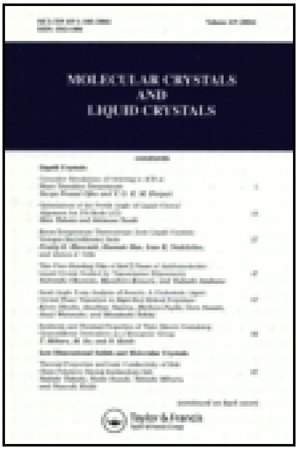

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Synthesis and Properties of Poly(9,9-Dipropargylfluorenylene-Biphenylene)

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Synthesis and Properties of Poly(9,9-Dipropargylfluorenylene-Biphenylene)

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Poly(9,9-dipropargylfluorenylene-biphenylene) was prepared by cross-coupling condensation of 9,9-dipropargylfluorene and 4,4′-diiodobiphenyl in high yield. The polymer structure was identified by various spectroscopic methods such as IR, ^{1}H-, ^{13}C NMR, UV-visible spectroscopies. The acetylenic units in the polymer main chain were found to be thermally crosslinked in the range of 167–278°C. The photoluminescence peak of the polymer is located 396 nm which corresponds to a photon energy of 3.13 eV.

Keywords: cross-coupling condensation; cross-linking; dipropargyl fluorene; internal acetylenic unit; photoluminescence

INTRODUCTION

π-Conjugated oligomers and polymers are intensively studied because of their interesting electrical, optical properties, and their potential utility in electronics and photonic applications [1–5]. Electroluminescent display has advantages of a fast response time, driven at low voltage, obviation of a backlight, an excellent luminance as well as a wide viewing angle [6–8]. A high performance device fabricated by Tang

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Address correspondence to Young-Woo Kwak, Department of Chemistry, Kyungpook National University, Sankyuk-dong, Buk-gu, Daegu 702-701, Korea. E-mail: ywkwak@knu.ac.kr and VanSlyke using two-layer light-emitting diodes (LEDs) with organic fluorescent dyes was a breakthrough in this field [6]. Since then, a number of organic materials have been developed as luminescent materials including low-molecular-weight systems and π-conjugated polymer systems [2–4,9].

Fluorene containing poly(phenylenevinylene) derivatives were good candidates as blue light-emitting organic materials for light-emitting devices [10–12]. The poly(fluorenyleneethynylene)s were prepared by alkyne metathesis of (9,9-dialkyl)fluoren–2,7-yleneethynylenes [13,14]. Some other acetytlenic polymers were also synthesized by palladium-catalyzed coupling reaction between the diiodobenzene and diethyldipropargyl malonate in high yield [15]. Curing of crystalline polydiacetylenes results in the formation of conjugated networks of alternating double and triple bonds still in crystalline arrays transverse to the polymer backbone [16,17]. We have reported the studies on the synthesis and electro-optical properties of 9,9-dipropargylfluorene derivatives with various functional groups [18,19]. And also we reported the spirocyclic conjugated polymers containing a fluorene unit by the cyclopolymerization of 9,9-dipropargylfluorene in the presence of Mo- and W-based transition-metal catalysts [20,21].

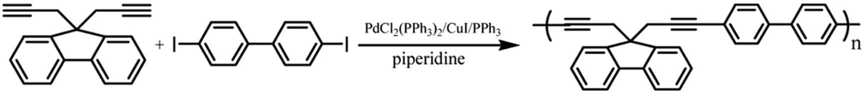
In this paper, we report the synthesis of fluorene-containing copolymer by palladium-catalyzed Heck reaction of 9,9-dipropargylfluorene (DPF) with 4,4′-diiodobiphenyl as well as the thermal behaviors and optical properties of the resulting polymer.

EXPERIMENTAL

Fluorene, 4,4′-diiodobiphenyl, bis(triphenylphosphine)palladium(II) dichloride, cuprous iodide, piperidine, and benzyltriethylammonium chloride were obtained from Aldrich Chemical Co. and used without further purification. The synthesis of 9,9-dipropargylfluorene (DPF) was carried out according to a literature procedure [22]. The polycondensation reaction of 9,9-dipropargylfluorene (0.2 g, 20 mmol) with 4,4′-diiodobiphenyl (0.27 g) were performed at 65°C in piperidine in the presence of $(PPh_3)_2PdCl_2/CuI$ (0.005 g) under nitrogen atmosphere. ^1H and ^{13}C NMR spectra were recorded on a Varian Gemini 200 MHz FT-NMR spectrometer in $CDCl_3$ and the chemical shifts were reported in ppm units with tetramethylsilane (TMS) as internal standard. Infrared spectra were obtained with a Mattson Instrument Genesis II spectrophotometer using a KBr pellet and frequencies were given in reciprocal centimeters. The molecular weights of the polymer were determined by a Shimadzu LC10A gel permeation chromatograph equipped with μ-Styragel columns using THF as an eluent. UV-visible spectra were measured in chloroform by a Thermo Aquamate UV-visible spectrophotometer. Aminco-Bowman II luminescence spectrophotometer (Xen150 W Xenon Lamp) was used for photoluminescence spectra. TGA and DSC thermograms were taken on a Shimadzu DTG60 and DSC60 under nitrogen atmosphere at a scanning rate of 10°C/min.

RESULTS AND DISCUSSION

The palladium-catalyzed coupling reaction was used for the synthesis of fluorene-containing polymer with acetylenic and arylene moieties in the polymer main chain. Poly(DPF-biphenylene) was prepared by palladium catalyzed reaction of DPF and 4,4′-diiodobiphenyl in 95% yield (Scheme 1)



SCHEME 1 Synthesis of poly(DPF-biphenylene).

The molecular weight (Mw) and polydispersity (Mw/Mn) of the resulting polymer were 7.21×10^3 and 2.18, respectively. Poly(DPF-biphenylene) was completely soluble in common organic solvents such as chloroform, chlorobenzene, toluene, and xylene. The polymer structure was characterized by various instrumental methods such as NMR, IR, UV-visible spectroscopies.

In the ^{13}C-NMR spectrum of poly(DPF-biphenylene), the signals for both the ethynylene carbons of DPF at the 80.58 ppm and 72.76 ppm were disappeared, and the new signals of internal ethynylene carbons were appeared at 87.95 ppm and 82.56 ppm, the former one is assigned to the signal of ethynylene carbon adjacent to benzene group in the main chain of the polymer. The ^{13}C-NMR spectrum exhibits 14 peaks, consistent with the chemical structure of repeating unit, which contains 14 different carbons. Using the DEPT technique, which allows one to distinguish between protonated and non-protonated carbons, we can see the various carbon peaks of one propargyl CH_2 and complicated aromatic CH. In the ^{1}H-NMR spectrum of poly(DPF-biphenylene), the CH_2 proton single peak of propargyl group was appeared at 3.01 ppm and the acectylenic proton peak ($\equiv$C$-$H) of DPF was disappeared. Integration ratio of aromatic group and propargyl group was 16.21:4, which matches with theoretical ratio (16:4).

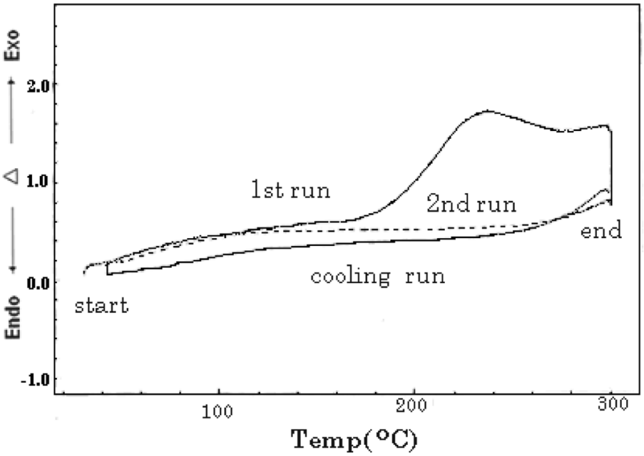


FIGURE 1 DSC thermogram of poly(DPF-biphenylene) [1st run (——) and 2nd run (--------)].

The IR spectrum of poly(DPF-biphenylene) did not show any absorption frequency at 3289 cm^{-1} due to the acetylenic $\equiv$C$-$H stretching absorption frequency, which had been observed in the IR spectrum of DPF. The resulting poly(DPF-biphenylene) were completely soluble in common organic solvents such as chloroform, chlorobenzene, toluene, and xylene.

The thermal behavior of poly(DPF-biphenylene) was examined by differential scanning calorimeter and thermogravimeter. From the DSC thermogram (Fig. 1) of poly(DPF-biphenylene), it was found that a broad exothermic peak was observed around 223°C (started at 151°C) in the first heating, whereas there was no exothermic peak in the second heating. The broad exothermic peak is probably due to the thermal crosslinking of the internal ethynyl groups in the polymer main chain. The TGA thermogram of poly(DPF-biphenylene) revealed that this polymer is thermally stable up to 360°C. The char yield of this polymer was 66% even after heating up to 600°C.

The UV-visible absorption and photoluminescence (PL) spectra of poly(DPF-biphenylene) was showed in Figure 2. The polymer containing biphenyl is not red shifted for the $\lambda_{\max}$ of UV when it is compared with that of poly(PDF) itself. This is probably due to no increase of the extent of π conjugation. The poly(DPF-biphenylene) solution emitted blue weak fluorescence at the excitation wavelength of 350 nm. The UV $\lambda_{\max}$ of poly(DPF-biphenylene) was very similar with those of

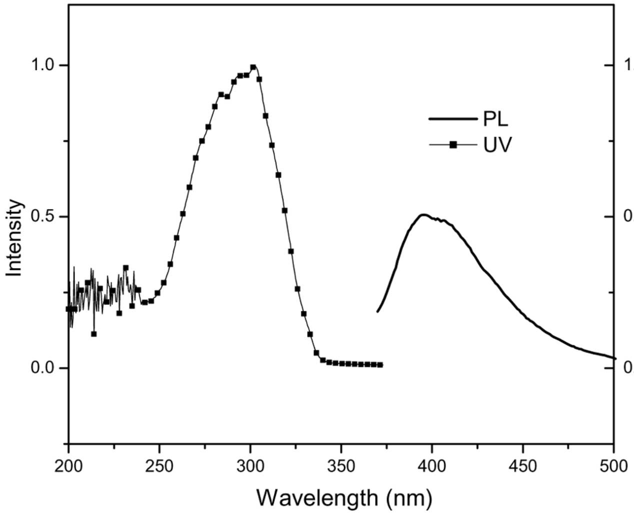


FIGURE 2 Absorption and emission spectra of poly(DPF-biphenylene) in solution.

poly(DPF) and poly(DPF-phenylene), which means no contribution of conjugation effect in polymer backbone. The PL quantum yield of poly(DPF-biphenylene) in chloroform (ca. 1×10^{-5} M) were measured by comparing to quinine sulfate (ca. 1×10^{-5} M) in 0.1 M H_2SO_4 as standard.

The quantum yield (43%) of poly(DPF-biphenylene) was higher than those of poly(DPF-phenylene) (24%) and poly(DPF) (27%) [19, 23]. More high quantum yield of poly(DPF-biphenylene) having biphenylene spaces in the polymer main chain may be explained by the extended conjugation length and/or the molecular bent structure of diethynyl-4,4′-biphenylene moieties.

TABLE 1 Optical Properties of poly(DPF), poly(DPF-phenylene) and poly(DPF-biphenylene)

Polymers	PL λ_{max} (nm)	Stokes shift (nm)	Q.Y. (%)	UV λ_{max} (nm)
Poly(DPF)	417	114	27	303
Poly(DPF-phenylene)	408	105	24	303
Poly(DPF-biphenylene)	396	94	43	302

CONCLUSIONS

Poly(DPF-biphenylene) containing ethynylene group in the polymer main chain was synthesized via palladium-catalyzed Heck-coupling reaction of 9,9-dipropargylfluorene with 4,4′-diiodobiphenyl in high yield. The resulting polymer exhibited good solubility in common organic solvents. The polymer structures were characterized by such spectroscopic methods as NMR, IR, and UV-visible spectroscopies. This polymer was found to be thermally crosslinked by the acetylenic moieties in the polymer main chain in the range of 167–278°C. The PL spectrum of polymer showed that the photoluminescence peak is located at 396 nm corresponding to the photon energy of 3.13 eV.

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