Application of Electropolymerized Poly(thiophen derivative)/NBR Composite Film to an Electroluminescence Emission Layer

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A semiconducting composite film of poly(3-substituted thiophen) and insulating nitrile butadiene rubber (NBR) was applied to an emission layer of polymer electroluminescence device. The uniform composite was deposited by electropolymerization of phenyl-, hexyl- and octylthiophen onto an indium-tin oxide glass pre-coated with NBR thin film. By utilizing indium as rectifying contact, visible light was observed from the composites under forward bias. The emission color depended on the substituents in thiophen units.

An electroluminescence (EL) device using a luminescent organic film has great advantages for flat panel display devices because of realizing large emission area, various color emissions, high brightness and so on. Recently, there are many active studies for applications of semiconducting π-conjugated polymer to the EL emission layer; poly(p-phenylenevinylene),[1] poly(alkylthiophen) (PAT),[2,3] poly(p-phenylene)[4] and these derivatives.[5-7] The applications of these polymers are expected to enhance the stability of the EL characteristics compared with low molecular materials. So far these polymer layers were almost formed by a mechanical technique as spin coating or dip coating from the solution containing the polymer which was chemically polymerized. Electrochemical polymerization is one of the most interesting wet processes for simultaneously both synthesizing and forming π-conjugated polymer films. In this letter, we present the application of electropolymerized film to EL emission layer which is compounded with an insulating polymer.

The electropolymerization was carried out under galvanostatic mode (80 μA cm^{-2} for a period of 8 min). This polymer film was prepared in acetonitrile (AN) solutions containing 0.1 mol dm^{-3} thiophen derivative monomer (Tokyo Chemical Industry Co., Ltd., used as received) and 0.1 mol dm^{-3} sodium perchlorate (Kanto Chemical Co., Inc.) as supporting electrolyte. One compartment cell was assembled with an indium-tin oxide (ITO) coated glass as a working-electrode, a Pt counter-electrode and an Ag/Ag$^+$(0.01 mol dm^{-3}) reference-electrode. ITO glasses were pre-coated with nitrile butadiene rubber (NBR) formed by dip coating method from 2-butanone solution containing 2 wt% NBR (Nippon Zeon Co., Ltd.). After the polymerization the composite film was undoped by applying a negative potential of −0.3 V. Indium electrode, rectifying contact, was deposited by vacuum evaporation onto the ITO modified with polymer. The emission area was 5 x 5 mm^2. All the measurements were carried out at room temperature in air.

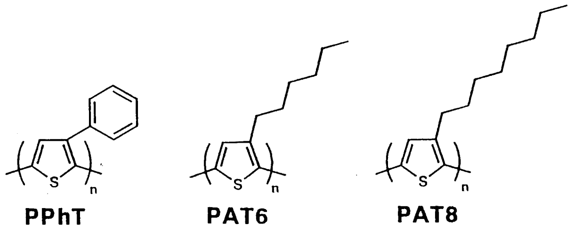
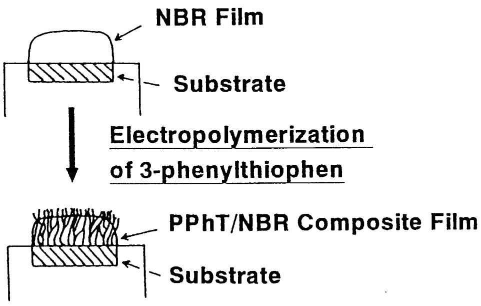


Figure 1. Molecular structures of poly(thiophen derivative)s; PPhT, PAT6 and PAT8.

By using various monomers as 3-alkylthiophen (alkyl chain length: n=1, 4, 6, 7, 8, 9, 12) and 3-phenylthiophen, which were soluble in AN, polymer films were deposited on bare ITO glasses by electropolymerization. Poly(3-phenylthiophen) (PPhT), poly(3-hexylthiophen) (PAT6) and poly(3-octylthiophen) (PAT8) films became relatively uniform, being confirmed by microscopic examination. Figure 1 shows the molecular structures of three polymers. The film thickness was about 2000 Å. However, a short current between ITO and In was leaked due to roughness of the polymer films. We observed no light emission from the device without pre-coating of NBR.

Using the ITO glass coated with NBR film, the poly(3-substituted thiophen)/NBR composite film was prepared by the technique which was almost the same as described in Ref. 8 (Scheme 1). By application of this composite to a device, the leakage was prohibited because of significant improvement in unformity of the film, being confirmed by SEM observation. Figure 2 shows the current-bias and bias-luminance characteris-



Scheme 1. Preparation process of PPhT/NBR composite film.

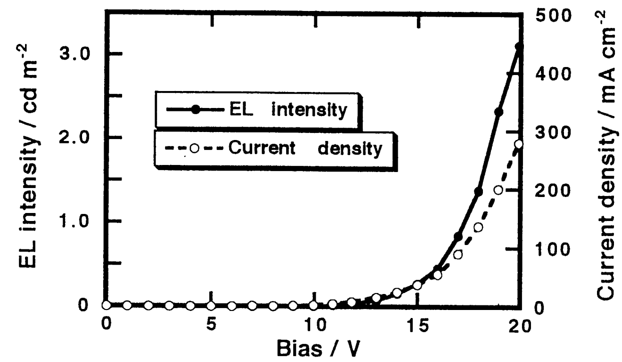


Figure 2. Dependence of current and EL intensity on bias voltage for the device using PPhT/NBR composite film.

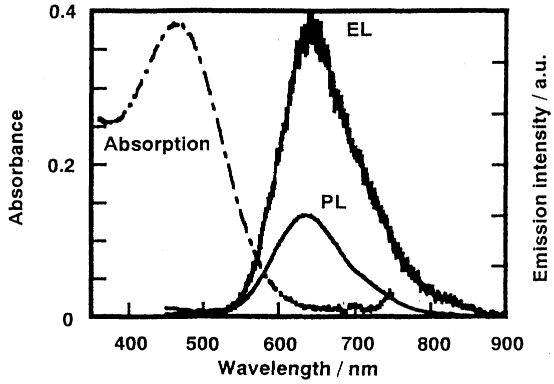


Figure 3. Absorption, PL and EL spectra of PPhT/NBR composite film.

tics of the device in the case of the PPhT/NBR composite film as an emission layer. The device indicated a rectification characteristic, and forward bias was obtained when the ITO was the positive and the In was grounded. As positive bias increases, light emission turns on at about 10 V as shown in Figure 2. The orange-red emission became visible under ordinary dim light. Other composite films for the PAT6/NBR and PAT8/NBR showed the same characteristics. The emission of the devices using the PAT6/NBR and PAT8/NBR composite film starts at about 22 V and 27 V, respectively. Since the insulating NBR film is non-fluorescent, these poly(thiophen derivative)s are confirmed to act as light emitter.

The absorption and PL spectrum of the PPhT/NBR film and the emission spectrum of the device are shown in Figure 3. The emission spectrum is similar to the PL spectrum of the PPhT/NBR film measured with an excitation wavelength of 450 nm. In Figure 3, the wavelength of the emission peaks corresponds to the edge of optical absorption which is attributed to the π–π^* transition of PPhT, and in Figure 2 the emission intensity increases with current density. These results, therefore, suggest that the emission is due to the recombination, at the PPhT, of electron and hole injected from each electrode.

The EL spectra of the devices utilizing various poly(thiophen derivative)/NBR composite films are shown in Figure 4. The spectrum characteristics of three composite polymers are similar to each other. However, there is a little difference in EL emission peaks. The emission peak of the device using the PPhT/NBR composite film appeared around 650 nm, while those of the PAT6/NBR and PAT8/NBR composite films appeared around 610 and 590 nm, respectively. The peak shift suggests that the EL spectra depend on the substituent in the 3-position of the thiophen. By Yoshino et al.,[9] light emitting diode using PAT (n≥12) spin-cast films polymerized by oxidizing reagent was reported. However, in our system shorter emission wavelength was observed from the composites due to the difference of the degree of polymerization and/or the conformation of polymer chain. Furthermore, dispersing fluorescent materials into NBR will be capable of controlling emission color and improving emission efficiency.

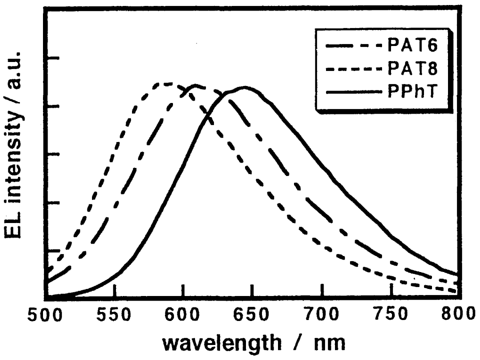


Figure 4. EL spectra of composite films of various poly(thiophen derivative) with NBR.

In conclusion, we succeeded in the application of electropolymerized film to polymer EL device. There is a high possibility for enhancement of the EL characteristics by control of the electrolysis condition and selection of emitting materials in the electropolymerization process.

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