S0032-3861(96)00190-5

Polymer Vol. 37 No. 16, pp. 3767–3769, 1996

0032-3861/96/$15.00 + 0.00

Synthesis and Ag^+-binding property of polyphenylacetylene with aza-crown cavity by cyclopolymerization of 2,6-bis[7′-(4″-ethynylphenoxy)-2′,5′-dioxaheptyl]pyridine

Toyoji Kakuchi*, Toshitaka Watanabe, Hiroyuki Kamimura and Shigeyuki Matsunami
Graduate School of Environmental Earth Science, Hokkaido University, Sapporo 060, Japan

and Kazuaki Yokota
Graduate School of Engineering, Hokkaido University, Sapporo 060, Japan
(Received 13 November 1995; revised 4 December 1995)

The cyclopolymerization of 2,6-bis[7′-(4″-ethynylphenoxy)-2′,5′-dioxaheptyl]pyridine was carried out using a rhodium complex catalyst to yield the polyphenylacetylene with an aza-crown ether cavity. The obtained polymer showed binding ability for metal cations, which was particularly high for Ag^+. Copyright © 1996 Elsevier Science Ltd.

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

Introduction

Conjugated polymers with a crown ether are expected to exhibit new functional properties based on the electrical conductivity of the main-chain[1] and the cation-binding ability of the crown cavity. For example, poly(thiophene)s[2] and poly(pyrrole)s[3] attached to crown ethers have been synthesized and the conducting properties were reported. Recently, we reported that two different types of poly(phenylacetylene)s with crown cavities were synthesized by the polymerization of 4′-ethynylbenzo-15-crown-5[4] and the cyclopolymerization of 1,14-bis(4′-ethynylphenoxy)-3,6,9,12-tetraoxatetradecane[5], respectively. They exhibited binding selectivity for alkali-metal cations, and an increase in electrical conductivity was produced by doping with I_2, with values in the semiconductor range[4].

We reported the synthesis of polymers with crown ether, thia-crown ether, cryptand, hemispherand, and crown lactone units using the cyclopolymerization of bifunctional monomers, such as α,ω-divinyl ether[6], α,ω-diepoxide[7], α,ω-diepisulfide[8], and allyloxyphenyl acrylate[9]. They showed binding characteristics toward appropriate metal cations, which depended on their ring sizes and the nature of the donor atoms. We have continued to expand the scope of the cyclopolymerization method in terms of the kind of polymerizable groups and macrocyclic units. Therefore, the synthesis of polymeric aza-crown ether using the cyclopolymerization method is interesting along with their cation-binding properties. Here we report the preparation of polyphenylacetylene with an aza-crown cavity **2** by the cyclopolymerization of 2,6-bis[7′-(4″-ethynylphenoxy)-2′,5′-dioxaheptyl]pyridine (**1**) using a rhodium complex catalyst. In addition, **2** is found to exhibit a remarkably high binding ability for Ag^+ (*Scheme 1*).

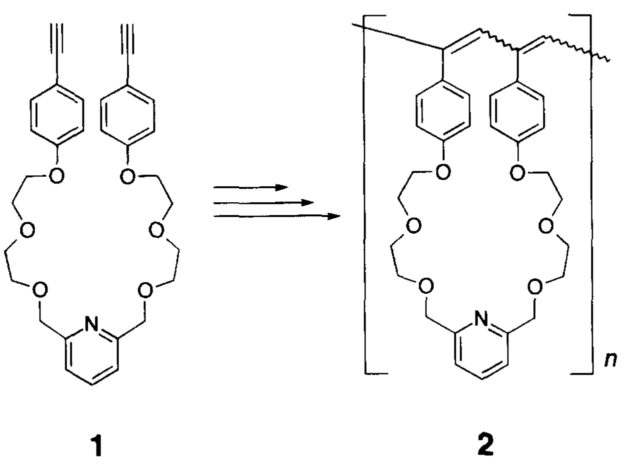
Experimental

Monomer. The synthesis of 2,6-bis[7′-(4″-ethynylphenoxy)-2′,5′-dioxaheptyl]pyridine (**1**) and intermediary compounds are outlined in *Scheme 2*. 5-(4′-Iodophenoxy)-3-oxapentanol (**4**) was prepared from 4-iodophenol and 5-chloro-3-oxapentyl tetrahyropyranyl ether (**3**), followed by the cleavage of the tetrahydropyranyl (THP) ether linkage. For the cross-coupling of diiodo compound **5** and trimethylsilylacetylene with bis(triphenylphosphine)palladium(II) chloride and copper (I) iodide, piperidine was used as the basic solvent. The deprotection of the disilyl compound smoothly progressed with Na_2CO_3 in methanol to give **1** (yield, 69% from **5**) as a yellow oil ^{1}H n.m.r. ($CDCl_3$) δ 3.00 (s, 2H, $\equiv$ CH), 3.73–3.79 (m, 8H, OCH_2CH_2), 3.85–3.89 (m, 4H, $PhOCH_2CH_2$), 4.10–4.15 (m, 4H, $PhOCH_2$), 4.67 (s, 4H, $PyCH_2$), 6.83–6.87 (m, 4H, PhH_{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). Anal. Calcd for $C_{31}H_{33}NO_6$: C, 72.21; H, 6.45; N, 2.72. Found: C, 71.18; H, 6.72; N, 2.74.

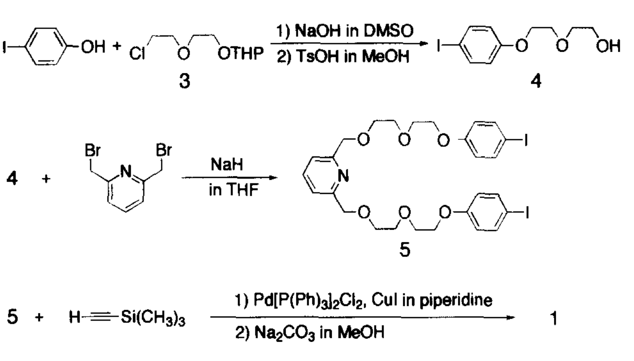
Cyclopolymerization. A typical polymerization procedure is as follows: To a solution of (bicyclo[2.2.1]-hepta-2,5-diene)rhodium(I) chloride dimer ([Rh(bhd)-Cl]$_2$) (2 mg, 4.5×10^{-3} mmol) in chloroform (0.3 ml), Et_2NH (33 mg, 0.45 mmol) was added under nitrogen. The mixture was warmed at 30°C for 30 min. To a solution of **1** (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 the large amount of methanol. The precipitate was filtered and then purified by

---

* To whom correspondence should be addressed



Scheme 1



Scheme 2

reprecipitation from chloroform/methanol several times to yield the polymer (128 mg, yield 55%).

Extraction experiment. The extraction of metal cation picrates was carried out using a procedure similar to that developed by Pedersen.[10]. A solution of polymer in chloroform ([aza-crown ether units] = 7×10^{-4} mol l^{-1}) was vigorously shaken in a culture tube with an aqueous solution of alkali hydroxide and picric acid ([picric acid] = 7×10^{-5} mol l^{-1} and [metal ion] = 0.01 mol l^{-1}). After separating the resulting two phases, the alkali picrate extracted into the chloroform was determined indirectly by measuring the absorbance of the picrate in the aqueous phase at 354 nm using a u.v.-visible spectrophotometer.

Results and discussion

Table 1 lists the results of the polymerization of **1**. $[Rh(bhd)Cl]_2$ did not exhibit catalytic activity but was combined with an appropriate amine as a cocatalyst to produce the polymers. The obtained polymers were yellow powders and were soluble in chloroform and dichloromethane except that substantial amounts of organic-solvent insoluble polymers were obtained for the polymerization with Et_2NH in toluene. The yields and the number-average molecular weights (M_ns) for the polymerizations with Et_2NH were higher than those with Et_3N. The condition with Et_2NH in $CHCl_3$ was most suitable. The M_n values ranged from 5300 to 16 000, corresponding to the number average degree of polymerization of 10.3 to 31.0.

Table 1 Cyclopolymerization of 2,6-bis[7′-(4″-ethynylphenoxy)-2′,5′-dioxaheptyl]pyridine (**1**) using (bicyclo[2.2.1]hepta-2,5-diene)rhodium(I) chloride dimer ($[Rh(bhd)Cl]_2$)[a]

Amine	Solvent	Yield[b] (%)	$M_n(M_W/M_n)$[c]	Extent of cyclization[d]
—	$CHCl_3$	0	—	—
Et_3N	$CHCl_3$	31 (trace)	5 300 (5.0)	0.99
Et_2NH	$CHCl_3$	55	16 000 (5.4)	0.99
Et_2NH	THF	Trace	12 000 (4.1)	0.89
Et_2NH	Toluene	Trace (47)	11 000 (3.4)	0.92

[a] [**1**] = 0.03 mol l^{-1}; [**1**]/[$[Rh(bhd)Cl]_2$] = 100; [amine]/[$[Rh(bhd)Cl]_2$] = 100; time, 12 h; temp., 30°C
[b] The yields of solvent-insoluble polymers in parentheses
[c] Measured in THF by g.p.c. using polystyrene as standards
[d] Determined by ^{1}H n.m.r. spectra

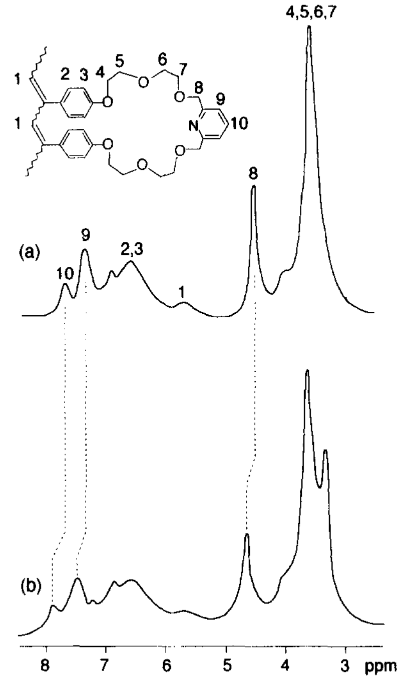


Figure 1 ^{1}H n.m.r. spectra of aza-crowned polymer **2** (a) and that with $AgClO_4$ (b) in DMSO-d_6

For the polymerization of **1**, $[Rh(bhd)Cl]_2$ was found to be a suitable polymerization catalyst, although WCl_6 and $MoCl_5$, which are excellent catalysts for the polymerization of substituted acetylenes,[11] did not exhibit catalytic activity. This was very similar to the results for the polymerizations of 4′-ethynylbenzo-15-crown-5[4] and 1,14-bis(4′-ethynylphenoxy)-3,6,9,12-tetraoxatetradecane[5].

Figure 1 shows the ^{1}H n.m.r. spectrum of the polymer obtained with $[Rh(bhd)Cl]_2/Et_2NH$. The characteristic absorption at 3.0 ppm due to the ethynyl proton has been remarkably diminished together with the appearance of an absorption at 5.5–5.9 ppm due to the proton in the conjugated main chain. The extent of cyclization, which was determined from the relative peak areas of the pyridyl (7.5–7.8 ppm) and ethynyl (3.0 ppm) protons in the ^{1}H n.m.r. spectra, was from 0.89 to 0.99. This means that the resulting polymer consisted of cyclic constitutional repeating units as the main structure with a small amount of pendant ethynyl groups, i.e., polyphenylacetylene with an aza-crown cavity, **2**.

The vinylic absorption due to the main-chain protons for **2** was broader than those for poly(phenylacetylene)s synthesized using rhodium complex catalysts[12]. In addition, we reported that the n.m.r. spectra of the polyphenylacetylenes with crown cavities showed sharp signals due to the main-chain atoms[4,5]. The lower regularity of the main-chain structure for **2** should be caused by the pyridyl unit in **1**, but this needs to be further studied.

The cation-binding properties of polymer **2** were estimated by the liquid–liquid extraction method using picrates of Fe^{2+}, Zn^{2+}, Cd^{2+}, Pb^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Ag^+ and Hg^{2+}. The extraction experiment was carried out with [aza-crown units in **2**]/[metal picrate] = 10. Although the pyridyl unit in the polymers participates with the acid–base reaction, picric acid was not extracted into the organic solution of the polymers in the absence of the metal cation. The binding ability was low for Fe^{2+} (6.2%), Zn^{2+} (3.3%), and Cd^{2+} (4.0%) and somewhat high for Pb^{2+} (25.4%), Co^{2+} (12.2%), Ni^{2+} (10.4%), Cu^{2+} (21.7%) and Hg^{2+} (14.1%). Polymer **2** exhibited remarkably high binding performance for Ag^+, attaining a 98.6% yield. In addition, a yield of 49.9% was found even for [aza-crown cavity units in **2**]/[metal picrate] = 2. Monomer **1** gave yields of 41.8 and 11.4% under the corresponding conditions. Polymer **2**, thus, was specific for binding with Ag^+. The complex between **2** and Ag^+ was confirmed by the ^{1}H n.m.r. measurement. As seen in *Figure 1*, the absorption at 3.0–4.2 ppm due to the methylene protons of the oxyethylene units was split into two parts. 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 relating to the pyridyl units after host–guest complexation. This means that the aza-crown moiety in **2** strongly formed a complex with Ag^+.

The geometric structure of polymer main-chain *cis* and *trans* forms, should affect the radius of aza-crown cavity. However this is not clear, so we cannot discuss the effect of conjugated main-chain structure on the cation-binding property. Further studies are underway to investigate the ionic and electrical conductivity and the electrochemical properties of **2** when it forms a complex with an appropriate cationic guest.

In summary, we synthesized a novel polymeric aza-crown ether using the cyclopolymerization method, i.e., polyphenylacetylene with an aza-crown ether cavity **2** was prepared from the cyclopolymerization of α,ω-diacetylene **1** with pyridyl unit using a rhodium complex catalyst. Polymer **2** showed binding ability for metal cations, which was particularly high for Ag^+. This binding property was specific among the polymers with various macrocyclic units prepared using the cyclopolymerization method.

References

1 Chien, J. 'Polyacetylen', Academic Press, Orland, FL, 1984

2 Le Moigne, J., Hilbere, A. and Strazielle, C. *Macromolecules* 1992, **25**, 6705

3 Matsunami, S., Kakuchi, T., Yokota, K. and Ishii, F. *Rep. Prog. Polym. Phys. Jpn* 1994, **37**, 517

4 Kakuchi, T., Matsunami, S., Kamimura, H., Ishii, F., Uesaka, T. and Yokota, K. *J. Polym. Sci., Part A: Polym. Chem.* 1995, **33**, 1431

5 Kakuchi, T., Kamimura, H., Matsunami, S. and Yokota, K. *Macromolecules* 1995, **28**, 658

6 (a) Kakuchi, T., Haba, O. and Yokota, K. *Macromolecules* 1992, **25**, 4854. (b) Kakuchi, T., Aoki, K., Haba, O. and Yokota, K. *Polym. J.* 1993, **25**, 839. (c) Yokota, K., Matsumura, M., Yamaguchi, K. and Takada, Y. *Makromol. Chem., Rapid Commun.* 1983, **4**, 721. (d) Yokota, K., Kakuchi, T., Yamanaka, M. and Takada, Y. *Makromol. Chem., Rapid Commun.* 1986, **7**, 633. (e) Kakcuchi, T., Sasaki, H. and Yokota, S. *Makromol. Chem.* 1988, **189**, 1279. (f) Kakuchi, T., Takaoka, T. and Yokota, K. *Makromol. Chem.* 1988, **189**, 2007. (g) Yokota, K., Kakuchi, T., Sasaki, H. and Ohmori, H. *Makromol. Chem.* 1989, **190**, 1269. (h) Kakuchi, T., Takaoka, T. and Yokota, K. *Makromol. Chem.* 1989, **190**, 2449. (i) Kakuchi, T., Haba, O. and Yokota, K. *Makromol. Chem.* 1991, **192**, 1601. (j) Yokota, K., Kakuchi, T., Yamamoto, T., Hasegawa, T. and Haba, O. *Makromol. Chem.* 1992, **193**, 1805

7 (a) Hashimoto, H., Kakuchi, T., Haba, O. and Yokota, K. *Macromolecules* 1992, **25**, 1828. (b) Kakuchi, T., Hashimoto, H., Harada, Y., Satoh, T. and Yokota, K. *J. Macromol. Sci., Pure Appl. Chem.* 1994, **A31**, 751. (c) Yokota, K., Hashimoto, H., Kakuchi, T. and Takada, Y. *Makromol. Chem., Rapid Commun.* 1984, **5**, 115. (d) Hashimoto, H., Kakuchi, T. and Yokota, K. *J. Org. Chem.* 1991, **56**, 6470. (e) Kakuchi, T., Harada, Y., Satoh, T., Yokota, K. and Hashimoto, H. *Polymer* 1994, **35**, 204

8 Yokota, K., Hashimoto, H., Kakuchi, T. and Takada, T. *Makromol. Chem., Rapid Commuun.* 1984, **5**, 767

9 Yokota, K., Hirayama, N. and Takada, T. *Polym. J.* 1975, **7**, 729

10 Pedersen, C. J. *Fed. Proc., Fed. Am. Soc. Exp. Biol.* 1968, **27**, 1305

11 (a) Masuda, T. and Higashimura, T. *Adv. Polym. Sci.* 1987, **81**, 121. (b) Masuda, T., Kawasaki, M., Okano, Y. and Higashimura, T. *Polym. J.* 1982, **14**, 371

12 (a) Furlani, A., Licoccia, S. and Russo, M. V. *J. Polym. Sci., Polym. Chem. Edn* 1986, **24**, 991. (b) Furlani, A., Napoletano, C., Russo, M. V. and Fest, W. J. *Polym. Bull.* 1986, **16**, 311. (c) Furlani, A., Napoletano, C., Russo, M. V., Camus, A. and Marsich, N. *J. Polym. Sci., Polym. Chem. Edn* 1989, **27**, 75. (d) Tabata, M., Yang, W., Yokota, K. and Shoma, J. *Polym. J.* 1990, **22**, 1105. (e) Tabata, M., Yang, W. and Yokota, K. *Polym. J.* 1991, **23**, 1135