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Electroluminescence of Photodegraded Poly(p-Phenylene- Vinylene) Derivatives by Ultraviolet Laser Light

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ELECTROLUMINESCENCE OF PHOTODEGRADED POLY(P-PHENYLENE-VINYLENE) DERIVATIVES BY ULTRAVIOLET LASER LIGHT

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Abstract We report the observations of electroluminescence of photodegraded poly(p-phenylenevinylene) derivatives film which was irradiated with laser light at a wavelength in the region of ultraviolet. EL spectral change for different polymers shows different behaviour. Electroluminescence and photoluminescence intensities of PPV decreases rapidly and the intensities in the blue region become relatively severe without peak shift. MEH-PPV shows the blue shift of the peak in EL spectra with negligible intensity decrement. Spectroscopic results of the PPV film degraded by UV light support the photodegradation occurred by chain-scission process.

INTRODUCTION

Since the first observation of the electroluminescence (EL) from a π -conjugated polymer by Cambridge group¹, there have been many researches conducted regarding the chemistry and physics of the polymers themselves and their devices.²⁻⁶ One of the important topics on the device performances is the reliability of polymer EL devices, since the mechanical and thermal properties of polymers are inferior to those of inorganic semiconductors. Many factors are related to the reliability of the device made of electroluminescent polymers, such as the film quality, the polymer-metal electrode interface, and environmental conditions during device fabrication and operation. Environmental conditions for preparation of polymer and for device fabrication are especially important because they affect the performance of the fabricated device.

Recently, as well as the oxygen effects on poly(p-phenylenevinylene) (PPV) during the elimination reaction⁷⁻⁹, there have been studies extensively on the environmental effect upon the EL polymer and the performance of EL devices¹⁰⁻¹³. One of the authors (Zyung) had observed that the photodegradation of the PPV film in air results in a significant loss in photoluminescence (PL) intensity, when irradiated with the

light at two wavelengths of 458 nm and 514.5 nm corresponding to the absorption maximum wavelength and to the peak emission wavelength of the EL¹⁰ respectively. The results indicated that the polymer light emitting diode may be degraded under an air environment by its own emission. In this study, wavelength region of the irradiation light resulting the photodegradation of the PPV film was extended to the ultraviolet and the EL behaviour of the irradiated film was investigated. EL from the MEH-PPV film irradiated with UV light was also studied and the results are discussed.

EXPERIMENTAL

Synthesis of the present PPV polymer was carried out via a precursor route using sulfonium salt¹⁴. Experimental details are shown in previous work¹⁰, except the laser light which has the wavelength of 351 nm from argon ion laser (Coherent, Innova 305) in the present study. Laser power was almost the same as that used in previous work¹⁰. The UV-visible, EL and PL intensities were measured as a function of irradiation time.

RESULTS AND DISCUSSION

Figure 1(a) shows UV-visible absorption spectra of the unirradiated PPV film and the irradiated PPV films with the light of 351 nm in air as a function of the irradiation time. UV-visible spectra of the PPV irradiated with the UV light in air show a drastic decrease in UV-visible absorbance. Main peak around 430 nm shows the blue shift during the irradiation, which may indicate the bond breaking in the main chain. When compared with the UV-visible absorption spectra of irradiated PPV films with the laser lights of 458 nm and 514.5 nm in air¹⁰, the UV-visible absorbance of PPV irradiated with laser light at 351 nm in air shows a more drastic decrease within a short period.

Figure 1(b) shows the normalized PL spectra of the irradiated PPV films. When each PL spectrum is compared with each other, the intensity in the blue region is relatively increased as the irradiation time increases. This happens similarly in EL spectra. For the PPV films bleached with the 351 nm light, EL spectra show also the drastic decrease in intensity without peak shift as the irradiation time increases as seen in Figure 2(a). Within 15 minute of the irradiation time, the EL intensity decrease by more than one-quarter. This shows the faster degradation in UV region, when compared with the results of previous work¹⁰. The degradation is more readily occurred with the UV light than the visible light. However, EL spectra of the MEH-PPV film degraded by UV light show the blue shift of the EL maxima by about 25 nm with the negligible intensity variation as the irradiation time increases. In the same irradiation time, MEH-PPV seems

more reliable than PPV. It is well known that the polymer with shorter conjugation length contribute to the increase in the EL or PL intensities in the blue region¹⁵. The results indicate that the irradiation of the UV light causes the conjugated backbone to be broken resulting in shorter conjugation length.

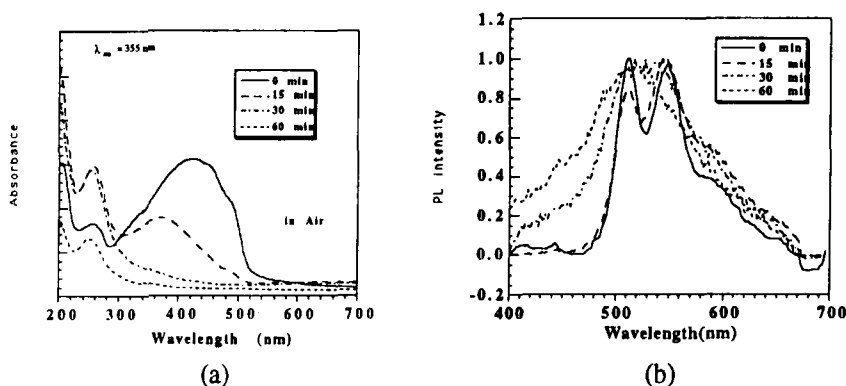


Figure 1. Absorption spectral change(a) and normalized PL(b) spectra of the PPV films irradiated with UV light at various irradiation time

Infrared spectra were also measured as a function of the irradiation time. The IR spectra of the PPV films irradiated at 351 nm in air are similar to those of irradiated with 458 and 514.5 nm. Similarly, new peaks at 1695 cm^{-1} and at 1278 cm^{-1} appear in the IR spectra of the irradiated films, which correspond to the carbonyl stretching vibrational band and C-O stretching vibrational band in a carboxyl group, respectively. Also, the very broad band ranging over $2400 - 3500 \text{ cm}^{-1}$ corresponds to O-H stretching vibrational band in a carboxylic acid groups and the sharp peak at 3023 cm^{-1} corresponds to a trans-vinylene C-H stretching band. These results support that the irradiation of PPV film with UV light yield also the same photoproduct as those irradiated with visible light, resulting from the chain scission process assisted by oxygen.

CONCLUSION

We describe the photodegradation of neat PPV thin films in air by the irradiation of ultraviolet laser light. The PL and EL intensities decrease very rapidly during laser irradiation. The degradation is more readily occurred with the UV light than the visible light. Spectroscopic results of the photodegradation support the chain scission process involving oxygen in air to yield terminal 4-vinylbenzoic acid groups. EL spectral behaviour in MEH-PPV is different from that in PPV within the same irradiation time, indicating degradation of MEH-PPV can be different from that of PPV.

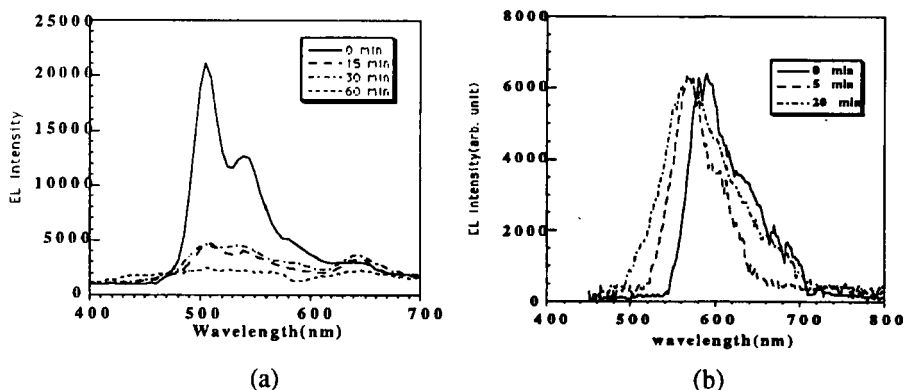


Figure 2. EL of the PPV film(a) and the MEH-PPV film(b) as a function of the irradiation time with 351 nm light

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