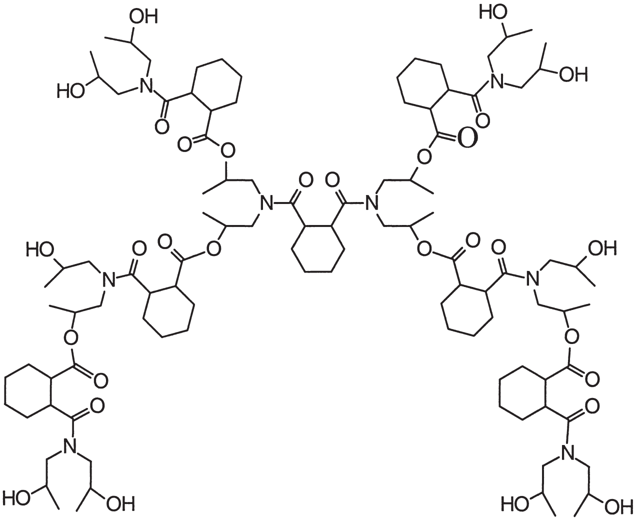

Figure 5. Approximate structure of a hyperbranched poly(ester amide) molecule.

As with dendrimers, it is possible to tune the properties of the hyperbranched poly(ester amide) through end group modification. We have prepared HYBRANE polymers with ester, carboxylic acid, amine, (meth)acrylate and alkoxysilane end groups. We have found that it is also possible to introduce functional end groups during the polymerization reaction, which can lead to products with a higher molecular weight and more end groups than via a two-step procedure.

The application potential of HYBRANE hyperbranched poly(ester amides) is currently under investigation. The cost price for producing these polymers is intrinsically lower than for dendrimers, which leads to a broader field of applications. Some examples, often based on appropriate end group modification, are enumerated in Table 2.

Table 2. Some application fields for HYBRANE hyperbranched poly(ester amides)

processing aids for thermoplastics
crosslinker for thermosets
dispersion aid for fillers and additives
surface active agents
toners
cosmetics
antifreeze additive for diesel fuels
dispersant in lubricants

Conclusions

The development of poly(propylene imine) dendrimers has led to a number of relevant industrial applications. The recently introduced economically attractive hyperbranched poly(ester amides) have opened a broad field for chemical modifications and concurrent new application potential.

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