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Cole Galey, and H. Park



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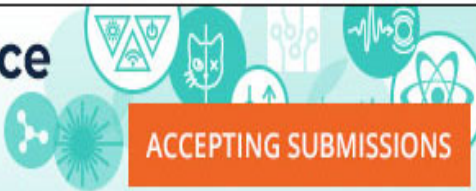
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Cole Galey and H. Park^{a)}

AFFILIATIONS

Department of Physics and Astronomy, Texas A&M University-Commerce, Commerce, Texas 75428, USA

^{a)}Corresponding author: heungman.park@tamuc.edu

ABSTRACT

The dynamics of photoluminescent response during optical degradation of MEH-PPV in films and chloroform solutions were investigated using various spectroscopic techniques (PL, UV-Vis, FTIR, and XRF). A significant blue shift in photoluminescence (PL) from MEH-PPV films during degradation indicated strong interchain exciton migration and a different photochemical reaction from that of solution. Two distinct wavelength-dependent dynamic PL responses were observed in MEH-PPV, and were attributed to photoactivation in the long side chain and polymer backbone. It was verified by a control experiment with BDMO-PPV which has symmetric side chains. The dynamic PL results indicate that the degradation process involves at least two-step photochemical reactions in the side chain and backbone. We also found that chlorine showed no effect on the optical degradation process.

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INTRODUCTION

The study of MEH-PPV, Poly[2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene], has been of great interest for its semiconducting properties. PPV derivatives such as MEH-PPV can be used to create thin films. Organic light emitting diodes (OLED) and solar cell devices can be produced from the thin films. It has been shown that the lifespan of these devices under standard atmospheric conditions is very short, on the order of a few minutes. Practical OLEDs and solar cells created with organic semiconducting materials must be prepared in a vacuum and sealed in such a way as to prevent oxygen and moisture from making contact with the material.^{1–5}

Not only does MEH-PPV degrade in solid films but also when prepared in solution. PPV derivatives (MEH-PPV, MEMO-PPV, BDMO-PPV, etc.) and most semiconductor polymers have been shown to rapidly degrade when exposed to oxygen, light, radiation, and heat in both solution and film.^{5–29} The degradation study has also been reviewed in several papers.^{30–34} The degradation process of film has been studied more closely since device failure occurs in thin films of MEH-PPV. However, several studies of the degradation of MEH-PPV in solution have also been performed.^{4–7,35–39} The process of making MEH-PPV thin films requires MEH-PPV to be dissolved in a solvent usually chloroform or chlorobenzene.

Degradation can occur if the solution is stored in ambient conditions leading to poorer quality devices.⁴⁰

This study confirms the previous data and further explains the different mechanisms responsible for the degradation of MEH-PPV in thin films and solutions. While studying the degradation of MEH-PPV solutions and thin films, it became apparent that the photoluminescence (PL) spectra of the degradation of MEH-PPV solutions and thin films differed. However, the UV-Vis spectra appeared very similar. Fourier-transform infrared spectroscopy (FTIR) and X-ray fluorescence (XRF) data were collected to determine what caused the difference in degradation of these materials.

EXPERIMENT

Powdered MEH-PPV ($M_n = 70,000 - 100,000$, PDI = 5, Sigma Aldrich 541435) and poly[2,5-bis(3',7'-dimethyloctyloxy)-1,4-phenylenevinylene] (BDMO-PPV, Sigma Aldrich 546518) purchased from Sigma Aldrich were dissolved in chloroform solutions at a concentration of 1.25 mg/mL. The solution was deposited on glass substrates using a dynamic spin coating method to create uniform thin films. The film thickness was measured by an ellipsometer to be about 10 nm. The films were dried for 2 hours under a 10 mTorr vacuum to ensure evaporation of the chloroform. These

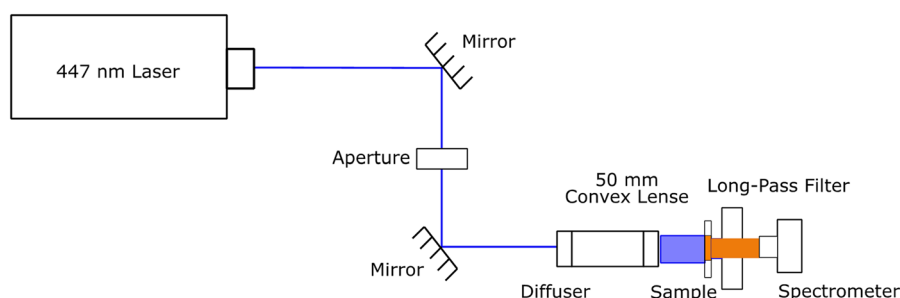


FIG. 1. Schematic diagram of optical setup for PL spectroscopy and degradation.

thin films were degraded using a 447 nm CW laser at an intensity of 120 mW/cm^2 . The Gaussian profile laser beam was expanded by an optical diffuser to obtain a tophat beam profile. The resulting beam was an approximately 2 cm diameter circular shaped, spatially uniform intensity beam which covered entire samples. During the degradation process, the PL and UV-VIS spectra were measured. The PL spectra were collected continuously without interrupting the degradation. An instrument response function was applied to the PL spectra to calibrate the relative PL intensity in each wavelength using a NIST traceable light source. A schematic experimental setup is shown in Fig. 1.

1 mL of the MEH-PPV solution diluted by 100 times was transferred to a cuvette. The cuvette of MEH-PPV solution was degraded using the same laser beam at the intensity of 120 mW/cm^2 . During the degradation process, PL and UV-VIS spectra were measured. The PL spectra were collected continuously without interrupting the degradation.

A thin film was created on a double polished undoped silicon substrate by static drop casting from the non-diluted solution to ensure the creation of a thicker film. The film was vacuum dried for 2 hours and an FTIR spectrum was measured before it was degraded. Then, the film was degraded for 4 hours by the laser beam and an FTIR spectrum was collected again. 1 mL of the MEH-PPV solution was transferred to a cuvette. The cuvette of the MEH-PPV solution was degraded using the laser beam at the intensity of 120 mW/cm^2 for 4 hours. The degraded solution was deposited on a silicon substrate by static drop casting. The film was vacuum dried for 2 hours before an FTIR spectrum was measured. Thus, FTIR spectra were collected from a pristine film, a degraded film, and a film from a degraded solution.

RESULT AND DISCUSSION

The MEH-PPV PL spectra of the chloroform solution and the film phase shows the typical difference, red-shifted spectra due to efficient interchain exciton migration and large domain size in films, as shown in Fig. 2.⁴¹ In addition, we observed that during photodegradation the dynamics of the PL response of the samples showed a significant difference (Fig. 3).

The initial PL spectrum of the MEH-PPV in chloroform solution has a main peak at 564 nm. As the sample degrades, the peak broadens, decreases in intensity, and shifts to a shorter wavelength. The blue shift typically attributed to decreased conjugation length due to chain scissoring and photochemical reaction.^{40,42,43} The initial PL of the MEH-PPV film has a main peak at 582 nm. As the

sample degrades, the peak broadens and decreases in intensity like the MEH-PPV solution. However, the blue shift is more significant in films. Our PL data in heavily degraded solution are different from those obtained by white light.⁴⁰ We discuss the difference at the end of the section.

We analyzed the dynamic PL responses during the degradation by plotting the PL intensity as it changed in time at several wavelengths (Fig. 4 and 5). Generally, PL decay in films is much faster than in solution due to the direct exposure in air mostly caused by photochemical reaction with oxygen and water. This decay involves an oxygen reaction with the vinyl double bond of the PPV backbone.^{27,29} The results in solution indicate that there are at least two types of photoactivation. Initially, the short and long wavelength regions show increasing PL and then decay to completely non-emissive states (Fig. 4). The two different time scales of the peaks (35 minutes at 500 nm and 25 minutes at 750 nm in Fig. 4) also support the two distinct photoactivations. At the long wavelength, the peak occurred much earlier than in the short wavelength. These contrasts may be attributed to the asymmetric structure of MEH-PPV side chains. It is known that water and oxygen molecules photochemically react with MEH-PPV reducing its PL ability. This may possibly be a two-step process. Photochemical reactions create new molecules which show increasing PL during the degradation, and then are photodegraded again becoming non-photoluminescent molecules. Therefore, the two types of photoactivation have at least three origins: two side chains and the polymer backbone.

To elucidate the origin of the photoactivation processes, we performed a control experiment with BDMO-PPV, which has symmetric side chains (Fig. S1 in [supplementary material](#)), dissolved in chloroform. Very similar time-dependent PL responses were

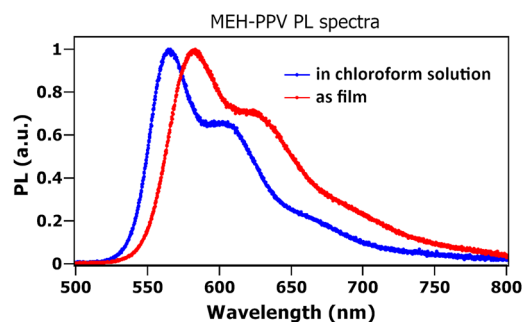


FIG. 2. Normalized PL spectra of MEH-PPV in chloroform solution and as film.

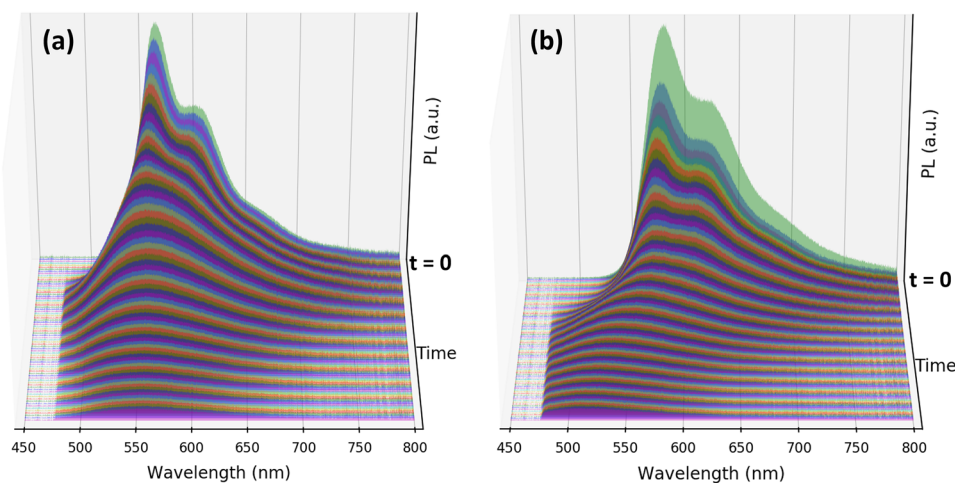


FIG. 3. (a) PL spectra over time as MEH-PPV in chloroform solution degrades. (b) PL spectra over time as MEH-PPV film degrades.

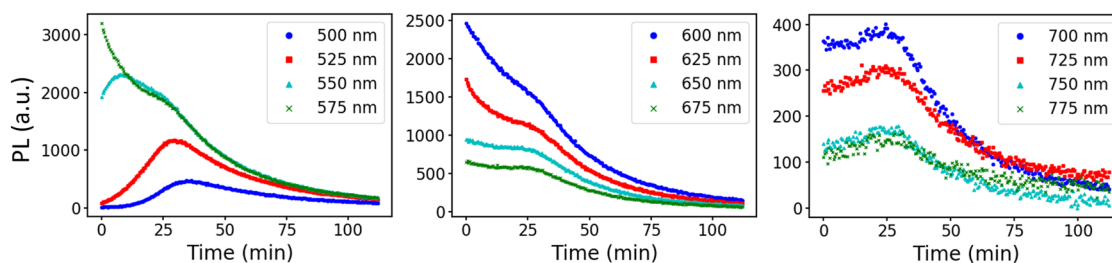


FIG. 4. PL changes in time during the photodegradation from MEH-PPV in chloroform solution at several wavelengths.

observed as shown in Fig. 6. This ensures that the short side chain of MEH-PPV does not contribute significantly to the PL dynamics during the photodegradation. The two-step processes occur in the polymer backbone and the long side chain in MEH-PPV.

The time-dependent PL responses from the films (Fig. 5) do not show the obvious increase in the PL at the long wavelengths. However, they show clear humps near 2 minutes (700, 725, 750, 775 nm data in Fig. 5). These result from the fact that all of the chains including the polymer backbone in films are in contact with nearby other chains. Therefore, the ensemble average of the PL from the films shows continuous broad responses, i.e. some long side chains are in contact with other long chains or the backbones, and some long side

chains are in contact with short side chains or the backbones. Therefore, it cannot exhibit two distinct responses. Only homogeneous photochemical changes are shown by the PL responses.

Due to the photoactivation and overlap in PL from multiple emission sites, the decay curves cannot be fit by single exponential curves. We fit the PL data with multi-peak Gaussian, Lorentzian, and Voigt functions. Since the PL curves come from multiple chromophores with different conjugation lengths including vibronic energy transitions, the choice of the fit function cannot be simply determined.^{44–46} However, our data indicated that Voigt and Gaussian fits showed similar results, but Lorentzian functions did not produce good fits. Though we fit the data with three Gaussian peaks

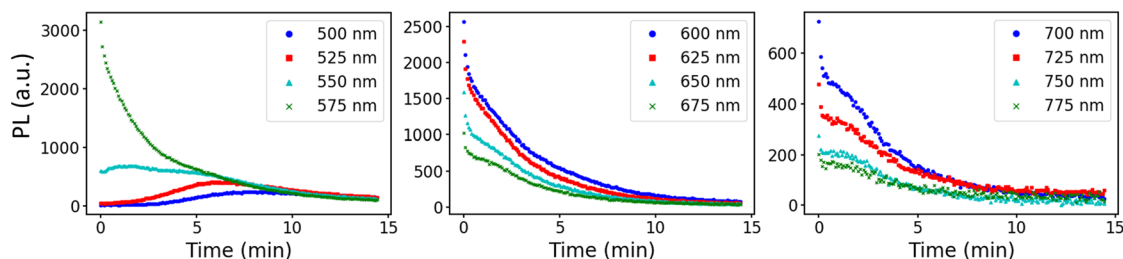


FIG. 5. PL changes in time during the photodegradation from MEH-PPV films at several wavelengths.

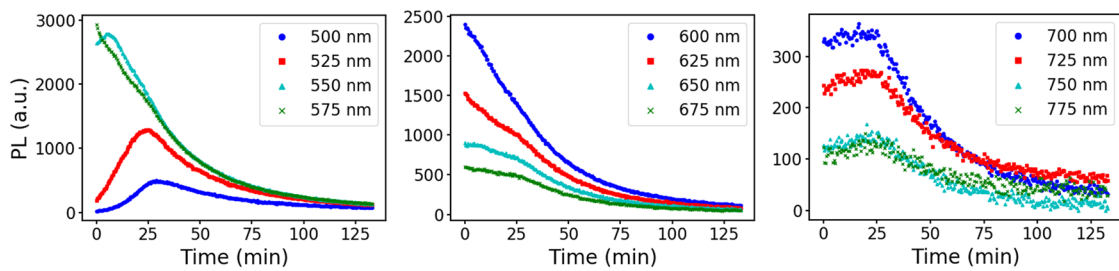


FIG. 6. PL changes in time during the photodegradation from BDMO-PPV in chloroform solution at several wavelengths.

(Fig. 7), actual contribution comes from several factors such as chain length and number of monomers in a chromophore. Similar results from multi-peak Gaussian fits were observed from BDMO-PPV with a more pronounced 2nd peak in BDMO-PPV film (Fig. 8). It implies that the long side chain in BDMO-PPV contributes to form more isolated emission sites in films. The PL figures of both of MEH-PPV and BDMO-PPV are shown for clarity in wavelength domain in the [supplementary material](#) (Fig. S2).

The UV-Vis absorbance spectrum of the MEH-PPV film has a peak at around 500 nm (Fig. 9). This peak diminishes in intensity, broadens, and shifts significantly to a wavelength of around 360 nm. The similarity of UV-Vis absorbance spectra in solution and film indicates that chain-to-chain contact in films does not affect the absorption significantly. However, the interchain contact affects exciton migration significantly in films as shown by red shifted PL spectrum in film compared to the PL spectrum in solution

(Fig. 2) which has been previously shown.^{35,36} Photo-created excitons migrate into near local energy minima sites where exciton recombination occurs. In good solvents such as chloroform and chlorobenzene, MEH-PPV polymers exist in extended conformation and excitons can migrate only along the chains. In films, chain-to-chain contact makes an orbital overlap resulting in a lower energy state than other nearby conjugated orbital states along chain. The red shift in films occurs from the interchain overlapped orbital states.⁴⁷

In a dilute solution, minimal interaction occurs between the polymer chains. Therefore, all exciton creation, migration, and recombination during degradation occur on one chain of an MEH-PPV molecule. The small PL peak shift during degradation in solution (Fig. 2-a) indicates that the entire domain of each recombination site is deactivated without leaving partial shorter chromophores. If a partial chain break is prevalent in exciton recombination domains, the time-dependent fluorescent spectra would show a

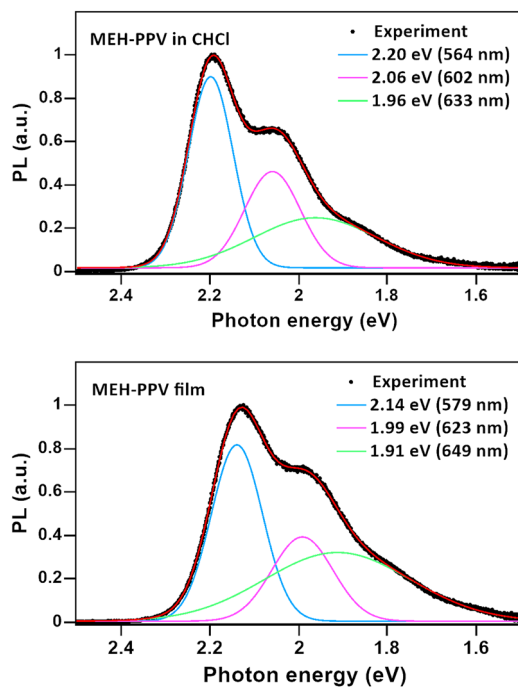


FIG. 7. Multi-peak Gaussian fits at the initial PL spectra of MEH-PPV.

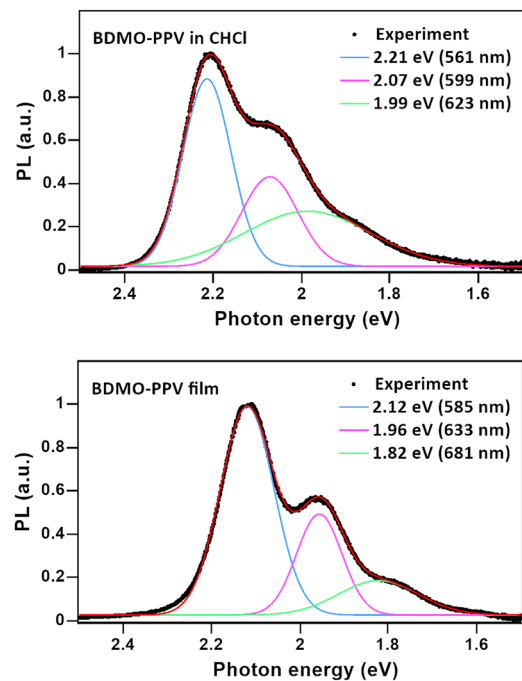


FIG. 8. Multi-peak Gaussian fits at the initial PL spectra of BDMO-PPV.

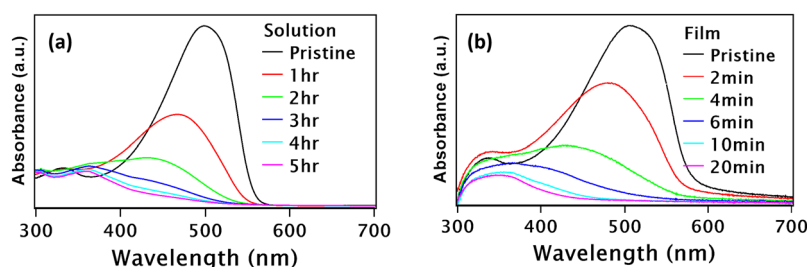


FIG. 9. (a) UV-Vis spectra as MEH-PPV solution degrades over time, (b) UV-Vis spectra as MEH-PPV film degrades over time.

significant blue shift. The broadening of the spectra suggests the formation of new molecules, chain scissoring, or a combination of the two processes as a result of the photo-degradation. This is supported by FTIR measurements which showed changes in the spectrum at $1700\text{--}1740\text{ cm}^{-1}$ which suggest the formation of hydroxides and a conversion from oxygen single bond (--O--) ethers to oxygen double bond (CO) esters, and also photochemical change in the backbone indicated by significant decrease at 3060 cm^{-1} .^{4,26,35,48}

The FTIR spectrum of the MEH-PPV solution is similar to the FTIR spectrum of the MEH-PPV film (Fig. 10). The degradation process in both samples involve common major photochemical reactions, possibly photo-oxidation even in the solution with residual low concentration oxygen molecules. The FTIR spectrum of pristine MEH-PPV film shows no evidence of chloroform carbon bonding ($850\text{--}550\text{ cm}^{-1}$) present in either the MEH-PPV film or solution samples.⁴⁹

The absence of chlorine atoms after complete photodegradation was confirmed by an XRF measurement (Fig. S3 in [supplementary material](#)). The XRF result does not show any significant peak for Cl signature which is different from gamma-ray-induced degradation in MEH-PPV.⁵⁰ When gamma-ray induced optical degradation occurs in MEH-PPV, Cl atoms are interplayed with the MEH-PPV backbone. Cl atoms excited by gamma-rays can be added into the backbone of MEH-PPV polymer by breaking C double bond and also replacing H atoms resulting in decreasing conjugation length. Thus, blue shift in absorption occurs after the irradiation.

Based on the observation and analysis above, there are at least two intermediate photoactivated states before complete degradation. Completely degraded solution and film by the laser beam are highly transparent (sample pictures are shown in Fig. S4 in

[supplementary material](#)). To explain the intermediate states of the polymers we propose the following steps during photodegradation in MEH-PPV.

1. Photoexcited MEH-PPV undergoes two types of photochemical reactions: Photo-Fri rearrangement and backbone oxidation.^{25,26}
2. Each type is responsible for new short and long wavelength PL responses.
3. These states are unstable and involve chain scission which results in further degradation.
4. In solid films of MEH-PPV, photo-induced interchain crosslinking occurs efficiently which is responsible for the large blue-shift in PL.

The photoactivated intermediate states are also supported by a recent study on MEH-PPV during photodegradation monitored by surface contact potential measurements. Palacios-Lidon et al.¹⁷ measured time evolution of surface photovoltage of MEH-PPV films using Kelvin probe microscopy during illumination by 480 nm light. They found that the blue light irradiation onto MEH-PPV induced two stage degradation which is similar to our results. However, our data resolved the two stage change spectroscopically which can give us more insight in understanding the degradation process.

Semiconducting polymers have limited distribution in their conjugation lengths due to conformation disorders relating to torsion angle, twisting, kinking, folding, and molecular defects. As the conjugation length decreases, the absorption and emission spectra are blue-shifted. If the photodegradation induces random chain scission, it is expected that the blue-shift is continuous during the degradation. However, our data in Fig. 3 showed finite blue shifts in both samples. In particular, the solution sample showed only about 20 nm peak shift in PL where interchain contact between polymers is minimal. This can be evidence to show that chain scission happens at weak parts of the polymers: twisted, or bent regions. The UV-Vis data in solution (Fig. 9) showed semi-continuous (greater than 3 hours) blue-shift during the degradation in contrast to the PL shift (Fig. 3 and 4) which shows less than 30 minutes. The UV-Vis and PL blue shifts are typically attributed to chain scission.⁴⁰ However, our data showed a difference in the time scale of the shifts between the UV-Vis and PL data. Unlike the experiment by Louis et al.⁴⁰ which used white light source, we used a 447 nm (2.77 eV) blue laser beam. It selectively creates excitons from some chromophores, and then the excitons migrate into lower energy (smaller than 2.77 eV) emission sites. This data is strong evidence for the creation of photoactivated intermediate photoluminescent molecules from PPV polymers.

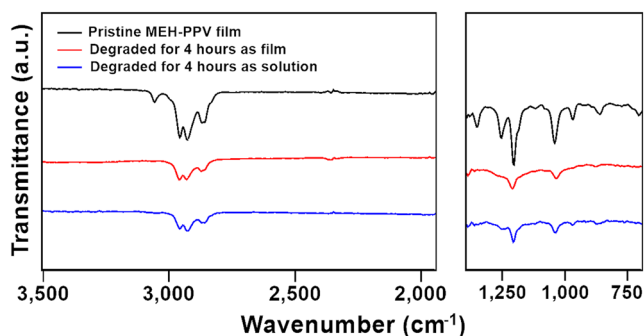


FIG. 10. FTIR spectra of MEH-PPV films in pristine, as degraded in film, and as degraded in solution. Noisy region ($1400\text{--}1800\text{ cm}^{-1}$) from water omitted.

SUMMARY

We have investigated the dynamics of the PL response during optical degradation in MEH-PPV organic semiconductor materials by utilizing PL, UV-Vis, XRF, and FTIR measurements. Chlorine plays no chemical role in the degradation process of MEH-PPV in chloroform solution or as a thin film. The difference in the PL spectra of the solution and film samples is not a result of a chemical structure between the two phases, but is caused by interchain exciton migration. Strong interchain exciton migration occurs in MEH-PPV films which is shown by a contrast between the 1st PL spectra in solution and film. As the MEH-PPV degrades, there is the possibility for different photochemical reactions between the solution and the film such as Photo-Fri rearrangement and backbone oxidation. The large blue shift during the degradation in the PL of the film is compelling evidence for this effect including chain crosslinking. The blue shift is much smaller in the solution because the molecules are too far apart for interchain interaction and exciton migration to take place. Though the UV-VIS and FTIR are similar in the two sample systems, unspecified interchain interaction involving exciton migration can occur in films. Two different dynamic PL responses in short and long wavelengths from solution are attributed to the long side chain and the polymer backbone, not to the asymmetric side chains of MEH-PPV. The photodegradation process involves at least a two-step process in the long chain and the backbone. The first step process involves a photoactivation in which PL increases at the short and long wavelengths, and followed by another process resulting in optically inactive states.

More research is required to elucidate the precise mechanism of the large blue shift of PL in film during photodegradation. This study will provide a greater understanding of the exciton dynamics and photoactivation during the degradation of organic semiconductor materials and eventually improve the device performance using the materials.

SUPPLEMENTARY MATERIAL

See [supplementary material](#) for schematic diagrams of the structures and PL responses of MEH-PPV and BDMO-PPV are shown in Fig. S1 and Fig. S2, respectively. An XRF data for chlorine signature from an MEH-PPV film degraded in a chloroform solution are shown in Fig. S3. Completely degraded MEH-PPV samples by the 447 nm laser beam are shown in Fig. S4.

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