

The influence of preparation method of OC₁OC₆-PPV films on the photo-oxidation process

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Abstract

Poly(*p*-phenylene vinylene) (PPV) derivatives are well known for their applications in polymer light emitting diodes (PLEDs). PPV derivatives are highly susceptible to photo-oxidation though, which is mainly caused by the scission of the vinyl double bond on the polymer backbone. In this work, we show that Langmuir–Blodgett (LB) films are less degraded than cast films of a PPV derivative (OC₁OC₆-PPV). Both films had similar thickness (~50 nm) to allow for a more realistic comparison. Degradation was monitored with UV–vis and FTIR spectroscopies. The results indicated that cast films were completely degraded in ca. 400 min, while LB took longer time, i.e. about four times the values for the cast films. The differences can be attributed to the more compact morphology in the LB than in the cast films. With a compact morphology the diffusion of oxygen in the LB film is hampered and this causes a delay in the degradation process.

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1. Introduction

Poly(*p*-phenylene vinylene) (PPV) derivatives have been investigated as possible candidate materials for polymer light emitting diodes (PLEDs). In comparison with small organic molecules such as 8-hydroxyquinoline aluminum (AlQ₃), PPV derivatives are advantageous for their easy processibility, stability and may serve for flexible displays. However, because of their conjugated nature, they are highly susceptible to photo-oxidation [1–6], as in the presence of oxygen light irradiation may lead to cleavage of vinyl double bonds on the polymer backbone [7] and to the incorporation of oxygen as carbonyl groups. This causes the conjugation length to decrease. Degradation may be monitored by the blue shift in the absorption spectrum of the polymer and appearance of

a band within 1740–1660 cm⁻¹ in the infrared spectrum, assigned to stretching of carbonyl groups. In derivatives with symmetrically substituted phenyl ring, e.g. poly(2-methoxy-5-(2-ethylhexyl-1,4-phenylene vinylene), MEH-PPV, photodegradation also causes the appearance of a band at 1600 cm⁻¹ assigned to asymmetric aromatic rings [2]. Photo-oxidation can in later stages lead to chain scission and decrease the polymer molecular weight. For the polymer in the solid state, as in the case of films used in PLEDs, several factors may affect the degradation rate, including oxygen concentration, sample thickness and the solvent used to prepare the sample [8].

The limitations of PPV derivatives mentioned above have prompted many searches into novel materials or processes to minimize photodegradation. It has been established that degradation requires illumination in the presence of oxygen [7], which is the reason why so much investment has been made toward developing methods of encapsulation for PLEDs. While encapsulation may prevent most of the photodegradation problems, it imposes

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technological limitations associated with cost and choice of materials to be used. It is therefore challenging to identify the mechanisms of photodegradation and try to minimize them, which is the topic of the present paper. Here, we investigate photodegradation of a PPV derivative, namely poly-(2-methoxy-5-hexyloxy-*p*-phenylene-vinylene), OC₁OC₆-PPV. Emphasis is placed on effects of film thickness, film-forming technique and use of different filters and light powers during irradiation.

2. Experimental

Poly-(2-methoxy-5-hexyloxy-*p*-phenylene-vinylene) (OC₁OC₆-PPV) was synthesized as described elsewhere [8]. Cast films were obtained by casting chloroform solutions of different concentrations onto B270 glass slides and dried at room temperature in the dark. 31-layer LB films were prepared from Langmuir films spread from chloroform solutions of OC₁OC₆-PPV (0.2 mg/mL) onto ultrapure water subphases. The Langmuir film fabrication and transfer of the LB films were carried out in a KSV 5000 LB trough, following the procedures described in detail in Ref. [9]. Photodegradation experiments were performed by illuminating the samples with white light from a halogen lamp (50 W, 12 V – Osram), placed at a fixed distance from the sample, yielding 17 mW/cm² of power at the sample surface. Irradiation was performed at room atmosphere at a controlled temperature of 25 °C (unless otherwise stated), with the polymer films always facing the lamp, resting over a white plain surface (no light exposure onto the bottom side of the sample). The UV–vis spectra were recorded in a Hitachi U2001 spectrophotometer in the transmission mode. For comparison, the samples were also irradiated with halogen lamps with intensities of 8 mW/cm² and 117 mW/cm². All filters used were purchased from Schott.

3. Results and discussion

Cast or LB films of OC₁OC₆-PPV were not degraded for more than 20 weeks if left in the dark under room conditions or if stored in a nitrogen atmosphere. Thermal stability was also good, as demonstrated in subsidiary experiments where freshly prepared samples, heated from 25 °C up to 98 °C in the dark, suffered only a 5% decrease in absorbance (results not shown). These control experiments indicate that degradation only occurs if the films are illuminated and in the presence of oxygen, consistent with previous findings for similar luminescent polymers [7]. Here we investigate how films from OC₁OC₆-PPV, produced with two distinct techniques, suffer photodegradation.

Photodegradation depends strongly on the film thickness, as it starts at the surface and then affects the inner layers of the material. For polypropylene films, for instance, Garcia et al. [10] observed the rate of degradation to be inversely proportional to the thickness, with the degradation profile showing stronger degradation closer to the exposed surface. Two main factors may affect the rates of photodegradation [10]. One is the decreasing light intensity across the sample bulk due to absorption, which has exponential thickness

dependence according to the Beer–Lambert law. The second one is the oxygen concentration throughout the material, which depends on the oxygen diffusion through the film.

For cast films of OC₁OC₆-PPV we confirmed a stronger photodegradation for a thin film, by plotting in Fig. 1 the normalized absorbance at 505 nm against time of irradiation for two samples with thicknesses of ca. 300 and 70 nm. Photodegradation also depends on the light intensity of the irradiating source, as indicated in Fig. 2 that shows the decrease in absorbance with time for lamps with three distinct intensities, for samples of similar thicknesses (± 70 nm). The lamp referred to as *A* has maximum density power of ca. 0.3 mW/cm² at 600 nm and an integrated intensity over the whole spectrum of 117 mW/cm² at the sample surface, while lamps *B* and *C* have maximum density powers of 0.05 mW/cm² and 0.02 mW/cm² at 600 nm, with integrated intensity of 17 mW/cm² and 8 mW/cm², respectively. Fig. 2 indicates that the level of photodegradation does not vary significantly for the low power sources (*B* and *C*), but it becomes much more pronounced with the high-intensity lamp *A*. The possibility of significant effects from the emission spectra of the lamps can be discarded, as these lamps display essentially the same spectra – shown in the inset of Fig. 2. Since lamp *B* has a slightly narrower spectrum, it was used in all subsequent experiments.

Photodegradation can be hindered to a considerable extension if filters are employed to prevent light that would otherwise be absorbed by the sample from reaching it. For instance, Fig. 3a shows a very small decrease in absorption (i.e. small photodegradation) for a sample that was protected by a filter (*R*) that absorbs light up to 650 nm. Note that the shaded area corresponds to the wavelengths absorbed. If the filters used are *G*, which allows light transmission between 500 and 600 nm, and *Y*, which absorbs up to 475 nm, photodegradation is increased. With filter *Y*, in particular, the OC₁OC₆-PPV film absorption was almost completely lost after 1500 min of irradiation. The latter experiments were carried out with the samples placed in a metallic vessel, with the filter at 10 mm from the sample closing the vessel. If the samples

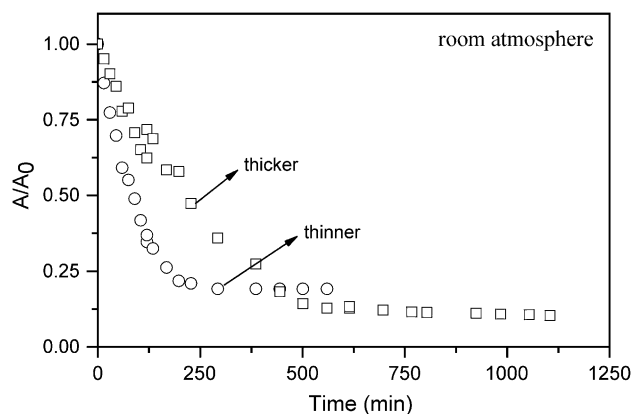


Fig. 1. Absorbance decay for films with different thicknesses upon white light irradiation.

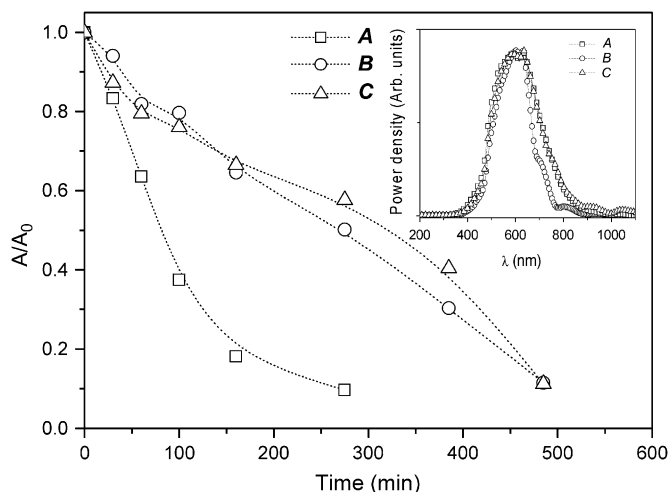


Fig. 2. Absorbance decay for samples illuminated with lamps of distinct intensities.

were more exposed to the air, the effects from the filters to prevent degradation were considerably reduced, as indicated in Fig. 3b. Degradation was now significant in all cases, even for the R filter for which only light within a narrow wavelength band was transmitted. For the samples in open air, degradation occurred almost three times faster than for the case in which the samples were in a closed, reflective holder. Taken

together, these results indicate that photodegradation requires absorbable light and oxygen at the sample, and may be partially hindered if absorption in the OC_1OC_6 -PPV film or availability of oxygen is decreased.

We have also confirmed that degradation occurs primarily in the vinyl group of OC_1OC_6 -PPV, consistent with earlier reports [11]. This was performed by monitoring the FTIR spectra of cast films – deposited onto silicon wafers under similar conditions used for the glass plates – following irradiation with a white light (lamp B) with no filters. The absorption areas were determined by integration using the valleys for baseline correction and, in order to minimize differences in thickness, the aromatic ring absorption band at 1500 cm^{-1} was used as the “thickness” band to calculate the relative areas [11]. A decrease in the $\text{CH}=\text{CH}$ absorption area was accompanied by an increase in the area associated with the carbonyl absorption, as shown in Fig. 4. A similar trend is observed by plotting the relative area of $\text{C}=\text{CH}$ stretching at 3050 cm^{-1} , which does not occur with other absorptions, indicating that oxidation occurs primarily in the vinyl group, confirming previous studies.

Another factor that can influence the rate of absorbance decay (or photodegradation rate) is the method used to produce the films. Cast and LB films of similar thicknesses were submitted to the photodegradation and the results are shown in Fig. 5. The slope of the curves is significantly different, with

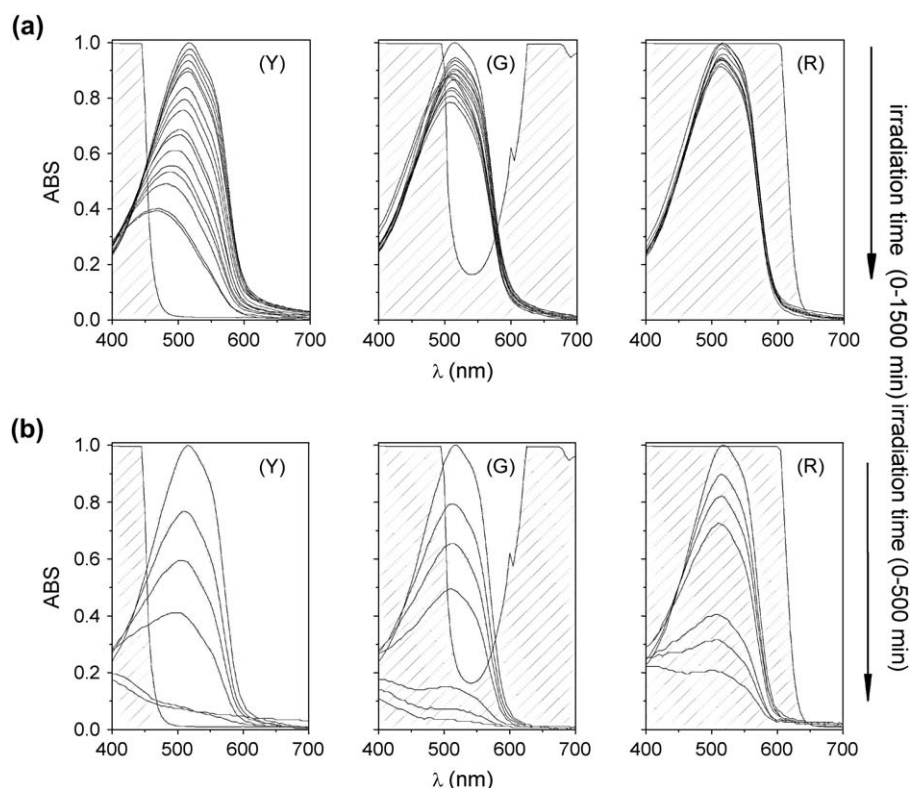


Fig. 3. Absorption spectra of OC_1OC_6 -PPV cast films with different filters, referred to as Y (yellow), G (green), and R (red), which coincide with their colors. The vertical arrow indicates increasing exposure times to light and the shaded area represents the wavelength region for the filter absorption, which in all cases covers also the range between 200 and 400 nm. (a) sample placed in an aluminum Petri dish of 10 mm high completely closed by the filter; (b) filter placed at 10 mm from the sample in open air.

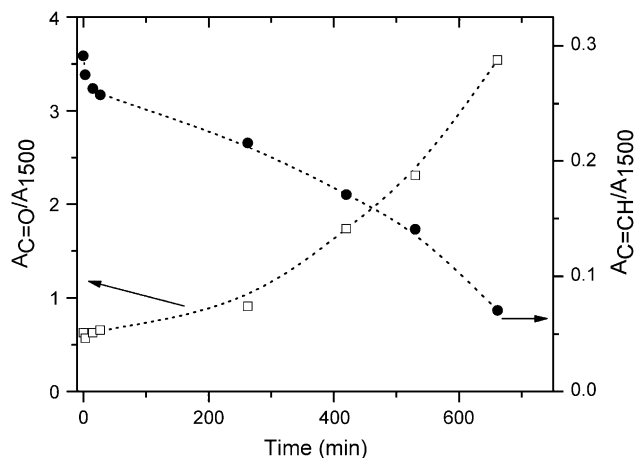


Fig. 4. Relative absorption areas of C=CH at 970 cm^{-1} and C=O. The lines are only to guide the eyes.

LB films degrading slower than the cast film, which was completely degraded in ca. 400 min. The LB films were completely degraded in ca. 1500 min, about four times longer. In this case, as the thickness of the samples prepared by different film-forming methods was similar, the decrease in light intensity described by the Beer–Lambert law was the same for the two samples shown in Fig. 5. However, the different film-forming techniques can lead to films with different morphologies. AFM images of LB and cast films showed that both are formed by globular structures, but the LB film displayed more globules for a given area [9], being thus more “dense”. This more compact morphology of the LB films, compared to the cast ones, can hamper oxygen diffusion and cause a delay in the degradation process.

The higher stability to oxidation of LB films was confirmed in experiments in which filters were used during exposure of the films to lamp B, similar to the experiments for the results in Fig. 3b. The results for the LB films are qualitatively the same as for the cast films, with higher degradation being observed with the yellow filter (Y). However, the exposure times

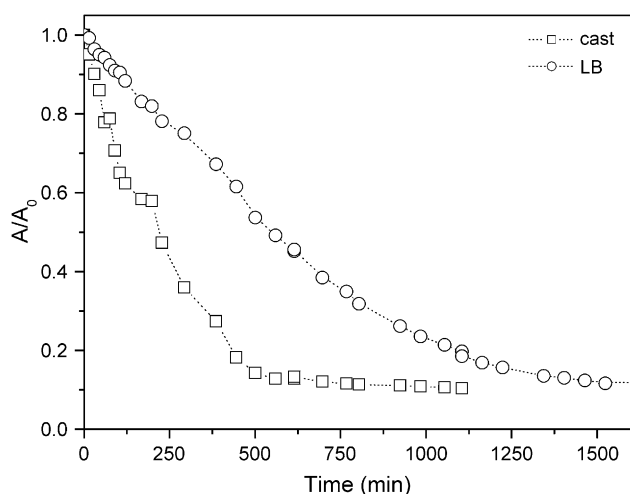


Fig. 5. Absorbance decay for cast and LB films of similar thicknesses.

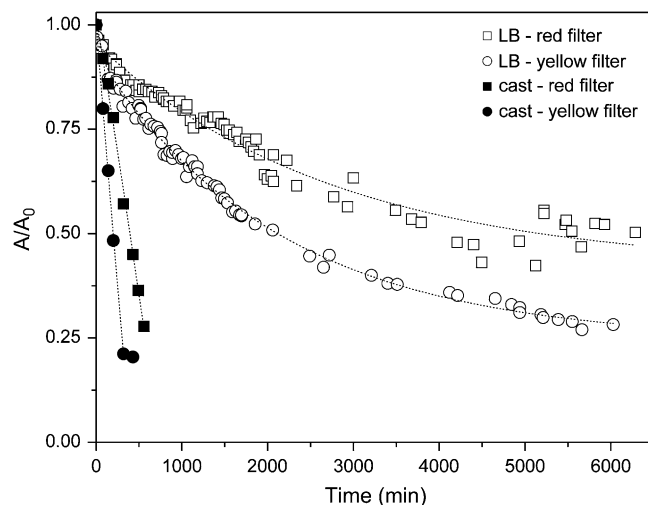


Fig. 6. Decay in absorbance for cast and LB films using red and yellow filters in open air.

required for degradation are now much longer than for the cast films, ca. 10 times longer, as one should expect. In order to illustrate this result, the normalized absorbance decays for cast and for the LB films submitted to degradation in open air, using the yellow and red filters, are shown in Fig. 6. In addition, we also confirmed with FTIR subsidiary measurements that photodegradation in LB films follows the same routes as the cast films.

In conclusion, confirming previous studies, the photodegradation of the PPV derivative only occurs with the presence of air and light that is absorbed by the sample. The rate of degradation varies with film thickness and depends on the film-forming technique. The films fabricated with the Langmuir–Blodgett technique showed a lower extent of photodegradation probably due to their more dense morphology that can hamper oxygen diffusion through the material and hence retard the photodegradation process.

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