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Melting-reactive dyes for mass coloration of synthetic fibres (II)—1,4-dihydroxyanthraquinone diglycidyl ether in nylon

Qinghua Meng, Deyin Huang*, Lin Chen, Shaohua Wei

School of Chemistry and Chemical Engineering, Shanghai Jiao Tong University, Shanghai 200240, PR China

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Abstract

Mass coloration of nylon using a melting-reactive dye is described. 1,4-Dihydroxyanthraquinone diglycidyl ether was synthesized as a novel melting-reactive dye in which the epoxy groups in the dye would react with amino groups of nylon by a nucleophilic addition mechanism. The dye was confirmed by UV–vis, IR and ^{1}H NMR spectroscopic analyses. The effect of the proportion of the added dye on the intrinsic viscosity of the polymer was studied. Thermal analysis showed high thermal stability and blending compatibilization. The light fastness of the coloured fibre was measured. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Mass coloration; Reactive dye; Nylon; 1,4-Dihydroxyanthraquinone diglycidyl ether; Chain-extending; Light fastness

1. Introduction

As nylon has a compact structure and high crystallinity, the choices of dyes and dyeing methods for nylon have long attracted research interest. Burkinshaw et al. have considered a series of reactive dyes (e.g. chlorodifluoropyrimidinyl dyes [1], α-bromoacrylamido dyes [2], vinyl sulphone and chlorotriazine dyes [3]), which would react with terminal amino groups in the nylon fibre via bi-molecular nucleophilic substitution (S_N2) reactions. Hrdina developed epoxy reactive dyes for the coloration of wool [4] which achieved technical importance because the reactivity of epoxy group was optimized with respect to the nucleophilic amino group of wool. By virtue of the covalent nature of the dye–fibre bond, these reactive dyes displayed excellent fastness to repeated washing without recourse to an aftertreatment [4].

Reactive blending offers the possibility of chemical reaction between different composites during melt blending [5], and we have successfully developed a melting-reactive dye (perylene-3,4,9,10-tetracarboxylic acid dianhydride) for the mass coloration of PET by this method [6]. The purpose of the present work was to develop an epoxy melting-reactive dye for the mass coloration of nylon. In this paper, 1,4-dihydroxyanthraquinone diglycidyl ether (DDE) was synthesized (Scheme 1) and the epoxy groups in DDE would react with amino groups of nylon by a nucleophilic addition mechanism in the mass coloration (Scheme 2).

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* Corresponding author. Tel.: +86-21-547-43270; fax: +86-21-547-43270.

E-mail address: qhmeng@mail1.sjtu.edu.cn (D. Huang).

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2. Experimental

2.1. Materials

Nylon10,10 was prepared by a typical polycondensation method from sebacic acid and 1,10-diaminodecane with the intrinsic viscosity of 0.889. The other reagents were commercially available and used without further purification.

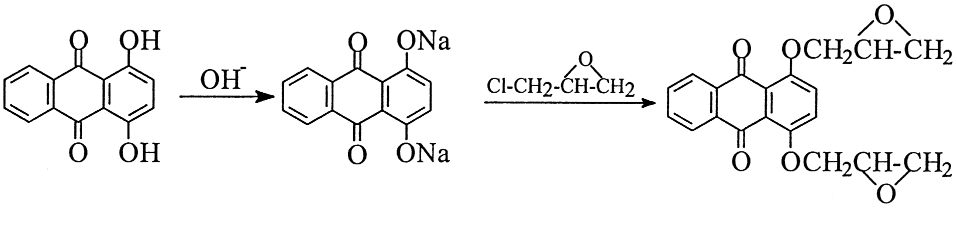
2.2. Instruments

UV–vis spectra were measured on a Lambda 20/2.0 spectrophotometer. IR spectrum was run as KBr pellet on a Pargon 1000 FT–IR spectrophotometer. The thermal stability of the sample was evaluated using a Perkin-Elmer TGA-7 thermal analyser at a heating rate of 20 °C/min in a nitrogen atmosphere. The DSC curves were recorded on a Perkin-Elmer Pyris I DSC under the protection of nitrogen and the scan rate was 20 °C/min. The intrinsic viscosity was measured in formic acid (90%) at 20 °C.

2.3. Procedures

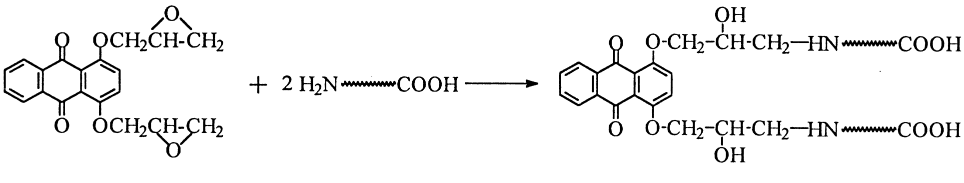
2.3.1. Preparation of 1,4-dihydroxyanthraquinone diglycidyl ether (DDE)

Two grams NaOH, 4 g 1,4-dihydroxyanthraquinone (DHA) and 20 ml toluene were added to a 250 ml flask equipped with a Dean–Stark apparatus. The resulting solution was refluxed for 2 h and then the toluene was distilled. 50 ml epichlorohydrin, 80 ml ethylene glycol and 0.2 g benzyltriethylammonium bromide were added to the flask. The mixture was vigorously agitated at 90 °C for 3 h, and then the excess epichlorohydrin was distilled from the flask at the pressure of 8 mm Hg. After the mixture was cooled, 50 ml chloroform was added to the flask and stirred for 20 min. The extracted solution was then washed with distilled water until the value of pH reached 7. After drying in a vacuum desiccator, the product was obtained as dark brown oil in a yield of 51%. λ_{max}: 424 nm; IR (KBr/cm^{-1}): 2878, 1660, 1256, 1126, 1065, 855; ^{1}H NMR (CDCl$_3$/δ, ppm): 8.17 (s, 2H), 7.73–7.53 (m, 2H), 7.39–7.27 (m, 2H),



(DDE)

Scheme 1. Synthesis of 1,4-dihydroxyanthraquinone diglycidyl ether (DDE).



(DDE) (Nylon)

Scheme 2. The nucleophilic addition mechanism in the mass coloration.

4.64–4.11 (m, 4H), 3.78–3.65 (m, 2H), 2.83–2.64 (m, 4H).

2.3.2. Mass coloration and spinning

Granulated Nylon10,10 and DDE were mixed carefully and then dried in an oven at 100 °C. Mass coloration was carried out in a Haake Rheocord 90 batch mixer equipped with roller blades. The mixing temperature, mixing speed and mixing time were maintained at 280 °C, 100 rpm and 6 min, respectively. The mixture (Nylon–DDE) was then extruded, cooled and pelletized. The resulting product was extracted with acetone in a Soxhlet Extractor, and dried in air. The single filament was formed under laboratory conditions by means of an Instron 4467 capillary rheometer. The diameter of the spinneret hole was 1.27 mm. The blend was extruded from the melt of 230 °C into air of 20 °C at the speed of 0.42 g/min. After passing through the atmospheric medium, the final

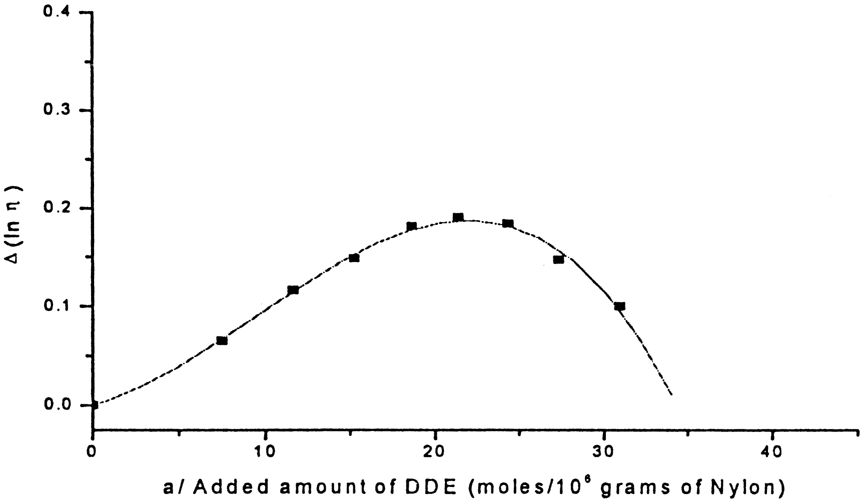


Fig. 1. Effect of added amount of DDE on intrinsic viscosity of nylon.

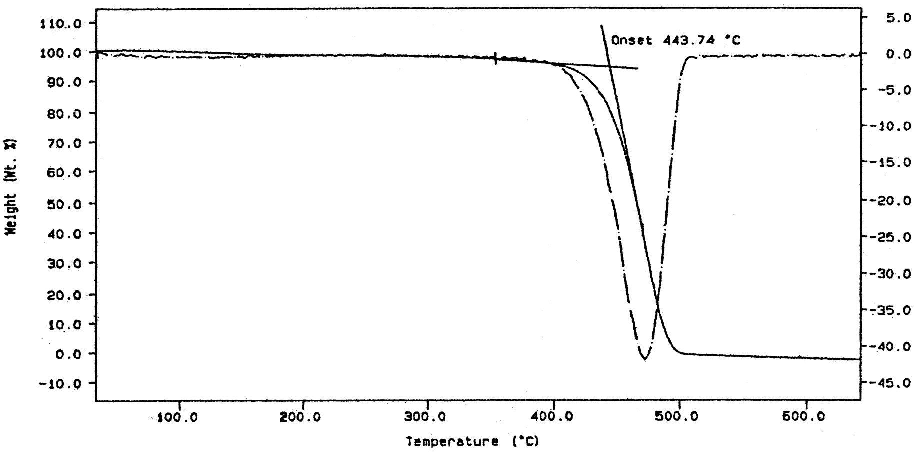


Fig. 2. TG analysis of Nylon–DDE.

fibre (42 dtex) was collected at a speed of 100 m/min. For testing light fastness, the sample and the standard were mounted on a frame partly covered with an opaque sheet, leaving the other half exposed in outdoors for 15 days. The faded sample was compared with the standard [7].

3. Results and discussion

3.1. Effect of added amount of DDE

To investigate the chain-extending reaction behavior of DDE, various amounts of DDE were added to the melt nylon. As seen from experimental results (Fig. 1), the intrinsic viscosity of nylon is increased and the maximum value of $\Delta(\ln \eta)$ was obtained as 0.19 when the added amount of DDE (a) reaches 21 moles per 10^6 g of nylon (0.74 wt.%). Compared with the dye of perylene-3,4,9,10-tetracarboxylic acid dianhydride in PET [6], DDE shows less effective chain-extending reactivity in nylon.

3.2. Solubility

To prove the existence of chemical bond between the dye moiety and polymer chain, the solubility analysis was carried out according to the technique proposed by Marechal [8]. The solubility of DDE, Nylon10,10, and the blend are listed in Table 1. DDE was soluble in ordinary organic solvents such as ethanol, acetone, THF, chloroform, DMF etc, but the dye in blend (Nylon–DDE) was insoluble in these solvents and showed similar behavior to nylon. The resistance to ordinary solvents unambiguously indicated that the dye was chemically bonded to the chain of nylon and could endure dry-cleaning process, which was an important property for the final textile [8].

3.3. Thermal analysis

In principle, dyes and pigments for mass coloration of synthetic fibres require high thermal stability in melt extruding and spinning. The blend (Nylon–DDE) was subjected to thermal analysis. The TG curve in Fig. 2 indicated that Nylon–DDE degraded at the temperature of 443.74 °C,

Table 1
Solubility of DDE and blend in organic solvents

	Ethanol	Acetone	THF	Chloroform	DMF	HCOOH
DDE	S	S	S	S	S	S
Nylon	I	I	I	I	I	S
Nylon–DDE	I	I	I	I	I	S

I, insoluble; S, soluble.

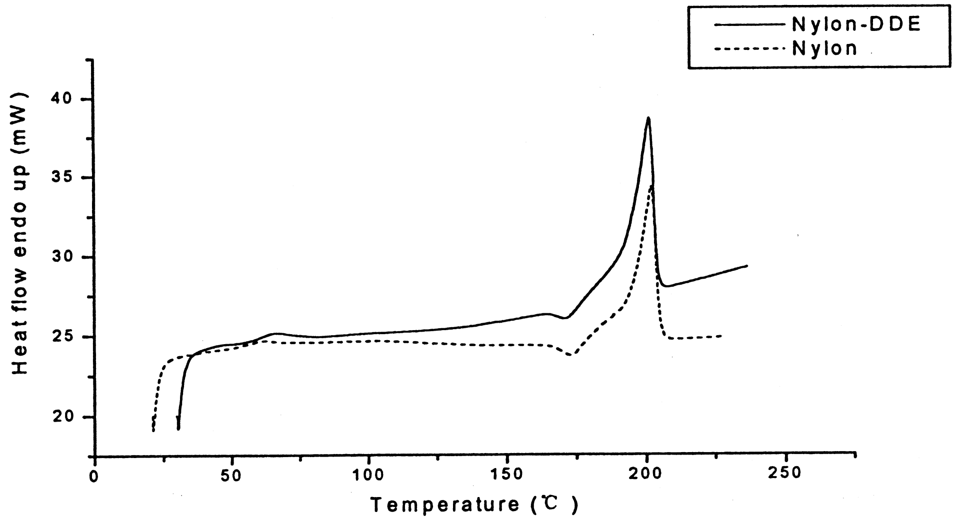


Fig. 3. DSC analysis of Nylon and Nylon–DDE fibres.

Table 2
DSC thermogram data of Nylon and Nylon–DDE fibres

	Glass transition		Crystallization		Fusion	
	T_g (°C)	ΔC_p (J/g °C)	T_c (°C)	ΔH_c (J/g)	T_m (°C)	ΔH_m (J/g)
Nylon	55.5	0.228	173.2	−8.426	201.9	71.156
Nylon–DDE	59.8	0.108	171.2	−1.665	201.3	68.842

which was more than adequately thermally stable for the application.

The DSC curves in Fig. 3 showed thermal behaviors of Nylon and Nylon–DDE in form of fibres. The glass transition, crystallization and fusion of fibres are summarized in Table 2. The single glass transition temperature (T_g) and single melting point (T_m) indicate blending compatibilization. By comparison, the raised T_g of Nylon–DDE indicates that the movement of the polymer chain is restrained by the chain extending reaction; the lower value of ΔH_c of Nylon–DDE fibre indicates less crystallinity, which shows that the crystallization perfection of the fibre was hampered in some sort by the addition of DDE.

3.4. Light fastness

Light fastness is one of the most important properties of textile fibres. The light fastness of the Nylon–DDE fibre was found to be 3–4. The observed low light fastness can be attributed to the photofading of the anthraquinone dye in nylon, which had a greater tendency to give light-induced reduction than polyester [9].

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