Photoirradiation Effects on Polymer Light-Emitting Devices

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Photoirradiation effects on polymer light-emitting devices (PLEDs) based on poly(3-dodecylthiophene), PAT12 and poly(3-octadecylthiophene), PAT18 have been studied. The PLEDs used have a semitransparent Al cathode to make the photodegradation rate of the polymer film in PLED comparable to that of a naked polymer film. Upon photoirradiation in air using an incandescent lamp (150 W), the electroluminescence from the devices rapidly diminished and was weakened so as to be undetected within several minutes. The quantum efficiency of electroluminescence as well as that of photoluminescence also dropped rapidly due to photoirradiation. These results imply that the photoinduced creation of defects acting as luminescence quenchers plays a crucial role in the photodegradation of PLEDs based on poly(3-alkylthiophene), PAT, rather than the degraded carrier-transport nature of the polymer due to scission of the main chain. On the other hand, the optical absorption due to π-π^* transition of the polymer film shows little change under the same photoirradiation condition. This indicates that most π-conjugation systems of polymer main chains survived photodegradation, which suggests a long diffusion length of excitons or a strong interchain interaction in PAT.

Key words: photoirradiation effect, poly(3-alkylthiophene), long diffusion length, strong interchain interaction

1. INTRODUCTION

The polymer light-emitting device (PLED) based on conjugated polymers is one of the most promising candidates for the active element in flat-panel displays, because simple and cheap techniques, such as spin coating and printing methods, can be employed for the fabrication of polymer thin film [1-3].

On the other hand, it is well known that conductive polymers are photosensitive materials. They are easily degraded upon photoirradiation in air. Generally, photodegradation of conductive polymers consist of two elemental phenomena, i.e. the scission of the main chain and the creation of defects. In poly(p-phenylene vinylene), PPV [4], the archetype of luminescent conductive polymers, and its derivatives, considerable bleaching of optical absorption corresponding to π-π^* transition of the polymer due to reduced π-conjugation, as well as rapid diminishing of photoluminescence due to defects quenching, is observed upon photoirradiation in air [5].

For photoirradiation effect of PLED based on conductive polymers, it is expected that the two elemental phenomena of photodegradation affect the emission properties of PLEDs in different ways. The scission of the main chain may reduce the carrier-transport ability of the polymer, while the photocreated defects can quench the luminescent species such as singlet excitons. The former effect will result in a suppressed supply of the parent charge carriers of excitons, which weakens the emission, but will not affect the quantum efficiency of electroluminescence. On the other hand, the latter may effectively reduce the quantum efficiency. Therefore, to understand the photodegradation mechanism of PLEDs, not only photophysical and photochemical investigations on the polymers but also studies on the complete devices are essential.

To investigate the photoirradiation effects on PLEDs, it is important to make the metal cathode as thin as possible, even though relatively thick metal cathodes have been used in most of the PLED studies carried out thus far to prolong the device lifetime. If we use such a thin cathode device, the photodegradation rate of the polymer film in the device can be comparable to that of a naked polymer film, and the photodegradation effects on devices and those on naked films (i.e. optical absorption, photoluminescence, etc.) can be directly compared.

Our recent study on PPV-based devices show that no notable change was induced in the external quantum efficiency of electroluminescence in the device after photoirradiation, while the photoluminescence quantum efficiency rapidly decreased upon similar photoirradiation [7]. These results imply that the reduced carrier-transport nature of the PPV derivatives and not defect quenching is the cause of the device degradation, and the recombination zone should be spatially separated from the photocreated defects in the polymer.

A number of material parameters, such as the exciton diffusion length, the strength of interchain interactions, and the conversion cross section of carriers to singlet excitons, influence the electroluminescence process in PLED. Therefore, the photodegradation mechanism of PLEDs may strongly depend on the conductive polymers used therein.

Polythiophene derivatives such as poly(3-alkylthiophene), PAT are also known to be a family of luminescent conductive polymers and have been extensively studied thus far [8, 9]. In this article, we report the photodegradation effects on PLEDs based on PATs, which have semitransparent Al cathodes. It will be shown that the photodegradation mechanism of PAT-based PLEDs is considerably different from that of PPV-based devices.

2. EXPERIMENTAL DETAILS

Figure 1 shows the schematic structure of the PLED used in this study as well as the molecular structures of Poly(3-dodecylthiophene), PAT12 and Poly(3-octadecyl-

thiophene), PAT18. The corresponding 3-alkylthiophene monomer purchased from TCI (Tokyo Chemical Industry Co., Ltd.) was polymerized with $FeCl_3$ and was carefully washed according to a method reported in the literature [10]. The PATs used here clearly have regiorandom conformations.
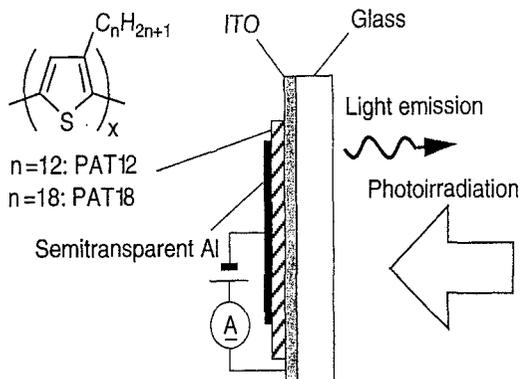

Figure 1. Schematic device structure of PLEDs used in this study. The molecular structures of PAT12 and PAT18 are also shown.

The devices were fabricated as follows. A film of PAT was spin-coated onto an ITO (indium-tin-oxide) film coated on a glass substrate from a chloroform solution. The thickness of the PAT film was on the order of 100 nm. The semitransparent Al film was vacuum deposited on the polymer surface as a cathode. The Al film was simultaneously deposited on a separate glass plate and its optical transmittance (%T) measured at 500 nm was used as an index of the thickness of the Al cathode. The results shown here were obtained from the devices with %T=24 % for PAT12 and %T=27 % for PAT18. The emission area of the devices was 1 cm². Photoirradiation was carried out in a slide projector with a 150 W incandescent lamp equipped with a thermal-cut filter.

The devices were operated in a dry box filled with nitrogen at room temperature and the emission intensity versus current-voltage properties were determined using a PC-controlled measurement system. The emission intensity was measured with a Si photodiode attached to the emission face of the device.

Optical absorption spectra were obtained with a Hitachi S3410 spectrophotometer and a Riken-Keiki AC-1 was used for the atmospheric UV photoemission spectroscopy. Photoluminescence spectra were measured with a homemade measurement setup including a photomultiplier tube attached to a monochromator as well as an Xe lamp combined with another monochromator as an excitation source. For these measurements, we used naked polymer films with the same thickness as the PLEDs, spin-coated onto glass plates.

3. RESULTS AND DISCUSSION

3.1 Electroluminescence from PLEDs based on PATs

Figure 2 shows the emission intensity versus voltage properties of PLEDs based on PAT12 after various photoirradiation times. The emission from the device rapidly diminished upon photoirradiation in air and was eventually weakened to become undetectable after photoirradia-

tion for 5 min.

On the other hand, the onset voltage of emission was found to be approximately 3 V and remained constant throughout the measurement. The reduction of the slope is clearly observed in the corresponding emission intensity versus current properties shown in Fig. 3, indicating that the external quantum efficiency of the emission from the PLEDs based on PAT12 is reduced upon photoirradiation.
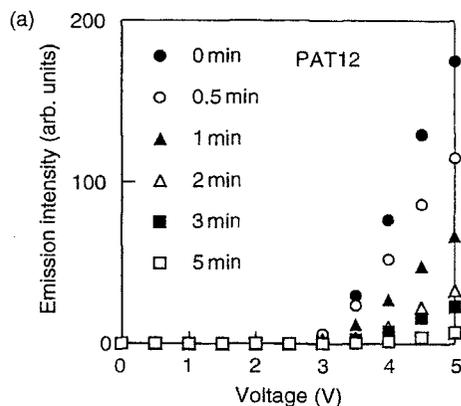

Figure 2. Emission intensity versus voltage properties of the PLED based on PAT12 after various photoirradiation time.
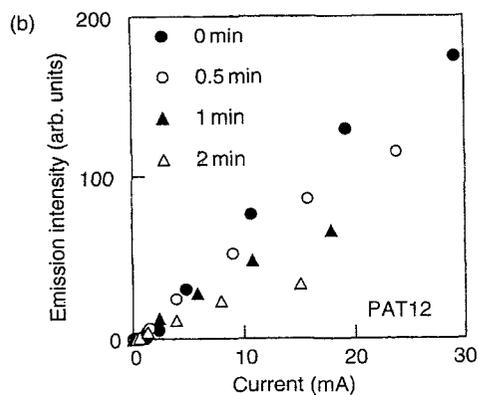

Figure 3. Emission intensity versus current properties of the PLED based on PAT12 after various photoirradiation time.

Similar behavior is also observed in the case of PLEDs based on PAT18. That is, as shown in Figs. 4 (a) and (b), the emission intensity decreased rapidly upon photoirradiation and became completely dark within 5 min; the external quantum efficiency of emission shows considerable decrease due to photoirradiation.

If the photodegradation of PLED originates from the reduction of carrier-transport ability of the polymer due to scission of the main chain, the external quantum efficiency of the device remains constant, as observed in the PLEDs based on a PPV derivative [7]. However, in the case of PATs, the reduction of quantum efficiency due to photoirradiation is observed. This suggests the following scenario: some defects which can quench luminescent species such as exitons, are created in the polymer layer upon photoirradiation; this defect quenching of luminescent species plays an important role in the photodegrada-

tion of PLEDs based on PATs, in contrast to those based on PPV derivatives.

Optical absorption spectra of PAT12 and PAT18 film after various photoirradiation times are shown in Figs 5 (a) and (b), respectively. While the electroluminescence from the devices based on PATs considerably diminished upon photoirradiation in air, the optical absorption spectra of PAT films show little change. This implies that most of the π-conjugation system in the PAT survives photodegradation, which suggests that the carrier-transport ability of the polymer layer in photoirradiated PLED is negligibly affected and thus supports the above-mentioned model of PLED photodegradation.
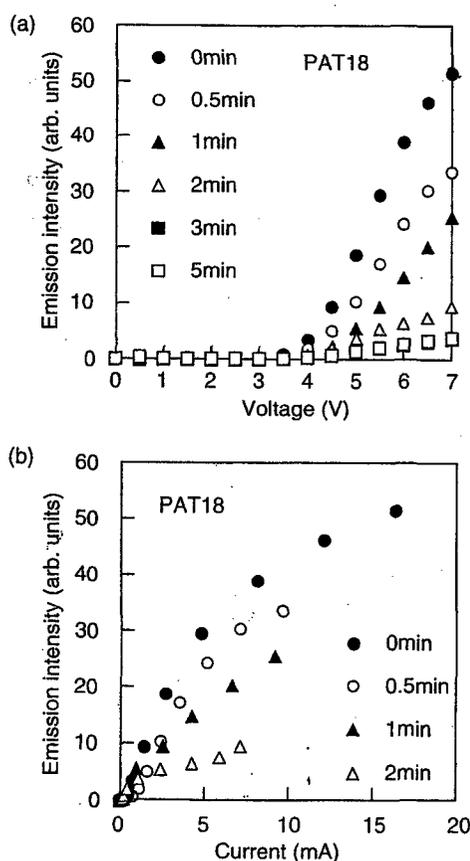

Figure 4. (a) Emission intensity versus voltage and (b) emission intensity versus current properties of the PLED based on PAT18 after various photoirradiation time.

Figure 6 shows the atmospheric UV photoemission spectra of the PAT films before and after photoirradiation for 5 min. The threshold energy for photoemission corresponds to the ionization potential at the surface of the sample. Although the slopes show little decrease due to photoirradiation, there is no shift in the ionization potentials, indicating that the degree of π-conjugation system of PAT films in the photoirradiated PLEDs is small even at the film surface.

Because of the quantum efficiency of electroluminescence of the PLEDs is considered to be proportional to the photoluminescence quantum efficiency, it is worthwhile to monitor the change in the photoluminescence spectra of polymer film due to photoirradiation. Figure 7 shows the photoluminescence spectra of the PAT18 film

after various photoirradiation times. The photoluminescence intensity decreased rapidly upon photoirradiation.

On the other hand, no notable changes in the spectral shift such as blue shift, were observed. Since the excitation wavelength used is 400 nm, where the absorbance of the polymer film remains constant throughout the measurement, as shown in Fig. 6, this result implies the reduction of photoluminescence quantum efficiency upon photoirradiation and thus the photoinduced creation of quenching defects is expected. Unfortunately, the photoluminescence from the PAT12 film is so weak as to be below the sensitivity of our measurement setup; nevertheless, it is expected that similar behavior is observed also in PAT12 film because the main chain structures of the two polymers are identical.
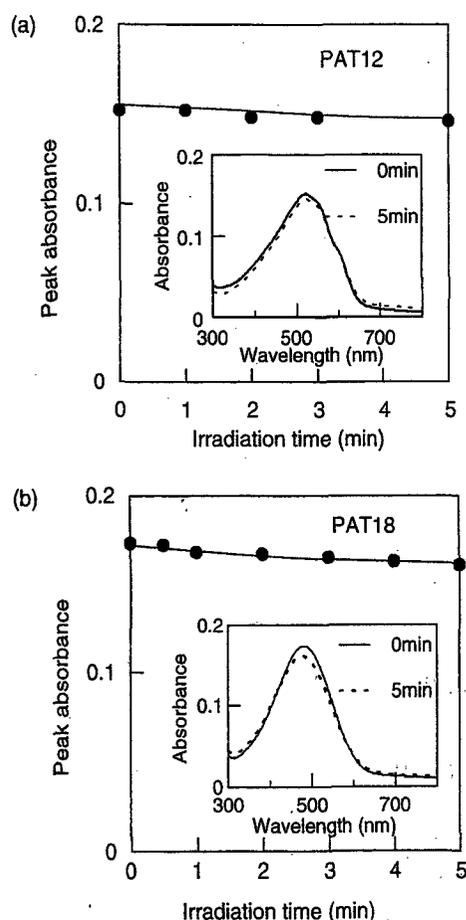

Figure 5. Dependence of the peak absorbance of (a) PAT12 and (b) PAT18 films on the photoirradiation time. Inset figures show the optical absorption spectra of relevant polymer films before and after photoirradiation for 5 min.

While the authors could not identify the chemical structure of the defects at this stage, it has already reported that the change of the PAT IR spectrum after photoirradiation in air indicates the formation of carbonyl groups as well as the decomposition of thiophene rings [11]. Since the carbonyl groups have such a strong electron affinity that they act as quenching defects for singlet excitons in PPV and its derivatives [5], it is likely that singlet excitons in PAT are also quenched by the carbon-
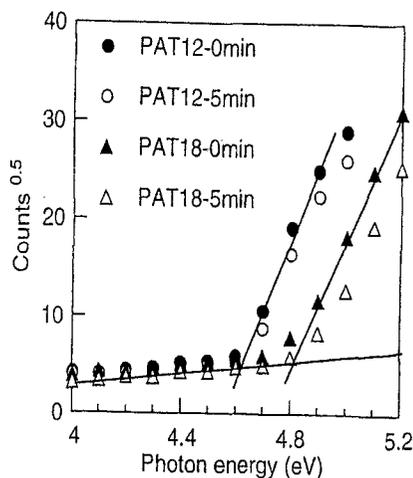
yl groups.

Figure 6. Atmospheric UV photoemission spectra of the PAT films before and after photoirradiation for 5 min.
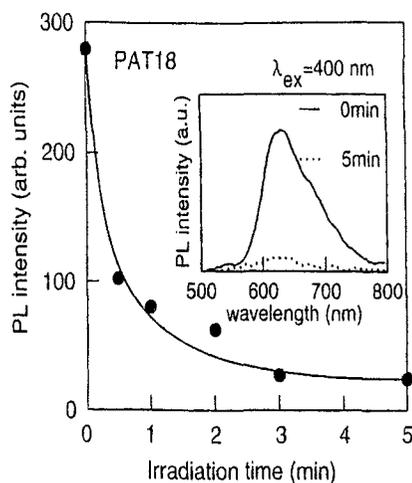

Figure 7. Dependence of photoluminescence intensity of the PAT18 film on photoirradiation time. The inset figure shows the photoluminescence spectra of the PAT18 film before and after photoirradiation for 5 min.

The finding that photoirradiation of PAT18 film for 5 min results in considerably weakened photo- and electroluminescence as well as no notable change in optical absorption, indicates that a low density of defects can effectively quench the luminescent species. Therefore, a long diffusion length of excitons or a strong interchain interaction in PATs is expected. This expectation is supported by the fact that PATs with longer alkyl side chains show stronger photoluminescence [12]. Figure 8 shows a schematic explanation for the electroluminescence process in photooxidized PATs.

4. CONCLUSIONS

In this paper, photoirradiation effects on PLEDs based on PAT12 and PAT18 have been reported. The experimental results can be summarized as follows.

(1) Upon photoirradiation in air using an incandescent lamp, the electroluminescence from the devices rapidly diminished and was weakened so as to be unde-

tectable within several minutes. Contrary to the case of PPV derivatives [7], the quantum efficiency of the devices rapidly decreased. In addition, the photoluminescence from the PAT18 film also rapidly diminished upon photoirradiation. These results imply that the photoinduced creation of quenching defects plays a dominant role in the photoirradiation of PLEDs based on PAT, rather than the degraded carrier-transport nature of the polymer due to scission of the main chain.
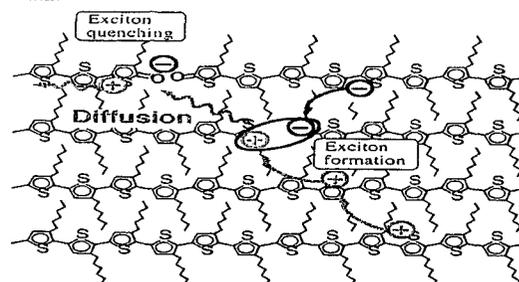

Fig. 8. Schematic explanation for the electroluminescence process in photooxidized PATs.

(2) On the other hand, the optical absorption and atmospheric UV photoemission spectra of the polymer film show little change under the same photoirradiation conditions. This indicates that most π-conjugation systems of polymer main chains survived photodegradation, which suggests a long diffusion length of excitons or a strong interchain interaction in PAT.

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