Hole-injection properties of annealed polythiophene films to replace PEDOT-PSS in multilayered OLED systems

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Abstract

Hole-injection properties of annealed poly(alkoxy- and alkylthiophene) films in OLEDs were studied. Among them, annealed poly(3,3'-dihexyloxy-2,2'-bithiophene) (aPHOBT) film exhibited good hole-injection properties and a triple-layered OLED with the structure ITO/aPHOBT/PVK/Alq3/Mg-Ag (device I) showed much higher performance than a double-layered device without the aPHOBT layer (device II, ITO/PVK/Alq3/Mg-Ag). Device I was slightly inferior to a device having a PEDOT-PSS layer as the hole injector (device III, ITO/PEDOT-PSS/PVK/Alq3/Mg-Ag) in the low-intermediate region of the applied voltage (6-11 V), but gave comparable luminance to III when the applied voltage exceeded 11 V.

Key words: Polythiophene; Hole-injection; OLED; Annealing

1. Introduction

Organic light emitting diodes (OLEDs) are attracting much attention because of their potential applications to flat panel displays and lighting. To achieve high

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performance of OLEDs, multilayered systems are usually employed, which are composed of discrete layers with different roles between electrodes. In those systems, poly(3,4-ethylenedioxythiophene)-poly(4-styrene sulfonate) (PEDOT-PSS) is commonly used as an excellent hole-injection material that facilitates hole-injection from anode (usually indium tin oxide (ITO)) to an organic layer lying on its surface, with good electron blocking. PEDOT-PSS is highly useful because it is insoluble in organic solvents and therefore, an organic layer can be prepared on its surface by solution processing, such as casting and spin-coating, using organic solvents. However, PEDOT-PSS also has some disadvantages. For example, the high acidity of PSS leads to corrosion of ITO particularly at high temperature [1]. In addition, the decomposition of PSS has been reported [2]. To develop novel materials that would be a good substitute for PEDOT-PSS, thermally [3] and photochemically [4] cross-linkable materials, whose cross-linking leads to the formation of solvent-resistant hole-injection layers, have been extensively studied. The electrochemical preparation of insoluble hole-injection layers on electrodes has been studied as well [5].

Recently, we demonstrated that poly(3-hexylthiophene) (PHT) films show good hole-transporting properties in multilayered devices of ITO/PHT/Alq3/Mg-Ag (Alq3 = tris(8-quinolinolato)aluminum), which are enhanced by annealing [6]. Since the films become insoluble in organic solvents by annealing, we decided to study the hole-injection properties of annealed polythiophene films in multilayered OLEDs. Recently, some poly(alkoxythiophene)s (PAOTs) were prepared as low-band gap materials [7], and we examined PAOTs together with PHT in the present study.

2. Experimental

2.1. Materials

Regio-regular PHT with the head-to-tail content of >97% and PVK were purchased from Aldrich Chemical Co. and Tokyo Kasei Kogyo Co., respectively, and were used as obtained. Alq3 was purchased from Tokyo Kasei Kogyo Co. and purified by sublimation. Diethyl ether was dried over sodium-potassium alloy and distilled immediately before use. Chloroform used as the reaction medium was dried over P_2O_5 and distilled immediately before use.

2.2. Preparation of 3,3'-dihexyloxy-2,2'-bithiophene.

To a solution of 2.0 g (11 mmol) of 3-hexyloxythiophene in 38 mL of diethyl ether was added 12 mmol of lithium diisopropyl amide (LDA) in 19 mL of diethyl ether at room temperature and the mixture was heated to reflux for 1 h. The mixture was cooled to -78°C and 1.6 g (12 mmol) of $CuCl_2$ was added in small portions. After stirring overnight at room temperature, the mixture was filtered to remove copper salts. The solvent was evaporated and the residue was subjected to silica gel column chromatography to give 0.58 g (29% yield) of the title compound as a colorless solid: ^{1}H NMR (δ in $CDCl_3$) 0.90 (6H, t, $J = 6.7$ Hz, CH_3), 1.35 (8H, m, CH_2CH_2), 1.52 (4H, m, CH_2), 1.84 (4H, m, CH_2), 4.08 (4H, t, $J = 6.3$ Hz, OCH_2), 6.83 (2H, d, $J = 5.5$ Hz, thiophene ring H), 7.06 (2H, d, $J = 5.5$ Hz, thiophene ring H); ^{13}C NMR (δ in $CDCl_3$) 14.05, 22.59, 25.73, 29.65, 31.56 ($CH_3CH_2CH_2CH_2CH_2$), 71.97 (OCH_2), 114.09, 116.03, 121.59, 151.92 (thiophene ring C); MS m/z 366 (M^+). Anal. Calcd for $C_{20}H_{30}O_2$: C, 65.53; 8.25. Found: C, 65.53; 8.15.

2.3. Preparation of PAOTs.

A mixture of 0.26 g (2.3 mmol) of 3-methoxythiophene, 1.5 g (9.2 mmol) of $FeCl_3$, and 46 mL of chloroform was stirred at -45°C for 120 h. To this was added 50 mL of 50% aqueous hydrazine and the mixture was stirred overnight at room temperature. After the resulting precipitates were filtered, the organic layer was separated and the aqueous layer was extracted with chloroform. The organic layer and the extracts were combined and dried over anhydrous magnesium sulfate. The solvent was evaporated and the residue was reprecipitated from chloroform-hexane to give 80 mg (31% yield) of poly(methoxythiophene) (PMOT) as a dark purple solid: ^{1}H NMR (δ in $CDCl_3$) 3.99 (3H, br s, OCH_3), 6.86-7.03 (1H, m, thiophene ring H).

Other PAOTs were prepared in a manner similar to that above, yielding dark purple solids (Table 1). Data for PHOT: ^{1}H NMR (δ in $CDCl_3$) 0.91-1.88 (11H, m, CH_3 and CH_2 of Hex), 4.13 (2H, m, OCH_2), 6.84-7.04 (1H, m, thiophene ring H). Data for PMEET: ^{1}H NMR (δ in $CDCl_3$) 3.36-4.29 (11H, m, $CH_3OCH_2CH_2OCH_2CH_2O$), 6.77-7.03 (1H, m, thiophene ring H). Data for PHOBT: ^{1}H NMR (δ in $CDCl_3$) 0.91-1.88 (11H, m, CH_3 and CH_2 of Hex), 4.13 (2H, m, OCH_2), 6.84-7.08 (1H, m, thiophene ring).

2.4. Fabrication of OLEDs with polythiophene hole-injection layers.

A thin film (ca. 5-10 nm) of PAOT or PHT was prepared by spin-coating from the chloroform solution on an ITO electrode. After heating the ITO electrode coated with the polymer film at 250°C for 20 min, PVK (60 nm) was spin-coated from the chloroform solution on the PAOT layer as a hole-transport layer. Then, an electron-transporting-emission layer was prepared by vacuum deposition of Alq3 at 1.3×10^{-3} Pa with a thickness of 60 nm on the PVK film. Finally, a layer of Mg-Ag alloy with an atomic ratio of 10:1 was deposited on the Alq3 layer as the top electrode at 1.3×10^{-3} Pa. The emitting area was 0.5×1.0 cm^2.

3. Results and discussion

3.1. Preparation of PAOTs.

PAOTs were obtained as dark purple solids by oxidative coupling of the respective alkoxythiophenes using $FeCl_3$ (Scheme 1). Table 1 summarizes the yields, molecular weights, and absorption maxima of the polymers prepared under optimized conditions. The rather low yield and low molecular weight of PMOT were due to the formation of insoluble substances that were removed by filtration, while those of PHOT and PMEET were probably the result of low reactivity of the monomers arising from the existence of sterically large substituents. To reduce steric effect on C-C bond formation, we prepared dihexyloxybithiophene and examined its polymerization. As expected, the resulting polymer (PHOBT) had much higher molecular weight than PHOT.

The UV absorption maxima of PAOTs appeared around 500 nm, which were red-shifted in the order of PMOT < PHOT < PHOBT < PMEET, presumably reflecting the molecular weights and electron donating properties of the substituents that would raise HOMO energy levels.

[Scheme 1 and Table 1]

3.2. Fabrication of OLEDs using annealed PAOT and PHT films.

Figure 1 presents spectral changes of a PHOBT film on annealing at 250°C in nitrogen atmosphere. The absorption band became broad and the absorption maxima slightly shifted to higher energies on annealing. At the same time, the absorbance decreased to approximately 1/3 of the original after annealing for 1 h. These results may be explained by the thermal cross-linking of thiophene units on annealing. Other PAOT films exhibited UV spectral changes on annealing, similar to those of PHOBT. PAOT films became insoluble after annealing at 250°C for 20 min, making it possible to prepare an organic layer by spin-coating on the annealed PAOT surface. At this stage, the polythiophene conjugated backbone was not completely decomposed but reacted only partly, as can be seen in Fig. 1. We also carried out thermogravimetric analysis (TGA) of PAOTs in nitrogen atmosphere and found that the weight loss was less than 5% at 250°C, indicating no significant degradation of the polymer chains.

[Figure 1]

To evaluate the hole-injection properties of the annealed PAOT (aPAOT) films, we fabricated OLEDs with the structure ITO/aPAOT (5-10 nm)/PVK (60 nm)/Alq3 (60 nm)/Mg-Ag, where PVK and Alq3 were a hole-transport layer and an electron-transporting emitter, respectively. Table 2 summarizes the performance of the devices examined. The device with aPHOBT (device I) showed the lowest onset voltage and the highest maximum current density and maximum luminance, indicating that the aPHOBT film is the best hole-injection material among the aPAOTs examined.

[Table 2 and Figure 2]

Figure 2 depicts current density-voltage (I-V) and luminance-voltage (L-V) characteristics of device I. A device without aPHOBT layer (device II, ITO/PVK/Alq3/Mg-Ag) and those having PEDOT-PSS and aPHT as the hole injector in place of aPHOBT (devices III and IV) were examined and the results are also presented in Fig. 2 and Table 2. Clearly, devices I, III, and IV having hole-injection layers showed much better performance with higher current density and luminance than device II, confirming the good hole-injection properties of aPHOBT, PEDOT-PSS, and aPHT films. Although device IV showed better I-V characteristics in the whole region of the applied voltage than device I, luminance from device I was always higher than that from device IV, indicating the superior electron-blocking properties of aPHOBT to aPHT. Compared with device III, devices I and IV showed lower current density in most of the applied voltage region except the 6-7 V region where device IV showed slightly higher current density. With respect to luminance, devices I and IV again showed lower values than device III in the low-intermediate region of the applied voltage (6-11 V). However, luminance from device I was comparable to that from device III in the high voltage region (> 11 V).

In conclusion, we demonstrated that conventional PHT and readily accessible PAOT are good precursors of hole-injection layers for solution-processed multilayered OLEDs. Although the properties of aPHOBT film were generally slightly inferior to those of PEDOT-PSS film, aPHOBT film showed comparable properties to PEDOT-PSS film regarding luminance in the high voltage region. Optimization of the polymer structure and the annealing process is under way.

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Table 1. Preparation of PAOTs

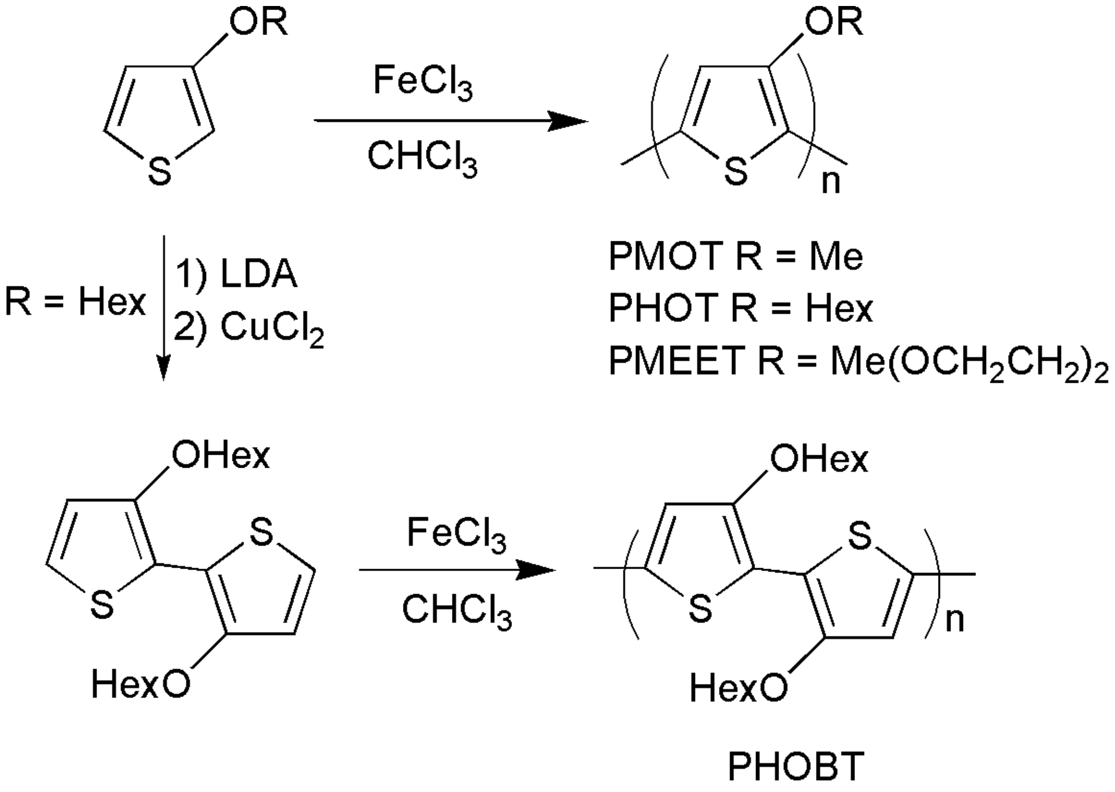
polym	conditions	yield[a]/%	Mw (Mw/Mn)[b]	UV λ_{max}[c]/nm
PMOT	-45°C, 120 h	31	2200 (1.2)	488
PHOT	-45°C, 72 h	36	2600 (1.3)	516
PMEET	0°C, 12 h	38	3200 (1.3)	530
PHOBT	0°C, 4 h	37	6200 (1.4)	526

[a] After reprecipitation. [b] Determined by GPC relative to polystyrene standards. [c] In $CHCl_3$.

Table 2. Performance of multilayered OLEDs having hole-injection layers

polym film	onset[a] voltage/V	max current density /mA·cm^{-2} (voltage[b]/V)	max luminance /cd·m^{-2} (voltage[b]/V)
aPMOT	6.5	470 (14)	7100 (13)
aPHOT	6.7	520 (14)	6700 (12)
aPMEET	6.6	530 (14)	7100 (13)
aPHOBT	6.3	590 (14)	12000 (12)
aPHT	6.5	710 (15)	8800 (13)
PEDOT-PSS	6.0	720 (14)	12500 (13)
Non	7.0	520 (17)	3900 (17)

[a] Applied voltage resulting in luminance of 10 cd·m^{-2}. [b] Applied voltage resulting in the maximum value.



Scheme 1. Synthesis of PAOTs.

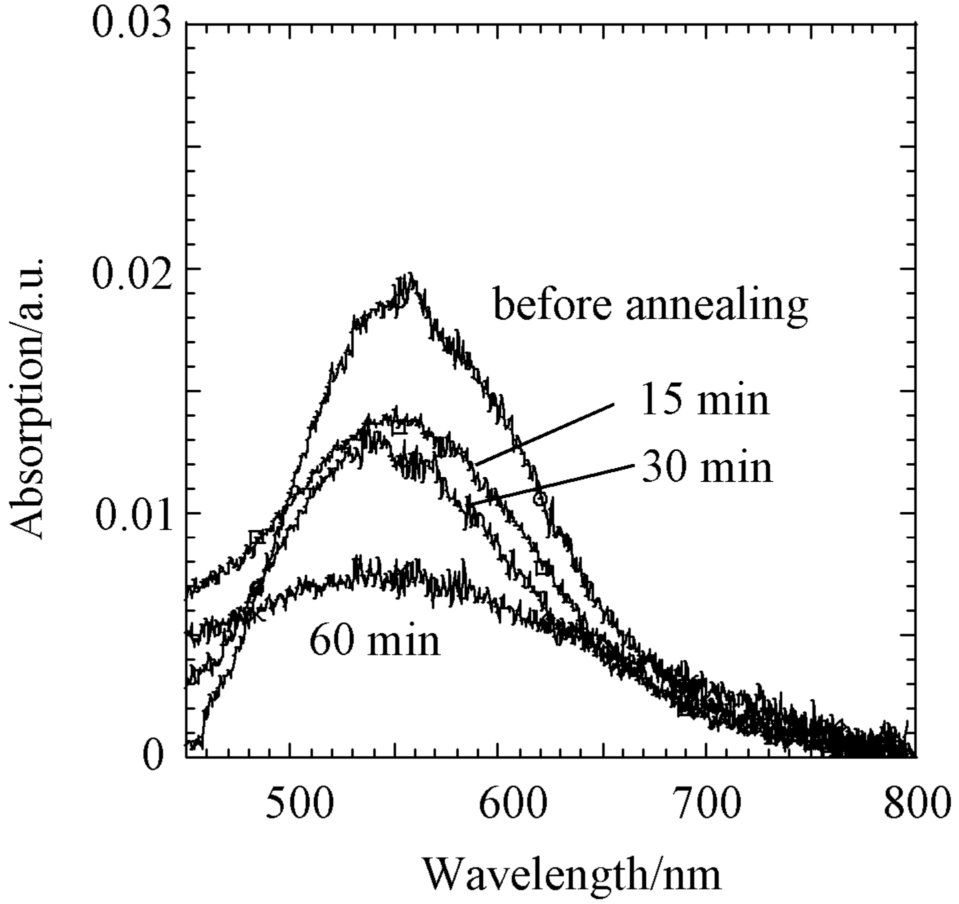


Figure 1. UV spectra of a PHOBT film spin-coated on a quartz plate, before and after annealing.

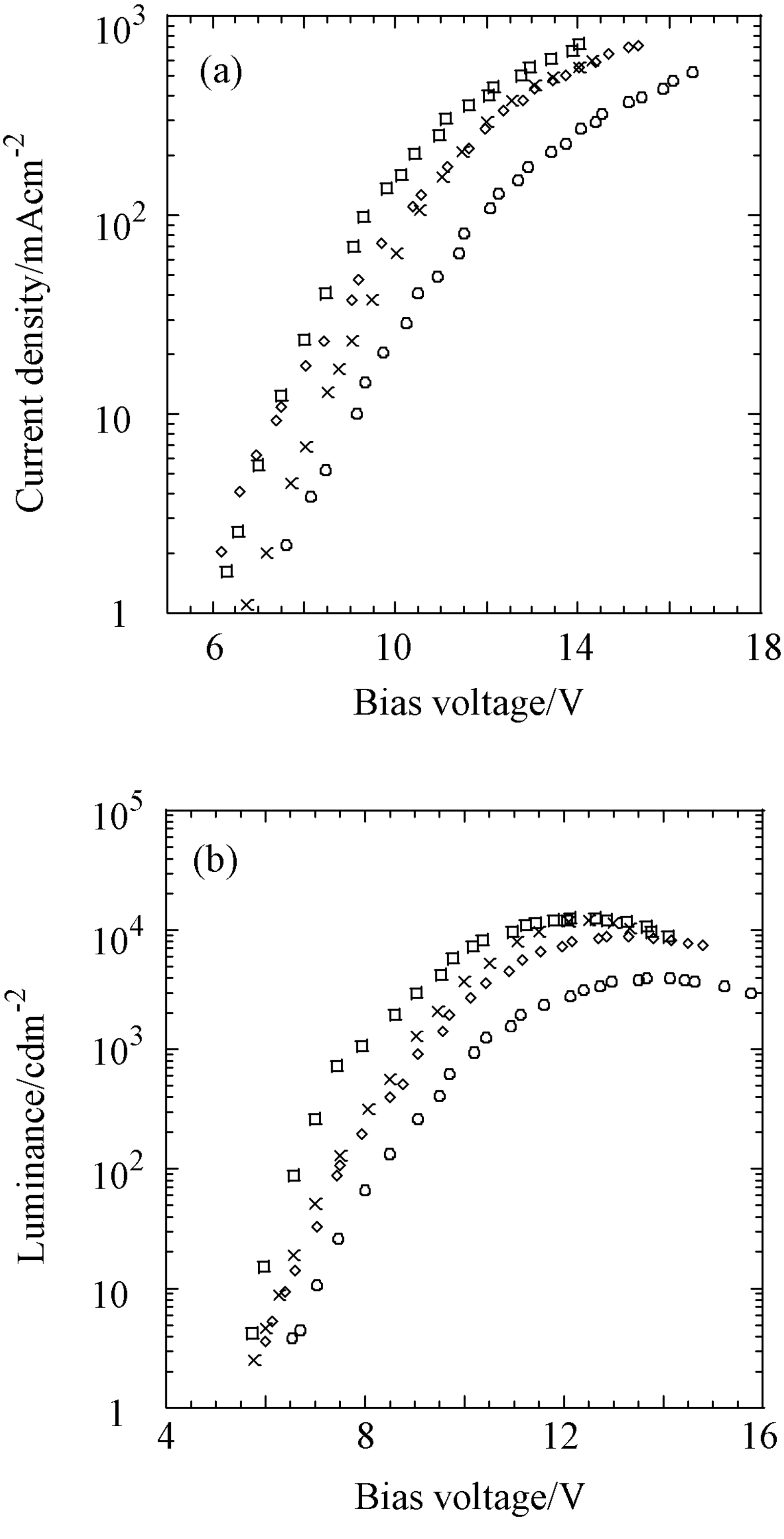


Figure 2. (a) Current density-voltage and (b) Luminance-voltage plots for multi-layered OLEDs (X) I, (O) II, (□) III, and (◇) IV.