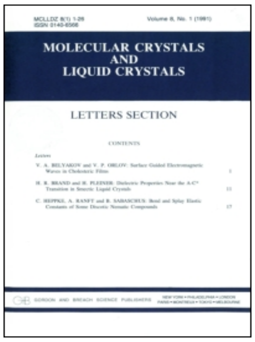
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Synthesis and properties of new fluorene-containing copolymer via the catalytic dehydrocoupling reaction of 9,9-dipropargyl fluorene and 4,4′-diphenyl-2,6-dibromo-dithieno-[3,2-b:2′,3′-d]silole

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ABSTRACT
New fluorene-containing copolymer was prepared via the catalytic dehydrocoupling reaction of 9,9-dipropargylfluorene and 4,4′-diphenyl-2,6-dibromo-dithieno-[3,2-b:2′,3′-d]silole in 44% yield. The resulting polymer was completely soluble in common organic solvents. The thermal behaviors and optical properties of the resulting polymer were measured and discussed. The chemical structure of polymer was characterized by NMR, IR, and UV-visible spectroscopies. The polymer showed characteristic wide UV-visible absorption band and blue PL maximum value at 440 nm, which is corresponding photon energy of 2.82 eV. The quantum yield (6.44%) of poly(DPF-DTS) was found to be 5 times higher than that of poly(DPF-bithiophene)).

KEYWORDS
dehydrocoupling; silole; photoluminescence; quantum yield; fluorene derivative; cross-linking; diacetylenic

Introduction

Polyacetylene is the most fundamental π-conjugated polymer, and this material has been the subject of extensive research since a doped polyacetylene film was found to be highly electrically conductive [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]. The electronics and photonics technologies have opened their materials base to organics, in particular π-conjugated oligomers and polymers [6–7]. Fluorene containing poly(phenylenevinylene) derivatives were good candidates as blue light-emitting organic materials for light-emitting devices and other purposes [8–10]. The oxidative-coupling of fluorene compound was used for the synthesis of diacetylene polymer [11] and the poly(fluorenyleneethylene)s were prepared by alkyne metathesis of (9,9-dialkyl)fluoren-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

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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 [19–22]. Silole derivatives having low-lying LUMO levels have been reported to be useful as electron-transporting materials in EL devices [23].

Herein, we report the synthesis of new silole-containing polymers via the catalytic dehydrocoupling reaction of 9,9-dipropargylfluorene and 4,4′-diphenyl-2,6-dibromo-dithieno-[3,2-b:2′,3′-d]silole 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 $NaOH/PhCH_2N^+Et_3Cl^-$ as described in the previous paper [24].

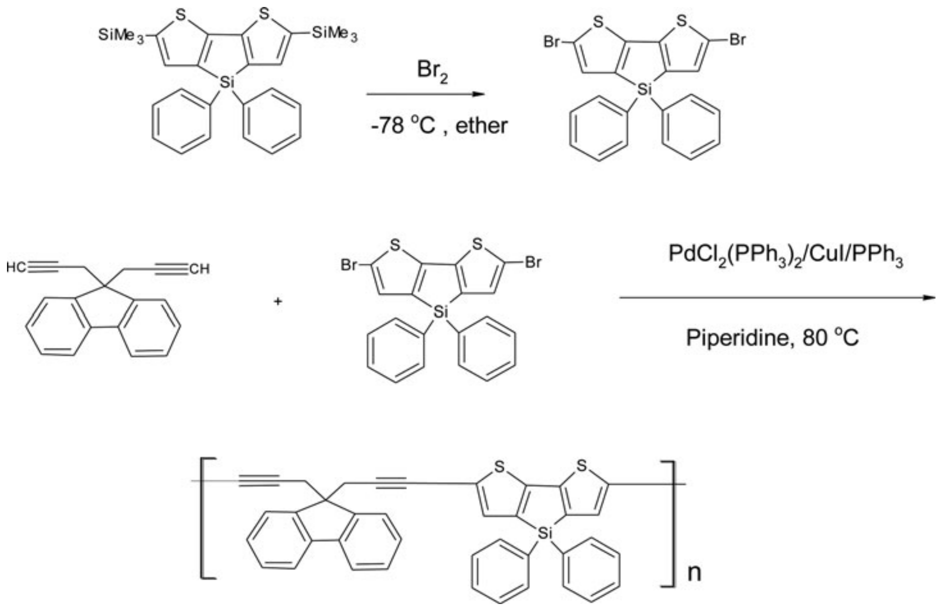
The palladium catalyzed heck coupling reaction of 9,9-dipropargylfluorene and 4,4′-diphenyl-2,6-dibromo-dithieno-[3,2-b:2′,3′-d]silole was used for the synthesis of fluorene-containing copolymer with acetylene moieties in the main chain as follows. 9,9-Dipropargylfluorene (0.46 g.1.9 mmol) and the corresponding 4,4′-diphenyl-2,6-dibromo-dithieno-[3,2-b:2′,3′-d]silole (0.84 g, 1.95 mmol), $PdCl_2(PPh_3)_2/CuI$ (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: 44%).

FT-IR spectra were obtained with a Mattson Instrument Genesis II spectrometer using a KBr pellet. NMR spectra were recorded on a Varian Gemini 200 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 electroluminescence spectra.

Results and discussion

The palladium-catalyzed dehydrocoupling 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 dehydrocoupling reaction of 9,9-dipropargylfluorene was performed at 80°C in the presence of $PdCl_2(PPh_3)_2/CuI$ under nitrogen atmosphere. This reaction proceeded homogeneously to give a moderate yield of polymer (44%). The resulting poly(DPF-DTS) was completely soluble in common organic solvents such as chloroform, chlorobenzene, toluene, and xylene. The weight-average molecular weight (Mw) and the polydispersity(Mw/Mn) of the present poly(DPF-DTS) were 1,810 and 1.28, respectively. This value is relatively low compared to those of the similar homologues obtained by using more simple dihaloaromatic compounds such as 1,4-diiodobenzene and 9,10-diiodoanthracene [21, 22]. It may be



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

caused by the bulkiness and relative low reactivity of 4,4′-diphenyl-2,6-dibromo-dithieno-[3,2-b:2′,3′-d]silole. The good solubility of polymer was judged to be originated by 9,9-dipropargylfluorene moieties in main chain and/or the relatively low molecular weight.

The polymer structure was characterized by such spectroscopic methods as NMR, IR, and UV-visible spectroscopies. Figure 1 shows the FT-IR spectra of DPF and poly(DPF-DTS). The IR spectrum of DPF shows strong absorption at 3289 cm^{-1} due to the acetylenic ≡C-H stretching absorption. The IR spectrum of poly(DPF-DTS) did not show any absorption at 3289 cm^{-1}, which is due to the complete reaction of terminal acetylenic functional groups. The internal acetylenic -C≡C- stretching vibration band of poly(DPF-DTS) was weakly observed at 2212 cm^{-1}. In the ^{1}H-NMR spectrum of poly(DPF-DTS), the methylene proton

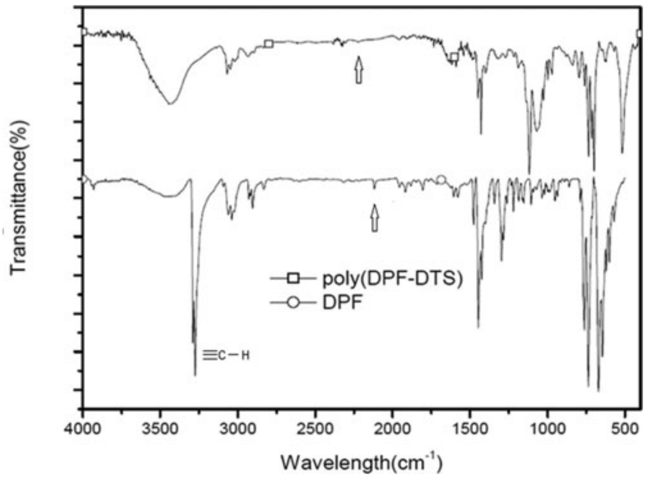


Figure 1. FT-IR spectra of DPF and poly(DPF-DTS) in KBr pellets.

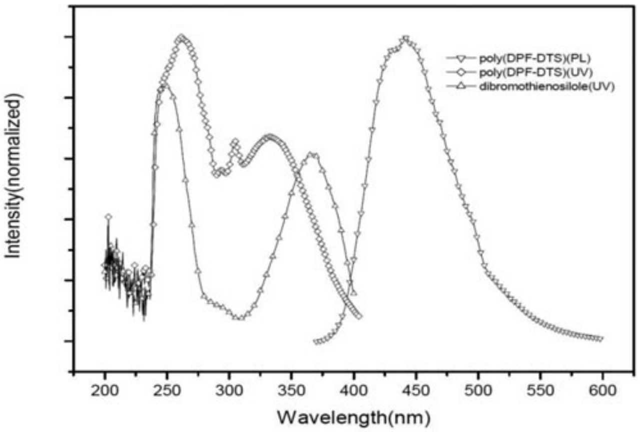


Figure 2. The UV-visible absorption and photoluminescence (PL) spectra of poly(DPF-DTS).

peaks of propargyl group (CH_2-C≡C-DTS) at 3.11 ppm and that of propargyl group (-CH_2-C≡C-C≡CH_2-) of poly(DPF) at 2.96 ppm were appeared. The broad aromatic fluorene and silole proton peaks of poly(DPF-DTS) were appeared at 6.87–7.82 ppm.

The thermal behavior of poly(DPF-DTS) was examined by differencial scanning calorimeter and thermogravimeter. From the DSC curve of poly(DPF-DTS), it was found that a broad exothermic peak was observed around 197°C (started at 157°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-DTS) was also examined. It showed first rapid weight loss in the range of 252–310°C and second rapid weight loss was observed in the range of 502–600°C. The char yield for poly(DPF-DTS) after heating up to 600°C was 37%.

Figure 2 shows the UV-visible and photoluminescence (PL) spectra of poly(DPF-DTS) measured from the solution (8.0×10^{-2} g/L) in chloroform at room temperature. The PL λ_{max} of poly(DPF-DTS) was observed in the range of 432–464 nm, which was similarly shifted in comparison with that of poly(DPF-bithiophene), a similar homologue with bithiophene moieties instead of DTS moieties. The solution of poly(DPF-DTS) emitted strong fluorescence at the excitation wavelength of 350 nm. The emission spectrum of poly(DPF-DTS) shows emission maximum at 440 nm, which is corresponding photon energy of 2.82 eV. The PL quantum yield of poly(DPF-DTS) in chloroform (1×10^{-5} M) was measured by comparing to quinine sulfate (1×10^{-5} M) in 0.1 M H_2SO_4 as standard. The quantum yield (6.44%) of poly(DPF-DTS) is the 5 times higher than that of a similar homologue, poly(DPF-bithiophene), which may be explained by the contribution of DTS group in polymer main chain.

Conclusions

A new fluorene-containing copolymer with acetylene moieties in the main chain was prepared via the palladium-catalyzed dehydrocoupling reaction of 9,9-dipropargylfluorene and 4,4′-diphenyl-2,6-dibromo-dithieno-[3,2-b:2′,3′-d]silole. 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-DTS) 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-DTS) is the 5 times higher than that of a similar homologue, poly(DPF-bithiophene), which is probably due to the contribution of silole moiety in the polymer main chain.

Acknowledgment

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