Cast Poly(vinyl alcohol) Films Containing Stacks of Imide Anion Radicals. Correlation of Spectra and Conductivity

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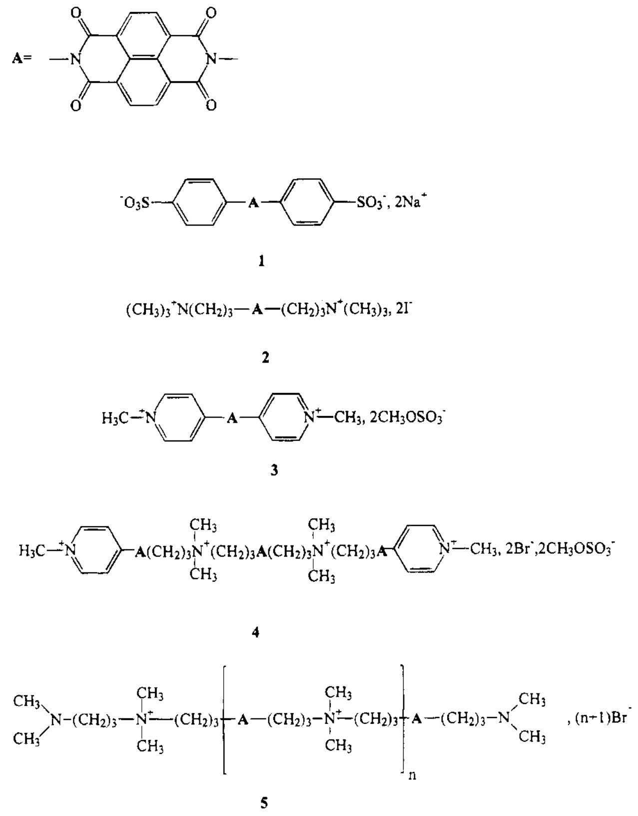
Aqueous solutions of naphthalene diimides, sodium dithionite reductant, and poly(vinyl alcohol) (PVA) were used to cast air stable n-doped films containing naphthalene diimide anion radicals in PVA. Both monomeric and oligomeric diimides, substituted with ionic phenyl sulfonate, propylammonium, or *N*-methylpyridinium groups, were employed. The loading of the film with anion radicals was varied as was the degree of reduction. Optical microscopy on the films showed no microcrystals of conductor, and samples with high conductivity appeared homogeneous. Characterization by vis, NIR, IR, and ESR spctroscopies showed that the anion radicals were present as π-stacks. Films formed from monomeric diimides had the stacks preferentially oriented in the film plane. Oligomers gave isotropic films. In the film plane, four-probe conductivities were in the range $10^{-3}-10^{-2}$ S cm^{-1} for films loaded with 5 wt % of diimide anion radicals. Spectroscopic and conductivity evidence for mixed valence stacks was found. The ratio of in-plane to across-the-plane conductivity ranged from 1 for spectroscopically isotropic samples to 10^5 for a mixed valence film from a monomeric diimide. Changes in the conductivity with diimide structure, loading, and extent of reduction were correlated with changes in the NIR and ESR spectra and are interpreted in terms of stack structure, stack anisotropy, and network formation.

Introduction

Experiments in this laboratory have shown that electrically conducting films can be formed by electroprecipitation of anion radical $\mathbf{1}^-$ (Chart 1) and a polycation.[1] These films were highly anisotropic and the conductivity was quite humidity sensitive. In a preliminary communication we have reported casting anisotropic films of anion radical $\mathbf{3}^-$ from aqueous poly(vinyl alcohol) (PVA) solutions.[2] It is this latter experiment which we herein elaborate. Elaboration seemed worthwhile because casting is widely applicable and the film properties were of some interest. We specifically note that this represents one of the few examples of air stable n-doped conducting polymers.[3] PVA is an especially useful host polymer because it is a good film former, it is biocompatible[4] and forms films from the ideal solvent, water.

Chart 1



In general this casting approach leads to conducting polymers which have a conducting phase of small molecules imbedded in the host polymer. It is sometimes possible to produce a film which has mechanical properties characteristic of the host polymer and electrical properties characteristic of the embedded conductor. In the best cases good conductivity can be obtained with low (<5%) loading with conductor. Jeszka and Ulanski and their co-workers[5] found such cases using charge transfer salts, e.g., TTF−TCNQ, embedded in various polymers. They showed the importance of forming a microcrystalline network of the conductor and revealed

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[1] Miller, L. L.; Zhong, C. J.; Kasai, P. *J. Am. Chem. Soc.* **1993**, *115*, 5982.

[2] Miller, L. L.; Zhong, C. J.; Hong, Y. *Synth. Met.* **1994**, *62*, 71.

[3] Skotheim, T. A. *Handbook of Conducting Polymers*; Marcel Dekker: New York, 1986; Vols. 1, 2.

[4] (a) Hirai, T.; Maruyama, H.; Suzuki, T.; Hayashi, S. *J. Appl. Polym. Sci.* **1992**, *45*, 1849. (b) Yoshida, R.; Sakai, K.; Okano, T.; Sakurai, Y. *J. Biomater. Sci., Polym. Ed.* **1992**, *3*, 243. (c) Shiga, T.; Hirose, Y.; Okada, A.; Toshio, T. *J. Appl. Polym. Sci.*, **1991**, *44*, 249.

[5] Jeszka, J. K.; Ulanski, J.; Kryszewski, M. *Nature* **1981**, *289*, 390. Ulanski, J.; Tracz, A.; M. Kryszewski, M. *J. Phys. D: Appl. Phys.* **1985**, *18*, 451. Tracz, A.; Jeszka, J. K.; Kryszewski, M. Ulanski, J. *Chemtronics* **1986**, *1*, 50. Jeszka, J. K. *Synth. Met.* **1993**, *59*, 151.

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some aspects of the crystallization phenomenon which takes place as the film solidifies. This work was extended to cation radical salts and to PVA using a water soluble TTF dicarboxylate to form conducting films of the cation radical.[6] If they were cast at high temperature, the films contained a microcrystalline network of the cation radical salt. The conductivity was anisotropic as were the ESR spectra.

In the present study we wanted to use PVA casting to gain insight into the structure and conductivity of naphthalene diimide anion radical films. These films appeared particularly interesting because they seemed not to contain crystals but to contain a conducting network of π-stacks.[2] These stacks have been primarily identified by their NIR absorption bands. Such "optical conduction bands" arise from excitation of π electrons along the stack. As such longer stacks of the same repeat unit give longer wavelength bands. These bands are also found for aqueous solutions of diimide anion radicals.[7] This provides the possibility of measuring π-stack spectra, which are uncomplicated by the film morphology and to compare the spectra of films and solutions.

In the present study we varied the structure of the anion radicals and the film forming conditions, and correlated the changes in the spectra and the conductivity. A further aspect, which we take up for the first time here, is the structure and conductivity of oligomers embedded in a polymer. Using diimide oligomers,[8] we provide insight into the possibilities for forming conducting films from polymers containing nonconjugated main chain redox groups. This has wide potential importance and is directly related to films formed from dendrimers that are under investigation in our laboratory.[9]

Results

General. Three monomeric naphthalene dimides, **1**−**3**, which have either phenylsulfonate, *N*-methylpyridinium, or propylammonium groups attached, were studied. In addition a compound containing three naphthalene diimide groups **4**, and an oligomer mixture containing, on average, five naphthalene diimide groups, **5**, were investigated.

The procedures used for film casting are detailed in the Experimental Section. In all but one case, that of **3**, the films were formed by spin casting at 65° from deaerated aqueous solutions containing the imide, the reducing agent sodium dithionite, and PVA. The loading is expressed as a weight percent, i.e., 10% means a weight ratio of diimide to PVA of 0.1 (a mole ratio of diimide to PVA repeat unit of less than 0.005). To the eye the films were usually homogeneous and of uniform thickness. The color was tan to glossy black, depending on the loading with anion radical. Free-standing films, typically 20 μm thick, could be easily peeled from the glass substrate and handled in air without physical or chemical degradation. These films, especially at low loading, are flexible and could be stretched up to 100% elongation without breaking.

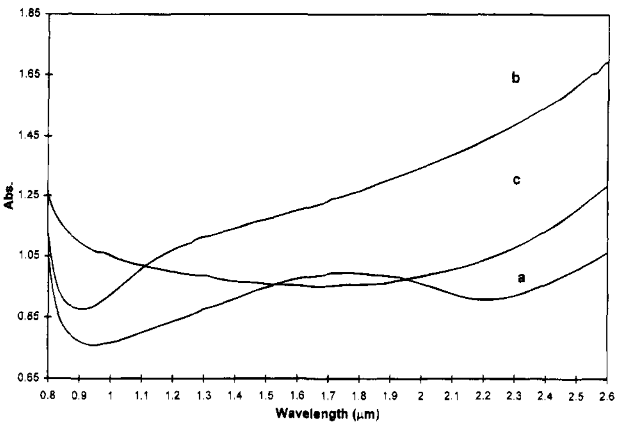

Figure 1. NIR spectra of 1^-/PVA films: (a) 5%, $1e^-$/imide; (b) 10%, $1e^-$/imide; (c) 10%, $0.38e^-$/imide.

The spin casting method improved the uniformity of the films and casting at 65°, instead of room temperature, improved the homogeneity and conductivity of the films (see below).

NIR, ESR, and, occasionally, vis and IR spectra were recorded for the films, and then four wires were attached for conductivity measurements. The spectra and the conductivity values were stable for at least a period of days and when tested the conductivity was unchanged after several weeks. All the conductivities were ohmic and showed no variation as current was passed over a period from 1 s to several hours.

1^-/PVA Films. Films were produced using 1.0−1.2 equiv of reductant, varying the loading with diimide **1** from 2.5 to 15 wt %. Although the films looked homogeneous to the eye, optical microscopy showed tiny brown "dots" of conductor in the clear PVA. As the loading was increased the density, but not the size, of the dots increased leading to a darker color. As shown in Figure 1a the film loaded at 2.5% showed a NIR maximum at 1700 nm. Increasing the loading led to a decrease in the intensity of this band and an increase in intensity at even longer wavelengths (Figure 1b). Using IR the maximum absorption of this band was found to be 3000 nm. The IR spectra also showed imide carbonyl bands at 1640 and 1527 cm^{-1}. These are typical for naphthalene diimide anion radicals.[7] The bands are shifted compared to the neutral diimide, which has symmetric and antisymmetric carbonyl bands at 1716 and 1670 cm^{-1}.

ESR spectra were recorded for films oriented parallel and perpendicular to the applied field (Figure 2). The spectra were anisotropic with a *g* value of 2.0049 for the parallel and 2.0053 for the larger peak of the perpendicular alignment spectrum. These spectra are quite similar to those recorded for a precipitated film of the anion radical salt **1^-,Na$^+$**.[7]

Conductivity studies of these fully reduced (one electron/diimide) films are summarized in Table 1. At 2.5% loading the conductivity was less than 10^{-6} S cm^{-1}. At 5% loading a conductivity threshold was reached and σ rose to 0.8×10^{-3} S cm^{-1}. Increasing the loading further to 15% only increased σ to 3×10^{-3} S cm^{-1}.

Our previous studies of solutions and films of diimide anion radicals have given no indication of the formation of mixed stacks. Thus, partially reduced materials,

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(6) Hong, Y.; Benz, M. E.; Miller, L. L. *Synth. Met.* **1995**, *68*, 287.

(7) Zhong, C. J.; Kwan, W. S. V.; Miller, L. L. *Chem. Mater.* **1993**, *4*, 1423.

(8) Penneau, J. F.; Stallman, B. J.; Kasai, P. H.; Miller, L. L. *Chem Mater.* **1991**, *3*, 791. Kwan, W. S. V., Ph.D. Thesis, University of Minnesota, 1993.

(9) Hashimoto, T.; Tabakovic, I.; Miller, L. L.; Swanson, D. R.; Tomalia, D. A. *Chem. Mater.* **1995**, *7*, 9.

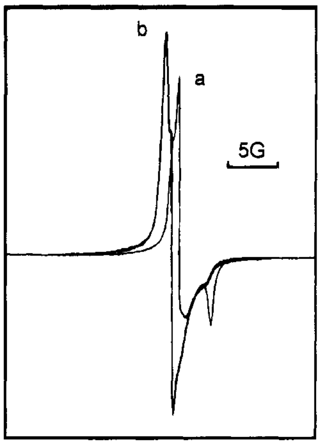

Figure 2. ESR spectra of 1^-/PVA film, 10%, 0.5e$^-$/imide. (a) film plane parallel; (b) perpendicular to the applied field.

Table 1. Conductivity of 1^-/PVA Films

loading	e$^-$/imide	$\sigma \times 10^3$ (S cm^{-1})
2.5%	1	$<10^{-3}$
5%	1	0.8
10%	1	2
15%	1	2.8
10%	0.75	15
10%	0.50	40
10%	0.38	25
10%	0.20	2

including **1**, reduced in D_2O with less than one electron/diimide, gave vis–NIR spectra which were simple additions of the spectra of anion radicals (one electron/diimide) and neutrals. In contrast to these previous reports **1^-/PVA** films gave both spectroscopic and conductivity evidence for mixed-valence stacks.

The conductivity data for films formed with 10% loading, but variable extents of reduction, are summarized in Table 1. Maximum conductivity (4×10^{-2} S cm^{-1}) was found for a film reduced with 0.5 electron/diimide. Films formed using 1–2 equiv of reductant had constant conductivity. NIR spectra on partially reduced films showed only the very long wavelength absorbance without the 1700 nm band (Figure 1c). It is noted that the film reduced with 0.37 electron/diimide has an anion radical loading of only 3.7% and in the absence of interaction between the neutrals and anion radicals would be expected to have a 1700 nm band. Thus, the mixture of neutrals and anion radicals give stacks with longer wavelength absorption, consistent with the conductivity data.

In preliminary experiments **1^-/PVA** films were cast at room temperature. These fims showed NIR spectra quite similar to those cast at 65° but were less homogeneous under the microscope and gave lower conductivity. A 10%, 0.5 electron/diimide room temperature film showed $\sigma = 3 \times 10^{-3}$ S cm^{-1}, compared to 4×10^{-2} S cm^{-1} for a 65° film.

2^-/PVA Films. PVA films formed from **2** with the reductant sodium dithionite were homogeneous to the eye and under the optical microscope, with the exception of a partially reduced film in which microcrystals of neutral **2** were present. No "dots" of precipitated particles of anion radical like those found for **1^-/PVA** were present. This may arise because of the better solubility of 2^- in the casting solution.

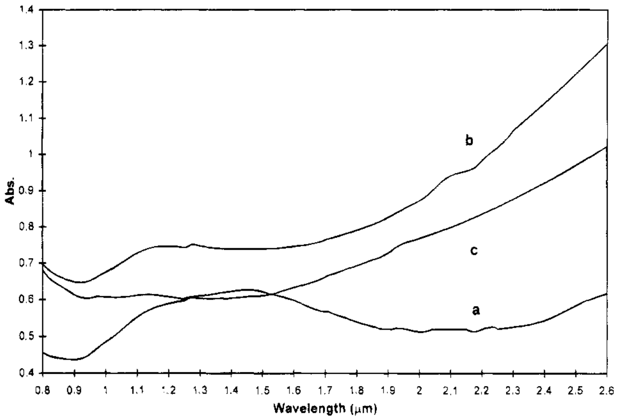

Figure 3. NIR spectra of 2^-/PVA films: (a) 2.5%, 1e$^-$/imide; (b) 10%, 1e$^-$/imide; (c) 10%, 0.25e$^-$/imide.

Table 2. Conductivity of 2^-, 4^-, 5^-/PVA Films

		$\sigma \times 10^3$ (S cm^{-1})		
loading	e$^-$/imide	2	4	5
2.5%	1	$<10^{-3}$	$<10^{-3}$	$<10^{-3}$
5%	1	0.4	$<10^{-3}$	$<10^{-3}$
10%	1	1.5	0.85	0.001
10%	0.5	9	2.5	1
10%	0.25	3	0.7	0.3

Table 3. ESR Intensities for 2^-, 4^-, 5^-/PVA Films

		ESR intensity ($\times 10^6$)		
loading	e$^-$/imide	2	4	5
2.5%	1	3.12	7.072	4.605
5%	1	4.245	12.51	7.944
10%	1	19.03	55.61	23.99
10%	0.5	22.10	74.91	31.50
10%	0.25	13.90	46.72	21.70

Solution studies of the anion radical 2^- in D_2O showed that it aggregated into short stacks with a NIR absorbance near 1350 nm. The NIR of **2^-/PVA** at low loading (2.5%) shows this absorbance, but there is also longer wavelength absorption (Figure 3a). As the loading was increased, the intensity of the longer wavelength NIR-IR absorbance increased (Figure 3b). As in the case of **1^-/PVA**, partial reduction (10% loading, 0.25 electron/diimide) led to a further relative increase of the NIR-IR absorbance (Figure 3c).

ESR spectra were similar to those in Figure 2 but not as anisotropic. Films aligned perpendicular gave $g = 2.0053$ and parallel $g = 2.0049$ for the larger peak. Shown in Table 3 are the relative ESR intensities (double integrated) for the various films. Higher loading or partial reduction gave a more intense ESR signal, although we emphasize that the signal is always weak.

Conductivity data for **2^-/PVA** are in Table 2. As for **1^-/PVA**, 2.5% loaded films are insulating, and at 5% loading the conductivity is much higher, 0.4×10^{-3} S cm^{-1}. Further increase in loading gives a small increase in σ. Partial reduction (0.5 electron/diimide) gives a substantial increase in conductivity. The 10%, 0.5 electron/diimide film is about 20 times as conductive as the 5%, 1 electron/diimide film, which has an equal number of anion radicals.

Across-the-film conductivity was measured for this mixed-valence sample (10%, 0.5 electron/diimide) using two probes. The conductivity was less than 10^{-7} S cm^{-1} (at the sensitivity limit). This high anisotropy, 10^5, has analogy in the films formed from 1^- and a polycation.[1] These values for the anisotropy are extremely high, especially since no specific effort to enhance the anisotropy, like elongation, has been employed.

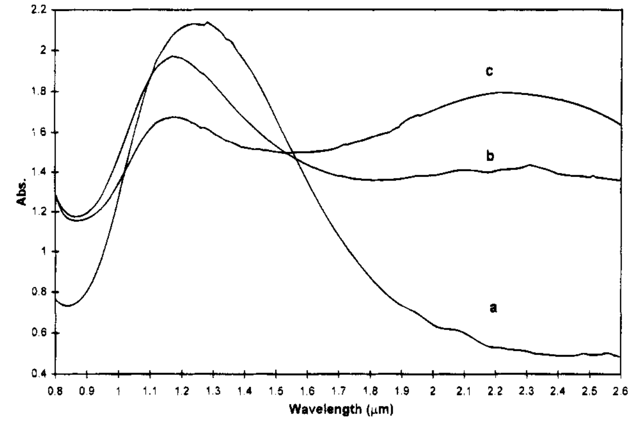

Figure 4. NIR spectra of 4^-/PVA films: (a) 5%, 1e$^-$/imide; (b) 10%, 1e$^-$/imide; (c) 10%, 0.5e$^-$/imide.

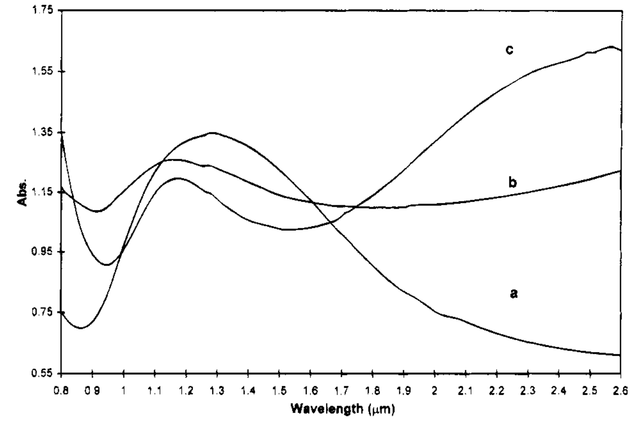

Figure 5. NIR spectra of 5^-/PVA films: (a) 5%, 1e$^-$/imide; (b) 10%, 1e$^-$/imide; (c) 10%, 0.5e$^-$/imide.

3^- PVA Films. Data on these films, which were simply cast at room temperature, not spin-cast at 65°, has been reported in a preliminary communication,[2] and we only summarize the results here. NIR spectra showed very long wavelength NIR-IR bands with the maximum near 3000 nm. ESR spectra were anisotropic and resembled those in Figure 2.

Optical microscopy showed that the visually homogeneous 10% loaded film contained some separated particles of conductor. Therefore, the threshold was higher than that for **1^-/PVA** or **2^-/PVA** and 5% loaded films were insulating. At 10% $\sigma = 4 \times 10^{-5}$ and 12% $\sigma = 10^{-4}$ compared to a pressed pellet $\sigma = 10^{-3}$ S cm^{-1}. In this case the conductivity was shown to be anisotropic with across-the-film conductivities of less than 10^{-6} S cm^{-1} even for highly loaded films.

4^-/PVA Films. Compound **4** was prepared by rational synthesis and is spectroscopically and chromatographically pure. From NMR we believe the counterions shown in the structural formula are present in about the ratio shown. Synthetic access to this trimer allowed for the first time an exploration of the π-stacking properties of a reduced main-chain oligomer in which the conducting units are separated by an insulating alkyl chain. This particular oligomer was designed to have water solubility due to the two ammonium groups and the two methylpyridinium end groups. We were particularly interested in the possibility that intramolecular aggregation would be important. Solution studies reported elsewhere[8] did not reveal such effects. The NIR spectrum of anion radical 4^- in D_2O with λ_{max} 1300 nm was, for example, quite similar to that of the monomeric 2^-.

PVA films containing 4^- were homogeneous under the optical microscope and had the good mechanical properties of films formed with monomeric analogues. The NIR spectra of 1 electron/diimide reduced, 2.5% and 5% loaded films showed a peak at 1300 nm and only weak absorbance in the NIR-IR (Figure 4a). A 10% film showed increased absorbance in the NIR-IR region (Figure 4b), and a 10% loaded, half reduced (0.5 electrons/diimide) film gave very long wavelength absorption in the NIR-IR which was very strong compared to that at 1300 nm (Figure 4c).

ESR spectra for **4^-/PVA** were isotropic, regardless of loading or extent of reduction. The spectra taken parallel and perpendicular to the field showed single lines with identical g values ($g = 2.0049$, with a width at half-height of 5 G). Although we have previously interpreted anisotropic spectra of diimide films as having an isotropic component,[1] this is the first example of a truly isotropic spectrum. Double integration of the spectra gave the intensity data shown in Table 3. As found for **2^-/PVA** the ESR intensity was highest for highly loaded and partially reduced films.

Conductivity data are found in Table 2. Similar to the results for **3^-/PVA**, which has the same methylpyridinium terminal groups, the conductivity threshold was around 10% loading for fully reduced films where it rose to 0.85×10^{-3} S cm^{-1}. Mixed-valence behavior was found when films were reduced with less than 1 equiv of dithionite. A 10% loaded, 0.5 electron/diimide film had $\sigma = 2.5 \times 10^{-3}$ S cm^{-1}, which is more than 10^3 times larger than a 5% loaded, fully reduced film.

5^-/PVA Films. The oligomeric mixture 5^- was produced by heating equal amounts of the appropriate dibromide and diamine.[8] Analyzed by HPLC and NMR, it contains on average five diimide groups and is primarily terminated with trimethylammonium groups as shown in the structural formula. The films from fully reduced **5** were not homogeneous under the optical microscope. **5** is not as water soluble as **4**, and it seems probable that precipitation took place while the films were still liquid, preventing dispersion of the anion radicals throughout the film.

The spectroscopic properties of **5^-/PVA** films corresponded quite closely to those of **4^-/PVA**. Thus the NIR spectra (Figure 5) showed bands near 1300 nm for fully reduced 5% loaded films, with increased absorbance at NIR-IR wavelengths for more highly loaded or partially reduced films. ESR spectra were isotropic, and a check on the anisotropicity of the NIR spectrum using linearly polarized light[1] showed that it was also isotropic, since there was less than 10% variation in the intensity and no change in shape as the incidence angle was varied from 90° to 30°. Like films of 2^- and 4^- the ESR intensity tracked the NIR-IR intensity and was largest for a 10% loaded, 0.5 electron/diimide film (Table 3).

Conductivity measurements on fully reduced films gave insulator properties because the conductor was precipitated into separated particles. Partially reduced films, which were microscopically homogeneous showed conductivities (Table 2) similar to **4^-/PVA**. Measurement of the across the film conductivity gave an identical value to that measured along the film plane, 1 ×

10^{-3} S cm^{-1}. Thus, the conductivity and spectroscopy are in agreement, showing that the sample is isotropic.

Discussion

In this section we first treat the general film qualities and the morphology and then discuss the spectroscopic and conductivity data.

The "embedded conductor" approach to conducting polymers can produce films with mechanical properties characteristic of the host polymer and conductive properties characteristic of the small molecule. The casting method developed here was reasonably successful in this regard. The mechanical properties of the films are quite good, and they are easily handled as free-standing films. The conductivity at loadings of less than 10% was only slightly less than that of the pure anion radical salt.

The stability of the films is remarkable. Because the radical anions that make up n-doped molecular conductors are usually sensitive to air oxidation and protonation by water, they are usually not stable under ambient conditions. Although these naphthalene diimide anion radicals are rapidly oxidized by oxygen in solution, the formation of π-aggregates embedded in PVA provides excellent stability. We have shown, as expected, that aggregation makes the reduction potential of the anion radicals considerably more positive, making them less reactive.

Morphology. In general the films were homogeneous to the eye but often had microscopic particles. When large precipitated particles were observed, it was from samples which had limited water solubility of the anion radical or (in the case of partially reduced samples) neutral diimide. Optical homogeneity and high conductivity require a certain dispersion of the conductor throughout the film. This will occur if the solubility is high enough to prevent precipitation at the early stages of casting, when the viscosity is still low enough to allow rapid diffusion to a few nucleation sites. Even in optically homogeneous samples, it may be true that there is phase separation into a conducting phase and a PVA phase as one goes to spacial resolutions less than that of the optical microscope. Such phase separation can produce a microcrystalline conducting network surrounded by PVA.[6] In the present case, however, there is no evidence for microcrystals. This is not surprising since the pure anion radical salts form films or powders when precipitated.

One further aspect of the film morphology, one of some interest, is the anisotropy. Thus, in every film formed from monomeric diimide anion radicals, whether it be a precipitated, pure film,[7] a PVA film, or film formed with polycations as both counterions and polymer,[1] the spectra and conductivity are anisotropic. The spectra reveal structural anisotropy of π-stacks that lie preferentially in the film plane. Since charge transport should be more effective along the stack direction than between stacks, the anisotropy in conductivity can be rationalized. It is interesting that the anisotropy is so high (conductivity ratios up to 10^5) for samples that have not been stretched. This must come from the forces present during casting. One possibility is that the stacks which have a long axis along the stack direction, preferentially lie with this axis at the interface with the substrate or vapor, and that this induces anisotropy throughout the sample.

Using the oligomers **4** and **5**, we found the first examples of diimide films that were isotropic in the NIR, ESR, and in their conductivity. This must result because the covalent attachment of the imide groups in one molecule prevents anisotropic organization. Long stacks are necessarily intermolecular stacks, and we propose that the different imides of one oligomer molecule are often involved in different intermolecular stacks. The three diimide groups of trimer **4** could be involved in three different stacks. For steric and entropic reasons these three stacks are not easily organized to run in the same direction and, therefore, are not oriented anisotropically.

Loading. We have focused on a variation over the narrow range 2.5–10 wt % (less than 1 mol % of diimide to PVA repeat unit). Below this range insulating behavior is observed, and above this range there are only small increases in conductivity. Considering only fully reduced films (1 electron/diimide) the effects of loading on spectra and conductivity are straightforward. A higher concentration of anion radicals leads to higher conductivity and to a more intense ESR signal. It also leads to a more intense absolute and *relative* absorbance in the NIR-IR. These bands are due to excitation of electrons along stacks, the so-called optical conduction bands. It is expected and confirmed from solution studies that longer stacks will be favored in more concentrated films. As the stack length increases, the wavelength will increase toward a limiting value. For these diimide stacks the limit in a variety of circumstances seems to be around 3000 nm.[1,2,7] When there is strong absorbance in this region from homogeneous films, the conductivity is higher as expected.

Mixed Valence Stacks. Although mixed valence π-stacks dominate the literature of conducting molecular salts,[10] this is the first demonstration of such stacks from diimides. The improved conductivity of partially reduced films is evidence for mixed valence stack formation and the increased relative intensity of the NIR-IR absorption correlates with this conclusion. Mixed-valence diimide stacks from neutrals and anion radicals have not been observed in solution, and it may be necessary to form them in a solid matrix like that provided by PVA. The concentrations in the films are some 10 times higher than those used in solution studies, but it is important to realize that what is observed is enhanced NIR-IR and conductivity from the presence of neutral in a film containing a constant concentration of anion radical. For example, a film loaded with 5% anion radical conducts 20 times better when there is also 5% neutral present (see entries 2 and 4 for compound **2** in Table 2).

ESR. The observations are self-consistent. Oligomeric diimides give isotropic spectra and monomeric diimides give anisotropic spectra. Anisotropic spectra from diimide films have been previously analyzed[1] and are consistent with the proposition that the radicals are associated with stacks that lie preferentially in the film plane. The isotropic spectra from oligomers are the first examples and require some comment. An isotropic ESR signal requires that the spin be distributed isotropically on the ESR time scale. A randomly oriented collection of ESR active stacks that did not communicate with one

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(10) (a) J. R. Ferraro, J. M. Williams, *Introduction to Synthetic Electrical Conductor*; Academic press: New York, 1987.

another would give a powder pattern and not an isotropic spectrum. If, as we hypothesized above, the diimide groups on any one oligomeric molecule are involved in different stacks, oriented in different directions, spin transfer between stacks is quite reasonable and an isotropic spectrum would result.

Although the ESR signals are weak and may not be due to the same species that are responsible for the NIR or the conductivity, there are interesting relationships between all this data. In addition to the correlation of spectral and conductivity anisotropy or the lack of it is the correlation of ESR intensity (Table 3) and conductivity (Tables 1 and 2). Disregarding the inhomogeneous samples that are insulating, we find more intense ESR spectra for the more highly conducting samples. This includes both fully and partially reduced samples and both isotropic and anisotropic films. Since the species responsible for the ESR signal is undefined and the signal is always weak, structural interpretation is not possible. We do note that there is no evidence for triplets (fine structure or half field lines) that would arise from stacks with singlet ground states, and low-lying triplets.

Conclusions

The casting route to conducting thin films is now firmly established using PVA and aqueous solutions, each of which has desirable properties for applications. Stable, n-doped, free-standing films were produced with good mechanical properties.

All these films have π-stacks as the elementary conducting unit, and the intensity of the NIR-IR band was a good indication that long stacks were formed. The highest conductivity was obtained for mixed valence films. Monomeric diimides formed anisotropic films, with the stacks in the film plane (conductivity ratios up to 10^5), oligomers formed isotropic ones (conductivity ratio of 1).

Formation of a network of π-stacks is necessary for conductivity. There were no microcrystals in these films, so the network was not visually evident, but whenever particles of conductor were precipitated, the conductivity was lowered.

The combination of spectroscopy, microscopy, and conductivity measurements gave considerable insight into the structure and morphology of these materials. The correlations of NIR and ESR intensities with high conductivity are not unexpected but have seldom been enucleated in such a clear fashion.

Experimental Section

PVA, 100% hydrolyzed, MW = 115 000 (Aldrich Chemical), and sodium dithionite ($Na_2S_2O_4$) (Mallinckrodt) were used without further purification. The syntheses of compounds **1**−**5** are reported elsewhere.[7,8] They were improved by the use of DMF in place of DMA solvent, which is easier to remove, and by shortening the imidization reaction time at 110 °C. All the compounds had satisfactory IR and ^1H NMR spectra. They were analyzed by HPLC using a Waters Associates system with a UV detector (380 nm), a VYDAC TF 218 C18 reverse-phase column, 50% CH_3CN/H_2O as eluant, flow rate 0.4 mL/min. Compounds **1**−**4** gave single peaks. Oligomer mixture **5** gave five peaks. Spectrometers have been previously described[1,2] as have the methods and equipment used for conductivity measurements.[1] All these measurements were made in air at room temperature.

The spin coater was constructed from a 12 V dc brushless micro fan (Radio Shack No. 273-244). This fan was modified by removing the electronics and half of the magnet so that the fan could be controlled externally by placing it on the top of a hot plate/magnetic stirrer. The modified microfan was mounted onto a glass plate using two-sided mounting tape. A glass bell jar was placed over the glass plate to cover the microfan and sealed with vacuum grease. The top opening of the bell jar was stopped with a rubber septum. To keep the environment under an inert atmosphere, a needle connecting to a source of argon was inserted through the rubber septum into the bell jar. A gas trap was also connected to the sidearm of the bell jar to monitor the argon flow. The film-casting temperature was varied by changing the temperature of the hot plate/magnetic stirrer. A 0.1 mm glass microslide (Clay Adams gold seal cover glass) was attached to the fan to provide the film forming surface.

PVA solutions (4 wt %) were prepared by dissolving the proper amount of PVA in distilled water at 90 °C. A weighed amount of diimide was added and the solution was heated and stirred at the casting temperature (65 °C). In the meantime, the solution was purged with argon to remove oxygen. In another vial, a weighed amount of sodium dithionite corresponding to a 10% molar excess was prepared. The vial was closed with a rubber septum and deoxygenated with argon. The PVA solution was first added into the vial with an airtight syringe for reduction and then transferred to the microslide attached to the spin coater. The spin coater was preheated to 65 °C and purged with argon for 30 min before film casting. During casting, a constant flow of argon was maintained to help evaporate the solvent. The speed of the spin coater was maintained at about 200 rpm. In general, 30−40 min is required to form circular shaped thin films of 1.5 cm diameter and thickness of 20−30 μm. These flexible films were peeled off from the glass substrate for further investigation.

Conductivity measurements[1] were made by embedding Ag wires into the surface of the film using silver paste to make contact. Two-probe measurements were used for the film conductivity. The contact resistance was corrected in the reported data. The contact resistance was calculated by subtracting the two-probe and the four-probe in-plane conductivity. And we assume the contact resistant is the same for both in-plane and cross-plane measurements. The validity of the method is confirmed since two-probe measurements on isotropic films yielded the same value for both in-plane and cross-plane conductivities.

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