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Red Pigmentary Polyimides from *N,N'*-Diamino-3,4,9,10-perylenetetracarboxylic Acid Bisimide

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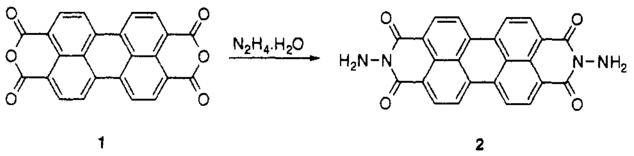
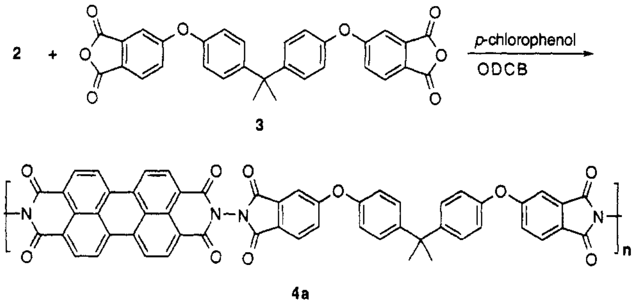
Introduction. The synthesis of soluble pigmentary polymers has generated much interest in the field of polymer chemistry during recent years.[1] Much of the stimulus for this increasing attention comes from the expectation that these materials should be useful because they are photoactive or photoconductive and can be used in optical devices. The direct incorporation of dyes into an appropriate soluble polymer has faced serious difficulties associated with low reactivity and solubility of the aromatic dyes used as monomers or low chemical and thermal stability particularly of many azo compounds.[2,3] Incorporation of monomers which are dyes containing naphthalene, perylene, and phthalocyanine derivatives into the polymeric backbone is difficult due to the rigid structure of the high melting and highly crystalline monomers. Attempted polymerization of these monomers results in low molecular weight materials coming out of solution during polymerization because of their insolubility and intractability. However, some aromatic dyes have found interesting applications as photosensitive materials[4] in addition to their use as pigments,[5] and they have been utilized as dispersions in a binding resin which then forms photoactive films.[6,7] These pigments are widely used in charge-generating coatings in xerography and electrophotography.[8] Only a few pigmentary polymers with aromatic chromophoric groups in the side chain, such as poly(1-vinylpyrene)s, are known. Syntheses of soluble dye-containing polyimides[1c] and low molecular weight polyarylenes[9] have been recently reported. These polymers contain solubilizing alkyl groups such as *tert*-butyl or long alkyl chains, and therefore their preparation methods generally require the use of expensive starting materials and reagents. The introduction of rigid perylene moieties into the backbone of polymers such as polyimides which themselves have low solubilities and are intractable has proven to be difficult. Attempts to make polyimides from 3,4,9,10-perylenetetracarboxylic dianhydride and modified caprolactams in several stages resulted in the formation of undesired gel during the reaction.[10]

Recently, we have reported[11] the synthesis of novel polyimides, poly(ether imide)s, and their copolymers containing naphthalene groups using hydrazine as a reactive diamine. As we were interested in exploring the potential of the *N*-aminoimide chemistry for introducing larger aromatic dye compounds into rigid polyimides, the bis(*N*-aminoimide) from 3,4,9,10-perylenetetracarboxylic dianhydride was prepared and its conversion into high molecular weight color poly(ether imide) and copoly(ether imide)s was studied. The polymers are very soluble in solvents such as chloroform, *sym*-tetrachloroethane (TCE) and *m*-cresol at room temperature, depending on the concentration of perylene moieties in the backbone of the polymers. Polymers with high concentrations of perylene groups are highly crystalline and have glass transition temperatures in the range 353–405 °C.

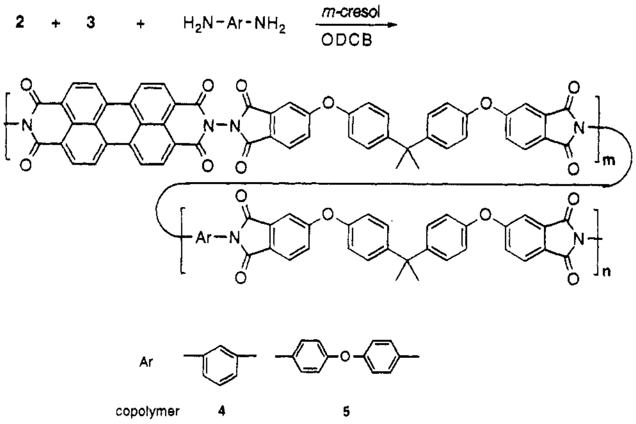
Scheme 1



Scheme 2



Scheme 3



Results and Discussion. The monomer *N,N'*-diamino-3,4,9,10-perylenetetracarboxylic acid bisimide (BNAP) (**2**) was prepared from the reaction of 3,4,9,10-perylenetetracarboxylic dianhydride (**1**) and hydrazine monohydrate in quantitative yield (Scheme 1). This material has been previously synthesized and used as a dye intermediate.[12] Hydrazine monohydrate was used in large excess in order to form a homogeneous suspension. The excess amount of hydrazine was removed under reduced pressure, and the resulting solid was kept in a vaccum oven at 80 °C for 48 h to ensure that all the open ring hydrazides are converted to imide rings. The product was obtained as a dark purple powder, and no further purification was required. The perylene monomer **2** is practically insoluble in most organic solvents. It is slightly soluble in *m*-cresol but readily dissolves in concentrated sulfuric acid. It does not show any melting point up to 400 °C. Polycondensation reactions involving monomer **2** with or without another diamino compound as a comonomer were carried out with Bisphenol A dianhydride (BPADA) (**3**) in a mixture of *m*-cresol and 1,2-dichlorobenzene (ODCB; Schemes 2 and 3). The high molecular weight homopolymer **4a**, copolymers **4b–d** using *m*-phenylenediamine, and copolymers **5a–c** using oxydianiline (ODA) as comonomers (Table 1) were isolated as red to dark reddish purple fibrous materials in excellent yield (92–95%). The polymerization reaction is dependent upon the dissolution of **2** into the solvent and takes 3–9 days depending on the amount of **2** in order to form high molecular weight polymer or copolymers. When a more acidic and higher boiling point solvent such as *p*-chlorophenol, in which **2** is more soluble, was used instead of *m*-cresol, the reaction time was considerably shorter.

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Table 1. Physical Properties of Poly(ether imide)s

polymer	BNAP[a] (mol %)	η_{inh} (dL/g)[b]	T_g (°C)	solubility[c]	film
4a	100	0.48	ND	*m*-cresol	dark red, brittle
4b	80	0.43	359	*m*-cresol, TCE	dark red, brittle
4c	50	0.53	317	TCE	red, flexible
4d	20	0.34	250	chloroform	red, flexible
5a	80	0.47	353	*m*-cresol, TCE	dark red, brittle
5b	50	0.36	304	TCE	dark red, flexible
5c	20	0.50	247	chloroform	red, flexible

[a] Based on the total amount of the diamino compound. [b] Inherent viscosities were measured at a concentration of 0.5 g/dL in *m*-cresol at 50 °C except for **4d** and **5c** which were measured in chloroform at 25 °C. [c] At room temperature.

Table 2. Thermal and Mechanical Properties of Poly(ether imide)s

polymer	TGA (°C)[a]		modulus (GPa)		tan
	N_2	air	25 °C	200 °C	δ(max) (°C)
4a	459	470	1.1	0.5	405
4b	453	468	1.5	1.1	366
4c	464	475	1.9	1.4	328
4d	496	505	0.9	1.4	245
5a	466	474	2.5	1.9	358
5b	470	489	2.1	2.4	315
5c	503	507	0.6	0.7	247

[a] Reported for 5% weight loss.

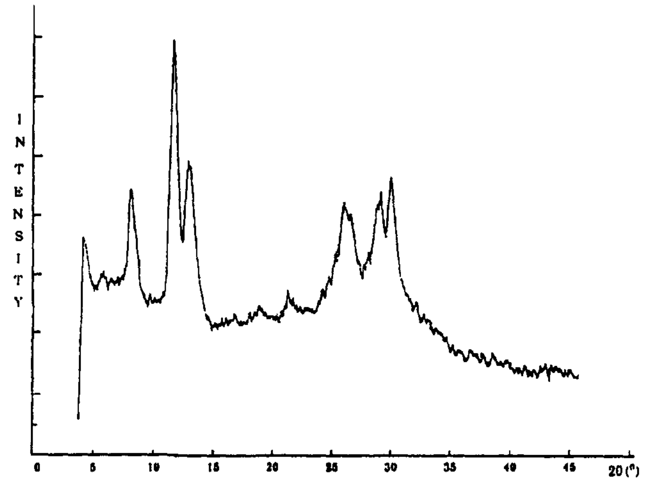

Figure 1. X-ray diffraction of homopolymer **4a**.

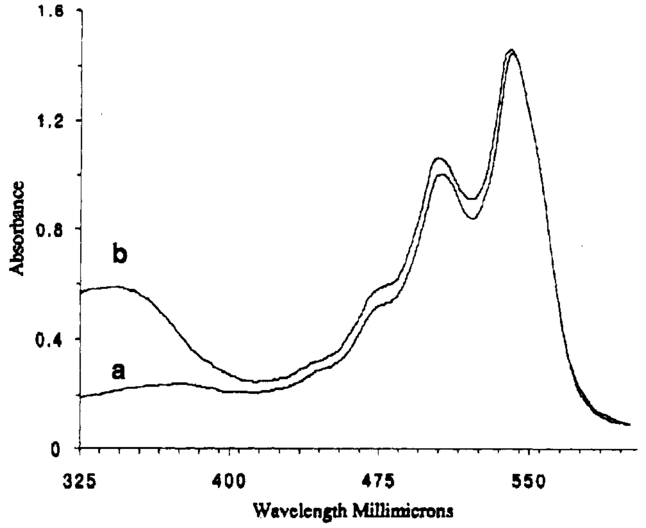

Figure 2. Absorption spectra of (a) perylene monomer **2** and (b) copolymer **4c** in *m*-cresol.

However, *p*-chlorophenol is considerably more difficult to remove from the resulting polymers. Solubility of the resulting polymers is also strongly dependent on the amnount of perylene-containing units in the polymer chain. Solubility decreases from copolymers **4d** and **5c** containing 20 mol % **2** which are readily soluble in chloroform to copolymers **4b** and **5a** with 80 mol % **2** which are only slightly soluble in TCE but readily soluble in *m*-cresol. Homopolymer **4a**, however, is only soluble in *m*-cresol and partially swells in TCE. Inherent viscosities of the polymers, measured in the appropriate solvent, were in the range of 0.34–0.53 dL/g. The ^{1}H NMR spectra of polymers **4d**, **5c**, and **4c** exhibit a broad peak around δ 8.1–8.7 which corresponds to all the protons of the perylene moiety. Integration of this signal and comparison with other signals such as the isopropylidene group show good agreement with the calculated amount of perylene **2** used in the polycondensation. Characteristically, the signals of the protons in the bay region of a perylene appear as a broad peak at lower field. This broadness does not seem to be due to slow motion of perylene rings which might be stacked together in the solution. This was shown by studying the effect of temperature on the shape of this broad peak which remains unchanged up to 100 °C. The isopropylidene moiety shows a resonance at δ 1.75 and other aromatic protons around δ 7.0–8.0. Glass transition temperatures (measured by differential scanning calorimetry, DSC) of the copolymers **4b–d** (359–250 °C) are slightly higher than those of copolymers **5a–c** (353–247 °C) (Table 1), presumably because of less restricted rotation present in the flexible ether linkage of the ODA moiety in copolymers **5a–c**. The T_g's of the copolymers **4b–d** and **5a–c** increase with increasing ratio of perylene monomer **2** to the other comonomer, from 247 to 359 °C (Table 1). Polymer **4a** did not show any transition in the DSC presumably because of its high degree of crystallinity. It started to decompose above 450 °C before it melted. Thermomechanical analysis (TMA) measurement, however, showed a T_g value of 405 °C for **4a** (Table 2). The high degree of restriction to rotation along the N–N bond and the rigid planar structure of the perylene diimide units which would be expected to stack together in the polymer matrix could account for the increase in glass transition temperatures observed in the copolymers. All polymers demonstrate excellent thermal stability by thermogravimetric analysis (TGA), with a 5% weight loss under an atmosphere of air and nitrogen in the temperature range 453–507 °C (Table 2). Tough, red, transparent, and flexible films of copolymers **4c,d** and **5b,c** were obtained by casting from chloroform or TCE. In the case of homopolymer **4a** and also copolymers **4b** and **5a**, which contained 80 mol % **2**, partial crystallization from solution occurred and the films were somewhat brittle. Slow evaporation of solvent over a 2-week period resulted in highly crystalline films of **4a,b** and **5a** which were quite brittle. The crystallinity of these samples was evaluated by X-ray diffraction measurement. As shown in the radial optical density trace of the X-ray powder pattern in Figure 1, homopolymer **4a** showed a high degree of crystalline character and exhibited strong reflection rings. The amount of crystallinity sharply decreased as some of the perylene units were replaced by *m*-phenylenediamine or ODA comonomers. The incorporation of the highly colored *N,N*-diamino-3,4,9,10-perylenetetracarboxylic acid bisimide units into the poly(ether imide)s is evidenced by their UV–vis spectra. In Figure 2, the spectrum of poly(ether imide) **4c** is shown together with that of the perylene **2**. The absorption of the monomeric perylene **2** at λ_{max} = 542 nm remains almost unchanged when this monomer is attached to the polymer backbone of these poly(ether imide)s. Extinction coefficients (ε) in M^{-1} cm^{-1} for all copoly(ether imide)s also confirmed the incorporation of perylene units in the polymer structure (e.g., ϵ = 47 600 for perylene monomer **2** and ϵ = 47 800 for polymer **4c**) (Figure 2). Dilute solutions of polymers with a low concentration of perylene exhibit strong orange fluorescence emission. When a thin film of polymer is excited, a red fluorescence emission is produced (λ_{em} = 670 nm).

A new class of high molecular weight dye-containing poly(ether imide)s and copoly(ether imide)s have been synthesized from the bis(*N*-aminoimide) prepared from 3,4,9,10-perylenetetracarboxylic dianhydride and hydrazine by reaction with Bisphenol A dianhydride using a solution polycondensation method. The polymers are soluble in organic solvents such as TCE and *m*-cresol at room temperature and can be readily cast into flexible, transparent, red-colored films. Their physical, thermal, and mechanical properties have been investigated.

Further work on photochemical and photophysical properties of these materials is in progress for their potential applications in electrophotography.

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