

Electrical Conductivity of Highly Organized Langmuir–Blodgett Films of Phthalocyaninato-Polysiloxane

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The electrical properties of phthalocyanine-polysiloxanes were investigated at room temperature. Polymers were deposited in LB films with high in-plane orientational anisotropy, allowing for a directional dependence of the conductivity to be measured. It was found that the conductivity parallel to the preferred orientation of the polymer chains is higher than the conductivity perpendicular to this direction. The orientational anisotropy could be manipulated by using different molecular weight polymers, and by annealing of the polymer films. Lower molecular weight materials showed the least orientational anisotropy, and annealing increased the orientational anisotropy. Using these strategies to intentionally alter the orientational anisotropy, corresponding changes in the conductivity could be detected. It was concluded that the charge transport was fastest along the polymer chains. Interchain charge carrier hops are assumed to be rate limiting, with the process facilitated by end to end orientation between polymer chains.

Introduction

The fabrication of electrical devices drives a constant search for new materials. The demands placed on these new materials include ease of synthesis and derivatization, facile processing, and the desired electrical properties. With respect to semiconductors, the most successful materials have traditionally been inorganic, but these have stringent requirements of purity and are expensive to process. Organic materials offer much more synthetic flexibility and can be designed with such features in mind as processability and conductivity/insularity. Another potentially useful feature to incorporate into such materials is a tendency toward self-organization, which could be exploited in the assembly of truly nanoscale devices.

An interesting category of molecules in this regard is the “hairy rod” polymer.⁴ These are stiff, rodlike polymers surrounded by a network of alkyl side chains. The juxtaposition of the rigidity of the backbone and the solvating effect of the alkyl chains allows these polymers to be processed by the Langmuir–Blodgett (LB) technique, forming well-defined multilayered structures with each monolayer on the order of subnanometers or nanometers thick. During the LB deposition process, the polymer backbones develop a preferential orientation parallel to the direction of dipping, induced by the inhomogeneous flow of the rigid molecules on the water surface during deposition.⁵ This preferential orientation is preserved in the LB film.

One group of hairy rod polymers with particularly interesting electrical properties is the phthalocyaninato-polysiloxanes (PcPS), shown in Figure 1.⁶ These consist of phthalocyanine rings cofacially bound by a siloxane backbone that passes through the center of the rings, with an inter-ring distance of 0.33 nm;⁷ rigidity of the backbone is imposed by the stacking of tightly bound planar rings. By judicious derivatization with four methoxy and four octoxy chains statistically placed around the perimeter of each ring, these polymers are sufficiently “solvated” to be assembled as Langmuir–Blodgett films.⁸

The most interesting electrical properties of these molecules are a result of the overlap between delocalized π systems that arises when the phthalocyanine rings are strung together by the polysiloxane backbone. The polymers examined in this work exhibit a blue shift in the electronic spectrum, indicating excitonic splitting of the π – π^* transition in adjacent phthalocyanine rings.⁹ An examination of the electrochemistry shows the π system interaction and charge delocalization to lower the oxidation potential of the individual rings.¹⁰ The latter work is corroborated by an electrochemical study of various well-defined phthalocyanine oligomers,¹¹ in which it is shown that the oxidation potential of the

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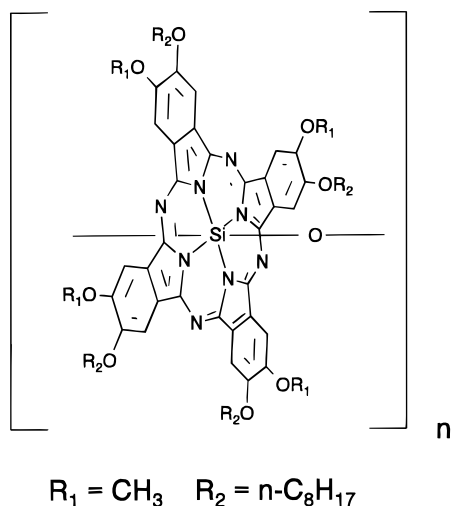


Figure 1. Molecular structure of PcPS.

phthalocyanine ring systematically decreases as oligomer size increases.

All of these results suggest interesting electrical properties of these polymers. The LB technique also offers the possibility to measure the conductivity of ultrathin films of these polymers, with each monolayer approximately 2.2 nm thick.⁷ In addition, these LB films provide a unique opportunity to measure the directional dependence of the conductivity in these materials. Because there is preferential orientation of the PcPS chains in the direction of dipping in the LB deposition process, one can compare and contrast the conductivity parallel to the preferential orientation of the chains with the conductivity perpendicular to the preferential orientation of the chains. This could provide great insight into the conductivity mechanisms in such materials, which at present are not clearly understood.

In the following work, the conductivity of PcPS in LB films is measured at room temperature. Previous work described the bulk conductivity and photoconductivity of PcPS,¹² and preliminary in-plane conductivity results.¹³ In this work, in-plane conductivities, parallel and perpendicular to the dipping direction, and bulk conductivities are compared, and a directional dependence for the conductivity is elucidated. Further evidence for this is collected by the examination of three polymers with different molecular weights, with different degrees of order in their respective LB films. A mechanism for conductivity at room temperature is proposed, and supported by measurements made under vacuum.

Experimental Section

The synthetic methodologies used to obtain the poly(tetra(methoxy)-tetra(octoxy)-phthalocyaninato)siloxane (PcPS) used in this work have been reported elsewhere.^{14,15} They all proceed through the unsymmetrically substituted phthalocyanine monomer, tetra(methoxy)-tetra(octoxy)-phthalocyaninato dichlorosilane.⁸ These monomers were triflated with thallium trifluoromethane sulfonate and then polymerized in a poly-

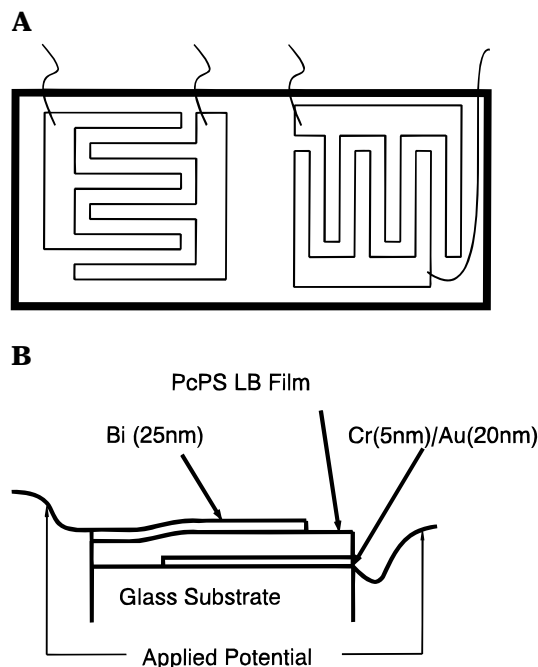


Figure 2. (a) Comb electrode configuration. (b) Sandwich electrode configuration.

condensation reaction. Three different polymer samples were examined, hereafter designated PcPSI, PcPSII, and PcPSIII, each prepared under different polymerization conditions, and as a result each having different molecular weights. PcPSI and PcPSII were prepared using a similar route, using a $[\text{Cu}(\text{CH}_3\text{CN})_4]\text{SO}_3\text{CF}_3$ catalyst, but different polymerization times, resulting in different molecular weights. PcPSIII was prepared as reported by Ferencz et al.¹⁰ by first synthesizing the tetra(methoxy)-tetra(octoxy)-phthalocyaninato siloxane dimers in pyridine.¹⁶ After the dimers were isolated, they were again triflated and polymerized further in diglyme. This gave higher molecular weight polymer than the first methodology.

All absorption spectra were measured on a Perkin-Elmer Lambda 9 UV-vis spectrometer equipped with a polarizer. Solution spectra were of 10^{-2} mg mL^{-1} chloroform solutions in quartz cuvettes, path length 1 cm. LB film spectra were of 15 monolayer films.

Transmission electron microscopy (TEM) was performed using a Philips CM 12 transmission microscope operating at 120 kV. LB monolayers of PcPS were transferred to copper TEM grids as described by Wu et al.¹⁷ LB deposition was effected on a piece of aluminum foil, supported by a glass slide and coated with a thin (5 nm) film of carbon. After deposition of one monolayer, the Al foil was dissolved in dilute HCl, and the remaining film of PcPS supported by carbon was floated onto a standard copper TEM grid.

All electrical characterization was performed with a Keithly Model 617 programmable electrometer at room temperature. Samples were held in an aluminum chamber, which could be evacuated to 10^{-5} mbar with a turbomolecular Balzers pump. Three current values were recorded at each applied voltage at 10 s intervals, to ensure a stable response. For final current-voltage plots, only the third value was used.

For the surface conductivity measurements, a comb electrode configuration was employed, as shown in Figure 2a, with electrode gaps of 10, 30, and 100 μm , and total electrode lengths of 123, 41, and 15 cm respectively. The latter comb electrodes were prepared by the consecutive resistive evapora-

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tion of Cr and Au through a mask in a Leybold evaporator at pressures $<10^{-5}$ mbar and rates of 0.2 nm s^{-1} and 0.7 nm s^{-1} , respectively. The 10 and $30 \mu\text{m}$ comb electrodes were obtained from Firma Heller, Wiesbaden, Germany. They were prepared using the lift-off technique. Fused silica glass slides were coated with a photoresist, illuminated in the inverse comb pattern and developed. Cr (3 nm) and Au (40 nm) were evaporated consecutively onto the substrate, and the remaining photoresist was removed. Each fused silica substrate had two sets of comb electrodes, one with teeth perpendicular and one with teeth parallel to the direction of dipping in the LB deposition process. This electrode configuration allowed for in-plane conductivity measurements in two directions, parallel and perpendicular to the direction of dipping for each LB film.

Bulk conductivity measurements were made using a sandwich electrode configuration as shown in Figure 2b, with a Au bottom electrode (20 nm) evaporated onto BK7 glass substrates modified with Cr (5 nm). Top electrodes in the sandwich configuration were of Bi (25 nm), deposited by evaporation onto the PcPS LB films. The area of the sandwich electrode configuration was typically 0.043 cm^2 . All electrode configurations were completed by attaching small contact wires to the electrodes with silver paint.

LB films were prepared on a LAUDA FW-1 Filmwaage. The aqueous subphase (Milli-Q Plus 185) was maintained at 6°C and kept under nitrogen during spreading, compression, and deposition of polymer films. Spreading solutions of PcPS in CHCl_3 were $0.1\text{--}0.2 \text{ mg mL}^{-1}$. These were spread dropwise in volumes of $300\text{--}500 \mu\text{L}$ with a $500 \mu\text{L}$ Hamilton syringe over a few minutes. The Langmuir film was then compressed immediately from one side at a rate of 1.5 cm min^{-1} to a surface pressure of 25 mN m^{-1} .¹⁸ After allowing 10 min for the film to stabilize, LB deposition was initiated at 1 cm min^{-1} . The substrate was positioned under the subphase prior to spreading of the PcPS solution, and so the first LB layer was formed on the upstroke. This first layer was suspended above the subphase for 30 min in order that it drain and dry. Subsequent layers were made with Y-type deposition, employing only short or no pauses between upstroke and downstroke. Transfer ratios of all films used in further measurements were 1.0 ± 0.1 . All annealing of films was at 160°C in air for 4 h.

Various substrates were used, but none showed any effect on the deposition process. The absorption measurements were performed with LB films on BK7 glass ($38 \times 25 \text{ mm}$ or $12 \times 25 \text{ mm}$), hydrophobized by treatment with hexamethylsilazane, following a standard cleaning procedure (CH_2Cl_2 bath, $\text{NH}_4\text{OH}/\text{H}_2\text{O}_2$ bath). The electron microscopy samples were prepared on carbon-coated Al foil, supported mechanically by a BK-7 glass slide ($60 \times 25 \text{ mm}$). When gold electrodes were required, these were supported on BK7 glass ($38 \times 25 \text{ mm}$: sandwich electrode configuration, $100 \mu\text{m}$ comb electrode configuration) or fused silica ($12 \times 25 \text{ mm}$: 10 and $30 \mu\text{m}$ comb configuration), modified first by a layer of chromium. When freshly evaporated, the gold was allowed to exist for a minimum of several hours in ambient conditions before LB deposition, during which time the gold became relatively hydrophilic, as observed qualitatively by the contact angle of the subphase water on the substrate. This produced the best LB deposition results.

Results

Polymer Samples. Analysis of the different polymer samples in order to determine molecular weights was not possible by conventional methods. This was partially due to the limited solubility of all polymer samples and partially due to the strong tendency of the polymers to aggregate end to end in solution. There were, however, features of the polymers that differed considerably between the three samples. One such feature

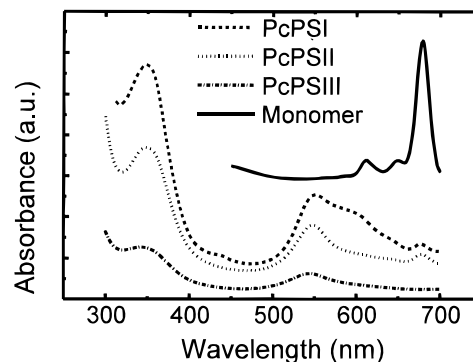


Figure 3. Absorption spectra of three PcPS samples and of the monomer in chloroform solutions, concentration $10^{-2} \text{ mg mL}^{-1}$.

was the solubility of the polymers in CHCl_3 , which decreased noticeably in the order PcPSI, PcPSII, PcPSIII.

The absorption spectra of the three polymers also differed to some extent. The solution spectra, together with the spectrum of the monomer in solution, are shown in Figure 3. All polymers show a Q-band blue-shifted from the Q-band of the monomer found at 680 nm. The shift is largest for PcPSIII (Q-band maximum 544 nm) and least for PcPSI (Q-band maximum 551 nm). In addition, the spectra of PcPSI and to a lesser extent PcPSII, show absorption shoulders red-shifted from the Q-band, although still blue-shifted from the monomer absorption, and a peak at 680 nm due to residual monomer.

A recent report¹⁷ showed transmission electron micrographs of LB films of PcPS. A discussion was included of the differences between micrographs of LB films of the three polymers examined here. Different chain lengths could be observed in the micrographs of each polymer sample, with PcPSI showing the shortest chains, and PcPSIII the longest. Furthermore, specific textures of liquid crystal type were observed in these LB films (see below), believed to be formed through long range order among the chains. Predictably, the highest long-range correlation between chains was detected in LB films of PcPSIII, and the lowest long-range correlation in films of PcPSI. However, in these micrographs one long chain cannot be distinguished from two shorter ones, aggregated end to end, and therefore no absolute molecular weight can be determined from these data.

In another study, matrix assisted laser desorption ionization (MALDI) was used to analyze the three different polymers.¹⁹ Although this method can only reveal a minimum molecular weight, with sensitivities dependent on the particular molecular fragment, the fragment profile of each polymer was distinct from the others. In particular, the profiles of PcPSI and PcPSII differed substantially. This work is still in preliminary stages.

Orientational Anisotropy in LB Films. LB films of "hairy rod" polymers are known to show definite orientation and anisotropy in the plane of the film, attributed to the inhomogeneous flow of the rigid rodlike molecules on the water surface during the LB deposition process.⁵ For the samples in this work, this order was

(18) Well-characterized surface pressure–area diagrams for these polymers were first reported in ref 7.

(19) Private communication from H. Rengel and G. Wegner.

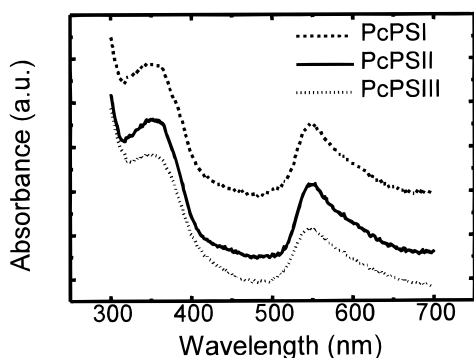


Figure 4. Absorption spectra of three PcPS samples in LB films, 15 monolayers.

Table 1. Absorption Anisotropy Data for LB Films of PcPSI, PcPSII, and PcPSIII

polymer	annealed	$A_{\text{perp}}/A_{\text{par}}$
PcPSI	no	1.8 ± 0.4
PcPSII	no	3.3 ± 0.8
PcPSIII	no	2.4 ± 0.5
PcPSI	yes	3.4 ± 0.7
PcPSII	yes	5.0 ± 0.7
PcPSIII	yes	1.8 ± 0.2

characterized by absorption measurements, and further demonstrated by electron microscopy.

Absorption Spectroscopy of Polymers in LB Films.

Figure 4 shows the spectra of the three different polymer samples in LB films. It should be noted that the shoulders that appear red-shifted from the Q-band for PcPSI and PcPSII in solution (Figure 3) are no longer present in the spectra of the LB films of the same polymer samples.

Anisotropy Measurements by Absorption Spectroscopy.

The anisotropy values from the absorption spectroscopy measurements for the three different polymers are listed in Table 1. All data are taken for LB films deposited on glass, although measurements were also done on films deposited on surface electrodes, to confirm that the surface electrodes had no effect on the ordering in the LB films. Two spectra were measured for every sample, one with light polarized perpendicular to the direction of dipping in the LB deposition process, and the other with light polarized parallel to the direction of dipping. The former spectra all showed higher absorbances than the latter in the Q-band, indicating that the phthalocyanine rings are oriented predominantly perpendicular to the direction of dipping, meaning that the polymer chains themselves are oriented parallel to the direction of dipping, as previously observed.⁵ The ratio of the Q-band absorbances from the two polarized spectra (A_{perp} = absorbance perpendicular to the direction of dipping, A_{par} = absorbance parallel to the direction of dipping) is used as a definition of the degree of orientational anisotropy in individual LB films, and these ratios ($A_{\text{perp}}/A_{\text{par}}$) are listed in Table 1.

No influence of film thickness on the degree of orientational anisotropy in LB films was discernible, although all data presented in Table 1 are for 15 monolayer films. Annealing had a noticeable effect, although this was different for different polymer samples. Unannealed films of the PcPSI showed the lowest orientational anisotropy. Annealing of these samples

increased the orientational anisotropy considerably. PcPSII showed the highest orientational anisotropy among nonannealed samples, and the effect of annealing on these samples was also to cause a considerable increase in the degree of orientational anisotropy, to produce LB films with the highest degree of orientational anisotropy out of all films examined. The PcPSIII films behaved somewhat differently. Initially, before annealing, their orientational anisotropy was slightly higher than that in the unannealed PcPSI films, but slightly lower than in the unannealed PcPSII films. Interestingly, annealing had the opposite effect on this polymer, causing a slight decrease in the degree of orientational anisotropy in the LB films.

Electron Microscopy. Figure 5 shows the transmission electron micrograph of a single monolayer of annealed PcPSIII. The inset shows a selected area electron diffraction pattern from this film, indicating the preferential orientation of PcPS chains. The wide angle equatorial reflection represents the interchain distance and the wide angle meridional reflection represents the inter-ring distance, as described in ref 17. Typical disclinations are marked D (strength $-1/2$) and E (strength $+1/2$), and they indicate the long-range correlation which exists in these liquid crystal-like textures.

Room-Temperature Electrical Conductivity of LB Films.

In-Plane Conductivity Measurements. The results from the surface comb electrode measurements are summarized in Table 2. All current–voltage responses were recorded in ambient conditions. They were observed to be ohmic between -10^3 V cm^{-1} and $+10^3$ V cm^{-1} , and the conductivities listed were measured at $+10^3$ V cm^{-1} . Conductivity measured for an unmodified 10 μm comb electrode at a field strength of $+10^3$ V cm^{-1} was less than 10^{-11} Ω^{-1} pS, whereas all the conductivities measured of PcPS were 10^{-9} Ω^{-1} or greater, and therefore the surface conductivity of the comb electrodes themselves is considered to be negligible in these experiments.

Specific conductivities (σ_s) are calculated using the following equation:

$$\sigma_s = \sigma_R g(d)$$

where σ_R is current divided by voltage at $+10^3$ V cm^{-1} , g is the gap between electrodes, d is the film thickness and l is the total length of electrodes. In this way, all conductivities are normalized for different electrode gaps and different film thicknesses.²⁰ Once this normalizing is done, no effect of electrode gap or film thickness was detectable for the range of experimental parameters investigated.

There was a substantial experimental error involved in these conductivity measurements, with large variation in conductivity from film to film. Thus, a range of specific conductivities is given in Table 2, rather than an average value. This range represents the lowest and highest specific conductivities measured for a given polymer. Each measurement was done on a fresh film. A given film showed a stable response over the time period of the measurement.

(20) It is assumed that the current flows through all layers equally.

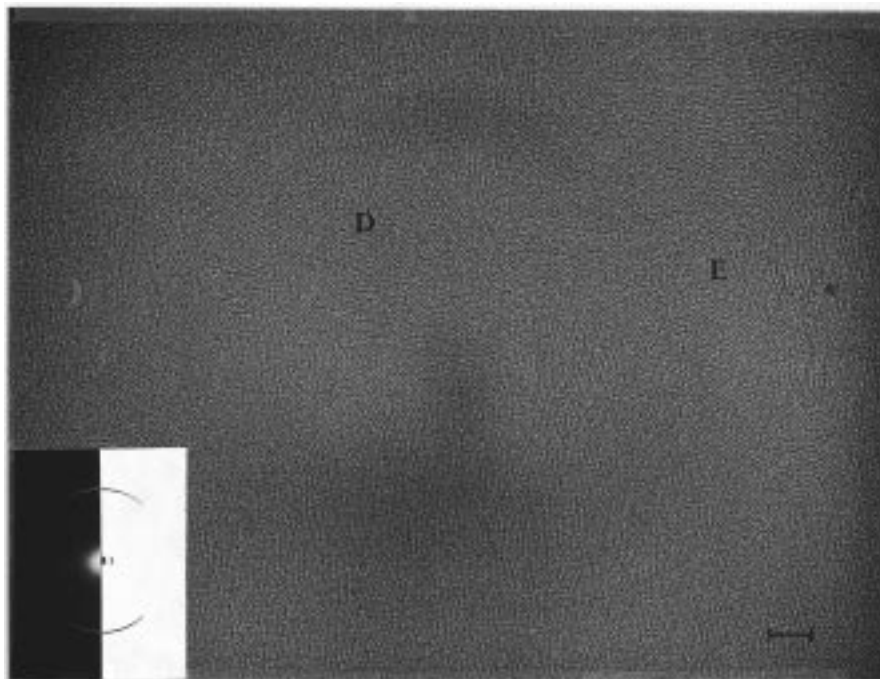


Figure 5. Transmission electron micrograph of one monolayer of annealed PcPSIII, with inset of selected area electron diffraction patterns. Scale bar in bottom right corner corresponds to 25 nm. D and E indicate typical disclinations of strength $-1/2$ and $+1/2$, respectively.

Table 2. Specific In-Plane Conductivities, σ^S , Measured with Surface Comb Electrode Configuration, for LB Films of PcPSI, PcPSII, and PcPSIII. All Films Were 15 Monolayers

polymer	annealed	direction (relative to chains)	σ^S ^a (nS cm ⁻¹)	$\sigma_{\text{par}}/\sigma_{\text{perp}}$ ^b
PcPSI	no	parallel	20–240	2.4 ± 1.0
		perpendicular	10–80	
PcPSII	no	parallel	70–300	2.8 ± 0.9
		perpendicular	30–130	
PcPSIII	no	parallel	160–1500	2.5 ± 0.5
		perpendicular	70–670	
PcPSI	yes	parallel	350–1500	12.9 ± 0.2
		perpendicular	30–120	
PcPSII	yes	parallel	470–5200	13.4 ± 0.7
		perpendicular	40–400	
PcPSIII	yes	parallel	40–350	2.9 ± 0.1
		perpendicular	10–120	

^a Specific conductivity values shown represent the lowest and highest values measured for a given polymer. Fresh films were taken for each measurement for typically six measurements.

^b Conductivity anisotropy values shown represent the average of all conductivity anisotropies for a given polymer. Each conductivity anisotropy value in the average was calculated from values of σ_{par} and σ_{perp} measured on the same film.

The surface comb electrodes employed here (see Figure 2a), with two sets of electrodes on each fused silica substrate, were useful in that the conductivity could be measured in two directions for one film. Therefore, the conductivity anisotropies given in Table 2 are the average of all the conductivity anisotropies measured for a given polymer, but each value in the average comes from one discrete film. This gave reproducible data on the conductivity anisotropy and partially avoided the problem of variation in absolute conductivity from film to film. The success of this approach can be seen in the experimental error in $\sigma_{\text{par}}/\sigma_{\text{perp}}$, which is much smaller for the conductivity anisotropy than it is for the absolute conductivities.

The anisotropy in conductivity was found to be quite pronounced. For all samples examined, the conductivity was higher in the direction parallel to the dipping direction in the LB deposition process. The extent of the anisotropy depended on many features.

Before annealing, the conductivities of PcPSI and PcPSII were similar, but PcPSIII exhibited a considerably higher conductivity. The anisotropies of the conductivities for the different polymers were all approximately the same in the unannealed samples, slight differences mirroring slight differences measured in the orientational anisotropy.

Annealing of these samples increased the absolute conductivities for PcPSI and PcPSII. Furthermore, the anisotropies of the conductivities increased for both of these polymers substantially. PcPSIII, however, showed a decrease in absolute conductivity upon annealing of the samples, and the anisotropy of the conductivities in the PcPSIII samples remained unchanged within the experimental error.

Bulk Conductivity Measurements. Figure 6 shows current–voltage responses of different PcPS sandwich electrode samples under various experimental conditions. Figure 6a is a typical, nonohmic current–voltage response of PcPS in a sandwich electrode configuration. The 31 monolayer film was of unannealed PcPSII, the medium molecular weight polymer. When measured in a vacuum (3×10^{-5} mbar), the current decreased by approximately 2 orders of magnitude, as shown in Figure 6b, but otherwise the diode response was the same. Annealing the film (before deposition of the top electrode) produced much lower currents, but still showed nonohmic behavior, as depicted in Figure 6c. When the higher molecular weight PcPSIII was used to form the film, the resulting current was also much lower, as can be seen in Figure 6d. Conductivities are

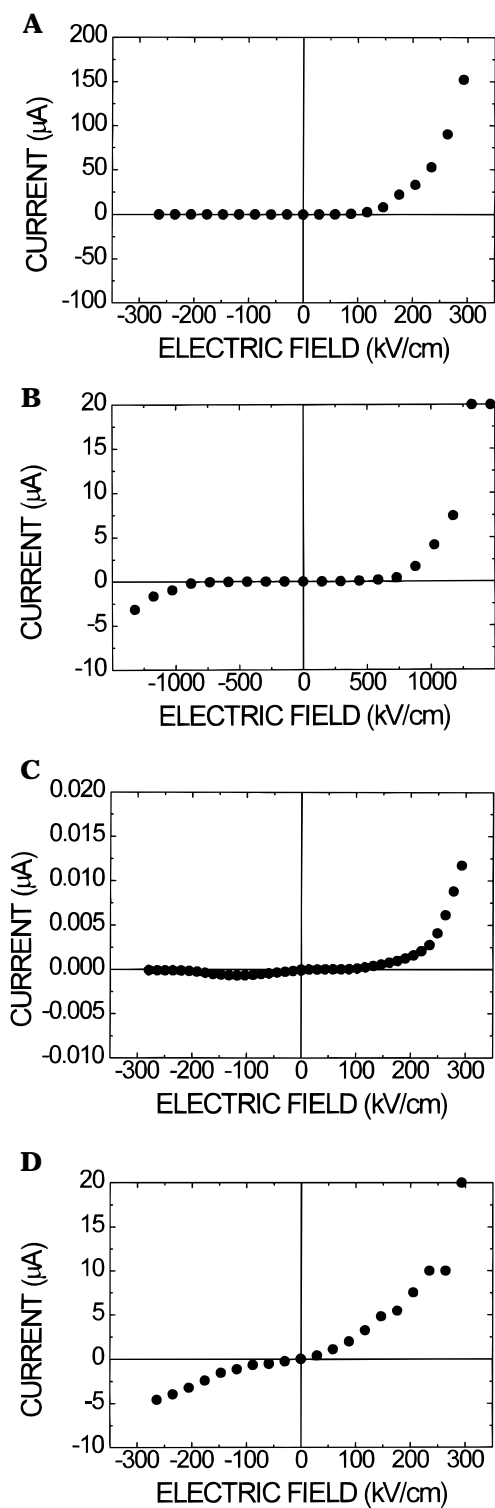


Figure 6. Current-voltage response of (a) 31 monolayers unannealed PcPSII, at atmospheric pressure, (b) 31 monolayers unannealed PcPSII, in a vacuum, (c) 31 monolayers annealed PcPSII, at atmospheric pressure, (d) 31 monolayers unannealed PcPSIII, at atmospheric pressure. All measurements made with sandwich electrode configuration.

difficult to quantify in the sandwich electrode configuration, due to the nonohmic response.

Discussion

Polymer Samples. From the differences observed in solubility for the three polymers, it is believed that

the molecular weight increases in the order PcPSI, PcPSII, PcPSIII. This is supported by the recent electron microscopy results¹⁷ and the preliminary MALDI studies.¹⁹

Further evidence for the molecular weight differences among the polymer samples comes from the absorption data in solution. The blue shift of the Q-band of the polymer from that of the monomer is attributed to excitonic splitting of the $\pi-\pi^*$ transition, which arises from π orbital overlap between adjacent phthalocyanine rings.⁹ Thus, the slight variation in Q-band maxima for the three polymers may be interpreted as an indication of the variation in molecular weight, with the largest shift from the monomer Q-band position (544 nm for PcPSIII) corresponding to the largest excitonic splitting, and therefore the highest molecular weight, and the smallest shift (551 nm for PcPSI) corresponding to the smallest excitonic splitting, and therefore the lowest molecular weight.

Further effect of the molecular weight on the absorption solution spectra can be seen in the absorbance shoulders appearing on the red side of the Q-band in the solution spectra of the two lower molecular weight polymers, PcPSI and PcPSII. These are attributed to a fraction of low molecular weight oligomers, which are suspected to be present in these two lower molecular weight polymer samples. This is supported by the preliminary MALDI data.¹⁹ In the spectrum of PcPSIII, no such shoulders are visible. It is interesting to note the disappearance of these shoulders in the LB films of the same polymer samples. It suggests that in the LB film formation, a certain degree of end-to-end order is imposed, even among these lower molecular weight fragments. This order appears to allow sufficient π orbital overlap for excitonic splitting to occur between rings on the ends of adjacent polymer and oligomer chains along the chains' trajectory, despite the presence of the alkoxy side chains on the perimeter of the rings.

Orientational Anisotropy in LB Films. The anisotropy in the polymer LB films was characterized by polarized absorption measurements and further demonstrated by electron microscopy. As mentioned, the film thickness appeared to have no effect on this anisotropy, although all films were over five monolayers thick, with the exception of the electron microscopy sample.²¹ Another parameter that seemed to have no effect was the substrate. In particular, the surface comb electrodes did not appear to impose any anisotropy through their own structure. The results are summarized in Table 1.

Before annealing, the three samples had surprisingly similar anisotropy within experimental error. It might be predicted that the longer chains would exhibit a greater anisotropy, as the inhomogeneity of the flow on the water surface during LB deposition would be most pronounced for the longest chains. However, this was not observed. To complement the absorption measurements, a transmission electron micrograph of annealed PcPSIII is shown (Figure 5). In this micrograph, it can

(21) The order in these LB films has been shown to develop quickly in the course of transfer from the aqueous subphase; at the top of one 60 mm substrate the anisotropy is equal to that observed for subsequent layers, according to ref 4. The electron microscopy samples was therefore taken at the end of a 60 mm substrate.

be seen that extensive anisotropic orientation is compromised by the formation of domains, defined by disclinations of various strengths. These domains are most pronounced for PcPSIII, slightly visible in films of PcPSII and undetectable in films of PcPSI. Thus, the effect of domain formation, to counteract the orientational anisotropy, increases in the order PcPSI, PcPSII, PcPSIII. This presumably offsets any difference in surface flow inhomogeneity between different molecular weight polymers. It can be concluded from the TEM results that, in addition to the externally imposed ordering that occurs during the flow of polymer chains on the water surface, some internally imposed self-ordering occurs as a result of the liquid crystalline nature of the monolayers at the air–water interface, in which chains arrange themselves into the aforementioned domains.

This is further observed after annealing the films. Thermally induced ordering is effected for the two lower molecular weight polymers, PcPSI and PcPSII, resulting in an increased orientational anisotropy in the films. The PcPSIII films, however, show lower orientational anisotropy after annealing.²² This suggests that the thermal and steric barriers to remove the disclinations and other defects are greater for the longest polymer chains than for the lower two molecular weight polymers, and cannot be overcome by the annealing procedure used here.²³

Thus, it appears that two factors are involved in the anisotropy observed in the PcPS LB films. The first is the inhomogeneous flow that occurs during the LB deposition process and results in alignment of the polymer chains parallel to the direction of dipping. The second factor is a self-organization into domains that occurs between chains and can occur on the water surface, but can also continue once deposition is completed, although the thermal and steric barriers to this are rather great, as they involve diffusion of the polymer molecules in the LB films and increase as a function of molecular weight.

Room-Temperature Electrical Conductivity of LB Films. *In-Plane Conductivity Measurements.* The in-plane conductivity, as measured for each film by two sets of surface comb electrodes oriented parallel and perpendicular to the direction of dipping, exhibited distinct anisotropy, being always higher parallel to the direction of dipping. Given the orientational anisotropy known to exist in the LB films of all of the polymer samples, this result implies that conductivity is higher along the chains than across the chains. This is perhaps not surprising, knowing from the shift in the Q-band from monomer to polymer that substantial energy delocalization occurs between cofacially oriented rings, and therefore the energy barrier to charge carrier transport along a chain could be low. This implies that the rate-limiting step in charge carrier transport through these films is the transfer of carriers from one chain to another, either from or to the middle of one chain, or an end to end transfer where the chain ends are not

cofacially aligned. Cofacial alignment of chains that leads to interchain excitonic splitting would be expected to facilitate interchain charge carrier transport. It is shown in this work (see Bulk Conductivity Measurements below) and in ref 12 that these charge carriers are holes and as such carry a positive charge.

For the unannealed films, the absolute conductivity is highest for the high molecular weight PcPSIII. This is presumably because the length of the chains minimizes the number of interchain hops required of the charge carriers. The anisotropy in the conductivity seems to correlate fairly well with the orientational anisotropy for all three polymers.

Annealing affects the absolute conductivities of the three polymer samples differently; this probably arises because the annealing affects the orientational anisotropy in each polymer film differently. The absolute conductivities of PcPSII and PcPSI increase upon annealing. Furthermore, the anisotropies of the conductivity for these two lower molecular weight polymers are greatly increased upon annealing. This agrees well with the observed influence of annealing on the orientational anisotropy for these two polymer samples, as improved orientational alignment would allow for more end to end cofacial orientation between chains and thus would be expected to increase the effectiveness of the charge transport in the direction of dipping.

An interesting observation is the increase in conductivity observed in the direction perpendicular to the chains. Although the reason for this is not at first clear, it may arise from the different mechanisms for interchain charge transport. Transport from the middle of one chain to the middle or end of an adjacent chain will always be hindered by the alkyl chain cushion surrounding each polymer backbone core, acting as a tunneling barrier. However, as mentioned above, when two chains are oriented end to end, charge transport between them is facilitated due to a certain amount of π orbital overlap between phthalocyanine end groups. The opportunities for end to end charge transport will obviously be limited by the number of polymer chains oriented end to end. It is known from the disappearance of the red-shifted shoulders on the Q-bands of PcPSI and PcPSII when going from solution to LB film that some end to end ordering in the LB films occurs. If the annealing process were to increase and optimize these end to end interactions, then the increased in-plane conductivity in both directions would be a logical result.

The lack of effect on the conductivity anisotropy of the annealing procedure for PcPSIII is probably due to the lack of further orientational anisotropy after annealing. The actual decrease observed in the absolute conductivity may be related to the disclinations and other packing defects observed in the transmission electron micrograph of these films and enhanced by annealing, but requires further investigation. In the context of a trapping mechanism in the charge carrier transport process, these features would be obvious traps, and their enhancement would be expected to cause a corresponding decrease in conductivity. Another effect of the annealing could be the removal of residual water from the LB films, which might result in a decrease in the absolute conductivity, but this seems rather unlikely to have a large effect, particularly an effect exclusive

(22) Similar results were observed in X-ray studies, probing through-plane order. Albouy, P.-A.; Schaub, M.; Wegner, G. *Acta Polym.* **1994**, *45*, 210.

(23) This has also been recently observed in polarization-modulation microscopy studies. Gupta, V. K.; Kornfeld, J. A.; Ferencz, A.; Wegner, G. *Science* **1994**, *265*, 940.

to the highest molecular weight polymer. Furthermore, in FTIR measurements on these films,⁶ no water was observed.

The relatively broad range of absolute conductivity values observed for all three polymers may be attributed to several experimental factors. Most likely are unavoidable differences in the histories of each sample, particularly with respect to the presence of air, as all samples are prepared and measured in air.²⁴ Impurities may also be introduced during the LB deposition process, and although every attempt is made to minimize these, the relatively low conductivity of these materials and the very thin films would ensure that even small amount of impurity would have some effect. However, the conductivity anisotropy data did not suffer from this variation from film to film, as they were calculated from values of σ_{par} and σ_{perp} measured on one discrete film. The comparative precision thus observed for the average conductivity anisotropy was considered evidence that the topography itself is reproducible for a given polymer and is not a source of the variation of the electrical properties from film to film.

Bulk Conductivity Measurements. The nonohmic behavior of the PcPS in a sandwich electrode configuration is a typical Schottky diode response, the flow of electrons from Bi to Au dictated by the difference in the Fermi levels of the respective metals. The large decrease in current when vacuum is applied suggests that the charge carriers are holes, assuming that one effect of the vacuum is the removal of oxygen, whose presence would stabilize holes. This decrease in current is reversible when air is admitted, supporting this assumption.

The annealing of the polymer film increases the orientational anisotropy, as determined by absorption spectroscopy. That this causes a decrease in current flow perpendicular to the film can be explained if it is accepted that the rate-determining step of the charge transport in these films is the interchain hopping of charge carriers. In that case, prior to annealing, some chains may exist that bridge neighboring LB layers, in order for charge to be transported from one layer to the next. This could arise through the imperfect orientation of these chains in their respective layer planes, observed by in-plane X-ray studies.²¹ The effect of annealing, however, is to improve the overall orientation of the chains, thus reducing the likelihood of chains that bridge neighboring LB layers and reducing the current flow.

The results for the high molecular weight polymer sample, PcPSIII, show this film to be of very low conductivity. To explain this, the interchain hopping of charge carriers must be subdivided into hopping from the middle of one chain to the middle or the end of another and hopping from the end of one chain to the end of another. As discussed for in-plane conductivity, it would be expected that the latter process would be much more favorable, particularly if the phthalocyanine end groups were cofacially oriented. Thus, more end to end orientation would increase the conductivity observed. In the LB films of the high molecular weight

polymer, PcPSIII, the stiffness and length of the chains might well act to minimize such end to end orientation, relative to what is observed in the two lower molecular weight samples. This would have an effect on both the charge transport through the LB layers, and in the plane of the LB layers, as discussed in the previous section.

Conclusions

The conductivity of a semiconducting organic polymer, poly(tetra(methoxy)-tetra(octoxy)-phthalocyaninato)siloxane, deposited as a Langmuir–Blodgett film, was determined at room temperature in three directions with respect to the direction of dipping in the LB deposition process. From these measurements, it was possible to extract information regarding conductivity mechanisms in these polymers, due to their high orientational anisotropy in the LB films. This information was further enhanced by the comparison of three different polymer samples, each of different molecular weights, and each exhibiting different levels of orientational anisotropy in the LB film arrangement.

The fastest charge transport appears to occur along the direction of the chains. This is not surprising, given the evidence in the absorption spectra of electronic interactions between neighboring phthalocyanine rings. Rate-limiting processes include the hopping of charge carriers from one chain to the next. This process is believed to be facilitated by end to end orientation of the phthalocyanine rings of adjacent polymers, something which is thought to occur in the LB films, as suggested by the disappearance of the oligomer Q-band in the absorption spectra of the films. The slowest process in charge transport is most likely the hopping of charge carriers from the middle of one chain to the middle or end of an adjacent chain, which would be substantially hindered by the alkyl side chains. Viewed in the context of a rate-limiting trapping process, any defect in the ideal structure of continuous parallel chains could be considered a trap for the charge-carrying holes. Disclinations observed in the LB films of the highest molecular weight polymer would be particularly effective traps and are believed to play an important role in the conductivity of these films.

The charge carrier mobility of electrons and holes has recently been measured in single chains of poly(phenylene) vinylene derivatives by a pulse-radiolysis time-resolved microwave conductivity technique.²⁵ These results showed much higher charge carrier mobilities along single chains than have been recorded in time-of-flight measurements on bulk material. Although the molecular structure of these polymers is different than that of PcPS, in both cases efficient intrachain charge transport is due to delocalized π electrons along the polymer backbone. These authors postulate that the high barriers to interchain charge transport inferred by bulk conductivity measurements do not arise from impurities alone and suggest a key role for more fundamental features such as domain and grain boundaries. This is consistent with our analysis of the results from directionally dependent conductivity measurements of PcPS.

(24) It is known from the results of the bulk conductivity measurements in this work that the presence of air greatly affects the electrical properties of the polymer, with oxygen acting as a dopant.

(25) Hoofman, R. J. O. M.; de Haas, M. P.; Siebbeles, L. P. A.; Warman, J. M. *Nature* **1998**, *392*, 54.

These materials offer numerous interesting possibilities in device design and fundamental studies of conductivity mechanisms. Their processability by the LB technique allows for ultrathin films of reproducible and controllable thicknesses to be formed, with well-defined orientational anisotropies. Because the electrical properties of the resulting films are dependent on these precisely defined parameters, these systems offer the opportunity of a semiconducting material with electrical properties predetermined in the processing stage. The organic polymer systems offer the further advantage of

monomer derivatization or molecular weight regulation to exert additional control over the electrical properties of the resulting materials.

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