Photoswitching Property of Ferrocene-doped Poly(methyl methacrylate) Thin Films Containing Chloroform Molecules

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Ferrocene-doped poly(methyl methacrylate) (PMMA) thin films prepared from solution in chloroform and modified under photoexcitation have exhibited interesting photoswitching property monitored by photoconductivity measurements in air. The results on photoconductivity have been discussed on the basis of formation of photoinduced charge-transfer complexes of ferrocene with chloroform molecules confined in PMMA thin films, dissociation of the complexes, secondary thermal reaction and photodegradation of PMMA. Photodegradation of PMMA, was studied by FTIR spectroscopy. The modified ferrocene-doped PMMA films could be used as photoswitching elements.

In the recent years, there is a growing research interest in searching new type of suitable organic switching devices[1,2] including photoswitches.[3] The display and telecommunication industries require cheap, fast, and stable optical switches. Organic/organometallic materials are attractive candidates for these applications because of their low cost, ease of processing and because their properties can be optimized by molecular design. Ferrocene (bis(cyclopentadienyl)iron: $(C_5H_5)_2Fe$; abbreviated as FcH; a technologically important material[4,5]) has shown interesting properties under photoexcitation.[6–9] In this letter, we report that FcH-doped PMMA thin films containing chloroform molecules modified under photoexcitation show an improved photoswitching property. To analyze the photodegradation in the PMMA films, FTIR spectra of the films were recorded before as well as after photoexcitation as a function of time.

Microcrystalline ferrrocene in powder form (Strem Chemicals, Newburyport, MA, U.S.A.) and poly(methyl methacrylate) [PMMA] (M_w 12000, Eastman Organic Chemicals, U.S.A.) were used after further purification. Several almost identical thin films (thickness ≈8000 Å) were cast,[7] from solutions in chloroform or benzene or mixtures of these two solvents, on cleaned glass plates at room temperature (≈300 K) and at about relative room humidity ≈70%. To allow evaporation of solvent molecules, the films were kept initially at room temperature for ca. 24 h and finally inside an oven at ca. 323 K for about 1 h. The films were cooled down to the room temperature before use and no further heating cooling treatment was given. Then the film under study was placed in a specially designed brass conductivity chamber fashioned with Teflon.[8,10] Electrical measurements (surface conductivity), in a normal air atmosphere (humidity ≈70%), were carried out by a programmable electrometer (model 617, Keithley Inst. Inc., Cleveland, OH, U.S.A.) connected with a PC through GPIB card using two-probe technique. Silver paste was used for electrical contacts. The electrodes (separation: 1 cm) were covered with black paper to avoid illumination of the electrodes. The measurements reported here, were performed after 2 h from the time of applied voltage (27 V, ohmic range). FTIR spectra were recorded by Magna-IR 750 spectrometer series II, Nicolet, U.S.A. and in all cases the photoexcitation (by a mercury lamp, 125 W) time was kept fixed (200 s). The experiment was repeated several times.

Doping of ferrocene molecule in PMMA film (≈1.7 mole/mole) prepared from chloroform as solvent showed an enhancement in both dark and photocurrent.

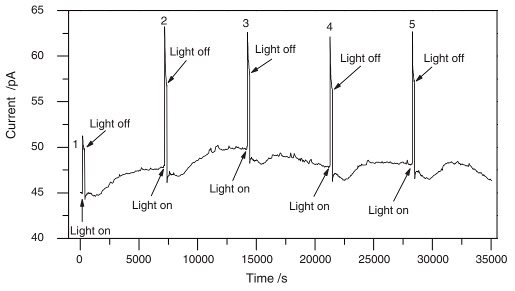

Figure 1. Current versus time plot for ferrocene-doped PMMA film (prepared from 100% chloroform) containing chloroform molecules.

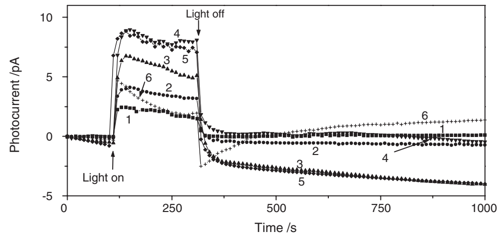

Figure 2. Photocurrent versus time for ferrocene-doped PMMA film containing different amount of chloroform molecules. Curves 1 to 6 refer to 0, 20, 40, 60, 80, and 100% chloroform in mixed solvents with benzene.

Figure 1 represents the change in current with time, in a ferrocene-doped PMMA thin film containing chloroform molecules, during repeated photoexcitation. This figure shows that the photocurrent is lowest for the first excitation and increased for next excitation. Further, Figure 1 does not show any significant change in the value of maximum photocurrent as well as in the nature of rise and decay of photocurrent during 2nd, 3rd, 4th, and 5th photoexcitations, indicating interesting photoresponse (photophysical changes) during repeated photoexcitations. It is noticed that the current before every excitation is not the same but the current after turning off the light varies with time in the same regular manner. The ferrocene-doped PMMA films showed very sharp response at light on and off position; verified for different applied voltages as well as for different concentrations of ferrocene in the films. The photocurrent intensity depends on the chloroform amount in the ferrocene-doped PMMA films (prepared from mixture of benzene and chloroform) as shown in Figure 2. The cause of decrease in current for the film prepared from 100% chloroform, compared to 60 and 80% chloroform, could be due to the trapping of charge carriers (contributing to photocurrent) by the additional chloroform molecules. The films prepared from 100% chloroform showed better photoswitching behavior.

Spectral analysis (UV–vis) showed that in the thin films of ferrocene-doped PMMA, some amount of chloroform molecules ($\approx 2.0 \times 10^{-6}$ M for the film in Figure 1) was present as impurities even after heat treatment of the films. It has been mentioned in an earlier communication that photoinduced charge transfer occurs between ferrocene (donor) and chloroform (acceptor) molecules confined in a PMMA thin film (acts as inert matrix to hold on ferrocene and chloroform molecules).[7] The primary step in the photoprocess is reported[11] to be the dissociation of the charge-transfer state to give ferricenium cation [$\mathrm{FcH^+}$], $\mathrm{Cl^-}$, and organic radical ($\mathrm{CHCl_2{\bullet}}$); on the basis of which one could consider the primary photochemical process as represented below:

$$\mathrm{FcH} + \mathrm{CHCl_3} \xrightarrow{h\nu} \mathrm{FcH^+} + \mathrm{Cl^-} + \mathrm{CHCl_2}^{\bullet} \qquad (1)$$

Traverso and Scandola have reported that in addition to the primary photochemical process some secondary thermal process induced by $\mathrm{CHCl_2{\bullet}}$ radical takes place.[11] The details of the secondary thermal process induced by the $\mathrm{CHCl_2{\bullet}}$ radical is not easily definable. In principle, the $\mathrm{CHCl_2{\bullet}}$ radicals could act in two different ways: (i) they could directly cause oxidation of ferrocene to ferricenium cation,[11] or (ii) they could react with molecular oxygen to give intermediate species capable of oxidizing ferrocene. However, ultimately the radicals could produce [FcH][$\mathrm{FeCl_4}$] reacting with intermediate species.[12]

Although the photochemical changes do not necessarily constitute photocurrent, the present experimental results indicate that the above-mentioned chemical reactions are active in controlling the electrical conductivity in ferrocene-doped PMMA films containing chloroform molecules. When the thin films of ferrocene-doped PMMA containing chloroform molecules are exposed to light, in addition to the occurrence of photoinduced charge transfer between ferrocene and chloroform molecules,[7] there is a possibility of photoinduced changes in the polymer itself. In fact, the FTIR spectra shown in Figure 3 indicate the photoinduced changes in PMMA. From the FTIR spectra a significant change in the intensity of the band at 1733 $\mathrm{cm^{-1}}$, which represents the carbonyl stretching frequency,[13] is clear. Siampiringue et al.[14] have discussed the possible reaction schemes for the photodegradation of PMMA in the presence of oxygen and according to them, either carbonyl group (ketonic) or hydroxy group was expected to be associated with the final product. From the enhancement in the intensity of the band at 1733 $\mathrm{cm^{-1}}$ in FTIR spectra, we definitely conclude that the carbonyl group (ketonic) is newly generated in the final product.

The photogenerated changes in the films after the initial photoexcitation were controlled by competing processes of photodegradation of PMMA and the secondary thermal reaction following the dissociation of the charge-transfer complex in the polymer matrix. The ferrocene-doped PMMA films (containing chloroform molecules) modified under photoexcitations have shown interesting photoswitching properties. Therefore, such films could be used as surface-type photoswitching elements. In the ferrocene-doped polymer films discussed so far, the response time for the photoinduced changes is about 20 times faster than the PMMA films without ferrocene. Further studies related to the effects of aging of the above discussed polymer films on the photoswitching property are on progress.

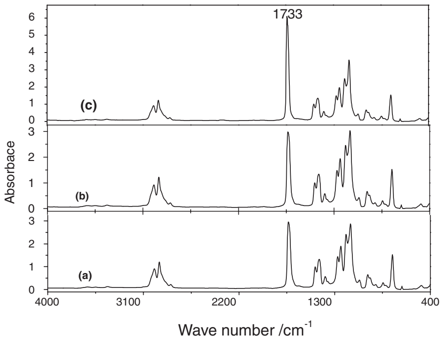

Figure 3. (a), (b), and (c) represent the FTIR spectra of FcH-doped PMMA film cast on polished side (1 0 0) of Si-wafer recorded before, immediately after and 2 h after photoexcitation, respectively.

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