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Dendrimers and dyes — a review

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Abstract

Dendrimers are a class of macromolecules characterized by a highly branched structure of great regularity, a compact shape, a large number of (reactive) end groups, and room between the branches for taking up guest molecules. Dyes have been used to probe the structure of dendrimers; special combinations of dyes and dendrimers can be used to capture and transfer photon energy. Modified dendrimers have been applied to extract dyes either in liquid–liquid systems or liquid–solid systems (dyeing of fibres). Furthermore, dendrimers have found a number of applications in inkjet printing and related techniques. For large-scale industrial use an economic alternative for dendrimers has been found in the hyperbranched polymers, which share many of the dendrimers' special properties. © 2001 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Most synthetic and naturally occurring macromolecules have a simple linear structure. They consist of a covalently linked chain of repeating monomeric building blocks, with an end group at each end of the chain. These two end group rarely play a part in the chemical or physical properties of the polymer material built up from the constituent linear macromolecules. Over the last 20 years polymer chemistry has created a number of non-linear variations on this simple polymer structure. These variations are commonly denoted as "macromolecular architectures" [1]. One of the new architectures arises from the introduction of a large number of branches during the polymer's synthesis, which leads to a macromolecule with many end groups.

Two classes of highly branched polymers are represented in Fig. 1: *dendrimers*, with a perfectly branched uniform structure, and *hyperbranched polymers* where the branching occurs in a more random fashion. The term "dendrimer" is drived from "dendron", the Greek word for tree. Due to their special structure, the physical and chemical properties of dendrimers and hyperbranched polymers (together also denoted as "dendritic polymers") are rather different from the usual linear polymers [2]. Characteristic are the compact shape, the large number of end groups, which are often reactive, and the possibility to take up guest molecules between the branches.

The large-scale availability of dendritic macromolecules has opened the road towards a broad

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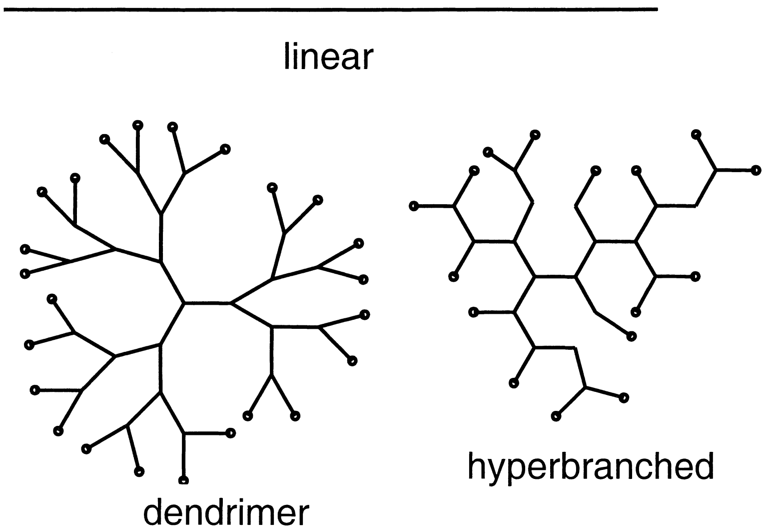


Fig. 1. Examples of macromolecular architectures: linear, dendrimer (perfectly and maximally branched structure) and hyperbranched.

scale of new applications, both with scientific and industrial relevance. This review gives a summary of the applicability of *combinations of dendrimers with dye molecules* for various purposes. The following topics are discussed:

- —dyes as structural probes for dendrimers
- —dyes combined with dendrimers for capture and transfer of photon energy
- —extraction and encapsulation of dyes by dendrimers
- —various applications
- —future developments

These topics are preceded by a short discussion of synthesis and properties of dendrimers.

2. Synthesis and properties of dendrimers

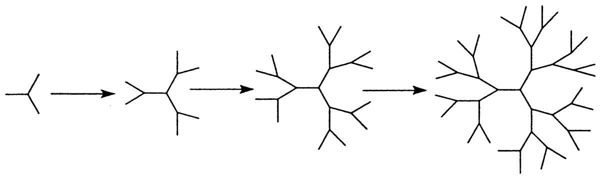
2.1. Synthesis

The synthesis of dendrimers requires a stepwise approach to build the perfectly regular structure. This differs from conventional polymerization reactions, which are either based on repeated addition of monomers to a growing chain with an activated end group (e.g. radical addition polymerization of vinyl monomers) or on the stepwise random combination of monomers and oligomers in polycondensation reactions.

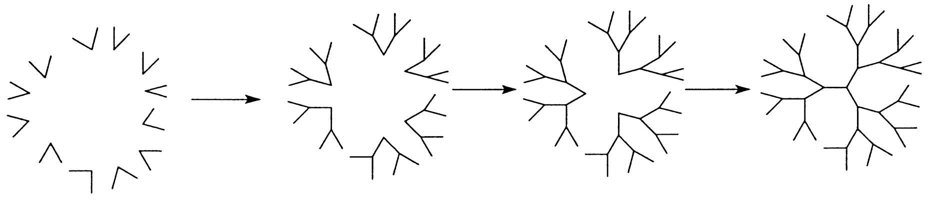
In dendrimer synthesis many chemical pathways can be followed, but there are two general strategies (Fig. 2). In the *divergent* route [3] the dendrimer is built up from a central polyfunctional core. In a repeated reaction cycle the building blocks are added layer by layer. Each next cycle leads to a higher *generation* of dendrimer. In the *convergent* synthesis [4] first complete wedges (“dendrons”) are prepared, which are subsequently coupled to a central core. An advantage of the convergent route is the possibility to separate and purify the intermediate products.

The divergent synthesis is especially suitable for upscaling to an industrial scale, as has been done by DSM [5] for its ASTRAMOL poly(propylene imine) dendrimers (Fig. 3). The convergent pathway is more usual for laboratory-scale production of tailor-made products. The end result of both methods is a collection of macromolecules of identical structure and molecular weight, similar to for example a protein or a nucleic acid.

The literature on dendrimers presently covers more than 2000 references, representing a variety of chemical structures. Next to the poly(propylene imine) dendrimers, other well-known dendrimers are the poly(amidoamine) [3] and the poly(benzyl ether) dendrimers [4].



divergent synthesis



convergent synthesis

Fig. 2. Two principal synthetic routes towards dendrimer: *divergent* synthesis starting from a central core; *convergent* synthesis starting with coupling of end groups into "dendrons", which are successively joined into larger units.

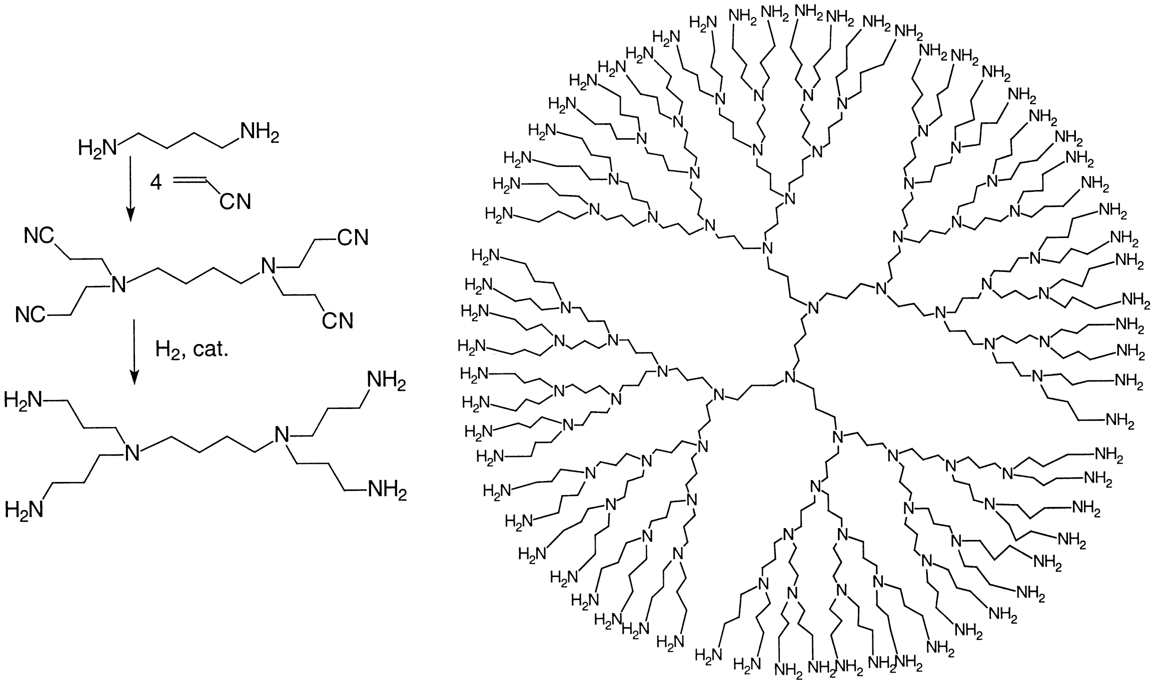


Fig. 3. Divergent synthesis of DSM's poly(propylene imine) dendrimers. Left: synthesis of first generation molecule; right: fifth generation dendrimer with 64 primary amine end groups.

2.2. Properties of dendrimers

Characteristic for all dendrimers is the presence of a large number of end groups, which often are reactive, and many branching points. The number of end groups is related to the number and functionality of the branching points. Many of the dendrimer's chemical and physical properties, such as state of aggregation, reactivity, stability and solubility are closely related to the nature of the end groups. Thus it is possible to tailor the dendrimer's properties by appropriate chemical modification of the end groups [2].

The spherical shape of the dendrimer molecule has important implications for its rheological properties both in bulk and in solution. The interaction of the spherical molecules with solvents or among themselves is very different from that of linear polymers [6].

Between the dendrimer's branches there is room for *guest molecules*. Guests can be, for example, simple solvents, but as we shall see it is generally possible for the dendrimer to take up larger species as well. The nature of the host–guest interaction is varied. Ionic (acid/base), donor-acceptor, Van der Waals and hydrogen-bonding interactions are known. A special case, elaborated in Section 5, is the *dendritic box*, where the guest is mechanically entrapped within the dendrimer.

3. Dyes as structural probes for dendrimers

In this type of application of dendrimers, dye molecules interact with some part of a dendrimer molecule, either end groups, branches or the core. The interaction leads to a change in the absorption or emission behavior of the dye, which can give information on the structure of the dendrimer or the interaction of the dendrimer with its environment. Generally, the results are compared with results obtained by other physical measurements (often spectroscopical methods) or for example computer simulations.

In a classical study, Fréchet [7] coupled the solvatochromic dye 4-(*N,N'*-dimethylamino)-1-nitrotoluene to the core of a poly(benzyl ether) dendrimer. In a solution of carbon tetrachloride the $\lambda_{\max}$ of the dye increased with higher dendrimer generation due to a shift of preferred interaction from dye–solvent to dye–dendrimer. Between generation 3 and 4 a marked discontinuity in the linear increase of $\lambda_{\max}$ was observed. The authors ascribe this jump to a transition in the dendrimer structure from an extended to a more globular configuration. This transition is also found from discontinuities in the intrinsic viscosity as a function of the generation. At a certain size the globular shape of the dendrimer starts to dominate its physical properties.

Russo [8] performed a complex investigation of the size of dendrimers, using a poly(amido amine) dendrimer equiped with a covalently coupled flourescent label. This author compared the apparent molecular size in aqueous solution as obtained from fluorescence photobleaching recovery with dynamic light scattering measurements. There was a marked difference between the two methods in the dependence of the dendrimer's diameter as a function of the salt concentration. The authors conclude theat fluorescent dye labeling of dendrimers gives a suitable diffusion probe.

An analogous study [9] was performed by the labeling of poly(amido amine) dendrimers with the fluorescent label 4-dimethylamino-4'-isothiocyanatoazobenzene (DABITC). The authors measured the apparent hydrodynamic radius of the dye-labeled dendrimers by holographic relaxation spectroscopy. They found a marked difference in swelling behavior in good and in bad solvents depending on the dendrimer's generation. Higher generations offer a larger interior surface area to interact with solvent molecules, which should explain the observed difference.

The divergent synthesis of dendrimers can lead to the occurence of minor structural faults. This can be detected by sophisticated mass or NMR spectroscopy techniques [5]. However, in an elegant study Newkome [10] showed the applicability of a reactive fluorescent dye (9-anthryl diazomethane) for the same purpose. The dye reacted with residual carboxylic groups resulting from incomplete reaction during the divergent buildup of an aliphatic poly(amide) dendrimer by peptide coupling chemistry. The fluorescence of dye-labeled defect structures could be used to detect defects at a concentration below 1%, which is much lower than can be realized by NMR.

Tomalia [11] has studied the interaction of the fluorescent hydrophobic dye *Nile Red* (phenoxazon-9) with a series of poly(amido amine) dendrimers of increasing generation. The hydrophobicity of the core of the divergently synthesized dendrimer was varied by using a series of diamines from 1,2-diaminoethane to 1,12-diaminododecane. When the latter compound was used as core, the fluorescence intensity of the dye strongly increased when dendrimer was added to a dye solution. Dendrimers with a more polar core had no effect. This indicates a hydrophobic interaction between dye and dendrimer core when the core is sufficiently apolar. Also the fluorescence polarization increased when dendrimer was added, which is explained by a restriction of motion in the dye due to its interaction with the dendrimer.

The same group [12] also investigated the effect of the dendrimer generation on the compactness of the macromolecule, using dye probes with luminescence, fluorescence and simple absorption techniques. From this work again follows that at increasing generations there occurs a transition from an open to a closed or more compact structure. This is reflected in the occurrence of stacked or aggregated dyes at the surface of dendrimers of higher generations, and in an incresed lifetime of luminescent probes.

Ford [13] has synthesized a poly(propylene imine) dendrimer with an equal number of hydrophilic and hydrophobic end groups on one molecule. This dendrimer can be described as a "unimolecular micelle", which can change conformation dependent on the solvent environment of the dendrimer. Using Reichardt's dye as a solvatochromic probe, it was found that in an aqueous solution the dendrimer's interior presents a wide range of polarities.

4. Dyes combined with dendrimers for capture and transfer of photon energy

4.1. Light harvesting with dendrimers

As has been discussed in the previous paragraphs, dendrimer molecules possess a distinct exterior and interior. This characteristic has been exploited in constructing dendrimers with light-absorbing chromophore groups at the outside, which subsequently transfer the absorbed photon energy to a single laser dye located at the dendrimer's core. In this way a "light harvesting" system is obtained, which presents a strong analogy to the photosynthetic system of nature. It should have the same function of absorbing light energy and concentrating it on a single active site (Fig. 4) This concept has first been elaborated theoretically [14], and has found a number of experimental realizations.

The practical synthesis of a dendrimer based light harvesting system has first been reported by Fréchet et al. [15]. They have synthesized a series of poly(benzyl ether) dendrimers of increasing generations, with the laser dyes Coumarin-2 at the dendrimer's core and Coumarin-343 at the periphery. The authors have shown [16] that this type of molecule is indeed acting as a spectral energy concentrating system, whith excellent absorption and emission characteristics. The same authors [17] are extending this concept towards the creation of a broad-band emission system using different absorbing and emission moieties coupled to core and periphery of the dendrimer.

4.2. Electroluminescence and LEDs

Analogous principles have been used for the construction of electroluminescent devices. A blue-emitting electroluminescent molecule was produced by Fomine [18] using modified coumarins as building blocks for a hyperbranched polyester.

A different concept for a dendrimer based electroluminescent molecule has been described recently [19]. The authors synthesized a completely conjugated dendrimer, based on porphyrin, anthracene and distyrylbenzene cores with stilbene based branches. It is suggested that fully conjugated dendrimers can form the basis for a polychromic light emitting diode. The combination of the conjugated dendrimer and poly(pyridine) appears to give a particularly efficient LED [20].

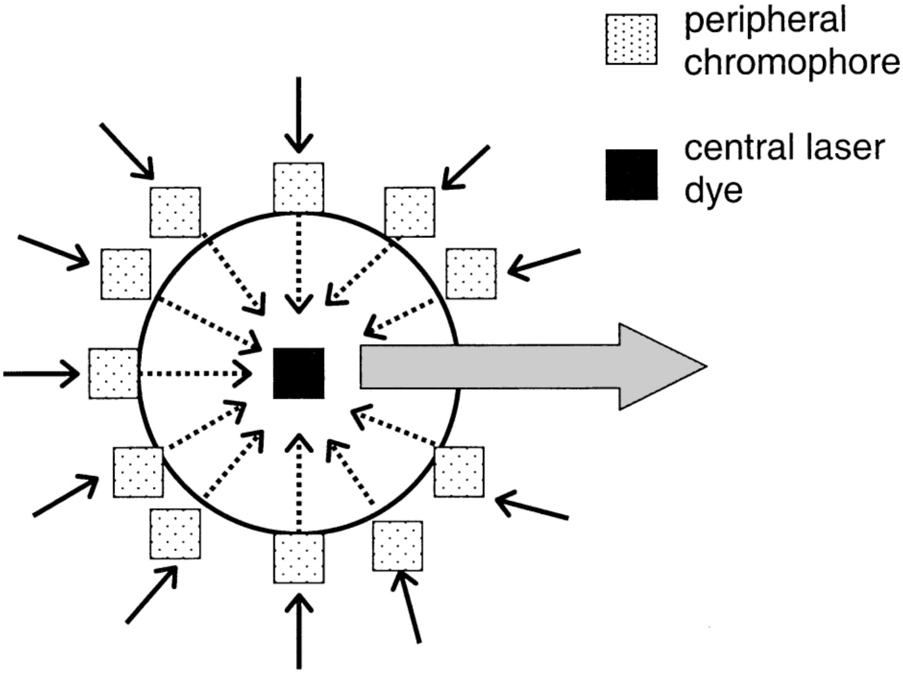


Fig. 4. Antenna function: light energy is absorbed by the chromophores coupled to the dendrimer's periphery, and transferred to the central laser dye which emits its own fluorescence.

4.3. Various light absorption systems

Dendrimers also have shown to be effective in the production of cadmium sulfide quantum dots. Here the dendrimer has no active function in light absorption of emission, but acts as a stabilizer for the CdS nanoparticles [21].

A photoresponsive dendrimer, which reversibly changes its conformation upon irradiation has been developed by McGrath [22]. By incorporation of an azobenzen chromophore in the core of a poly (benzyl ether) dendrimer, the molecule can change form an open structure with the core in the trans configuration to a closed structure with the core in the cis form. The authors envisage the possibility to use this concept for a light-activated system for molecular transport or controlled release.

5. Extraction and encapsulation of dyes by dendrimers

One of the features of dendrimers is the regular and highly branched structure of the molecule's interior. Even before the actual first synthesis of dendrimers, Maciejewski [23] already suggested that highly branched molecules should be able to act as a host for the encapsulation of guest molecules. Early experimental examples of this phenomenon are the solubilization of for example pyrene and aspirin by dendrimers in water. By appropriate modification of the dendrimer's exterior it is possible to emphasize the host behavior of dendrimers in specific environments. Two examples, where dyes have extensively have been used, are further elaborated in this review, viz. the dendritic box (Section 5.1) and the unimolecular micelle (Section 5.2). This second concept has already lead to an industrial development, viz. a dyeable poly(propylene) fibre.

5.1. The dendritic box

This concept was developed by Meijer and Jansen [24]. By constructing a dense, hydrogen-bonded shell around higher generations of poly(propylene imine) dendrimers in the presence of guest molecules, the guests can be trapped within the dendrimer.

The authors investigated a variety of dye molecules as guests. It was found that the shape of the dye molecule and the intra-dendrimer cavities, as well as the dendritic architecture determine the number of guest molecules that can be entrapped in this way (up to eight per dendrimer). Computer simulations of the entrapment process yielded the same results [25]. Moreover, by partial removal of the shell for example by mild hydrolysis), the shell becomes "leaky" and small guest molecules can be released again, while larger ones remain inside.

5.2. Dye extraction and the dyeing of PP fibres

In the "dendritic box" concept the capture of guest molecules is based on an accidental entrapment of guests during the closure of the shell. An active attraction of guest molecules by modified dendrimers was reported by Baars and Froehling [26], based on the extraction of acids from water by amines in an apolar solvent. They used poly(propylene imine) dendrimers with an end group modification of fatty acid amides, which results in a unimolecular micelle structure soluble in apolar media (Fig. 5).

The interior of this dendrimer consists of tertiary amine groups, which are able to give an acid–base interaction with acid dyes at sufficiently low pH. The authors showed that this system can act as a host towards a stoichiometric quantity of various acid dye molecules. In other words, a fourth generation dendrimer with 30 t-amine groups can absorb up to 30 dye molecules. With respect to the pH the extraction behavior is completely reversible: at higher pH the dendrimer releases the absorbed dye again. It appeared that low molecular weight amines such as trioctylamine are not able to extract dyes from water under these circumstances.

This extraction principle has also been applied by several other authors, for example by DeSimone [27] for the extraction of an acid dye with fluoralkyl modified dendrimers in supercritical CO_2.

The same kind of extraction has proven to be feasible for the dyeing of hydrophobic fibres such as poly(propylene) (PP) fibres, which cannot be dyed in conventional dyeing processes. In this case the alkylated dendrimer is blended with PP, and the blend is subsequently spun into a fibre. When this fibre is contacted with an appropriate dye solution, the dye is extracted into the fibre by the same acid–base mechanism as described above for the liquid–liquid extraction [28] (Fig. 6).

In the case of a weaker interaction between dendrimer and dye, it is still possible to extract or

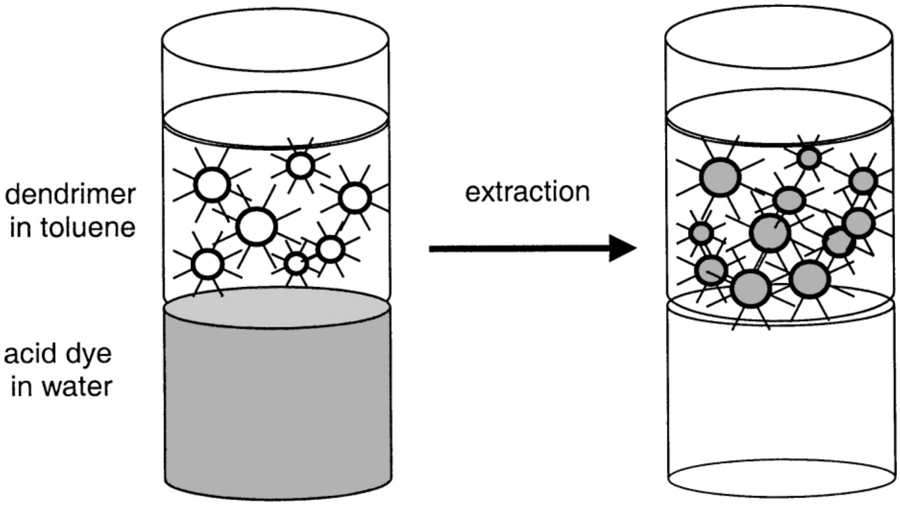


Fig. 5. Extraction of an acid dye from aqueous solution by an alkyl modified poly(propylene imine) dendrimer in toluene.

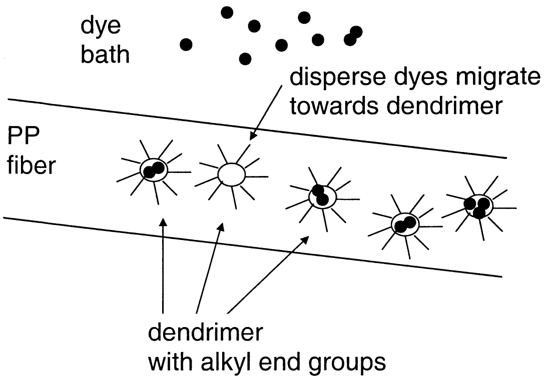


Fig. 6. Dyeing of poly(propylene) fibres. The fibre contains alkyl modified dendrimers or hyperbranched polymers, which extract the dyes out of the dye bath.

encapsulate dye molecules, but generally in smaller amounts compared to the acid–base extraction. Examples of this are reported by Frey [29] with alkylated hyperbranched poly(glycerol), Crooks [30] with fatty acid salts of poly(propylene imine) dendrimers and Smith [31], who solubilized proflavine using lysine-based dendrimers. The dyeing of PP fibers by using disperse dyes instead of acid dyes has also been developed [28].

Another way to encapsulate a dye in a dendritic macromolecule has been described by Froehling [32] and by Voit [33]. In their work a dendrimer or hyperbranched polymer with an apolar shell is precipitated from a solution containing dissolved dye molecules. In the precipitation a part of the dye is caught by the dendrimer, in analogy to the dendritic box. The dendrimer-encapsulated dye can for example be used to color materials which in themselves are incompatible with the often polar dye molecules. This concept offers the possibility to color apolar plastics using dyes instead of pigments, which can have a negative influence on mechanical or optical properties of plastics.

6. Various dye-related industrial applications of dendrimers

As was shown in Section 2, dendrimers possess a number of special properties which discern them from other macromolecules. Several industrial applications are based on these properties, as appears from the following examples from the patent literature.

The multitude of functional groups make dendrimers appropriate carriers for different functionalities on the same molecule. Thus the combination of dyes and specific receptors, antibodies or ligands coupled to a dendrimer can be used in senors or affinity assays [34,35].

The special rheological properties due to the compact form of dendrimer molecules in solution [6] has found applications in the area of ink jet printing, where low viscosity has to be combined with a high drying speed. Simultaneously, the large number of end groups on the dendrimer should contribute to the improvement of adhesion and water fastness of the ink [36–40].

The polyfunctionality of dendrimers is also found in its use as liquid toner in electrophotography [41], where an appropriately modified dendrimer combines the multiple functions of colorant, binder and charge director in a single molecule.

Finally, a combination of dendrimers and pigments has been described for application in printing inks [42].

7. Future developments

The first synthesis of dendrimers has been reported 15 years ago [43]. Since then numerous publications have been appearing on synthesis, characterization and properties of this new class of macromolecules. Applications based on the special properties of dendrimers have been reported as well [44]. The often complex multistep synthesis of dendrimers has so far precluded their commercial use on a large scale. An interesting alternative has been found in hyperbranched macromolecules [45], which share many of the dendrimers' features but can be produced in a one- or two-step polymerization reaction. Examples of hyperbranched polymers which are currently made on an industrial scale are the BOLTORN polyesters from Perstorp [46] and the HYBRANE polyesteramides from DSM [47].

It is expected that hyperbranched macromolecules will find commercial application in many areas. Thus, the numerous investigations on dendrimers over the past fifteen years have generated a deeper understanding into the possibilities of highly branched macromolecules in general, which will be put to industrial use by the application of hyperbranched polymers.

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