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Synthesis and fluorescent investigations of VBL-based waterborne polyurethane dye

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ABSTRACT

Fluorescent brightening agent VBL-based waterborne polyurethane dye (VBL–WPU) was synthesized by incorporation of VBL into waterborne polyurethane chains. The expected structure of polymeric fluorescent brightening agent was confirmed by FT-IR and UV–vis spectra. The molecular weight, average particle sizes and the contents of VBL segments in VBL–WPU were investigated. This polymeric dye exhibited intriguing optical behaviors. The absorption and emission maxima of VBL–WPU showed obviously hypsochromic shift in comparison with those of VBL. The fluorescence intensity of the polymer was prominently enhanced comparing with VBL because of the changes of micro-circumstance of VBL. Furthermore, the fluorescence of VBL–WPU was not sensitive to hydroquinone quencher.

1. Introduction

Chemical anchoring of small molecular fluorescent brightening agents (FBAs) onto polymer matrixes to afford polymeric fluorescent brightening agents (PFBAs) is of high interest because of the enhanced solvent resistance, resistance to migration, and better processability. Because FBAs are anchored in polymer chains through covalent bonds, their photostability and whitening performance can be enhanced, and fluorescence quantum yield can be increased. PFBAs can be applied not only in textiles, coating materials and paper making, but also in organic LEDs, fluorescent probes, etc.

Many polymeric fluorescent brightening agents have been reported in recent years based on many polymeric matrixes, for example, polyester, polystyrene, polyacrylonitrile, and poly(methyl methacrylate) [1–7]. However, most of them were solvent-borne polymeric fluorescent brightening agents and could cause severe pollution problems. The development of waterborne polymeric fluorescent brightening agent is the trend in the future and has generated interest at present [8–10]. In this work we synthesized a waterborne polyurethane dye, which was formed by attaching fluorescent brightening agent, disodium 4,4′-bis[(4-anilino-6-hydroxyethylamino-1,3,5-triazin-2-yl)amino]stilbene-2,2′-disulphonate (VBL), into waterborne polyurethane chains. Because VBL was anchored into polyurethane chains, dye migration could be avoided, and whitening performance could be preserved persistently with high fluorescence efficiency, solvent resistance and good rubbing resistance. Moreover, it was especially suitable for environmental protection that VBL–WPU was an emulsion.

2. Experimental part

2.1. Materials

Isophorone diisocyanate (IPDI, Aldrich Co.) was distilled under reduced pressure of 10 mmHg 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; and 2,2-dimethylol propionic acid (DMPA, Aldrich Co.) was dried at 120 °C for 48 h. *N*,*N*-dimethyl formamide (DMF), acetone and triethylamine (TEA) were distilled and kept in 4 Å molecular sieves before use. Fluorescent brightening agent VBL (Nantong Lisi Organic Chemicals Co., Ltd.), di-*n*-dibutyltin dilaurate (Aldrich Co.), acetic acid, lactic acid and acrylic acid were used as received.

2.2. Preparation

The synthesis processes of VBL–WPU were showed in Scheme 1. IPDI, PPG and DMPA (molar ratio IPDI:PPG:DMPA = 1:0.5:0.375) were poured into the flask equipped with a mechanical stirrer, thermometer, and a reflux condenser. A drop of di-*n*-dibutyltin

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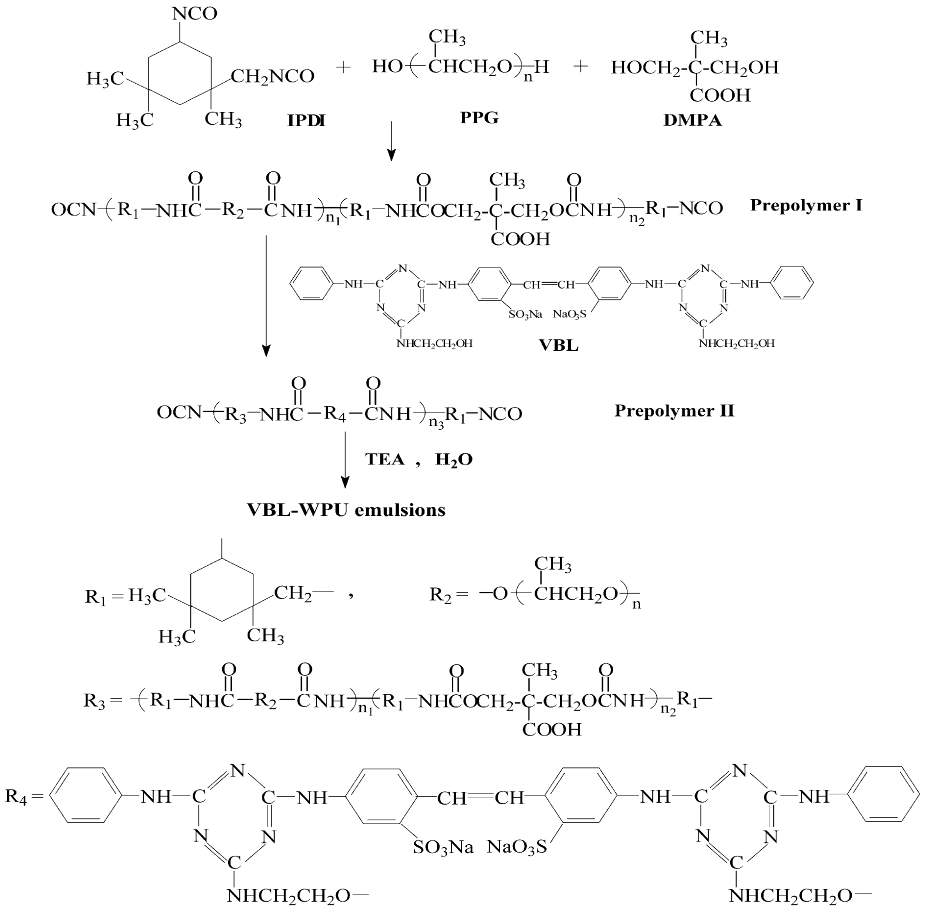

Scheme 1. Synthesis processes of VBL–WPU.

dilaurate was added to the flask with vigorous agitation. The reaction was carried out at 80 °C under N_2 atmosphere until the content of NCO group reached theoretical value to form NCO-terminated **prepolymer I**. The content of NCO was monitored by the standard dibutylamine titration method. In the final stage of this reaction, suitable amount of acetone was added into the system to reduce the viscosity of **prepolymer I**. Then, VBL (molar ratio IPDI:VBL = 1:0.06) dissolved in DMF was added and reacted with **prepolymer I** to form **prepolymer II** at 80 °C for 6 h. Subsequently, TEA as a neutralization agent was added to react with the carboxylic group in the side chain of **prepolymer II** for 30 min. The molar ratio of TEA to DMPA was 1.2:1 to ensure the complete neutralization. Finally, appropriate deionized water was added into the system with agitation at high shearing rates to emulsify the solution. After removal of the acetone by rotary vacuum evaporation under reduced pressure, the solid content of obtained VBL–WPU was about 30%.

2.3. Characterization

Films were prepared for further testing by casting the emulsions on a Teflon plate and drying at room temperature for 7 days, and then in a vacuum system at 50 °C for 2 days.

FT-IR spectra (a Bruker EQUIVOX55 IR spectrometer) were recorded using thin films, which were prepared by casting on KBr flake with dilute polymeric films in DMF and solvent vapored by heating under infrared lamp. The UV–vis spectra were recorded on a Shmadzu spectrophotometer UV-2401PC. Average particle sizes were determined by a Shmadzu SALD-7101 laser particle size analyzer. Fluorescence spectra were recorded on a Shmadzu RF-5301PC luminescence spectrometer. The temperature was measured with a thermocouple connected to the cell holder. The slit widths of monochromators were both 5 nm. Molecular weights and distribution were determined using gel permeation chromatography (GPC) with a series of linear Styragel columns. A Waters 1515 pump and Waters 2414 differential refractive index detector (set at 30 °C) were used. The eluent was DMF at a flow rate of 1.0 mL/min.

3. Results and discussion

3.1. Absorption spectra and characterization

The FT-IR spectra and UV–vis spectra of VBL–WPU were recorded in Figs. 1 and 2 where they were compared with the VBL. The FT-IR spectrum of VBL–WPU (Fig. 2) showed –N–H and –C=O of urethane stretching vibration at 3317 cm^{-1} (hydrogen bonded N–H) and 1706 cm^{-1} (hydrogen bonded), respectively. The –C–O of urethane and the C–O–C of PPG were observed at 1226 and 1095 cm^{-1}, respectively. Characteristic absorbance peaks of the Ar–C=C, –C–N of triazin and SO_3^- in VBL were observed at 1590, 1332 and 609 cm^{-1} in VBL–WPU, respectively. This demonstrated that the VBL had been anchored into the polyurethane chain. In addition, the absorbance peak at around 2275 cm^{-1} that attributed to N=C=O groups disappeared, which indicated a complete reaction between VBL and NCO-terminated prepolymers.

The UV–visible spectra of VBL–WPU (Fig. 2) showed an absorption peak at 333 nm due to stilbene units of VBL, which further confirmed that VBL was anchored to the polyurethane chains. Compared with VBL, VBL–WPU showed hypsochromic