Cyclopolymerization of 1,1-Dipropargyl-1-silacyclohexane by Transition Metal Catalysts

Yeong-Soon Gal,[†] In-Sook Lee, Eun-Hee Chang, Yun-Cheol Jeong,[‡] and Young-Woo Kwak[*]

Department of Chemistry, Kyungpook National University, Daegu 702-701, Korea. [*]E-mail: ywkwak@knu.ac.kr
[†]Polymer Chemistry Laboratory, College of General Education, Kyungil University, Hayang, Kyungbuk 712-701, Korea
[‡]R&D Center, Heesung Electronics LTD., Hosan-Dong, Dalseo-Gu, Daegu 704-230, Korea
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A conjugated spirocyclic polymer was synthesized *via* the cyclopolymerization of 1,1-dipropargyl-1-silacyclohexane with various transition metal catalysts. The monomer, 1,1-dipropargyl-1-silacyclohexane was synthesized by Grignard reaction of 1,1-dichloro-1-silacyclohexane with propargyl magnesium bromide. This polymerization proceeded well to give the corresponding poly(1,1-dipropargyl-1-silacyclohexane). The catalytic activity of WCl_6 was found to be similar with that of $MoCl_5$. The structure of polymer having the conjugated backbone with silacyclohexane moieties was characterized by such instrumental methods as NMR ([1]H-, [13]C-), IR, and UV-visible spectroscopies. The resulting polymers were mostly yellow or light-brown powders, depending on the catalyst systems used. This polymer was completely soluble in halogenated and aromatic hydrocarbons such as chloroform, 1,2-dichloromethane, benzene, toluene, and chlorobenzene, etc. The thermal and oxidative stabilities of polymer were also studied and discussed.

Key Words : Cyclopolymerization, Catalysts, Conjugated spirocyclic polymer, Polyacetylenes, Silacyclohexane

Introduction

Conjugated organic materials have attracted much attention because of their good ability to form thin films, good mechanical properties, and excellent electro-optical properties, etc.[1-5] Polyacetylene (PA), a prototypical conjugated polymer, is structurally the simplest one, and it can be made free-standing thin film by using Shirakawa catalysts $[Ti(OC_4H_9)_4-Al(C_2H_5)_3]$.[6] However, its intractability and instability have significantly limited its applications as a specialty material. The introduction of functional substituents into the polyacetylene causes important changes in the polymer, such as solubility, stability, melting, chemical, optical, electrical, and other properties.[7-10]

Various types of PA derivatives have been designed and synthesized.[7-15] The polymers having a conjugated backbone are expected to show unique properties such as electrical conductivity, paramagnetism, migration and transfer of energy, color, chemical reactivity, and complex formation ability.[10] Because of these properties, PA and its homologues have been promising as organic semiconductors,[16] as membranes for gas separation and for liquid-mixture separation,[17] as chiro-optical materials,[18] as side-chain liquid crystals,[8] as materials for chemical sensors,[19] and as materials for nonlinear optical property[10,20] and for photoluminescence and electroluminescence properties.[21-22]

Cyclopolymerization is an addition polymerization that leads to introduction of cyclic structures into the main chain of the polymer *via* an alternating intramolecular-intermolecular chain propagation.[23] α,ω-Alkadiynes are very interesting examples of substituted acetylenes, which can be susceptible to the ring-forming polymerization to give a new type of conjugated polymer backbone.[10,24] Gibson *et al.*

reported an insoluble 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 $Ti(OC_4H_9-n)_4$ and $Al(C_2H_5)_3$, using a specifically designed reactor.[25] Introduction of functional substituent to the methylene carbon at the 4-position of 1,6-heptadiyne solved the predescribed problems of poly(1,6-heptadiyne) and expanded the research areas of π-conjugated polymers. The polymerizations of various 1,6-heptadiynes having substituents had been carried out by Mo- and W-based catalysts.[10-13,26]

Silicon-containing dipropargyl monomers such as dimethyldipropargylsilane, methylphenydipropargylsilane, and diphenyldipropargylsilane were synthesized and cyclopolymerized.[27] And also silicon-containing mono- and disubstituted polyacetylenes were prepared by the transition metal catalyzed polymerization of the corresponding acetylene derivatives.[28-30] However, there have been no reports on the synthesis of conjugated polymers with silacycloalkane moieties. Now we report the synthesis of a spiro-type conjugated cyclopolymer by the polymerization of 1,1-dipropargyl-1-silacyclohexane by various transition metal catalysts and the characterization of the resulting polymer.

Experimental Section

Materials. 1,5-Dibromopentane (Aldrich Chemicals, 97%) and silicon tetrachloride (Aldrich Chemicals, 99%) were 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+%), WCl_6 (Aldrich Chemicals, 99.9+%), and $HgCl_2$ (Aldrich Chemicals, 99.9+%) were used without further purification.

Et$_3$SiH (Aldrich Chemicals, 99%) and EtAlCl$_2$ [Aldrich Chemicals, 25 wt % (1.8 M) solution in toluene] and Me$_4$Sn (Aldrich Chemicals, 95%) were used as received. Ph$_4$Sn (Aldrich Chemicals, 97%) was purified by recrystallizing twice from carbon tetrachloride. PdCl$_2$ (Aldrich Chemicals, 99.9+%) was used as received. The solvents were analytical grade materials. They were dried with an appropriate drying agent and distilled.

General procedures. GC analyses were performed on a Hewlett-Packard 5890 FID chromatograph, using a HP-5 (cross-linked 5% methylphenylsilicon) capillary column (30 m). NMR (^{1}H- and ^{13}C-) spectra were recorded on a Varian Mecury 300 MHz and Bruker AM-300 NMR spectrometer in CDCl$_3$ and the chemical shifts were reported in ppm units with tetramethylsilane (TMS) as an internal standard. Infrared spectra were obtained with Mattson Galaxy 7020A FT-IR spectrophotometer using a KBr pellet, and frequencies are given in reciprocal centimeters. Elemental analyses were performed with a FISONS EA1106 Elemental Analyzer. UV-visible spectra were measured in THF on a Shimadzu UV-2100 PC spectrophotometer. Molecular weights were determined by a gel permeation chromatography (Waters 254) equipped with μ-Styragel columns using CH$_2$Cl$_2$ as an eluent. Monodisperse polystyrene standard samples were used for molecular weight calibration. Thermal properties of polymer were performed with SSC 5200H TG/DTA 320 and 5200H DSC 220 under a nitrogen atmosphere at a heating rate of 10 ^{o}C/min.

Synthesis of 1,1-dichloro-1-silacyclohexane.[31] A 500 mL three-neck flask equipped with a mechanical stirrer and reflux condenser was charged with 50 mL of anhydrous ethyl ether and 11.0 g (0.45 mol) of magnesium turnings. A di-Grignard reagent was prepared by adding 27.3 mL (0.20 mol) of 1,5-dibromopentane dissolved in 150 mL of anhydrous ethyl ether under nitrogen atmosphere to the reaction mixture at ice-water temperature. After being stirred for an additional 3 hrs at room temperature, the resulting solution was transferred to a dropping funnel under a nitrogen atmosphere. The dropping funnel was then attached to one neck of 1000 mL three-neck flask equipped with mechanical stirrer and water condenser. The di-Grignard solution was then added dropwise with stirring under nitrogen to 20.6 mL (0.18 mol) of silicon tetrachloride in 500 mL of dry ethyl ether for 2 hrs at ice-water temperature. After completion of the addition, the reaction mixture was stirred for 1 hr at same temperature and then refluxed on the water bath for additional 4 hrs. The reaction mixture was then cooled and the precipitated magnesium salts were filtered from the etheral solution containing the product on the Büchner funnel, with use of suction. The salts were washed well with ether. Extraction and main portion were combined, washed with water and dried over MgSO$_4$. Distillation in a partial vacuum afforded 1,1-dichlorosilacyclohexane in 44% yield (0.08 mol).

MS m/z (relative intensity): 172 (M$^+$ +4, 3.4), 170 (M$^+$ +2, 20.5), 168 (M$^+$, 26.0).

Synthesis of 1,1-dipropargyl-1-silacyclohexane (DPSCH).

A 250 mL three-neck flask equipped with a mechanical stirrer and reflux condenser was charged with 125 mL of anhydrous ethyl ether and 7.9 g (0.32 mol) of magnesium turnings under ice-bath. A Grignard reagent was prepared by adding 24.6 mL (0.28 mol) of propargyl bromide and 0.28 g (1.03 mmol) of HgCl$_2$ dissolved in 25 mL of anhydrous ethyl ether to the reaction mixture at ice-water temperature under nitrogen atmosphere. After completion of the addition, the reaction mixture was stirred for 3 hrs at room temperature, the resulting solution was transferred to a dropping funnel under a nitrogen atmosphere. The dropping funnel was then attached to one neck of 500 mL three-neck flask equipped with mechanical stirrer and reflux condenser. The Grignard solution was then added dropwise with stirring under nitrogen to 12.1 g (72 mmol) of 1,1-dichloro-1-silacyclohexane in 25 mL of dry ethyl ether at dry ice/acetone bath. After completion of the addition, the reaction mixture was stirred at room temperature for an additional 7 hrs. Then the reaction mixture was quenched with saturated NH$_4$Cl solution and extracted with ethyl ether. The concentrated crude product was purified by fractional distillation (26 mmol, yield: 36%). MS m/z (relative intensity): 176 (M$^+$, 0.14). IR (cm^{-1}, KBr pellet): 3300 ($\equiv$C-H), 2919, 2853, 2117 (C$\equiv$C), 1399, 1182, 990, 910, 782, 626. ^{1}H-NMR (CDCl$_3$): δ 1.07-1.13 (m, 4H, silacyclohexyl protons), 1.66-1.75 (m, 2H, silacyclohexyl protons), 1.91 (d, 4H, 2CH$_2$-C$\equiv$C, J = 3.0 Hz), 1.96-2.02 (m, 4H, silacyclohexyl protons), 2.13 (t, 2H, 2C$\equiv$C-H, J = 3.0 Hz). ^{13}C-NMR (CDCl$_3$): δ 3.90, 11.28, 24.51, 29.93, 68.03, 81.21. Anal. Calcd for C$_{11}$H$_{16}$Si: C, 74.93; H, 9.15. Found: C, 74.13; H, 8.98.

Polymerization procedures. All procedures for the preparation of catalyst system and polymerization were carried out under dry nitrogen atmosphere because the active species are sensitive to moisture or oxygen.[13] Typical polymerization procedures are as follows.

Polymerization of DPSCH by WCl$_6$. In a magnetic-stirred 20 mL reaction vessel equipped with rubber septum, chlorobenzene (0.32 mL), 0.50 mL (0.05 mmol, M/C = 20) of 0.1 M WCl$_6$ solution, and 0.18 mL (1 mmol, [M]$_o$ = 1.0 M)) of DPSCH were added in that order given. And the polymerization was carried out in oil bath at 60 ^{o}C for 24 hrs under nitrogen atmosphere. Then, 10 mL of chloroform was added to the reaction mixture. The polymer solution was poured into an large excess of methanol, filtered from the solution, and then dried under vacuum at 40 ^{o}C for 24 hrs. The yield of polymer was 45%. ^{1}H-NMR (CDCl$_3$): δ 0.65-0.77 (4H, m, 2SiCH$_2$CC), 1.25-2.34 (10H, m, 2SiCH$_2$C=, 2SiCCH$_2$C, and CCH$_2$C), 6.60-7.07 (2H, m, vinyl protons). ^{13}C-NMR (CDCl$_3$): δ 12.43, 24.32, 25.10, 25.29, 29.71, 125.70, 129.09, 137.21, 141.73.

Polymerization of DPSCH by WCl$_6$-Ph$_4$Sn. In a magnetic-stirred 20 mL reaction vessel equipped with rubber septum, 0.18 mL (1 mmol, [M]$_o$ = 1.0 M) of DPSCH and chlorobenzene (0.42 mL) were added. Then the catalyst solution of 0.40 mL (0.04 mmol, M/C = 25) of 0.1 M WCl$_6$ solution and 17.1 mg (0.04 mmol) of Ph$_4$Sn was injected into the reaction vessel. After the polymerization was carried

out in oil bath at 60 °C for 24 hrs under nitrogen atmosphere, 10 mL of chloroform was added to the reaction mixture. The polymer solution was poured into an large excess of methanol, filtered from the solution, and then dried under vacuum at 40 °C for 24 hrs. The yield of polymer was 75%.

Polymerization of DPSCH by PdCl₂. In a magnetic-stirred 20 mL reaction vessel, 0.18 mL of DPSCH (1 mmol, $[M]_o$ = 1.0 M), 8.7 mg of PdCl₂ (0.05 mmol, M/C = 20), and DMF (0.82 mL) were added in that given order and sealed with a rubber septum after flushing with nitrogen gas. The polymerization was carried out at 60 °C for 24 hrs. Then the polymer solution diluted with DMF was poured into a large excess amount of methanol. The precipitated polymer was filtered and dried. The yield of polymer was 35%.

Results and Discussion

The cyclopolymerizable dipropargyl derivative with sila-cyclohexane, DPSCH, was prepared by using the Grignard reaction (Scheme 1). 1,1-Dichloro-1-silacyclohexane was easily prepared by the Grignard reaction of 1,5-dibromo-pentane with silicon tetrachloride in 44% yield. The second Grignard reaction of propargyl bromide and 1,1-dichloro-1-silacyclohexane gave DPSCH in 36% yield.

The cyclopolymerization of DPSCH was performed by various transition metal catalysts as follows (Scheme 2).

We used the W- and Mo-based catalysts, which have been found effective for the polymerization of some monosubstituted acetylenes and the cyclopolymerization of nonconjugated diynes.[10,13,27] Table 1 shows the results for the polymerization of DPSCH by various transition metal catalysts. In general, W-based catalysts were found to be very effective for the present cyclopolymerization. WCl₆ alone polymerize DPSCH monomer to give the polymer in 61% yield. As the mole ratio (M/C) of monomer to catalyst is increased, the polymer yields were generally decreased (exp. no. 1-3). In this
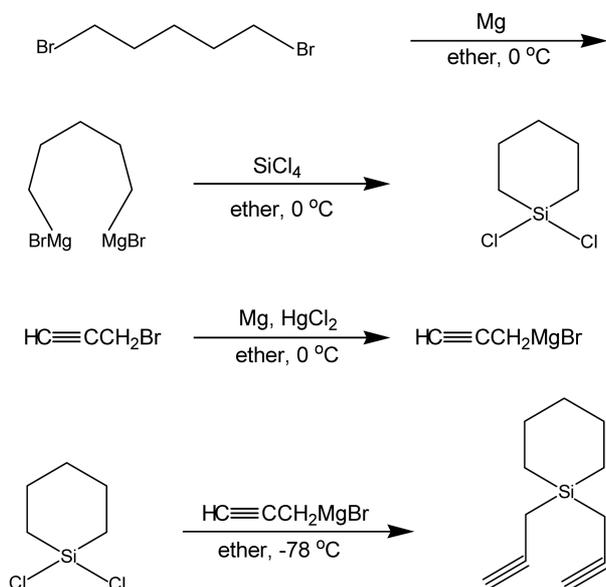
Scheme 1
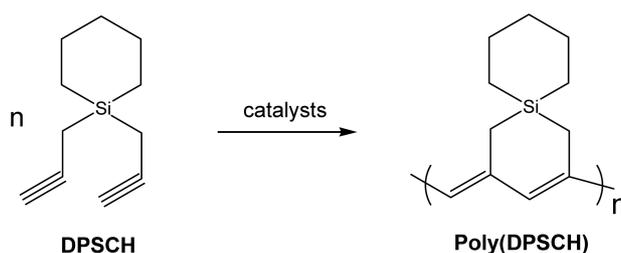
Scheme 2

Table 1. Cyclopolymerization of 1,1-Dipropargyl-1-silacyclohexane by Transition Metal Catalysts[a]

Exp. No	Catalyst	M/C[b]	P. Y. (%)[c]
1	WCl₆	15	61
2	WCl₆	20	46
3	WCl₆	25	41
4	MoCl₅	15	55
5	MoCl₅	20	50
6	MoCl₅	25	47
7	PdCl₂[d]	20	35

[a]Polymerization was carried out in chlorobezene (exp. no. 1-3) and in toluene (exp. no. 4-6) at 60 °C for 24 hrs. Initial monomer concentration was 1.0 M. [b]Mole ratio of monomer to catalyst. [c]Methanol-insoluble polymer. [d]The polymerization solvent was DMF.

polymerization of DPSCH, the catalytic activity of MoCl₅ (47-55%) was found to be very similar with that of WCl₆ (41-61%). The similar catalytic activity of WCl₆ and MoCl₅ catalysts also been observed for the polymerization of 1-ethynylcyclohexene,[32] triethyl α-propargylphosphono-acetate,[33] and 2-ethynyl-N-propargylpyridinium tetraphenyl-borate.[34] And also, we studied the polymerization behaviors of DPSCH by palladium(II) chloride. The polymerizations proceeded in more mild manner to give a 35% yield of polymer.

In addition, we studied the temperature effect for the polymerization of DPSCH by WCl₆ in chlorobenzene (M/C = 20, $[M]_0$ = 1.0 M). The temperature of 60 °C was found to be adequate for this cyclopolymerization. The yields of polymer at the temperatures of 40, 60, and 80 °C were 37, 46, and 31%, respectively.

Table 2 shows the results for the polymerization of DPSCH by WCl₆-based catalysts. The various organotin, organosilicon, and organoaluminium compounds were used as cocatalysts.[7,10] Ph₄Sn among three organotin compounds showed the highest cocatalytic activity for the present cyclopolymerization. Et₃SiH rather decreased the yield of polymer slightly. EtAlCl₂, which had showed the high cocatalytic activity for some cyclopolymerization of di-propargyl monomers such as dipropargyl ether,[35] dihexyl-dipropargylammonium salts,[36] and dipropargylfluorene,[37] increased the yield of polymer slightly. The molecular weights (Mw) of resulting poly(DPSCH)s were relatively low in the range of 3,300-5,200 and the polydispersities were in the range of 1.48-1.92.

Table 3 shows the solvent effect for the polymerization of DPSCH. The DPSCH was easily polymerized in aromatic

Table 2. Cyclopolymerization of 1,1-Dipropargyl-1-silacyclohexane by WCl$_6$-Based Catalysts[a]

Exp. No.	Catalyst system (mole ratio)[b]	P.Y. (%)[c]	Mn[d]	Mw[d]	PD (Mw/Mn)	Color[e]
1	WCl$_6$	41	2,100	3,400	1.62	l-b
2	WCl$_6$-Me$_4$Sn (1:1)	29	2,200	4,200	1.92	l-y
3	WCl$_6$-Ph$_4$Sn (1:1)	75	2,300	4,300	1.87	y
4	WCl$_6$-(n-Bu)$_4$Sn (1:1)	52	2,200	3,300	1.50	l-y
5	WCl$_6$-(n-Bu)$_4$Sn (1:2)	37	2,000	3,400	1.70	y
6	WCl$_6$-Et$_3$SiH (1:1)	35	2,700	4,000	1.48	y
7	WCl$_6$-Et$_3$SiH (1:2)	39	2,400	4,000	1.67	y
8	WCl$_6$-EtAlCl$_2$ (1:1)	55	3,000	5,200	1.73	y
9	WCl$_6$-EtAlCl$_2$ (1:2)	49	2,400	4,100	1.70	l-b

[a]Polymerization was carried out in chlorobezene 60 °C for 24 hrs. [b]Mixture of catalyst and cocatalyst solution was aged for 15 min at room temperature before use. The mole ratio (M/C) of monomer to catalyst and initial monomer concentration ([M]$_o$) were 25 and 1.0 M, respectively. [c]Methanol-insoluble polymer. [d]The molecular weights were measured with GPC. [e]The polymer color: y = yellow, l-b = light-brown, l-y = light-yellow.

Table 3. Solvent Effect for the Cyclopolymerization of 1,1-Dipropargyl-1-silacyclohexane by WCl$_6$[a]

Exp. No.	Solvent	P.Y. (%)[b]	Mn[c]	Mw[c]	PD (Mw/Mn)	Color[d]
1	1,2-dichloroethane	76	2000	3600	1.80	l-y
2	chloroform	70	3400	6600	1.94	l-b
3	cyclohexene	54	2700	4200	1.56	y
4	toluene	54	2900	5400	1.86	l-y
5	chlorobenzene	46	2600	4200	1.62	l-b
6	tetrahydrofuran	39	2400	3600	1.50	l-b
7	cyclohexane	35	2000	2500	1.25	l-y
8	tetralin	20	2100	2700	1.29	l-y
9	1,4-dioxane	12	1300	2000	1.54	l-b

[a]Polymerization was carried out by WCl$_6$ at 60 °C for 24 hrs. The mole ratio (M/C) of monomer to catalyst and initial monomer concentration ([M]$_o$) were 20 and 1.0 M, respectively. [b]Methanol-insoluble polymer. [c]The molecular weights were measured with GPC. [d]The polymer color: y = yellow, l-b = light-brown, l-y = light-yellow.

hydrocarbons such as chlorobenzene, and toluene. And, the high yields of polymer were obtained in the halogenated hydrocarbons such as 1,2-dichloroethane and chloroform. They are good solvents for not only the catalyst but also the resulting polymer. However, the relatively low yields of polymer were in the solvent of cyclohexane, tetralin, and 1,4-dioxane.

The solubility behaviors of the conjugated spirocyclic polymer are summarized in Table 4. This polymer was completely soluble in halogenated and aromatic hydrocarbons such as dichloromethane, chloroform, benzene, toluene, and chlorobenzene, and partially soluble in ethyl ether and DMF, but insoluble in n-hexane, methanol, and acetone.

The polymer structure of poly(DPSCH) was characterized by NMR (^{1}H- and ^{13}C-), infrared, and UV-visible spectroscopies. Figure 1 shows the FT-IR spectra of DPSCH and poly(DPSCH) in KBr pellet. The IR spectrum of poly-(DPSCH) did not show any acetylenic C≡C bond stretching (2117 cm^{-1}) and ≡C-H bond stretching (3300 cm^{-1}) frequencies. Instead, the C=C stretching frequency peaks of conjugated polymer backbone was observed at around 1602 cm^{-1}. The aliphatic C-H stretching peaks were observed at 2853 and 2919 cm^{-1}. A very strong peak of Si-C linkages of polymer was observed at 794 cm^{-1}.

The ^{1}H-NMR spectrum of poly(DPSCH) in CDCl$_3$ did not show the acetylenic proton peak of monomer. Instead, the new vinyl protons of conjugated polymer backbone were

**Table 4**. Solubility Behavior of Poly(1,1-dipropargyl-1-silacyclo-hexane)[a]

Solvent	Solubility[b]	Solvent	Solubility[b]
Toluene	+ +	THF	+ +
Benzene	+ +	Carbon tetrachloride	+ +
Chlorobenzene	+ +	1,4-Dioxane	+ +
Cyclohexene	+ +	Ethyl ether	+ −
Chloroform	+ +	DMF	+ −
Triethylamine	+ +	*n*-Hexane	− −
Dichloromethane	+ +	Methanol	− −
1,2-Dichloroethane	+ +	Acetone	− −

[a]The solubility test was performed for powdery samples in excess solvent. [b]Solubility; + + : soluble, + − : partially soluble, − − : insoluble

observed in the range of 6.60-7.07 ppm. The peaks of the methylene protons of silacyclohexane adjacent to the silicon atom were observed at 0.65-0.77 ppm. And the peaks of the three methylene protons of silacyclohexane and two methylene protons adjacent to the vinylic carbons were observed at 1.25-2.34 ppm. The ^{13}C-NMR spectrum of poly(DPSCH) in CDCl$_3$ did not show any acetylenic carbon peaks (68.03, 81.21 ppm) of DPSCH. Instead, the spectrum of poly-(DPSCH) exhibited the new olefinic carbon peaks of the conjugated polymer backbone at the region of 125.70-141.73 ppm. The peaks of various methylene carbons of poly(DPSCH) were observed at the region of 12.43-29.71 ppm. Figure 2 shows the typical UV-visible spectrum of
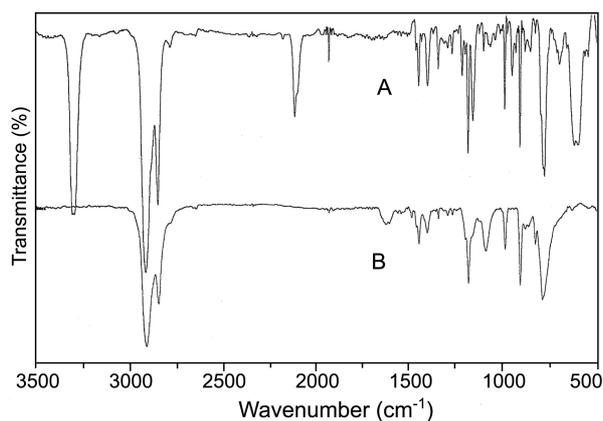
Figure 1. FT-IR spectra of DPSCH (A) and poly(DPSCH) (B) in KBr pellet.
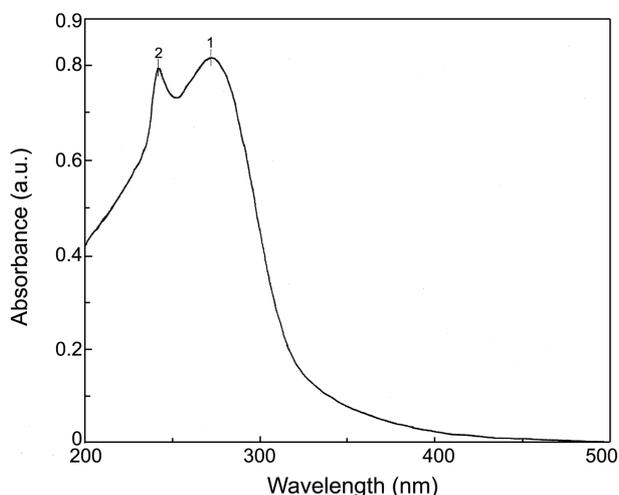
Figure 2. UV-visible spectrum of poly(DPSCH) in THF.

poly(DPSCH) in THF. This spectrum showed a characteristic UV absorption band at 280 nm, which is originated from the $\pi \rightarrow \pi^*$ transition of the conjugated polymer backbone. These spectral data indicated that the present poly(DPSCH) have a conjugated backbone system having spiro cyclic recurring units.

The resulting poly(DPSCH)s by W- and Mo-based catalysts were yellow or light-brown powders, whereas the polymer prepared by PdCl$_2$ were mostly black powder. As mentioned previously, PA and poly(1,6-heptadiyne) itself were easily oxidized in air at room temperature.[38] Thus we studied the oxidative stability of poly(DPSCH). Figure 3 shows the IR spectra of poly(DPSCH) as a function of exposing time in air. The IR spectrum of poly(DPSCH), which had been
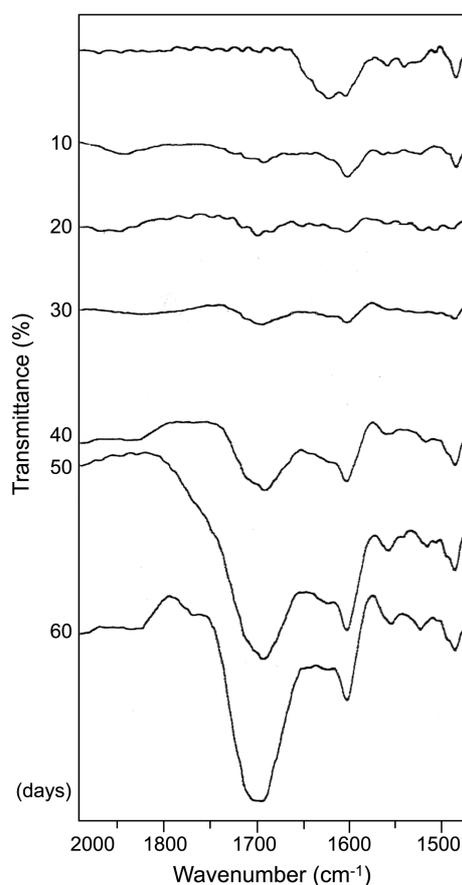

Figure 3. The change of absorption peak at the region of carbonyl peak of poly(DPSCH) as a function of exposing time in air.

exposed for 10 days to air at room temperature, showed a very small new carbonyl absorption band at 1700 cm^{-1}. This polymer was found to be more stable to air oxidation than those of PA and poly(1,6-heptadiyne) itself. As the exposing time was increased, the carbonyl peak intensities were gradually increased. This phenomenon was caused by air oxidation of the conjugated polymer backbone as suggested in Scheme 3.

The TGA thermogram of poly(DPSCH) in Figure 4 showed that this polymer start to decompose after 167 $^{\circ}$C and it retains 97.5% of its original weight at 200 $^{\circ}$C, 87.3% at 300 $^{\circ}$C, 54.2% at 500 $^{\circ}$C, 47.4% at 600 $^{\circ}$C, and 34.3% at 1000 $^{\circ}$C. The high residual weight even after 850 $^{\circ}$C may be deduced to be due to the formation of Si-C matrices. Figure 5 shows the DSC thermogram of poly(DPSCH) under nitrogen atmosphere. This polymer did not show the characteristic glass-transition temperature (T$_g$) peak as like
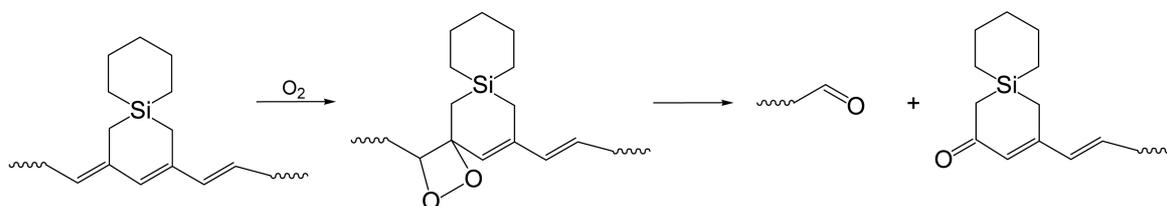
Scheme 3
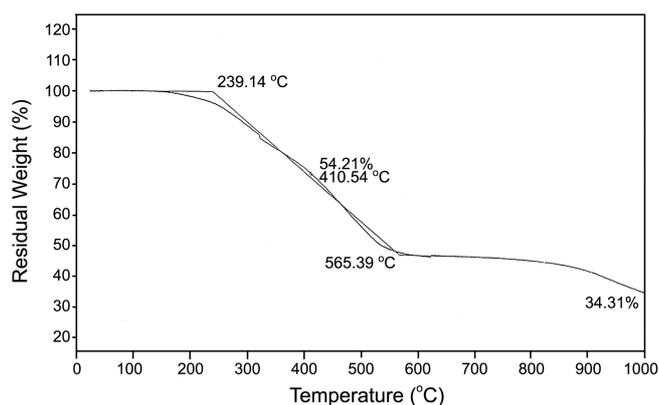
Figure 4. TGA thermogram of poly(DPSCH) measured under nitrogen atmosphere at a heating rate of 10 °C/min.
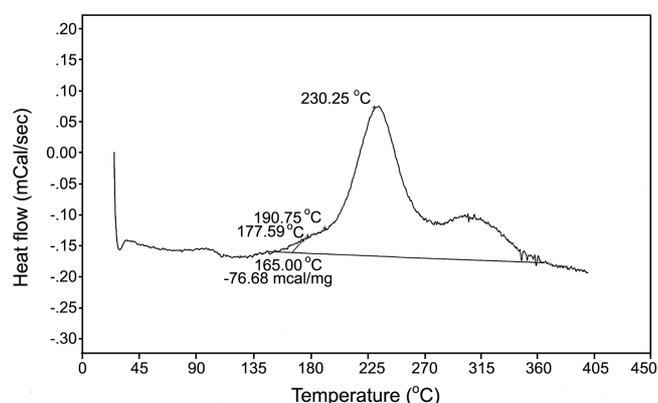
Figure 5. DSC thermogram of poly(DPSCH) measured under nitrogen atmosphere at a heating rate of 10 °C/min.

those other similar conjugated polymers.[39] An exothermic peak started at 165 °C, which is related with the thermal cross-linking of conjugated polymer backbone.

Conclusions

We prepared poly(DPSCH), a conjugated spirocyclic polymer, by the cyclopolymerization of DPSCH in the presence of various transition metal catalysts in moderate yields. The tungsten and molybdenum chlorides were found to be effective for the polymerization of DPSCH and showed similar catalytic activities. Ph_4Sn was very effective cocatalyst for the polymerization of DPSCH by WCl_6. The chemical structure of poly(DPSCH) having the conjugated backbone with silacyclohexane moieties was characterized by various instrumental methods. The polymers were generally soluble in halogenated and aromatic hydrocarbons such as dichloromethane, chloroform, benzene, toluene, and chlorobenzene. The high char yield of poly(DPSCH) even after heating up to 850 °C was possibly due to the formation of Si-C matrices.

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