Synthesis and Characterization of a New p-type Amorphous Conjugated copolymer for Solution Process OTFT Material

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Abstract

A new p-type conjugated copolymer, poly(9,10-diethynylanthracene-alt-9,9-didodecylfluorene (PDADF) was synthesized through a Sonogashira coupling reaction. A solution-processed thin film transistor device showed a carrier mobility value of 6.0 X 10^{-4} cm^2/Vs with a threshold voltage of -17 V and a capacitance (C_i) of 10 nF/cm^2.

1. Introduction

Poly(arylenethynylene)s of general formular [Ar-C≡C-Ar']n are promising candidate among the conjugate polymers for use as organic semiconducting molecules such as the active layer in light-emitting diodes[1-2] or as organic thin film transistors.[3-4] Polymer semiconductors for OTFTs have advantages such as good film-forming[5-6] attribute; moreover, they enable solution processability through the use of spin-coating and inkjet printing involving inexpensive solution deposition techniques.[7-8]

In here, a new ethynyl-linked alternating anthracene/fluorene copolymer for an organic thin film transistor is designed. The newly designed copolymer is expected to have high mobility and ambient stability due to the ethynyl-linked anthracene and fluorene with a feasible π-system. Furthermore, the introduction of long alkyl group on the fluorene can increase the degree of orderness by self-assembly and can increase the solubility in the most common organic solvents.

2. Experimental

9,10-Bis(trimethylsilanylethynyl)anthracene was efficiently synthesized by the reaction of trimethylsilylethynyl and dibromoanthracene obtained from the bromination of anthracene in the presence of $PdCl_2(PPh_3)_2$, PPh_3, and CuI using a 3:1 mixture of toluene/diisopropylamine as a solvent. 9,10-Diethynylanthracene was synthesized by deprotection of 9,10-Bis(trimethylsilanylethynyl)anthracene with 1*N*-NaOH in methanol/diethyl ether. 2,7-Diiodo-9,9-didodecyl-fluorene was obtained by diiodination following the alkylation process. The newly conjugated copolymer was synthesized through a palladium(II)-catalyzed Sonogashira coupling reaction with 9,10-diehtynylanthracene, 2,7-diiodo-9,9-didodecyl-fluorene, $PdCl_2$(dppf), and CuI in THF (150 mL) and triethylamine (30 mL). After polymerization, the polymer was end-capped with 2-ethynylnaphthalene to remove the terminal iodo group that can deteriorate the property of the polymer.

3. Results and discussion

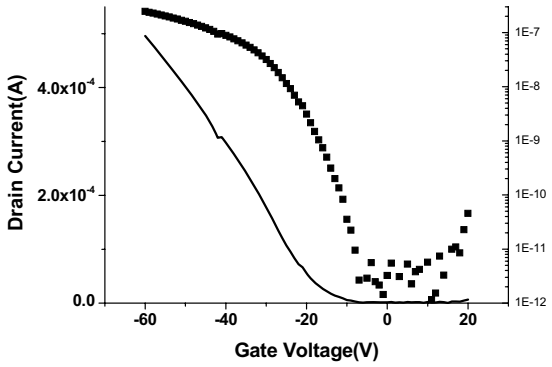
The obtained copolymer is highly soluble in common organic solvents (1.0 wt%) such as chloroform, methylene chloride, chlorobenzene, and toluene at room temperature. The copolymer was determined through gel permeation chromatography (GPC) analysis to have a number-average molecular weight (Mn) of 22,800 and a weight-average molecular weight (Mw) 29,300. The polydispersity

index (PDI) was 1.29 with respect to a polystyrene standard. The structure of the copolymer was confirmed by ^{1}H-NMR, ^{13}C-NMR, FT-IR, and elemental analysis. The thermal properties of the copolymer were evaluated by TGA and DSC. The glass transition temperature (Tg) of the polymer was not observed after heating 300 ℃. Table 1 shows a normalized UV-vis absorption maximum and PL emission maximum of a solution ($CHCl_3$) and of spin-coated film, respectively. The absorption maximum for the film was broadened and red-shifted as compared to that of the solution. This result suggests that the polymer will have good mobility due to its high intermolecular interaction. Moreover, a large red shift from the solution to the film, suggesting that the polymer can form π-π stacking by aggregation, was observed. The electrochemical properties of the polymer were investigated by cyclic voltammetry (CV). The oxidation onset of the polymer was 1.19 eV. The optical band gap of the polymer was 2.03 eV as calculated from the threshold of the absorption edge at 610 nm. The HOMO level of the polymer was determined to be – 5.62 eV.

TABLE 1. Photochemical property

	UV_{max}		PL_{max}	
Value	solution	film	solution	film
	514 nm	522nm	568 nm	608 nm

The polymer thin-film transistor was found to exhibit p-channel FET type characteristic in the transfer and output curves (Figure l). The carrier mobility of PDADF was 6.0 X 10^{-4} cm^2/Vs with a measured capacitance (C_i) of 10 nF/cm^2. In order to elucidate the crystal structure of the polymer, grazing incident angle X-ray diffraction (GIXD) was utilized.



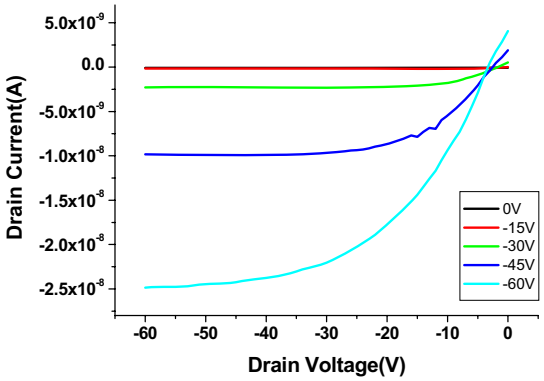
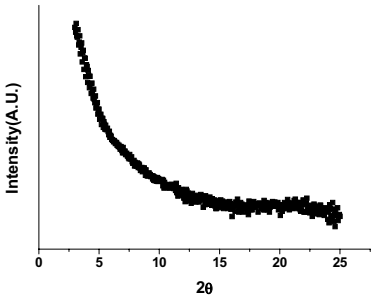


Fig. 1. OTFT characteristics of the PDADF

Figure 2 shows a out-of-plane and in-plane GIXD patterns of spin-coated polymer on SiO_2 dielectric surface that show only an amorphous halo near $2\Theta=20^0$. No Bragg peaks and only a broad amorphous halo indicate no long range order and only the existence of a short range order consisting of the most probable distances between neighboring atoms, or an amorphous state. From the X-ray diffraction result, it is suggested that the relatively low mobility of the polymer is due to its amorphous morphology.

(a)



(b)

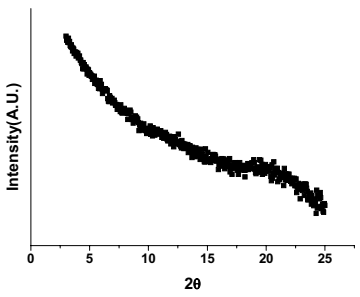


Fig. 2. Out-plane (a) and In-plane (b) grazing incidence XRD data for PDADF.

4. Summary

A new ethynyl-linked alternating anthracene/fluorene copolymer was designed in this study. It has a relatively planar configuration for an organic thin film transistors due to the introduction of ethynyl moieties. The polymer showed not only good thermal stability but also high π-stacking due to intermolecular interaction. A thin-film transistor with this polymer was found to exhibit typical p-channel FET characteristic with a hole mobility of 6.0 X 10^{-4} cm^2/Vs cm^2 V^{-1} s^{-1} and an on/off ratio of 10^4 with a threshold voltage of -17 V and a capacitance (C_i) of 10 nF/cm^2.

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