A Study of Poly(p-Xylylene)-Coated AsF$_5$-Doped Polyacetylene

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Synopsis

Electrical conductivity measurements and scanning electron microscopy have been used to study uncoated and poly(p-xylylene)-coated samples of polyacetylene doped with AsF$_5$. These initial results indicate a considerable reduction in the decay rate of conductivity in the presence of oxygen as well as a decreased rate of thermal decomposition of the dopant when heated between 50°C and 115°C in vacuum by the coating.

INTRODUCTION

Recently, it has been demonstrated that when free-standing films of polyacetylene, (CH)$_x$, are exposed to the vapors of electron acceptors, such as AsF$_5$ and I$_2$, the electrical conductivity of the films can be increased in excess of 12 orders of magnitude, covering the full range from insulator to semiconductor to metal.[1-3]   However, the mechanical and electrical properties of the (CH)$_x$ films, both undoped and doped, degrades upon exposure to air and/or heat.[4,5] When oxidized in air, the films become brittle, and their electrical conductivity decreases. This slow oxidation can easily be detected by carbonyl peaks appearing at 1680 cm^{-1} and 1730 cm^{-1} in the IR spectra of the undoped films.

Earlier, it has been shown[6] that when AsF$_5$-doped polyacetylene, [CH(AsF$_5$)$_y$]$_x$, is heated at elevated temperatures (50–130°C) under continuous vacuum pumping, the conductivity of the sample decreases, the rate of conductivity decrease being faster at higher temperatures. This conductivity decrease is caused by decomposition of AsF$_6^-$ into AsF$_3$, F$_2$, and As.[6]   The average activation energy for this first-order decomposition process was found to be 16 kcal/mol as determined by three different experimental techniques.[6]   Similar studies under progress for iodine-doped (CH)$_x$ show that these films are less stable at higher temperatures than the [CH(AsF$_5$)$_y$]$_x$, films.[7]

It has been reported that coating films with paraffin reduces the oxidation rate of the films.[8]   In this paper, we wish to report the results of some preliminary attempts to protect polyacetylene films doped with AsF$_5$ from oxidation and from dopant degradation by using poly(p-xylylene), parylene, coatings applied by a pyrolytic polymerization technique.

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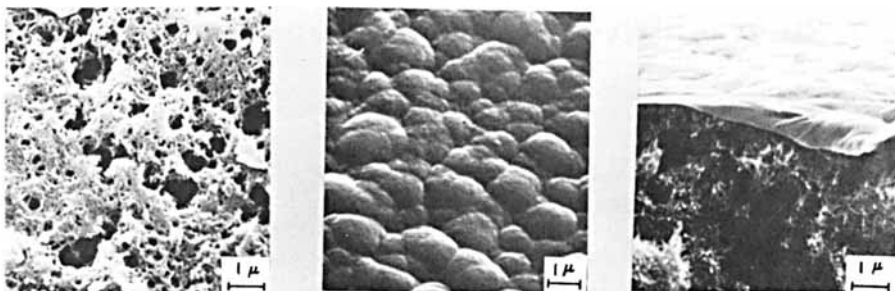† Department of Chemical Engineering.
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Fig. 1. Scanning electron micrographs of (a) an AsF_5-doped polyacetylene film, dull surface; (b) a poly(p-xylylene)-coated AsF_5-doped polyacetylene film, dull surface, coating thickness 2 μm; (c) a poly(p-xylylene)-coated AsF_5-doped polyacetylene film, cross section, coating thickness 2 μm.

EXPERIMENTAL

The $(CH)_x$ films used in this work were prepared according to the technique developed by Shirakawa et al.[9-12] An acetylene uptake of ~100 torr resulted in a film of polyacetylene polymerizing on the surface of the $Ti(OC_4H_9)_4$—$Al(C_2H_5)_3$—toluene solution at $-78°C$. The thickness of the film was ~0.1 mm as determined by scanning electron microscopy. The cis-isomer was isomerized to the $trans$-isomer by heating at 150°C for 2 h. Infrared spectra of the resulting film indicated a $trans$ content of 95%.

The doping was carried out by exposing films to a 1-torr pressure of AsF_5-vapor. The doped samples were pumped in vacuum (less than 10^{-3} torr) for 2 days in order to get a constant dopant concentration. After 2 days of pumping, the sample composition was $[CH(AsF_5)_{0.11}]_x$ as determined by weight uptake. The conductivity of the sample was found to be 260 $\Omega^{-1}\cdot cm^{-1}$. All the conductivity measurements in this work were done using the standard four-probe technique. The samples, typically 1 cm^2 in size, were mounted on Teflon frames. Platinum wires and an inert low-resistance contact cement were used to make electrical contacts. The contacts were checked to be Ohmic up to 200 mA. The electrical conductivity measurements were typically carried out between 100 μA and 5 mA. All sample handling took place using Schlenk-tube techniques, an inert atmosphere or vacuum. The samples were exposed to air only when the electrical contacts were made and during transfer to the apparatus used for the coating process. Usually, the total air exposure amounted to 10–20 min.

The parylene coatings were applied using a pyrolytic vapor-deposition technique developed by Gorham[13] and modified by Yasuda et al.[14] The dimer di-p-xylylene (Union Carbide Co.) is vaporized at 160°C, the vapor pressure being 0.1 torr. The dimer vapor is then let through a pyrolysis zone maintained at 660°C. During the pyrolysis, the dimer is cleaved into two molecules of p-xylylene. p-Xylylene spontaneously polymerizes on condensation. It coats all surfaces in the deposition chamber, which is kept at room temperature.

RESULTS AND DISCUSSION

The advantage in using vapor-deposited parylene coatings over mechanically applied wax or polymer coatings on $(CH)_x$-substrates is that the p-xylylene monomer behaves as a reactive medium surrounding the $(CH)_x$ samples placed
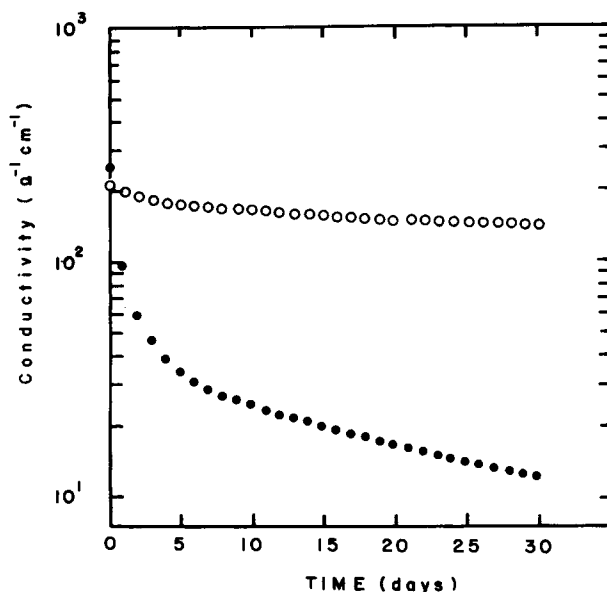
Fig. 2. Conductivity decrease as a function of time of $[CH(AsF_5)_{0.11}]_x$ exposed to air. (●) Uncoated; (O) parylene-coated.

in the deposition chamber. For these reasons, films of uniform thickness are deposited on all surfaces, including sharp edges, crevices, and the inside of holes. These features are achieved only with great difficulty using mechanically applied coating techniques. Furthermore, since the parylene coating is a linear polymer without any crosslinking, it does not create any significant stress on the substrate that might affect its mechanical properties. Parylene exhibits excellent chemical resistance and electrical and barrier properties and has outstanding dimensional stability.[13]

Figures 1(a–c) show electron micrographs of uncoated and parylene-coated $[CH(AsF_5)_{0.11}]_x$. As it turned out, the dull surface of the film (the surface in direct contact with the acetylene gas during the polymerization) required a coating thickness of about 1 μm in order to completely cover the porous structure of the surface. On the other hand, the shiny surface, which was in direct contact with the glass wall during the polymerization, shows a surface layer of flattened fibrils that are packed more closely than on the dull side. Coatings of parylene less than 1 μm thick completely smooth out the shiny surface.

TABLE I
Rate Constants and Activation Energies for Uncoated and Parylene-Coated AsF_5-Doped Polyacetylene

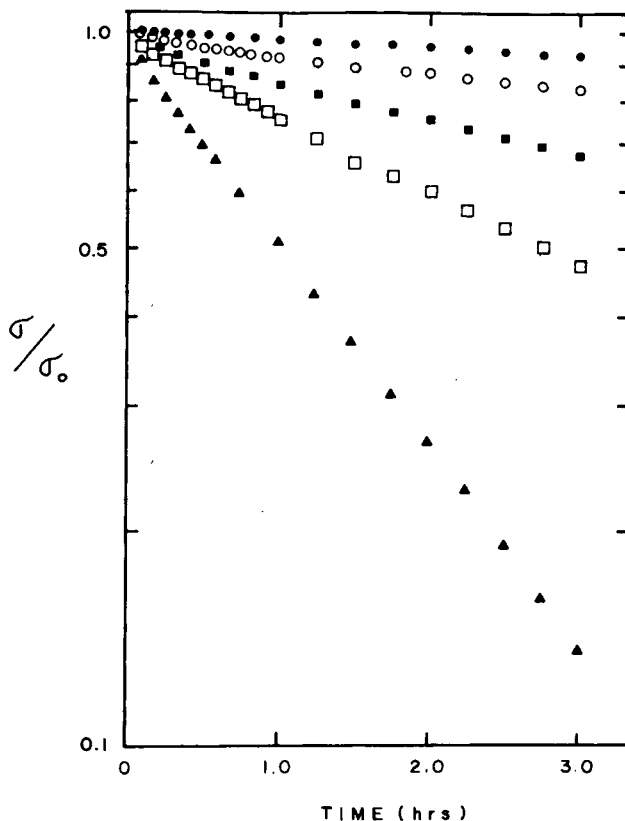|	Uncoated	Parylene-coated
k (50°C)	3.4×10^{-6} s^{-1}	1.1×10^{-6} s^{-1}
k (70°C)	1.4×10^{-5} s^{-1}	5.9×10^{-6} s^{-1}
k (85°C)	3.3×10^{-5} s^{-1}	1.3×10^{-5} s^{-1}
k (100°C)	6.6×10^{-5} s^{-1}	4.4×10^{-5} s^{-1}
k (115°C)	1.8×10^{-4} s^{-1}	9.1×10^{-5} s^{-1}
E_a (kcal/mol)	14.8 ± 1.5	17.2 ± 1.3

Fig. 3. Decrease in conductivity with time at higher temperatures.   Uncoated $[CH(AsF_5)_{0.11}]_x$.
($\bullet$) 50°C; (O) 70°C; ($\blacksquare$) 85°C; ($\square$) 100°C; ($\blacktriangle$) 115°C.

An experiment was carried out to investigate the effect of air oxidation upon the electrical conductivity of both uncoated and parylene-coated $[CH(AsF_5)_{0.11}]_x$. Both uncoated and coated samples were kept in air at constant humidity (57%) for 1 month, and the electrical conductivity was measured with 1-day intervals. The coating thickness was 2 μm.   Figure 2 shows the decrease in electrical conductivity of the samples as a function of time exposed to air.   The initial conductivity of the parylene coated sample was about 20% lower than that of the uncoated sample.   This reduction was probably caused by air exposure during the sample transfer to the deposition chamber.   Nevertheless, the parylene-coated sample shows a considerable stabilization against air oxidation.   Its electrical conductivity decreased by only 10% in 24 h compared to the uncoated sample having a conductivity decrease by a factor of 3 during the same period of time.   After 1 month of air exposure, the conductivity of the parylene-coated sample had decreased by a factor of 1.4 while the conductivity of the uncoated sample fell by a factor of more than 20.   The final conductivities after 1 month were 150 $\Omega^{-1}\cdot cm^{-1}$ and 11 $\Omega^{-1}\cdot cm^{-1}$ for the coated and uncoated sample, respectively.

Electrical conductivity measurements vs. time were carried out at constant temperatures between 50°C and 115°C in order to compare the thermal stability between coated and uncoated $[CH(AsF_5)_{0.11}]_x$.   The electrical conductivity of

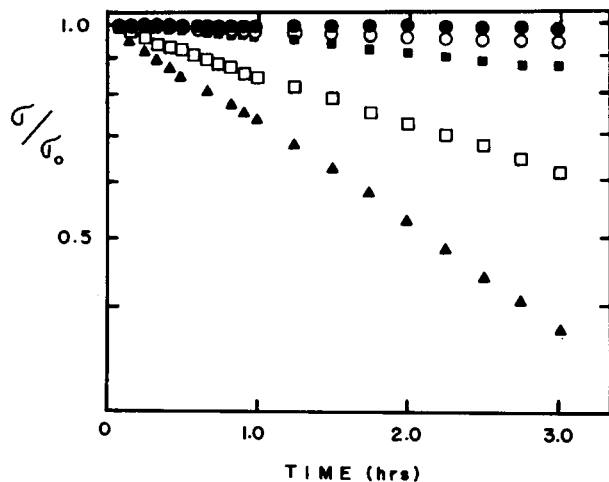Fig. 4. Decrease in conductivity with time at higher temperatures. Parylene-coated [CH(AsF$_5$)$_{0.11}$]$_x$. (●) 50°C; (○) 70°C; (■) 85°C; (□) 100°C; (▲) 115°C.

the sample 15 min after the heat was initiated was chosen as the initial value, σ_0, for each temperature. During this initial heating period, the conductivity first increased until the sample temperature became stabilized, a typical semi-
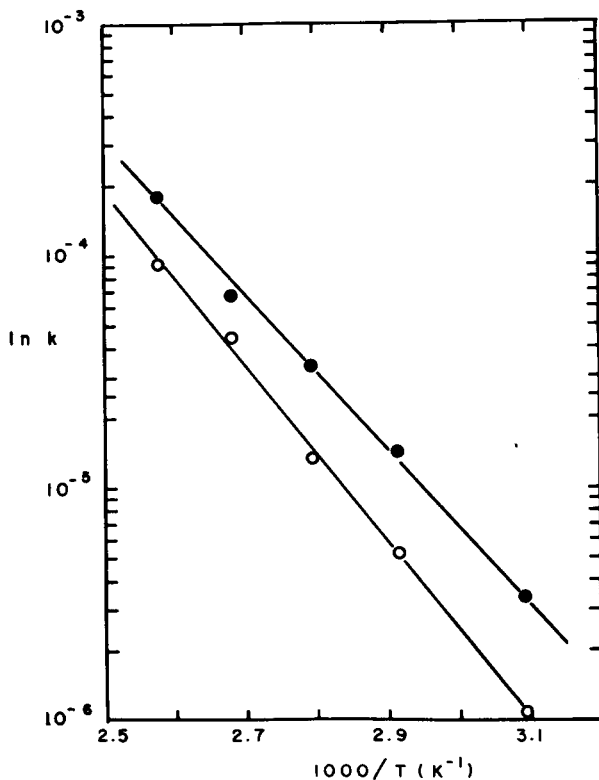

Fig. 5. Rate of conductivity decrease vs. $1/T$. [CH(AsF$_5$)$_{0.11}$]$_x$: (●) uncoated; (○) parylene-coated.

conductive behavior.   After the initial heating period, $\ln \sigma/\sigma_0$ decreased linearly with time, the rate of decrease becoming faster as the temperature is increased. Figure 3 (uncoated sample) and Figure 4 (coated sample) show plots of $\ln \sigma/\sigma_0$ vs. time at different temperatures.   This linearity indicates that the thermal decomposition of both uncoated and parylene-coated $[CH(AsF_5)_{0.11}]_x$ follows first-order kinetics.   The rate constants calculated from the slopes of the $\ln \sigma/\sigma_0$ vs. time plots, given in Table I, are used to construct the Arrhenius plots shown in Figure 5.   The activation energies obtained from these plots are 14.8 ± 1.5 kcal/mol and 17.2 ± 1.3 kcal/mol for the uncoated and parylene-coated samples, respectively.   This activation energy for the uncoated sample is in agreement with earlier observations.[6]

The parylene coating tends to stabilize the AsF_5 dopant as shown by a significant reduction in the decomposition rate throughout the temperature range employed.   This fact is promising enough to suggest that vapor-deposited parylenes might have useful applications as coatings on undoped and doped polyacetylene to stabilize them from air oxidation and from thermal decomposition at moderate temperatures.   Use of substituted poly(p-xylylene) such as poly-(chloro-p-xylylene), which has much better barrier properties to permanent gases and to moisture,[13] instead of unsubstituted poly(p-xylylene), might improve the stabilization of polyacetylene films even more.

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