Available online at www.sciencedirect.com

SCIENCE DIRECT®

Organic Electronics 4 (2003) 49–59

Organic Electronics

www.elsevier.com/locate/orgel

Development of a new class of hole-transporting and emitting vinyl polymers and their application in organic electroluminescent devices

Daisuke Mutaguchi, Kenji Okumoto, Yutaka Ohsedo, Kazuyuki Moriwaki, Yasuhiko Shirota *

Department of Applied Chemistry, Faculty of Engineering, Osaka University, 2-1 Yamadaoka, Suita, Osaka 565-0871, Japan

Abstract

A new class of hole-transporting vinyl polymers, poly{4-vinyl-4′-[bis(4′-*tert*-butylbiphenyl-4-yl)amino]biphenyl} (PVBAB) and poly{4-vinyl-4′-[*N*,*N*-bis(9,9-dimethylfluoren-2-yl)amino]biphenyl} (PVFAB), and a new emitting vinyl polymer, poly(2-{4-[4-vinylphenyl(4-methylphenyl)amino]phenyl}-5-dimesitylborylthiophene) (PVPhAMB-1T), were designed and synthesized. These new vinyl polymers form smooth amorphous films with high glass-transition temperatures of ca. 200 °C. PVBAB and PVFAB possess electron-donating properties, and PVPhAMB-1T possesses bipolar character with both electron-donating and accepting properties, exhibiting strong fluorescence in solution and as films. Organic electroluminescent devices using PVBAB or PVFAB as a hole-transport layer and *N*,*N*′-dimethylquinacridone-doped tris(8-quinolinolato)aluminum as an emitting layer were thermally stable and exhibited very high performance. The use of PVPhAMB-1T as an emitting material also permitted the fabrication of a high-performance, green-emitting organic EL device.

Keywords: Hole-transporting polymer; Emitting polymer; Organic electroluminescent device

1. Introduction

Organic electroluminescent (EL) devices have attracted a great deal of attention in view of both academic interest and technological applications for full-color, flat-panel displays and lighting [1–3]. The performance of organic EL devices depends on materials functioning in various specialized roles, including emitting, charge-transporting, and charge-blocking materials. It is therefore of crucial importance to develop high-performance materials for the fabrication of high-performance devices. Both polymers and small molecules that form stable amorphous glasses, namely, amorphous molecular materials, have been studied extensively for use in organic EL devices [4–6]. We have performed a series of studies on the creation of amorphous molecular materials [5], and have investigated organic EL devices using amorphous molecular materials [5,7–11].

---

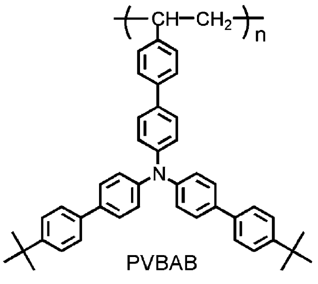
[*] Corresponding author. Tel.: +81-6-6879-7364; fax: +81-6-6879-7367.

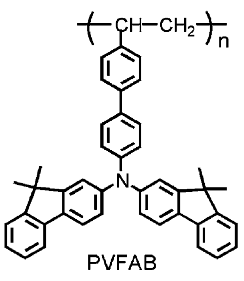
E-mail address: shirota@ap.chem.eng.osaka-u.ac.jp (Y. Shirota).

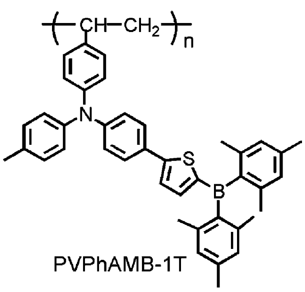
1566-1199/$ - see front matter © 2003 Elsevier B.V. All rights reserved.
doi:10.1016/j.orgel.2003.08.001

Polymers permit the formation of large-area, homogeneous films with high mechanical strength by wet processes. π-Conjugated polymers have been extensively studied for use in organic EL devices. Pendant polymers are also good candidates for organic EL materials. Generally, pendant polymers have advantages over π-conjugated polymers in solubility and processability. Vinyl polymers with triphenyldiamine side groups have been reported to function as good hole transporters in tris(8-quinolinolato)aluminum (Alq$_3$)-based organic EL devices [12,13]. The glass-transition temperatures (T_gs) of the reported polymers, however, are in the range from 130 to 150 °C [12]. It has been reported that vinyl polymers with side groups such as trifluoromethyl substituted quaterphenyl, 2,5-diphenyl-l,3,4-oxadiazole, and diphenylquinoxaline serve as electron-transporting materials in organic EL devices [14,15]. In addition, several pendant polymers have been reported to function as emitters, which include poly(*N*-vinylcarbazole), polymethylmethacrylate having a naphthalimide side group, and poly{9-(4-vinylphenyl)anthracene} [16–18]. However, the performance of organic EL devices using these pendant polymers as emitters are relatively low, luminances being less than 1000 cd m^{-2}. Hole-transporting polymers with higher T_gs remain to be developed for the fabrication of thermally stable organic EL devices. It is also a subject of great interest and significance to develop pendant polymers that function as good emitting materials for organic EL devices.

We report here the design and synthesis of a new class of hole-transporting and emitting vinyl polymers with high T_gs, and the fabrication and performance of organic EL devices using the synthesized polymers. The polymers developed in the present study are poly{4-vinyl-4′-[bis(4′-*tert*-butylbiphenyl-4-yl)amino]biphenyl} (PVBAB) and poly{4-vinyl-4′-[*N*,*N*-bis(9,9-dimethylfluoren-2-yl) amino]biphenyl} (PVFAB) as hole-transporting materials and poly(2-{4-[4-vinylphenyl(4-methylphenyl)amino]phenyl}-5-dimesitylborylthiophene) (PVPhAMB-1T) as an emitting material.


PVBAB


PVFAB


PVPhAMB-1T

2. Experimental

2.1. Materials

Aniline, 4-bromostylene, *N*-bromosuccinimide, dibromothiophene, dimesitylboron fluoride, diphenylamine, *N*,*N*′-diphenylquinacridone, fluorene, 4-iodotoluene, tetrakis(triphenylphosphine)palladium(0), and trimethyl borate were obtained commercially. Tris(8-quinolinolatoaluminum) (Alq$_3$) and poly(4-stylenesulfonate)-doped poly(3,4-ethylenedioxythiophene) (PEDOT; PSS) were obtained from Shin-nittetsu Kagaku Co. Ltd. and Bayer Co. Ltd., respectively.

2.2. Synthesis

2.2.1. Synthesis of *N*,*N*-bis(4′-*tert*-butylbiphenyl-4-yl) aniline (*II*)

Aniline (2.0 g, 21 mmol), 4-*tert*-butyl-4′-bromobiphenyl (**I**) (12 g, 41 mmol), bis(dibenzalacetone)palladium(0) (120 mg, 0.2 mmol), and 1,1′-bis (diphenylphosphino)ferrocene (200 mg, 0.3 mmol) were dissolved in distilled toluene and heated to 90 °C. Then, sodium *tert*-butoxide (5.0 g, 52 mmol) was added and stirred under reflux for 15 h. The resulting solution was poured into water, and *N*,*N*-bis(4′-*tert*-butylbiphenyl-4-yl)aniline (**II**) was extracted with toluene. It was purified by silica-gel column chromatography using toluene/hexane as an eluent. Yield: 6.1 g (56%).

2.2.2. Synthesis of N,N-bis(4′-tert-butylbiphenyl-4-yl)-4-bromoaniline (*III*)

N,*N*-bis(4′-*tert*-butylbiphenyl-4-yl)-4-bromoaniline (**III**) was synthesized by bromination of *N*,*N*-bis (4′-*tert*-butylbiphenyl-4-yl)aniline **(II)** (5.1 g, 10 mmol) with *N*-bromosuccinimide (1.8 g, 10 mmol) in chloroform at room temperature for 1 h. **III** was purified by silica-gel column chromatography using hexane as an eluent. Yield: 5.8 g (98%).

2.2.3. Synthesis of 4-vinyl-4′-bis(4′-tert-butylbiphenyl-4-yl)aminobiphenyl

4-Bromostyrene (3 g, 16 mmol) was reacted with magnesium (400 mg, 16 mmol) in distilled THF under nitrogen. The resulting Grignard reagent was reacted with trimethylborate (3 g, 29 mmol) at −20 °C, followed by hydrolysis with water to yield styrene-4-boronic acid. Then, 4-bromo-bis(4′-*tert*-butylbiphenyl-4-yl)aniline (**III**), tetrakis(triphneyl-phosphine)palladium(0) (180 mg, 0.15 mmol), and sodium carbonate (4.5 g, 7.6 mmol) aqueous solution were added, and the solution was stirred for 24 h at 80 °C to yield VBAB. It was purified by silica-gel column chromatography. Yield: 3.5 g (75%).

VBAB: MS: m/e 611.5(M^+). EA: Found: C, 90.30; H, 7.41; N, 2.29% Calcd for $C_{36}H_{21}N$: C, 90.29; H, 7.43, N, 2.33%. ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.51 (4H, d), 7.47 (4H, d, $J = 8.8$ Hz), 7.44 (4H, d, $J = 8.5$ Hz), 7.28 (2H, dd, $J = 8.1$, 7.5 Hz), 6.71 (1H, dd, $J = 10.9$, 17.6 Hz), 5.78 (1H, d, $J = 17.6$ Hz), 5.25 (1H, d, $J = 10.8$ Hz), 1.36 (18H, s).

2.2.4. Synthesis of PVBAB

Benzene solution of VBAB (1.0 M) containing 0.01 M azobisisobutyronitrile was placed in a glass tube and repeatedly degassed by freeze, pump, and thaw cycles. Polymerization was carried out at 65 °C for 36 h. The solution was poured into methanol to precipitate polymers. The resulting polymer was precipitated repeatedly from benzene/methanol. Yield: 40%.

PVBAB: ^{1}H NMR (750 MHz, $CDCl_3$): δ (ppm) 7.58–6.91 (24H, broad), 1.22–1.42 (21H, broad).

2.2.5. Synthesis of 2-iodofluorene (*IV*)

2-Iodofluorene (**IV**) was synthesized by iodination of fluorene (100 g, 602 mmol) with iodine (80 g, 320 mmol) in the presence of *ortho*-periodinic acid (H_5IO_6) (20 g, 88 mmol) in 80% acetic acid aqueous solution at 80 °C for 4 h under nitrogen atmosphere. After cooling, the solvent was removed by decantation and a brown solid was obtained. This was dissolved in toluene and washed with 5% $NaHSO_3$ aqueous solution to remove the remaining iodine. Then, the resulting solid was purified by alumina column chromatography using toluene as an eluent, followed by recrystallization from toluene. Yield: 105 g (60%).

2.2.6. Synthesis of 9,9-dimethyl-2-iodofluorene (*V*)

2-Iodofluorene (60 g, 205 mmol) was dissolved in THF and treated with potassium *tert*-butoxide (24 g, 214 mmol) to give a red solution, followed by methylation with methyliodide (30.4 g, 214 mmol). This procedure was repeated once more to yield 9,9-dimethyl-2-iodofluorene (**V**). This was purified by silica-gel column chromatography using hexane as an eluent, followed by vacuum distillation. Yield: 49.2 g (75%).

2.2.7. Synthesis of N,N-bis(9,9-dimethylfluoren-2-yl)aniline (*VI*)

N,*N*-bis(9,9-dimethylfluoren-2-yl)aniline (**VI**) was synthesized by the Ullmann reaction of 9,9-dimethyl-2-iodofluorene (50 g, 156 mmol) with aniline (5.5 g, 59 mmol) in mesitylene at 170 °C for 8 h in the presence of copper powder (7.5 g), potassium carbonate (35 g), and 18-crown-6-ether (1.5 g) and purified by silica-gel column chromatography using toluene/hexane as an eluent, followed by recrystallization from toluene/hexane. Yield: 20 g (71%).

2.2.8. Synthesis of N,N-bis(9,9-dimethylfluoren-2-yl)-4-bromoaniline (*VII*)

N,*N*-bis(9,9-dimethylfluoren-2-yl)-4-bromoaniline (**VII**) was synthesized by bromination of

N,*N*-bis(9,9-dimethylfluoren-2-yl)aniline (**VI**) (10 g, 21 mmol) with *N*-bromosuccinimide (3.6 g, 21 mmol) in chloroform at room temperature for 1 h. It was purified by silica-gel column chromatography using toluene as an eluent, followed by recrystallization from toluene. Yield: 11.3 g (95%).

2.2.9. Synthesis of 4-vinyl-4′-[N,N-bis(9,9-dimethylfluoren-2-yl)amino]biphenyl

4-Bromostyrene (1.2 g, 6.6 mmol) was reacted with magnesium (150 mg, 6.0 mmol) in distilled THF under nitrogen flow to give a Grignard reagent. It was reacted with trimethylborate 0.62 g (6.0 mmol) at −78 °C, followed by hydrolysis with water to yield styrene-4-boronic acid. Then, *N,N*-bis(9,9-dimethylfluoren-2-yl)-4-bromoaniline (**VII**), tetrakis(triphneylphosphine)palladium(0) (64 mg, 0.04 mmol), and 2N potassium carbonate aqueous solution were added, and the solution was stirred for 20 h at 70 °C to yield VBAB. Yield: 0.42 g (37%).

VFAB: MS: m/e 579(M^+). ^{1}H NMR (750 MHz, $CDCl_3$): δ (ppm) 7.65 (2H, d, $J = 7.5$), 7.61 (2H, d, $J = 8.1$), 7.58 (2H, d, $J = 8.4$), 7.52 (2H, d, $J = 8.7$), 7.47 (2H, d, $J = 8.2$), 7.40 (2H, d, $J = 7.5$), 7.32 (2H, t, $J = 7.5$), 7.28-7.23 (6H, m), 7.13 (2H, d, $J = 8.2$), 6.74 (1H, dd, $J = 11.0$, $J = 17.6$), 5.78 (1H, d, $J = 17.6$), 5.20 (1H, d, $J = 10.8$), 1.40 (12H, s).

2.2.10. Synthesis of PVFAB

Benzene solution of VFAB (0.4 M) containing 0.01 M azobisisobutyronitrile was placed in a glass tube and repeatedly degassed by freeze, pump, and thaw cycle. Polymerization was carried out at 65 °C for 36 h. The solution was poured into methanol to precipitate polymers. The polymer was precipitated repeatedly from benzene/methanol. Yield: 73%.

PVBAB: ^{1}H NMR (750 MHz, THF-d_8): δ (ppm) 7.35–6.90 (22H, broad), 2.45 (2H, s), 2.30 (1H, s), 1.18 (12H, s).

*2.2.11. Synthesis of 4-[4-bromophenyl(4-methylphenyl)amino]benzaldehyde (**IX**)*

Phosphoryl chloride (13.5 g, 89 mmol) was dropped into DMF at 0 °C and heated to 40 °C for 5 min to prepare Vilsmeier reagent. It was dropped into DMF solution of *N*-(4-bromophenyl)-*N*-(4-methylphenyl)aniline (**VIII**) (15 g, 44.5 mmol) and the solution was stirred at 60 °C for 12 h. After DMF was removed by evaporation, sodium hydroxide aqueous solution (1 M) was added and stirred at 60 °C for 2 h to give 4-[4-bromophenyl(4-methylphenyl)amino]benzaldehyde (**IX**). It was purified by silica-gel column chromatography using toluene as an eluent. Yield: 8.0 g (49%).

*2.2.12. Synthesis of 4-[4-bromophenyl(4-methylphenyl)amino]vinylbenzene (**X**)*

n-Butyllithium (1.0 M, 23.9 ml) was dropped into THF solution of methyltriphenylphosphonium bromide (9.8 g, 38 mmol). It was dipped into THF solution of 4-[4-bromophenyl(4-methylphenyl)amino]benzaldehyde (**IX**) (6.9 g, 19 mmol) and the solution was stirred for 17 h at room temperature to yield 4-[4-bromophenyl(4-methylphenyl)amino]vinylbenzene (**X**). It was purified by silica-gel column chromatography using toluene as an eluent. Yield: 2.5 g (36%).

2.2.13. Synthesis of 2-bromo-5-dimesitylborylthiophene

2,5-Dibromothiophene was lithiated with *tert*-butyllithium pentane solution (1.46 M, 30.7 ml) in dry THF under nitrogen flow at −77 °C. Then it was reacted with dimesitylboron fluoride (6.0 g, 22.4 mmol) THF solution to give 2-bromo-5-dimesitylborylthiophene. After THF and 2,5-dibromothiophene were removed by evaporation, the product was purified by silica-gel column chromatography using hexane as an eluent. Yield: 4.5 g (50%).

2.2.14. Synthesis of 2-{4-[4-vinylphenyl(4-methylphenyl)amino]phenyl}-5-dimesitylborylthiophene

4-[4-Bromophenyl(4-methylphenyl)amino]vinylbenzene (**X**) (1.0 g, 2.75 mmol) was reacted with magnesium (150 mg, 6.0 mmol) in dry THF under N_2 flow at room temperature for 12 h to prepare a Grignard reagent (**XI**), followed by reaction with trimethylborate (0.29 g, 2.8 mmol) to give a boronic acid (**XII**). Then, THF solution of 2-bromo-5-dimesitylborylthiophene (1.0 g, 2.44 mmol), tetrakis(triphneylphosphine)palladium(0) (350 mg, 0.3 mmol), and 2N potassium carbonate aqua were added, and the solution was stirred at 70 °C for 8 h to yield VPhAMB-1T. It was purified by silica-gel column chromatography using toluene/hexane as an eluent and recrystallization from hexane.

VPhAMB-1T: MS: m/e 615(M$^+$). ^{1}H NMR (750 MHz, THF-d$_8$): δ (ppm) 7.57 (2H, d, $J = 8.7$), 7.48 (1H, d, $J = 3.8$), 7.35 (1H, d, $J = 3.8$), 7.31 (2H, d, $J = 8.6$), 7.18 (2H, t, $J = 7.5$), 7.13–6.98 (8H, m), 6.80 (4H, s), 6.65 (1H, dd, $J = 17.6$, $J = 10.9$), 5.65 (1H, d, $J = 17.6$), 5.10 (1H, d, $J = 10.9$), 2.29 (3H, s), 2.26 (6H, s), 2.13 (12H, s).

2.2.15. Synthesis of PVPhAMB-1T

Toluene solution of VPhAMB-1T (0.165 M) containing 0.005 M azobisisobutyronitrile was placed in a glass tube and repeatedly degassed by freeze, pump, and thaw cycle. Polymerization was carried out at 80 °C for 40 h. The solution was poured into methanol to precipitate polymers. The polymer was repeatedly from benzene/methanol. Yield: 73%.

PVPhAMB-1T: ^{1}H NMR (750 MHz, CDCl$_3$) δ (ppm): 7.59–6.23 (broad, 18H), 2.36–1.85 (broad, 24H).

2.3. Cyclic voltammetry

Cyclic voltammetry was carried out for dichloromethane solution of PVBAB and PVFAB and THF solution of PVPhAMB-1T (1.0×10^{-3} M) containing tetra-*n*-butylammonium perchlorate (0.1 M), using a platinum disk (1.6 mm in diameter) and a platinum wire as the working and counter electrodes, respectively, and Ag/AgNO$_3$ (0.01 M in acetonitrile) as the reference electrode. Scan rates were 100 mV s^{-1} for PVBAB and PVFAB and 500 mV s^{-1} for PVPhAMB-1T.

2.4. Fabrication of organic EL devices

The ITO electrode (ca. 14 Ω sq.$^{-1}$, Sanyo Vacuum Industries) was cleaned by being immersed in an ultrasonic bath of 1,1,1-trichloroethane, followed by exposure to hot acetone vapor and UV ozone immediately before use. Poly(4-stylenesulfonate)-doped poly(3,4-ethylenedioxythiophene) (PEDOT;PSS) in water/methanol (purchased from Bayer, BYTRON P AI 4083) was deposited onto the ITO electrode by spin coating with a speed of 1000 rpm. It was annealed at ~150 °C for 3 min under nitrogen atmosphere. Then, a THF solution of the synthesized polymer was deposited by spin coating with a speed of 3000 rpm. The thin films of 5,5′-bis(dimesitylboryl)-2,2′-bithiophene (BMB-2T) and tris(8-quinolinolato)aluminum (Alq$_3$) were formed by vacuum deposition. The *N*,*N*-dimethylquinacridone (QA)-doped Alq$_3$ layer was formed by simultaneous vacuum deposition of QA and Alq$_3$ from separate sources. The vacuum deposition of the organic materials was carried out at a deposition rate of 0.2–0.3 nm s^{-1} at 10^{-5} Torr. Finally, lithium fluoride and aluminum as a cathode were successively deposited in vacuo onto the organic multilayer. The emitting area was ~4 mm^2.

2.5. Measurement of the thermal stability of organic EL device

The organic EL device was placed in a cryostat at 10^{-1} Torr, heated to a given temperature, held at that temperature for 5 min, and then the constant current to give a luminance of 300 cd m^{-2} at 20 °C was applied to the device to measure the luminance at each given temperature.

2.6. Apparatus

Number-average and weight-average molecular weights of the polymers were determined by gel permeation chromatography by use of a Waters 600E. Electronic absorption spectra were measured with a HITACHI U-3500 spectrophotometer. Differential scanning calorimetry (DSC) was carried out with a Seiko Instruments DSC220C. Cyclic voltammetry was performed using a BAS 100B. Photoluminescence (PL) and EL spectra were measured with a Hitachi model F-4500 fluorescence spectrometer. The current versus voltage and luminance versus voltage characteristics were measured using an Advantest TR6143 electrometer and a photoluminance meter Minolta LS-100. Temperature control of organic EL device was done with an Oxford ITC502.

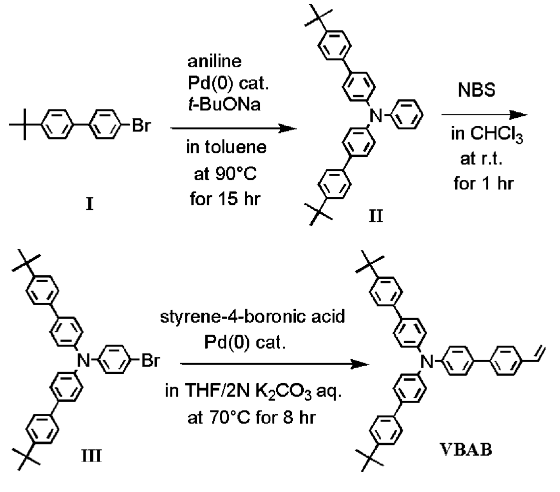
3. Results and discussion

3.1. Design and synthesis of new vinyl polymers, PVBAB, PVFAB, and PVPhAMB-1T

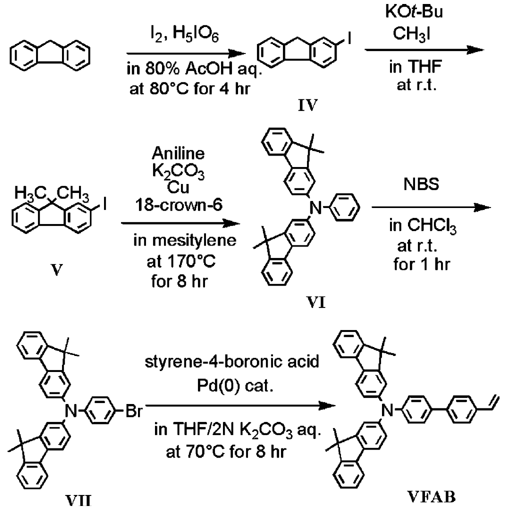
Glass-transition temperature (T_g) is a measure of thermal stability of amorphous materials. We have reported that the incorporation of rigid moieties such as phenothiazine, carbazole, biphenyl, and fluorene groups constitutes one of the guidelines for raising T_g of amorphous molecular materials [19–24]. In the present study with the aim of developing new hole-transporting polymers with high T_gs, we have designed and synthesized new vinyl polymers containing pendant arylamines with biphenyl or fluorene groups, PVBAB and PVFAB.

The emitting layer in organic EL devices functions as the recombination center for holes and electrons injected from the anode and cathode, respectively. Therefore, the materials for use in the emitting layer should have bipolar character, accepting both holes and electrons. In addition, emitting materials should also have high luminescence quantum efficiencies. Based on this concept, we have reported the first clear-cut examples of emitting amorphous molecular materials with desired bipolar character, e.g., 2-{4-[bis(4-methylphenyl)amino]phenyl-5-(dimesitylboryl)thiophene (PhAMB-1T) [25,26]. In the present study, we have synthesized a new emitting vinyl polymer having the PhAMB-1T moiety as the pendant group, PVPhAMB-1T.

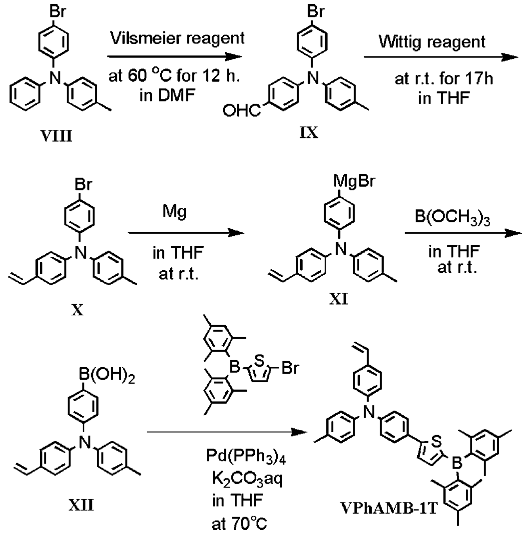
PVBAB, PVFAB and PVPhAMB-1T were synthesized by radical polymerization of the corresponding new vinyl monomers, VBAB, VFAB and PVPhAMB-1T. Synthetic routes for the new monomers, VBAB, VFAB and VPhAMB-1T, are shown in Schemes 1–3.



Scheme 1. Synthetic route of VBAB.



Scheme 2. Synthetic route of VFAB.



Scheme 3. Synthetic route of VPhAMB-1T.

Table 1
Number-average and weight-average molecular weights (Mn and Mw) and molecular-weight distributions (M_w/M_n) of PVBAB, PVFAB and PVPhAMB-1T

Polymer	M_n[a]	M_w[a]	Mw/Mn
PVBAB	21,000	39,000	1.86
PVFAB	42,000	163,000	3.88
PVPhAMB-1T	25,000	39,000	1.56

[a] M_n and M_w were determined by gel permeation chromatography in THF using polystyrenes as standards.

3.2. Properties of PVBAB, PVFAB and PVPhAMB-1T

Table 1 summarizes the number-average and weight-average molecular weights and molecular weight distributions of PVBAB, PVFAB and PVPhAMB-1T. The number-average molecular weights were determined to be above 20,000 for all the polymers. PVBAB, PVFAB and PVPhAMB-1T are soluble in common organic solvents such as toluene, chloroform, and THF. They form smooth, uniform amorphous films by spin coating from solution. As discussed later, PVBAB and PVFAB function as hole-transporting materials, and PVPhAMB-1T as an emitting material in organic EL devices.

All the synthesized polymers, PVBAB, PVFAB and PVPhAMB-1T, exhibited high T_gs of 229, 204, and 194 °C, respectively. Fig. 1 shows DSC curves of PVBAB and PVFAB. The T_gs of the present new hole-transporting vinyl polymers, PVBAB and PVFAB, are higher than those of the previously reported ones with pendant triphenyldiamine moieties owing to the incorporation of rigid biphenyl and fluorene moieties.

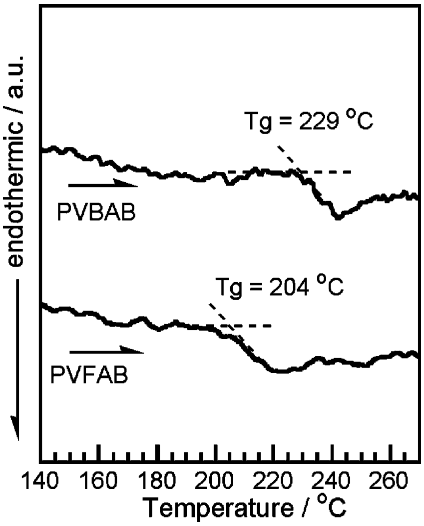


Fig. 1. DSC curves of PVBAB and PVFAB. Heating rate: 5 °C min^{-1}.

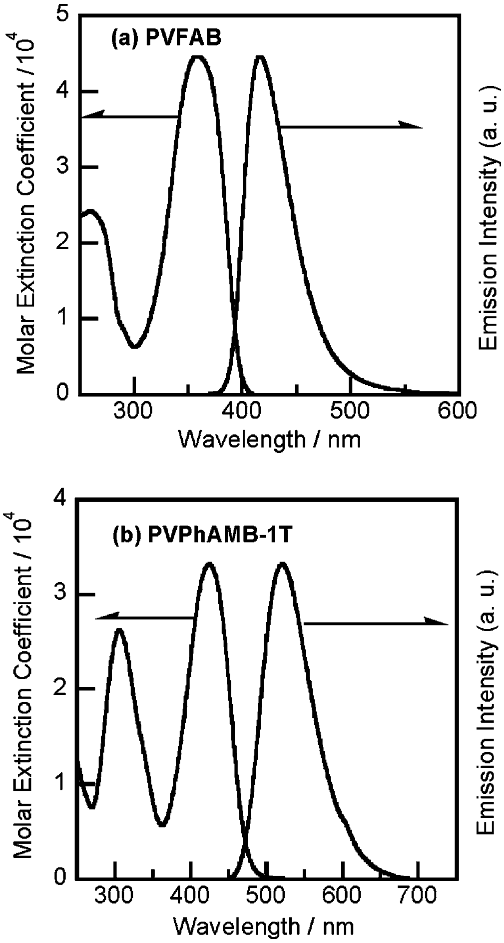


Fig. 2. Electronic absorption and fluorescence spectra of (a) PVFAB and (b) PVPhAMB-1T in THF.

Fig. 2 shows the electronic absorption and fluorescence spectra of PVFAB and PVPhAMB-1T in THF solution. Table 2 summarizes the electronic absorption band maxima, molar extinction coefficients, fluorescence band maxima, and fluorescence quantum efficiencies of PVBAB, PVFAB and PVPhAMB-1T in THF solution. Both the electronic absorption and fluorescence bands of PVPhAMB-1T are in the longer wavelength region than those of PVBAB and PVFAB, and understood in terms of intramolecular charge-transfer from the electron-donating triarylamine moiety to the electron-accepting dimesitylboryl moiety in the pendant π-electron system [25]. PVPhAMB-1T emits bright green light peaking at 520 nm with a relatively high fluorescence quantum efficiency of 0.58 in THF solution. PVBAB and PVFAB, which function as hole-transporting materials, also emit blue–violet fluorescence with relatively high fluorescence quantum efficiencies (Table 2).

Fig. 3 shows cyclic voltammograms of PVBAB, PVFAB and PVPhAMB-1T. PVBAB and PVFAB undergo reversible anodic oxidation with oxidation potentials of 0.58 and 0.51 V versus Ag/Ag$^+$, respectively. PVPhAMB-1T undergoes both reversible anodic oxidation and cathodic reduction with oxidation and reduction potentials of 0.58 and −2.25 V versus Ag/Ag$^+$, respectively. Thus, PVPhAMB-1T possesses desired bipolar character that is required for emitting materials in organic EL devices.

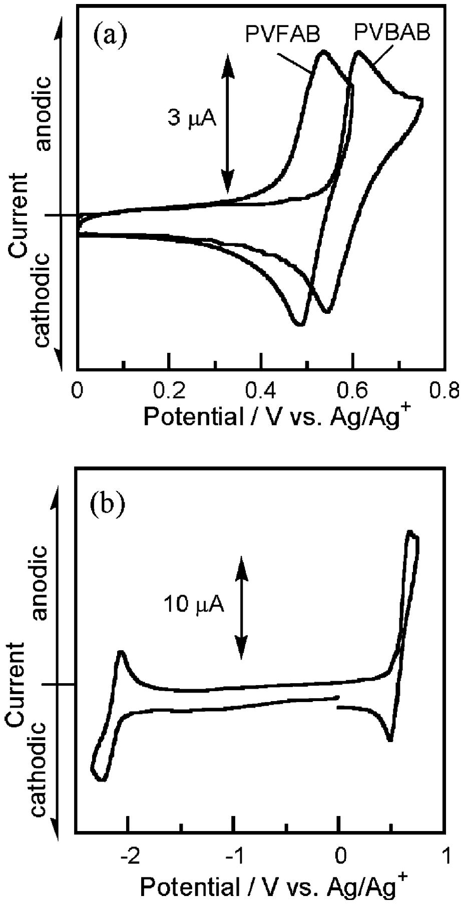


Fig. 3. Cyclic voltammograms for (a) anodic oxidation of PVBAB and PVFAB (1.0×10^{-3} M) in dichloromethane and (b) anodic oxidation and cathodic reduction of PVPhAMB-1T (1.0×10^{-3} M) in THF. Scan rates were 100 mV s^{-1} for PVBAB and PVFAB and 500 mV s^{-1} for PVPhAMB-1T.

3.3. Organic EL devices using PVBAB and PVFAB as hole transporters

The polymers PVBAB and PVFAB are expected to function as hole transporters, permitting the fabrication of thermally stable organic EL devices. Multilayer organic EL devices using PVBAB or PVFAB as a hole-transport layer were fabricated, where poly(4-stylenesulfonate)-doped

Table 2

Electronic absorption band maxima ($\lambda_{\max}^{\rm abs}$), molar extinction coefficients (ε), fluorescence band maxima ($\lambda_{\max}^{\rm f}$), and fluorescence quantum efficiencies ($\Phi_{\rm f}$) of PVBAB, PVFAB and PVPhAMB-1T

Polymer	$\lambda_{\max}^{\rm abs}$(nm)[a]	log ε[a]	$\lambda_{\max}^{\rm f}$ (nm)[a]	$\Phi_{\rm f}$[b]
PVBAB	346	4.74	408	0.49
PVFAB	358	4.65	416	0.48
PVPhAMB-1T	425	4.52	521	0.58

[a] In THF solution.

[b] Determined with reference to aqueous sulfuric acid solution of quinine sulfate.

poly(3,4-ethylenedioxythiophene) (PEDOT;PSS) [27] was used as a hole injection layer, *N*,*N*-dimethylquinacridone (QA)-doped tris(8-quinolinolato)aluminum (Alq_3) as an emitting layer, and Alq_3 as an electron transport layer: ITO/PEDOT;PSS (50 nm)/PVBAB (50 nm)/0.8wt% QA-doped Alq_3 (30 nm)/Alq_3 (20 nm)/LiF(0.5 nm)/Al (Device A) and ITO/PEDOT;PSS (50 nm)/PVFAB (50 nm)/0.8wt% QA-doped Alq_3 (30 nm)/Alq_3 (20 nm)/LiF(0.5 nm)/A1 (Device B). The structures of these devices are shown in Fig. 4(a).

Both devices A and B emitted green light originating from QA, as shown in Fig. 5. The voltage–current density and voltage–luminance characteristics for device B are shown in Fig. 6. Device A also showed almost similar voltage–current density and voltage–luminance characteristics. Table 3 summarizes turn-on voltages, maximum luminances, and luminous and external quantum efficiencies for devices A and B. These devices are characterized by low turn-on voltages below 3 V, high maximum luminances above 90,000 cd m^{-2}, and high luminous and external quantum efficiencies of 3.9 lm W^{-1} and 1.9%, respectively. Fig. 7 shows temperature dependence of the luminance for device B. The device was found to operate even at 170 °C without any significant decrease in luminance. PVBAB and PVFAB with high T_gs above 200 °C are promising candidates for hole-transporting materials for thermally stable organic EL devices.

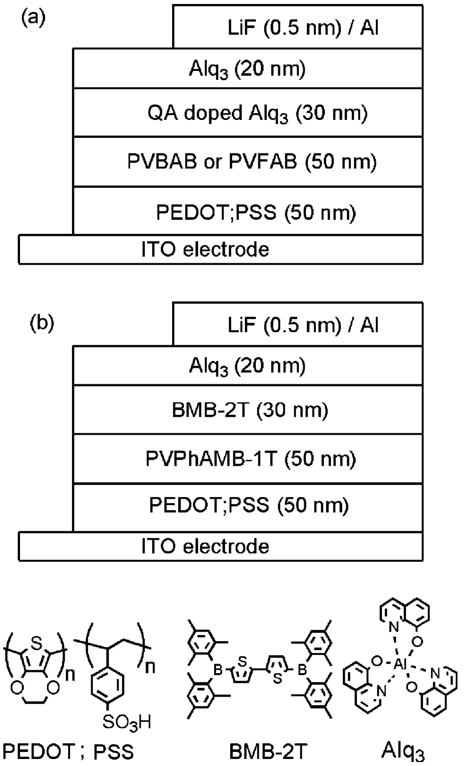


Fig. 4. Side views of multilayer organic EL devices and molecular structures of materials used.

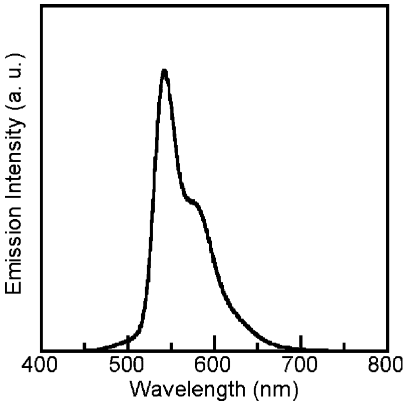


Fig. 5. EL spectrum of device A.

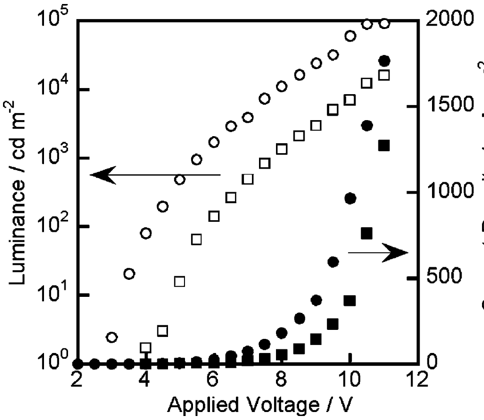


Fig. 6. Luminance–voltage characteristics for device B (open circle) and device C (open square), and current density–voltage characteristics for device B (closed circle) and device C (closed square).

Table 3
Maximum luminances, luminous efficiencies, and external quantum efficiencies for devices A, B and C

Device	Turn-on voltage (V)[a]	Maximum luminance ($cd\,m^{-2}$)	Luminous efficiency ($lm\,W^{-1}$)[b]	External quantum efficiency[b]
A	2.5	95,000 (at 10.5 V)	3.9	1.9%
B	3.0	91,000 (at 11.0 V)	3.9	1.9%
C	3.5	15,600 (at 11.0 V)	1.4	0.9%

[a] Voltage to obtain a luminance of 0.1 $cd\,m^{-2}$.
[b] At a luminance of 300 $cd\,m^{-2}$.

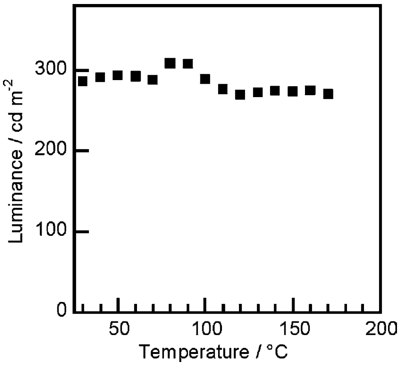


Fig. 7. Temperature dependence of the luminance of device B.

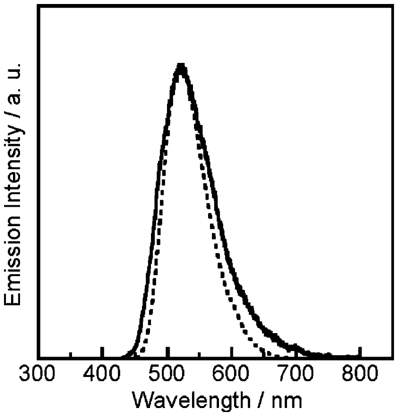


Fig. 8. EL spectrum of device C (solid line) and PL spectrum of PVPhAMB-1T film (dotted line).

3.4. Organic EL devices using PVPhAMB-1T as an emitting material

PVPhAMB-1T is expected to function well as a new emitting material for organic EL devices. A multilayer organic EL device using PVPhAMB-1T as an emitting layer was fabricated, where PEDOT;PSS was used as a hole injection layer, and 5,5′-bis(dimesitylboryl)-2,2′-bithiophene (BMB-2T) [28] and Alq_3 were used as double electron-transport layers: ITO/PEDOT;PSS (50 nm)/PVPhAMB-1T (50 nm)/BMB-2T (30 nm)/Alq_3 (20 nm)/LiF(0.5 nm)/A1 (device C). The structure of device C is shown in Fig. 4(b). This device emitted bright green light resulting from PVPhAMB-1T. Fig. 8 shows the EL spectrum of device C, which was in good agreement with the PL spectrum of PVPhAMB-1T as films. The voltage–current density and voltage–luminance characteristics for device C are shown in Fig. 6 together with those for device B. Performance characteristics for device C are included in Table 3. The present device exhibited much higher performance than previously reported organic EL devices using vinyl polymers as emitters [16–18]. The present study shows that PVPhAMB-1T is a promising candidate for emitting materials for use in organic EL devices, paving the way for the development of a variety of further new charge-transporting and emitting polymers for organic EL devices.

4. Conclusion

In the present study, a new class of hole-transporting vinyl polymers with T_gs above 200 °C, PVBAB and PVFAB, and a new emitting vinyl polymer with a T_g above 190 °C, PVPhAMB-1T, were developed, and their spectroscopic and electrochemical properties characterized. These new vinyl polymers form smooth amorphous films from solution. PVBAB and PVFAB were found to function as good hole transporters in thermally stable, high-performance organic EL devices.

PVPhAMB-1T was also found to be a good candidate for emitting materials, permitting the fabrication of a high performance, green-emitting organic EL device.

References

[1] C.W. Tang, S.A. Vanslyke, Appl. Phys. Lett. 51 (1987) 913.

[2] J.H. Burroughes, D.D.C. Bradley, A.R. Brown, R.N. Marks, K. Mackay, R.H. Friend, P.L. Burns, A.B. Holmes, Nature 347 (1990) 539.

[3] M.A. Baldo, D.F. O'Brien, Y. You, A. Shoustikov, S. Sibley, M.E. Thompson, S.R. Forrest, Nature 395 (1998) 151.

[4] A. Kraft, A.C. Grimsdale, A.B. Holmes, Angew. Chem. Int. Ed. 37 (1998) 402.

[5] Y. Shirota, J. Mater. Chem. 10 (2000) 1.

[6] U. Mitschke, P. Bäuerle, Chem. Mater. 10 (2000) 1471.

[7] Y. Shirota, Proc. SPIE-Int. Soc. Opt. Eng. 3148 (1997) 186.

[8] Y. Shirota, S. Nomura, H. Kageyama, Proc. SPIE-Int. Soc. Opt. Eng. 3476 (1998) 132.

[9] Y. Shirota, T. Noda, H. Ogawa, Proc. SPIE-Int. Soc. Opt. Eng. 3797 (1999) 158.

[10] Y. Shirota, K. Okumoto, Proc. SPIE-Int. Soc. Opt. Eng. 4105 (2000) 158.

[11] Y. Shirota, M. Kinoshita, K. Okumoto, Proc. SPIE-Int. Soc. Opt. Eng. 4464 (2002) 203.

[12] E. Bellmann, S.E. Shaheen, R.H. Grubbs, S.R. Marder, B. Kippelen, N. Peyghambarian, Chem. Mater. 11 (1999) 399.

[13] S.E. Shaheen, G.E. Jabbour, B. Kippelen, N. Peyghambarian, J.D. Anderson, S.R. Marber, N.R. Armstrong, E. Bellmann, R.H. Brubbs, Appl. Phys. Lett. 74 (1999) 3212.

[14] J. Pommerehne, A. Selz, K. Book, F. Koch, U. Zimmermann, Chr. Unterlechner, J.H. Wendorff, W. Heinz, H. Bässler, Macromolecules 30 (1997) 8270.

[15] S. Dailey, W.J. Feast, R.J. Pease, I.C. Sage, S. Till, E.L. Wood, J. Mater. Chem. 11 (2001) 2238.

[16] J. Kido, K. Hongawa, K. Okuyama, K. Nagai, Appl. Phys. Lett. 63 (1993) 2627.

[17] F. Cacialli, R.H. Friend, C.-M. Bouche, P. Le Barny, H. Facoetti, F. Soyer, P. Robin, J. Appl. Phys. 83 (1998) 2343.

[18] S. Shirai, J. Kido, Chem. Lett. (2002) 386.

[19] A. Higuchi, H. Inada, T. Kobata, Y. Shirota, Adv. Mater. 3 (1991) 549.

[20] Y. Kuwabara, H. Ogawa, H. Inada, N. Noma, Y. Shirota, Adv. Mater. 6 (1994) 677.

[21] H. Ogawa, H. Inada, Y. Shirota, Macromol. Symp. 125 (1997) 171.

[22] Y. Shirota, K. Okumoto, H. Inada, Synth. Met. 111–112 (2000) 387.

[23] K. Okumoto, Y. Shirota, Chem. Lett. (2000) 1034.

[24] K. Okumoto, T. Ohara, H. Noda, Y. Shirota, Synth. Met. 121 (2001) 1655.

[25] Y. Shirota, M. Kinoshita, T. Noda, K. Okumoto, T. Ohara, J. Am. Chem. Soc. 122 (2000) 11021.

[26] H. Doi, M. Kinoshita, K. Okumoto, Y. Shirota, Chem. Mater. 15 (2003) 1080.

[27] S.A. Carter, M. Angelopoulos, S. Karg, P.J. Brock, J.C. Scott, Appl. Phys. Lett. 70 (1997) 2067.

[28] T. Noda, Y. Shirota, J. Am. Chem. Soc. 120 (1998) 9714.