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Influence of Annulene Ratio on the Electrochemical and Spectroscopic Properties of Methano[10]Annulene−Thiophene Random Copolymers

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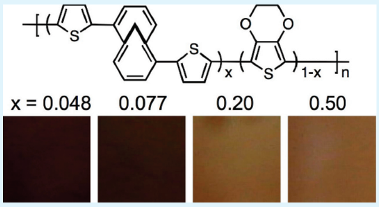

ABSTRACT: We describe a series of copolymerization studies whereby the nonbenzenoid aromatic methano[10]annulene is incorporated into three different types of random copolymers, two based on polythiophenes (from bithiophene and terthiophene monomers) and one based on poly(ethylene dioxythiophene). Copolymers where the annulene component was in the majority had optical and electrochemical behaviors reminiscent of the annulene homopolymer. In contrast, we found that the annulene influenced polymer electronics at very low feed ratios where the commercial comonomer was in the majority. Copolymerizations are useful approaches to dilute the complex annulene monomers into functional polymers without losing the optoelectronic properties of the annulene homopolymers. These electrochemical results provide important design rules that can be employed for the chemical synthesis of related random copolymers.

KEYWORDS: electropolymerization, conducting polymers, polythiophenes, annulenes, spectroelectrochemistry

INTRODUCTION

Increasing attention has been paid to the construction of exotic monomer precursor units usable as new components for molecular and polymeric active materials for organic electronic devices.[1−7] New molecular entities are prepared through chemical synthesis with useful properties that render them easier to reduce or oxidize chemically or electrochemically, provide them with a specific optical bandgap, or allow them to form different degrees of thin film crystallinity. They may also be designed with reactive functionality to allow for inclusion into more complex π-conjugated materials via cross-coupling reactions. These synthetic modifications often come with a substantial cost in terms of lengthy or difficult chemical steps that can limit the quantity at which these materials can be prepared. Electrochemical copolymerization routes have enabled the preparation of complex conjugated polymers from monomer components whose percentages can be dialed in experimentally without up-front synthesis of an oligomeric "macromonomer." In some cases, the resulting copolymers present electronic properties that are true blends of the individual monomer components while others have superimposable spectral signatures that can be attributed to the molecular monomeric contributions.[8−11] In addition to electronic structure modifications, the addition of low-oxidation potential polymerizable additives has also been employed in copolymer synthesis to lower the oxidation potentials required for polymer deposition on electrodes and to enable the extraction of unusual mechanistic features.[12,13]

We recently reported a general strategy to enhance the effective conjugation lengths of π-conjugated polymers through the inclusion of unusual aromatics as exemplified by several studies with methano[10]annulene.[14−16] The motivation behind these studies was to incorporate nonbenzenoid aromatics into π-conjugated backbones to take advantage of their lower degrees of resonance stabilization energies relative to the benzenoid counterparts.[17] Therefore, when the polymers adopted the quinoidal electronic structures as a function of electrochemical oxidation/doping, the energetic cost to disrupt aromaticity would be lessened. This process is relevant to many optoelectronic devices where the electronic structure of the π-conjugated active layer must be polarizable under other operation-relevant scenarios (e.g., field-effect doping or incident solar radiation). We have explored several types of annulene copolymers containing thiophene, furan and other types of conjugated groups (Chart 1), where the "comonomer" ratio was set by the composition of the oligomeric macromonomer precursors prepared independently. For example, we prepared oligoaromatic annulene macromonomers flanked with two thiophene units and with two bithiophene units leading to conjugated alternating copolymers with 2:1 and 4:1 thiophene:annulene ratios, respectively.[15] These macromonomers were polymerized electrochemically, and we found that the annulene polymers had very broad and ill-defined spectroscopic signatures in the oxidized states when compared to the corresponding benzenoid polymers. We also found that as the annulene percentage increased in the polymer backbone, the oxidation potentials decreased, as attributed to the cation stabilizing abilities well-established for the annulene core.[18]

The nonplanar geometry and the racemic nature of the annulene core hold exciting promise in the development of amorphous charge transporting materials that can be processed from solution with minimal reliance on the inclusion of solubilizing alkyl tails: amorphous materials might enable more reliable solution processing and be less susceptible to long-term phase segregation or other morphology changes within bulk-heterojunction

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Chart 1. Recent Examples of Annulene−Oligoaromatic Alternating Copolymers

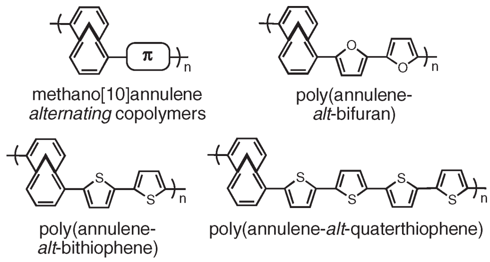
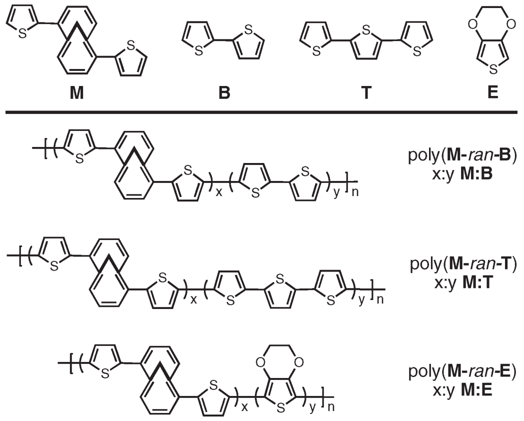


Chart 2. Monomers (top) and Random Copolymers (bottom) Studied Herein



photovoltaics or other electronic devices.[19−22] Although the methano[10]annulene hydrocarbon can be produced in the lab routinely on tens of grams scale,[23] and for pilot-plant production on larger scale, this is nowhere near the scale on which more common benzenoid building blocks can be synthesized or purchased commercially. Copolymer studies would enable a more viable extension of this exotic monomer into functional conjugated polymers because a systematic study of new amorphous polymers with different annulene ratios becomes prohibitively difficult if specific tailored annulene macromonomers must be synthesized individually. These studies would be equally relevant for electrochemical synthesis and as a preliminary screen to offer compositional structural guidance for the analogous chemically copolymerized materials.

We report here a detailed study of copolymers whereby the polymerizable annulene monomer 2,7-dithienylmethano-[10]annulene (**M**)[15] was mixed in defined ratios with readily available electropolymerizable oligo-α-thiophenes (bithiophene, **B**, and terthiophene, **T**) and ethylene dioxythiophene (**E**) monomers thus leading to random copolymers as shown in Chart 2. The purpose of this study is to understand at what point and to what extent does the incorporation of the unusual polymerizable annulene monomer as a minority component perturb the electronics of the resulting copolymers. Although the present report deals exclusively with polymers generated through electropolymerization, the results can be used to guide the synthesis of other annulene−oligothiophene macromonomers useful for preparing related copolymers with more defined chemical composition.

■ EXPERIMENTAL SECTION

Annulene monomer **M** was prepared through Stille coupling between 2,7-dibromomethano[10]annulene[24] and tributylstannyl thiophene as described previously.[15] Bithiophene (**B**) and terthiophene (**T**) were purchased from Aldrich and used without purification. Ethylene dioxythiophene (**E**) was obtained from Aldrich and Bayer and used as received. n-Bu_4NPF_6 was purchased from Aldrich and recrystallized from ethanol/water and dried under high vacuum before use. Solvents for electrochemistry were purified by passage through activated alumina columns and degassed before use. Stock solutions of all monomers were prepared in 0.1 M n-Bu_4NPF_6 in CH_2Cl_2. Comonomer solutions were prepared from these stock solutions such that the overall concentration of electropolymerizable species was ca. 2.5 mM. These comonomer solutions were subjected to cyclic voltammetry (CV) in three electrode, one chamber cells at 2 mm^2 platinum button working electrodes with quasi-internal Ag/Ag^+ reference electrodes (silver wire immersed in 0.01 M $AgNO_3$ and 0.1 M n-Bu_4NPF_6 in acetonitrile, separated from the cell with a porous Vycor frit, obtained from Bioanalytical Systems, Inc.) and platinum counter electrodes using a scan rate of 100 mV/s. The half-wave potential ($E_{1/2}$) of the Fc/Fc^+ couple was used as an external standard, but all potentials are reported relative to Ag/Ag^+. The potentials for the CV experiments were cycled using either an Autolab PGSTAT 302 bipotentiostat or a PARSTAT 2273 potentiostat with the presumption being that the monomer feed ratio was reflected in the composition of the resulting copolymers. Thin films for spectroelectrochemical analysis were grown on glass coated with indium tin oxide (Aldrich, 70−100 Ω/sq surface resistivity) and UV−vis measurements were taken with a Varian Cary 50 Bio UV−vis spectrophotometer. A polymer-modified ITO plate placed in the light path was used as the working electrode in a three-electrode cell set up in a quartz cuvette for spectroelectrochemical measurements. The ITO electrode was held at progressively more positive potentials prior to UV−vis measurements. Polymer films for conductivity measurements were grown on electrically shorted gold interdigitated electrode arrays as described for standard CV such that polymer spanned the whole array. Drain currents were recorded between the two working electrodes of the array (15 μm spacing) at a 5 mV/s scan rate with a potential difference of 40 mV between the two working electrodes; the devices were purchased from Abtech Scientific, Inc. (IME 1550.5 M Au U).

■ RESULTS AND DISCUSSION

M:B Copolymers. In line with our work to prepare annulene−thiophene copolymers from polymerizable macromonomers, we explored compositional variations of the annulene (**M**) with bithiophene (**B**). We surveyed concentration ranges between 1000:1 **M:B** and 1:1000 **M:B** but only report representative data here. The onset of oxidation (E_{on}) and the potential of peak anodic current ($E_{p,a}$) for **M** were around 700 and 970 mV, respectively. It is slightly harder to oxidize **B** as reflected in the more positive E_{on} and $E_{p,a}$ values relative to **M** (950 and 1500 mV, respectively). The fact that the E_{on} values were only separated by 250 mV suggests that CV should be an effective means to ensure incorporation of both monomers into random copolymers without the application of excessive overpotentials. No unusual polymerization effects in terms of E_{on} and $E_{p,a}$ were found in **M:B** comonomer solutions where **B** was the minority component, and all initial CV scans resembled **M** solutions (Figure 1a). In contrast, films prepared from **B**-rich solutions showed a marked lowering of the onset of anodic activity. Typically, it was required that we scan beyond the $E_{p,a}$ to achieve reasonable polymer growth. In the **M:B** mixtures where **B** was the major

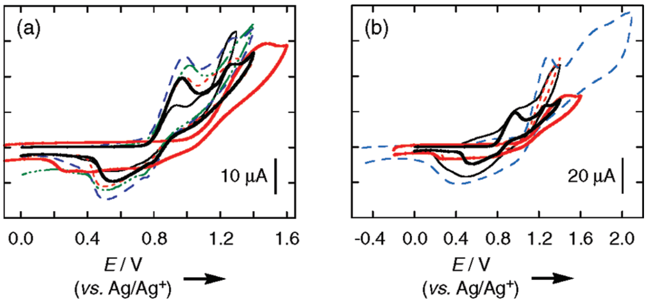


Figure 1. First CV scans of **M:B** comonomer solutions, where total electroactive species concentration is 2.5 mM in 0.1 M *n*-Bu_4NPF_6 in CH_2Cl_2. CV conditions: 100 mV/s scan rate at a 2 mm^2 Pt button working electrode vs a quasi-internal Ag/Ag^+ reference. (a) **M**-rich **M:B** solutions: **M**, bold black line; 1:1, thin black line; 13:1, dotted red line; 120:1, dashed blue line; 1000:1, green line; **B**, bold red line. (b) **B**-rich **M:B** solutions: **M**, bold black line; 1:1.2, black line; 1:10, dotted red line; 1:1000, dashed blue line; **B**, bold red line.

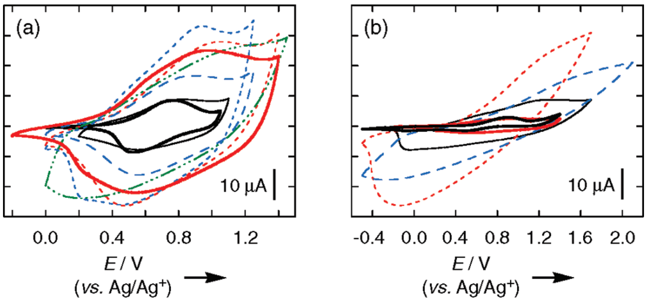


Figure 2. **M:B** random copolymer CVs in monomer-free electrolyte, conditions as listed in Figure 1. (a) **B**-rich **M:B** copolymers: poly(**M**), bold black line; 1:1.1, black line; 1:2.5, dotted red line; 1:4.4, dashed blue line; 1:9, green line; 1:18, dotted blue line; poly(**B**), bold red line. (b) Greater **B** compositions: poly(**M**), bold black line; 1:10, black line; 1:97, dotted red line; 1:1000, dashed blue line; poly(**B**), bold red line.

component, the presence of **M** lowered the effective $E_{p,a}$ thus leading to a less harsh oxidative polymerization (Figure 1b).

Continued CV cycling led to the adsorption on insoluble polymer films of the working electrodes. These modified electrodes were rinsed and placed in monomer-free electrolyte to record the corresponding polymer CVs. Both the poly(**M**) and poly(**B**) homopolymer films had comparable CV profiles although the poly(**M**) film had a more pronounced and quasi-reversible oxidation with an $E_{1/2}$ value of 700 mV. Copolymers grown from **M**-rich monomer solutions were qualitatively quite similar albeit with greater degrees of hysteresis, all exhibiting non-Nernstian quasi-reversible anodic behavior with apparent $E_{1/2}$ values around 650−700 mV. In the case of the **B**-rich copolymers, the film CVs had a strong resemblance to poly(**M**) homopolymers at **B** monomer ratios below 1:5 **M:B** (Figure 2a). A transition to more ill-defined polymer CVs was observed at **B** monomer ratios greater than 1:9 **M:B** leading to much stronger hysteresis responses (Figure 2b). This hysteresis could be envisioned to arise from more ordered thin films of polymers due to polymer thickness effects or better packing of the oligothiophenes formed locally at the electrode surface during the polymerization, thus requiring overpotentials to achieve film reorganization and electrolyte influx during charging cycles.[25] Similar voltammetric behavior has been observed for solid films of oligothiophenes and polythiophenes derived from terthiophene

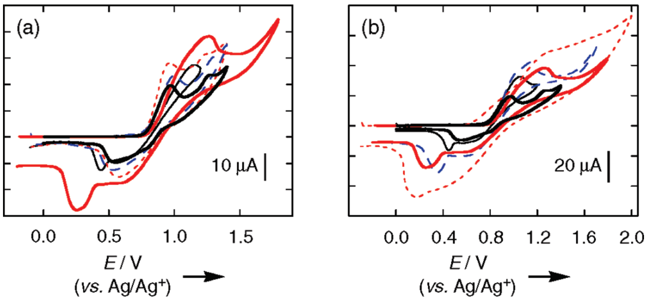


Figure 3. First CV scans of **M:T** comonomer solutions, where total electroactive species concentration is 2.5 mM. Other conditions as listed in Figure 1. (a) **M**-rich **M:T** solutions: **M**, bold black line; 0.81:1, black line; 8.7:1, dotted red line; 85:1, dashed blue line; **T**, bold red line. (b) **T**-rich **M:T** solutions: **M**, bold black line; 1:0.86, black line; 1:9.1, dotted red line; 1:79, dashed blue line; **T**, bold red line.

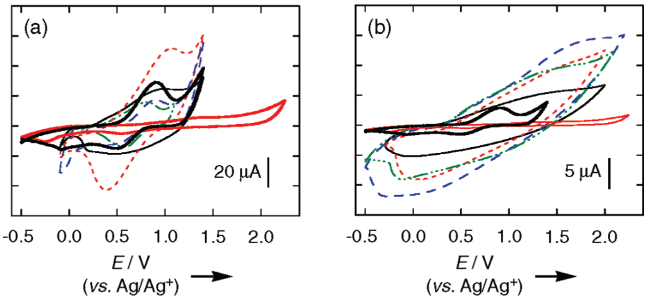


Figure 4. **M:T** random copolymer CVs in monomer-free electrolyte, conditions as listed in Figure 1. (a) **M**-rich **M:T** copolymers: poly(**M**), bold black line; 0.81:1, black line; 8.7:1, dotted red line; 86:1, dashed blue line; 880:1, green line; poly(**T**), bold red line. (b) **T**-rich **M:T** copolymers: poly(**M**), bold black line; 1:0.86, black line; 1:9.1, dotted red line; 1:79, dashed blue line; 1:900, green line; poly(**T**), bold red line.

monomers.[26,27] Although it seems that greater **B** percentages in the comonomer feed lead to more polymer film current, in some cases film instabilities were noted with continued CV sweeping resulting in diminished current intensities. It is clear that the annulene ring is still able to exert a noticeable influence on the copolymer electronics even at the ca. 1:5 **M:B** ratio, corresponding to 8% annulene composition in the random copolymer.

M:T Copolymers. The same general trends found in the **M:B** copolymers above held for terthiophene (**T**) copolymers, the only major difference being that the E_{on} values for **T** and **M** were the same (700 mV). **M**-rich **M:T** comonomer solutions showed basically the same E_{on} values with $E_{p,a}$ values ranging between 960 and 1030 mV (Figure 3a). As the comonomer solution became more **T**-rich, the onsets remained comparable but the $E_{p,a}$ values shifted slightly more positive (between 1060 and 1310 mV, approaching that found for **M**-free solutions of **T** at 1270 mV, Figure 3b). Noticeable in the CV of the ca. 1:1 **M:T** monomer feed ratio solution was the presence of a sharp cathodic process at 440 mV quite similar to the cathodic feature at 250 mV found during the growth of poly(**T**) homopolymer. This pronounced hysteresis is well-known for polythiophenes prepared from poorly soluble oligothiophenes as alluded to above in the **M:B** copolymer systems.

M-rich **M:T** copolymers had CV profiles comparable to the pure poly(**M**) homopolymer with quasi-reversible $E_{1/2}$ values around 700 mV (Figure 4a). The 1:1 **M:T** copolymer had more broad and ill-defined CV features, and the more **T**-rich copolymers were markedly hysteretic (Figure 4b). In comparison, poly(**T**) homopolymers prepared under the same conditions passed much less current than did even those with trace amounts of **M** in the polymerization solution. We attribute this to a more robust copolymer film that remains adhered to the electrode surface: poly(**T**) homopolymers prepared under these same conditions readily rinsed off of the electrode surface following oxidative polymerization. This poor deposition would be problematic for the preparation of ITO-modified electrodes, so we did not collect **M:T** copolymer spectroelectrochemical data.

M:B Copolymer Spectroelectrochemistry. Annulene-containing polymers have been shown to encourage longer delocalization lengths within the conducting charged backbones as observed through spectroelectrochemical measurements.[14−16] This is due to the energetic ease with which the annulene electronics can be polarized in order to stabilize a charged defect or carrier by way of a quinoidal electronic structure. We therefore wanted to assess how the annulene as a minority component of a random copolymer would affect this delocalization. As a representative example, we probed **M:B** copolymer films at 1:1, 10:1, and 1:10 compositions to observe how the annulene incorporation would influence optical properties of the oxidized quinoidal structures. The 10-fold ratios were chosen as these were where the most dramatic polymer changes were observed in CV measurements of the comonomer solutions and copolymer films.

The spectroelectrochemical experiment allows us to characterize the changes in electronic structure that accompany polymer redox events. For electrochromic conducting polymers, this usually involves a structural reorganization from the localized aromatic form associated with the neutral form of the polymer semiconductor to the delocalized quinoidal form associated with the charge carriers generated upon electrochemical oxidation.[28] This also gives a defined UV−vis spectral profile to the distinct chromic responses associated with typical electrochromic thin films. Annulene-containing polymers typically have very broad polaronic absorption profiles, a feature that we attribute to the existence of materials with varying conjugation lengths within the thin films (due to different oligomeric materials for example) leading to a broad superposition of polaronic absorptions present for the heterogeneous electronic population. Both the 1:1 (Figure 5a) and 1:10 (Figure 5b) M:B copolymers similarly show this featureless and broad low-energy absorption while the poly(**B**) homopolymer shows a sharper absorption signature at moderate doping levels centered around 720 nm (Figure 5c). Figure 5d shows a normalized plot of the neutral UV−vis absorptions for poly(**M**) and poly(**B**) homopolymers along with the 1:1 and 1:10 **M:B** copolymers. The 10:1 copolymer was in essence an overlay of the poly(**M**) homopolymer. Although the overall differences in absorption maxima are not dramatic (ca. 20 nm difference among samples), it is apparent that the red fine structure of the poly(**B**) homopolymer (an indicator of a more ordered film common for oligothiophenes) is less of a presence in the 1:10 copolymer. Thus, even at the ca. 4% loading, the nonplanar annulene core is able to impart noticeable disorder to the adsorbed conjugated polymer film.

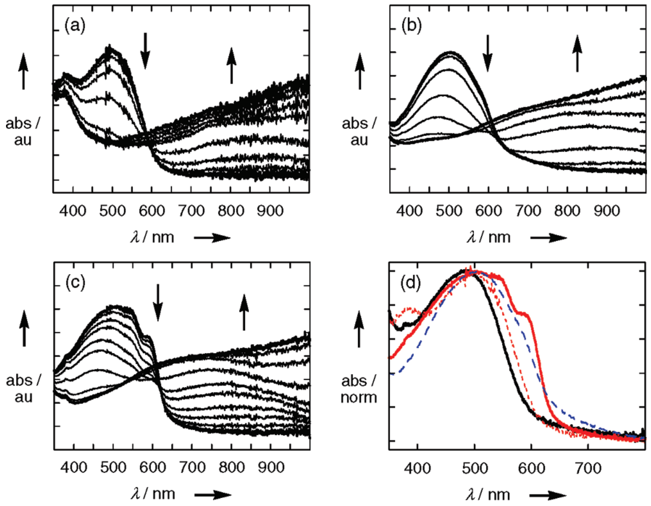


Figure 5. Spectroelectrochemical profiles for (a) 1:1 **M:B** copolymer held between 320 and 1080 mV, (b) 1:10 **M:B** copolymer held between 310 and 1090 mV, and (c) poly(**B**) homopolymer held between 200 and 1060 mV. All films were deposited onto transparent ITO electrodes and held at increasingly more positive applied potentials (arrows indicate trends in absorption as applied potentials are increased in ca. 70−120 mV increments over the potential ranges indicated above). (d) Neutral polymer UV−vis profiles for: poly(**M**) homopolymer, bold black line; 1:1 **M:B** copolymer, dotted red line; 1:10 **M:B** copolymer, dashed blue line; and poly(**B**) homopolymer, bold red line. Other conditions as listed in Figure 1.

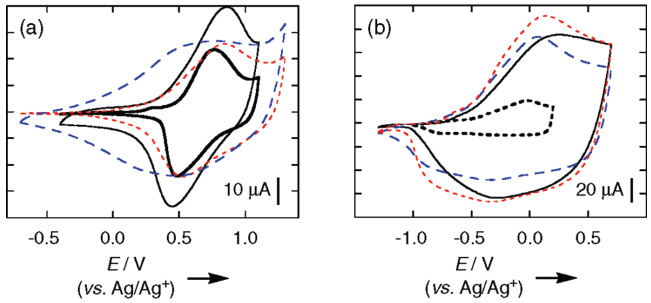


Figure 6. **M:E** random copolymer CVs in monomer-free electrolyte, conditions as listed in Figure 1. (a) **M**-rich **M:E** copolymers: poly(**M**), bold black line; 20:1, black line; 4:1, dotted red line; 1:1, dashed blue line. (b) **E**-rich **M:E** copolymers: poly(**E**), dashed bold black line; 1:4, black line; 1:12, dotted red line; 1:20, dashed blue line.

M:E Copolymers. EDOT (**E**) is a versatile monomer used to prepare the ubiquitous poly(EDOT) formulations that have been used as hole-transporting conductive coatings for a variety of organic electronics applications.[29,30] It has also been employed in several established electrochemical copolymerization studies.[9,10] We thus prepared **M:E** copolymers in line with the oligothiophene copolymers above. In practice, the use of EDOT led to much thicker copolymer films with greater degrees of quasi-reversibility compared to the oligothiophene copolymers (especially **T**-rich **M:T** copolymers, where the CVs showed pronounced hysteresis).

Comonomer electrolyte solutions for CV and subsequent polymerization were prepared between 20:1 and 1:80 **M:E** ratios, and representative data is discussed here. The E_{on} values for anodic activity leading to polymer growth were ca. 800 mV in all cases (for reference, E_{on} values for **E** and **M** monomer solutions were 800 and 700 mV, respectively). **M**-rich **M:E** copolymers had CV profiles very similar to the quasi-reversible oxidation of poly(**M**) homopolymer ($E_{1/2}$ values between 620 and 670 mV, Figure 6a). In contrast, the **E**-rich **M:E** copolymers showed progressive $E_{p,a}$ shifts to less positive potentials as the EDOT percentages were increased (Figure 6b). All **E**-rich **M:E** copolymer films showed much greater CV currents than did the pure poly(**E**) homopolymer.

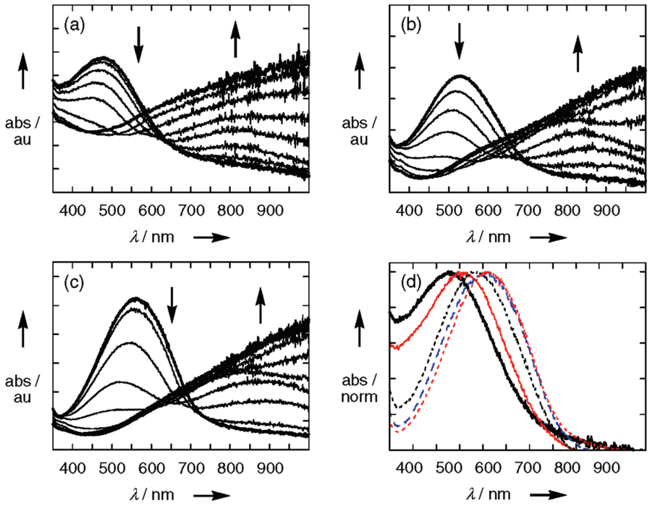


Figure 7. Spectroelectrochemical profiles for (a) 4:1 **M:E** copolymer between −170 and +1210 mV, (b) 1:4 **M:E** copolymer between −360 and +1020 mV, and (c) 1:20 **M:E** copolymer between −670 and +1210 mV. All films were deposited onto transparent ITO electrodes and held as tincreasingly more positive applied potentials (arrows indicate trends in absorption as applied potentials are increased in ca. 150−200 mV increments over the potential ranges indicated above). (d) Neutral polymer UV−vis profiles for **M:E** copolymers: 4:1, bold black line; 1:1, red line; 1:4, dotted black line; 1:12, dashed blue line; and 1:20, dotted red line. Other conditions as listed in Figure 1.

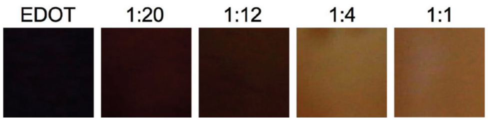


Figure 8. Thin films of EDOT homopolymer (left) and **M:E** random copolymers of given ratios prepared through anodic polymerization of the respective monomer solutions on ITO electrodes. Each panel represents ca. 6 × 6 mm area.

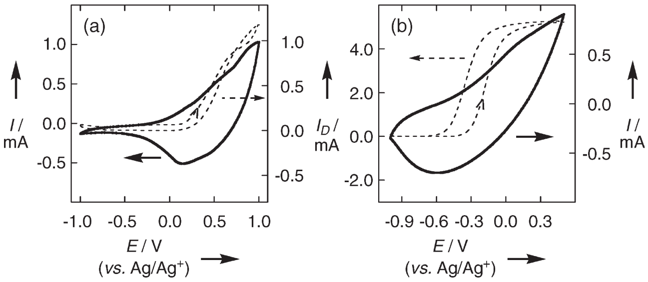


Figure 9. CV (bold) and in situ conductivity profiles (dotted) for (a) 1:1 **M:E** copolymer and (b) 1:12 **M:E** copolymer acquired on 15 μM spaced interdigitated electrode arrays. The drain current (I_D) was recorded in situ by dropping a 40 mV offset potential between the two working electrodes comprising the interdigitated array and subsequently scanning both channels independently with a scan rate of 5 mV/s. The arrows on the drain current correspond to the trace of the initial forward CV scan (to more positive potentials necessary to create positive charge carriers). Other conditions as listed in Figure 1.

Spectroelectrochemical analyses were conducted on the **M:E** copolymers. Unlike the situation for the **M**-oligothiophene copolymers, the EDOT copolymers grew very well on ITO leading to thick and strongly absorbing films. **M**-rich **M:E** copolymers (between 4:1 and 20:1 **M:E** ratios) had absorption profiles in both the neutral (λ_{max} ca. 475−480 nm) and progressively more doped states that mirrored those found for poly(**M**) homopolymers grown under the same experimental conditions. The λ_{max} values shifted almost 80 nm as the **M:E** ratios were varied from 4:1 (477 nm, Figure 7a) to 1:12 (555 nm, Figure 7b), reaching apparent saturation at 1:20 (560 nm, Figure 7c). Although the λ_{max} values steadily increased in this interval (Figure 7d), the absorption onsets were not as dramatically impacted. Even at the 1:20 level, the annulene influence is apparent: the low energy λ_{max} of poly(**E**) homopolymer in the reduced state shows pronounced vibronic structure (at ca. 600−620 nm, leading to an apparent midnight blue color), whereas the neutral 1:20 **M:E** copolymer shows a broad and featureless absorption λ_{max} at 560 nm. Visually, the colors of the copolymers (Figure 8) span qualitatively from red-purple (1:20) to brown-orange (1:1 and greater **M** percentages).

Finally, we obtained in situ conductivity data for the **M:E** copolymers. These measurements were conducted according to Wrighton's method using interdigitated microelectrode arrays.[31] In brief, these transistor-like measurements provide information on how the relative conductivity of the polymer is influenced by the applied oxidation potential. The assumption is that, if a film spanning the electrode array is conductive, an applied potential strong enough to oxidize the polymer should subsequently lead to a drain current between the electrodes in the device due to the injection of charge carriers. Problematic polymer adhesion onto the interdigitated devices has limited the application of this technique to annulene-based conjugated polymers, but the facile polymerization propensities of the EDOT monomer to polymerize into thick films allow us to apply it here for the **M:E** copolymers.

In situ conductivities were recorded for the 1:1 **M:E** copolymer along with the **E**-rich **M:E** copolymers. The 1:1 copolymer showed an onset of conductivity at fairly high applied potential (170 mV, Figure 9a). More **E**-rich copolymers displayed much less positive onsets (−430 mV for the 1:12 **M:E** copolymer, Figure 9b). The sigmoidal hysteresis and conductivity plateau at higher applied potentials is characteristic of the in situ profile observed for poly(**E**) homopolymer and indicates the oxidized conducting polymer maintains bipolaron-like metallic mobile carriers.[32−34]

Comparisons to Polymers Prepared under More Controlled Conditions. We made the assumption that the monomer feed ratios were reflected in the final polymer compositions, but the differences in reactivities that may exist between the comonomers renders this assumption not entirely accurate. As such, comparisons to polymers prepared from different monomers or under more controlled synthesis conditions would be informative. Earlier, we reported the preparation of a polymer derived from the oxidative homocoupling of bis(bithienyl) methano-[10]annulene (MBT, related to the **M** monomer described here but replacing the thienyl with a bithienyl).[14] This monomer would lead to a polymer with a 4:1 annulene:thiophene ratio as set explicitly by the composition of the macromonomer and would be related conceptually to the 1:1 **M:B** random compositions explored here. Poly(MBT) was shown to have a non-Nernstian quasi-reversible $E_{1/2}$ value of 655 mV, comparable to the 650−700 mV values found for the 1:1 **M:B** and related compositions (Figure 2a). In addition, the λ_{max} of poly(MBT) in the neutral state was 480 nm, whereas that of the 1:1 **M:B** copolymer was 495 nm. Although not exact, it suggests that the electronic compositions of the two polymers are sufficiently comparable and that the random polymers are not simply arising from preferred polymerization of one of the comonomers present in the feed.

Complex monomer syntheses (of what should be very insoluble materials) would be required to probe these trends at larger bithiophene ratios, so chemical copolymerizations would be better able to address these compositional issues. In our preliminary studies,[35] we found that copolymers prepared by Stille coupling with compositions identical to the 1:1 **M:E** copolymers were insoluble in common halogenated solvents even at elevated temperatures. There were no solubilizing chains on this step-growth copolymer, and our ongoing work is addressing the inclusion of such groups to facilitate solution processing and structural characterization. These groups necessarily influence polymer electronics through the substituent electron donation and the torsional effects along the conjugated backbone, so their abilities to serve as direct comparisons of defined compositional makeup to the random copolymers discussed here will be limited.

CONCLUSIONS

In this report, we presented several electroanalytical investigations on random copolymers containing the methano[10]-annulene core. In all cases, dilution of the exotic annulene monomer with more standard and commercially available thiophene-derived monomers allowed for some of the electronic properties of the annulene to be imparted to the random copolymer without the need for difficult chemical synthesis of a specific polymerizable monomer. Importantly, annulene compositions as low as 4% were able to impart marked differences to polymer optoelectronic properties indicating that the costly annulene component can be diluted effectively with more readily available comonomers. At these loadings, the annulene is also able to influence the film intermolecular order as determined through polymer UV−vis measurements. These findings will provide important experimental guidance applicable to the design and synthesis of solution-processable annulene polymers synthesized through chemical polymerization strategies.

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