



## Synthesis of Acyclic Polyethers Bearing Thioamide End-Groups and Selective Sensing of Silver Ion

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**Abstract.** A series of acyclic polyethers bearing thioamide end-groups and lipophilic alkyl chains were successfully synthesized with moderate yields. Transport measurements in a bulk liquid membrane (BLM) system indicated a very high selectivity of silver ion over other metal cations. Thermodynamic parameters ( $\Delta H$ ,  $T\Delta S$ , and  $\log K$ ) for ligand-metal ion complexations were determined by solution calorimetric titration in methanol at 25 °C. The complexations were enthalpy driven and silver ion exhibited a high selectivity over other metal ions due to the increase of covalent binding between the soft acid ( $\text{Ag}^+$ ) and soft base (sulfur).

**Key words:** polyether, thioamides, complexation, ion selectivity, transport, thermodynamic parameter.

### 1. Introduction

Selective transport of metal cations using acyclic polyethers (podands) has long been studied from the viewpoints of selective separation, recovery, volume reduction, and selective instrumental sensor applied in most industrial fields [1–7]. In particular, selective separation of silver ion from industrial waste has been remarkably focused [8, 9]. We have reported that a series of acyclic polyethers **1** in ion selective electrodes (ISE), solvent extraction, and transport experiments with a bulk liquid membrane show an excellent selectivity of  $\text{Pb}^{2+}$  over other transition metal ions [10]. Sulfur-containing podands were reported to show a selective complexation with silver ion over other metal ions [11]. With those points of views, we have been interested in transformation of the diamide functional group into a dithioamide end-group to study the complexation behavior with specific metal ions as well as the possibility for the participation of the sulfur atom in covalent binding with the metal ion. Therefore, we have synthesized a series of sulfur-containing

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acyclic polyethers which varies the donor atom, the length of the ether linkage, and lipophilicity to elucidate the extent to which the individual building blocks control the selectivity of complex formation with cations. In addition, we report the results for the synthesis of the corresponding podands and their complexation behavior with silver ion along with thermodynamic parameters obtained from the solution calorimetric titration experiment.

## 2. Experimental

### 2.1. SYNTHESIS

#### 2.1.1. *Chemicals and instruments for analysis*

IR spectra were obtained with a Perkin-Elmer 1600 Series FT-IR on potassium bromide pellets.  $^1\text{H}$  NMR spectra were recorded with a Bruker AF-300 spectrometer with the chemical shifts ( $\delta$ ) reported downfield from the internal standard, tetramethylsilane. Elemental analysis was performed by a Vario EL Elemental Analyzer in the Korea Basic Science Institute in Seoul. Unless specified otherwise, reagent grade reactants and solvents were obtained from chemical suppliers and used as received. Dry solvents were prepared as follows: methylene chloride was freshly distilled from lithium aluminum hydride. Toluene was pre-dried over molecular sieves (3Å) and distilled. Acyclic polyether dicarboxylic acids [12] and the corresponding diamides (**1**, **2** and **6**) [13] were prepared by the method described in the literature.

#### 2.1.2. *1,2-bis[2-(2'-N,N-diethylacetamidooxy)phenoxy]ethane (3)*

Under nitrogen, a solution of 1,2-bis[2-(2'-N,N-diethylacetamidooxy)phenoxy]ethane (4.72 g, 10.0 mmol) and 2,4-bis(4-methoxyphenyl)-1,3-dithia-2,4-diphosphetane-2,4-disulfide (Lawesson's reagent) (4.01 g, 10.0 mmol) in 100 mL of toluene was refluxed for 10 h. The solvent was removed *in vacuo* to give a brownish oil. 100 mL of water and 100 mL of methylene chloride were added. The organic layer was separated and washed with water several times followed by drying over anhydrous magnesium sulfate. Purification by column chromatography on silica gel with ethyl acetate-hexane (1 : 2) ( $R_f = 0.4$ ) gave a white solid with an 80% yield. Mp. 186–188 °C. IR (neat): 1594, 1508, 1459, 1257, 1208, 1125, 1021, 738  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  0.91 (t, 12 H), 3.37 (q, 8 H), 4.40 (s, 4 H), 4.72 (s, 4 H), 6.91–7.10 (m, 8 H). Anal. calculated for  $\text{C}_{26}\text{H}_{36}\text{N}_2\text{O}_4\text{S}_2$ : C, 61.90; H, 7.14. Found; C, 61.77; H, 7.26.

#### 2.1.3. *1,2-bis[2-(2'-N,N-dipropylacetamidooxy)phenoxy]ethane (4)*

Synthetic procedures were the same as for compound **3**. Yield 68%. Mp. 122–124 °C. IR (neat): 1598, 1513, 1467, 1255, 1205, 1125, 1027  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  0.85 (t, 12 H), 1.10–1.50 (m, 8 H), 3.31 (t, 8 H), 4.38 (s, 4 H), 4.71 (s, 4 H),

6.91–7.11 (m, 8 H). Anal. calculated for  $C_{30}H_{44}O_4S_2$ : C, 64.29; H, 7.86. Found; C, 64.37; H, 7.76.

#### 2.1.4. *1,2-bis[2-(2'-N,N-dipentylacethioamidooxy)phenoxy]ethane (5)*

Synthetic procedures were the same as for compound **3**. Yield 77%. Mp. 84–87 °C. IR (neat): 1595, 1510, 1465, 1253, 1208, 1125, 1206  $cm^{-1}$ .  $^1H$  NMR ( $CDCl_3$ ):  $\delta$  0.85 (t, 12 H), 1.12–1.81 (m, 24 H), 3.29 (t, 8 H), 4.40 (s, 4 H), 4.70 (s, 4 H), 6.91–7.12 (m, 8 H). Anal. calculated for  $C_{38}H_{60}O_4S_2$ : C, 67.85; H, 8.92. Found; C, 67.67; H, 8.85.

#### 2.1.5. *1,5-bis[2-(2'-N,N-dipentylacethioamidooxy)phenoxy]-3-oxapentane (7)*

Synthetic procedures were the same as for compound **3**. Yield 80%. Mp. 186–188 °C. IR (neat): 1599, 1512, 1467, 1255, 1205, 1127, 1022  $cm^{-1}$ .  $^1H$  NMR ( $CDCl_3$ ):  $\delta$  0.78 (t, 12 H), 1.10–1.82 (m, 24 H), 3.69–3.94 (m, 12 H), 4.18 (t, 4 H), 5.10 (s, 4 H), 6.91–7.12 (m, 8 H). Anal. calculated for  $C_{40}H_{64}O_5S_2$ : C, 67.04; H, 8.93. Found; C, 67.17; H, 8.86.

## 2.2. SOLUTION CALORIMETRIC TITRATION

The calorimetric determination was carried out using a TRONAC model 1250 isoperibol titration calorimeter equipped with a 25 mL glass Dewar flask as the reaction vessel and a 10 mL-precision constant-rate burette for titrant delivery. The thermostat was maintained at  $25 \pm 0.02$  °C with a TRONAC model 40 precision temperature controller. Procedures, calibrations, and data analyses including the stability constant,  $\Delta H$ , and  $T\Delta S$  values by nonlinear regression methods adopted recommendations previously reported [14]. The ligand solution (1.0 mM of the ligand, 25.0 mL) was titrated with 10.0 mM  $M(NO_3)_n$  in methanol solution. The heat of dilution for the metal nitrate was measured in separate experiments by titrating the metal nitrate into methanol solution. The heat of dilution for the ligand was measured by titrating the methanol solution into 1.0 mM of the ligand solution. Stability constants, enthalpy changes, and entropy changes were simultaneously obtained using the least squares program FS101E and FS101ET.

## 2.3. BULK LIQUID MEMBRANE

Membrane transport experiments were carried out using a bulk liquid membrane cell based on the concept of the Schulman bridge at 25 °C [15]. The bottom half of the cell was filled with 3.0 mL of 1.0 mM solution of the organic ligand in chloroform and a glass tube inserted. The interior of the tube above the organic medium was filled with 0.8 mL of 0.1 M metal ion solution as the source phase. The outer cylinder was filled with 5.0 mL of deionized water as the receiving phase. The details of the transport conditions are summarized in the footnotes of Table I.

Table I. Single ion transport of metal ions from an aqueous source phase into the receiving phase through a bulk organic liquid membrane using various podands<sup>a</sup>

Ligand	Flux value ( $\times 10^{-8}$ mol s <sup>-1</sup> m <sup>-2</sup> )						
	Ag <sup>+</sup>	Cd <sup>2+</sup>	Pb <sup>2+</sup>	Cu <sup>2+</sup>	Ni <sup>2+</sup>	Co <sup>2+</sup>	Zn <sup>2+</sup>
2	0.78 $\pm$ 0.01	0	1.71 $\pm$ 0.03	0	0	0	0
3	68.9 $\pm$ 5.99	0	0	0	0	0	0
4	99.37 $\pm$ 8.28	0	0	0	0	0	0
5	136.23 $\pm$ 2.43	0	0	0	0	0	0
6	3.32 $\pm$ 0.03	0	4.67 $\pm$ 0.43	0	0	0	0
7	103.36 $\pm$ 9.59	0	0	0	0	0	0

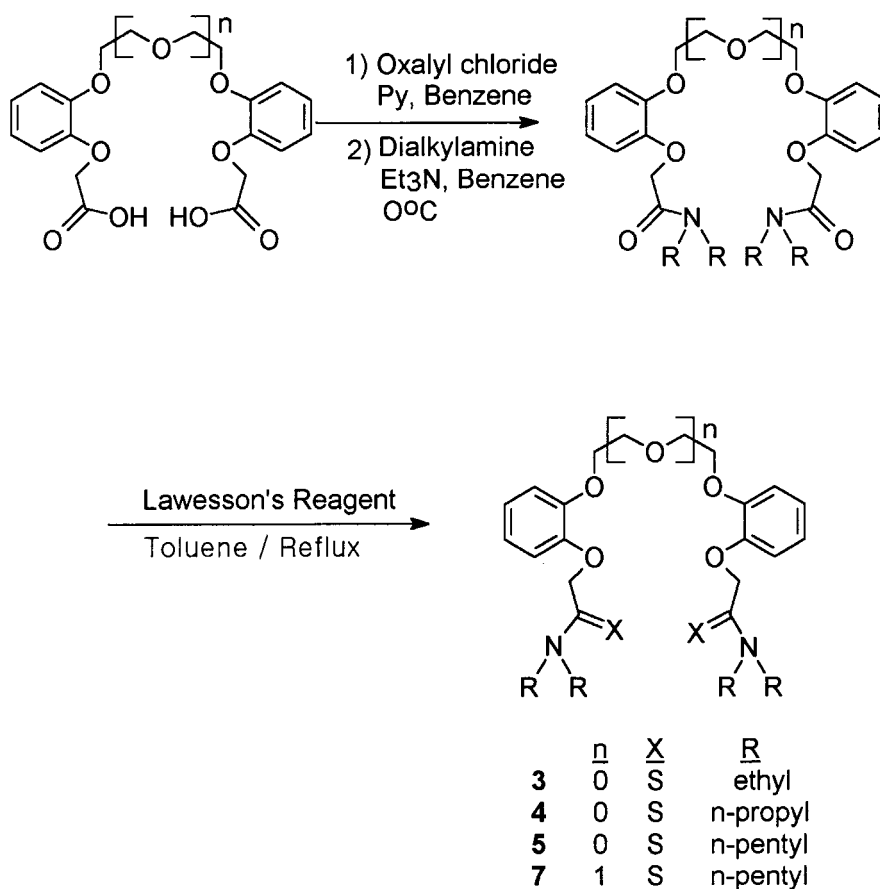
<sup>a</sup> Transport conditions: source phase (aqueous solution of nitrate, 0.8 mL), M(NO<sub>3</sub>)<sub>n</sub> = 0.1 M; membrane phase (CHCl<sub>3</sub>, 3.0 mL), (carrier) = 1.0 mM; i.d. of glass vial = 18 mm, stirred by 13 mm Teflon-coated magnetic stirring bar driven by a Hurst Synchronous motor; receiving phase (deionized water, 5.0 mL). The average value of three independent determinations. The experimental values deviate from the reported values by an average of 10%.

The receiving phase was sampled after 24 h stirring with 120 rpm at 25 °C and analyzed for cation concentration using an atomic absorption spectrometer.

### 3. Results and Discussion

#### 3.1. SYNTHESIS

Synthetic routes for the preparation of acyclic polyether diamides and dithioamides are described in Scheme 1. Previously we developed and reported synthetic procedures from dicarboxylic acid to diamide [10]. Chlorination of the dicarboxylic acid with oxalyl chloride in the presence of a catalytic amount of pyridine provides 1,5-bis[2-(chloroacetyloxy)phenoxy]-3-oxapentane in quantitative yield as a yellowish oil. The corresponding acid chloride was used in the next reaction step without any further purification. Subsequently, the reaction of the corresponding acid chloride with dialkylamine and triethylamine as a base in benzene gave the corresponding diamide compounds as a colorless oil. The synthetic method for transformation of the amide into the thioamide has been well studied. One of the best reagents is known to be Lawesson's reagent, 2,4-bis(4-methoxyphenyl)-1,3-dithia-2,4-diphosphetane-2,4-disulfide, which is able to give a quantitative yield [16]. Refluxing of a mixture of the acyclic polyether diamide and Lawesson's reagent in toluene as a solvent gave 60% yields in all cases in this study. Variation of the length of the *N*-alkyl chain (ethyl to propyl to pentyl) was to study the influence of the ligand lipophilicity on metal ion complexation in solution. In addition, length variation of the ethylene glycol unit connecting two benzene rings was to investigate the size effect on formation of the pseudo-cyclic structure which is able



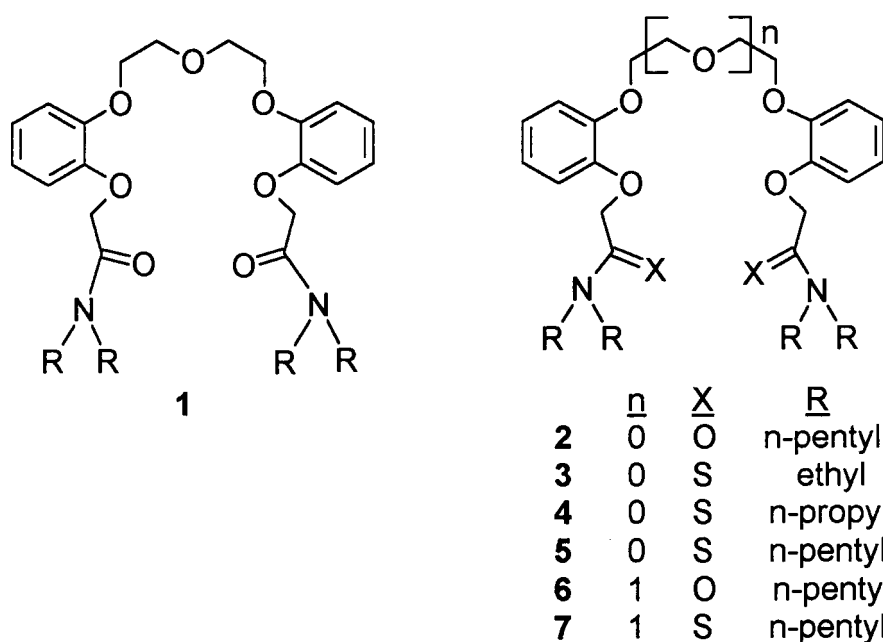
Scheme 1. Synthetic route for preparation of acyclic polyether dithioamides.

to wrap the specific metal ion. The acyclic polyether diamides and dithioamides mainly investigated in this study are listed in Scheme 2.

### 3.2. COMPLEXATION STUDIES

#### 3.2.1. Solution calorimetric titration

In determination of the complex stability there are many known methods such as potentiometry [17], polarography [18], calorimetry [19], and spectrophotometry [20]. We have used solution calorimetry to obtain the thermodynamic parameters which give an important and more detailed information on the complexation behavior. The complexation enthalpies, entropies, free energies, and log K values determined by the solution calorimetric titration technique are listed in Table II. This illustrates the effect of substitution of sulfur for oxygen on the change of enthalpy in structural variation of the podands. Complexations of all metal ions



Scheme 2. Acyclic polyether diamides and dithioamides.

with the acyclic polyether diamide and thioamide are observed to be exothermic but entropy changes are negative, indicating that the interactions of the corresponding podands with metal ions are enthalpy driven. In contrast to cyclic compounds such as pre-organized crown ethers, acyclic polyethers change the conformation from a linear framework to a pseudo-cyclic conformation in a *wrap around fashion* to bind a specific metal ion. So, this phenomenon definitely gives rise to negative entropy changes.

Podand **6** shows a selective heat change for lead ion while no heat change was observed for silver and copper ion. Interestingly, for **4**, **5** and **7** having thioamide end-groups,  $\text{Ag}^+$  represents significant heat changes compared with other metal ions, providing relatively high  $\log K$  values. For  $\text{Pb}^{2+}$ , podands **4**, **5** and **7** were observed to show small heat changes. Silver ion was known to be suitable for the sulfur atom with respect to HSAB theory [21]. From the above experimental data and reported theory, we assume that the sulfur rather than the nitrogen atom in the thioamide side chain participates in the complexation with  $\text{Ag}^+$ . Investigating the influence of the ether linkage length between two benzo groups on the heat change for the complexation, the shorter ether linkage (**5**) results in somewhat better complexation than **7** having diethylene glycol units, of which propensity is in good agreement with the results of the bulk liquid membrane experiment (vide infra). The alkyl chain length of the organic ligand in this study could also play an important role governing the extent of metal ion complexation. Compared to **4** in which an *n*-propyl chain is attached, compound **5** having *n*-pentyl chains on nitro-

Table II. Thermodynamic parameters for the interactions of several cations with podands in methanol at 25 °C

Compound	Parameter	Metal cations					
		Ag <sup>+</sup>	Pb <sup>2+</sup>	Cu <sup>2+</sup>	Na <sup>+</sup>	K <sup>+</sup>	Ca <sup>2+</sup>
<b>4</b>	Log K	3.80 ± 0.00	3.04 ± 0.04	3.16 ± 0.00	–	–	a
	ΔG <sup>b</sup>	–5.19 ± 0.00	–4.15 ± 0.06	–4.31 ± 0.00	–	–	a
	ΔH <sup>b</sup>	–34.09 ± 2.42	–8.06 ± 0.41	–24.02 ± 0.47	–	–	a
	TΔS <sup>b</sup>	–28.90 ± 2.44	–3.91 ± 0.46	–19.71 ± 0.47	–	–	a
<b>5</b>	Log K	3.35 ± 0.06	3.34 ± 0.07	3.32 ± 0.84	a	a	a
	ΔG <sup>b</sup>	–4.57 ± 0.08	–0.15 ± 0.09	–4.40 ± 0.06	a	a	a
	ΔH <sup>b</sup>	–50.03 ± 0.17	–8.21 ± 0.67	–9.59 ± 0.83	a	a	a
	TΔS <sup>b</sup>	–45.46 ± 0.09	4.06 ± 0.58	–5.19 ± 0.77	a	a	a
<b>6</b>	Log K	a	3.88 ± 0.12	a	3.08 ± 0.00	3.86 ± 0.08	3.30 ± 0.04
	ΔG <sup>b</sup>	a	–5.30 ± 0.08	a	–4.20 ± 0.00	–5.27 ± 0.07	–4.50 ± 0.05
	ΔH <sup>b</sup>	a	–11.78 ± 0.14	a	–5.31 ± 0.24	–5.33 ± 0.14	–8.26 ± 0.84
	TΔS <sup>b</sup>	a	–6.48 ± 0.22	a	–1.11 ± 0.24	–0.06 ± 0.01	–4.12 ± 0.78
<b>7</b>	Log K	3.22 ± 0.00	3.16 ± 0.06	3.16 ± 0.00	–	–	a
	ΔG <sup>b</sup>	–4.39 ± 0.05	–4.27 ± 0.06	–4.13 ± 0.00	–	–	a
	ΔH <sup>b</sup>	–36.42 ± 2.16	–8.43 ± 0.18	–18.29 ± 0.64	–	–	a
	TΔS <sup>b</sup>	–32.03 ± 2.22	–4.16 ± 0.17	–13.18 ± 0.64	–	–	a

Titant: 0.01 M M(NO<sub>3</sub>)<sub>n</sub> in MeOH. Titrate: 0.001 M ligand in MeOH.

<sup>a</sup> The heat of reaction is so small that log K and ΔH cannot be determined.

<sup>b</sup> Unit: kcal mol<sup>–1</sup>.

gen atoms shows a larger negative enthalpy change, probably due to the slightly stronger electron-donating effect of the pentyl group. However, log K values were obtained with a reverse trend probably because of entropic disfavor by suffering *wrapping around* of the larger alkyl chain.

### 3.2.2. Bulk liquid membrane transport

To further study the influence of structural variation of amide and thioamide end-groups on metal ion complexation by considering the amount transported from the source phase to the receiving phase by an organic medium, we used a bulk liquid membrane system. The results of single ion transport are described in Table I. First of all, in the single ion transport stage, compounds **2** and **6**, both having amide end-groups, show low flux values for both  $\text{Ag}^+$  and  $\text{Pb}^{2+}$ . Interestingly, ligands **3–5** bearing thioamide instead of amide end-groups exhibit an excellent silver ion selectivity over other metal ions (transition and heavy metal ions). Transport of silver ion was not in agreement with calorimetry titration results which do not show any selectivity. The reason seems to be that there is a considerable anion effect. In membrane transport, two  $\text{NO}_3^-$  anions must accompany one metal cation in the case of  $\text{M}^{2+}$  such as  $\text{Cu}^{2+}$  and  $\text{Pb}^{2+}$ , whereas only one  $\text{NO}_3^-$  anion is necessary for  $\text{Ag}^+$  to be transported. The number of accompanying anions per cation is of importance in affecting the distribution coefficient of the cation transport due to the fact that the corresponding anions should be first dehydrated in solution.

On increasing the chain length from ethyl (**3**) to propyl (**4**) to pentyl (**5**) on the thioamide end-group, the amount of  $\text{Ag}^+$  transported is found to gradually increase. This is attributed to the increased solubility of the ligand-metal complex in organic medium as the lipophilicity of the organic ligand increases to give an increasing transport rate. In the chain length effect of the ether linkage, compound **5**, having only one ethylene glycol unit, shows a higher transport value than does compound **7** having a diethylene glycol unit. So, we can assert that the best combination of structural variation for  $\text{Ag}^+$  complexation so far consists of a monoethylene glycol unit between two benzo groups as well as a dipentyl lipophilic chain on the thioamide end-group, namely podand **5**. A competitive transport experiment was also conducted to provide an excellent  $\text{Ag}^+$  ion selectivity over other metal ions for all organic ligands (Table III) even though we could not suggest proper reasons for the different selectivities according to the structural variation (**3–5** and **7**).

## 4. Conclusions

Syntheses of novel acyclic polyethers bearing thioamide end-groups were successfully accomplished with quantitative yields. From the results of solution calorimetry, and bulk liquid membrane transport, compound **5** containing a monoethylene ether linkage and a dipentyl group on the thioamide end-group exhibits an excellent selectivity for  $\text{Ag}^+$  over other metal ions. For metal complexation of acyclic polyether dithioamides, participation of the sulfur instead of the nitrogen atom in



*Table III.* Competitive transport of metal ions from an aqueous source phase into a receiving phase through a bulk organic liquid membrane by using various podands.<sup>a</sup>

Compound	Flux value ( $\times 10^{-8}$ mol s <sup>-1</sup> m <sup>-2</sup> )					
	Ag <sup>+</sup> /Cd <sup>2+</sup>	Ag <sup>+</sup> /Pb <sup>2+</sup>	Ag <sup>+</sup> /Cu <sup>2+</sup>	Ag <sup>+</sup> /Co <sup>2+</sup>	Ag <sup>+</sup> /Ni <sup>2+</sup>	Ag <sup>+</sup> /Zn <sup>2+</sup>
<b>3</b>	161.12 ± 6.79	122.25 ± 6.69	144.80 ± 14.37	134.53 ± 0.54	134.61 ± 13.97	146.91 ± 12.26
	/0	/0	/0	/0	/0	/0
<b>4</b>	135.03 ± 6.80	142.17 ± 10.81	200.24 ± 2.37	243.79 ± 24.22	250.44 ± 24.98	178.73 ± 10.65
	/0	/0	/0	/0	/0	/0
<b>5</b>	148.46 ± 10.27	129.83 ± 12.24	149.77 ± 14.11	195.83 ± 9.52	185.75 ± 17.89	169.98 ± 1.51
	/0	/0	/0	/0	/0	/0
<b>7</b>	145.18 ± 10.59	223.47 ± 2.47	264.17 ± 2.64	358.48 ± 22.75	276.59 ± 8.93	203.39 ± 16.87
	/0	/0	/0	/0	/0	/0

<sup>a</sup>Experimental conditions are the same as shown in Table I. The experimental values deviate from the reported values by an average of 10%.

the thioamide was indicated by membrane transport experiments and calorimetric titration by comparing with those of the acyclic polyether diamide.

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