Synthesis and properties of amphiphilic hyperbranched polyethers as pigment dispersant

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Abstract. Hyperbranched polymers possess prominent properties such as low viscosity, good solubility, high rheological property, environmental non-toxic,and so on, which have potential applications in coatings. In this study, the amphiphilic hyperbranched polyethers (AHPs) consisting of hydrophobic hyperbranched polyethers core and hydrophilic poly (ethylene glycol) arms with different degree of branching (DB) under various reaction temperatures was prepared by the cation ring-opening polymerization. Their structures were characterized by IR, ^{13}CNMR and GPC. Their dispersion properties for pigment particles were investigated. The AHP_{47} with 0.47 DB was found to have good dispersion properties for Yellow HGR. This work would provide experimental data and theoretical foundation for the application of hyperbranched polyethers in environmental protection coating.

1. Introduction

Coating pigment particles are prone to form agaggregates because of their high surface energy, which affected seriously the quality of the coating. To make use of high-quality dispersant in pigment dispersing process is the best strategy. Dispersants play a very important role in the production of coatings. The stability of the dispersion system can avoid many coating problems and coating film defects. If the formula is reasonable, adding dispersant properly can effectively reduce the cost and improve the coating performance. Good pigment dispersant can have the following functions: (1) enhancing the luster and increasing the effect of levelling; (2) preventing floating; (3) improving the tinting strength; (4) reducing viscosity and increasing pigment loading; (5) reducing the flocculation; (6) preventing back coarse and increasing the storage stability; (7) increasing the colour saturation; (8) increasing transparency (organic pigment) or covering power (inorganic pigment); (9) improving the grinding efficiency and reducing production cost; (10) prevent sedimentation [1, 2].

Hyperbranched polymers with a special topological structure possess many unique and useful properties, such as high degree of branching (DB), lack of chain entanglement, high solubility, low melting point and low solution viscosity [3-5]. They have received considerable attention in recent years, and have potential applications in coatings [6, 7]. In this paper, a series of hyperbranched polyethers with different DB were synthesized under various reaction temperatures, and the amphiphilic hyperbranched polyether with a poly(3-ethyl-3-oxetanemethanol) core and multiple linear poly-(ethylene glycol) arms (AHP) was obtained as the pigment dispersant. Their structures and dispersion properties for pigment particles were investigated. It would be helpful to promote the hyperbranched polyethers for applying in environmental protection coating.

2. Experimental

2.1. Reagents and methods

Boron trifluoride etherate $BF_3O(C_2H_5)_2$ was purchased from Fluka. All other chemical reagents used in this experiment were obtained from commercial sources and were of the highest purity available. CH_2Cl_2 was dried by distillation in presence of CaH_2 under reduced pressure. Fourier transform infrared spectroscopy (FTIR) tests were conducted on a Spectrum 100 FTIR spectrometer (PerkinElmer, US) using KBr discs. ^{13}C NMR spectra were recorded on a Varian MERCURYplus 400 NMR spectrometer operating at 100 MHz. Molecular weight distributions were determined by using gel permeation chromatography (GPC) on Waters 2690 separations module using a waters 2410 refractive index detector with THF as an eluentand polystyrene as calibration standards. The viscosity was measured by Brookfield digital viscometer. The sagging test was carried out the sagging coating machine with 50-270 μm film thickness.

2.2. Synthesis and characterization

The synthetic route of amphiphilic hyperbranched polyether (AHP) was shown in figure 1. According to the reaction formula, the detailed synthesis process was described as below.

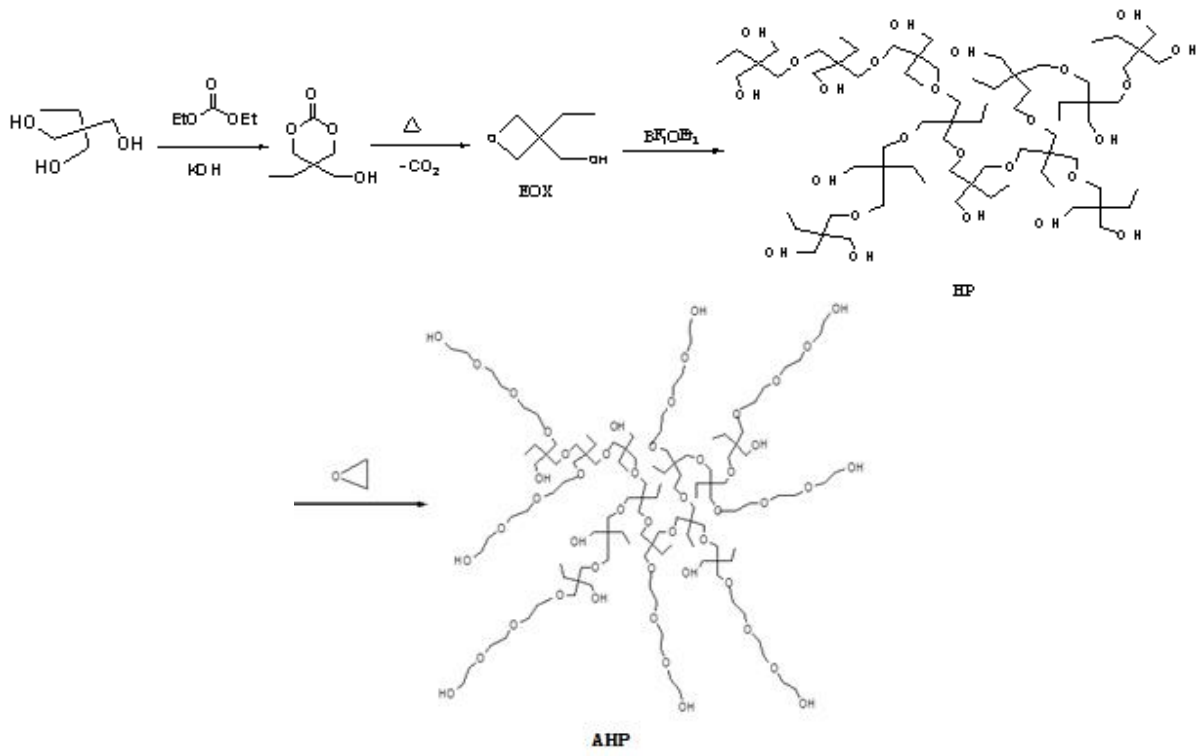

Figure 1. Synthetic routes of amphiphilic hyperbranched polyether (AHP)

2.2.1. Synthesis of 3-ethyl-3-oxetanemethanol (EOX). 3-Ethyl-3-oxetanemethanol (EOX) was prepared from trimethylolpropane according to the previous report with minor modifications [8]. Briefly, trimethylolpropane (26.8 g), diethyl carbonate (23.6 g) and potassiumhydroxide (10 mg) dissolved in absolute alcohol (0.5 mL) was refluxed at 105°C for 4h, and the mixture was heated above 180°C for 2h. The crude product was subjected to reduced pressure distillation, and the pure product (EOX) was obtained as a fraction boiling at 84–84.5 °C at 2.8 mmHg.FT-IR (cm^{-1}): 3413 (O-H), 2958, 2875 (C-H), 1050 (C-O), 976 (C-O-C).

2.2.2. Synthesis of hyperbranched polyethers (HPs). HPs were synthesized by cation ring-opening polymerization according to the previous report with minor modifications [9, 10]. Into a four-necked round-bottomed flask equipped with a PTFE stirrer, a funnel and a thermometer, nitrogen was flowed for 30 min to expel the oxygen from the system, then 80 mL of solvent CH_2Cl_2 and 6.4 mL of catalyst $BF_3O(C_2H_5)_2$ (0.05 mol) were added via syringe, espectively. The monomer EOX (0.1 mol, 11.6 mL) was introduced through the funnel within 10 min, and the reaction temperature was kept constant throughout the polymerization process. The polymerization was quenched with ethanol after 48 h. Then the mixture was precipitated into distilled water and immersed overnight. Finally, the resulting solid was obtained by filtration and then dried at 80°C under high vacuum. The same reaction was repeated at different temperatures. The samples prepared at 0°C, 10°C, 30°C and 50°C were named as HP_{35}, HP_{41}, HP_{47} and HP_{51}, respectively, according to the DB value. FT-IR (KBr, cm^{-1}): 3450, 2956, 2927, 2877, 1471, 1383, 1105, 1048, 752. ^{13}C NMR (100 MHz): δ (ppm) 7.9 (–CH_3), 22.8(–CH_2–), 43.5(–C), 63.0 (–CH_2OH), 67.0– 72.0 (–CH_2–O–CH_2–).

2.2.3. Synthesis of amphiphilic hyperbranched polyethers (AHPs). HP and ethylene oxide were stirred for 24 h, and the hyperbranched polyether with a poly(3-ethyl-3-oxetanemethanol) core and multiple linear poly-(ethylene glycol) arms was obtained. FT-IR (KBr, cm^{-1}): 3347, 2958, 2930, 2881, 1480, 1385, 1111, 1050, 758. ^{13}C NMR (100 MHz): δ (ppm) 7.9 (–CH_3), 23.5 (–CH_2–), 43.7(–C), 62.0 (–CH_2OH), 67.0– 73.0 (–CH_2–O–CH_2–).

3. Result and discussion

3.1. DB analysis

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. DB is expressed below in equation (1) [11]. L, D and T represent linear unit, dendritic unit and terminal unit, respectively.

$$DB = \frac{D+T}{D+T+L} \qquad (1)$$

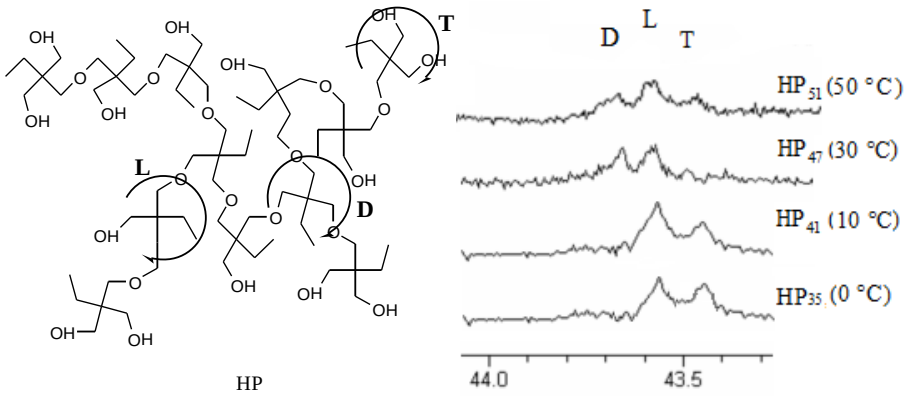

Figure 2. Structure of HP and ^{13}C NMR spectra of HP for the variation of the three peaks near 43.5 ppm in detail.

From figure 2, it showed in more detail the magnified signal region near 43.5 ppm in ^{13}C NMR spectra, which was attributed to quaternary carbon atoms of the D, L and T. [12] The DB value can be calculated by integrating the signals of different quaternary carbon atoms. The DB values for the samples prepared at 0°C, 10°C, 30°C and 50°C were 0.35, 0.41, 0.47, and 0.51, and the sample was labelled respectively HP_{35}, HP_{41}, HP_{47} and HP_{51}, which showed that the DB increased with increasing

reaction temperature. That is, the structure of the resulting polyether depends on the reaction temperature: at low temperature, the linear addition is preferred, which leads to mostly linear products; at higher temperatures, the addition reaction becomes a random process resulting in hyperbranched polymers, which are consistent with previous reports [9, 10].

3.2. GPC analysis

The molecular weights of amphiphilic hyperbranched polyethers (AHPs) were determined by gel permeation chromatography (GPC), and the result was listed in table 1. As seen from the table, the weight average molecular weight (Mw) of the AHP varied from 2300 to 3400, and showed unregularity.

Table 1. The synthesis condition and characterization data of AHP.

Sample	T (°C)	Yield (%)	DB	Mw
HP_{35}	0	83	0.35	3037
HP_{41}	10	85	0.41	3379
HP_{47}	30	90	0.47	2385
HP_{51}	50	88	0.51	2655

3.3. Dispersion performance analysis

Pigments are usually insoluble in the used medium, and mostly in the form of aggregates. In order to obtain good coloring power, transparency, chromaticity, and so on, the aggregate of pigment must be prevented. If the pigment does not have good dispersion, many defects are likely to occur, such as flocculation, loss of light, color offset, floating, sedimentation, etc. In this paper, the viscosity, color and sagging performance were discussed. Table 2 showed the dispersion performance of AHPs for Yellow HGR in xylene and propylene glycol methyl ether acetate. It showed that AHP with different DB had different dispersion performance for Yellow HGR. The AHP_{47} with 0.47 DB owned the lowest viscosity and good color, and the sagging began from 150 μm film thickness, which was superior to other AHPs.

Table 2. The dispersion performance of AHPs on the Yellow HGR.

Sample	Viscosity (5rpm, cps)	Viscosity (50rpm, cps)	Color	Sagging (μm)
AHP_{35}	1668	1078	too light	75
AHP_{41}	1179	803	consistent	88
AHP_{47}	896	457	good	150
AHP_{51}	995	769	light	100

As previously reported that the structure of dispersing agent had important influence on the dispersion of pigment [13-16], the AHP_{47} with medium DB and lowest Mw among the products of AHP (figure 2) might interact with pigment particles better, and improve the dispersion performance. As seen from the table 2, the AHP_{47} could obviously reduce the viscosity of the color paste obtained, thus the loading capacity of the pigment could be increased and the production efficiency could be improved.

4. Conclusion

The amphiphilic hyperbranched polyethers (AHPs) with a poly(3-ethyl-3-oxetanemethanol) core and multiple linear poly-(ethylene glycol) arms were synthesized by simple and easy chemical reaction

method. The AHPs owned good dispersion performance for coating pigment particles. Among the products of AHP, AHP_{47} with 0.47 DB had good potentiality in coating applications. The further study is underway.

Acknowledgments
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