Synthesis of Poly(phenylacetylene) with a Crown Cavity by Cyclopolymerization of 1,14-Bis(4-ethynylphenoxy)-3,6,9,12-tetraoxatetradecane

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Introduction. Polyacetylenes with various substituents have been designed and synthesized for polymeric materials possessing electrical conductive, magnetic, liquid-crystalline, and nonlinear optical properties. We have previously reported on the synthesis and characterization of poly(4′-ethynylbenzo-15-crown-5),[1] polyacetylene with a crown cavity. Polyacetylenes of this type, which have not been studied to date, are expected to exhibit high electrical and ionic conductivities because of the cation-binding property of the crown cavity.

For the synthesis of poly(crown ether), the cyclopolymerization of a bifunctional monomer, such as α,ω-divinyl ether[2] and α,ω-diepoxide,[3] is a facile method. The cyclopolymerizations of 1,6-heptadiyne and its derivatives have been studied in terms of the cyclic constitutional units and the electrical and other properties of the conjugated polymers obtained.[4] There has been no attempt to cyclopolymerize α,ω-diacetylenes capable of forming large-membered rings. Of interest, therefore, are the molecular design of such an α,ω-diacetylene and the synthesis of a polyacetylene with a crown cavity via the cyclopolymerization method. In this paper, we report on the cyclopolymerization of 1,14-bis(4-ethynylphenoxy)-3,6,9,12-tetraoxatetradecane (**1**) with rhodium, tungsten, and molybdenum catalysts and the characterization of poly(phenylacetylene) **2**.

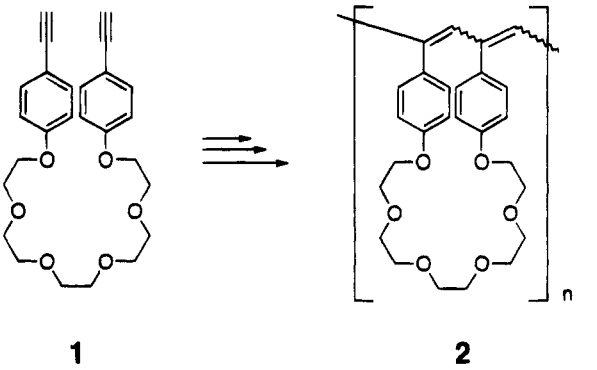
Results and Discussion. The synthesis of α,ω-diacetylene 1,14-bis(4-ethynylphenoxy)-3,6,9,12-tetraoxatetradecane (**1**) and intermediary compounds is outlined in Scheme 2. For the cross-coupling of diiodo compound **3** and (trimethylsilyl)acetylene with the Pd(0)/Cu(I) catalyst system, piperidine was used as the basic solvent. The deprotection of disilyl compound **4** smoothly progressed with Na_2CO_3 in methanol.

Table 1 lists the results of the cyclopolymerizations of α,ω-diacetylene **1** with transition metal catalysts. All the polymerizations with the catalyst system consisting of (bicyclo[2.2.1]hepta-2,5-diene)rhodium(I) chloride dimer ([Rh(bhd)Cl]$_2$) and triethylamine (Et_3N) proceeded homogeneously. The obtained polymers were yellow powders that were soluble in chloroform and dichloromethane and insoluble in benzene and THF, and their number-average molecular weights ranged from 12 000 to 30 000.

On the other hand, for the polymerizations with WCl_6[5] in toluene and $W(CO)_6/h\nu$ in CCl_4,[6] small amounts of polymer were obtained but they were insoluble in chloroform, THF, and other organic solvents. In addition, no reactions occurred using $MoCl_5$[5] and $Mo(CO)_6/h\nu$.[6] These results indicate that the oligoether unit in **1** deactivates the catalytic activities of WCl_6 and $MoCl_5$ for the polymerization of the ethynyl group in **1**.

To clarify the effect of the oligoether unit on the acetylene polymerization, phenylacetylene (**PA**) was polymerized using rhodium, tungsten, and molybdenum catalysts in the presence of 1,14-diphenoxy-3,6,9,12-tetraoxatetradecane (**5**). Table 2 lists the results of the polymerizations of **PA**. For the polymerizations using

Scheme 1



Scheme 2

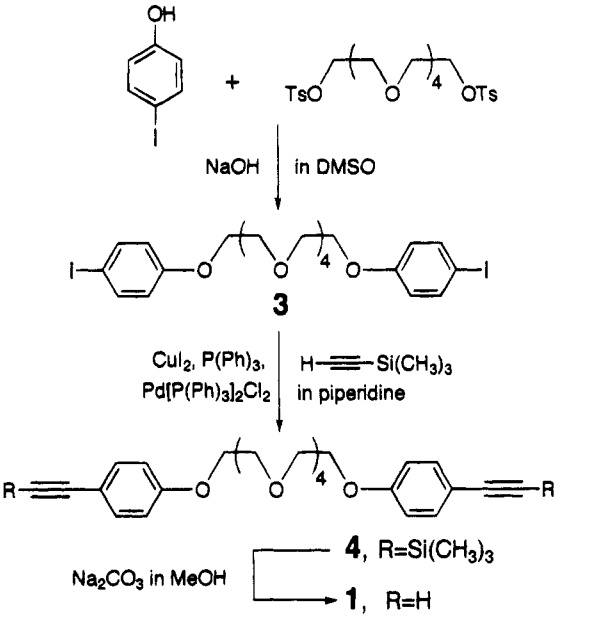


Table 1. Cyclopolymerization of 1,14-Bis(4-ethynylphenoxy)-3,6,9,12-tetraoxatetradecane (1) with Rh, W, and Mo Catalysts[a]

catalyst (Cat.)	solvent	[1] (mol·L^{-1})	[1]/[Cat.]	yield (%)	$M_n \times 10^{-4}$ [b]	M_w[b]/M_n
[Rh(bhd)Cl]$_2$/Et_3N[c]	$CHCl_3$	0.05	100	65.9	3.0	4.5
		0.02	40	63.8	1.2	3.4
		0.01	20	76.6	1.8	2.9
WCl_6	$C_6H_5CH_3$	0.1	12.5	16.1[d]		
$W(CO)_6/h\nu$	CCl_4	0.1	25	7.1[d]		
$MoCl_5$	$C_6H_5CH_3$	0.1	12.5	0		
$Mo(CO)_6/h\nu$	CCl_4	0.1	25	0		

[a] Time, 24 h; temperature, 30 °C. [b] Determined by GPC (polystyrene standards). [c] [Rh(bhd)Cl]$_2$, (bicyclo[2.2.1]hepta-2,5-diene)rhodium(I) chloride dimer; Et_3N, triethylamine; [Rh(bhd)Cl]$_2$/[Et_3N] = 100. [d] Insoluble in chloroform.

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Table 2. Effect of 1,14-Diphenoxy-3,6,9,12-tetraoxatetradecane (5) on the Polymerization of Phenylacetylene (PA) with Rh, W, and Mo Catalysts[a]

	PA		PA/5[b]	
catalyst	yield (%)	M_n (M_w/M_n)[c]	yield (%)	M_n (M_w/M_n)[c]
$[Rh(bhd)Cl]_2$[d]	95	3.5×10^4 (2.0)	92	3.6×10^4 (3.1)
WCl_6[e]	85	1.1×10^4 (2.2)	0	
$MoCl_5$[f]	12	9.1×10^3 (2.1)	0	

[a] [**PA**] = 0.5 mol·L^{-1}; temoperature, 30 °C; time, 20 h. [b] [**PA**]/[**5**] = 2. [c] Determined by GPC in $CHCl_3$ using polystyrene standards. [d] $[Rh(bhd)Cl]_2$, (bicyclo[2.2.1]hepta-2,5-diene)rhodium(I) chloride dimer; [**PA**]/$[Rh(bhd)Cl]_2$ = 100, $[Rh(bhd)Cl]_2/[Et_3N]$ = 100; solvent, $CHCl_3$. [e] [**PA**]/$[WCl_6]$ = 50; solvent, $C_6H_5CH_3$. [f] [**PA**]/$[MoCl_5]$ = 50; solvent, $C_6H_5CH_3$.

$[Rh(bhd)Cl]_2$, the yield and the M_n of the obtained poly(phenylacetylene)s (**PPAs**) were almost the same in value regardless of whether **5** was added or not. On the other hand, **5** obviously affected the catalytic activity of WCl_6 and $MoCl_5$; none of the polymer and oligomer were formed when **5** was added, while appropriate **PPAs** were obtained in the absence of **5**. These results mean that the oligoether unit interferes with the catalytic activity of WCl_6 and $MoCl_5$ for the acetylene polymerization.

The polymerization character of **1** apparently differs from that of the acetylenes having alkyl or aryl substituents; i.e., the oligoether unit in **1** caused the deactivation of the common catalysts WCl_6 and $MoCl_5$ for the acetylene polymerization. The cyclopolymerization of **1**, however, was successful using the rhodium complex catalyst to produce the gel-free polyacetylene in a high yield.

Figure 1 shows the ^1H and the ^{13}C NMR spectra of the polymer obtained with $[Rh(bhd)Cl]_2/Et_3N$. The characteristic absorptions at 2.99 ppm due to the acetylenic proton and at 75.88 and 83.60 ppm due to the acetylenic carbon have completely disappeared, and the absorptions due to the proton and the carbon in the conjugated main chain were observed at 5.5–6.0 and 132–140 ppm, respectively. This means that the resulting polymer essentially consists of cyclic repeating units caused by the cyclopolymerization mechanism; i.e., the extent of cyclization was 100%.

Furlani et al.[7] and Tabata et al.[8] reported that **PA** polymerized with rhodium complex catalysts to produce highly cis-transoidal regulated **PPAs** whose NMR spectra showed sharp signals due to the main chain atoms. For polymer **2**, relatively sharp absorptions attributed to the main chain atoms were also observed, which suggests that the structure of the main chain for polymer **2** should be the cis-form. However, signals at 5.62, 5.65, and 5.68 ppm for protons and at 135.0, 136.5, and 139.5 ppm for quaternary carbons were observed, and their detailed assignments have been studied in relation to the stereochemistry of the main chain.

The cation-binding property of polymer **2** was estimated by the one-plate extraction experiment[9] using lithium, sodium, potassium, rubidium, and cesium picrates. Table 3 lists the results of the extraction at [crown cavity units in polymer **2**]/[metal picrate] = 10. The extraction yield increased with increasing cation radius, i.e., $Li^+ < Na^+ < K^+ < Rb^+ < Cs^+$. This means that the cyclic units in polymer **2** act as a crown cavity in the host–guest complexation.

The electrical conductivity of polymer **2** at 25 °C was 3.6×10^{-9} S·cm^{-1}, a value larger than that of about

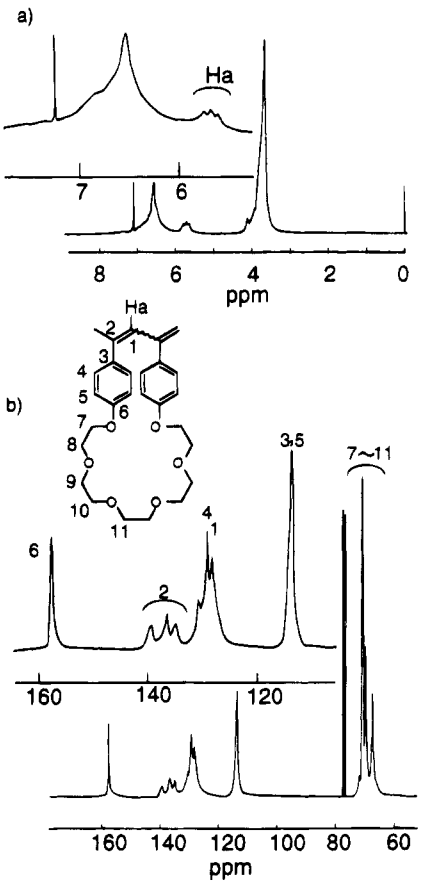

Figure 1. ^1H and ^{13}C NMR spectra of the polymer prepared by the cyclopolymerization of 1,14-bis(4-ethynylphenoxy)-3,6,9,12-tetraoxatetradecane (**1**) with (bicyclo[2.2.1]hepta-2,5-diene)rhodium(I) chloride dimer ($[Rh(bhd)Cl]_2$) in $CHCl_3$ ($[Rh(bhd)Cl]_2/[1]$ = 100; $[Rh(bhd)Cl]_2/[Et_3N]$ = 100; temperature, 30 °C; time, 20 h).

Table 3. Extraction Yield (%) of Alkali Metal Picrate by Polymer 2[a]

Li^+	Na^+	K^+	Rb^+	Cs^+
3.2	5.6	8.6	9.7	15.6

[a] [Crown cavity units in polymer **2**] = 7.0×10^{-4} mol·L^{-1}, [picric acid] = 7.0×10^{-5} mol·L^{-1}, and [alkali metal hydroxide] = 0.1 mol·L^{-1}.

10^{-14} S·cm^{-1} for the **PPAs** prepared using Rh catalysts. An increase in conductivity was found for the I_2-doped polymer at a value of 8.5×10^{-6} S·cm^{-1}.

We have successfully synthesized poly(phenylacetylene) **2** with a crown cavity by the cyclopolymerization of α,ω-diacetylene **1** using a rhodium catalyst. Polymer **2** exhibited a binding characteristic for alkali metal cations. Further studies are currently in progress to investigate ionic and electrical conductive and electrochemical properties of polymer **2** when it forms a complex with the appropriate cationic guest.

Experimental Section. Measurements. The ^1H and ^{13}C NMR spectra were recorded with a Bruker AMX 300 instrument. Gel permeation chromatograms (GPC) were obtained at 40 °C with a Jasco HPLC system (PU-980 intelligent HPLC pump and 830-RI intelligent RI detector) equipped with three polystyrene gel columns (Waters A-802, A-803, and A-805). Chloroform was the carrier solvent at a flow rate of 1.0 mL/min. The molecular weights of the polymers were determined using a calibration curve with polystyrene standards.

Synthesis of 1,14-Bis(4-iodophenoxy)-3,6,9,12-tetraoxatetradecane (3). A solution of 57.0 g (259

mmol) of 4-iodophenol and 12.7 g (318 mmol) of sodium hydroxide in 120 mL of dimethyl sulfoxide was heated at 80 °C with stirring until sodium hydroxide was completely dissolved. Then 32.3 g (117 mmol) of 1,14-dichloro-3,6,9,12-tetraoxatetradecane was added to the mixture. After stirring at 100 °C for 4 h, the reaction mixture was diluted with 200 mL of water and extracted with four 200 mL portions of toluene. The extracts were washed with 200 mL of 2 mol·L^{-1} aqueous sodium hydroxide solution and water, dried over anhydrous sodium sulfate, and evaporated under reduced pressure. The residue was recrystallized from toluene to give 52.3 g of **3** (yield, 69.4%) as a white powder. Mp: 102–103 °C. ^{1}H NMR ($CDCl_3$): δ 3.64 (s, 4H, CH_2), 3.68 (s, 8H, CH_2), 3.75–3.95 (m, 4H, $ArOCH_2CH_2$), 3.95–4.20 (m, 4H, $ArOCH_2$), 6.68, 7.53 (d, 8H, J = 9.01 Hz, aromatic). Anal. Calcd for $C_{22}H_{28}I_2O_6$ (642.27): C, 41.14; H, 4.39; I, 39.52. Found: C, 41.09; H, 4.40; I, 39.63.

Synthesis of 1,14-Bis{[4-(trimethylsilyl)ethynyl]-phenoxy}-3,6,9,12-tetraoxatetradecane (4). To a solution of 23 g (35.8 mmol) of **3**, 1.1 g (1.57 mmol) of bis(triphenylphosphine)palladium(II) chloride, and 228 mg (0.72 mmol) of copper(I) iodide in 300 mL of dry piperidine was added 12 mL (85 mmol) of (trimethylsilyl)acetylene at 50 °C. After 7 h, the white precipitate was removed. The precipitate was then washed with toluene. The filtrate was evaporated, and the residue was treated with 200 mL of water and extracted with toluene (100 mL × 4). The extracts were dried, filtered, and evaporated. The residue was chromatographed on silica gel with hexane/methanol (v/v, 97:3) and then with dry chloroform. A raw product free from solvent was recrystallized from hexane/ether (v/v, 50:50) to give 15.6 g of **4** (yield, 75.0%) as a light beige flake crystal. Mp: 77–78 °C. ^{1}H NMR ($CDCl_3$): δ 0.25 (s, 18H, $SiCH_3$), 3.65 (s, 4H, CH_2), 3.69 (s, 8H, CH_2), 3.75–3.93 (m, 4H, $ArOCH_2CH_2$), 4.10–4.20 (m, 4H, $ArOCH_2$), 6.86, 7.43 (d, 8H, J = 9.01 Hz, aromatic). Anal. Calcd for $C_{32}H_{46}O_6Si_2$ (582.89): C, 65.94; H, 7.95. Found: C, 65.92; H, 7.90.

Synthesis of 1,14-Bis(4-ethynylphenoxy)-3,6,9,-12-tetraoxatetradecane (1). A solution of 5.0 g (8.57 mmol) of **4** and 3.1 g (29.1 mmol) of Na_2CO_3 in 100 mL of MeOH was stirred at 30 °C for 3 h. The reaction mixture was diluted with 500 mL of water and then extracted with five 200 mL portions of toluene. The extracts were dried over anhydrous sodium sulfate, filtered, and evaporated. The residue was chromatographed on silica gel with hexane/methanol (v/v, 97:3) and then with dry chloroform to produce a raw product. The compound was recrystallized from ether to give 3.3 g of **1** (yield, 88%) as a light yellow flake crystal. Mp: 51–52 °C. ^{1}H NMR ($CDCl_3$): δ 2.99 (s, 2H, HC≡), 3.64 (s, 4H, CH_2), 3.67 (s, 8H, CH_2), 3.72–3.89 (m, 4H, $ArOCH_2CH_2$), 4.04–4.17 (m, 4H, $ArOCH_2$), 6.83, 7.40 (d, 8H, J = 9.01 Hz, aromatic). ^{13}C NMR ($CDCl_3$): δ 67.42 ($ArOCH_2$), 69.56 ($ArOCH_2CH_2$), 70.81, 70.58, 70.58 (CH_2), 75.88 (HC≡), 83.60 (≡C–), 114.27, 133.49, 114.54, 159.10 (aromatic). Anal. Calcd for $C_{26}H_{30}O_6$ (438.52): C, 71.21; H, 6.90. Found: C, 71.31; H, 6.93.

Cyclopolymerization. The polymerizations were carried out with WCl_6 and $MoCl_5$ in toluene, with $W(CO)_6/h\nu$ and $Mo(CO)_6/h\nu$ in CCl_4, and with $[Rh(bhd)Cl]_2$ in chloroform. After 24 h at 30 °C, the polymerization mixture was poured into a large amount of *n*-hexane, and the polymer was purified by reprecipitation from chloroform/ether.

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CORRECTIONS

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The expression under eq 2 should read $\sigma_1 \propto x = l/P$.

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