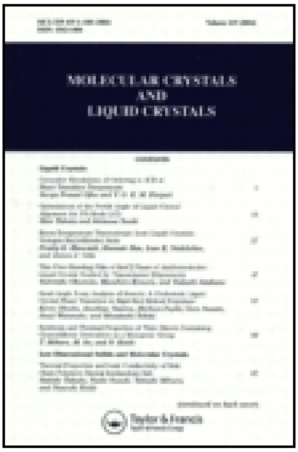

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Solvent Effects on the Photodegration of a PPV Derivative

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Solvent Effects on the Photodegration of a PPV Derivative

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ABSTRACT
The photodegradation of soluble electroluminescent polymers is one of the greatest problems to be overcome in order to improve their technological applications. Here we will report on preliminary evaluation of the effects of commonly used solvents on the photodegradation of poly(3-methoxy-5-dodecyloxy-*p*-phenylene-vinylene), MD-PPV. We prepared solutions of similar concentration of MD-PPV in different solvents and recorded the ultraviolet-visible spectra before and after the exposure to a 250 mW/cm^2 light intensity. Also, we prepared cast films with the same solutions (with similar thickness) in order to observe if the solvent also affects the properties of the films. The results showed that the solvent polarity seems to be not the unique factor affecting the photodegradation, since no direct correlation could be made. Among the solvents tested, tetrahydrofuran was the best solvent for preparing films in order to minimize the photodegradation process.

Keywords: PPV derivatives, photodegradation

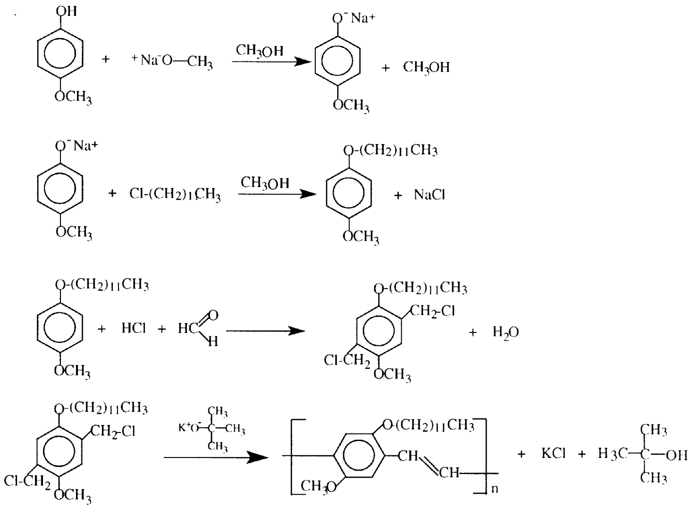
INTRODUCTION

The photodegradation of soluble electroluminescent polymers, and in particular of the PPV derivatives that are soluble in organic solvents, is one of the greatest problems to be overcome in order to improve their technological applications[1-3]. Generally, to build up the electroluminescent devices, the polymer is processed from organic solvent solutions, in the form of cast or spin coated films. The conformation of polymer molecules in solution depends on the interaction between solvent molecules and the polymer, and can affect the polymer absorption spectra in the ultraviolet-visible region[4]. Also, it was observed that the absorption spectrum of the cast films, in many cases, depends on the solvent they were cast from. And as the degradation occurs mainly under exposure to light and air, in the excited state rather than in the ground state, the solvatochromic processes can affect the extent of photodegradation reactions. Thus, as the solvents used in film preparations can be an important factor influencing the final properties of films, it should be interested to characterize what kind of solvatochromic effects the electroluminescent polymers present and also what role the solvents plays on the photodegradation process. Here we report on preliminary evaluations of the effects of commonly used solvents on the photodegradation of poly(3-metoxi-5-dodecyloxy-*p*-phenylene-vinylene) (MD-PPV).

EXPERIMENTAL

Polymer Synthesis: The synthesis of MD-PPV was carried out according to the scheme 1.

Photodegradation Experiments: Solutions of similar concentration (0.01mg/ml) of MD-PPV in different solvents were prepared and the ultraviolet-visible spectra were recorded before and after the exposure to a 250 mW/cm^2 light intensity for various periods of time. Also, cast films with similar thickness were prepared and the photodegradation was followed in the same way. Prior to the measurements, the films were treated in vacuum at 50 °C for 2 hours to remove residual solvents.



Scheme 1 – Synthesis of MD-PPV.

RESULTS AND DISCUSSION

Fig1 and 2 show the UV-Vis spectra of the solutions, respectively before and after 24 hours exposure to light.

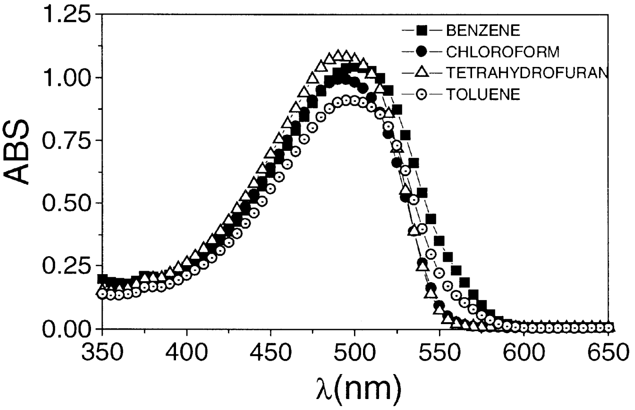


FIGURE 1 – UV-Vis spectra of MD-PPV in different solvents in dark

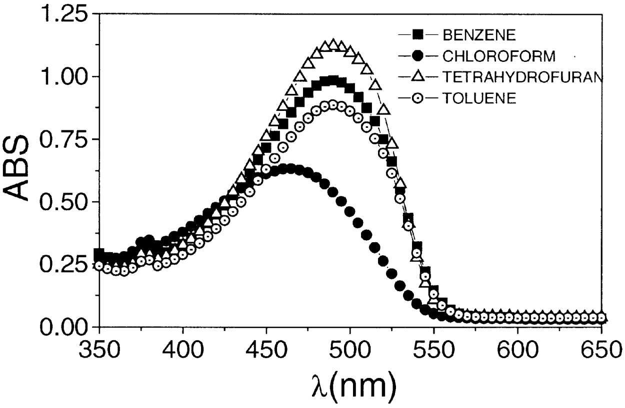


FIGURE 2 – UV-Vis spectra of the solutions showed in figure 1, after 24 hours exposure to light

Chloroform, the most commonly used solvent to prepare films of PPV derivatives, showed the greater extent of photodegradation, while tetrahydrofuran showed the smaller extent, although they present similar polarity indexes. Thus the solvent polarity seems to be not the unique factor affecting the photodegradation.

There is almost no distinction between the behavior of photodegradation in the two aromatic hydrocarbons. Although the decrease in the absorbance was not significant, a shift of λ_{max} towards longer wavelengths occurred.

In all cases, the comparison between the solution (fig.1.) and films spectra (fig.3.). in dark showed larger absorption bands in the latter ones, and also a shift towards longer wavelengths. The shift was very slightly in the aromatic hydrocarbons, but significant in tetrahydrofuran and chloroform, indicating a possible aggregation and different morphologies of the films, depending on the solvent used to prepare them.

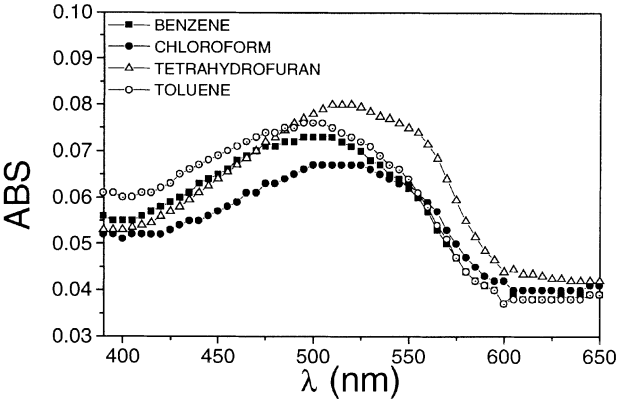


FIGURE 3 – UV-Vis spectra of MD-PPV films cast from different solvents in dark.

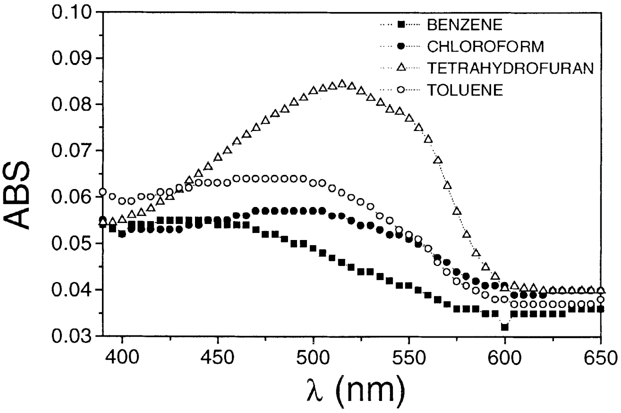


FIGURE 4 – UV-Vis spectra of MD-PPV films cast from different solvents after 30 minutes of exposure to light.

As in the solution, also in the solid stated the films cast from tetrahydrofuran showed the lower extent of degradation (fig.4), although no significant differences were observed within the other solvents. For example, tetrahydrofuran films presented an absorbance 10% lower after one hour of light exposure and the other ones presents absorbance decreases around 50%. After 24 hours, all films were completed degraded. Thus tetrahydrofuran seems to be the best solvent for preparing films in order to retard the photodegradation process.

Since solvent polarity is not the unique effect, the chemical nature of the solvent and the polymer-solvent interactions may take an important role in the photodegradation process reported here. Tetrahydrofuran is known to react in the presence of oxygen and light to form peroxides, thus it can be acting also as an antioxidant. Also, tetrahydrofuran is not a good solvent for MD-PPV and thus polymer-polymer interactions may be stronger than polymer-solvent interactions. This leads to more condensed polymer morphology and the possible formations of aggregates which can difficult and retard the photodegradation, since the polymer chains in the inner part will be less accessible. Further experiments are being carried out in order to confirm the reasons why the photodegradation process is retarded by tetrahydrofuran.

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