Wide band gap cross-linkable semiconducting polymer LED

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Abstract

A new derivative (PVK-Ox) of poly(vinyl carbazole) (PVK) was prepared by tethering oxetane pendants to the carbazole group through the decamethylene spacer. Photo-patternability of this new PVK-based polymer was investigated through photo-crosslinking reaction under UV light illumination (λ = 312 nm). We show that the chemical modifications as well as the cross-linking reaction do not degrade the optoelectronic performance of the starting polymer. The potential use of wide band gap cross-linkable polymers as electron-blocking layer is demonstrated. The results indicate that photolithography based on photo-crosslinking is a viable device fabrication tool for organic electronics.

Keywords: Poly(vinyl carbazole); Crosslink; LED; Polymer; Photolithography

1. Introduction

The production of conjugated polymer-based electronics requires a wide range of processing techniques to address the broad range of applications being envisaged. The photo-crosslinking functionality that enables the use of photolithography compatible processes is one potential path that is being explored. The reports on cross-linkable light emitting polymers include single and multilayer devices [1–3] as well as photo-patterned devices [4–6] which are based on the synthesis of new polymers that carry cross-linkable, luminescent pendent groups. The photo-initiated cross-linking method renders the exposed parts of the film insoluble and hence allows for multilayer deposition (from solution) as well as standard photolithography resolution. In a recent, paper it was shown that cross-linking can also be introduced using a material formulation approach [7]. In that paper, a cross-linkable arylamine blue polymer is used as a host for orange, yellow, and green emitting PPVs. Since the processing reported in Ref. [7] preserved the PPVs electroluminescent properties, it seems that UV cross-linking is not necessarily a function that contradicts photoluminescent properties. In this paper we perform a comparison between poly(vinyl carbazole) (PVK) and PVK bearing cross-linkable oxetane side groups (PVK-Ox). We find that the addition of the cross-linking functionality on the carbazole pendants has no effect on the material properties compared to the noncross-linkable polymer. We demonstrate its use as a device building block in a double layer conjugated peptide LED where it serves as an electron-blocking layer.

2. Experimental

2.1. Synthesis of PVK-Ox

Poly(vinyl carbazole) (PVK, $M_n = 124,600$ and $M_W = 667,500$), $n$-butyllithium (2.5 M solution in hexane), [4-[(2-
hydroxytetradecyl]oxyl-phenyl]phenyldonium hexa-fluoroantimionate (photo-initiator) were purchased from Aldrich Chem. Co. (USA). Synthesis of PVK-Ox is outlined in Scheme 2. Synthetic details of PVK-Ox are to a solution of PVK (I, 2.00 g/10.3 mmol) in purified THF (120 mL) was added dropwise at −78 °C a solution (3.30 mL/10.3 mmol) of 2.5 M n-butyllithium in hexane via a syringe over a period of 30 min followed by dropwise addition of a solution of the bromodecyloxymethyl-substituted (II, 2.63 g/10.3 mmol) in THF at −78 °C. The mixture was slowly warmed up to and maintained at room temperature for 12 h with continuous stirring. The reaction mixture was washed several times with water, dried over anhydrous MgSO4, and filtered. The solvent in the filtrate was removed by evaporation under a reduced pressure (ca. 10−1 Torr). The recovered product was dissolved in THF and the solution was poured into 500 mL of methanol to precipitate the polymer. The resulting polymer was redissolved in THF and again reprecipitated into 500 mL of methanol. The collected polymer was further purified by Soxhlet extraction through methanol to remove the low molecular weight oligomers and impurities. The precipitated polymer was dried in a vacuum oven to yield 1.80 g (70%) of PVK-Ox (III).

2.2. Film preparation

All film preparation, cross-linking steps and cyclic voltammogram (CV) measurements were made inside an inert glove box (<1 ppm O2 and H2O). Films were spin coated from PVK-Ox solution in THF (15 mg/mL), which additionally contained 1 wt.% (relative to PVK-Ox) of the photocatalyst, (4-[2-(hydroxytetradecyl)-oxyll]-phenyl]-phenyldoniumhexafluoroantimionate, as initiator (see Scheme 1) for the cationic polymerization of the oxetane units. The solution of PVK-Ox was spin coated at 1000 rpm for 1 min and dried at 70 °C for 30 min under vacuum. Films were irradiated by standard handheld UV lamp (λmax = 312 nm) for 3 min at 130 °C, dried for 30 min on a hot plate at the same temperature, washed by THF and dried for 3 min on a plate at +150 °C. The irradiation was carried out at close to Tg temperature to enhance the chain motion and thus increase the cross-linking efficiency.

2.3. Thermal transition measurements

The thermal transition temperatures were determined under N2 atmosphere using a Mettler Toledo DSC 821e (Greifensen, Germany) differential scanning calorimeter. The heating and cooling rates were kept at 10°C/min. Indium was utilized as reference for calibrating the temperature. Tg was estimated to be the midpoint temperature of the endothermic baseline shift.

2.4. Cyclic voltammogram, PL quantum efficiency, UV–vis spectra, and LED preparation

The samples for cyclic voltammogram measurements were prepared as films on ITO substrate as a working electrode by spin coating. The samples were examined at the scan speed 0.1 V/s in a cell containing 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF6) as supporting electrolyte in anhydrous acetonitrile. Platinum wire was used as a counter electrode and an Ag/AgNO3 (0.01 M in acetonitrile) as a reference electrode, respectively. The onset potential (Eonset) of p-doping has been used to determine the HOMO energy level by means of the empirical relationship proposed in Ref. [9]. This relationship connects the solid-state IP (HOMO) to the Eox using the relations IP (EHOMO) = −(Eox + 4.4) (eV), where EHOMO is the HOMO energy level below the vacuum. The value of 4.4 represents the difference between the vacuum level potential of the saturated calomel electrode (SCE) and the potential of the Ag/AgNO3 electrode. The LUMO level is deduced based on the optical absorption gap.

The PL spectral measurements and PL quantum efficiency measurements were performed on an integrated system based on the FS920 fluorimeter by Edinburgh Instruments Ltd. (UK). The PL quantum efficiency measurements were carried out using IS-040-SL Integrating sphere (Labsphere) that was fiber coupled to the FS920 and the procedure was as described in Ref. [10].

The UV–vis absorption spectra of polymer films (ca. 100 nm thick) were recorded on a Beckman (CA, USA) DU-640 spectrometer.

The LEDs were prepared on patterned glass/ITO substrates purchased from Psiotec Ltd. (UK). The ITO was cleaned by solvents and oxygen plasma (conditions equivalent to etch of 350 nm of polyimide) prior to the deposition of the PEDOT layer. All the following steps were performed inside an inert glove box. PEDOT was annealed at 110 °C under dry vacuum for 3 h. The semiconducting polymer film was spun coated on top of the PEDOT layer and later exposed to UV (315 nm) light. The final film was washed and then annealed at 110 °C under dry vacuum for 3 h. Top contact was 10 nm of Ca followed by 200 nm of Al both evaporated at 0.1 nm/s and at a pressure of ~5 × 10−7 Torr.

3. Results and discussion

3.1. 1H NMR analysis and the molecular weight definition of synthesized PVK-Ox

As shown in Scheme 2 PVK (I) was first lithiated by reacting with n-butyllithium at −78 °C, which then was alkylated by o-bromoalkyloxymethyloxetane (II). According to elemental and 1H NMR analysis, the obtained polymer (III) contains 10 mol% of substituted PVK unit as depicted in Scheme 2. The possibility of the presence of the disubstituted structure was neglected, because lithiation on the both phenyl rings of the PVK repeating unit is expected to be much less probable.

The molecular weight of PVK-Ox determined by GPC measurement with polystyrene as the calibration standard was...
Scheme 2. Synthesis route for PVK-Ox.

Fig. 1. CV of PVK-Ox films in 0.1 M solution of CH\textsubscript{3}CN + TBAPF\textsubscript{6}. The dashed and solid lines were measured for a film before and after the cross-linking process, respectively.

$$M_n = 121,000 \text{ and } M_w = 667,000 \text{ with a polydispersity index (PDI) of (5.5). The molecular weight the PVK sample measured by us under the same condition was } M_n = 124,600 \text{ and } M_w = 539,800. \text{ It is believed that the chemical reactions performed on PVK did not degrade the polymer chains as expected. The } T_g \text{ of PVK-Ox (150} ^\circ \text{C}) \text{ is significantly lower than that of the PVK polymer (200} ^\circ \text{C}) \text{ most probably due to the presence of the long pendant groups.}

3.2. Optoelectronic characterization

Cyclic voltametry of PVK-Ox before and after the cross-linking process are shown in Fig. 1. The measurement procedure is outlined in Section 2. The deduced HOMO and LUMO levels are 5.2 and 1.7 eV, respectively (see also Table 1). These values are exactly the same as those (5.2 and 1.7 eV) of unsubstituted PVK.

In order to quantify the cross-linking efficiency we measured the absorption and PL spectrum of the as prepared and of the cross-linked, and washed films (see Fig. 2). From the absorption spectrum we deduce the relative fraction of the film that was left after the thorough washing and define it as the cross-linking efficiency. This cross-linking efficiency was about 80%. To follow the photoluminescence properties of PVK-Ox through the various processing stages we measured its PL quantum efficiency after each step. Table 1 describes the properties of the PVK-Ox materials under various stages: (1) the pristine

<table>
<thead>
<tr>
<th>Sample</th>
<th>Excitation (nm)</th>
<th>PL peak (nm)</th>
<th>PL quantum efficiency (%)</th>
<th>Band gap (eV)</th>
<th>HOMO (eV)</th>
<th>LUMO (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PVK-Ox, without PI</td>
<td>345</td>
<td>420</td>
<td>6</td>
<td>3.5</td>
<td>5.2</td>
<td>1.7</td>
</tr>
<tr>
<td>PVK-Ox + 1% PI, no X-linked</td>
<td>345</td>
<td>420</td>
<td>4</td>
<td>3.5</td>
<td>5.2</td>
<td>1.7</td>
</tr>
<tr>
<td>PVK-Ox + 1% PI, X-linked and washed</td>
<td>345</td>
<td>420</td>
<td>6</td>
<td>3.5</td>
<td>5.2</td>
<td>1.7</td>
</tr>
<tr>
<td>PVK-Ox, Aldrich</td>
<td>345</td>
<td>420</td>
<td>5</td>
<td>3.5</td>
<td>5.2</td>
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<td>PVK, Aldrich</td>
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film without photo-initiator (PI), (2) the film with 1 wt.% PI, and (3) the film with the PI after cross-linking and washing. For reference we also included two PVK polymers of different $M_w$ as purchased from Sigma–Aldrich. We note that the non-reacted photo-initiator (PI) quenches 30% of the PL and that after the cross-linking process this quenching disappears. As Table 1 shows, the PL quantum efficiency (PLQE) of PVK-Ox (6%) is the same as the PLQE measured for PVK without the oxetane side groups.

After deducing that the photoluminescence properties of cross-linked PVK are as good as those of pristine PVK films we prepared as a final test single layer LEDs. Fig. 3 shows the current–voltage characteristics of the PVK-Ox LED as well as the external electroluminescence efficiency as a function of applied voltage. The turn on voltage is typical of the large band gap PVK and the external efficiency (0.25%) is relatively high for PVK type LEDs.

The effectiveness of the cross-linking process and the energy levels of PVK-Ox suggest that it should be suitable for other functionalities, such as electron-blocking layer [11] in a double layer device structure. To test this hypothesis we tested LEDs where the active layer is a conjugated peptide polymer [8] having HOMO and LUMO levels at 5.0 and 2.5 eV, respectively. Fig. 4a shows the chemical structure of the optoelectronic peptide used as active layer and Fig. 4b shows schematically the structure of a double layer LED where the PVK-Ox serves as an electron-blocking (hole transporting) layer. Fig. 4c shows the characteristics of two LEDs one of which is a single layer LED (full line) and the second is such that a PVK-Ox layer is inserted between the active peptide layer and the PEDOT layer (dashed line). This figure shows that both the luminance (right axis) and luminance efficiency (left axis) are enhanced by a factor a bit larger than 5. The corresponding enhancement indicates that the PVK-Ox is indeed functioning as an electron-blocking layer as one would expect based on the relative energy levels.

4. Conclusion

Wide band gap cross-linkable materials have been synthesized and characterized. We have shown that the synthesis route as well as the cross-linking procedure does not degrade the performance of the polymer with respect to the same polymer without the cross-linking moiety. To substantiate the photexcitation data we also constructed blue LEDs that are cross-linked and insoluble having efficiency values similar to the non-modified PVK polymer. Finally, we showed that the energy levels of PVK combined with the cross-linking functionality provided by the oxetane side groups makes PVK-Ox a good electron-blocking layer.

The results presented here together with those presented earlier for the formulation procedure [7] indicate that photolithography [12] based on cross-linkable luminescent films is a viable fabrication tool. The wide band gap of the polymer used here makes it a good device building block that could serve either as a host for red, green, and blue polymers on top of being a hole transporting & electron-blocking layer. Namely, extending the cross-linkable family of polymers to wider band gap ones is of real importance.

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References