Polymer 53 (2012) 2001–2007

Contents lists available at SciVerse ScienceDirect

Polymer

journal homepage: www.elsevier.com/locate/polymer

Synthesis and characterization of fluorene-derived PU as a thermo cross-linked hole-transporting layer for PLED

Ching-Nan Chuang [a], Chao-Hui Kuo [a], Yu-Shan Cheng [a], Chih-Kai Huang [a], Man-kit Leung [a,c,*], Kuo-Huang Hsieh [a,b,*]

[a] Institute of Polymer Science and Engineering, National Taiwan University, Taipei 106, Taiwan
[b] Department of Chemical Engineering, National Taiwan University, Taipei 106, Taiwan
[c] Department of Chemistry, National Taiwan University, Taipei 106, Taiwan

ARTICLE INFO

Article history:
Received 19 December 2011
Received in revised form
5 March 2012
Accepted 8 March 2012
Available online 15 March 2012

Keywords:
PLED
Polyurethane
Hole-transporting material

ABSTRACT

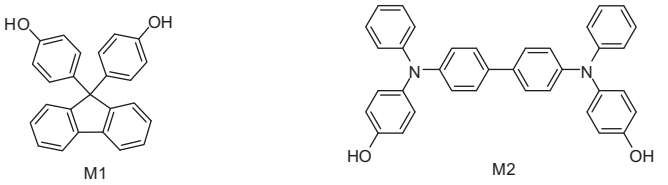
Novel hole-transporting polyurethane, denoted as **P1**, resulting from the condensation of 9, 9-bis(4-hydroxyphenyl)fluorene and isophorone diisocyanate (denoted as IPDI) has been developed. When **P1** is thermally consolidated in the presence of 2-(phosphonooxy)ethyl methacrylate (**P2M**), it forms a distinguished hole-transport layer that leads to an extremely good performance of the phosphorescent PLED. In the study, the device of ITO/PEDOT: PSS/**P1**-**P2M**/Ir(ppy)$_3$-*t*-PBD-PVK/Mg/Ag shows a high current efficiency of 27.6 cd/A and a low turn-on voltage of 6 V. In particular, the stable output efficiency of 17–22 cd/A within the range of 420–4400 cd/m^2 at 12–20 V makes **P1** a promising hole-transport material for phosphorescent PLED applications.

1. Introduction

Organic electronic polymers have attracted considerable interest because of their applications in polymer light-emitting diodes (PLEDs) [1–5], organic thin-film transistors (OTFTs) [6–8], flexible flat-panel display [9] and photovoltaic cells [10,11]. Among the classes of electroluminescent (EL) conjugated polymers, poly(*p*-phenylenevinylene)s (PPVs) [12] and poly(9,9-dialkylfluorene)s (PFs) [13] are two families that have attracted a lot of attention during the past decade. PFs and their derivatives are promising blue-light-emitting materials that are widely used in PLEDs due to their excellent thermal and chemical stability, as well as their high photoluminescence (PL) quantum yield [14–17] and π-electron excessive (electron-rich) in nature and hence have better hole-injection and hole-transporting ability [18–21]. However, the mismatched HOMO energy level of 5.8 eV [22,23] builds up a high hole-injection barrier, and an unbalance charge injection could lead to poor performance of the organic electronic devices. To solve this problem, there are two strategies have been adopted, one is through appropriate design of chemical structure and the other is optimized of the device structure. For the first strategy, the incorporation of hole-transporting moieties on a main or side chain, such as triphenylamine, is usually adopted to improve hole-injection from anode [24,25]. For the second strategy, multilayer devices are required and fabricated by adding an extra hole-transporting layer (HTL), such as poly(styrenesulphonate):poly(3,4-ethylenedioxythiophene) (PEDOT: PSS), to reduce the hole-injection barrier from anode [26,27]. An ideal device should have a smooth charge carrier injection, and balanced charge transport properties in the polymer layer. The presence of a high injection barrier usually results in a high driving voltage, which leads to an increased thermal loading for the polymer layer; therefore, a good hole-transporting layer (HTL) plays a very important role in fabricating a high efficiency multilayer PLED. It bridges the hole-injection from an indium tin oxide (ITO) anode into a light-emitting layer (EML), which results in balanced charge-injection/transport and better device performance. Material to be used as an efficient HTL in multilayer PLEDs has to possess very good solvent resistance for multilayer processing. To achieve this purpose, either photo- or thermally cross-linked hole-transporting materials or a suitable solvent combination are usually employed to consolidate the bottom layer [28–37]. Recently, Wong reported that fluorene derivatives show good charge transport behavior [38,39]. Certain challenges are posed, however, for carrier-transport properties that are both fundamental and practical interest, because linear conjugated polymers in films generally have a strong tendency to form crystalline domains. Although sporadic reports exist oncarrier-transport

* Corresponding authors. Institute of Polymer Science and Engineering, National Taiwan University, Taipei 106, Taiwan. Tel.: +886 2 33663044; fax: +886 2 33661673.
E-mail addresses: mkleung@ntu.edu.tw (M.-k. Leung), khhsieh@ntu.edu.tw (K.-H. Hsieh).

0032-3861/$ – see front matter © 2012 Elsevier Ltd. All rights reserved.
doi:10.1016/j.polymer.2012.03.023



Scheme 1. Structure of **M1** and **M2**.

properties as a function of polymer lengths in crystalline states of some conjugated polymers, such as polythiophenes and polyacenes [40–44], however, they give no representation of the generally amorphous (disordered) situation in polymer films. To obtain a truly amorphous film to study, diaryl substituents have been introduced at the C9 of fluorene, leading to enhanced morphological stability of the amorphous phase and exhibiting intriguing non-dispersive ambipolar carrier-transport properties. The other method was to isolate the function group, such as ether linkage, silane, alkyl chain, urethane, etc. The usage of this kind of linkage realizes an unlimited mixing of active side groups and causes a stable morphology, since both migration and aggregation are significantly suppressed by fixing the active molecules as side groups [45,46].

Polyurethanes (PUs) are common polymers that are widely used in industrial applications due to their properties: elasticity, flexibility, thermal stability, and excellent chemical resistance [47–52]. Several studies on the applications of PUs on PLEDs have recently been reported [53–57]. In our previous reports [36,47,54,55], we demonstrated that polymers with urethane linkages enhance hole-injection performance between PEDOT: PSS and EML.

In this work, two series of polyurethanes were synthesized and characterized: the first series comprised the homopolymers of fluorene type polyurethane (**P1**) and triphenylamine type polyurethane (**P5**). The second series comprised the copolymers of triphenylamine-co-9, 9-bis(4-hydroxyphenyl)fluorene derivatives (**P2**–**P4**) [58–62]. PUs were ideal candidates in our study due to their metal-ion-free synthetic pathway. A low level of metal-ion contaminants is an essential requirement for high performance electronic polymers. PUs were prepared from condensation of diols and diisocyanates, in which no metal-ion-containing reagents were involved so that metal-ion contaminations could be avoided.

2. Experimental

2.1. Materials

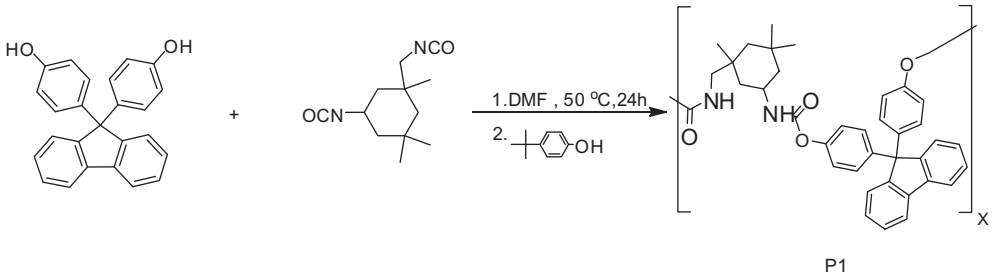
N, N′-bis(4-hydoxyphenyl)-*N, N′*-diphenylbenzidine was prepared in our previous work [55]. Reagent grade chemicals and solvents were purchased from Aldrich, ACROS, Fluka, and Lancaster Chemical Co. THF, dichloromethane and DMF were dried over sodium/benzophenone, P_2O_5 and calcium hydride respectively and freshly distilled before use. Tetrabutylammonium perchlorate (TBAP) was recrystallized twice from ethyl acetate and vacuum-dried for two additional days. The other chemicals were used without further purification. The chemical structures for all of the products were confirmed by ^{1}H NMR spectroscopy, mass spectra (FAB) and elemental analyses.

2.2. Characterization methods

^{1}H NMR spectra were measured on a Bruker 400 MHz spectrometer. Elemental analyses were measured using an EA Heraeus Vario EL-3 analyzer. FT-IR spectra were recorded on a Jasco-480 spectrometer. UV–Vis analyses were obtained from a Jasco V-570 UV–Vis spectrophotometer. The number-average and weight-average molecular weight of the polymers were determined by a Waters GPC-480 system with a column of AM GPC Gel (10 μm) from the American Polymer Standard Company. Dimethylformamide (DMF) was used as eluent and polystyrene as the standard in the GPC experiments. TGA and DSC were performed on a TGA Perkin–Elmer TGA-7 and a DSC Du Pont 2010 analyzer under nitrogen atmospheric conditions at a heating rate of 10 °C min^{-1}. The thickness of the polymer films was measured using an Alpha step Dektak 3030 profilometer. PL spectra of the polymers were recorded using a Hitachi-4500 spectrofluorometer. Cyclic voltammetric measurements of the material were made in DMF with 0.1 M tetrabutylammonium perchlorate (TBAP) as the supporting electrolyte at a scan rate of 100 mV/s. Platinum wires were used as both the counter and working electrodes, and silver/silver ions (Ag in 0.1 M AgCl solution) was used as the reference electrode. Ferrocene was used as an internal standard, and the potential values were obtained and converted to vs. SCE (saturated calomel electrode) [63]. Electroluminscence was recorded on a Minolta CS-100A instrument. The *I–V* and *L–V* characteristics of the devices were measured by integrating a Keithley 2400 source-meter as the voltage and current source and a Minolta CS-100A instrument as the Luminance detector. All of the measurements and device fabrications were performed at room temperature in a dust-controlled environment.

2.3. Device fabrication

Two kinds of device structures were adopted in this study. The first type of device was fabricated with ITO/PEDOT: PSS/PUs/Ir(ppy)$_3$ + PVK+*t*-PBD/Mg/Ag where there was no thermal cross-linked agent contained in the PUs layer. The second device contained a cross-linked agent [2-(phosphonooxy)ethyl methacrylate (**P2M**)] in the PU layer which was thermally cross-linked prior to metal vapor deposition. The ITO surface was cleaned by sonication, and rinsed sequentially in de-ionized water, Triton-100 water solution, de-ionized water, acetone, and methanol. For the previous structure, the hole-injection material: PEDOT: PSS was spin-coated



Scheme 2. PUs synthetic route of the fluorene type (**P1**).