Synthesis, Characterization, and Electrical Properties of Diazophenylene Bridged Co, Ni, Cu, Ce, and Er Phthalocyanine Polymers

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ABSTRACT: In this research, diazophenylene bridged metal-phthalocyanine (Pc) polymers were produced from diazonium salt of 1,4-diaminophenylene and presynthesized 1,8,15,22-tetraamino metal-Pcs. 1,8,15,22-Tetraamino metal-Pc complexes of Co, Ni, Cu, Ce, and Er were obtained by reducing 1,8,15,22-tetranitro metal-Pc complexes synthesized from 3-nitrophthalic anhydride, urea, metal salt, and ammonium molybdate catalyst. Complexes and polymers were characterized by Fourier transform infrared (FTIR), ultraviolet–visible (UV–vis), and X-ray powder diffraction spectroscopes. X-ray analysis of the polymers showed that there were short-range orientations in the polymers. Thermal analysis of the complexes and the polymers were done by differential scanning calorimeter (DSC) and thermal gravimetric analysis (TGA) at a heating rate of $10°C$ min^{-1} under nitrogen atmosphere. Ash analysis was performed to determine the metal content of the polymers. Viscosimetry and ebullioscopy measurements of the soluble part of the polymers were done for molecular weight analysis of the soluble part in tetrahydrofuran (THF) at $25°C$. Four-probe conductivity measurements on isothermal conditions revealed that the polymer samples showed 10^4 fold increases in their electrical conductivities when doped with iodine. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 106: 378–385, 2007

Key words: phthalocyanine polymers; azo polymers; conducting polymers; electrical conductivity

INTRODUCTION

Phthalocyanine (Pc) is a planar 18π electron heterocyclic aromatic system. A large variety of complexes of the planar macrocycle Pc^{-2} and its derivatives have been described in the literature.[1–3] Main group metals such as Si and Ge as well as numerous transition metals such as Fe, Co, or Ni serve as central units. New materials are constructed by the variation of substituents at the ligand and the metal ion in the core of the ligand.[4,5] Pcs are mostly used as dyes and pigments (absorption at 660–730 nm with ϵ 10^5 L mol^{-1} cm^{-1}), and the usage of Pc dyes is around 80,000 tons per year. Applications are also realized as a catalyst, that is, the oxidation of sulfur compounds in gasoline fractions called as Merox Process in the petroleum industry, as photoconductors in xerographic double layers of laser printers and copy machines, as photosensitizers in the photodynamic therapy of cancer, and as active materials in writable disks. Other properties with potential applications are coming out from the use of Pcs as sensors, as molecular organic semiconductors in organic photovoltaic cells and as active electron transfer compounds in catalysis, photochemistry, and photoelectrochemistry.[6–11]

The combination of a metal ion, a ligand, and the chemical environment (such as a macromolecule) determines the chemical and physical behavior of Pcs. The preparative chemistry gives way for the synthesis of various combinations of Pcs with macromolecules. These functionalized macromolecules are part of the field of macromolecular metal complexes, which mean the combination of a metal cluster, metal ion, metal complex, or metal chelate with a macromolecule. These combinations are given as follows.

In the first combination, the Pc ligand is part of a polymer network or chain. In general, these polymers are insoluble in organic solvents, but films or coatings on suitable carriers can be prepared.[12–16] The polymers exhibit good thermal stability, high electrical conductivity, and good catalytic or electrochemical activity.

In the second combination, the metal ion in the core of the Pc ligand is part of a polymer chain. The stacking of the Pcs results in high electrical conductivity of the polymers.[17–20]

In the third combination, Pcs are covalently bound via the ligand to an organic or inorganic macromolecule. Characteristic properties of these materials are

electron or photoelectron transfer, catalytic or photo-catalytic activity.[21,22]

In the fourth combination, the interaction of a Pc occurs coordinatively between the metal of a Pc and a polymer donor ligand or electrostatically between a charged Pc and a charged polymer chain. The materials are mainly investigated for their activity in catalysis or photocatalysis.[23]

Fifth combination is the simplest combination dealing with physical incorporation of Pc into the matrix of an organic or inorganic macromolecule. These materials are of interest as dye stuffs, photo-conductors, active electrode coatings in photoelectro-chemistry, and catalysts.

Essentially important to the properties is the avail-ability of π-electrons of the macrocyclic ring system and d-electrons of the central metal ion in the core of the ligand for electron transfer. Second, under irradi-ation with visible light, electron, or energy transfer from the excited state can occur.

Diazophenylene bridged Cu-Pc, and diazodiphenyl-ene bridged Cu-Pc polymers were synthesized and characterized in our previous studies,[24,25] and diazo linkage increased conjugation in the systems because of the π electrons of benzyl and the nonbonding elec-trons on nitrogen. Increasing conjugation in a poly-meric system affects the electronic properties and results in a material with different properties.

Most of the azo polymers, which have been reported in the literature, may be classified into three groups: i) polymers formed by the modifica-tion of existing polymers, ii) addition polymers, which have azo structures appended to the polymer backbone obtained from azo compound carrying ole-fin groups, and iii) polymers that have azo group as an integral part of the main chain, which represents the polymers synthesized in this work.

EXPERIMENTAL

Chemicals

Copper (I) chloride (CuCl), nickel sulfate hexahydrate ($NiSO_4 \cdot 6H_2O$), cobalt sulfate heptahydrate ($CoSO_4 \cdot 7H_2O$), cerium (II) sulfate tetrahydrate ($CeSO_4 \cdot 4H_2O$), erbium (III) chloride ($ErCl_3$), urea, 3-nitrophthalic acid, ammonium molybdate, 1,4-dinitrobenzene, methanol, tin (II) chloride ($SnCl_2$), sodium nitrite ($NaNO_2$), so-dium acetate (CH_3COONa), hydrochloric acid (HCl), methanol, THF, and nitrobenzene were all commer-cially available and were used without further puri-fication.

Instrumentation

Heidolph VV micro rotovapor was used in the reduc-tion processes. Nüve FN 400 oven was operated to supply 180°C constant temperature for 5 h during the synthesis of 1,8,15,22-tetranitro metal-Pc complexes. Complexes and polymers were dried under vacuum in a Şimşek Laborteknik vacuum incubator till con-stant weight. Ash tests were performed in a high tem-perature oven.

FTIR spectra of the polymers were recorded on a Nicolet 510 FT-spectrophotometer. A Shimadzu UV-1601 model spectrophotometer was employed in the determination of UV–visible (UV–vis) spectra of complexes and polymers. X-ray diffraction spectros-copy measurements were made using Rigaku Gei-gerflex X-ray powder diffractometer. This is a gen-eral purpose diffractometer, which can be used to characterize powders and polycrystalline materials. X-ray spectra of polymers were taken in 0°–35° angles in 35 min.

Ash analysis was performed in a high temperature oven. The temperature was increased to 800°C in 2 h and maintained at that temperature for 8 h. Metals in the core of the Pc units were assumed to be con-verted to metal oxides of maximum oxidation states. Theoretical and experimental metal weight percen-tages were calculated according to the following equations:

$$\% \text{ Metal(experimental)}$$
$$= \{[W_{ash} - ((W_{ash}/MW_{metaloxide}) \times n_o \times 16.00)]/W_{sample}\} \times 100 \quad (1)$$

$$\% \text{ Metal(theoretical)} = (MW_{metal}/MW_{repeat\ unit}) \times 100 \quad (2)$$

where W is the weight, MW, the molecular weight, and n_O, number of oxygen atoms in the complex. Ash analysis was repeated three times for all of the polymers and average values were used.

Thermal analysis of complexes and polymers was done by DSC 910S of TA Instruments Differential Scanning Calorimetry. A constant heating rate of 10°C min^{-1} was used during DSC measurements. Thermal stability of the polymers was measured using Setaram Labsys TGA instrument with a heat-ing rate of 10°C min^{-1} between 20 and 800°C in an isothermal nitrogen atmosphere.

Ebullioscopy measurements were performed by a special design ebullioscopy apparatus and Beckmann thermometer was used for the determination of tem-perature differences in the ebullioscopy experiments. Viscosity measurements were performed by Ubbe-lohde viscometers in THF as a solvent at 25°C and [η]'s of samples were determined.

Four-probe system with Keithley 617 Program-mable Electrometer was operated to determine the electrical conductivities of the polymers. Conductiv-ity values were the average of 10 precise measure-
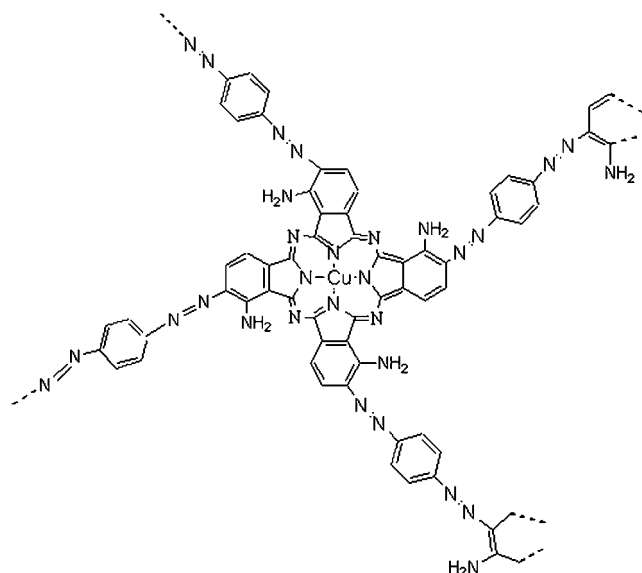
Figure 1 One of the possible structure of diazophenylene bridged Cu-phthalocyanine polymer.

ments. By doping low molecular weight Pcs with iodine from the gas phase or from solution, partial oxidation to radical cations occurs. Iodine doping is also effective in increasing the conductivity of diazophenylene bridged polymers. Doping of polymer with iodine was achieved by the help of a U-tube and it is performed at 50°C in an oven. Iodine itself is a nonconductor. Yet, it increases the conductivity of conjugated systems by forming ions. When it is in excess, it may form a nonconducting separate phase decreasing the conductivity.

Synthesis of materials

Reduction of 1,4-dinitrobenzene to 1,4-diaminobenzene

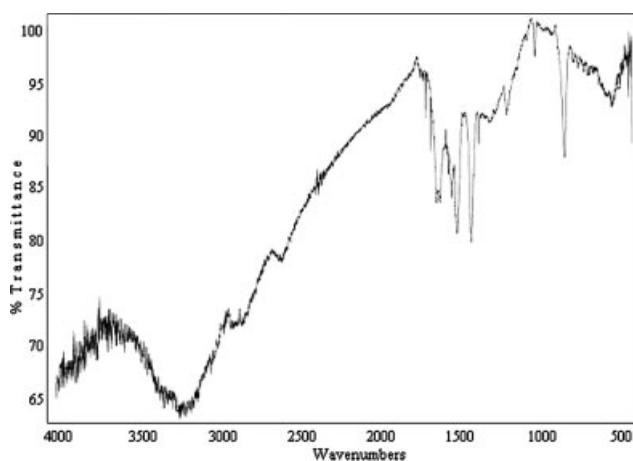Concentrated HCl (10 mL) is added in small portions to a mixture of 1.00 g of the nitro compound

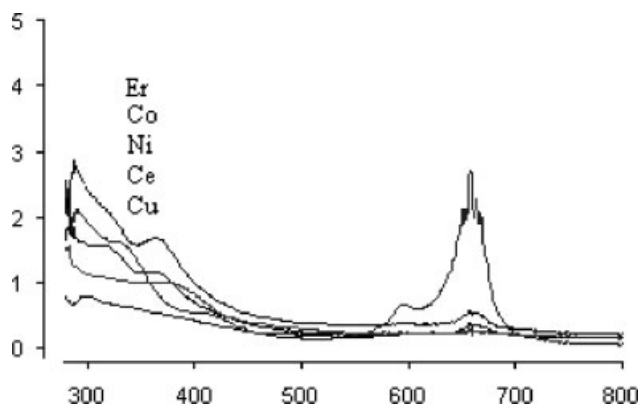**Figure 2** FTIR spectrum of 1,4-diazophenylene bridged Cu-phthalocyanine polymers.

Figure 3 UV–vis spectrum of diazophenylene bridged metal-phthalocyanine polymers recorded in THF.

and 3.00 g of granulated Tin (II) chloride in a small flask fitted with a micro rotovapor. The flask is rotated well (to ensure thorough mixing) during the addition of the acid. Temperature is maintained at 100°C for 10 min to ensure complete dissociation of nitro compound. The 1,4-diaminobenzene compound was isolated by diethyl ether extraction. Melting point of the obtained 1,4-diaminobenzene was measured as 139°C.

Synthesis of metal 1,8,15,22-tetranitrophthalocyanine, metal (II) 1,8,15,22-tetraaminophthalocyanine, and diazophenylene bridged metal-phthalocyanine polymers

Synthesis of Cu (II) 1,8,15,22-tetranitrophthalocyanine[26,27] and Cu (II) 1,8,15,22-tetraaminophthalocyanine was performed according to the literature.[22] For the synthesis of the other metals 1,8,15,22-tetranitrophthalocyanine complexes, the same procedure was applied and stoichiometric amount of NiSO$_4$·6H$_2$O for Ni(II) 1,8,15,22-tetranitrophthalocyanine complex, CoSO$_4$·7H$_2$O for Co(II) 1,8,15,22-tetranitrophthalocyanine, CeSO$_4$·4H$_2$O for Ce(IV) 1,8,15,22-tetranitrophthalocyanine, and ErCl$_3$ for Er(III) 1,8,15,22-tetranitrophthalocyanine was used.

TABLE I
UV–Visible Absorption Maximums of Diazophenylene Bridged Metal Phthalocyanine Polymers in Nanometers

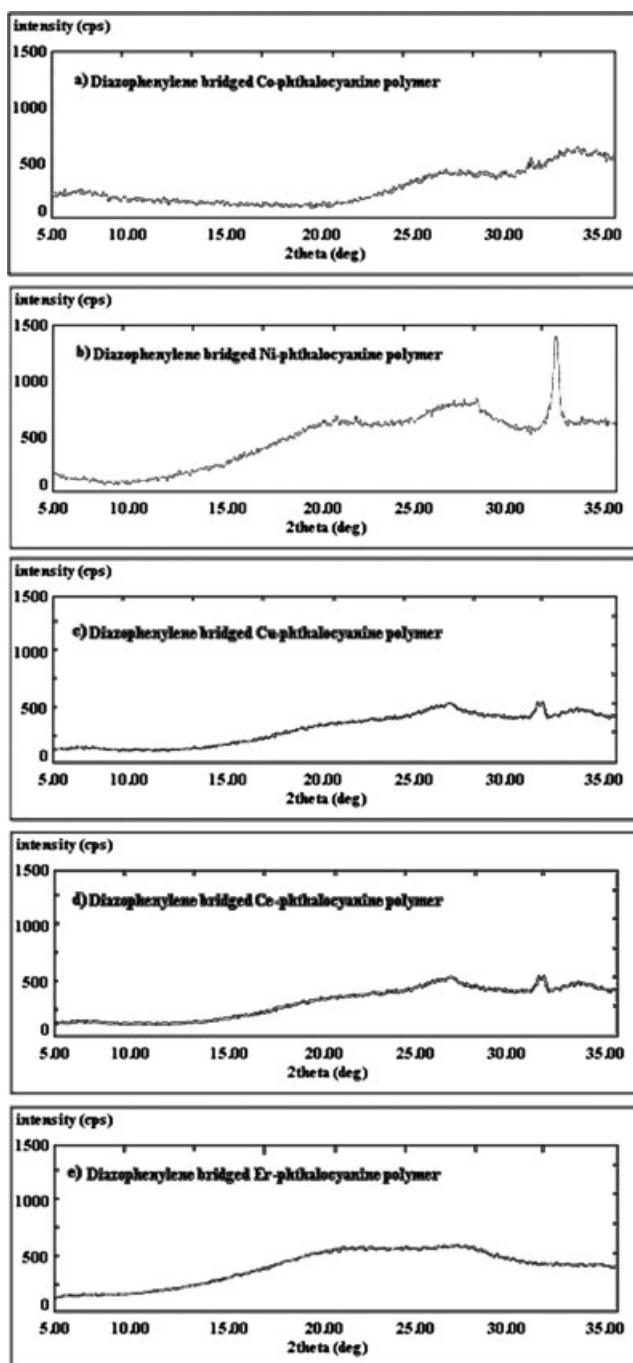| Diazophenylene Bridged Metal-Phthalocyanine Polymer	Absorption Maximums (nm)
Diazophenylene bridged Co-phthalocyanine polymer	292, 315, 411, 593, 650
Diazophenylene bridged Ni-phthalocyanine polymer	295, 305, 378, 415, 580, 650
Diazophenylene bridged Cu-phthalocyanine polymer	298, 399, 660
Diazophenylene bridged Ce-phthalocyanine polymer	305, 388, 670
Diazophenylene bridged Er-phthalocyanine polymer	290, 375, 581, 652

Figure 4 X-ray powder diffraction spectrum of diazophenylene bridged metal-phthalocyanine polymer.

Melting temperatures of Co, Ni, Cu, Ce, and Er 1,8,15,22-tetraaminophthalocyanine complexes are 256.03 °C (and 263.28 °C), 269.48 °C, 256.03 °C, 280.34 °C, and 285.02 °C, respectively. Melting temperatures found by DSC are reproducible for these complexes.

Synthesis of diazophenylene bridged Cu(II) Pc polymers was carried out according to our previous work.[24] About 0.54 g (5 mmol) of 1,4-diamino benzene is dissolved in a hot mixture of 2.40 mL concentrated HCl and 20 mL of water. Temperature is decreased to 0°C and the solution is tetraazotized by the addition of 0.70 g (10 mmol) of NaNO2 in 5.00 mL of water within 1 min. Tetraazo solution is left in ice for 5 min and then added to a suspension of 0.5 g of tetraamino Cu-Pc and 4.00 g of crystallized CH_3COONa in 50 mL of water. It is stirred well and allowed to stand for 1 h. Then resultant mixture is heated up to 80°C. Purification is made by washing with hot water. The yield of this process is around 90%.

Other diazophenylene bridged metal-Pc polymers (Co, Ni, Ce, and Er) were synthesized by the same procedure. Figure 1 shows one of the possible structures of the resultant polymers. The amino groups bonded to the Pc units in the structure of the polymers are a general result of the polymerization reaction.

RESULTS AND DISCUSSION

Diazophenylene bridged metal (Co/Ni/Cu/Ce/Er)-Pc polymers are found to be partially soluble in THF and dichloromethane. Both the soluble and the insoluble parts of the polymer were assumed to have the same structure on the basis of FTIR spectroscopy.

Spectroscopic analysis

FTIR spectroscopy

The synthesis and the chemical structures of metal 1,8,15,22-tetranitrophthalocyanine complexes, metal 1,8,15,22-tetraaminophthalocyanine complexes, and diazophenylene bridged metal-Pc polymers were determined by FTIR spectra[28–32] taken in KBr. Metal 1,8,15,22-tetranitrophthalocyanine complexes have characteristic NO_2 peaks at 1340 and 1540 cm^{-1}. The characteristic nitro peaks in metal 1,8,15,22-tetrani-

TABLE II
Theoretical and Experimental Values of Metal Percentages and Degradation
Temperatures in Diazophenylene Bridged Metal Phthalocyanine Polymers

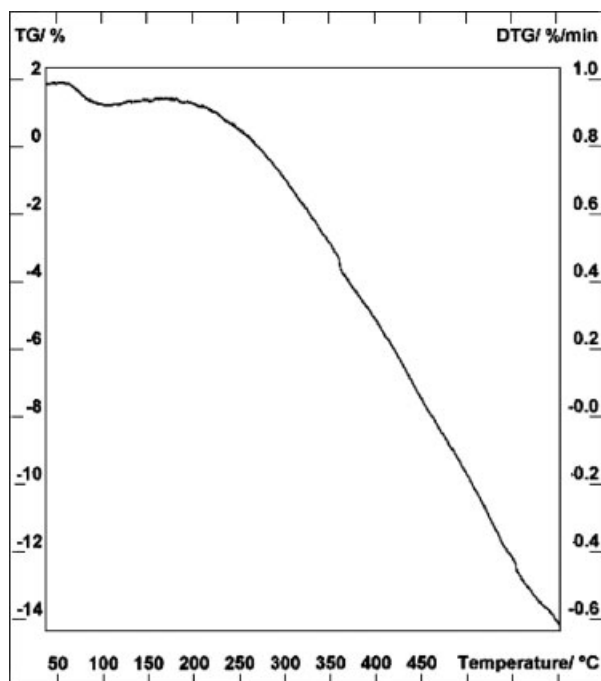|	Metal Content (%)		Degradation
	Exp.	Theo.	Temperature (°C)
Diazophenylene bridged Co-phthalocyanine	7.81	7.09	96.98
Diazophenylene bridged Ni-phthalocyanine	7.66	6.59	122.66
Diazophenylene bridged Cu-phthalocyanine	7.21	6.62	102.34
Diazophenylene bridged Ce-phthalocyanine	15.71	14.41	124.22
Diazophenylene bridged Er-phthalocyanine	16.83	16.74	110.16

Figure 5 TGA graph for diazophenylene bridged Cu-phthalocyanine polymer.

trophthalocyanine complexes disappeared after the reduction of the complexes. Metal 1,8,15,22-tetraaminophthalocyanine complexes show the stretching vibration of the NH_2 group at around 3540 cm^{-1}. The characteristic bands for Pc groups in metal 1,8,15,22-tetranitrophthalocyanine complexes, metal 1,8,15,22-tetraaminophthalocyanine complexes, and diazophenylene bridged Pc polymers were 3540 cm^{-1} for NH_2, 3100 cm^{-1} and 2900 cm^{-1} for aromatic C—H stretching, 1610 cm^{-1} for C=C conjugation, and 1540, 1250, 1100, and 750 cm^{-1} in FTIR spectra. The peaks at around 1405 cm^{-1} in diazophenylene bridged metal-Pc polymers were due to N=N bond stretching. The characteristic bands of phenylene groups in diazophenylene bridged metal-Pc polymers were at around 1620, 1480, and 820 cm^{-1} wavelengths. FTIR spectrum of diazophenylene bridged Cu-Pc polymer in Figure 2 is in agreement with

FTIR spectra of the other diazophenylene bridged metal-Pc polymers.

UV–vis spectroscopy

UV–visible (UV–vis) spectroscopy is one of the most versatile method for Pc characterization.[32,33] The simplest Pc unit is a 18π electron system giving electronic transitions at several different wavelengths. The most prominent bands is the one at around 650–700 nm. This peak is accepted as the evidence of Pc unit for such systems. If a Pc unit is amino functionalized, UV–vis spectroscopy produces a peak at around 300 nm. The evidence of polymerization is the formation of a shoulder at around 370–420 nm due to N=N transition. The UV–vis spectra for Cu(II) 1,8,15,22-tetranitrophthalocyanine and Cu(II) 1,8,15,22-tetraaminophthalocyanine complexes, and diazophenylene bridged Cu-Pc polymer were given in the previous study explicitly. Figure 3 represents UV–vis spectra of the diazophenylene bridged metal-Pc polymers, that are summarized in Table I.

It is clear from the Table that the wavelengths of UV–vis absorption bands for the diazophenylene bridged metal-Pc polymers change with the metals in the core of the Pc units.

X-ray powder diffraction spectroscopy analysis

Diazophenylene bridged metal-Pc polymers are amorphous materials. The peaks observed are low in intensity and broad showing short-range ordering in the polymers. This short-range ordering was observed at a maximum in diazophenylene bridged Ce-Pc as shown in Figure 4.

Thermal analysis

The metal contents of the polymers were determined by ash analysis in which the temperature was increased stepwise. Metal oxides were formed at high temperatures. The weight percentages of metals in diazophenylene bridged metal-Pc polymers were calculated according to the equations given in the Experimental section [Eqs. (1) and (2)] and tabulated

TABLE III
Summary of Thermal Gravimetric Analysis of Polymers

Polymer	Degradation Temperatures and Weight Losses			
	First Degradation	Weight Loss (%)	Second Degradation	Weight Loss (%)
Diazophenylene bridged Co-phthalocyanine	97	2	200–600	17.5
Diazophenylene bridged Ni-phthalocyanine	123	2.5	225–600	20
Diazophenylene bridged Cu-phthalocyanine	102	1.2	240–600	14
Diazophenylene bridged Ce-phthalocyanine	124	1	225–600	8
Diazophenylene bridged Er-phthalocyanine	110	5	230–600	35

TABLE IV
Number-Average Molecular Weights (g mol^{-1}) of Complexes and Soluble Parts of Polymers Determined by Boiling Point Elevation Technique (Ebullioscopy)

	1,8,15,22-Tetraamino Complexes	Diazophenylene Bridged Polymers
Co-phthalocyanine	754	Higher than detection limits
Ni-phthalocyanine	822	29,000
Cu-phthalocyanine	822	29,000
Ce-phthalocyanine	904	Higher than detection limits
Er-phthalocyanine	924	Higher than detection limits

in Table II as theoretical values were calculated from the residual metal oxides.

The difference in the metal content in the experimental and the theoretical values may be due to the relatively low coupling of diazonium salt with 1,8,15,22-tetraaminophthalocyanine complexes.

Figure 5 shows TGA thermogram for the degradation of diazophenylene bridged Cu-Pc polymer. A complete table showing degradation temperatures of all of the polymers are tabulated in Table III.

As seen in Table III, the degradations started at approximately the same temperatures at around 100°C, which can be elimination of water molecules rather than decomposition of nitrogenous products.

The residual part after the first degradation is heat resistant Pc units, which are known as temperature resistant materials up to 600°C.[22,34–36]

Molecular weight analysis

Classical molecular weight determination methods known in polymer chemistry are very difficult to apply to Pc polymers.[37] This difficulty is due to the insolubility or very poor solubility of the polymers in organic solvents.[1–3] Determination of number-average molecular weight of soluble part of polymers by using colligative properties is very commonly used. In this study, ebullioscopic measurements were used for this purpose. THF was used as solvent and its ebullioscopic constant, K_b, was determined using azobenzol. Molecular weights of the complexes and the polymers are tabulated in Table IV.

The molecular weight analysis for tetraamino metal-Pc complexes is an easy task, since a considerable change in temperature can be observed. However, in some cases, such as diazophenylene bridged Co, Ce, and Er-Pc polymers ebullioscopy method did not give useful results.

Viscosity is based on the classical Huggins equation ($\eta_{sp}/c = [\eta] + bc$) that expresses the specific viscosity of the polymer (η_{sp}) as a function of concentration (c). Solution viscosity measurements of the polymers were determined by Ubbelohde viscometer in THF solution at 25°C and their [η] values were determined both for the complexes and the polymers, which are given in Table V.

It is well known that "k" and "a" parameters in Mark-Houwink-Sakurada relationship is dependent on solvent, temperature, and polymer type, and there is a logarithmic relation between intrinsic viscosity and molecular weight, that is, an increase in intrinsic viscosity means a logarithmic increase in molecular weight. If "k" and "a" values for complex and polymers were assumed to be similar, their intrinsic viscosities can be compared to get an idea about their viscosity average molecular weights. [η] values for the polymers were larger than that of the complexes implying polymerization.

TABLE V
Intrinsic Viscosity [η] of Soluble Parts of Polymers Determined by Dilute Solution Viscosimetry

	1,8,15,22-Tetraamino Complexes	Diazophenylene Bridged Polymers
Co-phthalocyanine	0.0014	0.0054
Ni-phthalocyanine	0.0165	0.0371
Cu-phthalocyanine	0.0109	0.0324
Ce-phthalocyanine	0.0237	0.0332
Er-phthalocyanine	0.0163	0.0218

TABLE VI
Electrical Conductivities of Metal 1,8,15,22-Tetraaminophthalocyanine Complexes and Diazophenylene Bridged Metal Phthalocyanine Polymers (S m^{-1})

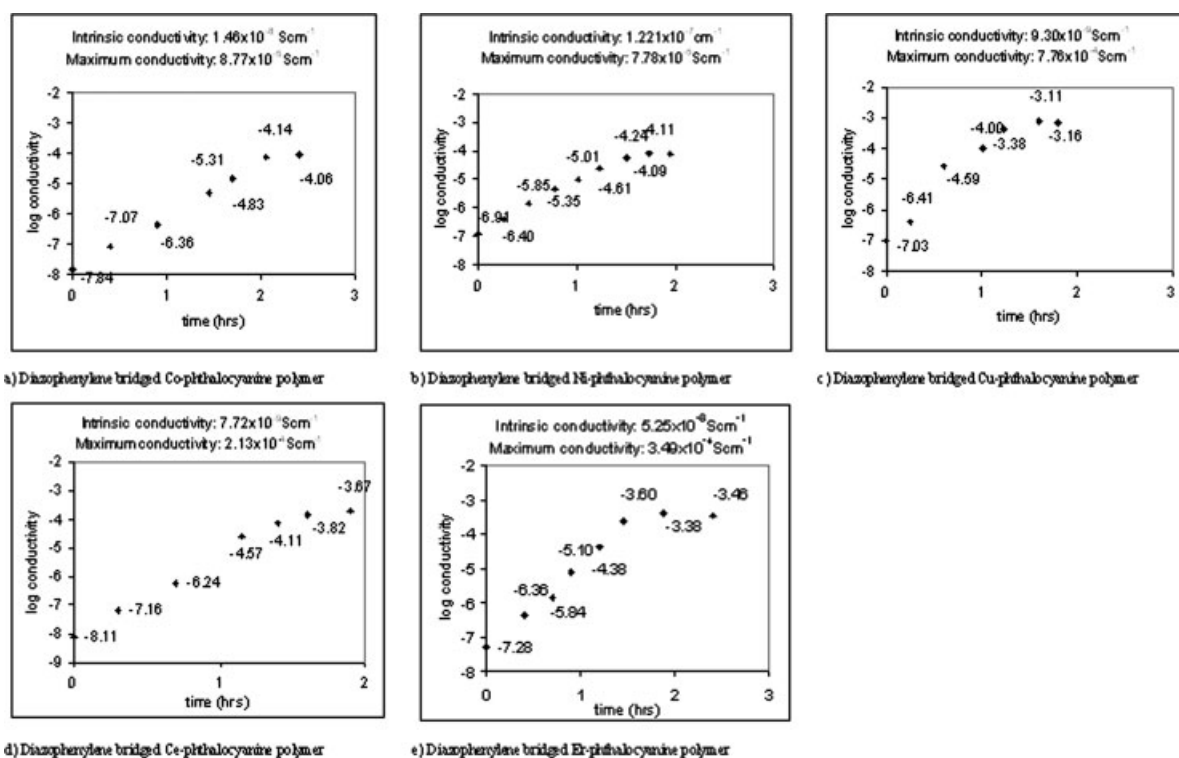|	Conductivity
Co 1,8,15,22-tetraaminophthalocyanine complex	2.08×10^{-7}
Ni 1,8,15,22-tetraaminophthalocyanine complex	1.17×10^{-7}
Cu 1,8,15,22-tetraaminophthalocyanine complex	1.30×10^{-6}
Ce 1,8,15,22-tetraaminophthalocyanine complex	3.34×10^{-5}
Er 1,8,15,22-tetraaminophthalocyanine complex	1.34×10^{-4}
Diazophenylene bridged Co-phthalocyanine polymer	2.10×10^{-7}
Diazophenylene bridged Ni-phthalocyanine polymer	1.21×10^{-7}
Diazophenylene bridged Cu-phthalocyanine polymer	6.80×10^{-6}
Diazophenylene bridged Ce-phthalocyanine polymer	2.40×10^{-9}
Diazophenylene bridged Er-phthalocyanine polymer	5.25×10^{-8}

Figure 6 Effect of iodine doping on electrical conductivity of diazophenylene bridged phthalocyanine polymers.

Electrical properties

Metal complexes and their polymeric derivatives have become interesting because of the possibility to yield organic conductors.[38,39] Conductivities of complexes were tabulated in Table VI. It is clear from the table that conductivity of the complexes increased in a similar manner as the metallic conductivity for transition metals in the core of the Pcs. Although, Er and Ce have lower metallic conductivities compared to Co, Cu, and Ni, their complexes had higher electrical conductivities. This is probably due to the effect of atomic sizes or possible formation of double- or triple-layered products by Ce and Er. Lantanide Pcs are especially prepared in double-layered sandwich form because of their high intrinsic conductivity. The formation of double- or triple-layered products was also expected to increase the conductivity of the polymers, however a decrease by Ce and Er in the polymers was observed revealing that extend of formation of double or triple-layered products by Ce and Er was very restricted in the polymers.

Conductivity is enhanced by suitable doping in electronic materials. Figure 6 shows the results of iodine doped conductivity of diazophenylene bridged metal Pc polymers. The increase in conductivity by iodine doping slows down after a critical concentration where iodine starts to form a separate phase decreasing electrical conductivity.

The maximum enhancement of conductivity by iodine doping was observed in diazophenylene bridged Ce-Pc polymer with the conductivity value of 2.13×10^{-4} S cm^{-1}.

CONCLUSIONS

The combination of Pcs and macromolecules is an excellent example of macromolecular metal complexes and this study contributes greatly on this subject by the novel synthesis of diazophenylene bridged Co/Ni/Cu/Ce/Er Pc polymers.

Co/Ni/Cu/Ce/Er-1,8,15,22-tetranitrophthalocyanine complexes were synthesized and reduced to Co/Ni/Cu/Ce/Er-1,8,15,22-tetraaminophthalocyanine complexes. The FTIR band at 1340 cm^{-1} was characteristic for nitro compounds. The characteristic band for amino compounds was observed at around 3450 cm^{-1}. The transition bands of Pc complexes were observed at around 650–700 nm region in the UV–vis spectra. The tetraamino complexes were soluble in some solvents and therefore, they were used for the comparison of molecular weights of soluble parts of diazophenylene bridged metal Pc polymers to metal-tetraaminophthalocyanine complexes.

Diazophenylene bridged polymers were characterized by FTIR and UV–vis spectroscopies. The cross-linked structure and low solubility of the polymers restricted the spectroscopic characterization to some extent. Short-range orientations in the polymer structures were detected by X-ray diffraction spectroscopy analysis and it was more apparent in diazophenylene bridged Ni-Pc polymer.

Thermal characterization of the polymers was performed by ash analysis, differential scanning calorimetry, and thermal gravimetric analysis (TGA). Ash analysis of the polymers showed that polymers accommodated metals at the core of the Pc units. The positive deviation from theoretical quantities were due to the aggregating salts of Sn. DSC and TGA measurements were consistent with each other and showed thermal stability of the crosslinked polymers.

The polymers were partially soluble in some solvents such as dichloromethane and tetrahydrofurane (THF). Also, the number-average molecular weights of some polymers were determined by ebullioscopic method. Viscometric measurements were done in THF solvent and showed that soluble parts of the polymers had higher molecular weights than complexes.

Conductivity of the polymers was in the order of magnitude of 10^{-8}–10^{-9} S cm^{-1}. These polymers were extrinsic conductors and their conductivities could be increased up to 10^{-3} S cm^{-1} when doped with iodine. Conductivities of the polymers were dependent on the central metals and the conductivity increased in the order of Cu < Co < Ni < Ce < Er in diazophenylene bridged polymers.

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