Synthesis and Application of Polymeric Dyes Containing the Anthraquinone Structure

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Received 20 December 2000; accepted 12 February 2001

ABSTRACT: Two polymeric dyes containing the anthraquinone structure were prepared via solution polycondensation. Their monomers were prepared through reactions between 1,5-dichloroanthraquinone and nucleophiles. The polymeric dyes were characterized with NMR and thermogravimetry. Their ultraviolet spectra, intrinsic viscosity, and solubility were also measured. Then, the polymeric dyes were applied to the mass coloration of poly(ethylene terephthalate) with good compatibility. © 2002 John Wiley & Sons, Inc. J Appl Polym Sci 83: 1252–1257, 2002

Key words: polymeric dyes; mass coloration; 1,5-bis(2-hydroxyethylamino)anthraquinone (BHAA); 1,5-bis(2-hydroxyethoxy)anthraquinone (BHEA); polymerization; compatability; thermal properties

INTRODUCTION

Poly(ethylene terephthalate) (PET) typically has a compact structure and high crystallinity; the method used at present for the coloration of PET has some drawbacks. The use of a polymeric dye has been proposed as a new effective technique in which the dye is chemically bonded to the polymer.[1] As polyesters are usually prepared via melt-phase polycondensation, the monomers or dye monomers must be stable under the necessary conditions (>260°C, 4 h). The preparation of such a polymeric dye containing the anthraquinone structure has met this problem.[2] In this study, copolyesters containing the anthraquinone structure (Scheme 1) were prepared via solution polycondensation. As high-chromophore-content polyesters, these polymeric dyes could be applied to the mass coloration of synthetic fibers. Scanning electron microscopy (SEM) photomicrographs of colored fibers indicated good compatibility between the polymeric dyes and PET.

EXPERIMENTAL

Materials

Terephthaloyl dichloride was commercially available and was purified by crystallization in petroleum ether. Other reagents were commercially available and were used without further purification.

Syntheses of Monomers

Synthesis of 1,5-Bis(2-hydroxyethylamino)anthraquinone (BHAA)

The synthesis procedure was carried out according to the literature[3] with some modifications. A mixture of 1,5-dichloroanthraquinone (13.8 g,

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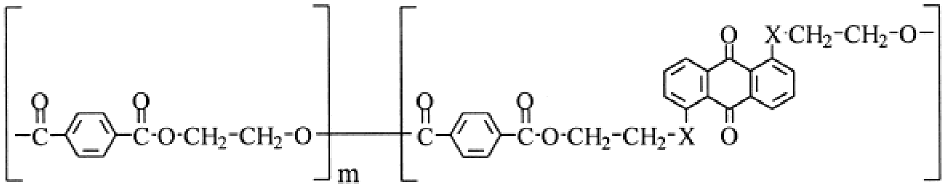
Journal of Applied Polymer Science, Vol. 83, 1252–1257 (2002)

DOI 10.1002/app.2296



Scheme 1 Polymeric dyes containing the anthraquinone structure.

0.05 mol), ethanolamine (20.0 g, 0.33 mol), and ethylene glycol (100 mL) was heated to about 120°C for 18 h with good agitation. The dark-red reaction mixture was cooled to about 40°C, and water (300 mL) was added to precipitate the product. It was collected by filtration, washed with demineralized water, and air-dried to yield 14.8 g of product (91% of the theoretical yield), with a melting temperature (T_m) of 266–267°C and an absorption maximum at 513.0 nm in the visible absorption spectrum in chloroform.

Synthesis of 1,5-Bis(2-hydroxyethoxy)anthraquinone (BHEA)

A mixture of 1,5-dichloroanthraquinone (10.0 g, 0.036 mol), KOH (5.0 g, 0.089 mol), and ethylene glycol (150 mL) was heated to about 120°C for 24 h with good agitation. The dark-brown reaction mixture was cooled to about 40°C, and water (400 mL) was added to precipitate the product. It was collected by filtration and air-dried to yield 10.9 g of the crude product (T_m = 127–132°C). The crude product was purified by column chromatography or repeated recrystallization from acetic acid/water in the presence of charcoal, and a brilliant yellow product was obtained in a yield of 7.6 g (64% of the theoretical yield). The resulting product had a T_m of 185–186°C and an absorption maximum at 381.9 nm in the visible absorption spectrum in chloroform.

Syntheses of Polymeric Dyes

BHAA (0.435 g, 1.33 mmol) and ethylene glycol (1.57 g, 25.4 mmol) were thoroughly dissolved in 10 mL of pyridine and 30 mL of chloroform in a 150-mL Erlenmeyer flask fitted with a reflux condenser. Terephthaloyl dichloride (5.42 g, 26.7 mmol) was dissolved in 25 mL of chloroform and was added to the former solution slowly. After reacting at 80°C for 1.5 h, the mixture was allowed to cool. The red solid was collected as a precipitate and washed with ethanol. After a period of drying in a vacuum desiccator, 3.38 g (39.93 %) of polymeric dye (poly-BHAA) was obtained (λ_{max} = 518.0 nm in phenol/tetrachloroethane, $[\eta]$ = 0.29 dL/g).

The polymeric dye of poly-BHEA was also prepared by the aforementioned method with a yield of 54.35% (λ_{max} = 391.8 nm in phenol/tetrachloroethane, $[\eta]$ = 0.24 dL/g).

Mass Coloration of Polyester Fiber

PET with an intrinsic viscosity of 0.6 was prepared by a typical polycondensation method from bis(β-hydroxyl terephthalate). Granulated PET

Table I Products Indicated by HPLC MS

Product	Retention Time (min)	Area (%)	MS: m/z (M + H)[a]		Substitute	
			Calcd	Found	1-Position	5-Position
BHEA	3.3	71.45	329.3	329.1	—OCH_2CH_2OH	—OCH_2CH_2OH
BY-1	4.0	10.22	269.3	269.1	—OCH_2CH_2OH	—H
BY-2	4.2	4.74	303.7	303.0	—OCH_2CH_2OH	—Cl
BY-3	4.5	11.41	285.2	285.1	—OCH_2CH_2OH	—OH

[a] Data were recorded on HP1100-LC/MSD.

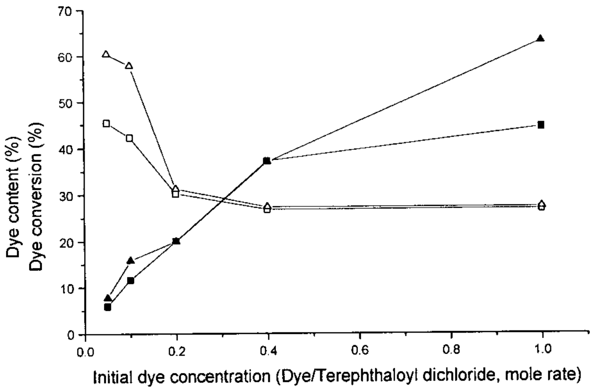


Figure 1 Effect of the initial dye concentration on polycondensation: (▲) dye content of poly-BHAA, (■) dye content of poly-BHEA, (△) dye conversion in poly-BHAA, and (□) dye conversion in poly-BHEA.

and the prepared polymeric dye (2%) were mixed carefully and then dried in an oven at 130°C to a moisture content of less than 0.01 wt %. 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 was then extruded, cooled, and pelletized. The resulting product was extracted with acetone in a Soxhlet extractor and dried in air. The colored PET fiber was formed under laboratory conditions with an Instron 4467 capillary rheometer. It was extruded from the melt at a temperature of 273°C into air at a temperature of 20°C. After passing through the atmospheric medium, the colored fiber was collected at a speed of 100 m/min. The intrinsic viscosity of the colored fibers was measured to be 0.58 dL/g.

Characterization

T_m was determined on a Yanaco Mp-500 apparatus. The intrinsic viscosity was measured in phenol/tetrachloroethane (50/50 v/v) at 25°C. Ultraviolet–visible spectra were measured on a Lambda 20/2.0 spectrophotometer. ^{1}H-NMR spectra were recorded on a Gemini 2000 (300 Hz; Varian, Ltd.) in CF_3COOD as a solvent. The dye contents were measured on the basis of ^{1}H-NMR spectra. The thermal stability of the sample was evaluated with a TGA-7 thermal analyzer (PerkinElmer) at a heating rate of 20°C/min under a nitrogen atmosphere. The colored fibers were cryogenically fractured in liquid nitrogen. The surfaces of the fractured specimens were gold-sputtered and observed on a Hitachi S-2150 scanning electron microscope operated with secondary electron imaging at 20 kV.

RESULTS AND DISCUSSION

Synthesis of Monomeric Dyes

The chlorine atom at the 1-position of anthraquinone shows activity in substitution reactions and makes 1-chloroanthraquinone, 1,5-dichloroanthraquinone, and 1,8-dichloroanthraquinone, a group of readily available materials for the preparation of anthraquinone compounds.[3–5] X-ray diffraction analysis of a single crystal shows that chlorine at the 1-position is obviously repelled by the nearby oxygen atom (carbonyl group). Such a repelling force may enhance chlorine's leaving tendency in a substitution reaction.[6] The yields and purity of the direct substitution reaction depended on the nucleophiles. Because of the weaker nucleophilicity of ethylene glycol, the preparation and purification of BHEA were more laborious than those of BHAA. The crude product of BHEA was studied with high-performance liquid chromatography (HPLC) mass spectrometry (MS), and the results are shown in Table I. Three byproducts (BY-1, BY-2, and BY-3) were identified, in addition to BHEA. Pure BHEA for poly-

Table II Solubility of Monomeric and Polymeric Dyes in Organic Solvents

	Ethanol	Acetone	THF	Chloroform	DMF	Phenol/Tetracholoroethane
BHAA	S	S	S	S	S	S
BHEA	S	S	S	S	S	S
Poly-BHAA	I	I	I	I	I	S
Poly-BHEA	I	I	I	I	I	S
PET	I	I	I	I	I	S

I = insoluble; S = soluble.

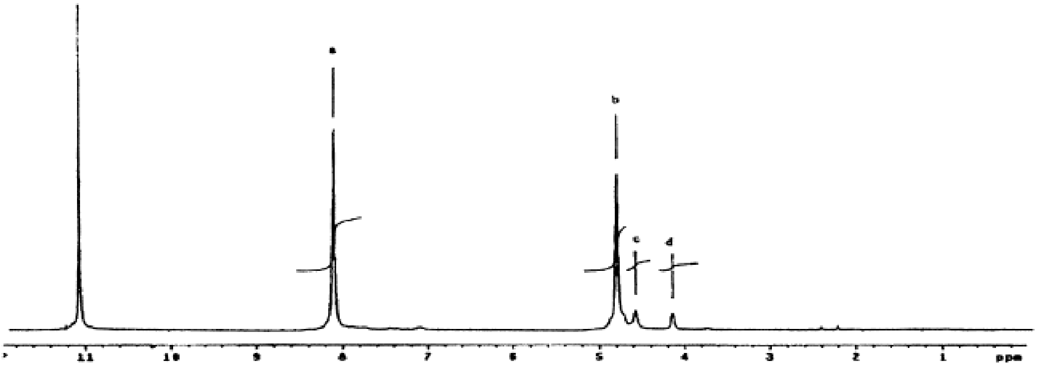


Figure 2 ^{1}H-NMR spectrum of poly-BHEA.

condensation could be obtained by column chromatography or repeated recrystallization.

Syntheses of Polymeric Dyes

Although the syntheses of polymeric dyes in solution polycondensation avoided the destruction of the anthraquinone structure, some disadvantages appeared, such as low intrinsic viscosity and the use of uncovered toxic solvents. From the Mark–Houwink relationship,[7] the viscosity-average molecular weights of poly-BHAA and poly-BHEA were calculated to be 8500 and 6700, respectively. As shown in Figure 1, an increase in the quantity of the dye in the reaction mixture resulted in an increase in the concentration of the polymeric dye but a decrease in the dye conversion. This should be considered with respect to a suitable dye content for economic purposes.

Solubility Analysis

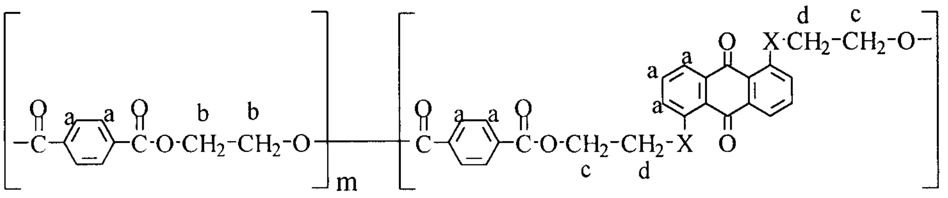
To prove the existence of a chemical bond between the dye moiety and polymer chain, we carried out a solubility analysis according to the technique proposed by Marechal.[2] The solubility of the monomeric and polymeric dyes is listed in Table II. Monomeric dyes were soluble in common organic solvents such as ethanol, acetone, tetrahydrofuran (THF), chloroform, and dimethylformamide (DMF), but the polymeric dyes were insoluble in these solvents. Polymeric dyes showed solubility behavior similar to that of PET, and the only solvent for them was a mixture of phenol and tetracholoroethane. This result unambiguously indicated that the dyes were chemically bonded to the chain of PET and could endure a dry-cleaning process; this latter property is important for the final textile.[2]

^{1}H-NMR Analysis

As a method of directly observing the chemical environment of bonded hydrogen, ^{1}H-NMR analysis was applied to the characterization of the polymeric dyes. ^{1}H-NMR spectra of the two polymeric dyes were similar. The spectrum of poly-BHEA is shown in Figure 2. The general polymer structure with functional groups was identified (Scheme 2). Proton spectra for the terephthaloyl and anthraquinone groups are taken as the peak of a (δ = 8.1). The proton spectra for the peaks of b, c, and d are summarized in Table III and Scheme 2. No evidence was obtained for the presence of any free monomers in the polymers.

Thermal Analysis

In principle, the thermal stability of polymeric dyes is important for their application in a color



Scheme 2 Identification of the poly-BHEA structure by the ^{1}H-NMR spectrum.

Table III ^{1}**H-NMR Chemical Shift of Polymeric Dyes**

	Position (δ/ppm)			
—X—	a	b	c	d
—O—	8.1	4.8	4.6	4.2
—NH—	8.1	4.8	4.5	4.1

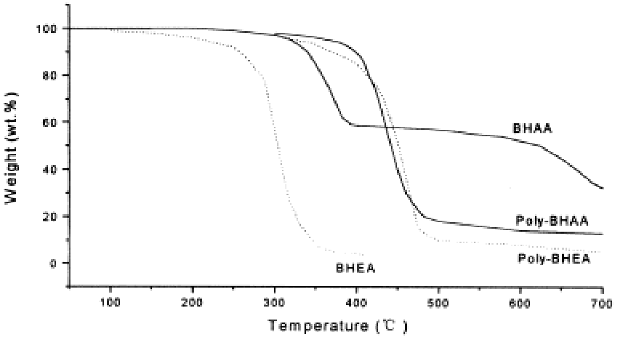


Figure 3 Thermogravimetric curves of monomeric and polymeric dyes.

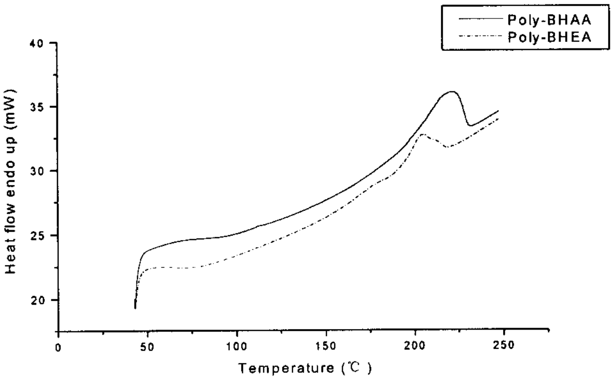


Figure 4 DSC analysis of polymeric dyes.

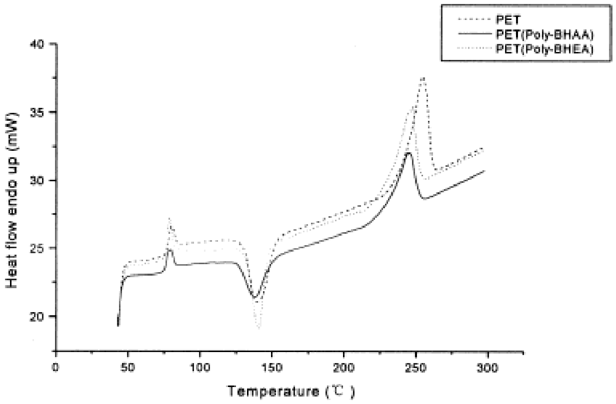


Figure 5 DSC analysis of colored fibers.

master batch.[2] Thermogravimetric curves of monomeric and polymeric dyes are shown in Figure 3. It is obvious that the polymeric dyes had better thermal stability than monomeric dyes, which qualified them for the mass coloration of PET. The prepared polymeric dyes were then applied to mass coloration, and the blend could be spun under the same conditions as PET.

The differential scanning calorimetry (DSC) curves in Figure 4 show thermal behaviors of polymeric dyes. The T_m's are indicated in the curves, but no glass transition and cold crystallization are observed. The polymeric dyes with low molecular weights did not exhibit typical thermal properties of PET.

The DSC curves in Figure 5 show thermal behaviors of PET and colored PET in the form of fibers. The glass transition, cold crystallization, and fusion of fibers are summarized in Table IV. The single glass-transition temperature (T_g) and single T_m indicated blending compatibility. The peak that appeared at T_g was probably due to stress residue, which was formed in the process of spinning. In comparison, the values of ΔH_c and T_m of colored PET fiber were smaller than those of uncolored fiber, which indicated lower crystallinity. The crystallization perfection of the fibers was

Table IV DSC Thermogram Data of Fibers

	Glass Transition		Cold Crystallization		Fusion	
	T_g (°C)	ΔC_p (J/g °C)	T_c (°C)	ΔH_c (J/g)	T_m (°C)	ΔH_m (J/g)
PET	76.7	0.336	139.7	−32.4	254.7	51.7
PET (poly-BHAA)	75.2	0.385	138.3	−25.5	244.7	47.0
PET (poly-BHEA)	75.6	0.385	140.7	−29.9	248.1	51.4

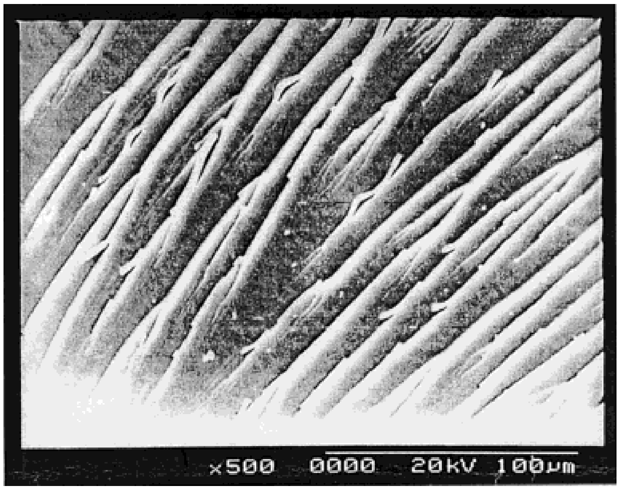


Figure 6 SEM fractured-surface study of fiber colored by poly-BHAA.

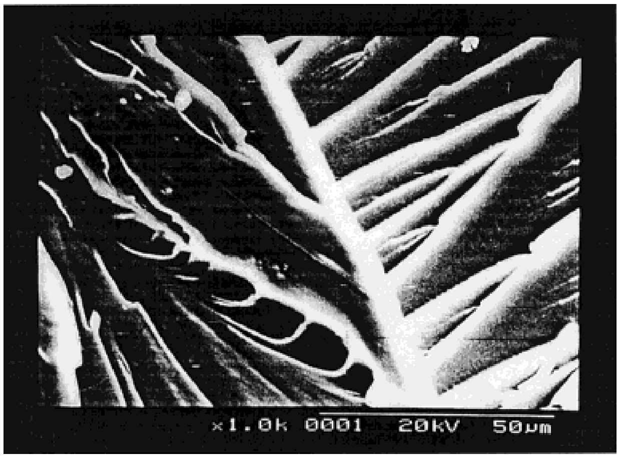


Figure 7 SEM fractured-surface study of fiber colored by poly-BHEA.

probably hampered in some way by the addition of polymeric dyes.

Compatibility

Figures 6 and 7 show SEM photomicrographs of the tensile fracture surfaces of colored PET fibers. Excellent oriented structures are observed, and no large granular particles are found on either fracture surface. The clean surface morphology indicates that the polymeric dyes were compatible with PET. This was probably due to the resemblance of the polymeric dyes and PET in the polarity and flexibility of their polymer chains.

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