

Synthesis, Electrooxidation, and Characterization of Bis(diphenylamine)naphthalene Diimide

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Received July 10, 1995. Revised Manuscript Received February 9, 1996[Ⓞ]

We have synthesized a new poly(imide) precursor for solution electrodeposition onto conducting surfaces. The new monomer, *N,N*-bis[*p*-phenylamino(phenyl)]-1,4,5,8-naphthalenetetracarboxylic diimide (DNTD), contains a central naphthalene diimide moiety flanked by two dimerizable diphenylamine groups. DNTD was oxidatively electrodeposited onto Au-, Pt-, and In-doped SnO₂ surfaces from DMSO, CH₃CN, and CH₂Cl₂. The cyclic voltammetry is consistent with initial radical cation formation of diphenylamine groups, and then para C–C coupling of radicals to form dimers and higher order oligomers. IR spectroscopy was used to determine the average degree of polymerization and confirm para coupling. The resulting material shows electrochemically reversible 1e⁻ and 2e⁻/monomer unit reduction waves corresponding to the naphthalene tetracarboxylic diimide radical anion and dianion. Also a quasireversible 1e⁻ and 2e⁻/monomer unit oxidation corresponding to the oxidation of diphenylbenzidine unit is shown. Visible–NIR spectroelectrochemistry shows low-energy absorptions in the NIR (~1100 nm) corresponding to diphenylbenzidine radical cation π -dimer in CH₂Cl₂ whereas in DMSO and CH₃CN at the same potential, no low-energy bands are observed. Variable-angle transmission spectroscopy on air-oxidized dry films prepared from CH₂Cl₂ shows band shifts from 1100 to 950 nm and almost no shift of the 845 nm band of films formed in DMSO. This is consistent with the anisotropic nature of the material from CH₂Cl₂. We interpret these spectra as arising from π -stacks parallel to the surface. Scanning electron micrographs show small domains (~300–500 nm) for films composed mostly of dimers and smooth films for relatively higher molecular weight materials.

Our objective is to make electropolymerizable materials that incorporate various functional units into the main chain. Along this line we sought a general, synthetically accessible monomer where the end units could undergo electrochemically induced coupling. Polyaniline (PA), formed from head-to-tail oxidative coupling of aniline, has been extensively studied because of its high conductivity and chemical stability.^{1–4} To study the mechanism of aniline polymerization and to search for new conducting polymers, the properties of many aniline derivatives have been studied. Among these derivatives, diphenylamine (DPA) and its related compounds were shown to dimerize and/or polymerize depending on conditions.^{5–10} Also diphenylamine and its derivatives have been used as redox indicators since they have intense absorption bands upon oxidation.

Since the mechanism of coupling, although not totally understood, has sufficient literature precedence, we chose the diphenylamine group as our electropolymerizable end group.

In contrast to PA, polyimides are very useful materials because of their low dielectric, highly insulating properties, and thermal/oxidative stability.¹¹ However, polyimides in solution are electroactive and can transport electrons and ions.^{12–14} The electrochemical and spectroscopic properties of different imides, diimides, and polyimides have been extensively reported.^{13,15–20} The most important electrochemical property of aromatic diimide-based compounds is the existence of a stable 1e⁻ and 2e⁻ reduced states. Recently Miller and co-workers reported that an imide radical could form π -stacked dimers and higher order π -stacked oligomers.²¹ Also an imide radical could be electrostatically bound to a polycation to form a π -stacking polymer film

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Ⓞ Abstract published in *Advance ACS Abstracts*, May 1, 1996.

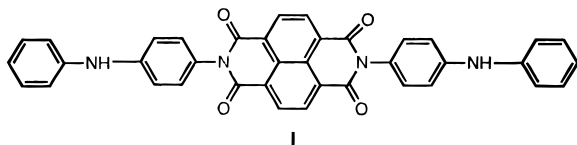
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that shows anisotropic conductivity.²² Organic radicals that are π -stacked have been shown to be semiconductive, conductive, and, under some conditions, superconductive.²³ Wurster (TMPD), TCNQ, TTF, and viologen salts are examples of materials in this class where conduction is anisotropic and follows the π -stacking axis. These organic conductors can be compared to the "main-chain" type conductors such as polyaniline, polypyrrole, polythiophene, and polyacetylene where the mechanism of bulk conduction is believed to be some combination of intrachain and interchain charge hopping.²⁴ An important point is that alignment of chains increase the possibility for π -stacking interactions and has been shown to increase the bulk conductivity.²⁵ Partial alignment of fibrils has been accomplished by stretching films²⁶ or by growing them in an anisotropic media.^{25,27} Our objective is to demonstrate the alignment of polymer chains through reversible π -stacking interactions.

The voltammetry of the oxidatively coupled dimer of diphenylamine, diphenylbenzidine, shows that the second oxidation occurs only 120 mV more positive of the first oxidation.²⁸ These overlapping redox waves make it challenging to quantitate the different oxidation levels spectroscopically. This is important since upon partial oxidation many diamine salts such as tetramethylbenzidine show low-energy electronic absorption bands beyond 700 nm. Also, in this case the spectra are temperature dependent, indicating weakly bound π -dimers or higher order oligomers.²⁸ This behavior is also observed for the radical cations of short thiophene oligomers.²⁹

In this paper, we describe the synthesis of a new compound, DNTD (**I**), which contains two types of electroactive groups, a naphthalenetetracarboxylic diimide group and two flanking diphenylamine groups.



In designing this polymer precursor, we thought of two possible ways to align chains through π -stacking interactions. We could reduce the polymer by one electron to form the imide radical anion or oxidize the benzidine to its radical cation. Either of these species could form π -dimers which would bring adjacent chains into registration.

We report the electrochemistry of this compound and the resulting material electroprecipitated onto electrodes from various solvents. Characterization is based on spectroscopic methods such as visible and IR spectroscopies. From the results of visible-NIR spectro-

electrochemistry, we postulate the formation of π -stacking in the oxidized diphenylbenzidine unit and no π -stacking in the $1e^-$ reduced diimide group. The morphology, anisotropic nature, and degree of polymerization is highly solvent dependent.

Experimental Section

Reagents and Materials. DMSO, DMF, CH₃CN, and CH₂Cl₂ were obtained from Fischer Scientific Co. and distilled from CaH₂ (Aldrich Chemical Co.) (in vacuum for DMF, DMSO, and CH₃CN). Trifluoroacetic acid (Aldrich) was used as received. Tetrabutylammonium hexafluorophosphate, TBAPF₆ (Aldrich), was recrystallized twice from the mixture of ethanol and acetone (1:1 v/v). 1,4,5,8-Naphthalenetetracarboxylic dianhydride (Aldrich) and *N*-phenyl-1,4-phenylenediamine (Aldrich) were used as received. ¹H NMR spectra were obtained on a Bruker 250 multiprobe spectrometer. Elemental analyses were performed by Atlantic Microlabs. Mass spectrometry data were provided by the Auburn Mass Spectrometry Laboratory. Melting points were obtained on a Perkin-Elmer DSC-7 differential scanning calorimeter.

Synthesis of DNTD. *N*-Phenyl-1,4-phenylenediamine (0.60 g) was dissolved in 20 mL DMF. This solution was heated to 90 °C. Then 0.30 g of dianhydride was added into the above solution portionwise over 10 min. The temperature of the mixture solution was raised to 130 °C and held constant for 19 h. The product was precipitated out with the diethyl ether and filtered. Then the solid product was stirred in diethyl ether for 5 min and filtered again. The above purification procedure was done three times to extract residual DMF, yield 80%, mp 418 °C (dec). Mass spectrum (DMSO/TFA solvent, DCI): (M + H)⁺ = 601. Elemental anal. calcd for C₃₈H₂₄N₄O₄·H₂O: C, 73.79%; H, 4.21%; N, 9.06%. Found: C, 73.84%; H, 4.19%; N, 9.07%. NMR (CF₃COOD) δ 9.18 (4H), τ 7.95 (8H), τ 7.79–7.82 (10H); NMR (DMSO-*d*₆) τ 6.90 (2H), τ 7.17–7.31 (20H). IR (cm⁻¹) 3392, 1711, 1667, 1594, 1519, 1495, 1446, 1405, 1345, 1323, 1248, 1211, 1196, 1175, 1137, 1118, 980, 880, 853, 826, 769. UV-vis (nm) DMSO 381, 361, 342.

Midinfrared Spectroscopy. Grazing angle reflectance IR (GIR) spectra were recorded on a Mattson RS-1 FTIR spectrometer with a Specac Graseby Reflection accessory set at an 86° angle of incidence. All the IR data were collected at a spectral resolution of 4 cm⁻¹ with 1000 sample scans using a high D* MCT-A detector with N₂ purge of the sample compartment. Au films were thermally evaporated at a pressure of <10⁻⁵ Torr in a Denton DV-502A high-vacuum evaporator from 99.99% pure wire onto borosilicate microscope slides.³⁰

Electrochemistry. Cyclic voltammetry was performed on a modified AFRDE4 potentiostat (Pine Instrument Co.) and a three-electrode cell degassed with Ar. Voltammograms were recorded on Yokogawa 3025 X-Y recorder. The reference electrode was Ag/AgCl saturated KCl, the counter electrode was a spiral Pt wire, and the working electrodes were typically either a 1.5 mm diameter Au or Pt disk.

Visible-NIR Spectroelectrochemistry. Conductive indium tin oxide (ITO) coated borosilicate slides (75 × 25 × 0.9 mm, 40 Ω /square) were purchased from Delta Technologies, Ltd. The reference electrode was Ag/AgCl. The electropolymerization/precipitation was performed in the long-path-length spectroelectrochemical cell. This cell consisted of a front and rear window of ITO-coated glass with a 2.5 cm Teflon solution compartment between. Three holes had been drilled for degassing the solution, the counter and reference electrode. The front window was used for the working electrode and a Pt mesh was used for the counter electrode. The UV-vis experiments were performed on a Hitachi U-2000 spectrophotometer, a CV-27 potentiostat, and an X-Y recorder. NIR experiments were performed on Mattson RS-1 FTIR spectrometer using a PbSe detector, quartz-halogen source with 32 cm⁻¹ resolution.

Mass Spectrometry. Negative ion FAB mass spectra were obtained with a VG70EHF sector mass spectrometer. The

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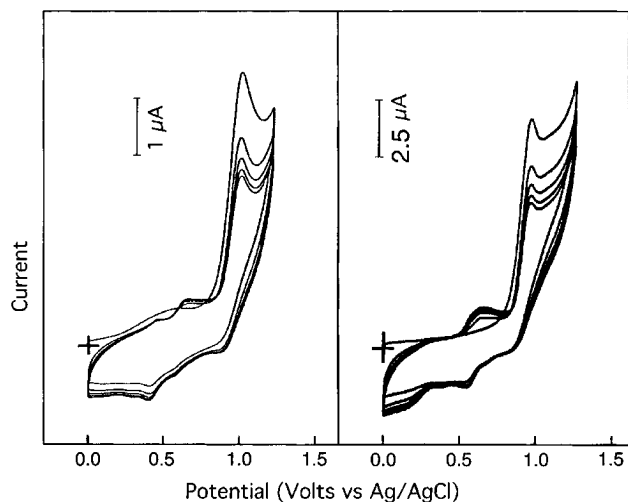


Figure 1. Cyclic voltammograms of (left) 0.46 mM DNTD and (right) 1.0 mM diphenylamine in DMSO containing 0.1 M TBAPF₆ at a Au disk electrode (area = 0.018 cm²), scan rate = 200 mV/s.

sample was obtained by electrooxidizing DNTD onto a large surface area Pt mesh electrode from CH₂Cl₂. The electrode was removed and placed in a beaker containing boiling 1:3 v:v MeOH/NH₄OH for 30 min. The resulting solution was evaporated at elevated temperature to one-third volume. A 2 μL sample was dispersed in the matrix of the FAB probe tip and bombarded with 7 kV xenon fast atoms produced by an Ion-Tech saddle field gun operated at 1.2 mA. Pentamethylene glycol was used as the sample matrix.

Scanning Electron Microscopy. Scanning electron micrographs were obtained on a Zeiss Model 940 digital scanning electron microscope using 2 kV electrons and a magnification of 5000×. The substrates were Au wires of 0.5 mm diameter with DNTD electrooxidized as above and contacted to the stage with conductive tape.

Results and Discussion

DNTD Electrochemistry at Au and SnO₂ Electrodes in DMSO Solvent. Figure 1 (left) shows the cyclic voltammetry at a Au disk electrode of a 0.46 mM solution of DNTD in DMSO containing 0.1 M TBAPF₆ with a scan range of 0.0–1.20 V. This potential range reflects the redox chemistry of the diphenylamine groups in DNTD. During the first positive scan an irreversible peak at 1.0 V vs Ag/AgCl is observed. This peak occurs at a similar potential to the 1 e⁻ oxidation of diphenylamine to form a radical cation.⁶ During the first negative-going scan and the second positive scan, two sets of peaks are observed. The peak potential separations of each set are ca. 60 mV. Subsequent scans show a decrease in large irreversible peak consistent with either decreased concentration of DNTD at the surface or hindered e⁻ transfer. In DMSO the oxidative peaks between +0.3 and +0.9 V increase until the fourth scan, at which time the voltammetry remains the same. This voltammetry is very similar to that of diphenylamine oxidized under the same conditions (Figure 1, right). This corresponds to diphenylamine voltammetry at a Pt electrode in CH₃CN solvent^{5,6} and the solution voltammetry of diphenylbenzidine under similar conditions. The diimide group, therefore, does not perturb the electrochemical properties of the diphenylamine groups. This is consistent with literature reports of no spin density at the imide nitrogen in imide radical anions and suggests no electronic interaction

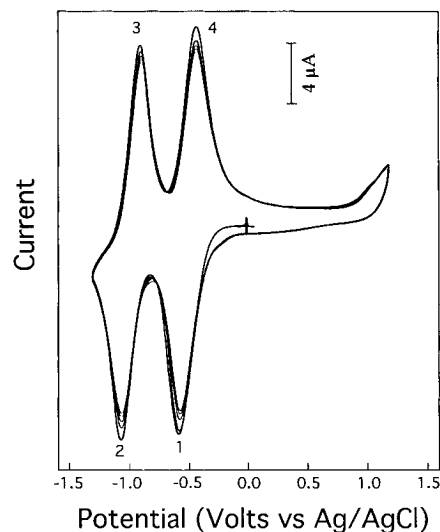


Figure 2. Cyclic voltammogram of DNTD film, prepared from DMSO solution, in 0.1 M TBAPF₆, DMSO solution, scan rate = 200 mV/s.

between the diimide group and the diphenylamine group.³¹

After the above electrode is rinsed with fresh DMSO, no observable material was seen on the electrode. The electrode was placed in a degassed DMSO solution containing only electrolyte and no voltammetric waves were observed. The electrode was again cycled in the above DNTD solution, but the scan range was increased from +1.20 to -1.30 V. The oxidative peaks are similar to those in Figure 1, but two sets of peaks with $E_{1/2}$'s of -0.46 and -0.92 are observed on the reductive sweep. Both waves increase in current with increasing number of scans. After electrochemical cycling for 30 min, a blue film is observed on the surface of the electrode. Upon emersion, rinsing with fresh solvent, and immersion into solvent containing supporting electrolyte, the voltammetry in Figure 2 is observed. The electrode shows ill-defined voltammetry at positive potentials and two sets of chemically reversible reduction peaks at $E_{1/2}$'s of -0.51 and -0.98 V. The peak current dependence on scan rate is consistent with a surface-confined species. These peaks are similar to the electrochemistry of naphthalene diimide reduction in DMF.¹⁶ The first set of waves is consistent with the formation of the radical anion and the second set with the dianion. Assuming 1 e⁻/monomer unit, integration of peak 1 yields 1.08×10^{-8} mol of DNTD/cm². Repetitive cycling results in only a small (<5% total) loss of surface material. Also, we have applied the Scotch tape test, which does not remove the dry film. These experiments show that the film adheres well to the electrode. While the best films are produced with repetitive cycling, similar films can also be produced by holding the electrode potential at +1.2 V for 20 min. The electrochemistry of these films is consistent with noninteracting diimide radicals, without π -stacking in DMSO. Also the ill-defined electrochemistry at positive potentials probably means that the diphenylamine end groups and resulting diphenylbenzidine groups in the surface-confined film are not electroactive under these conditions.

The IR spectrum of the monomer, DNTD, and the grazing angle IR (GIR) spectrum of the surface film are

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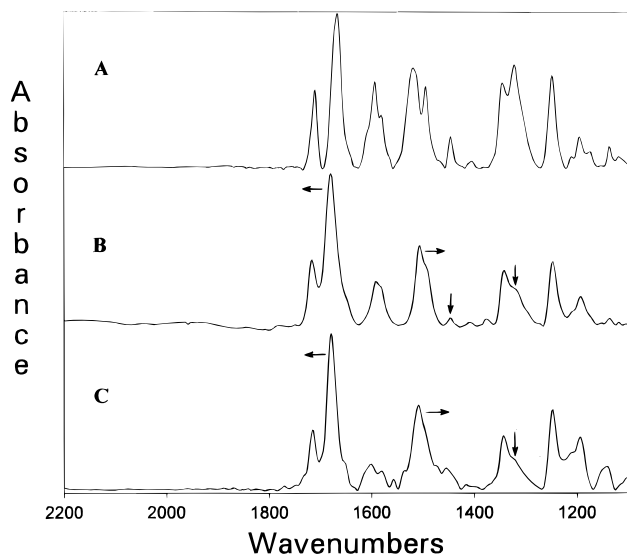


Figure 3. Infrared spectroscopy of (A) DNTD monomer dispersed in KBr (transmission spectroscopy), (B) DNTD electrooxidized onto a Au-coated glass slide from DMSO solvent (grazing angle spectroscopy), (C) DNTD electrooxidized onto a Au-coated glass slide from CH_2Cl_2 solution (grazing angle spectroscopy).

shown in Figure 3. For the monomer (Figure 3A), the bands at 1518 and 1405 cm^{-1} were assigned to the semicircle stretch modes of the para-substituted benzene ring, and 1495 and 1446 cm^{-1} bands were assigned to the semicircle stretch modes of the monosubstituted benzene ring at each end of DNTD.³² The intensity ratio of 1667 cm^{-1} diimide asymmetric stretch to 1446 cm^{-1} band, $I_{\text{diimide}}/I_{\text{end}}$ was 5.0 for DNTD. For the surface film (Figure 3B), the 1495 cm^{-1} becomes a shoulder of larger 1507 cm^{-1} which is shifted to lower energy from 1518 cm^{-1} in the monomer. The intensity ratio of the 1680 cm^{-1} diimide band to that of 1446 cm^{-1} is 23.5. The degree of DNTD polymerization, n , could be estimated via the following equation:

$$n = \frac{(I_{\text{diimide}}/I_{\text{end}})_{\text{polymer}}}{(I_{\text{diimide}}/I_{\text{end}})_{\text{monomer}}} \quad (1)$$

where I_{diimide} is the intensity of the asymmetric diimide band and I_{end} is the intensity of the monosubstituted benzene stretch. The average degree of polymerization was 4.7. This leads to an average molecular weight of 2800 for the DNTD chains.

In addition to electropolymerization at Au electrodes, a surface film of DNTD could also be prepared on transparent ITO electrodes from DMSO. The transmission UV-vis spectrum of the electrooxidized film on ITO in pure electrolyte solution at different applied potentials and the neutral DNTD monomer in solution are shown in Figure 4. The peaks at 342, 361, and 382 nm in the monomer (Figure 4A) are assigned to the naphthalene diimide group.²¹ The spectrum of the film at 0.00 V (Figure 4B) is similar to the monomer except that the 342 nm peak is shifted to 327 nm. The spectrum of the film at +1.50 V (Figure 4C) is similar. The potential of -0.75 V corresponds to $1e^-$ reduction per monomer unit. This radical anion shows absorptions at 474, 606, 701, and 786 nm, with corresponding

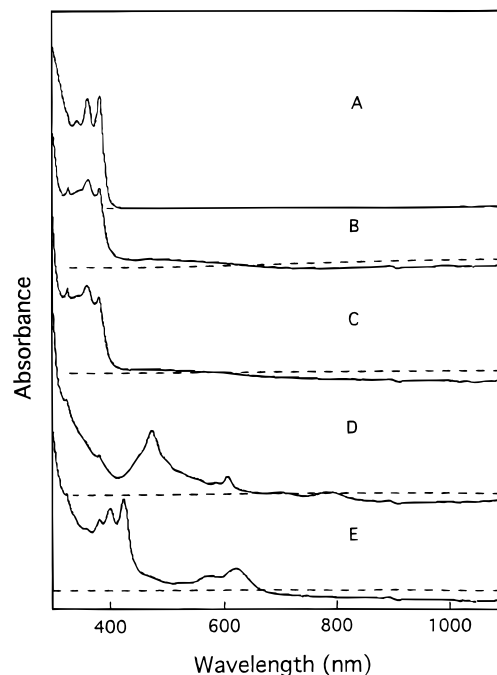


Figure 4. UV-visible-near IR spectra of (A) DNTD monomer in DMSO, and the polymer film on a ITO glass electrode in DMSO containing 0.1 M TBAPF₆ with the potential (B) 0.00, (C) 1.50, (D) -0.75 , and (E) -1.50 V . All potentials are referenced to an aqueous Ag/AgCl. The film was prepared from a DMSO solution.

decreases of the bands at 361 and 382 nm (Figure 4D). This spectrum resembles that of the reported solution diimide-based anion radical in DMF.²¹ Figure 4E is the spectrum at -1.50 V , past the second reduction wave. Four new absorptions at 400, 424, 571, and 620 nm occur corresponding to those reported for the naphthalene diimide dianion.²¹ Even though these species are surface-confined as evidenced through the cyclic voltammetry and there is no loss of material during repeated cycling in a solution of pure electrolyte, the spectroscopy of the material does not resemble that of aggregates.

The spectrum Figure 4D is similar to that obtained via the reduction of the DNTD monomer by zinc amalgam (Zn/Hg) in DMSO containing 0.1 M TBAPF₆. This implies that the radical anions could also be prepared by chemical reduction, and the polymeric form of the radical anion is similar to the monomeric solution form. This is consistent with linkage through the diphenylamine units (as opposed to oxidation of the diimide group) and the diphenylbenzidine linkage does not electronically perturb the diimide.

DNTD Electrochemistry at Au and SnO₂ Electrodes in CH_2Cl_2 Solvent. Figure 5 shows the cyclic voltammogram of DNTD at a Au electrode in CH_2Cl_2 containing 0.1 M TBAPF₆. The negative potential peaks due to diimide reduction were similar to that observed in DMSO. The first positive scan results in a single electrochemical oxidation wave at fast scan rates. However on the second and subsequent scans a new oxidation peak at $+0.86\text{ V}$ appears. This is consistent with the diphenylbenzidine linkage being formed. At platinum electrodes the electrochemistry is the same and a gold-covered film was formed (gold on gold is difficult to distinguish). In the above experiment on a Au electrode, after the third scan the electrode is removed from solution and the cyclic voltammogram in fresh CH_2Cl_2 containing 0.1 M TBAPF₆ is recorded in

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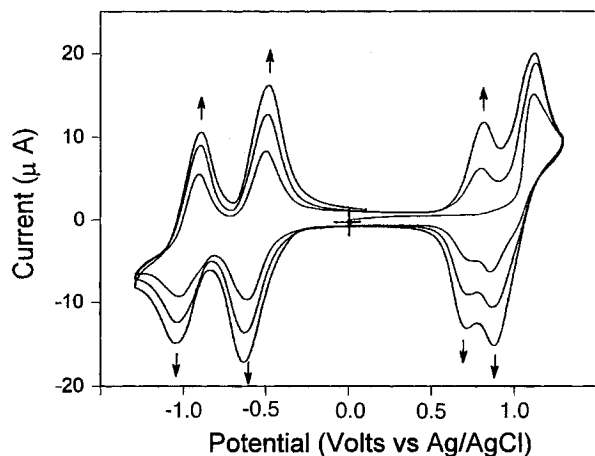


Figure 5. Cyclic voltammogram of 0.5 mM DNTD in CH_2Cl_2 containing 0.1 M TBAPF_6 at a Au disk electrode (area = 0.018 cm^2), scan rate = 200 mV/s.

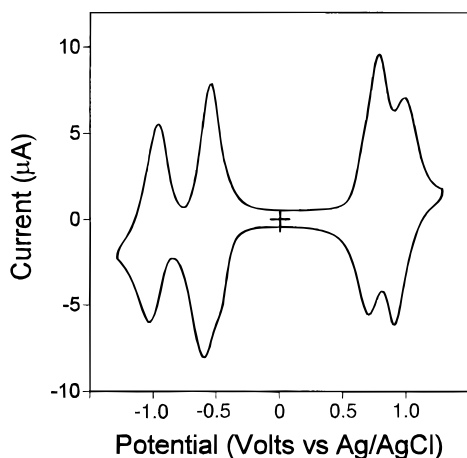


Figure 6. Cyclic voltammogram of DNTD film prepared from CH_2Cl_2 solution in 0.1 M TBAPF_6 , CH_2Cl_2 solution, scan rate = 200 mV/s.

Figure 6. We observe two reduction waves corresponding the production of the radical anion and dianion, respectively. On the positive sweep we observe two waves corresponding to the radical cation and dication of benzidine. We make this conclusion based on the comparison of the voltammetry of an authentic sample of diphenylbenzidine in CH_2Cl_2 as shown in Figure 7. In comparing the electrooxidation product of DNTD with the solution-phase diphenylbenzidine, there are two oxidation waves centered at ~ 0.72 and ~ 0.92 V for both compounds. The only real differences between the two voltammograms is that Figure 6 is a surface-confined species and has the naphthalene diimide unit in the chain where Figure 7 is a solution species with the diffusional tail.

We studied this film using grazing angle mid-IR spectroscopy as shown in Figure 3C. Using the same end-group analysis as above we find an average degree of polymerization, $n = 2.0 \pm 0.1$. This is a lower degree of polymerization than for films derived from DMSO, yet the spectrum clearly is not the spectrum of the monomer. Also while the monomer can easily be dissolved off a surface, this dimer film is insoluble and persistent.

Although we conclude from IR and electrochemical evidence that the coupling between monomers results in a diphenylbenzidine linkage, a more direct proof of this linkage was necessary. Thus we turned our atten-

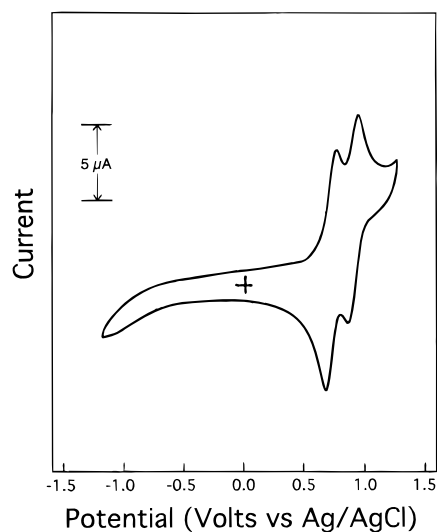


Figure 7. Cyclic voltammogram of a 1.0 mM diphenylbenzidine solution in 0.1 M TBAPF_6 , CH_2Cl_2 solution at a Pt disk electrode (area = 0.018 cm^2), scan rate = 200 mV/s.

tion to mass spectrometry. The precipitate itself is completely insoluble in all organic solvents attempted (more than 50 tried), which is not surprising since most polyimides are very insoluble. However, even strongly complexing Lewis acid solvents such as refluxing AlCl_3 /nitromethane³³ did not dissolve the precipitate. To get a soluble sample for mass spectrometry, we cleaved the diimide groups of a film oxidized from CH_2Cl_2 with refluxing $\text{CH}_3\text{OH}/\text{NH}_4\text{OH}$ and analyzed the resulting solution using FAB-MS. We observed a strong peak in the negative ion MS at 153 mass units corresponding to the biphenyl group. Neither the matrix with NH_4OH nor the monomer **1** under the same conditions showed the peak at m/z 153. Since the biphenyl unit was not observed in the FAB-MS of the monomer, we can rule out any gas-phase rearrangements and deduce it had arisen from oxidative dimerization.

Figure 8 is the spectroelectrochemistry of the film in CH_2Cl_2 . The spectrum of the neutral film (Figure 8A) was the same as the monomer with bands at 361 and 382 nm. When the potential was changed to 0.90 V, two peaks in the visible region (460 and 613 nm) and one peak in the near-IR region (the peak was beyond 1100 nm, Figure 8B) were observed. At more positive potentials the bands at 460 nm and in the near IR region decreased (Figure 8C, 1.00 V) and disappeared (Figure 8D, 1.33 V). At these potentials the band with a peak at 613 nm increased. The spectrum of the film in the visible region at -1.00 V (Figure 8E) was the same as those of the films prepared from DMSO and CH_3CN solvents and reflect the diimide radical anion. The spectrum at -1.70 V (Figure 8F) had an intense band with the peak at 602 nm and a smaller peak at 761 nm in the visible region similar to the diimide dianion. Figure 9 is the near-IR spectrum of the film at 0.90 V showing the peak at (8540 cm^{-1}) 1171 nm. This is the extension of the visible spectrum shown in Figure 8B. This shows the extent of the NIR bands, and from the peak width it is clear it is not the overtone of a vibrational peak and electronic in origin.

Films produced from CH_2Cl_2 upon exposure to air show absorbances in the near-IR region presumably from O_2 oxidation. Interestingly enough variable-angle

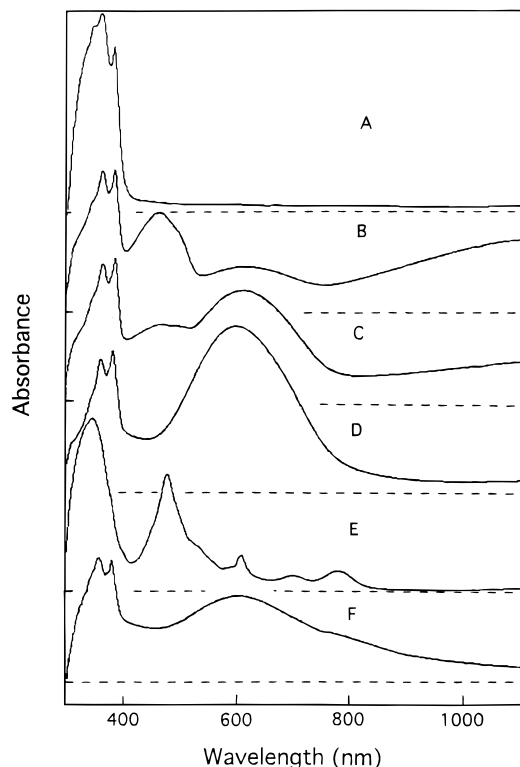


Figure 8. UV-visible-near IR spectra of the DNTD polymer film on an ITO glass electrode in CH_2Cl_2 containing 0.1 M TBAPF_6 with the potential (A) 0.00, (B) 0.90, (C) 1.00, (D) 1.33, (E) -1.00 , and (F) -1.70 V. All potentials are referenced to a Ag/AgCl reference electrode. The film was prepared from a CH_2Cl_2 solution.

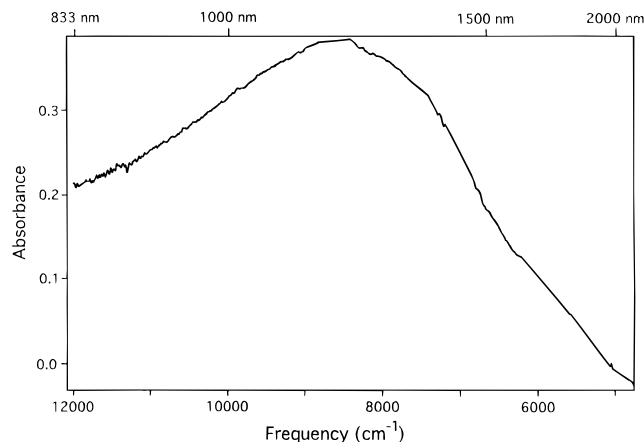


Figure 9. Near-IR spectrum of the DNTD polymer film on a ITO glass electrode in CH_2Cl_2 containing 0.1 M TBAPF_6 with the potential of $+0.90$ V vs Ag/AgCl .

transmission spectroscopy shows NIR band shifts to higher energies with greater angles of incidence. In Figure 10 is shown a dry film where the lowest energy band maxima shifts monotonically from 1070 nm for 0° to 955 nm for 70° angle of incidence. Also a band around 510 nm is seen when the low-energy NIR band appears, and it shifts to longer wavelengths as the angle of incidence increases. Both bands are observed in solution at potentials around $+0.90$ V vs Ag/AgCl . From these results we suggest that the preferred direction of the π -stacking interaction is parallel to the substrate. An angular dependence to charge-transfer bands has been observed in other systems though the bands tend to increase or decrease in intensity as opposed to shifting.³⁴ We observe low energy bands in dry films

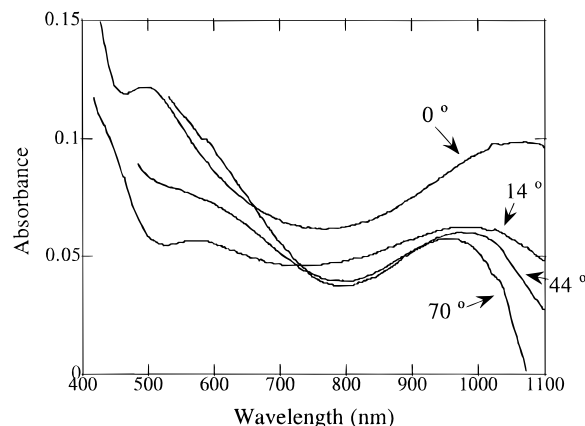


Figure 10. Variable-angle visible-near IR spectra of a dry DNTD film removed from solution at 0.0 V potential. The angles refer to the angle of incidence of the illuminating beam. 0° refers to normal incidence.

from DMSO solution although the band maxima are at slightly higher energies (826 nm at 54° angle of incidence) and unpolarized.

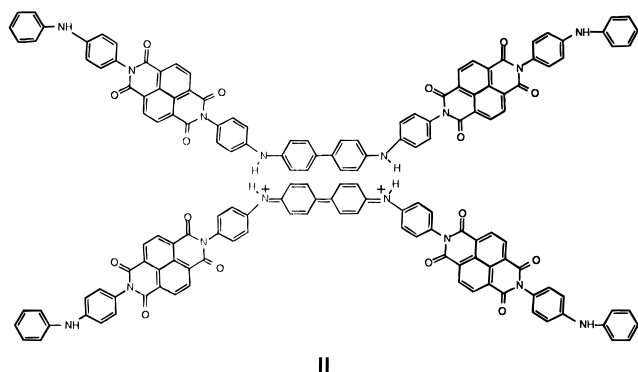
The differences between the films oxidized from DMSO and CH_2Cl_2 interested us, especially the observation of NIR bands. We decided to examine the morphology of the films to further elucidate these differences. Figure 11 shows scanning electron micrographs (SEM) of gold wires coated with the DNTD electrooxidized material. The top SEM is a film electrooxidized from CH_2Cl_2 , where the bottom is from a DMSO solution. The surface coverages are approximately equal and represent $\sim 1 \times 10^{-7}$ mol/ cm^2 of monomer units. The major difference between these two SEM is that the film from CH_2Cl_2 shows many domains of the 300–500 nm size regime where the DMSO film is rather contiguous with few domains. This is consistent with the picture of precipitation of smaller, organized π -stacked *p*-phenyl coupled dimers from CH_2Cl_2 and longer, disorganized oligomeric and polymeric chained material that does not have aligned chains from DMSO. The lack of NIR bands can be rationalized as the lack of chain alignment and thus inhibition of interchain hopping (from one diphenylbenzidine unit to the next) in the DMSO film.

Cyclic Voltammetry of DNTD in CH_3CN Solvent.

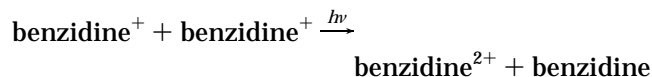
Films oxidized from CH_3CN show voltammetric waves for oxidation and reduction similar to CH_2Cl_2 . Repeated cycling increases the amount of material on the electrode surface in a monotonic fashion much like Figure 5. Although qualitatively the electrooxidation and subsequent surface confinement are similar, the starting concentration (determined by the maximum solubility of the monomer) is ~ 30 μM . Consequently the growth at 200 mV/s is determined as 2.1×10^{-10} mol/ cm^2 per scan. The same experiment from a 0.5 mM CH_2Cl_2 solution gives a growth rate of 8.1×10^{-9} mol/ cm^2 per scan. The important point is growth of relatively thick films ($\Gamma \sim 10^{-7}$ mol/ cm^2) while easily achieved from CH_2Cl_2 , is difficult from CH_3CN . Spectroelectrochemistry of these films is similar to the film formed in DMSO (Figure 4). No NIR bands were observed upon oxidation into and past the oxidation wave at 0.84 V vs Ag/AgCl .

(34) Miller, L. L.; Zhong, C.-J.; Kasai, P. *J. Am. Chem. Soc.* **1993**, *115*, 5982.

The solvents chosen have different effects on the growth and morphology of the films. DMSO stabilizes radical cations presumably through its high dielectric strength and accessible lone pairs. The radical cations being more soluble allows more time for polymerization before eventual precipitation onto the surface. DMSO also solubilizes the benzidine group thus π -dimers do not form. CH_2Cl_2 does not solvate radical cations as well, so the resulting dimers and trimers precipitate from solution without undergoing further chain elongation. The pertinent question is, why is the precipitated material anisotropic? The covalently coupled dimers possess one diphenylbenzidine unit which when oxidized by $1e^-$, could form a π -stacked dimer with another. If the resulting π -dimer aggregate of C-C coupled dimer (**II**) precipitated on the surface the π -stack axis would



be parallel to the surface. Thus the charge-transfer band



would be polarized along the benzidine-benzidine axis, parallel to the plane of the substrate. For the material formed from oxidation in DMSO, the greater degree of polymerization and longer chains would be harder to align than the covalently linked dimers. Without alignment the formation of the benzidine π -dimer would be unfavorable as seen in the spectroscopy shown in Figure 4. Originally, we expected some interactions between the diimide radical anions in the solid film. However, spectra in both Figures 4D and 8E, taken at potentials after the first reduction but before the second reduction, show the same peaks identified in the literature as the noninteracting diimide radical anion.²¹ Since there are five available redox states with different spectroscopic properties, we are investigating this and other similar materials as electrochromic materials. We are now undertaking AFM and STM characterizations of these materials³⁵ to better understand the nature and role of morphology on electronic properties.

Conclusion

We have synthesized DNTD and polymerized it in DMSO and CH_3CN by electrooxidation. The polymer

(35) Wang, L.; Demir, U.; Shannon, C. G.; Cammarata, V., work in progress.

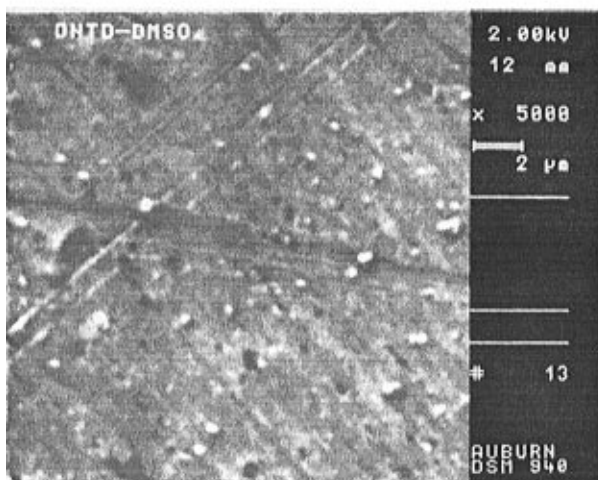
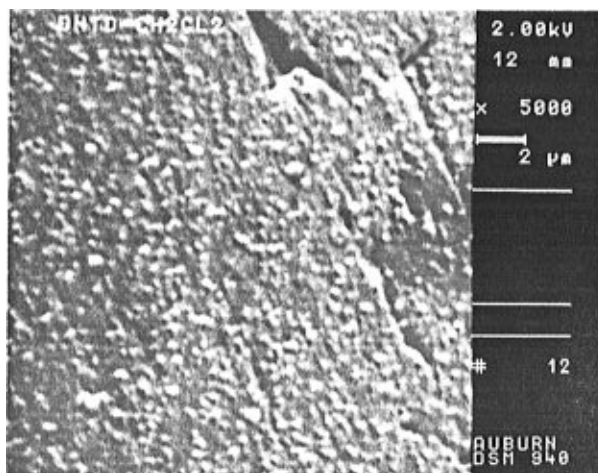


Figure 11. Scanning electron micrographs using 2 keV electrons with 5000 \times magnification on a Au wire with DNTD electrooxidized from (top) CH_2Cl_2 solution and (bottom) DMSO solution.

film was precipitated onto various electrode surfaces, and at Au electrodes the degree of polymerization was ~ 5 . The precipitation of the material was enhanced by cycling of the film through both the oxidative and reductive waves. The properties of the films produced in CH_2Cl_2 solvent were significantly different from those in DMSO and CH_3CN . In CH_2Cl_2 , DNTD mainly dimerized through para C-C coupling and then electroprecipitated on the electrode surface in π -stacks. DMSO and CH_2Cl_2 led to different morphologies of the film. The longer chains which were not aligned tended to be smooth, whereas the π -dimers of covalent dimers showed small grains similar to nucleation and growth type materials. Thus shorter chains can align better and stack to form oriented domains.

Acknowledgment. We would like to acknowledge partial financial support from The Petroleum Research Foundation and the Department of Energy. B.J.S. would like to acknowledge The Petroleum Research Foundation for a summer faculty fellowship. We also would like to acknowledge and thank Dr. Alfred Brown for help with the scanning electron microscopy.