Conductivity of Triiodide Salts in Vapor-Swollen Commodity Polymers

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Iodine is the most common chemical oxidant used to produce conducting polymers. Iodine oxidation has been used for conjugated oligomers and polymers of virtually every type,[1] including polyacetylenes, polythiophenes, polypyrroles, polyphenylenevinylenes, and even polyisoprene, which should be very difficult to oxidize. In general, the conductivity of the resulting material has been discussed in terms of the structure of the oxidized polymer, for example, cation radicals, polarons or bipolarons. We have recently used iodine oxidation to produce some "vapoconductive" polymers: materials that increase their conductivity in the presence of organic vapors.[2] We realized that the iodine reduction products, triiodide or polyiodides, could play an important role as charge carriers[3] in these films, but we, like so many others, had not investigated that aspect. To begin to fill that void, we have now studied the conductivity of triiodide salts in common polymers and report some unexpected results. Because a variety of inexpensive films can be simply produced and these have different, large, and reversible vapoconductive responses, these materials may be useful as sensor components.[4,5]

The experimental method[6] is quite simple. Solutions of tetrahexylammonium iodide plus the polymer of interest (weight ratio 1/4) were used to cast films. The polymers and respective casting solvents were poly(vinyl chloride) (PVC) from DMF, poly(methyl methacrylate) (PMMA) from $CHCl_3$, polystyrene (PS) from DMF, poly(ethylene oxide) (PEO) from $CHCl_3$, and poly(vinyl acetate) (PVAc) from DMF. The films, cast over two Pt wires and dried under vacuum at 60 °C, appeared homogeneous under an optical microscope. In contrast, tetraethylammonium iodide gave crystals and inhomogeniety. The films (nominal thickness of 15 μm determined with a surface profiler) were placed in iodine vapor for 2 h. The color became yellow to dark mahogany, depending on the polymer. In a few hours the excess iodine sublimed out, generally leaving dark yellow films. The conductivity values were as follows: PVAc, 8×10^{-8} S/cm; PEO, 7×10^{-5} S/cm; PVC, 8×10^{-10} S/cm; PS, 3×10^{-5} S/cm; PMMA, 6×10^{-9} S/cm. Studied by UV−vis spectroscopy, the films showed absorption peaks at 366 and 295 nm, which have been assigned to triiodide.[3] They lacked UV absorbance for iodide at 220 nm and vis absorbance due to I_2. Although we recognize that polyiodides could be present in addition to triiodide, we will hereafter refer to these films as polymer/triiodide films.

Table 1. σ/σ^0 **for Films Exposed to Vapors**

vapor/polymer	PVC[a]	PMMA[a]	PVAc[a]	PEO[a]	PS[a]	PMMA[b]
acetone	2×10^6	5×10^5	2×10^5	2×10^2	70	5×10^3
CH_2Cl_2	1×10^6	1×10^6	2×10^5	2×10^2	20	2×10^4
CH_3CN	1×10^6	5×10^5	5×10^4	90	20	8×10^3
THF	3×10^5	4×10^5	4×10^3	1×10^2	8	2×10^1
$CHCl_3$	1×10^5	2×10^5	4×10^4	40	3	6×10^3
EtOAc	2×10^5	2×10^5	5×10^2	60	3	1×10^3
MeOH	2×10^5	3×10^4	3×10^4	30	7	3×10^3
EtOH	3×10^4	2×10^3	1×10^3	8	2	3
Et_2O	1×10^4	3×10^3	7×10^2	40	2	4
IprOH	1×10^4	1×10^3	50	4	1	4
toluene	5×10^3	1×10^4	1	20	1	6
cyclohexane	1	1	50	2	1	1

[a] Tetrahexylammonium iodide polymer films treated with I_2. Tabulated values after 20 s of vapor exposure. [b] Tetrabutylammonium triiodide polymer films. Tabulated values after 4 min of vapor exposure.

In Table 1 are results obtained when the films described above were exposed to 12 volatile organic compounds. The procedure simply involved placing the film in a closed round-bottom flask containing a small amount of the organic liquid. The vapor pressure of the organic compound at room temperature then caused the changes in conductivity. The increases were generally quite rapid so the data shown in Table 1 were taken after 20 s of exposure. Longer exposure times often lead to even larger σ, but we chose to compare the responses at one (arbitrary) unit of time. In general, the increases were rapidly reversed within tens of seconds when the cell was taken back into the laboratory atmosphere. This could be repeated several times with good reproducibility (Figure 1) if care was taken to depolarize the device for a few minutes between measurements.

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(6) Solutions used to cast the films were prepared by dissolving the polymer and salt in a minimum (∼0.5 mL) of solvent, followed by 5 min in an ultrasonic bath. Films were cast by dipping a two-point probe (two Pt wires sealed into a glass rod and ground off flat) into the solution, removing the excess solution, and drying the film in air and then in a 60 °C vacuum oven. The dry films were then treated with iodine vapor in an enclosed vessel for 2 h. Currents measured with a picoammeter ranged from 10 pA to 0.1 mA.

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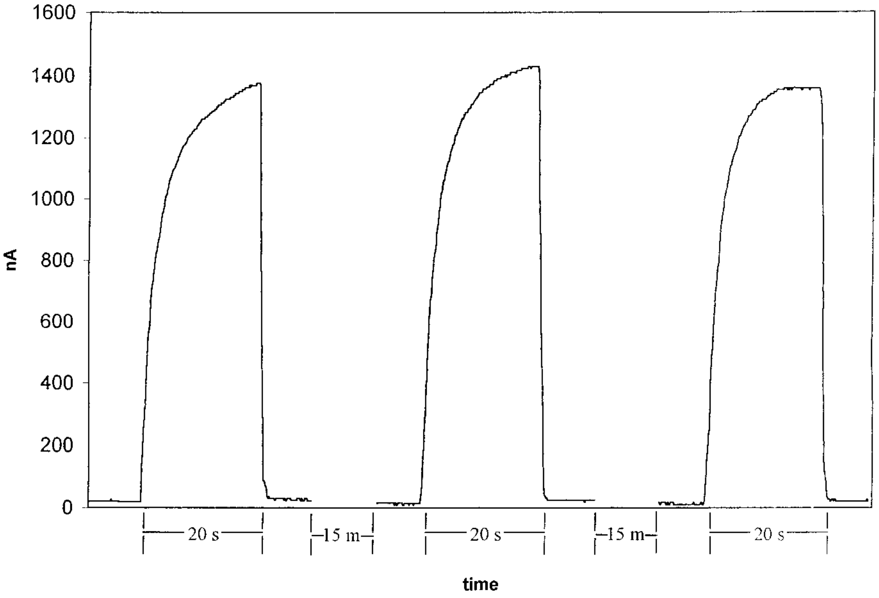

Figure 1. Vapoconductive response for a PMMA/tetrahexylammonium iodide film treated tih I_2, exposed to CH_2Cl_2 vapor three times for 20 s/exposure at a potential of +0.50 V. The film was depolarized for 15 min at a potential of −0.50 V between exposures.

Several aspects of the results are remarkable. (1) The changes are extremely large. Tabulated as conductivity with vapor divided by the conductivity in air (σ/σ^0), values ranging up to 2×10^6 were determined, and many vapors gave increases of more than 10^3. Cyclohexane gave the smallest responses for all the polymers, but over PVAc even this vapor changed σ/σ^0 by 50. Changes of this magnitude have been documented in only one other case.[5] (2) Quantitatively, different vapoconductive effects were observed with each of the polymers. The more insulating films gave the largest σ/σ^0 values. (3) The magnitude of the response from a particular vapor was generally different for each of the polymers. Choosing diethyl ether as an example, the triiodide polymers gave the following σ/σ^0 values: PVC (1×10^4), PMMA (3×10^3), PVAc (7×10^2), PEO (40), and PS (2). (4) A qualitative ranking of the σ/σ^0 values for a given polymer can be obtained by examining any column in Table 1. Comparing these rankings for the five polymers shows great similarity between them. Indeed, the vapors are listed in descending order according to their average rank. Acetone ranks first followed in order by methylene chloride, acetonitrile, tetrahydrofuran, chloroform, ethyl acetate, methanol, ethanol, diethyl ether, 2-propanol, toluene, and cyclohexane.

These results, which are important to the field of iodine oxidized conductors, were amplified by an exploratory study of vapor effects on the conductivity of tetrabutylammonium triiodide in PMMA. The σ/σ_0 results are shown in the last column of Table 1. The σ_0 value was difficult to measure, but the changes are rather large and qualitatively similar to those for the tetrahexylammonium triiodide films.

Because the resistance of these films increases as thickness decreases, this phenomenon is bulk, not surface conductivity. We have also studied vapor uptake using a quartz crystal microbalance. Because films treated with iodine lost weight during the measurements, we used tetrahexylammonium iodide films or films of tetrabutylammonium triiodide, each in PMMA. The mass gain upon solvent exposure, $\Delta M/M_0$, data are found in Table 2. It can be seen that considerable amounts of vapors are absorbed, but that there is not a good correlation with the magnitude of the change of conductivity. This is not surprising because the material is complex and the chemical effects of the vapor, not just the amounts, must be important.

Table 2. QCM Data ($\Delta M/M_0 \times 10^{-2}$) for Solvent Uptake by PMMA/Alkyl Ammonium Iodide Films Exposed to Vapors for 20 s

vapor/salt	$N(hex)_4I/I_2$	$N(butyl)_4I_3$
acetone	7	0.4
CH_2Cl_2	>30[a]	>50[a]
CH_3CN	9	0.4
THF	0.9	3
$CHCl_3$	10	5
EtOAc	2	0.8
MeOH	10	5
EtOH	10	4
Et_2O	20	2
IPrOH	3	0.2
toluene	0.7	0.2
cyclohexane	0.9	8

[a] Maximum value obtained prior to film failure due to excessive uptake of vapor.

We propose that even though the conducting material is being diluted with the absorbed vapor, this change increases the conductivity by allowing more molecular motion and a faster rate of electron transfer through the film. Following Shriver et al., we suggest that this might involve electron hopping between triiodide molecules. The results demonstrate that each polymer is different, but that the vapor has some similar effects on the conducting network of triiodide ions, regardless of the surrounding polymer matrix. The conductivity mechanism is under study.

In summary, we have discovered new molecular conductors based on ordinary commodity polymers. On the basis of these and previous results,[2,5,7] we suggest

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that the large effects of swelling on conductivity will often be observed for materials in which molecular motion improves conductivity. The iodine oxidized dendrimers that we previously reported[2] have vapoconductive effects similar to these triiodide responses, but the rank order of vapor response is not the same as that observed here. We note that vapor effects of this magnitude have not been reported for conducting polymers such as oxidized polypyrrole and that carbon particles imbedded in commodity polymers such as those employed here usually give small decreases in conductivity when exposed to vapors. Because these two types of materials have been most widely employed for the construction of electronic noses, redox materials of the type employed here may prove to be useful because of their very different responses. Beyond that we wish to emphasize the large effects that swelling can have on conductivity. Important in this regard are so-called in situ measurements of conductivity in which the films were prepared electrochemically and then investigated in solution.[8] Finally, we reiterate that these new conductors are extremely sensitive in their differentiation of organic vapors. This may lead to applications as sensor materials.

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(8) See for example Zotti, G.; Salmaso, R.; Gallazzi, M. C.; Marin, R. A. *Chem. Mater.* **1997**, *9*, 791. Kittleson, G. P.; White, H. S.; Wrighton, M. S. *J. Am. Chem. Soc.* **1984**, *106*, 7389. Marsella, M. J.; Newland, R. J.; Carroll, P. J.; Swager, T. M. *J. Am. Chem. Soc.* **1995**, *117*, 9842.