Synthesizing Hyperbranched Azo Polymer through Azo-coupling Reaction

Pengchao Che, Yaning He, Yue Zhang, and Xiaogong Wang*
Department of Chemical Engineering, School of Materials Science and Engineering, Tsinghua University, Beijing 100084, P. R. China

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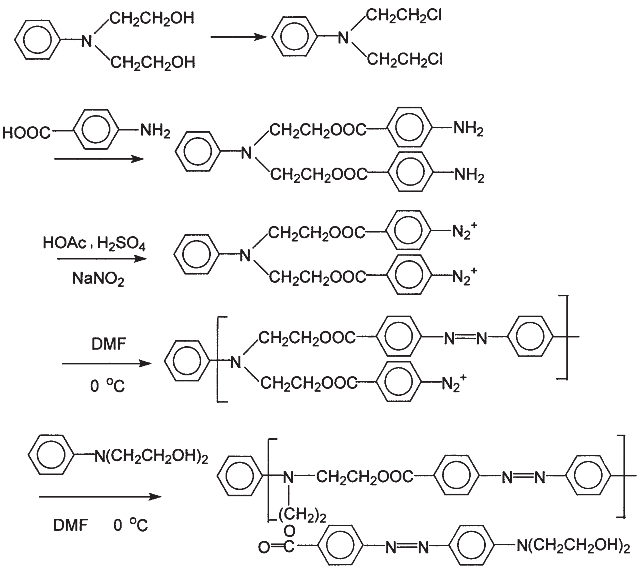
An AB_2 monomer *N*,*N*-bis[2-(4-aminobenzoyloxy)ethyl]aniline was synthesized by nucleophilic substitution reaction between *N*,*N*-bis(2-chloroethyl)aniline and 4-aminobenzonic acid. Based on the monomer, the azo-coupling reaction was explored for the first time to prepare a hyperbranched azo polymer. The results showed that the scheme was a feasible way to synthesize hyperbranched azo polymers under extremely mild conditions.

Hyperbranched polymers (HBPs) have attracted considerable attention in recent years.[1] HBPs possess unique properties of dendritic polymers such as high solubility, low solution and melt viscosity compared to linear analogues, and amorphous nature in solid state. Existence of a large number of end functional groups enables HBPs to react with other reactive groups and to significantly modify properties of the polymers. HBPs are generally prepared from AB_x (where x is usually 2 or 3) monomers through a one-step polymerization process.[2] Polycondensation reactions have been widely used for preparing HBPs, in which strict reaction conditions such as high temperature and vacuum are required.[3] Linear azo polymers have been extensively studied in recent years for a wide range of applications such as reversible optical storage systems, EO modulators, holographic gratings and sensors. However, up to now, only few hyperbranched azo polymers have been synthesized.[4] In a previous paper, we reported a way to obtain azobenzene-containing HBPs through the esterification reaction.[5] In this letter, we further report that azo coupling reaction was used to synthesize an azobenzene-containing HBP. To our knowledge, no HBPs or even linear polymers have been prepared through this route.

The hyperbranched polymer was prepared through the route shown in Scheme 1. *N*,*N*-bis(2-chloroethyl)aniline was synthesized by the reaction between *N*,*N*-bis(2-hydroxyethyl)aniline and phosphorus oxycholride. In the reaction, *N*,*N*-bis(2-hydroxyethyl)aniline (10 g, 0.055 mol) was added slowly into phosphorus oxychloride (10.2 mL, 0.11 mol) under ice-bath cooling. After the addition was completed, the mixture was heated to 110 °C and reacted at that temperature for 1 h. The solution was then poured into benzene (50 mL). After repeatedly washed with water and then dried by using anhydrous magnesium sulfate, the product was finally obtained by removing the benzene. Yield: 82%. ^1H NMR (DMSO-d_6), $\delta = 7.20$ (2H, m), 6.67 (3H, m), 3.72 (8H, t). mp: 43 °C.

N,*N*-Bis[2-(4-aminobenzoyloxy)ethyl]aniline was prepared by nucleophilic substitution reaction between *N*,*N*-bis(2-chloroethyl)aniline and 4-aminobenzonic acid. In the reaction, *N*,*N*-bis(2-chloroethyl)aniline (1.308 g, 6 mmol) and 4-aminobenzonic acid (2.888 g 2.4 mmol) were dissolved in DMSO (80 mL). Potassium carbonate (8 g) and potassium iodide (2 g) were added into the DMSO solution. The mixture was reacted at 110 °C for 7 h with stirring and then precipitated into an excessive amount of water. The product was collected by filtration and dried under vacuum at 70 °C for 24 h. Yield: 80%, mp = 160 °C. The ^1H NMR spectrum (DMSO-d_6) of the compound and assignment are given in Figure 1a.



Scheme 1.

The hyperbranched polymer was prepared by azo coupling reaction. The *N*,*N*-bis[2-(4-aminobenzoyloxy)ethyl]aniline (0.520 g 1.4 mmol) was dissolved in a homogeneous mixture of glacial acetic acid (11.2 mL) and sulfuric acid (1.0 mL). Aqueous solution of sodium nitride (0.242 g 3.5 mmol in 0.6 mL of water) was added dropwise into the solution at 0 °C. Then the clear solution of diazonium salt was added into DMF (40 mL) and stirred at 0 °C for 8 h. After the reaction, a solution of *N*,*N*-bis(2-hydroxyethyl)aniline (0.253 g 1.4 mmol in 10 mL of DMF) was added into the solution and kept in 0 °C with stirring for 5 h, which enabled the remaining diazonium salt groups on the periphery to be completely reacted through azo coupling reaction. The mixture was then poured into an excessive amount of water. The precipitate was collected by filtration, washed repeatedly with water, and dried. The product was dissolved in DMF (20 mL) and then dropped into ethanol slowly with stirring. The precipitate was collected by filtration, washed repeatedly with ethanol, and dried under vacuum at 70 °C for 48 h. Yield: 60%.

The ^1H NMR spectrum of the hyperbranched azo polymer and assignment are shown in Figure 1b. The resonance ($\delta = 6.62$ ppm, Figure 1a) corresponding to anilino moieties at the focal points can no longer be observed from the ^1H NMR spectra of the final products, which indicates a high reaction yield. The UV–vis spectrum of the hyperbranched azo polymer in DMF solution is shown in Figure 2. The spectrum shows typical absorption behavior of the pseudo-stilbene type of azo chro-

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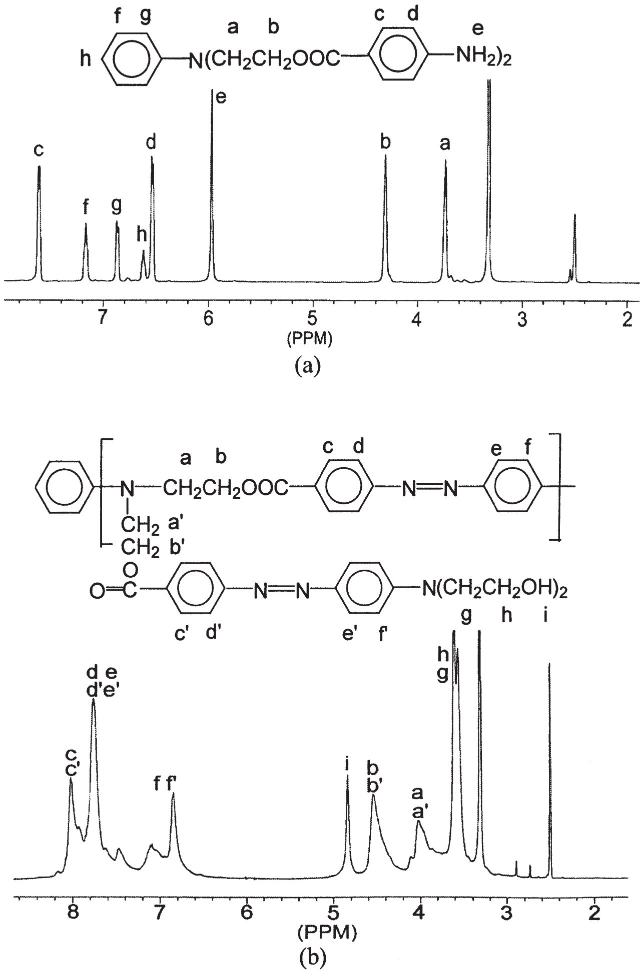

Figure 1. ^{1}H NMR spectrum of monomer (a) and hyperbranched azo polymer (b) in DMSO-d_6.

mophores, which confirms the polymerization carrying out through the formation of the azobenzene units. The number-average molecular weight of the hyperbranched polymer and the polydispersity index were estimated to be 7074 and 1.5, respectively by GPC. The Tg of the polymer obtained from the DSC curve was 106 °C. The hyperbranched azo polymer can be very well dissolved in the solvents such as DMF and NMP and can be dissolved in chloroform with a limited solubility. However, it cannot be dissolved in alcohols such as methanol. The degree of branching (DB) proposed by Frechet has been used to characterize the ratio of dendritic units to linear units in hyperbranched polymers.[3] In current case, the resonances corresponding to dendritic units and linear units can not be well distinguished from the ^{1}H NMR spectrum (Figure 1b). As suggested by Frey, DBs of hyperbranced polymers formed from the one-pot polymerizations of AB_2 monomers tend to be close 0.5.[6] The

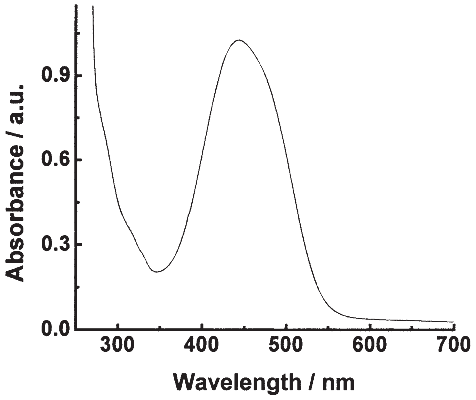

Figure 2. UV–vis spectrum of hyperbranched azo polymer in DMF.

results suggest that the polymer with high molecular weight has been successfully synthesized through azo coupling reaction. Compared with the polycondensations used to synthesize hyperbranched polymers, the scheme reported in this work shows advantages for not using strict reaction conditions such as high temperature and vacuum.

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