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Electrically Conducting Dendrimers

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Abstract: Generations 1–5 of poly(amidoamine) (PAMAM) dendrimers were peripherally modified with cationically substituted naphthalene diimides. Reduction with sodium dithionite in water or formamide formed anion radicals on the diimide moieties. Evaporation of water under argon produced powders of the reduced dendrimers that were electrically conductive. Using formamide as solvent, films were cast of reduced generation-3 modified dendrimers. Fully reduced films (1.1 e/diimide) gave conductivities under ambient conditions of about 10^{-3} S/cm. Films formed from these dendrimers that were half-reduced (0.55 e/diimide) gave $\sigma = 10^{-2}$ S/cm. Near-infrared (NIR) spectra on the films showed the formation of π -stacks with maximum absorbance beyond 2000 nm. The wavelength and intensity of this absorbance correlated with the conductivity. The conductivity increased with increased humidity above the films reaching values as high as 18 S/cm at 90% relative humidity. The conductivity was in all cases electronic and isotropic. The conductivity–humidity effect was probed by NIR spectroscopy, X-ray powder diffraction, and quartz crystal microbalance measurements. These studies suggest that the amorphous films absorb water from the air and at high humidity they are plasticized, allowing faster stack-to-stack electron hopping and increased conductivity.

Introduction

Dendrimers, like conventional polymers, are built from smaller repeating subunits, but instead of forming linear chains, the subunits branch out in a well-defined pattern from a central point. Through either divergent or convergent syntheses, dendrimers can be made with high regularity and controlled molecular weight.¹ The nonlinear and accurately controlled covalent structure of these polymers has spurred a wide range of studies.² Only recently, however, have dendrimers been examined with an eye toward materials chemistry. The present paper expands upon previously communicated results³ concerning the first examples of electrically conducting dendrimers.

Most organic conductors are understood as one-dimensional conductors because the electrons (or holes) mainly travel through conjugated chains or stacks of π -conjugated molecules.⁴ We felt that the three-dimensional structure of dendrimers might lead to quite different structures and electrical properties. Interest in 3-D structures is emphasized by the results reported for C₆₀.⁵ This fullerene, reduced to the trianion stage, forms electrically conducting films which have the highest T_c of any molecular material. It has been proposed that this results in

part from the three-dimensional nature of its molecular structure. Dendrimers have flexible molecular structures and cannot be thought of in the same way as fullerenes. It seemed clear, however, that the three-dimensional scaffold of the dendrimers would exert some control over the structure and morphology of these materials and we hoped that this would lead to interesting new properties and, conversely, lead to some new insight into dendrimer structures.

The specific materials of interest here involve diimide anion radicals as the conducting moieties. Previous studies from this laboratory have shown that these anion radicals aggregate into π -stacks in solution⁶ and solids and form electrically conducting films.⁷ Of particular pertinence to the present work are films produced by co-electrodeposition of a diimide anion radical and the polycation poly(diallyldimethylammonium).^{7a} These films have a highly anisotropic conductivity, which increases with increased humidity above the film. Measured at 90% relative humidity (RH) at room temperature, conductivity in the film plane was 10^{-1} S/cm; across the film plane, $\sigma = 5 \times 10^{-8}$ S/cm. Anisotropic conducting films have also been formed by imbedding the diimide anion radicals in poly(vinyl alcohol).^{7b} In both cases near-infrared (NIR) spectroscopy was used to understand the structure and conductivity mechanism.

We have reported on the synthesis and characterization of the diimide modified dendrimers⁸ which are the subject of the present study. Well-characterized poly(amidoamine) (PAMAM) dendrimers were modified with cationically substituted diimide groups, chosen to enhance the water solubility of the products. These modified dendrimers were characterized and shown to be highly loaded (>65% in all cases) with diimides. It was

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also shown that reduction in water or formamide solution with dithionite produces dendrimeric poly(anion radicals) in which each diimide group had taken up one electron. The reduced dendrimers were characterized by optical spectroscopy, electrochemistry, and ESR. Importantly, the anion radical moieties are stable in these solvents in the absence of oxygen. In degassed formamide stability is complete even at 120 °C for several hours.

To our knowledge the only other study of conducting dendrimers is one in which dendritic polyesters were prepared with two, four, or eight TTF units.⁹ Conductive charge transfer salts with $\sigma = 2 \times 10^{-3}$ S/cm were precipitated as powders by addition of TCNQ.

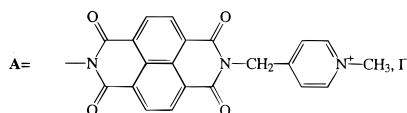
The present study provides thin film materials with humidity dependent conductivities as high as 18 S/cm. This value is the highest reported for an air-stable n-doped polymer. Previously examples of air-unstable n-doped polymers are polyacetylene reduced with sodium naphthalide (film, $\sigma = 80$ S/cm),¹⁰ polypyridine reduced with sodium naphthalide (powder, $\sigma = 0.1$ S/cm),¹¹ and a film of electrochemically polymerized, cathodically reduced dithienylvinylene (bathed in acetonitrile, tetraethylammonium perchlorate solution, $\sigma = 2$ S/cm).¹²

Results

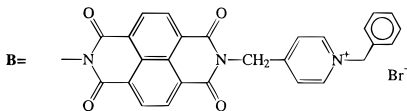
Ammonia core, poly(amidoamine) (PAMAM) dendrimers, generations 1–5, were modified with diimide **A** yielding **D-A**

D = generation 1–5 PAMAM dendrimers, NH₃ Core.

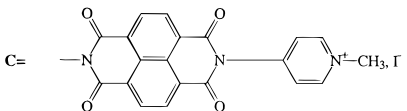
D—A



D—B

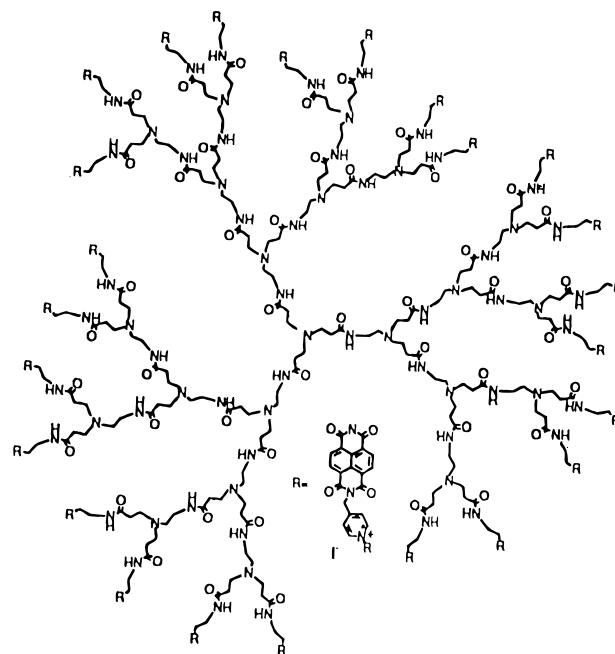


D—C



as previously reported.⁸ The generation-3 dendrimer (**D3**), which is terminated with 24 amine groups, was modified with three different diimide groups, yielding **D3-A**, **D3-B**, and **D3-C**. Diaminoethane core, generation-3 PAMAM (36 terminal amines) was similarly modified producing **D3-A**.

Initial attempts to cast films utilized the dendrimers **D-A** in aqueous solution, reduced with 1.1 equiv of sodium dithionite. Using various temperatures and concentrations it proved impossible to form homogeneous and coherent films. The precipitated powders formed by evaporation of water at room temperature under flowing argon were, however, collected and pressed into pellets. Four probe conductivity measurements were performed



D3-A

at room temperature. The conductivity of **D1-A** was below 10^{-7} S/cm. **D2-A** gave $\sigma = 1 \times 10^{-4}$ S/cm. The conductivities of **D3-A**, **D4-A**, and **D5-A** were about 7×10^{-4} S/cm.

In a search for a polar solvent more suitable for film casting, formamide was discovered to have useful properties. The reduced dendrimers are more soluble and the diimide anion radicals attached to the dendrimers aggregated into π -dimers and π -stacks in this solvent.⁸ **D3-A** exhibited better solubility and better film forming properties than other **D-A** generations and it was chosen for extensive study. An apparatus appropriate for casting films from formamide was constructed, which allowed control of the temperature and kept the sample under flowing argon during film casting. The dendrimers, reduced with 1.1 equiv of sodium dithionite, gave dark brown films on glass slides. These films were rather brittle and were not removed from the glass.

Optical spectra were recorded for **D3-A** films.³ Films cast at 120 °C showed an intense NIR peak at 1140 nm, assigned from previous studies to a π -dimer of two anion radicals coming together face-to-face.⁶ Casting at 60 °C gave rise to a 2300-nm absorption with a weaker π -dimer peak. The longer wavelength absorption is characteristic of excitation of conduction electrons along π -stacks.^{6,13} When 0.55 equiv of dithionite (0.55 e/imide) was used for reduction, the π -dimer peak was even weaker and the π -stack absorption was shifted to the IR region with maximum at 3000 nm. The IR spectra also showed imide carbonyl bands at 1640 and 1527 cm^{-1} . These are typical for naphthalene diimide anion radicals.⁶ The bands are shifted compared to the neutral diimide, which has carbonyl bands at 1716 and 1670 cm^{-1} . Visible spectra of these films showed a peak at 450 nm, consistent with previous solution studies on these compounds and other imide derivatives.⁶

D3-B films were cast from formamide at 60 °C. The solubility of both neutral and reduced forms of **D3-B** is better than for **D3-A** and this resulted in more homogeneous films. Films formed on a silicon-coated paper substrate could be bent 30° above or below the film plane without any noticeable crack

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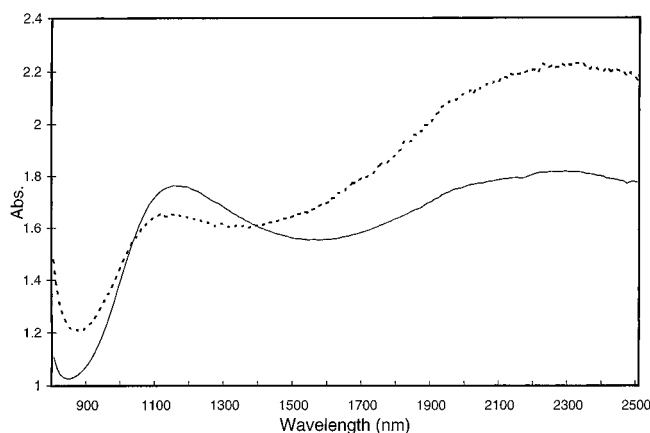


Figure 1. NIR of **D3-B** films cast at 60°C: 1.1 e/imide reduced (solid line) and 0.55 e/imide (dashed line).

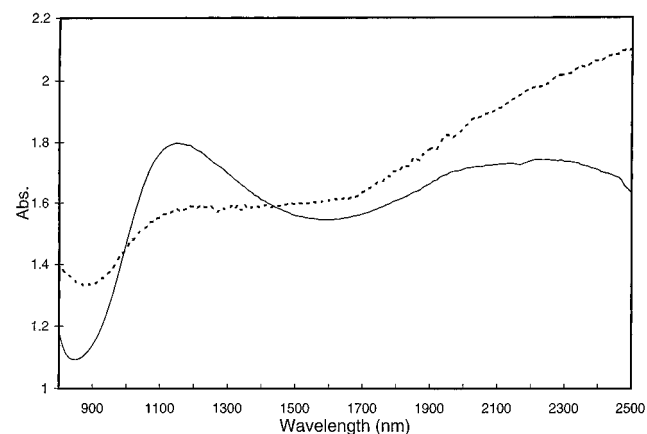


Figure 2. NIR of **D3-A** films cast at 60°C: 1.1 e/imide reduced (solid line) and 0.55 e/imide (dashed line).

lines, and using a sharp blade, films could be removed from the substrate providing flexible, freestanding films. Fully reduced films showed NIR peaks at 1140 and 2200 nm (Figure 1). Using 0.55 e/imide, half-reduced films showed a small peak at 1140 nm and major absorption at 2200 nm.

D3-C was of interest because when reduced, it showed somewhat longer NIR absorption in solution. Unfortunately, it precipitated too rapidly upon reduction in formamide and we were not able to cast films. A NIR spectrum of the solid was measured by coating the powder onto a glass slide. A fully reduced sample showed a small peak at 1140 nm, while in a half-reduced sample, the 1140-nm peak has completely disappeared in favor of a longer wavelength (>2200 nm) band. Pressed powder conductivities were 4×10^{-3} and 6×10^{-2} S/cm for fully reduced and half-reduced samples, respectively, slightly higher than for powders of **D-A**.

D3-A films (ethylenediamine core) were similarly cast at 60 °C from formamide. NIR on fully reduced films showed a peak at 1140 nm and a relatively large absorption peak at 2300 nm extending into the IR region (Figure 2). For half-reduced films, the 1140-nm peak appears as a shoulder in the spectrum with the main absorption peak at 3000 nm.

Four-probe conductivity measurements were made on **D3-A**, **D3-B**, and **D3-A** films at about 25% relative humidity (RH) at room temperature (Table 1). The in-plane conductivities were generally higher for films cast at 60 °C, not 120 °C, and for films reduced with 0.55 e/imide, not 1.1 e/imide. The values ranged from 2×10^{-3} to 5×10^{-2} S/cm. The conductivities were ohmic, and there was no evidence for depletion or polarization when current was passed for several hours and then

Table 1. Dendrimer Films Conductivity (S/cm)

	1.1 e/imide 25% RH	0.5 e/imide 25% RH	1.1 e/imide 90% RH	0.5 e/imide 90% RH
D3-A	1.2×10^{-3}	4.7×10^{-2}	0.12	11
D3-B	1.7×10^{-3}	5.0×10^{-2}	0.08	15
D3-C	1.9×10^{-3}	4.2×10^{-2}	0.11	18

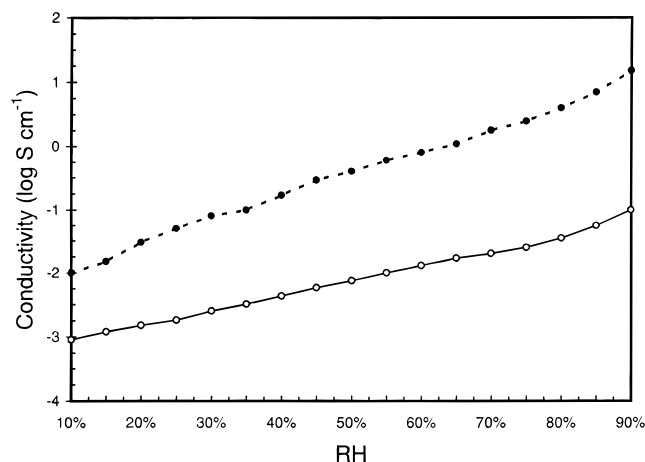


Figure 3. Conductivity vs relative humidity of **D3-B** films: 1.1 e/imide reduced (solid line) and 0.55 e/imide (dashed line).

switched. The values were stable for samples stored in air for several weeks. Conductivity for a sample film placed between two glass plates and sealed with epoxy was stable for several months. Two probes were used to measure in-plane and cross-plane conductivities across the same distance and gave identical values. Alternatively two-probe, across-the-film measurements were compared to four-probe measurements along the film, which were corrected for the contact resistance. Again, the values were the same indicating isotropic conductivity.

Films of **D3-A**, **D3-B**, and **D3-A** exhibited enhanced conductivity when placed in a humid atmosphere. Using controlled humidity argon the change was shown to be reversible and about two orders of magnitude between 10 and 90% (RH). At 90% RH, fully reduced **D3-A**, **D3-B**, and **D3-A** have conductivity values (Table 1) of about 0.1 S/cm. Half-reduced samples have conductivities of about 10 S/cm. At 100% RH (rain), a half-reduced **D3-B** film showed $\sigma = 25$ S/cm. The conductivity was always ohmic and no evidence for polarization was observed even at extreme humidity levels. The values are repeatable (within 2%) through several 10–90% RH reversible cycles before the films develop crack lines. After that, conductivity drops dramatically. Plots of conductivity vs RH (Figure 3) reveal that between 15 and 65% RH the conductivity increase is almost linear with changes of less than one order of magnitude. A more rapid change is observed above 65% RH. In all our tests, conductivities responded quickly to changes in humidity (Figure 4). Specifically, it took less than 5 min for the conductivity to reach its steady state value when RH was increased from 30% to 40% RH.

In order to assess the effect of humidity on structure, one side of a 1-cm quartz cell was coated with a **D3-A** film. A NIR spectrum was taken after the closed cell was dried and held under argon for 24 h. Another NIR was taken after the cell was filled with water-saturated argon for 2 h. The base line of the wet film shifted up about 10% but there was no change in the shape of the spectrum.

A wide-angle X-ray diffraction instrument was fitted with a homemade device to control the humidity above the sample being analyzed. Data were recorded on both dry and wet films.

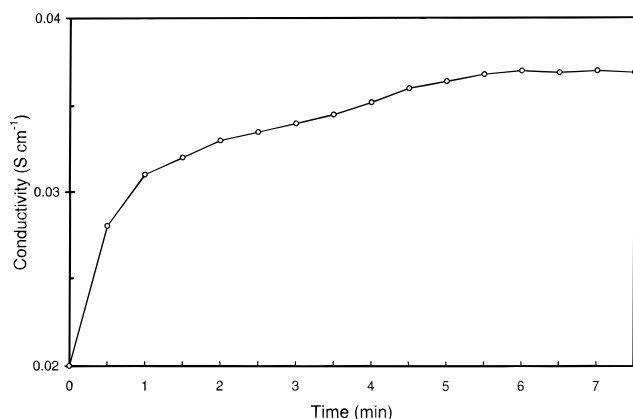


Figure 4. Conductivity vs time for **D3-B**. Relative humidity stepped from 30% to 40% at $t = 0$.

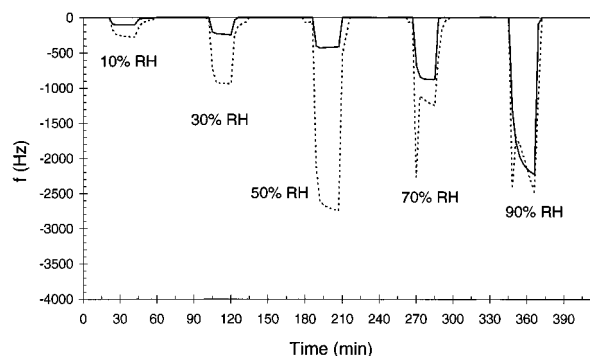


Figure 5. **D3-A** films QCM frequency response to relative humidity: neutral (solid line); reduced (dashed line).

In both cases, the films gave only a broad peak corresponding to expectations for an amorphous film without crystalline structure.

The quartz crystal microbalance was used to study film hydration. **D3-A** and **D3-B** in both neutral and reduced forms were coated on calibrated 9-MHz quartz crystals. Samples were mounted in a stainless steel box. The humidity was varied between 10 and 90% in 10% increments. Twenty minutes were given to each humidity level to allow the film to reach equilibrium. Another 20 min of purging with dry nitrogen allowed films to dehydrate. After dehydration they were brought up to the next humidity level. Consider first the data (Figure 5) for unreduced **D3-A** and **D3-B**. Change in the RH led to a rapid decrease in the frequency due to the absorption of water by the film, then a relatively constant frequency indicating equilibration was complete. After each dehydration the frequency returned to its original value. Using the Sauerbrey equation¹⁴ the weight of the absorbed water was calculated from the frequency. In Figure 6 the weight is plotted as a function of RH. Above 60% RH the weight of water increases rapidly, reaching 37% and 47% of the dry film weight at 90% RH for **D3-A** and **D3-B**, respectively.

The reduced films behave the same up to 60% RH except that, comparing the same initial weight of film, the reduced films take up more water. For example, at 50% RH unreduced **D3-A** takes up 10% of its original weight, and reduced **D3-A** takes up 26%. Above 60% RH the experimental curves for the reduced dendrimers (Figure 5) are irregular. When the humidity is turned on, the frequency decreases as expected, then rises and drops again as time passes. Clearly, major changes in the film structure are occurring and one cannot use these data to weigh the absorbed water.

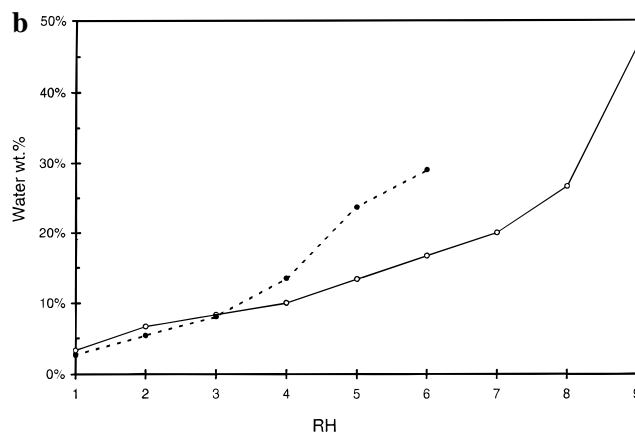
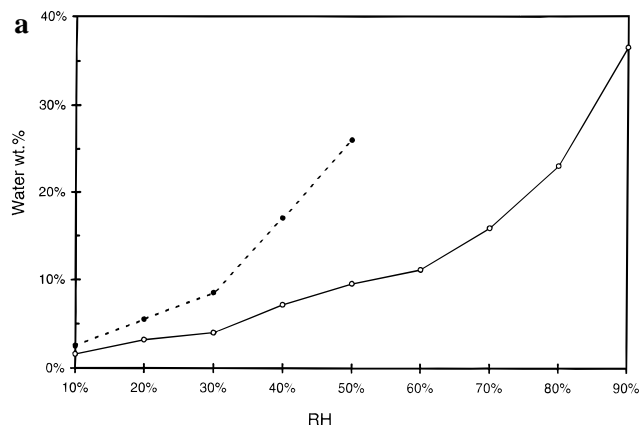


Figure 6. Weight percent water in films held at different relative humidity: neutral (solid line), reduced (dashed line); (a) **D3-A**, (b) **D3-B**.

Discussion

These films constitute the first examples of electrically conducting dendrimers and one of the few examples of dendrimers used for materials chemistry. The results are interesting in the context of dendrimer structure and in the context of conducting polymers. As noted above, n-doped conducting polymers are not air stable and only a few reliable conductivity values have been reported. The values, >10 S/cm, reported here for hydrated, mixed valence films are reasonably high and suggest that further structural development may give conductivities as high as more traditional oxidized (p-doped) conjugated polymers like polythiophenes or poly(phenylenevinylene). In terms of structure and morphology the dendrimer films are, of course, quite different from typical conducting polymers, which have long conjugated chains and improved conductivity for oriented, partially crystalline samples. Dendrimer films rely on π -stack interactions, they are amorphous, and improved conductivity is achieved by hydration, a process which seems (see below) to involve plasticization. Therefore, in addition to their intrinsic importance these new materials introduce some new perspectives on conducting materials.

On the negative side we found it difficult to form high-quality thin films. Even with the good fortune of developing formamide as a casting solvent only a few of the dendrimers gave good films. In only one case, **D3-B**, could a reduced film be used as a free-standing film. This poor film-forming quality results, in part, because the modified, reduced dendrimers are salts, and, perhaps in part, because there is little interpenetration of the chains of neighboring dendrimer molecules. It should be quite feasible, of course, to use other modifying groups and other dendrimer structures to improve on this situation.

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Insight into the structure and conductivity of these materials can be best made by comparison with other diimide anion radical conductors.^{6,7} Previous studies of reduced diimides as pure salts, as salts imbedded in PVA, or as electroprecipitated diimide/polycation films demonstrated that the conducting films contained π -stacks of anion radicals oriented in the film plane. This was reflected in the anisotropy of the conductivity and NIR spectra. Here also the data demonstrate a relationship between structure, NIR spectra, and conductivity. All the conducting films had very long wavelength absorption bands in the NIR/IR. These bands are characteristic of conductors and in this case the wavelength is qualitatively characteristic of the delocalization length along π -stacks. Comparison of dendrimer films with the other diimide anion radical films demonstrates that covalent attachment of the anion radicals to the dendrimer scaffold did not inhibit stack formation.

On a larger scale the relatively high conductivity values demand that these stacks be organized into a conducting network. This requires interaction between the diimides on neighboring dendrimer molecules. Since the conductivity values for the dry dendrimer films are as high as those for pure diimide anion radical films, it indicates that this intermolecular interaction and network formation is effective even though much of the mass is PAMAM, not conductor. In contrast to films formed using small diimide molecules these films are isotropic in their structure and conductivity. It means that the 3-dimensional structure of the dendrimer led to a 3-dimensional network.

The relationship between structure, NIR spectra, and conductivity is also demonstrated for partially reduced films. In solution no evidence has been found for mixed valence (neutral plus anion radical) stacks. In these films, however, partially reduced films show increased NIR/IR absorbance (more intense and longer wavelength) and higher electrical conductivity. Higher conductivity for mixed-valence π -stack materials is commonly observed and theoretically predicted.⁴ Indeed, we cannot rule out the possibility that even in our "fully reduced" materials, there are some neutral diimide moieties which contribute to formation of highly reduced, but mixed stacks.

The humidity/conductivity phenomenon is of obvious interest because the effect on conductivity is quite large and because we believe these are electronic, not ionic conductors. The measurements reported above demonstrate that the films hydrate rapidly and reversibly and this absorption of water is responsible for the increased conductivity. This hydration would be expected to enhance ionic conductivity and, although some ionic conductivity cannot be ruled out, we find no evidence for this effect. It is not probable that ionic conductivity would be high enough to contribute significantly with the high levels of electronic conductivity. Since the dendrimer is so large, inorganic ions, sodium or iodide, associated with the reduced dendrimer as counterions are the species most likely to carry ionic current. If they do migrate, the concentrations of these ions would become polarized, and depleted by electrolysis at the electrodes, and show the usual effects of ionic conductivity. These are not observed. It is postulated, therefore, that absorbed water somehow improves the electronic conductivity. Since the NIR spectra do not change very much with hydration and there is no evidence for crystallization in the hydrated films, we conclude that the water enhances charge transport between stacks in this amorphous material.

The quartz crystal microbalance measurements are extremely interesting in this regard. The data on unreduced films show that considerable amounts of water are absorbed. It is known that the PAMAM core is hydrophilic, but the pyridinium iodide salt moieties can be involved in this phenomenon as well. The

reduced films take up even more water, presumably because they are more ionic. In the low RH range, the films appear to be sufficiently rigid so that the Sauerbrey equation¹⁴ can be used to estimate the water uptake, but at high humidity the QCM measurements indicate that a more complicated phenomenon is occurring. It is easy to observe that the films become much less brittle and somewhat sticky when the room humidity is high and it seems likely that hydration plasticizes the materials leading to a viscoelastic film. It is known that such a material does not respond to the vibration of the quartz crystal as a rigid body.^{14,15} The experimental observations (Figure 5) can then be explained as follows. When the humidity is turned on the QCM frequency decreases as water is absorbed, but sufficient water leads to a phase change to the viscoelastic phase. This loss of rigidity causes the frequency to increase, followed eventually by a further frequency decrease due to the absorption of more water.

It is this new, viscoelastic phase that leads to the highest conductivity values for both fully reduced and partially reduced films. The correlation of the change in phase with the change in conductivity above 60% suggests that the phase change is responsible for the conductivity change. Since there is no evidence that hydrated films have different stack structures we suggest that the increase in conductivity results from the increased mobility of stacks in the highly hydrated films. Many studies of redox polymers which conduct by electron (and counter ion) hopping from one redox site to a neighboring site have shown that solvating the polymer film increases the hopping rate and it has been suggested that the mobility of the species in the polymer is important in this phenomenon. It could of course be true that the barrier to inter-stack hopping could also be lowered by solvation of the ions involved.

Our results are interesting in the field of conducting polymers because conjugated chain conducting polymers usually give higher conductivity from more organization.¹⁶ One interesting example of the effects of solvation on conductivity has been reported by Murray and co-workers for films of the ladder polymer poly(benzimidazobenzophenanthroline).¹⁷ As a dry film this polymer has electronic conductivity of 0.2 S/cm. Wetted with acetonitrile the conductivity is ionic and smaller (10^{-5} – 10^{-3} S/cm). This counter example shows that swelling of a conducting polymer film with solvent can actually decrease the electronic conductivity to a level at which ionic conduction dominates.

Increased conductivity from increased humidity was previously reported for polyaniline and for a black powder obtained from the anodic oxidation of thionaphtheneindole.¹⁸ In the latter case it was shown that the conductivity increased from about 10^{-5} to 7×10^{-4} S/cm at 85% RH. The majority of the conductivity increase occurred between 40% and 80% RH. The time response of these powders was on the order of ten hours, much slower than the dendrimer films, which have a response time comparable to a commercial PACER hygrometer.

Finally, we turn to the dependence of conductivity on structure. For the set **D-A**, **D-B**, **D-C**, all stacked similarly and gave similar conductivities. Although we thought that the larger dendrimers might force the diimide groups into closer proximity, there is also little difference between the packed powder

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conductivities of **D2-A**–**D5-A**. **D1-A**, which has only 6 diimide groups, is a much worse conductor, but the 96 diimides on **D5-A** offer no advantage compared to the 12 on **D2-A**. We postulate that only short π -stacks are formed on any dendrimer, so the conducting network is similar for all the cases studied. It is clearly true on the other hand that there is sufficient flexibility in the PAMAM core to allow π -stack interactions both intra- and intermolecularly.

In conclusion we have developed the first examples of a new class of conducting polymers. The structure and conductivity can be understood to a certain extent in terms of π -stacks, the 3-dimensional nature of dendrimers, and the hygroscopic nature of the material. A number of interesting experiments are envisaged in future work.

Experimental Section

Materials. The syntheses of the modified dendrimers have been reported elsewhere.⁸ Sodium dithionite ($\text{Na}_2\text{S}_2\text{O}_4$) was used without further purification. UV studies showed that a 10% excess was needed to ensure complete reduction.

Film Casting. A digital controlled temperature hot plate (Mirak Thermolyne) was used for film casting. A microslide (Clay Adams gold seal cover glass) which provided the film-forming surface was placed onto a glass plate. The glass plate was covered with a glass bell jar and sealed with vacuum grease. The top opening of the bell jar was closed with a rubber septum. Two needles allowing a flow of high purified argon were inserted through the rubber septum into the bell jar. A gas trap was connected to the side arm of the bell jar to monitor. Film casting temperature was varied by changing the temperature of the hot plate placed directly under the bell jar.

Solutions of modified dendrimer (10 wt %) were prepared by dissolving the proper amount of compound in formamide (Aldrich Chemicals, 99+% grade). The solution was heated at the casting

temperature and was purged with argon to remove oxygen. In another vial, a weighed amount of sodium dithionite was prepared. The vial was closed with a rubber septum and deoxygenated with argon. The solution was first added into the vial with an air-tight syringe for reduction, and then transferred onto the microslide. Depending on the casting temperature, 2 to 6 h were required to form a dark brown colored film with a thickness of 3 to 5 μm . For samples that do not form films, the dried powder was collected from the glass slides and pressed into a pellet for further studies.

Vis and NIR spectra were taken directly on the films formed on the microslides. A reference spectrum with just the microslide was obtained to correct the base line. All of the Vis and NIR data were collected with a computer-controlled Cary 17 spectrometer at room temperature. Samples for IR measurements were prepared by coating the films onto a slice of silicon wafer.

Conductivity measurements were performed with a standard 4-probe method. Four silver wires (Ted Peller) were parallel attached to the surface of the sample with silver paste. The sample was held in a bell jar equipped with a PACER hygrometer model DH200/300 humidity sensor. One stream of argon is allowed to pass through a distilled water bath and then combined with a stream of dry argon before introduction into the bell jar. The humidity was controlled by varying the ratio of the two argon streams. To record the conductivity number at a specific humidity, the humidity was maintained for 5 min before the conductivity reading was recorded.

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