

# Synthesis and Characterization of Poly(1,4-dihydroxyanthraquinone terephthalate)

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**ABSTRACT:** A novel polymeric dye containing an anthraquinone ring was prepared by solution polycondensation. The molecule geometry was fully optimized on the basis of the AM1 method. The hydrogen bond was formed and retained coplanarity in the molecular structure. In its UV spectrum, a large hypsochromic shift and a hypochromic effect were observed due to polyesterification. The polymeric dye was also characterized by means of IR and TG. Its thermal degradation mechanism was elucidated. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 81: 2246–2248, 2001

**Key words:** 1,4-dihydroxyanthraquinone (DHA); poly(1,4-dihydroxyanthraquinone terephthalate) (P-DHA); Polymeric dye; thermal degradation mechanism

## INTRODUCTION

Investigation of third-order nonlinearity is important for all-optical switching, optical bistability, and optical logic.<sup>1</sup> Organic structures provide flexibility to tailor their molecular structure and use molecular engineering to maximize the optical nonlinearity. Almost all third-order nonlinear optical materials are induced by  $\pi$ -electron oriented intra- and intermolecular interactions. Most dyes have large  $\pi$ -conjugated structures and are thus valuable candidates for nonlinear optical materials.<sup>2,3</sup>

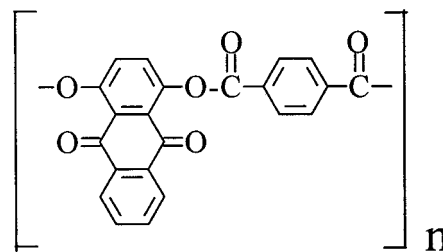
In this article, we report on a novel polymeric dye- Poly(1,4-dihydroxyanthraquinone terephthalate) (P-DHA), containing anthraquinone rings (Fig. 1). Anthraquinone has a coplanar structure and two-dimensional delocalized  $\pi$ -electron distribution.<sup>4</sup> The interlayer  $\pi$ - $\pi$  interaction may lead to three-dimensional molecular stacking in the crystal zone of the polymer. This will be helpful to produce

large third-order nonlinear optical susceptibility. As a high chromophore-contained polyester, the polymeric dye may also be applied in mass coloration of synthetic fibres or plastics with good compatibility.<sup>5</sup>

## EXPERIMENTAL

### Materials and Equipment

The 1,4-dihydroxyanthraquinone (DHA) and terephthaloyl dichloride were commercially available, and were purified by crystallization in ethanol



**Figure 1** Poly(1,4-dihydroxyanthraquinone terephthalate) (P-DHA).

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and petroleum ether. Other reagents were commercially available and used without further purification.

The melting point was determined on a Yanaco Mp-500 apparatus. The intrinsic viscosity was measured in *N,N*-dimethylacetamide (25°C). UV/VIS spectra were measured on a Lambda 20/2.0 spectrophotometer. IR spectra were run as KBr pellets on a Pargon 1000 FTIR spectrophotometer. The thermal stability of the sample was eval-

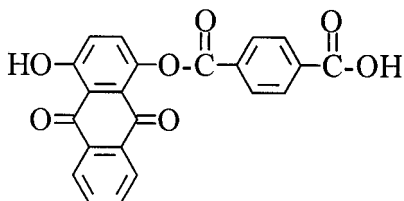


Figure 2 Model compound (DAT).

uated using a TGA-7 thermal analyzer (Perkin-Elmer) at a heating rate of 20°C/min in nitrogen atmosphere.

#### Preparation of Poly(1,4-dihydroxyanthraquinone terephthalate)

1,4-Dihydroxyanthraquinone (2.4 g) and terephthaloyl dichloride (2.0 g) were thoroughly dissolved by 60 mL pyridine in a 150-mL Erlenmeyer flask fitted with a reflux condenser. After reaction at 115°C for 1.5 h, the mixture was allowed to cool. The bright yellow solid was collected as precipitate and washed by ethanol. After being dried in a vacuum desiccator, 4.1 g (94%) of polymeric dye was then obtained; m.p. > 300°C,  $[\eta]$  0.41 g/dL.

#### Computational Approach

The molecule geometry was fully optimized on the basis of the semiempirical AM1 Hamiltonian in

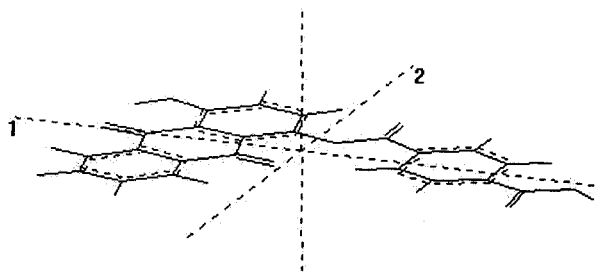


Figure 3 Three-dimensional structure of DAT.

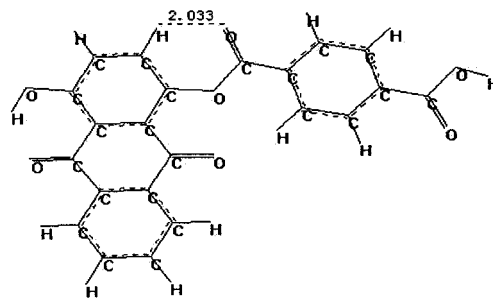


Figure 4 Hydrogen bond formed in DAT.

the MOPAC package. The PRESICE option was used as a convergence criterion for geometry calculation.

## RESULTS AND DISCUSSION

### Geometric Structures

The overall three-dimensional structure of 1,4-dihydroxyanthraquinone (DHA) was reported by G. D. Nigam, and it showed perfect coplanarity.<sup>4</sup> As single crystals of polymers for the X-ray diffraction technique were nearly impossible to obtain, we introduced a model compound (DAT) (Fig. 2) instead of poly(1,4-dihydroxyanthraquinone terephthalate) (P-DHA), and optimized its geometry by the AM1 method.

A general three-dimensional view of DAT is shown in Figure 3. In Figure 4, an intramolecular contact distance of 2.033 Å indicated the formation of hydrogen bonds. Even when bonded with a terephthaloyl group by esterification, the integral dye molecule retained its coplanarity, due to the hydrogen bond between O atoms in the ester site

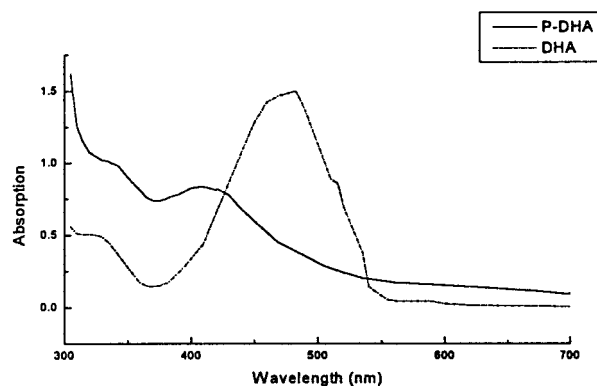
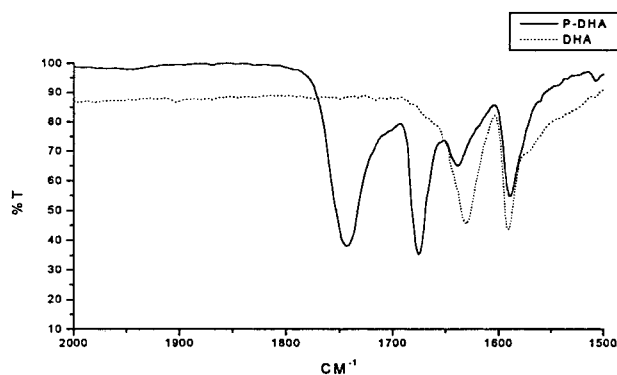


Figure 5 UV/VIS absorption spectra of P-DHA ( $1.67 \times 10^{-4}$  M) and DHA ( $1.01 \times 10^{-3}$  M).

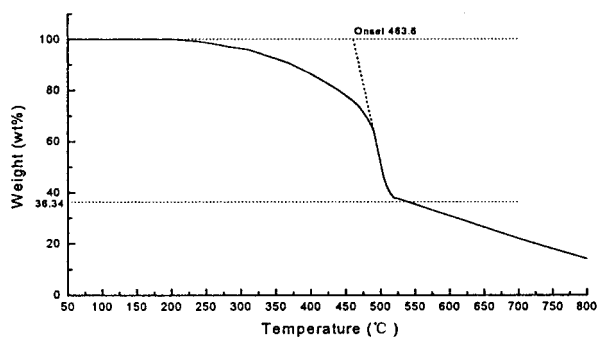


**Figure 6** Infrared spectra of P-DHA and DHA.

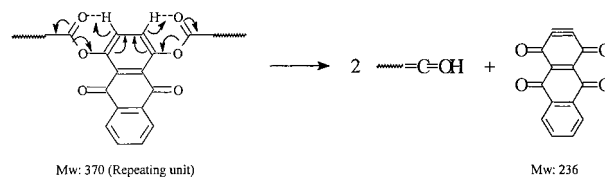
and H atoms in the anthraquinone ring. As a result, the coplanar structure would play an important role in producing three-dimensional molecular stacking, and then might lead to better optical nonlinearity and a more brilliant hue. This polymeric dye has a melting point of  $>300^{\circ}\text{C}$ , which is attributed to the rigid molecular stacking behavior as well.

### Spectroscopic Analysis

It could be found in the UV/VIS spectra (Fig. 5), that absorption spectrum of P-DHA was different from that of DHA.  $\lambda_{\text{max}}$  of DHA and P-DHA were 481.01 and 407.75 nm, respectively, which indicated a large hypsochromic shift of 73.26 nm as a result of polyesterification. In addition, a marked



**Figure 7** Infrared spectra of P-DHA and DHA.



**Scheme 1** Thermal degradation mechanism of P-DHA.

hypochromic effect was observed, and  $\epsilon_{\text{max}}$  of P-DHA was only 1/10.6 that of DHA. In the IR spectra (Fig. 6), reaction of DHA with terephthaloyl dichloride was confirmed by the appearance of absorption peak at  $1744\text{ cm}^{-1}$  (ester group in P-DHA). A hypsochromic shift of  $44\text{ cm}^{-1}$  was also observed for carbonyl groups in the midring of the anthraquinone.

### Thermal Analysis

In principle, thermal stability of polymeric dyes is important for their application in optical materials and the color master batch. P-DHA was then subjected to the thermal analysis. The TG curve of P-DHA is shown in Figure 7, which indicates thermal degradation behavior similar to ordinary polyesters. The thermal degradation process of P-DHA can be explained by the mechanism (Scheme 1), which involves a transition structure of a six-member ring with the assistance of the hydrogen bonding mentioned above (Fig. 4). Such a mechanism was supported by the weight loss in the TG curve (Fig. 7) as 63.66 wt % (Calcd. 63.78 wt %).

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