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UV-induced acid–base chemistry within the PVC matrix

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Abstract

PVC films containing methyl violet have been subjected to UV irradiation to induce dehydrochlorination leading to capture of the released HCl by the dye. It is demonstrated that a process similar to the indicator colour change in an aqueous solution can also be induced within the PVC matrix by the action of light. It is also shown that this process can be utilised for lithographic purposes. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Poly(vinyl)chloride; UV induced dehydrochlorination; Acid–base indicators

1. Introduction

It is well established that poly(vinyl chloride), PVC, loses HCl (dehydrochlorination) upon exposure to heat [1,2], energetic particles like photons [3], protons [4] and neutrons [5]. Therefore, a substantial effort has concentrated on developing additives to prevent this dehydrochlorination [1,2]. An equal amount of work has concentrated on understanding the mechanism of the process, where possibilities of (i) a radical, (ii) an ionic and (iii) an autocatalytic process have been discussed [6–9]. Photodegradation and photochemical modifications of PVC and the resulting polyenes have also been extensively studied for improving electrical conductivity of the films [10–12]. It was even claimed that dehydrochlorinated PVC gave polyacetylene-like material [13]. By incorporation of electrically conducting polymers like polyaniline or polypyrrole into PVC, either by blending and/or forming composites, mechanically stable and highly conducting films (in the range of 10^{-5}–1 S/cm) have also been obtained [14–19]. In our previous work we were able to show that it was possible to make use of this dehydrochlorination by capturing the evolved acid (HCl) with in situ basic traps [20]. Specifically, polyaniline in its non-conducting (basic) form was incorporated into the PVC matrix and the increase in the electrical conductivity upon UV (or γ-ray) exposure was attributed to the conversion of the non-conducting polyaniline to its conducting form as a result of doping by the HCl released. UV–Vis, IR and XPS spectroscopic techniques were carried out to substantiate these arguments. It was also demonstrated that the process could be reversed (i.e. the electrical conductivity and conductivity-related spectroscopic features decreased) by further exposure of the polymer films to ammonia vapours. In this contribution we extend our work by using the same UV-induced loss of HCl to create optical (colour) change within the PVC matrix via incorporation of a suitable acid–base indicator, methyl violet, which captures the HCl, and leads to macro- and micro-scale lithographic applications. We had also reported a similar study using bromocresol green within the PVC matrix where, however, both the dye (bromocresol green) and PVC underwent photochemical modifications [21].

2. Experimental

The blend films were prepared by dissolving PVC and the basic dye (methyl violet) in a 10:1 weight ratio in freshly distilled tetrahydrofuran (THF) and casting into 10–50 μm thick films by evaporation of the solvent under saturated THF atmosphere at room temperature. UV-irradiation was accomplished by using a low pressure Hg lamp which radiates mostly at 254 nm. The visible spectra of the films (before and after irradiation) and aqueous solutions of the indicator were recorded using a Cary 5E spectrometer. The macro-scale pattern was imprinted by irradiating the solvent cast blend film through a 200 μm steel mask with 254 nm source. The steel mask was cut with an industrial CO_2 laser to write the script “BILKENT” on it, and placed right on top of the sample. For the micro-scale lithographic study, a

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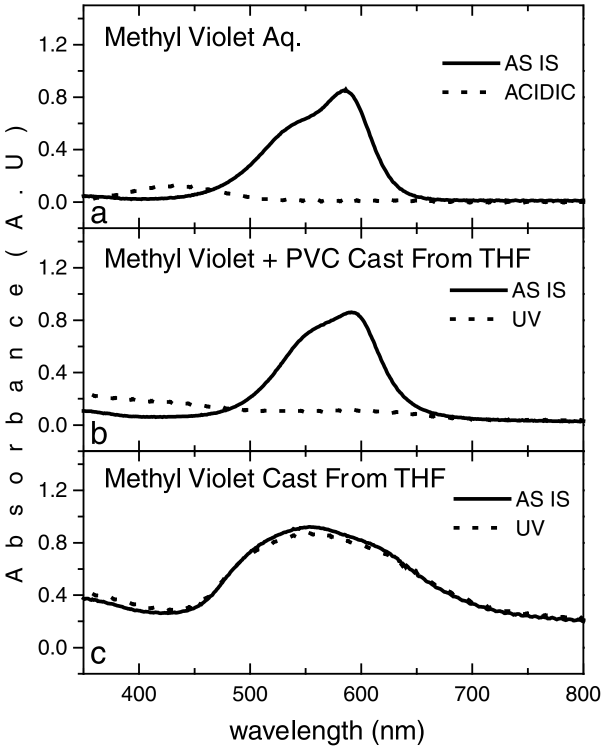


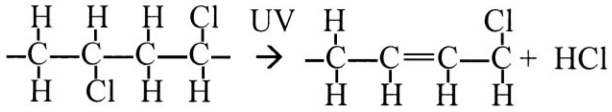
Fig. 1. (a) Visible spectrum of an aqueous methyl violet solution before and after acidifying it. (b) Visible spectrum of ca. 15 μm PVC film containing (10:1 by weight) methyl violet cast from THF before and after exposure to 254 nm UV light.(c) Spectrum of a very thin methyl violet (only) film before and after exposure to UV.

Zeiss UMSP 80 microscope spectrometer equipped with a 75 W Xe source was used. The sample was placed on a scanning *x*–*y* stage with sub-micron resolution. The micro-scale pattern was imprinted by irradiation of the blend film through a quartz mask. The mask, which had a previously printed pattern on, was placed right after the monochromator and the shadow of the mask was projected on the sample. After irradiation at 300 nm, the lateral absorbance change of the pattern at 600 nm was recorded, and the photograph of the pattern was taken with 40× magnification.

3. Results and discussion

The PVC matrix itself is slightly acidic probably due to ever-existing HCl during preparation of the powder. Therefore, different indicators/dyes were tried since some were UV-sensitive and others had an unsuitable range for their colour change [21]. Methyl violet which changed its colour around pH = 1 was found to be the most suitable [22]. The visible spectra of methyl violet in aqueous solution before and after acidifying the medium are shown in Fig. 1a. The complex absorption band between 500 and 600 nm disappears upon acidifying which makes the solution colourless. Exactly the same change can also be induced within the PVC matrix upon UV irradiation as shown in Fig. 1b. The similarity between the changes in the aqueous phase and the PVC matrix is remarkable. In Fig. 1c the spectrum of a very thin film of methyl violet cast from THF solution is also displayed which shows a slightly different absorption pattern when compared with its solution spectrum. The absorption features, however, are not altered upon UV irradiation which is a further proof that it is the HCl derived from PVC upon irradiation which causes this simple solvent free acid–base chemistry leading to the optical changes. The process can simply be formulated as follows:

Fig. 2. Photograph of macro-scale lithographic example of PVC film containing methyl violet (10:1 by weight).



$$-\underset{H}{\overset{H}{C}}-\underset{Cl}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{Cl}{C}}- \xrightarrow{UV} -\underset{H}{\overset{H}{C}}-\underset{H}{C}=\underset{H}{C}-\underset{H}{\overset{Cl}{C}} + HCl$$

$$HCl + M.V.\ (\text{basic form}) \rightarrow M.V.\ (\text{acidic form})$$

Discolouration of PVC upon UV exposure (yellowing) and irradiation with high-energy radiation have long been studied for imaging and for electron beam dosimetry. Even incorporation of acid-sensitive dyes into PVC for dosimetric purposes had been reported [23]. However, stability of the optical changes and the shelf life have been the major obstacle for their wider use [23] in addition to the underestimated photomodification of the dyes used [24]. We have also utilised this process to create macro-scale (Fig. 2) and micro-scale (Fig. 3a) optical writing which have been stable for more than one year kept at room temperature. The stability of our optical modification must be related to the right combination of the dye and the preparation conditions. Fig. 3b shows the same micro-scale pattern in terms of absorbance change at 600 nm along the *x*-axis and in the middle of the print in Fig. 3a (note that all the three slits have different widths which are faithfully reproduced in their optical density patterns). Since the pattern was imprinted via the shadow projection method, the pattern lacks fidelity to some extent (blurring and spots). We believe this is mainly the artefact of our lithographic tools rather than the photochemical process, which can be improved using different techniques, or custom designed samples.

The cause of the optical and/or electrical changes can easily be stated as the dehydrochlorination of PVC itself. However, the actual mechanism of the process, its wavelength dependence, the nature of the polyenes formed, and,

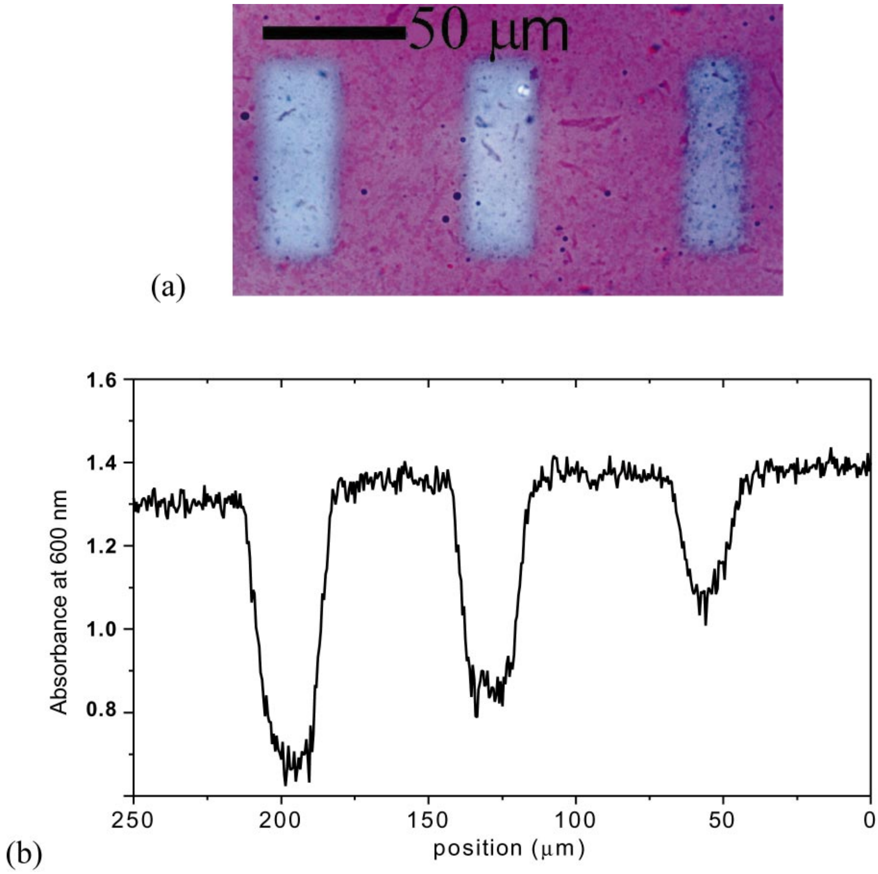


Fig. 3. (a) Photograph of micro-scale lithographic example of PVC film containing methyl violet (10:1 by weight). (b) Lateral absorbance changes of the micro-scale pattern at 600 nm along the *x*-axis and in the middle of the print in Fig. 3a note that all the three slits have different widths and this is faithfully reproduced in the optical density pattern).

especially, the role of impurities both in the photochemical process and in the stability of the products all require further, careful investigation.

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