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Synthesis of a novel water-soluble crosslinking polymeric dye with good dyeing properties

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Abstract

A novel yellow polymeric dye was synthesized by the reaction of 2,4-dinitrochlorobenzene with polyallylamine prepared from the homopolymerization of monoallylammonium chloride. The structure of the polymeric dye was characterized by using IR, UV–visible, TLC and ^{1}H NMR analysis, and the λ_{max} of this polymeric dye in water is 361 nm. The effects of the concentration of amino group, the mole ratio of Na_2CO_3 to amino group, the reaction temperature, and the reaction time of the reaction are discussed in detail. Furthermore, the silk and cotton dyed with this polymeric dye were fixed by the use of crosslinking agent, 2-chloro-4,6-di(aminobenzene-4′-β-sulphatoethylsulphone)-1,3,5-*s*-triazine, they have high fixation and the polymeric dye shows very good fastness to washing and rubbing.

Keywords: Polymeric dyes; Polyallylamine; Crosslinking dyeing

1. Introduction

Polymeric dyes are composed of optically chromophoric groups bound to or into polymers [1]. They are classified as block type and graft type according to their structures. Either block polymeric dyes or graft polymeric dyes offer the advantage of allowing a range of physical properties, such as solubility, absorption, migration and viscosity, that are tunable. The range of products possible offered by the joining of the fields of polymer chemistry and color chemistry is virtually inexhaustible [2,3]. Now, they have been applied in fibre [4–6], hair dyes [7,8], solid-state polymeric dye lasers [9,10], jet-printing [11,12], and electrokinetic chromatography [13].

Polymeric water-soluble dyes, which are of considerable biological and technological interest because of their various properties [14,15], have been little investigated [16–19]. One reason for this is that the vast majorities of chromophores are not available in a water-soluble form [20], and thus cannot be converted into water-soluble materials by the polymerization of easily prepared monomers. To prepare water-soluble polymeric dyes constructed of fundamentally water-insoluble chromophores, the chromophore must somehow be attached to, or be made a part of, a polymeric system which otherwise contains the required solubilizing functionality.

Polyallylamine [21] is a water-soluble polymer, which can provide straightforward synthetic approaches to materials of this type. In this paper, we synthesized a new water-soluble polymeric dye thereof polyallylamine as backbone and 2,4-dinitrobenzene as chromophore. Moreover, there are many reactive groups (amino group), which can be used to crosslink with fibre and polymeric dye by the use of crosslinking agent. It has high dye fixation and good wet fastness on silk and cotton.

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2. Experimental

2.1. Reagents and instruments

Poly(allylammonium chloride) was prepared from homopolymerization of monoallylammonium salts with azo-initiators, and the number average molecular weight of 8500 was obtained from membrane osmometry in 1 mol/l NaCl aqueous solution [21]. Crosslinking agent, 2-chloro-4,6-di(aminobenzene-4′-β-sulphatoethylsulphone)-1,3,5-*s*-triazine was prepared according to the method described by Lewis [22]. 2,4-Dinitrochlorobenzene, methanol and Na_2CO_3 were of analytical grade quality.

Varian INOVA 400 NMR Spectrometer, FT/IR-430 Spectrophotometer, and HP-8453 UV–Visible Spectrometer were used to confirm the structure of the polymeric dye.

2.2. Preparation of the polymeric dye

Poly(allylammonium chloride) (1.9 g, 20 mmol amine) and Na_2CO_3 (4.2 g, 40 mmol) were dissolved in 80 ml water with stirring, and heated to 60 °C. Then, 1.2 g (6 mmol) 2,4-dinitrochlorobenzene was added, the mixture was heated to 80 °C, and kept at 80 °C until the reaction was over, and the reaction termination was determined by TLC (Silica GF254, benzene:dioxane: acetic acid = 90:25:4, v/v). The resultant dye solution was poured into 320 ml methanol, 6 mol/l HCl was dropped into this mixture solution and yellow precipitate was obtained. The product was dried to constant weight in an oven at 40 °C in the presence of P_2O_5 to yield 2.6 g product (97%).

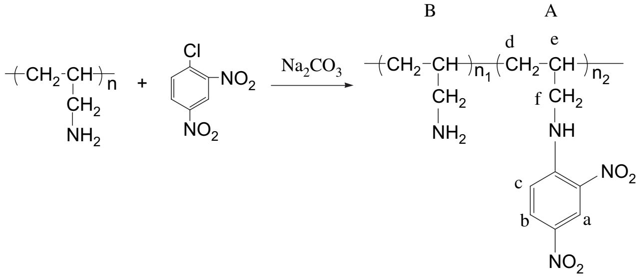
2.3. Dyeing and fixing process

Dyeing with polymeric dye on silk and cotton was carried out using a "3-dip-3-nip" padding operation at room temperature. The concentration of the dye-bath was 5% (wt/wt). After dyed fibre became dry, it was dipped into fixing-bath containing 6% (wt/wt) crosslinking agent for 3 min and nipped once. Then the fibre was heated to 50 °C and kept for 3 min in an oven. At last, the dyed fibre was rinsed with water completely.

3. Results and discussion

3.1. Synthesis of polymeric dye

The reaction of 2,4-dinitrochlorobenzene with polyallylamine can be considered as nucleophilic aromatic substitution. As amino group attacks the carbon bearing the chlorine, a negative sigma complex is formed. The negative charge is delocalized over the *ortho* and *para* carbons, stabilized by the electron-withdrawing nitro groups. These two nitro groups stabilize the negative charge through the inductive effect and resonance with a partial carbon–nitrogen double bond. 2,4-Dinitrochlorobenzene is grafted on polyallylamine after the chloride is dropped from the sigma complex. In this paper, the polymeric dye was prepared by the reaction of polyallylamine with 2,4-dinitrochlorobenzene (Scheme 1).



Scheme 1. Synthesis of polymeric dye.

The factors, i.e., the concentration of amino group, the mole ratio of Na_2CO_3 to amino group, the reaction temperature, and the reaction time were discussed in detail. The degree of substitution of chromophore was calculated by the use of calibration curve of yellow crosslinking polymeric dye (Fig. 1).

The abscissa in Fig. 1 represented the concentration of chain A, and when the reaction was over, 1 ml reactive mixture was taken out, diluted to 100 ml and the absorbance was determined by UV–visible, then the concentration of chain A was calculated by the use of Fig. 1, the degree of substitution of chromophore was calculated based on the concentration of chain A.

3.2. Structure confirmation

The polymeric dye was characterized by the use of TLC, IR, UV–visible and ^{1}H NMR. The R_f of the polymeric dye is 0, and the R_f of 2,4-dinitrochlorobenzene is 0.71. During the reaction, we didn't find the hydrolytic product of 2,4-dinitrochlorobenzene (R_f = 0.86) by TLC. Fig. 2 illustrates the absorbance of the diluted polymeric dye solution measured by a

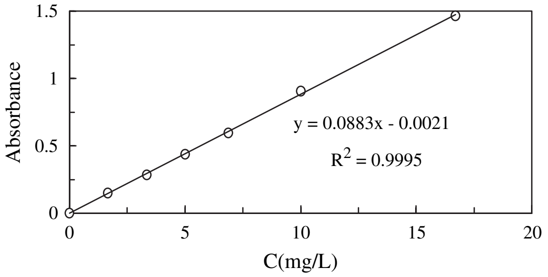


Fig. 1. Calibration curve of yellow crosslinking polymeric dye.

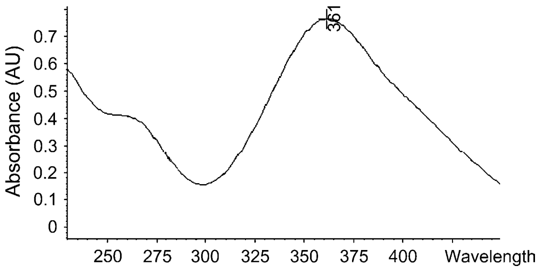


Fig. 2. Absorption curve of polymeric dye.

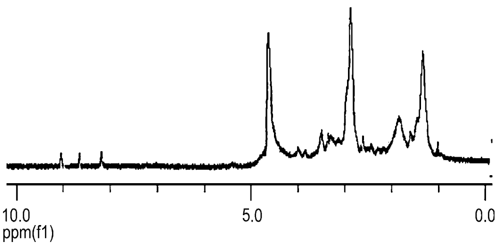


Fig. 4. ^{1}H NMR spectrum of polymeric dye.

UV–visible Spectrophotometer and the λ_{max} of this polymeric dye is 361 nm.

The infrared absorption spectrum of polymeric dye in a KBr disk is shown in Fig. 3. The absorption bands due to NH_2 existed at 3432 and 1617 cm^{-1}; the absorption bands at 1519 and 1334 cm^{-1} were assigned to NO_2.

As a method of directly observing the chemical environment of bonded hydrogen, ^{1}H NMR analysis (D_2O) was applied to the characterization of the polymeric dye. The spectrum of polymeric dye is shown in Fig. 4. The proton spectra for benzene groups were taken as the peaks of a ($\delta = 9.1$), b ($\delta = 8.6$) and c ($\delta = 8.2$). The peak of g ($\delta = 4.7$) was assigned to water, and the peaks of d ($\delta = 1.3$), e ($\delta = 1.9$) and f ($\delta = 2.9$) were assigned to polyallylamine.

3.3. Effect of the concentration of amino group on the degree of substitution of chromophore

The effects of the concentration of amino group on the degree of substitution of chromophore are summarized in Fig. 5. It was clear that with the increase in the concentration of amino group from 0.25 mol/l to 1.0 mol/l, the degree of substitution of chromophore decreased from 29.3% to 23.6% gradually. That was because that polyallylamine had an extended chain conformation when the concentration was low, which was helpful to the reaction of polyallylamine with 2,4-dinitrochlorobenzene, but with the increase in concentration, the intermolecular association of polyallylamine caused the association of polymer coil, which went against the reaction.

3.4. Effect of the mole ratio of Na_2CO_3 to amino group on the degree of substitution of chromophore

The effects of the mole ratio of Na_2CO_3 to amino group on the degree of substitution of chromophore are summarized in Fig. 6. It showed that the degree of substitution of chromophore first increased with the increase in the mole ratio of Na_2CO_3 to amino group, and then decreased. During the reaction, the role of Na_2CO_3 was not only to neutralize the HCl of poly(allylammonium chloride), but also to trap the HCl produced from the reaction. Moreover, the amination of 2,4-dinitrochlorobenzene was a nucleophilic aromatic substitution, the alkaline condition was helpful for it. But too much alkaline would lead to the side-reaction of hydrolysis of 2,4-dinitrochlorobenzene. As the ratio was lower than 2, the amount of Na_2CO_3 was not enough to neutralize the HCl either from raw material or from the reaction. So the degree of substitution of chromophore reached maximum when the mole ratio of Na_2CO_3 to amino group was 2.

3.5. Effect of the reaction temperature on the degree of substitution of chromophore

Polyallylamine was hygroscopic and freely soluble in water. However, it was insoluble in organic solvents such as acetone, dioxane, tetrahydrofuran, DMF,

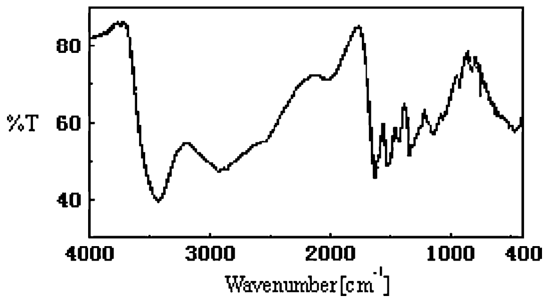


Fig. 3. IR spectra of polymeric dye.

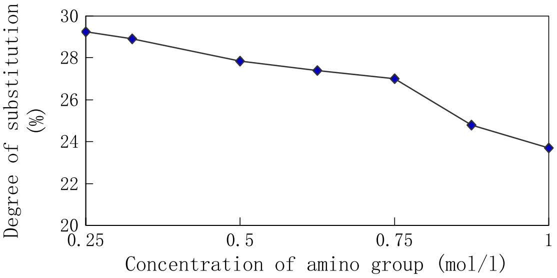


Fig. 5. Effect of the concentration of amino group on the degree of substitution.

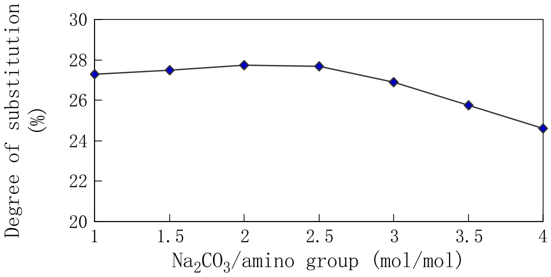


Fig. 6. Effect of the mole ratio of Na_2CO_3 to amino group on the degree of substitution.

DMSO, benzene and chloroform. However, 2,4-dinitrochlorobenzene was insoluble in water, but when temperature reached 56 °C, 2,4-dinitrochlorobenzene melted into liquid. The reaction between polyallylamine and 2,4-dinitrochlorobenzene can be carried out by violent stir in order to develop emulsion. But if the temperature was too high, the hydrolysis of 2,4-dinitrochlorobenzene would become serious. Fig. 7 illustrates that the degree of substitution of chromophore increased from 24.0% to 28.7% as the temperature increased from 60 °C to 80 °C whereas decreased from 28.7% to 27.7% as the temperature continued to increase to 90 °C.

3.6. Effect of the reaction time on the degree of substitution of chromophore

The relationship between the reaction time and the degree of substitution of chromophore in polymeric dye is shown in Fig. 8. It was clear that the degree of substitution of chromophore reached a maximum at 20 h.

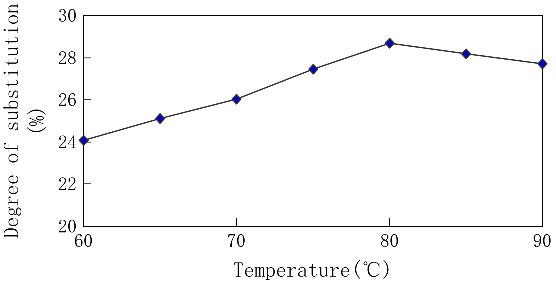


Fig. 7. Effect of the reaction temperature on the degree of substitution.

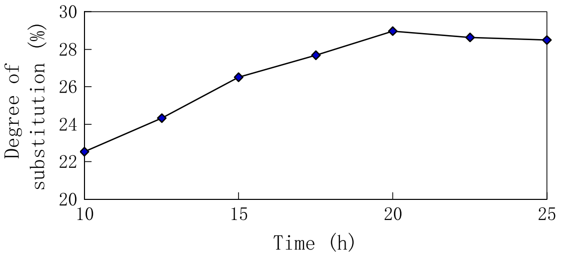


Fig. 8. Effect of the reaction times on the degree of substitution.

3.7. Dyeing properties

Dyeing properties of polymeric dye on silk and cotton are listed in Table 1. It can be seen that the fixation of polymeric dye either on silk or on cotton fixed by crosslinking agent, 2-chloro-4,6-di(aminobenzene-4′-β-sulphatoethylsulphone)-1,3,5-*s*-triazine, at pH value 8.5 can reach 99%. It was because that plenty of nucleophilic groups (amino group) in polymeric dyes thereof polyallylamine as backbone were released because of the neutralization of ammonium groups in the alkaline condition, at the same time, the reaction of 2-chloro-4,6-di(aminobenzene-4′-β-sulphatoethylsulphone)-1,3,5-*s*-triazine with polymeric dye and fibre, respectively, was nucleophilic substitution during the crosslinking–fixing process, so the alkaline condition was helpful for fixation of the polymeric dye. Both washing-fastness and rub-fastness can reach 4 grade and 4–5 grade, respectively.

4. Conclusion

A water-soluble polymeric dye was synthesized by the reaction of 2,4-dinitrochlorobenzene with polyallylamine in alkaline condition. The degree of substitution of chlorophore in polymeric dye reached 29.3% under the conditions of 0.25 mol/l amino groups, 2/1 mol/mol (Na_2CO_3/NH_2), 80 °C, and 20 h. Silk and cotton were dyed with this polymeric dye and fixed by the use of crosslinking agent. The fixation can reach 99%, and wash-fastness, rub-fastness can reach 4 grade and 4–5 grade, respectively.

Table 1
Dyeing characteristics of polymeric dye

Fibre	Fixation	Wash-fastness			Water-fastness			Light-fastness	Rub-fastness	
		Change	Cotton	Silk	Change	Cotton	Silk		Dry	Wet
Silk	≥99%	4–5	5	5	4–5	5	4–5	3–4	4	4
Cotton	99%	4	4	4	4–5	5	4–5	3–4	4	4

Acknowledgement

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