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Crowned polyacetylene: 3. Synthesis and cation-binding property of polyphenylacetylene with azacrown cavity by cyclopolymerization of α,ω-bis(4'-ethynylphenoxy)oligooxyethylene containing a pyridyl unit

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The cyclopolymerizations of 2,6-bis[7'-(4"-ethynylphenoxy)-2',5'-dioxaheptyl]pyridine (**1a**) and 2,6-bis[10'-(4"-ethynylphenoxy)-2',5',8'-trioxadecyl]pyridine (**1b**) were carried out using the (bicyclo[2.2.1]-hepta-2,5-diene)rhodium(I) chloride dimer. The yellowish powdery, organic solvent-soluble polymers were obtained using an amine as a cocatalyst. The resulting polymers consisted of cyclic constitutional repeating units as the main structure along with pendant acetylenic groups, i.e. the extent of cyclization was from 0.89 to 0.99 for the polyphenylacetylenes with an azacrown cavity, **2a** and **2b**, obtained from monomers **1a** and **1b**, respectively. Polymer **2** exhibited cation-binding ability for alkaline earth metal, heavy metal, and transition metal ions and, in particular, for Ag^+. The complex of **2** with Ag^+, which was confirmed by the ^1H n.m.r. spectrum, consisted of the azacrown cavity and Ag^+ with a ratio of 2. © 1997 Elsevier Science Ltd. All rights reserved.

(Keywords: cyclopolymerization; α, ω-diacetylene; polyphenylacetylene)

INTRODUCTION

Conjugated polymers with macrocyclic cavities are expected to exhibit new functional properties based on the electrical conductivity of the main-chain and the cation-binding ability of the macrocyclic cavity. For instance, polythiophene and polypyrrole having a crown ether[1-6], azacrown ether[7], cyclam[8], and calixarene[9] have been designed and synthesized, and changes in the electrical properties were observed before and after host–guest complexation.

We reported the synthesis of poly (4'-ethynylbenzo-15-crown-5) which exhibited a binding property in the order of $K^+ > Rb^+ >> Cs^+ >>> Na^+$, Li^{+}[10,11]. In addition, the electrical conductivity increased by doping with I_2 to values in the semiconductor range. Polyphenylacetylene with a crown cavity was also synthesized by the cyclopolymerization of 1,14-bis(4'-ethynylphenoxy)-3,6,9,12-tetraoxatetradecane[12]. This was the first attempt at the cyclopolymerization of α, ω-diacetylene leading to the polymeric crown ether.

The cation-binding characteristics of macrocyclic hosts depend on their ring-sizes and the nature of the donor atoms. For example, macrocycles containing nitrogen and sulfur, aza- and thiacrown ethers, show higher binding properties towards transition metal cation, such as silver[13]. These properties are different from those of crown ethers. We have developed a strategy for producing polymers with macrocyclic cavities by the cyclopolymerization of bifunctional monomers. For example, α, ω-divinyl ether, α, ω-diepoxide, α, ω-diacetylene and α, ω-diepisulfide are cyclopolymerized to produce poly(crown ether), poly(cryptand), poly(hemispherand) and poly(thiacrown ether), which exhibited respective metal cation-binding properties depending on the size of the macrocyclic units and the kind of donor atoms[14].

To grasp the scope of the cyclopolymerization method in terms of the kind of polymerizable groups and macrocyclic units, we have focused here on the conjugated polymers with azacrown cavities. Recently, we demonstrated the first successful synthesis of poly-(azacrown ether) **2a** by the cyclopolymerization of α, ω-diacetylene with a pyridyl unit, 2,6-bis[7'-(4"-ethynylphenoxy)-2',5'-dioxaheptyl]pyridine (**1a**), using a rhodium complex catalyst[15]. In addition, poly(azacrown ether) exhibited a higher binding ability towards a silver cation.

In this paper, we report on the newly synthesized 2,6-bis[10'-(4"-ethynylphenoxy)-2',5', 8'-trioxadecyl]pyridine

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(**1b**), and an attempt at its cyclopolymerization to produce the polymeric azacrown ether **2b** whose ring size is larger than that of **2a**. The cation-binding properties of **2a** and **2b** are characterized by a liquid–liquid extraction method using the picric salts of various metal cations. In addition, for the complex between **2** and Ag^+, the azacrown/Ag^+ ratio in the polymers is determined by the method of continuous variation.

1a, 2a: n=1; 1b, 2b: n=2
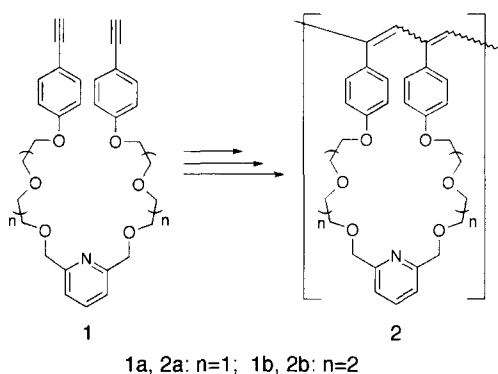
Scheme 1

EXPERIMENTAL

Measurements

[1]H and [13]C n.m.r. spectra were recorded using a JEOL EX-270 instrument. U.v. spectra were measured using a Jasco 660 u.v./vis. spectrophotometer. Gel permeation chromatograms were obtained at 40°C with a Jasco high-performance liquid chromatography (h.p.l.c.) 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). Tetrahydrofuran (THF) was the carrier solvent at a flow rate of $1.0 \, ml \, min^{-1}$. The molecular weights of the polymers were determined using a calibration curve with standard polystyrene.

Materials

Bis(triphenylphosphine)palladium(II) chloride and (trimethylsilyl)acetylene (TMSA) were obtained from N. E. Chemcat and Shinetsu Chemical Industry, respectively. Copper (I) iodide, and the (bicyclo[2.2.1]hepta-2,5-diene)rhodium(I) chloride dimer ([Rh(bhd)Cl]$_2$) were purchased from Aldrich and used without further purification. Piperidine, chloroform, toluene and triethylamine were dried over CaH_2 and distilled under a nitrogen atmosphere.

5-(4′-Iodophenoxy)-3-oxapentane-1-ol (**4a**): procedure A.

A solution of 105.2 g (0.48 mol) of 4-iodophenol and 19.1 g (0.48 mol) of NaOH in 500 ml of dimethyl sulfoxide (DMSO) was heated at 80°C with stirring until the sodium hydroxide was completely dissolved. Then, 90.7 g (0.43 mol) of 5-chloro-3-oxapentyl tetrahyropyranyl ether (**3a**) was added to the mixture. After stirring at 100°C for 7 h, the reaction mixture was diluted with 500 ml of water and extracted with four 200 ml portions of ether. The extracts were washed with 200 ml of aqueous sodium hydroxide solution and water, dried over anhydrous sodium sulfate, and evaporated under

reduced pressure to give 170 g of crude 5-(4′-iodophenoxy)-3-oxapentyl tetrahydropyranyl ether, which was used without further purification.

A mixture of the crude 5-(4′-iodophenoxy)-3-oxapentyl tetrahydropyranyl ether and 2 g of Amberlyst in 500 ml of methanol was stirred for 24 h at 30°C. After separating the Amberlyst, the methanol solution was evaporated under reduced pressure. The residue was chromatographed on silica gel with ethyl acetate to give 90.4 g of **4a** (yield 68%) as pale yellow needles. M.p. 45.2°C R_f 0.44 (AcOEt). [1]H n.m.r. (CDCl$_3$: δ 2.07 (broad, 1H, OH), 3.65–3.68 (m, 2H, CH_2OH), 3.76 (m, 2H, CH_2CH_2OH), 3.84–3.88 (m, 2H, $PhOCH_2CH_2$), 4.09–4.12 (m, 2H, $PhOCH_2$), 6.69–6.72 (m, 2H, Ph–H$_{ortho}$), 7.54–7.57 (m, 2H, Ph–H$_{meta}$). [13]C n.m.r. (CDCl$_3$): δ 61.79, 67.52, 69.55, 72.57, 83.14, 117.01, 138.25, 158.55. Analysis ($C_{10}H_{13}IO_3$): C 38.98%, H 4.25%, I 41.19 (calculated); C 39.11%, H 4.23%, I 40.99% (found).

2,6-Bis[7′-(4″-iodophenoxy)-2′,5′-dioxaheptyl]pyridine (**5a**): procedure B.

To 1.56 g of 60% NaH in oil, which was washed with dry *n*-hexane and then dry THF, a solution of 10.0 g (32.5 mmol) of **4a** in 120 ml of dry THF was carefully added. After the evolution of H_2 ceased, a solution of 5.16 g (32.5 mmol) of 2,6-bis(bromomethyl)pyridine in 30 ml of dry THF was added, and the resulting mixture was stirred for 12 h. The solvent was removed under reduced pressure, and residue was added to 70 ml of water and then shaken with three 30 ml portions of ether. The aqueous layer was extracted with two 30 ml of ether. The combined solvents were dried with anhydrous Na_2SO_4 and evaporated under reduced pressure, and the residue was chromatographed on silica gel with ethyl acetate to give 8.85 g of **5a** (yield 76%) as a pale yellow solid. M.p. 49.7°C. R_f 0.29 (AcOEt). [1]H n.m.r. (CDCl$_3$): δ 3.72–3.79 (m, 8H, OCH_2CH_2), 3.84–3.87 (m, 4H, $PhOCH_2CH_2$), 4.07–4.13 (m, 4H, $PhOCH_2$), 4.67 (s, 4H, $PyCH_2$), 6.66–6.72 (m, 4H, Ph–H$_{ortho}$), 7.35 (d, $J = 7.59$ Hz, 2H, 3,5-Py–H), 7.50–7.55 (m, 4H, Ph–H$_{meta}$), 7.65 (t, $J = 7.59$ Hz, 1H, 4-Py–H). [13]C n.m.r. (CDCl$_3$): δ 67.48, 69.57, 70.18, 70.70, 73.98, 82.87, 116.98, 119.86, 137.13, 138.07, 157.74, 158.59. Analysis ($C_{27}H_{31}I_2NO_6$): C 45.08%, H 4.34%, I 35.28%, N 1.95% (calculated); C 45.71%, H 4.44%, I 35.64%, N 2.02% (found).

2,6-Bis[7′-(4″-ethynylphenoxy)-2′, 5′-dioxaheptyl]pyridine (**1a**): procedure C.

A mixture of 8.9 g (12.3 mmol) of **5a** 691 mg (0.98 mmol) of bis(tripheylphosphine)palladium(II) chloride ([(C$_6$H$_3$)$_5$P]$_2$PdCl$_2$), 94 mg (0.49 mmol) of copper(I) iodide and 194 mg (0.74 mmol) of triphenylphospine in 150 ml of dry piperidine was stirred for 1 h at room temperature under an atmosphere of nitrogen. To the solution was added 2.9 g (30 mmol) of TMSA, and the entire mixture was stirred for 1 h at room temperature and then for 100 h at 50°C. After the mixture cooled, the precipitate was removed and the solvent was evaporated to produce a black oil. The residue was dissolved in 100 ml of ether. The ethereal solution was washed with saturated aqueous ammonium chloride five times and dried over anhydrous sodium sulfate. The ether was evaporated, and the residue was chromatographed on silica gel with ethyl acetate. The solvent was evaporated under reduced

pressure to give 7.3 g of 2,6-bis{7′-[4″-(trimethylsily-lethynyl)phenoxy]-2′,5′-dioxaheptyl}pyridine as a brown oil, which was used without further purification.

A mixture of 7.2 g of the crude bis(trimethylsilyl) compound and 3 g of sodium carbonate in 150 ml of methanol was stirred for 7 h at 30°C. After evaporating the solvent, the residue was dissolved into 200 ml of ether and washed with saturated aqueous sodium chloride solution. The organic layer was separated, dried with anhydrous Na_2SO_4, and evaporated. This residue then was chromatographed on silica gel with ethyl acetate to give 4.4 g of **1a** (yield, 69% from **5a**) as a yellow oil. R_f 0.34 (AcOEt). ^1H n.m.r. (CDCl$_3$): δ 3.00 (s, 2H, $\equiv$CH), 3.73–3.79 (m, 8H, OCH$_2$CH$_2$), 3.85–3.89 (m, 4H, PhOCH$_2$CH_2), 4.10–4.15 (m, 4H, PhOCH$_2$), 4.67 (s, 4H, PyCH$_2$), 6.83–6.87 (m, 4H, Ph–H$_{ortho}$), 7.35 (d, J = 7.59 Hz, 2H, 3,5-Py–H), 7.38–7.42 (m, 4H, Ph–H$_{meta}$), 7.64 (t, J = 7.59 Hz, 4-Py–H). ^{13}C n.m.r. (CDCl$_3$): δ 67.37, 69.53, 70.14, 70.68, 73.96, 75.79, 83.50, 114.22, 114.47, 119.82, 133.41, 137.10, 157.74, 159.04. Analysis (C$_{31}$H$_{33}$NO$_6$): C 72.21%, H 6.45%, N 2.72% (calculated); C 71.18%, H 6.72%, N 2.74% (found).

8-(4′-Iodophenoxy)-3,6-dioxaoctane-1-ol (4b).

Procedure A was applied to 121 g (0.55 mol) of 4-iodophenol, 22 g (0.55 mol) of NaOH and 90.8 g (0.54 mol) of 8-chloro-3,6-dioxaoctane-1-ol (3b) in 500 ml of DMSO. The residue was chromatographed on silica gel with ethyl acetate to give 151.2 g of **4b** (yield 80%) as a pale yellow solid. M.p. 48.0°C. R_f 0.30 (AcOEt). ^1H n.m.r. (CDCl$_3$): δ 2.2 (broad, 1H, OH), 3.60–3.65 (m, 2H, CH$_2$OH), 3.69–3.75 (m, 6H, OCH$_2$), 3.83–3.87 (m, 2H, PhOCH$_2$CH_2), 4.08–4.11 (m, 2H, PhOCH$_2$), 6.69–6.72 (m, 2H, Ph–H$_{ortho}$), 7.53–7.56 (m, 2H, Ph–H$_{meta}$). ^{13}C n.m.r. (CDCl$_3$): δ 61.72, 67.43, 69.56, 70.30, 70.80, 72.45, 83.00, 116.94, 138.09, 158.44. Analysis (C$_{12}$H$_{17}$IO$_4$): C 40.93%, H 4.87%, I 36.03% (calculated); C 41.05%, H 4.84%, I 36.09% (found).

2,6-Bis[10′-(4″-iodophenoxy)-2′,5′,8′-trioxadecyl]-pyridine (5b).

Procedure B was applied to 5.3 g (15 mmol) of **4b**, 2.0 g (7.55 mmol) of 2,6-bis(bromo-methyl)pyridine, and 0.91 g of 60% NaH. The residue was chromatographed on silica gel with ethyl acetate to give 4.0 g of **5b** (yield, 65%) as a yellow oil. R_f 0.20 (AcOEt). ^1H n.m.r. (CDCl$_3$): δ 3.72 (s, 16H, OCH$_2$CH$_2$), 3.83–3.87 (m, 4H, PhOCH$_2$CH_2), 4.07–4.11 (m, 4H, PhOCH$_2$), 4.66 (s, 4H, PyCH$_2$), 6.66–6.71 (m, 4H, Ph–H$_{ortho}$) 7.36 (d, J = 7.59 Hz, 2H, 3,5-Py–H), 7.50–7.56 (m, 4H, Ph–H$_{meta}$), 7.66 (t, J = 7.59 Hz, 1H, 4-Py–H). ^{13}C n.m.r. (CDCl$_3$): δ 67.52, 69.62, 70.23, 70.59, 70.70, 70.86, 73.99, 82.92, 117.03, 119.95, 137.26, 138.16, 157.85, 158.66. Analysis (C$_{31}$H$_{39}$I$_2$NO$_8$): C 46.11%, H 4.87%, I 31.43%, N 1.73% (calculated); C 46.15%, H 4.79%, I 31.16%, N 1.81% (found).

2,6-Bis(10′-(4″-ethynylphenoxy)-2′,5′,8′-trioxadecyl]-pyridine (1b).

Procedure C was applied to 9.14 g (11.3 mmol) of **5b**, 397 mg (0.57 mmol) of [(C$_6$H$_5$)$_3$P]$_2$PdCl$_2$, 64 mg (0.34 mmol) of CuI, 178 mg (0.68 mmol) of triphenylphosphine and 2.67 g (27 mmol) of TMSA in 150 ml of dry piperidine. The crude 2,6-bis{10′-[4″-(trimethylsilylethynyl)phenoxy]-2′,5′,8′-trioxadecyl}pyridine was treated with 3 g of Na$_2$CO$_3$ in 150 ml, and then the raw product was chromatographed on silica gel with ethyl acetate to give
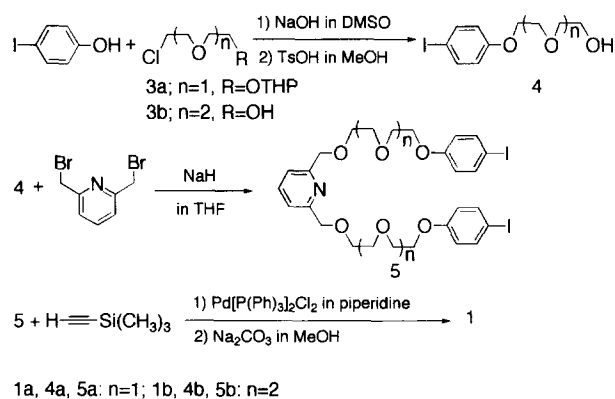
Scheme 2

5.82 g of **1b** (yield, 85% from **5b**) as a yellow oil. R_f 0.15 (AcOEt). ^1H n.m.r. (CDCl$_3$): δ 3.00 (s, 2H, $\equiv$CH), 3.72 (s, 16H, OCH$_2$CH$_2$), 3.83–3.87 (m, 4H, PhOCH$_2$CH_2), 4.10–4.13 (m, 4H, PhOCH$_2$), 4.66 (s, 4H, PyCH$_2$), 6.82–6.85 (m, 4H, Ph–H$_{ortho}$), 7.35 (d, J = 7.59 Hz, 2H, 3,5-Py–H), 7.38–7.41 (m, 4H, Ph–H$_{meta}$), 7.66 (t, J = 7.59 Hz, 4-Py–H). ^{13}C n.m.r. (CDCl$_3$): δ 67.69, 69.85, 70.47, 70.83, 70.95, 71.11, 74.26, 76.05, 83.84, 114.54, 114.81, 120.14, 130.77, 137.44, 158.12, 159.38. Analysis (C$_{35}$H$_{41}$NO$_8$): C 69.63%, H 6.85%, N 2.32% (calculated); C 69.77%, H 6.90%, N 2.28% (found).

Cyclopolymerization

A typical polymerization procedure is as follows. To a solution of the (bicyclo[2.2.1]hepta-2,5-diene)rhodium(I) chloride dimer ([Rh(bhd)Cl]$_2$) (2 mg, 4.5 × 10^{-3} mmol) in chloroform (0.3 ml), Et$_2$NH (33 mg, 0.45 mmol) was added under nitrogen. The mixture was warmed at 30°C for 30 min. To a solution of **1a** (232 mg, 0.45 mmol) in chloroform (14.6 ml), the catalyst solution was added using a syringe with stirring at 30°C under nitrogen. After stirring for 12 h, the polymerization was quenched by adding a small amount of acetic acid, and then the mixture was concentrated under reduced pressure. The residue was poured into a large amount of methanol. The precipitate was filtered and then purified by reprecipitation from chloroform/methanol several times to yield the polymer (128 mg, yield 55%). The M_n and M_w/M_n were 16 000 and 5.4, respectively.

Extraction experiment

The extraction of alkali metal picrates was carried out using a procedure similar to the one developed by Pedersen[16]. A solution of polymer in dichloromethane ([azacrown ether units] = 2.1 × 10^{-4} mol l^{-1}) was vigorously shaken in a culture tube with the aqueous solution of metal cation picrate ([alkali earth chloride], [FeCl$_2$], [CoCl$_2$], [NiCl$_2$], [HgCl$_2$], [Cu(NO$_2$)$_2$], [Zn(NO$_2$)$_2$], (Cd(NO$_2$)$_2$], [AgNO$_2$], [Pb(NO$_2$)$_2$], 0.1 mol l^{-1}; [picric acid], 7 × 10^{-5} mol l^{-1}). After separating the resulting two phases, the metal cation picrate extracted into the dichloromethane was indirectly determined by measuring the absorbance of the picrate in the aqueous phase at 357 nm using a u.v./vis. spectrophotometer.

The molar ratio of [azacrown units in **2**]/[Ag$^+$] was determined by the method of continuous variation. The initial ratio of [azacrown units in **2**]$_{organic\ phase}$ and
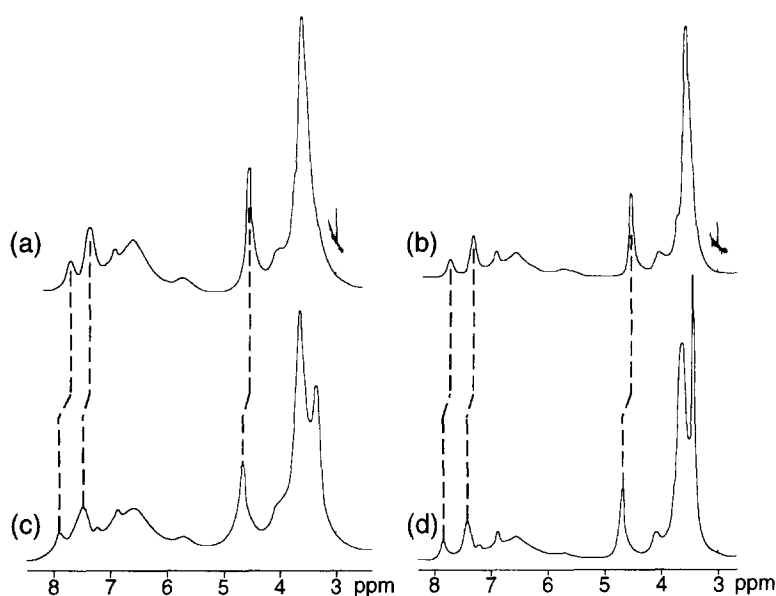
Figure 1 ^{1}H n.m.r. spectra of azacrowned polymers (a) **2a** and (b) **2b**, (c) **2a** · AgClO$_4$, and (d) **2b** · AgClO$_4$ in DMSO-d_6

Table 1 Cyclopolymerization of 2,6-bis[7′-(4″-ethynylphenoxy)-2′,5′-dioxaheptyl]pyridine (**1a**) and 2,6-bis[10′-(4″-ethynylphenoxy)-2′,5′,8′-trioxadecyl]pyridine (**1b**) using (bicyclo[2.2.1]hepta-2,5-diene)rhodium(I) chloride dimer^a

		1a			**1b**		
Amine	Solvent	Yield (%)^b	f_c^{c}	$M_n(M_w/M_n)^d$	Yield (%)^b	f_c^{c}	$M_n(M_w/M_n)^d$
–	CHCl$_3$	0	–	–	0	–	–
Et$_3$N	CHCl$_3$	31	0.99	24 000 (3.3)	20 (10)	0.89	11 000 (3.1)
Et$_2$NH	CHCl$_3$	55	0.99	16 000 (5.4)	53	0.94	29 000 (2.2)
Et$_2$NH	THF	Trace	0.92	12 000 (4.1)	3.5	0.93	5 800 (3.3)
Et$_2$NH	Toluene	Trace (47)	0.92	11 000 (3.4)	11 (67)	0.99	14 000 (5.0)

^{a} [M] = 0.03 mol l^{-1}, [M]/[catalyst] = 100; [amine]/[catalyst] = 100; temperature, 30°C; time, 12 h
^{b} The values in parentheses were yields of organic solvent-insoluble polymers
^{c} The mole fraction cyclized units in the polymers (f_c) determined by ^{1}H n.m.r. spectra
^{d} Measured by g.p.c. in THF using polystyrene as the standard

[Ag picrate]$_{aqueous\ phase}$ was varied while maintaining their total concentration at 7.0×10^{-5} mol l^{-1}.

RESULTS AND DISCUSSION

Cyclopolymerization

The synthesis of α,ω-diacetylenes, 2,6-bis[7′-[(4″-ethynylphenoxy)-2′5′-dioxaheptyl]pyridine (**1a**) and 2,6-bis[10′-(4″-ethynylphenoxy)-2′,5′,8′-trioxadecyl]pyridine (**1b**), and the intermediary compounds is outlined in *Scheme 2*. 5-(4′-Iodophenoxy)-3-oxapentane-1-ol (**4a**) was prepared from 4-iodophenol and 5-chloro-3-oxapentyl tetrahydropyranyl ether (**3a**), followed by the cleavage of the tetrahydropyranyl (THP) ether linkage. 8-(4′-Iodophenoxy)-3,6-dioxaoctane-1-ol (**4b**) was obtained from 4-iodophenol and 8-chloro-3,6-dioxaoctane-1-ol (**3b**). For the cross-coupling of diiodo compound **4** and TMSA with the Pd(0)/Cu(I) catalyst system, piperidine was used as the basic solvent. The deprotection of the disilyl compound smoothly progressed with Na$_2$CO$_3$ in methanol to yield **1**.

The polymerizations of **1a** and **1b** were carried out using the (bicyclo[2.2.1]hepta-2,5-diene)rhodium(I) chloride dimer ([Rh(bhd)Cl]$_2$) and the results are listed in *Table 1*. For both monomers, ([Rh(bhd)Cl]$_2$) did not exhibit catalytic activity but performed the polymeriza-

tion only in the presence of a small amount of Et$_2$NH or Et$_3$N. All the polymerizations proceeded homogeneously and were terminated by adding a small amount of acetic acid. The obtained polymers were yellow powders and soluble in chloroform and THF. However, substantial amounts of organic solvent-insoluble polymers were obtained for the polymerization with Et$_2$NH in toluene. The yields and the M_n values for the polymerizations with Et$_2$NH were higher than those with Et$_3$N. Under the condition with Et$_2$NH in THF, the polymers were only slightly obtained. The M_n ranged from 5300 to 16 000 for **1a** and from 5800 to 22 000 for **1b**.

WCl$_6$ and MoCl$_5$, which are excellent catalysts for the polymerization of substituted acetylenes, did not exhibit catalytic activity for the polymerizations of **1a** and **1b**. This result indicates that the donor atoms in **1** deactivates the catalytic activities of WCl$_6$ and MoCl$_5$ for the polymerization of the ethynyl group in **1**. On the other hand, [Rh(bhd)Cl]$_2$ was found to be a polymerization catalyst for **1**. These polymerization characteristics were similar to those for the polymerizations of 4′-ethynylbenzo-15-crown-5 and 1,14-bis(4′-ethynylphenoxy)-3,6,9,12-tetraoxatetradecane.

Figure 1 shows the ^{1}H n.m.r. spectra of the polymers obtained from **1a** and **1b** using [Rh(bhd)Cl]$_2$/Et$_2$NH. The characteristic absorption at 5.5–6.0 ppm due to the proton in the conjugated main chain appeared instead of

Table 2 Extraction of metal cation picrates by polyphenylacetylenes with azacrown cavities, **2a** and **2b**[a]

Cations	Extraction yield (%)	
	2a	**2b**
Mg^{2+}	2.3	6.9
Ca^{2+}	6.6	9.6
Sr^{2+}	2.0	4.1
Ba^{2+}	2.2	7.4
Fe^{2+}	6.2	6.5
Zn^{2+}	3.3	3.8
Cd^{2+}	4.0	3.9
Pb^{2+}	25.4	27.7
Co^{2+}	12.2	7.5
Ni^{2+}	10.4	6.4
Cu^{2+}	21.7	13.7
Ag^{+}	98.6	96.9
Hg^{2+}	14.1	14.6

[a] [Metal cation] $= 1 \times 10^{-2}\,mol\,l^{-1}$ and [picric acid] $= 7.0 \times 10^{-5}\,mol\,l^{-1}$ in the aquous phase; [azacrown units in **2**] $= 7.0 \times 10^{-4}\,mol\,l^{-1}$ in the CH_2Cl_2 phase

Figure 2 Continuous variation plots for **2a** and Ag picrate ($\bigcirc$) and **2b** and Ag picrate ($\bullet$); [azacrown units in **2**]$_{organic\ phase}$ + [Ag picrate]$_{aqueous\ phase}$ $= 7.0 \times 10^{-5}\,mol\,l^{-1}$

the diminishing absorption at 3.0 ppm due to the ethynyl proton. The extent of cyclization was determined by the area ratio of the pyridyl and ethynyl protons in the [1]H n.m.r. spectrum, and varied from 0.89 to 0.99 for the polymers from both monomers, **1a** and **1b**. This means that the resulting polymers consisted of cyclic constitutional repeating units as the main structure along with pendant acetylenic groups, i.e. the polyphenylacetylenes with an azacrown cavity, **2a** and **2b**.

For bifunctional monomer cyclopolymerized to produce a polymeric macrocyclic host, α, ω-diacetylene is a useful monomer for the synthesis of not only the poly(crown ether) but also the poly(azacrown ether) where the rhodium complex catalyst combined with appropriate amine serves as the polymerization catalyst.

Cation-binding property

The cation-binding properties of polymer **2** were estimated by the liquid–liquid extraction method using picrates of alkali metal ions (Li^+, Na^+, K^+, Rb^+ and Cs^+), alkaline earth metal ions (Mg^{2+}, Ca^{2+}, Sr^{2+} and Ba^{2+}), heavy metal ions (Hg^{2+}, Zn^{2+}, Cd^{2+} and Pb^{2+}) and transition metal ions (Co^{2+}, Ni^{2+}, Cu^{2+}, Ag^+ and Fe^{2+}). *Table 2* lists the results of the extraction experiment at an [azacrown cavity units in polymer **2**]/[metal picrate] ratio of 10. Although the pyridyl unit in the polymers is basic, picric acid in the aquous phase without a metal cation was not extracted into the organic phase containing the polymers. The extraction for alkali cations could not be determined, because both polymers slightly dissolved into the aqueous phase. For polymers **2a** and **2b**, the increasing order of the extraction yield is as follows: transition metal ions > heavy metal ions > alkaline earth metal ions. Although the relation between the cavity sizes of azacrown ether units in **2** and cation radii is unclear, the yields that exceed 10% are shown in Pb^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+} and Hg^{2+} for **2a** and Pb^{2+}, Cu^{2+} and Hg^+ for **2b**.

Both polymers exhibited remarkably high binding ability for Ag^+, and the yields were 98.6 and 96.9% for **2a** and **2b**, respectively. In addition, the yields of 49.9 and 46.7% for **2a** and **2b**, respect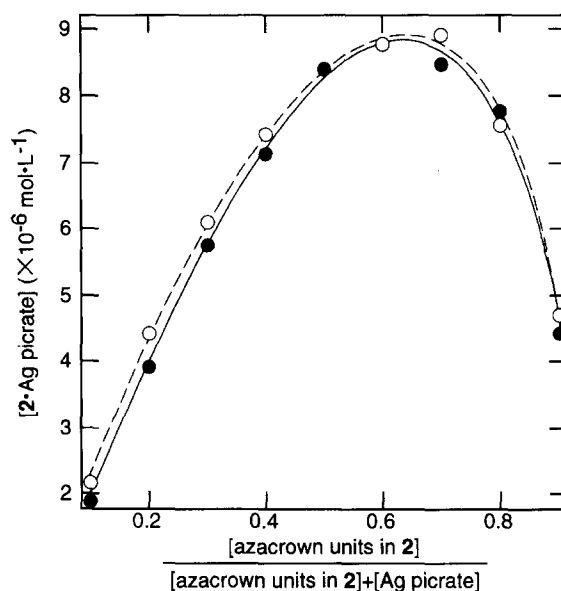ively, were found even under the condition of the [azacrown cavity units in **2**]/[picrate of Ag^+] ratio of 2. The ratio of the azacrown cavity and Ag^+ units in **2** can be determined using the method of continuous variation. *Figure 2* shows the plots of the extraction yields of Ag^+ *versus* the initial mole composition between the azacrown cavity in the polymer and Ag^+. For both host–guest systems, the maximum yields were observed at compositions of 0.62–0.68. This means that two azacrown cavities form the complex with one Ag^+, i.e. a 2:1 complex.

The complex between **2** and Ag^+ was confirmed by the [1]H n.m.r. measurement. $(CD_3)_2SO$ (DMSO-d_6) was used because the complex between **2** and $AgClO_4$ was insoluble in $CDCl_3$. After the host–guest complexation, the absorptions at 3.0–4.2 ppm due to the oxyethylene protons were split into two parts, as shown in *Figure 1*. Moreover, downfield shifts were observed for the methylene (4.3–4.7 ppm) and methine (7.1–7.5 and 7.5–7.9 ppm) proton signals of the pyridyl units. This means that the azacrown cavities units in **2a** and **2b** firmly formed the complexes with Ag^+.

[2.2.2]Paracyclophane was found to form the complex with Ag^+, in which the phenyl rings acted as π-binding sites[17]. The π-binding abilities of phenyl rings and conjugated main chain in **2** were estimated using poly(phenylacetylene), but it did not exhibit any binding property towards Ag^+. Therefore the oxygen and nitrogen atoms in **2** dominantly act as cation-binding sites for Ag^+.

For the cation binding property, the relation between the binding selectivity and the size of azacrown cavity in **2** was not obvious, which is caused by the fact that the donor atoms are not regularly arranged in the macrocyclic units. Therefore a more sophisticated molecular design is needed, for example using the propargyl group instead of the 4-ethynylphenyl group in the α, ω-diethynyl monomer. Further studies are underway to synthesize such a monomer and investigate the ionic and

electrical conductive and electrochemical properties of polymer **2** when it forms a complex with an appropriate cationic guest.

CONCLUSION

α,ω-Diacetylenes containing pyridyl units, 2,6-bis[7'-(4"-ethynylphenoxy)-2',5'-dioxaheptyl]pyridine **(1a)** and 2,6-bis[10'-(4"-ethynylphenoxy)-2',5',8'-trioxadecyl]pyridine **(1b)**, were polymerized with a rhodium catalyst to yield polyphenylacetylenes with azacrown cavities, **2a** and **2b**, using an amine as the cocatalyst. Polymer **2** exhibited the binding abilities for alkaline earth, heavy metal and transition metal cations and, in particular, for Ag^+. The complex of **2** and Ag^+, which was confirmed by the ^1H n.m.r. spectrum, consisted of the azacrown cavity and Ag^+ with a ratio of 2.

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