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Cyclopolymerization of α-Methylbenzyl Dipropargylamine by Transition Metal Catalysts

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Introduction

π-Conjugated oligomers and polymers are intensively studied mainly because of their interesting electrical and optical properties and, more importantly, their potential utility in electronics and photonic applications.[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 [$Ti(OC_4H_9)_4$-$Al(C_2H_5)_3$].[6] However, the drawbacks are that PA is insoluble, infusible, and unstable to air oxidation. Thus it was difficult for practrical applications to opto-electronic devices as an active material. To overcome these problems of PA itself, more stable heterocycle-based polymers such as polypyrrole[7] and polythiophene[8] were prepared, and these materials can be easily obtained in their oxidized conducting form by means of one-step electrochemical synthesis.

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And also, a number of substituted PAs has been prepared by the simple linear polymerization of the corresponding acetylene monomers by various catalyst systems.[9-14] 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.[15] Because of these properties, polyacetylene and its homologues have been promising as organic semiconductors,[16,17] as membranes for gas separation and for liquid-mixture separation,[18] as chiro-optical materials,[19] as side-chain liquid crystals,[10,20] and as materials for nonlinear optical property[21,22] and for photoluminescence and electroluminescence properties.[23-26]

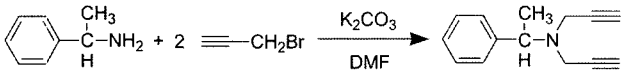
Cyclopolymerization of nonconjugated diynes is very interesting method for the synthesis of conjugated polymer system via an alternating intramolecular-intermolecular chain propagation.[27] 1,6-Heptadiyne itself has been polymerized by various transition metal catalysts into a polyene of cyclic structure.[28,29] The resulting poly(1,6-heptadiyne)s obtained were dark red or black, which indicates a high order of conjugation in the polymer. However, the poly(1,6-heptadiyne)s were also insoluble in any organic solvent and unstable to air oxidation as like with that of PA.[28] Introduction of substituents at 4-position of 1,6-heptadiyne can help enhance the processibility and stability of the polyene systems, thus a variety of substituted poly(1,6-heptadiyne)s were designed and synthesized.[9,30-32]

In recent years, nitrogen-containing polymers have received unabated attention in the design and synthesis of multifunctional polymers.[9] Unlike other π-conjugated polymers, they contain nitrogen heteroatom either in the main chains or in the side chains that provide facile quaternarization reaction and protonation of the nitrogen sites.[9,15]

Now, we report the synthesis of new conjugated cyclopolymer by the cyclopolymerization of a dipropargylamine derivative and the characterization of the resulting conjugated polymer.

Experimental

Materials. α-Methylbenzylamine (Aldrich Chemicals, 99%) and *N,N*-dimethylformamide (Aldrich Chemicals, 99.9+%) were used as received. Propargyl bromide (Aldrich Chemicals, 80 wt% solution in toluene) was dried with CaH_2 and distilled under reduced pressure. Potassium carbonate was dried *in vacuo* at 150 °C for 24 h prior to use. $PdCl_2$ (Aldrich Chemicals, 99.9+%), (Bicyclo[2.2.1]hepta-2,5-diene) dichloropalladium (II) [(bchd)$PdCl_2$, Aldrich Chemicals], $PtCl_2$ (Strem), and $RuCl_3$ (Aldrich Chemicals) were used as received. $MoCl_5$ (Aldrich Chemicals, 99.9+%), WCl_6 (Aldrich Chemicals, 99.9+%), and $EtAlCl_2$ (Aldrich Chemicals, 25



Scheme I. Synthesis of MBDPA.

wt% solution in toluene) were also used without further purification. The solvents were analytical grade materials. They were dried with an appropriate drying agent and distilled.

Synthesis of Monomer. α-Methylbenzyl dipropargylamine (MBDPA) was prepared according to the Scheme I. The detailed procedures for each step are as follows. A mixture of α-methylbenzylamine (10 g, 82.5 mmol) and anhydrous potassium carbonate (34.2 g, 247 mmol) in 200 mL of DMF was stirred and propargyl bromide (29.4 g, 247 mmol) was added dropwise at 50 °C. After the addition, temperature was raised to 100 °C, and stirred for 12 h. DMF was distilled under reduced pressure, and water was added. The organic layer was separated and the aqueous layer was extracted with ether. The combined ether solution was dried over anhydrous $MgSO_4$. After removal of ether, the residue was distilled under reduced pressure (yield: 75%). ^{1}H-NMR ($CDCl_3$, δ, ppm): 1.37 (d, 3H), 2.22 (s, 2H), 3.50 (s, 4H), 3.64 (q, 1H), 7.22~7.36 (m, 5H). ^{13}C-NMR ($CDCl_3$, δ, ppm): 21.44, 39.68, 60.60, 72.72, 79.08, 127.16, 128.44, 144.17. IR (KBr pellet, wavenumber, cm^{-1}): 909, 1155, 1279, 1326, 1433, 1492, 1719, 2121, 2818, 2979, 3069, 3270.

Polymerization of MBDPA by $PdCl_2$. In a 20 mL reactor equipped with rubber septum, 1.0 g (5.07 mmol) of MBDPA, 0.0299 g (0.169 mmol, M/C=30) of $PdCl_2$, and 9 mL of DMF ($[M]_0$=0.5 M) were added in that order given. Then the polymerization was carried out at 90 °C for 24 h under nitrogen atmosphere. The polymerization proceeded in homogeneous manner. After a given time of polymerization, 10 mL of DMF was added to the polymerization solution. The polymer solution was precipitated into a large excess of ether, filtered from the solution, and then dried under vacuum at 40 °C for 12 h. The brown polymer powder was obtained in 52% yield.

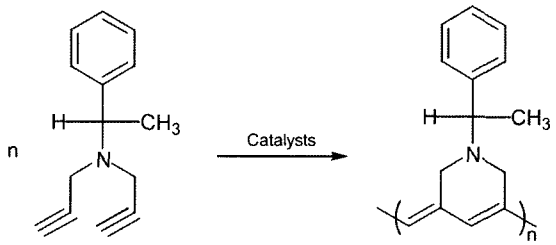
Polymerization of MBDPA by $MoCl_5$-$EtAlCl_2$. In a 20 mL reactor equipped with rubber septum, 1.0 g (5.07 mmol) of MBDPA, and chlorobenzene (2.01 mL, $[M]_0$=1.0 M) were added. Then the catalyst solution of 1.014 mL (1.014 mmol, M/C=50) of 0.1 M $MoCl_5$ solution and 1.014 mL (2.028 mmol) of 0.2 M $EtAlCl_2$ solution after shaking the catalyst solution at room temperature for 15 min, was injected into the polymerization reactor. After a given time of polymerization at 90 °C, 10 mL of chloroform was added to the polymerization solution. The polymer solution was poured into an excess of ether, filtered from the solution, and then dried under vacuum at 40 °C for 12 h. The polymer yield was 61%.

Instruments and Measurement. NMR (^{1}H- and ^{13}C-) spectra of polymers were recorded on a Varian 500 MHz FT-NMR spectrometer (Model: Unity INOVA) in DMSO-d_6 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 FISONS EA1110 elemental analyzer. UV-visible spectra were taken in THF on a JASCO V-530 spectrophotometer. Molecular weights were determined by a gel permeation chromatographer (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 optical absorption spectra were measured by a HP 8453 UV-visible spectrophotometer. The photoluminescence spectra were obtained by Perkin Elmer luminescence spectrometer LS55 (Xenon flash tube) utilizing a lock-in amplifier system with a chopping frequency of 150 Hz.

Results and Discussion

The cyclopolymerization of a dipropargyl monomer, MBDPA, was carried out by various transition metal catalysts (Scheme II).

Table I shows the results for the polymerization of MBDPA by transition metal catalysts. We firstly tested this cyclopolymerization of MBDPA by palladium, platinum, and ruthenium chlorides in DMF solvent. These catalyst systems have been known to be effective for the polymerization of nitrogen-containing acetylene derivatives such as dipropargylamine,[33] dipropargylammonium bromides,[34,35] and tripropargylamine.[36] As shown in this table, $PdCl_2$ polymerized the MBDPA in a moderate yield (52%). $PtCl_2$ and $RuCl_3$ catalysts also the similar catalytic activity with that of $PdCl_2$. The polymer yields for the polymerization of MBDPA by $PdCl_2$ according to the reaction time were measured. This polymerization proceeded more fastly in the initial reaction times, and then the polymer yield was gradually increased to 12 h and the polymer yield reaches upto 52%. These polymerizations



Scheme II. Cyclopolymerization of MBDPA.

Table I. Cyclopolymerization of α-Methylbenzyl Dipropargylamine by Transition Metal Catalysts[a]

No	Catalyst System[b]	Solvent	M/C[c]	$[M]_0$[d]	P.Y.(%)[e]	*Mn*[f]
1	$PdCl_2$	DMF	30	0.5	52	4,100
2	$PtCl_2$	DMF	30	0.5	45	3,500
3	$RuCl_3$	DMF	30	0.5	60	3,800
4	(bchd)$PdCl_2$	DMF	30	0.5	48	3,200
5	WCl_6	Chlorobenzene	50	1.0	9	-
6	WCl_6-$EtAlCl_2$(1:2)	Chlorobenzene	50	1.0	46	8,600
7	$MoCl_5$	Chlorobenzene	50	1.0	57	9,500
8	$MoCl_5$-$EtAlCl_2$(1:2)	Chlorobenzene	50	1.0	61	9,300

[a]Polymerization was carried out at 90 °C for 24 h. [b]Mixture of catalyst and cocatalyst solution was aged for 15 min at room temperature before use. [c]Monomer to catalyat mole ratio. [d]Initial monomer concentration. [e]Ethyl ether-insoluble polymer. [f]The molecular weights were determined by GPC.

proceeded in homogeneous manner. The (bchd)$PdCl_2$, which showed good solubility in the polymerization solvent, also polymerized MBDPA in homogeneous manner to give the corresponding polymer in 48% yield.

Mo- and W-based catalysts, which were found to be very effective for the metathesis polymerization of cycloolefins and the metathesis cyclopolymerization of dipropargyl monomers, were also used for the present polymerization. WCl_6 alone only gave a trace amount of solid products (< 10%). The cocatalyst, $EtAlCl_2$, activated the polymerization of MBDPA by WCl_6 to give 46% yield of polymer. $MoCl_5$ alone and $MoCl_5$-$EtAlCl_2$, which had been found to be very effective for the cyclopolymerization of dipropargyl monomers,[9-13] also found to be effective to give a moderate yield of polymer (57%, 61%, respectively). In our previous works, it was found that the Mo-based catalysts are very effective for the polymerization of such dipropargyl monomers without nitrogen atom as diphenyldipropargylmethane, diethyl dipropargylmolonate, and dipropargylfluorenes to give a quantitative yield of polymer.[9,36] The relatively low yields for the present polymerization of dipropargyl monomer with nitrogen atom may be due to the slight deactivation of Mo-catalyst by the nitrogen atom.

The resulting poly(MBDPA) was found to be completely soluble in such organic solvents as chloroform, chlorobenzene, DMF, DMSO, etc, whereas some similar conjugated polymers obtained from dipropargylamine derivatives such as dipropargylamine,[33] dipropargylammonium bromide,[33] and tripropargylamine[35] were insoluble in any organic solvents. This may be due to the ideal conjugated cyclopolymer structure by the increase of cyclopolymerizability of MBDPA by bulky methylbenzyl substituents and/or the increased solubility of monomer and polymer to the polymerization solvent.

The chemical structure of conjugated cyclopolymer obtained from MBDPA was characterized by elemental analysis, NMR (^{1}H- and ^{13}C-), infrared, and UV-visible spectroscopies. The elemental analysis data of reprecipitated poly(MBDPA) agreed well with the theoretical value: Calcd for ($C_{14}H_{15}N$): C, 85.23%; H, 7.66%; N, 7.10%, Found: C, 85.10%; H, 7.55 %; N, 7.12%.

Figure 1 shows ^{1}H-NMR spectra of poly(MBDPA) in DMSO-d_6. It showed the methyl and methine proton peaks at 0.5-2.3 ppm. The peaks of methylene protons adjacent to the conjugated carbons were observed at 3.4 ppm. The vinyl protons of conjugated polymer backbone were also observed at the region of 4.8-6.8 ppm, whereas the phenyl protons were observed around 7.2 ppm.

Figure 2 shows the typical ^{13}C-NMR spectrum of poly(MBDPA) in DMSO-d_6. This spectrum did not show any acetylenic carbon peaks (72.72, 79.08 ppm) of MBDPA. Instead, the ^{13}C-NMR spectrum of poly(MBDPA) showed the phenyl carbons at 124-127 and 142-146 ppm, and more broad olefinic carbon peaks of the conjugated polymer backbone at the region of 114-142 ppm. The peak of the methine carbons was observed at 64.26 ppm, whereas the peak of methylene carbons of poly(MBDPA) was observed at 57.20

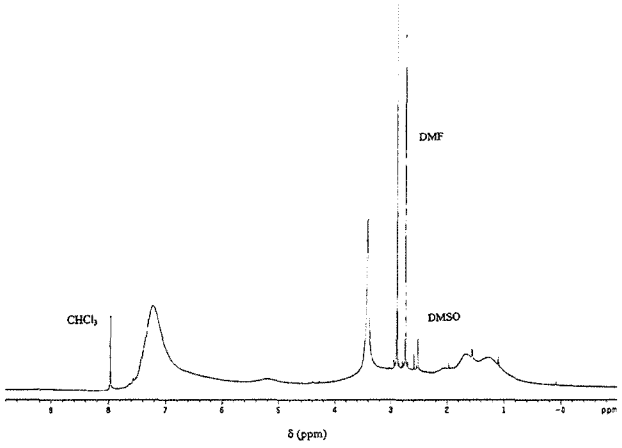


Figure 1. ^{1}H-NMR spectrum of poly(MBDPA) in DMSO-d_6.

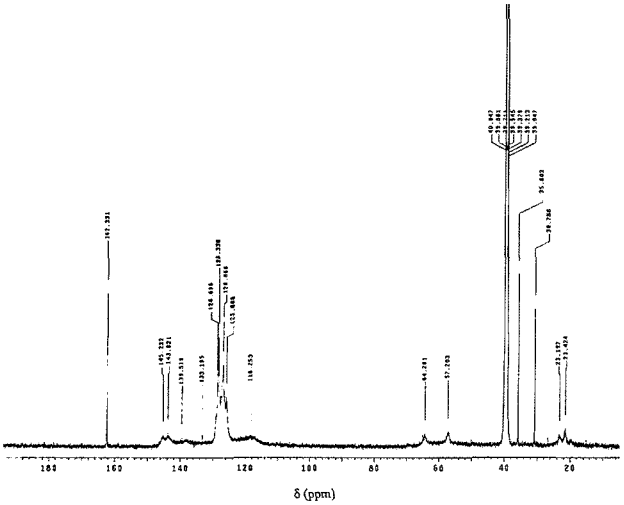


Figure 2. ^{13}C-NMR spectrum of poly(MBDPA) in DMSO-d_6.

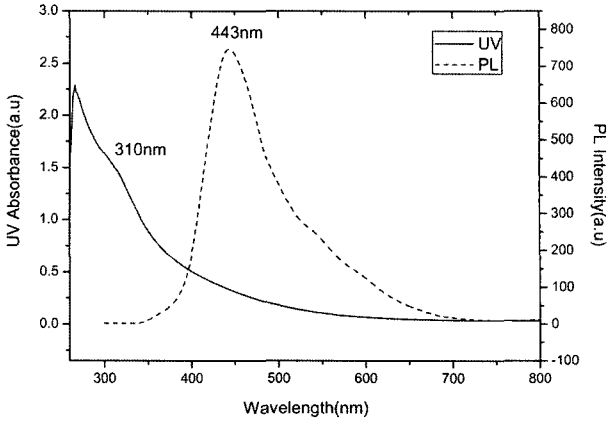


Figure 3. Optical absorption and photoluminescence spectra of poly(MBDPA) polymer solution.

ppm (downfield shift to the methylene carbon peaks of propargyl functional group of MBDPA, 39.68 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.[37,38] 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 (57-58 ppm) and six-membered rings (54-55 ppm), respectively. Unfortunately, the present polymer has no quaternary carbons. However, the present polymers showed two methyl carbons (21.42, 23.20 ppm) and two aromatic carbons (143.82, 145.23 ppm), indicating different environments. This means that the present poly(MBDPA) contains the mixtures of five and six-membered ring moieties, which the carbon peaks of high field shift can be assignable as ones of six-membered ring moieties.

In the IR spectrum of poly(MBDPA), the acetylenic ≡C-H and C≡C bond stretching peaks at 3270 and 2121 cm^{-1} were mostly disappeared. And the C=C double bond stretching frequency peak of conjugated polymer backbone at around 1668 cm^{-1} was strongly observed.

The morphologies of poly(MBDPA) were also investigated by X-ray diffraction analysis. 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,[15,36] the present polymers are mostly amorphous.

TGA thermogram of poly(MBDPA) revealed that this polymer showed an abrupt weight loss above 200 °C. It exhibited that the polymer retains 99% of its original weight at 200 °C, 84% at 300 °C, 67% at 400 °C, 57% at 500 °C, and 54% at 700 °C.

DSC thermogram of poly(MBDPA) showed two irreversible exothermic processes, one peaking at 118 °C and the other at 234 °C. The lower process is originated from the rearrangement of exo double bond of poly(1,6-heptadiyne) homologues to convert to the polymer from a helical structure to a nearly planar polyene backbone configuration. The isomerization temperature of linear polyacetylene was reported as 155 °C.[9] The higher temperature process is assumed to be due to the exo to endo rearrangement and/or the thermal decomposition reaction.

The electro-optical properties of poly(MBDPA) was measured and discussed. Figure 3 shows the UV-visible spectra and photoluminescence (PL) spectra of poly(MBDPA) solution (0.1 wt%, DMF). Poly(MBDPA) showed characteristic absorption at the visible region and blue PL spectrum at 443 nm corresponding to the photon energy of 2.80 eV.

Conclusions

In this article, we demonstrated the synthesis of a new conjugated cyclopolymer by the cyclopolymerization of MBDPA, and elucidated the polymer structure by NMR, IR, and UV-visible spectroscopies. The polymerization proceeded well by various transition metal catalysts to give a moderate yield of polymer. The spectroscopic studies on the microstructures of this cyclopolymer indicated that the polymer backbone contains the mixtures of five and six-membered ring moieties. The polymers were generally soluble in halogenated and aromatic hydrocarbon solvents such as chloroform, chlorobenzene, DMF, DMSO, etc. The X-ray diffraction analyses revealed that the present conjugated cyclopolymers are mostly amorphous.

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ment of 500 MHz NMR spectra of polymers.

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