Solid-State Ordering and Potential Dependence of Conductivity in Poly(2,5-dialkoxy-*p*-phenyleneethynylene)

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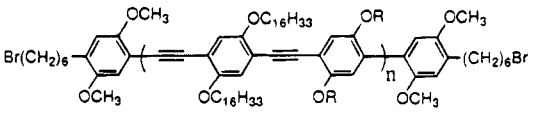
Solution-cast films of four different poly(2,5-dialkoxy-*p*-phenyleneethynylene) molecules, **I**–**IV**, with varying backbone chain lengths and varying alkoxy substituent chain lengths, and an alternating copolymer of 1,4-diethynyl-2,5-dihexadecyloxybenzene and 9,10-dibromoanthracene, **V**, have been characterized electrochemically and by X-ray diffraction (XRD) and differential scanning calorimetry (DSC). XRD and DSC show that the polymers have varying degrees of order and crystallinity based on long-range lamellar structure. Cyclic voltammetry in liquid SO_2/electrolyte shows that the onset of oxidation for **I**–**IV** occurs at ~1.05 V vs SCE with the more crystalline polymers having slower electrochemical response than the less crystalline ones. In situ characterization of the potential dependence of conductivity in the same medium shows that the maximum conductivities of **I**–**IV** range from ~0.2 to ~5 Ω^{-1} cm^{-1}, suggesting that higher conductivity is associated with lower long-range order in the polymer films but showing little dependence on average polymer chain length. **I**–**IV** all have maximum conductivity at ~1.6 V vs SCE and finite potential windows of high conductivity ~0.55 V wide, indicating that the potential of maximum conductivity and the width of the window of high conductivity are determined by molecular rather than bulk properties. For **V**, the onset of oxidation occurs at ~0.8 V vs SCE, the potential of maximum conductivity is ~1.5 V vs SCE, and the width of the potential window of high conductivity is ~0.85 V.

Introduction

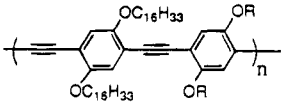
This paper reports the potential dependence of the conductivity, and the solid-state bulk structural characterization, of rigid-rod conjugated poly(*p*-phenyleneethynylene) polymers **I**–**V** (Scheme 1). These polymers are soluble, and we have elsewhere reported on their synthesis, characterization, and solution fluorescence.[1] The results reported here show that these polymers tend to organize in the solid state and that they can be reversibly oxidized in liquid SO_2/electrolyte. **I**–**V** have finite potential windows of high conductivity, a feature that has been shown to be characteristic of conjugated polymers.[2,3] The differences between the maximum conductivities of these polymers arise from differences between their molecular structures and/or their bulk ordering.

Studies of rigid-rod polymers have shown that they can be made soluble in common organic solvents and that they form highly crystalline layered solids when derivatized with long aliphatic side chains.[4,5] Some of these polymers have been shown to display liquid-crystalline phases. Likewise, soluble rigid-rod poly(*p*-phenyleneethynylene) molecules have been synthesized by incorporating long-chain alkoxy substituents.[1,6,7]

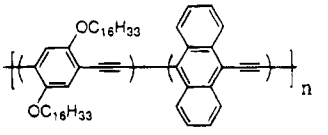
Scheme 1. Structures and Average Lengths (*n*) for Polymers I–V



I R = $C_{16}H_{33}$; n_{ave} = 12
II R = $C_{16}H_{33}$; n_{ave} = 20
III R = C_8H_{17}; n_{ave} = 20



IV R = 50% C_8H_{17}; 50% CH_3; n_{ave} = 100



V n_{ave} = 11

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These poly(*p*-phenyleneethynylene) molecules have been shown to be highly fluorescent and to be capable of highly efficient energy transfer to emitting anthracene end-cap groups.[1] An investigation of the non-linear optical properties of a polymer similar to **V** has also been reported.[8]

Accounts of the chemical oxidation of chemically prepared poly(*p*-phenyleneethynylene) have not reported high conductivity for the polymer. In one case, exposure to AsF_5 vapor yielded a conductivity of 10^{-3} Ω^{-1} cm^{-1},[9] while in another, exposure to AsF_5 or I_2 vapors yielded conductivities of 6.6×10^{-8} or 4×10^{-5} Ω^{-1} cm^{-1}, respectively.[10] It was later reported that films produced by the electrochemical reduction of α,α,α,α′,α′,α′-hexachloro-*p*-xylene and assumed to be poly(*p*-phenyleneethynylene) had conductivities of 3×10^{-7} Ω^{-1} cm^{-1} upon exposure to I_2 vapor and 70 Ω^{-1} cm^{-1} upon exposure to SO_3 vapor,[11] but the structure of the material under investigation was not confirmed. Recently it has been reported that while under exposure to I_2 vapors, films of poly(2,5-dibutoxy-*p*-phenyleneethynylene) have conductivities of $\sim 10^{-6}$ Ω^{-1} cm^{-1} at room temperature and 5×10^{-3} Ω^{-1} cm^{-1} at 80 °C.[7]

In fact, high conductivities have not been found for any organic ethynylene-based conjugated polymers. Conductivities measured for polydiacetylenes exposed to I_2 vapors have not exceeded 10^{-3} Ω^{-1} cm^{-1}.[12] It has been reported that no appreciable conductivity could be measured for poly(2,5-thienyleneethynylene) exposed to I_2,[13] and conductivities measured for a series of poly(2,5-ethylenethiophenediylethynylene) films exposed to I_2 or AsF_5 did not exceed 2.2×10^{-6} Ω^{-1} cm^{-1}.[14] A polymer purported to be polyethynylene itself was reported to have a conductivity of 2.1×10^{-4} Ω^{-1} cm^{-1} upon exposure to I_2.[15] Only upon inclusion of metals in such polymers, e.g., poly(copper-yne), were conductivities up to 10 Ω^{-1} cm^{-1} reported.[15,16] In general, polyynes are more difficult to oxidize than their polyene analogues because acetylenic systems do not as readily stabilize carbocations. The resistance to oxidation of ethynylene-based polymers and their instability when they are oxidized may account for the lack of high conductivities in previous studies.[14]

Electrochemical studies of poly(*p*-phenyleneethynylene) have not been reported to date. Poly(*p*-phenyleneethynylene) has been calculated to have an ionization potential of 5.6 eV, which is 0.5 eV greater than that calculated for its polyene analogue, poly(*p*-phenylenevinylene).[17] The onset of electrochemical oxidation for poly(*p*-phenylenevinylene) has been reported to occur at ~0.30−0.35 V vs SCE.[18] Poly(2,5-dimethoxy-*p*-phenylenevinylene) is more easily oxidized, with the onset of oxidation reported at ~0 V vs SCE,[19,20] and with conductivities up to 500 Ω^{-1} cm^{-1} having been obtained by electrochemical oxidation.[19] The results reported here show that poly(*p*-phenyleneethynylene) films are indeed relatively difficult to oxidize but that in a suitable medium, they can be reversibly oxidized and exhibit in situ high conductivities at intermediate levels of oxidation. The use of liquid SO_2/electrolyte should enable in situ measurement of high conductivities in other oxidized ethynylene-based conjugated polymers. We speculate that the SO_2/electrolyte allows the study of highly oxidized organic materials because degradation of the oxidized organic material via nucleophilic processes is minimized.

Experimental Section

Synthesis and Characterization of Polymers. Synthesis of polymers **I**, **II**, **IV**, and **V** was accomplished using a catalyzed cross-coupling reaction of aryl acetylenes and aryl halides[1,21] and is reported elsewhere along with characterization of the polymer structures and average degree of polymerization as determined by NMR end group analysis, gel permeation chromatography (GPC), and elemental analyses.[1,22] **III** was synthesized using the same conditions and stoichiometry as were used in the synthesis of **II**[1] (PIb in ref 1), except that 1,4-diethynyl-2,5-dioctyloxybenzene was used instead of 1,4-diethynyl-2,5-dihexadecyloxybenzene. Polymer dispersity indices (PDI) for **I**−**V** are all approximately 2.[1]

X-ray scattering (XRD) data were obtained using a Rigaku RU300B rotating anode X-ray generator and fully automated powder diffractometer, operated in reflection mode with Cu Kα radiation, and $^1/_2$° divergence slit, $^1/_2$° scatterer slit, and 3 mm receiving slit. Samples for XRD were prepared by solution-casting ~1-mm-thick films of **I**−**V** onto Al substrates. Samples either were used as cast or were first heated under inert atmosphere to above their melting temperature (~180 °C), annealed for $^1/_2$ h at 150 °C, and then slowly cooled to room temperature. **V** did not melt but was otherwise treated in the same way. Differential scanning calorimetry (DSC) data were collected using a Perkin-Elmer DSC4 at a scan rate of 20 °C/min.

Casting of Polymer Films. We have, in a previous publication,[23] reported on the design and microfabrication of 0.23 cm × 0.15 cm arrays of eight, individually addressable, interdigitated, Pt macro- and microelectrodes. Films of **I**−**V** were cast onto such arrays from solutions made by dissolving ~3 mg of polymer in 1 or 2 mL of solvent. **I**−**IV** were dissolved in $CHCl_3$ or toluene. For **I** and **II**, it was necessary to keep the solvent warm in order to prevent gelling of the polymer. **V** was dissolved in *o*-dichlorobenzene, and this too was warmed to keep all the polymer in solution. Films were cast using 0.1 or 0.25 μL capillary pipets. Cyclic voltammograms were also obtained for films cast from 0.5 μL capillary pipettes onto 0.5 cm × 0.5 cm Pt flag electrodes.

Electrochemistry and Conductivity Measurements. SO_2 and $[(n\text{-}Bu)_4N]AsF_6$ were prepared and electrochemical

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experiments in liquid SO_2/electrolyte were performed as have been described previously.[2,23] The use of microfabricated electrode arrays to measure the potential dependence of conductivity,[2,24] and the different configurations that can be used with the arrays of eight individually addressable macro- and microelectrodes,[23] has been described previously, and is briefly summarized here:

When a small fixed potential, V_D, is maintained between two individually addressable electrodes connected by a film of redox-active polymer, the magnitude of the current between the electrodes, I_D, is directly proportional to the conductivity of the polymer. The conductivity of the polymer changes as its electrochemical potential, V_G, is changed. Therefore a plot of I_D vs V_G gives relative conductivity vs potential.

Actual conductivities were calculated by using the known quantities of polymer cast, areas of polymer films, and electrode array dimensions and by assuming a density of 1 for the polymer films in order to estimate their thicknesses.

Results

Solid-State Characterization. Figure 1A shows the XRD scattering plot of **II**. **I** and **II** display identical diffraction patterns with a prominent first order reflection at a d spacing of 33.2 Å accompanied by at least 5 higher orders of reflection with even reflections having suppressed intensities. These data indicate a highly ordered layered structure. Well-defined intense peaks are observed at d spacings of ~4 Å. **III** (Figure 1B) shows a first-order peak at a d spacing of 25.6 Å and at least 4 higher order reflections, with no suppression of the even reflections. The higher order reflections are not as sharp as those of **II**, indicating that **III** has considerably less long-range order, and the wide-angle reflections at d spacings of ~4 Å are also considerably less intense and sharp than those for **II**. The XRD scattering plot for **IV** (Figure 1C) shows two broad first-order reflections at d spacings of 31.4 Å and 22.5 Å. The breadth of the peaks and the lack of higher order reflections indicate that **IV** does not adopt a long-range ordered layered structure to any appreciable extent. The XRD scattering plot for **V** (Figure 1D) shows a prominent first-order reflection at a d spacing of 25.2 Å and 2 higher order reflections. The scattering plots of both **IV** and **V** have broad indistinct features at wide angles. XRD data for as-cast unannealed films of **I**–**V** are slightly less sharp.

Figure 2A shows DSC traces for **II** (again, identical data were obtained for **I**), which shows two very distinct phase transitions with endothermic peaks at 117 and 167 °C upon heating, and exothermic peaks at 143 and 105 °C upon cooling. The DSC for **III** (Figure 2B), lacks the well-resolved transition at lower temperature and is considerably more complicated than that for **II**, with the high-temperature phase changes appearing to be composed of two transitions close together in temperature. Endothermic peaks are at 77, 166, and 179 °C upon heating (there may also be broad peaks at 87 and 131 °C), and exothermic peaks are at 153, 142, and 123 °C upon cooling, the latter peak being very small and broad. The XRD scattering plots and DSC traces for **II** and **III** are virtually identical to those that have been reported for two analogous poly(2,5-dialkoxy-*p*-phenylene-2,5-dihexadecyloxyterephthalate) polymers,[5] one having $-OC_{16}H_{33}$ side chains on the alternate phenylene units and the other having $-OC_6H_{13}$ side chains.

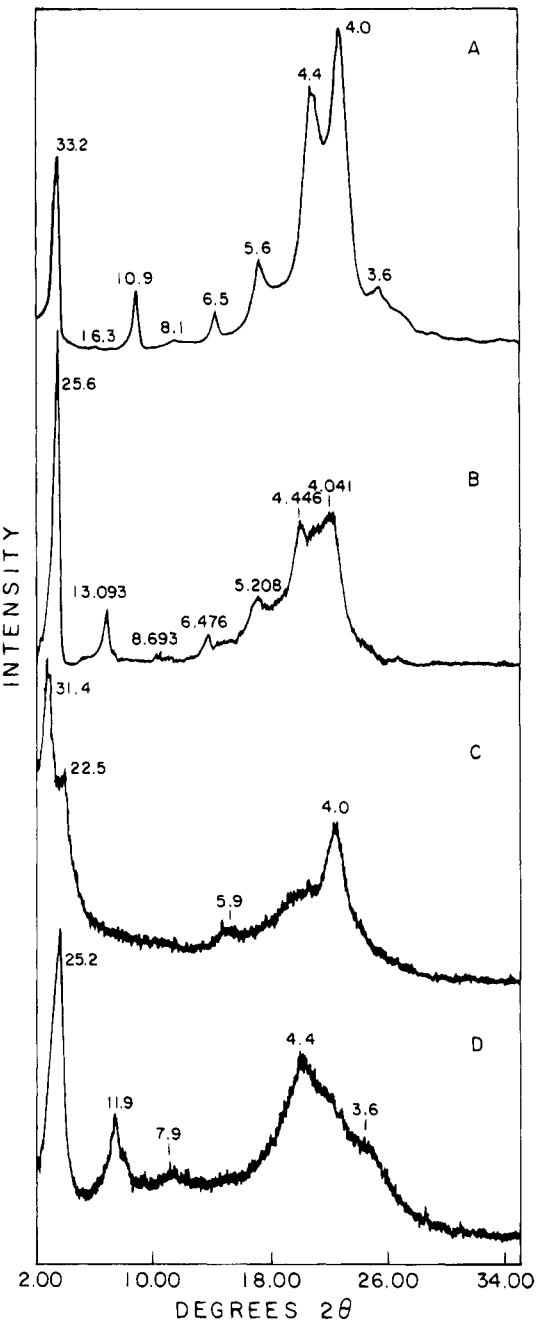

Figure 1. XRD scattering plots for annealed samples of **II**–**V** under Cu Kα irradiation: plot A, **II**; plot B, **III**; plot C, **IV**; plot D, **V**. Peaks are labeled with d spacings in angstroms.

Electrochemical Oxidation and Potential Dependence of Conductivities. Figure 3 shows cyclic voltammetry and the I_D–V_G characteristic for **IV** on a Pt macro/microelectrode array in liquid SO_2/0.1 M [(n-Bu)$_4$N]AsF$_6$ at −70 °C. The voltammogram shows two principal pairs of anodic and cathodic peaks, and these are associated with the potentials of onset and decline of drain current (I_D) in the I_D–V_G characteristic. The increase and decrease of I_D define a finite potential window of high conductivity. Such potential windows of high conductivity have been shown to be a general feature of conjugated conducting polymers.[2,3] There is sweep-rate-independent hysteresis in the I_D–V_G characteristic which correlates with hysteresis in the cyclic

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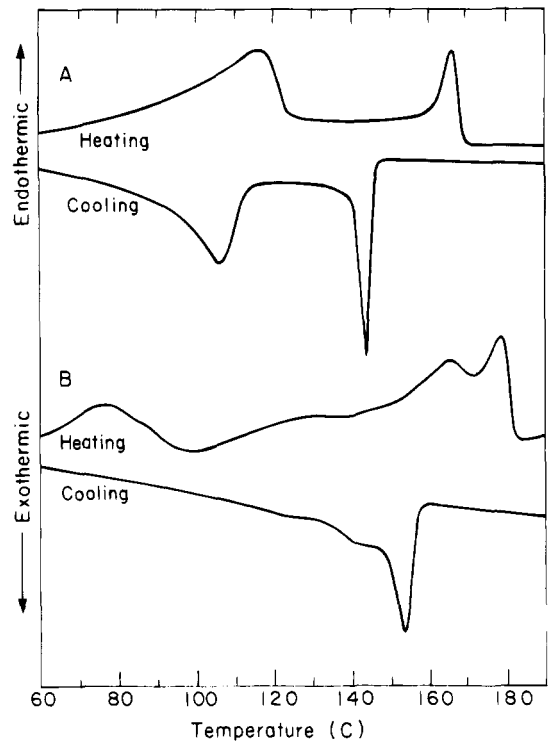

Figure 2. DSC scans for **II** and **III**: scan A, **II**; scan B, **III**.

voltammogram. Such hysteresis is characteristic of potential-dependent phenomena in conjugated polymers and is a consequence of charge injection being accompanied by structural distortions in these systems.[25] The magnitude of I_D is higher on the positive potential sweep than on the negative sweep, and these magnitudes are reproduced on subsequent scans, indicating that the difference is not a consequence of degradation of the polymer. Similar behavior has been noted for all the conjugated polymers for which oxidative finite potential windows of high conductivity have been characterized.[2,3,23]

The cyclic voltammogram shows the onset for oxidation of **IV** at ~0.65 V vs a poly(vinylferrocene) (PVFc) internal standard, corresponding to ~1.05 V vs SCE.[26] This is ~0.7 V positive of the onset of oxidation for poly(*p*-phenylenevinylene) and ~1.05 V positive of the onset of oxidation for poly(2,5-dimethoxy-*p*-phenylenevinylene). The onset of oxidation for **I**–**III** (Figures 4 and 5) occurs at the same potential and is so far positive that in attempts to oxidize films and measure their conductivity in CH_3CN/0.1 M $[(n\text{-}Bu)_4N]PF_6$, it was not possible to significantly oxidize the polymers without irreversibly degrading them.

With the gate potential held at 0 V vs PVFc and **IV** in the neutral state, measurement of the resistance between the electrodes used to obtain the I_D–V_G characteristic indicates that the conductivity of the neutral polymer is $\leq 5 \times 10^{-6}$ Ω^{-1} cm^{-1}, or at least 6 orders of magnitude lower than that of the oxidized polymer at its potential of maximum conductivity (~5 Ω^{-1} cm^{-1} at ~1.2 V vs PVFc). Measurement of the I_D–V_G characteristic at more sensitive current scales indicates that at the positive potential limit shown, ~1.57 V vs PVFc,

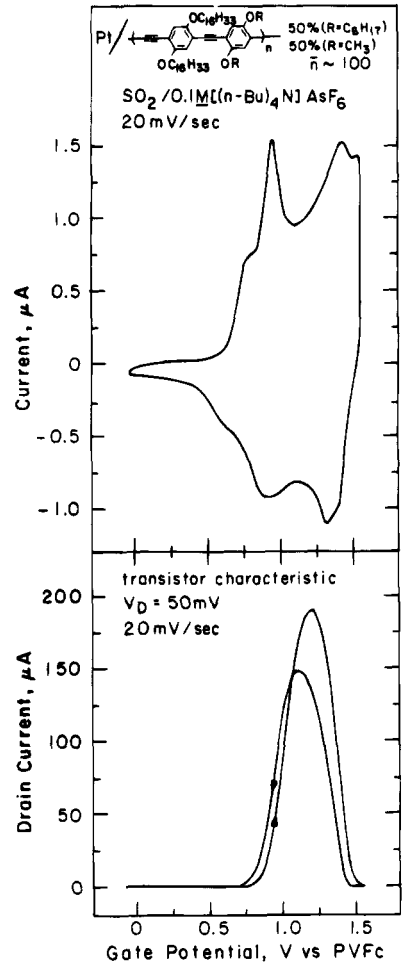

Figure 3. Top: cyclic voltammetry of a film of **IV** containing 9.5×10^{-10} mol of ethynylarene repeat units on a Pt macro/microelectrode array in SO_2/0.1 M $[(n\text{-}Bu)_4N]AsF_6$ at −70 °C. Bottom: I_D–V_G characteristic in the same medium for the macro/microelectrode array configured to function as two coplanar electrodes separated by 36 μm over a 1.5 mm length.[23]

the conductivity is not less than 10^{-4} Ω^{-1} cm^{-1}. The polymer slowly degrades at such a positive potential, precluding the halting of the potential scan in order to make more accurate conductivity measurements. Nevertheless, it is clear that when oxidized to the positive potential limit shown, **IV** is at least 20 times more conducting than when in its neutral state.

Figure 4 shows that the cyclic voltammetry and the I_D–V_G characteristic for **III** are very similar to those for **IV**. The onset of oxidation, the cyclic voltammetric peak positions, and the potentials of maximum conductivity for both positive and negative sweeps are the same for both polymers. However, in the case of **III**, a thinner film has been cast on the Pt macro/microelectrode array, enabling the polymer to maintain potential equilibrium with the electrodes at faster scan rates. This has made it possible to scan to more positive potentials, in this case ~1.81 V vs PVFc, without significant degradation of the polymer. Upon scanning to this more positive potential, a distinct new set of cyclic voltammetric peaks begins to appear, but the I_D–V_G indicates that they are not associated with significant changes in conductivity. I_D–V_G measurements at more sensitive current settings indicate that the conductivity of **III** in the potential range 1.6–1.8 V vs. PVFc does not change much and that, as observed for **IV**, it is significantly

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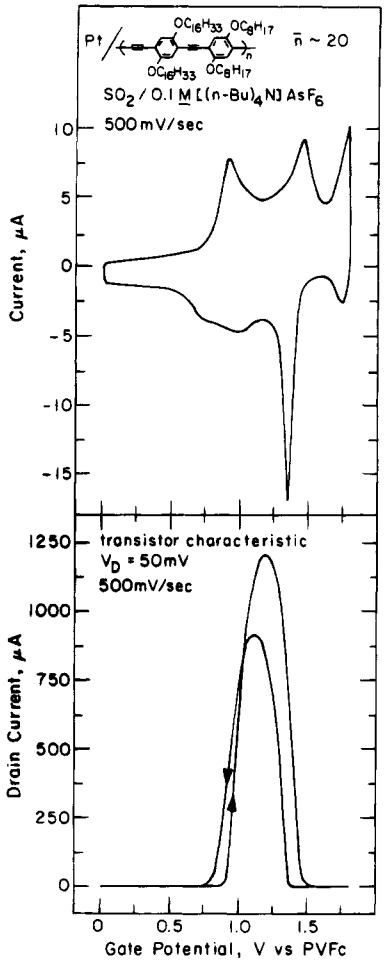

Figure 4. Top: cyclic voltammetry of a film of **III** containing ~2 × 10^{-10} mol of ethynylarene repeat units on a Pt macro/microelectrode array in SO_2/0.1 M [(*n*-Bu)$_4$N]AsF_6 at −70 °C. Bottom: I_D−V_G characteristic in the same medium for the fully interdigitated macro/microelectrode array (configured to function as two coplanar electrodes separated by 4 μm over a 21 cm length).[23]

higher than the conductivity of the neutral polymer and not lower than a factor of 10^4−10^5 less than the maximum conductivity.

It is noteworthy that the cyclic voltammogram of **III** shows a minimum in anodic current at ~1.63 V but that the current is still significantly above baseline. Integration of the voltammogram indicates that, at this potential, the polymer has been oxidized by ~0.5−0.6 electron/ethynylarene repeat unit, suggesting that the highest occupied electronic band of the polymer remains partially populated giving rise to significant conductivity.[2]

Figure 5 shows the cyclic voltammetry and I_D−V_G characteristic for **II**. The electrochemical behavior and the potential dependence of conductivity for **I** are indistinguishable from those for **II**. The principal differences between **II** and **III** or **IV** are that **II** has much slower electrochemical response and is less conducting (Table 1, vide infra). **II** also chemically degrades more rapidly at positive potentials than do **III** or **IV**. Therefore, to characterize the entire potential window of high conductivity, a scan rate has been used at which the film of **II** is not quite in potential equilibrium with the electrode array, causing some distortion of the data. At slower scan rates, the cyclic voltammetry looks much more like that for **III** or **IV**, and the peak

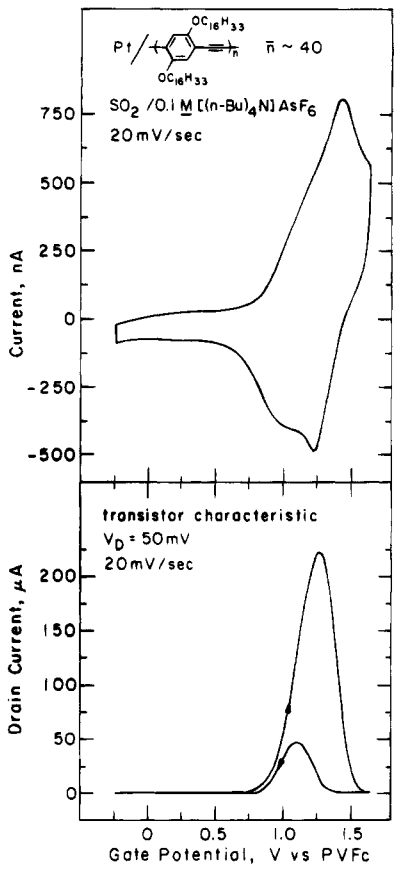

Figure 5. Top: cyclic voltammetry of a film of **II** containing 2.5 × 10^{-10} mol of ethynylarene repeat units on a Pt macro/microelectrode array in SO_2/0.1 M [(*n*-Bu)$_4$N]AsF_6 at −70 °C. Bottom: I_D−V_G characteristic in the same medium for the fully interdigitated macro/microelectrode array.

Table 1. Conductivity and Electrochemical Data for I−V (Confidence Limits Are ±1 Standard Deviation (±S))

	σ_{max}[a] (Ω^{-1} cm^{-1})	window[b] width(V)	$V_{\sigma_{max}}$[c]	ox. level[d] $V_{\sigma_{max}}$	ox. level[e] V_+
I	0.18 ± 0.04	0.55	1.2	0.39 ± 0.08	0.79 ± 0.17
II	0.29 ± 0.17	0.55	1.2	0.33 ± 0.07	0.71 ± 0.15
III	1.6 ± 0.8	0.55	1.2	0.26 ± 0.05	0.53 ± 0.08
IV	4.5 ± 0.8	0.55	1.2	0.37 ± 0.13	0.71 ± 0.24
V	0.12 ± 0.03	0.85	1.1	0.25 ± 0.05	0.62 ± 0.07

[a] Maximum conductivity. [b] Width of the potential window in which conductivity is at least 10% of σ_{max}. [c] Potential vs PVFc of maximum conductivity on positive sweep. [d] Extent of oxidation in electrons per ethynylarene repeat unit at $V_{\sigma_{max}}$. [e] Extent of oxidation at the positive sweep limit, V_+ (1.57−1.63 V vs PVFc for **I**−**IV** and 1.67−1.70 V vs PVFc for **V**).

for the positive sweep of the I_D−V_G curve occurs at ~1.2 V vs PVFc. Nevertheless, even at the 20 mV/s scan rate used for Figure 5, **II** undergoes significant degradation. An I_D−V_G scan made subsequently to the one in Figure 5 showed a maximum I_D of 90 μA on the positive sweep, as opposed to the 225 μA shown. As the polymer degrades, its maximum conductivity declines drastically, and its electroactivity, as revealed by the integral of its cyclic voltammogram, declines more slowly. But interestingly, the remaining electrochemical response of **II** becomes more rapid, and the cyclic voltammogram, although smaller than before in current and area, looks much like that of **III** or **IV** at comparable scan rates, even though the maximum conductivity of the polymer has been substantially diminished.

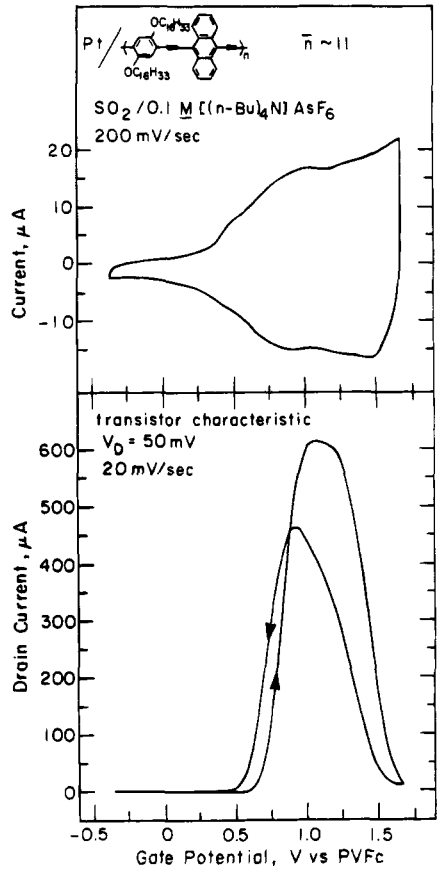

Figure 6. Top: cyclic voltammetry of a film of **V** containing 1.9×10^{-9} mol of ethynylarene repeat units on a 0.2 cm^2 Pt electrode in SO_2/0.1 M $[(n\text{-}Bu)_4N]AsF_6$ at −70 °C. Bottom: I_D−V_G characteristic in the same medium for a film of **V** containing 2.0×10^{-9} mol of ethynylarene repeat units on a Pt macro/microelectrode array in fully interdigitated configuration.

The rigid-rod structures of these polymer molecules and their tendency to organize suggest that their conductivity should be anisotropic and that enhanced conductivity might be obtained by ordering the molecules with their long axes oriented across the interelectrode gaps. Two methods of electric field poling were attempted. A 50 V potential was put across the interdigitated macro/microelectrode array (a field of 1.25×10^5 V/cm) while films were being cast from solution, or for films that were already cast, the 50 V potential was applied while heating the cast film and electrode array to 50 °C for 10−60 min under inert atmosphere. However, subsequent I_D−V_G measurements for these films indicated that attempts at electric field poling of **II** and **III** to orient the polymers in the interelectrode gaps did not lead to any enhancement of conductivity. Likewise, annealing of cast films at 150 °C in the absence of an electric field had no influence on conductivity.

Figure 6 shows the cyclic voltammetry and I_D−V_G characteristic of **V**. This polymer has ethynylanthracene units alternating with the ethynylbenzene units in its backbone as opposed to the all ethynylbenzene backbones of **I**−**IV**. There are a number of important differences between the behavior of **V** and that of **I**−**IV**. **V** has a more negative potential for onset of oxidation (~0.4 V vs PVFc), a more negative potential of maximum conductivity, and a wider potential window of high conductivity. Solutions of **V** absorb at significantly longer wavelength than do those of **I**−**IV** (λ_{max} = 545 nm for **V**, 446 nm for **I**−**III**, and 452 nm for **IV**).[1,27] This and the more negative onset of oxidation are consistent with increased conjugation resulting from incorporation of anthracenyl units into the polymer backbone.

Table 1 summarizes the electrochemical and conductivity data for **I**−**V**. **I**−**IV** have identically wide potential windows of high conductivity, and they have the same potential of maximum conductivity. The only significant differences between **I**−**IV** are in the magnitdues of their maximum conductivities. These polymer conductivities are independent of the average backbone chain length: **I** and **II** have different average length backbones but no significant difference in conductivity, while **II** and **III** have the same average backbone chain length but have significantly different conductivities. It is also noteworthy that **I**−**IV** have essentially the same absorption λ_{max} in solution.

Table 1 gives the extents to which **I**−**V** are oxidized at the potential of maximum conductivity and at the positive sweep limit, which approximates the positive potential limit of high conductivity. These values are calculated by integration of cyclic voltammograms. There do not appear to be significant differences between the extents to which **I**−**V** are oxidized. However, there are sizable deviations in these data, and this probably reflects the difficulty in accurately and precisely delivering the small volumes of solution from which films are cast. This is also a likely source of deviations in the maximum conductivity data.

I−**V** can be oxidized somewhat reversibly beyond the extents listed in Table 1 as is indicated for **III** in Figure 4. Such further oxidation is shown in the cyclic voltammograms for **V** and **III** (Figure 7). Another set of well-defined peaks appears for both polymers (and for **I**, **II**, and **IV**), and they bear some resemblance to cyclic voltammetric peaks of conventional redox polymers in that they are relatively narrow and lacking in hysteresis. This is indicative of greater electronic localization for sites undergoing oxidation at these potentials than there is at the potential region of high conductivity, and it is consistent with the low conductivities of the polymers in this potential region.[2,28] However, the polymers degrade rapidly at these potentials, precluding determinations of conductivity to any extent beyond that already discussed for **III** at ~1.81 V vs PVFc (Figure 4). Upon sweeping to even more positive potentials, there is rapid increase in anodic current, with little of the additional charge injected being recovered upon sweep reversal.

Discussion

The striking similarity between the XRD and DSC data for **II** and **III** and those for the poly(2,5-dialkoxy-*p*-phenylene-2,5-dihexadecyloxyterephthalate) molecules studied by Wegner et al. justifies the use of their structural model[5] (Scheme 2) in interpreting the data presented here. In general, these polymers adopt a lamellar structure, with the aryl units of each conjugated chain being coplanar and forming π-stacks with other conjugated main chains, and the alkyl chains

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(28) Flanagan, J. B.; Margel, S.; Bard, A. J.; Anson, F. C. *J. Am. Chem. Soc.* **1978**, *100*, 4248.

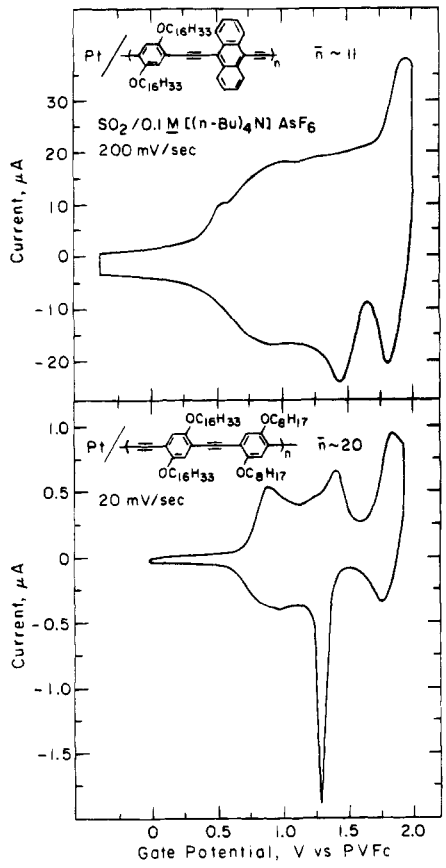
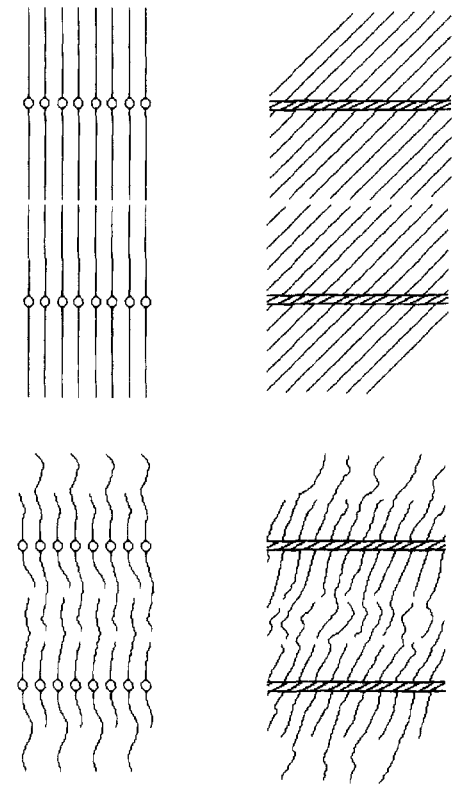


Figure 7. Top: cyclic voltammetry of a film of **V** containing 1.9×10^{-9} mol of ethynylarene repeat units on a 0.2 cm^2 Pt electrode in SO_2/0.1 M $[(n\text{-}Bu)_4N]AsF_6$ at −70 °C. Bottom: cyclic voltammetry in the same medium for a film of **III** containing 4.1×10^{-10} mol of ethynylarene repeat units on a Pt electrode.

extending laterally within the planes of their respective main chains. The alkyl chains are orthogonal to the axis of π-stacking but tilted with respect to the conjugated main-chain axis. The first-order small-angle reflections (large d) in the XRD data are caused by the separation between adjacent π-stacks or the separation between adjacent coplanar polymer chains, whereas the prominent reflections at wide angle (small d) are caused by the separation between polymer chains in the π-stacking direction and by the separations between adjacent side chains.

The many higher order reflections in the XRD data for **II** are indicative of long-range order. As with the analogous poly(2,5-dihexadecyloxy-*p*-phenylene-2,5-dihexadecyloxyterephthalate),[5] high crystallinity of the alkyl side chains is indicated by the sharpness and intensity of the wide angle peaks at $d \approx 4$ Å and by the sharpness and intensity of the low-temperature peaks (117 °C endotherm and 105 °C exotherm) in the DSC which are assigned to a melting or disordering of the side chains. The high-temperature DSC peaks are assigned to a bulk isotropic melting transition. A structure in which the side chains of coplanar adjacent polymer molecules are not interdigitated and are tilted with respect to the backbone axis accounts for the 33.2 Å d spacing between coplanar backbones and for the oscillation of higher order scattering intensities. The region of low electron density between the ends of side chains in adjacent layers superimposes a $d/2$ periodicity of diminished scattering.

Scheme 2. Possible Structures for the Solid-State Ordering of I and II (Top) and III (Bottom)[a]



[a] Right: viewed down conjugated main-chain axis. Left: viewed down the π-stacking axis (adapted from ref 5)

III is less ordered than **I** and **II**. As with the analogous poly(2,5-dihexyloxy-*p*-phenylene-2,5-dihexadecyloxyterephthalate),[5] the lack of sharpness and intensity of the wide-angle XRD peaks and of the low-temperature DSC peaks indicate that there is little crystallinity of the alkyl side chains. The 25.6 Å d spacing and the lack of oscillation in higher order scattering intensities indicate that the alkyl side chains of coplanar adjacent polymer molecules are interdigitated. The complexity of the DSC, and particularly the 166 °C endotherm and the 142 °C exotherm, suggests that **III** may have a liquid-crystalline phase. The XRD data indicate that both **IV** and **V** have substantially less long-range order than **III**.

The oxidation of **I**−**IV** occurs at such positive potentials as to make it unlikely that they can be reversibly oxidized to a high extent in electrochemical solvents other than liquid SO_2. The magnitudes of differences between the oxidation potentials of conducting polymers are expected to be the same as the differences between their ionization potentials.[29] The electrochemical data show that, relative to poly(*p*-phenylenevinylene) or poly(2,5-dimethoxy-*p*-phenylenevinylene), **I**−**IV** are oxidized at much more positive potentials than might be expected from calculations of the ionization potentials of poly(*p*-phenylenevinylene) and poly(*p*-phenyleneethynylene).[17] Our results indicate that, as has been previously suggested,[14] the lack of other observations of high conductivity in ethynylene-based polymers is due to their being very difficult to oxidize.

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Our use of SO_2/electrolyte allows study of highly oxidized organic materials, enabling in situ measurements of electrical conductivity to be made for **I**–**V**. Considering the quality of these measurements from sample to sample, we can speculate on the origin of differences in the maximum conductivities for **I**–**V**, despite the fact that those differences are rather small (less than 50-fold). There is not a significant difference between the maximum conductivities of **I** and **II**, even though the average chain length of **II** is about twice that of **I**, whereas the maximum conductivities of **II** and **III** which have the same average chain length are significantly different. Although conclusions regarding the relationship between conductivity and chain length in these polymers might be disputed on the grounds of their high PDIs (~2),[1] it has been shown that the solution absorption and emission spectra of **I**–**IV** are indeed largely insensitive to molecular weight,[1] showing that, despite their rigid linear structures, the longest effective conjugation length in these polymers is less than the minimum average polymer length, or ~24 phenyleneethynylene repeat units in the case of **I**. We have previously found that for low-polydispersity polyacetylene oligomers, maximum conductivity showed little chain length dependence for samples longer than ~60 double bonds,[23] and analogous results have been reported for oligothiophenes,[30] indicating a critical length beyond which backbone chain length has little influence on conductivity of conjugated polymers. This observation in poly(*p*-phenyleneethynylene) polymers is particularly compelling because they are intrinsically straight "rigid rods" and should not contain any "kinks".

Compared to **I** or **II**, the maximum conductivities of **III** and **IV** are about an order of magnitude larger, and we note the trend in maximum conductivity (**IV** > **III** > **II** and **I**) follows the trend in disorder for the neutral polymers as well as the trend in weight fraction of insulating alkyl side chains. While disorder inferred from X-ray diffraction data for the neutral polymers is not necessarily applicable to the oxidized and conducting polymers, we note the similar findings for poly(3-alkylpyrroles)[31] and for poly(3-alkylthiophenes),[32,33] which suggest that with increasing side chain length, the tendency toward greater long-range order appears to have a more significant influence on conductivity than does the increase in insulating alkyl weight fraction.

V has somewhat lower conductivity compared to **I**–**IV**. The longer wavelength absorption, more negative onset of oxidation, and wider potential window of high conductivity of **V** relative to those of **I**–**IV** are all indicative of a narrower bandgap and greater bandwidth. This is consistent with theoretical calculations[34] and experimental observations[35] for the effects of benzannelation on conducting polymer backbones. These considerations might lead to the expectation that **V** would be more highly conductive than it is. It may be that anthracenyl units in the polymer backbone have a tendency to localize charge relative to the phenyl units. This is suggested by fluorescence data showing that anthracenyl units tend to act as low-energy traps in a photoexcited anthracene-capped poly(*p*-phenyleneethynylene).[1]

The greater crystallinity of **I** and **II** accounts for their sluggish electrochemical response compared to that of **III** or **IV**. Electrochemical redox activity requires that there be penetration by solvent and electrolyte between polymer strands, and this is likely to be quite hindered in the more crystalline material. The reason that **I** and **II** decompose more rapidly than **III** and **IV** is less apparent. Perhaps less charge mobility (lower conductivity) and less penetration, and therefore less Coulombic screening, by solvent and electrolyte lead to more charge localization and more rapid reaction of the polymer with itself (cross-linking). Whatever the mechanism by which films of **I** and **II** decompose, it probably lessens their crystallinity and therefore allows their electrochemical response to quicken.

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