Dispersion of Inorganic Pigments by Amphiphilic Hyperbranched Polyethers Dispersant

Qing Xu¹, Yungui Liu², Anlu Long² and Yuanjing Zhou²,*

¹ Institute of Biology, Guizhou Academy of Sciences, Guiyang 550009, China
² Institute of Analysis and Testing, Guizhou Academy of Sciences, Guiyang 550002, China
* E-mail: zhoyuanjing-8006@163.com

Abstract. The self-made amphiphilic hyperbranched polyethers (AHPs) dispersant were applied to inorganic pigments dispersion system, and their dispersibility to inorganic pigments was investigated. The results showed that AHPs had a good dispersing effect on inorganic pigments. When the branching degree of hyperbranched polyether was 0.47 and the dosage was 9% of the quality of pigment, the dispersing effect of AHP 47 on titanium dioxide was the best with the dispersion force as high as 98%. The dispersion stabilities for other inorganic pigments were also studied, and the dispersion effect was titanium white > iron oxide red > titanium nickel yellow > cobalt blue > copper-chromium black. AHPs had the characteristics of high solubility, low viscosity, good rheological properties and no pollution, which provided a new idea for the development of new efficient inorganic pigment dispersants.

1. Introduction
Inorganic pigments are inorganic powder colorants containing metal elements and have the advantages of high temperature resistance, weather resistance and strong covering power. They are widely used in various fields of people's life [1, 2]. However, inorganic pigments are insoluble in water, organic solvents and other media. Pigment particles have high surface energy, easy to agglomerate. With the increase of particle size of pigments, the pigments system is extremely unstable, which seriously affects its practical application. Therefore, before use, inorganic pigments must be surface treated to improve their dispersibility[3, 4].

Pigment dispersant is a functional additive specially developed for dispersing and stabilizing some solid particles in liquid. Hyperbranched polymers are highly branched polymers with high solubility, low viscosity, good rheological properties, and no pollution. They have great potential in pigment dispersion [5-8]. A series of amphiphilic hyperbranched polyethers (AHPs) with different branching degrees were synthesized in our previous work and it was found that the AHPs had good dispersing effect on pigment yellow [9]. Here, we applied them to inorganic pigments and investigated their dispersibility to inorganic pigments in order to expand their application.

2. Experimental

2.1. Materials and Instruments
AHPs dispersant was prepared by ourselves according to reference 9. Titanium white, cobalt blue, titanium nickel yellow, iron oxide red, and copper chrome black were obtained from commercial sources.
AB205-N analytical balance (Shanghai mettler toledo company), Milli-Q element water purification system (Millipore Co., Billerica, MA, USA), KQ2200DE numerical control ultrasonic cleaner (Kunshan ultrasound instrument Co., Ltd.), NDJ-5S viscometer (Guangzhou huruiming instruments Co., Ltd.), SU8020 field emission scanning electron microscope (Hitachi, Japan).

2.2. Preparation of Pigment Dispersion System
A certain amount of pigment, AHP and deionized water were weighed, mixed and stirred evenly. The pigment dispersed system was obtained by using JKQ2200DE numerical control ultrasonic cleaner to disperse the pigments with 800 W powers for a certain time.

The blank control system without hyperbranched polyether dispersant was prepared under the same conditions.

2.3. Determination of Dispersion Performance
Place the dispersed pigment system on the test tube rack, stay overnight, observe the settlement, record the location of the suspension settlement at intervals (Figure 1), and calculate the dispersion force (F) as follows (1):

\[ F = \frac{(H - h)}{H} \times 100\% \]

In the formula (1): h means settlement height (mm), H means total height (mm), and F means dispersion force (%). The greater the dispersion force, the better the dispersion.

2.4. SEM Analysis
The pigment dispersed system and the blank system without dispersant were first dried for 12 hours in an oven at 40 °C, and then analyzed by scanning electron microscopy (SEM) with SU8020 field emission scanning electron microscope.

3. Result and Discussion
3.1. Effect of Branching Degree of Amphiphilic Hyperbranched Polyethers on Dispersion Property
The DB of a hyperbranched polymer is a measurement on the content of branches in the molecular structure and is considered to be a main structural feature affecting the properties. Our previous research showed that the DB had important influence on the dispersion of pigment [9]. A series of amphiphilic hyperbranched polyethers (AHPs) consisting of hydrophobic hyperbranched polyether core and hydrophilic poly (ethylene glycol) arm with different DB under various reaction temperatures by the cation ring-opening polymerization, named as AHP35, AHP41, AHP47 and AHP51, respectively, according to the DB value were prepared. Among the products of AHP, AHP47 with 0.47 DB had good dispersion performance for Yellow HGR, owned the lowest viscosity, good color, and the highest sagging starting point. Here, we applied these AHPs to the dispersion of inorganic pigments, and investigated the dispersion stability of them to titanium white, cobalt blue, titanium nickel yellow, iron oxide red, and copper chrome black.

It was reported that the structure of dispersing agent had important influence on the dispersion of pigment. The structure of polymer dispersant is mainly composed of hydrophobic group and hydrophilic group. The proportion of hydrophobic group and hydrophilic group in polymer dispersant has great influence on the dispersion performance of polymer. If the proportion of hydrophilic groups is too high, the dispersant is easy to fall off from the surface of solid particles, and the hydrophilic chains are easily entangled, which leads to flocculation. If the hydrophobic chains are too long, they can not be completely adsorbed on the surface of particles to form rings or combine with the surface of adjacent particles, resulting in "bridging" flocculation between particles [10, 11].

The dispersion effect of AHPs with different DB on titanium dioxide was shown in Figure 2. With the increase of DB value, the dispersion effect of hyperbranched polyethers on titanium dioxide increased first and then decreased. When DB = 0.47, the dispersion force was the best. According to DB formula [12], with the increase of DB value, the dendritic unit and terminal unit in molecular structure increased, that is, the hydrophilic group of polyethylene glycol in polymer increased,
hydrophilic ability increased, on the contrary, hydrophilicity decreased, and the stability of pigment would decreased after dispersion; when DB = 0.47, the hydrophobic and lipophilic reached equilibrium, and the dispersion effect was the best.

![Figure 1. Dispersion force of testing method.](image)

![Figure 2. The effect of DB of AHP on dispersion property.](image)

The blank experiment showed that settlement was completed in less than 1 hour.

### 3.2. Effect of Dispersant Dosage on Dispersion Property

As can be seen from Figure 3, when the dosage of dispersant increased, the stability of the system increased first, and then tended to be stable, and finally tended to decrease. This might be due to the fact that when the dosage of dispersant was small, the dispersant could not completely cover the surface of the pigments, and could not form a complete adsorption layer on the surface of the pigments. The uncovered part of the surface of the pigments aggregated in order to reduce the surface energy, so that the pigments aggregated and dispersed unstably. When the dosage of dispersant was further increased, enough dispersants were adsorbed on the surface of the pigments in order to prevent particle agglomeration. When the dosage of dispersant increased to a certain extent, polymer molecular chains entangled with each other, resulting in the re-aggregation of pigment particles, but the dispersion stability of pigments decreased. Only when the dispersant formed a dense monomolecular adsorption layer on the surface of the pigment particles, the dosage of the dispersant would be optimum.

![Figure 3. The effect of dispersant dosage on dispersion properties.](image)
3.3. Dispersion Stability of Different Pigment Dispersion Systems with the Same Dispersant

The disperse efficiency of AHP$_{47}$ on different pigments was shown in Figure 4.

![Figure 4. The disperse efficiency of AHP$_{47}$ on different pigments.](image)

As shown in Figure 4, AHP$_{47}$ had the best dispersion stability for titanium dioxide with the dispersion force as high as 98%, followed by iron oxide red with the dispersion force as high as 95%, which all exceeded the results reported in the literature [13, 14], and the worst dispersion effect for copper chrome black. It was related to the structural characteristics of the pigment particles themselves and the structural properties of hyperbranched dispersant AHP$_{47}$. The AHP$_{47}$ with medium DB and lowest Mw among the products of AHP might interact with pigment particles better, and improve the dispersion performance [9].

3.4. SEM Analysis

Figure 5 and Figure 6 showed respectively the titanium dioxide pigment powders and iron oxide red pigment powders SEM photos before and after dispersion treatment.

![SEM photos](image)
As can be seen from Figure 5 and Figure 6, the pigment powders had a large amount of agglomeration, and the adhesion between particles was serious. After treatment with AHP\textsubscript{47} dispersant, the aggregates decreased obviously and the particle distribution was more uniform.

4. Conclusion
The amphiphilic hyperbranched polyethers (AHPs) with a poly (3-ethyl-3-oxetanemethanol) core and multiple linear poly-(ethylene glycol) arms had good dispersing effect on pigments. When DB was 0.47 and the dosage was 9\%, the dispersing forces of AHP\textsubscript{47} to titanium dioxide and iron oxide red were all more than 95\%. AHPs had the characteristics of low viscosity and no pollution, and had great potential in the application of pigment dispersants.

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6. References
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