

Insoluble Lithium Complex of Polyether Carboxylic Acids Consisting of Naphthalene Repeating Unit and Its Stable Monolayer on Aqueous Surfaces

Kazuhiro Taguchi,^{*,†,‡,§} Teiichi Murakami,[†] Masahiro Higuchi,^{†,‡} Midori Goto,[†] Kazuhisa Hiratani,[†]
Akemi Okada,^{†,‡} Sadatoshi Akabori,^{†,‡} Yasuhito Miyake,^{†,‡,§} and Mikiji Miyata^{†,‡,§}

[†]Nanoarchitectonics Research Center, National Institute of Advanced Industrial Science and Technology (AIST),
Tsukuba, Ibaraki 305-8565

[‡]CREST, Japan Science and Technology Corporation (JST)

[§]Department of Chemistry, Faculty of Science, Toho University, Funabashi, Chiba 274-8510

^{§§}Department of Material and Life Science, Graduate School of Engineering, Osaka University, Suita, Osaka 565-0871

(Received August 13, 2001; CL-010786)

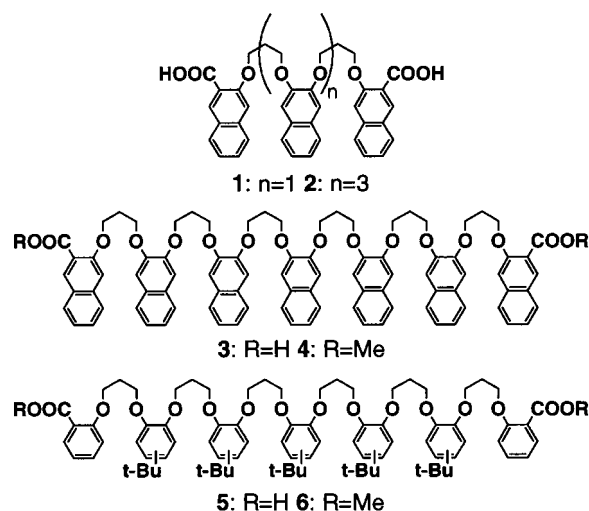
We synthesized several polyether dicarboxylic acids with naphthalene and trimethylene groups as repeating units. The polyethers selectively formed complexes with lithium, an alkali metal. In contrast to the typical polyethers, their alkali metal complexes exhibited very low solubilities for water and hydrophobic organic solvents such as chloroform and toluene. Polyethers having seven naphthalene units formed a stable monolayer on an aqueous subphase, only when alkali metal hydroxides were added, but not acid.

After the discovery of macrocyclic ethers, also called crown ethers, a number of open-chain polyethers (podants) were also extensively investigated as hosts that can take metal cations into the pseudo-cavity formed by the folded ether chain.¹ The host polyethers surround the guest species facing the oxygen atoms inward and methylene groups outward, and often form a coiled structure.^{1,2} 1,2-Phenylene and ethylene units are commonly used for the polyethers mainly because they are superior in material acquisition for preparation, reaction processing, and product properties, e.g. solubilities of the free and the complex forms in common organic solvents.

Obtaining a novel polyether with a well-packed coiled conformation in the metal complex seems to insure excellent selectivity for a certain metal ion. In this work, we introduced 2,3-naphthalene (trimethylene) units in the polyether chains instead of 1,2-phenylene (ethylene). A 2,3-naphthalene unit can provide stronger interaction based on π - π stacking than benzene rings and may form a better-packed conformation. Trimethylene is also a flexible chain unit and tends to form a smaller pseudo-cavity than an ethylene unit,³ though the chain is longer. In fact, dibenzo-14-crown-4,⁴ which consists of two 1,2-phenylene and two trimethylene units, unexpectedly has a small cavity suitable for incorporation of a lithium metal cation. The smaller cavity may also mean better-packed conformation of the polyether. Following this strategy, we designed polyethers having *tert*-butyl-1,2-phenylene (residual group of *tert*-butylcatechol) and trimethylene groups as the repeating units, (5), and confirmed the excellent lithium selectivity and the coiled conformation of the polyether.⁵

Using a method slightly modified from our previous report,⁵ we prepared polyether carboxylic acids **1**, **2**, and **3** by typical step-wise Williamson's reactions between hydroxy groups on the naphthalene rings and terminal chloride of intermediates in the presence of alkali. The final products were characterized by IR, NMR, FABMS,⁶ and GPC.

The solubilities of the free polyethers were comparable to the



common polyethers (more than 30 mg in 1 mL of chloroform), so we used them for competitive metal extraction experiments⁷ by contacting the dichloromethane solution with an aqueous solution containing the same molar amount of LiOH, NaOH, and KOH. Adding the polyether solution to the aqueous solution of alkali metals caused an immediate precipitation on the interface, and we recovered the theoretical amount of the white complex after shaking the solutions. As expected, we observed a band shift of the carbonyl stretching region from 1735 to 1586 cm^{-1} (Li-complex), indicating formation of a carboxylate accompanied by complexation. After acidifying the precipitate by adding diluted hydrochloric acid, we quantitatively analyzed alkali metals, extracted into the aqueous phase, by the elemental absorption method (Table 1). This experiment also confirmed the stoichiometry of the complexes to have a ratio of 1 to 2 of polyether and metal. The long chain polyether, **3**, had better lithium selectivity against sodium and potassium than did polyethers **1** and **2**, and probably the phenylene-based polyethers (**5**),⁵ even though the selectivity was analyzed in a liquid membrane experiment.⁸ X-ray powder diffraction of the Li-complex prepared in the same way revealed a crys-

Table 1. Competitive complexation of the polyethers with alkali metals and the lithium selectivity

Polyether	2	3
Li	49%	70%
Na	30% (Li/Na 1.6)	16% (Li/Na 4.2)
K	21% (Li/K 2.3)	14% (Li/K 5.0)

talline pattern with sharp peaks, while Na- and K-complexes were rather amorphous. Because the pseudo-cavity of **3** is not large enough to incorporate sodium or potassium ions with an ionic radius exceeding that of lithium ion, the complexes could not form a well-packed conformation of the polyether chain, resulting in rather amorphous precipitates. We assumed that the low solubility for the solvent and superior lithium selectivity should reflect a compact coiled conformation with a simple symmetry derived from tight multiple stacking among the naphthalene units.

Very low solubility⁹ of the complexes for water encouraged us to apply the polyethers to a monolayer study, although the polyethers are not typical amphiphilic compounds but have aliphatic long chains. On pure water and aqueous solutions of a diluted sulfuric acid and alkali hydroxide, **1** did not induce an increase of surface pressure upon compression, probably due to its being hydrophilic. Rather hydrophobic polyethers **2** and **3** did not form a reproducible, stable monolayer either. However, on aqueous solutions of alkali hydroxides, **3** formed a stable monolayer. This monolayer was strong enough to prepare Langmuir-Blodgett films on a solid substrate by common methods. This feature was in striking contrast to aliphatic carboxylic acid (e.g. stearic acid) monolayers, which are stable only for acidic and neutral subphases. The π -A isotherms depended slightly on ionic size of metals; the limiting areas¹⁰ in aqueous solutions of lithium hydroxide, sodium hydroxide, potassium hydroxide, and cesium hydroxide were 1.82, 2.00, 2.05, and 2.18 nm² molecule⁻¹ ($\pm 3\%$), respectively. We used a Brewster angle microscope to observe the monolayer morphology of **3**. When we spread the polyether **3** on an aqueous lithium hydroxide solution, homogeneous solid phase appeared immediately, floated on the subphase like ice plates on water, and did not change in size during compression. However, we always observed inhomogeneous aggregates in pure water during spreading and compression. In contrast, phenylene-type polyether carboxylic acid **5**, which must be more hydrophobic than the naphthalene polyether due to the butyl group on the phenylene unit, did not exhibit an increase in surface pressure with compression (data not shown). Methyl esters **4** and **6**, which were the intermediates for the corresponding polyether carboxylic acids, did not form a stable monolayer either, even though they were more hydrophobic (Figure 1 (e) for **4**). These monolayer properties of **3** in an aqueous alkali solution

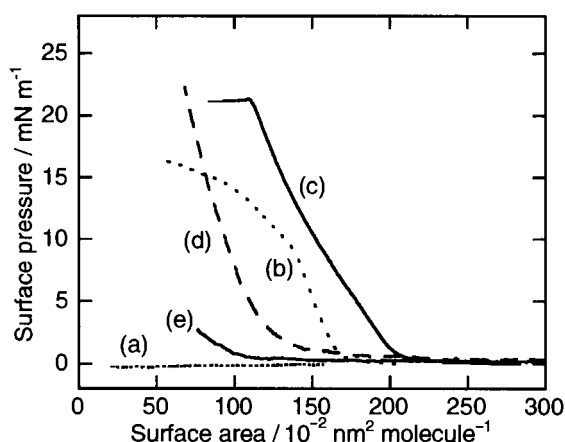


Figure 1. π -A isotherms of the monolayers from chloroform solutions (0.2–0.3 g/dm³) at 25 °C, (a) **1**, (b) **2**, (c) **3**, and (e) **4**, on 0.01 mole dm⁻³ LiOH and 0.01 mole dm⁻³ LiCl, and (d) **3** on pure water.

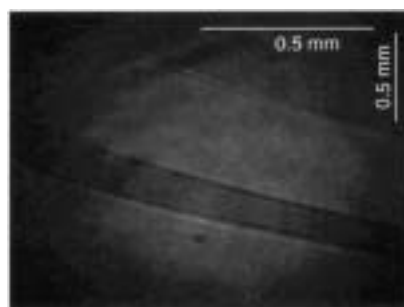


Figure 2. Brewster angle microscope observation of the monolayer **3** on an aqueous subphase containing LiOH (before compression). Dark region: bare water surface.

suggest a unique coiled conformation of polyether. Each naphthalene unit must form multiple stackings to withstand the surface pressure. Furthermore, hydrophilic groups are enclosed inside and do not dissolve into the subphase.

References and Notes

- F. Vogtle and E. Weber, "The Chemistry of Ethers, Crown Ethers, Hydroxy Groups and Their Sulphur Analogues," ed. by S. Patai, John Wiley & Sons, Chichester, New York, Brisbane, Toronto (1980).
- a) N. Kasuga, S. Nakahama, K. Yamaguchi, Y. Ohashi, and K. Hori, *Bull. Chem. Soc. Jpn.*, **64**, 3548 (1991). b) H. Kuboniwa, S. Nagami, K. Yamaguchi, A. Hirao, S. Nakahama, and N. Yamazaki, *J. Chem. Soc. Chem. Commun.*, **1985**, 1468.
- a) K. Hiratani, *Chem. Lett.*, **1982**, 1021. b) K. Hiratani, *Bull. Chem. Soc., Jpn.*, **58**, 420 (1985).
- a) N. K. Dalley, W. Jiang, and U. Olsher, *J. Inc. Phen. Mol. Rec. Chem.*, **12**, 305 (1992). b) R. A. Sachleben and J. H. Burns, *J. Chem. Soc., Perkin Trans. 2*, **1992**, 1971. c) G. Shoham, W. N. Lipscomb, and U. Olsher, *J. Chem. Soc., Chem. Commun.*, **1983**, 208.
- K. Hiratani and K. Taguchi, *Bull. Chem. Soc. Jpn.*, **60**, 3827 (1987).
- 3**: mp 113–116 °C. IR(KBr) $\nu_{C=O}$ 1739 cm⁻¹. ¹H NMR(300 MHz, CDCl₃, TMS) δ 8.57 (s, 2H), 7.74 (d, $J=8.2$ Hz, 2H), 7.65–7.69 (m, 2H), 7.56 (d, $J=8.2$ Hz, 2H), 7.43–7.49 (m, 2H), 7.34–7.38 (m, 4H), 7.21 (s, 2H), 7.19 (s, 2H), 4.57 (t, $J=6.0$ Hz, 4H), 4.40 (t, $J=5.8$ Hz, 4H), 2.53–2.57 (m, 4H). Anal. Calcd for C₃₈H₃₂O₈: C, 74.01; H, 5.23%. Found: C, 73.87; H, 5.22%. FABMS 617 ([M+1]). **4**: mp 87–88 °C. $\nu_{C=O}$ 1735 cm⁻¹. δ 8.67 (s, 2H), 7.81 (d, $J=8.0$ Hz, 2H), 7.63 (d, $J=8.0$ Hz, 2H), 7.55–7.57 (m, 4H), 7.45–7.48 (m, 4H), 7.27–7.38 (m, 6H), 7.19–7.22 (m, 2H), 7.15 (s, 2H), 7.13 (s, 2H), 7.12 (s, 2H), 7.01 (s, 2H), 4.46 (t, $J=6.1$ Hz, 4H), 4.32 (t, $J=6.1$ Hz, 4H), 4.26 (m, 8H), 2.35–2.44 (m, 8H). FABMS 1018 ([M+1]). **5**: mp 113–116 °C. $\nu_{C=O}$ 1737 cm⁻¹. δ 8.65 (s, 2H), 7.79 (d, $J=7.6$ Hz, 2H), 7.19–7.63 (m, 28H), 7.10 (bs, 6H), 7.05 (s, 4H), 6.99 (s, 2H), 4.42 (t, $J=6.3$ Hz, 4H), 4.30 (t, $J=6.3$ Hz, 4H), 4.18–4.25 (m, 16H), 2.31–2.40 (m, 12H). Anal. Calcd for C₉₀H₈₀O₁₆: C, 76.25; H, 5.69%. Found: C, 76.05; H, 5.67%. FABMS 1418 ([M+1]).
- We performed competitive metal complexation by stirring the polyether (15 mg) in 10 mL of dichloromethane with 1 mL of an aqueous alkali solution containing 0.1 mol dm⁻³ of LiOH, NaOH, and KOH over night at room temperature. The complex was recovered as an insoluble precipitate by filtration and thorough washing with pure water. The incorporated metals were extracted from the precipitate dispersed in chloroform with 2 mol dm⁻³ of HCl and quantitatively analyzed by elemental absorption.
- The phenylene-base polyether **5** formed a soluble complex with alkali metals. Ion selectivity was measured by an active transport experiment through a liquid membrane: Li/Na 2.4, Li/K 2.8.
- We did not apply NMR, UV-vis, or fluorescence analysis to the complex of **3** due to the very low solubility in common solvents such as chloroform, benzene, and THF. We observed weak spectra derived from the very small amount of metal-free polyether remaining in the precipitate. Complex **1** with magnesium exhibited exceptionally a weak NMR spectrum with a complicated broad pattern after prolonged accumulation.
- The limiting areas were comparable to the least molecular section area (1.7 nm² molecule⁻¹) estimated by a CPK molecular model based on a assumption that the coiled chain wraps two metal ions at the termini and the longitudinal axis lies along the surface.