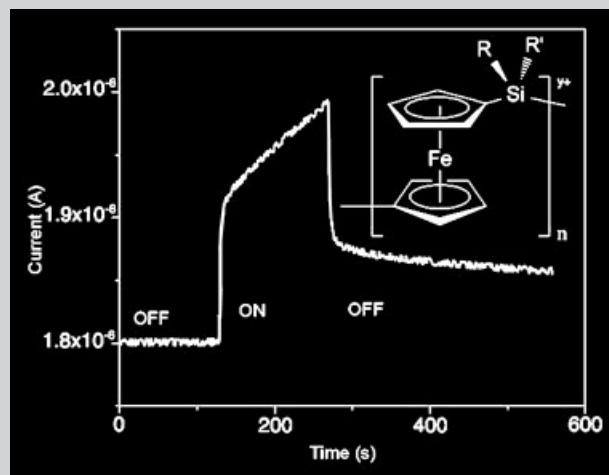


**Full Paper:** Irradiation of thin films of poly(ferrocenylmethylphenylsilane) ( $[\text{Fe}(\eta^5\text{-C}_5\text{H}_4)_2\text{SiMePh}]_n$ ) cast from chloroform solution with UV light leads to photooxidation of ferrocene centers in the polymer main chain. The extent of the polymer oxidation can be controlled in the range ca. 0–5% by the duration of the irradiation exposure and by the concentration of chloroform. The photooxidized polyferrocenylsilane material is conductive, with an increased conductivity of greater than three orders of magnitude relative to the unoxidized material. In addition, the photooxidized polymers have been found to be photoconductive. The photooxidation process can be reversed by means of chemical reduction using hydrazine or decamethylferrocene, leading to the regeneration of the neutral polymers. However, substantial molecular weight decline was detected during the photooxidation/reduction process, presumably as a result of chain cleavage reactions induced by the anionic or radical chlorinated photoproducts. Methylation of the cyclopentadienyl rings of the ferrocene moiety in the polymer was found to lead to materials which are significantly more stable.



Time trace of the current at constant applied voltage of 100 V for a PFS film upon illumination. The ON and OFF states were created by using a mechanical shutter.

## Photooxidation and Photoconductivity of Polyferrocenylsilane Thin Films

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**Keywords:** conducting polymers; inorganic polymers; photochemistry; photoconductivity

### Introduction

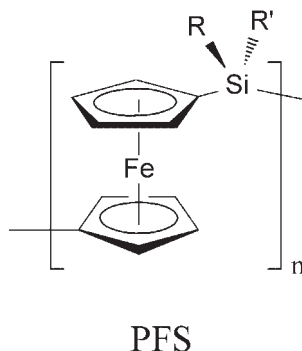
Intense interest in semiconducting,  $\pi$ -conjugated polymers exists due to their potential for incorporation into light-weight, flexible and efficient devices. This area of research has grown rapidly, and electroluminescent devices, photovoltaic devices, and field-effect transistors have all been realized.<sup>[1–3]</sup> However, compared to the organic polymers, metal-containing polymers still represent a relatively undeveloped field. Recent advances in the controlled synthesis of high molecular weight examples of these materials have led to growing interest in this area.<sup>[4–6]</sup> Such polymers have considerable potential in materials science due to the pre-

sence of the metal atoms, which can impart unique electrical, optical and magnetic properties. As well, chemical modification of the polymer involving the metal atoms allows tunability of the polymer properties. All of these aspects endow metal-containing polymers with the ability to achieve functionality often not readily available in organic polymers.

Polyferrocenylsilanes (PFSs) represent a novel class of metallopolymers, which are relatively easy to synthesize and can be prepared with high molecular weights ( $\bar{M}_w > 10^6$ ,  $\bar{M}_n > 10^5$ ).<sup>[7]</sup> These materials are highly processible and the high metal content has been found to give rise to many interesting properties.<sup>[7]</sup> Polyferrocenylsilanes possess the well-known, redox-active ferrocene unit in the main chain. The polymers exhibit two reversible redox waves, the first of which arises from the initial oxidation of

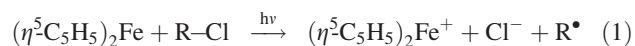
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alternating ferrocene units as a result of metal–metal interactions.<sup>[8–11]</sup>



The intrinsic conductivity of PFS is on the order of  $10^{-11} \Omega^{-1} \cdot \text{cm}^{-1}$ ; however, vapor-phase  $\text{I}_2$  doping of films of the polymer leads to an increase in conductivity of more than 8 orders of magnitude and yields p-type semiconducting films.<sup>[12–15]</sup> This has led to interest in the use of PFS as protective, charge dissipation materials.<sup>[16]</sup> Oxidation of iron centers in PFS changes its electrical, optical and physical properties, and thus motivates the exploration of methods of controlled oxidation to allow incorporation of PFS into responsive devices.

The photochemistry of ferrocene has been well studied.<sup>[17]</sup> Ferrocene is known to undergo charge-transfer due to solvent photochemistry with halocarbon solvents, resulting in production of ferrocenium cation and reduction of the halocarbon, as shown in Equation (1).<sup>[18,19]</sup> Further reactivity involving the radical generally occurs, with substitution reactions on the cyclopentadienyl ring and/or decomposition of the ferrocenium species possible, as well as oxidation of another ferrocene unit.<sup>[17,20,21]</sup>



The charge-transfer to solvent property has been previously used for the photoelectrochemical reduction of halocarbons by electrode-confined methacrylate- and siloxane-based polymers containing ferrocene and cobaltocene, respectively.<sup>[22]</sup> The charge-transfer to solvent between ferrocenes and  $\text{CHCl}_3$  in a PMMA matrix has also been investigated, and photogeneration of the ferrocenium cation was observed.<sup>[23,24]</sup> The resulting composite material was reported to exhibit photoconductivity.<sup>[25]</sup> Because of our interest in the electrical properties of ferrocene-containing polymers, we have explored the potential of photooxidation of PFS in the presence of  $\text{CHCl}_3$ .

In the present paper we have studied the influence of the photooxidation of thin films of poly(ferrocenylmethylphenylsilane) ( $[\text{Fe}(\eta^5\text{-C}_5\text{H}_4)_2\text{SiMePh}]_n$ , PFMPS) in the presence of chloroform on the molecular weight, optical and electrical properties of the polymer. We demonstrate that

this type of photooxidation significantly increases the conductivity of the films and makes them photoconducting.

## Experimental Part

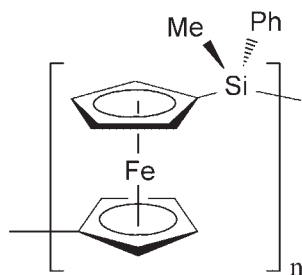
PFMPS<sup>[26]</sup> and poly[(dimethylferrocenyl)dimethylsilane]<sup>[27]</sup> (PDMFS) were prepared as previously reported. Molecular weights were determined by gel permeation chromatography (GPC) using a Waters 2690 Separation Module equipped with a column heater, Ultrastaygel column (pore sizes of  $10^3$ – $10^5$  Å), in-line degasser and a differential refractometer. The eluent was THF, and a flow rate of  $1.0 \text{ mL} \cdot \text{min}^{-1}$  was used. Molecular weights ( $\bar{M}_n$ ) are reported relative to polystyrene standards, which were purchased from American Polymer Standards, and are based on an average of at least three separate samples. Films of the polymer were cast from concentrated chloroform solutions onto glass or indium tin oxide (ITO)/glass substrates by a mechanically-driven blade technique and allowed to dry in air. The cast films were in the range of 10–20  $\mu\text{m}$  thick, as measured using a Dektak3 surface step profiler. The UV treatment was performed in air using an Optical Associates Inc. near-UV source equipped with a 450 W Hg lamp followed by selective reflectors and a collimator, delivering at the output a spatially homogeneous light spot in the spectral range 350–450 nm. For UV exposures in the presence of chloroform vapor, the sample was supported on an inverted glass dish such that it was ca. 1 cm above the level of chloroform in a shallow glass Petri dish. The dish was covered with a larger Petri dish lid to prevent rapid evaporation of chloroform during the irradiation time. Hydrazine hydrate and decamethylferrocene were purchased from Aldrich and used as supplied. Solutions of hydrazine (ca. 15 wt.-% in methanol) and decamethylferrocene (ca. 0.2 wt.-% in 1:1 hexane/acetone) were prepared in air. Chemical reduction of the oxidized polymer films was performed by soaking the film in a sufficient volume of the appropriate solution to cover the film entirely. The optical spectra were measured in transmission mode using a Cary 500 spectrophotometer. The extent of photooxidation was estimated from the optical spectrum of the films by using the ratios of the extinction coefficients<sup>[28]</sup> of ferrocene and the ferrocenium ion at the appropriate wavelengths. Electrical measurements were obtained using an Agilent 4155C semiconductor parameter analyzer; films were deposited on glass substrates with interdigitated structures of conducting ITO for which the interelectrode spacing was 0.5 mm and the total length was 19 cm. The photoconductivity was measured by illumination from a fiber optic illuminator equipped with a 150 W projection lamp.

## Results and Discussion

### Photooxidation of PFMPS in the Presence of Chloroform

PFMPS is an amorphous material with a  $T_g$  of 90 °C. The lack of crystallinity was regarded as an attribute for studying the electrical properties of polyferrocenes, as complications arising from sample thermal history would be

minimized. We have found that UV irradiation of PFMPS films cast from  $\text{CHCl}_3$  solutions results in photooxidation of the material.



PFMPS

Qualitatively, the process is readily monitored visually, with the originally orange films becoming increasing blue-green in appearance during the UV irradiation. The photooxidation can be followed spectroscopically as shown in Figure 1. The optical spectrum of the untreated PFMPS film (curve A) shows the well known<sup>[28]</sup> visible region band at 2.75 eV, which arises due to d–d electronic transitions localized on the Fe centers. After exposure of the film cast from  $\text{CHCl}_3$  (in air) to UV light (curve B) a band at 1.92 eV develops which is ascribed to a ligand-to-metal charge transfer (LMCT) transition, indicative of the ferrocenium centers formed upon oxidation.<sup>[28]</sup> The percent oxidation of this sample was reproducible, and was estimated to be ca. 1%. The UV light exposure in the presence of chloroform vapor (curve C) increases the amplitude of this band by a factor of 4 and an additional band at 0.93 eV appears, which is ascribed to intervalence charge transfer (IT) between

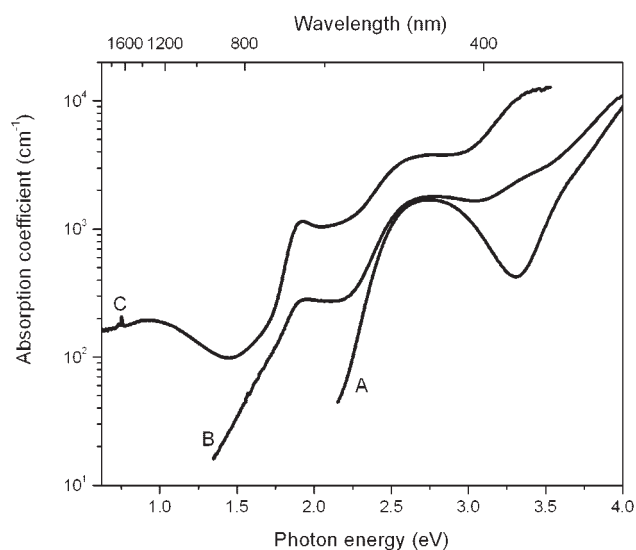


Figure 1. Absorption coefficient spectra of a PFMPS film cast from  $\text{CHCl}_3$  (A) without irradiation, (B) UV-treated in air, and (C) UV-treated in  $\text{CHCl}_3$  vapor.

Fe(II) and Fe(III) states as has been noted in related mixed-valence oligoferrocene<sup>[9,29,30]</sup> and polyferrocene<sup>[31]</sup> derivatives. Samples exposed to UV irradiation in chloroform vapor reproducibly gave a percent oxidation of ca. 5%. The optical absorption spectrum measured after UV treatment of  $\text{CHCl}_3$  solutions of the polymer shows the same features qualitatively. However the IT band is more intense in the solution samples than observed for the films cast from  $\text{CHCl}_3$ . The appearance of the LMCT and IT bands was demonstrated previously for the case of electrochemically oxidized PFS gels.<sup>[7,31]</sup>

The oxidation also causes changes in the high energy absorption region which can be explained by the difference in the energy and the oscillator strength of the optical transitions in the oxidized state. The spectrum of the relative changes in the absorption coefficient illustrates the spectral ranges of maximal change, which occur at 1.92 and 3.33 eV (Figure 2). The saturation of the changes after 45 min UV exposure of this film suggests the exhaustion of the oxidizing agent ( $\text{CHCl}_3$ ). Consistent with this, we observed that for thinner films, this saturation occurs on a shorter timescale than for thicker films. By ensuring a significantly large source of oxidizing agent, either by placing the films in chloroform vapor or by performing the oxidation in solution, we were able to induce a higher degree of oxidation in the polymer and to observe the IT absorption band at 0.93 eV.

#### Reduction of Photooxidized PFMPS

The photooxidized films may be chemically reduced, and we have studied this using hydrazine ( $\text{N}_2\text{H}_4$ ) and

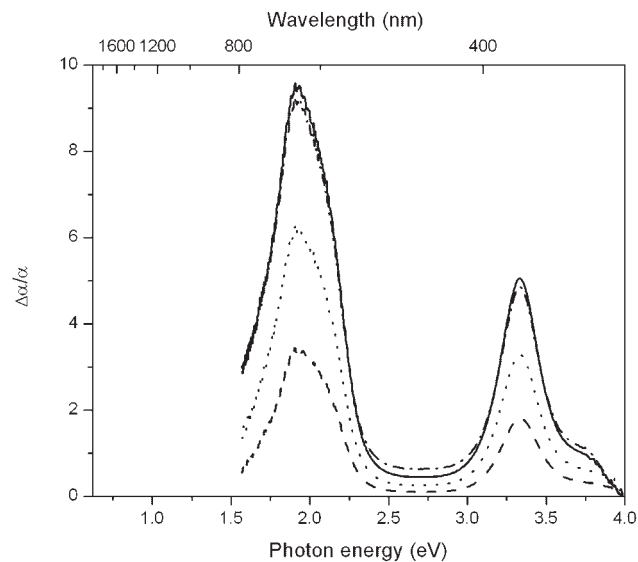


Figure 2. Relative changes in the absorption coefficient after the UV treatment in air of a 17  $\mu\text{m}$  thick film of PFMPS as a function of the exposure time for 15 min (dashed line), 30 min (dotted line), 45 min (dash-dotted line), and 60 min (solid line).

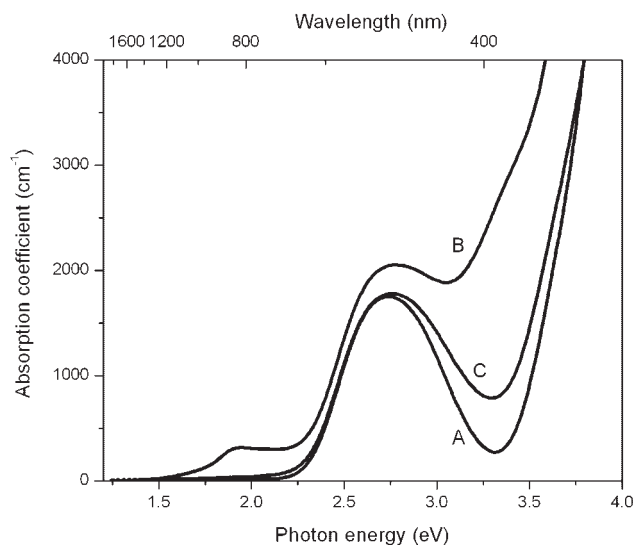


Figure 3. Absorption coefficient spectra of PFMPS films cast from  $\text{CHCl}_3$  (A) before irradiation, (B) after UV exposure for 1 h, and (C) after chemical reduction.

decamethylferrocene ( $\text{Cp}_2^*\text{Fe}$ ) as reducing agents. The reduction of the polymer films was monitored spectroscopically as the reduced material has no LMCT absorption band in the visible region – the disappearance of the band at 640 nm (1.92 eV) in the optical spectrum serves as a good indicator of the reduction process. Figure 3 shows representative transmission spectra of a PFMPS polymer film cast from  $\text{CHCl}_3$  (A), after photooxidation via UV irradiation (B), and after chemical reduction (C). Though the spectroscopic features of the reduced films are the same as prior to the photooxidation treatment, visible cracks form in the films after reduction and drying in air. However, the photooxidized films are of high optical quality, comparable to that of the film prior to irradiation. The quality of the films was judged from the absence of visible cracks and defects, as well as a flat baseline with high transmission in the optical spectrum at wavelengths (ca. 750–1200 nm) outside the absorbing region, where scattering effects would appear in films of lower quality.

The oxidation is reversible, however fragmentation of the polymer occurs during the overall photooxidation/reduction process. GPC measurements indicate a reduction of the molecular weight from  $\bar{M}_n = 220\,000$  to 8 000 after photooxidation and reduction by methanolic hydrazine solutions (Table 1, sample 4). Control samples of films cast from  $\text{CHCl}_3$  which were not irradiated with UV light, and either exposed to methanolic hydrazine or just methanol were also studied. Without treatment with hydrazine, no significant molecular weight decline was observed, while exposing the films to hydrazine resulted in a slight decrease of the molecular weight from  $\bar{M}_n = 220\,000$  to 190 000 (Table 1, samples 1 and 3), with no observed spectroscopic changes in these samples. Given that the polydispersity of

Table 1. Molecular weight data for PFMPS thin films.

Sample	$\bar{M}_n$ (PDI) <sup>a)</sup>
1 <sup>b)</sup>	220 000 (2.25)
2 <sup>c)</sup>	212 000 (2.25)
3 <sup>d)</sup>	190 000 (2.08)
4 <sup>e)</sup>	8 000 (2.08)
5 <sup>f)</sup>	21 000 (1.89)
6 <sup>g)</sup>	14 000 (2.01)

a) GPC data are averages of at least 3 separate samples.

b) PFMPS powder as prepared.

c) PFMPS film cast from  $\text{CHCl}_3$ .

d) PFMPS film cast from  $\text{CHCl}_3$  exposed to  $\text{N}_2\text{H}_4$  solution.

e) PFMPS film cast from  $\text{CHCl}_3$ , exposed to UV irradiation for 60 min then reduced with  $\text{N}_2\text{H}_4$  solution for 3 h.

f) As for sample 4, except reduced with  $\text{Cp}_2^*\text{Fe}$  solution for 10 min.

g) PFMPS film cast from  $\text{CHCl}_3$ , exposed to UV irradiation for 60 min in the presence of  $\text{CHCl}_3$  vapor, then reduced with  $\text{Cp}_2^*\text{Fe}$  solution for 10 min.

the polymer before and after the photooxidation/reduction cycle does not change substantially (Table 1), and as a bimodal molecular weight distribution is not detected after the treatment, it would seem that the fragmentation of the polymer occurs via chain scission along the polymer backbone in a moderately uniform, rather than totally random, manner. With this in mind, we thus estimate the number of chain cleavages that are occurring during the process as  $[(\bar{M}_n(\text{before})/\bar{M}_n(\text{after})) - 1]$  where the before and after terms refer to the polymer as prepared and after the photooxidation/reduction cycle, respectively. Thus, photooxidation followed by hydrazine treatment results in about 26 chain scissions.

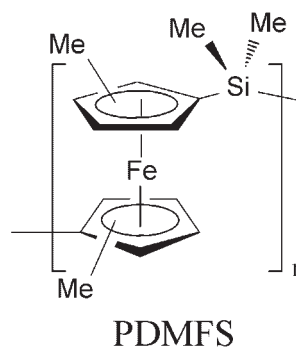
To examine the effects of UV light on the polymer films, PFMPS films were also cast from toluene. In contrast to the  $\text{CHCl}_3$  cast films, the toluene cast films show no changes in their optical spectra upon exposure to UV irradiation. The effects on molecular weight of UV irradiation and treatment with hydrazine solution on toluene cast films are negligible compared with those observed for the  $\text{CHCl}_3$  cast films. No change in molecular weight was observed for films of PFMPS cast from toluene after UV treatment for 1 h, and only a slight decrease in  $\bar{M}_n$  (from 220 000 to 176 000) is observed for toluene cast PFMPS films exposed to UV irradiation for 60 min, followed by treatment with methanolic hydrazine. This molecular weight decline is thus most likely a result of reaction with hydrazine, as the  $\bar{M}_n$  value is comparable to that observed for treatment of an unoxidized  $\text{CHCl}_3$  cast film (see above). In comparison, substantial molecular weight decline occurs for the films cast from  $\text{CHCl}_3$  undergoing the same treatments. Thus, the presence of  $\text{CHCl}_3$  is necessary for the photooxidation to occur, and the significant decline in the molecular weight of the polymer is concomitant with the photooxidation/reduction process.

The non-negligible molecular weight decline observed after exposure of the unoxidized films (cast either from toluene or  $\text{CHCl}_3$ ) to hydrazine indicates that hydrazine is not an “innocent” reducing agent. Facile reduction of oxidized ferrocene-containing dendrimers using  $\text{Cp}_2^*\text{Fe}$  has been reported,<sup>[32]</sup> and we also examined its use for the reduction of the photooxidized films. Decamethylferrocene is a more favorable reducing agent in our systems than hydrazine. No molecular weight change was observed for an unoxidized film cast from  $\text{CHCl}_3$  which was treated with  $\text{Cp}_2^*\text{Fe}$ . As well, the reduction of the photooxidized PFMPS films was much more rapid as observed visually, with the film color changing from blue to orange within ca. 5 min (complete reduction confirmed by UV-vis), compared to > 60 min for the hydrazine-treated samples. The molecular weight decline measured in the samples reduced using  $\text{Cp}_2^*\text{Fe}$  was less than that of the hydrazine-reduced materials (Table 1, samples 4 and 5), however the fragmentation of the polymer main chain during the photooxidation/reduction process is still significant. The reduced material possessed an  $\bar{M}_n$  value of 21 000, compared to the hydrazine reduced films, which showed  $\bar{M}_n = 8\,000$ . This corresponds to an average of 9 chain scission events per chain.<sup>b</sup> The optical quality of the films reduced by  $\text{Cp}_2^*\text{Fe}$  was also found to be higher than those reduced using  $\text{N}_2\text{H}_4$ , with less visible fracturing, and a lower scattering loss in the optical spectra of the films.

The nature of the fragmentation process for PFMPS during the photooxidation process and subsequent reduction is currently unclear. However, the main chain of the oxidized polymer is expected to be more susceptible to fragmentation due to the potentially more labile Si–Cp and Fe–Cp bonds. Indeed, in preliminary studies, molecular weight decline has been noted during oxidation/reduction cycles for PFS materials in solution when using a variety of chemical oxidants. It was also found that the nature of the anion affects the stability of the oxidized polymer.<sup>[33]</sup> For example, oxidized PFS possessing  $\text{PF}_6^-$  counterions was found to be significantly more resilient to main chain cleavage than analogous  $\text{I}_3^-$  containing polymers, possibly due to the greater nucleophilicity of the triiodide anion.<sup>[33]</sup> In the present study, presumably  $\text{Cl}^-$  is the counterion present in the photooxidized material, and this is anticipated to be a non-innocent anion which may degrade the oxidized polymer via reaction with Si–Cp or Fe–Cp bonds.

Functionalization of the Cp rings of the ferrocenyl centers with electron-donating groups has the potential to stabilize the oxidized materials, as well as lowering the

oxidation potential of the ferrocene center in the neutral species.<sup>[34,35]</sup> We have previously discussed the preparation and properties of Cp-methylated PFSs.<sup>[27]</sup> We thus undertook a preliminary study to test the durability of such materials in the photooxidation with  $\text{CHCl}_3$  and reduction with  $\text{Cp}_2^*\text{Fe}$  process, using the same conditions applied to the PFMPS films. For the case of poly[(dimethylferrocenyl)dimethylsilane] (PDMFS), significant molecular weight decline was again observed, from  $\bar{M}_n = 73\,000$  (PDI = 1.94) for the polymer as prepared to  $\bar{M}_n = 12\,000$  (PDI = 1.94) for the polymer after reduction. Considering the much lower molecular weight of the starting material in the methylated polymer case compared to the PFMPS experiments discussed earlier, this is a promising result – the number of scissions per chain has been reduced to ca. 5 compared to 9 for the PFMPS case. This encouraging result has prompted us to begin to explore the utility of the photooxidation process with new PFS derivatives with different substituents on the Cp rings which are electron donating and/or sterically bulky in order to stabilize the materials towards the chain scission reactions.



The photooxidation of PFS/ $\text{CHCl}_3$  most likely occurs via a route analogous to that accepted for the ferrocene system,<sup>[17]</sup> whereby the ferrocene centers are oxidized to give ferrocenium units, a chloride ion, and the  $\cdot\text{CHCl}_2$  radical species. The generated radical may further react with the PFS chain to either oxidize another ferrocene unit and generate the highly reactive  $\text{CHCl}_2^-$ , or cleave a Si–Cp or Fe–Cp bond. Likewise, the  $\text{Cl}^-$  ion may react to cleave a Si–Cp bond adjacent to, or an Fe–Cp bond involving, an Fe(III) center. It is worth noting however that, regardless of the molecular weight of the polymer, the photooxidized species which is generated exhibits the characteristic increase in conductivity of doped PFS,<sup>[12,13]</sup> and interestingly also shows photoconductive properties, which has not previously been observed in doped PFS materials.

#### Conductivity Measurements on Photooxidized PFMPS Films

Prior to UV exposure of films of PFMPS cast from  $\text{CHCl}_3$ , the materials are very poorly conducting ( $\sigma = 6.0 \times 10^{-11} \text{ } \Omega^{-1} \cdot \text{cm}^{-1}$ ). However, upon treatment with UV

<sup>b</sup> The estimated number of chain scissions is nearly the same as the number of oxidation sites calculated based on the optical spectrum (1% oxidation = ca. 8 ferrocenium centers per polymer chain). This would suggest that every oxidation results in chain cleavage.

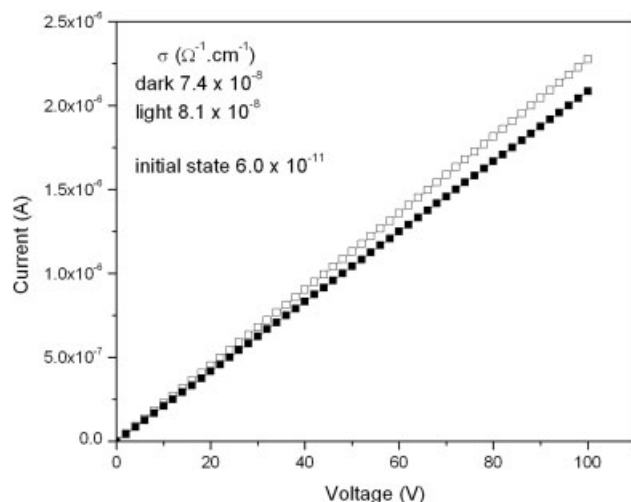


Figure 4. Current–voltage data for the film treated by UV light for 60 min in  $\text{CHCl}_3$  vapor. The solid symbols are for dark measurements and the open symbols are for measurements under halogen lamp illumination.

light, the material becomes semiconducting, consistent with oxidative doping of the PFMPs as reported previously using  $\text{I}_2$  doping.<sup>[12–14]</sup> The photooxidation results in a significant change in the dark conductivity of the PFMPs films of about three orders of magnitude (to  $7.4 \times 10^{-8} \Omega^{-1} \cdot \text{cm}^{-1}$ ), as indicated in Figure 4. The current–voltage characteristics of the used structures show exact straight lines (Figure 4) and high reproducibility allowing the derivation of a well-defined value for the conductivity. The stability of the dark current also rules out the contribution of ionic current. The latter is illustrated once again in Figure 5 for the first 120 s of the experiment before starting the illumination.

The same cannot be said for the case of using the combination of applied electric field and light illumination from a halogen lamp of 150 W. Figure 5 shows that after light illumination the current increases stepwise, and after that continues to increase slowly. After removing the light the current drops again stepwise, followed by a very slow decay having a saturation level higher than the initial one. Obviously, the combination of electric field and white light illumination continues the oxidation process and/or leads to definite rearrangements in the film structure. Despite these difficulties, one can clearly and reproducibly detect changes in the current upon illumination. For the light source used we have detected relative changes in the conductivity of several percent upon illumination (Figure 4). This was sufficient for us to perform photocurrent spectral measurements, which will be presented in a forthcoming paper.<sup>[36]</sup> Photooxidation of ferrocene with chloroform within a poly(methyl methacrylate) (PMMA) matrix has recently been reported to give a photoconductive material.<sup>[25]</sup> However, examples of photoconductivity in polymeric ferrocene-based materials are exceptionally rare. Nishihara et al.

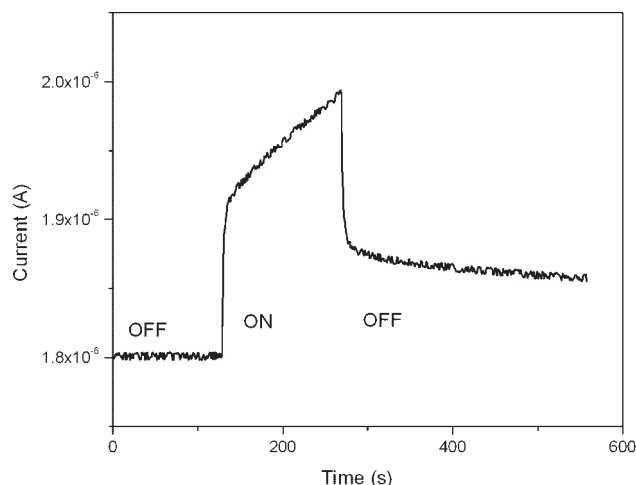


Figure 5. Time trace of the current at constant applied voltage of 100 V for the same film and the same illumination as in Figure 4. The ON and OFF states were created by using a mechanical shutter.

have reported that doping of oligoferrocenylenes with tetracyanoethylene (TCNE) gives charge-transfer complex-bearing materials that exhibit photoconductivity, though the molecular weights of the materials studied were all under 5000.<sup>[37,38]</sup> Ferrocene-containing conducting polymers<sup>[39]</sup> and self-assembled materials<sup>[40]</sup> have recently shown promise in photovoltaic applications. Thus, the photooxidation of PFSs in the presence of  $\text{CHCl}_3$  represents an interesting technique, offering the potential of photo-patterning and optical control of the electrical properties, to prepare (photo)conducting organometallic polymeric materials. In addition to chemical modification of PFSs in order to prepare more stable materials with the possibility of fully reversible photooxidation/reduction processes, we are also interested in improving the electrical conductivity and photoconductivity of the photooxidized materials by addition of e.g. radical scavengers or electron acceptors (such as TCNE). We are also now exploring the utility of this method for device applications.

## Conclusions

We have shown that photooxidation of PFMPs thin films in the presence of chloroform and UV light leads to a significant increase in conductivity. In addition, we have found that the resulting films are photoconductive, a new result for PFS materials. Chemical reduction of the photooxidized polymers is readily accomplished, however substantial molecular weight decline is apparent. This is probably a result of main chain cleavage reactions induced by the chlorinated photoproducts. A PFS derivative bearing methyl groups on the Cp rings of the ferrocene moiety in the polymer undergoes fewer chain scissions during the

photooxidation/reduction process, suggesting the potential for optimization of the materials to provide more stable photooxidized species.

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