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Poly(5,6-dimethoxyindole-2-carboxylic acid) (PDMICA): A Melanin-Like Polymer with Unique Electrochromic and Structural Properties

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ABSTRACT: 5,6-Dimethoxyindole-2-carboxylic acid has been electrochemically polymerized to form a polymer that is chemically similar to melanin, a conjugated polymer found in nature. The poly(5,6-dimethoxyindole-2-carboxylic acid) (PDMICA) films are green and electrochromic, changing color from transparent to green and then to purple as the voltage applied increases continuously from −1 to +1 V. This result is distinct from other synthetic and natural melanins, which are dark brown and have broadband adsorption that is believed to be derived from their chemical disorder. In addition, electrochemically polymerized PDMICA has a degree of crystallinity that has not been seen in melanins, as shown by 1.39, 0.32, and 0.28 nm spacings in wide-angle X-ray diffraction patterns and a nanofibrous structure, as seen in scanning electron micrographs.

Introduction

Melanins are conjugated polymers found in the skin, hair, eyes, ears, and brain. In humans and other animals, the two main types of melanin are eumelanin, which consists mostly of dihydroxyindole repeat units, and pheomelanin, which consists of benzothiazine repeat units.[1] The structure−function relationships inherent to these polymers are not entirely clear, especially in the ear and brain, where the melanin is not exposed to sunlight.[2−4] Therefore, it is of interest to study both natural and synthetic versions of melanin to understand their biological functions and also to try to utilize them as biomaterials. Most synthetic versions of melanin have been chemically or electrochemically polymerized from the monomers L-3,4-dihydroxyphenylalanine (L-DOPA)[5−8] or tyrosine.[9−12] These polymerizations produce dark brown, amorphous, insoluble polymers or oligomers that contain many different chemical species and thus have broadband UV−visible absorption.[13] d'Ischia et al. recently reviewed current advances in synthetic melanin preparation, characterization, and possible device utilitzation.[14] We are interested in producing novel synthetic melanin derivatives that have well-defined structures and can be used to investigate the optical, electronic, and biological properties of melanin.

Electrochromic conjugated polymers have been developed and studied over the past 15 years for various display and "smart" optical applications.[15] By changing the chemical structure of the main chain or pendant groups, researchers have been able to adjust the band gap of these conjugated polymers and therefore have control over the colors displayed.[16] In addition, the stability, switching time, and optical contrast of many polymers have been optimized.[15,17,18] Most of these electrochromic polymers are derivatives of polythiophene, polypyrrole, and polyaniline. Although some simple polyindoles have been studied for their electrochromic properties,[19,20] polyindoles that have side groups similar to melanin have not been investigated.

In our attempts to synthesize melanin-like polymers, we electrochemically polymerized the monomer 5,6-dimethoxyindole-2-carboxylic acid (structurally similar to the melanin repeat-unit 5,6-dihydroxyindole-2-carboxylic acid, Figure 1). The resulting poly(5,6-dimethoxyindole-2-carboxylic acid) (PDMICA) is green, displays electrochromic activity, and has a significant degree of crystallinity. The electrochemical, spectroscopic, and structural characterization of the electrochemically polymerized films are presented in this contribution.

Experimental Methods

Electrochemical Polymerization. 5,6-Dimethoxyindole-2-carboxylic acid (DMICA, Alfa Aesar) was electrochemically polymerized onto ITO-coated glass (Delta Technologies) in a two-electrode cell using an Autolab PGstat12 Potentiostat/Galvanostat (EcoChemie) with a platinum wire counter electrode. The films were electrochemically polymerized in acetone with tetrabutylammonium perchlorate (TBAP) counterion, unless otherwise stated. Other counterions were found to be suitable including lithium perchlorate (LP, SigmaAldrich), tetrabutylammonium hexafluorophosphate (TBAPF6, Fluka), and the ionic liquid 1-butyl-3-methylimidazolium tetrafluoroborate (Aldrich), which serves as the solvent and the counterion. These other counterions also produced electrochromic PDMICA but are not described in detail in this manuscript. All films were polymerized galvanostatically using a current density between 0.1 and 0.2 mA/cm^2 for 10 min and rinsed with acetone after polymerization.

Cyclic Voltammetry and UV−vis Spectrophotometry. The polymer films were subjected to cyclic voltammetry (CV) using the same Autolab potentiostat/galvanostat with a platinum counter electrode, a saturated calomel reference electrode and phosphate-buffered saline electrolyte (PBS, Hyclone Media). Cycling was performed between −1 and +1 V with a scan rate of 0.01 V/s. UV−vis spectrometry was performed on the PDMICA films between 200 to 800 nm using a Cary UV50 UV−vis

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spectrometer (Varian). The absorption was determined before CV and immediately after the films were subjected to different stages of the voltage cycle.

X-ray Photoelectron Spectroscopy. Chemical analysis was performed on PDMICA films using a PHI 5600 X-ray photoelectron spectrometer with a monochromatic aluminum X-ray source (Al Kα = 1486.6 eV) and a hemispherical electron energy analyzer. The pass energy for the survey spectra and characteristic region spectra were 187.85 and 58.7 eV, respectively. A takeoff angle of 45° was used, and the base chamber pressure was $< 2 \times 10^{-9}$ Torr. Additional XPS was performed on the DMICA monomer using a Kratos Axis Ultra DLD X-ray photoelectron spectrometer with a monochromatic aluminum X-ray source and chamber pressure between 1×10^{-8} and 1×10^{-9} Torr. Survey pass energy was 160 eV, and characteristic region pass energy was 20 eV. All spectra were referenced to the C−C/C−H peak at 285.0 eV.

X-ray Diffraction. Thin-film X-ray diffraction (XRD) experiments were conducted using a Bruker D8 Discover diffractometer equipped with a HI-STAR 2D detector. A copper fixed-tube 2.2 kW generator was operated at 40 kV, 40 mA for all experiments. A point-focus beam formed by a 500 μm monocapillary collimator was used, and the instrument was calibrated using a NIST1976 flat plate XRD standard. Data were collected with an incident beam angle of 5° and the detector at an angle of 15° with a camera length of ~15 cm. Molecular modeling of the potential crystal structures was performed using Materials Studio 4.4 (Accelrys) software.

Scanning Electron Microscopy. Morphological studies were conducted using a JEOL JSM-7400F field emission scanning electron microscope at 3 kV operating voltage. The PDMICA films were sputter-coated for with gold−palladium for 40 s to provide a more conductive surface.

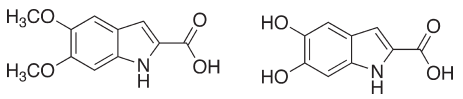


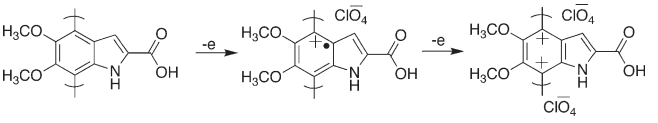
Figure 1. Monomer used in this study, 5,6-dimethoxyindole-2-carboxylic acid (DMICA) (left), and one of the components of melanin, 5,6-dihydroxyindole-2-carboxylic acid (DHICA) (right).

Results and Discussion

Electrochemical polymerization of 5,6-dimethoxyindole-2-carboxylic acid produced green PDMICA films that undergo distinct color changes during CV, shown in Figure 2. At negative voltages, the polymer is transparent, around 0 V, the polymer is green, and above 0.5 V, the polymer turns purple. The color changes and corresponding CV peaks are reversible for approximately three cycles. After this point, the PDMICA film comes off the ITO electrode (in the case of perchlorate and hexafluorophosphate counterions) or remains intact but loses its electrochromic activity, whereas cycling continues (in the case of ionic liquid counterion).

Scheme 1 demonstrates reversible structural changes that are possible during CV and can result in color change. As the potential increases, PDMICA is oxidized (p-doping) and may form radical cation and dication states. These charged states are lower in energy than the neutral form and should have higher wavelength absorption.[15] To investigate the optical changes further, we measured the absorptive properties of the PDMICA films (Figure 2f). Whereas the monomer does not have any

Scheme 1. Transition of the PDMICA from a Neutral Species to Oxidized States (Radical Cation and Dication) during Cyclic Voltammetry[a]



[a] The scheme represents the transparent (neutral), green (radical cation), and possibly purple (dication) states of the film. There may be other irreversible chemical reactions that alter the chemical structure of the purple form. In addition, it is possible that the polymer couples through the three position, but 4,7-coupling is shown for simplicity.

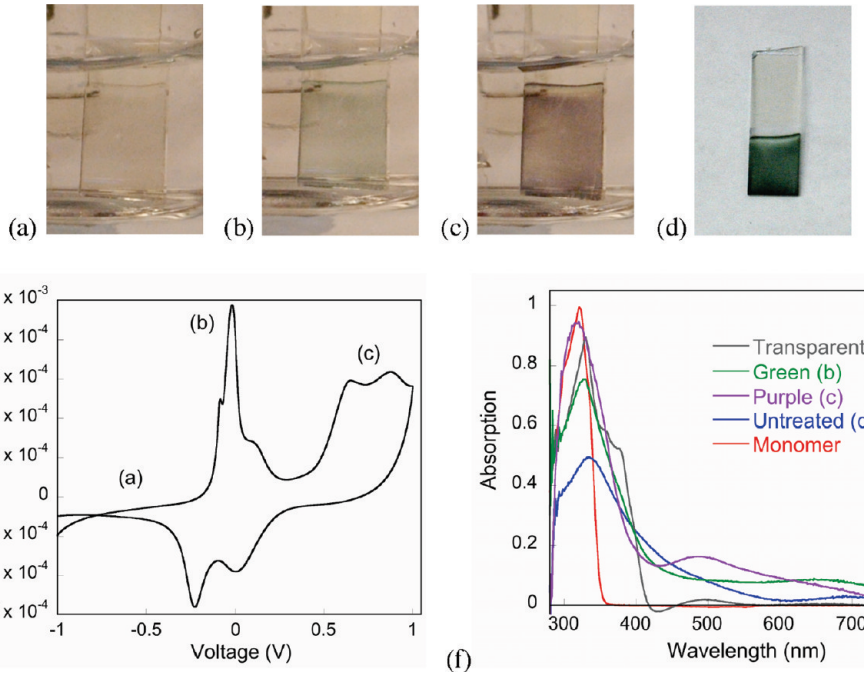


Figure 2. Electrochromic PDMICA: the films are transparent when subjected to (a) negative voltages, (b) green near 0 V, and (c) purple above 0.5 V. (d) The as-polymerized films are also green. (e) The cyclic voltammetry curve shows the voltage range for each color. (f) UV−vis absorption spectra demonstrate different energy absorptions depending on the state of the PDMICA.

absorption above 360 nm, the resulting films have longer wavelength absorption, confirming the formation of extended conjugation by electrochemical polymerization. The transparent films show very little absorption above 420 nm, and besides a peak near the monomer absorption at 330 nm, there are two smaller shoulders around 350 and 380 nm. Because the film does not have significant absorption in the visible wavelength region, the film looks transparent. The green films have a broader peak around 330 nm and a small, broad peak around 670 nm. This new peak could be explained by radical cation formation because this peak is lower in energy than any of the peaks seen in the transparent polymer. The highly oxidized or purple form of the polymer has broad absorption peaks around 320 and 500 nm. The 500 nm peak is higher in energy than the 670 nm peak seen in the green films and cannot be explained by dication formation. Because the films lose their electrochromic activity after three cycles, it is likely that this form results from an irreversible chemical reaction. If a dication state is also present, then the absorption may be higher in wavelength than the measured range. Therefore, we can speculate that the chemical structure of the polymer changes irreversibly in the purple form. In addition, the cycling irreversibility may be resolved by cycling in a controlled atmosphere that is free of oxygen and water.

Whereas the complete chemical structure of PDMICA has not been elucidated, XPS of the films indicates that the monomer unit remains intact during electrochemical polymerization. Because films that are made with TBAP counterion could have nitrogen peaks from both the tetrabutylammonium and the PDMICA, films made with LP counterion were also investigated. The survey spectrum (Figure 3a) demonstrates that all of the expected elements are present: carbon, oxygen, and nitrogen from PDMICA and chlorine from the perchlorate counterion. The C 1s characteristic region (Figure 3b) and the N 1s characteristic region (Figure 3c) provide more detailed information about the bonding of these elements. In the C 1s spectra, there appear to be peaks present around 285, 286.5, and 289 eV, which correspond to C−C/C−H, C−O/C−N, and C═O bonding, respectively.[21] These peaks are also confirmed in the monomer C 1s spectrum (Supporting Information) and occur in relatively the same ratio. These results indicate that the methoxy and carboxylic acid functional groups are present in the polymer and that the carbon frame has not been disrupted. PDMICA films made with TBAP have a more prominent C−C/C−H peak, most likely because of the presence of tetrabutylammonium cation. Although the cation should not be incorporated into the film as a dopant, it could be trapped in the film during polymerization or present as residual material that was not removed during washing. The N 1s spectra also support the conclusion that tetrabutylammonium is present in PDMICA TBAP films. A second nitrogen peak around 402 eV is present in the PDMICA TBAP spectrum and is absent in the PDMICA LP spectrum. This peak also varies in intensity based on the amount of TBAP present in the film. The presence of only one nitrogen peak in PDMICA LP films indicates that the nitrogen only has one bonding configuration in the polymer. This information, along with the supporting evidence that the nitrogen peak occurs at almost the same binding energy in the monomer N 1s spectrum as the polymer N 1s spectra (~400.7 eV), indicates that the amine functional group remains intact in PDMICA. However, the C−C bonding structure between polymer repeat units is still unclear. The repeat units could be connected through the nonfunctionalized carbons at positions three, four, or seven.

XRD patterns of the PDMICA films reveal a surprising amount of structural order. Figure 4 presents the 2D diffraction patterns and azimuthally averaged data for the transparent, green and purple films. The 2θ peaks at 21.40, 30.45, 35.25, 36.20, and 37.40° are from diffraction off the ITO electrode. The 6.35, 27.50,

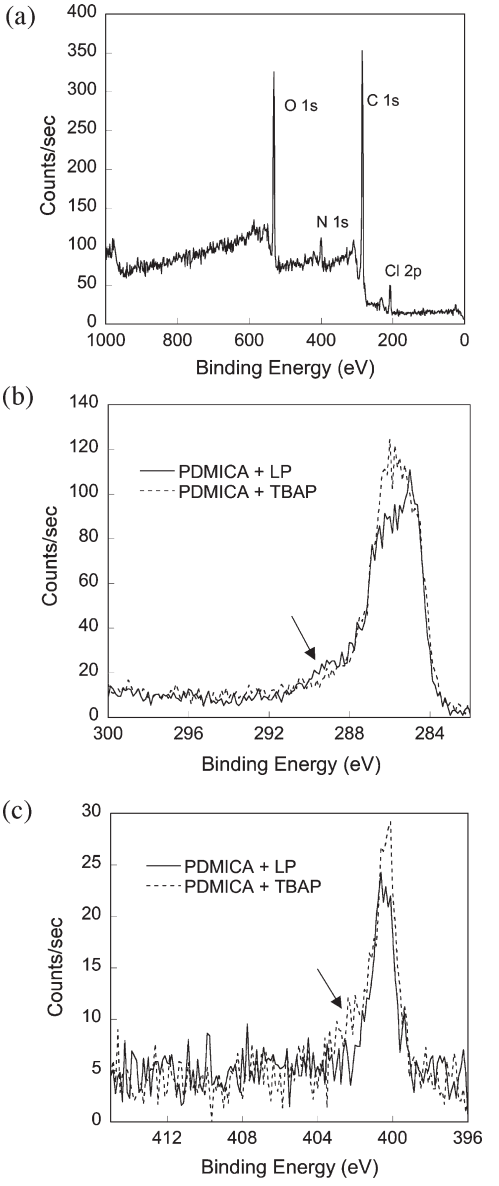


Figure 3. XPS spectra of PDMICA films: (a) survey spectrum demonstrating the presence of carbon, oxygen, nitrogen, and chlorine. (b) C 1s spectra of PDMICA with lithium perchlorate (LP) and tetrabutylammonium (TBAP) counterions. The arrow highlights the small peak for C═O, indicating the presence of the COOH functional group. (c) N 1s spectra of PDMICA with LP and TBAP counterions. The arrow highlights the nitrogen peak for tetrabutylammonium, which varies in intensity based on the amount of residual or trapped TBAP in the film.

and 31.70° peaks, which correspond to *d* spacings of 1.39, 0.32, and 0.28 nm, are diffraction peaks from the PDMICA films. Initial estimates of the solid-state packing of the melanin derivatives using molecular modeling indicate that the 1.39 nm spacing corresponds to the distance between PDMICA chains edge-to-edge, whereas the spacings near 0.32 and 0.28 nm may correspond to the packing of PDMICA face-to-face. The 0.32 nm spacing is similar to but somewhat smaller than the interlayer spacing in graphite (0.335 nm).[22] Further study is needed to determine the exact packing structure of the molecules within the unit cell. These may include more experimental studies such as diffraction and transmission electron microscopy, along with crystal structure modeling.

The scattering intensity from the transparent films (Figure 4a) is weaker than the scattering from the green (Figure 4b) and purple (Figure 4c) films. The transparent films should contain

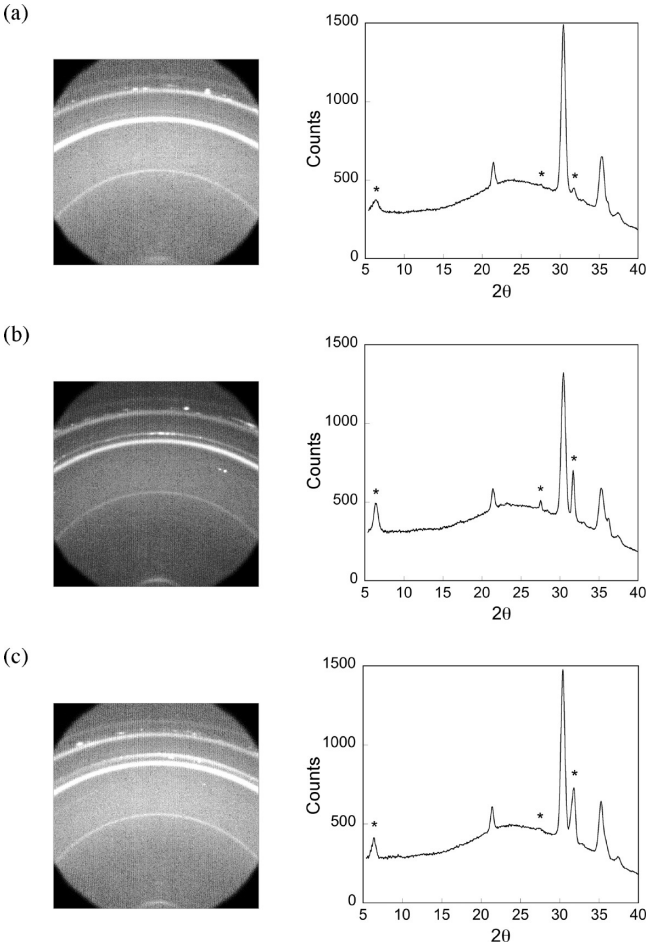


Figure 4. X-ray diffraction data for (a) transparent, (b) green, and (c) purple PDMICA. Left: 2D scans of scattering intensity from a thin film of PDMICA, 0° 2θ at the bottom middle of the Figure. Right: Azimuthally averaged scans of intensity as a function of 2θ. The marked peaks represent scattering from PDMICA, and all other peaks are produced by the ITO substrate.

neutral PDMICA. Because the initially prepared PDMICA-conjugated polymer backbone is positively charged, there are negative counterions, such as perchlorate ions, coordinated to the backbone of the polymer. The switch from positive to neutral backbone will cause these counterions to be released from the film, which may disrupt the structure of the polymer, thus weakening the scattering intensity.

The relatively sharp diffraction peaks from PDMICA are unique compared with synthetic and natural melanin polymers. Structural studies in literature demonstrate that previous melanin-like synthetic polymers and natural eumelanins are largely disordered but contain nanosize aggregates consisting of stacked parallel sheets of indole oligomers.[23−27] Interestingly, XRD patterns of these materials have extremely broad peaks with d spacings near 0.3 to 0.4 nm,[27] and transmission electron microscopy has demonstrated $\pi-\pi$ stacking of melanin layers with spacings between 0.37 and 0.40 nm.[28] Although they are slightly larger, these results are similar to the 0.32 nm spacing seen in the XRD patterns of PDMICA. However, PDMICA also appears to have well-defined edge-to-edge packing (at ∼1.4 nm), which has not been seen in synthetic or natural eumelanins.

The scanning electron micrographs of PDMICA films, shown in Figure 5, also support the conclusion that PDMICA is semicrystalline. The micrographs demonstrate that the films are extremely porous and contain nanofibers of PDMICA. Figure 5c shows how these fibers are approximately 30 nm in diameter and

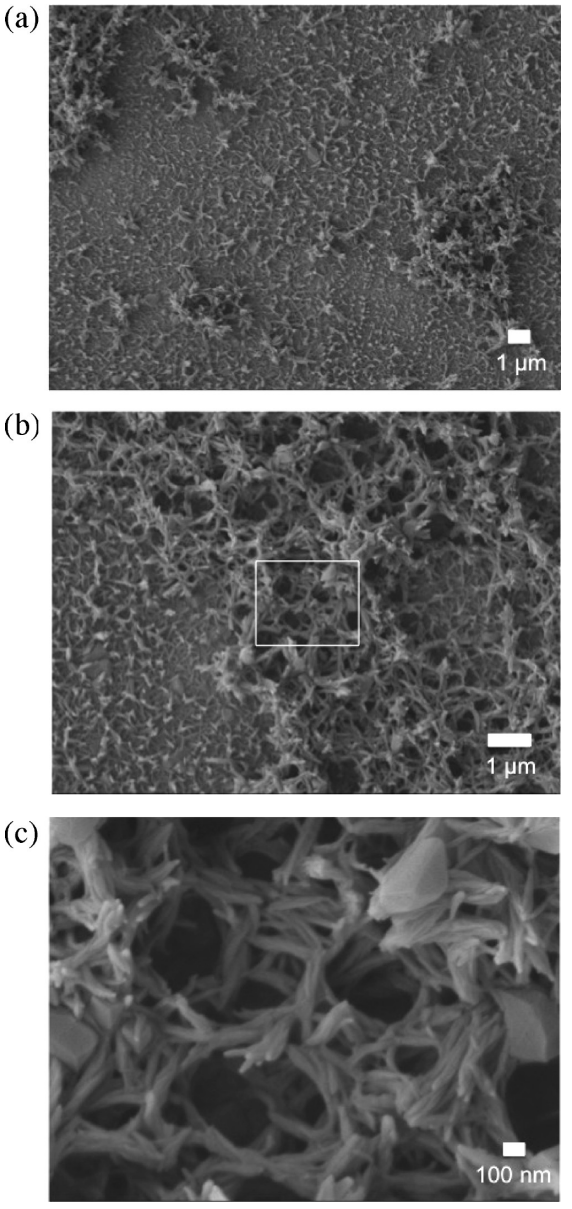


Figure 5. Scanning electron micrographs of PDMICA at (a) lower magnification to show the clustering of polymer in certain regions, (b) medium magnification to demonstrate the porous nature of the films, and (c) high magnification of the inset in part b to show the nanofibrous structure of the polymer.

are bundled together to form the porous structure. Although fibers or rods are formed, they do not appear to have any preferred orientation, either in the SEM images or when examined for birefringence in optical microscopy.

Conclusions

We have electrochemically polymerized PDMICA, a green melanin-like polymer that changes color when subjected to CV. The polymer changes from transparent, to green, and then to purple as the voltage applied scans from −1 to +1 V. The optical properties of the polymer are different from those of L-DOPA melanin, which has broadband UV−vis absorption. In addition, the polymer films have more structural order than synthetic and natural melanins, as shown by sharp XRD peaks and a nanofibrous structure in SEM images. These results demonstrate how changes in monomer chemical structure can greatly influence the optical and structural properties of melanin-like polymers.

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Supporting Information Available: The survey, C 1s, O 1s, and N 1s X-ray photoelectron spectra for 5,6-dimethoxyindole-2-carboxylic acid. This material is available free of charge via the Internet at http://pubs.acs.org.

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