

ORIGINAL ARTICLE

Effect of polymer chain structure on electroluminescence of poly(4-diphenylaminostyrene)/Alq₃ blend films

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Three types of poly(4-diphenylaminostyrene) (PDAS) having different polymer chain structures were prepared by living anionic polymerization, and the electroluminescence of PDAS/tris(8-hydroxyquinoline) aluminum (Alq₃) blend films was examined to obtain basic information of PDAS for application to organic light-emitting diodes (OLEDs). The hole drift mobility of PDAS was on the order of 10⁻⁴ to 10⁻⁵ (cm²V⁻¹s⁻¹) with a negative slope, and it increased with an increase in the syndiotactic configuration in the polymer chain. The current density, turn-on voltage and brightness were also improved with an increase in the syndiotactic configuration of PDAS.

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INTRODUCTION

Poly(4-diphenylaminostyrene) (PDAS), a stable and soluble triphenylamine-containing polymer, has been recognized as an attractive hole-transport semiconducting polymer for optoelectronic applications.^{1–11} It is important for such applications to characterize the relationship between polymer chain structure and properties. Therefore, a number of polymerization studies of 4-diphenylaminostyrene (DAS), the monomer of PDAS, have been carried out using anionic,^{1,3} radical and living radical^{1,2,4–11} methods to obtain PDAS with a well-defined and well-controlled polymer chain structure. However, the controlled polymerization of DAS is considerably difficult, even using living radical polymerization. To our knowledge, only the dependence of the glass transition temperature on the degree of polymerization of PDAS has been examined by Behl *et al.*⁴

Recently, we attempted the anionic polymerization of DAS to obtain PDAS with a well-defined polymer chain structure.^{12–14} As a result, the first successful example of the living anionic polymerization of DAS using the alkyllithium/amine system was discovered (Scheme 1). The method involved the synthesis of homopolymers and block copolymers with narrow-range polydispersity indices, controlled molecular weight and well-defined polymer chain structures. Subsequently, the stereoregularity of PDAS was revealed.^{12,14} With respect to PDAS, the polymer chain structure strongly affected the hole drift mobility and photoluminescence (PL), whereas it did not significantly affect the highest occupied molecular orbital/lowest unoccupied molecular orbital energy levels and ultraviolet/visible (UV/vis) absorption.¹⁴

To obtain basic information of PDAS for application to organic light-emitting diodes (OLEDs), we herein report the electroluminescence (EL) of PDAS/tris(8-hydroxyquinoline) aluminum (Alq₃, a typical light-emitting material) blend films. The effect of the polymer chain structure of PDAS is also described in detail.

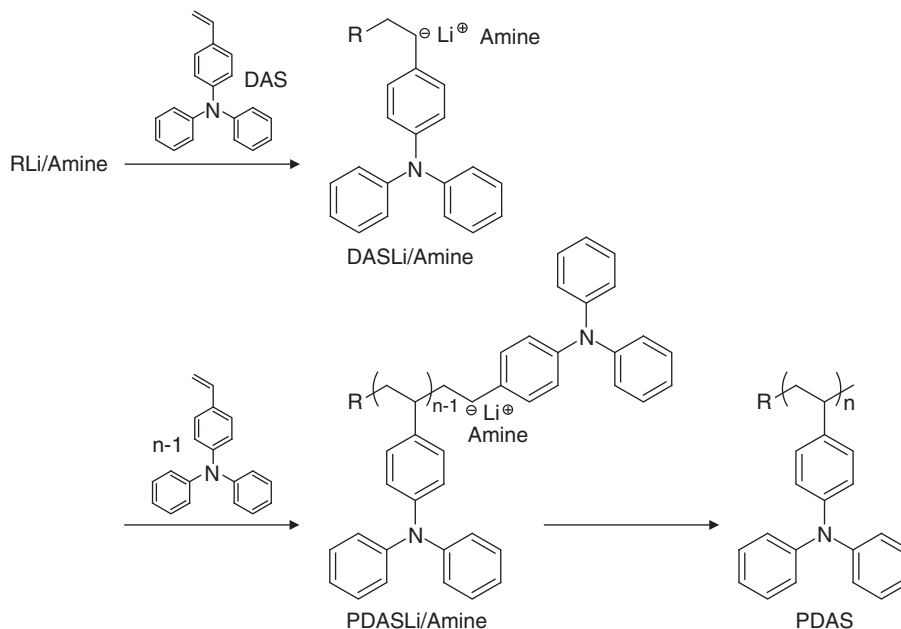
EXPERIMENTAL PROCEDURE

Materials

Toluene (≥99.8%), cyclohexane (99.5%) and *N,N,N',N'*-tetramethylethylenediamine (TMEDA, ≥99.5%) were refluxed over calcium hydride (CaH₂, 95%) and then distilled under dry argon. All other reagents were used as received, unless otherwise stated. DAS was prepared by means of a previously reported standard Wittig reaction.¹² All reagents were purchased from Sigma-Aldrich (St Louis, MO, USA).

General procedure for the living anionic polymerization of DAS

A well-dried 50-ml Schlenk tube was purged with dry argon, and 5.0 ml of polymerization solvent (toluene or cyclohexane) was injected at room temperature (~25 °C) using a syringe. Alkyllithium was supplied to the solution with a syringe, TMEDA was added to the solution under dry argon and the mixture was stirred for 10 min to form the alkyllithium/TMEDA (1.00/1.25) system. DAS (0.185 mol l⁻¹ solution in polymerization solvent) was added to this solution, and the reaction mixture was magnetically stirred under dry argon at room temperature. To terminate the reaction after polymerization, dry methanol was injected into the reaction mixture in an equimolar amount to the lithium atoms present. The polymerization mixture was then poured into a large volume of methanol to precipitate the polymer, which was then separated by filtration. The product was dried under reduced pressure at room temperature for 24 h, resulting in a white powdery polymer.¹²



Scheme 1 Living anionic polymerization of DAS with the alkyllithium/amine system.

Fabrication of EL devices

Before device fabrication, indium tin oxide (ITO) on glass substrates was patterned as 2 mm-wide stripes with a resistivity of $30 \Omega/\square$. The substrates were cleaned by sonication in soap solution, rinsed with deionized water, sonicated in isopropanol and methanol and dried with nitrogen. A 35 nm layer of PEDOT (poly(3,4-ethylenedioxythiophene))-PSS (poly(styrenesulfonate)) was spin-coated onto the substrate at 4000 r.p.m. and baked in air at 100°C for 1 h. The PDAS/Alq₃ (94/6, (wt/wt)) blend was dissolved in tetrahydrofuran at a concentration of 10.0 wt%, and was spin-coated onto the PEDOT-PSS layer at 3000 r.p.m. to form a 60 nm polymer layer (The thickness of each polymer layer (that is, PDAS/Alq₃ blend) was almost same (~ 60 nm)). A 50 nm-thick layer of 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline (BCP) was deposited by thermal evaporation from a resistivity-heated tantalum boat onto the polymer-coated substrate. After BCP film deposition, the chamber was vented and a shadow mask with a 2 mm width stripe was placed on the substrate, perpendicular to the ITO stripes. A 0.5 nm LiF layer and a 150 nm aluminum (Al) layer were then deposited sequentially as the cathode.

Measurements

The number-average molecular weight (M_n), weight-average molecular weight (M_w) and polydispersity indices (PDI, M_w/M_n) were determined using a gel permeation chromatography apparatus equipped with a differential refractive index detector and a Shimadzu Shim-pack GPC-80 M column (Shimadzu, Kyoto, Japan) (column length: 300 mm; diameter: 8 mm; effective molecular weight range: 100–4 000 000) at 40°C . Tetrahydrofuran was used as the eluent at a flow rate of 1.0 ml min^{-1} . A molecular weight calibration curve was obtained using polystyrene standards. ^1H nuclear magnetic resonance (Jeol ECA500, Jeol, Tokyo, Japan) spectra of the polymers were measured in deuterated chloroform at 500 MHz. UV/vis (Shimadzu UV-3101 PC) and PL (Shimadzu RF-5300 PC) spectra were measured in tetrahydrofuran (10 mg l^{-1}) using quartz cells. Drift mobility was determined by a time-of-flight method with a device consisting of an Al/Ti-phthalocyanine/polymer film/Au cell, a xenon flash lamp (L2359, Hamamatsu Photonics, Shizuoka, Japan) and a digitizing oscilloscope (DSO630, Gould, Valley View, OH, USA). The EL devices were operated using a Kenwood PSR-60M DC power supply (Kenwood, Tokyo, Japan). The current density was measured with an Advantest R6441A digital multimeter (Advantest, Tokyo, Japan), and the EL intensity was measured with a Minolta LS-100 luminance meter (Konica-Minolta,

Tokyo, Japan). The thickness of polymer films was determined using a profilometer (Dektak II, Sloan, Goleta, CA, USA).

RESULTS AND DISCUSSION

Preparation of PDAS

To examine the effect of polymer chain structure on the EL of PDAS/Alq₃ blend films, three types of PDAS having different polymer chain structures were synthesized by the living anionic polymerization of DAS with the *tert*-butyllithium (1.70 mol l^{-1} in pentane)/TMEDA (1.00/1.25) system in toluene or with the *n*-butyllithium (1.60 mol l^{-1} in *n*-hexane)/TMEDA (1.00/1.25) system in cyclohexane, according to the procedure previously reported (Scheme 1).^{12,14} The M_n and polymer chain structures of the three types of PDAS were subsequently examined using gel permeation chromatography and ^1H nuclear magnetic resonance spectroscopy. The results are summarized in Table 1.

The M_n of each PDAS depended on the molar ratio of $[\text{DAS}]_0/[\text{Li}]_0$ because of the living nature of the polymerization.^{12–14} PDAS-1 and -2 had almost the same M_n (~ 2000), and the M_n of PDAS-3 ($\sim 20\,000$) was 10 times higher than that of PDAS-1 and -2.

Figure 1 shows typical ^1H nuclear magnetic resonance spectra of PDAS obtained in this study. As we reported previously, the polymer chain structure of PDAS is strongly affected by the M_n and polymerization solvent, and the ratio of isotactic/syndiotactic structures (I/S) can be determined by the ratio of the area of isotactic methine proton peaks (downfield of 2.20 p.p.m.) versus the area of syndiotactic methine proton peaks (upfield of 2.20 p.p.m.).^{12,14} From the ^1H nuclear magnetic resonance spectra of Figure 1, the I/S of PDAS-1 to -3 were 69/31, 31/69 and 5/95, respectively (Table 1).

Optical properties of PDAS and Alq₃

Figure 2 shows the UV/vis (Figure 2a) and PL (Figure 2b) spectra of PDAS-1 to -3 and Alq₃. The UV/vis spectra of PDAS-1 to -3 showed absorption bands in the region from 260 to 380 nm,¹⁴ and the main absorption band of Alq₃ was in the region from 350 to 450 nm. With respect to the PL spectra, the emission maxima ($\lambda_{\text{max}}^{\text{em}}$) of PDAS-1 to

Table 1 List of evaluated polymers^a

No.	Initiator system	[DAS] ₀ /[Li] ₀	Solvent	Yield (wt%)	<i>M_n</i> (g mol ⁻¹) ^b	PDI ^b	I/S ^c
PDAS-1	<i>t</i> -BuLi/TMEDA (1.00/1.25)	7.80	Toluene	100	1910	1.10	69/31
PDAS-2	<i>n</i> -BuLi/TMEDA (1.00/1.25)	7.80	Cyclohexane	98	2140	1.12	31/69
PDAS-3	<i>t</i> -BuLi/TMEDA (1.00/1.25)	74.5	Toluene	99	21 600	1.12	5/95

Abbreviations: GPC, gel permeation chromatography; NMR, nuclear magnetic resonance; I/S, isotactic/syndiotactic structures; *M_n*, number-average molecular weight; PDAS, poly(4-diphenylaminostyrene); PDI, polydispersity indices; PSt, polystyrene; *t*-BuLi, *tert*-butyllithium; *n*-BuLi, *n*-butyllithium; TMEDA, *N,N,N',N'*-tetramethylethylenediamine.

^aPolymerization was carried out under dry argon at room temperature for 24 h. DAS/solvent=0.500 g/15.0 ml.

^b*M_n* and PDI were estimated by GPC using PSt as a standard.

^cThe ratio of isotactic/syndiotactic structures. Determined by ¹H NMR.¹⁴

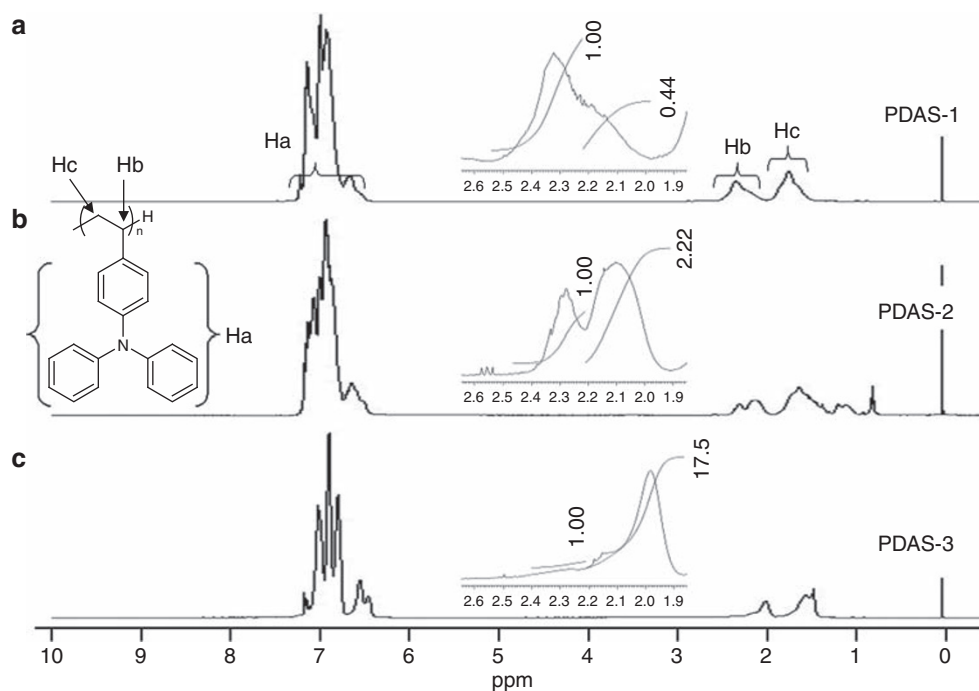


Figure 1 ¹H nuclear magnetic resonance spectra of PDAS measured in a 3.0 wt% solution of CDCl₃ at 50 °C. (a) *M_n*=1910, PDI=1.10; (b) *M_n*=2140, PDI=1.12; (c) *M_n*=21600, PDI=1.12. PDI, polydispersity indices.

-3 were observed in the region from 360 to 390 nm. The intensity of $\lambda_{\text{max}}^{\text{em}}$ decreased with an increase in the syndiotactic configuration because of the intramolecular excimer-forming fluorescence of PDAS, as we reported previously.¹⁴ The $\lambda_{\text{max}}^{\text{em}}$ of Alq₃ was observed to be ~530 nm. The regions of UV/vis absorption of Alq₃ and PL of PDAS-1 to -3 overlapped well. However, an obvious fluorescence resonance energy transfer from PDAS to Alq₃ was not observed in PDAS/Alq₃ blend films (Figure 3).

Hole drift mobility of PDAS

As we reported previously,¹⁴ the hole drift mobility of PDAS is strongly affected by the stereoregularity of the polymer chain. On the other hand, the molecular weight does not significantly affect the hole drift mobility of PDAS.

To examine the hole drift mobility of each PDAS obtained in this study, three kinds of transparent polymer films with thicknesses on the order of 1.0–3.0 μm were prepared by the bar-coating method using *o*-xylene solutions of PDAS-1 to -3 (PDAS/*o*-xylene=0.03 g/1.00 g).

The hole drift mobilities, μ , of PDAS-1 to -3 films were determined using a standard time-of-flight method, calculated according to the following equation:

$$\mu = L^2/t_T V,$$

where L is the polymer film thickness, t_T is the transit time and V is the applied voltage. The value for t_T was determined from $\log i$ (current) vs $\log t$ (time) plots.

The logarithm values of the hole drift mobilities for PDAS-1 to -3 are plotted against the square root of the applied field ($E^{1/2}(\text{V cm}^{-1})^{1/2}$) in Figure 4. The stereoregularity of the polymer chain strongly affected the hole drift mobility of PDAS. The hole drift mobility for PDAS-1 and -2 was on the order of 10^{-5} (cm²V⁻¹s⁻¹) with a negative slope, whereas that for PDAS-3 was on the order of 10^{-4} to 10^{-5} (cm²V⁻¹s⁻¹) with a negative slope. The order of hole drift mobility was PDAS-1 < PDAS-2 < PDAS-3, that is, an increase in the hole drift mobility is observed with an increase in the syndiotactic configuration (PDAS-1 < PDAS-2 < PDAS-3; Table 1). Therefore, the syndiotactic

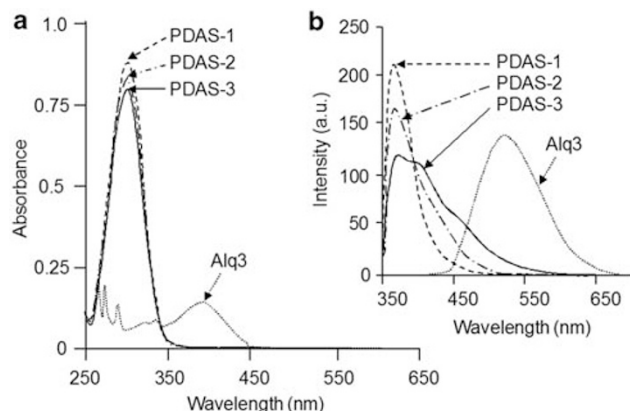


Figure 2 UV/vis and PL spectra of PDAS and Alq₃. (a) UV/vis spectra of PDAS-1 to -3 and Alq₃. PDAS (or Alq₃)/THF=0.10 mg/10.0 ml. (b) PL spectra of PDAS-1 to -3 and Alq₃. PDAS (or Alq₃)/THF=0.10 mg/10.0 ml. Excitation wavelength of 300 nm (PDAS) or 395 nm (Alq₃). THF, tetrahydrofuran.

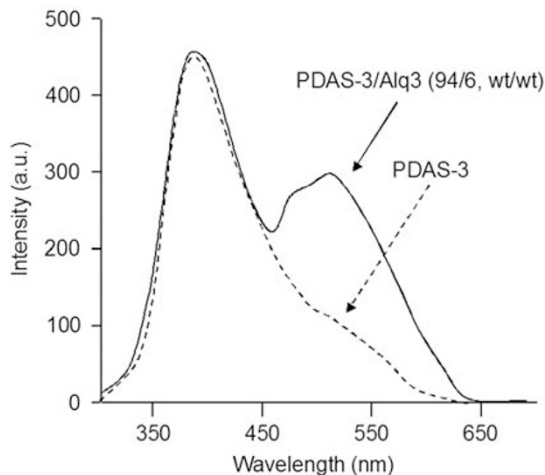


Figure 3 PL spectra of PDAS-3 film and PDAS-3/Alq₃ (=94/6 (wt/wt)) blend film. Excitation wavelength of 300 nm.

configuration in the polymer chain is a main factor that enhances the hole drift mobility of PDAS, as revealed previously.¹⁴

Effects of the polymer chain structure on EL

To examine the effects of polymer chain structure of PDAS on EL of PDAS/Alq₃ blend films, a 10.0 wt% tetrahydrofuran solution of PDAS/Alq₃ blend (94/6 (wt/wt)) was used to form an emissive layer in a device with the following structure: ITO/PEDOT-PSS/PDAS-Alq₃/BCP/LiF/Al, as shown in Figure 5. The PEDOT-PSS layer functions to both planarize the substrate and efficiently inject holes into the emissive layer. The PDAS/Alq₃ blend layer functions as the emissive layer. The BCP layer functions to efficiently block holes and inject electrons into the emissive layer. In devices of this type, only the emission from Alq₃, leading to green emission, was observed.

Figure 6 shows the current density–voltage characteristics of an ITO/PEDOT-PSS/PDAS-Alq₃/BCP/LiF/Al device. The current density of each device increased with the forward bias voltage applied, showing the rectification properties, and an increase in the current density was observed with an increase in the syndiotactic configuration

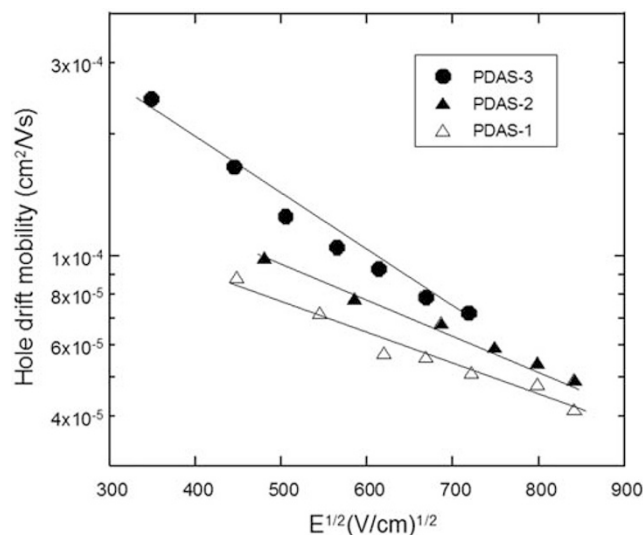


Figure 4 Dependence of the hole drift mobility on the applied field for thin films of PDAS (PDAS-1 to -3).

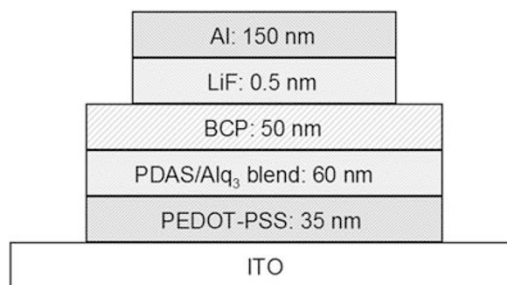


Figure 5 OLED construction: ITO/PEDOT-PSS/PDAS-Alq₃/BCP/LiF/Al. Both PEDOT-PSS and PDAS/Alq₃ blend layers were solution processed, whereas the BCP, LiF and Al cathode layers were vacuum deposited.

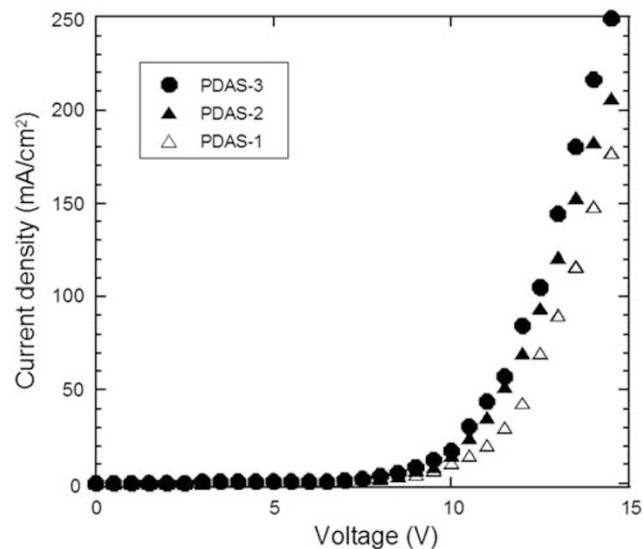


Figure 6 Current density–voltage characteristics of ITO/PEDOT-PSS/PDAS-Alq₃/BCP/LiF/Al devices.

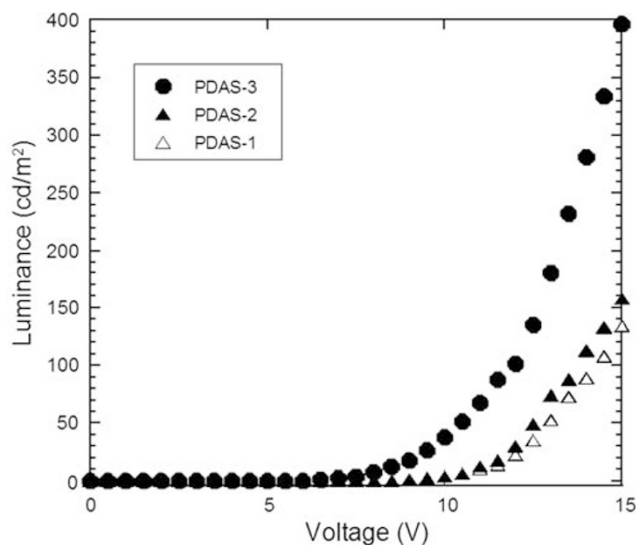


Figure 7 Luminance–voltage characteristics of ITO/PEDOT-PSS/PDAS-Alq₃/BCP/LiF/Al devices.

of PDAS (PDAS-1 < PDAS-2 < PDAS-3; Table 1). PDAS-1 and -2 had almost the same M_n (~ 2000), but different stereoregularities (PDAS-1: I/S=69/31; PDAS-2: S/I=31/69). The current density of PDAS-2 was higher than that of PDAS-1 at the same bias voltage. Therefore, the syndiotactic configuration in the polymer chain seems to be the appropriate structure to obtain high current density in PDAS/Alq₃ blend films.

Figure 7 shows the luminance–voltage characteristics of an ITO/PEDOT-PSS/PDAS-Alq₃/BCP/LiF/Al device. Each device showed green emission with different turn-on voltages and brightnesses. The device containing PDAS-1/Alq₃ blend film had a turn-on voltage of 9.0 V and a luminance maximum of 134 cd m⁻² at 15 V. The device containing PDAS-2/Alq₃ blend film had a turn-on voltage of 8.5 V and a luminance maximum of 159 cd m⁻² at 15 V. The device containing the PDAS-3/Alq₃ blend film had a turn-on voltage of 6.0 V and a luminance maximum of 396 cd m⁻² at 15 V. Thus, the turn-on voltage and brightness improved with an increase in the syndiotactic configuration of PDAS. Meanwhile, there was no notable difference of EL spectra between isotactic-rich PDAS and syndiotactic-rich PDAS.

The different EL properties of the ITO/PEDOT-PSS/PDAS-Alq₃/BCP/LiF/Al devices seem to result from the difference of the hole-transporting ability of PDAS (Figure 4). The most effective recombination is thought to occur in the PDAS-3/Alq₃ blend film. Therefore, the syndiotactic configuration of PDAS is thought to be the appropriate structure for application to OLEDs.

CONCLUSION

Three types of PDAS having different polymer chain structures were prepared by living anionic polymerization, and the EL of PDAS/Alq₃ blend films was examined to obtain basic information of PDAS for application to OLEDs. The hole drift mobility of PDAS was on the order of 10⁻⁴ to 10⁻⁵ (cm² V⁻¹ s⁻¹) with a negative slope, and it was increased with an increase in the syndiotactic configuration in the polymer chain. An increase in the current density in an ITO/PEDOT-PSS/PDAS-Alq₃/BCP/LiF/Al device was also observed with an increase in the syndiotactic configuration of PDAS. Turn-on voltage and brightness were also improved with an increase in the syndiotactic configuration of PDAS. Therefore, the syndiotactic configuration of PDAS was thought to be the appropriate structure for the application to OLEDs.

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