

Synthesis of New Hole Transport Polymers Based on *N, N'*-Diphenyl-*N, N'*-bis(4-methylphenyl)-1,4-phenylenediamine

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ABSTRACT: New hole transport polymers were prepared by polyaddition of *N, N'*-diphenyl-*N, N'*-bis(4-methylphenyl)-1,4-phenylenediamine (PDA) with divinyl or diisopropenyl benzene and were characterized by ¹H NMR, differential scanning calorimetry (DSC), UV absorption spectra and cyclic voltammetry. These polymers exhibit high glass transition temperatures and low oxidation potentials. Two-layer electroluminescent (EL) devices, in which the polymers were spin cast on ITO anode as the hole transport layer and aluminum tris(8-hydroxyquinoline) (Alq) was used as the emitting layer, gave a high brightness of above 10000 cd m⁻² with an operating voltage of less than 15 V.

KEY WORDS Hole Transport Polymer / Electroluminescent Device / Polyaddition / *N, N'*-Diphenyl-*N, N'*-bis(4-methylphenyl)-1,4-phenylenediamine / Diolefin /

There has been considerable interest attracted in the field of organic electroluminescent (EL) devices because of their potential application as full-color flat panel displays.^{1–8} Over the past few years, much progress has been made concerning the improvement of efficiency and stability of organic EL devices. The use of charge transport materials, hole transport materials or/and electron transport materials, between emitter and electrode has been proved to be an efficient way to achieve high device efficiency, due to the improved balance of hole and electron injection. Therefore, present research is focused on charge transport materials as well as light-emitting materials.

In an EL device, the hole transport material facilitates the hole injection and blocks the electrons, thus confines the emission away from the metal electrode, which leads to increase the device performance. Triarylamines have been most widely studied as hole transport materials in organic EL device, based on the fact that they can form stable aminium radical cations.^{1,9–12} The vacuum-deposited triarylamines are difficult to maintain the long-term stability due to recrystallization and low glass transition temperature. Polymeric materials are a good choice to improve the device stability. And they are able to form a film through spin casting. Guest-host system has been used to achieve polymeric materials, however, phase separation may occur even at ambient conditions. Thus, the synthesis of polymers containing triaryamine is of particular interest, from the standpoints of processing and improving device performance. There have been some reports related to this issue.^{13–19} To prepare polymers, triarylamines have been usually functionalized with specific groups, *e.g.*, vinyl group. This approach involves the complicated processes in monomer synthesis, correspondingly results in a relatively low yield.

In our previous attempt,²⁰ 4-tolyldiphenylamine (TDPA) was polymerized with diolefin in the presence of an acid catalyst. Soluble polymers were obtained in a

high yield, suggesting that the polyaddition provides a simple route for the preparation of new triaryamine-based polymers. Moreover, structure characterization showed that the reaction occurred at meta-position of TDPA as well as para-position.

We report herein on the synthesis of new hole transport polymers through the polyaddition between *N, N'*-diphenyl-*N, N'*-bis(4-methylphenyl)-1,4-phenylenediamine (PDA) and diolefin. Furthermore, the performance of EL devices based on these polymers as a hole transport layer is described.

EXPERIMENTAL

Materials

1,3-Diisopropenylbenzene (IPB, purity over 95%, TOKYO KASEI) was used as received. Solvents used in polymerization and acetonitrile were distilled over NaH and kept under nitrogen. Other reagents and solvents were used without further purification, unless otherwise noted. *N, N'*-diphenyl-*N, N'*-bis(4-methylphenyl)-1,4-phenylenediamine and 1,4-divinylbenzene were synthesized as described below.

Synthesis of Monomers

N, N'-diphenyl-*N, N'*-bis(4-methylphenyl)-1,4-phenylenediamine (PDA). PDA was synthesized by Tosoh method.²¹ A 500 mL dried flask fitted with a magnetic stirrer and a condenser was charged with 21.92 g (80.0 mmol) of *N, N'*-diphenyl-1,4-phenylenediamine, 27.36 g (160 mmol) of 4-bromotoluene, 18.39 g (192 mmol) of *t*-BuONa, 0.0359 g (0.16 mmol) of palladium acetate, 0.64 mmol of *p*(*t*-Bu)₃ and 200 mL of dry xylene under a nitrogen atmosphere. The resulting mixture was heated to 120°C for 3 h. After cooling, distilled water was added to the flask. The organic phase was separated, washed with water for three times, and evaporated to remove the solvent. The crude product was purified by fresh silica gel

column (toluene/hexane: 1/1) to afford a white solid in 62% yield. ^1H NMR (in CDCl_3) δ from tetramethylsilane (TMS), 2.3 ppm (6H, s), 6.8–7.4 ppm (22H, m). ^{13}C NMR (in CDCl_3) δ from TMS, 20.8, 121.8, 123.1, 124.6, 125.1, 129.1, 129.9, 132.4, 142.9, 145.4, 148.3 ppm.

1,4-Divinylbenzene (DVB). The mixture of chloromethylstyrene (30.5 g, 0.2 mol) and sodium iodide (30 g, 0.2 mol) in 250 mL of acetone was stirred at room temperature for 12 h. After filtration, the solution was added to triphenylphosphine (52 g, 0.2 mol) dissolved in 150 mL of acetone. The white solid was collected and dried under vacuum after stirring for an additional 24 h. Then 50 g (0.1 mol) of white solid was dissolved in 250 mL of dichloromethane, followed by gradual addition of formaldehyde solution (37%, 50 mL) and the aqueous solution of NaOH (2 M, 200 mL). The resulting solution was stirred for 5 h. Thereafter, organic phase was separated by a separatory funnel and washed with water for three times. Removal of the solvent by rotary evaporation resulted in a white solid, which was then poured into hexane. The solution was filtered to remove the insoluble portion. After evaporating the solvent, the residue was distilled under reduced pressure to afford product as a white solid in 73% yield. B.p. $50^\circ\text{C}/3$ mmHg. ^1H NMR (in CDCl_3) δ from TMS, 5.22 ppm (2H,d), 5.72 ppm (2H,d), 6.68 ppm (2H,m), 7.35 ppm (4H,s). ^{13}C NMR (in CDCl_3) δ from TMS, 113.7, 126.4, 136.6, 137.3 ppm.

General Polymerization Procedure

The polymerization of PDA with diolefin was performed in a glass ampoule flushed with dry nitrogen. *p*-Toluenesulfonic acid (purity over 98%) was used as a catalyst and chlorobenzene as a solvent. The reaction mixture was poured into an excess amount of acetone. Then recovered polymer was purified by reprecipitation of toluene solution into acetone twice, followed by drying under vacuum.

Measurements

NMR spectra were recorded on a JEOL α -500 spectrometer operating at 500 MHz for ^1H and 125 MHz for ^{13}C . All spectra were taken in CDCl_3 at 50°C with TMS as a standard. Gel permeation chromatograms (GPC) were obtained by using a column packed with styrene/divinylbenzene gel beads, and CHCl_3 as an eluent at a 0.5 mL min^{-1} flow rate. The molecular weight was calibrated by using polystyrene standards (Shodex). UV spectra were recorded in chloroform solutions on a JASCO Ubest-30 UV-VIS spectrometer. Differential scanning calorimetry (DSC) was carried out at a scan rate of $10^\circ\text{C min}^{-1}$ under nitrogen atmosphere using the Rigaku Thermoplus 2 DSC 8230 910 instrument. Cyclic voltammetry was conducted on a typical three-electrode cell with a Pt wire as the counter electrode and an Ag/AgCl electrode as the reference electrode, and polymer-coated Pt as the working electrode, which was prepared by coating from the toluene solution of polymer. Supporting electrolyte is 0.1 M tetrabutylammonium perchlorate (Bu_4NClO_4) in dry acetonitrile. All measurements were conducted at room temperature under nitrogen atmosphere.

EL devices were fabricated on ITO-coated glass sub-

strates with a sheet resistance of $20\ \Omega/\text{sq}$, which was ultrasonically cleaned successively in hydrochloric acid (3 M), isopropanol and methanol. Polymer layer (50 nm) was prepared by spin coating from chlorobenzene solution (12 g L^{-1}). Aluminum tris(8-hydroxyquinoline) (50 nm) was coated onto the polymer film by vacuum vapor deposition. The Mg : Ag alloy cathode with a thickness of 200 nm was thermally evaporated at a pressure of 10^{-5} Torr. The light emission was measured using a luminance meter (MINOLTA LS-100), and an I-V characteristic using an electrometer (AD-VANTEST, R6451A).

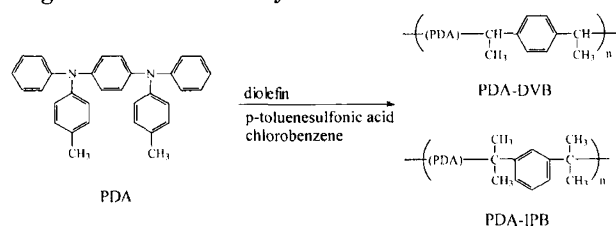
RESULTS AND DISCUSSION

Polymerization

The reaction of benzene with olefin, in the presence of Lewis acid or protonic acid, has been known to yield alkylate benzene.²² The amino group in triarylamine is an activating group for the electrophilic substitution of benzene ring. It was, therefore, anticipated that polymers could be obtained by the electrophilic aromatic substitution of triarylamine with diolefin. Our previous work, in which the reaction of TDPA with diolefin yielded soluble polymers, indicated that this method is effective to synthesize triarylamine-based polymers.

The polymerization of PDA with DVB or IPB was performed using *p*-toluenesulfonic acid as a catalyst in chlorobenzene, as outlined in Scheme 1. In both cases, the reaction mixtures became green-black during polymerization, due to the protonation of amine from the acid catalyst. When the polymerization solutions were precipitated into acetone, the products were yielded as white solids. Table I shows results for various polymerization conditions.

PDA was polymerized with DVB at 60, 90, and 105°C to investigate the temperature dependence of the polymerization. The results indicate both molecular weight and yield of resulting polymer increase as the reaction temperature increases. At 60°C , when the polymerization was carried out for 24 h, the M_w of polymer is 0.59×10^4 , while it becomes 0.87×10^4 at 90°C only for 6 h. When using 3 mol% catalyst for 3 h, the polymer was obtained with an increased yield of 73% at 105°C in comparison with the 56% yield at 90°C . On the other hand, increasing the catalyst amount enhances the yield as well as the molecular weight of PDA-DVB polymer. The yield increased from 33 to 71% with the increase of catalyst amount from 1 mol% to 5 mol%, when the reaction temperature was set at 90°C . The polymer, prepared using 5 mol% catalyst at 105°C for 3 h, has a molecular weight of 7.51×10^4 at a yield of 89%.



Scheme 1. Synthetic route of polymers.

Table I. Polymerization conditions and results

	Conc. ^a	Temp.	Catalyst	Time	Yield	M_w	M_w/M_n ^b
	mol L ⁻¹	°C	mol%	h	%	× 10 ⁻⁴	
PDA-DVB	2	60	1	24	31	0.59	3.24
	2	90	1	6	33	0.87	1.64
	2	90	3	3	56	5.21	4.78
	2	90	5	3	71	6.18	4.72
	2	105	3	3	73	5.71	4.14
	2	105	5	3	89	7.51	4.06
PDA-IPB	2	90	3	24	38	0.22	1.45
	2	105	3	24	67	0.53	1.51
	4	105	3	24	75	1.20	1.49
	2	105	5	24	92	1.16	1.67

^a Total monomer concentration. ^b Determined by gel permeation chromatography using polystyrene standards.

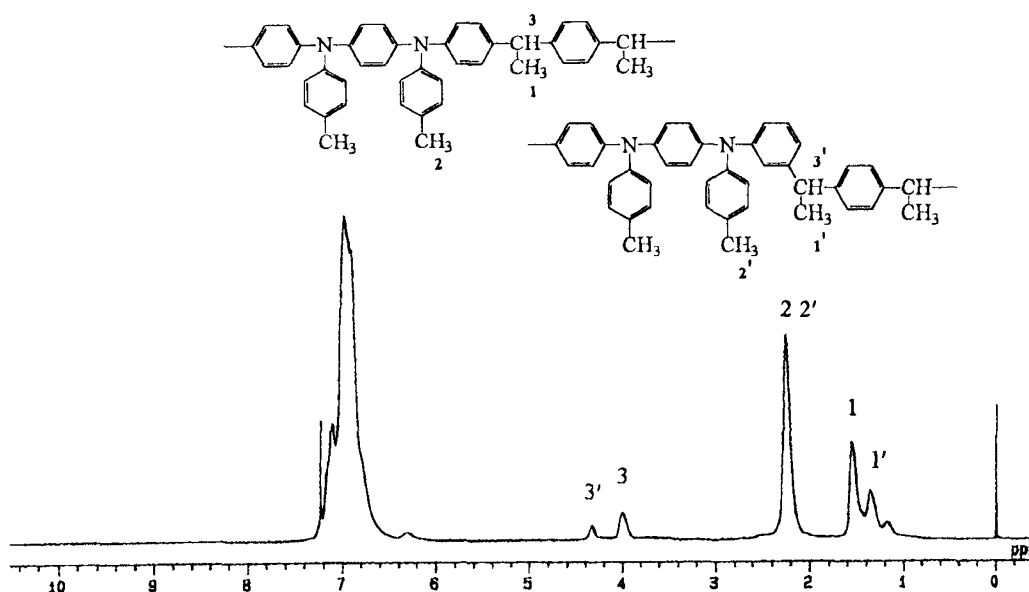


Figure 1. ¹H NMR spectrum (CDCl₃, 500 MHz, 50°C) of polymer PDA-DVB.

Similar observations were obtained in the polymerization of PDA with IPB. However, the molecular weights of PDA-IPB polymers were much lower than those of PDA-DVB polymers, even at a longer reaction time, indicating relatively low reactivity of IPB. This can be explained that the tertiary cation produced by the protonation of IPB is more stable than the secondary cation derived from DVB. The PDA-IPB polymer having a M_w of 0.53×10^4 was obtained as the polymerization was carried out using a total monomer concentration of 2 mol L^{-1} and 3 mol% catalyst at 105°C for 24 h. Use of a higher monomer concentration of 4 mol L^{-1} was found to yield the polymer with a higher M_w of 1.20×10^4 . However, the increase of either reaction time or monomer concentration results in insoluble gel for the preparation of PDA-DVB polymer. In addition, the synthesized PDA-IPB polymers show narrow molecular weight distribution between 1.4 and 1.7, in contrast with those of PDA-DVB polymers (1.6–4.8). Both polymers are soluble in common organic solvents such as chloroform, tetrahydrofuran and toluene to be light green solutions.

Structural Characterization

The ¹H NMR spectrum of PDA-DVB polymer is shown in Figure 1. More signals than those expected for the Scheme 1 are observed in the spectrum of PDA-DVB

polymer. On the basis of the results of our previous work,²⁰ it can be deduced that the polymerization of PDA with DVB occurs not only at the para position but also at meta position of phenyl group in PDA unit. The large signal at 1.6 ppm is assigned to methyl protons from DVB unit linked at para position, and the signal of corresponding methine protons appears at 4.0 ppm. While the small signals detected at 1.3 and 4.3 ppm are assigned to methyl protons and methine protons from DVB unit linked at meta position, respectively. The presence of meta linkage can be considered the reason for the broader molecular weight distribution and the formation of cross linked polymer, which finally lead to an insoluble gel as the product. In addition, a comparison of a series of spectra revealed that the intensity of signals at meta position increases with increasing the polymer molecular weight.

As shown in Figure 2, the spectrum of PDA-IPB polymer is less complex and in agreement with the para-linked structure. The large signal at 1.6 ppm is assigned to the methyl protons from IPB unit linked at para position. The methyl protons in PDA unit and the aromatic protons exhibited signals at 2.3 ppm and 6.8–7.2 ppm, respectively. Also, relative intensity of each signal is consistent with the expected structure.

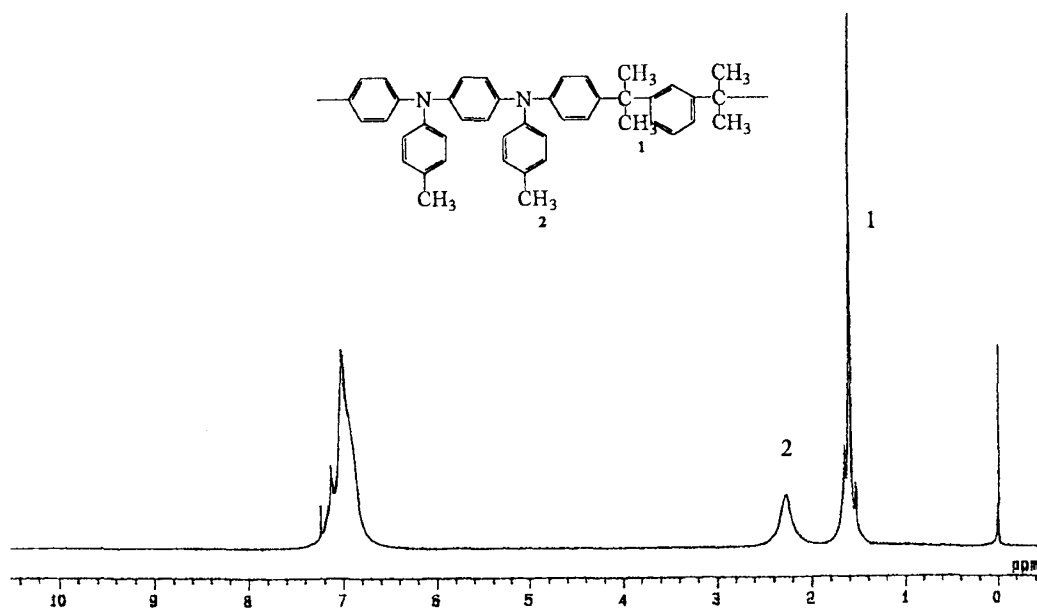


Figure 2. ^1H NMR spectrum (CDCl_3 , 500 MHz, 50°C) of polymer PDA-IPB.

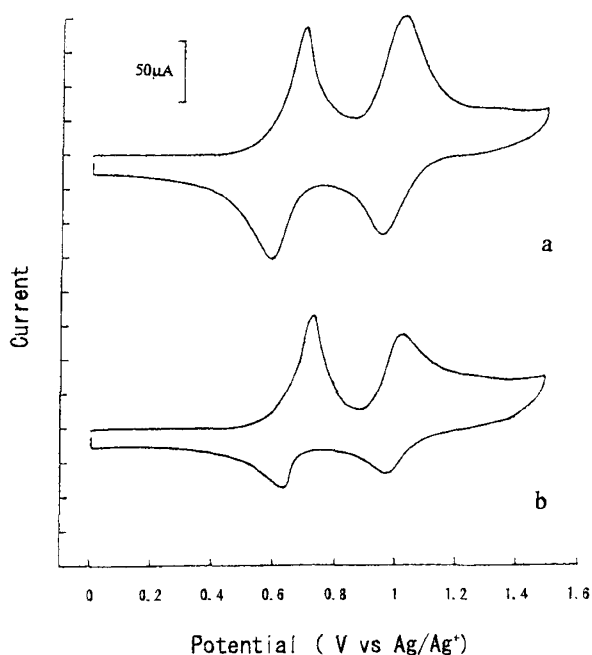


Figure 3. Cyclic voltammograms for films of PDA-DVB (a) and PDA-IPB (b) polymers on a Pt electrode scanning from 0.0 to +1.5 V at a scan rate of 200 mV s^{-1} .

Other Characterizations

The resulting polymers of PDA-DVB and PDA-IPB showed glass transition temperatures (T_g) at 174 and 151°C , respectively, which are higher than those of typical triarylamine monomers.^{12, 23} UV absorption spectra of both polymers were measured in CHCl_3 solution. The maximum absorption of PDA-DVB polymer appeared at 317 nm, and PDA-IPB polymer showed the maximum absorption at 318 nm. The peak absorption around 315 nm is a characteristic of PDA monomer, indicating that incorporation of PDA into polymer main chain does not greatly change its electronic structure.

Table II. Characteristics of the synthesized polymers

Polymer	T_g^a	λ_{max}^b	Redox potential ^c	
	$^\circ\text{C}$	nm	$E_{\text{pa}1,2}/\text{V}$	$E_{\text{pc}1,2}/\text{V}$
PDA-DVB	174	317	0.68, 1.03	0.57, 0.94
PDA-IPB	151	318	0.65, 0.98	0.59, 0.95
(PDA)	—	315	0.58, 1.02	0.52, 0.95

^a Determined by differential scanning calorimetry with a scan rate of $10^\circ\text{C min}^{-1}$. ^b Absorption spectrum in chloroform solution. ^c Determined by cyclic voltammetry in 0.1 M $\text{Bu}_4\text{NClO}_4/\text{acetonitrile}$ vs. Ag/AgCl .

The charge transport occurs through hopping involving redox reaction of charge transport molecules. The redox properties of the polymers have been examined by cyclic voltammetry in acetonitrile containing 0.1 M tetrabutylammonium perchlorate (Bu_4NClO_4) vs. Ag/AgCl . Figure 3 shows cyclic voltammograms of polymer films coated onto Pt working electrode. Both films showed two one-electron processes, which have been attributed to the removal of two electrons from each PDA unit.^{24, 25} For the PDA-DVB case, two anodic waves were observed at 0.68 and 1.03 V vs. Ag/AgCl , associated with two cathodic peaks at 0.57 and 0.94 V (Figure 3a). PDA-IPB polymer film displayed two redox processes at 0.65/0.59 and 0.98/0.95 V (Figure 3b). These peak potentials are similar to those of PDA monomer as shown in Table II. It revealed that redox behavior of PDA is retained after polymerization with diolefin.

Characteristics of EL Devices

Two-layer EL devices were prepared using PDA-DVB and PDA-IPB polymers as hole transport layer (HTL) and aluminum tris(8-hydroxyquinoline) (Alq) as the electron transport and emitting layer. Polymer layer was spin-coated on ITO anode with a thickness of 50 nm. The peak position of PL for both PDA-DVB and PDA-IPB polymers was observed at ca. 420 nm. The EL spectra of two-layer devices are shown in Figure 4. Both de-

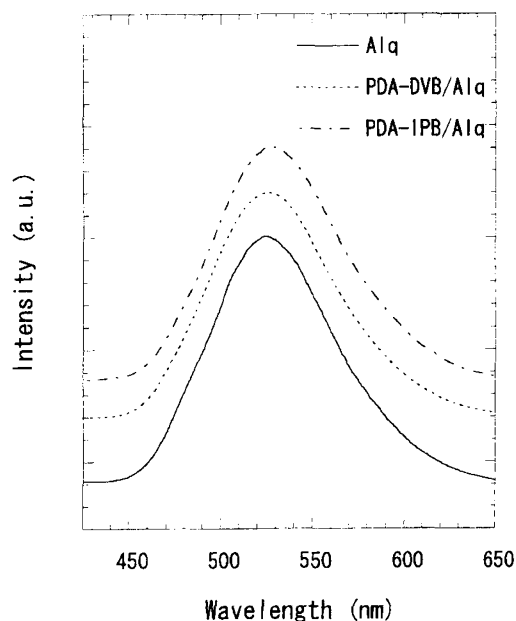


Figure 4. Electroluminescence spectra of ITO/polymer/Alq/Mg : Ag devices and photoluminescence spectrum of Alq.

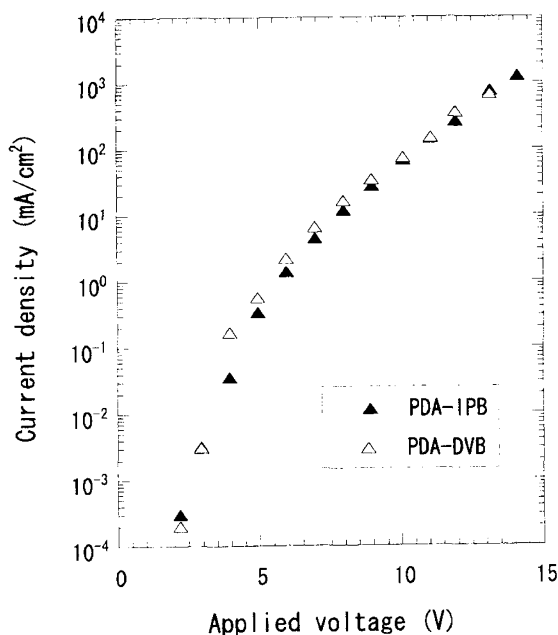


Figure 5. Current-voltage characteristics of ITO/polymer/Alq/Mg : Ag EL devices.

vices yielded light-green EL with emission maximum at *ca.* 525 nm, which corresponds to the Alq emission spectrum, indicating that excitons are generated from Alq and the polymers function only as a hole transport layer.

Figure 5 shows the current *vs.* voltage curves of devices fabricated using PDA-DVB and PDA-IPB. In these devices, similar current-voltage dependences are obtained. Current injection started from as low as about 2.5 V and increased with increasing the operating voltage. The PDA-DVB device showed a slightly high current density, compared to the PDA-IPB device. The characteristics of brightness *vs.* voltage are presented in Figure 6. Both EL devices exhibit high brightness (above

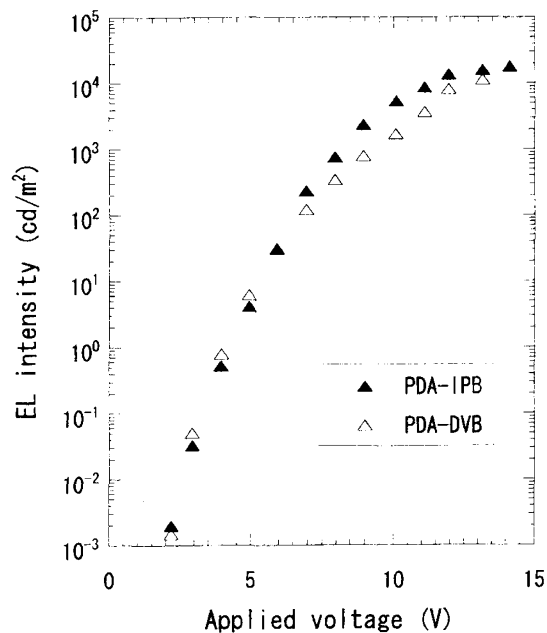


Figure 6. Brightness-voltage characteristics of ITO/polymer/Alq/Mg : Ag EL devices.

Table III. EL performance for ITO/polymer/Alq/Mg : Ag devices

HTL polymer	Turn-on voltage ^a	Max. EL intensity	Max. luminous efficiency
	V	cd m ⁻²	lm w ⁻¹
PDA-DVB	3.2	11280	1.50
PDA-IPB	3.3	17960	2.40

^a Light emission at this voltage equals 0.1 cd m⁻².

10000 cd m⁻²) at an operating voltage of less than 15 V. For polymer PDA-DVB, the turn-on voltage, defined as a voltage for light emission of 0.1 cd m⁻², is 3.2 V, and the light intensity increased rapidly with an increase in operating voltage up to 13 V. This device showed a maximum intensity of 11280 cd m⁻² at 13 V. A similar turn-on voltage for light emission was observed in the device using PDA-IPB polymer. However, at relatively high operating voltage, the brightness of PDA-IPB device is stronger than that of PDA-DVB device. A maximum intensity of 17960 cd m⁻² was achieved at 14 V. Moreover, the maximum luminous efficiency is 2.40 lm w⁻¹ near 200 cd m⁻² for PDA-IPB device and 1.50 lm w⁻¹ near 100 cd m⁻² for PDA-DVB device. The device performances of both polymers are comparable to those of molecular triarylamines.²³ In addition, the higher EL performance observed in PDA-IPB device may be due to the smooth film of high quality in comparison to PDA-DVB polymer film, in which the impurities result in the formation of a slight amount of granule. Table III summarizes the device data for these polymers as a hole transport layer.

CONCLUSION

We have synthesized new polymers containing triarylamine units in main chain by one-step reaction from *N,N'*-diphenyl-*N,N'*-bis(4-methylphenyl)-1,4-phenylenediamine (PDA) and diolefin. The resulting polymers, PDA-DVB and PDA-IPB, exhibit high glass transition

temperatures and electroactivity. Both polymers are soluble in common organic solvents, which allows yielding thin films of good quality through spin casting. Two-layer EL devices were fabricated with a hole transport layer of the synthesized polymers, an emitting layer of Alq, an ITO anode and Mg : Ag alloy cathode. These devices showed a higher brightness than 10000 cd m^{-2} with an operating voltage of less than 15 V and a low turn-on voltage around 3 V, which suggest that the present polymers are promising candidates for hole transport materials.

REFERENCES

1. C. W. Tang, and S. A. VanSlyke, *Appl. Phys. Lett.*, **51**, 913 (1987).
2. C. Adachi, T. Tsutsui, and S. Saito, *Appl. Phys. Lett.*, **55**, 1489 (1989).
3. J. H. Burroughes, D. D. C. Bradley, A. R. Brown, R. N. Marks, K. Mackay, R. H. Friend, P. L. Burn, and A. B. Holmes, *Nature*, **347**, 539 (1990).
4. P. E. Burroed, V. Bulovic, S. R. Forrest, L. S. Sapochak, D. M. McCarty, and M. E. Thompson, *Appl. Phys. Lett.*, **65**, 2922 (1994).
5. C. W. Tang, and J. E. Littman, U.S. Patent, 5294869, (1994).
6. J. Kido, M. Kimura, and K. Nagai, *Science*, **267**, 1332 (1995).
7. J. Bettenhausen, P. Strohriegel, W. Brutting, H. Tokuhisa, and T. Tsutsui, *J. Appl. Phys.*, **82**, 4957 (1997).
8. M. Thelakkat and H. W. Schmidt, *Adv. Mater.*, **10**, 219 (1998).
9. M. Van der Auweraer, F. C. De Schryver, P. M. Borsenberger, and J. J. Fitzgerald, *J. Phys. Chem.*, **97**, 8808 (1993).
10. K. Naito and A. Miura, *J. Phys. Chem.*, **97**, 6240 (1993).
11. Y. Yang, Q. Pei, and A. J. Heeger, *J. Appl. Phys.*, **79**, 934 (1996).
12. J. Louie, J. F. Hartwig, and A. J. Fry, *J. Am. Chem. Soc.*, **119**, 11695 (1997).
13. C. Hosokawa, N. Kawasaki, S. Sakamoto, and T. Kusumoto, *Appl. Phys. Lett.*, **61**, 2503 (1992).
14. E. S. Kolb, R. A. Gaudiana, and P. G. Metha, *Macromolecules*, **29**, 2359 (1996).
15. J. Kido, G. Harada, and K. Nagai, *Polym. Adv. Technol.*, **7**, 31 (1996).
16. J. M. Son, Y. Sakaki, K. Ogino, and H. Sato, *IEEE Trans. Electron Devices*, **44**, 1307 (1997).
17. Y. Q. Liu, M. S. Liu, X. C. Li, and K. Y. Jen, *Chem. Mater.*, **10**, 3301 (1998).
18. E. Bellmann, S. E. Shaheen, S. Thayumanavan, S. Barlow, R. H. Grubbs, S. R. Marder, B. Kippelen, and N. Peyghambarian, *Chem. Mater.*, **10**, 1668 (1998).
19. E. Bellmann, S. E. Shaheen, R. H. Grubbs, S. R. Marder, B. Kippelen, and N. Peyghambarian, *Chem. Mater.*, **11**, 399 (1999).
20. X. Q. Wang, M. Nakao, K. Ogino, H. Sato, and H. M. Tan, *Macromol. Chem. Phys.*, in press.
21. M. Nishiyama, T. Yamamoto, and Y. Koie, *Tetrahedron Letters*, **39**, 2367 (1998).
22. C. C. Price, "Organic Reactions", John Wiley & Sons, New York, N.Y., 1959, Vol. 3, p 1.
23. S. Tokito, H. Tanaka, K. Noda, A. Okada, and Y. Taga, *IEEE Trans. Electron Devices*, **44**, 1239 (1997).
24. R. Campton, M. E. Laing, A. Ledwith, and I. I. Abu-abdoun, *J. Appl. Electrochem.*, **18**, 431 (1988).
25. J. F. Ambrose, L. L. Carpenter, and R. F. Nelson, *J. Electrochem. Soc.*, **122**, 876 (1975).