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Ionic Functionality and the Polyacetylene−Oxygen Charge-Transfer Complex

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S Supporting Information

INTRODUCTION

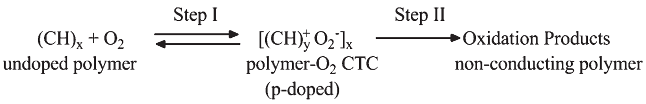
In recent years, considerable research has been focused on the use of conjugated polyelectrolytes (CPEs) for applications such as photovoltaics, polymer light-emitting electrochemical cells (PLECs), organic field-effect transistors, chemical sensors, and electrochromic devices.[1−5] Interest in CPEs stems in part from their solution processability, which facilitates thin-film fabrication through a variety of casting techniques such as spin-coating, spray-casting, layer-by-layer deposition, and inkjet printing.[6−9] It is also well established that the presence of mobile counterions has a dramatic impact on the electronic and optical properties of CPE-based devices. For example, mobile ions can impact charge injection through polarization at electrode boundaries,[10−12] and ionic centers can impact photoluminescence and electronic charge carrier mobilities by affecting film morphology and interchain interactions.[13,14]

Despite the emerging importance of CPEs, the influence of CPE ionic groups on the interaction of the conjugated backbone with molecular oxygen has been only marginally explored.[15] While the oxidation and degradation mechanisms of conjugated polymers have been extensively researched by various groups,[16−19] little or no work has been undertaken to investigate the corresponding mechanisms in their ionically functionalized analogues. Herein we report a study of the interaction of molecular oxygen, under ambient photo-oxidative conditions, with an anionically functionalized polyacetylene derivative and with respect to the chemical nature of the counterion. It was hypothesized that the intermediate polymer−O_2 charge-transfer complex (CTC), common to the oxidation of most conjugated polymers (Scheme 1),[16,20] would be stabilized through ionic interactions with high-charge-density ions such as alkali metal cations. The bound anion should aid in this stabilization by compensating the positive charge on the polymer backbone resulting from doping by oxygen. The formation of such a stabilized intermediate would have direct implications to the fabrication of CPE-based devices as well as their conditions of operation. The presence of a CTC with oxygen can dramatically alter material properties such as absorbance, conductivity, photoluminescence, and solubility. Hence, substantial alteration in either the thermodynamics or kinetics of its formation could be critically important to the operation of CPE-based devices and their sensitivity to trace alkali metals and oxygen.

EXPERIMENTAL SECTION

To determine the effect of ionic functionality on the formation and stabilization of the oxygen CTC, thin films of the anionic polyacetylene derivative poly(2-cyclooctatetraenylethanesulfonate) with tetramethylammonium ($TMAPA_A$) or alkali metal (MPA_A, M = Na^+, Li^+) counterions and the nonionic derivative poly(trimethylsilylcyclooctatetraene) (PA_{TMS}) were fabricated. The $TMAPA_A$ and PA_{TMS} films were spray or spun-cast from solutions of the corresponding polymers in methanol and chloroform, respectively. The syntheses for these polymers are described elsewhere.[21,22] The resulting films were typically 50−100 nm in thickness as determined by stylus or optical profilometry. The MPA_A films were prepared using solid-state ion exchange: films of $TMAPA_A$ were submerged in an acetonitrile solution containing 0.1 M sodium triflate (NaOTf), lithium triflate (LiOTf), or sodium tetrafluoroborate ($NaBF_4$) for 3 min followed by submersion in clean acetonitrile for 3 min and then rinsed before drying under vacuum for ∼12 h. The ion exchange was confirmed using XPS analysis. To monitor the formation and subsequent degradation of the CTC, UV−vis−NIR and FTIR spectroscopy were used to monitor spectral changes associated with the doped intermediate state. These data were used as a metric to determine the stabilizing effect of ions on the CTC based on the relative rates of formation and photobleaching of associated absorbances. Illuminated films were exposed to fluorescent lighting (∼0.4 mW/cm^2) under ambient laboratory conditions. Unless otherwise specified, all experiments were performed in air. NaOTf (Aldrich, ≥98%) was recrystallized (4 times) from ethyl acetate and dried under vacuum for 5 days at 80 °C. LiOTf (Aldrich, 99.99%) and $NaBF_4$ (Aldrich, ≥98%) were used as received. High-purity acetonitrile (Burdick & Jackson) was distilled from molecular sieves (3 Å) and stored under N_2 until used.

Scheme 1. Generalized Oxidation Mechanism of Polyacetylene



RESULTS

A dramatic enhancement of the stability of the polyacetylene−O_2 CTC as a result of ionic functionality and, in particular, the chemical nature of the counterion was observed.

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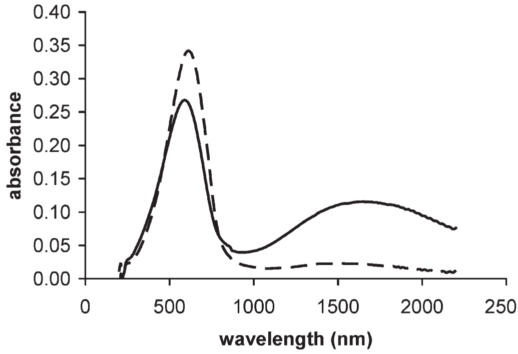


Figure 1. Absorbance of TMAPA$_A$ film before (dashed line) and after (solid line) ion exchange to the sodium salt.

Figure 1 shows the UV−vis−NIR spectra of a TMAPA$_A$ thin film before and after ion exchange to the sodium salt. Each film had been exposed to ambient oxygen for ∼10 min at this point, and further evolution of the spectral features was slow relative to this time scale. The broad spectral feature centered at ∼1650 nm results from a midgap soliton state associated with the doped polymer.[23] The minor presence of this feature in the case of the TMAPA$_A$ film is due to the doping effect of ambient oxygen resulting in the formation of a small amount of the O_2 CTC, and it is reversible when the sample is placed under vacuum, as has been demonstrated by various groups studying the air stability of polyacetylene.[16,24] No such change was observed for the nonionically functionalized analogue PA$_{TMS}$ after similar exposure to ambient O_2. A much larger increase in the intensity of the NIR 1650 nm absorbance and a decrease in the visible absorbance at ∼600 nm was observed following ion exchange with NaOTf and subsequent exposure to ambient O_2, occurring on the time scale of seconds to minutes. Control exchange experiments carried out using neat acetonitrile, or solutions containing alkylammonium cations showed no increase in the NIR. Sodium exchange experiments conducted under O_2-free conditions also showed no increase in the NIR. These controls indicate that the substantial doping in the NaPA$_A$ is due to the formation of the polymer−O_2 CTC influenced by the presence of the sodium cation. XPS analyses confirmed the exchange of the TMA ion for Na^+ as well as determined the lack of residual triflate anions, which could affect interpretation of the data (see Supporting Information).

To further confirm the formation of the CTC, FTIR spectroscopy was used to analyze films before and after ion exchange (Figure 2). The salient features seen are the intense, broad bands at ∼1400 and 850 cm^{-1}, which are seen to grow substantially upon ion exchange and O_2 exposure. These bands are assigned to charge-coupled molecular vibrations associated with the doped polymer backbone.[25−27] The appearance of a band at 1140 cm^{-1}, assigned to the C−O stretch, is further evidence of the formation of the CTC.[17]

It is important to note that the intensity of the spectral features in the NIR and IR regions of the nonexchanged polymer do not increase significantly with increased O_2 exposure, but rather they diminish as the polymer degrades. Furthermore, unlike the TMAPA$_A$ films and traditional polyacetylene, the NaPA$_A$ films display no reversibility of the polymer−O_2 complex even after weeks under vacuum. Concomitant with the changes in optical properties was a significant reduction in the film's electrical resistance consistent with oxygen doping.[16,17] Identical analyses of the nonionic PA$_{TMS}$ as well as a cationic polyacetylene film displayed none of the spectral features associated with the stabilized formation of the CTC.

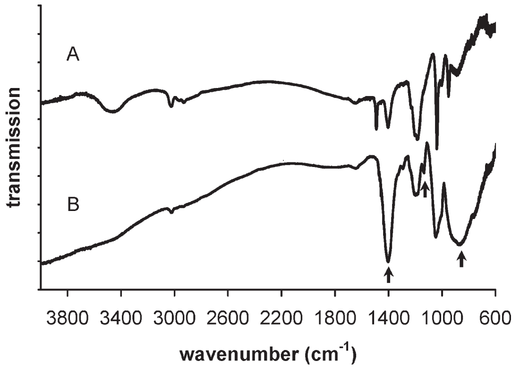


Figure 2. FTIR of a TMAPA$_A$ film: (A) as deposited and (B) following Na^+ exchange. The film had been exposed to air for ∼10 min in both cases. The broad, intense bands at ∼1400 and 850 cm^{-1} correspond to the doped polymer backbone, while the band at ∼1140 cm^{-1} corresponds to the C−O stretch of the CTC.

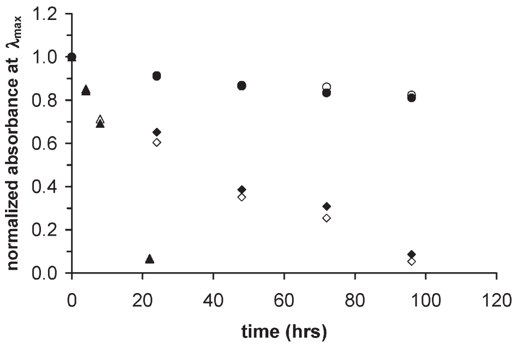


Figure 3. Normalized absorbance of thin films of PA$_{TMS}$ (triangles), TMAPA$_A$ (diamonds), and NaPA$_A$ (circles) at the initial wavelength of maximum absorbance (530, 600, and 590 nm, respectively). The open and filled symbols represent two samples exposed to identical photo-oxidative conditions. Film thicknesses were 70 nm (TMAPA$_A$ and NaPA$_A$) and 70 and 100 nm (PA$_{TMS}$).

To determine the influence of the ion-stabilized CTC on the subsequent degradation of the polymer (Scheme 1, step II), films exposed to ambient photo-oxidative conditions were monitored via UV−vis−NIR spectroscopy over a prolonged period of time. The rate of photobleaching of the absorbance in the visible region was used as a metric to determine the influence of the stabilized CTC on the subsequent degradation of the film. Figure 3 shows the normalized absorbances at the initial wavelength of maximum absorbance (λ_{max}) for the three films. As can be seen, the PA$_{TMS}$ films completely bleach in the visible region in a period of ∼22 h. This is expected as polyacetylene is known to rapidly degrade under photo-oxidative conditions. The TMAPA$_A$ films completely bleach in ∼96 h, while the NaPA$_A$ films displayed only ∼19% loss in absorbance over the same period of time. Also associated with the reduction in absorbance is a blue shift of the λ_{max}, consistent with a reduction in conjugation length as the polymer degrades to carbonyl products. The magnitude of this shift with NaPA$_A$ films was minimal in comparison to that of TMAPA$_A$ (see Supporting Information).

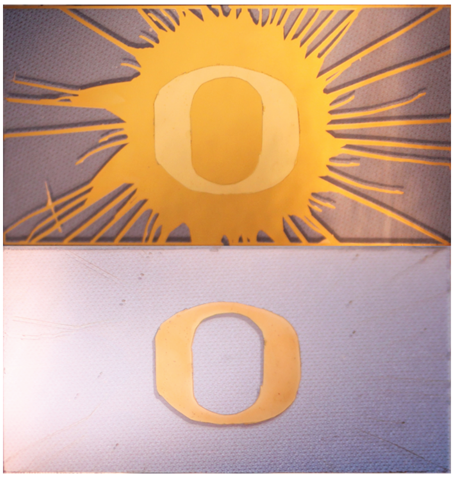


Figure 4. Patterned ion exchange of a TMAPA$_A$ films (~200 nm) immediately after exchange (top) and after ~15 days exposure to photo-oxidative conditions (bottom). The O-shape is the area exchanged for Na$^+$.

Thin films exchanged using NaBF$_4$ and LiOTf also displayed similar absorbance changes to the NaPA$_A$ films over the same period of time.

To highlight the observed visual changes associated with CTC formation and subsequent inhibited photobleaching, a simple experiment was conducted in which a paper mask (O-shaped) saturated with NaOTf solution was placed atop a spun-cast TMAPA$_A$ film (Figure 4). The ion-exchanged region under the mask displayed a change in visible absorption (bleaching) in a manner analogous to the solution phase exchange upon CTC formation, resulting in the transfer of the mask pattern to the substrate. Subsequent exposure of the film to photo-oxidative conditions resulted in the inhibited bleaching of the patterned area relative to the nonexchanged region.

In work by Arroyo-Villan et al. on the photo-oxidative stability of sulfonate functionalized polythiophenes,[15] it has been suggested that polymer degradation is inhibited in the presence of alkali metal counterions due to an increase in the hydrophilicity of the polymer film. This results in a greater uptake of ambient water, which acts as a singlet oxygen quencher. A singlet oxygen degradation mechanism is believed to occur in solution as well as in amorphous polymer films. To address this possibility, TMAPA$_A$ and NaPA$_A$ films were prepared in quartz cuvettes and redissolved in nanopure H_2O (18.2 MΩ). These solutions were then subjected to the same photo-oxidative conditions and analysis as the polymer films. Figure 5 shows a plot of the normalized absorbance at the initial λ_{max} as a function of time. As can be seen, the Na$^+$ exchanged polymer bleaches at a rate slower than that of the TMA polymer in a similar manner as seen in the solid films. These data suggest that singlet oxygen quenching due to the presence of water is not solely responsible for the inhibition of degradation, as this would be expected to result in both solutions bleaching at the same rate. Furthermore, as seen in the IR spectra (Figure 2), the intensity of the O−H stretch in the TMAPA$_A$ film is greater than that of the film following Na$^+$ exchange, again, suggesting that H_2O is not the primary degradation inhibitor.

Other groups have found that morphological changes resulting from alteration of polymer packing can have an impact on the rate of photodegradation.[28] This change was attributed to decreases in oxygen permeability due to the formation of polymer aggregates. To address this possibility, AFM was performed on TMAPA$_A$ films before and after exchange to the sodium salt. The results showed no observable alteration of surface morphology or aggregate formation (see Supporting Information).

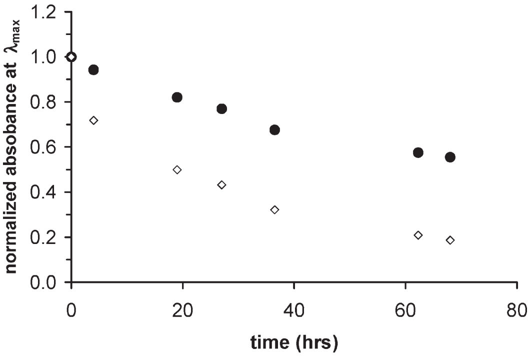


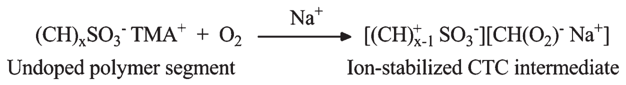
Figure 5. Normalized absorbance of aqueous solutions of TMAPA$_A$ (diamonds) and NaPA$_A$ (circles) at the initial wavelength of maximum absorbance (592 and 589 nm, respectively). Solutions have the same concentrations and were exposed to identical photo-oxidative conditions.

■ DISCUSSION

The spectral data suggest that the presence of small alkali metal counterions has a significant impact on the rate of formation of the CTC. Likewise, the slower rate of photobleaching of the visible absorbance of the ionically functionalized films suggests that the presence of ionic functionality has a significant impact on stabilization of the polymer−O_2 CTC. To rationalize the results, a mechanism is proposed in which sodium ion migration from the bound sulfonate stabilizes the negative charge of the CTC (Scheme 2). Likewise, the resulting positive charge on the polymer backbone is compensated by the bound sulfonate anion, as demonstrated by several groups in electrochemical doping experiments of CPEs.[22,29] The increase in stabilization of the CTC by the Na$^+$ (or Li$^+$) vs TMA counterion is not unexpected as the larger charge density of the alkali metal ion will more strongly associate with the negative charge on the oxygen. As this intermediate state is stabilized more effectively by alkali metal cations, subsequent reaction to form the carbonyl degradation products is inhibited. This stabilizing effect is also manifest in the lack of reversibility of the CTC. Extensive work has been reported on the oxidation of polyacetylene in which the formation of the CTC, via oxygen doping, has been shown to be reversible by placing the film under vacuum within a short period of time.[16,24] Under these conditions, the spectral features associated with the CTC are reversed as the polymer reverts to the undoped state. The conductivity of the polymer also returns to that of the undoped state without significant degradation of the polymer. Research into the environmental stability of other polymer films, such as polythiophene, has shown a similar reversibility.[30] However, in the case of the MPA$_A$ films, the spectral features are not reversible even with extended time under vacuum. Whether CTC stabilization is kinetically or thermodynamically controlled is currently under investigation.

While alteration of polymer conformation cannot be completely discounted, the AFM and spectral data suggest that its impact

Scheme 2. CTC Stabilization by Sodium Ion Migration



$$(CH)_xSO_3^-\,TMA^+ + O_2 \xrightarrow{Na^+} [(CH)^+_{x-1}\,SO_3^-][CH(O_2)^-\,Na^+]$$

is not significant. Following ion exchange, a small blue shift is observed in the λ_{max} in the visible region (~10−20 nm), which can be attributed to chain twisting or kinking. However, a more likely cause is the reduction in conjugation length from the formation of the polymer−O_2 complex itself. Furthermore, the lack of any observable changes in surface morphology and given the very small values for polymer diffusion coefficients in the solid state,[31] it is unlikely that conformational changes are responsible for the reduction in the rate of photodegradation of the CTC intermediate. This is supported by solution phase experiments, which show only a minor blue shift of the λ_{max} of $NaPA_A$ relative to $TMAPA_A$ (~3 nm).

The rapid formation of the CTC also appears to be unique to the anionically functionalized polymer. When analogous experiments were conducted using nonionic PA_{TMS} or cationically functionalized polyacetylene derivatives, no spectral changes associated with CTC formation or inhibited degradation were observed. This can be explained by the proposed mechanism through the synergistic effect of the ability of the bound sulfonate to compensate the net positive charge and the sodium stabilized negative charge associated with the CTC. While it has been reported that chemical or electrochemical p-doping of conjugated polymers will inhibit O_2 oxidation and degradation, no examples of the inhibition of conjugated polymer degradation resulting from an internally ion-stabilized polymer−O_2 complex in the solid state have been reported. In the former case, the doped state is compensated by an introduced dopant anion. In this case, XPS analysis confirmed that no triflate anions were present in the exchanged films, supporting the proposed mechanism. Preliminary results on sulfonate functionalized polythiophenes show an analogous effect as the result of alkali metal cation exchange, suggesting the CTC stabilization may be general with anionic CPEs.

CONCLUSION

We have demonstrated that in the presence of alkali metal cations and molecular oxygen anionically functionalized polyacetylenes rapidly oxidize to form the intermediate CTC. This complex is stabilized by the alkali metal cations more effectively than with larger alkylammonium cations, resulting in decreased rates of photobleaching and the prevention of the reverse reaction to re-establish the undoped polymer. Comparison of polyacetylene CPEs to nonionic TMS derivatives indicate that the presence of ionic functionality, in general, affects the stabilization of the CTC. These results have significant implications for the fabrication and operation of CPE-based devices such as light-emitting devices and photovoltaics. If extreme care is not taken to avoid the introduction of oxygen in the presence of even trace amounts of alkali metal cations, the irreversible formation of the CTC complex will result in altered device performance or the possibility for misinterpreting results if its presence is not recognized. The effects of the CTC on device performance can manifest as decreased quantum efficiencies in devices such as PLECs or reduction in photovoltaic efficiencies, as the result of exciton quenching by the CTC. The preliminary observation of a similar counterion effect in sulfonate functionalized polythiophenes suggests that this phenomenon may be a general effect with anionic CPEs. These results suggest that the interaction of CPEs with molecular oxygen may be far more complex than has been seen in the studies of nonionic conjugated polymers, requiring detailed investigations to elucidate the chemical mechanisms in order to optimize the performance of devices based on this class of materials.

ASSOCIATED CONTENT

Supporting Information. XPS, AFM, UV−vis spectra, and sample prep. This material is available free of charge via the Internet at http://pubs.acs.org.

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