

Synthesis and Properties of Conjugated Cyclopolymers Bearing Fluorene Derivatives

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Abstract: Fluorene-containing, spiro-type, conjugated polymers were synthesized via the cyclopolymerization of dipropargylfluorenes (2-substituted, X=H, Br, Ac, NO₂) with various transition metal catalysts. The polymerization of dipropargylfluorenes proceeded well using Mo-based catalysts to give a high polymer yield. The catalytic activities of the Mo-based catalysts were found to be more effective than those of W-based catalysts. The palladium (II) chloride also increased the polymer yield of the polymerization. The polymer structure of poly(dipropargylfluorene)s was characterized by such instrumental methods as NMR (¹H-, ¹³C-), IR, UV-visible spectroscopies, and elemental analysis as having the conjugated polymer backbone bearing fluorene moieties. The ¹³C-NMR spectral data on the quaternary carbon atoms in polymers indicated that the conjugated cyclopolymers have the six-membered rings majorly. The poly(dipropargylfluorene) derivatives were completely soluble in halogenated and aromatic hydrocarbons such as methylene chloride, chloroform, benzene, toluene, and chlorobenzene. The poly(dipropargylfluorene) derivatives were thermally more stable than poly(dipropargylfluorene) itself, and X-ray diffraction analyses revealed that the polymers are mostly amorphous. The photoluminescence peaks of the polymers were observed at about 457-491 nm, depending on the substituents of fluorene moieties.

Keywords: catalysts, conjugated polymer, cyclopolymerization, polyacetylenes, photoluminescence.

Introduction

Conjugated polymers have attracted much attention because of their good ability to form thin films, good mechanical properties, excellent electro-optical properties, etc.¹⁻⁵ Among the π -conjugated polymers, the polyacetylene (PA) is structurally the simplest one, and it can be made free-standing thin film by using Shirakawa catalysts [Ti(OC₄H₉)₄-Al(C₂H₅)₃].^{6,7} However, the drawbacks are that PA is insoluble, infusible, and unstable to air oxidation. To overcome these problems of PA itself, various types of PA derivatives have been designed and synthesized.⁸⁻¹⁶

A number of mono- and disubstituted PAs has been prepared by the simple linear polymerization of the corresponding acetylene monomers by various catalyst systems.⁸⁻¹⁶ The polymers having a conjugated backbone are expected

to show unique properties such as electrical conductivity, paramagnetism, migration and transfer of energy, color, and chemical reactivity and complex formation ability.⁸ Because of these properties, PA and its homologues have been promising as organic semiconductors,^{11,17-19} as membranes for gas separation and for liquid-mixture separation,^{12,20} as chiro-optical materials,^{13,21} as side-chain liquid crystals,^{10,22} as materials for chemical sensors,²³ and as materials for nonlinear optical property^{11,24-26} and for photoluminescence and electroluminescence properties.²⁷⁻³¹

Cyclopolymerization is a type of chain-growth addition polymerization that leads to cyclic structure in the polymer main chain via an alternating intramolecular-intermolecular chain propagation.³² 1,6-Heptadiyne and its homologues are very interesting examples of substituted acetylenes, which can be susceptible to the ring-forming polymerization (cyclopolymerization) to give a new type of conjugated polymer backbone system.^{33,34} In contrast to simple mono-

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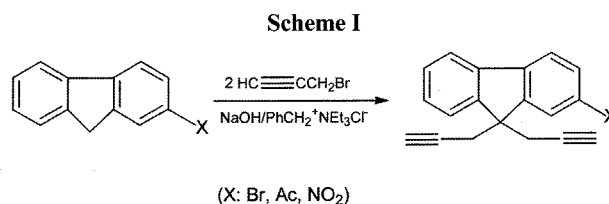
and disubstituted polyacetylenes, in which the coplanarity is generally hindered by the bulky substituents adjacent to the polymer backbone, the presence of a cyclic ring in the cyclopolymer of nonconjugated diynes tends to make the conjugated polymer backbone more coplanar. Gibson *et al.* reported a free-standing film with metallic luster by the polymerization of 1,6-heptadiyne on the surfaces of concentrated solutions of Ziegler-type homogeneous catalyst derived from $\text{Ti}(\text{OC}_4\text{H}_9\text{-}n)_4$ and $\text{Al}(\text{C}_2\text{H}_5)_3$, using a specifically designed reactor.³⁵ However, the resulting poly(1,6-heptadiyne)s, besides low molecular weight of oligomers, were insoluble in organic solvents and very susceptible to air oxidation, regardless of the catalysts used and the polymerization conditions.³⁵ Introduction of substituent to the methylene carbon at the 4-position of 1,6-heptadiyne solved the pre-described problems of poly(1,6-heptadiyne) and expanded the research areas of π -conjugated polymers. The polymerizations of various 1,6-heptadiynes having substituents have been carried out by Mo- and W-based catalysts.^{10,11,14-16,36-38}

Fluorene containing poly(phenylene vinylene) derivatives were good candidates as blue light-emitting organic materials for light-emitting devices for display and other purposes.³⁹ The diacetylene polymer via oxidative coupling of fluorene compound⁴⁰ and poly(fluorenylene ethylene)s by alkyne metathesis of (9,9-dialkyl)fluorene-2,7-ylene ethylenes⁴¹ were prepared and characterized. In 9,9'-spirofluorene in the polymer chains, the fluorene rings are orthogonally arranged and connected via a common tetracoordinated carbon.⁴² 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.⁴²

In our previous paper,⁴³ we reported the synthesis of poly(dipropargylfluorene) by the cyclopolymerization of dipropargylfluorene (DPF) with spiro-skeletal units in the polymer chain. The present article deals with the polymerization behaviors of 9-substituted dipropargylfluorenes (substituent: Br, Ac, NO_2) and the properties of the resulting conjugated cyclopolymers.

Experimental

Materials. 2-Bromofluorene, 2-acetylfluorene, and 2-nitrofluorene (Aldrich Chemicals) were used as received. Benzyltriethylammonium chloride (Aldrich Chemicals, 99%) was used as received. Propargyl bromide (Aldrich Chemicals, 80 wt% solution of toluene) was dried with CaH_2 and distilled under reduced pressure. MoCl_5 (Aldrich Chemicals, 99.9+%), MoCl_4 (Aldrich Chemicals), Cp_2MoCl_2 (Aldrich Chemicals, 98%), WCl_6 (Aldrich Chemicals, 99.9+%) were used without further purification. Et_3Al , Et_2AlCl , and EtAlCl_2 [Aldrich Chemicals, 25 wt% (1.8 M) solution in toluene] and Me_4Sn (Aldrich Chemicals, 95%) were used as received. Ph_4Sn (Aldrich Chemicals, 97%) was purified by



recrystallizing twice from carbon tetrachloride. The solvents were analytical grade materials. They were dried with an appropriate drying agent and distilled.

Synthesis of 2-Substituted Dipropargylfluorenes. 2-Substituted dipropargylfluorenes, the aromatic acetylene compounds, were synthesized by the reaction of 2-substituted fluorene and propargyl bromide with the catalyst of $\text{NaOH}/\text{PhCH}_2\text{N}^+\text{Et}_3\text{Cl}^-$ in high yields (Scheme I).

2-Acetyl-9,9-dipropargylfluorene (DPF-Ac). A two-neck flask equipped with a reflux condenser was charged with 2-acetylfluorene (10 g, 48.0 mmol), propargyl bromide (13 mL, 146 mmol), 50% aqueous NaOH solution (60 mL), and benzyltriethylammonium chloride (0.6 g, 2.63 mmol). The reaction mixture was heated at 70°C for 5 h, and then diluted with toluene, washed once with dilute acid, and twice with water. The organic layer was separated and dried over magnesium sulfate. Toluene was removed under reduced pressure and the product was purified by recrystallization from methylene chloride to give a pure yellowish monomer (yield = 91%). M.P $111\sim 112^\circ\text{C}$; $^1\text{H-NMR}$ ($\text{DMSO-}d_6$): 8.34 (s, 1H), 8.04 (dd, $J=7.95, 1.42$ Hz, 1H), 7.97 (s, 1H), 7.94-7.92 (m, 1H), 7.78-7.75 (m, 1H), 7.44-7.41 (m, 2H), 2.97-2.95 (m, 4H), 2.62 (s, 3H), 2.61-2.60 (m, 2H). $^{13}\text{C-NMR}$ ($\text{DMSO-}d_6$): 197.49, 149.47, 148.49, 144.92, 138.95, 135.72, 128.96, 128.49, 128.09, 123.68, 123.14, 121.07, 119.96, 80.68, 72.79, 51.22, 27.09, 26.80. FT-IR (KBr, cm^{-1}): 3265, 3059, 2116, 1663 (-OAc), 1609, 1573, 1428, 1362, 1277, 1249, 1227, 959, 844.

2-Bromo-9,9-dipropargylfluorene (DPF-Br). The synthesis was also carried out using the similar method as for DPF-Ac with 2-bromofluorene (15 g, 61.2 mmol), propargyl bromide (17 mL, 191 mmol), 50% aqueous NaOH solution (85 mL) and benzyltriethylammonium chloride (1.0 g, 4.39 mmol). The crude product was purified by recrystallization from ethanol to give a pure yellowish monomer (yield = 92%). M.P $119\sim 120^\circ\text{C}$; $^1\text{H NMR}$ ($\text{DMSO-}d_6$): 7.95 (d, $J=1.66$ Hz, 1H), 7.83 (d, $J=6.48$ Hz, 1H), 7.79 (d, $J=8.11$ Hz, 1H), 7.72 (d, $J=8.10$ Hz, 1H), 7.57 (d, $J=8.11$ Hz, 1H), 7.40-7.36 (m, 2H), 2.91 (d, $J=2.45$ Hz, 4H), 2.62 (t, $J=2.40$ Hz, 2H). $^{13}\text{C NMR}$ ($\text{DMSO-}d_6$): 150.57, 147.90, 139.49, 139.00, 130.69, 127.94, 127.62, 126.60, 123.47, 121.76, 120.15, 80.50, 72.76, 51.24, 27.03. FT-IR (KBr, cm^{-1}): 3272, 3059, 2116, 1602, 1569, 1465, 1442, 1271, 1184, 1063, 1005, 824.

2-Nitro-9,9-dipropargylfluorene (DPF- NO_2). The synthesis was carried out using the similar method as for DPF-Ac with 2-nitrofluorene (15 g, 71.0 mmol), propargyl bromide (19 mL, 213 mmol), 50% aqueous NaOH solution (85

mL), and benzytriethylammonium chloride (0.8 g, 3.51 mmol). The crude product was purified by recrystallization from EtOH/THF to give a pure yellowish monomer (yield=89%). M.P 138-139°C; ^1H NMR (DMSO- d_6): 8.65 (d, $J=2.08$ Hz, 1H), 8.30 (dd, $J=8.45$, 2.22 Hz, 1H), 8.10 (d, $J=8.41$ Hz, 1H), 8.03-8.00 (m, 1H), 7.81-7.78 (m, 1H), 7.49-7.46 (m, 2H), 3.03 (dd, $J=11.76$, 2.60 Hz, 4H), 2.60 (t, $J=2.50$ Hz, 2H). ^{13}C NMR (DMSO- d_6): 149.90, 149.48, 147.12, 146.59, 138.01, 129.34, 128.32, 124.10, 123.75, 121.67, 120.65, 118.86, 80.27, 72.92, 51.79, 26.79. FT-IR (KBr, cm^{-1}): 3296, 3081, 2129, 1613, 1591, 1515 ($-\text{NO}_2$), 1467, 1445, 1421, 1335 ($-\text{NO}_2$), 1263, 1082, 759.

Polymerization Procedures. All procedures for catalyst system preparation and polymerization were carried out under dry nitrogen atmosphere because the active species are sensitive to moisture or oxygen. Typical polymerization procedures are as follows.

Polymerization of DPF-Br by MoCl_5 . In a magnetic-stirred 30 mL reactor equipped with rubber septum, 0.5 g (1.56 mmol) of DPF-Br, chlorobenzene (5.42 mL, $[M]_0=0.25$ M), and 0.31 mL (0.031 mmol, $M/C=50$) of 0.1 M MoCl_5 solution were added in that order given. And the polymerization was carried out at 30°C for 24 h under nitrogen atmosphere. The polymerization proceeded very rapidly in the initial time of reaction. After a given time of polymerization, 10 mL of chloroform was added to the polymerization solution. The polymer solution was precipitated into an excess of methanol, filtered from the solution, and then dried under vacuum at 40°C for 12 h. The polymer yield was quantitative.

Polymerization of DPF-Br by MoCl_5 - EtAlCl_2 . In a magnetic-stirred 30 mL reactor equipped with rubber septum, 0.5 g (1.56 mmol) of DPF-Br and chlorobenzene (5.09 mL, $[M]_0=0.25$ M) were added. Then the catalyst solution of 0.31 mL (0.031 mmol, $M/C=50$) of 0.1 M MoCl_5 solution and 0.31 mL (0.0622 mmol) of 0.2 M EtAlCl_2 solution after shaking the catalyst solution at room temperature for 15 min, was injected into the polymerization reactor. After a given time of polymerization, 10 mL of chloroform was added to the polymerization solution. The polymer solution was precipitated into an excess of methanol, filtered from the solution, and then dried under vacuum at 40°C for 12 h. The polymer yield was 87%.

Polymerization of DPF-Br by PdCl_2 . In a magnetic-stirred 30 mL reactor, DPF-Br (1.0 g, 3.11 mmol), PdCl_2 [18.4 mg, 0.104 mmol, monomer to catalyst mole ratio (M/C)=30], and DMF (5.23 mL, $[M]_0=0.5$) were added in that given order and sealed with a rubber septum after flushing with purified argon gas. The polymerization was carried out at 90°C for 24 h. The polymerization proceeded in more mild manner. Then the polymer solution diluted with DMF was precipitated into a large excess amount of methanol. The precipitated polymer was filtered and dried. The polymer yield was 93%.

Instruments and Measurement. NMR (^1H - and ^{13}C -) spectra of polymers were recorded on a Varian 500 MHz FT-NMR spectrometer (Model: Unity INOVA) in CDCl_3 and the chemical shifts were reported in ppm units with tetramethylsilane as an internal standard. FTIR spectra were obtained with a Bruker EQUINOX 55 spectrometer using a KBr pellet, and frequencies are given in reciprocal centimeters. Elemental analyses were performed with FISON S EA1110 elemental analyzer. UV-visible spectra were taken in THF on a JASCO V-530 spectrophotometer. Molecular weights were determined by a gel permeation chromatograph (Waters 150C) equipped with μ -Styragel columns using THF as an eluent. Monodisperse polystyrene standard samples were used for molecular weight calibration. Thermogravimetry (TG) was performed under a nitrogen atmosphere at a heating rate of 10°C/min. with a DuPont 2200 thermogravimetric analyzer. X-ray diffractograms were obtained with a PHILLIPS X-ray diffractometer (Model: XPert-APD). The emission spectra were obtained for dilute ($\sim 10^{-6}$ M) solutions with a Hitachi F4500. Each polymer film was excited with several portions of visible light from a xenon lamp.

Results and Discussion

Cyclopolymerization of Dipropargylfluorene Derivatives. The polymerization of 2-substituted dipropargylfluorenes were carried out by various transition metal catalysts as follows (Scheme II).

Table I shows the results for the polymerization of DPF-Br by various Mo-based catalysts. In general, Mo-based catalysts were found to be very effective for the present polymerization. MoCl_5 alone polymerize DPF-Br monomer to give a quantitative yield of polymer. In more severe reaction condition (exp. no. 1), the resulting polymers were mostly insoluble, although the polymer yields were quantitative. The monomer to catalyst mole ratio (M/C) of 100 was found to be adequate in the viewpoints of polymer yield and solubility. The DPF-Br was easily polymerized in aromatic hydrocarbons such as chlorobenzene, benzene, and toluene. They are good solvents for not only the catalyst but also the resulting polymer. However, the polymerization did not proceed in nitrobenzene. The MoCl_4 also showed the similar catalytic activity with that of MoCl_5 . Such organotin and organoaluminium cocatalysts as Me_4Sn , Ph_4Sn , and EtAlCl_2

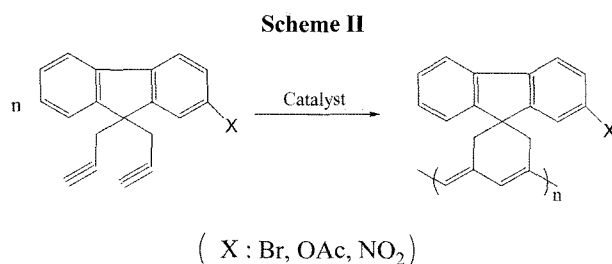


Table I. Polymerization of 2-Bromo-9,9-dipropargylfluorene by Mo-Based Catalysts^a

Exp. No.	Catalyst System ^b (mole ratio)	Solvent	M/C ^c	[M] ₀ ^d	Temp. (°C)	P.Y. (%) ^e	M _n ^f
1	MoCl ₅	Chlorobenzene	50	0.25	60	100	insoluble
2	MoCl ₅	Chlorobenzene	50	0.125	30	100	15,700
3	MoCl ₅	Chlorobenzene	100	0.125	30	98	20,100
4	MoCl ₅	Chlorobenzene	250	0.125	30	65	16,900
5	MoCl ₅	Toluene	100	0.25	30	100	17,800
6	MoCl ₅	Benzene	100	0.25	30	95	16,500
7	MoCl ₅	Chloroform	100	0.25	30	64	11,200
8	MoCl ₅	THF	100	0.25	30	13	-
9	MoCl ₅	Nitrobenzene	100	0.25	30	-	-
10	MoCl ₅ -Me ₄ Sn(1:2)	Chlorobenzene	100	0.25	30	95	16,500
11	MoCl ₅ -Ph ₄ Sn(1:2)	Chlorobenzene	100	0.25	30	92	16,000
12	MoCl ₅ -EtAlCl ₂ (1:2)	Chlorobenzene	100	0.25	30	87	18,300
13	MoCl ₅ -Et ₃ Al(1:2)	Chlorobenzene	100	0.25	30	81	14,400
14	MoCl ₄	Chlorobenzene	100	0.25	30	100	18,900
15	Cp ₂ MoCl ₂ -EtAlCl ₂ (1:2)	Chlorobenzene	100	0.25	30	81	4,250

^aPolymerization was carried out for 24 h. ^bMixture of catalyst and cocatalyst solution was aged for 15 min at room temperature before use.

^cMonomer-to-catalyst mole ratio. ^dInitial monomer concentration of DPF-Br. ^eMethanol-insoluble polymer. ^fThe molecular weights were measured with GPC.

were also used for the polymerization of DPF-Br by MoCl₅. However, the polymer yields were slightly decreased. The Cp₂MoCl₂-EtAlCl₂ catalyst system, which was effective for the polymerization of phenylacetylene and some dipropar-

Table II. Polymerization of 9,9-Dipropargylfluorene and 2-Substituted-9,9-dipropargylfluorenes by MoCl₅ and WCl₆-EtAlCl₂ Catalyst Systems^a

Exp. No.	Monomer	Catalyst System ^b (mole ratio)	Polymer Yield (%) ^c	M _n ^d
1	DPF	MoCl ₅	62	16,500
2	DPF-Br	MoCl ₅	98	20,100
3	DPF-Ac	MoCl ₅	32	8,500
4	DPF-NO ₂	MoCl ₅	5	-
5	DPF	WCl ₆ -EtAlCl ₂ (1:2)	25	4,100
6	DPF-Br	WCl ₆ -EtAlCl ₂ (1:2)	13	3,400
7	DPF-Ac	WCl ₆ -EtAlCl ₂ (1:2)	5	-
8	DPF-NO ₂	WCl ₆ -EtAlCl ₂ (1:2)	0	-

^aPolymerization was carried out in chlorobenzene at 30 °C for 24 h. The monomer-to-catalyst mole ratio (M/C) and initial monomer concentration ([M]₀) were 100 and 0.125 M, respectively. ^bMixture of catalyst and cocatalyst solution was aged for 15 min at room temperature before use. ^cMethanol-insoluble polymer. ^dThe molecular weights were measured with GPC.

gyl monomers,^{44,45} were also found to be effective for the polymerization of DPF-Br. In general, the WCl₆-based catalysts were found to be less effective to give only low yield of polymer. The polymerization behaviors of DPF-Br by Mo- and W-based catalysts were found to be very similar with that of DPF itself. The reaction state and polymer yield according to the polymerization time were consecutively checked from the precipitation of the solution taken from the polymerization reactor. The polymer yields according to the polymerization time revealed that this polymerization proceeds rapidly at early 1 h, reached about 50% yield, and then finally 98 % after 24 h (exp. no. 3). The number-average molecular weights were in the range of 4,250-20,100, depending on the polymerization conditions.

Table II shows the results for the polymerization of DPF and its derivatives by MoCl₅ and WCl₆-EtAlCl₂ catalyst systems. In the case of DPF and DPF-Br by using MoCl₅ catalyst, the polymerization proceeded well to give relatively high yield of polymer. The DPF-Ac by MoCl₅ gave a moderate yield of polymer, whereas DPF-NO₂ gave only a low yield of polymer. When the WCl₆-EtAlCl₂ catalyst system was used, the polymer yield were found to be generally lower than those of MoCl₅ catalyst. Especially, in the cases of dipropargyl monomers carrying acetyl and nitro functional groups, the polymer yields were very low. It might be due to the poisoning effect of these functional groups to the catalyst systems.

Table III. Polymerization of 9,9-Dipropargylfluorene and 2-Substituted-9,9-dipropargylfluorenes by PdCl₂^a

Exp. No.	Monomer	Polymer Yield (%) ^b	M _n ^c
1	DPF	86	7,500
2	DPF-Br	93	7,600
3	DPF-Ac	77	9,900
4	DPF-NO ₂	92	9,300

^aPolymerization was carried out at 90 °C in DMF for 24 h. The monomer-to-catalyst mole ratio (M/C) and initial monomer concentration ($[M]_0$) were 30 and 0.5 M, respectively. ^bMethanol-insoluble polymer. ^cThe molecular weights were measured with GPC.

We also tested the present polymerization of DPF and its derivatives by palladium(II) chloride. Table III shows the results for polymerization of DPF and its derivatives by palladium(II) chloride. The polymerizations proceeded well in homogeneous manner at more elevated temperature (90 °C) to give a high yield of polymer, regardless of the functionalities of monomer, although the molecular weights were somewhat low (7,500-9,900). The same polymerizations at lower temperature (50 °C) were also proceeded in homogeneous manner to give a moderate yield of polymers (polymer yield: 35-52%).

Characterization of Polymer Structure. The polymer structures of conjugated cyclopolymers obtained from dipropargylfluorene derivatives were characterized by elemental analysis, NMR (¹H- and ¹³C-), infrared, and UV-visible spectroscopies. The elemental analysis data of reprecipitated poly(DPF-Br) agreed well with the theoretical value: Calcd for (C₁₉H₁₃Br): C, 71.05%; H, 4.08%; Br, 24.87%, Found: C, 70.16%; H, 4.17%; Br, 25.67%.

Figure 1 shows ¹H-NMR spectra of poly(DPF) and its homologues in CDCl₃. They all showed the aromatic fluorene proton peaks at the aromatic region of 7.0-7.0 ppm. The vinyl protons of conjugated polymer backbone were also observed simultaneously at the aromatic proton region. The peaks of methylene protons adjacent to the conjugated carbons were observed at 1.6-4.0 ppm. Figure 2 shows the typical ¹³C-NMR spectrum of poly(DPF-Br) prepared by MoCl₅ in CDCl₃. This spectrum did not show any acetylenic carbon peaks (72.76, 80.50 ppm) of DPF-Br. Instead, the ¹³C-NMR spectrum of poly(DPF-Br) showed the aromatic carbons of fluorene groups and the olefinic carbon peaks of the conjugated polymer backbone at the region of 118-156 ppm. The peaks of the methylene carbons of poly(DPF-Br) were observed around 46 ppm. More informations on the microstructures of poly(1,6-heptadiyne)-based conjugated cyclopolymers can be obtained from the studies on the resonance for the quaternary carbon atoms.⁴⁶ It has been reported that the two clusters of resonances for the quaternary carbon atoms in poly(diethyl dipropargylmalonate) can be assigned to the quaternary carbons in five-membered rings (57-

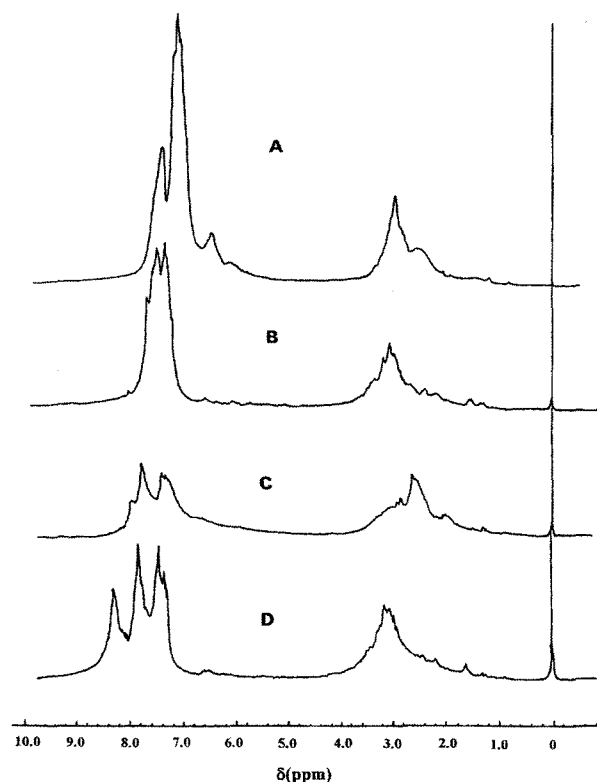


Figure 1. ¹H-NMR spectra of poly(DPF) [A], poly(DPF-Br) [B], poly(DPF-Ac) [C], and poly(DPF-NO₂) [D] in CDCl₃.

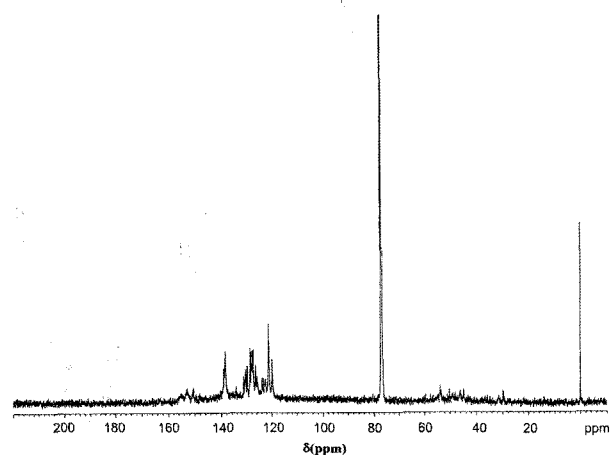


Figure 2. ¹³C-NMR spectrum of poly(DPF-Br) in CDCl₃.

58 ppm) and six-membered rings (54-55 ppm), respectively. As shown in Figure 2, there is only one peak at around 54 ppm. This observation infers that the present poly(DPF-Br) has the six-membered ring structure majorly in the polymer main chains. It was also found that other two homologues [poly(DPF-Ac), poly(DPF-NO₂)] have the six-membered ring moieties majorly in the polymer structure.

Figure 3 shows the FTIR spectra of poly(DPF) and its

homologues in KBr pellet. They did not show any acetylenic $C \equiv C$ bond stretching and $=C-H$ bond stretching frequencies. Instead, the $C=C$ stretching frequency peaks of aromatic fluorenes around 1600 cm^{-1} became more intense because of the the $C=C$ stretching frequency of conjugated polymer backbone than those of dipropargyl monomers. A carbonyl

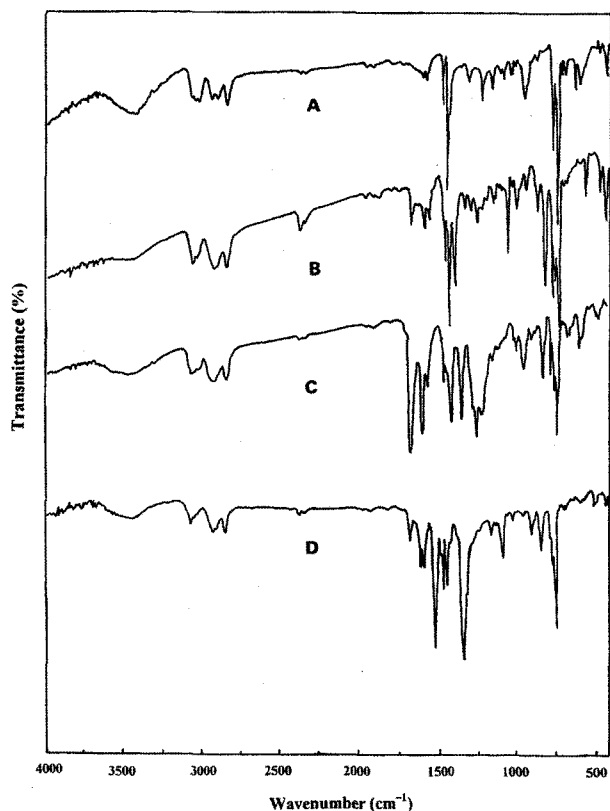


Figure 3. FTIR spectra of poly(DPF) (A), poly(DPF-Br) (B), poly(DPF-Ac) (C), and poly(DPF-NO₂) (D).

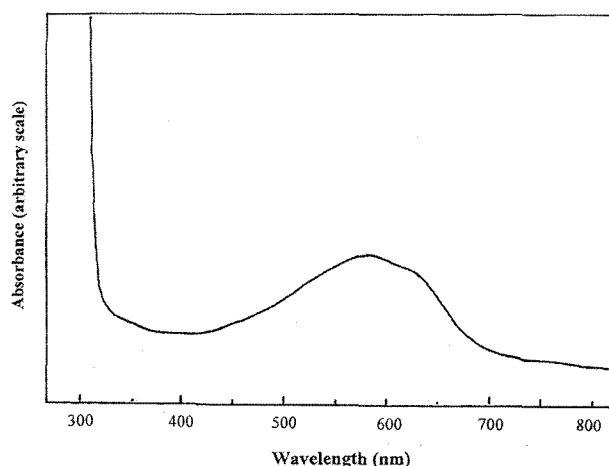


Figure 4. UV-visible spectrum of poly(DPF-Br) prepared by MoCl₅ (solvent: DMF).

stretching frequencies of acetyl functional groups in poly (DPF-Ac) are observed at 1679 cm^{-1} . In spectrum D [poly (DPF-NO₂)], the symmetrical and antisymmetrical NO₂ stretching frequencies of aromatic nitro compounds are seen at 1339 and 1521 cm^{-1} , respectively. Figure 4 shows the typical UV-visible spectrum of poly(DPF-Br) in the visible region. This spectrum showed a characteristic absorption peak at the visible region because of the conjugated polymer backbone. It showed a characteristic peculiar absorption peak at about 580 nm . The absorption spectra of the polymerization solution according to the polymerization time were also checked. The interesting absorption peak at around 580 nm was newly observed even after the polymerization time of 30 min as the polymerization proceed. This bathochromic shift of absorption peaks indicated that the conjugated polymer system was formed. These spectral data indicated that the present poly(DPF) derivatives have a conjugated backbone system having 6-membered cyclic recurring units majorly.

Polymer Properties. The resulting poly(DPF) derivatives prepared by Mo- and W-based catalysts were majorly brown powders, whereas the same samples prepared by PdCl₂ were mostly black powders. The solubility test was performed for powdery samples in excess solvent. The poly(DPF-Br)s were completely soluble in halogenated and aromatic hydrocarbons such as methylene chloride, chloroform, benzene, toluene, and chlorobenzene, but insoluble in ethyl ether, hexanes, and methanol. Poly(DPF-Ac) and poly(DPF-NO₂) showed similar solubility behaviors with that of poly(DPF-Br).

The thermal properties of the resulting polymers were studied by thermogravimetric analysis method. The TGA thermogram of poly(DPF-Br) showed that this polymer start to decompose after 260°C and it retains 98% of its original weight at 200°C , 95% at 290°C , 90% at 325°C , 70% at 391°C , 60% at 618°C , and 55% at 700°C . The slight weight losses at relatively low temperatures are due to the absorbed moisture and/or organic residues in the polymer. In the case of poly(DPF-Ac), an abrupt weight loss was

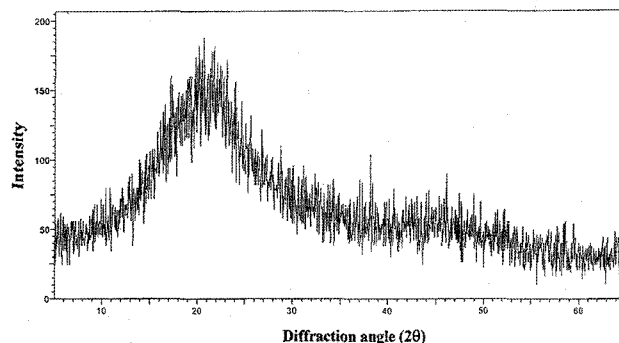


Figure 5. X-ray diffractogram of poly(DPF-Br) prepared by MoCl₅.

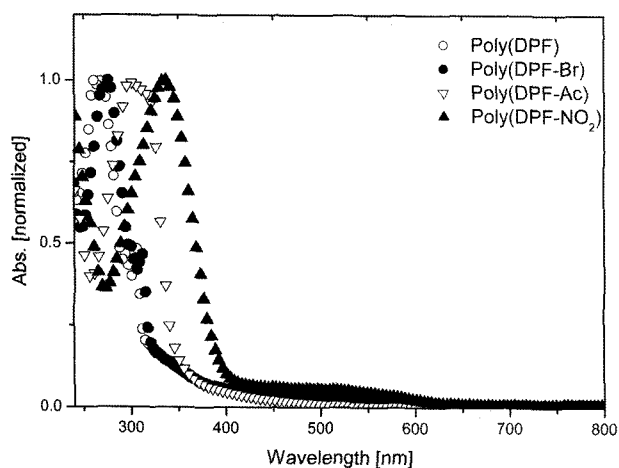


Figure 6. Optical absorption spectra of poly(DPF) and its homologues in chloroform solution.

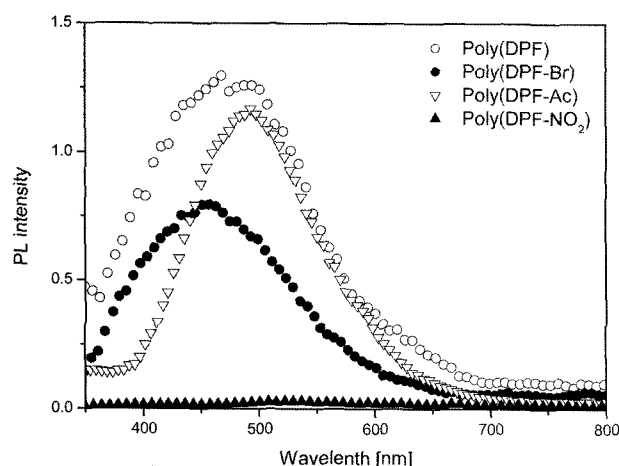


Figure 7. Emission spectra of poly(DPF) and its homologues in chloroform solution.

observed after 350 °C. The char yields of poly(DPF-Br), poly(DPF-Ac), and poly(DPF-NO₂) after heating up to 700 °C were 55, 45, and 65%, respectively, whereas the char yield of poly(DPF) itself was 19%.

The morphology of poly(DPF) derivatives was also investigated by X-ray diffraction analysis. Figure 5 shows the typical X-ray diffractogram of poly(DPF-Br) prepared by MoCl₅. Because the peak in the diffraction pattern is broad and the ratio of the half-height width to diffraction angle ($\Delta 2\theta/2\theta$) is greater than 0.35, other two polymers showed similar diffractograms. Thus the present poly(DPF) derivatives are mostly amorphous.

Figure 6 shows the optical absorption spectra of poly(DPF), poly(DPF-Br), poly(DPF-Ac), and poly(DPF-NO₂) in chloroform solution. The absorption spectra of the present polymers have two peaks at around 263–336 and 419–620 nm, which originate from the fluorene substituents and π -

conjugated main chains, respectively. The peak due to the fluorene units is the major portion compared to the absorption λ_{max} due to the π - π^* transitions of conjugated main chains.

Figure 7 shows emission spectra of the poly(DPF), poly(DPF-Br), poly(DPF-Ac), and poly(DPF-NO₂) in chloroform solution. When the polymer solutions were excited at maximum absorption wavelength of each polymer, emission peaks of the present polymers are observed at about 457–491 nm, which depends on the substituents of fluorene units. However, poly(DPF-NO₂) was difficult to obtain the emission peak, due to the nitro substituent on fluorene units.

Conclusions

In this article, we demonstrated the synthesis of a series poly(1,6-heptadiyne) homologues by the cyclopolymerization of 9,9-dipropargylfluorene derivatives, and elucidated the polymer structure by NMR, IR, and UV-visible spectroscopic analyses. The polymerization proceeded well by Mo-based transition metal catalysts. And PdCl₂ was also found to be very effective to give high yield of polymer, regardless of the substituents. The spectroscopic studies on the quaternary carbon atoms in these cyclopolymers indicated that the present polymers has the six-membered ring structure majorly in the polymer main chain. The polymers were generally soluble in halogenated and aromatic hydrocarbons such as methylene chloride, chloroform, benzene, toluene, and chlorobenzene. The X-ray diffraction analysis data for the polymers revealed that the present conjugated cyclopolymers are mostly amorphous. It was concluded that the emission properties of poly(1,6-heptadiyne)-based cyclopolymer system depend on the substituents of fluorene side chain.

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