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Synthesis of transparent covalently self-colored polyurethane based on anthraquinone chromophore chain extenders

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ABSTRACT

The hydroxyl terminated polyurethanes covalently bonded anthraquinone chromophores into skeleton were successfully synthesized based on 1-amino-4-hydroxy-2-(6-hydroxy-hexyloxy) anthraquinone (AHHA) and dimethylolpropionic acid (DMPA) as chain extenders. The UV–visible spectroscopy of polyurethane solution revealed that the conjugated structure of chromophore was not affected after bonding into polyurethane. Owing to the absorption of chromophore in the range of 360–630 nm, the polyurethane with 0.12 wt% AHHA in backbone possessed high transmittance of 94.6% in the range of 630–800 nm and that of polyurethane with 0.89, 1.32, 2.13 wt% AHHA were 87.9%, 82.5%, 78.6%, respectively. Interestingly, the optical transmittance of corresponding polyurethane was 80.5% in the range of 630–800 nm. Transparency was strongly related to the phase separation and crystallization behavior. The DSC curve revealed no endothermic peak and XRD showed a broad diffraction peak, demonstrating that chromophore-incorporated polyurethane with different AHHA amounts had no distinct phase separation and crystallization that accounted for good transparency.

1. Introduction

Polyurethane (PU) is a versatile polymer for various applications such as foams, adhesives, coatings and composites [1]. Its diverse properties can be tailored by the selection of a huge list of chain extenders to meet various performance demands. 1,4-butane diol (BDO) is the usual chain extender for thermoplastic polyurethane with best mechanical properties among aliphatic diols [2]. Compared to diol chain extender, the synthesized PU with diamino chain extenders are able to pack more efficiently and provide higher level of crystallinity [3]. Increasing the length of the amide chain extender, the modulus and the melting temperature of PUE were increased without changing the good low temperature properties [4]. Traditional solvent-borne polyurethane possesses some inevitable drawbacks such as the evaporation of volatile organic compounds (VOC), toxicity, flammability. These drawbacks can be effectively addressed by water borne polyurethane which is a binary colloidal system and polyurethane particle dispersed in continuous water medium [5]. Dimethylolpropionic acid possesses pendant acid group neutralized by alkali with the increased water solubility of polyurethane. With nontoxic, environmental friendliness and excellent adhesion to matrix, water borne polyurethanes are widely utilized in coatings, paintings and adhesives.

A traditional coloration method of polyurethanes is to mix dyes or pigments with them, provided with some shortcomings such as dye migration, poor brightness and rubbing resistance due to the poor compatibility between dyes and polyurethanes [6,7]. An effective method to overcome these defects is to permanently incorporate chromophore into polyurethane matrix via covalent bonding. The chromophore containing one hydroxyl or amino group can be bonded into polyurethane chain through the reaction with isocyanate-terminated polyurethane prepolymer, such as fluorescent dye [8–10], the amount of chromophore is dependent on the amount of NCO group from both ends. For those reactive dyes with large molecule, it is difficult to incorporate into polyurethane due to steric hindrance effect. A polymer chain containing hydroxyl is first synthesized and then reacted with vinyl sulfone group [11–13]. Chromophores with glycol or diamine can be used as chain extender to bonded in polyurethane backbone such as fluorescent dye [14], anthraquinone dye [15] and azo dye [16]. Chromophore-bonded polyurethanes offer the advantages of migration resistance, storage stability, and water resistant property due to the good compatibility between chromophore and polyurethane.

Transparency is an important performance of polyurethane and can enhance the product value. When light encounters polyurethane, it can be absorbed, reflected, scattered and transmitted. Transparency means allowing most of light to throw polyurethane, but the nature of polyurethane such as phase separation and crystallization behavior in the hard segment can cause light scattering, which leads to decreased transparency [17]. Some attempts have been done to prepare

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transparent polyurethane. There are primarily two aspects that are important for the preparation of transparent polyurethane, namely, decreasing the crystallinity of hard segment and increasing the miscibility between hard and soft segment. The crystallinities descend while mixed chain extenders [17] or dissocyanates [18] are selected as materials in the synthesis of polyurethane. In addition, polyurethanes synthesized from bio-based chain extender showed a slightly lower crystallinity in the hard segment structure than that synthesized from BDO as the chain extender [19]. The miscibility between hard and soft segment can be achieved by choosing the structure of soft segment. The miscibility of polycarbonate segment is better than polyether segment [20]. Transparent polyurethane can be used as substitutes for ordinary optical glass, coating and painting.

In our previous work [21], disperse dyes have been successfully incorporated into polyurethane skeleton via covalent bonding to overcome defects such as the security, thermal migration, poor solvent resistance of traditional dye with low molecular weight. In this work, we focus on the synthesis of transparent self-colored polyurethane with different content of 1-amino-4-hydroxy-2-(6-hydroxy-hexyloxy) anthraquinone. Color and transparency are competitive property. Transparency means visible light through the polyurethane while color demonstrates the absorption of light. In order to obtain good transparency, non-symmetric IPDI and dimethylolpropionic acid are selected to destroy crystalline structure. Meanwhile, the dimethy lolpropionic acid provides the polyurethane with water solubility for purification. Polyethylene glycol 1000 is used as soft segment. The structure, molecular weight, crystallinity and thermal properties of dye-bonded polyurethane are investigated. Such synthetic polyurethane with self-color and transparency is able to be employed as coatings on glass only need some cured agent to be a film or textile without other auxiliaries.

2. Experimental details

2.1. Materials

Isophorone diisocyanate (IPDI), a mixture of isomers, was available from Aladdin (Shanghai) Co., Ltd. 1-amino-4-hydroxy-2-(6-hydroxy-hexyloxy) anthraquinone (as shown in Scheme 1) was obtained from FILO Color & Chemicals (Wuxi) Co., Ltd. Dimethylolpropionic acid (DMPA) was purchased from Huaxia (Chengdu) Co., Ltd. Polyethylene glycol 1000 (PEG1000), triethylamine (TEA), dibutyltin dilaurate (DBTDL), acetone and dichloromethane were supplied by Sinopharm Chemical Reagent Co., Ltd. IPDI trimer was available from Jining Baichuan Chemical Co., Ltd. PEG1000 was dehydrated at 80 °C in a vacuum oven overnight before use. Acetone was stored with 4 Å type molecular sieves for a week for further use. Other chemicals were utilized without any purification.

2.2. Synthesis of polyurethane

Chromophore-bonded polyurethanes with different AHHA amount were synthesized via a two-step condensation reaction[22], shown as follows (Scheme 1). The formulations of chromophore-bonded polyurethanes were summarized in Table 1. IPDI was firstly placed in a three-necked round bottom flask, which equipped with a condenser and electric stirrer. The temperature was heated up to 70 °C. PEG1000 was dissolved in 10–15 mL acetone then added dropwise to react with IPDI at 70 °C for 2 h to obtain an isocyanate terminated prepolymer. AHHA and DBTDL were utilized as chain extender and catalyst, respectively. The reaction was carried out at 70 °C for 3 h. Afterwards, DMPA was poured into the system to react with residual NCO group at 70 °C for additional 4 h, forming hydroxyl terminated polyurethane. Acetone was added to reduce the viscosity of reaction and prevent the implosion. The temperature was cooled to 50 °C, then TEA was utilized to neutralize carboxyl group in DMPA, the reaction was kept for 0.5 h. Thereafter, the acetone was removed via rotary evaporation for the precipitation of unreacted AHHA then subsequently 50–100 mL deionized water was added to obtain polyurethane solution. The solution was followed by centrifugation and filtration to remove residual dyes and insoluble product. Water was removed via rotary evaporation. For control sample (PU0), DMPA was utilized instead of AHHA.

2.3. Preparation of polyurethane films

Hydroxyl terminated chromophore-incorporated polyurethane was dissolved in dichloromethane with a solid content of 20%, 10 wt% IPDI trimer was added to the dispersion. Afterwards, dispersion was poured into a glass container. The evaporation of dichloromethane and reaction between isocyanate group and hydroxyl group were taken place at room temperature for 5 days. The thickness of films was in a range of 0.69-0.79 mm.

2.4. Characterization and measurement

Fourier transform infrared spectroscopy (FTIR) was used to identify the presence of characteristic functional groups in the chromophore-incorporated polyurethane films. The FTIR spectra were obtained using NICOLET. Is 10 (made in Thermo Fisher Scientific) with an attenuated total reflectance (ATR) mode. The scanning range was from 4000 to 500 cm^{-1}.

^{1}H NMR spectrum were conducted with a NMR spectrometer (Aduance Ш 400 Hz, Bruker). Deuterium dimethyl sulfoxide (DMSO-d) and tetramethylsilane (TMS) were utilized as solvent and internal standard respectively.

Molecular weight and polydispersity index of polyurethane samples were estimated by gel permeation chromatography (GPC, Waters THF, USA) with tetrahydrofuran as eluent and calibrated with polystyrene standard. Polyurethane specimens were dissolved in tetrahydrofuran at a concentration of 5 mg/mL and 20 μL of the test solution was injected into the GPC apparatus with wide-distribution sample injection.

Thermogravimetric measurements of polyurethane were carried out with an A TGA/SDTA851e thermogravimetric analyzer. About 10 mg samples were heated under nitrogen atmosphere at a heating rate of 10 °C/min to 500 °C.

Differential scanning calorimetry (DSC) experiments were carried out in a TA-Q200 DSC apparatus in the range of −80–200 °C. 4–6 mg polyurethane film was sealed in an aluminum pan at a heating rate of 10 °C/min under a dry nitrogen gas atmosphere at a constant flow rate of 40 mL/min. The melting temperature was defined as the endothermic peak maxima.

UV–vis absorption spectrum was determined on UV-2600 (made in Shimadzu Corporation) in a range of 800 nm to 360 nm. The transparency of PU films was measured with a transmittance mode and utilized air as the reference medium. The amount of chromophore in polyurethane was obtained via dissolving polyurethane samples in acetone. The standard curve of monomolecular AHHA was obtained by a concentration of 2.45 mg/L, 4.80 mg/L, 9.60 mg/L, 12.00 mg/L, 14.40 mg/L, 19.20 mg/L, 24.00 mg/L. The concentration of dye-bonded polyurethane was 0.8 g/L.

The color parameters (K/S value, L*, a*, b*, C*, h°) of polyurethane films were performed with an Xrite-8400 spectrophotometer with the D65 illuminant and a 10° standard observer. Each sample was measured for three times with a cotton fabric in the background to avoid the transmission of visible light.

An X-ray diffractometer instrument (D8 Advances, Bruker) was used to analyze the crystallinity of chromophore-incorporated PU films. The scanning of 2θ angles between 5° and 50° below the scan speed of 5.0000° min^{-1} was carried out.