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Hyperbranched Polymers as a Novel Class of Pigment Dispersants

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Summary: Hyperbranched polymers form a novel class of materials that are employed as components of resin formulations. They are appreciated for their low intrinsic viscosities, which is ascribed to their spherical shape. It was envisaged to devise pigment dispersants with hyperbranched moieties as structural elements. Commercially available hyperbranched polymers with polyester, polyesteramide and polyethylene imine backbones were chemically modified to develop a range of disperants with core- and shell-type pigment anchoring mechanisms. Both the shell- and core-type anchoring principles generally can be used for pigment dispersion and stabilisation at a low viscosity level.

Keywords: dendrimers, pigment dispersants, viscosity, coatings, polymers

Introduction:

Hyperbranched polymers belong to a class of polymers characterized by densely branched structures and a large number of reactive groups. Typical is the tree-like structure, which is obtained by polymerisation of ABx-type monomers.[1] Currently, the importance of hyperbranched structures has been identified by researchers in various industries and the polymers are being investigated in a broad range of coating applications.[2] This mainly was stimulated by the fact that several types of this polymer class have been made commercially available recently.[3,4]

The large number of functional groups on these polymers has a significant influence on the final physical and chemical properties. This allows various possibilities to derivatise (part of) these groups to obtain a certain desired property, such as reactivity, viscosity, compatibility or solubility and the use in different applications with their specific requirements. For example, the end groups can be transformed into unsaturated fatty acid esters or amides (for alkyd systems), acrylate- (radiation curing) or epoxy-terminated (for 2-pack systems), grafted with other polymers to obtain compatibilizers, equipped with ionic groups (for water solubility) or in particular with non-reactive groups for viscosity, polarity and compatibility adjustment.[5]

As a preliminary achievement, it has been recognized that hyperbranched structures show a non-

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Newtonian relationship between viscosity and molecular weight, and these rheological properties (low viscosity at high molecular weight due to reduced chance of chain entanglement) are combined with other characteristics, such as reactivity, chemical resistance, mechanical properties. For coating applications, if used as a binder component, this can mean a lower solvent content with advantageous film properties, which is highly interesting for environmental reasons.[4]

Hyperbranched Polymers

Classical examples of hyperbranched structures, are those which are built up from monomers of the AB_2-type and are called dendrimers, *dendron* being the Greek work for tree. The first commercial available dendrimers, polypropylene imines and polyamido amines were monodisperse polymers, meaning that costly stepwise build up and purification steps were required, limiting their use to high added value products like medicinal applications. [6] Recently, one-pot polyester types *(PES)* are commercially available, which consist of a multifunctional core from which branches extend to give a highly branched inherent structure with a large number of hydroxyl groups.[3] The AB_2-monomer is 2,2-dimethylolpropionic acid. The polymers are described by exponential growth and defined as polydisperse hyperbranched polymers of which the molecular weight is controlled by stoichiometry without the use of protective groups. The geometric structure is sphere-like consisting of three different regions: the *iniator core* (polyfunctional Bx starter), the *intermediate layer* (tree-structure by monomers AB_2) and the *shell* (reactive groups at the peripheral surface). The term *generation* is used to describe the size of the polymer and represents one repetitive step during the synthesis. The interior ester functions are shielded by the dense tree-structure, showing a higher hydrolytic and chemical stability.[5]

A second class of polymers are hyperbranched polyesteramides *(PEA)* as possible starting materials for this study. They have been developed and commericialized at the end of the 1990's, being polymers with a large number of multifunctional groups.[4] Besides hydroxyl and carboxyl-groups, hyperbranched PEA can be modified with a broad range of functional groups such as tertiary amines, alkyl chains and unsaturated groups. The synthesis takes place as a one-pot reaction in which monomers such as cyclic anhydrides (*e.g.* phthalic anhydride, succinic anhydride and others) are reacted with diisopropylamine. A rearrangement of the reactive species leads to a complex branched polycondensation product.[7] Variations in the ratio between the two starting materials leads to a molecular weight (MW) range of hyperbranched PEA. The obtained polymers can be further reacted with monocarboxylic acids, cyclic anhydrides, dialkyl amines and ethyleneoxide grafted chains. Investigated application fields for these polymers are crosslinkers for (powder) coatings, toner resins, high-solid air-dying alkyds, polyolefin dyeing and as surfactants.[4] In these applications the high chemical and mechanical resistance is pointed out.

Another interesting starting point are polyethylene imines *(PEI)*. These products are polymeric amines based on homopolymers of ethyleneimine (aziridine).[8] The geometry is branched and spherical with a well defined ratio of primary, secondary and tertiary amine functions, where statistically this ratio is about 1:1:1. They can be reprensented by the partial structural formula -$(CH_2\text{-}CH_2\text{-}NH)_n$- with $n = 10 - 10^6$.

Depending on their molecular weights, they vary in viscosity. Their affinity for polar surfaces (adhesion) can be explained by the branched nature with many anchoring points, and especially the adhesion to pigment surfaces has been highlighted. The pure polymer is described as pigment dispersant and flocculant in one compound.[8] At amounts below 1% on solid pigment, or if high molecular weight PEI are used, flocculation is observed; at higher amounts or with low molecular derivatives, stable dispersions are obtained. The amine functions react readily with ketones and aldehydes, furthermore, amidisation reactions with a wide range of carboxylic acids can be carried out. It is known that PEI can be reacted with polyesters, polyetherketones, polyolefines etc. Some of these functionalised grades have been commercialised as dispersants, however generally they show a poor solubility and a tendency to crystallisation under use conditions.[9]

Dispersing Agents

In the study described below, it was envisaged to use hyperbranched polymers as basic building block for the design of polymeric dispersing agents, and to overcome at the same time mentioned disadvantages. In the EFKA technology, polymeric or high molecular weight dispersants are used to wet and stabilise dispersions of inorganic and organic pigments in pigment concentrates or by direct grinding.[10] This principle provides dispersions with a long term stable viscosity at high pigment loading and constant colour strength, without reflocculation and sedimentation of the solid pigment particles. For this purpose EFKA provides polymers based on two kinds of patented chemistry, namely acrylic copolymers and polyurethanes.[11, 12] In a simplyfied view both systems are based upon a linear backbone, from which functional side chains are pending. These functional groups consist of compatibility-enhancing moieties, such as polyester or polyether chains and pigment affinic groups, so-called anchoring groups, which are designed to adsorp onto the pigment surface, therefore enveloping the pigment particle with the polymeric dispersant. Compatibility enhancing chains in this representation extend into the liquid grinding medium and interact positively with the binder molecules and the solvent. Their main action is to induce the steric stabilisation mechanism, which prevents the penetration of the chains of neighbouring polymer/pigment complexes and subsequently their mutual agglomeration.[13] In addition, carboxylic acid groups can be connected to the backbone, which render a possibility to make the polymer water soluble after neutralisation.

These polymeric dispersants have proven to be efficient and are well established additives for the paint industry, however there exists some room for improvement, like in state of the art automotive paints. They lack an optimum low viscosity at a high pigment loading with certain organic pigments and show occasionally an undesired build-up of a high yield value (thixotropic behaviour, which can be reversibly broken down by low shear forces like stirring and shaking). This phenomenon can be explained by the specific polymeric structure, being linear and showing average MW's of 5,000 to 25,000 $g \cdot mol^{-1}$ in a distribution that includes MW's as high as 100,000 $g \cdot mol^{-1}$. Such linear polymers with pending polar groups can interact inter- and intramolecularly or with functional groups of binder molecules by polar forces which prevent Newtonian flow of the paste. We have identified two ways to investigate the solution to this phenomenon:

- by applying controlled polymerisation techniques to obtain much narrower molecular weight distributions and defined polymeric architectures.
- by using hyperbranched building blocks to avoid linear polymer geometries.

The first approach is considered outside the socpe the current study, whereas the latter principle will be presented in this paper. It was anticipated that hyperbranched systems, due to their characteristics of offering low viscosities at high molecular weights together with the possibility to functionalise the outer shell with the appropriate chemistry, can offer the solution to overcome viscosity build-up.

In the general concept, hyperbranched polymers would be reacted with side chains that provide solubility and specific anchoring moieties to ensure adsorption of the polymer to the pigment surface. Both dendrimeric PES and hyperbranched PEA, as well as PEI fulfill the requirements for further functionalisations.

Concept based on Dendrimeric Polyesters *(PES)*

In a first approach, dendrimeric PES were investigated, having 2, 3 and 4 generations, representing MW's of ca. 2000, 3500 and 5000 g·mol^{-1} with respectively 16, 32 and 64 reactive hydroxyl groups. Due to the extreme polar structure of the outer shell, these solid polymers dissolve readily in water and methanol at ambient or slightly elevated temperatures, but both solvents are unsuitable starting points for many organic chemical reactions. It was found that melting the solids (> 40 °C) in a liquid reactive system (such as cyclic esters and fatty acids), would render an adduct, which remains liquid at room temperature and dissolves in common coating solvents like aromatics, esters and ketones. Furthermore, the extension of the outer shell with one molecule of *e.g.* caprolactone would increase the molecular weight and extend the spherical structure of the dispersant. It was expected that the body of the dendrimer would take part in the required steric stabilisation of the pigment dispersion and steric side chains could be shorter (< 1000 g·mol^{-1}) than in the classical linear systems.[12]

Table 1. Dispersants based on dendritic polyesters (PES).

sample	MW of PES (g·mol^{-1})	hydroxy-carboxylic acid [a)]	capping agent [b)]	aromatic group [c)]	tert. amine [d)]	approx. MW (g·mol^{-1})
4	3500	32 Cl	16 UFA	10 BA	-	12900
5	3500	16 CL	16 UFA	10 BA	-	11000
6	3500	16 CL	16 UFA	-	16 TA	16200
7	3500	16 CL	22 UFA	-	10 TA	15500
8	3500	16 CL	16 UFA	6 BA	10 TA	14500
9	3500	64 CL	-	-	10 TA	14900
10	3500	16 RA	16 UFA	-	15 TA	18800
11	2000	16 CL	6 UFA	-	5 TA	7500
12	2000	16 CL	6 UFA	4 PAH	4 TA	7700
13	2000	16 CL	6 UFA	-	5 TA	7500
14	5000	64 CL	-	-	15 TA	18400

[a)] CL= caprolactone and RA = ricinoleic acid; [b)] UFA = unsaturated fatty acid;
[c)] BA = benzoic acid and PAH = phthalic acid anhydride; [d)] TA = isocyanate-functionalised tertiary amine

In a typical example, PES (table 1, sample **4**) was reacted with an equimolar amount of caprolactone, then 16 terminal hydroxyl groups (50%) being extended with fatty acids leading directly to a compatibilising chain. Then 10 parts of benzoic acid were reacted. The remainder hydroxy groups were not functionalised. The thus obtained colourless polymer was diluted with solvents to ca. 50% and tested as a dispersant in an oil-free polyester based pigment concentrate with a standard pigment. As a reference a commercial linear polyacrylate dispersant and two competitive commercially available products were used. The pigment concentrate was measured on viscosity and subsequently applied with melamine on a sheet and cured at 130 °C, for determining gloss, seeding and transparency.

In a similar way, more samples were prepared (see table 1). The variation consisted of the amount of caprolactone initially applied to elongate the core dendrimer (12-hydroxy unsaturated fatty acid, ricinoleic acid, can also be used), the amount of fatty acid to cap some of the hydroxy groups, the utilisation of aromatic systems such as benzoic acid and phthalic acid anhydride as possible pigment affinic groups, or isocyanate-functionalided tertiary amines to enhance the anchoring efficiency, the structure of which is not disclosed for patent filing reasons.[14]

Table 2. Formulation for dispersant testing.

Components for **I** and **II** [a]	Amount (g)
Oil-free polyester	10.0
Dispersant	3.2 (at 50% solids)
Alkylbenzene	28.8
Irganzin DPP Red BTR	8.0
Glass beads	100
Total (**I**)	150 [b]
Above pigment concentrate (**I**)	2.50
Oil-free polyester	3.91
Melamine	1.67
Alkylbenzene	1.89
Silicone levelling agent	0.03
Total of (**II**)	10.0 [c]

[a] I = pigment concentrate and II = pour-out formulation

[b] grinding 1.5 h (Scandex) to < 5 µm ; c) mixed (dispermat) and poured out on plastic sheet, cured 0.5 h at 130 °C.

The above samples were selected by their gloss values at 20° to be above 70, and having no to only slight haze. The pastes were measured by their viscosity at different speeds with a Brookfield apparatus at different speeds (5 and 50 rounds per minute, *rpm*). The paste formulation that was used is based on an oil-free polyester as grinding medium, the pigment Irgazin Red BTR (16%), the dispersant at a level of 20% active material on pigment and solvent. An example of a typical formulation is given (table 2). Irgazin DPP Red BTR was chosen as a model pigment. It is based on diketopyrrolo pyrrole chemistry, and has a small particle size (BET = 15 $m^2 \cdot g^{-1}$) and known to easily build up viscosity after grinding.[15]

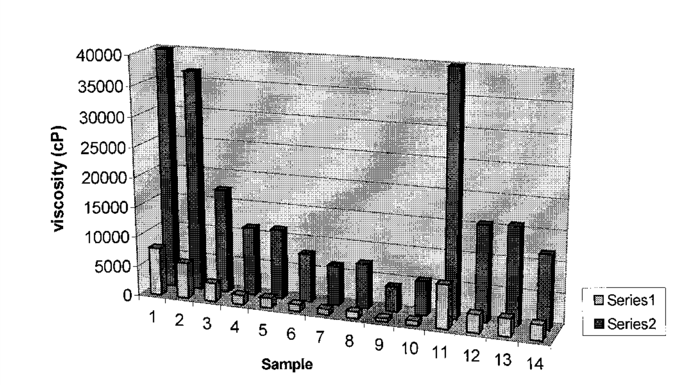

Figure 1. Viscosity measurements of selected pigment pastes. Series 1 and 2 measured at 50 rpm and 5 rpm respectively (Brookfield, spindle 4).

Figure 1 shows that dendrimers based on a PES with 3500 $g \cdot mol^{-1}$ (samples **4** to **10**) show lower viscosities in the pigment paste as compared to the reference linear polyacrylate (**1**) and two other competitive products (**2** and **3**). A decrease of the size of the dendrimer (2000 $g \cdot mol^{-1}$, **11** to **13**) gives a rise in viscosity. The chart also clearly shows that tertiary amine anchoring groups are more effective in viscosity reduction (**6** to **10**) as compared to the same polymer structure with merely aromatic anchors (**4** and **5**), this implying a stronger attachment of the dispersant to the pigment surface and therefore better dispersion.

Concept based on Hyperbranched Polyesteramides *(PEA)*

To investigate hyperbranched PEA, the results of the above dendritic polyesters were used for functionalisation. As a model structure, a PEA based on the condensate of succinic anhydride and diisopropanolamine having 8 hydroxyl groups throughout the branched structure with ca. 1200 $g \cdot mol^{-1}$ was chosen. This is lower than the used dendrimers and most similar to a PES with 2000 g·mol^{-1}, however with only half of the reactive groups.

The core polymer of the PEA-type, which shows low solubility and a solid state, was melted and reacted with caprolactone, followed by esterification of 3 hydroxy-groups with unsaturated fatty acids. The resulting polymer was treated with respectively 5, 3 and 1 equivalents of isocyanate-funtionalised tertiary amine, leading to three samples (table 3, **15** to **17**), which were submitted to the same application test with pigment Irgazin DPP Red BTR as described in table 2.

Table 3. Dispersants based on hyperbranched PEA.

sample	MW of PEA (g·mol^{-1})	hydroxy-carboxylic acid [a]	capping agent [b]	aromatic group	tert. amine [c]	approx. MW (g·mol^{-1})
15	2000	8 CL	3 UFA	-	5 TA	5800
16	2000	8 CL	3 UFA	-	3 TA	5000
17	2000	8 CL	3 UFA	-	1 TA	4100

[a] CL= caprolactone [b] UFA = unsaturated fatty acid [c] TA = isocyanate-functionalised teritary amine

All three samples showed an unexpected higher viscosity than any of the reference samples and competitive materials. Nevertheless, the gloss values of the three samples were high, at levels of 80 to 90 at 20°, showing good dispersion of the pigment. The undefined branched structure of this building block might be the reason of higher viscosities due to formation of linear structures. In addition, the low MW of this commerical product might be not sufficient for effective separation of the dispersed pigment particles, as it was the case with PES.

Concept based on Hyperbranched Polyethylene Imines *(PEI)*

The special feature of this concept is, that here the core of the polymer, the branched amine structure can be seen as the anchoring moiety, leading to the simplyfication that merely compatibility enhancing steric groups need to be connected to the core.

It appeared practical to block 50% of the available -NH- and -NH_2 groups of the PEI with MW's of respectively 800, 1300 and 2000 g·mol^{-1} with unsaturated fatty acids. The remainder 50% of amino groups was treated with caprolactone, such that chains of 8 to 12 monomer units were connected to each available amine functionality. To avoid any viscosity build-up by terminal hydroxyl groups of the polyester chain, they were subsequently esterified with lauric acid. The thus obtained products (**18** to **20**) were first submitted to application testing (see table 2) for a range of pigments to determine which of the three PEI cores would be the most suited for further investigation. Table 4 shows that the increase of the size of the anchoring core of the hyperbranched dispersant leads to higher gloss values and lower viscosities in the pigment pastes. The PEI with MW of 2000 g·mol^{-1} (**20**) lead to better results than an comparisive linear polyacrylate dispersant (**1**).

Table 4. Performance results of PEI-based dispersants in pigment concentrates.

sample	**18**	**19**	**20**	**1** (ref.) [a]
MW of dispersant (g·mol^{-1})	10600	17600	26500	25000
(MW of PEI) (g·mol^{-1})	(800)	(1300)	(2000)	(n.a.)
Pigment used in formulation				
Heliogen Blue L 7072 D	**49** [c]	**81**	**98**	**92**
with EFKA-6745 [b]	0 [d]	++	+++	0
Heliogen Blue L 7072 D	**74**	**77**	**87**	**85**
	-	-	+	0
Irgazin Red 2030	**22**	**35**	**55**	**66**
	+	+	++	0
Irgazin DPP Red BTR	**62**	**80**	**92**	72
	--	-	+	0
Colour Black FW 200	**94**	**93**	**92**	**92**
	0	+	++	0
Kronos 2310	**82**	**90**	**85**	**89**
	0	-	+	0

[a] EFKA-4401; [b] synergist for phthalocyanine pigments; [c] gloss (20°); [d] relative viscosity (reference set at 0).

Analysis of Results

From the above results, the PEI core appears to be the most promising building block for dispersant design. This can be visualised by comparing the geometrical structures of the resulting dispersants. Both PES and PEA lead to shell-type dispersants, while the PEI give core-type structures. In the first case, the anchoring groups are equally distributed over the surface of the ideally spherical shaped polymer, preventing an efficient pigment attachment of all the anchors, while core-types would experience a firm attachment by the core itself, avoiding the build-up of physical structures between the polar anchors and functional moieties of resins and others in the formulation. Generally it appears, that hyperbranched dispersants need sufficient MW (above ca. 15,000 g·mol^{-1}) in order to reach low viscosity levels. At lower MW's the volume of the polymer might not be sufficient for particle separation and as a consequence mutual interactions may prevent effective viscosity reduction. Further studies and optimization of the PEI dispersant architecture are required to determine the influence of the length and the amount of the steric side chains. The current results have provided insight in the structure-performance relationship of dispersants on the basis of which we are currently developing a new generation of polymeric dispersants, based on a new chemistry, which show an enhanced level of perfomance with regard to compatibility, a reduced tendency to crystallise and being liquid at room temperature.

Summary and Conclusion

It has been shown that the use of hyperbranched cores as carrier for the functional groups of a polymeric dispersant is a useful tool to improve the rheologic behaviour of polymeric dispersants in the described application fields. This is explained by the spherical shape of the polymers, leading to reduced interactions with polar groups in the liquid medium. The availability of numerous functional groups on the hyperbranched building blocks allows functionalisation of the core through versatile methods with desired moieties, such as pigment affinic groups and steric side chains.

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