

Optical control over photoconductivity in polyferrocenylsilane films

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(Received 11 June 2003; accepted 29 October 2003)

We report the study and elucidate the origin of the photoconductivity of polyferrocenylsilanes achieved through photooxidation performed by ultraviolet irradiation in the presence of chloroform. The persistence over months of the changes in the optoelectronic properties allowed more detailed studies of the charge photogeneration process. The photocurrent spectrum mimics that of the absorption indicating that the photooxidized material is not a mechanical mixture of oxidized and unoxidized polymer units. Photomodulation spectroscopy revealed the existence of long-lived photoexcited states with a lifetime in the millisecond range. They have been interpreted as trapped excitons at the oxidized sites where the polymer is deformed due to the presence of the chloroform derived counter ions. Because of the relatively long lifetime of the trapped excitons they can dissociate and the formed charge carriers can be separated in an externally applied electric field. The effect of the polymer chain deformation around the oxidized unit extends over the neighboring polymer units. In light of the potential applications of this class of polymers in various electronic and photonic devices, the clarification of such a basic process as the photocurrent generation will be a key factor for further technological development. © 2004 American Institute of Physics. [DOI: 10.1063/1.1635808]

I. INTRODUCTION

The promise of light-weight, efficient, low-cost electronic and optical devices continues to drive research into the chemistry, physics, and engineering aspects of polymers. By far the vast majority of effort has focused on organic, π -conjugated polymers and block co-polymers.^{1,2} A less studied, but very promising, class of materials is polymers into which transition metal atoms have been incorporated.^{3,4} These materials have shown novel physical properties which are attributable to the presence of the metal atoms within the polymer. Polyferrocenylsilanes (PFSs) are a class of organometallic polymers whose unusual physical properties^{5,6} arise due to the presence of iron atoms which are contained within the polymer via the presence of the ferrocene group in the backbone chain. A wide range of potential applications is envisioned, for example, in chemo-mechanical sensors, ceramic precursors, electrochromic materials, electrode mediators, and variable refractive-index materials.⁷⁻¹² Another attractive application is in nanocrystal/polymer composites¹³

where the polymer with appropriate functional groups is intended to replace the surface ligands and simultaneously to deliver electronic excitations to the nanocrystals in a light emitting device.

We have recently demonstrated¹⁴ an effective optical method for increasing the conductivity and photoconductivity of PFS. The ability to control optically the electrical properties of this class of conductive polymers opens the door to flexible engineering solutions, such as programmable two-dimensional keys, reconfigurable optical code-division multiple-access correlators, etc., employing materials of this type.

The attractiveness of such applications has motivated past work to achieve photoconductivity in ferrocene-based materials. Nishihara *et al.*¹⁵⁻¹⁷ have demonstrated photoconductivity for oligo- and polyferrocenylenes oxidized partially by tetracyanoethylene (TCNE). Thander and Mallik¹⁸⁻²⁰ have studied the photooxidation of ferrocene with chloroform confined in a poly(methyl methacrylate) matrix, and have demonstrated photoconductivity in this composite material. Oxidation of PFS, in particular by iodine vapor-phase doping, leads to a significant increase in conductivity of several orders of magnitude.^{10,21,22} The photooxidation method

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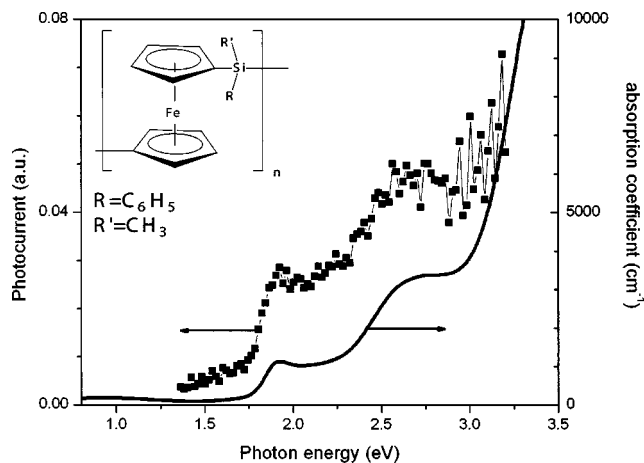


FIG. 1. Photoconductivity spectrum of a film photooxidized by using prefiltered UV light from a Hg lamp in an atmosphere of chloroform vapor (the corresponding absorption coefficient spectrum is shown for comparison). The inset shows the chemical structure of PFMPS.

of PFS demonstrated recently¹⁴ not only increases the polymer film conductivity but also results in remarkable and stable photosensitivity.

This development motivates the clarification of the electronic processes in the oxidized state, in particular the mechanism of charge transport and photogeneration. In the present paper, we present a detailed study of the spectral behavior of the photocurrent and of the photoexcited states in oxidized poly(ferrocenylmethylphenylsilane) (PFMPS), and we demonstrate how a particular photooxidation method influences details of the electronic structure of the material.

II. EXPERIMENT

PFMPS was synthesized as previously described,¹⁴ the chemical structure of which is shown in the inset of Fig. 1. Films were blade cast from chloroform solution onto glass substrates with, in cases, interdigitated structures of conducting indium tin oxide (ITO). The interelectrode spacing was 0.5 mm and the total length was 19 cm. The film thickness was measured by a surface step profiler.

We performed photooxidation using three methods:

- (1) illumination by a Xe lamp at ambient atmosphere;
- (2) illumination using collimated, filtered (350–450 nm) UV light from a Hg lamp at ambient atmosphere;
- (3) illumination using collimated, filtered (350–450 nm) UV light from a Hg lamp in chloroform vapor.

Photocurrent spectra were taken by applying a DC voltage of 100 V and measuring the voltage drop across a resistor. The samples were illuminated using monochromatic light from a tungsten halogen lamp passed through a single grating monochromator TRIAX 190. Long pass filters were used to reject the higher diffraction orders. The light was mechanically chopped at 32 Hz and the signal was detected by a lock-in amplifier SR 830. The presented data are normalized for the spectral distribution of the irradiation light. The photomodulation experiments were performed using the 442 nm line of a continuous-wave HeCd laser as pump beam and a

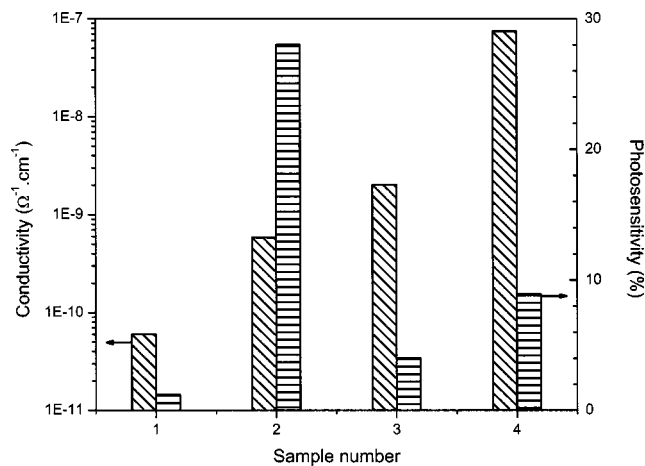


FIG. 2. Dark conductivity and photosensitivity, defined as the relative change of the conductivity upon illumination, for a pristine film (1), film photooxidized by using Xe lamp in air (2), film photooxidized by using prefiltered UV light from a Hg lamp in air (3) and in an atmosphere of chloroform vapor (4).

tungsten halogen lamp as probe beam. The probe beam was focused on the sample using mirror optics and spectrally analyzed by a single grating monochromator TRIAX 320. A combination of longpass filters was used to suppress the second-order light. A silicon detector was used for the spectral range 430–1100 nm, and an InGaAs detector for the range 930–1600 nm. The detector output was amplified using a current-to-voltage pre-amplifier (Perkin-Elmer 5182) and measured using a lock-in amplifier SR830. The samples were placed in the vacuum chamber of a closed-cycle He cryostat. Temperature-dependent transmission measurements were performed with the same setup using a single beam method. Control transmission measurements were performed at room temperature using a Cary 500 spectrophotometer.

III. RESULTS

A. Photocurrent studies

As has been already reported¹⁴ the photooxidation of PFS in the presence of chloroform (CHCl_3) results in a significant increase of the conductivity, in an unambiguous appearance of photocurrent generation, and in changes of the optical absorption spectra. We have found that oxidation can be achieved by different combinations of the illumination source, atmosphere, exposure time, etc. We can group the photooxidation procedures according to the different electronic properties which they produce.

Figure 2 shows the dark conductivity and the photosensitivity, defined as the relative change of the conductivity upon illumination from a fiber optic illuminator equipped with a 150 W projection lamp,¹⁴ for

- (i) a pristine film (sample 1);
- (ii) films photooxidized using Xe lamp in air (sample 2);
- (iii) films photooxidized using filtered UV light from mercury lamp in air (sample 3); and
- (iv) films photooxidized using filtered UV light from a mercury lamp in chloroform vapor (sample 4).

The dark conductivity is highest ($\sim 10^{-7} \Omega^{-1} \text{cm}^{-1}$) for photooxidation performed in the presence of CHCl_3 vapor. Chloroform is needed for the photooxidation process, and thus a sufficient supply of CHCl_3 molecules is necessary to achieve a high degree of oxidation.¹⁴ The exposure time is another critical parameter, as has been discussed earlier.¹⁴ The experimental results presented are for samples treated long enough that the photooxidation reached saturation.¹⁴ Any further illumination with much weaker light intensity during the spectral measurements of the photoconductivity and the photoexcitation experiments was found not to affect significantly the film properties, which was confirmed by the good reproducibility of the results. The UV treatment with the Hg lamp was performed for a longer time than the Xe illumination (60 versus 6); however, a notable difference between the two methods is that the oxidation by the Xe lamp results in heating of the samples. The effect of the increased temperature could be the reason for the higher photosensitivity of the Xe treated samples. The photosensitivity for the UV treated samples, however, increases together with the dark conductivity suggesting the same origin for the increase of the dark conductivity and for the photocurrent generation. This change of the optoelectronic properties is persistent after storage of the samples for several months in air.

The photocurrent was highest in the sample which was UV-treated in CHCl_3 vapor. In this case we were able to resolve spectrally the photoconductivity. The result is shown in Fig. 1 together with the corresponding absorption spectrum. The photocurrent spectrum follows exactly the absorption coefficient profile resulting in a spectrally constant photoconductive gain, as is typical for measurements with symmetric configuration of the electrodes and with equal charge generation and collection over the entire spectral range studied. The fact that the absorption band at 1.93 eV, created after the photooxidation,¹⁴ contributes to the photocurrent equally as the absorption band that is present also in the pristine state suggests the same photogeneration mechanism in both cases. Considering also that we observed significant photosensitivity (Fig. 2) only after the photooxidation of the material, i.e., after the formation of the absorption band at 1.93 eV, we conclude that the energy state associated with the 1.93 eV band has a key role in the photogeneration process.

B. Photoexcitation studies

In order to reveal some details of the nature of this state we have used photomodulation spectroscopy to study changes in its occupancy after photoexcitation. This technique also gives information on the generation and recombination of the photoexcited carriers. Figure 3 compares the photomodulation spectra of the four types of films first presented in Fig. 2. The spectra represent the in-phase signal after numerical phase rotation such that the out-of-phase signal becomes zero in the spectral range below 2.1 eV. The ability to zero the out-of-phase signal in this spectral range suggests that the features—a bleaching and absorption band—have equal frequency dependence, i.e., they are characterized by the same lifetime, suggesting a common origin. There are some differences between the samples oxidized by

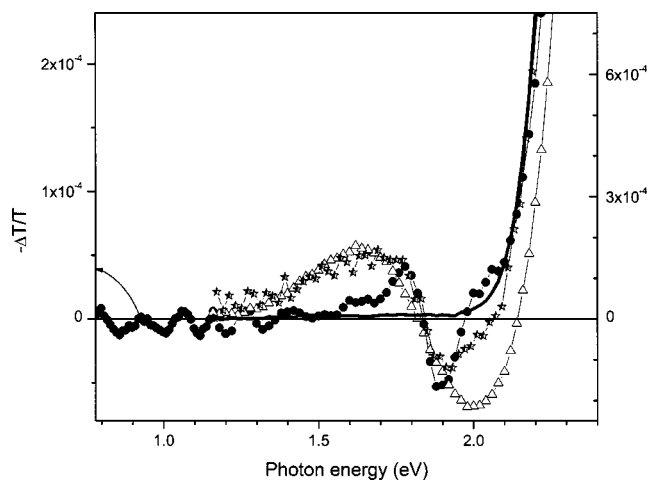


FIG. 3. Photomodulation spectra of a pristine film (solid line), film photooxidized by using Xe lamp in air (up triangles), film photooxidized by using prefiltered UV light from a mercury lamp in air (stars), and in an atmosphere of chloroform vapor (circles).

different methods. The bleaching band peaks at 2 eV for the Xe treated sample and at 1.9 eV for the UV treated film in chloroform vapor. At nearly the same energy are the maxima in the absorption spectra for these two films, as illustrated in Fig. 4. The zero crossing point at 1.83 eV is almost the same for all films; however, the photoinduced absorption band in the spectral range lower than 1.83 eV is very narrow for the film UV treated in chloroform vapor and is much broader for the other samples. The former film shows thermal modulation of the refractive index leading to the oscillations seen at energy below 1.4 eV in Fig. 3. The thermal origin is confirmed by measuring the spectra in vacuum and in air. The different thermal isolation in these two cases changes the amplitude of the oscillations; however, the other features retain the same intensity.

The photomodulation spectra at energies higher than 2.1 eV show photoinduced absorption (Fig. 3). For the pristine

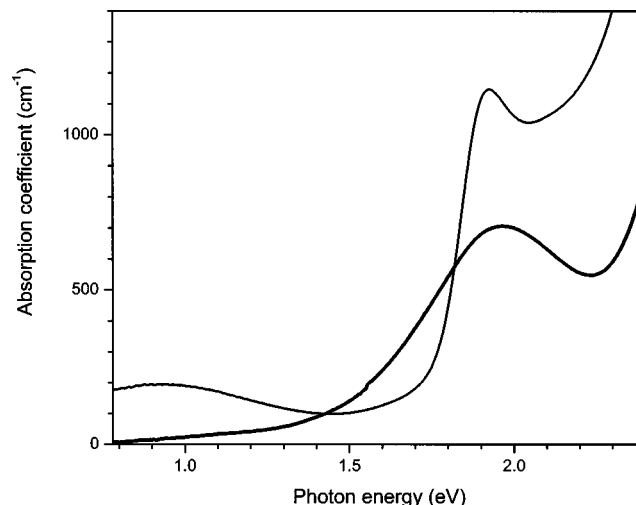


FIG. 4. Absorption coefficient spectrum of a film photooxidized by using Xe lamp in air (thicker line) and a film photooxidized by using prefiltered UV light from a mercury lamp in an atmosphere of chloroform (thinner line).

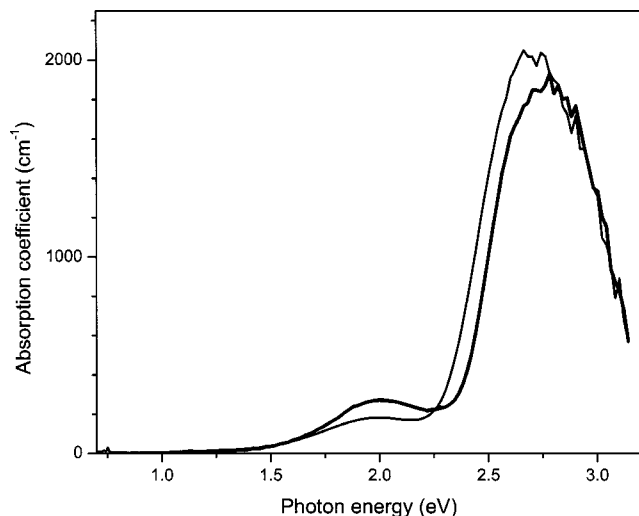


FIG. 5. Absorption coefficient spectra of a film photooxidized by using Xe lamp in air at room temperature (thinner line) and at 50 K (thicker line).

films, the photoinduced absorption (PIA) in this spectral range is due to thermal modulation of the absorption edge. All treated films show the same feature. However, the frequency dependence indicates an additional contribution to the PIA signal after photooxidation. This topic will be addressed later in the present work.

In order to clarify the thermal contribution to the modulation spectra, the temperature dependence of the absorption was studied for the Xe treated films (Fig. 5). Similar to the results for ferrocene,²³ the maximum of the absorption band at about 2.74 eV shifts to higher energy upon cooling at the expense of the large decrease of the intensity of the transitions at the low-energy side of the band. The amount of this shift is, however, lower for the case of PFMPS compared to that in ferrocene.²³ The absorption feature induced by the photooxidation process at 2 eV grows in intensity upon cooling (Fig. 5). These results would predict thermal modulation at the absorption edge and thermal bleaching at the band at 2 eV. For the case of a pristine PFMPS film, we have calculated from the temperature-dependent transmission measurements an average shift of the absorption edge of $1.8\text{--}2.2 \times 10^{-4}$ eV/K. This is a typical value for solid state materials.²⁴

Figure 6(A) (circles) shows the frequency-dependence of the photoinduced absorption for a pristine film at 2.22 eV. The curve above 10 Hz follows the ω^{-1} dependence. This is typical for single exponential behavior, which in the case of a thermal process has a characteristic change in the slope²⁵ from ω^0 to ω^{-1} at a frequency determined by the thermal properties of the film usually in the sub-Hertz region. The frequency-dependence for the films treated by UV light shows very different behavior than mentioned above, suggesting the participation of additional processes—in particular changes in the occupation of already existing states—giving rise to photoinduced absorption above 2.1 eV.

As mentioned, the bleaching and absorption bands below 2.1 eV have the same frequency dependence. The data for the bleaching band in Fig. 6(B) show that their frequency dependence is different from that for the absorption edge

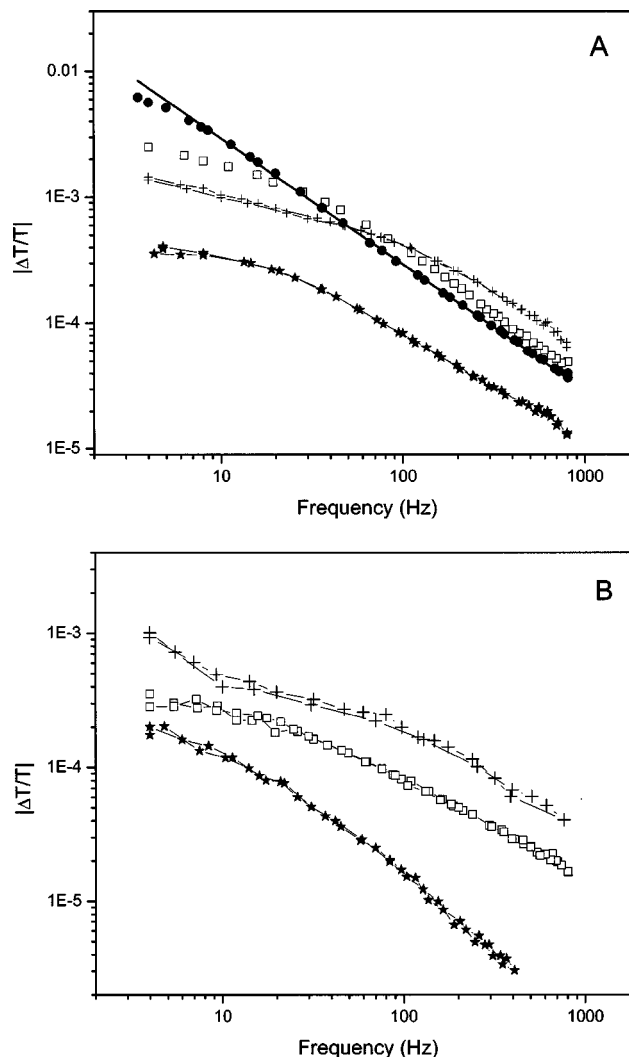


FIG. 6. Frequency dependence of the photoinduced absorption in the range higher than 2.2 eV (A) and within the photobleaching band (B) for a Xe lamp treated film (squares), for UV treated film in air (crosses) and in chloroform vapor (stars), and for the pristine sample (circles) which does not show any photobleaching. The line in (A) is a fit by a $f \sim \omega^{-1}$ to the data of the pristine film.

region. This, together with the following evidence, excludes the assignment of the bleaching band to thermal effects:

- (i) The zero crossing in the photomodulation spectra is nearly constant at 1.83 eV for all oxidized films. Such zero crossing is not expected from the temperature dependence of the absorption coefficient in Fig. 5.
- (ii) The modulation of the refractive index, mostly due to thermal effects, was changed by using different conditions for the sample measurement (in air or in vacuo); however, this is not the case for the main features shown in Fig. 3.
- (iii) The absorption coefficient spectra for the films UV treated in air and in CHCl_3 vapor are nearly the same at energies higher than 1.3 eV (not shown). If the thermal modulation is the reason for the observed bands in the photomodulation spectrum then there will be no difference in the shape of the bleaching and absorption band for the two types of films. In fact, the

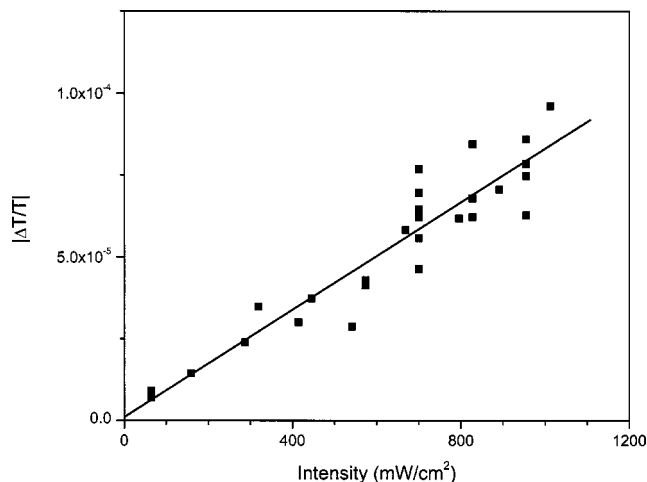


FIG. 7. Intensity dependence of the photoinduced absorption signal at 1.68 eV at 33 Hz modulation frequency for a film photooxidized by UV light in air. The line is a linear fit.

film treated in chloroform vapor shows a much narrower photoinduced absorption band below 1.8 eV.

The frequency dependence of the photogenerated states can in principle give their lifetime. If there is not a unique lifetime, then the analysis is ambiguous and in most cases limited to qualitative statements. We have fit the data using the expression for square modulation²⁵ with multiple curves with fixed lifetime and the generation constant as a variable. The results show that the lifetime of the photogenerated states is more than 8 ms for the case of the UV treated film in CHCl_3 vapor. The analysis for the film UV treated in air and for the Xe treated sample revealed the presence of similar long-lived states of 8 ms, but also of such states having a lifetime around 2 ms and even shorter than 1 ms. The use of the mechanical chopper allows the determination of lifetimes above ~ 0.4 ms. The intensity dependence of the photoinduced absorption band presented in Fig. 7 is linear. We can conclude that within the intensities used in our experiment the recombination is monomolecular.

The photomodulation experiments on solutions showed poor reproducibility because the photooxidation continues during the experiments. The precipitation of small particles led either to spurious signals due to light scattering influenced by the pump beam, or to direct deposition of these particles on the quartz cell window. However, the optical absorption data of the photooxidized solutions are qualitatively the same as those for the films UV photooxidized in CHCl_3 vapor.

IV. DISCUSSION

Photooxidation of the PFMPS films changes the electronic structure of the material. The increase in the dark conductivity and photosensitivity and the appearance of new absorption bands and of long-lived photoexcited states are some of the macroscopic signatures of this change we have observed. As discussed previously,¹⁴ the photooxidation takes place at the iron atom and a chloroform-derived counter ion (Cl^-) presumably remains in the near vicinity of

the oxidized iron atom to ensure charge neutrality. The percent oxidation of the samples was found to be less than 5%.¹⁴ Thus, the optical properties of the photooxidized polymer can be considered as a superposition of the properties of the ferrocene units and the ferrocenium ion units. According to the well established interpretation,^{26–28} the band at 1.92 eV is ascribed to a ligand-to-metal charge transfer (LMCT) transition within the ferrocenium centers and the absorption band at 2.74 eV is ascribed to transitions within the ferrocene units. Similar changes in the optical spectra of polyferrocenylsilane co-polymers oxidized electrochemically have also been observed.⁶ Obviously, the individual properties of the separate building blocks of this class of polymer are preserved with small modifications depending on the exact polymer structure and the way the oxidation is done. We have used such an approach in our previous paper.¹⁴ A detailed investigation of the electronic structure of polyferrocenylsilanes which can verify the applicability of such an approach is still not yet available. The experimental data in the present paper are more directed towards investigation of the excited state of the PFMPS films which makes the analysis without having a detailed electronic scheme even more difficult. For that reason we are proposing a simplified model for the explanation of the appearance of long living excited states, i.e., the appearance of the photoinduced absorption and bleaching band, and the photocurrent generation.

As mentioned above the chloroform-derived counter ion (Cl^-) satisfies the charge neutrality at the oxidized ferrocene unit. However, it does not contribute directly to the absorption at energy lower than 1.92 eV, i.e., all the associated levels are placed at higher energy. On the other hand, the presence of this species in close vicinity to the polymer chain leads to distortion in the polymer structure at this site. Such distortions are generally the reason for the appearance of states at lower energy trapping the molecular excitations.²⁹ Furthermore, both recombination and ionization of the trapped excitation is hampered leading to the appearance of long-lived photoexcitations and thus to bleaching of the ground state. The bleaching and absorption band in the photomodulation experiment at 1.92 and 1.78 eV are signatures of the above described process. The formation of the trap state and its exact energy location depend on the ability of the polymer chain to respond to the presence of the extrinsic chloroform-derived ion within the mechanical constraints of the solid film.

The very sharp absorption feature at 1.92 eV in the optical spectra of the samples UV treated in CHCl_3 vapor indicates that this type of treatment results in well-defined trap levels. The film treated in CHCl_3 vapor was observed to be gel-like: Penetration of the vapor made the film tacky. Surface scratches or strain accumulated during the deposition process are recovered by treating the film in CHCl_3 vapor for tens of minutes. Since the photooxidation was performed in the gel-like state, the polymer structure is more relaxed. This may account for the narrower features in the photomodulation spectrum in Fig. 3, as well as for the better defined lifetime of the photogenerated states derived from the frequency dependence in Fig. 6. The difference between samples treated in air and in CHCl_3 vapor is much more

pronounced in the photoinduced absorption feature below 1.84 eV. Remarkably, the width of this feature is nearly the same in the films treated in air but using the different light sources (Xe lamp and filtered UV light) supporting the concept that mechanical constraint of the solid film hinders the relaxation of the polymer around the oxidized sites. The observed monomolecular recombination mechanism confirms the localization of the process of generation, trapping of the molecular excitations and recombination around the ferrocenium ion.

The trapped photoexcitation can dissociate into a separated trapped electron and a free hole, the latter contributing to the hole photoconduction. According to this scheme the carrier generation is spatially limited to the ferrocenium ion site and the ferrocene units remain quasi-passive in the photocurrent generation, being only the conductive path for the separated holes. If this is the case and if the absorption of the ferrocenium ion is considered²⁶ then the band at 2.72 eV characteristic only for the ferrocene units has not to appear in the photocurrent spectrum in contrary to the experimental results in Fig. 1. Therefore, the influence of the trap state has to extend beyond the oxidized polymer site. This seems to be logical because the polymer chain distortion is difficult to contain only within one polymer unit and most probably extends over several units. This way the absorption at 2.72 eV within the unoxidized polymer unit is followed by rapid relaxation of the excitation to the trap state similarly as the absorption at 1.9 eV within the oxidized unit can produce an excitation trapped at the same trap state. As a result the photocurrent spectrum and the optical absorption spectrum show almost the same intensity of these two absorption bands. Additional experiments are needed for more detailed clarification of the photocurrent generation mechanism.

Mixing of the electronic systems of the oxidized and unoxidized sites of the polymer chain is not unexpected. The absorption band at 0.92 eV (Fig. 4) was previously reported for electrochemical oxidation of polyferrocenylsilane co-polymers⁵ and in well-defined linear oligo(ferrocenyldimethylsilanes)³⁰ and is ascribed to intervalence charge transfer (IT) between Fe(II) and Fe(III) states, assuming definite overlap between the wave functions of the two sites. The IT band is well-defined in the photooxidized PFMPS solutions as well as in the films treated in CHCl_3 vapor. The photomodulation spectra do not show signatures of this band (Fig. 3) because the trap state responsible for the bleaching of the band at 1.9 eV is at energy significantly higher than 0.92 eV.

The above discussion about the formation of the photoinduced states is of applied interest in view of the observation of significant photocurrent in the photooxidized films. The capturing of the photogenerated electron at the defect levels allows separation of the electron-hole pair. The fact that the captured electron is in a long-lived state shows that the recombination with a hole from such a state is a slow process in which the holes have enough time to drift in the applied external field. The effective capture of the photoexcited carriers at the defect state is most probably responsible for the constant generation of the photocurrent across the entire spectral range studied (Fig. 1).

The optical spectrum of the pristine material¹⁴ exhibits exponential behavior below 2.39 eV which is typical for disordered materials³¹ and formation of tail states. The formula of Tauc³¹ yields an Urbach energy of 85 meV, indicating greater disorder than in organic films.³² However, after the photooxidation process, the tail states are no longer the same as in the pristine PFMPS film, as indicated by the recombination dynamics of the PIA signal at $h\nu > 2.2$ eV (Fig. 6). In the pristine film this signal is truly thermally modulated. After UV light treatment, an additional process contributes to the photoinduced absorption signal. A probable candidate is the change in the occupancy of the tail states. The lowering of the molecular weight observed¹⁴ supports the argument that the material has to have a lot of disorder, and so the induced tail states could contribute to the photoinduced absorption at $h\nu > 2.1$ eV.

V. CONCLUSIONS

Photooxidation of PFMPS results in a significant increase of the dark conductivity and photoconductivity, the appearance of new absorption bands, and the photogeneration of long-lived states. The oxidation process, and the presence of a chloroform-derived ion in the close vicinity of the oxidized site, leads to deformation of the polymer chain and to the appearance of an energy state effectively trapping the molecular excitations. The trapped excitons have increased lifetime leading to increased probability for their dissociation. The charge carriers produced by this dissociation process contribute to the photocurrent generation. The exciton trap state extends over the neighboring ferrocene units in the polymer chain and thus the photooxidized polymer is not a mechanical mixture of oxidized and unoxidized polymer sites. Direct manifestation of this effect is the close resemblance of the absorption coefficient profile in the photocurrent spectra. The photosensitizing of the polyferrocenylsilane gives additional functionality to this class of polymers. Although the magnitude of the photocarrier generation efficiency is currently lower than that of the well studied inorganic semiconductors, the photocurrent generation achieved is of particular importance in combination with the intriguing redox, catalytic, magnetic, and nonlinear optical properties of this polymer class. The understanding of the photogeneration process helps to find ways to increase this effect by material optimization as well as to envision application areas of the photoconductive material which are very promising in combination with the advantageous properties of the organometallic polymer compared to purely organic systems.

ACKNOWLEDGMENTS

The authors would like to thank Professor Z. H. Lu for providing the opportunity to use the UV illumination source. The interdigitated ITO structures have been kindly provided by Professor Dr. W. Brütting, University of Bayreuth. E.H.S. and I.M. thank the Canada Research Chairs Foundation, and the Ontario Research and Development Challenge Fund.

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