

Synthesis and Properties of Phenylene-containing Copolymer *via* the Catalytic Heck Coupling Reaction of Dipropargyl Group and Terphenyl Group

Bon Kweon Koo^{†,*} and Sang Gu Lee^{‡,*}

[†]Department of Chemistry, Daegu Catholic University, Gyeongsan 38430, Korea. *E-mail: bkkoo@cu.ac.kr

[‡]Research Facilities Center, Daegu Catholic University, Gyeongsan 38430, Korea.

*E-mail: leesg@cu.ac.kr

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INTRODUCTION

As a highly conductive material, polyacetylene which is the most fundamental π -conjugated polymer has been the subject of extensive research.¹⁻³ The conjugated oligomers and polymers are commonly used in electronic devices because of electrical properties and their potential utility in photonic and electronics application.^{4,5} Homocoupling of alkynes for obtaining di- and polyacetylenic compounds, electron-rich compounds that play different roles in biological systems and in industry,⁶ are reactions of considerable interest in organic synthesis.⁷ The reaction can be catalyzed by a variety of metal-based catalytic systems.⁸ The electronics and photonics technologies have opened their materials based to organics, in particular π -conjugated oligomers and polymers.^{9,10} The oxidative-coupling of fluorene compound was used for the synthesis of diacetylene polymer¹¹ and the poly(fluorenyleneethylene)s were prepared by alkyne metathesis of (9,9-dialkyl)fluorene-2,7-yleneethylenes.¹² In 9,9'-spirofluorene of the polymer chains, the fluorene moieties are orthogonally arranged and connected *via* a commonly tetracoordinated carbon.¹³

Dipropargyl monomers offer a variety of synthetic pathways to different polymer structures.^{4,14,15} New crosslinkable acetylenic polymers were prepared by the palladium-catalyzed carbon-carbon coupling reactions between the diiodobenzene and diethyldipropargyl malonate in quantitative yield.¹⁶ The thermal curing behaviors of the resulting materials are related to the polymer structures.^{17,18} In our previous works, we reported the studies on the synthesis and electro-optical properties of 9,9-dipropargylfluorene having reactive acetylenic functionalities.¹⁹⁻²³

Herein, we report the synthesis of new terphenyl-containing polymers *via* the catalytic Heck-coupling reaction of 9,9-dipropargylfluorene and diiodoterphenyl as well as

the thermal behaviors and optical properties of the resulting polymer.

EXPERIMENTAL

Fluorene (Aldrich Chemicals., 98%) was used without further purification. Propargyl bromide (Aldrich Chemicals, 80 wt % solution in toluene) was dried with CaH_2 and distilled under reduced pressure. 9,9-Dipropargylfluorene was prepared by the reaction of fluorene and propargyl bromide with the catalyst of $\text{NaOH/PhCH}_2\text{N}^+\text{Et}_3\text{Cl}^-$ as described in the previous paper.¹⁷

The palladium catalyzed Heck coupling reaction of 9,9-dipropargylfluorene and di-iodoterphenyl was used for the synthesis of fluorene-containing copolymer with acetylene moieties in the main chain as follows. 9,9-Dipropargylfluorene (0.46 g, 1.9 mmol) and the corresponding di-iodoterphenyl (0.84 g, 1.95 mmol), $\text{PdCl}_2(\text{PPh}_3)_2/\text{CuI}$ (0.005 g), and piperidine (12 mL) were introduced in the reaction flask. The reaction was performed at 80 °C for 6 hrs under nitrogen atmosphere. The reaction mixture was poured into 200 mL MeOH with stirring. The precipitated polymer was filtered, and washed with methanol, and then dried in vacuum to give a yellowish powder (polymer yield: 65%).

FT-IR spectra were obtained with a Mattson Instrument Genesis II spectrometer using a KBr pellet. NMR spectra were recorded on a Varian 300 MHz FT-NMR spectrometer in CDCl_3 . The molecular weights of the polymers were determined by a gel permeation chromatographer (Shimadzu LC10A) equipped with μ -Styragel columns using THF as an eluent. TGA and DSC thermograms were taken on a Shimadzu DTG60 and DSC60 under nitrogen atmosphere at a scan rate of 10 °C/min. The UV spectra were measured by a Thermo Aquamate UV-VIS Spectrometer. Shimadzu Spectrofluorophotometer RF-5301PC (Xen150W

Xenon Lamp) was used for photo- and electro-luminescence spectra.

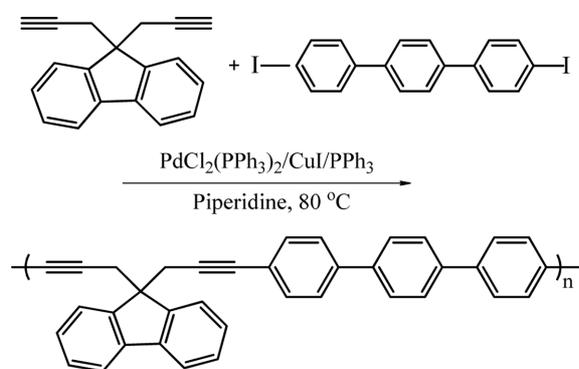
RESULTS AND DISCUSSION

The palladium-catalyzed Heck coupling polymerization reaction of terminal diacetylenic compound and dibromoaromatic compound was used for the synthesis of fluorene-containing polymer with acetylene moieties in the main chain (*Scheme 1*).

The Heck coupling reaction of 9,9-dipropargylfluorene was performed at 80 °C in the presence of PdCl₂(PPh₃)₂/CuI under nitrogen atmosphere. The reaction proceeded homogeneously to give a moderate yield of polymer (65%). The resulting poly(DPF-terphenyl) was completely soluble in common organic solvents such as chloroform, chlorobenzene, toluene, and xylene. The weight-average molecular weight (M_w) of the polymer containing 9,9-dipropargylfluorenes was 3,375 relative to polystyrene standards in gel permeation chromatography.

The polymer structure was characterized by such spectroscopic methods as NMR, IR, and UV-visible spectroscopies. *Fig. 1* shows the FT-IR spectra of DPF and poly(DPF-terphenyl). The IR spectrum of DPF shows strong absorption at 3,275 cm⁻¹ due to the acetylenic ≡C-H stretching absorption. The IR spectrum of poly(DPF-terphenyl) did not show any absorption at 3275 cm⁻¹, which is due to the complete reaction of terminal acetylenic functional groups. The internal acetylenic -C≡C-C≡C- stretching vibration band of poly(DPF-terphenyl) was weakly observed at 2230 cm⁻¹. In the ¹H-NMR spectrum of poly(DPF-terphenyl), the methylene proton peaks of propargyl group (CH₂-C≡C-terphenyl) at 2.51-3.43 ppm was appeared. The broad aromatic fluorene and terphenyl peaks of poly(DPF-terphenyl) were appeared at 7.32-8.35 ppm.

The thermal behavior of poly(DPF-terphenyl) was exam-



Scheme 1. Synthesis of poly(DPF-terphenyl).

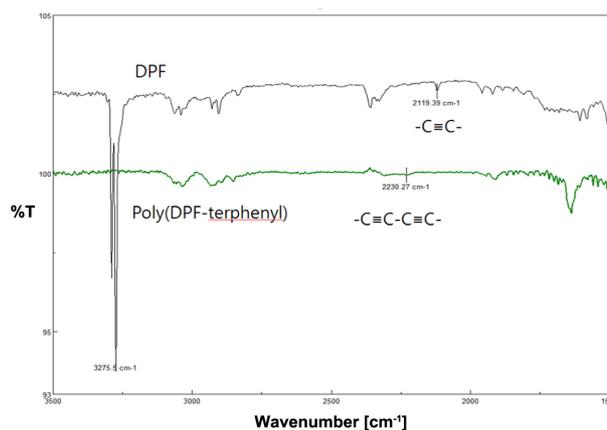


Figure 1. FT-IR spectra of DPF and poly(DPF-terphenyl).

ined by differential scanning calorimeter and thermogravimeter. From the DSC curve of poly(DPF-terphenyl), it was found that a broad exothermic peak was observed around 259 °C and 360 °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 acetylenic groups in the main chain of the polymer. The thermal stability of poly(DPF-terphenyl) was also examined. It showed first rapid weight loss in the range of 325-372 °C and second rapid weight loss was observed in the range of 593-600 °C. The char yield for poly(DPF-terphenyl) after heating up to 600 °C was 62%.

Fig. 2 shows the UV-visible and photoluminescence (PL) spectra of poly(DPF-terphenyl) measured from the solution (8.0×10^{-2} g/L) in chloroform at room temperature. The PL λ_{max} of poly(DPF-terphenyl) was observed in the range of 347-469 nm, which was similarly shifted in comparison with that of poly(DPF-phenyl), a similar homologue with phenylene moieties instead of phenyl moieties. The

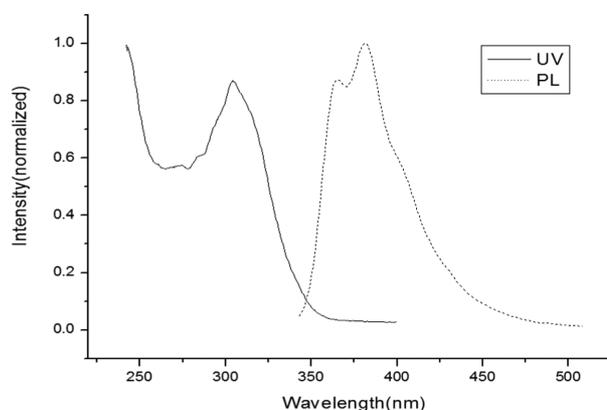


Figure 2. The UV-visible absorption and Photoluminescence spectra of poly(DPF-terphenyl).

solution of poly(DPF-terphenyl) emitted strong fluorescence at the excitation wavelength of 350 nm. The emission spectrum of poly(DPF-terphenyl) shows emission maximum at 382.5 nm, which is corresponding photon energy of 3.24 eV. The PL quantum yield of poly(DPF-terphenyl) in chloroform (1×10^{-5} M) was measured by comparing to quinine sulfate (1×10^{-5} M) in 0.1 M H₂SO₄ as standard. The quantum yield (49.0%) of poly(DPF-terphenyl) is the 2 times higher than that (23.9%) of a similar homologue, poly(DPF-Phenyl), which may be explained by the contribution of terphenyl group in polymer main chain.

CONCLUSIONS

A new fluorene-containing copolymer with acetylene moieties in the main chain was prepared via the palladium-catalyzed Heck coupling reaction of 9,9-dipropargylfluorene and diiodoterphenyl. The resulting polymer was completely soluble in common organic solvents such as chloroform, chlorobenzene, toluene, and xylene. The polymer structure was characterized by such spectroscopic methods as NMR, IR, and UV-visible spectroscopies. Poly(DPF-terphenyl) was found to start the thermal crosslinking of the internal ethynyl moieties at the polymer main chain around 197 °C. The quantum yield of poly(DPF-terphenyl) is the 2 times higher than that of a similar homologue, poly(DPF-phenyl), which is probably due to the contribution of terphenyl moiety in the polymer main chain.

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