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Iodine-Doped Ferrocenylene−Silylene and −Germylene Polymers

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Iodine doping of polyferrocenylenesilylene(germylene) thin films, $[(\eta^5\text{-}R_2EC_5H_4)Fe(\eta^5\text{-}C_5H_4)]_n$, E = Si, Ge, transforms them from insulators to conducting materials. The process was monitored by IR, Raman, and UV/vis spectroscopy and occurs via irreversible electron transfer to form of ferrocenium ion centers with $[I_3]^-$ counteranions. The latter further react with I_2 to form $[I_5]^-$ polyiodide anions in a reversible manner. A Mössbauer spectrum of the doped polymer suggests that alternate Fe centers have been oxidized. Treatment of the doped films with NH_3 results in a typical compensation process.

Introduction

The synthesis and properties of ferrocenylene−silylene, −germylene, and −stannylene polymers $[(\eta^5\text{-}R_2EC_5H_4)Fe(\eta^5\text{-}C_5H_4)]_n$, E = Si, Ge, Sn, and related complexes have been of recent interest due to the capacity of the ferrocenyl group to provide unique properties not generally associated with organic polymer materials.[1−3] For example, the materials possess two distinct redox processes when examined by cyclic voltammetry; they form electrochromic thin films; they can be used as variable refractive index sensor materials;[4a,b] and they have potential preceramic properties.[4c]

Such materials can form charge-transfer complexes and have been reported to form conducting materials upon doping with iodine.[3a,e,f] These latter systems are related to the so-called conductive low-dimensional halogenated materials whose electrical properties are controlled by the level of oxidation, by the type of $[I]^-\cdot nI_2$ anions formed, and by their mutual packing.[5] Here we report a study on the nature of the species formed upon iodine doping, relating their conductivity to optical, vibrational, and Mössbauer spectroscopic properties to permit an understanding of the processes involved in this doping procedure.

Experimental Section

General Procedures. The various polymeric materials were synthesized using published routes.[1,2] Doping was performed, in vacuo, by exposing thin films of the polymers, spin-coated or cast from benzene solutions (500−6000 Å on quartz, KBr or CaF_2 substrates), to iodine vapor. Conductivity measurements were obtained using published techniques on these samples,[3a] and UV/vis spectra were recorded concurrently. Doping was continued until constant conductivity values and constant electronic spectra were obtained. In all cases the constancy of both occurred at the same level of doping. UV/vis spectra were recorded on Perkin-Elmer λ-14 or Carl Zeiss M-40 spectrometers, Raman spectra on a Jobin-Yvon T64000

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Table 1. Electrical Properties of Iodine-Doped (Ferrocenylenesilylene) and (Ferrocenylenegermylene) Polymers, $(FCER_2)_n$, FC = $(\eta^5\text{-}C_5H_4)Fe(\eta^5\text{-}C_5H_4)$[a]

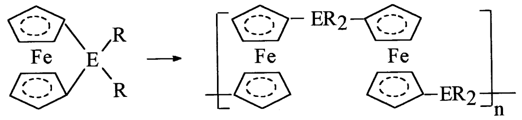
ER_2	thickness (Å)	$\sigma_{(saturated)}$ $(cm\ \Omega)^{-1}$	$\sigma_{(final)}$ $(cm\ \Omega)^{-1}$
MePhSi	1966	3×10^{-4}	2.0×10^{-5}
$MePhSi/Me_2Si$	1477	1.3×10^{-5}	3.0×10^{-6}
Et_2Ge	1291	1.8×10^{-4}	6.0×0^{-7}
Me_2Ge	2131	3.0×10^{-4}	6.0×10^{-6}
Bu_2Ge	1040	3.0×10^{-6}	2.0×10^{-7}

[a] Polymers were synthesized by thermal ring-opening of appropriate ferrocenophane as reported in ref 2b. Molecular weights were in the range 10^4−10^5 with a polydispersity of 1.3−1.8; film thickness measured by a Dektek 2A profilometer, ±70 Å.

instrument, IR on a Perkin-Elmer 1600 FTIR or Carl Zeiss M 82 spectrophotometer, and Mössbauer spectra on standard instrumentation with a 1.13 GBq cm^{-2} ^{57}Co source maintained at room temperature. Isomer shifts are reported relative to αFe at room temperature.

Results and Discussion

The ferrocenylene−silylene and −germylene polymers investigated in this study, $[(\eta^5\text{-}R_2EC_5H_4)Fe(\eta^5\text{-}C_5H_4)]_n$, E = Si, R_2 = Me_2, MePh, Me_2/MePh; E = Ge, R_2 = Et_2, n-Bu_2, were synthesized by the ring-opening of the corresponding ferrocenophanes, eq 1. The polymers were readily doped by iodine as thin films supported on quartz, KBr, or CaF_2 substrates. In this manner we were able to study the conductivity and electronic spectra of the samples (supported on quartz slides) under the same conditions. Raman spectra were recorded on the same samples. Separate studies on the IR properties were performed using films cast on KBr and CaF_2 plates.



(1)

The undoped polymers **1** are insulators, >10^{-14} Ω^{-1} cm^{-1}. Upon doping, the pale yellow films slowly turned light brown and then progressively darker. Both the conductivity and electronic spectra were measured concurrently, and as the samples became darker, the conductivity increased. After complete doping, i.e., when a constant value for the resistance and a nonchanging electronic spectrum had been obtained, the sample was evacuated and pumping was continued until new constant values for the resistance and reproducible spectra were again obtained. The highest levels for conductivity obtained were in the range 10^{-4}−10^{-5} Ω^{-1} cm^{-1}. In no case, after vacuum treatment, was the original insulating material recovered, and the final conductivities were in the range 10^{-7} Ω^{-1} cm^{-1}. This lack of reversibility is in contrast to the results obtained with thin films of $[(\eta^5\text{-}\{Me_2Si\}_6C_5H_4)Fe(\eta^5\text{-}C_5H_4)]_n$, where not only was the Si−Si bond stable to the iodine but several reversible oxidation/reduction cycles were observed.[3a] The values determined for the conductivity of the polymers under the conditions of saturated doping and final state doping as described above are presented in Table 1 and agree with previously published data.[3e] A typical sequence of the electronic spectra of the doped materials, along with their respective resistances obtained during the vacuum de-doping process, are presented in Figure 1.

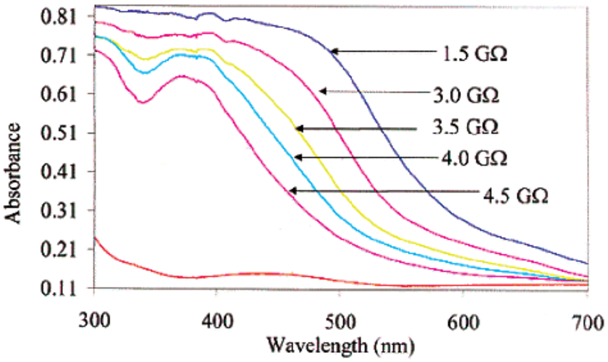


Figure 1. Sequence of optical spectra obtained during pumping on an iodine vapor saturated film of $[(\eta^5\text{-}Me_2SiC_5H_4)Fe(\eta^5\text{-}C_5H_4)]_n$. The initial saturated sample has a resistance of 1.5 GΩ, progressively increasing with pumping until the final equilibrium value of 4.5 GΩ. The spectrum at the bottom of the figure is that of the initial undoped polymer on the same scale.

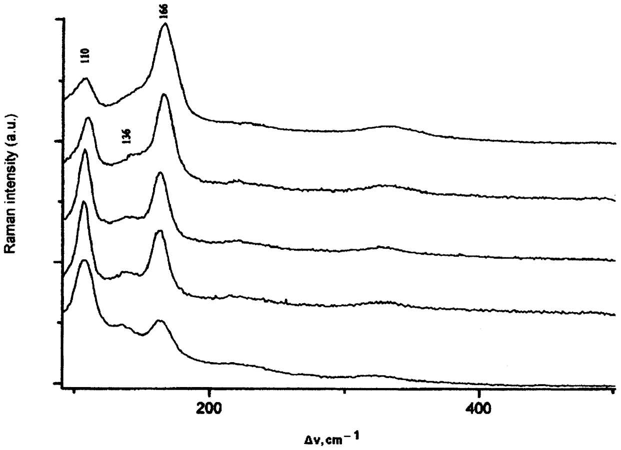


Figure 2. Raman spectra of a series of iodine-doped films of $[(\eta^5\text{-}MePhSiC_5H_4)Fe(\eta^5\text{-}C_5H_4)]_n$: from the top with progressively decreasing iodine content.

From the data recorded in Figure 1 it is clear that there is a permanent nonreversible process that occurs upon iodine doping. The original undoped samples possess the typical low extinction coefficient absorbance at ∼450 nm associated with the ferrocenylene groups in the polymer backbone. After doping, and pumping the samples until constant resistance and constant optical spectra were obtained, a residual absorbance band at ∼380 nm was observed, Figure 1. This band is characteristic of the I_3^- species and suggests that the polymer has been oxidized to create ferrocenium ions for which $[I_3]^-$ is the counteranion.[6]

To verify this assignment, we performed a Raman study on the thin films. A typical sequence of Raman spectra, covering the range 80−500 cm^{-1}, from the saturated to final state doping after pumping is recorded in Figure 2. Two major features may be seen, a band at ∼106 cm^{-1} and another at ∼170 cm^{-1}. The former band is well-documented to be derived from the $[I_3]^-$ ion and confirms the assignment noted above.[7] The second band,

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~170 cm^{-1}, has been established to be due to the polyiodide species $[I_5]^-$ that involves I_2 weakly bound to $[I_3]^-$.[8] It is clear from Figure 2 that the relative amount of I_5^- increases with greater levels of doping. The increasing amounts of $[I_5]^-$ coincide with the red shift of the UV absorption observed in Figure 1 and the increasing conductivity of the thin films. The extra I_2 binding observed with continued doping is reversibly removed in vacuo to form $[I_3]^-$ as the remaining anionic species. We have been unable to locate a reliable and documented electronic spectrum for the $[I_5]^-$ species; however, it seems reasonable to suggest that the spectra observed in Figure 1 upon increased doping, and increased conductivity, are a reflection of the increasing levels of $[I_5]^-$. It is established that increasing amounts of iodine can cause progressively higher polyiodides to be formed, $[I_7]^-$, $[I_9]^-$, etc.;[9] therefore, the precise content of the various polyiodide species that are formed at the highest doping levels is not clear at this time. All these polyiodides are in reality $[I_3]^-$ weakly bound to 1, 2, 3, etc., I_2 molecules, so that the electronic spectrum may be closely related to that of I_2. However, it is clear that pumping at high vacuum can remove the weakly bound I_2 from the higher polyiodides, and ultimately the removal of the excess I_2 results in the sole presence of the $[I_3]^-$ ion. These observations shed light upon very recent results in which the resistance of some analogous polymers doped with I_2 was found to be a function of aging and atmospheric pressure.[3f] The decreases in conductivity observed are thus seen as the loss of I_2 from polyiodides, predominantly $[I_5]^-$, formed during the oxidation of the polymer films. Each of the polymers used in this study possessed behavior similar to that noted in Figures 1 and 2, although with varying values for the conductivity of the samples. The thicker the film used in our studies, the more difficult it was to remove the iodine from the polyiodide anions, and with thick films the process of doping to the higher levels was effectively irreversible on a time scale of hours. Treatment of iodine-doped films with NH_3 did result in a so-called "compensation effect" and re-formed an insulating material. Such an effect has been observed from other iodine-doped polymers.[10]

Cyclic voltammetric analysis of the ferrocenylene-silylene(germylene) polymers has shown that oxidation of the polymers occurs in two discrete steps. Initially alternative Fe centers are oxidized, and then at a higher oxidation potential the remaining Fe centers can be oxidized.[1,2] The second process requires more energy due to the electronic effect of the neighboring ferrocenium ions created in step 1. To assess the extent of oxidation of the iron centers in the iodine doping process, we have performed an initial Mössbauer analysis on the samples described above when excess iodine has been removed in vacuo.

The Mössbauer spectrum of a doped sample of $[(\eta^5\text{-}MePhSiC_5H_4)Fe(\eta^5\text{-}C_5H_4)]$ at 293 K is presented in Figure 3. It consists of a doublet (with isomer shift $\delta(1) = 0.45 \pm 0.03$ mm/s, quadrupole splitting $\Delta(1) = 2.27 \pm 0.03$ mm/s, and line width $\Gamma(1) = 0.24 \pm 0.03$ mm/s) and an inner singlet (with isomer shift $\delta(2) = 0.46 \pm 0.03$ mm/s and line width $\Gamma(2) = 0.48 \pm 0.03$ mm/s). The singlet is actually an unresolved doublet which, being least-squares fitted by Lorentzian line shapes, gives $\Delta E_Q = {\sim}0.2$ mm s^{-1} with equal intensities and line widths of the two components. These doublet and singlet parameters are in agreement with those reported for Fe(II) atoms in ferrocene and its derivatives and for Fe(III) in ferricenium triiodide.[11] Thus not all the Fe centers in the polymer have been oxidized, since both Fe^{2+} and Fe^{3+} species are present. Both localized[12a] and delocalized[12b] Fe(II)/Fe(III) mixed valence ferrocene systems have been reported, and the present spectrum shows that in the doped polymers the centers are localized; that is, there is no electron-hopping between the two Fe centers on the Mössbauer time scale. The ratio of the two spectral component areas is close to 1, suggesting that the two forms of iron may be in approximately equal amounts.

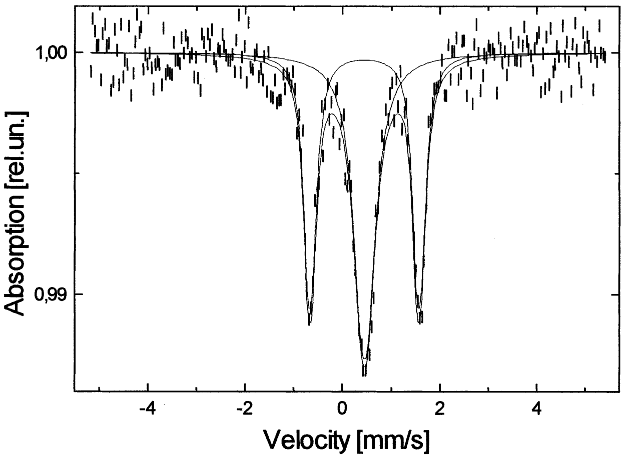

Figure 3. Mössbauer spectrum of the doped sample of $[(\eta^5\text{-}MePhSiC_5H_4)Fe(\eta^5\text{-}C_5H_4)]_n$ taken at room temperature.

There are many reports on the oxidation of ferrocene by iodine to yield ferrocenium ions including a series of studies by the Hendrickson group on species with two or more ferrocene centers.[12b] These authors suggested that infrared spectroscopy can be useful in analyzing the degree of oxidation in the resulting complexes. They reported that a band at ~813 cm^{-1} is associated with the Fe^{II} form of ferrocene and that upon oxidation to Fe^{III} it was transformed to a band at ~845 cm^{-1}. The IR spectrum of undoped phenyl(methyl)silylene polymer exhibits bands at 817 and 833 cm^{-1}. Upon high levels of doping, these bands diminish in intensity and ultimately almost disappear to be replaced by the intense band at 862 cm^{-1}. Upon removal of the polymer film from the I_2 environment, and with pumping to an equilibrium condition, this latter band itself diminishes and the lower frequencies are partially recovered such that the two sets are of approximately equal intensity. If the Hendrickson analysis is indeed appropriate, then

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the IR-calculated amounts of [Fc] and $[Fc]^+$ at this stage happily coincide with the estimate noted above based upon the Mössbauer data and collected on the same sample.

The overall result is that in the doped polymer form studied alternative iron centers have been oxidized, a result that parallels the data obtained from cyclic voltammetric analysis of undoped samples. Furthermore, our results are in agreement with studies by the Manners group on model oligomeric compounds.[13] They showed that linear oligomeric ferrocenylenesilylenes, containing up to nine units, are readily oxidized by I_2 to yield materials with alternating Fe(III) and Fe(II) iron centers, with concurrent formation of $[I_3]^-$ anions.

However, as originally noted, this analysis must be used with some caution[12b] and is beyond the scope of the present report, but may serve as a starting point for further study. For example, with very high I_2 doping levels the IR data suggest that all the Fc units can be oxidized to $[Fc]^+$. To date we have no evidence for this from Mössbauer spectroscopy since we have used this technique only in the absence of an excess iodine environment. It is well-established that the charge-transfer complex of ferrocene and TCNE is stable in the solid state and in acetonitrile, but readily dissociates to recover ferrocene and TCNE upon addition of the nonpolar cyclohexane, which does not facilitate the stabilization of charge separation. It seems that a similar situation may be present in this study where the large amount of excess I_2 stabilizes complete metal oxidation, but the second, more energy demanding oxidation step is readily reversible upon removal of the I_2.

Doping of $(\eta^5\text{-}Me_3SiC_5H_4)_2Fe]$. We have also examined the model system 1,1′-bis(trimethylsilyl)ferrocene, $(\eta^5\text{-}Me_3SiC_5H_4)_2Fe]$, **2**, using UV/visible, Raman, and IR spectroscopy in the undoped and doped forms. From such a study it was apparent that after the initially formed $[(\eta^5\text{-}Me_3SiC_5H_4)_2Fe]^+I_3^-$ (a crystalline substance) no further reaction with I_2 occurs to form higher polyiodides. There is no evidence for the Raman band at 170 cm^{-1} associated with $[I_5]^-$, Figure 4, and the electronic spectrum reveals only the absorbance at ∼380 nm associated with $[I_3]^-$. Analysis of the IR spectra of the doped and undoped samples of **2** was not productive. The IR spectrum of the undoped material in the analytical region of 700−900 cm^{-1} exhibited bands at 898 (m), 863 (m, sh), 833 (bd, st), 820 (bd, st, sh), 753, and 691 cm^{-1} that preclude the simple analysis noted above to monitor the oxidation process. Upon doping, all the bands remained, with a slight shift of the broad band in the 820−833 region to 833−840 cm^{-1}.

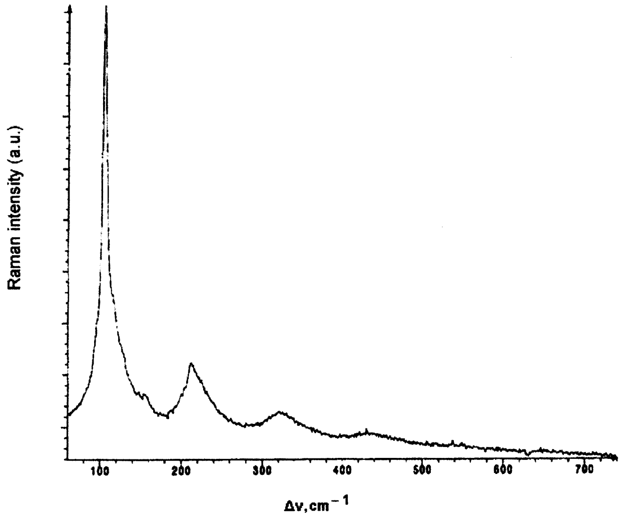

Figure 4. Raman spectrum of iodine-doped $[(\eta^5\text{-}Me_3SiC_5H_4)_2Fe]$.

The results obtained from the iodine reaction with **2**, and the results of studies on the oligomeric ferrocenylenesilylenes, which result only in the formation of the $[I_3]^-$ counteranion, show that it is the polymeric nature of the ferrocenylene−silylene and −germylene materials that is responsible for the extra binding of iodine to form the higher polyiodides. In general the materials are semicrystalline/amorphous polymers,[1g,2b,h] and in the amorphous regions there is sufficient space to permit the formation of the more bulky polyiodide counterions. However upon I_2 doping of **2** and the oligomeric materials, crystalline materials are formed that apparently preclude further formation of such species. It is also clear that the polyiodides are responsible for both the longer wavelength absorbance and enhanced conductivity noted from the data in Figure 1. Whether the extra conductivity is associated simply with the polyiodides per se or via a more ordered form of the polymer that is induced by their formation is open to question. From detailed studies on mixed valence state $[\text{biferrocene}]^+I_3^-$ compounds, Nakashima and co-workers were able to conclude that *neighboring metal centers interacted directly in the unsubstituted biferrocene, but via the triodide anions for the 1′,1‴-diethylbiferrocenium analogue.*[14] Thus, substituents on the cyclopentadienyl ring have a dramatic effect upon metal−metal interactions. Changes in the anion structure were also shown to facilitate valence-detrapping in the biferrocene mixed valence compounds.[14] The increased conductivity of the silyleneferrocenylene polymers upon transformation of the $[I_3]^- \rightarrow [I_5]^-$ $([I_3{\cdot}I_2]^-)$ can therefore be related to such structural features since the conductivity of mixed valence ferrocene-based polymers has been shown to be consistent with an electron-hopping model.[15]

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