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Conjugated Polymeric Phthalocyanines by Polycyclotetramerization and Electropolymerization

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Summary: Polymeric phthalocyanines are prepared by polycyclotetramerization of tetracarbonitriles and electropolymerization of amino- or pyrrole-substituted phthalocyanines. The conjugated polymers are characterized by a long wavelength absorption and a high electrical conductivity.

Introduction

Low molecular weight phthalocyanines **1** are interesting as catalysts, photocatalysts, in photoelectrochemical and photovoltaic cells, as photoconductors, as sensor, etc.[1] The advanced properties of these materials are determined by the kind of metal ion in the core of the ligand and the substituents at the annelated benzene rings of the tetraazaporphyrin macrocycle. In contrast to numerous reports about the synthesis and properties of low molecular weight phthalocyanines only relatively few papers describe the combination of phthalocyanines with macromolecules.[2] One possibility is that the ligand of the phthalocyanine is part of a macromolecule.[2-4] This paper describes some aspects of such polymeric phthalocyanines.

Polymeric phthalocyanines by cyclotetramerization reactions

Low molecular weight phthalocyanines **1** are prepared, for example, from unsubstituted or substituted phthalonitriles in the presence of a metal or metal salt by a cyclotetramerization reaction. In the case of a polycyclotetramerization, bifunctional monomers based on tetracarbonitriles such as 1,2,4,5-tetracyanobenzene for polymers **2**[3,5] or various with R oxy-, arylenedioxy- and alkylenedioxy-bridged diphthalonitriles for polymers **3**[3,6] are employed. The

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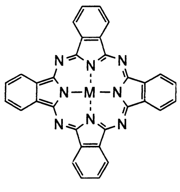
following points for the polymers must be considered: structural uniformity (possible formation of polynitriles or polytriazines as side products), nature of end groups, metal content and degree of polymerisation.



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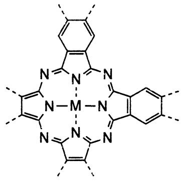

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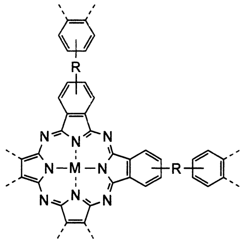

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The synthesis of powdered polymeric phthalocyanines must be carried out under carefully selected reaction conditions to fulfil the criteria of structurally defined polymers. The polycyclotetramerizations occur after stoichiometric equations as shown in Eq. 1 - 4 ($C_{10}H_2N_4$: 1,2,4,5-tetracyanobenzene). The reaction of tetracarbonitriles with $CuCl_2$ at 300 - 400°C (Eq. 1) results in structurally uniform polymers **2** or **3** with nitrile end groups due to UV/Vis and IR analysis data.[5,6] After quantitative IR analysis the average values of the molecular weight show that the values increase with increasing flexibility between the two reactive sides of a tetracarbonitrile or the bridging group R: for **2** >4000; for **3** with R= -0- >12000; for **3** with R= -O-arylene-O- > 60000; for **3** with R= -O-alkylene-O- up to infinity. For a polycyclotetramerization in a solvent, tetracarbonitriles were heated in pentanol-1 in the presence of Li pentanolate (Eq. 2).[3] Addition of metal salts (acetates of Zn^{2+}, Co^{2+}, Cu^{2+} etc.) results in the formation of different metal containing polymeric phthalocyanines.

$$2n(C_{10}H_2N_4) + nCuCl_2 \rightarrow [(C_{20}H_4N_8)^{2-}Cu^{2+}]_n + nCl_2 \qquad (1)$$

$$2n(C_{10}H_2N_4) + \text{alcohol} + 2nLi + \rightarrow [(C_{20}H_4N_8)^{2-}Li_2^{+}]_n + \text{oxidized alcohol} \qquad (2)$$

$$2n(C_{10}H_2N_4) + nCu^{\circ} \rightarrow [(C_{20}H_4N_8)^{2-}Cu^{2+}]_n \qquad (3)$$

$$2n(C_{10}H_2N_4) + 0.5nCo(CO)_8 \rightarrow [(C_{20}H_4N_8)^{2-}Co^{2+}]_n + 4nCO \qquad (4)$$

For various investigations with respect to electrical, photoelectrical, catalytic and photocatalytic properties, the preparation of thin films on flat surfaces (e.g. glass, Ti, glass/ITO (indium tin oxide), KCl) or coatings on particles (e.g. SiO_2, TiO_2,

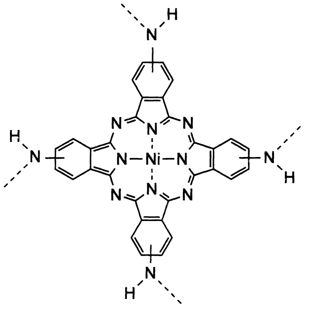
Al_2O_3) is necessary. Because polymeric phthalocyanines are insoluble and not vaporizable, special techniques must be employed. The reaction of Cu-films (thickness 1,5 - 20 nm) with gaseous tetracarbonitriles at T>350°C yields films of structurally uniform polymers (thickness 46 - 230 nm) (Eq. 3).[7-9] The mechanism of film growth is as follows. After formation of a first phthalocyanine film, the metal from the metal film diffuses to the growing polymer film surface in order to react with tetracarbonitriles. At first octacyanophthalocyanine, then oligomeric and then polymeric phthalocyanines are formed.

For the synthesis of metal phthalocyanines on the surface of powdered SiO_2 or TiO_2 (surface area around 300 m^2/g) different metal carbonyls such as $Co_2(CO)_8$ were in the first step adsorbed on the carriers and then heated with carbonitriles at ~180°C (Eq. 4).[10]

Polymeric phthalocyanines by electropolymerizations

Differently structured polymeric phthalocyanines are obtained by an oxidative electropolymerization of phthalocyanines bearing electron-rich substituents. Besides publications about the polymerisation of amino-, pyrrolyl- and thienyl-substituted tetraphenylporphyrins[11], reports on phthalocyanines concentrates on the electropolymerization of amino-[12] and recently tetrapyrrole-substituted phthalocyanines.[13,14]

The electropolymerization of 2,9,16,23-tetraaminophthalocyanines and 2,9,16,23-tetra-(pyrrole-1-ylalkoxy)-phthalocyanines to polymers with the idealized structures **4**, **5** were carried at ITO as working electrodes in DMF or dichloromethane containing 10^{-3} mol/L monomer and 0.1 mol/L supporting electrolyte (e.g. tetrabutylammonium perchlorate or hexafluorophosphate) under potentiodynamic or potentiostatic conditions.[13,14] The amino-substituted phthalocyanine display upon oxidative scanning a first reversible one-electron oxidation (ligand oxidation for M= 2H, Ni, Zn; metal oxidation for M= Co) at ~0.2 V vs. SCE and a second irreversible peak (NH_2 oxidation) at ~0.8 V vs. SCE whereas the pyrrole-substituted monomers exhibit the reversible peak at ~0.7 V vs. SCE and the irreversible one at ~1.2 V vs. SCE (pyrrole oxidation). The second irreversible oxidation peaks correspond to the polymerization. Film thickness, roughness and consumed charge over polymerisation time was studied in detail.[13,14]



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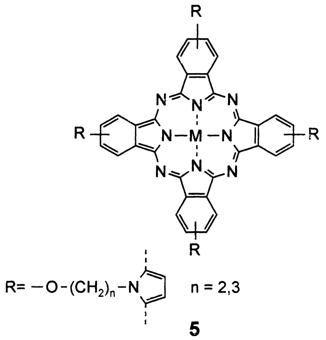

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The polymeric phthalocyanines **2**, **4** consist of connected conjugated phthalocyanine units whereas in the polymers **3, 5** the π-conjugation is interrupted. These structural evidences are proven by UV-Vis spectra and electrical conductivities. Exemplarily, Figure 1 shows the UV-Vis reflectance spectra of the polymers **2** and **3** (**3** with R= -O-C_6H_4-O-). Low molecular weight phthalocyanines exhibit the Q-band transition at ~680 nm which is seen for the polymers **3** at ~700 nm. In contrast, the long wavelength absorption for the polymers **2** is found at ~1200 nm[3] which is indicated by ZINDO/S calculations (Figure 2). For the conjugated polymers **4** the longest wavelength absorptions are at >1000 nm and for the not-conjugated polymers **5** at ~680 nm.[13,14] The conductivities of low molecular weight phthalocyanines are in the order of 10^{-11} - 10^{-15} S/cm. Thin film of the polymers **2** and **4** exhibit conductivities of 10^{-2} and 4 S/cm whereas the values of the polymers **3** and **5** are ~10^{-8} and 10^{-5} S/cm, respectively.[7,13,14] For polymeric phthalocyanines on inorganic carriers or as thin films the following properties are pointed out: catalysts for the oxidation of sulfur compounds,[10,15] Faradaic activity,[9] electrochromic charge/discharge.[7,16]

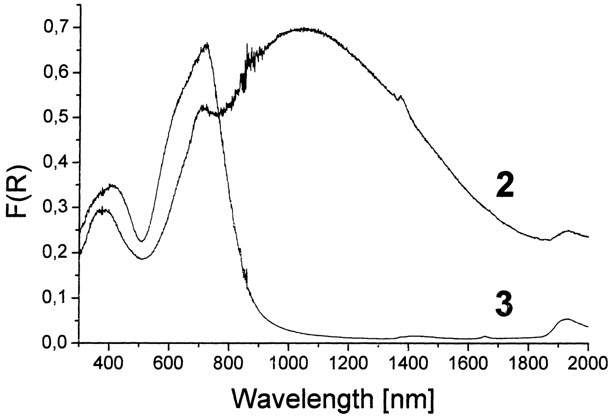

Figure 1. UV-Vis reflectance spectra of the polymers **2**, **3** in $BaSO_4$.

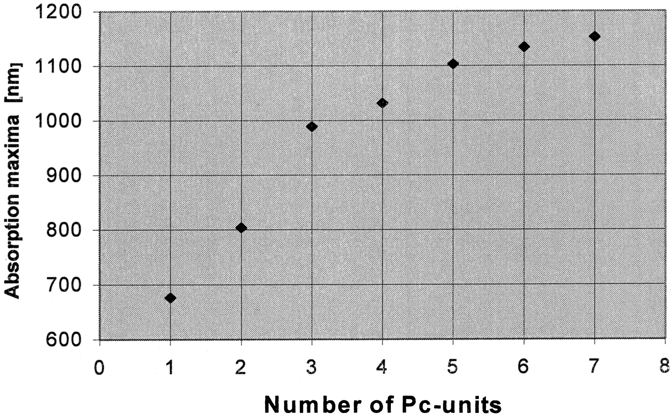

Figure 2. Calculated HOMO/LUMO-transitions of polymer **2** (Hyperchem 5.02 with ZINDO/S).

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