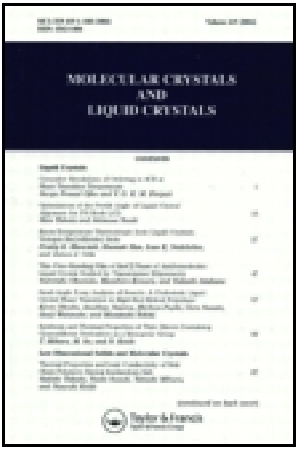

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Synthesis and Optical Properties of Poly(2-substituted-9,9-dipropargylfluorene)s

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Poly(9,9-dipropargylfluorene) and poly(2-substituted-9,9-dipropargylfluorene)s ($X = Ac$, Br, NO_2) were prepared by the palladium-catalyzed dehydrocoupling polymerization reaction of 2-substituted-9,9-dipropargylfluorenes. The thermal and optical properties of the polymers have been investigated. The diacetylenic functions in polymer main chain started to be thermally crosslinked in the range of 143–177°C. The photoluminescence spectra of polymers were in the range of 407–410 nm, which are corresponded to the photon energy of 3.05–3.03 eV. The quantum yield of poly(DPF-Br) is the highest value (55.84%), which means probably the contribution of electron-donating character of Bromine at the 2-position of fluorene.

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

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1. INTRODUCTION

Recently, the electronics and photonics technologies have opened their materials base to organics, in particular π-conjugated oligomers and polymers [1–3]. 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 [4–6]. A high performance device fabricated by Tang and VanSlyke using two-layer light-emitting diodes (LEDs) with organic fluorescent dyes was a breakthrough in this field [4]. Since then, a number of organic materials have been developed as luminescent materials including small molecular systems and π-conjugated polymer systems [7]. Conjugated polymers offer the possibility of combining the desirable processing and structural properties of polymers together with the electronic functionality of a metal or semiconductor [8]. Among the π-conjugated polymer systems, poly(*p*-phenylenevinylene) [9–16] and poly(9,9-dialkylfluorene) [17–20] derivatives are considered as promising candidate materials for polymeric LEDs. Fluorene containing poly (phenylenevinylene) derivatives were good candidates as blue light-emitting organic materials for light-emitting devices for display and other purposes [3–5]. The oxidative-coupling of fluorene compound was used for the synthesis of diacetylene polymer [21] and the poly (fluorenyleneethylene)s were prepared by alkyne metathesis of (9,9-dialkyl)fluoren-2,7-yleneethylenes [22]. In 9,9′-spirofluorene of the polymer chains, the fluorene rings are orthogonally arranged and connected via a commonly tetracoordinated carbon [23]. This structural features would be expected to reduce the probability of interchain interactions and prevent the close packing of the polymer chains, resulting in good solubility of polymers.

Dipropargyl monomers offer a variety of synthetic pathways to different polymer structures [24–26]. Many of these linear polymers can be cured (crosslinked) via the photochemical or thermal reaction of the diacetylene linkages [21]. New crosslinkable acetylenic polymers were prepared by the palladium-catalyzed carbon-carbon coupling reactions between the diiodobenzene and diethyldipropargyl malonate in quantitative yield [27]. The thermal curing behaviors of the resulting materials are related to the polymer structures [28]. Cure 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 [29]. In our previous paper, we reported the synthesis and electro-optical properties of 2-substituted 9,9-dipropargylfluorene having reactive acetylenic functionalities [30]. And also the cyclopolymerization of dipropargylfluorenes by various transition-metal catalysts gave conjugated cyclopolymer in high yields [31].

In this study, we report the synthesis of new fluorene-containing polymers via catalytic dehydrocoupling reaction of 2-substituted-9,9-dipropargylfluorenes as well as the thermal behaviors and optical properties of the resulting polymers.

2. EXPERIMENTAL

2-Bromofluorene, 2-acetylfluorene, 2-nitrofluorene, and benzyltriethylammonium chloride were obtained from Aldrich Chemical Co. and used without further purification. Propargyl bromide (Aldrich Chemical Co., 80 wt % solution of toluene) was dried with CaH_2 and distilled under reduced pressure. 2-Substituted 9,9-dipropargylfluorenes, the aromatic diacetylene compounds, were prepared by the reaction of 2-substituted fluorene and propargyl bromide with the catalyst of $NaOH/PhCH_2N^+Et_3Cl^-$ in high yields. More detailed synthetic procedures and spectral data for 2-substituted-dipropargyl fluorenes were given in the previous paper [28]. The palladium-catalyzed dehydrocoupling reaction of 9,9-dipropargylfluorene were carried out at 65°C in piperidine under nitrogen atmosphere. A typical procedure was as follows : A 30 mL round flask was purged with nitrogen and 0.3 g (1.23 mmole) of 9,9-diproparylgylfluorene, 4.3 mg of copper iodide, 10 mg of triphenylphospine, 1 mg of (triphenylphosphine)palladium dichloride, and 6 mL of piperidine were placed to the flask under nitrogen. The flask was purged by nitrogen for 3 min and heated by oil bath at 65°C. After stirring for 12 h under nitrogen atmosphere reaction mixture was poured into 200 mL of MeOH with sirring. The precipitated polymer was filtered, washed with methanol, and then dried in vacuo to give a yellowish polymer. Yields of the products were calculated on the basis of the isolated products.

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.

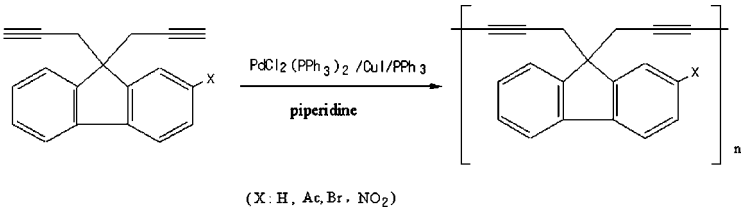
3. RESULTS AND DISCUSSION

The palladium-catalyzed dehydrocoupling polymerization reaction of the diacetylenic compounds, which are 2-substituted-9,9-dipropargylfluorenes, were used for the synthesis of fluorene-containing polymer with acetylene moieties in the main chain (Scheme 1).

The dehydrocoupling polymerization reaction of 2-substituted-9,9-dipropargylfluorene were performed at 65°C in piperidine in the presence of $PdCl_2(PPh_3)_2/CuI$ under nitrogen atmosphere. This reaction proceeded well to give a high yield of polymer. Yields of the polymers were in the range of 67–98% according to the substituents (Table 1). The low yield of poly(DPF-Br) may be due to the possible side reaction of Heck reaction with bromine atom on the fluorene. The weight-average molecular weights (Mw) of the polymers of 2-substituted-9,9-dipropargylfluorenes were in range of 6310–10395 relative to polystyrene standards in gel permeation chromatography(GPC). In the cases of poly(PDF-NO_2) and poly(DPF-Br), the corresponding polymers with low molecular weight were obtained.

The polymer structure was characterized by such spectroscopic methods as NMR, IR, UV-visible spectrometers. Figure 1 shows the ^{13}C-NMR spectrum of poly(DPF-Br) in $CDCl_3$. As shown in this spectrum, the signals for both the ethynylene carbons of DPF-Br at the 80.58 ppm and 72.76 ppm were disappeared as the polymerization proceeded, and the new signals of internal ethynylene carbons were appeared at 68.07 ppm and 74.45 ppm, the latter one is assigned to the signal of ethynylene carbon adjacent to the other ethynylene group in the main chain of the polymer. This indicates that the carbon-carbon bond between ethynyl groups of DPF-Br was formed during the polymerization.

Figure 2 shows the IR spectra of poly(DPF) and its three homologues in KBr pellet. The IR spectrum of poly(DPF) did not show any absorption at 3289 cm^{-1} due to $\equiv$C$-$H stretching absorption, which had been observed in the IR spectrum of DPF itself. The IR spectra



SCHEME 1 Synthesis of poly(DPF) and its homologues (X = Ac, Br, NO_2).

TABLE 1 Properties of Poly(2-substituted-9,9-dipropargylfluorenes ($X = H$, Ac, Br, NO_2)

Polymer	Mw	Yield (%)	Quantum yield (%)	UV, $\lambda_{max}(\varepsilon)$
Poly(DPF)	10395	94	27.08	303 (1200)
Poly(DPF-NO_2)	6310	98	2.57	334 (14080)
Poly(DPF-Ac)	9903	94	8.11	320 (15330)
Poly(DPF-Br)	6997	67	55.84	309 (1700)

of poly(DPF-Ac), poly(DPF-Br), and poly(DPF-NO_2) also did not show the acetylenic C–H stretching absorptions at $3275\,cm^{-1}$ of DPF-Ac, $3266\,cm^{-1}$ of DPF-Br and $3279\,cm^{-1}$ of DPF-NO_2 in Figure 3. The resulting poly(DPF) and its homologues were completely soluble in common organic solvents such as chloroform, chlorobenzene, toluene, and xylene.

The thermal behavior of poly(DPF) and its homologues were examined by differential scanning calorimeter and thermogravimeter. From the DSC curve of poly(DPF-NO_2) in Figure 4, it was found that a broad exothermic peak was observed around 195°C (started at 161°C) in the first heating, whereas there was no exothermic peak in the second

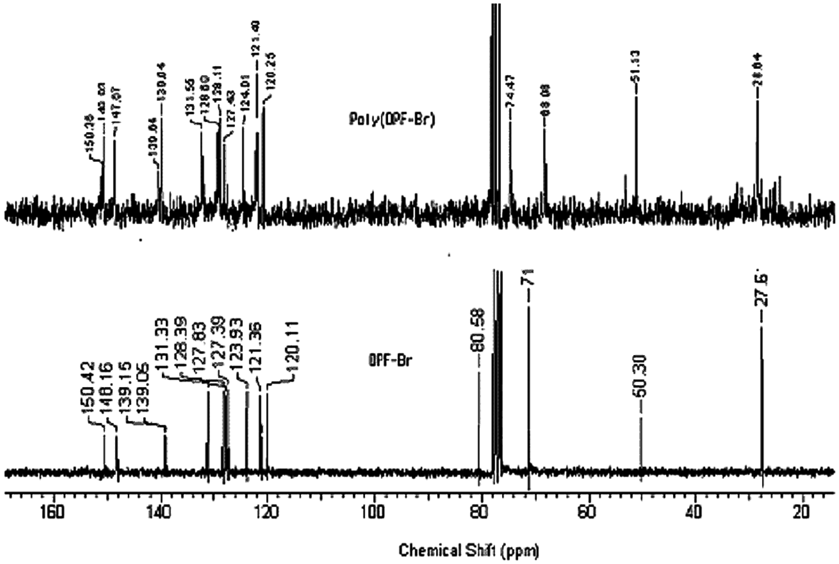


FIGURE 1 ^{13}C-NMR spectrum of poly(DPF-Br) (upper) and DPF-Br (down) in $CDCl_3$.

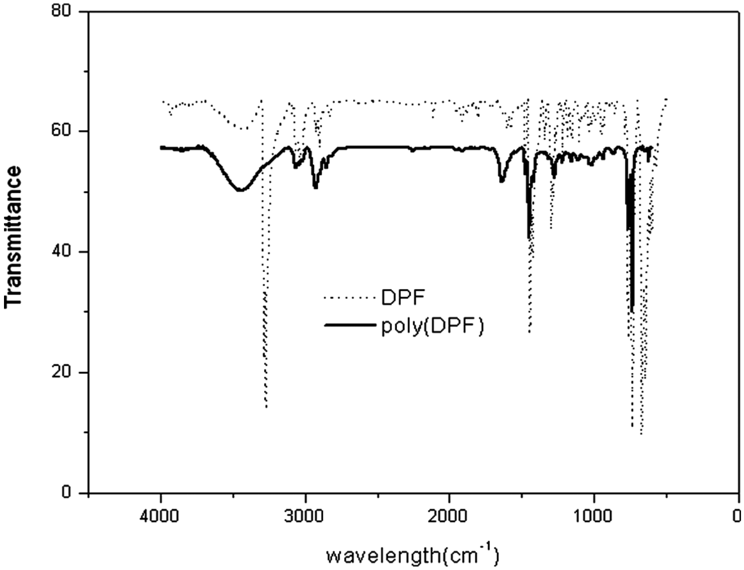


FIGURE 2 IR spectrum of DPF (––––––) and poly(DPF) (——).

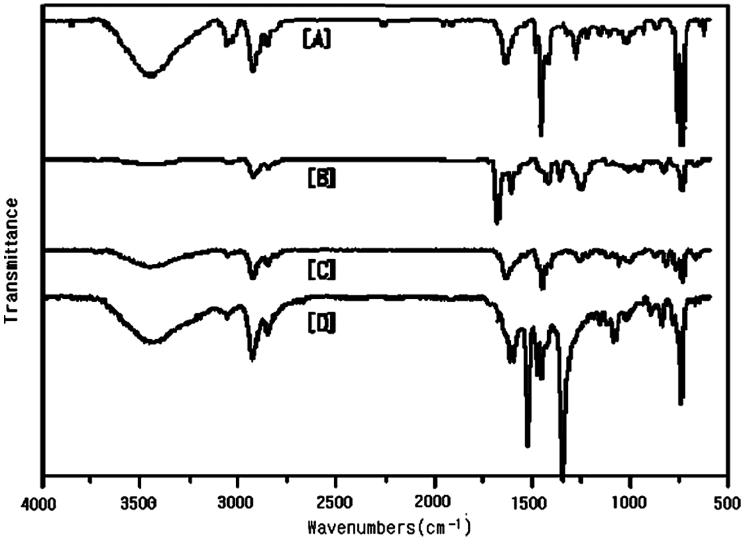


FIGURE 3 IR spectrum of poly(DPF) [A], poly(DPF-Ac) [B], poly(DPF-Br) [C] and poly(DPF-NO_2) [D].

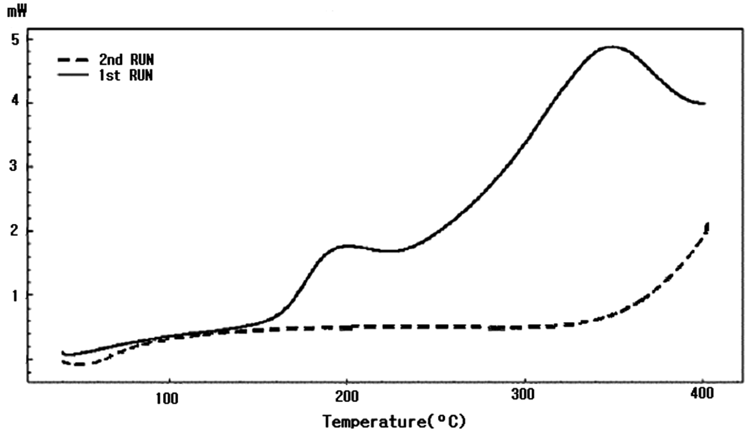


FIGURE 4 DSC thermogram of poly(DPF-NO_2) [1st run (——) and 2nd run (– – – – –)].

heating. The broad exothermic peak is probably due to the thermal crosslinking of the internal ethynyl groups in the main chain of the polymer. The exothermic peaks on other polymers started at 143°C for [poly(DPF)], 150°C for [poly(DPF-Br)], and 177°C for [poly(DPF-Ac)], respectively. The thermal stabilities of the resulting polymers

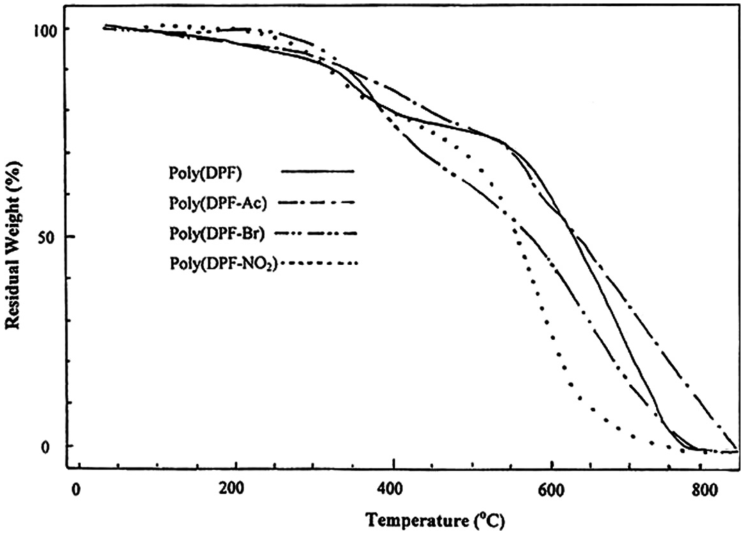


FIGURE 5 TGA thermograms of poly(DPF) and its three homologues.

were also examined. Figure 5 shows the TGA thermograms of poly(DPF) and its three homologues. These polymers showed similar thermal stability up to 300°C. Its first rapid weight losses were observed in the range of 250–310°C and the second weight losses were observed in the range of 460–550°C. The char yields for the polymers after heating up to 600°C were found to be 60% for [poly(DPF)], 57% for [poly(DPF-Ac)], 43% for [poly(DPF-Br)], and 27% for [poly(DPF-NO_2)], respectively. The poly(DPF-NO_2) showed first weight loss at 250°C and second weight loss at 480°C.

The absorption spectra of the polymers were summarized in Table 1. The λ_{max} of the polymers were observed in the range of 320–339 nm, which are depending on the substituents at the 2-position of fluorene. The molar extinction coefficients(ε) of poly(DPF-NO_2) and poly(DPF-Ac) having the electron-withdrawing substituents were more higher than those of poly(DPF) itself and poly(DPF-Br). Figure 6 illustrates the typical absorption and emission spectra of poly(DPF-NO_2).

The solution of poly(DPF-NO_2) emitted blue weak fluorescence at the excitation wavelength of 350 nm. As shown in Figure 6, the emission spectrum of poly(DPF-NO_2) shows emission maximum at 417 nm. The PL quantum yields of poly(DPF) and its homologues in chloroform (ca. 1×10^{-6} M) were measured by comparing to quinine sulfate

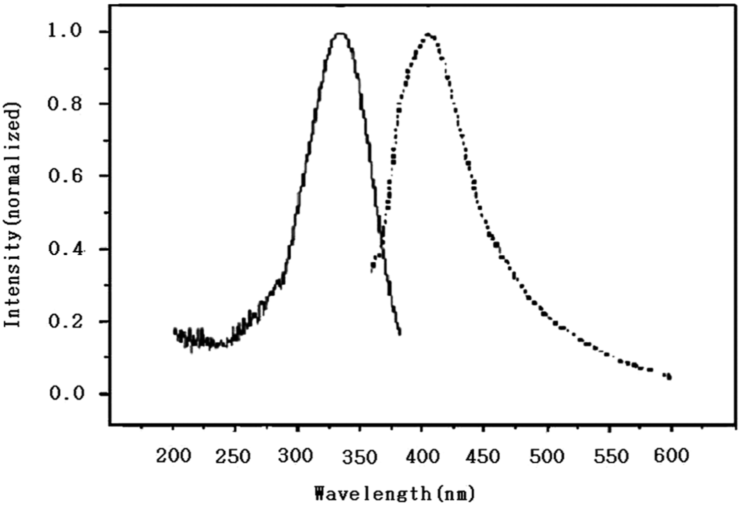


FIGURE 6 UV-visible and emission spectra of poly(DPF-NO_2) [UV (——) and Emission (– – – – –)] measured from the solution (1×10^{-5} M) in chloroform at room temperature.

(ca. 1×10^{-6} M) in 0.1 M H_2SO_4 as standard (Table 1). The quantum yield of poly(DPF-Br) is the highest value (55.84%), which means probably the contribution of electron-releasing character of Bromine at the 2-position of fluorene.

4. CONCLUSIONS

We have prepared poly(2-substituted-9,9-dipropargylfluorenes)s by the palladium-catalyzed dehydrocoupling reaction of 2-substituted-9,9-dipropargylfluorene in high yields . The resulting polymers exhibited good solubility in common organic solvent. The polymer structures were characterized by such spectroscopic methods as NMR, IR, and UV-visible spectrometers. These polymers were started to be thermally crosslinked by the internal ethynyl moieties in the main chain of the polymers in the range of 143–177°C. The quantum yield of poly(DPF-Br) is the highest value (55.84%), which means probably the contribution of electron-releasing character of Bromine at the 2-position of fluorene. Further studies on the synthesis and optical properties of the copolymer systems having various aromatic groups are in progress.

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