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Syntheses and properties of PVK modified with perylene structures

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Abstract

A perylene dye monomer, *N*-(3,5-dimethyl-) phenenyl-*N*′-allyl-3,4:9,10-perylene tetracarboxylic diimide, was synthesized and copolymerized with *N*-vinyl carbarzole to produce perylene-modified PVK structures. The monomeric and polymeric dyes were characterized by infrared, absorption, and fluorescence spectroscopies, the results of which indicated little difference between the two forms. Intrinsic viscosity studies revealed that the molecular weights of the polymeric dyes were not very high. © 2000 Published by Elsevier Science Ltd.

Keywords: Perylene dyes; PVK; Polymeric dyes; Synthesis; Intrinsic viscosity

1. Introduction

In recent years, perylene colorants were found to be useful as electrophotographic materials [1]. For example, Tang used C.I. Pigment Red 149 coupled with CuPc to form p–n hetero-junction solar cells, in which the conversion efficiency reached 1.00% [2]. Perylene reds have also been used as substrates for OPC materials [3], liquid crystal displays [4,5], laser dyes [6] and fluorescent light collectors [7].

In our previous studies, a series of perylene pigments were synthesized and their sutability as substrates for n-type organic semiconductors in solar cells and as charge generation materials in electrophotography was examined. These Ag/ClAlPc/MePTC/SnO_2 based cells showed excellent photoelectric properties, as their conversion efficiency reached 1.0% with a fill factor of 54.0% [8]. While the use of perylene red pigments in electrophotography also gave good results [9], their low solubility restricted utility in this area. Studies aimed at enhancing solubility have been reported [10,11].

The present paper pertains to the synthesis of perylene-modified polymer structures, which had the combined characteristic of polymers and perylene dyes. In this regard, a perylene dye monomer was designed, synthesized, and copolymerized with *N*-vinyl carbazole. Subsequently, the properties of the monomeric and polymeric compounds were determined.

2. Experimental

2.1. General

Perylene dianhydride was obtained from Anshan Dyestuff Factory and was used without further purification. *N*-vinyl carbazole was purified by

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recrystallization five times from CH_3OH. All other chemicals were reagent grade and were used directly.

IR spectra were recorded on a Nicolet Ft IR spectrophotometer and combustion analyses were performed using a Carlo Erba MOD 1106 automatic microanalyser. Absorption spectra were recorded on a Shimadzu UV-3100 UV–Vis spectrophotometer and fluorescence spectra were recorded by a Shimadzu RF-5000 fluorimeter.

2.2. Synthesis of N-*(3,5-dimethyl-) phenenyl-3,4:9,10-perylenetetracarboxylic monoanhydride monoimide* (**2**) [11]

A mixture of 3,4:9,10-perylenetetracarboxylic dianhydride (**1**; 7.8 g, 0.02 mol), water (80 ml) and triethylamine (12 ml) was stirred at 90°C for about 1 h, whereupon dissolution occurred. Pyridine (20 ml) and 3,5-dimethylaniline (2.7 ml, 0.02 mol) were added, and the reaction mixture was cooled to 20–25°C. The pH was adjusted to 6.4–6.7 with 85% H_3PO_4, and the reaction mixture was heated slowly to 90°C, with stirring, and held at that temperature for 6 h.

The cooled reaction mixture was acidified with 10% HCl and the precipitate was collected by filtration, and washed with 10% HCl and water to remove the amine. The wet filter cake was dissolved in hot 5% KOH (200 ml) and KCl (20 g) was added. The precipitated potassium salt of **2** was collected, and the dissolution/precipitation process was repeated until the filtrate was colorless, indicating that **1** was completely removed. The resultant filter cake was dissolved in hot 5% KOH and filtered quickly. The filtrate was heated and filtered until there was no collectable byproduct **3**. The filtrate was acidified with 10% HCl, filtered, and the solid was washed with water and dried. The yield of **2** was 37.8%.

Compound **2** had a melting point >350°C and had very low solubility in most commonly available organic solvents, preventing further purification. IR spectrum (KBr) ν (cm^{-1}): 1768, 1725 (anhydride), and 1695, 1652 (imide).

2.3. Synthesis of perylene dye monomer (**4**)

A mixture of **2** (2.0 g, 0.004 mol), allylamine (4 ml, 0.07 mol), pyridine (40 ml) and water (15 ml) was stirred at 90°C for 6 h, and then cooled and filtered. The solid was dispersed in hot 5% KOH and filtered quickly. The filter cake was washed with water and dried, giving crude **4** (85%). Recrystallization from nitrobenzene gave IR (KBr) ν (cm^{-1}): 1694, 1651 (imide).

Elemental analysis. Found: C 78.65%, H 7.12%, N 5.24%. Calcd: C 78.43%, H 7.08%, N 5.26%. Absorption spectrum (NMP): 525 nm (λ_{max}), 488 nm. Fluorescence spectrum (NMP): 535 nm (λ_{max}), 577 nm.

2.4. Copolymerization of perylene dye monomer and N-*vinyl carbazole*

A mixture of *N*-vinyl carbazole (1.0 g), dye monomer **4** (0.005, 0.01, or 0.015 g) was stirred at 65°C for 10 min under an N_2 atmosphere. Toluene (30 ml) and BPO (0.005 g) were added, and reaction was at reflux under an N_2 atmosphere for 24 h. After cooling to room temperature, the reaction mixture was filtered. The filtrate was diluted with CH_3OH and the precipitate was collected by filtration. The following process was repeated three times: the collected solid was dissolved in NMP and the insolubles filtered. The filtrate was diluted with CH_3OH and the mixture was filtered. The final cake was dried under vacuum to give a dark red powder.

IR spectrum (KBr) of the polymers showed moderately intense carbonyl bands at 1694 and 1651 cm^{-1} (imide).

2.5. Intrinsic viscosity measurements

About 0.01 g of the polymeric dyes was dissolved in 25 ml NMP and an Ubbelohde viscometer was used to measure the flow times of polymer solutions and the pure solvent. Intrinsic viscosities were then calculated using the following equations:

$$[\eta] = [2(\eta_{sp} - \ln \eta_r)]^{1/2}/C$$

$$\eta_{sp} = \eta_r - 1$$

$$\eta_r = \rho t[1 + K(1/t_0^2 - 1/t^2)]/\rho_0 t_0$$

where $[\eta]$ is the intrinsic viscosity; ρ and ρ_0 are the densities of the polymer solution and the pure solvent; t and t_0 are the flow times of the solution and the pure solvent, and K is the instrument constant.

3. Results and discussion

3.1. Synthesis of perylene dyes

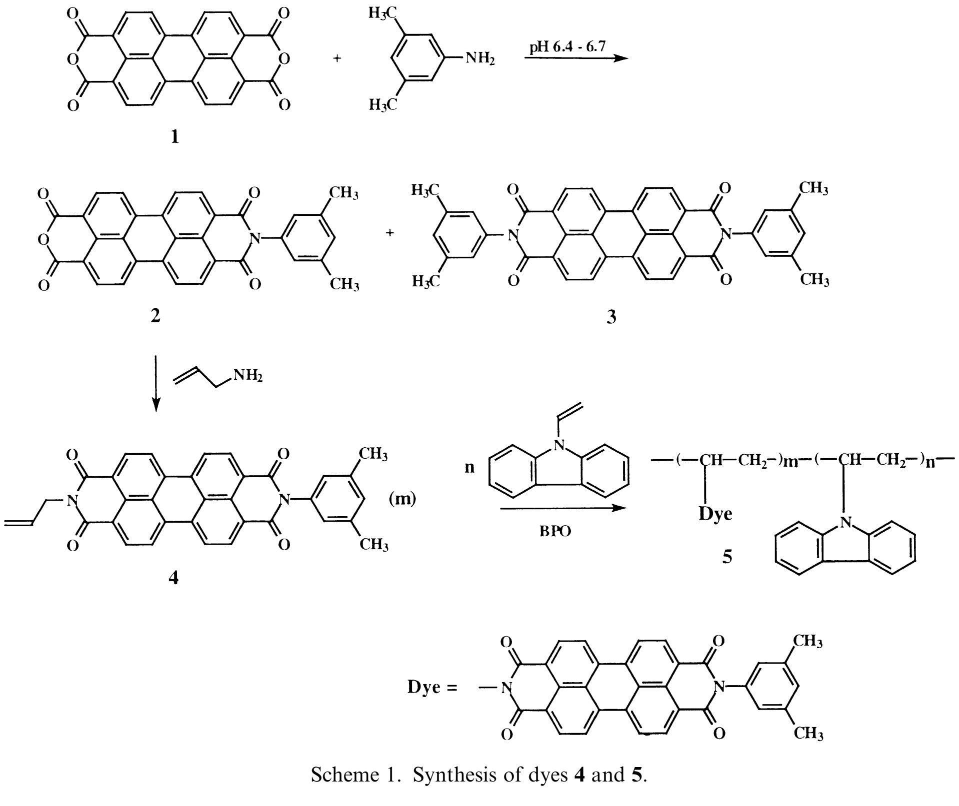
The synthesis of the target dyes is outlined in Scheme 1. Compound **1** was dissolved with the aid of triethylamine (TEA), forming the tetraammonium salt. In the condensation between **1** and 3,5-dimethylaniline, pH control was critical. Since the ammonium compound that arises from the reaction between **1** and TEA would not condense with the aniline derivative, a mixture of H_3PO_4, TEA, and pyridine was used to transform **1** to its monoanhydride diammonium salt. The optimum pH for forming dye **2** was 6.4–6.7. When the pH was below that level, **1** existed as the dianhydride and the proportion of **3** increased, sharply decreasing the yield of **2**.

Separation of **1**, **2** and **3** took advantage of their widely different solubilities in cold and hot KOH solutions. Perylene **1** could be easily dissolved as the potassium tetraammonium salt in cold or hot KOH solution. Perylene **2** was soluble only in hot KOH solution as the diammonium salt. Perylene **3** was insoluble in hot or cold KOH solution, because it could not be salified.

Condensation of perylene **2** with allylamine gave the target dye monomer **4**.

3.2. Properties of polymer dyes

The results shown in Table 1 indicate that the intrinsic viscosities of copolymers of perylene dye monomer **4** and *N*-vinyl carbazole were low. When the content of perylene dye monomer increased, intrinsic viscosity decreased. The reactivity of perylene dye monomer was much lower



Scheme 1. Synthesis of dyes **4** and **5**.

Table 1
Intrinsic viscosities of the polymeric dyes

Code no.	Monomeric dye (g)	*N*-vinyl carbazole (g)	$[\eta]$ (ml g^{-1})
5-1	0.015	1	23.14
5-2	0.010	1	30.86
5-3	0.005	1	37.55

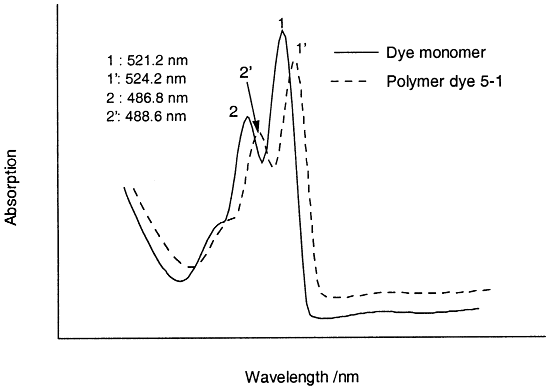


Fig. 1. Absorption spectra of perylene dye monomer and polymer dye **5-1**.

than that of *N*-vinyl carbazole, due to steric hindrance. This led to a low average molecular weight.

The absorption spectra of the polymeric dyes in NMP with different perylene monomer contents were similar. The absorption maxima of the polymers were very close to that of the monomeric dye, with only a 3 nm red shift (Fig. 1). Fluorescence spectra were also very close to that of the perylene dye monomer (Fig. 2). Within the concentration range of 10^{-6}–10^{-5} g/ml, a linear relationship between fluorescence intensity and concentration was observed (Fig. 3), which is characteristic of fluorescent dyes. These results indicate that the incorporation of a perylene dye into a polymer chain did not alter its properties.

The polymeric dyes had good solubility in organic solvents such as acetone, THF, DMF, and NMP, and were easy converted to film form. SEM photographs showed that the films were very uniform.

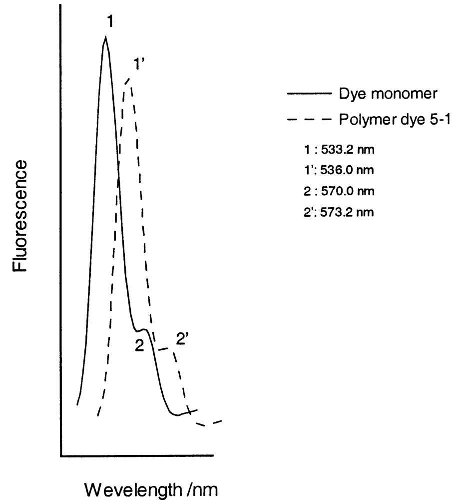


Fig 2. Fluorescence spectra of perylene dye monomer and polymer **5-1**.

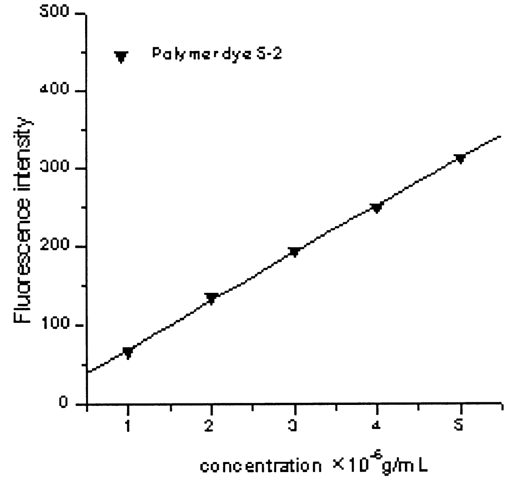


Fig 3. Relationship between fluorescence intensity and polymeric dye concentration.

Previous investigations indicated that PVK-co-CuPc(COOH)$_3$ polymers had better photoconductivities than that of the corresponding CuPc monomers [12]. When the present polymers were deposited as Charge Generation Layers of organic photo-conductors, the photosensitivity was unsatisfactory.

Acknowledgements

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