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Synthesis of waterborne polyurethane functionalized with Alizarin Red S dye for enhanced color fastness

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Abstract

The water-based polyurethane-based covalently linked anthraquinone dye has been synthesized very efficiently by combining Alizarin Red S dye with a polyurethane skeleton. The number-average and weight-average molecular weights of this innovative polymeric dye are about 6.24 k and 10.3 k, respectively, indicating its improved structural properties. The dye has maximum absorption wavelengths of 260 nm, 520 nm and 555 nm – which shows hypsochromic response compared to traditional micromolecule dyes, i.e., it has increased absorption capacity. The covalently linked micromolecule dyes to the polyurethane framework significantly increase its thermal tolerance and centrifugal stability. This water-based WPU-ARS exhibits excellent solubility and color stability in various pH environments, which makes it more effective. Compared to a mixture of ordinary dyes and polyurethane, the thermal transfer properties of this newly modified polymeric dye have been improved by up to 85%. Increased color stability under centrifugation, acidic and alkaline environments, and high temperatures have enabled this polymeric dye product to achieve significant potential and qualitative excellence in use as a dye, coating, or printing ink.

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I. Introduction

Polyurethane is a versatile material, whose extraordinary processability and structural diversity make it suitable for a wide range of applications. Excellent elasticity is achieved in its films through the use of various diols and chain-extenders. Amine-extended polyurethanes, commonly known as polyurethane-urea, exhibit superior mechanical and physical properties compared to diol-extended polyurethanes due to the strong hydrogen bonding of the urea group. By incorporating hydrophilic extenders such as 2,2-dimethylolpropionic acid (DMPA) in the pre-polyerization stage, polyurethanes can be converted from solvent-based dispersions to water-based disprsions—a unique example of environmental friendliness. Waterborne polyurethane (WPU) reduces the risk of environmental pollution by reducing the emission of volatile organic compounds (VOCs) into the environment, while maintaining the main properties of solvent-based polyurethanes, such as low temperature tolerance, flexibility and force tolerance. For this reason, WPU is currently widely used in various fields, including grouting materials, adhesives, and coatings, which are able to easily withstand microcracks or cracks. Developing more durable properties has become an important strategy in modern materials technology to ensure long-term durability [1-3].

Typically, waterborne polyurethane (WPU) resins are prepared by directly mixing with dyes or dye pastes, or by post-application coloring. However, due to the presence of multiple phases and complex interactions, additional adjuvants are often required to maintain the stability of the dispersion. The process of preparing dye pastes is laborious and time-consuming on the one hand, and its application also faces various technical challenges. Often, colored coatings fail to achieve the desired performance due to insufficient color stability, abrasion resistance, migration resistance, and durability. To overcome these limitations, the addition of modern polymeric dyes has emerged as an effective solution, which is capable of ensuring improved color stability, high performance, and long-lasting colored coatings in the case of coloring. As a result, not only the quality of the colored surfaces is increasing, but also the processing is becoming easier and more efficient [4,5].

Polymeric dyes are a type of colored polymer that is made by chemically linking the dye chromophore to the main or side chain of the polymer. These dyes combine the color properties of dyes with the stability of polymers. As a result of the chemical bond, they are heat-resistant, solvent-resistant, and resistant to color transfer. Due to their large molecules and stability, they are not absorbed into the skin, thus posing little health risk. They ensure high color fastness at low doses, and some dyes also exhibit photoresponsive properties. As a result, polymeric dyes have become a potential material for use in textiles, coatings, printing inks, foods, cosmetics, and lighting devices [6,7].

Recently, waterborne polyurethane-based polymeric dyes have become the focus of increasing interest among researchers. Although most polyurethane polymeric dyes are currently based on covalent bonding with fluorescent dyes, which are used in fluorescent detection and photoelectric devices. In addition, some reactive and anthraquinone-based dyes have also been incorporated as part of the polyurethane chain, which ensures improved film formation and strong adhesion to the surface of colored polymers and glass. However, since reactive dyes are usually composed of complex structures, their reactivity with the terminal isocyanate groups of the prepolymer is limited—resulting in low dye penetration into the polymer. To overcome this limitation, anthraquinone dyes are being considered as a potential alternative, offering simple structures, bright colors, and relatively improved migration resistance and solvent tolerance [8-10].

Alizarin and its derivatives, especially Alizarin Red S (ARS), have long been used as an important class of mordant dyes in the textile industry due to their bright colors and long-lasting properties. Compared with other alizarin-derived dyes, ARS is particularly well known for its water solubility and versatile functionality. This dye is important not only in textile dyeing but also in biomedical research, such as the detection of calcium in tissues and the identification of specific spots in bone cells in histological examinations. According to the structure shown in Scheme 1, ARS is an anthraquinone-based dye, which enriches its chemical properties through the presence of two adjacent hydroxyl groups. This structure establishes ARS as an effective and versatile dye. There are few studies in the literature so far on the incorporation of anthaquinone dyes into the polymer chain with anthraquinone-based cationic polyurethanes, which indicates a new potential direction for future research [11,12].

This study focuses on enhancing the stability of ARS dyes by covalent bonding with WPU. The synthesis materials—isophorone diisocyanate (IPDI), polyethylene glycol 400 (PEG 400), methyldiethanolamine (MDEA), and ARS—were used to prepare dye-impregnated waterborne polyurethane (WPU-ARS). The structure, molecular weight, and thermal properties of the dye-impregnated polyurethane were analyzed in detail. In addition, the color stability of WPU-ARS and monomolecular ARS dyes was compared. Notably, the excellent dispersion ability of WPU-ARS establishes it as a self-sufficient dye and adhesive material, which does not require the use of additional dispersants, stabilizers, or binders. As a result, such ARS-impregnated waterborne polyurethanes have emerged with revolutionary potential, which can ensure multiple effective applications in various industrial sectors such as water-based coatings, printing inks, textile and paper dyeing and finishing.

II. Experimental

2.1. Materials

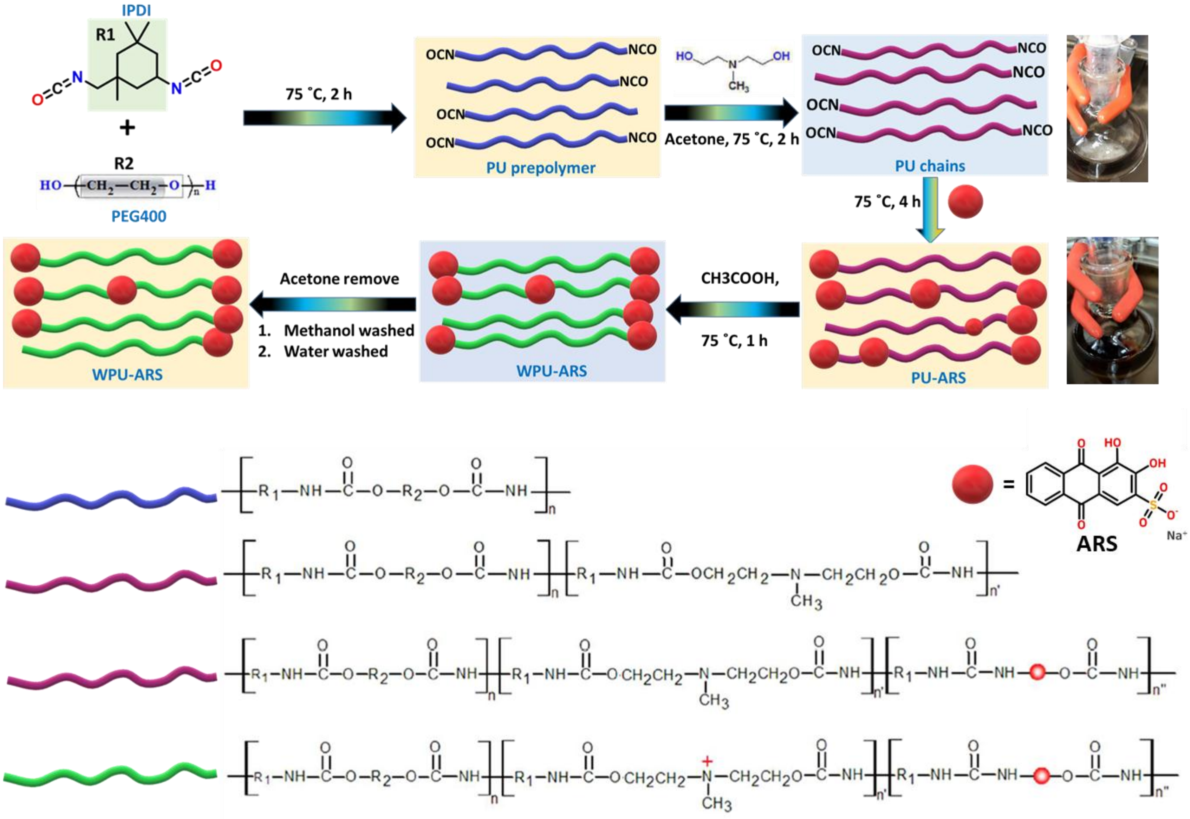
Isophorone diisocyanate (IPDI) was bought from innochem (Beijing) Co., Ltd. Alizarin Red S (ARS) was available from innochem (Beijing) Co., Ltd. Methyldiethanolamine (MDEA), polyethylene glycol 400 (PEG400) and glacial acetic acid (HAc), which were separately used as chain extender, soft segment and neutralizer, were procured from Sinopharm Chemical Reagent Co., Ltd. MDEA and PEG400 were vacuum-dried at 60℃ for about 24 h prior to use. Acetone bought from Sinopharm Chemical Reagent Co., Ltd., was dried and always kept with 4Å molecular sieve before utilization.

2.2. Methods

The structure of ARS and WPU-ARS were characterized by a NICOLET is10 transform infrared instrument (Thermo Fisher Scientific, Co. Ltd., China). Measurements were carried out within the wave number range of 400-4000 cm^{-1} at room temperature *via* the KBr pellet (1 mg/100 mg) technique. UV-vis spectra of ARS and WPU-ARS in deionized water were examined by a UV–vis Spectrophotometer (Cary 50, Varian) at room temperature in the wavelength range of 200-800 nm. Thermogravimetric analysis (TGA) of WPU-ARS were performed in nitrogen and in air atmospheres by A TGA/SDTA851e thermogravimetric analyzer (Mettler-Toledo). The molecular weight of WPU-ARS was investigated by gel permeation chromatography (GPC) (Waters 1515 Isocratic HPLC, USA) with eluent tetrahydrofuran (THF) at 35 ℃.

2.3. Synthesis of WPU-ARS

The WPU-ARS polymer was prepared by addition polymerization, as illustrated in Scheme 2. In a three-way flask equipped with a mechanical stirrer and reflux condenser, IPDI (44 mmol) and PEG400 (28 mmol) were added together with vigorous stirring. Then, the mixture was prepolymerized at 75℃ for 2 h to form an isocyanate-terminated prepolymer. In the next step, MDEA (10 mmol) dissolved in dry acetone (10 mL) was slowly added to the prepolymer to cause chain extension and was further run at 75℃ for 2 h. After this, ARS (2 mmol) was added to the reaction mixture, which reacted with the NCO groups and after 4 h a dye-terminated polyurethane was formed. After the reaction, the mixture was cooled to about 50℃ and the amino group was neutralized by adding acetic acid (5 mmol) for 1 h, thereby forming WPU-ARS. Next, acetone was removed from the viscous WPU-ARS by vacuum distillation. Finally, methanol (80-100 ml) was added to the WPU-ARS with continuous stirring, and a reddish precipitate was visible. This precipitate was filtered off, washed with hot methanol successively, and dried at room temperature until completely dry. In an alternative purification method, the concentrated WPU-ARS was dissolved in water and centrifuged, and the unreacted ARS was removed by filtration to obtain the pure WPU-ARS solution. IPDI acts as a strong segment, which ensures high mechanical strength and reliability in the polymer structure. On the other hand, PEG 400 is added as a flexible segment, which provides the necessary flexibility and elasticity in the polymeric dyestuff. MDEA, used as a chain extender, increases the water solubility in addition to increasing the length of the polyurethane chain, resulting in a significant improvement in the overall mechanical properties and solubility. ARS is incorporated into the polymer structure as a chromophore, which imparts color to the polyurethane chain and imparts color properties. During the pre-polymerization and chain extension steps, a small amount of acetone is added to complete the reaction by reducing the viscosity, which makes the entire reaction system more efficient and easier. In this way, each component plays a specific role and collectively maximizes the structure and functionality of the polymer.



Scheme1. Synthesis of ARS-bonded waterborne polyurethane

2.4. Characterization

2.4.1. FTIR and TGA

FTIR measurements were carried out within the wave number range of 400-4000 cm^{-1} at room temperature *via* the KBr pellet (1 mg/100 mg) technique. TGA samples ranging from 4 to 6 mg in weight were heated from 25 to 650 °C at a heating rate of 20 °C min^{-1} and under a nitrogen flow of 10 ml/min.

2.4.2. UV-vis spectra and pH sensitivity

0.1 N HCl and 0.1 N NaOH solution were used to adjust the pH values of dyes dispersed in deionized water. Subsequently, the samples were examined via UV-vis spectra at room temperature in the wavelength range of 200-800 nm.

2.4.3. Molecular weight

Near-monodisperse polystyrene (PS) standards were employed for molecular weight calibration. Eight PS standard samples, with peak molecular weights (Mp) ranging from 2,000 to 300,000 g/mol, were individually dissolved in tetrahydrofuran (THF). Molecular weight spectrograms were acquired using a scanning wavelength range of 190–800 nm and a controlled flow rate of 0–20 cm^3/min. The resulting data and chromatographic curves for both the PS standards and the WPU-ARS samples were accurately recorded and analyzed using the Breeze 2 software integrated with the Waters HPLC system.

2.4.4. Centrifugal stability

The absorbance ratio is considered as an indicator of centrifugal stability. The dyes were uniformly dispersed in pure deionized water and centrifuged at 4000 rpm for 30 min. Then, the light absorbance of the dye at the maximum absorption wavelength was determined using a UV-vis spectrophotometer (Cary 50, Varian). Finally, the absorbance ratio (γ) of the dye was calculated based on the obtained absorbance data, which was used as a measure of stability.

$$\gamma = \frac{A}{A0} \times 100\%$$

where A_0 represents the absorbance of the dye solution prior to centrifugation, and A denotes the absorbance measured after the centrifugation process.

III. Results and discussion

3.1. Structural characterization

The structure of ARS and WPU-ARS was analyzed using FTIR in the range of 400–4000 cm⁻ ¹ using KBr pellet method. In Figure 1A, the FTIR spectrum of ARS shows the O-H and N-H stretching vibrations at 3460 and 3250 cm⁻ ¹, and the peaks related to C=O and benzene ring at 1580–1630 and 1450–1525 cm⁻ ¹. In Figure 1A, the spectrum of WPU-ARS shows the N-H, C=O and C-O vibrations at 3365, 1730 and 1305 cm⁻ ¹, confirming the polyurethane structure. The absence of the C-O-C peak of PEG400 at 1240–1110 cm⁻ ¹ and the -NCO at 2280 cm⁻ ¹ is evidence of complete reaction. The peaks at 1450–1550 cm⁻ ¹ indicate successful incorporation of the ARS dye.

3.2. Thermal property

The thermal stability of polymeric dyes is a very important performance indicator in their practical applications, as many dyeing processes are carried out at high temperatures. The thermal behavior of ARS-bonded polyurethane through methanol washed (WPU-ARS), water washed (WPU-ARS-2), and dye molecule ARS by TGA in a N_2 atmosphere is presented in Figure 1B. Two distinct degradation steps can be observed in the TGA curve of WPU-DR. In the first step, about 10% weight loss (T_{10}%) occurs at temperatures around 100–150°C, which is thought to be mainly due to the evaporation of moisture and residual acetic acid. As the temperature is further increased, the main degradation occurs in the range of 250 to 580°C, where weight losses ranging from 10% to 90% ($T_{1\ 0}$ %–$T_{9\ 0}$ %) are observed. At this stage, the decomposition of the hard part and then the soft part of the structure of the dye-based WPU occurs, indicating the gradual termination of chain formation. On the other hand, the weight loss in WPU-ARS-2 begins at around 150°C, which is comparable to that of WPU-ARS. The study shows that the thermal decomposition of the hard part of polyurethane generally occurs faster than that of the soft part, indicating that the overall thermal stability is mainly dependent on the hard part. Notably, an anthraquinone-based ARS monomer with a higher decomposition temperature was incorporated as a hard part into the polyurethane chain. As a result, the thermal stability of the synthesized dye-based WPU is clearly improved compared to the simple mixture of dye and polyurethane alone.

3.3. Molecular weight

The molecular weight of dye-based aqueous polyurethane has a significant effect on its color and performance. If the molecular weight is too high, the color becomes unattractive due to the low concentration of dye chromophores in the chain and the tactile feel of the substrate is also poor. On the other hand, if the molecular weight is too low, the amount of polar groups in the polyurethane decreases, which reduces the color fastness. Therefore, the correct molecular weight selection is very important to form a suitable structure. To control this molecular weight, polyethylene glycol with a molecular weight of 400 is used as the soft segment and the NCO/OH ratio (R value) is set to 1.2. Through GPC experiments (Figure 1C), it was found that the number-average molecular weight (Mn) of WPU-ARS is about 6.24 kilodaltons and the mass-average molecular weight (Mw) is about 10.3 kilodaltons. In addition, its poly-dispersity index is 1.65, which indicates a relatively narrow molecular weight distribution.

3.4. UV-vis absorption spectroscopy

In the wavelength range of 200-800 nm, the UV-vis absorption spectra of WPU-ARS and ARS (Figure 1D) show that the curves of both are almost identical, indicating that ARS is successfully attached to the aqueous polyurethane chain. The presence of anthraquinone-based chromophore and auxochrome (-OH, $-NH_2$) leads to clear absorption peaks in the 250-300 nm and 450-600 nm ranges due to the $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ electronic transitions. The maximum absorption wavelengths of ARS are at 265, 525 and 565 nm, while the peaks of WPU-ARS are at 260, 520 and 555 nm—indicating a hypsochromic shift of 5-10 nm. A major reason for this shift is the elimination of the intermolecular hydrogen bond between α-NH_2 /OH and C=O in the anthraquinone structure. Furthermore, the carbonyl group in the urethane bond acts as an electron-withdrawing and exerts an inductive effect on the chromophore, resulting in a decrease in the π electron conductivity and an increase in the energy level of the π^* orbital. This results in an additional energy requirement for the $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions, resulting in a shift of the absorption wavelength to shorter wavelengths and a slightly lighter color.

3.5. pH sensitivity

The –OH group attached to the anthraquinone ring is sensitive to pH changes, resulting in distinct color variations under different acidic and alkaline conditions. Figure 1E present a comparative analysis of the λ max shifting of ARS and WPU-ARS in pH range 2-12. The color of ARS changes from light red to purple red in the pH range 2-12, indicating a bathochromic shift due to the increased electron donating tendency of the OH-alkali reaction in the anthraquinone. When ARS is added to the PU chain, the color variation is no longer observed with pH changes, indicating high color stability. However, WPU-ARS loses its solubility under alkaline conditions, because the quaternary ammonium group is deactivated by alkali, rendering the polymer insoluble (Figure 1F). The solubility is restored upon addition of acid. These results demonstrate that the covalent addition of small molecular dyes to WPU significantly enhances color stability and solubility.

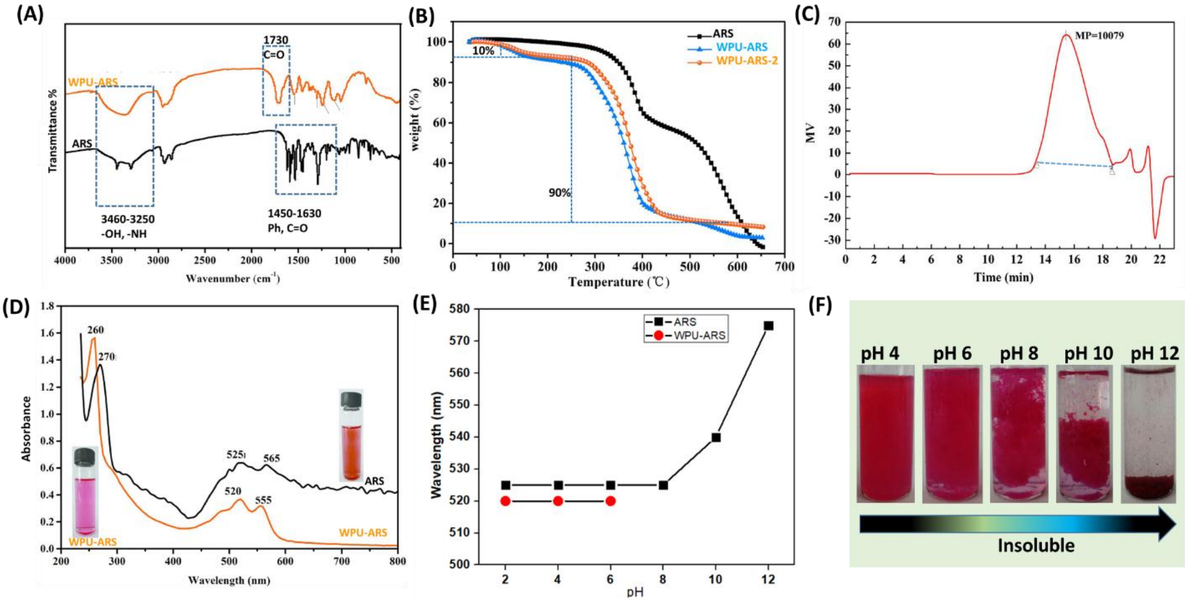


Figure 1. FT-IR (A), TGA (B), Molecular weight (C), UV-vis spectra (D), λ max shifting in various pH solution (E), and solubility (F) of ARS-bonded waterborne polyurethane and ARS

3.6. Centrifugal stability

To evaluate the centrifugal stability of PU-based dyes, WPU-ARS, WPU-ARS-2 and reference ARS were dispersed in deionized water without any additional dispersant and centrifuged at 2000-4000 rpm (30 min). The adsorption ratio of ARS decreased from 24% to 8% and that of WPU-ARS-2 from 25% to 9%, indicating a decrease in stability with increasing centrifuge speed. However, the adsorption ratio of WPU-ARS remained at 99% even after 15 min of centrifugation at 4000 rpm. This high stability confirms that ARS is successfully chemically linked to the PU chain and exhibits good water solubility. This property of PU-based dyes ensures the long-term stability of waterborne polyurethane dispersions by reducing the tendency of stratification and sedimentation. Additionally, since this stability is achieved without additional components or mechanical support, the application process is simplified and production costs are reduced.

IV. Conclusion

Cationic dye-bound waterborne polyurethane (polymeric dye) was successfully synthesized using anthraquinone disperse dye via acetone process. The color and stability of dye-bound WPU, the corresponding micromolecular dye and dye-blended WPU were comparatively analyzed. The number-average and weight-average molecular weights of the mentioned polymeric dyes were 6.24k and 10.3k, respectively, and the polydispersity index was 1.65, indicating a narrow molecular weight distribution. The maximum absorption wavelengths of the dye-bound WPU were located at 260, 520 and 555 nm with hypsochromic shifts of 5-10 nm. It exhibited excellent centrifugal stability as 99% absorption was maintained even after 15 min centrifugation at 4000 rpm, indicating covalent binding of the dye. It maintains good solubility in acidic environments and the color remains unchanged over a wide pH range. The transfer rate of dye-incorporated WPU is only 8%, while that of mixed dyes is 35%, which is a significant difference. Its improved color stability and solubility make it a potential material for textile dyeing and coating.

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