

Conductivity Measurements of Electrochemically Oxidized Langmuir–Blodgett Films of Phthalocyaninato–Polysiloxane

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The dark electrical conductivity of Langmuir–Blodgett assemblies of phthalocyaninato–polysiloxane (PcPS) has been measured at room temperature as a function of the degree of electrochemical oxidation. The conductivity is observed to increase from $<10^{-6}$ S/cm for unoxidized PcPS to 10^{-5} S/cm at an oxidation level of 20%, and to decrease upon further oxidation. The initial increase in conductivity upon oxidative doping is believed to arise from the introduction of charge carriers with mobilities of approximately 10^{-6} cm²/Vs, while the subsequent decrease in conductivity at higher oxidation levels is attributed to reduced charge carrier mobility in the highly charged polymer.

Introduction

Phthalocyaninato–polysiloxanes (PcPS) (Figure 1) are polymers with phthalocyanine (Pc) macrocycles covalently connected in a cofacial geometry through a polysiloxane backbone.^{1,2} When the Pc rings are derivatized with alkoxy chains around their perimeter, the resulting polymers are soluble and can be processed by the Langmuir–Blodgett (LB) technique into ultrathin films. Because of their excellent thermal and electrochemical stability, PcPS LB films have been the subject of numerous investigations, including electrical, electrochemical, and photoelectrical studies.^{3–9} Although there is no orbital overlap between the Pc macrocycles, there is strong evidence that electron mobility parallel to the stack is high.⁹ Dark conductivities at room temperature between 10^{-9} and 10^{-6} S/cm, depending on sample history and environment, have recently been reported for PcPS LB assemblies.^{7,9} The analysis of the space-charge limited currents yielded mobilities between 10^{-7} and 10^{-5} cm²/Vs, depending on temperature.⁹

The conductivity of organic solid materials can be augmented by increasing the number of charge carriers, or “doping” by chemical or electrochemical means. In the present work, this is achieved electrochemically by the generation of mobile charge carriers through an electron-transfer reaction between the organic compound and the working electrode. This is already common in electropolymerized materials such as polyaniline, in which increases in conductivity up to 6 orders of magnitude can be observed.¹⁰ This was attributed to reduced mobility of charge carriers in a fully charged polymer. This suggests that, to optimize the conductivity through electrochemical doping, it is not sufficient to fully oxidize the polymer, but rather there exists a specific potential at which doping is optimized to give the highest conductivity. Previous studies of other phthalocyanine compounds which crystallize in a stacked fashion reported substantial changes in the electrical conductivity upon chemical doping, with values of σ_{RT} up to 700 S/cm.¹¹

In this work, the effect of electrochemical doping on the dark conductivity of PcPS LB assemblies is investigated. Spectro-

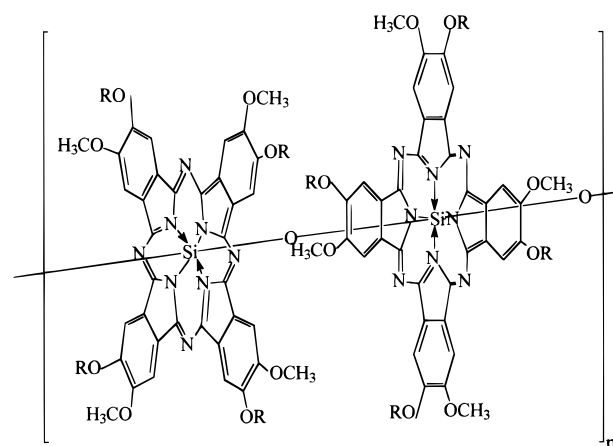


Figure 1. Structure of phthalocyaninato–polysiloxanes. For this work, R = C₈H₁₇.

electrochemical investigations as well as investigations of the electron spin density have already shown that PcPS can be oxidized electrochemically to the radical cation.⁴ It was observed that the single charged radical cation is formed for potentials up to 0.8 V and the double charged cation is generated for higher potentials. One characteristic feature of this process is a clear maximum in the ESR signal.¹² The radical cation is very stable and reproducible cyclovoltammograms have been recorded over more than 15 000 cycles. Our experimental results show that doping increases the electrical dark conductivity up to approximately 10^{-5} S/cm, and in contrast to crystalline samples of Pc compounds, there is a significant decrease for doping levels larger than 0.1.

Experimental Section

The phthalocyaninato–polysiloxane examined in this work was poly(tetra(methoxy)tetra(octoxy)phthalocyaninato)siloxane (PcPS), with four methoxy and four octaoxy groups randomly located around the perimeter of each ring. The synthesis of this polymer is reported elsewhere.⁴ LB film deposition was effected on a 6 °C water (Milli-Q) subphase at a surface pressure of 25 mN/m and a dipping rate of 23 mm/min, using a LAUDA-FW1 film balance. Upon transfer, the polymers are oriented prefer-

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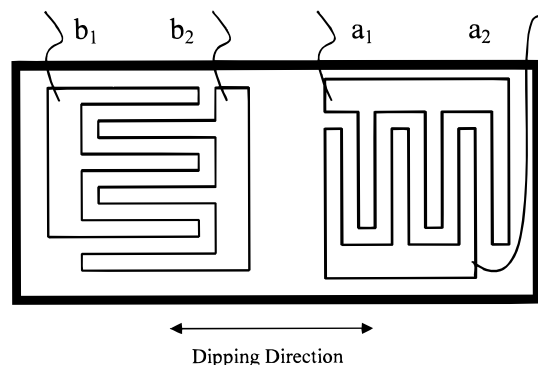


Figure 2. Configuration of the two interdigitated pairs of gold surface comb electrodes: distance between teeth = $10\ \mu\text{m}$; width of teeth = $10\ \mu\text{m}$.

entially parallel to the dipping direction.¹³ For each film, 21 monolayers were transferred. Prior to all measurements, each film was annealed for at least 12 h at $110\ ^\circ\text{C}$ in air.

The substrates for LB deposition were surface comb electrodes (Au on Cr supported on fused silica) with $10\ \mu\text{m}$ “teeth” and $10\ \mu\text{m}$ gaps between “teeth”. The exact electrode configuration is shown in Figure 2. Each fused silica substrate has two pairs of comb electrodes (contact pads a_1/a_2 , b_1/b_2) oriented perpendicular to one another, allowing for in-plane conductivity measurements both parallel and perpendicular to the direction of dipping for each film. Each interdigitating comb electrode structure covered an area of $5 \times 5\ \text{mm}^2$ (excluding contact pads).

Electrochemical measurements were performed using a Princeton Applied Research 270 potentiostat. All experiments were done in aqueous $0.1\ \text{M LiClO}_4$, with a Ag/AgCl reference electrode and a Pt counter electrode. All reported potentials are with respect to the Ag/AgCl reference electrode. The working electrode was formed by connecting together the four surface comb electrode contact pads (a_1 , a_2 , b_1 , b_2). A sweep rate of $50\ \text{mV/s}$ was used for the cyclic voltammetry. For the potential pulse experiments, the chronocoulometry mode was used, in which the applied potential was stepped from an open circuit potential to the desired applied potential, and current was recorded as a function of time. Applied potentials were held for 120 s, at which point only capacitive current was observed.

After each electrochemical measurement, the sample film was rinsed and dried, and the four surface comb electrodes were disconnected from one another. Conductivity was measured with a Keithley model 617 programmable electrometer. Current values were recorded at applied potentials of 0.1 and $-0.1\ \text{V}$ in air at atmospheric pressure and ambient temperatures for each pair of electrodes, and the conductivity was calculated from this response.

Results

The cyclic voltammogram of a PcPS LB film on a set of gold comb electrodes is shown in Figure 3. A reversible oxidation peak is observed at $E^\circ = +0.36\ \text{V}$ versus Ag/AgCl, as reported previously.⁴ The correlation between the doping level in PcPS and the conductivity was investigated by varying the potential applied at the working electrode for doping purposes. Each potential was applied for 120 s, after which only non-Faradaic current was observed. The total charge transferred to the film (from integration of chronoamperometric data) for various applied potentials is shown in Figure 4a. Significant charge is transferred at potentials larger than $0.3\ \text{V}$, as expected from electrochemical data. Assuming an area per monomer unit of about $0.8\ \text{nm}^2$ and the known film thickness of 21 mono-

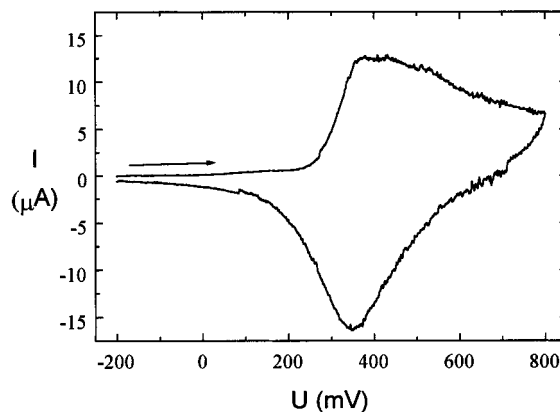


Figure 3. Cyclic voltammogram of 21 monolayers of PcPS on a gold surface comb electrode set. Potentials are with respect to Ag/AgCl.

layers, the average degree of oxidation per monomer unit can be calculated from the charge transferred. Cyclic voltammetry indicates an average degree of oxidation of 60% at a potential of $800\ \text{mV}$. In this calculation, the polymer accessible to oxidation is assumed to be that which covers the whole surface comb structure, including polymer covering comb teeth and polymer between comb teeth.¹⁴ However, it should be pointed out that this assumption leads to a lower limit of doping. Were some of the chains to be inaccessible to doping, the accessible chains would necessarily contain a larger proportion of oxidized rings.

Figure 4b shows the film conductivity as a function of the electrochemical potential. Conductivities both parallel (σ_{par}) and perpendicular (σ_{perp}) to the direction of dipping in the LB deposition process were measured, using comb electrode pairs b_1/b_2 and a_1/a_2 , respectively. In both cases, virtually no charge is transferred at potentials below $0.3\ \text{V}$ and the conductivity remains nearly unchanged. At higher applied electrochemical potentials, the conductivity increases by more than 1 order of magnitude. But while the film doping level increases continuously with increasing potential, the film conductivity reaches a maximum at about $500\ \text{mV}$. Oxidation beyond this potential results in a decrease in conductivity. The doping of PcPS molecules was also investigated by UV–vis absorption spectroscopy of the polymer films, in which the characteristic absorption of the radical cation could be clearly resolved.⁴ (This observation supports the assumption that doping occurs in the regions between the interdigitating electrode strips).

Figure 5 shows the conductivity as a function of the oxidation level, as calculated by the charge transferred per monomer unit. The conductivity reaches its maximum value at an oxidation level of about 15%. Considering an average chain length of $108\ \text{\AA}$, corresponding to 32 repeating units,¹⁵ five phthalocyanine rings would be oxidized per polymer chain at this oxidation level. Assuming a regular distribution of the charges, each radical cation is separated by five unoxidized monomer units. At low doping levels the conductivity increases almost linearly with the number of charges transferred during the electrochemical doping process (inset). Again, these doping levels represent lower limits to the doping levels per oxidized chain.

Conductivities are higher parallel to the dipping direction, which is the direction of preferential orientation of the PcPS polymer chains. This conductivity anisotropy has been previously demonstrated.⁷ The conductivity anisotropy is relatively constant for all doping levels.

To determine the long-term stability of the oxidized state, the film was oxidized at $500\ \text{mV}$ vs Ag/AgCl, as described

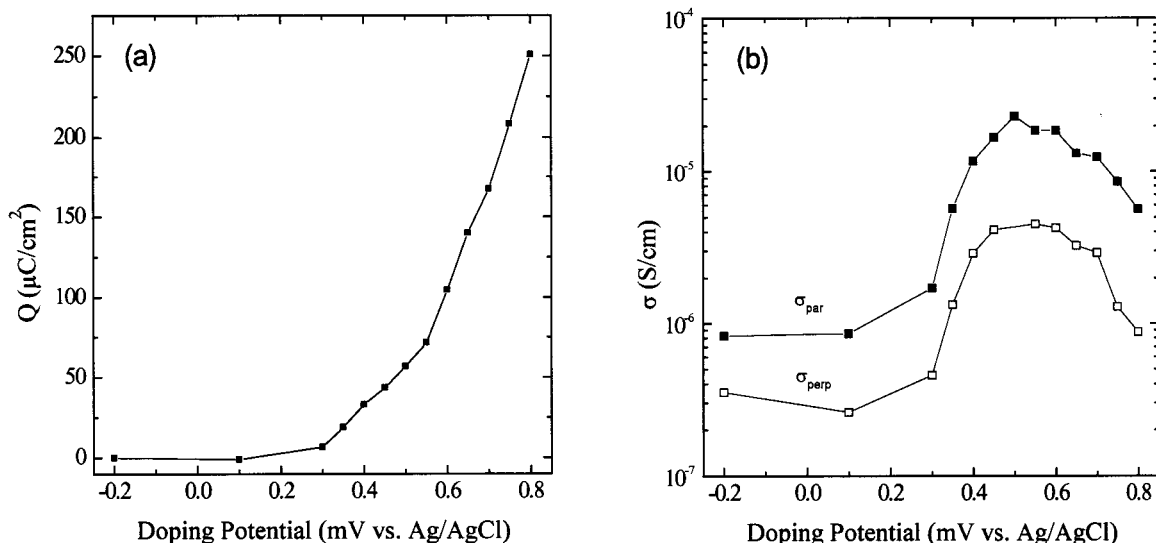


Figure 4. (a) Total charge transferred to the film at various electrochemical potentials. (b) Electrical conductivity of 21 monolayers of PcPS measured parallel and perpendicular to the dipping direction as a function of the electrochemical potential.

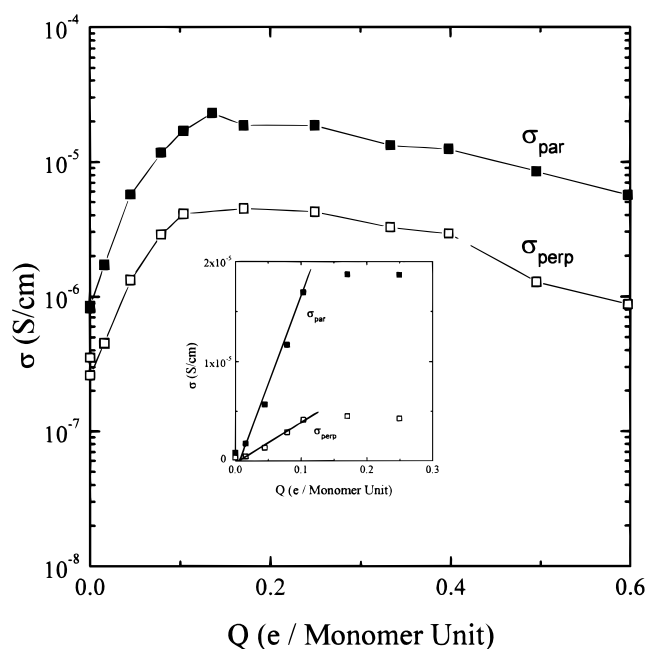


Figure 5. Electrical conductivity as a function of the oxidation level, represented by charge per monomer unit. (inset) Same, for doping levels lower than 0.1.

above. Then, the current parallel to the dipping direction was measured in nitrogen atmosphere for a period of 15 h with a constant field applied. During this period of time, the conductivity decreased only by a factor of 2. Assuming an exponential decay, a half time of about 40 h can be determined from these data.

Discussion

A relatively smooth monotonic increase of the number of transferred charges with increasing potential from 100 to 800 mV is observed (Figure 4a), suggesting a continuous distribution of oxidation sites in the PcPS. Presumably this increase will level off at higher potentials when a maximum doping level is reached. Higher potentials were avoided to minimize the possibility of secondary redox reactions in the polymer and the risk of secondary reactions with the charge carriers. In any case, doping levels were imposed up to and beyond those observed

to achieve the maximum increase in conductivity. This maximum conductivity is 10^{-5} S/cm, which is 1 order of magnitude larger than the dark conductivity of the undoped PcPS film measured under otherwise identical conditions.¹⁶

At low doping levels y for the PcPS examined in this work, which is also characterized as a localized carrier semiconductor, the conductivity increases almost linearly with y . If we assume that doping does not change the electronic structure of the material, the conductivity should follow the relation

$$\sigma = ye\mu/v_{\text{pc}} \quad (1)$$

where $v_{\text{pc}} = 1.7 \text{ nm}^3$ is the volume per Pc ring, e is the elemental charge, and μ is the charge carrier mobility. From the slope of the conductivity increase in the inset of Figure 4, a charge carrier mobility of $\mu_{\text{p}} = 1\text{--}2 \times 10^{-6} \text{ cm}^2/\text{V s}$, parallel to the dipping direction, can be derived. The room-temperature mobility has been determined from dark conductivity experiments on undoped PcPS LB films on interdigitated surface comb electrodes to be $\mu_{\text{p}} \approx 2 \times 10^{-7} \text{ cm}^2/\text{V s}$.⁹ This is rather consistent with a description of the doping process at low doping levels to be the introduction of "mobile" charge carriers into an organic semiconductor, where the charge carrier mobility is determined by the hopping of charge carriers in an energetically broadened distribution of density of states (DOS).^{9,17}

The most surprising result of these investigations is that the conductivity of doped PcPS samples saturates at relatively low doping levels, with no apparent semiconductor to metal transition being observed. Despite the fact that the absolute doping levels reported here represent only a lower limit to doping capacity, the absence of a phase transition is indisputable. This is in direct contrast to results on related $[\text{SiPcO}]_n$ polymers.^{18,19} As-polymerized $[\text{SiPcO}]_n$ crystallizes in an orthorhombic structure. Oxidation is accompanied by a first-order structural phase transition to the tetragonal packing. Once in this more open structure, the doping level y can be continuously tuned from $y = 0$ to 0.5 and, at the same time, the electrical conductivity at RT changes over 5 orders of magnitude, reaching 10^{-1} S/cm. This behavior is interpreted by a transition at $y \approx 0.2$ from a localized carrier semiconductor, with the conductivity given by hopping of the charge carriers between localized sites, to a molecular metal.

Although the decrease in conductivity above doping levels of 20% is perhaps surprising, little is known about the nature

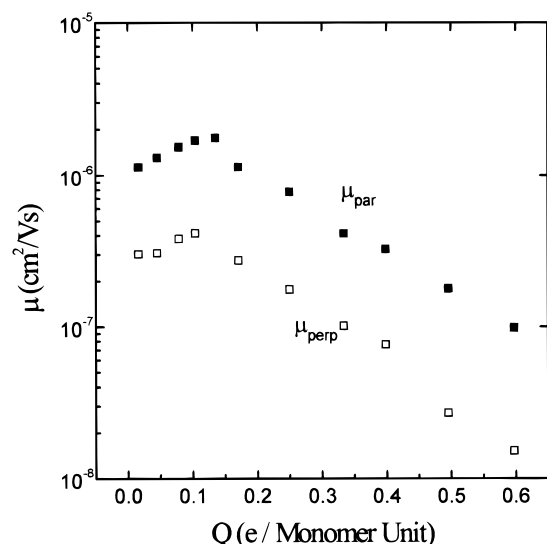


Figure 6. Charge carrier mobilities parallel and perpendicular to the dipping direction as a function of the doping level. Mobilities were derived from the data shown in Figure 5 using eq 1.

of the cation and its delocalization on the PcPS chain. Spectroelectrochemistry of the PcPS monomer, dimer, and polymer has shown that the absorption band of the radical cation occurs at the same wavelength for all three species.¹⁵ It was concluded that the cation is localized on one Pc ring on the time scale of the absorption experiment (fs). On the other hand, cyclic voltammograms of (SiPcO)_n oligomers (*n* = 1–4) exhibit a continuous shift of the oxidation and reduction potential.²⁰ For the tetramer, four reversible redox couples are observed. The significant lowering of oxidation potential for successive oxidation steps (ca. 0.4 V) has been attributed to a delocalization of charges among the Pc rings on the time scale of the cyclic voltammetry experiments (typically seconds to minutes). With respect to the charge transport along a chain, these observations indicate that the hopping of a hole onto a segment of the PcPS chain which already bears a radical cation will be energetically hindered. As a result, the DOS for partially doped PcPS is expected to be broadened, resulting in a decrease in charge carrier mobility. Figure 6 shows the plot of the mobility vs doping level, which indicates an almost exponential decay of μ for values of $y > 0.1$. No indication of a sharp transition is observed.

The contrast between the PcPS studied here and the related [SiPcO]_n polymers mentioned above is primarily the lack of semiconductor to metal transition upon doping in the former. This transition in the [SiPcO]_n materials is attributed to a first-order phase transition from an orthorhombic crystal structure to a more open tetragonal packed structure, which promotes increased charge mobility. The PcPS material studied here is deposited in an LB film architecture with liquid crystalline properties, as recently revealed by TEM studies.²¹ PcPS bears a peripheral alkoxy chain substitution. In the LB assembly these side chains form a disordered amorphous matrix for the hexagonally ordered PcPS cylinders, with a random orientation of the alkoxy dipoles. Also, rotational motion of the rings in the solid state has been confirmed by solid-state NMR spectroscopy.¹² As a consequence, a charge carrier travelling along a PcPS cylinder is expected to experience large energetic disorder. Proof for this comes from the rather low “trap-free” intracolumnar mobility of only 10^{–2} cm²/V s, as determined by pulse-radiolysis time-resolved microwave conductivity experiments.⁹ In contrast, crystalline samples of monomeric Pc

compounds usually yield values above 10^{–1} cm²/V s.²² The difference between conductivity measurement techniques employed for the LB films described here and for the characterization of the crystalline [SiPcO]_n species could contribute to differences in absolute conductivity values. However, it is believed that even with a proportion of the polymer chains being inaccessible to oxidation in the present technique, a semiconductor to metal transition would still be clearly manifested in the variation of conductivity as a function of doping level in the present data, if such a transition were to occur. Therefore, we conclude that the lack of a transition to metal-like conductivity is due to the considerable structural disorder in the PcPS LB assembly.

Conclusion

The dependence of the electrical conductivity of PcPS as a function of the level of electrochemical doping differs significantly from the behavior found in crystalline monomeric and polymeric Pc materials. The conductivity is limited to a rather low value of approximately 10^{–5} S/cm, and it even decreases at doping levels above 20%. This behavior can be interpreted by structural considerations. Specifically, the covalent link between the Pc rings does not allow for structural transitions of the packing of the individual Pc rings in the polymer chain. Furthermore, the amorphous side chain region as well as the rotation of the rings even in the solid state introduces significant structural disorder, which finally gives rise to a broadening of the distribution of site energy. As a consequence, it is expected that the charge carriers remain localized even at high doping levels and no semiconductor-to-metal transition can occur.

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References and Notes

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