Synthesis and Dispersion of Organic Pigments by Amphiphilic Hyperbranched Polyesteramides Dispersant

Qing Xu¹, Shangjun Long², Guohua Liu¹, Xuelin Zhang³ and Yuanjing Zhou²*,

¹Institute of Biology, Guizhou Academy of Sciences, Guiyang 550009, China
²Institute of Analysis and Testing, Guizhou Academy of Sciences, Guiyang 550002, China
³Center for Research and Development of Fine Chemicals of Sun Yat-sen University

*Corresponding author

**Abstract.** The amphiphilic hyperbranched polyesteramides (AHPAs) consisting of hydrophobic hyperbranched polyether cores and hydrophilic poly(ethylene glycol) arms with urethane bonds in the molecular structure were synthesized by solution polymerization in chloroform using hexamethylene diisocyanate (HMDI) as a coupling agent. And their chemical structures were confirmed by FT-IR and ¹³C NMR. Further, the AHPAs were applied to disperse organic pigments and their dispersibilities were investigated. The results showed that AHPAs had good dispersing effect on organic pigments. When the dosage of AHPA was 12% (on the weight of pigment), the dispersing effect of AHPA on phthalocyanine green was the best with the lowest relative settlement rate, viscosity and particle size. The dispersibilities of AHPA on organic pigments were phthalocyanine green > benzidine yellow G > pigment red F5R. AHPAs have the characteristics of high solubility, low viscosity, good rheological properties and no pollution and would be the ideal materials for using as the pigment dispersants.

1. Introduction

Hyperbranched polymers with a three-dimensional dendritic architecture exhibiting special properties have aroused extensive attention. Especially, there are a large number of terminal functional groups in their molecular structures. By modification of these end-groups, the properties of hyperbranched polymers such as glass transition temperature, solubility, melt viscosity and surface properties are significantly modulated to define mainly possible applications [1-5]. In recent year, the emergent applications of hyperbranched polymers including biomedicine, electrical conductivity, chemical sensing, and catalyst carrier have been explored successfully [6-9].

Organic pigments have the characteristics of small particle size, large specific surface area and low polarity. In order to give full play to the coloring effect of organic pigments, measures must be taken to make them uniformly and stably disperse in the medium. Traditional organic small molecules or inorganic dispersants show effective dispersing effect in the medium, but they do not adsorb firmly on the surface of organic pigment particles, and the long-term stability of the system is not good. They also have adverse effects on the appearance, hardness and aging resistance of the paint film [10, 11]. A series of amphiphilic hyperbranched polyethers (AHPs) with different branching degrees were synthesized in our previous work and applied as pigment dispersant on pigment yellow with good dispersing effect [12]. Here, we prepared their derivatives (AHPAs) through modification of end groups and applied them to organic pigments. Their dispersibility to organic pigments was investigated.
2. Experimental

2.1. Reagents and Instruments
All chemical reagents used in this study were bought from Sinopharm Chemical Reagent Co., Ltd and were of the highest purity available. Methoxy polyethylene glycol (mPEG, Mn=600, 1000, 2000) was dried by azeotropic distillation with benzene. CH₂Cl₂ and CHCl₃ were dried by distillation in presence of CaH₂ under reduced pressure.

Fourier transform infrared spectroscopy (FT-IR) tests were conducted on a Spectrum 100 FT-IR spectrometer (Perkin-Elmer, US) using KBr discs. ¹³C NMR spectra were recorded on a Varian MERCURY plus 400 NMR spectrometer operating at 100 MHz.

2.2. Synthesis of Amphiphilic Hyperbranched Polyesteramides (AHPAs)
By two-step reactions, AHPAs were synthesized. First, the hydroxyl end-group of mono methoxy polyethylene glycol (mPEG) reacted with one NCO group of hexamethylene diisocyanate (HMDI) to obtain the isocyanate-terminated intermediate (mPEG-NCO). And then, the unreacted other NCO group in the mPEG-NCO reacted with the hydroxyls of HP to obtain the amphiphilic hyperbranched polyesteramide. The detailed synthesis process was described as below.

2.2.1 Synthesis of mPEG-NCO. Methoxy polyethylene glycol (mPEG1000, 27 g) was dissolved in dry CH₂Cl₂ (80 mL). Under nitrogen, the reactor was heated to 40 °C in an oil bath, and then hexamethylene diisocyanate (HMDI) (48 mL) was slowly added by a drip funnel. After 8 h, the reaction mixture was precipitated in petroleum ether and filtered to obtain the light yellow intermediate mPEG-NCO. FT-IR (KBr, cm⁻¹): 3440, 2890, 2270, 1715, 1540, 1110, 848, 755.

2.2.2 Synthesis of hyperbranched polyesteramides (AHPAs). HP was synthesized by cation ring-opening polymerization according to the previous report [12]. Under nitrogen, the HP was dissolved in dry CHCl₃. After the reactor was heated to 50 °C, mPEG-NCO in dry CHCl₃ was slowly added into the reactor by a drip funnel. When the reaction went on for 12 h, the reaction product was precipitated in alcohol and filtered to obtain the yellow waxy solid. FT-IR (KBr, cm⁻¹): 3438, 2885, 1715, 1540, 1110, 848, 752. ¹³C NMR (100 MHz): δ (ppm) 7.9 (–CH₃), 22.8 (–CH₂–), 43.5 (–C), 63.0 (–CH₂OH), 67.0–72.0 (–CH₂–O–CH₂–).

2.3. Preparation of Pigment Dispersion System
A certain amount of pigment AHPA and deionized water were 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.

2.4. Determination of Dispersion Performance
The dispersion stability, viscosity and particle size of dispersion system were determined.

2.4.1 Dispersion stability. Place the dispersed pigment system on the test tube rack, observe the settlement, record the location of the suspension settlement at intervals, and calculate the relative settlement rate (R) as following (1) [13].

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

In the formula (1): h means settlement height (mm), H means total height (mm).

2.4.2. Viscosity. The viscosity of dispersed pigment system was measured by Brookfield digital viscometer at room temperature.
2.4.3 Particle size. The particle size of dispersion system was measured by ZS-90 Nano particle analyzer at room temperature.

3. Result and Discussion

3.1. Synthesis and Characterization of Amphiphilic Hyperbranched Polyesteramides (AHPAs)

The synthetic route of AHPAs was shown in Scheme 1. By controlling the reaction temperature and the amount of reactants, one NCO group of HMDI was first introduced onto the hydroxyl end-group of mono methoxy polyethylene glycol (mPEG) to obtain the isocyanate-terminated intermediate (mPEG-NCO). And then, the other unreacted NCO group of mPEG-NCO was grafted onto the hydroxyls of HP.

Scheme 1. Synthetic routes of amphiphilichyperbranched polyesteramides (AHPAs).

Figure 1 gave the FT-IR spectra of mPEG-NCO and AHPA. The FT-IR spectrum of mPEG-NCO (Figure 1(a)) showed a strong hydroxyl peak at 3440 cm⁻¹ for hydroxyl, a strong absorption peak at around 2890 cm⁻¹ for methyl and methylene groups, a sharp peak at about 2270 cm⁻¹ for NCO groups, a sharp peak at 1715 cm⁻¹ for C=O groups, at 1540 cm⁻¹ for NH groups, at 1110 cm⁻¹ for ether bonds.
By grafting mPEG-NCO onto HP, the NCO peak at 2270 cm\(^{-1}\) disappeared in the FT-IR spectrum of AHPA (Figure 1(b))\(^{[11]}\), which meant that the NCO group had been changed into the carbonate group, and the absorption of amide NH groups at 1540 cm\(^{-1}\) and ether bonds at 1100 cm\(^{-1}\) were retained. These results suggested that graft hyperbranched polyesteramides, AHPAs, were formed via the reactions of the two NCO groups of HMDI with hydroxyls of mPEG and HP, respectively.

![Figure 1. FT-IR spectra of mPEG-NCO (a), AHPA (b).]

The chemistry structure of AHPAs was further confirmed by the \(^{13}\)C NMR measurement. As shown in Figure 2, the triple peaks at around 43.7 ppm represented linear unit (L), dendritic unit (D) and terminal unit (T) of hyperbranched polymer, respectively. The characteristic mPEG carbons from the polymerized methylenes were seen at about 71.2 ppm. These results indicated the formation of the graft hyperbranched polyesteramides (AHPAs)\(^{[12]}\).

![Figure 2. \(^{13}\)C NMR spectrum of AHPA in CDCl\(_3\).]

3.2. Dispersion Stability
Settlement method is the most direct and simple method to observe the stability of dispersed systems\(^{[13]}\). Figure 3 showed the change of relative settlement rate (R) with natural settlement time. The
smaller the relative settlement rate, the better the dispersion. The relative sedimentation rate of the sample with dispersant (S1, S2) was obviously lower than that of the sample without dispersant (S0). Figure 4 showed the change of relative settlement rate with addition of dispersant. When the dosage of dispersant increased, the relative settlement rate of the system decreased first, and then increased. 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 unsteadily. 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.

3.3. Viscosity
Dispersants can not only maintain the dispersion stability of the pigment system, but also reduce the viscosity of the system. As can be seen from Figure 5, the addition of dispersant significantly reduced the viscosity of pigment system. However, with the increase of dispersant dosage, the viscosity of the system increased inversely. Therefore, the dosage of dispersant in the dispersion system was not the higher the better, which was consistent with the experimental results of sedimentation (Figure 3).
3.4. Particle Size
Figure 6 showed the effect of AHPA on the particle size of different pigment system. The particle size of phthalocyanine green, benzidine yellow G, and pigment red F5R was around 180, 205, and 250 nm, respectively. This is related to the molecular structure of pigments themselves, the molecular structure of dispersants, and the interaction between pigments and dispersants.

4. Conclusion
By solution polymerization using hexamethylene diisocyanate as a coupling agent, the amphiphilic hyperbranched polyesteramides (AHPAs) consisting of hydrophobic hyperbranched polyethers cores and hydrophilic poly(ethylene glycol) arms with urethane bonds in the molecular structure were synthesized. Being used as the pigment dispersant, AHPAs had good dispersing effect on organic pigments, and had great potential in the application of pigment dispersants. Further research will continue.

Acknowledgments
This work was financially supported by the Science and Technology Project of Guizhou Province, China ([2016]1139, JZ [2015]2006, Z [2015]6013), and [2017]01).

References
[1] Huang Y, Wang ST and Zhu XY 2017 Acta Polym. Sin. 2245
[2] Mahmoodi Y, Dodel T, Moieni M, Hasanzadeh M, Horak D, Haghi A and Zaikov G 2014 Key Engineering Materials 1133
[3] Zhang J, Xie S, Zhang X, Lu Z, Xiao H, Li C, Li G, Xu X, Chen X and Bo Z 2017 Chem. Commun. 53537
[4] Mu B, Liu T T AND Tian W 2018 Macromol. Rapid Comm. e1800471
[5] Qi M, Huang W, Xiao G, Zhu X, Gao C and Zhou Y 2017 Acta Polym. Sin. 2 214
[6] Gurunathan T, Mohanty S and Nayak, S K 2016 Polym-Plast Technol. 55 92
[7] Tirthankar J 2016, Paintindia 66 59
[8] Nabae Y and Kakimoto M A 2018 Polymers 12 10
[9] Han J R, Liu T, Zhang S, Hao C, Xin J N, Guo B H and Zhang J W 2019 Ind. Eng. Chem. Res. 16 6466
[10] Rojin B and William P 2018 Paint & Coatings Industry 4 86
[11] Nagose S, Rose E and Joshi A 2019 Prog. Org. Coat 33 55
[12] XuQ, Zhou YJ, Long S J, Liu Y G and Li J H 2017 Materials Science and Engineering 292 12109.
[13] Liu A H, Wu B Y and Jiang Z D 1996 Coatings Industry 4 7