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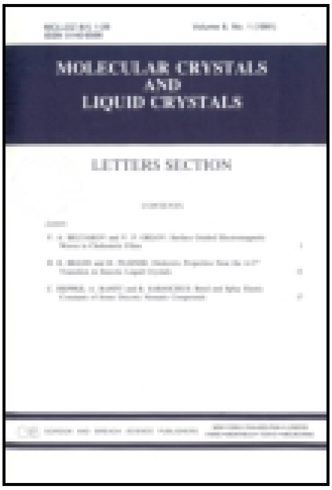

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Synthesis and Optical Properties of New Fluorene-Containing Copolymer via the Catalytic Dehydrocoupling Reaction of 9,9-Dipropargyl Fluorene and Diiodoanthracene

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Synthesis and Optical Properties of New Fluorene-Containing Copolymer via the Catalytic Dehydrocoupling Reaction of 9,9-Dipropargyl Fluorene and Diiodoanthracene

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New fluorene-containing copolymer was prepared via the catalytic dehydrocoupling reaction of 9,9-dipropargylfluorene and diiodoanthracene in 75% yield. The resulting polymer was completely soluble in common organic solvents. 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 445 nm, which is corresponding photon energy of 2.79 eV. The quantum yield (27.8%) of poly(DPF-anthrylene) was found to be slightly higher than that (23.9%) of poly(DPF-phenylene).

Keywords dehydrocoupling; anthracene; photoluminescence; quantum yield; fluorene derivative; cross-linking; diacetylenic

Introduction

The conjugatd polymers have been promising as transparent antistatic coatings, electromagnetic shielding, separation membranes, electrochromic windows, supercapacitors, transistors, photovoltaic cells, conducting photoresists, chemical sensors, light emitting diodes, and lasers [1–4]. The electronics and photonics technologies have opened their materials base to organics, in particular π-conjugated oligomers and polymers [5–7]. Fluorene containing poly(phenylenevinylene) derivatives were good candidates as blue light-emitting organic materials for light-emitting devices for display 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].

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Dipropargyl monomers offer a variety of synthetic pathways to different polymer structures [1, 14–16]. New crosslinkable acetylenic polymers were prepared by the palladium-catalyzed carbon-carbon coupling reactions between the diiodobenzene and diethyldipropargyl malonate in quantitative yield [17]. The thermal curing behaviors of the resulting materials are related to the polymer structures [18–19]. In our previous works, we reported the studies on the synthesis and electro-optical properties of 9,9-dipropargylfluorene having reactive acetylenic functionalities [20, 21].

Herein, we report the synthesis of new anthracene-containing polymers via the catalytic dehydrocoupling reaction of 9,9-dipropargylfluorenes and 9,10-diiodoanthracene as well as the thermal behaviors and optical properties of the resulting polymer.

Experimental

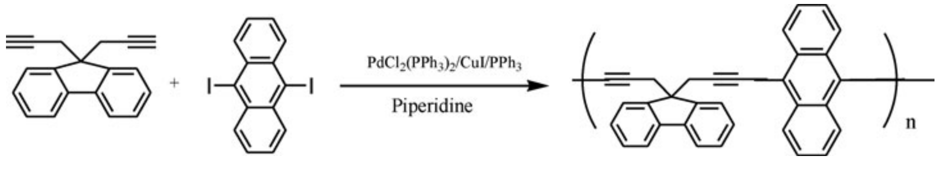
Fluorene (Aldrich Chemicals, 98%) was used without further purification. Propargyl bromide (Aldrich Chemicals, 80 wt% solution in toluene) was dried with CaH_2 and distilled under reduced pressure. 9,9-Dipropargylfluorene was prepared by the reaction of fluorene and propargyl bromide with the catalyst of $NaOH/PhCH_2N^+Et_3Cl^-$ as described in the previous paper [20].

The palladium catalyzed heck coupling reaction of 9,9-dipropargylfluorene and 9,10-diiodoanthracene 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 9,10-diiodoanthracene (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: 75%).

NMR spectra were recorded on a Varian Gemini 200 MHz FT-NMR spectrometer in $CDCl_3$. FT-IR spectra were obtained with a Mattson Instrument Genesis II spectrometer using a KBr pellet. 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. 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. 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 dehydrocoupling polymerization reaction of terminal diacetylenic compound and diiodoaromatic compound was used for the synthesis of fluorene-containing polymer with acetylene moieties in the main chain (Scheme 1).



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

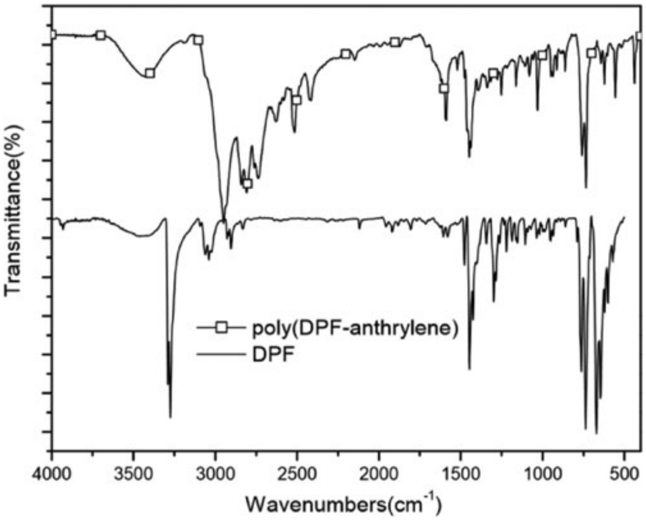


Figure 1. FT-IR spectra of DPF and poly(DPF-anthrylene) in KBr pellets.

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 well to give a relatively high yield of polymer (75%). The resulting poly(DPF-anthrylene) was completely soluble in common organic solvents such as chloroform, chlorobenzene, toluene, and xylene. The weight-average molecular weight (Mw) of the polymer containing 9,9-dipropargylfluorenes was 11,200.

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-anthrylene). 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-anthrylene) 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-anthrylene) was weakly observed at 2212 cm^{-1}. In the ^{1}H-NMR spectrum of poly(DPF-anthrylene), the methylene proton peaks of polymer was broadly observed at 2.71-3.82 ppm and the broad aromatic fluorene and anthracene proton peaks of poly(DPF-anthrylene) were appeared at 6.87-8.46ppm.

The thermal behavior of poly(DPF-anthrylene) was examined by differencial scanning calorimeter and thermogravimeter. From the DSC curve of poly(DPF-anthrylene), it was found that a broad exothermic peak was observed around 191–283 °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 acetylenic groups in the main chain of the polymer. The thermal stabilities of poly(DPF-anthrylene) were also examined. It showed the smooth weight losses in the long range of 100-410 °C. The char yield for poly(DPF-anthrylene) after heating up to 600 °C was 51%.

Figure 2 shows the UV-visible and photoluminescence (PL) spectra of poly(DPF-anthrylene) measured from the solution (8.0×10^{-2} g/L) in chloroform at room temperature. The λ_{max} of poly(DPF-anthrylene) was observed in the range of 401–424 nm, which was red shifted in comparison with that of poly(DPF-Ph), a similar homologue with phenylene moieties instead of anthrylene moieties [22]. The solution of poly(DPF-anthrylene) emitted

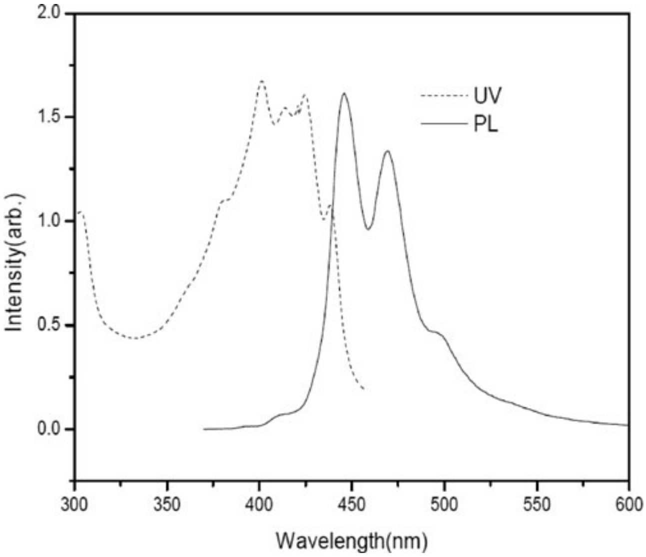


Figure 2. The UV-visible absorption and photoluminescence (PL) spectra of poly(DPF-anthrylene).

strong fluorescence at the excitation wavelength of 350 nm. The emission spectrum of poly(DPF-anthrylene) shows emission maximum at 445 nm, which is corresponding photon energy of 2.72 eV. The PL quantum yield of poly(DPF-anthrylene) 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 (27.8%) of poly(DPF-anthrylene) is the slightly higher than that (23.8%) of a similar homologue, poly(DPF-phenylene), which may be explained by the contribution of anthrylene group in the back main chain.

Conclusions

A new fluorene-containing copolymer with acetylene moieties in the main chain was prepared by the palladium-catalyzed dehydrocoupling reaction of 9,9-dipropargylfluorene and 9,10-diiodoanthracene in relatively high yield. The polymer structure was characterized by such spectroscopic methods as NMR, IR, and UV-visible spectroscopies. Poly(DPF-anthrylene) was found to start the thermal crosslinking of the internal ethynyl moieties at the polymer main chain in the range of 191–283 °C. The quantum yield of poly(DPF-anthrylene) is the slightly higher than that of a similar homologue, poly(DPF-phenyl), which is probably due to the contribution of anthracene moiety in the backbone of poly(DPF-anthrylene).

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