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Synthesis, characterization and fluorescence performance of a waterborne polyurethane-based polymeric dye

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ABSTRACT

A novel anionic waterborne polyurethane-based fluorescent dye WPU-DV26 was synthesized by incorporating the molecular structure of disperse violet 26 (DV26) into the polyurethane chain. The structure of WPU-DV26 was confirmed by means of Fourier transform infrared spectroscopy and UV–vis absorption analysis. Comparing to the UV–vis spectrum of DV26, WPU-DV26 showed a hypsochromic shift from the absorption maxima of 518, 558, 609 nm to 510, 548, 586 nm, respectively. WPU-DV26 can form stable latex in water. The number average molecular weight and its distribution index, and average latex particle size for WPU-DV26 were determined to be 2.33×10^4, 1.36 and 80 nm, respectively. The improved thermal stability of WPU-DV26 can be attributed to the embedded anthraquinone unit of DV26. It was found that both the intensity and stability of the fluorescence of WPU-DV26 latex were improved significantly compared with those of DV26.

1. Introduction

Polymeric dyes have received sustained attention during past years due to distinct properties and potential applications in a wide variety of fields. However, most of them are solvent-based, and can be dissolved only in organic solvents which may cause some environment pollution problems. The development of water-borne polymeric dyes is going to be a trend in the near future and has aroused some interests [1–5]. Some scientists prepared polymeric dyes by means of introducing dye structure into polyurethane repeating units, functionalizing side groups of polyurethane with dye chromophore, or copolymerizing with dye moieties [6–12]. Buruiana et al. synthesized cationic polyurethane with chromophore (azobenzene, quinone, stilbene and anthracene) and covalently bound the chromophore into the side group or the main chain of polyurethanes [13–18]. However, few polymeric fluorescent dyes of waterborne polyurethane-based were reported in the literature. Only a few polyurethanes containing the anthraquinone component were reported owing to the difficulty in preparing such structure by traditional methods.

Disperse violet 26 (DV26) is a disperse dye and has the advantages of material compatibility and color fastness, especially in dyeing of polyester fabrics as well as plastics. Mogi et al. found that the polylactide fabrics dyed with DV26 showed a high *K*/*S* value and the light fastness higher than grade 4 [19]. In this paper, we prepared anionic water-borne polyurethane dye (WPU-DV26) with the chromophoric anthraquinone units by using DV26 through the prepolymer mixing process. Because the chromophore was covalently bonded into the polyurethane chain, dye migration could be avoided, and the color could be preserved permanently with brightness, solvent resistance and also good rubbing resistance. Additionally, WPU-DV26 is aqueous dispersion and is suitable for the environmental protection. Special fluorescence performances of WPU-DV26 are also discussed in detail.

2. Experimental

2.1. Main materials

2,4-Tolylene diisocyanate (TDI, Shanghai Chemical Reagent Co., Ltd.) was purified by distilling under reduced pressure at 120 °C. Poly(propylene glycol) (PPG, $M_n=1000$ g/mol, Basf Co.) was dried under the pressure of 10 mmHg at 110 °C for 12 h. 2,2-Dimethylol propionic acid (DMPA, Aldrich Co.) was dried in an oven at 120 °C for 48 h. Acetone and *N*,*N*-dimethyl formamide (DMF) were distilled and kept with 4 Å molecular sieve before use. Disperse violet 26 (DV26, Afine Chemicals Ltd.), di-*n*-butyltin dilaurate (DBTDL, Aldrich Co.), triethylamine (TEA) formic acid, acetic acid and acrylic acid were used as received.

2.2. Synthesis of WPU-DV26

The fluorescent emulsion of WPU-DV26 was prepared according to the procedure shown in Scheme 1. TDI, PPG and DMPA were

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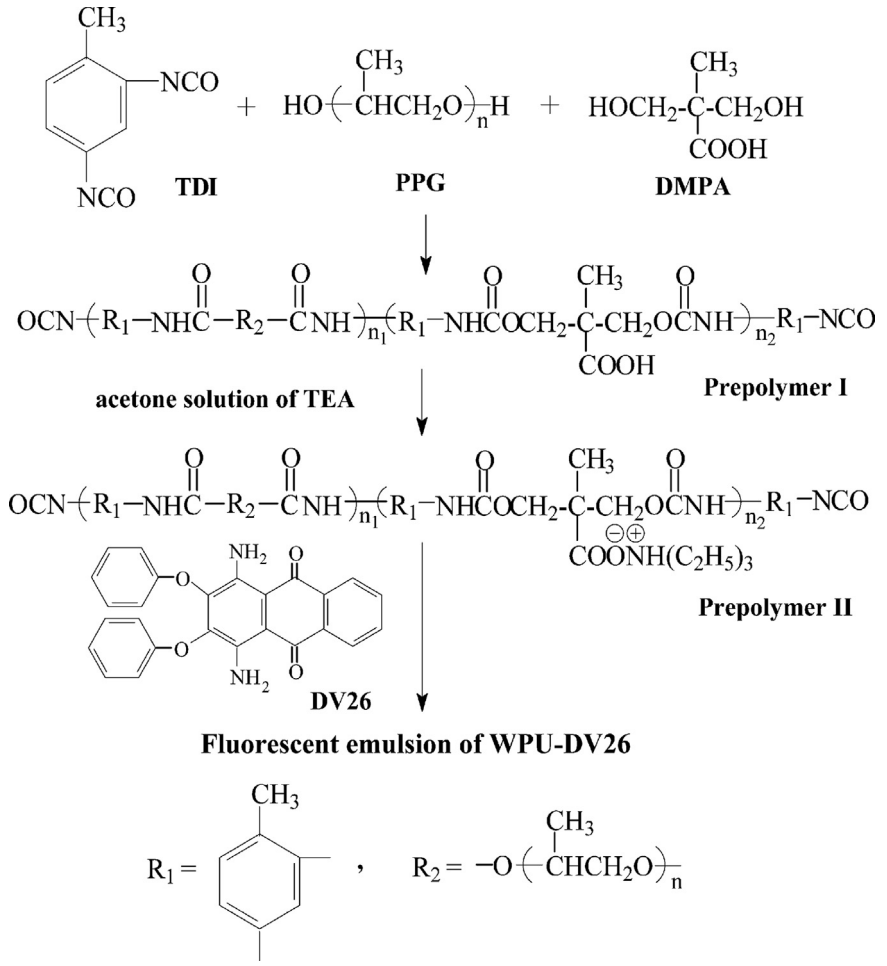

Scheme 1. Preparation process of WPU-DV26 fluorescent emulsion.

first added into a dry four-necked flask equipped with a mechanical stirrer, a thermometer, and a reflux condenser according to a suitable molar ratio of TDI:PPG:DMPA=1:0.4:0.38. DBTDL was added dropwise to the flask under stirring (molar ratio of TDI: DBTDL=1:0.02). The prepolymerization of polyurethane was carried out at 80 °C under N_2 atmosphere until NCO content reached a theoretical value to produce NCO-terminated prepolymer I. The NCO content was monitored via a standard dibutylamine titration method [20]. When the reaction mixture was slowly cooled down to 30 °C, the acetone solution of TEA (6 wt%) was added to the system and reacted with the carboxylic group in the side chain of prepolymer I for 30 min to form quaternized NCO-terminated prepolymer II. The molar ratio of TEA to DMPA was 1.2:1 to ensure the complete neutralization. DV26 aqueous solution (1.8 wt%) was added into the reaction mixture (molar ratio of TDI:DV26=1:0.16) until the system was cooled down to 5 °C, and further reacted with NCO group of prepolymer II for 30 min under vigorous agitation. The fluorescent emulsion of WPU-DV26 was formed after acetone was removed from the emulsion using a rotary evaporator. The solid content of obtained WPU-DV26 fluorescent emulsion was about 30%.

2.3. Sample preparation and measurements

The latex film with thickness of about 150 μm for further testing was prepared by casting the fluorescent emulsion on a Teflon plate and drying at ambient temperature for 7 days, and then in a vacuum system at 50 °C for 2 days.

Fourier transform infrared (FTIR) spectrum (a Bruker EQUIVOX55 IR spectrometer) was recorded in the range of 4000–500 cm^{-1} using thin film prepared by casting dilute DMF solution of the latex on KBr flake and then evaporating DMF by heating under reduced pressure. Ultraviolet–visible (UV–vis) spectrum was recorded on a Shimadzu spectrophotometer UV-2501PC using water solution of DV26 and WPU-DV26 emulsion with the concentration of 1.0×10^{-5} mol/L at 25 °C. Fluorescence spectrum was recorded on a Shimadzu RF-5301PC luminescence spectrometer. All solvents used were purified to eliminate interference for fluorescence.

Average particle size of the emulsion was determined by using a Shimadzu SALD-7101 laser particle size analyzer. Differential scanning calorimetric (DSC) curve was recorded using a Perkin-Elmer Pyris-1 at a constant heating rate of 10 °C/min. The thermogravimetric characteristics were investigated by a thermogravimetric analyzer (TGA) of Shimadzu TGA-50H under nitrogen atmosphere. Gel permeation chromatography (GPC) analysis was performed on an apparatus with a Waters 1515 pump and a Waters 2414 differential refractive index detector using two linear Styragel columns HT3, HT4 at column temperature of 35 °C. The eluent was DMF, and flow rate was 1.0 mL/min.

3. Results and discussion

3.1. Structure analysis of WPU-DV26 by FTIR

The chain structure of WPU-DV26 was confirmed by FTIR spectroscopy. FTIR spectra of WPU-DV26 and DV26 are shown in