

INFLUENCE OF TRACES OF WATER ON THE SYNTHESIS AND ELECTROLUMINESCENCE PROPERTIES OF POLY(2-METHOXY, 5-(2'-ETHYLHEXYLOXY)-1,4-PHENYLENE VINYLENE)*

Yue-qi Mo, Jian Huang, Jia-xin Jiang, Xian-yu Deng, Yu-hua Niu and Yong Cao**

*Institute of Optoelectronic Materials & Devices, College of Material Science and Engineering,
South China University of Technology, Guangzhou 510640, China*

Abstract It was found that traces of water in the reaction medium would result in a great increase of gel and a decrease of molecular weight of the poly(2-methoxy, 5-(2'-ethylhexyloxy)-1,4-phenylene vinylene) during the polymerization, which ultimately led to inferior film qualities and device properties. The device (ITO/PEDOT/MEH-PPV/Ba/Al) with MEH-PPV prepared under dry conditions has an external quantum efficiency of above 2.0%.

Keywords Poly(phenylene vinylene), Light-emitting diodes

INTRODUCTION

Poly(*p*-phenylene vinylene)(PPV) and its derivatives have been one of the most popular conjugated polymers applied in light-emitting diodes since 1990^[1]. The first soluble PPV – poly(2-methoxy, 5-(2'-ethylhexyloxy)-1,4-phenylene vinylene) (MEH-PPV)^[2] – is a very important and widely utilized light-emitting polymer due to its low cost, simplicity of synthesis and high yield. Since MEH-PPV has relatively high external quantum efficiency, it is extensively used in many laboratories. However, the synthesis of MEH-PPV is difficult to control due to gelation during the polymerization^[3]. The origin of the gelation during MEH-PPV polymerization and its influence on the device properties were investigated in this study.

EXPERIMENT

Materials

2-Methoxy, 5-(2'-ethylhexyloxy)-1,4-bismethylchlorobenzene was synthesized according to the literature^[2], *t*-BuOK was purchased from Aldrich. Dioxane was refined by refluxing with sodium under N₂ flow for 2 days and distilled off before use^[4]. Water rich dioxane is prepared by adding water to dioxane.

Polymerization

1 g 2-Methoxy, 5-(2'-ethylhexyloxy)-1,4-bismethylchlorobenzene (3 mmol) dissolved in 150 mL dioxane was stirred at 97°C under N₂ flow, and 2 g *t*-BuOK (18 mmol) dissolved in 30 mL dioxane was added within 0.5 min. After refluxing for 1/2 h, the mixture was cooled down and 150 mL ethanol/water solution (1:1) was added to precipitate out the red polymer (first precipitation). The red precipitate was collected and washed with water and ethanol for 3 times and dried under vacuum at room temperature. The polymer was re-dissolved in 150 mL xylene and filtered through a glass filter (pore size = 30–50 μm, G2) to remove the insoluble gel (second

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** Corresponding author: Yong Cao (曹镛), E-mail: poycao@scut.edu.cn

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precipitation). Ethanol was added to the resulting red solution to precipitate out the MEH-PPV polymer. The polymer obtained was dried in a vacuum oven at RT for 24 h. The precipitate was dissolved in xylene inside a dry box filled with nitrogen and the solution was filtered through 5 μm filter (Millipore) before spin-coating.

Measurement

The water content in refined dioxane was determined by a Shimadzu GC-17A gas chromatograph. The molecular weight of MEH-PPVs was measured with a HP GPC 1011 instrument. IR spectra of MEH-PPV in KBr matrix were recorded on a Vector33 FTIR spectrometer.

Fabrication of Devices and Their Characterization

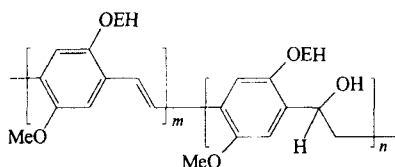
The emission spectra were recorded with an Oriel Instaspec-4 CCD detection system. Photoluminescence PL spectra were excited using the 325 nm line of an Omnichrome Series 56 HeCd Laser (Melles Griot).

Polymer light-emitting diodes (PLEDs) were fabricated using MEH-PPV as the active luminescent layer. The thickness of the emitting layer was 70 nm, as determined by surface profilometer (Tencor, Alfa-Step 500). Indium/tin oxide (ITO) was used as the anode. A 200 nm thick PEDOT-PSS Baytron P (Bayer Corporation product for ITO surface mending and hole injection enhancing) was incorporated by spin coating between ITO and emitting layer. A thin layer of Ba was deposited on the top of emitting layer as the cathode. Finally, 200 nm thick Al layer were thermally evaporated onto the top of Ba as a capping layer. The deposition rates of Ba and Al the thickness of the evaporation layers were monitored by a thickness/rate meter (Sycon) at a deposition rates of 0.05–0.1 nm/s and 1–2 nm/s, respectively. The cathode area defined the size of the emitting area as 0.15 cm². All the experimental steps were carried out in a nitrogen glove box except for spin-coating of PEDT-PSS. The current versus voltage (*I*-*V*) curve, the light output versus voltage (*L*-*V*) curve and the external quantum efficiency were measured with a Keithley 236 source-measure unit and a calibrated silicon photodiode.

RESULT AND DISCUSSION

Influence of Trace of Water on the Synthesis of MEH-PPV

In order to find out whether trace water in the polymerization medium is responsible for the gelation, a small amount of water was introduced purposely into the well purified dioxane for comparison. It was found that the water content in dioxane purified according to the standard procedure was 0.0086% measured from its gas chromatogram. Additional 0.1% water was added to such purified dioxane. The yield and solubility of MEH-PPV prepared by polymerization in refined dioxane (sample A) and in dioxane with additional 0.1% water (sample B) were given in Table 1, indicating that MEH-PPV polymerized in water-rich medium has higher gel content and lower solubility in *p*-xylene. There are at least other 3 structural features: (1) The molecular weight of sample B is higher than that of sample A; (2) There is a larger amount of hydroxyl groups in sample B



Scheme 1 Molecular structure of MEH-PPV containing hydroxyl groups

Table 1. Gel content and solubility of two kinds of MEH-PPVs

Sample	Water content in dioxane	Weight remained after 1 st precipitation	Weight remained after 2 nd precipitation	Weight loss after filtration with G2 filter	Max. concn. of MEH-PPV in xylene*	Filtration through 5 μm filter
A	0.0086%	0.40g	0.25g	0.15g	0.5%–0.7%	easy
B	0.1086%	0.45g	0.10g	0.35g	0.2%–0.3%	hard

* Maximum concentration which can be reached without visible precipitation.

(Scheme 1). (3) There are larger amounts of crosslinking or branching structures in sample B than in sample A (structure C in Scheme 2).

Molecular Weight of MEH-PPV

The molecular weight of sample A and B (after it was filtered through 5 μm filter) was given in Table 2.

Table 2. Molecular weight of sample A and B			
Sample	M_w (10^4 g/mol)	M_n (10^4 g/mol)	M_w/M_n
A	93.622	12.255	7.6393
B	32.257	2.800	11.5170

It was found that the molecular weight of sample A was much higher than that of B, whereas A has better solubility than sample B (Table 1). This means that MEH-PPV with very high molecular weight ($M_w >$ about 0.9 million for sample A) can still have excellent solubility in organic solvent such as tetrahydrofuran and chloroform, *etc.* Unfortunately, the high M_w fraction ($M_w >$ 0.4 million) in sample B has formed the gel and been filtered off.

IR Analysis

IR spectra of sample A (spectrum A) and B (spectrum B) after filtration through a 5 μm filter and sample B before filtration (spectrum C) are shown in Fig. 1.

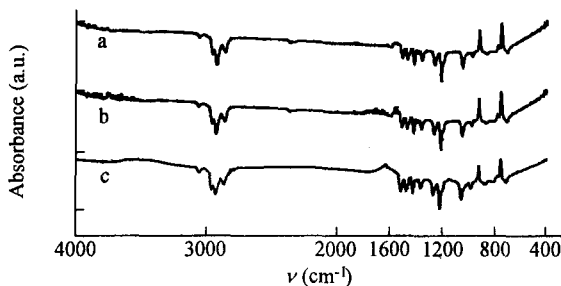


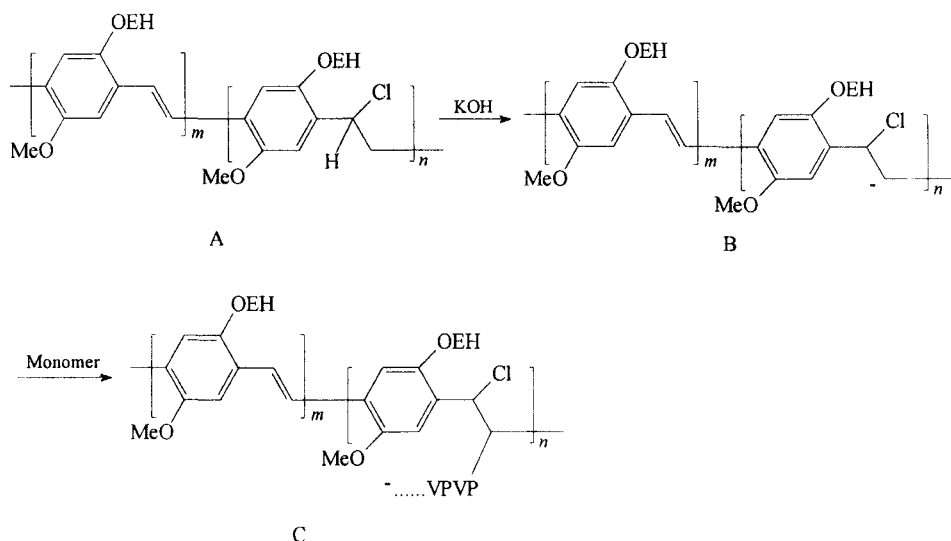
Fig. 1 IR spectra of sample A (spectrum A) and B (spectrum B) after filtration through 5 μm filter and sample B before filtration (spectrum C)

The second possibility is that there are larger amounts of hydroxyl groups in sample B (Scheme 1). It was deduced from the fact that the polymerization was carried out in the dioxane with additional water in the case of sample B, the precursor of MEH-PPV may be hydrolyzed (replacing chloride atoms). Hydroxyl groups attached to main chain of MEH-PPV may limit the solubility of the resulting MEH-PPV in non-polar organic solvent such as *p*-xylene and THF.

It was found that there are no obvious differences between the IR spectra A, B and C. The absorption vibrations at 3056 cm^{-1} and 968 cm^{-1} which are assigned to the olefinic C—H stretch and the *trans*-substituted olefinic C—H bend respectively are very evident. No obvious —OH stretching vibrations (3200–3600 cm^{-1}) are observed in the IR spectra even in sample B with gel. Additionally, C—O stretching vibration ($\sim$ 1100 cm^{-1}) of the secondary alcohol is not found. There are no distinguishable differences in the ^1H -NMR spectra of sample A and B, either.

As there are no characteristic IR bands related to the hydroxyl group either in sample A or in sample B, the amount of hydroxyl group present in MEH-PPV must be below the detection limit (*i.e.*, $< 1\%$ – 2%) of the instrument. It is hardly thinkable that a hydroxyl group content less than 1% – 2% could lead to such low solubility. We prefer the third hypothesis according to which a minimal amount of crosslinking or branching will decrease the solubility of polymer rapidly. *t*-BuOK will be hydrolyzed in the water-containing medium and turned into KOH, which is insoluble in dioxane. The precursor polymer chains would attach these micro-particles

and α -H atoms would be stripped off and the anion polymerization begun (Scheme 2). Further ^{13}C -NMR could cast light upon this problem.



Scheme 2 Supposed mechanism of crosslinking or branching during polymerization

Properties of Device

The electroluminescence spectra (Fig. 2) of sample A and B are almost identical with an emission maximum at 585 nm. The I - V / L - V characteristics of the devices prepared from sample A and B fabricated under the same conditions are shown in Fig. 3. It was found that the turn-on voltages of both samples were 3.0 V, while the electroluminescence intensity of sample A (1000 cd/m^2 at 4.2 V and 2800 cd/m^2 at 5.0 V) was much higher than that of sample B (100 cd/m^2 at 4.2 V and 300 cd/m^2 at 5.0 V). Figure 4 shows the QE- V and L- V characteristics of sample A and B. It was found that the external quantum efficiency was about 2.4% and 1.2% for sample A and sample B, respectively at 4.2 V. These results clearly indicate that a little modification in the chemical structure of emitting polymer has remarkable influence on the device performance. It will be interesting to see how a further decrease in water content of dioxane used in MEH-PPV polymerization could affect the device performance. In order to keep the water content extremely low in the reaction medium, it is important to remove the water fully from the solvent and all starting materials in the polymerization reaction, and to assure thorough drying of all the apparatus used during polymerization. Work in this direction is in progress.

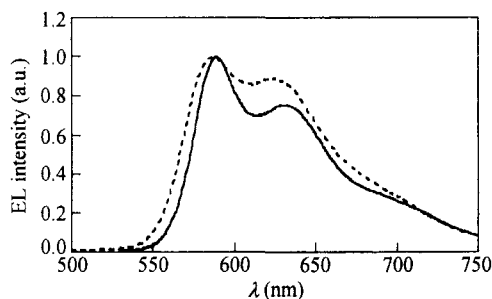


Fig. 2 EL spectra of sample A (—) and B (---)

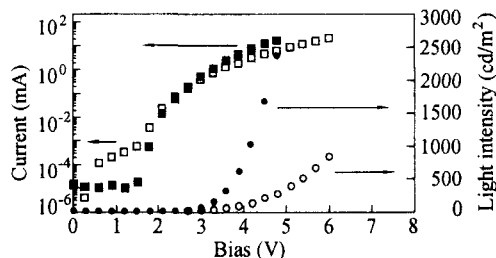


Fig. 3 I- V ($\square$, $\blacksquare$) and L- V ($\circ$, $\bullet$) characteristics of sample A ($\blacksquare$, $\bullet$) and B ($\square$, $\circ$)

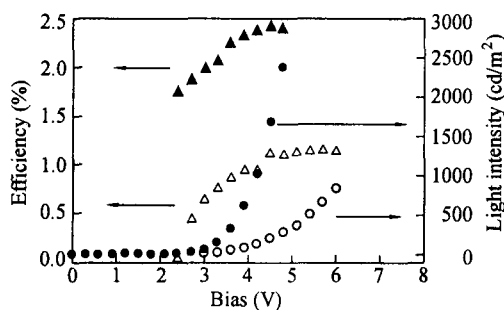


Fig. 4 QE-V (Δ , $\blacktriangle$) and L-V ($\circ$, $\bullet$) of sample A ($\blacktriangle$, $\bullet$) and B (Δ , $\circ$)

CONCLUSION

Trace of water during the polymerization resulted in an increase of gel and a decrease of solubility of MEH-PPV, which, in turn, will impair the device performance. The device made from polymer prepared under the dry conditions shows improved external quantum efficiency of above 2.0%.

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