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Synthesis, characterization and TG-DTA study of diethyl 5-(4-hydroxyethoxyphenylazo)isophthalate

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Abstract A novel AB_2-type monomer diethyl 5-(4-hydroxyethoxyphenylazo)isophthalate for preparing hyperbranched azo polymers (HBPAZO) was synthesized. The monomer obtained was characterized by IR spectra, UV–Vis spectra, ^1H NMR spectrum and C NMR spectrum. The TG-DTG/DTA curves show that the decomposition of the monomer proceeds in four steps. During the second-step decomposition, the mass loss occurs between 480.5 K and 579.0 K and the phenomena of condensing to HBPAZO for the melted monomer was found. So it is inferred that this temperature range is the best for polycondensation of the melted monomer, which is very important for synthesizing of HBPAZO.

Keywords Diethyl 5-(4-hydroxyethoxyphenylazo) isophthalate · Synthesis · Characterization · Thermal decomposition · TG-DTG/DTA

Introduction

In recent years, azobenzene-containing hyperbranched polymers (HBPAZO) have been extensively investigated [1–8] due to their potential applications such as liquid crystal displays and devices, reversible optical storage systems, nonlinear optical waveguides, photorefractive switches, and holographic gratings [9–12]. A good monomer is very important for obtaining hyperbranched polymers with excellent performance. Diethyl 5-(4-hydroxyethoxyphenylazo)isophthalate, whose structure formula is shown in Fig. 1, is a novel AB_2-type monomer for preparing HBPAZO. To our knowledge, synthesis and thermal property of this monomer has not been investigated so far. In this article, we reported the synthesis of the novel AB_2-type monomer. The structure of the monomer was confirmed by IR, UV–Vis, ^1H NMR and C NMR. The thermal behavior of the monomer was studied by TG-DTA.

Experimental

Chemicals and materials

Chloroform and tetrahydrofuran (THF) were used after distillation over P_2O_5 and sodium, respectively. Other solvents and reagents were used directly as purchased without further purification.

Material preparation

The synthetic stages of diethyl 5-(4-hydroxyethoxyphenylazo)isophthalate was shown in Scheme 1. Isophthalic acid (16.6 g, 0.2 mol) and concentrated sulfuric acid (32 mL)

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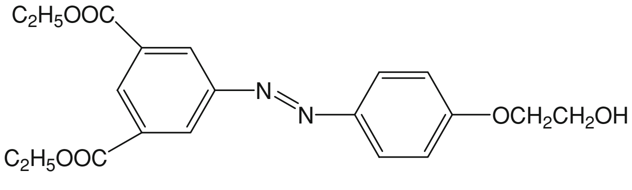
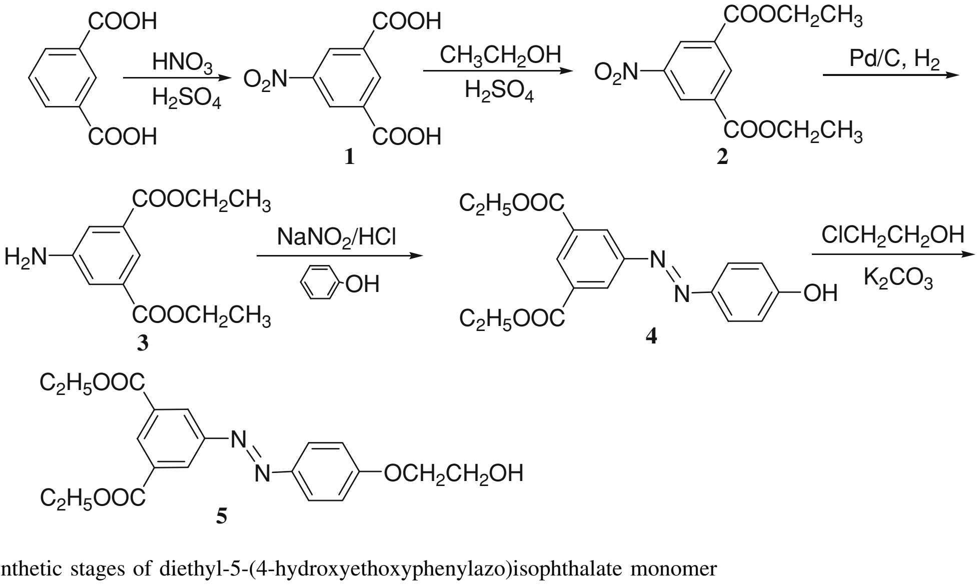


Fig. 1 Structure formula of diethyl 5-(4-hydroxyethoxyphenylazo)-isophthalate

were added to a 250 mL three-neck flask equipped with reflux condenser and mechanical stirrer. The mixture was stirred at 333 K for10 min. 65% nitric acid (22 mL) was added and the temperature of the solution was raised to 356 K and kept the temperature for 1 h. Then the mixture was poured into brash ice. The solid obtained was filtered and recrystallized from water to give 5-nitrylisophthalic acid (compound 1). Melting point: 533–534 K. Yield: 83.4%. Compound 1 (2.11 g, 0.01 mol), ethanol (20 mL) and concentrated sulfuric acid (3 mL) were added to a 100 mL round-bottom flask equipped with reflux condenser. The mixture was heated under reflux for 20 h, and on cooling to room temperature, the crude product crystallized from the ethanol solution as a white solid. The solid was recovered by filtration, washed with cold water, and recrystallized from ethanol to yield diethyl 5-nitro-isophthalate (compound 2). Melting point: 358–359 K. Yield: 82.6%. Compound 2 (2.67 g, 0.01 mol), 10% Pd/C catalyst (0.2 g), absolute ethyl alcohol (10 mL) and tetrahydrofuran (10 mL) were placed a 50 mL conical flask with a magnetic stirrer and a hydrogen gas inlet. The reaction mixture was stirred at the same time hydrogen was added. The Pd/C catalyst was removed by filtering until the hydrogen was not been consumed. The filtrate was poured into water and the solid obtained was filtered and recrystallized to afford diethyl 5-amino-iaophthalate (compound 3). Melting point: 390–391 K. Yield: 94.1 %. Compound 3 (1.0 g, 0.0054 mol), water (10 mL) and hydrochloric acid (1.3 mL) were placed a 100 mL conical flask with a magnetic stirrer. The reactive substrate was cooled to 273 K and 3.12 mol L^{-1} $NaNO_2$ was added slowly with stirring for 15 min to obtain clarifying diazosalt solution. 0.18 mol L^{-1} sodium phenate was added to the diazosalt solution obtained above. The reaction was conducted at 273 K with stirring for 30 min. The reaction mixture was filtered, washed with ethanol and recrystallized with 5% NaCl solution. The product of diethyl 5-(4-hydroxyphenylazo)isophthalate (compound 4) was obtained. Melting point: 425–426 K. Yield: 92.5%. To a 50 mL round-bottomed flask equipped with a reflux condenser and a thermometer were added compound 4 (0.86 g, 0.0025 mol), chlorethanol (3 mL), K_2CO_3 (0.69 g), KI (0.2 g) and DMF (15 mL). The reaction was conducted for 7 h. After reaction the reactive mixture was poured into 400 mL water. The solid obtained was filtered, washed and recrystallized with CCl_4. The AB_2-type monomer, diethyl 5-(4-hydroxyethoxyphenylazo)isophthalate (compound 5) was obtained. Melting point: 392.4–393.0 K. Yield: 93.9%.

Methods of characterization

The ^{1}H NMR spectrum and the C HNMR spectrum were obtained on a Bruker AV 500 MHz spectrometer. The IR spectra were measured on an IR spectrophotometer (Bruck



Scheme 1 The synthetic stages of diethyl-5-(4-hydroxyethoxyphenylazo)isophthalate monomer

Equinox 55) using the KBr pellet technique. The UV–Vis spectra of the monomer were recorded by a Shimadzu UV-240 spectrometer in THF solutions.

The thermal decomposition of the monomer was investigated with Perkin Elmer Diamond TG/DTA from room temperature to 1073 K at a heating rate of 10 K min^{-1} under nitrogen atmosphere. Alumina crucibles were used in this experiment.

Results and discussion

Structure characterization of diethyl 5-(4-hydroxyethoxyphenylazo)isophthalate

The ^{1}H NMR spectrum and the C NMR spectrum of the obtained monomer and the assignment of the resonance peaks at different position are shown in Fig. 2.

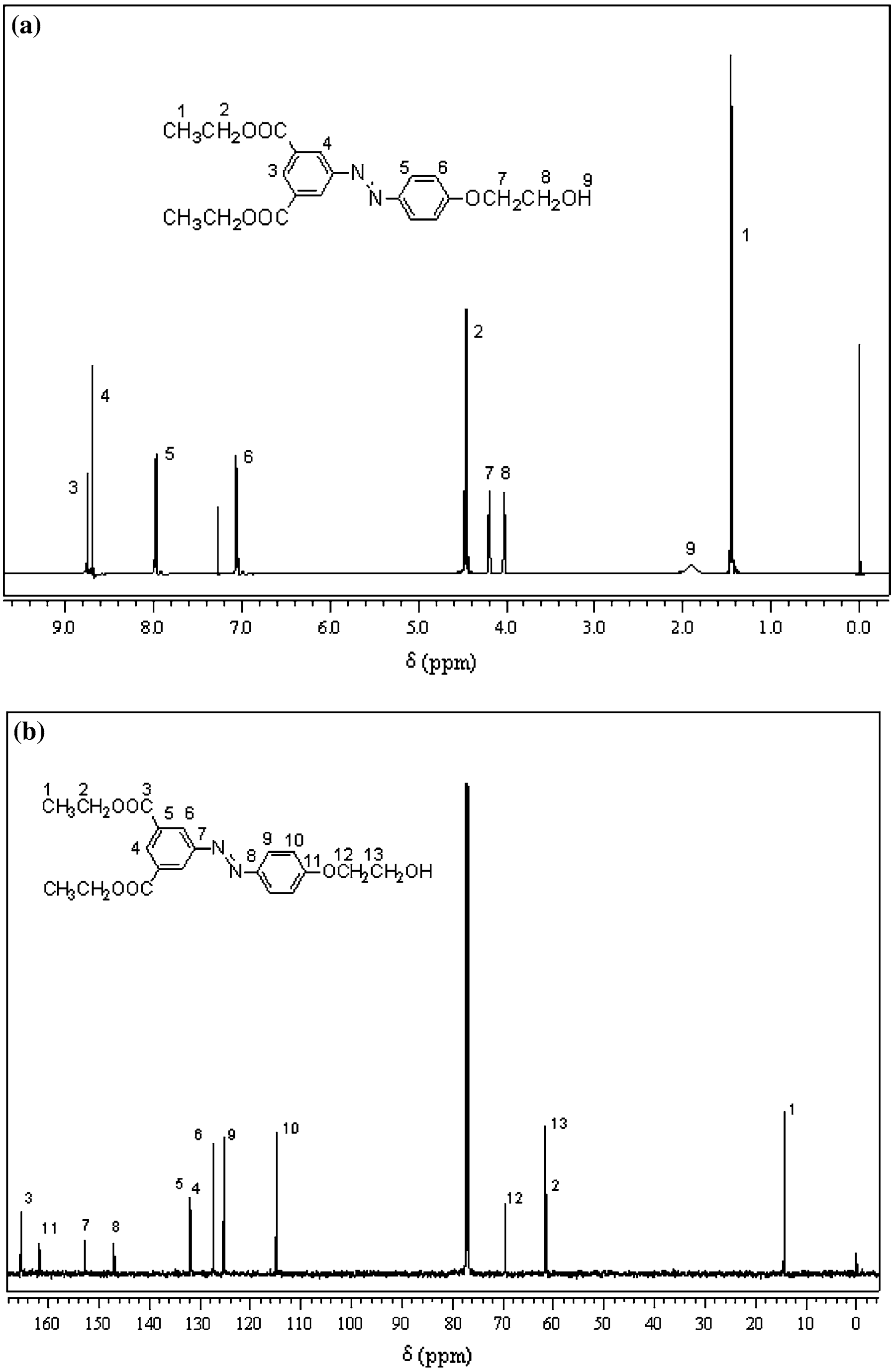


Fig. 2 ^{1}H NMR spectrum (**a**) and C NMR spectrum (**b**) of diethyl 5-(4-hydroxyethoxyphenylazo)isophthalate

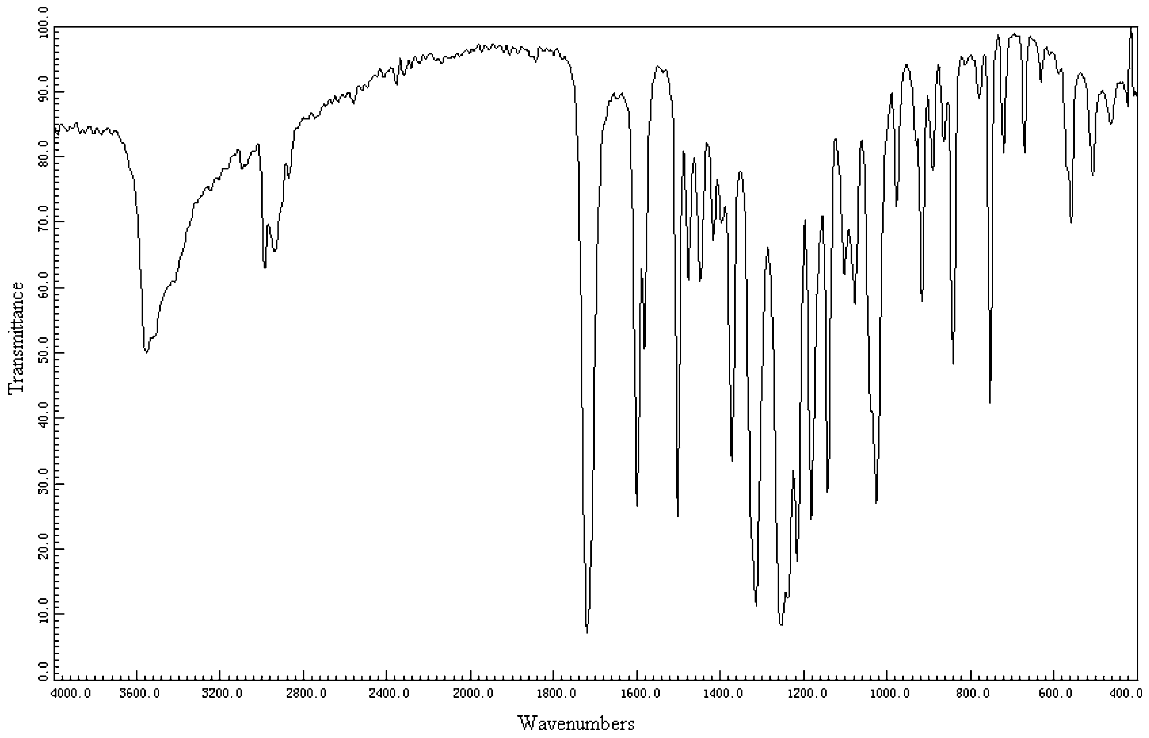


Fig. 3 IR spectra of diethyl 5-(4-hydroxyethoxyphenylazo)isophthalate

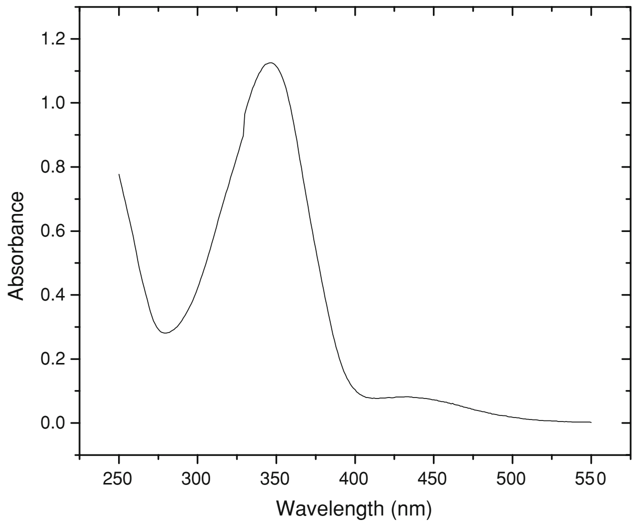


Fig. 4 UV–Vis spectra of diethyl 5-(4-hydroxyethoxyphenylazo)-isophthalate

Figure 3 gives the IR spectra of this monomer. The assignment of the vibration peaks is as follows: 3548 cm^{-1} (v–OH), 3096 cm^{-1}(Ar–H), 2984 cm^{-1} and 2940 cm^{-1} (–CH_2, –CH_3), 1720 cm^{-1}(C=O), 1600 cm^{-1}, 1580 cm^{-1}, 1502 cm^{-1} and 1478 cm^{-1}(Ar), 1252 cm^{-1} and 1142 cm^{-1}(–C–O–C–), 842 cm^{-1} and 752 cm^{-1}(–Ar).

Figure 4 shows the UV–Vis spectra of this monomer in the $CHCl_3$ solution. The curve shows typical absorption behavior of the azo chromophores, e.g. band corresponding to the π–π^* transition exhibits strong absorption at about 346 nm and band corresponding to the n–π^* transition displays week absorption at about 444 nm.

Thermal decomposition of diethyl 5-(4-hydroxyethoxyphenylazo)isophthalate

The TG-DTG curves of the diethyl 5-(4-hydroxyethoxyphenylazo)isophthalate monomer are shown in Fig. 5a. The TG-DTG curves of the monomer show four-step mass loss behavior. The first step indicates a 4–5% mass loss at temperatures up to 480.5 K. This step can be attributed to the expulsion of water molecule. The second-step mass loss occurs between 480.5 K and 579.0 K. The mass loss observed is 12.2% against calculated 11.9%, showing that ethanol molecule is expelled. During this step, the melted monomer condenses to HBPAZO by the ester-interchange reaction. So it is inferred that 480.5 K is the low limit value of temperature for polycondensation of the melted monomer, and 579.0 K is the upper limit value of the temperature. The third-step is in continuation with the second step from 579.0 K to 618.8 K. The mass loss observed is 7.2% against calculated loss of 7.25%, corresponding to the elimination of nitrogen molecule, which is due to the decomposition of azo structure of HBPAZO [13, 14]. The fourth-step mass loss is from 618.8 K to 854.7 K. The mass loss observed is 38.1% against calculated loss of 37.8%, which is attributed to the decomposition of alkyl.

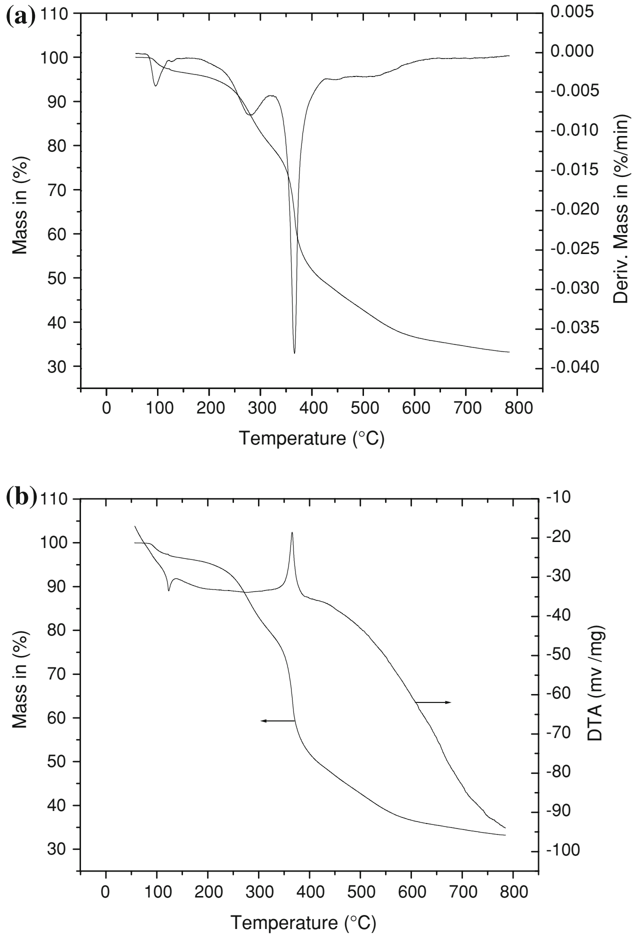


Fig. 5 **a** TG-DTG curves of diethyl 5-(4-hydroxyethoxyphenylazo)isophthalate. **b** TG-DTA curves of diethyl 5-(4-hydroxyethoxyphenylazo)isophthalate

The total mass loss in the heating process form ambient temperature to 854.7 K corresponds to 57.5% of the initial sample mass, remaining 42.5% black residual (calculated value: 43.5%) in the crucible, which maybe is the carbon obtained by decomposing ester carbonyl and benzene. The TG-DTA curves of the monomer are shown in Fig. 5b. A sharply endothermic peak assigned to melting of the monomer was observed, with the peak temperature of $T = 396.3$ K. When the temperature was higher than 476.9 K, the other sharply exothermic peak associated with the thermal decomposition of the monomer appeared in the temperature range from 476.9 K to 854.7 K with the peak temperature at $T = 638.9$ K.

Conclusion

A novel AB_2-type monomer diethyl 5-(4-hydroxyethoxyphenylazo)isophthalate for preparing HBPAZO was synthesized. The TG-DTG/DTA curves show that the decomposition of the monomer proceeds in four steps. During the second-step decomposition, it is found that the melted monomer condenses to HBPAZO. So it is inferred that 480.5 K and 579.0 K are the low and upper limit temperatures for polycondensation of the melted monomer. This temperature range is very important for synthesizing of HBPAZO, which is the aim of our next work.

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