Synthesis of Novel Soluble Poly(Aryl Ether)s Bearing Covalently Bound Naphthalocyanine Units

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SYNTHESIS OF NOVEL SOLUBLE POLY(ARYL ETHER)S BEARING COVALENTLY BOUND NAPHTHALOCYANINE UNITS

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ABSTRACT

Thermally stable poly(aryl ether)s bearing covalently bound zinc(II) naphthalocyanine units have been synthesized by treatment of the dicyanoarylene-containing poly(aryl ether)s with excess amounts of naphthalocyanine molecules and zinc dust in bromonaphthalene. These polymers are soluble in common organic solvents. Their maximum absorption wavelength is 770 nm.

INTRODUCTION

Since the discovery of phthalocyanines [1] in the early 1930s, a rich and varied chemistry and technology has developed around these interesting materials. There are literally thousands of publications and patents concerned with phthalocyanine and its analogs [2, 3]. Recently, there has been renewed interest in phthalocyanine compounds because of their applications in optical data processing [4–8].

Phthalocyanine compounds have high thermal, hydrolytic, and oxidative stabilities. They show high absorption intensities at long wavelengths. This latter property is even more significant since one of the goals of contemporary optical storage instrument design is to use solid semiconductor lasers for writing purposes [9]. These solid-state lasers emit at wavelengths greater than 800 nm, i.e., in the infrared (IR) region. Naphthalocyanine compounds absorbs in the near-IR or in the IR

region, depending on the complexed metal ions or substituents on the naphthalocyanine rings [10–12].

Despite the excellent properties, considerable difficulty has been reported [13] in utilizing these properties because of the extreme insolubility of unsubstituted phthalocyanine and naphthalocyanine compounds, which hinders fabrication into useful devices. In addition, the utility of phthalocyanine and naphthalocyanine systems is limited by crystal size, brittleness, and stability of the matrix materials that hold the dispersed phthalocyanine compounds. Some of these problems could be avoided if phthalocyanine units were covalently incorporated into polymer systems, especially thermooxidatively stable polymers. Although there are reports on the synthesis of small naphthalocyanine compounds [14], there have been no reports on the synthesis of polymers containing naphthalocyanine units.

This paper describes the synthesis of poly(aryl ether)s bearing covalently bound naphthalocyanine units in the polymer main chains. Their physical properties are presented.

EXPERIMENTAL

Materials

Polymers **IV**, **V**, and **VI** were prepared according to our previous procedure [17]. All other chemicals were purchased from Aldrich Chemical Co. and used without further purification. Naphthalocyanine (**X**) was prepared according to the procedure reported [15].

Synthesis of Polymers Bearing Naphthalocyanine Units: Typical Procedure for Polymer VII

To a 100-mL 3-neck flask equipped with an Ar gas inlet and a condenser were added 2 g of polymer **IV**, 4.5 g (7.2 equivalent to polymer **IV**) of 2,3-naphthalenedicarbonitrile, 0.52 g of zinc dust, a catalytic amount of potassium hydroxide and ammonium molybdate (AmMo), and 50 mL of 2- bromonaphthalene. The mixture was heated to 270°C under an atmosphere of argon for 10 hours. Part of the solvent was removed by vacuum distillation, and then the mixture was poured into methanol. A dark blue-green precipitate was collected and washed with methanol, acetone, water, dilute hydrochloric acid, and finally by water and ethanol. The precipitate was collected by filtration and then extracted by chloroform, using a Soxhlet extractor. The chloroform solution was concentrated and precipitated into methanol. The dark green fibrous powder was dried at 180°C for 24 hours. The yield of polymer **VII** is 16% based on polymer **IV**.

Polymers **VIII** and **IX** were synthesized by similar procedures using 30 equivalents of 2,3-naphthalenedicarbonitrile per 2,3-naphthalenedicarbonitrile units in polymers **V** and **VI** to give a yield of 24% for polymer **VIII** and 18% for polymer **IX**, respectively.

Characterization
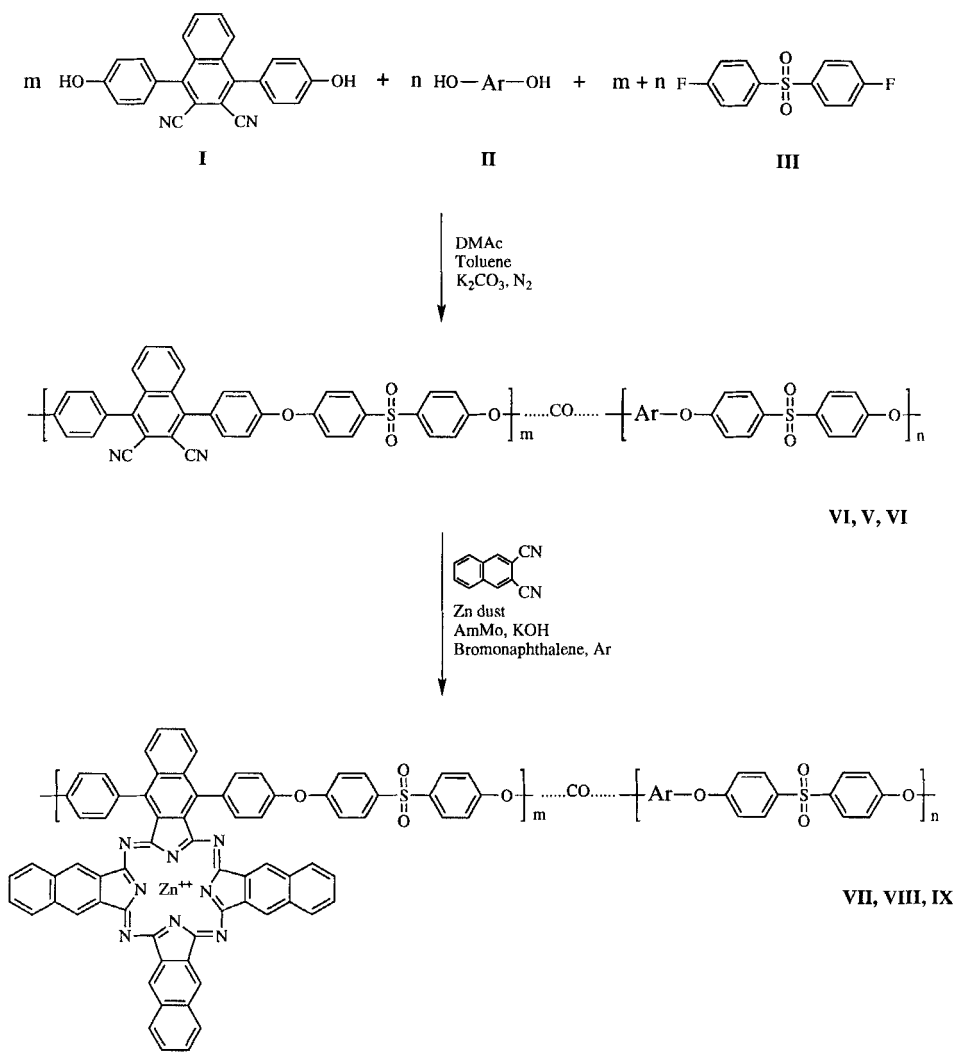
^{1}H-NMR spectra were recorded on a Gemini-200 and Varian Unity-500 spectrometer using dimethylsulfoxide (DMSO) and methylene chloride-d_2 (CD$_2$Cl$_2$) as solvent. UV-Visible absorption spectra were recorded in chloroform solution or

films on a Hewlett-Packard 8452A UV-Vis spectrophotometer. Inherent viscosities were measured using an Ubbelohde viscometer at 25°C at a concentration of 0.5 g/dL. Apparent molecular weights were determined by size exclusion chromatography on a Waters 510 HPLC with a UV detector. Glass transition temperatures (T_gs) were determined by a Seiko 220 DSC instrument at a heating rate of 20°C/min under nitrogen atmosphere. In all cases the middle point of the change in the slope of the base line on the second heating scan was taken as the T_g. Thermogravometric analysis (TGA) data were collected using a Seiko TG/DTA 220 instrument at a heating rate of 20°C/min in N_2 and air. Mechanical properties were measured on a Seiko TMA/SS 120 instrument, using cast films. Films were cast from chloroform. Elemental analysis data were provided by Galbraith Laboratories Inc., Knoxville, Tennessee, USA.

RESULTS AND DISCUSSION

Synthesis and Characterization of Poly(Aryl Ether)s (VII, VIII, IX) Bearing Covalently Bound Naphthalocyanine Units

The naphthalocyanines referred to throughout this paper are the zinc(II) naphthalocyanines. Zinc(II) naphthalocyanines are relatively easy to prepare and can be characterized by NMR spectroscopy. The synthesis of the small naphthalocyanine compounds were undertaken in the melt state [15, 16] and in solution [11, 15]. The solution reaction conditions were utilized in our synthesis of polymeric naphthalocyanines because it was assumed that these reaction conditions would provide a more homogeneous reaction media. The synthesis of polymers VII, VIII, and IX is illustrated in Scheme 1. Polymers IV, V, and VI were synthesized by condensation of bisphenol monomers I and II with the difluoride monomer III in an aprotic dipolar solvent [17]. Treatment of polymers IV, V, and VI with 2,3-naphthalenedicarbonitrile in the presence of zinc dust and a catalytic amount of potassium hydroxide and ammonium molybdate (AmMo) in 2-bromonaphthalene at 270°C under an atmosphere of argon for 10 hours yielded polymers VII, VIII, and IX that contain naphthalocyanine units. The crude products were dark blue-green fine solids and gave a dark blue-green solution. The isolated solids consisted of large amounts of insoluble naphthalocyanine small molecules resulting from the reaction of 2,3-napthalenedicarbonitrile itself and some crosslinked polymers. They were easily separated from the soluble polymers by filtration. From the solution, polymers VII, VIII, and IX were isolated as described in the Experimental section. The final polymers formed dark blue-green fibrous powders. An excess of 2,3-naphthalenedicarbonitrile was used because the possibility existed that two 2,3-naphthalenedicarbonitrile units in the same or different polymer chains could become incorporated into the same naphthalocyanine unit. Although it has been reported that 1,4-diphenyl-2,3-naphthalenedicarbonitrile itself does not form a naphthalocyanine [15], it is possible to form a naphthalocyanine ring by the combination of two 1,4-diphenyl-2,3-naphthalenedicarbonitrile units in polymer chains and two 2,3-naphthalenedicarbonitrile molecules. This would cause crosslinking and insolubility. For this reason the content of 2,3-naphthalenedicarbonitrile structural units in the polymer was kept low (50, 20, and 10% in polymers IV, V, and VI, respectively), and a very large excess (7.2 equivalents for VII, and 30 equivalents for VIII

Polymer	Ar	m/n
VI, VII	$-\!\!\left\langle\right\rangle\!\!-\!\!C\!\!\begin{smallmatrix}CF_3\\CF_3\end{smallmatrix}\!\!-\!\!\left\langle\right\rangle\!\!-$	1
V, VIII	$-\!\!\left\langle\right\rangle\!\!-\!\!\left\langle\right\rangle\!\!-$	1/4
VI, IX	$-\!\!\left\langle\right\rangle\!\!-\!\!\left\langle\right\rangle\!\!-$	1/9

SCHEME 1.

and for **IX**) of 2,3-naphthalenedicarbonitrile was used [18]. Furthermore, the use of dilute reaction conditions was expected to minimize this type of crosslinking. The yield of the soluble naphthalocyanine-containing polymers depends on the content of 2,3-naphthalenedicarbonitrile structural units. The higher content gave lower yield of soluble polymer. Treatment of a homopolymer containing 100% of 2,3-naphthalenedicarbonitrile structural units with 2,3-naphthalenedicarbonitrile resulted in completely insoluble dark blue-green solids which are probably highly crosslinked.

Polymers **VII**, **VIII**, and **IX** were characterized by ^{1}H-NMR spectroscopy, UV-Visible absorption spectroscopy, gel permeation chromatography (GPC), and elemental analysis. ^{1}H-NMR spectra of polymer **VII** and the small naphthalocyanine molecule **X** (see its structure in Fig. 1b) are shown in Fig. 1. The spectrum of small naphthalocyanine molecules was obtained at 95°C because the solubility of naphthalocyanine is very poor at room temperature. The spectrum of polymer **VII** was obtained at 95°C for comparison. It is the same as that obtained at room temperature. The broad signal peak of polymer **VII** (Fig. 1a) at 9.54 ppm was assigned to the protons of type **a** and that at 8.47 ppm to the protons of type **b**. The signals of the type **c** protons are overlapped at 7.33 ppm. Because of the strong aromatic ring current of naphthalocyanine molecules, NMR signals of the type **a** and **b** protons appear at a much lower field than aromatic protons of a benzene ring. The signals of the corresponding protons in the small naphthalocyanine molecules appear at an even lower field than in the polymeric naphthalocyanine molecules, as seen in Fig. 1(b). This is probably due to aggregation of small naphthalocyanine molecules. Chemical shifts of protons of phthalocyanine molecules are different in the aggregated and unaggregated states [19, 20]. Given that the backbones of the polymers bearing naphthalocyanine units are fully aromatic, it is expected that there would be difficulties for the polymeric naphthalocyanine molecules to pack together [18]. A very thin film of polymer **VII** was examined under a cross-polarized microscope. No birefringence was observed and the cross-polarized light was completely blocked. It is known [21] that the aggregated phthalocyanine molecules form liquid crystalline phases. If there were liquid crystalline phases present, birefringence would have been observed, and if there were occluded small naphthalocyanine molecules, the cross-polarizing light would pass through the very thin film. The NMR and microscopic results show that naphthalocyanine units are covalently bound in polymer chains and not merely occluded in the polymeric matrices.

Figure 2 shows the UV-Visible absorption spectrum of polymer **VII** in chloroform. The dilute chloroform solution of polymer **VII** is green in color. The maximum absorption appears at 770 nm, comparable to the reported maximum absorption wavelength for small naphthalocyanine molecules [10, 11, 12, 14, 15]. By measuring the absorption intensity of polymer **VII** at 770 nm in bromonaphthalene at a concentration of about 10^{-5} M against the intensity of the small naphthalocyanine in the same solvent, it was estimated that the content of naphthalocyanine structural units in polymer **VII** is 26.5%. In the same way, the contents of naphthalocyanine units in polymers **VIII** and **IX** were estimated to be 5.2 and 9.5%, respectively. Results of elemental analysis of zinc in the polymers are in agreement with the UV-absorption measurements. The content of the structural units containing 2,3-naphthalenedicarbonitrile moiety in polymer **IV**, **V**, and **VI** is 50, 10, and 20%,
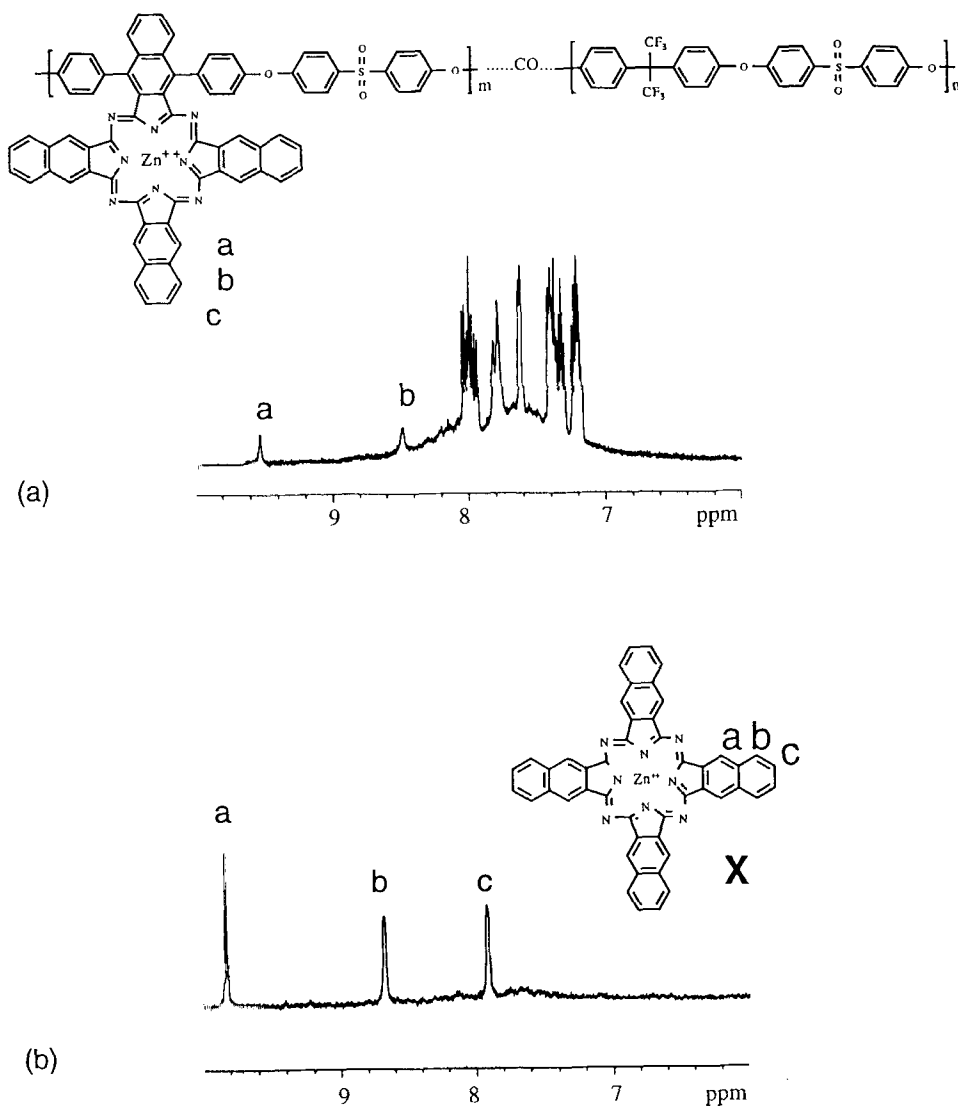
FIG. 1.   ¹H-NMR spectra of polymer **VII** (a) and naphthalocyanine, **X** (b).

respectively, and the conversion of these units in polymers **IV**, **V**, and **VI** to naph-
thalocyanine units in polymers **VII**, **VIII**, and **IX** are 53, 52, and 43%, respectively.

Properties of Poly(Aryl Ether)s (VII, VIII, IX) Bearing Covalently Bound Naphthalocyanine Units

Properties of the polymers bearing covalently bound naphthalocyanine units
(**VII, VIII, IX**) are summarized in Table 1. Properties of the corresponding precur-
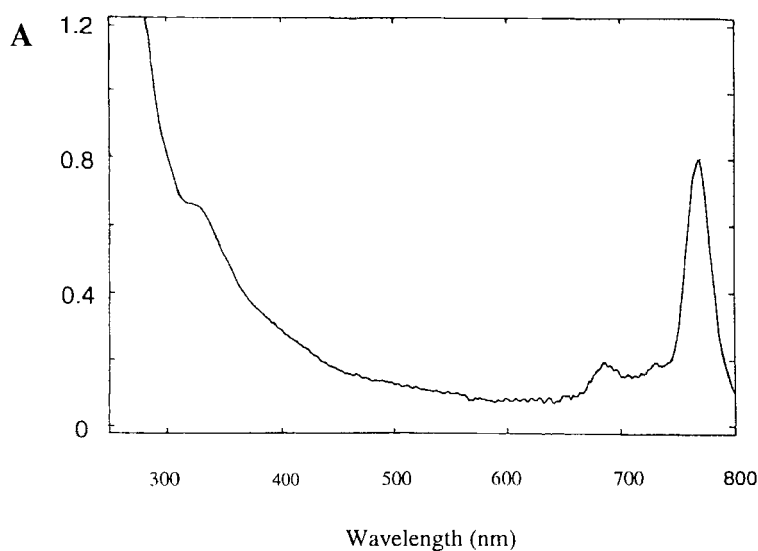sor polymers (**IV, V, VI**) are also listed in Table 1 for comparison. Polymer **VII** is

A

FIG. 2. UV-Absorption spectrum of polymer **VII**.

not end-capped and is of high molecular weight. Polymers **VIII** and **IX** were obtained from the end-capped polymers **V** and **VI** [17] in order to control the molecular weight and minimize formation of insoluble crosslinked polymers. When the molecular weight of the precursor polymer was high, as in the case of polymer **IV**, the resulting naphthalocyanine-bearing polymer **VII** had a very broad molecular weight distribution and the conversion to soluble polymer was also low. All of the naphthalocyanine-bearing polymers (**VII, VIII, IX**) are amorphous and can be cast into tough and flexible films. The inherent viscosities of the polymers range from 0.40 for polymer **VIII** and 0.41 for polymer **IX** to 1.28 for polymer **VII**. The increase in viscosities is probably due to the formation of bulky naphthalocyanine rings in polymer chains, which may result in a significant straightening of polymer chains and the formation of some higher molecular weight polymers by coupling of chains through naphthalocyanine units. Apparent molecular weights were measured by size exclusion chromatography, using polystyrene standards. The molecular

TABLE 1. Properties of Polymers

Polymer	η_{inh}	MW	T_g,°C	T, °C $(-5\%wt)$	E', GPa (25°C)	λ_{max}, nm
IV	0.72	114,500	250	538	2.59	
V	0.33	24,536	201	510	2.80	
VI	0.36	25,347	210	507	2.41	
VII	1.28	432,000	319	442	0.72	770
VIII	0.40	31,325	215	434	0.86	770
IX	0.41	33,210	225	452	0.93	770

weights of polymers **VII**, **VIII**, and **IX** are 432,000, 31,325 and 33,210, respectively, and are larger than those of the corresponding precursor polymers **IV**, **V**, and **VI**. The changes in molecular weights are in agreement with the changes in inherent viscosities.

The glass transition temperatures (T_gs) of the naphthalocyanine-bearing polymers **VII**, **VIII**, and **IX** are higher than those of the corresponding precursor polymers **IV**, **V**, and **VI**. The T_g for polymer **VII** is 319°C, 69°C higher than the T_g of polymer **IV**. The T_gs of polymers **VIII** and **IX** are 215 and 225°C, 14 and 15°C higher than those of the corresponding polymers **V** and **VI**, respectively. The content of naphthalocyanine structure units is the highest in polymer **VII**; therefore, the increase in T_g for polymer **VII** is the most significant. The significant increases in the glass transition temperatures are additional strong evidence that naphthalocyanine rings are covalently bound to the polymer chains. Polymers **VII**, **VIII**, and **IX** are film-forming materials. Their 5% weight loss temperatures as measured by TGA are less and Young's modulus values are smaller than those of the corresponding precursor polymers **IV**, **V**, and **VI**. Phthalocyanines are known to be very thermooxidatively stable; however, phthalocyanine formation is not a quantitative reaction and the above results probably indicate the presence of some unstable dimeric and trimeric intermediates which could be formed during the cyclization reaction [22]. To avoid this problem, our current efforts are directed toward the synthesis of phthalocyanine-containing monomers.

CONCLUSIONS

High temperature poly(aryl ether)s bearing covalently bound naphthalocyanine units were synthesized by treatment of the dicyano group containing poly(aryl ether)s with excess amounts of naphthalocyanine molecules and zinc dust in bromonaphthalene. These polymers are soluble in common organic solvents. Their maximum absorption wavelength is 770 nm.

ACKNOWLEDGMENTS

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