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Communications

Synthesis of Donor-Acceptor Alternating Copolymer by Uncatalyzed Condensation Polymerization

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Introduction

Organic semiconductors that consist of conjugated polymers (CPs) are the subject of considerable current research interest, owing to their fundamental optoelectronic properties and their potential applications ranging from photodiodes to light emitting devices (LEDs), thin-film transistors (TFTs), and photovoltaic cells (PVs).[1-8] Solution-processable organic semiconductors are required for printing low-cost TFT circuits *via* solution deposition/patterning processes.[9,10] Donor-acceptor (D-A) copolymer systems are known for intrachain push-pull charge transfer, which has been used to synthesize more conjugated, lower band gap polymers having extended overlap with the solar spectrum.[11-13] Many researchers have also sought to reduce the band gap by using a D-A approach. Recently, D-A copolymers can be increased in its mobility due to increasing intermolecular interaction. Thus, organic thin-film transistors (OTFT) using D-A as semiconductor, is for also the studies of mobility. In addition, the charge injector is also very important for organic light emitting devices (OLED) as this can be a shred by balanced charge recombination. Thus, various donor-acceptor copolymers have been developed for such applications. In order to synthesize donor-acceptor, various coupling reaction such as Stille, Suzuki, and Yamamoto coupling, etc were used. Various coupling reaction using catalyst can deterolate their properties, especially, the very small amount of catalyst impurity affects the efficacy and life time of OLED device.

The most interesting CPs are polyfluorene derivatives (PFs), which are reported electroluminescent polymer, and have several advantages as an emitting material.[14-17] The PFs exhibit high photoluminescence (PL) efficiency, good charge transport, thermal stability, and tunability of physical parameters through chemical modification and copolymerization.[14-17] Moreover, substitution at the 9-position with various moieties has also been examined as a mean to control the color emitted by PFs.[18] The physicochemical properties of PFs can be tuned *via* side chain substitution without substantial changing the electronic properties of backbone.[18]

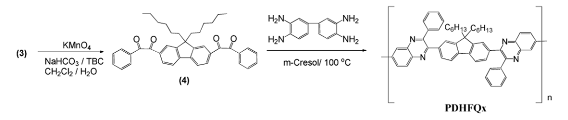
The first soluble PFs was synthesized by the oxidative coupling of 9,9-dihexylfluorene with $FeCl_3$.[19] They have a low molecular weight and structural defects due to the oxidative coupling that does not proceed strictly with regioselectively.[16] The metal-catalyzed cross-coupling reactions require monomers to be functionalized in the 2 and 7 positions which were introduced for the enormous synthetic improvement that guarantee perfect regioselectivity.[16] The Ni(0)-catalyzed Yamamoto and the Pd(0)-catalyzed Suzuki condensation reactions were the most prominent types of reactions used to prepare PFs.[20,21] These reactions are among the most powerful tools in polymer synthesis. However, the significant disadvantage of these reactions is the high cost of the synthesis process. In addition, it is also difficult to remove residual metallic impurities; a potential problem for electroluminescent devices.

To overcome these problems, the design and synthesis of new copolymer with high purity and easy purification are desirable.

In this paper, we report the design and synthesis of acceptor-donor-acceptor (A-D-A) type copolymer, poly[2,2′-(9,9-dihexylflourene-2,7-diyl)-6,6′-bis(3-phenylquinoxaline)] containing 9,9-dihexylfluorene and phenylquinoxaline unit by uncatalyzed condensation reaction (Scheme I).

Results and Discussion

The synthetic procedure used to prepare the monomer and polymer is outlined in Scheme I. The fluorene was treated with *n*-buthyllithum and *n*-hexylbromide to afforded 9,9-



Scheme I. Synthesis of PDHFQx.

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*Corresponding Authors. E-mails: jaeyoung@gnu.ac.kr or ykim@gnu.ac.kr dihexylfluorene **1**, which is purified and further treated with bromine and $FeCl_3$ to afford **2**. Sonogashira coupling of **2** with phenylacetylene gave **3** in yield of 82%. The fourth step of the procedure involved the oxidation of the triple bond to diketone **4**. The polymerization was carried out through condensation reaction of obtained 2,7-bis(phenyloxoacetyl)-9,9-dihexyl-9*H*-fluorene (**4**) and purchased 3,3-diaminobenzidine in *m*-cresol solvent at 100 °C for 24 h. The polymer was isolated by pouring the reaction mixture into methanol. The crude polymer was washed with methanol, water, and methanol again, successively. The polymer dissolves well in common organic solvents including chloroform, dichloromethane, tetrahydrofuran and toluene, and the films can be easily made. The good solubility of the polymer may be originated from the hexyl substituted fluorine unit. The chemical structure identification of polymer was carried out by using FTIR, ^{1}H, and ^{13}C NMR (Figure S1). In the infrared spectrum as shown in the Figure S1 (see the Supplementary Information (SI)), we observed the band around 3051-2846 cm^{-1} region which may be due to the aliphatic -CH_2 and -CH_3 vibrations of hexyl group in PDHFQx. The appearance of the strong band at 2225 cm^{-1} indicates the formation of C=N groups. The absence of the absorption of NH_2, C=O, and presence of C=N group confirms the conversion of PDHFQx. As illustrated in Figure 1, the NMR spectrum indicates the successful synthesis of the PDHFQx. The aliphatic hexyl protons of dihexylfluorene and aromatic protons of phenylquinoxaline and flourene appeared at 0.40-1.23 ppm, and at around 7.18-8.55 ppm, respectively. The integration ratio of aromatic protons and aliphatic protons are also well matched. Furthermore, the area ratio of aromatic and aliphatic carbons was consistent with suggested structure of the copolymer. The copolymer, PDHFQx successfully synthesized by uncatalyzed condensation reaction.

The weight average molecular weight of the copolymer was determined by gel permeation chromatography (GPC) using polystyrene stands for the calculation. A GPC analysis revealed that the weight average molecular weight (M_w) of copolymer of 9,600 with polydispersity index of 1.2. The thermal stability of the polymer was investigated with thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) under nitrogen atmosphere. As shown in the Figure S2 (see the SI), the 5% weight loss was observed at 440 °C for PDHFQx and its glass transition temperature (T_g) was found at 140 °C. From the TGA and DSC thermogram, the resulting polymer had good thermal stability with high T_g. This T_g value is much higher than that about 55 °C of typical poly(9,9-dihexylfluorene),[22] indicating that the incorporation of phenylquinoxaline unit significantly enhances the thermal stability of the dihexylfluorene-based copolymer. It is implied that the polymer will be stable during the manufacturing or operation process of a device at high temperatures. From this point of view, the polymer PDHFQx can be a promising candidate for PLEDs applications.

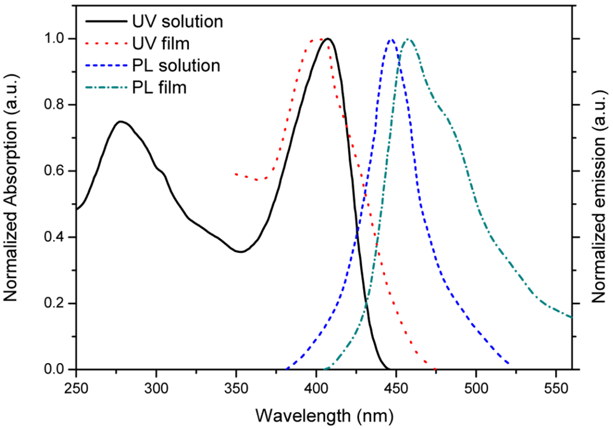

Figure 1. Absorption and PL spectra of PDHFQx in solution and film state.

The photophysical characteristics of PDHFQx were investigated by absorption spectra in $CHCl_3$ solution and in the film spin-coated on glass substrates. Typical absorption spectra of dilute solutions of poly(9,9-dialkylfluorenes) show a sharp peak with max at 375 nm of π-π^* transition.[23,24] Figure 1 shows UV-visible absorption and photoluminescence (PL) spectra of the polymer in solution and film. In solution, the absorption maximum of PDHFQx is red-shifted compared to typical poly(9,9-dialkylfluorenes), due to the presence of phenylquinoxaline acceptor groups in polymer. The optical band gap energy of PDHFQx was calculated to be 2.64 eV from the onset of absorption band at 470 nm. When the dilute solution of PDHFQx in chloroform was excited at 407 nm, the photoluminescence (PL) exhibited a maximum peak at 448 nm, corresponding to blue light emission. The PL spectrum is quite narrow with a full width at half maximum (FWHM) of 36 nm in solution state.

The PL quantum yield of the polymer in $CHCl_3$ solution, measured using anthracene (Φ=0.27) as standard reference is 0.24. The solid PL spectrum showed a maximum peak as 457 nm. Even donor-acceptor type copolymer, the slight red shifted can be explained by twisted backbone caused by steric strain between backbone and phenyl side groups. As a result, the obtained copolymer can be candidate for organic light emitting device as blue emitter polymer.

Cyclic voltammetry (CV) was performed on a film of the copolymer deposited on a carbon electrode measured in $AgNO_3$ (0.01 M)/Bu_4NBF_4 (0.1 M)/acetonitrile with a platinium counter electrode and a silver reference electrode, calibrated against ferrocene-ferrocenium. As shown in Figure S3 (see the SI), the measured oxidation peak potentials of the copolymer were measured to be E_{ox}=0.98 V. The energy levels of the highest occupied molecular orbital (HOMO), the lowest unoccupied molecular orbital (LUMO), and the band gap were estimated from the oxidation onset by using CV and the onset of the absorption spectra. The HOMO and LUMO energy levels for copolymer are 5.38

and 2.74 eV, respectively.

In this study, a new blue-emitting polymer which was composed with fluorene and quinoxaline, was successfully synthesized by uncatalyzed condensation reaction. The molecular structure of polymer was confirmed by FTIR, ^{1}H and ^{13}C NMR studies. The synthesized PDHFQx showed good solubility and higher thermal stability with high T_g of 140 °C. The PL spectrum of PDHFQx showed the blue emission without long wavelength emission due to excimer formation. In particularly, the PDHFQx can be used in low cost solution processable fabrication technologies. These results indicate that polymer can be a candidate blue light emitter in OLEDs.

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Supporting Information: Experimental details, FTIR, ^{1}H, and ^{13}C NMR spectroscopic data, TGA and DSC thermograms, and cyclic voltammogram of PDHFQx. The materials are available *via* the Internet at http://www.springer.com/13233.

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