Synthesis and characterization of highly soluble 9,10-diphenyl-substituted poly(2,6-anthracenevinylene)

Peihua Ren, Yanli Zhang, Haichang Zhang, Xueheng Zhang, Wen Li, Wenjun Yang*

Key Laboratory of Rubber-plastics (QUST), Ministry of Education, School of Polymer Science and Technology, Qingdao University of Science and Technology, 53 Zhengzhou Road, Qingdao 266042, China

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ABSTRACT

We report the synthesis and optoelectronic properties of highly soluble poly(9,10-bis(3′,4′-di(2″-ethyl-hexyloxy))phenyl)-2,6-anthracenevinylene) (HSM-PAV). The key intermediate for the synthesis of HSM-PAV is 2,6-dimethyl-9,10-dibromoanthracene, and the high solubility of HSM-PAV is from the incorporation of lateral 3,4-di(2-ethylhexyloxy)phenyl moieties into the 9,10-positions of anthracene units. The increase of side alkyloxy groups endows HSM-PAV with higher molecular weight ($M_n = 3.2 \times 10^4$) and better electro-luminescence performances ($L_{max} = 590$ cd/m^2, $LE_{max} = 0.27$ cd/A) compared with the poly(2,6-anthrace-nevinylene) with lateral monoalkyoxy moieties ($M_n = 1.9 \times 10^4$, $L_{max} = 340$ cd/m^2, $LE_{max} = 0.17$ cd/A). The electrical conductivity of doped HSM-PAV film with iodine is 5×10^{-2} S cm^{-1} that is several order higher than that of doped 9,10-anthracene-based polymers, further demonstrating that linkage position has a dramatic effect on the optoelectronic properties of anthracene-based conjugated polymers.

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1. Introduction

Since the discovery of electroluminescence (EL) in poly(*p*-phe-nylenevinylene) (PPV) [1], a variety of optoelectroactive conjugated backbone structures, such as poly(*p*-phenylene vinylene) [1], poly-(*p*-phenylene) [2], polythiophene [3], and polyfluorene [4] have been synthesized for application in light-emitting diodes. Among vast kinds of conjugated polymers, poly(arylene vinylene)s are extensively studied, such as poly(phenylene vinylene)s [1], poly(naphthalene vinylene)s [5], poly(thiophene vinylene)s [6], poly(fluorene vinyl-ene)s [7], poly(9,10-anthracene vinylene)s [8] and their copolymers that have been reported in the past. During the development of organic optoelectronics, anthracene is a very important aromatic unit. For instance, organic electroluminescence was first demonstrated from its single crystals [9]. Due to its promising light-emitting prop-erties and charge carrier transport properties, anthracene has been widely used as a building block for conjugated small molecules [10], oligomers [11] and polymers [12] with excellent optoelectronic properties. The anthracene unit could be in principle linked into polymer backbone in two different ways, 9,10- or 2,6-positions, to allow a quinoid character and to form an efficient conjugation. Several groups have reported oligomers and polymers composed of 9,10-linked anthracene derivatives, including poly(9,10-anthrylene)s [13]

and poly(9,10-anthrylenevinylene) [8]. The apparent drawback of 9,10-linkage is that the main chain of the conjugated molecules is strongly twisted because of the high steric hindrance of 1,8-positions in the anthracene ring, resulting in poor conjugation along the back-bone and low molecular weight [14]. In comparison with 9,10-linkage, 2,6-linkage should enable elimination of the detrimental effect of steric hindrance on molecular conjugation and benefit high fluo-rescence efficiency. There have been a few reports on poly(2,6-anthrylene)s and oligo(2,6-anthrylene)s [15]. However, to date few poly(2,6-anthracenevinylene)s have been reported before due to their synthetic inaccessibility to the best of our knowledge. 2,6-Anthrace-nevinylene-based homopolymers and copolymers should provide a novel class of poly(arylene vinylene)s whose optoelectronic prop-erties were still unclear. Recently, McNamara et al. reported the first synthesis of the poly(arylene vinylene)s containing 9,10-dihydro-2,6-anthracenevinylene using anthraquione-1,5-diol as a key starting material [16]. These copolymers containing 2,6-anthracenevinylene showed low molecular weight and poor solubility which limited the further investigation of their optoelectronic properties. Very recently, we have developed a new and facile approach to the synthesis of 9,10-diphenyl-substituted poly(2,6-anthracene vinylene)s starting from isoprene and 1,4-benzoquinone [17]. However, a soluble poly(9,10-bis-(*p*-(2-ethylhexyloxy)phenyl)-2,6-anthracenevinylene) was only obtained by Gilch polymerization in the presence of an equal molar amount of 4-*tert*-butylbenzyl bromide which acts as a molecular weight adjustor. Although the relative molecular weight of 2,6-PAV ($M_n = 1.9 \times 10^4$) was the highest among the reported poly(arylene

* Corresponding author.
E-mail address: ywjph2004@qust.edu.cn (W. Yang).

vinylene)s containing anthracenevinylene [13,14,16], the degree of polymerization of 2,6-PAV was still limited and also much smaller than that of other poly(arylene vinylene)s such as poly(1,4-phenylene vinylene). Moreover, when 2,6-PAV solution was filtered through a PTFE filter, it remained a certain amount of gel, which implies that the real solubility of as-synthesized 2,6-PAV was limited. Therefore, it is necessary to synthesize highly soluble and high molecular weight poly(2,6-anthracene vinylene) derivatives and to further investigate their optoelectronic properties.

It has been shown that the improved processability of aromatic conjugated polymers can be achieved by increasing the numbers of flexible side chains on the polymer backbone [18]. In this work, we report the highly soluble and high molecular weight 9,10-diphenyl-substituted poly(2,6-anthracenevinylene) derivate with two lateral 3,4-di(2-ethylhexyloxy)phenyl moieties on the 9,10-positions of anthracene ring, HSM-PAV (Scheme 1). The introduction of phenyl moieties on the 9,10-positions of anthracene not only can eliminate the reactive 9,10-hydrogens of anthracene but also can reduce the aggregation of the polymer due to an out-of-plane twist of more than 60° between benzene and anthracene. The increase of flexible side alkyloxy chains not only improves the solubility of HSM-PAV but also gives rise to both sterical hindrance along the polymer backbone and high stability against photooxidation [18]. The well-separated conjugated polymer chains may improve the fluorescence efficiency [18] and the LED performance [19]. The increased solubility should allow the synthesis of high molecular weight conjugated polymer having good film forming and mechanical properties. On the other hand, it has been reported that the enhanced electrical conductivity in 9,10-anthracene-based polymers is independent on the extended conjugation along the chain [20]. This might be because of the low degree of conjugation along the polymer backbone induced by strong steric hindrance of 1,8-hydrogens on anthracene ring [21]. To poly(2,6-anthracenevinylene)s, there is a good conjugation along the polymer backbone. Our primary result shows that HSM-PAV exhibits a significantly enhanced electrical conductivity after doping with iodine.

2. Experimental section

2.1. Characterization

NMR spectra were recorded on a JEOL JNM-LA300 (300 MHz) spectrometer in chloroform solutions with tetramethylsilane (TMS) as an internal standard. Molecular weight was determined by gel permeation chromatography (GPC) by a Waters 1515 HPLC using SDVB column at 25 °C. The calibration was made with a series of mono-dispersed polystyrene standards in chloroform. UV–vis spectra were recorded on a HP-8453 UV–VIS system, and the photoluminescence (PL) spectra were measured on an Aminco Bowman series 2 luminescence spectrometer. The fluorescence quantum yields were determined in chloroform by the literature method using coumarin in methanol as the reference. The elemental analysis was performed on Perkin–Elmer 2400. Thermogravimetric analysis (TGA) was carried out on a ZETZSCH TG209 at a heating rate of 10 °C/min under a nitrogen flow. Differential scanning calorimetry (DSC) was run on a ZETZSCH DSC204 at a heating rate of 10 °C/min under a nitrogen flow.

Indium–tin-oxide (ITO)-coated glass with a sheet resistance of 50 Ω/cm^2 was used as substrate. The substrate pre-patterned by photolithography to give an effective device size of 4 mm^2. Pre-treatment of ITO includes a routine chemical cleaning using detergent and alcohol in sequence, followed by oxygen plasma cleaning. The poly(3,4-ethylenedioxythiophene) (PEDOT) doped with poly(styrenesulfonic acid) (PSS) was spin-coated from its water dispersion, yielding a 100 nm thick layer after drying (ca. 105 °C; 5 min). A ca. 100 nm layer of the polymer was spin cast from its chloroform solution (7 mg/mL) onto the hole-transport layer (HTL) of PEDOT: PSS. The polymer solution in chloroform was filtered through a 0.45 μm PTFE filter. Finally, a 200 nm Barium cathode was thermally deposited and then capped with aluminum onto the organic film in the vacuum with a back pressure of 5×10^{-4} Pa. Electroluminescent (EL) spectra were measured by a PR-650 spectro-scan spectrometer. The luminance–current–voltage characteristics were recorded simultaneously with the measurement of the EL spectra by combining the spectrometer with a Keithley 2400 programmable electrometer. All measurements were carried out at room temperature under ambient conditions. Electrical conductivity of HSM-PAV film doped with iodine was measured on SZT-2000 (Shanghai, China), a four-point-probe measuring system.

2.2. Materials

All starting materials are obtained from commercially available resources. Pd(PPh$_3$)$_4$, NBS, n-BuLi, B(OCH$_3$)$_3$ are purchased from Aldrich or Alfar Chemical Co. THF was distilled over sodium and benzophenone. 9,10-Dibromo-2,6-dimethyl-anthracene is from previous work [17].
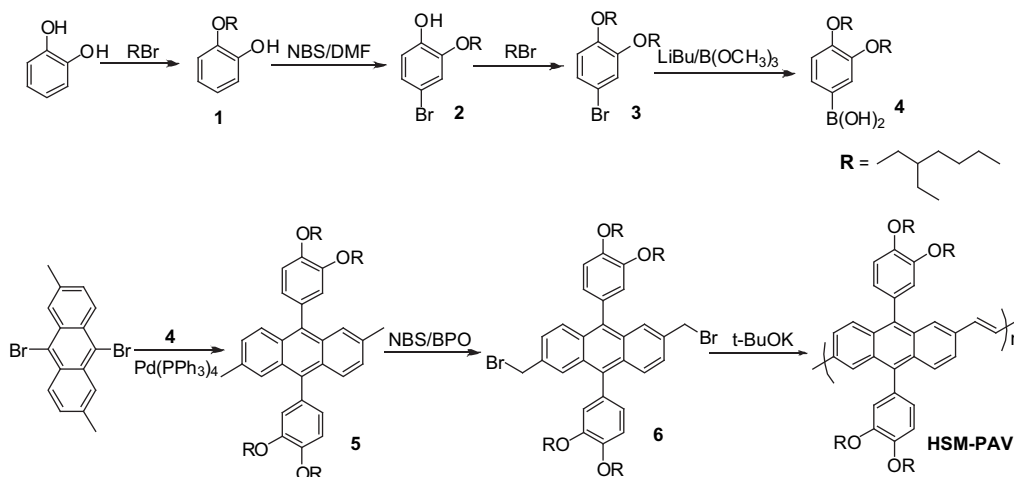
Scheme 1. Synthesis and structure of the polymer HSM-PAV.

2.3. Synthesis

2.3.1. 2-(2′-Ethylhexyloxy)phenol (**1**)

A mixture of 1,2-dihydroxybenzene (11.1 g, 100 mmol), 2-ethyl-hexyl bromide (19.8 g, 100 mmol), K_2CO_3 (20.8 g, 150 mmol) in DMF (150 mL) was heated at 100 °C and stirred for 12 h. The resulting mixture was poured into large amount of water and extracted with dichloromethane. The solvent was evaporated and crude product was purified by column chromatography on silica gel using hexane/ethyl acetate (6/1) as the eluent to afford colorless liquor. Yield 16.9 g (76%). ^{1}H NMR (300 MHz, CDCl$_3$): δ 6.93 (m, 1H), 6.85 (m, 3H), 5.61 (s, 1H), 3.93 (d, 2H, $J = 6.0$ Hz), 1.77 (m, 1H), 1.47 (m, 4H), 1.33 (m, 4H), 0.94 (m, 6H).

2.3.2. 2-(2′-Ethylhexyloxy)-4-bromophenol (**2**)

Bromide (8.0 g, 50 mmol, in 30 mL CHCl$_3$) was added dropwise to a solution of 2-(2′-Ethylhexyloxy)phenol (11.1 g, 50 mmol) in CHCl$_3$ (80 mL) at 0 °C and stirred for 1 h. The solvent was evaporated and crude product was purified by column chromatography on silica gel using hexane/ethyl acetate (6/1) as the eluent to afford colorless liquor. Yield 13.1 g (87%). ^{1}H NMR (300 MHz, CDCl$_3$): δ 6.97 (m, 2H), 6.80 (d, 1H, $J = 9.0$ Hz), 5.54 (s, 1H), 3.90 (d, 2H, $J = 6.0$ Hz), 1.77 (m, 1H), 1.46 (m, 4H), 1.32 (m, 4H), 0.94 (m, 6H).

2.3.3. 4-Bromo-1,2-bis-(2-ethyl-hexyloxy)-benzene (**3**)

A mixture of 2-(2′-ethylhexyl-oxy)-4-bromophenol (5.25 g, 17.4 mmol), 2-ethylhexyl bromide (4.02 g, 20.1 mmol), K_2CO_3 (3.88 g, 28.1 mmol) in DMF (50 mL) was heated at 100 °C for 24 h. The mixture was poured into large amount of water and extracted with dichloromethane. The solvent was evaporated and crude product was purified by column chromatography on silica gel using hexane as the eluent to afford colorless liquor. Yield 5.48 g (76%). ^{1}H NMR (300 MHz, CDCl$_3$): δ 6.97 (m, 2H), 6.72 (d, $J = 9.0$ Hz, 1H), 3.82 (d, $J = 6.0$ Hz, 4H), 1.70 (m, 2H), 1.32–1.50 (m, 16H), 0.92 (m, 12H).

2.3.4. 3,4-Bis-(2-ethyl-hexyloxy)benzene boronic acid (**4**)

10.0 mL of butyllithium (1.6 M in hexanes, 16.0 mmol) was added to a solution of 4-bromo-1,2-bis-(2-ethyl-hexyloxy)-benzene (5.30 g, 12.8 mmol) in anhydrous THF (40 mL) at −78 °C under nitrogen. The mixture was stirred at that temperature for 1 h and then trimethyl borate (2.7 mL, 24.6 mmol in 15 mL of THF) was slowly added. The mixture was stirred for 1 h at −78 °C and for 4 h at room temperature. After quenching with water, the mixture was extracted with dichloromethane and the solvent was evaporated. The crude product was purified by short column chromatography on silica gel using ethyl acetate/hexane (1:5) followed by ethyl acetate/hexane (1:2) as the eluent to afford viscous liquor. 3.93 g (81% yield). ^{1}H NMR (300 MHz, CDCl$_3$): δ 7.82 (d, $J = 9.0$ Hz, 1H), 7.68 (d, $J = 3.0$ Hz, 1H), 7.00 (d, $J = 9.0$ Hz, 1H), 4.01 (d, $J = 6.0$ Hz, 2H), 3.96 (d, $J = 6.0$ Hz, 2H), 1.82 (m, 2H), 1.32–1.52 (m, 16H), 0.92 (m, 12H).

2.3.5. 9,10-Bis-(3,4-bis(2-ethyl-hexyloxy)-phenyl)-2,6-dimethyl-anthracene (**5**)

2,6-Dimethyl-9,10-dibromoanthracene (1.5 g, 4.12 mmol) was dissolved in toluene (50 mL). To this solution 2.0 M Na_2CO_3 aqueous solution (40 mL), Aliquat®336 (5 drops), 3,4-bis(2′-ethyl-hexyloxy)benzene boronic acid (3.75 g, 9.91 mmol) was added. The reaction mixture was bubbled with nitrogen for 5 min and then the catalyst Pd(PPh$_3$)$_4$ (0.16 g) was added under nitrogen. The mixture was refluxed under vigorous stirring for 36 h. The resulting mixture was extracted with toluene and solvent was removed. The crude product was purified by column chromatography on silica gel using hexane/MC (20/1) as the eluent to produce a wax solid. 3.12 g (87% yield). Mp < 50 °C; ^{1}H NMR (300 MHz, CDCl$_3$): δ 7.66 (d, $J = 9.0$ Hz, 2H), 7.50 (s, 2H), 7.17 (dd, $J_1 = 9.0$ Hz, $J_2 = 3.0$ Hz, 2H), 7.11 (d, $J = 6.0$ Hz, 2H), 6.97 (m, 4H), 4.04 (d, $J = 6.0$ Hz, 4H), 3.85 (m, 4H), 2.41 (s, 6H), 1.88 (m, 2H), 1.79 (m, 2H), 1.28–1.64 (m, 32H), 0.89–1.04 (m, 24H). Anal. Calcd for $C_{60}H_{86}O_4$ (871.32): C, 82.71; H, 9.95; O, 7.34. Found: C, 82.72; H, 9.91.

2.3.6. 9,10-Bis-(3,4-bis(2-ethylhexyloxy)-phenyl)-2,6-bis-bromomethyl-anthracene (**6**)

A mixture of 9,10-bis-(3,4-bis(2-ethylhexyloxy-phenyl)-2,6-dimethyl-anthracene) (2.9 g, 3.33 mmol), NBS (1.3 g, 7.30 mmol) and BPO (41 mg, 0.16 mmol) in anhydrous CCl$_4$ (60 mL) was bubbled with nitrogen for 3 min and then was refluxed for 3 h. The succinimide was filtered off and the mother liquor was washed with aqueous sodium metabisulfite (10%) and water. After drying over Na_2SO_4, the solvent was evaporated. The crude product was purified by flash column chromatography on silica gel using hexane/ethyl acetate (30:1) as the eluent. 2.43 g (71% yield). ^{1}H NMR (300 MHz, CDCl$_3$): δ 7.67 (d, $J = 9.0$ Hz, 2H), 7.50 (s, 2H), 7.16 (d, $J = 9.0$ Hz, 2H), 7.11 (d, $J = 6.0$ Hz, 2H), 6.97 (m, 4H), 4.55 (s, 4H), 4.04 (d, $J = 6.0$ Hz, 4H), 3.85 (m, 4H), 1.88 (m, 2H), 1.79 (m, 2H), 1.28–1.64 (m, 32H), 0.89–1.04 (m, 24H). Anal. Calcd for $C_{60}H_{84}Br_2O_4$ (1029.11): C, 70.03; H, 8.23; Br, 15.53; O, 6.22. Found: C, 70.10; H, 8.20.

2.3.7. Poly{9,10-bis[4-(2-ethylhexyloxy)phenyl]-2,6-anthracenevinylene} (HSM-PAV)

A solution of 9,10-bis-(3,4-bis(2-ethylhexyloxy)-phenyl)-2,6-bis-bromomethyl-anthracene (0.48 g, 0.47 mmol) in anhydrous THF (40 mL) was bubbled with nitrogen for 3 min at 0 °C. t-BuOK (0.35 g, 3.12 mmol) in anhydrous THF (10 mL) was added to above solution at once under stirring and nitrogen protect. The resulting mixture was stirred for another 5 h and then 4-tert-butylbenzyl bromide (102 mg, 0.45 mmol) was added to terminate the reaction. After further stirring 1 h, the mixture was precipitated by methanol and the resulting precipitate was re-precipitated twice with chloroform–methanol. After drying in vacuum, 0.26 g of a yellow solid were obtained (66% yield). ^{1}H NMR (300 MHz, CDCl$_3$): $\delta = 7.79$ (m, 2Hz), 7.73 (broad, 2H), 7.19–7.31 (m, 4H), 7.21–7.22 (broad, 2H), 7.16 (m, 4H), 4.06 (m, 4H), 3.86 (m, 4H), 1.87 (m, 2H), 1.79 (m, 2H), 1.28–1.64 (m, 32H), 0.89-1.04 (m, 24H). Anal. Calcd for $C_{60}H_{82}O_4$ (867.29): C, 83.09; H, 9.53; O, 7.38. Found: C, 83.42; H, 9.41.

3. Results and discussion

3.1. Synthesis

The synthesis of 9,10-diphenyl-substituted poly(2,6-anthracene vinylene) derivative, HSM-PAV, is depicted in Scheme 1. The key intermediate 9,10-dibromo-2,6-dimethyl-anthracene was readily available to us [18]. The mono-alkylation reaction of benzene-1,2-diol with 2-ethylhexyl bromide in the presence of K_2CO_3 gave **1** followed by reaction with NBS in DMF to afford bromide **2**. Using this intermediate, one could fix the position of the following substituent which may be useful to some molecular designs. **2** was further alkylated with 2-ethylhexyl bromide to afford 4-bromo-1,2-bis-(2-ethyl-hexyloxy)-benzene (**3**). The boronic acid **4** was obtained by treating **3** with n-butyllithium in anhydrous THF followed by adding trimethyl borate. The Suzuki coupling of **4** and 9,10-dibromo-2,6-dimethyl-anthracene catalyzed by tetrakis-(triphenylphosphine) palladium(0) in toluene yielded **5**, which was a wax-like solid with a low melting point due to the introduction of four branched alkyloxy moieties. Radical-initiated bromination of **5** gave monomer **6**. Polymerization of **6** catalyzed by potassium tert-butoxide in anhydrous THF yielded the desirable polymer HSM-PAV (Scheme 1).

Unlike the synthesis of 2,6-PAV, here 4-*tert*-butylbenzyl bromide was added in the later period of polymerization and acted as end-capping agent. The number average molecular weight of HSM-PAV measured by gel permeation chromatography (GPC) analysis with a polystyrene standard calibration was obviously higher than previous 2,6-PAV (1.9×10^4) and reached to 3.2×10^4. Although HSM-PAV had a relatively high molecular weight, it was completely soluble in chloroform, THF, and toluene at room temperature. It should be noted that 2,6-PAV synthesized by the same procedure as described for HSM-PAV gave a poorly soluble polymer. The reason for this high solubility of HSM-PAV must be from the increasing numbers of flexible side chains on the polymer backbone.

3.2. Thermal properties

The thermal properties of the polymer were determined by Differential scanning calorimetry (DSC) and thermal gravimetric analysis (TGA) under a nitrogen atmosphere at a heating rate of 10 °C/min. DSC trace showed that HSM-PAV had neither a glass transition nor a crystal melting transition was observed in the temperature range from 25 to 300 °C (the inset in Fig. 1), indicating that the polymer has a fully rigid chain and an amorphously aggregated structure. This property should prevent the deformation of polymer morphology and degradation of the polymer as film devices. TGA measurement revealed that HSM-PAV had a good thermal stability with a decomposition temperature of 368 °C (5 wt% weight loss) in a nitrogen atmosphere (Fig. 1).

3.3. Photoluminescence and optical stability

The optical properties of chloroform solution (10^{-4} M of repeating unit) and as-prepared film of HSM-PAV are displayed in Figs. 2 and 3. Fig. 2 shows that the absorption spectrum of HSM-PAV in dilute solution has two absorption maxima around 348 nm and 446 nm. The intense absorption band around 348 nm in the violet region is from the absorption of anthracene moiety and the weaker band in the range of 400–500 nm is due to the absorption of the conjugated backbone. The as-prepared HSM-PAV film exhibits two absorption maxima around 352 nm and 451 nm which are only red-shifted by several nanometers compared to that in solution. HSM-PAV shows a green emission with a maximum at 496 nm and 503 nm in solution and film state respectively. The fluorescence quantum yield is 0.50 measured in chloroform with quinine as
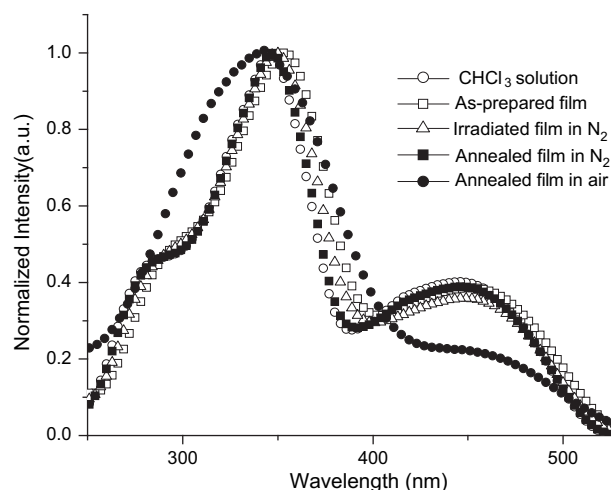

Fig. 2. UV–vis absorption spectra of HSM-PAV in chloroform ($\circ$), in as-prepared film ($\square$), in film irradiated under N_2 ($\triangle$), in films annealed under N_2 ($\blacksquare$) or air ($\bullet$).

a standard in 1 N H_2SO_4 ($\varphi = 0.546$) [15]. Both absorption and PL spectra in solid state show slight red-shifts compared to that in solution, indicating that there is almost no conformation change for this fully rigid polymer backbone from solution to film state. Meanwhile, no new peak corresponding to aggregation was observed, which probably ascribed to that the twist phenyl groups and the four branched alkyloxy moieties on the side of anthracene ring can suppress the close packing of the polymer chain. The fluorescence quantum yield of HSM-PAV (0.50) is somewhat higher than that of 2,6-PAV (0.44), which might result from the well-separated rigid polymer chains that was beneficial to solid fluorescence and EL performance.

The negative properties of the poly(arylenevinylene) derivatives are probably the sensitivity of double bonds to heat and light. In the case of anthracene-based derivatives, the additional dimerization or ednoperoxidation of anthracene rings through the 9- and 10-positions may happen upon heating and light irradiating. This would reduce the maximum absorption and emission of the polymer and also make them blue-shift. To examine the stability of HSM-PAV, we put the polymer film coated on glass slides into a flask under nitrogen atmosphere. As displayed in Figs. 2 and 3,
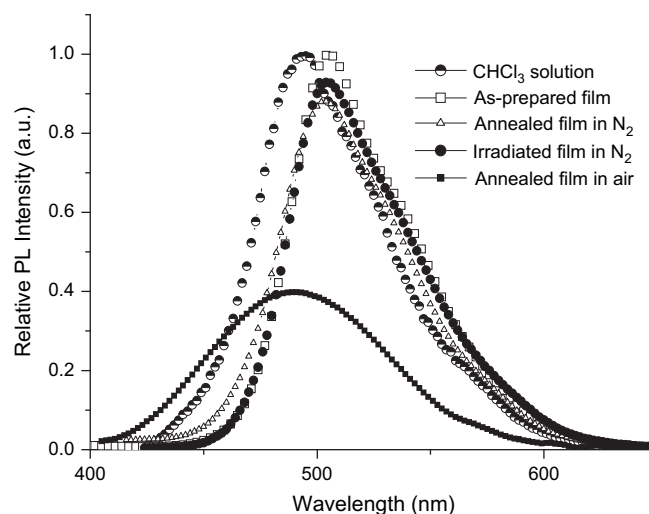

Fig. 1. TGA thermogram and DSC trace of HSM-PAV.

Fig. 3. PL spectra of HSM-PAV in chloroform ($\circ$), in as-prepared film ($\square$) in films annealed under N_2 ($\triangle$) or air ($\blacksquare$) and in film irradiated under N_2 ($\bullet$).
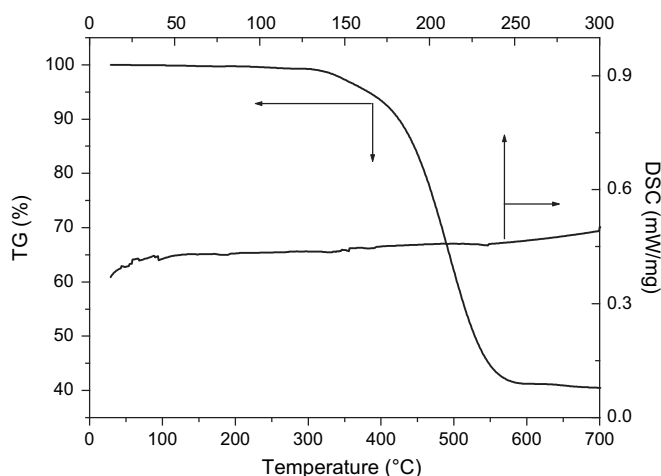
after annealing of HSM-PAV film in nitrogen for 24 h at 120 °C, only slightly decreased both absorption and PL intensity were observed. Upon irradiation of HSM-PAV film with an ordinary light bulb (60 W) in nitrogen for 24 h at room temperature, the situation was similar to annealing in both the absorption and PL spectra. These results indicate that HSM-PAV exhibits good thermal and optical stability in inert atmospheres. Since the reactivity between anthracene rings depended on not only the anthracene density but also the anthracene mobility and mutual accessibility, HSM-PAV has a fairly rigid backbone which should hinder the accessibility of anthracene to anthracene. The out-of-plane twisting of more 60° between benzene and anthracene should suppress the face to face reaction of anthracene units. It has been reported that poly-(thiophene) and poly(1,4-phenyenevinylene)s substituted by alkyl-oxyphenyl side groups showed reduced aggregation and increased stability. Therefore, 9,10-diphenyl with four branched alkyloxy moieties have played an important role for the stability and the separation of HSM-PAV backbone. However, upon annealing HSM-PAV film in air for 24 h at 120 °C, the intensity of the absorption and the emission decreased obviously, moreover, the fluorescence emission showed obviously blue-shifted (Figs. 2 and 3). Although these changes must result from the oxidation of anthracene rings or double bonds in polymer backbone, it is difficult to conclude that, based on the limited data, which is prone to be oxidized.

3.4. Electroluminescence properties

Although many conjugated anthracene-based polymers have been synthesized, the studies on their electroluminescence (EL) characteristics are still scarce. In order to compare with the EL properties of 2,6-PAV reported previously, same simple devices with the configuration ITO/PEDOT: PSS/HSM-PAV/Ba/Al were fabricated. As shown in Fig. 4, the EL spectrum of HSM-PAV is very similar to its film PL one (Fig. 2), and is also the same as that of 2,6-PAV. They are all bluish green emissive materials with the CIE coordinate around (0.28, 0.51). Fig. 5 demonstrates that the HSM-PAV-based device exhibits a voltage-independent and stable EL spectrum. Upon increasing the applied voltages from 5.5 to 13 V, we observed no significant change in the EL spectra, indicating that polymer HSM-PAV is of good color stability.

The EL device characteristics of polymer HSM-PAV are shown in Fig. 5. The device shows a turn-on voltage of about 5.0 V, which is similar to that of previous 2,6-PAV. The maximal brightness and the maximal luminous efficiency of the device with HSM-PAV as an
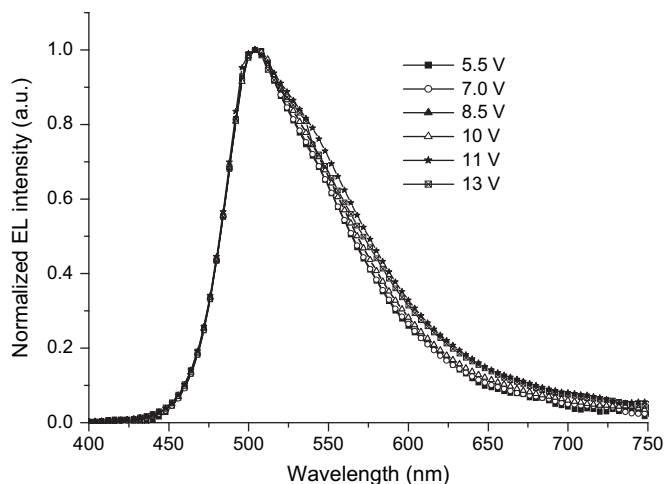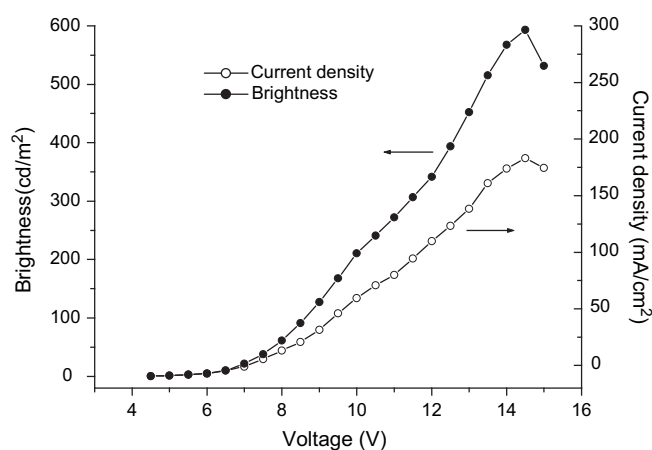
Fig. 5. Current density–voltage–luminance characteristics of the device ITO/PEDOT:PSS/HSM-PAV/Ba/Al.

emitter are 590 cd/m^2 and 0.27 cd/A respectively. Although the device performance of HSM-PAV is not among the best performances reported for poly(arylenevinylene)s, the EL properties of HSM-PAV are much better than those of many other conjugated anthracene-based polymers reported. Furthermore, HSM-PAV-based device shows relatively higher brightness, luminous efficiency and damage-voltage over 2,6-PAV (340 cd/m^2, 0.17 cd/A and 12 V). This might be attributed to the well-separated conjugated polymer chains and the improved film forming of HSM-PAV due to the incorporation of the twist phenyl and an increased number of branched alkyloxy moieties on the side of anthracene.

3.5. Electrical conductivity of HSM-PAV

Iodine doping of HSM-PAV film was carried out in dried and evacuated flask, which can avoid possible complications due to the degradation of the polymer [12e]. Under such doping conditions the electrical conductivity of HSM-PAV film rose from $\sigma < 10^{-5}$ S cm^{-1} (before doping) up to $\sigma = 2.5 \times 10^{-1}$ S cm^{-1} (after doping with iodine for 24 h). This value was several order higher than that of doped 9,10-anthracene-based polymers [20,21], which is ascribed to improved molecular conjugation along polymer backbone [15a,d] and further indicate that the electronic and photonic properties of anthracene-based conjugated polymers are highly dependent on both the nature of the active building blocks and the way in which they are linked. Further investigation of their optoelectronic properties is under the way.

4. Conclusions

This study has shown that it is possible to prepare highly soluble, high molecular weight poly(2,6-anthracenevinylene)s (HSM-PAV). The strategy is the introduction of increased number of branched alkyloxy groups into the lateral phenyl rings. The similar absorption and emission spectra in solution and film indicate that the as-synthesized poly(2,6-anthracenevinylene) is fairly rigid and no aggregation is formed in the solid state. HSM-PAV film doped with iodine shows a high electrical conductivity (2.5×10^{-1} S cm^{-1}) due to a good conjugation pathway formed by 2,6-linkage. The increased solubility and molecular weight not only endow poly(2,6-anthracenevinylene) with improved electroluminescence properties but also enable the synthesis of soluble copolymers containing 2,6-anthracenevinylene unit. This work has laid a material foundation on further investigation of other optoelectronic properties of 2,6-anthracenevinylene-based polymers.

Fig. 4. EL spectra of the device ITO/PEDOT:PSS/HSM-PAV/Ba/Al recorded at various voltages.

Acknowledgment

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