Combined Electrical and Optical Characterization of Polydiacetylene
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ABSTRACT: Polydiacetylene (PDA) is a conductive polymer that has mechanochromism. When the polymer is exposed to mechanical stresses, change in temperature (thermochromism), pH (ionochromism), and so forth, the structural perturbation can be seen by the change in its color. Although it presents interesting electrical and optical properties, the relationship between these signals has rarely been investigated. We studied the correlation between the electrical conductivity and the absorption spectra of PDA. Upon UV irradiation, PDA absorption spectra presented a blue shift, which coincided with the decrease in the electrical conductivity.

INTRODUCTION
Conductive polymer has garnered attention since the breakthrough in 1977 due to its interesting conducting mechanism and its unique combined characteristics of flexibility and conductivity that can be used for applications such as flexible displays and touch sensors. Among them, polydiacetylene (PDA) has poor electrical conductivity that originates from the difficulty in doping due to its rigid crystal microdomains. Thus, it was once considered a secondary candidate for electronics applications. However, recent advance in nanofabrication techniques enabled the electrical characterization of nanostructured PDA, which presented an unexpected high conductivity (\(\sigma = 10^{-2} \text{ S/cm, semiconductor range}\)). It is because scaling down the sample size increased the surface to volume ratio, promoting the doping efficiency. In addition, nanosized PDA is expected to have high mobility (\(\mu = 20 \text{ m}^2/\text{Vs}\) predicted optically) because it is a single crystal.

On the other hand, PDA became a popular material due to its mechanochromism. When the polymer is exposed to a mechanical stress, change in temperature (thermochromism), pH (ionochromism), and so forth, the structural perturbation can be seen by the change in its color or in its fluorescence intensity. An enormous number of papers have been published within the past decade for attempts to use PDA as chromic and fluorescence sensors for the detection of ions, peptides, ligands, bacteria, and so forth. However, these optical studies have been rarely combined with the electrical characterization of PDA. Therefore, the correlation between the optical signals and the electrical ones is left elusive.

In this work, we study the electrical properties of PDA in relation to its optical chromism. The combined study will provide better insight for understanding the mechanism of PDA mechanosensitivity and a possibility to develop double readout (optical and electrical) sensors.

MATERIALS AND METHODS
Sample Fabrication. 10,12-tricosadiynoic acid (TRCDA, #L10231, AlfaAesar, U.K.) was dissolved in chloroform (#C/4960/15, Fisher Scientific, UK) at 25 mg/mL as a stock solution. Interdigitated gold electrodes (Material: Ti/Au; electrode width: 10 \(\mu\)m; electrode gap: 10 \(\mu\)m; number of feet: 90 pairs; thickness: 50/150 nm) fabricated on glass substrates (#IDE-Au, micrux technologies, Spain) were gently wiped with ethanol, rinsed with filtered water (EMD Millipore, USA), and dried with a nitrogen gun. TRCDA (0.2 mg) was deposited at the center of the interdigitated electrode and placed in a vacuum for 2–4 h to remove the solvent. The samples were polymerized with a UV cross-linker (CL-1000, UVP, CA, USA) for a desired UV dose. Even for the highest UV dose used in this work, the UV box temperature did not reach more than around 37 °C. Therefore, the blue-to-red transition induced by UV irradiation is not due to the increase in temperature because the thermochromism of PDA requires much higher temperature (>60 °C).

UV–Vis Spectroscopy. For the absorption measurements, the samples were made via the same procedure as that described above but on glass coverslips. V-670 (Jasco, USA) was used with a scan rate of 50 nm/min and a signal integration of 1.2 s/nm. The samples deposited on glass coverslips were fixed with a handmade sample holder. Absorption spectra were presented after removal of the background (the spectra obtained with monomers).

Electrical Characterization. The electrical characterization was performed with a two-electrode setup with a potentiostat Autolab (Metrohm AG, Switzerland). The voltage was scanned at a scan rate of 0.2 or 0.1 V/s inside a faraday cage under a dark environment. For the electrical contact between the chip and the potentiostat, we used a chip holder (#ED-DROP-...
CELL, Micrux Technologies, Spain). The current measured in this work is close to the detection limit of the instrument; thus, the background electrical noise was unavoidable. We selected a certain sampling rate (the time resolution of the experiments or the speed of the cyclic voltammetry) that matches with the noise frequency to present the data less noisy. The resistance values in Figure 3 were estimated from six samples and presented as the average and the standard deviation as error bars.

Estimation of the PDA Thickness by Confocal Laser Scanning Microscopy (CLSM). The thickness of the PDA was roughly estimated by taking 3D images by CLSM (Confocal A1, Nikon AG, JP) with a 60× oil objective (CFI PLAN APO LBDA 60XH, Nikon, JP) with a green filter setting (488/525). Fluorescence images were presented in a false color. The resolution in the z direction set by the pinhole was in the range of a few hundreds of nanometers. Therefore, the technique was used just to estimate the order of magnitude of the thickness. The bright field images were taken with the same inverted microscope with a color camera (Digital Camera Head DS-Fi2, Nikon, JP).

Temperature-Induced Blue-to-Red Transition Monitored by Electrical Measurements. The samples were prepared as described above but with a lower amount of TRCDA (0.1 mg) on the chip to ensure the uniform blue-to-red transition induced by heat. The electrical measurements were performed as described above but without the faraday cage because we needed to access the sample for heating. The temperature increase was induced by maintaining a soldering iron (#WHS 40D, Weller, USA) 2 mm above the sample (without any contact) until blue PDA visibly turned into red. At this moment, the temperature of the sample was approximately 100 °C. The process was monitored with chronoamperometry at V = 1 V. Additional I−V curves were taken before and after the chronoamperometry.

■ RESULTS AND DISCUSSION

The PDA samples were fabricated by depositing chloroform-dissolved 10,12-tricosadiynoic acid (Figure 1A) on cleaned glass coverslips, removing chloroform under vacuum overnight, followed by subsequent UV irradiation (see the Materials and Methods section for details). We selected 10,12-tricosadiynoic acid as a monomer because it is known to form lamellar bilayers10 and similar lipids have been commonly used for PDA electrical characterization.11 Different UV doses yielded PDA samples that appeared to be blue-to-red by the naked eyes. Figure 1B shows the absorption spectra of these samples. After polymerizing at a UV dose of 0.01 J/cm², a clear peak developed at 650 nm (arrow i in Figure 1B). This is the reason why this state of PDA appears to be blue (called blue state PDA) because a large fraction of red light (650 nm) is absorbed by the sample and only the rest of the light is reflected. When the samples were irradiated with a higher UV dose, the peak at 650 nm diminished while another peak at 500 nm (ii in Figure 1B) was enhanced. This PDA is called red state PDA. These spectra shifts upon polymerization are characteristic of PDA, explained by the broadening of the band gap that originates from the structural change of the polymer.11

The same PDA samples were also deposited on chips with patterned gold electrodes (see the Materials and Methods section for details). A two-electrode setup was used to obtain I−V curves at different UV doses. Figure 2A shows the I−V curves of PDA polymerized for 0−0.4 J/cm². Without polymerization, 10,12-tricosadiynoic acid is an insulator. As the samples were cross-linked, the conductance increased (0−0.4 J/cm²). However, further UV irradiation (2−6 J/cm²) rather decreased the conductance (Figure 2B). To visualize the transition of the PDA conductivity, the resistance of the sample is plotted against the UV dose in Figure 3 (black squares).

Figure 3 shows the calculated resistance of PDA samples at different UV doses (black squares). It has a valley at 0.5 J/cm² with a minimum resistance of ~1 GΩ. The height of the blue peak at λ = 650 nm obtained from the absorption spectra in Figure 1B is plotted against the UV dose on the right axis (blue squares in Figure 3). The height of the blue peak roughly
The Journal of Physical Chemistry B

represents the amount of blue PDA contained in the sample. It initially increases during the low UV dose (0–0.5 J/cm²) because the monomers polymerize and form blue PDA. However, further UV irradiation (0.5–12 J/cm²) decreases it because at these UV doses, the created blue PDA transforms into red PDA, which shows an absorption peak at 500 nm. The blue peak height maximizes at 0.5 J/cm², when the sample resistance is the lowest. It indicates that the blue PDA is more conductive than the red PDA. The result agrees with the previous electrical characterization of PDA with a field-effect transistor. The chromism of PDA is explained by the change in the electron orbital overlap in the conjugation. The distance between two carbons in the conjugated backbone is mainly governed by the monomer packing at the initial phase of polymerization. For most diacetylene monomers, they cross-link upon UV with a conformation that is not in the perfectly relaxed state because of the effect of the head group and the other monomer packing conditions (blue state). When the system is perturbed (e.g., by UV), the polymer tries to relax into the real energy minimum that has less overlap in the electron orbitals, which broadens the band gap and causes a blue shift in the absorption wavelength (red state). Therefore, it is reasonable that the red state has a smaller conductance than the blue state due to less overlap of the orbitals (and thus a larger band gap where fewer electrons are excited to the conduction band at room temperature). The exact mechanism of how the external perturbation changes the orbital overlap had been under a debate for a couple of decades. Historically, a model based on the transition from the one-ene structure to the butatriene structure was proposed but was rejected based on X-ray diffraction, nuclear magnetic resonance (NMR), and theoretical studies. In 1987, Dobrosavljevic and Stratt theoretically explained the chromism by a twist of the side chain, using real-space renormalization group methods to calculate the density of states and localization length for a simple tight binding model. This model could also explain the lipid head group dependence of the chromism reported experimentally because the lipid head group affects the rotation of the side chain. To obtain direct experimental evidence is extremely difficult. It is because the atomic structure of blue PDAs cannot be easily studied by X-ray diffraction techniques because the irradiation with X-ray induces the blue-to-red transition. As a result, many of the reported PDA structures are probably that of red PDAs, making it difficult to compare the side chain angles between blue and red states. This is the first systematic study that clearly shows the correlation between the PDA conductance and the blue-to-red transition of PDA.

To estimate the order of magnitude of the resistivity from the obtained resistance, the thickness of the PDA samples was characterized by CLSM. Figure 4A,B shows the bright field images of the blue and the red PDA on glass substrates from an identical position. They present an inhomogeneous distribution of PDA over the surface. Note that the electrode distance used in the conductivity measurement is 10 μm, which is smaller than the size of the PDA islands observed in the bright field images (Figure 4A,B). Before and after UV irradiation, the size of the islands did not change significantly, but the morphology within each island appeared slightly different, as has been previously reported. This morphological change may have also affected the electrical conductance. Red PDA is fluorescent, while the fluorescence pathway is forbidden in blue PDA. Nevertheless, in reality, “blue PDA” is also slightly fluorescent because a small amount of red PDA is mixed due to the spontaneous polymerization during the storage. We used this fluorescence to obtain a 3D image of blue PDA samples by CLSM (Figure 4C). Although the sample thickness was not homogeneous, it was on the order of a few micrometers. With it, the resistivity was roughly estimated to be ρ ≈ 50 MΩm (σ ≈ 2 × 10⁻¹⁰ S/cm in conductance) for the blue PDA (R ≈ 1 GΩ at 0.5 J/cm²). It is of the same order of magnitude as the reported conductivity of bulk PDA crystals without doping.

Finally, we attempted to use PDA as a double optical and electrical sensor to monitor the change in temperature. Heating PDA at 60–100 °C is well-known to induce the blue-to-red transition, as shown in the inset photos in Figure 5A. Figure 5A shows the current of PDA at V = 1 V over time. When the sample was blue PDA, the current at 0.4 ± 0.1 nA was observed (see the inset in Figure 5A). During the heating, the current increased. It is a typical behavior of a semiconductor (PDA) because more electrons are excited from the valence band to the conduction band at high temperature. After the heat source was removed and the sample temperature came back to room temperature, the current at 0.1 ± 0.1 nA was monitored for the red PDA. I–V curves obtained before and after heating also

Figure 3. Resistance (black) and absorption of the blue peak (blue) at λ = 650 nm against the UV dose.

Figure 4. Bright field and CLSM images of PDAs. A bright field image of (A) blue and (B) red PDA. (C) The 3D reconstitution of CLSM images taken with a blue PDA sample deposited on a glass substrate. The sample surface was scratched by the backside of a razor blade to locally remove PDA. It gives a contrast between the PDA deposited area and the glass substrate.
Figure 5. Temperature-induced blue-to-red transition monitored electrically and by naked eyes. (A) Current from PDA over time, while applying V = 1 V. The inset shows the same data on a different scale. The blue PDA presented a higher conductance compared to the red PDA after heating. The inset photos show the sample before (left side) and after (right side) heating. (B) I-V curves before and after heating, where the voltage was swept 0 → 1 → −1 V.

presented the increase in the resistance after heat treatment (Figure 5B). Note that the morphology of the PDA samples observed by bright field microscopy changed slightly before and after heating (similarly to Figure 4A,B). It may have also affected the conductance.

**CONCLUSIONS**

We presented a systematic decrease of PDA electrical conductance that coincides with the blue shift of the PDA absorption spectra upon UV irradiation. The result agrees with the well-accepted mechanism of PDA mechanochromism. Almost all of the previously reported PDA sensors used only the optical properties for detecting temperature, pH, binding of molecules, and so forth. The presented work implies that PDA can be used as a double optical and electrical sensor to enhance its sensitivity or to expand its applications.

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**Notes**

The authors declare no competing financial interest.

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