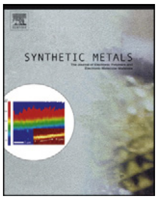
Synthetic Metals 161 (2011) 1186–1193

Contents lists available at ScienceDirect

Synthetic Metals

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



Increasing of stability depended on the position of alkoxy group in PPV

Suhee Song[a], Sung Heum Park[b,e], Jaeyeon Jung[a], Il Kim[c], Kwanghee Lee[e], Youngeup Jin[d,*], Hongsuk Suh[a,**]

[a] Department of Chemistry and Chemistry Institute for Functional Materials, Pusan National University, Busan 609-735, Republic of Korea
[b] Department of Physics, Pukyong National University, Busan 608-739, Republic of Korea
[c] The WCU Center for Synthetic Polymer Bioconjugate Hybrid Materials, Department of Polymer Science and Engineering, Pusan National University, Busan 609-735, Republic of Korea
[d] Department of Industrial Chemistry, Pukyong National University, Busan 608-739, Republic of Korea
[e] Department of Materials Science and Engineering Gwangju Institute of Science and Technology, Gwangju 500-712, Republic of Korea

ARTICLE INFO

Article history:
Received 22 February 2011
Received in revised form 24 March 2011
Accepted 25 March 2011
Available online 14 May 2011

Keywords:
PLED
Color stability
PPVs
Fluoro

ABSTRACT

In order to prevent the photo oxidation of the vinylene group of poly(*p*-phenylenevinylene) (PPV) series, the poly(*p*-phenylenedifluorovinylene) (PPDFV) derivatives with difluoro groups on vinylene unit were synthesized by Gilch polymerization using potassium tertbutoxide. The stability of the PPDFV backbone is attributed to the electron-withdrawing effect of the fluoro groups which prohibit the initial step of [2+2] cycloaddition for the oxidation of the vinylene unit. In photo-degradation experiments with white light, the PL spectra of *m*-EHOPh-PPDFV film is blue shifted about 19 nm and the optical density of the side peak at 380 nm is increased to 0.5 atomic unit. In case of *p*-EHOPh-PPDFV, the PL spectra show almost same maxima peaks at 448–450 nm after irradiation from 1 h to 5 h. *p*-EHOPh-PPDFV with *para*-alkoxy phenyl group shows very stable PL spectra against photo oxidation as compared to the case of *m*-EHOPh-PPDFV with *meta*-alkoxy phenyl group.

1. Introduction

Various kinds of conjugated polymers have been developed for polymer light-emitting diodes (PLEDs) [1–3], organic photovoltaics (OPVs) [4–6], thin-film transistors [7–8], and sensors [9]. PLEDs attract scientific and industrial interests due to several advantages such as tunable emission colors and favorable solution processability [10] including ink-jet printing [11] and roll-to-roll process [12]. Many conjugated polymers, such as poly(*p*-phenylene) (PPP) [13], poly(phenylenevinylene) (PPV) [14], polyfluorene (PF) [15] and poly(4*H*-cyclopenta[*def*]phenathrene) (PCPP) [3,16], have attracted much attention for optoelectronic devices[17] and a large number of studies have been reported.

Although PPVs have advantage of facile polymerization to provide high molecular weight and easy color tuning, color stability of the device is a problem caused by photo-oxidative degradation after irradiation with white light or operation of the device [18–20]. It is reported that singlet oxygen adds in a 2π–2π cycloaddition to the double bond which connects phenylene groups in PPV derivative [18]. Electron rich olefins are known to readily yield dioxetanes upon reaction with singlet oxygen [21]. In order to reduce oxidation of the vinylene group, fluorinated vinylene was introduced in PPV backbone, which reduced the electron delocalization of the polymer backbone caused by the electron-withdrawing effect of fluoro atoms [22–24]. The absorption spectra of PPV polymers with fluorinated vinylene units have shown a blue-shift as compared to non-fluorinated PPV polymers, which was attributed to the reduction of the effective conjugation length [22,25].

In this paper, we report the synthesis and properties of new conjugated polymers for EL utilizing new back-bone, poly(1-(3′-(2-ethylhexyloxy)-1′-phenyl)-2,5-phenylenevinylene) (*m*-EHOPh-PPV), poly(1-(3′-(2-ethylhexyloxy)-1′-phenyl)-2,5-phenylenedifluorovinylene) (*m*-EHOPh-PPDFV), poly(1-(4′-(2-ethylhexyloxy)-1′-phenyl)-2,5-phenylenevinylene) (*p*-EHOPh-PPV), and poly(1-(4′-(2-ethylhexyloxy)-1′-phenyl)-2,5-phenylenedifluorovinylene) (*p*-EHOPh-PPDFV). In order to reduce photo-degradation, *m*-EHOPh-PPDFV and *p*-EHOPh-PPDFV were synthesized using of vinylene unit substituted with difluoro groups. *p*-EHOPh-PPDFV with *para*-alkoxy phenyl group and difluoro substituted vinylene unit was found to have higher stability against photo oxidation than *m*-EHOPh-PPDFV with *meta*-alkoxy phenyl group. Our investigation was focused on the stability of the PPDFV series against photo-oxidation, and optical properties in the solid state.

---

* Corresponding author. Tel.: +82 51 629 6426.
** Corresponding author. Tel.: +82 51 510 2203; fax: +82 51 516 7421.
E-mail addresses: yjin@pknu.ac.kr (Y. Jin), hssuh@pusan.ac.kr (H. Suh).

0379-6779/$ – see front matter. Crown Copyright © 2011 Published by Elsevier B.V. All rights reserved.
doi:10.1016/j.synthmet.2011.03.032

Table 1
Polymerization results and thermal properties of polymers.

Polymer	M_n[a]	M_w[a]	PDI[a]	DSC (T_g)[b]	TGA (T_d)[c]
m-EHOPh-PPV	35,000	130,000	3.7	77	412
m-EHOPh-PPDFV	25,000	40,000	1.6	88	402
p-EHOPh-PPV	125,000	252,000	2.0	79	400
p-EHOPh-PPDFV	8000	14,000	1.6	74	385

[a] Molecular weight (M_w) and polydispersity (PDI) of the polymers were determined by gel permeation chromatography (GPC) in THF using polystyrene standards.

[b] Glass transition temperature measured by DSC under N_2.

[c] Onset decomposition temperature (5% weight loss) measured by TGA under N_2.

2. Results and discussion

2.1. Synthesis and characterization

The general synthetic routes toward the monomers and polymers are outlined in Schemes 1 and 2. The 3-bromophenol **(1)** and 4-bromophenol **(10)** were alkylated with ethylhexylbromide **(2)** using KOH to generate 3-bromophenyl-2-ethylhexyl ether **(3)** and 4-bromophenyl-2-ethylhexyl ether **(11)**, respectively. The compounds **3** and **11** were coupled with the Grignard reagent prepared by adding 2-bromo-*p*-xylene to generate 3-(2-ethylhexyloxy)-2′,5′-dimethyl-1,1′-biphenyl **(4)** and 4-(2-ethylhexyloxy)-2′,5′-dimethyl-1,1′-biphenyl **(12)**, respectively. Compounds **4** and **12** were then brominated with NBS in CCl_4 and light source (300 W) to afford 2,5-bis(bromomethyl)-3′-(2-ethylhexyloxy)-1,1′-biphenyl **(5)** and 2,5-bis(bromomethyl)-4′-(2-ethylhexyloxy)-1,1′-biphenyl **(13)**, respectively. The resulting dibromides were fluorinated with TBAF by nucleophilic substitution reaction using fluoride ion to afford 3-(2-ethylhexyloxy)-2′,5′-bis(fluoromethyl)-1,1′-biphenyl **(6)** and 4-(2-ethylhexyloxy)-2′,5′-bis(fluoromethyl)-1,1′-biphenyl **(14)** which were brominated again using NBS and light source in CCl_4 to generate monomers, 2′,5′-bis(bromo(fluoro)methyl)(1,1′-biphenyl)-3-yl-2-ethylhexyl ether **(7)** and 2′,5′-bis(bromo(fluoro)methyl)(1,1′-biphenyl)-4-yl-2-ethylhexyl ether **(15)**, respectively. The monomers (5, 7, 13 and 15) were used for the preparation of *m*-EHOPh-PPV, *m*-EHOPh-PPDFV, *p*-EHOPh-PPV and *p*-EHOPh-PPDFV, respectively, by Gilch polymerization, employing an excess amount of potassium *tert*-butoxide in THF at 0 °C for 24 h. The resulting polymers were soluble in organic solvents such as chloroform, tetrahydrofuran (THF), dichloromethane, and chlorobenzene.

Table 1 summarizes the polymerization results including molecular weights, PDIs and thermal stability of the copolymers. The polymers have number-average molecular weight (M_n) of 8000–35,000 and weight-average molecular weight (M_w) of 14,000–252,000 with PDI (poly dispersity index, M_w/M_n) value of 1.6–3.5. The thermal properties of the polymers were evaluated by differential scanning calorimetry (DSC) and thermo gravimetric analysis (TGA) under nitrogen atmosphere. All of the polymers show good thermal stability, with glass transition temperature (T_g) of polymers at around 77 °C for *m*-EHOPh-PPV, 88 °C for *m*-EHOPh-PPDFV, 79 °C for *p*-EHOPh-PPV and 74 °C for *p*-EHOPh-PPDFV, estimated by DSC performed in the temperature range from 30 to 250 °C. As shown in Fig. 1, their decomposition temperatures (T_d), which correspond to a 5% weight loss upon heating during TGA, are 412, 402, 400 and 385 °C for *m*-EHOPh-PPV, *m*-EHOPh-PPDFV, *p*-EHOPh-PPV and *p*-EHOPh-PPDFV, respectively. The decomposition temperatures of *m*-EHOPh-PPDFV and *p*-EHOPh-PPDFV were slightly lower than that of the polymers without fluoro groups. The polymers exhibit good thermal stability which is important for the application of the polymers in organic light emitting diodes.

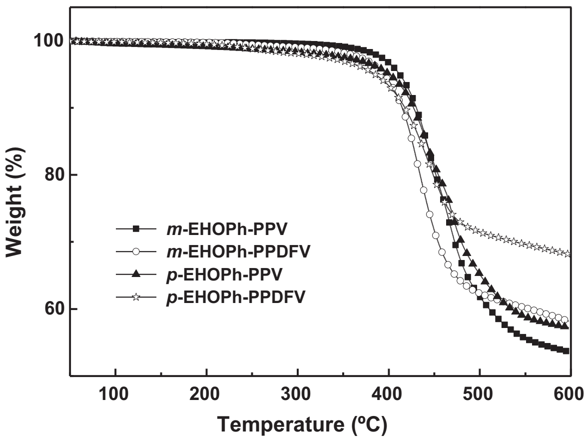


Fig. 1. Thermogravimetric analysis of the polymers under N2.

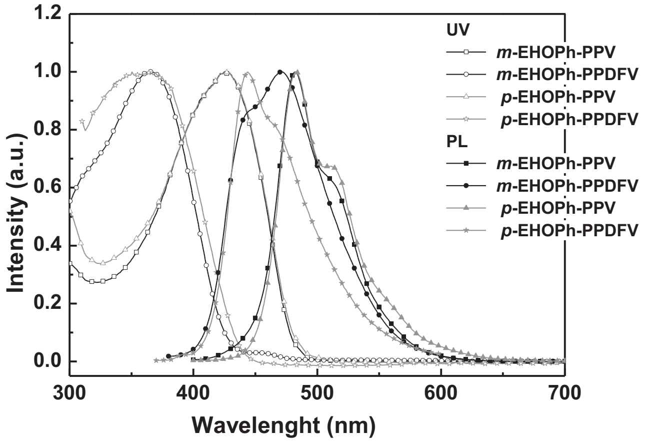


Fig. 2. UV–vis absorption and photoluminescence spectra of the polymers in the chloroform solution.

2.2. Optical properties

The UV–vis absorption and photoluminescence (PL) emission spectra of the polymers as solution and thin film are shown in Figs. 2 and 3 and summarized in Table 2. The solution was prepared using chloroform as solvent and the thin film was prepared by spin-coating on quartz plates from the polymer solutions in chlorobenzene. The maximum absorption peaks appeared at

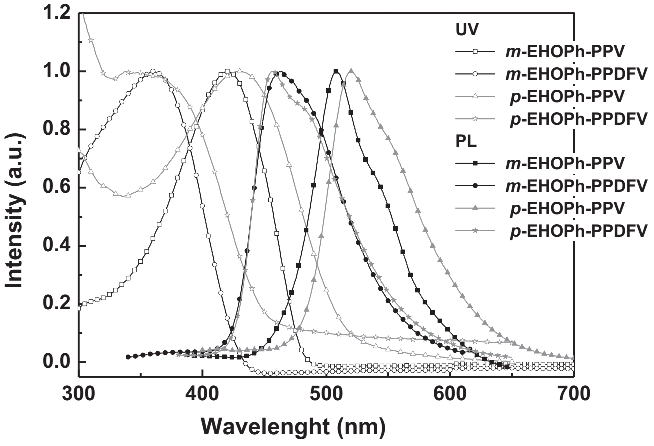


Fig. 3. UV–vis absorption and photoluminescence spectra of polymers in thin film.