

# A waterborne polyurethane-based polymeric dye with covalently linked disperse red 11

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## ABSTRACT

A red fluorescent sulfonated waterborne polyurethane-based dye WPU-DR11 was synthesized by conjugating Disperse Red 11 (DR11) into polyurethane backbones. The expected structure of WPU-DR11 was characterized by FT-IR and UV–vis spectra. Containing the well-known dye of anthraquinone chromophores, WPU-DR11 exhibits intriguing optical behaviors. Compared with DR11, WPU-DR11 shows an obvious bathochromic shift in absorption spectra, whereas a evident hypsochromic shift in emission spectra. The fluorescence intensity of WPU-DR11 is dramatically enhanced compared with that of DR11. The fluorescence intensity of WPU-DR11 increases with the temperature, which is different from that of ordinary fluorescent materials. It is found that the fluorescence intensity of WPU-DR11 gradually increase with the increase of concentration, and then decrease. Migration rate of WPU-DR11 are only 2.0–4.0%, which is well below migration rate of DR11. The polyester fibers dyed with WPU-DR11 show high color yield, excellent breaking strength retention, good air permeability and anti-wrinkle resistance. According to the experimental results, WPU-DR11 exhibits excellent fluorescent and dyeing performance.

## 1. Introduction

In the 21st century, polymeric dyes with small molecular dyes chemically anchored in the main or side chains have gained much attention due to good application prospects in many high-tech fields [1–8]. Although various polymer dyes have been studied in the literature, most of them are solvent-based and may cause environmental pollution problems in the application [9–12]. Recently, waterborne polymeric dyes have received plenty of interests owing to their versatile, nontoxic and environmental friendly properties [13–15].

Waterborne polyurethane (WPU) is a type of multifunctional and eco-friendly material to meet the highly diversified demands such as textiles, chemosensor, biological materials, etc. Nowadays, a few waterborne polyurethane-based dyes (WPU-DRs) have been researched [15–17]. WPU-DRs can significantly enhance the color depth and fastness, and have the obvious anti-wrinkle, antistatic performance and good air permeability in the coating and finishing process [18,19]. The carboxylated waterborne polyurethane-based dyes with anthraquinones, naphthalimides and azobenzene have been reported previously [20,21]. Most attention is focused on chemical synthesis and commercial applications. In contrast to carboxylated waterborne polyurethane (CWPU), sulfonated waterborne polyurethane has better hydrophilicity, heat resistance, solid content and stability than CWPU [22]. Although a

few sulfonated waterborne polyurethane-based dyes have been reported, their research focuses on chemical synthesis, rarely in luminescent properties and finishing effect.

Herein, a red fluorescent sulfonated waterborne polyurethane-based dye, WPU-DR11, was synthesized by covalently incorporating Disperse Red 11 into the polyurethane backbones. Special absorbance and fluorescence performances of WPU-DR11 were discussed in detail. Because DR11 is attached to the polyurethane chains through covalent bonding, it has excellent thermal-migration resistance and color fastness. The polyester fibers dyed with WPU-DR11 show high color yield, excellent breaking strength retention, good air permeability and anti-wrinkle resistance. Besides, WPU-DR11 is water as a solvent, especially suitable for environmental protection.

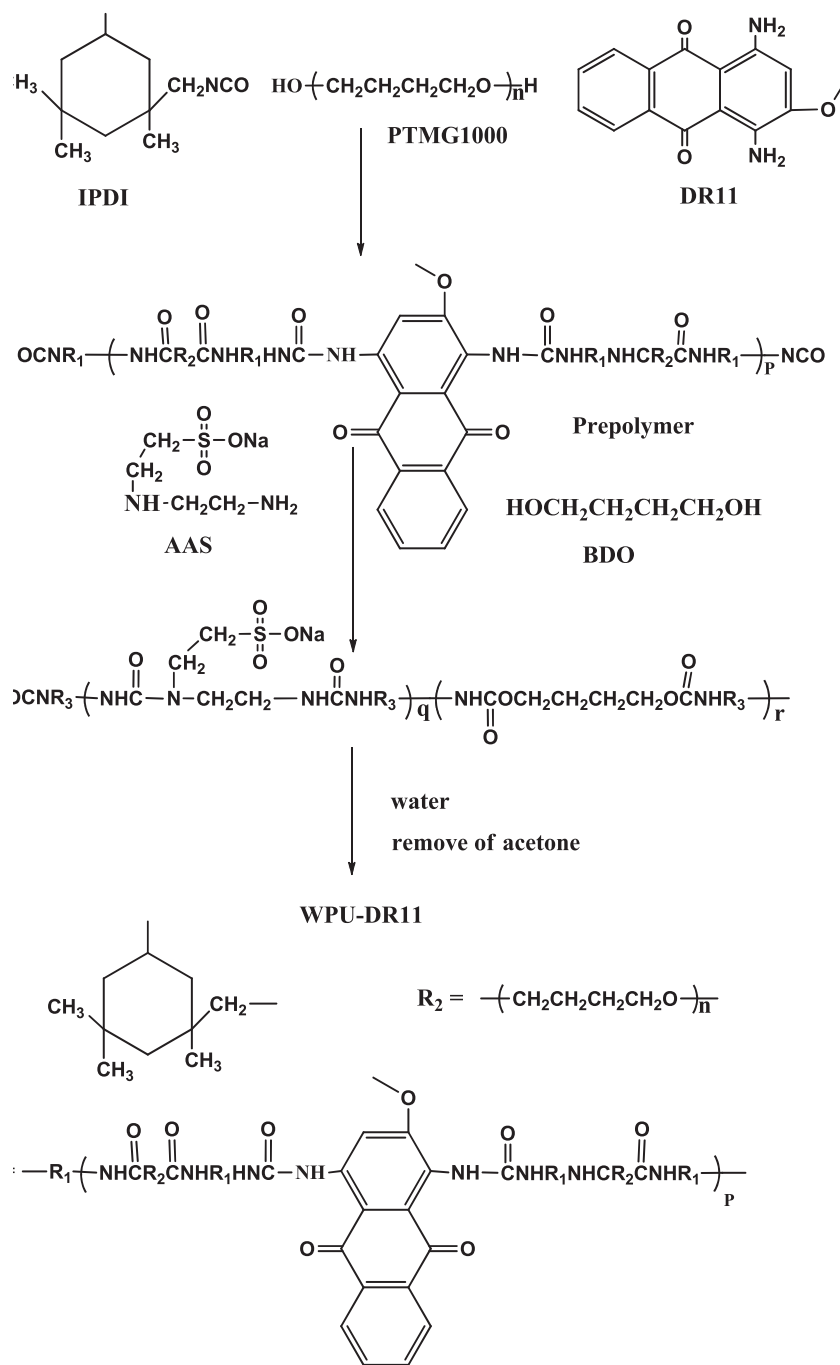
## 2. Experimental

### 2.1. Materials

Isophorone diisocyanate (IPDI) was purified by distillation under a reduced pressure of 1330 Pa at 120 °C. Poly (tetramethylene ether) glycol (PTMG,  $M_n = 1000$  g/mol) was dried under a pressure of 1330 Pa to 110 °C before use. Disperse Red 11 (1, 4-diamino-2-methoxy anthraquinone, C. I. 62015, DR11) was dried in an oven at 120 °C for

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Scheme 1. Synthetic process of WPU-DR11.

48 h before use. IPDI, Disperse Red 11 and PTMG are purchased from Bayer Co., German Sodium. 2-((2-aminoethyl) amino)ethane-1-sulfonate (AAS, Aladdin Co., Shanghai) was used as received. Methacrylic acid, acetic acid and acrylic acid were used as received. Acetone (AC), 1-methylpyrrolidine (NMP) and *N,N*-dimethyl formamide (DMF) were distilled and kept on a 4A molecular sieve before use. Stannous octoate (OS) was used as received. Methacrylic acid, acetic acid, acrylic acid, AC, DMF and OS are obtained from Shanghai Chemical Reagent Co., Ltd. Fabric: polyester fiber, 10 Tex warp yarn, 10 Tex weft yarn, ends per inch 255 root/10 cm. Wuhu Zhongtian Printing and Dyeing Co. LTD.

## 2.2. Synthesis of WPU-DR11

WPU-DR11 fluorescent emulsion was synthesized according to a polycondensation reaction, as illustrated in Scheme 1. IPDI, PTMG, and DR11 dissolved in DMF were charged into the four-necked separable flask equipped with a mechanical stirrer, thermometer, nitrogen inlet, and reflux condenser with a drying tube. The temperature of the mixture was slowly raised to 80 °C with vigorous agitation under  $\text{N}_2$  atmosphere until the amount of residual-NCO reached the theoretical value, determined by the standard dibutylamine titration method [23]. During the polymerization, the catalytic stannous octoate was added to the flask dropwise (0.2 wt%) and a suitable amount of acetone was charged to dilute the viscosity of the reaction system. The reaction system was slowly cooled down to 60 °C. AAS was added dropwise to

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