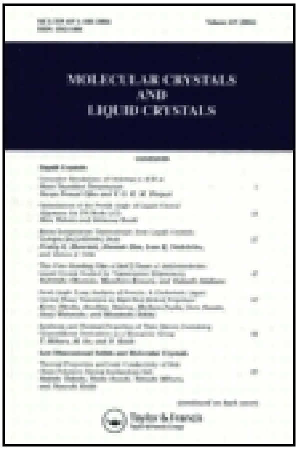

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Synthesis and Characterization of Poly(9,9-Dipropargylfluorenylene-Phenylene)

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Synthesis and Characterization of Poly(9,9-Dipropargylfluorenylene-Phenylene)

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Poly(9,9-dipropargylfluorenylene-phenylene) was prepared by cross-coupling condensation, known as the Heck reaction of 9,9-dipropargylfluorene (DPF) and 1,4-diiodobenzene in high yield. The polymer structure was identified by various spectroscopic methods such as IR, ^1H-, ^{13}C NMR, UV-visible spectroscopies. The acetylenic units in the polymer main chain were found to be thermal intermolecularly crosslinked in the range of 147–256°C. The photoluminescence of the polymer in chloroform solution appeared at 408 nm, which corresponds to a photon energy of 3.04 eV.

Keywords: acetylenic unit; cross-coupling condensation; cross-linking; fluorene derivative; phase image; photoluminescence; quantum yield

INTRODUCTION

In the field of optics and electronics, polymeric materials are traditionally used in applications such as packaging, electrical insulators, and photoresists [1–3]. However, new opportunities emerged with the discovery of conducting polyacetylene in 1977 [4,5]. π-Conjugated oligomers and polymers are intensively studied because of their

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interesting electrical, optical properties, and their potential utility in electronics and photonic applications [6,7]. The conjugated polymers have been promising as transparent antistatic coatings, electromagnetic shieldings, separation membranes, electrochromic windows, supercapacitors, transistors, photovoltaic cells, conducting photoresists, chemical sensors, light-emitting diodes, and lasers [8–11]. 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 [12–14]. 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 [12]. Since then, a number of organic materials have been developed as luminescent materials including low-molecular-weight systems and π-conjugated polymer systems [15]. Fluorene containing poly(phenylenevinylene) derivatives were good candidates as blue light-emitting organic materials for light-emitting devices [16–18]. The poly(9,9-dialkyl)fluoren-2,7-yleneethynylene)s were prepared by alkyne metathesis [19]. In 9,9′-spirobifluorene units of the polymer chains, the fluorene rings are orthogonally arranged and connected via a commonly tetracoordinated carbon [20]. 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.

The linear acetylenic polymer with fluorene moieties from the oxidative coupling reaction of dipropargylfluorene was prepared and its photochemical or thermal reaction properties were investigated [21,22]. Other acetytlenic polymer was also synthesized by palladium-catalyzed coupling reaction between the diiodobenzene and diethyldipropargyl malonate in high yield [23]. 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 [24,25]. We recently reported the synthesis and electro-optical properties of 9,9-dipropargylfluorene derivatives with various functional groups [26]. And also we reported that a spirocyclic conjugated polymer containing a fluorene unit, poly(dipropargylfluorene), was synthesized via the cyclopolymerization of 9,9-dipropargylfluorene in the presence of Mo- and W-based transition-metal catalysts [27]. In this paper, we report the synthesis of fluorene-containing copolymer by palladium-catalyzed Heck reaction of 9,9-dipropargylfluorene (DPF) with 1,4-diiodobenzene as well as the thermal behaviors and optical properties of the resulting polymer for the application in carrier-transporting materials.

EXPERIMENTAL SECTION

Materials

Fluorene, 1,4-diiodobenzene, bis(triphenylphosphine)palladium(II) dichloride, cuprous iodide, piperidine, and benzyltriethylammonium chloride were obtained from Aldrich Chemical Co. and used without further purification. Propargyl bromide (Aldrich Chemicals 80 wt% solution of toluene) was dried with CaH_2 and distilled. The synthesis of 9,9-dipropargylfluorene (DPF) was carried out according to a literature procedure [21]. The palladium-catalyzed reaction of DPF and 1,4-diiodobenzene was carried out at 65°C in piperidine under nitrogen atmosphere. A typical procedure was as follows: A mixture of 0.3 g (1.2 mmol) of DPF, 0.4 g (1.2 mmol) of 1,4-diiodobenzene, 4.3 mg (2.3×10^{-2} mmol) of cuprous iodide, 10 mg (3.8×10^{-2} mmol) of triphenylphospine, 1 mg (1.4×10^{-3} mmol) of bis(triphenylphosphine)palladium(II) dichloride in 7 mL of piperidine was stirred at 65°C for 12 h under nitrogen atmosphere. The reaction mixture was poured into 200 mL of methanol. The precipitated polymer was filtered, washed with methanol, and then dried in vacuo to give yellowish polymer (0.37 g, 95% yield).

General Procedures

^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. GC analyses were performed on a Hewlett-Packard 5890 FID chromatograph, using a HP-5 (cross-linked 5% methylphenylsilicon) capillary column (30 m). Infrared spectra were obtained with a Mattson Instrument Genesis II spectrophotometer using a KBr pellet and frequencies were given in reciprocal centimeters. The molecular weight of the polymer was 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 (Xen150W 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. AFM measurements were conducted with a Digital Instruments Nanoscope IIIa, in constant force mode, at room temperature. The very sharp TM-AFM tip (TESP $f = 320$ kHz, L 125 μm, W 30 μm) glides over the surface (scan size 100 μm^2) and tracks the profile line by line. Each line is a convolution between the tip and the local roughness profile of the sample. The images consist of 256 lines with 256 pixel per line. The samples were dried and heated at 150° in air. The surface roughness was evaluated by determination of the average plane roughness (ra), root mean square (rms), and surface area.

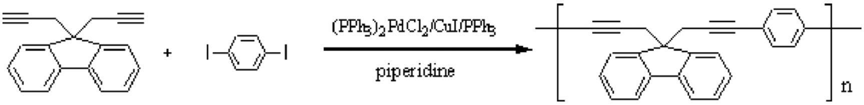
RESULTS AND DISCUSSION

The palladium-catalyzed coupling reaction was proceeded for the synthesis of fluorene-containing polymer with acetylenic and arylene moieties in the main chain as shown in the Scheme 1. The poly (dipropargylfluorenylene-phenylene), poly(DPF-phenylene), was prepared by palladium catalyzed reaction of DPF and 1,4-diiodobenzene.

The polymerization reaction of DPF with 1,4-diiodobenzene was performed in piperidine at 65°C in the presence of $(PPh_3)_2$ $PdCl_2/CuI$ under nitrogen atmosphere. This reaction proceeded well to give a high yield of polymer (0.37 g, 95%). The average molecular weight (Mw) and polydispersity (Mw/Mn) of the resulting polymer were 8.4×10^3 and 2.18, respectively. Poly(DPF-phenylene) 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, and UV-visible spectroscopies.

Figure 1 shows the ^{13}C NMR spectrum of poly(DPF-phenylene) and DPF in $CDCl_3$. As shown in these spectra, the signals for both terminal acetylenic carbons of DPF observed at the 80.58 ppm and 72.76 ppm were disappeared in the ^{13}C NMR spectrum of poly(DPF-phenylene). The new signals of internal acetylenic carbons were appeared at 82.84 ppm and 88.86 ppm, because there may be some electron delocalization, the latter one is assigned to the signal of acetylenic carbon connected to phenylene group in the main chain of the polymer. This means that the carbon-carbon bond between acetylene of DPF and phenylene groups was formed during the coupling reaction.

The ^1H NMR spectrum of poly(DPF-phenylene) did not show the acetylenic proton signal (≡C-H) of DPF itself at 2.0 ppm in Figure 2. The methylene proton signals of the polymer originated from the propargyl group of DPF was appeared at 3.01 ppm. The aromatic



SCHEME 1 Synthesis of poly(DPF-phenylene).

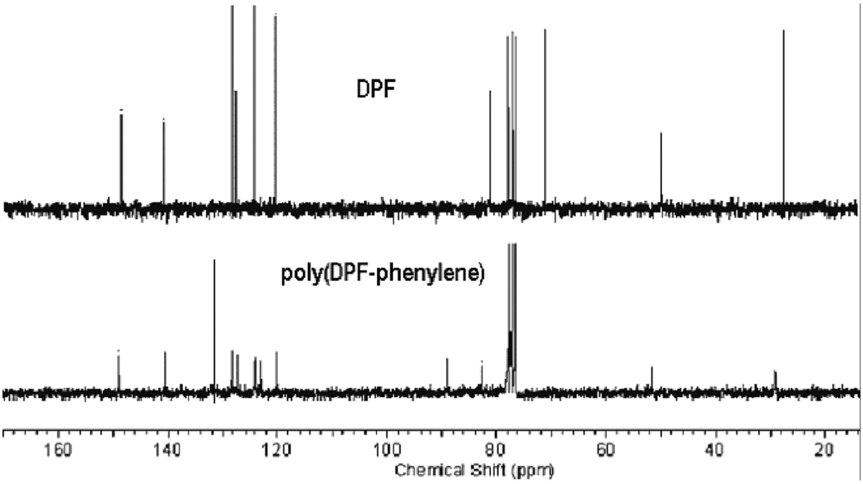


FIGURE 1 ^{13}C NMR spectra of DPF and poly(DPF-phenylene).

proton signals of fluorenylene and phenylene groups were observed at 7.21–7.85 ppm.

The ^{13}C NMR and the corresponding distortionless enhancement by polarization transfer (DEPT) spectra of poly(DPF-phenylene) are depicted in Figure 3. The ^{13}C NMR spectrum exhibits 12 peaks, which are well matched with those of ideal repeating unit of poly(DPF-phenylene). Using the DEPT technique, which allows one to distinguish between protonated and non-protonated carbons, it is possible to see that the signals of methylene carbons of propargyl

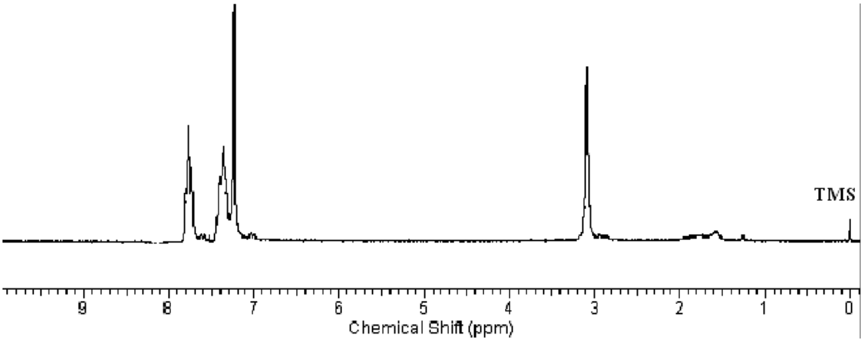


FIGURE 2 ^{1}H NMR spectrum of poly(DPF-phenylene).

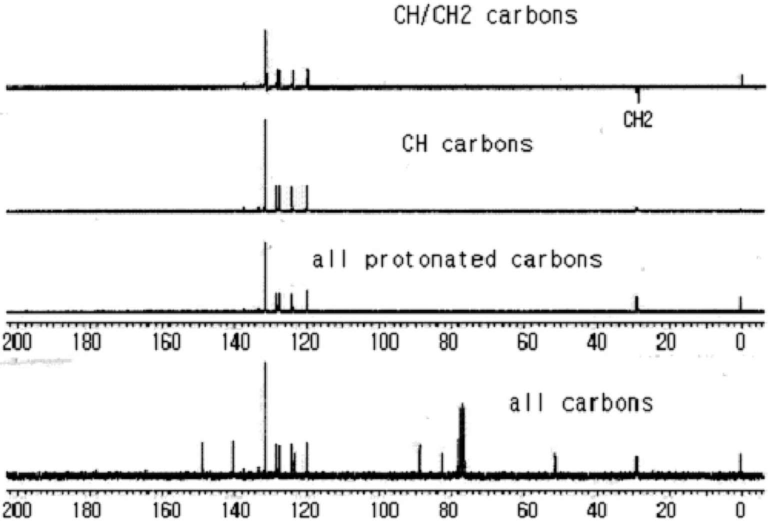


FIGURE 3 DEPT ^{13}C NMR spectrum of poly(DPF-phenylene).

group and five protonated aromatic carbons are presented in the all protonated carbons of Figure 3. The methylene carbon signal of propargyl unit of the polymer is assigned at 28.99 ppm from DEPT ^{13}C NMR spectrum which show that the signal of CH_2 is negative. The signals of protonated aromatic carbons of fluorenylene group appears at 128.18, 127.47, 123.95 and 120.05 ppm, while the signal of protonated carbon of phenylene group appears at 131.56 ppm. The signals of quarternary aromatic carbons (140.27, 148.81 ppm) of fluorenylene moiety and the one of quarternary aromatic carbon of phenylene group (123.13 ppm) were disappeared in all protonated carbons DEPT spectrum of poly(DPF-phenylene) in Figure 3.

The IR spectra of poly(DPF) and poly(DPF-phenylene) in Figure 4 did not show any absorption at 3289 cm^{-1} which is due to the acetylenic (≡C-H) stretching frequency of DPF itself. In the case of poly(DPF), the weak C≡C-C≡C stretching frequency of diacetylenic group was observed at 2253 cm^{-1}, whereas the C≡C stretching frequency of acetylenic unit in poly(DPF-phenylene) was observed at 2225 cm^{-1}. The stretching frequencies of aromatic C-H and methylene C-H bonds occur at 3060 cm^{-1}, 2936 cm^{-1}, and 2812 cm^{-1}, respectively.

The thermal behaviors of poly(DPF-phenylene) were examined by differential scanning calorimeter (DSC). The DSC thermogram of poly(DPF-phenylene) in Figure 5 measured under nitrogen atmosphere at a heating rate of 10°C/min. A broad exothermic peak was

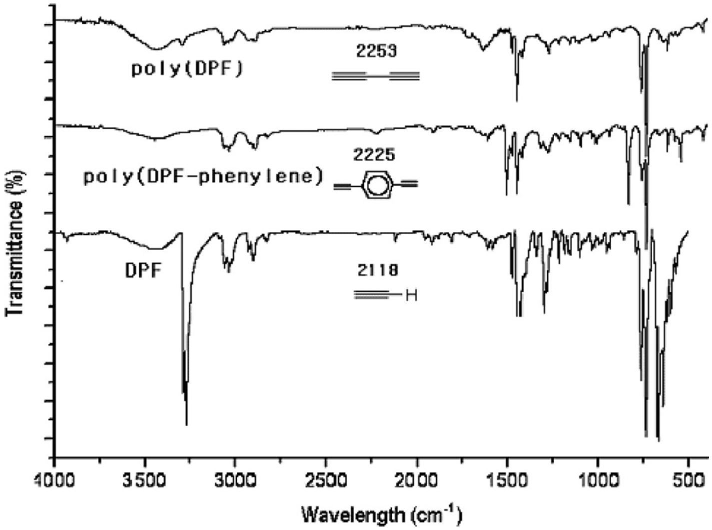


FIGURE 4 IR spectrum of DPF, poly(DPF) and poly(DPF-phenylene) measured by using KBr pellet.

observed around 223°C (started at 151°C) in the first heating, whereas no exothermic peak was observed in the second heating. The broad exothermic peak is probably due to the thermal crosslinking of acetylenic groups in the main chain of polymer. In our previous

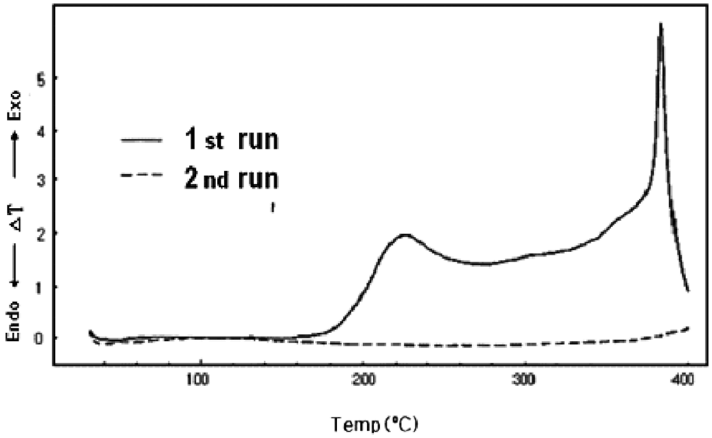


FIGURE 5 DSC thermogram of poly(DPF-phenylene) [1st run (——) and 2nd run (- - - - - - - -)].

investigation [22], it was reported that the same exothermic peak for poly(DPF) homopolymer appeared at 195°C (started at 143°C).

Figure 6 shows the TGA thermograms of DPF itself and poly(DPF-phenylene). The poly(DPF-phenylene) was found to be stable up to 300°C without any weight loss, whereas the most DPF was disappeared at the same temperature. The first smooth weight loss was observed in the range of 250–310°C and the second rapid weight loss was observed in the range of 520–600°C. The char yields of the polymer after heating up to 600°C was 57%. It was also found that the poly(DPF-phenylene) is thermally more stable than that of poly(DPF) which is stable up to 240°C [22].

Figure 7 shows the IR spectra of poly(DPF-phenylene) on the ITO plate before and after heating at 150°C for 20 min. In the spectrum of poly(DPF-phenylene) after aging, the stretching frequency of C=C bond which was formed from the crosslinking process appears broadly at $1545 \sim 1646\,\text{cm}^{-1}$. The optical properties of the polymer were summarized in Table 1.

The absorption and emission spectra of polymer illustrated in Figure 8. The absorption maximum of the polymer solution in chloroform was very similar to that of poly(DPF) itself ($\lambda_{\max} = 303\,\text{nm}$). It implies that the absorption of the polymer may be mainly originated from fluorenylene moiety in the polymer.

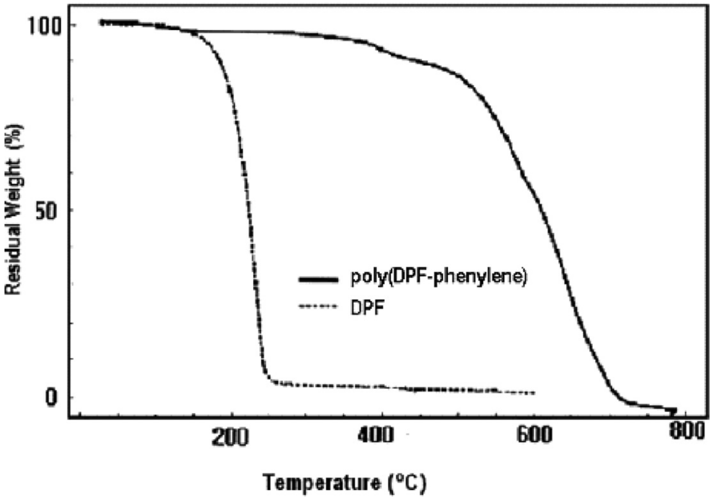


FIGURE 6 TGA thermogram of poly(DPF-phenylene) and DPF under nitrogen atmosphere at a heat rate of 10°/min.

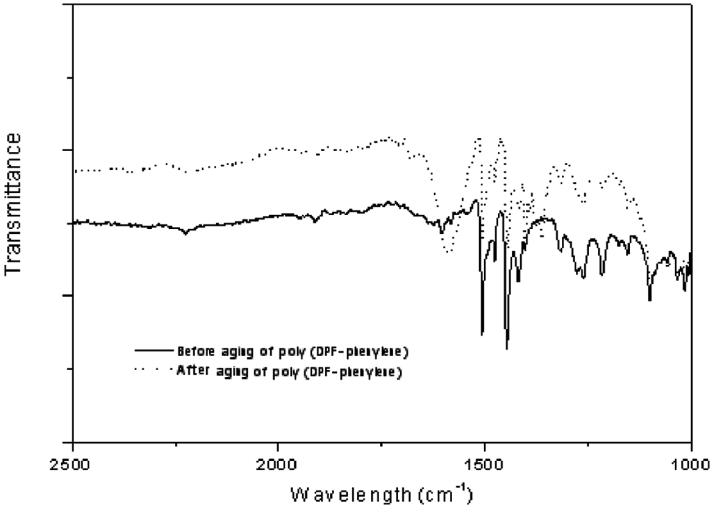


FIGURE 7 IR spectra of poly(DPF-phenylene) on the ITO plate before and after aging at 150°C.

The PL spectrum of the polymer solution is slightly red shifted as compared to that of the polymer film. This is probably due to the polarity of the solvent. The solution of poly(DPF-phenylene) emitted weak blue fluorescence when it is excited at 350 nm. Before thermal aging, the poly(DPF-phenylene) in film exhibited the emission maximum at 387 nm. After thermal aging, its PL spectrum peaked at 387 and 409 nm in Figure 8. The PL quantum yields of poly(DPF)

TABLE 1 Optical Properties of Poly(DPF-phenylene)

	ΔEg/eV[a]	PL λ_{max} (nm)	Stokes shift (nm)	Quantum yield (%)[c]	UV λ_{max}
Ploy(DPF) (solution)	3.93	417[b]	114	27.1	273, 305
Poly(DPF-phenylene) (solution)	3.93	408	105	23.9	275, 303
Poly(DPF-phenylene) (film: before aging)	3.93	387	82	–	275, 303
Poly(DPF-phenylene) (film: before aging)	–	387, 409	96, 104	–	–

[a] Optical band gap taken from the absorption spectre.
[b] Cited in ref. [22].
[c] Quantum yield relative to quinine sulfate. 10^{-5} M quinine sulfate in 0.1 M H_2SO_4.

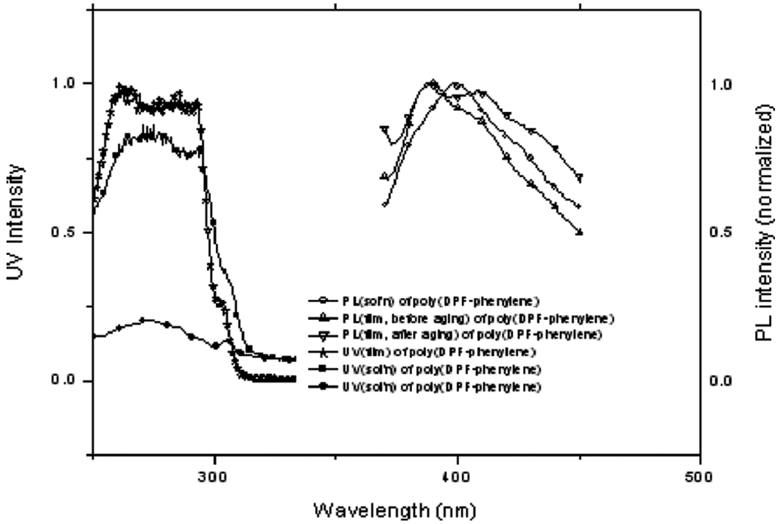


FIGURE 8 UV absorption spectra and photoluminescence spectra of poly(DPF-phenylene) measured in thin film (before and after aging) and solution (1×10^{-5} M) in chloroform at room temperature.

and poly(DPF-phenylene) in chloroform solution (ca. 1×10^{-5} M) were measured by comparing with quinine sulfate (ca. 1×10^{-5} M) in 0.1 M H_2SO_4 as standard (Table 1) [28]. As previously described, the λ_{max} of UV absorption of poly(DPF-phenylene) was very similar to that of poly(DPF) itself, however, the quantum yield (23.9%) of poly(DPF-phenylene) was somewhat lower than that (27.1%) of poly(DPF) itself.

Figure 9 shows the atomic force microscope (AFM) image of poly(DPF-phenylene) film obtained at scan frequency of 0.8 Hz. The thermal aging was performed for 20 min at 150°C. The TM-AFM phase image of the polymer film surface after thermal aging is more smooth than that of the polymer film surface before aging. The value (rms: 0.491) of surface roughness was decreased to the value (rms: 0.195) by annealing at 150°C for 20 min. As the annealing time is increased, the surface roughness of film was gradually decreased. This change in roughness may be attributed to the formation of a new gel-like phase which is made from the molecular rearrangement. The gelation is similar to the crosslinking which is interacted with inter- or intramolecularly between polymer chains. The morphology of poly(DPF-phenylene) powder was also investigated by X-ray diffraction analysis.

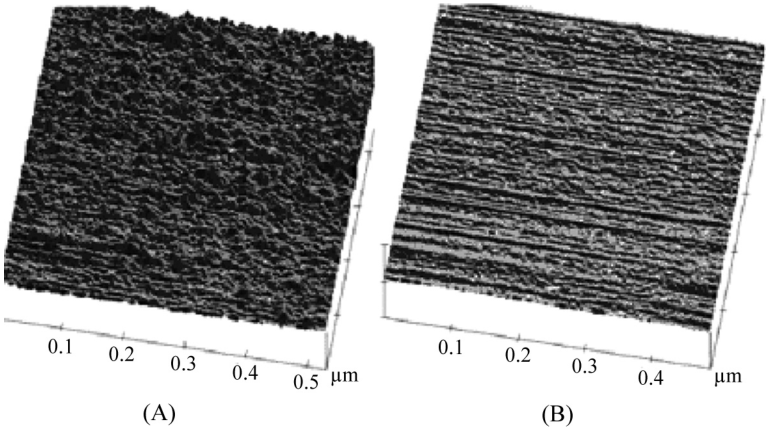


FIGURE 9 Phase 3D images of poly(DPF-phenylene) [before aging (A) and after aging (B)].

As shown in Figure 10, since the peak in the diffraction pattern was broad and the ratio of the half-height width to diffraction angle ($\Delta 2\theta/2\theta$) is greater than 0.35, the polymer appears to be mostly amorphous [29].

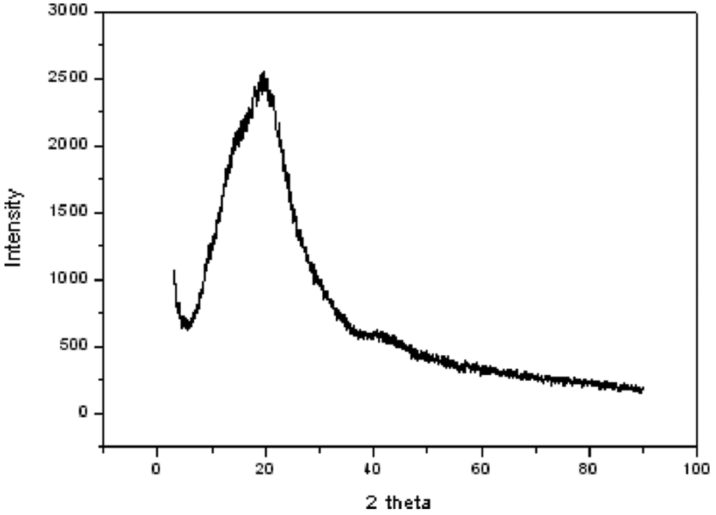


FIGURE 10 X-ray diffractogram of poly(DPF-phenylene).

CONCLUSIONS

The poly(DPF-phenylene) has been synthesized via palladium-catalyzed Heck-coupling reaction of 9,9-dipropargylfluorene with 1,4-diiodobenzene 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 cross-linked by the acetylenic moieties in the polymer main chain in the range of 143–256°C. The thermal stability of poly(DPF-phenylene) is more stable than poly(DPF) itself. The decrease of surface roughness by annealing may be attributed to the formation of a new gel-like phase by the interchain crosslinking of the acetylenic groups in the polymer backbone.

REFERENCES

[1] Leclerc, M. (2001). *J. Polym. Sci.: Part A: Polym. Chem.*, *39*, 2867.
[2] Bredas, J. L., Beljonne, D., Coropceanu, V., & Cornil, J. (2004). *Chem. Rev.*, *104*, 4971.
[3] Hoeben, F. J. M., Jonkheijim, P., Meijer, E. W., & Schenning, A. P. H. J. (2005). *Chem. Rev.*, *105*, 1491.
[4] Shirakawa, H., Louis, E. J., MacDiarmid, A. G., Chiang, C. K., & Heeger, A. J. (1977). *J. Chem. Soc. Chem. Commun.*, 578.
[5] Heeger, A. J. (2001). *Angew. Chem. Int. Ed.*, *40*, 2591.
[6] Masuda, T. & Higashimura, T. (1984). *Acc. Chem. Res.*, *17*, 51.
[7] Choi, S. K., Gal, Y. S., Jin, S. H., & Kim, H. K. (2000). *Chem. Rev.*, *100*, 1645.
[8] Gal, Y. S., Jin, S. H., & Choi, S. K. (2004). *J. Mol. Cat. A: Chem.*, *213*, 115.
[9] Buchmeiser, M. R. (2005). *Adv. Polym. Sci.*, *176*, 89.
[10] Lam, J. W. Y. & Tang, B. Z. (2005). *Acc. Chem. Res.*, *38*, 745.
[11] Gal, Y. S., Jin, S. H., & Kim, S. H. (2006). *J. Ind. Eng. Chem.*, *12*, 235.
[12] Tang, C. W. & VanSlyke, S. A. (1987). *Appl. Phys. Lett. 51*, 913.
[13] Braun, D. & Heeger, A. J. (1991). *Appl. Phys. Lett.*, *58*, 1982.
[14] Ohmori, Y., Uchida, M., Muro, K., & Yoshino, K. (1991). *Jpn. J. Appl. Phys.*, *30*, L1938.
[15] Dai, L., Winkler, B., Dong, L., Tong, L., & Mau, A. W. H. (2001). *Adv. Mater.*, *13*, 915.
[16] Cho, H. N., Kim, D. Y., Kim, Y. C., Lee, J. Y., & Kim, C.Y. (1997). *Adv. Mater.*, *9*, 326.
[17] Cho, H. N., Kim, J. K., Kim, D. Y., Kim, C. Y., Song, N. W., & Kim, D. (1999). *Macromolecules 32*, 1476.
[18] Jin, S. H., Park, H. J., Kim, J. Y., Lee, K., Lee, S. P., Moon, D. K., Lee, H. J., & Gal, Y. S. (2002). *Macromolecules*, *35*, 7532.
[19] Pschirer, N. G. & Bunz, U. H. F. (2000). *Macromolecules*, *33*, 3961.
[20] Chiang, C. L. & Shu, C. F. (2002). *Chem. Mater.*, *14*, 682.
[21] Tregre, G. J. & Mathias, L. J. (1997). *J. Polym. Sci.: Part A: Polym. Chem.*, *35*, 587.
[22] Lee, S. G., Kwak, Y. W., Park, J. W., Jin, S. H., & Gal, Y. S. (2005). *J. Nonlinear Optical Phys & Mater.*, *14*, 573.

[23] Jin, S. H., Kim, S. H., & Gal, Y. S. (2001). *J. Polym. Sci.: Part A: Polym. Chem.*, *39*, 4025.

[24] Nielsen, M. B. & Diederich, F. (2005). *Chem. Rev.*, *105*, 1837.

[25] Baughman, R. H. (2006). *Science*, *312*, 1009.

[26] (a) Lee, S. G., Kwak, Y.-W., Park, J. W., Jin, S. H., & Gal, Y. S. (2005). *Curr. Appl. Phys.*, *5*, 59; (b) Lee, S. G., Kwak, Y.-W., Koo, B.-K., Jin, S.-H., & Gal, Y.-S. (2006). *Mol. Cryst. Liq. Cryst.*, *458*, 237.

[27] Gal, Y. S., Jin, S. H., Park, J. W., Lee, W. C., Lee, H. S., & Kim, S. Y. (2001). *J. Polym. Sci.: Part A: Polym. Chem.*, *39*, 4101.

[28] Chen, Z.-K. & Huang, W. (2000). *Macromolecules*, *33*, 9015.

[29] Lee, J. H., Park, J. W., & Choi, S. K. (1996). *J. Polym. Sci.: Part A: Polym. Chem.*, *34*, 1617.