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Organic vapors, organic polymers and electrical conductivity

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ABSTRACT: Recent studies have shown that the electrical conductivity of certain organic polymer films change when the films are exposed to organic vapors. Here, results using polymers that conduct via redox hopping and conjugated polymers such as polyaniline are emphasized. In these cases extremely large vapor-induced increases in conductivity, up to a factor of 10^6, have been measured. These vapoconductivity effects result in part from morphological changes, especially plasticization. The results are of interest for the development of sensors. Copyright © 2000 John Wiley & Sons, Ltd.

KEYWORDS: organic vapors; organic polymers; electrical conductivity; sensors

INTRODUCTION

Electrical conductivity has been a major focus of work on organic materials chemistry. The discovery of highly conducting organic polymers, such as polyacetylene oxidized with iodine, spurred interest in the general subject of electrical conductivity in polymers, and led to an extensive literature on conjugated, oxidized polymers. This has led in turn to a number of studies on the effects of vapors on polymer conductivity. In this paper we give some background information on the materials and the mechanisms of conductivity and then describe experimental results. We emphasize studies of redox and conjugated-chain polymer films because that has been the focus of our research work. Although physical organic chemistry will provide our perspective, a driving force for much of the activity in this area is vapor sensors and we briefly address these applications as well.

Molecular Conductivity

Of interest here are molecular solids.[1] This world can be divided into ionic conductors in which ions must diffuse to the two electrodes where they are oxidized and reduced, and electronic conductors in which electrons (or holes) move through the sample to the electrodes. Chemists usually imagine electronic conductivity in terms of electrons moving through the solid by jumping from molecule to molecule. Physicists expand this idea to include positively charged holes, denoting the absence of an electron, but the idea is the same. If electrons are not delocalized intermolecularly, then the electron must, indeed, hop from molecule to molecule through the sample. Hopping is an activated process analogous to solution-phase single-electron transfer so widely studied by chemists. If, however, there is delocalization between molecules then the solid has a band structure and the electron can move more freely. A single-crystal metal has a band structure that allows electrons to move from one electrical contact through the crystal to the other contact without hopping.

The situation for conducting polymers is seldom simple. Consider first the case in which electron hopping is involved. An example of such a material is a mixture of a cation radical and a neutral molecule dispersed in a polymer matrix. Conductivity involves electron hopping from neutral to cation radical. It is common, however, that such species form stacked, mixed valence aggregates. This aggregation can form single crystals with delocalization of electrons along the stacks. Clearly, such aggregation is an important phenomenon in polymers, a phenomenon that will affect the observed conductivity behavior.

More widely studied are oxidized, conjugated-chain polymers, such as polyacetylene or polythiophene oxidized with iodine. These polymers have electrons delocalized along segments of their chains and may also have electrons delocalized between chains. Highly conductive polymers have metallic properties, but typically these materials are semiconductors. They have

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conductivities less than that of metals and the conductivity increases with increasing temperature. Of particular importance here are considerations of electron transfer between chains or between domains of the solid. These processes are usually relatively slow, so they limit the rate and the conductivity. Although little is understood about these aspects, it is expected that the electron transfer will require molecular motion, and that the conductivity will be sensitive to this motion.

In addition to considerations of molecular structure and molecular motion it is important to remember that conductivity is a bulk property and requires a conducting network through the sample. We shall see the importance of this below, but consider that many of the polymers of interest are composed of more than one species. An example is a conducting polymer as a minor component in an insulating polymer, used to obtain desirable electrical and mechanical properties. In such cases phase separation is an important consideration. High electrical conductivity requires that the conductor form a continuous phase within the insulator.

Here we are interested only in d.c. conductivity and the measurements are fairly simple. The values are also fairly accurate and, wonderfully, the spread of values is huge, perhaps the largest of any values a chemist might encounter. Insulators have conductivities, σ, reported in S cm^{-1} (where S, the siemens, is a reciprocal ohm) as low as 10^{-12} S cm^{-1}. Most polymers are good insulators and some are used for insulation around wires. The highest reported conductivity for a polymer is for oriented and iodine-oxidized polyacetylene at 10^5 S cm^{-1}. Ionic conductors such as lithium salts in poly(ethylene oxide) have room temperature conductivities of 10^{-6}–10^{-2} S cm^{-1}. Many conjugated and oxidized polymers, such as polythiophene oxidized with iodine, give values around 1–10^2 S cm^{-1} depending on the exact method of preparation.

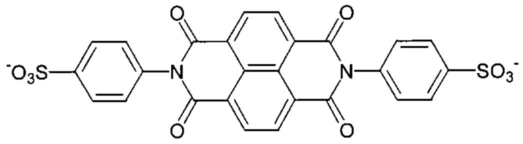
Some of the current activity in the field of conducting polymers is directed toward applications as gas sensors, or as components in gas sensor arrays.[2] Because conducting polymers such as oxidized polypyrrole or carbon particles imbedded in inert polymers change conductivity when exposed to organic vapors, they are candidates for this use and, indeed, have been used to develop commercial devices. When sensors or sensor arrays are combined with suitable signal processing and pattern recognition systems, the device is described as an 'electronic nose.'[2] Such systems are applicable as a nondestructive method for the detection and discrimination of gases and odors, for quality assurance in the food and beverage industry and in breath analysis. Electronic noses can be based on a variety of different sensing materials including semiconducting metal oxides, lipid coatings and phthalocyanines in addition to polymer films. Conducting polymer films have the advantages of operating at room temperature, sensitivity to a wide variety of volatile organic compounds and being inexpensive to fabricate relative to other sensing materials.

In summary, the materials of primary interest to this paper are polymers containing oxidized or partially oxidized organic species. Electron hopping is important for the conductivity, and an understanding must involve considerations of both the structure of the molecular species and the morphology of the material. When the polymers absorb vapors, the structure and conductivity change and this provides an opportunity for applications in the field of sensors.

RESULTS

Our first experience with the effects of vapors on conductivity involved a polymer composed of a small molecule anion radical and a polymeric polycation.[3] Our idea was that the polymer would serve as the counter ion for the anion radical, and would also provide the polymeric material so that mechanically useful films could be prepared. As the anion radical we chose the naphthalene diimide, **1**$^-$. Previous studies had demonstrated that **1**$^-$ could be formed in aqueous solution and was stable in the absence of oxygen. It had also been demonstrated that **1**$^-$ formed π stacks in aqueous solution and in solids as a sodium salt. Therefore, it seemed that a conducting material would result if we used the polycation poly(dimethydiallylammonium) (PDDA) to form **1**$^-$/PDDA.

(1)



We devised a method for the production of **1**$^-$/PDDA films that involved the reduction of **1** in the presence of PDDA in water on a mercury pool electrode. A black, shiny film formed on the surface of the liquid mercury that could be easily removed, washed, dried and stored in air, provided that the humidity was not too high. As such, this procedure yielded an unusual example of an air stable n-doped (negatively doped) conducting polymer. Conductivity measurements of the dried film along the film plane showed that the polymer was semiconducting with a room temperature conductivity of 10^{-4} S cm^{-1} in dry nitrogen or air. The conductivity was much lower across the film plane, only about 10^{-7} S cm^{-1}. ESR and visible–near–infrared (NIR) studies showed that the structure was anisotropic with π stacks of anion radicals oriented primarily in the film plane.

Of special interest was the observation that the conductivity of these films depended on the humidity above the sample. In a humid atmosphere the film became sticky and the conductivity increased. At 90% relative humidity the conductivity was 0.1 S cm^{-1}. The effect was reversible so that when the humidity was removed the conductivity rapidly returned to its original value. Because the film became sticky we proposed that water uptake caused plasticization of the film and that (somehow) this led to higher conductivity. Further investigation of the conductivity showed that there was evidence for polarization of the sample at high humidity. This suggested that the material might be considered a redox conductor.[4] If electron hopping between stacks was important in determining the conductivity, then absorption of water into the film might improve the local mobility, and therefore the rate of hopping. This would increase σ, but since $\mathbf{1}^-$/PDDA contained such a variety of ionic materials the mechanism of the vapoconductive effect remained unclear.

These studies rationalized the sensitivity of the $\mathbf{1}^-$/PDDA films to humidity and set the stage for further investigation of the phenomenon. In order to develop a method for preparing similar films using a non-electrochemical method, we studied the water-soluble polymer poly(vinyl alcohol) in mixture with $\mathbf{1}^-$ and similar water-soluble diimides.[5] Free-standing films of this system with varied loading and degree of reduction of the diimide conductor were readily obtained by spin casting. The conducting films that were produced were anisotropic, but not very sensitive to humidity. This made it clear that the presence of anion radicals, even as π stacks, was insufficient to explain the humidity effect. The new results suggested that PDDA was somehow involved with the water uptake and that this led to the humidity effect.

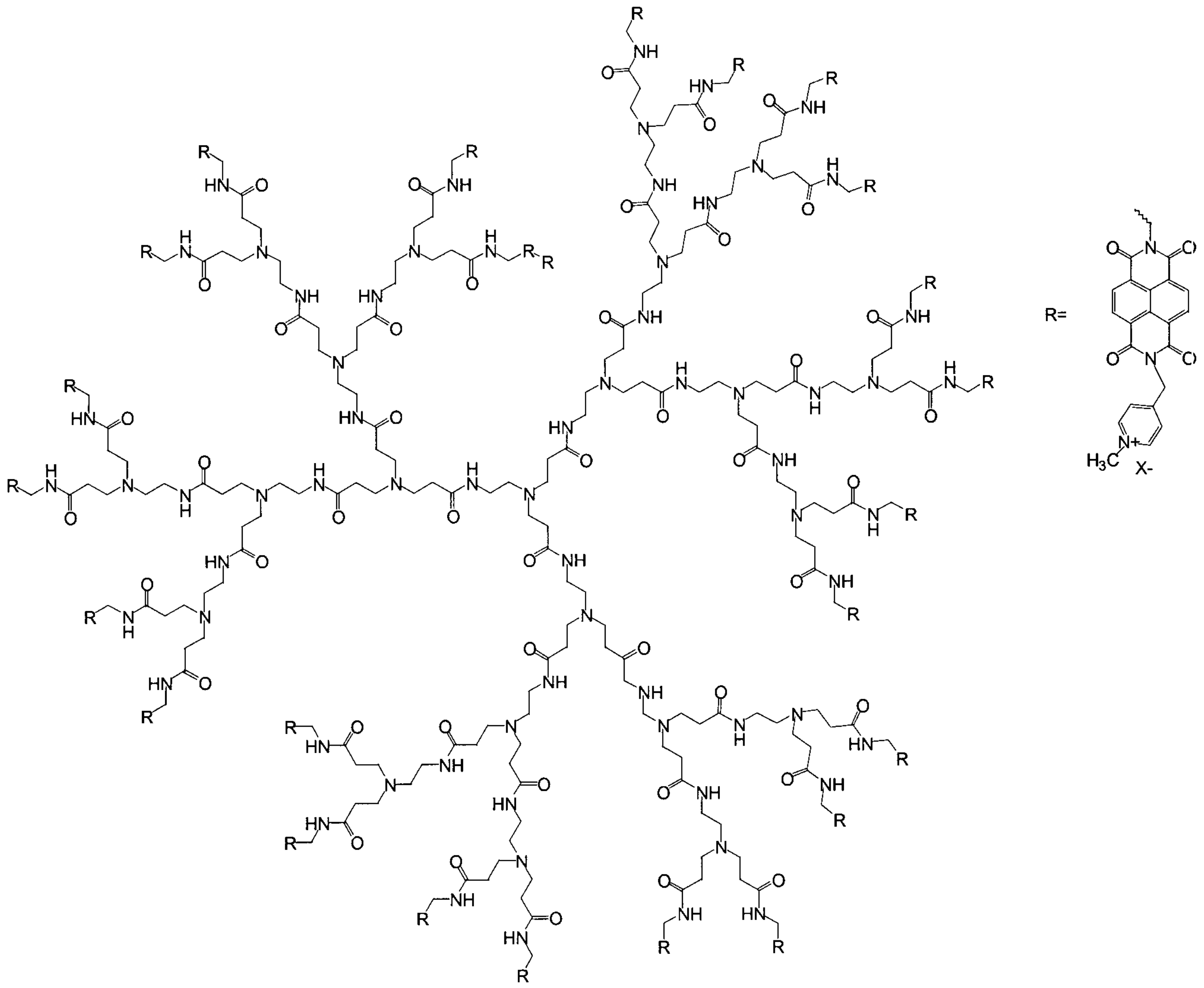
In all the work on conjugated chain conducting polymers, linear polymers were used. It was, therefore, of general interest to study branched-chain polymers. As a start in this field we chose dendrimers. Dendrimers are highly branched polymers, synthesized in a stepwise fashion to give a final product with a very narrow molecular weight distribution. Tomalia's group had developed the synthesis of polyamidoamine (PAMAM) dendrimers and provided amine-terminated polymers with increasing molecular weights, generations 1–4. We modified these dendrimers by attaching diimide groups to the periphery giving, for example, the third-generation dendrimer $\mathbf{D_{3\pi}A}$ with up to 192 diimide groups per molecule.[6] In aqueous solution, NIR spectroscopy showed that the diimide anion radicals formed π dimers, but not the larger π stacks found with the monomeric anion radicals such as $\mathbf{1}^-$. Films cast from water produced electrically conducting powders, but not films. This may be due to the branched dendrimeric structure which can inhibit intermolecular interpenetration. Dissolving the dendrimer **2** in formamide, and reducing with sodium dithionite gave stable solutions of the anion radicals, which could be spin cast into useful films. Although the solutions gave anion radicals that reacted with oxygen in the air, the cast films were stable in dry air.

Fully reduced films (1.1 electrons/diimide) gave conductivities under ambient conditions of about 10^{-3} S cm^{-1}. Films formed from these dendrimers that were partially reduced (0.55 electrons/diimide) gave $\sigma = 10^{-2}$ S cm^{-1}. This is consistent with the idea that conduction involves electron hopping. Electron exchange between two anion radicals necessarily produces a dianion and a neutral in an endothermic process. Electron hopping from an anion radical to a neutral in a mixed valence film is thermoneutral.

Spectroscopic studies on these films showed NIR absorption out to 2000 nm with stronger intensity at long wavelengths for mixed valence films. This is consistent with the formation of the conducting entities involving anion radical aggregation. Although there are geometric constraints on the aggregation of anion radicals, the fact that they are on the periphery of the dendrimer means that there is a high local concentration, which is favorable for aggregate formation. Interestingly, these films are isotropic, that is, there is no preferred orientation of the anion radical aggregates in the film plane of the type found for $\mathbf{1}^-$. Clearly, the dendritic structure controls morphology in this sense.

The first indication that these films would be sensitive to humidity was obtained when it was observed that the current flowing through a film rose and fell with the breathing rate of the observer. The humidity in his exhaled breath increased the conductivity of the film. More careful studies quantified this effect. In the case of the partially reduced film, the conductivity rose from 0.01 S cm^{-1} at zero humidity to 15 S cm^{-1} at 90% humidity, an increase by a factor of 1500. The reversible change for a film about 20 μm thick took place in a few minutes after the humidity was changed. This phenomenon was probed using a quartz crystal microbalance (QCM). The vibrational frequency of the quartz crystal depends on the weight of the film attached to its surface, and in certain circumstances the mass of absorbed water can be measured. In practice we found that large quantities of water were absorbed, with increasing amounts at high humidity. Above 50% relative humidity the device became unstable as the wet film became heavier and more plastic. Spectroscopic studies showed no difference between wet and dry films. Therefore, there is no evidence for changes in the structure of the conducting entities and we suggest that plasticization and increased mobility explain the increase in conductivity.

These results on PAMAM dendrimers modified with anion radicals led us to extend our results to cation radical-modified dendrimers. Oxidized species are more air stable and more widely used for materials chemistry, so this extension would connect our results to those in the literature on other conductors. In collaboration with Newkome we prepared polyamido dendrimers modified with oligothiophenes such as **2** and **3**.[7] It had been established that oligothiophenes could be oxidized to give stable cation radicals. The conductivity and spectra of such salts had been reported and so we had a sufficient



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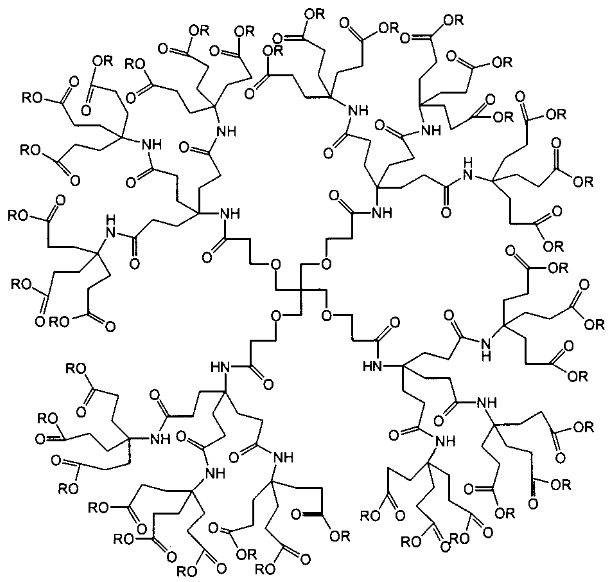

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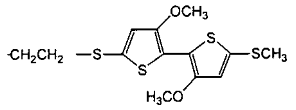

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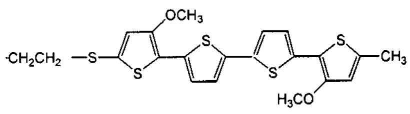


(3)

background to undertake the study. The specific dendrimers had the oligothiophenes attached via thioalkanol groups. The thio group gave added stability to the cation radical, and the alcohol allowed attachment to the dendrimer via an ester linkage. Spectroscopic measurements indicated that the loading with oligothiophenes was 60–70%. Oxidation in methylene chloride solution gave optical spectra demonstrating that cation radical π-dimers were formed. This indicated an enhanced disposition toward dimerization for the dendrimer compared to monomeric analogs at the same concentration.

The cation radicals did not form good films under casting conditions, so we cast films of the neutral species and oxidized them with iodine vapor. The conductivity of these films for either the bithiophene or quaterthiophene examples was 10^{-3} S cm^{-1}. Rapid switching of the current and long-term current passage indicated that the conductivity was not ionic. This conductivity is similar to or slightly lower than those of pure quaterthiophenes oxidized with iodine, indicating that the dendrimer structure has only a small effect on the conductivity.

Vapoconductivity experiments revealed a new phenomenon. Water vapor had only a small (factor of two) effect on the conductivity, but organic vapors increased the conductivity (σ/σ_0, where σ_0 is measured in air) by factors of up to 800. The increase, which took place over a period of a few minutes for films of thickness 10 μm, was rapidly reversed when the vapor was removed. In Table 1 are shown the changes in conductivity (σ/σ_0) for a variety of volatile organic compounds. The data show that there is a range of responses, with certain polar organic vapors giving the largest values. Non-polar vapors such as toluene gave very small changes. Comparison of the two dendrimers **2** with bithiophene cation radicals and **3**, with quaterthiophene cation radicals gave similar results, but the ordering of vapoconductive effects was different. Acetone gave the largest effect with **2**. Diethyl ether gave the largest increase with **3**. It was realized that the sensitivity of these polymers to organic vapors allowed the possibility of sensor applications. In particular, it was reasoned that qualitative organic analysis could be performed based simply on the observed conductivity value.

QCM studies were performed on these polymers exposed to organic vapors. There was a decrease in frequency (increase in weight) over a period of minutes. When the vapor was removed, the weight returned to a value similar to that of the initial sample, also over a period of minutes. In Table 1 is shown the percentage increase in mass. It can be seen that the films are taking up every vapor including those that do not have a large effect on the conductivity. The mass of absorbed vapor amounts to about 5–10% (w/w). It was physically observed that the films under acetone vapor became sticky, while the films under water vapor remained hard to the touch.

Table 1. Conductivity and mass changes of iodine-oxidized films of **2** and **3** exposed to various vapors

	2		**3**	
Vapor	σ/σ_0	$(\Delta M/M_0)\times 100$	σ/σ_0	$(\Delta M/M_0)\times 100$
Acetone	800	11	190	9.6
Ethanol	380	10	290	7.8
Ethyl acetate	280	4	210	3.6
Ether	240	6.4	350	7.3
Acetonitrile	140	6.2	310	6
Dichloromethane	47	9.2	31	9.1
Methanol	35	18	44	15
Toluene	1.5	4	4.2	3.9
Water	1.3	17	2.1	20
Hexane	1.5	4.3	1.2	3.7

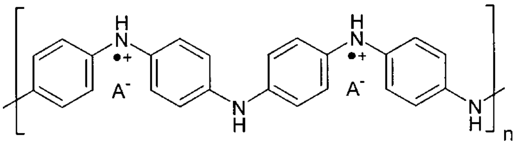
It will be recognized that these oxidized dendrimer films contain not only oligothiophene cation radicals, but also counter ions, triiodide or polyiodides. These halide species are known to give conductivity in poly(ethylene oxide) and could contribute to the conductivity in this case.[8] Preliminary tests (D. C. Boyd, unpublished results) indicate that this is the case and that triiodide salts can be used to develop inexpensive and reversible vapoconductive films. An example is tetrahexylammonium iodide in PVC, treated with iodine vapor. This film, in which triiodide is found spectroscopically, is insulating with $\sigma = 8 \times 10^{-10}$ S cm^{-1}. In the presence of acetone the conductivity rises to 2×10^{-3} S cm^{-1}. When the acetone vapor is removed, the conductivity returns to its original value. This huge (six orders of magnitude) change is reversible for a number of cycles. Other vapors (Table 2) give different, but large effects, and even toluene increased the conductivity by 5000.

The magnitude of these effects is much larger than found in an extensive series of studies on oxidized polypyrrole based sensors.[2] These studies usually used electrochemically prepared polypyrrole. The counterion for the cationic polymer came from the electrolyte and was varied. Although changes of 100 have been found, in most cases the size of the effect was a few per cent increase or decrease. The thrust of this work was to use such materials for sensors and even small vapoconductive effects could be used if an array of sensors was employed.

Table 2. Vapoconductivity effects for tetrahexylammonium triiodide–PVC films

Vapor	σ/σ_0	Vapor	σ/σ_0
Acetone	2×10^6	Methanol	2×10^5
Dichloromethane	1×10^6	Ethanol	3×10^4
Acetonitrile	1×10^6	Diethyl ether	1×10^4
Tetrahydrofuran	3×10^5	Isopropyl alcohol	1×10^4
Chloroform	1×10^5	Toluene	5×10^3
Ethyl acetate	2×10^5	Cyclohexane	1

(4)



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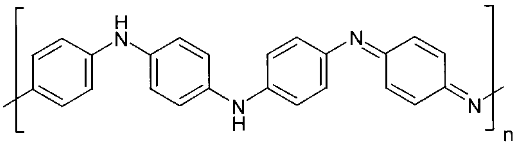

Table 3. Vapoconductivity changes for protonated polyaniline films after 30 s exposure

Vapor	σ/σ_0	Vapor	σ/σ_0
Methanol	7.4×10^5	Dimethylformamide	2.0×10^1
Ethanol	6.0×10^5	Tetrahydrofuran	1
Isopropyl Alcohol	1.3×10^4	Acetonitrile	1
Isobutyl Alcohol	6.2×10^2	Ethyl acetate	1
tert-Butyl Alcohol	5.4×10^2	Diethyl ether	1
Acetone	3.4×10^1	Toluene	1
Methyl ethyl ketone	1.0×10^1		

Since iodine has been the oxidant of choice in this field, the above results also have some general significance for the field of conducting polymers.[1] Examples range from oxidation of polyacetylene using iodine in carbon tetrachloride, to make the most highly conducting polymer known, to many examples of iodine-oxidized polythiophenes, poly(phenylenevinylene)s and even polyisoprene. We suggest that if the conductivity is not too high and if the samples are not too dry, triiodide conduction could be important.

The large vapoconductive effects from organic vapors described above were soon related to an ongoing study of a soluble polyaniline obtained from Dr Pat Kinlen at Monsanto. The polymer was solubilized by a large counterion, dinonylnaphthalene sulfonate. The material also contained excess dinonylnaphthalenesulfonic acid and a plasticizer in *p*-xylene. Although the polyaniline was in the protonated (conducting) form (**4**), films cast from *p*-xylene gave a very low conductivity. This was expected from previously published work, as was the result when the film was washed with methanol.[9] The methanol wash sharply increased the conductivity to values near 20 S cm^{-1}. Although it was possible that the methanol was washing away some non-conducting material, it seemed equally reasonable that the polar solvent allowed the ionic polyaniline to unfold and aggregate to give bulk conductivity. We reasoned that if the latter was true then methanol vapor could have a similar effect.

Tested experimentally,[10] it was determined that methanol vapor, indeed, caused a rapid increase in conductivity of this Monsanto polyaniline material cast from *p*-xylene. The initial conductivity of 3×10^{-5} S cm^{-1} changed to 20 S cm^{-1} after exposure to methanol vapor for 1 min. When the film was transferred to air the conductivity did not change. Indeed, even heating the film to 70 °C to drive off any absorbed methanol did not change the high conductivity value. On the other hand, the conductivity could be rapidly decreased by exposure to a non-polar vapor such as chloroform or toluene. In this way the film could be put through several cycles of high and low conductivity. Seen in a different sense, chloroform could be used to deactivate the film in preparation for another methanol measurement.

The large dynamic range of the effect allowed us to differentiate a number of different vapors. Table 3 gives several examples. Notable are the small effects of dichloromethane and other non-polar vapors and the very large effects of polar vapors such as dimethylformamide, acetone and alcohols. Polarity is very much a factor as seen in the effects of methanol, ethanol, propanol and butanol. The notion that this film could be used to differentiate different vapor pressures of the same material was tested using alcohol–water mixtures. Extrapolation of the data indicated that it would be possible to determine ethanol down to about 0.05% in liquid water. Of more practical interest was the differentiation of lite beer ($\sigma/\sigma_0 = 60$) from ale ($\sigma/\sigma_0 = 1260$) *before tasting.*

QCM studies (Fig. 1) showed that the film rapidly absorbed large quantities of ethanol vapor. Removal of the vapor led to rapid loss of the absorbed ethanol from the film. It is not established that all of the ethanol departed, however. Spectroscopic studies showed only minor spectral changes with ethanol absorption. Wide-angle x-ray scattering showed some evidence for increased crystallinity when the film was treated with ethanol vapor. Our conclusion again is that the film is swollen with the volatile organic compound and that this allows reorganization of the morphology. In this case, more crystallinity may be important for the conductivity increase. Crystallization, or at least organization into polyaniline networks, has received support from a recent study of polyaniline gels.[11] These gels were formed using emaraldine base and an excess of organic sulfonic acids such as dinonylnaphthalenesulfonic acid in formic acid. They show TEM evidence for organized fibrils and x-ray scattering evidence for crystalline phases. The conductance of these gels is lower (10^{-2} S cm^{-1}) than that for our high-conductivity films, but it seems clear that in the presence of vapors such as formic acid we could also be forming a gel phase and that network morphologies are formed under conditions comparable to those we employed.

We have also studied the neutral, insulating form of polyaniline (**5**) (J. S. Bankers, unpublished results). The initial conductivity of a film of this commercial material,

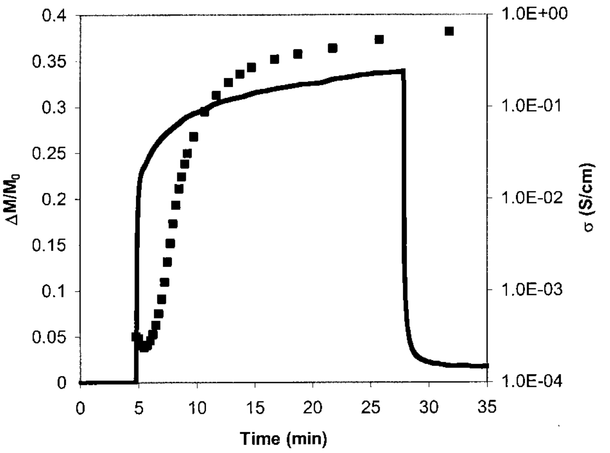

Figure 1. Conductivity (squares) and mass changes from QCM for 1 μm polyaniline films exposed to the vapor above a 20:80 ethanol–water mixture by volume. Sample placed in the vapor after 5 min

cast from *N*-methyl-2-pyrrolidinone, is about 10^{-10} S cm^{-1}. When the film was exposed to organic vapors the conductivity rose substantially as shown in Table 4. The UV–visible spectra of the film before and during exposure to vapor show a broad maximum at 625 nm as expected for the base form of polyaniline. These spectra show that the vapor does not protonate the polyaniline. Additionally, experiments have shown that the maximum conductive response decreases with repeated exposure to vapors. By reversing the bias on alternating exposures, this phenomenon is greatly reduced. It was thought that this phenomenon might be due to ions, not properly removed during the conversion from the salt to base form, migrating to the electrodes during bias. However, elemental analysis does not support this hypothesis. A comparison of the relative sensitivity of the protonated and unprotonated forms of polyaniline to organic vapors shows some differences, and in this base form material there are no obvious candidates for carriers.

Still, the films exhibited increases in conductivity as large as 10^6 when exposed to methanol vapors. Although the changes in conductivity were not entirely reproducible from exposure to exposure, an acceptable method has been devised to standardize the response. Using this method, the conductivity changes were sufficient to differentiate 10 volatile organic compounds in a blind test.

Previous studies of vapoconductivity (or vaporesistivity) have focused useful attention on three types of polymers. Oxidized conjugated-chain polymers such as polyaniline, polypyrrole and polythiophene have received attention. Bartlett and co-workers have published extensively on such materials.[2] They have made devices, including arrays, and developed the electronics and software to make these measurements useful in applications. Of interest are artificial neural networks for the identification of vapors. Of importance are methods to calibrate the responses. There is often a concern with baseline drift and reproducibility of the response. Because these materials are in a high oxidation state they are susceptible to reduction by amines and other volatile reducing agents, and this tends to change the property in an irreversible manner. On the other hand, this type of redox or acid–base behavior has been widely touted for sensitive detection using such polymers.

In comparison with the redox polymers of interest here, these conjugated chain conductors have higher conductivities, but show smaller vapoconductivity effects. A typical change (usually an increase) is a few per cent compared with the 10^3–10^6 changes we have measured. Little has been reported that makes a convincing case for one material allowing the differentiation of a variety of vapors. Instead, arrays are proposed for qualitative identification of volatile organics.

Ionic conductors have also been employed as organic vapor sensors. The sensitivity of polymers containing non-redox ions to humidity is well known. Also well known is the effect of plasticizers on the ionic conductivity of lithium salts in poly(ethylene oxide) of the type used for battery applications. A recent paper reports a survey of a number of polymers, plasticizers and organic salts to organic vapors such as ethanol and toluene.[12] All three components are required to obtain the vapoconductive response. The conductivity in the absence of vapor is of the order of 10^{-6} S cm^{-1}. It appears that the vapors typically cause increases on the order of a few per cent, but can be up to 100 and are reversible. It was possible to construct very stable devices

Table 4. Base form of polyaniline: vapoconductivity changes compared with the change for methanol vapor

Vapor	$(\sigma_{vapor}/\sigma_{methanol}) \times 10^{-3}$	Vapor	$(\sigma_{vapor}/\sigma_{methanol}) \times 10^{-3}$
Ethanol	127	Dimethylformamide	20
Acetone	119	Isopropyl alcohol	10
Methyl ethyl ketone	48	Tetrahydrofuran	5.3
Dichloromethane	39	Acetonitrile	2.7
		Ethyl acetate	2.3
		Isobutyl alcohol	1.8

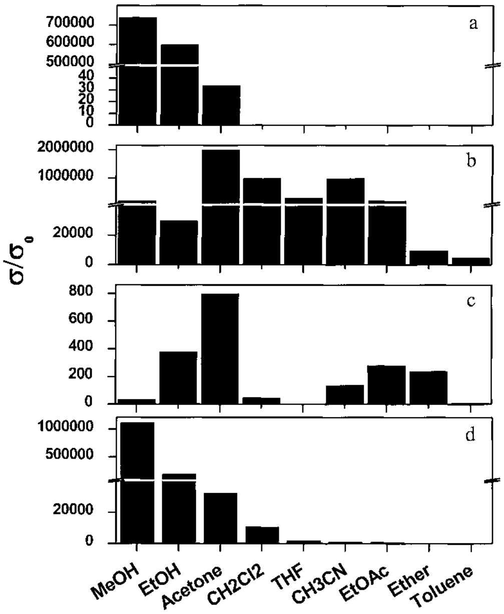

Figure 2. Comparison of the vapoconductive effects of four polymer films: (a) protonated polyaniline; (b) tetrahexylammonium triiodide–PVC; (c) dendrimer **2** oxidized with iodine; (d) base form of polyaniline

with good reproducibility and use them for quantitation of the amount of organic vapor in air.

Of interest is the development of a set of vapor-sensitive films with different responses. Such a set would have greater possibilities for analytical use than a set in which all the members gave similar responses. Figure 2 compares the vapoconductive responses for the four polymer systems described above. In the case of the base form of polyaniline the absolute values are not exact because the initial conductivity is so low, but the relative values are meaningful in this context. It can be seen that there is not a similar pattern in the observed responses. Polar vapors tend to give larger increases in conductivity, but the details change dramatically. Hence it appears that this new phenomenon could have utility for sensor components.

Acknowledgements

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