

# Melting-Reactive Dyes for Mass Coloration of Nylon Based on Blend Compatibilization: Perylene-3,4,9,10-tetracarboxylic Acid Dianhydride

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**ABSTRACT:** The mass coloration of nylon-1010 with a melting-reactive dye, an economically favorable and environmentally friendly method of coloration, is described. Perylene-3,4,9,10-tetracarboxylic acid dianhydride (PTAD) was used as a melting-reactive dye for nylon-1010, and it showed high thermal stability. A chain-extending reaction was confirmed by an ultraviolet–visible spectroscopic analysis. The effect of the proportion of added PTAD on the intrinsic viscosity of the polymer was studied, and increased amounts resulted in increased intrinsic viscosity. The light fastness of the colored fibers was found to be 4. © 2002 John Wiley & Sons, Inc. *J Appl Polym Sci* 83: 2164–2167, 2002

**Key words:** reactive dyes; mass coloration; nylon-1010; perylene-3,4,9,10-tetracarboxylic acid dianhydride (PTAD); chain-extending; reactive extrusion; compatibility; thermal property

## INTRODUCTION

Synthetic fibers (polyester and nylon) typically have compact structures and high crystallinity. Dyes and dyeing methods for them have long attracted researchers.<sup>1–3</sup> Reactive blending offers attractive opportunities for developing new materials with useful combinations of properties.<sup>4</sup> Thus, new covalent bonds are generated *in situ* during melt blending. Therefore, this method can also be used for the mass coloration of synthetic fibers and has been successful in the coloration of polyester.<sup>5</sup>

In this study, perylene-3,4,9,10-tetracarboxylic acid dianhydride (PTAD), a useful melting-reactive dye containing two carboxylic anhydrides,

was reacted with amino groups in nylon and hydroxyl groups in polyester. Chain-extending reactions took place during the blending of PTAD and nylon in the melt phase (Scheme 1). Such a method is particularly useful because it avoids the pollution problems of traditional dyeing methods.<sup>6</sup>

## EXPERIMENTAL

### Materials

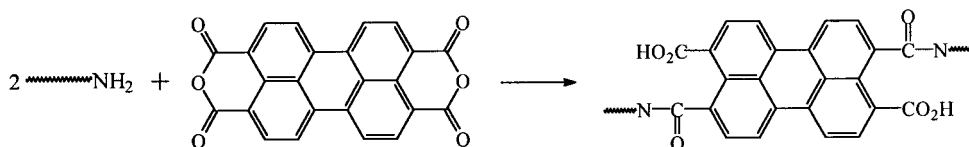
The reagents were commercially available and were used without further purification.

### Instruments

Ultraviolet–visible (UV–vis) spectra were measured on a PerkinElmer Lambda 20 UV–vis spectrophotometer (PerkinElmer, Norwalk, CT) in a

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Scheme 1 Chain-extending reaction.

phenol/tetrachloroethane solution ( $10^{-5}$  M). The intrinsic viscosity was measured in phenol/ethanol (2/1) at 30°C. The thermal stability of the samples was evaluated with a TGA-7 thermal analyzer (PerkinElmer) at a heating rate of 20°C/min in a nitrogen atmosphere. Differential scanning calorimetry (DSC) curves were recorded on a PerkinElmer Pyris I differential scanning calorimeter (PerkinElmer) under nitrogen, and the scan rate was 20°C/min. Mechanical properties of the fibers were evaluated with an Instron 4465 tensile tester (U.S.A.) at a crosshead speed of 25 mm/min. For testing the light fastness, the sample and standard were mounted on a frame partly covered with an opaque sheet, with the other half exposed outdoors for 15 days. The faded sample was compared with the standard.

### Procedures

Nylon-1010 was prepared with a typical polycondensation method from the nylon salt of decanediamine and decanedioic acid and had an intrinsic viscosity of 0.889 dL/g and a melting point of 201°C. Granulated nylon-1010 and PTAD (21.4 mol/10<sup>6</sup> g of nylon) were mixed carefully and then dried in an oven at 100°C. Mass coloration was carried out in a Haake Rheocord 90 batch mixer (Berlin, Germany) equipped with roller blades. The mixing temperature, mixing speed and mixing time were maintained at 240°C, 100 rpm, and 6 min, respectively. The mixture (nylon-PTAD) was then extruded, cooled, and pelletized. The resulting product was washed with acetone in a Soxhlet extractor and dried in air. The colored nylon fiber was formed under laboratory conditions with an Instron 4467 capillary rheometer. It was extruded from the melt at a temperature of 230°C into air with a temperature of 20°C. After passing through the atmospheric medium, the colored fiber was collected at a speed of 100 m/min.

## RESULTS AND DISCUSSION

### Spectroscopic Analysis

UV-vis spectra of PTAD and nylon-PTAD are given in Figure 1, and the  $\lambda_{\text{max}}$  values are 519.8

and 535.7 nm, respectively, indicating a marked bathochromic effect of 15.9 nm. Obviously, this is the result of the reaction of PTAD with terminal amino groups of nylon.

### Effect of Added PTAD on the Intrinsic Viscosity of Nylon

To investigate the reactivity of PTAD, we added various amounts of PTAD to molten nylon under the same process conditions, and we measured the changes in their intrinsic viscosity. The results shown in Figure 2 indicate a behavior similar to the chain-extending reaction in poly(ethylene terephthalate).<sup>7</sup> As seen in the experimental results, the maximum value of the intrinsic viscosity obtained was 1.15 (dL/g) when the added amount of PTAD reached 21.4 (mol/10<sup>6</sup> g of nylon). Therefore, PTAD is beneficial for the spinning of colored nylon.

To evaluate the effectiveness of the chain extender quantitatively, we introduced the extending-efficiency (EE) parameter:

$$\text{EE (\%)} = \frac{r}{a} \quad (1)$$

where  $a$  is the amount of PTAD added to nylon (mol/10<sup>6</sup> g of nylon) and  $r$  is the amount of PTAD

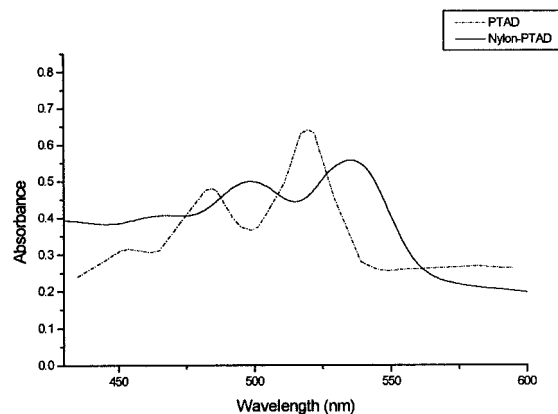
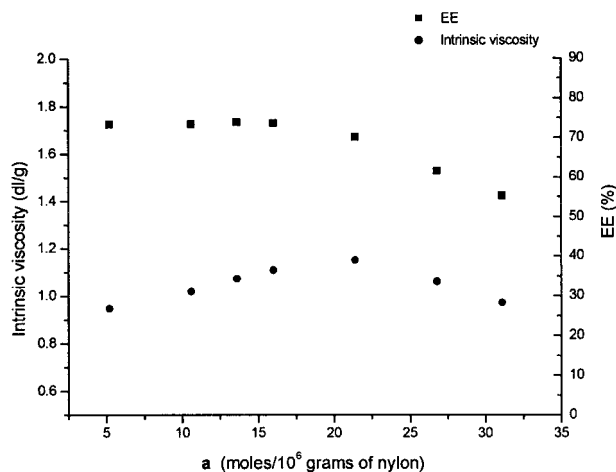


Figure 1 UV-vis spectra of PTAD and nylon-PTAD.



**Figure 2** Effect of added PTAD on the intrinsic viscosity of nylon.

bonded to the terminal groups of nylon (mol/10<sup>6</sup> g of nylon).

From Scheme 1,

$$n = n_0 + a - 2r \quad (2)$$

where  $n_0$  and  $n$  are the amounts of molecules for the initial nylon and the blend (mol/10<sup>6</sup> g), respectively.

Because the viscosity-average molecular weight ( $M_\eta$ ) approximates the number-average molecular weight ( $M_n$ ),  $n_0$  and  $n$  in eq. (2) can be calculated from  $\eta$  with the Mark-Houwink equation:

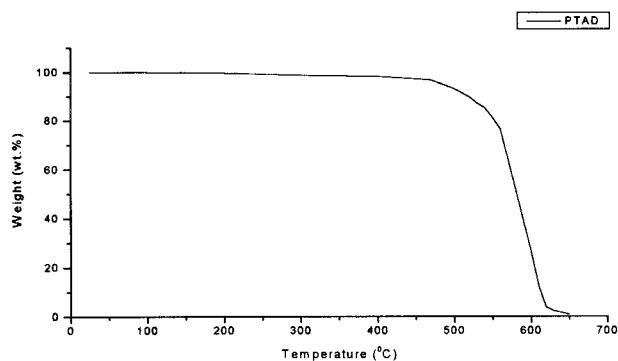
$$\eta = KM_\eta^\alpha = KM_n^\alpha = K\left(\frac{10^6}{n}\right)^\alpha \quad (3)$$

where  $\eta$  is the intrinsic viscosity of the polymer and  $\alpha$  and  $K$  are the constants in the Mark-Houwink relationship.

Therefore,

$$\begin{aligned} \text{EE} (\%) &= \frac{r}{a} = \frac{n_0 - n}{2a} + \frac{1}{2} \\ &= \frac{10^6}{2a} \left[ \left(\frac{K}{\eta_0}\right)^{1/\alpha} - \left(\frac{K}{\eta}\right)^{1/\alpha} \right] + \frac{1}{2} \quad (4) \end{aligned}$$

The EE values of PTAD in blending were calculated with eq. (4), and the results are shown in Figure 2.

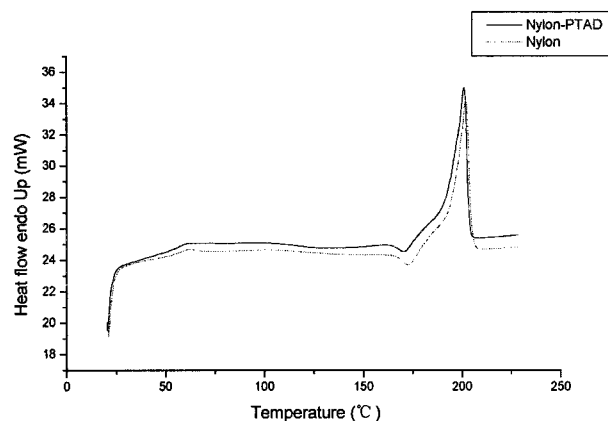


**Figure 3** Thermogravimetric analysis of PTAD.

### Thermal Analysis

In principle, dyes and pigments for the mass coloration of synthetic fibers require high thermal stability in melt extruding and spinning. PTAD, the reactive dye used here, was subjected to thermogravimetric analysis, and the results are shown in Figure 3. PTAD decomposed at 560°C, much higher than the processing temperatures in reactive blending and spinning. Thus, PTAD is more than adequately thermally stable for the application.

The DSC curves in Figure 4 show the thermal behaviors of nylon and nylon-PTAD (in the form of a fiber), and Table I summarizes the values of the glass transition, crystallization, and fusion. Blending compatibilization is characterized by the presence of a single glass-transition temperature and a single melting temperature<sup>4</sup> due to the chemical interactions between blend components. The area under the exothermic crystallization peak ( $\Delta H_c$ ) is a measure of the amount of crystallinity,<sup>8</sup> so the reduction of  $\Delta H_c$  suggests a



**Figure 4** DSC analysis of nylon and nylon-PTAD.

**Table I** DSC Thermogram Data of Nylon and Nylon-PTAD

	Glass Transition		Crystallization		Fusion	
	$T_g$ (°C)	$\Delta C_p$ (J/G°C)	$T_c$ (°C)	$\Delta H$ (J/g)	$T_m$ (°C)	$\Delta H$ (J/g)
Nylon	55.5	0.228	173.2	-8.426	201.9	74.2
Nylon-PTAD	57.3	0.349	170.8	-6.101	201.2	78.2

$T_g$  = glass-transition temperature;  $\Delta C_p$  = specific heat at constant pressure;  $T_c$  = crystallization temperature;  $\Delta H$  = enthalpy;  $T_m$  = melting temperature.

low amount of nylon crystallinity. PTAD possibly restricts the crystallization of nylon. However, the higher heat of fusion of nylon-PTAD cannot be easily explained.

### Mechanical Properties

Stress-strain curves for fibers of nylon and nylon-PTAD are shown in Figure 5. The neat nylon shows the typical tensile property of a crystalline polymer. The stress-strain curve for nylon-PTAD is affected by the chain-extending reaction to some extent. The strength and modulus are increased relative to neat nylon, but the elongation at break is decreased. PTAD bonded with nylon probably acts as a hard segment in the polymer chain.

### Light Fastness

Light fastness is one of the most important properties of textile fibers. The light fastness of nylon-PTAD colored fiber was found to be 4, but the

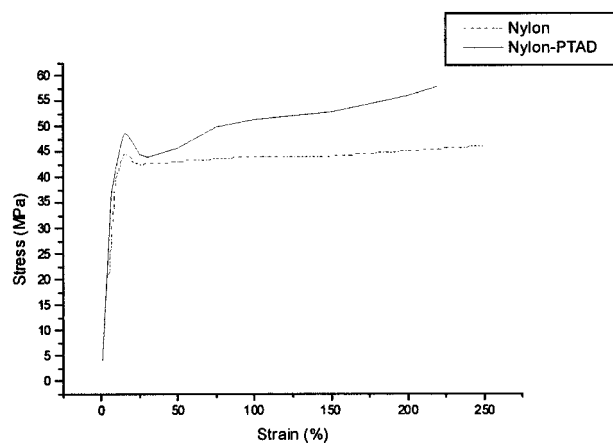
light fastness of the same dye used in polyester was found to be 7.<sup>9</sup> This is probably due to the photofading of dyes on nylon because nylon has a greater tendency for light-induced reactions than polyester.<sup>10</sup>

### CONCLUSIONS

On the basis of experimental results, we find that reactive mass coloration is an economically more favorable and environmentally more friendly method of dyeing. The reactive dye that we used showed high thermal stability and resulted in increased intrinsic viscosity of nylon through a chain-extending reaction. Blend compatibilization was indicated by DSC but suggested low crystallinity. The light fastness of the colored fiber was found to be 4.

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**Figure 5** Stress-strain curves for fibers of nylon and nylon-PTAD