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An Electrically Conducting Dendrimer

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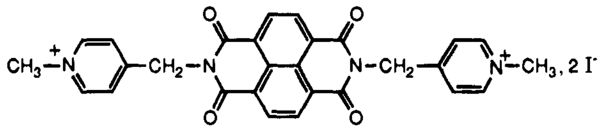
We report the first example of a dendrimer that is electrically conducting. The conducting film was formed from a poly(amidoamine) (PAMAM) dendrimer that had been modified on its periphery with naphthalene diimide anion radicals. These anion radicals, aggregated into a π-stacked network, provide the pathway for conductivity.

Because conducting polymers typically have conjugated main chains,[1] and because dendrimers are a relatively new class of polymers,[2] it is not surprising that this is the first example of a conducting dendrimer. On the other hand, we must comment on the paucity of examples of well-characterized conducting polymers formed from any polymer with redox groups attached to a nonconjugated main chain.[3] The present investigation has its origins in previous studies that established that diimide anion radicals like $\mathbf{1}^-$ (made water soluble with the pyridinium groups) aggregate into π-stacks in aqueous solution[4] and form stable conducting polymer films when embedded in PVA or a cationic polymer.[5] These materials are interesting because they are *n*-doped and yet do not oxidize in dry air, and because they have an anisotropic structure, with the stacks lying preferentially in the plane of the thin films.

PAMAM dendrimers were chosen for their water solubility and synthetic accessibility. These modified dendrimers are not defect free, but they have a very narrow molecular weight range.[2e] We have reported the peripheral modification of generations 1−6 with ionic diimide groups, forming a set of polymers exemplified by **G3**.[6] We have also reported chemical and electrochemical reduction of the diimide groups to form poly(anion radicals) in solution. We were able to achieve high loading with anion radical units and show spectroscopically that anion radical π-stacking occurred in aqueous solution. Here we take advantage of the aggregation phenomenon to form a three-dimensional network that leads to the observed bulk conductivity.



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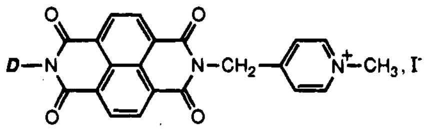

G3 (*D* = PAMAM dendrimer)

Initial studies using several generations of the previously reported dendrimers[6] showed that generation 3 (**G3**) had better film-forming properties than the other modified, unreduced dendrimer generations, and it was thus chosen for study. As analyzed by visible spectroscopy, the samples were $>70\%$ loaded (there is some associated water). Coulometric analysis gave $>80\%$ loading. Reduced **G3** ($\mathbf{G3}^-$) was formed with a 10% molar excess of $Na_2S_2O_4$ to give anion radicals on each diimide group. This solution was syringed onto a heated glass slide or silicon wafer (for IR) held under a flowing atmosphere of argon in a modified bell jar. Dark brown films, 3−5 μm thick, resulted after a few hours at the chosen casting temperature. When water was used as the casting solvent, the film quality was poor, and the conductivity was $<10^{-4}$ S cm^{-1}. Speculating that this was due to premature precipitation of the polymer,[5,7] we turned to formamide as an alternative, very polar solvent that would be favorable for forming stacks. Reduction with $Na_2S_2O_4$ went smoothly in formamide, as evidenced by the optical spectra of the solutions (near-IR $\lambda_{max} = 1200$ nm), and the resulting films were more homogeneous.

Standard four-probe conductivity measurements were made in the film plane at room temperature in the laboratory atmosphere. All of the conductivities were ohmic, there is no evidence of polarization on switching the current direction, and the conductivity values remained constant for several hours. This demonstrates that the conductivity is electronic, not ionic. (Note that there is sodium iodide in the films.) Films cast at 60 °C had $\sigma = 2 \times 10^{-3}$ S cm^{-1}, 10 times higher than the values for those cast at 120 °C. We suggest that stacking is improved at the lower temperature without significant detriment to the solubility and film homogeneity. For films reduced with 0.55 e/imide and cast at 60 °C, the conductivities are even higher, 6×10^{-2} S cm^{-1}. This strongly suggests mixed valence stacks.[8,9] When two-probe measurements, corrected for contact resistance, were employed for cross-plane conductivity measurements, the films exhibited isotropic conductivity. This contrasts with the anisotropic character of previously formed films using monomeric anion radicals like $\mathbf{1}^-$.

Vis−near-IR spectra of cast films were interpreted by comparison with solution spectra of monomeric diimide anion radicals, i.e., $\mathbf{1}^-$, that aggregate in water.[4,6] It has been shown that π-dimers of these anion radicals absorb at 1140 nm, and conducting π-stacks absorb at longer wavelengths in the near-IR or even IR. Figure 1 shows spectra of $\mathbf{G3}^-$ films cast from

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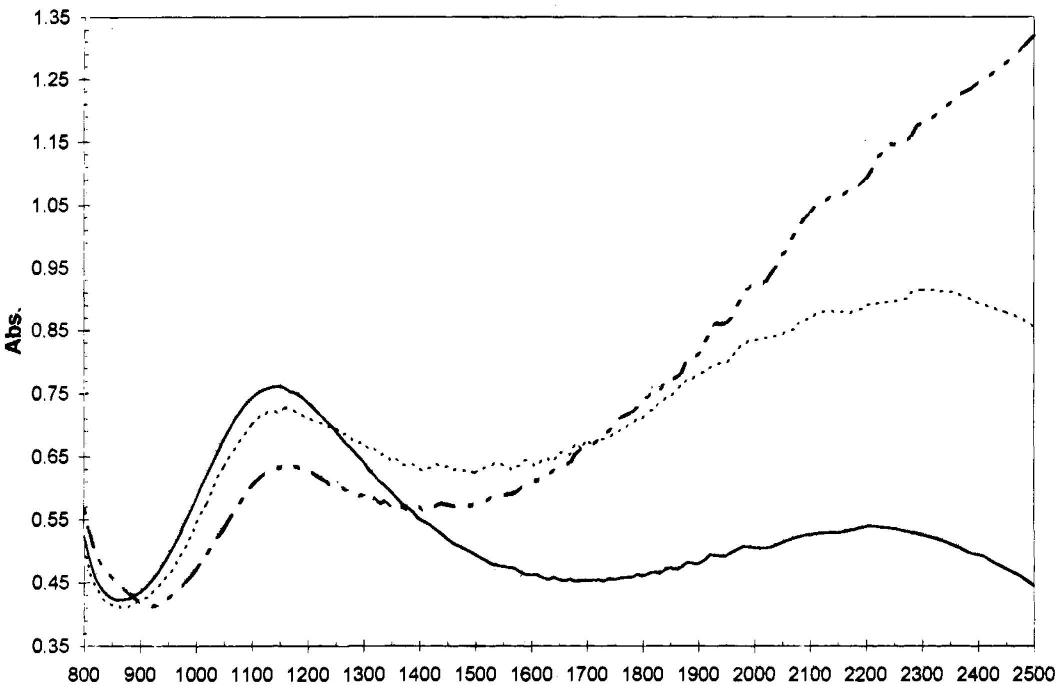

Figure 1. Near-IR spectra of films of **G3**$^-$. Fully reduced film cast at 120 °C (solid line) and at 60 °C (thin dashed line); partially reduced film cast at 60 °C (thick dashed line).

formamide solution. Cast at 120 °C, the film has only a small absorbance near 2200 nm. At 60 °C, π-aggregation is enhanced, and a more intense π-stack peak is present. Using only 0.55 equiv of reducing agent diminished the π-dimer peak and increased the π-stack absorption. The λ_{max} was now in the IR region near 3000 nm. This shift in the optical conduction band is consistent with formation of mixed valence stacks containing both neutral diimide and anion radical diimide moieties. The IR spectrum also showed imide carbonyl bands at 1640 and 1527 cm^{-1}, which are typical for these aggregated anion radicals. Visible spectra of the films showed λ_{max} near 450 nm, as expected.[4]

It was noticed that breathing on the films immediately increased the conductivity. Humidity-dependent conductivity was previously reported for diimide/polycation films,[5b] so it was hypothesized that this effect resulted from the moisture in exhaled air. The effect was documented (Figure 2) using a controlled humidity device. The conductivity, which was still electronic, not ionic, responded quickly and reversibly to the humidity change. High humidity increased fully reduced film conductivities to 0.12 S cm^{-1} and increased partially reduced film conductivities to values as high as 11 S cm^{-1}.

This conductivity is actually higher than the conductivities reported for pure diimide anion radical salts[4] or those with ion radicals embedded in polymers[5b,7,9] and is only slightly lower than the conductivities of many conjugated chain polymers, like polypyrrole.[1] Because dendrimeric structures may produce π-stack formation in three dimensions, a structural feature different from the usual 1-D structures of small molecule stacks, but reminiscent of fullerene structures, the isotropic nature of these dendrimer films is of particular interest. Future studies will develop the material properties and further investigate the structure and conductivity of these unusual films.

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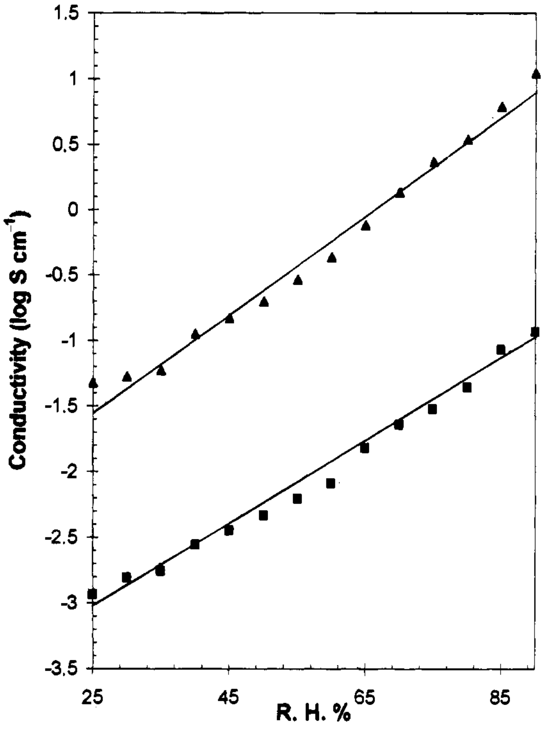

Figure 2. Humidity dependence of the conductivity. Fully reduced film (■) and partially reduced film (▲).

Supporting Information Available: Procedure for the preparation and characterization of **G3**, as well as the method for film casting (3 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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