J Mater Sci (2007) 42:1325–1329
DOI 10.1007/s10853-006-1193-2

Synthesis and light-emitting properties of poly[9-(4′-tert-butyl-phenylenemethene)-fluoroene-co-9,9-dioctylfluorene]

Zongqiang Yu · Songting Tan · Zhuling Yuan · Yingping Zou · Benhu Fan · Yongfang Li

Received: 30 November 2005 / Accepted: 1 February 2006 / Published online: 30 November 2006
© Springer Science+Business Media, LLC 2006

Abstract A novel copolymer, poly[9-(4′-tert-butyl-phenylenemethene)-fluoroene-co-9,9-dioctylfluorene], has been synthesized through the Yamamoto coupling method. The copolymer has good solubility and thermal stability with a glass transition temperature at 85 °C. The PL spectrum of the copolymer shows a maximum emission peak at 530 nm. A polymer light-emitting diode (PLED) with the configuration ITO/PEDOT/copolymer/Ca/Al has been fabricated. The device emits green light with an emission peak at 540 nm. A maximum brightness of 603 cd/m^2 was achieved at a drive voltage of 24.3 V.

Introduction

Polyfluorenes (PFs) have been widely studied because they are promising candidates of new high performance materials for blue polymer light-emitting diodes (PLEDs) [1]. The interest in these polymers arose because they showed high photoluminescence (PL) quantum yields, excellent chemical and thermal stability as well as good solubility and film-forming properties [2–4]. PFs are the most promising candidates for blue light-emitting polymers because of their high photoluminescence and electroluminescence efficiencies [5]. Functionalization of fluorene at C-9 position offers the control of polymer solubility and interchain interactions in film state [6–8]. Among the polyfluorenes, poly(9,9-dialkyl)fluorenes have been shown to be stable blue light-emitting polymers [9, 10]. The charge carrier mobility of these polymers is, however, limited by their steric inability to exhibit the two-dimensional lamellar π-stacking morphology. To address this limitation, recently, a series of PFs such as poly[9-(dicyanomethylene)]-fluorene and poly{9,9-bis(2-ethylhexyl)fluorene-2,7-diyl-*co*-[aza(2,7-fluorene-9-ylidene) methyl]-diphenylamine} have been reported [11–13]. This type of polymers have lower band gap than poly(9,9-dialkyl)fluorenes since the double bonds on the C-9 position of the fluorene unit improve the planarity and intermolecular π-stacking [14].

In this paper, we report on the synthesis and characterization of a novel copolymer, poly[9-(4′-tert-butyl-phenylenemethene)-fluoroene-co-9,9-dioctylfluorene]. A 4-tert- butyl-phenylenemethene group was introduced into the side chain of the fluorene unit. The physical and photoluminescence properties of the copolymer were studied. In addition, an electroluminescence (EL) device of copolymer was fabricated, and the luminescence and current density were measured. The new copolymer with more planar conformation is expected to have lower band gap and better charge carrier mobility than poly(9,9-dialkyl)fluorenes. The

Z. Yu · S. Tan (✉) · Z. Yuan
College of Chemistry and Institute of Polymer Materials, Xiangtan University, Xiangtan, Hunan 411105, P.R. China
e-mail: tanst2008@163.com

Z. Yu · S. Tan · Z. Yuan
Key Laboratory of Advanced Materials & Rheological Properties of Ministry of Education, Xiangtan University, Xiangtan 411105, P.R. China

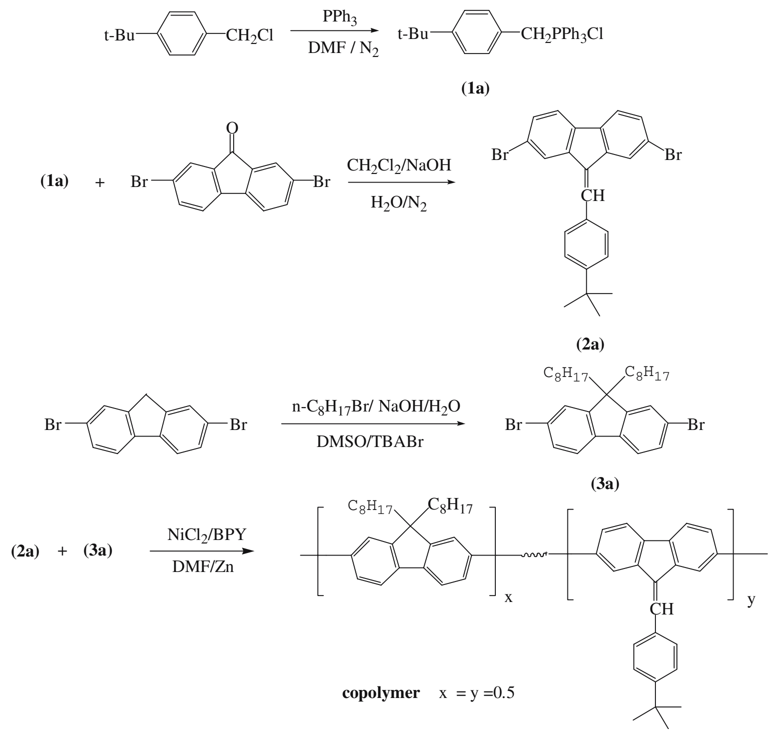
Y. Zou · B. Fan · Y. Li
CAS Key Laboratory of Organic Solids, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100080, P.R. China

synthetic route and details are given in Scheme and in experimental section.

Experimental procedure

Synthetic routes to the monomers and polymer are showed in Scheme 1.

Scheme 1 Synthetic routes of the monomers and copolymer



2,7-Dibromo-9-(4-tert-butyl-phenylenemethene)-fluorene (Monomer 2a) was synthesized following the procedures reported in literature [15]. It was prepared in two steps from 4-tert-butyl-benzenyl triphenyl phosphonium chloride, followed by conversion to monomer 2a by a Wittig reaction (0.4725 g, yield: 56%, mp: 136–137 °C). IR (KBr, cm^{-1}): 1065 (Ar–Br st), 691 (C = CH trans); ^{1}H-NMR(CDCl$_3$, TMS) δ (ppm): aromatic 7.90 (s, 2H), 7.75 (s, 1H), 7.43 (m, 8H), aliphatic 1.43 (s, 9H).

2,7-Dibromo-9,9′-dioctylfluorene (3a) was synthesized according to the procedures outlined in literature [16].

The copolymer named poly[9-(4′-tert-butyl-phenylenemethene)-fluoroene-co-9,9-dioctylfluorene] was synthesized by Yamamoto coupling method according to literature [17]. Monomer 2a (0.1710 g, 0.375 mmol) and 3a (0.2050 g, 0.375 mmol), nickel chloride (0.0095 g, 0.750 mmol), zinc (0.2260 g, 3.450 mmol), triphenylphosphine (0.2950 g, 1.125 mmol), bipyridine (0.0117 g, 0.0750 mmol), and *N*,*N*-dimethylformamide (DMF) (2.0 mL) were added under nitrogen. Then the mixture was stirring at 90 °C for 48 h. The pale green solids were precipitated into a large excess of 20% hydrochloric acid/methanol solution. The crude product was washed with methanol, distilled water, and methanol sequentially, and dried in vacuum at 40 °C for 24 h to afford pale yellow solids (0.1630 g, yield 63%). IR (KBr, cm^{-1}): 3065 (ArC-H st), 3013 (ArC-H st), 2945 (C-H st), 2928(C-H st), 2860 (C-H st), 1597 (ArC-C-C), 1453 (CH$_2$), 1363 (CH$_2$), 740 (-C-(CH$_2$)$_6$-C-, st). ^{1}H-NMR (CDCl$_3$, TMS) δ (ppm): aromatic 7.99–7.049 (m, 16H), aliphatic (C–H) 2.2 (s, 4H), 1.9–1.1 (m, 24H), 0.53–0.16 (m, 12H).

FT-IR spectra were measured on a Perkin-Elmer Spectra One spectrometer. UV–vis and PL spectra of the copolymer were obtained using a Perkin-Elmer Lamada 25 and LS-55 luminescence spectrometer, respectively. ^{1}H-NMR spectra were collected on a Bruker AVANCE 400 spectrometer. The molecular weights of polymer were determined by a WATER 2414 gel permeation chromatography with THF as eluent and polystyrene as standard. Cyclic voltammetry was conducted with an EG & G Princeton applied research model 273 potentiostat/galvanostat with a Pt wire electrode, a Pt plate counter electrode, and a Ag/Ag$^+$ reference electrode (Ag/0.1 M AgCl/acetonitrile) immersed in 0.1 M Bu$_4$NClO$_4$ in anhydrous acetonitrile purged with dried N$_2$. The thin polymer films were formed on Pt wire working electrodes via dip-coating from the polymer solution. The scanning rate was 50 mV/s, and all electrochemical potentials were calibrated with the ferrocene/ferrocenium (Fc/Fc^+) standard. Thermo-gravimetric analysis (TGA) was performed under nitrogen at a heating rate of 20 °C/min with Netzsch TG 209 analyzer. Differential scanning calorimetry (DSC) of the copolymers was performed with a Perkin Elmer DSC-7 instrument under nitrogen at a heating rate of 20 °C/min. The single-layered EL device was fabricated with the configuration ITO/PEDOT/copolymer/Ca/Al. PEDOT was spin-coated on top of the ITO and dried at 100 °C for 1 h under vacuum. A 90 nm layer of copolymer was spin-coated from its toluene solution onto the PEDOT layer under nitrogen. A 10 nm thick calcium cathode was deposited on the copolymer film by vacuum evaporation at a pressure less than 2×10^{-6} Torr, followed by a protective coating of aluminum for 180 nm. The EL spectra were recorded on an Instaspec 4 CCD spectrophotometer (Oriel Co.). The current–voltage–brightness characteristics of the device were measured with Keilthley 236 source analyzer.

Results and discussion

The synthesized copolymer was highly soluble in common organic solvents such as chloroform, tetrahydrofuran, methylene chloride, toluene and so on. The molecular weight determined by GPC is Mw = 7255, Mn = 3965, calibrated to a polystyrene standard, and the polydispersity is 1.83. The thermal property of the synthesized polymer was evaluated by the means of TGA and DSC under nitrogen atmosphere. The TGA thermogram and DSC heating curve are shown in Fig. 1. Like other PFs, the copolymer also exhibits good thermal stability, showing 5% weight loss at higher than 427 °C. As shown in Fig. 1a, the decomposition of the copolymer involved two steps. The first step starts from 290 °C and has a sharp loss until 51% of the mass. The second step starts from 535 °C. The first step might be assigned to the side chain decomposition and the second step to the main chain. Figure 1b shows a glass transition at around 85 °C for the copolymer as determined by DSC. Neither a melting point nor any other first-order phase transition was observed in either the heating or cooling cycles, indicating that the copolymer was amorphous.

Figure 2 shows the UV–vis absorption spectra and PL spectra of the copolymer in chloroform solution and thin film. The copolymer has a maximum absorption at 355 nm in dilute chloroform, which red-shifts to 376 nm in film state. The optical band gap of the copolymer determined from the absorption onset is found to be 2.38 eV. As compared to polyalkylfluorene [18], the band gap of the copolymer has been reduced for about 0.57 eV. Moreover, the copolymer with planar conformation and intermolecular π-stacking is high enough to be stable to oxidation in air [19].

The PL spectra of the copolymer show an emission peak at 421 nm. The quantum efficiency was determined as $\Phi_{sol} = 0.42$ in chloroform solution using dilute quinine sulfate as a standard (1×10^{-3} g/L solution in 0.1 M H_2SO_4) [20]. The PL emission maximum of the polymer is at about 530 nm in film state, which red-shifts for 109 nm compared with that of the polymer in solution, indicating a significant bathochromic shift of the emission. The intermolecular interactions in the solid state may favor coplanar arrangements of the aromatic rings in the polymer chain and may be responsible for the enhanced conjugation [21].

The HOMO and the LUMO are measured by electrochemical cyclic voltammetry (CV). When Ag/AgCl electrode is used as the reference electrode, the correlation can be expressed as [22].

$$E_{\mathrm{HOMO}} = -|\mathrm{IP}| = -|\mathrm{e}E_{\mathrm{ox}} + 4.37|$$

$$E_{\mathrm{LUMO}} = -|\mathrm{EA}| = -|\mathrm{e}E_{\mathrm{red}} + 4.37|$$

$$E_{\mathrm{g}} = |\mathrm{IP}| - |\mathrm{EA}| = E_{\mathrm{LUMO}} - E_{\mathrm{HOMO}}.$$

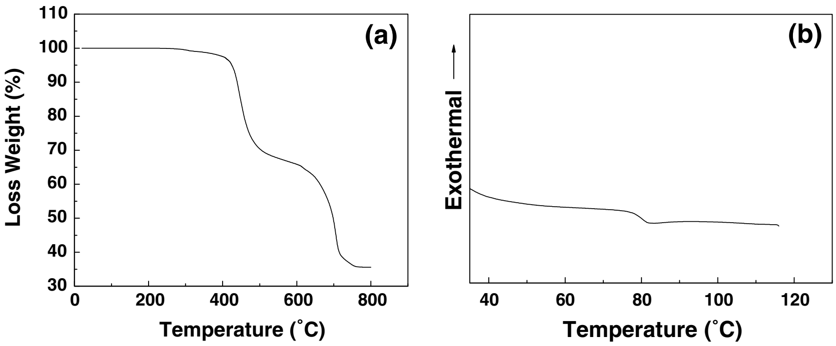


Fig. 1 TGA thermograms (**a**) and DSC heating curve (**b**) of the copolymer

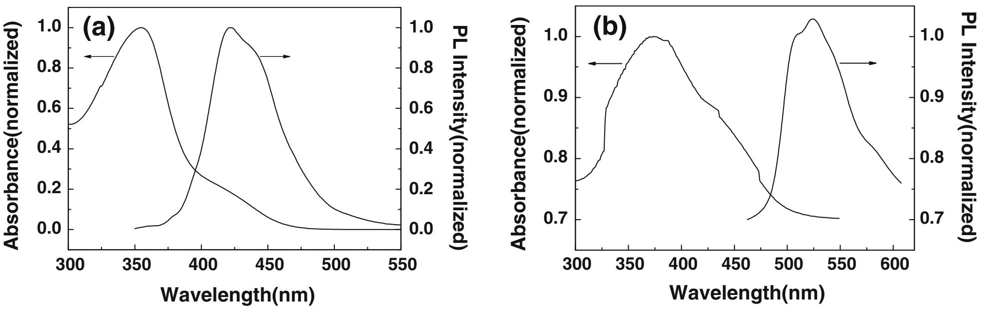


Fig. 2 Absorption and PL spectra of the copolymer in chloroform solution (**a**) and solid film (**b**)

E_{ox} and E_{red} are onset potential of the oxidation and reduction process, respectively. As for the copolymer, the onset potential of oxidation occurs at 0.95 eV, so the HOMO level is calculated as –5.32 eV. The HOMO level of the copolymer has been increased 0.48 eV than that of polyalkylfluorene (–5.8 eV) [18]. The band gap (E_g) is estimated as 2.38 eV from the UV–vis absorption spectrum. The LUMO level is calculated as –2.94 eV, which has been decreased 0.82 eV as compared to the LUMO level of polyalkylfluorene (–2.12 eV). The HOMO level of the copolymer facilitates hole transport and is suitable to the work function of ITO-glass. However, the LUMO level of the copolymer would not favor electron injection and act as an electron trap which might affect the performance of the single-layer device [23].

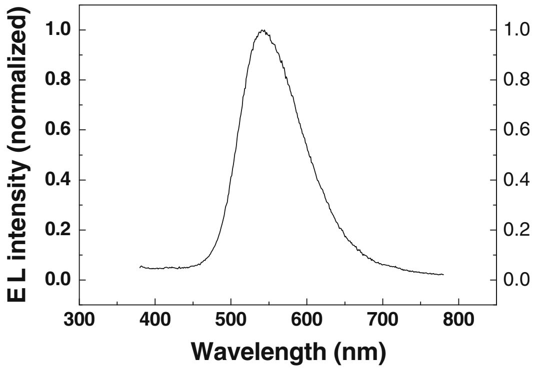


Fig. 3 EL spectrum of ITO/PEDOT/copolymer/Ca/Al device

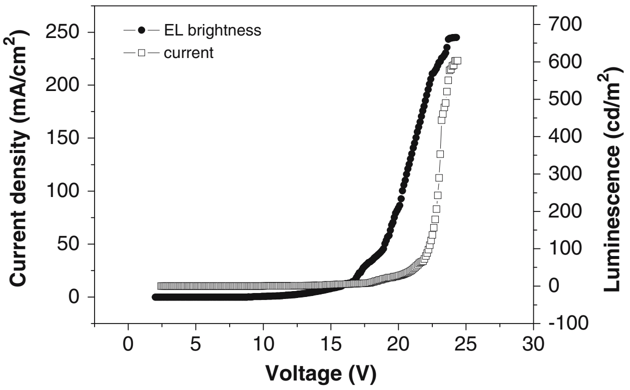


Fig. 4 Current–brightness–voltage curves of an ITO/PEDOT/copolymer/Ca/Al device

An EL device with the configuration ITO/PEDOT (30 nm)/copolymer (96 nm)/Ca (10 nm)/Al (180 nm) was fabricated and characterized as a function of applied voltage. Figure 3 shows that the EL spectrum of the device emits green light with a peak at 540 nm, which is similar to the PL spectra of the polymer film. Figure 4 shows the current–voltage–luminance characteristics of the EL device. The turn-on voltage of this device is at about 10.6 V, which is higher than polyalkylfluorene (8 V). The relative high turn-on voltage of the copolymer is probable due to the unsuitable LED configuration. It seems that the single-layer device of the copolymer is not optimized in terms of electron injection at cathode [24–25]. The maximum brightness of the device is 603 cd/m^2 at 24.3 V (245.7 mA/cm^2). Figure 5 shows current efficiency–current density characteristics of the device. The current efficiency is stable at about 0.05 cd/A when the current density is higher than 70 mA/cm^2. However, the current efficiency is relative lower than that of the similar configuration ITO/PEDOT/PFO/Ca/Al (about 0.2 cd/A). It could be that poly(4-tert-butyl-phenylene-methene)-fluorene has a sp^2-hybridized carbon at the

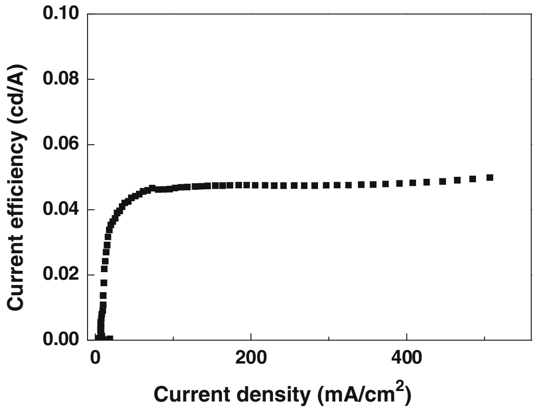


Fig. 5 Current efficiency–current density characteristics of an ITO/PEDOT/copolymer/Ca/Al device

9-position, which permits the alkyl chains to adopt a coplanar conformation relative to the polymer backbone, thus facilitating cofacial aggregation [26]. Aggregation formation and relative low molecule weight could be the major reason of low efficiency for the copolymer LED.

Conclusions

Our results show that a 4-tert-butyl-phenylenemethene group was introduced into the side chain of the fluorene unit to improve the planarity. The synthesized copolymer is amorphous with good solubility and thermal stability. The EL device with the configuration ITO/PEDOT/copolymer/Ca/Al emits green light with an emission peak at 540 nm the turn on voltage is about 10.6 V. The maximum brightness of 603 cd/m^2 can be obtained at a driving voltage of 24.3 V (245.7 mA/cm^2).

Acknowledgement This work was supported by the National Nature Science Foundation of China (No 50473045).

References

1. Scherf U, List EJW (2002a) Adv Mater 14:477
2. Pei Q, Yang A (1996) J Am Chem Soc 188:7416
3. Grell M, Long X, Bradely DDC (1997) Adv Mater 9:798
4. Cho NS, Hwang DH, Lee JI, Jung BJ, Shim HK (2002) Macromolecules 36:1224
5. Becker S, Ego C, Grimsdale AC, List EJW, Marsitzky D, Pogantsch A, Setayesh S, Leising G, Mullen K (2002) Synthetic Met 125:73
6. Kreyenschmidt M, Klaerner G (1998) Macromolecules 31:1099
7. Klarner G, Lee JI (1999) Adv Mater 11:115
8. Lee JI, Klaerner G (1999) Chem Mater 11:1083
9. Scherf U, List EJW (2002b) Adv Mater 14:477
10. Leclerc M (2001) Polymer 39:2867
11. Heeney M, Bailey C, Giles M (2004) Macromolecules 37:5250
12. Wong WY, Liu GL (2003) Eur J Org Chem 32:365
13. Hwang DH, Park MJ (2004) Synthetic Met 146:145
14. Osikowicz W, Murdey R, Giles M, Heeney M (2004) Chem Phys Lett 385:184
15. Kim YH, Ahn JH, Shin DC (2004) Polymer 45:2525
16. Xia CJ, Advincula RC (2001) Macromolecules 34:5854
17. An BK, Kim YH, Shin DC (2001) Macromoleculars 34:3993
18. Bradley DDC, Grell M, Giebeler C (1998) Appl Phys Lett 73:2453
19. Leeuw DMD, Simenon MMJ, Brown AR, Einerhand REF (1997) Synthetic Met 87:53
20. Demas JN, Crosby GA (1971) J Phys Chem 75:991
21. Jenekhe SA, Osaheni JA (1994) Science 265:75
22. Morgado J, Acialli CF, Friend RH (2001) Macromolecules 34:3094
23. Fanshun M, Yong C, He T (2003) Eur Polym J 39:1325
24. Brown TM, Friend RH, Millard IS (2003) J Appl Phys 13:93
25. Shang-Fang Lim B, Cacialli F (2005) Adv Funct Mater 15:981
26. Heeney M, Bailey C,Mc Culloch I (2004) Macromolecules 37:5250