

Poly(*p*-phenylenevinylene)의 전기냉광 및 산소 존재하에서의 광열화

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Electroluminescence and Photoinduced Degradation of Poly(*p*-phenylenevinylene) by Laser Light under Oxygen Environment

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요약: Poly(*p*-phenylenevinylene) 고분자의 전기냉광과 전기냉광시의 스펙트럼 상에서 피이크에 해당하는 파장의 빛을 레이저로 poly(*p*-phenylenevinylene) 고분자에 조사하였을 때 광열화가 일어나는 것을 관찰하였다. 광냉광의 특성이 공기 중에서는 급격히 열화하며 진공하에서는 일어나지 않았다. 이것은 공기 중의 산소가 광열화를 촉진하는 것을 나타내며, 이 가설은 자외선-가시광 흡수 분광과 자외선 분광법으로 확인하였다.

ABSTRACT: We report the observations of electroluminescence and photodegradation of poly(*p*-phenylenevinylene) polymer when the polymer film was irradiated with laser light at a wavelength corresponding to the peak wavelength of electroluminescence. Degradation in photoluminescent properties was significant in an air environment but not under vacuum. This indicates that the oxygen in air aids photodegradation and this hypothesis was confirmed by UV-VIS absorption and infrared spectroscopy.

Keywords: electroluminescence, conducting polymer, photodegradation, poly(*p*-phenylene vinylene).

INTRODUCTION

Electroluminescence (EL) from π -conjugated polymers has great potential for applications in information displays and light emitting diodes. There have been many researches conducted regarding the chemistry and physics of the polymers themselves and their devices.¹⁻⁶ Advantages of polymer EL devices include processibility, luminous efficiency and wavelength controllability. However, there are still the areas to be investigated for improving the EL devices made of semiconducting polymers

such as the optical and physical properties of the electroluminescent polymers.

Many factors are related to the reliability of the device made of electroluminescent polymers, such as the film quality, the polymer-metal electrode interface, environmental conditions during device operation and so on. Environmental conditions for preparation of polymer and for device fabrication are important because they affect the performance of the fabricated device. Oxygen effects on poly(*p*-phenylenevinylene) (PPV) during the elimination reaction have been studied extensively,⁷⁻⁹ but there are few

studies on the photodegradation reaction even though it has an important effect upon the performance of EL devices. In this paper, we report the degradation of the PPV film in air atmosphere when irradiated with laser light at a wavelength corresponding to the peak emission wavelength of the electroluminescence. The degradation was investigated by decay of photoluminescence (PL) intensity, optical ultra-violet-visible (UV-VIS) and infrared (IR) spectroscopy. It is important to understand the mechanism of photodegradation for improvement of the device performance such as the life-time.

EXPERIMENTAL

Materials. Synthesis of the present PPV polymer was carried out via a precursor route using sulfonium salt.¹⁰ A reaction scheme is shown in Fig. 1. Starting from the monomer disulfonium salt, water-soluble precursor polymer is prepared and then spin coated on the transparent electrode such as indium tin oxide (ITO) for measurement of EL spectrum. Dialkyl sulfide and hydrogen halide were eliminated by thermal treatment for several hours at 200 °C in a vacuum oven to obtain the fully converted PPV. For IR measurement, the free standing film was obtained by spin-casting the polymer on the substrate and peeling off carefully after complete drying in vacuum at room temperature.

Methods. The device structure for EL measurement is shown in Fig. 2. The polymer was spin coated on the transparent electrode with the thickness of 70 nm and the metal electrode for cathode was vacuum deposited on the polymer at a pressure of 1×10^{-6} torr after thermal treatment. In order to investigate the photodegradation, the polymer films were irradiated with laser light under air and vacuum environment. Two

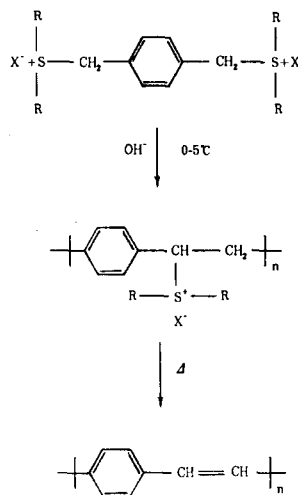


Figure 1. Precursor route for preparation of PPV.

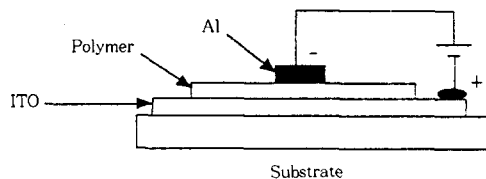


Figure 2. Device structure for measurement of electroluminescence.

wavelengths of 458 nm and 514.5 nm from argon ion laser (Spectra-Physics 2020) were used, which are close to the absorption maximum and the EL maximum, respectively. The laser beams were expanded to a diameter of 1 cm and irradiated onto the film for periods up to several hours. The incident beam was split into two beams, one as the reference monitoring the laser intensity fluctuation and the other for excitation of the sample. The incident power of laser light was a few tens of mW. Absorption spectra were obtained using a Hitachi U-3501 UV-VIS spectrophotometer. The PL intensities were measured as a function of time at 511 nm when excited at 458 nm and at 550 nm when excited at 514.5 nm, and were recorded on a chart recorder. The irradiated samples were taken for the measurement of

infrared spectra using a Bomem Michelson series (MB-100) Fourier Transformed IR spectrophotometer with the resolution of 4 cm^{-1} .

RESULTS AND DISCUSSION

The EL spectrum of the thermal treated PPV polymer is shown in Fig. 3, which is obtained under the forward bias of 7 V. The spectrum agrees well to the results already reported.² The forward bias is obtained when the ITO electrode is positively biased and the metal electrode negatively. EL spectrum shows two peaks located at 510 and 540 nm. The spacing of two peaks is about 30 nm (0.14 eV), which is expected for optic phonon modes corresponding to lattice vibrations of the carbon backbone. One of the strongest Raman modes located at 0.146 eV agrees well with the observed spacing.¹¹

The PL intensity of a PPV film, normalized by the reference laser beam intensity, decreased drastically down to 30% of the initial intensity in short period when the film was irradiated with 458 nm laser light in air environment, as shown in Fig. 4. The loss in luminescence intensity upon irradiation with 458 nm laser light on the precursor polymer¹² or partially converted polymer¹³ was also observed by others. However, we observe that the PL intensity, even when excited at 514.5 nm where the EL peak is located as shown in Fig. 3, decreases to about half of its initial intensity for fully converted PPV. This fact indicates that the polymer light emitting diode may be degraded under an air environment by its own emission. On the contrary, PL intensities show negligible change for both excitation wavelengths in a vacuum environment. These results suggest that oxygen in air may assist the photodegradation of PPV polymer. It is well known that oxygen effects on the PPV during the elimination reaction leads to low quantum efficiency due to the forma-

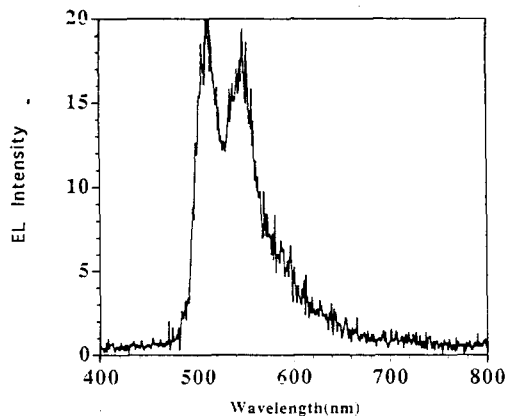


Figure 3. Electroluminescence spectrum of PPV.

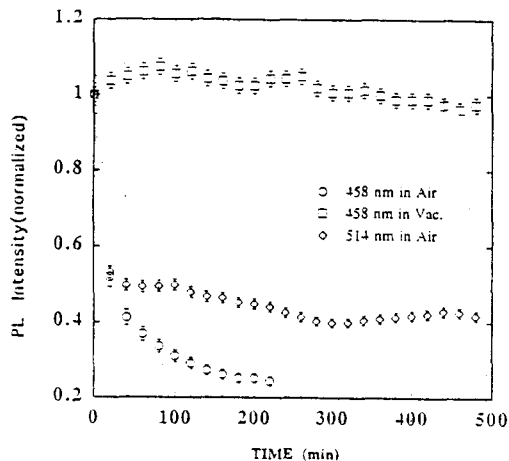


Figure 4. Photoluminescence intensity decay of PPV films during laser irradiation at 458 and 514.5 nm.

tion of carbonyl groups which act as quenching sites.^{6,8}

In order to investigate the photodegradation mechanism, we took several optical spectroscopic measurements. Fig. 5 shows UV-VIS absorption spectra of the unirradiated PPV film and the irradiated PPV films with laser lights of 458 nm and 514.5 nm in air and in vacuum. The absorption spectrum of PPV irradiated at 458 nm wavelength in vacuum is almost the same as that of the unirradiated PPV film. However, the UV-VIS

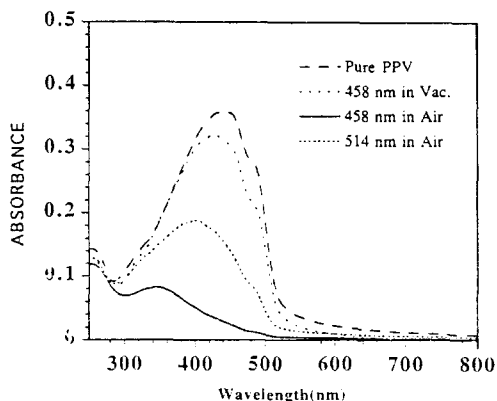


Figure 5. Absorption spectra of the unirradiated and the irradiated PPV films. The films were irradiated at 30 mW for a day.

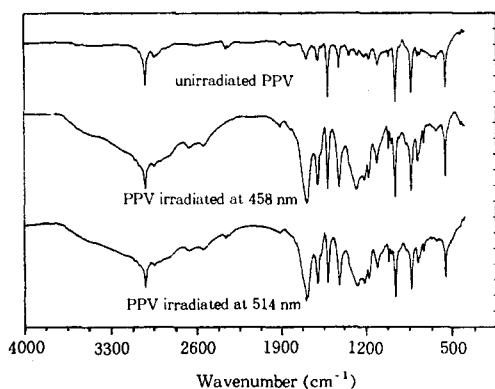


Figure 6. Infrared spectra of the unirradiated and the irradiated PPV films. The films were irradiated at 30 mW for a day.

spectra of the PPV irradiated with laser light at both wavelengths in air show a drastic decrease in UV-VIS absorption peak. The original yellow color of the film changed to brown after irradiation. The color is not recovered even after the sample was annealed at the elevated temperature (200 °C) in vacuum. The above results indicate that the chemical structure of the PPV changed during irradiation in atmospheric oxygen. This was confirmed by infrared spectroscopic measurements.

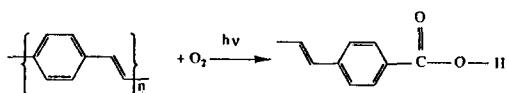
Table 1. Peak Assignments for Unirradiated and Irradiated PPV

cm ⁻¹	unirradiated	irradiated
2400-3500	—	Carboxylic OH stretch
3023	trans-vinylene CH stretch	trans-vinylene CH stretch
2950	aliphatic CH stretch	aliphatic CH stretch
1694	—	carbonyl stretch
1599	quadrant ring stretch	quadrant ring stretch
1515	semi-circle ring stretch	semi-circle ring stretch
1421	semi-circle ring stretch	semi-circle ring stretch
1278	—	carboxylic C-O stretch
1210	vinylene CH in-plane bend	vinylene CH in-plane bend
1177	<i>p</i> -phenylene CH in-plane bend	<i>p</i> -phenylene CH in-plane bend
1108	<i>p</i> -phenylene CH in-plane bend	<i>p</i> -phenylene CH in-plane bend
1018	<i>p</i> -phenylene CH in-plane bend	<i>p</i> -phenylene CH in-plane bend
963	trans-vinylene CH out-of-plane bend	trans-vinylene CH out-of-plane bend
835	<i>p</i> -phenylene out-of-plane bend	<i>p</i> -phenylene out-of-plane bend
557	<i>p</i> -phenylene out-of-plane ring bend	<i>p</i> -phenylene out-of-plane ring bend

Infrared spectra shown in Fig. 6 provide more detailed information about the photodegradation of PPV polymers. The infrared spectrum of the unirradiated PPV film is nearly identical to published spectra¹⁴ so that the peaks can be easily assigned; see Table 1. The absence of a peak at 630 cm⁻¹ corresponding to precursor C-S stretching vibrational mode in the unirradiated sample indicates that the elimination reaction was complete. However, both IR spectra of the films irradiated at 458 and 514.5 nm in air are similar, and show significant differences from that of the unirradiated PPV. 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 cm⁻¹ corresponds to O-H stretching vibrational band in a carboxylic acid groups¹⁵ and the sharp peak at

3023 cm^{-1} corresponds to a trans-vinylene C-H stretching band.¹⁴

However, the peaks corresponding to the *p*-phenylene C-H in-plane band¹⁴ at 1177 cm^{-1} , the *p*-phenylene C-H out of plane band at 836 cm^{-1} , the *p*-phenylene out-of-plane ring band at 557 cm^{-1} , and the tran-vinylene C-H out-of-plane band at 963 cm^{-1} show no changes even after the irradiation. This means that the *p*-phenylene group still remains in the reaction products even after photodegradation. Based on these observations, we can deduce the photodegradation mechanism of PPV in air as a chain scission reaction ;



When we compared the spectra of the irradiated sample with the IR spectrum of 4-vinylbenzoic acid, we found that those spectra are nearly the same. The change of the chemical structure is irreversible so that recovery of the yellow color was not possible. The product of photodegradation does not luminesce and hence the PL intensity decays during laser irradiation.

CONCLUSION

We describe the photodegradation of neat PPV thin films in air by the irradiation of laser light at a wavelength of 514.5 nm which is the peak wavelength of electroluminescence. The PL intensity decreases to half of the initial intensity during laser irradiation. The photodegradation reaction is a chain scission process involving oxygen in air to yield terminal 4-vinylbenzoic acid groups. This result indicates that the oxygen-sensitive electroluminescent

polymers can be degraded by their own emitted light in an oxygen environment. This photodegradation of conducting polymer may effect seriously on the performance of electroluminescence devices. Therefore, it is important to keep the device from the oxygen in air not only for protection of the easily oxidizable metal electrode but also for protection against photodegradation, resulting in enhancement of the lifetime of EL device.

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전기전도성 폴리아닐린/폴리스티렌 블렌드의 전기전도도에 영향을 미치는 인자들에 관한 연구

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Studies on the Factors Affecting Electric Conductivity of Conducting Polyaniline/Polystyrene Blends

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요약: Emeraldine base (EB) 형태로 합성된 polyaniline (PANI)과 polystyrene (PS)의 블렌드의 전기전도도에 영향을 미치는 인자들에 관하여 연구하였다. 블렌드는 m-cresol을 용매로 사용하여 용액 블렌딩 방법에 의하여 제조하였으며, 혼입제로는 dodecylbenzenesulfonic acid (DBSA)와 camphorsulfonic acid (CSA) 두 가지를 사용하였다. 혼입제의 구조와 양에 따른 블렌드의 전기전도도의 변화를 살펴보고 용매 증발시의 조건이 전기전도도에 미치는 영향도 살펴보았다. 또한 PS를 함유하지 않은 도핑된 순수 PANI착체의 전기전도도에 영향을 미치는 인자들에 관해서도 연구하였다. 순수 PANI착체나 블렌드 모두 CSA를 사용했을 때에 비해 DBSA를 사용했을 때 높은 전기전도도를 얻었으며 혼입제의 함량이 당량비로 0.5일 때 최고의 전기전도도를 나타내었다. 블렌드의 경우 PANI착체의 함량이 증가할수록 전기전도도는 증가하였고 DBSA를 혼입제로 사용했을 경우 PANI착체의 함유량이 5 wt%만 되어도 약 5 S/cm의 높은 값을 나타내었다. 또한 용매 증발시의 조건에 따라 블렌드의 전기전도도는 크게 달라짐을 알 수 있었으며, 이는 상분리와 밀접한 관계가 있음이 밝혀졌다. 전기전도도와 상분리 사이의 상호관계를 규명하기 위하여 분자량이 다른 세 가지의 단분산 PS를 사용하여 블렌드를 제조하여 분자량이 전기전도도에 미치는 영향도 검토하였다.

ABSTRACT: The factors affecting electric conductivity of blends of emeraldine base polyaniline (PANI) with polystyrene (PS) were investigated. Blend specimens were prepared using m-cresol as a solvent. Dodecylbenzenesulfonic acid (DBSA) and camphorsulfonic acid (CSA) were employed as dopants. The effects of dopant type and content, and the solvent evaporation conditions on the electric conductivity of pure (PANI+dopant) complexes and their blends with PS were studied. In both cases, DBSA was found to be more superior dopant to CSA. The maximum electric conductivity were obtained when 0.5 mole of dopant were used. For the blends, the electric conductivity was increased with the amount of PANI complex. And it was also found that the solvent evaporation conditions affect very significantly the electric conductivity of blends due to the phase separation behaviors. Three nearly mono-disperse PS's differing in molecular weight were employed to investigate this behavior in more detail.