

Synthesis and Discussion of 3-hexylthiophene related rigid copolymers for Optical Devices

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Abstract

Two conjugated copolymers, poly{(9,9-dihexyl-fluorene)-random-(3-hexylthiophene)} (PTFR) and poly{(9,9-dihexyl fluorene)-alt-(3-hexylthiophene)} (PTFA) were obtained by using Kumada coupling based on 3-hexylthiophene moiety unit. The fluorescence (PL) and ultraviolet (UV) optical properties of these polymers were compared with poly(9,9-dihexylfluorene) and poly(3-hexylthiophene), and the fluorescence light emitting range cover from 400 to 550 nm which can be used for polymer white light emitting device and organic solar cell.

Keywords: conjugated polymer, organic solar cells, Kumada coupling.

1. Introduction

Since the first report of polymer light-emitting diodes (PLEDs) in 1990, the development of conjugated polymers are huge. Especially, polythiophene and its derivatives (PTs), which are special conductive and optoelectronic materials [1-3]. Polyfluorenes are attractive class of polymer semiconducting material for electroluminescent, which synthesis easy and color tunable. To combine these two materials via nickel-catalyzed Kumada cross-coupling method, a random and a alternative copolymers base on 3-hexylthiophene and 9,9-dihexyl-2,7-dibromofluorene repeating units were synthesized.

2. Experimental details

The detail synthesis steps and chemical structures of the copolymers are shown in Fig. 1 and Fig. 2.

All monomer have purified by crystallization, reduce pressure distillation, or reaction under dry nitrogen atmospheres. Polymers were purified via flash column chromatography to remove nickel catalysis.

3. Results and Discussion

Figure 3 shows copolymers PTFR and PTFA structure identify by using proton nuclear magnetic resonance spectra (NMR), which characters of poly(3-aklythiophene) are around 2.8 ppm and 6.9 ppm [5]. If these two peaks are broaden with multiple

peaks, that means conformation of 3-aklythiophene is in random type (Fig. 3a.). If the peaks are indented, the polymer structure is in regular conformation. Fig. 3b shows two peaks at the position of 6.9 ppm and 7.05 ppm respectively were resulted from different regular arrangement, head to tail form (H-T) and tail to tail form (T-T).

Figure 4 and Figure 5 are UV-Vis absorption spectra and fluorescence spectra of PTFA.

Figure 4 indicates PTFA and PTFR have similar energy gap from UV-Vis absorbance. The energy gape was approximately between 2.7 ~ 2.8 eV in solid film. PTFA and PTFR both have similar maximum absorption around 375 nm in UV-Vis absorbance in solution and solid film. The width of these absorption peaks across ~ 100 nm shown that these two materials have stable energy gap.

In figure 5, PTFA PL spectra had red shift about ~60nm from solution to solid film. PTFR only slightly shifted about 10 nm - 20 nm, which indicates that PTFA have regular conformation and results in better structural aggregation in solid film as than PTFR.

4. Conclusions

The 3-hexylthiophene related rigid copolymers were obtained. The PL and UV spectra show that they cover wide range of visible light area and can be used in white light emitting diode and organic solar cell. The PTFA has regular structure which is easier resulting in aggregation form while comparing to PTFR random form.

References

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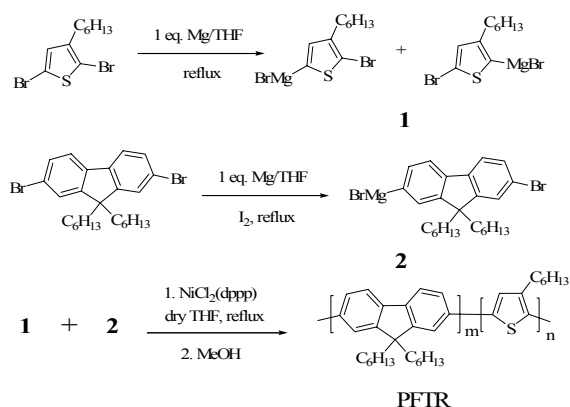


Fig. 1. Synthesis of PTFR

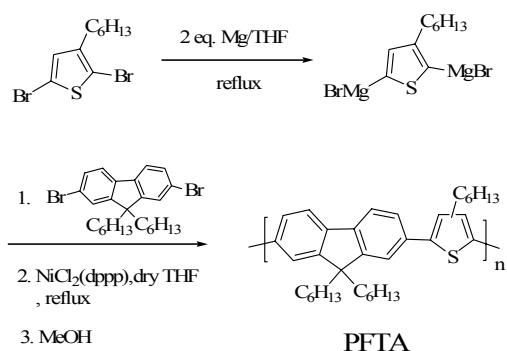


Fig. 2. Synthesis of PTFA

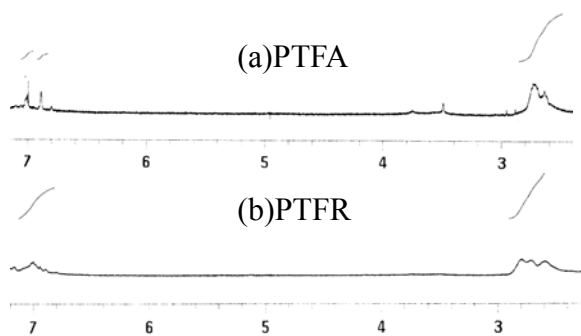


Fig. 3. ¹H NMR spectra of (a)PTFA and (b) PTFR

Table 1. Number average (M_n) and weight average (M_w) of PTFR and PTFA. Determine by GPC, RI detector.

Polymer	M_n	M_w	M_w/M_n
PTFR	2900	9200	3.17
PTFA	2600	7000	2.69

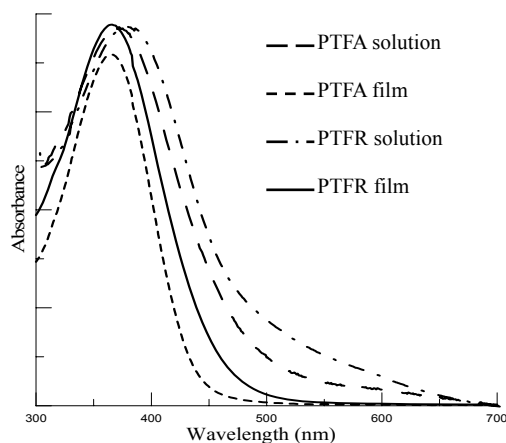


Fig. 4. The PTFA and PTFR measured from the films on quartz plates and 0.1 wt% CHCl_3 solution in quartz cell at room temperature.

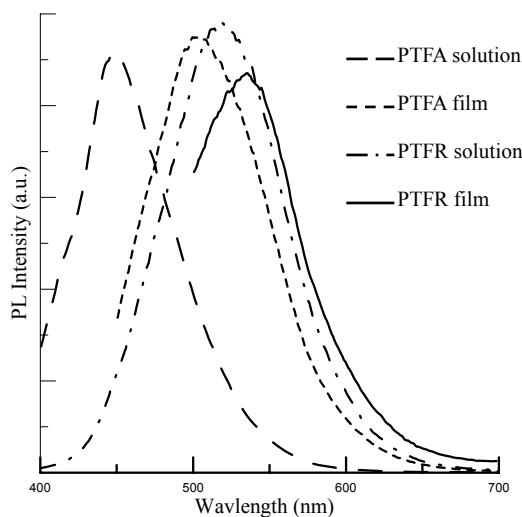


Fig. 5. The PL spectra of PTFA and PTFR measured from the films on quartz plates and 0.1 wt% CHCl_3 solution in quartz cell at room temperature.