

NOTES

Polymer Possessing Diaza-18-crown 6-Ether Linked by π -Conjugated Aminopenta-2,4-dienylidene Groups Generated by Ring-opening of Pyridinium Ring

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Polymers possessing crown ether and diazacrown ether have attracted much attention due to their potential usability for separators of ionic species, chemosensors, and ion conductors.^{1–4} The structures of units linked to the crown ether and the diazacrown ether in the polymers are important for their applications since chemical properties of the polymers are affected by the structures of the linkers. For example, polymers containing the diazacrown ether linked by amide groups or imide groups show unique optical and electrochemical properties on the basis of functionalities of the linkers.^{5,6} To the best of our knowledge, there is no report on main chain polymers possessing the diazacrown ether linked by π -conjugated chains. Such a polymer will show interesting chemical properties upon complexation of the diazacrown ether with metal ions since the π -conjugated system may expand through the metal complex of the diazacrown ether. Investigation of the chemical properties of the polymer will give new fundamental information for construction of polymers having ion sensing and separating functionalities.

We previously reported synthesis of π -conjugated polymers by reaction of *N*-(2,4-dinitrophenyl)pyridinium chloride (**1**) with 2,5-dimethyl-1,4-phenylenediamine.⁷ The polymers were consisted of 5-(2,5-dimethyl-1,4-phenylene)penta-2,4-dienylideneammonium chloride unit and *N*-2,5-dimethyl-1,4-phenylene diaza[12]annulanium dichloride unit that were generated by ring-opening of the pyridinium ring of **1**.

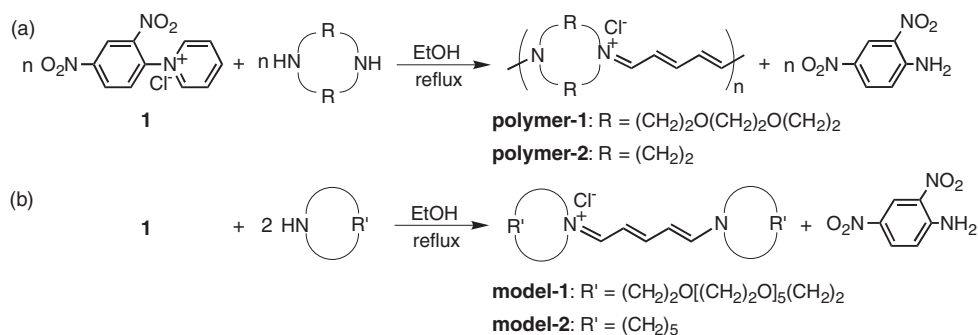
In addition, we have found that reaction of **1** with aliphatic diamines provides structurally controlled polymers consisted of 5-alkane-penta-2,4-dienylideneammonium chloride unit. These polymers have a positive charge on the iminium group ($-(R)N^+=C-$) that may induce unique optical and electrochemical properties.

In this work, we describe results of the reaction of **1** with 4,13-diaza-18-crown 6-ether (DA18C6), the structure, optical and electrochemical properties, and metal complexation of the polymer. A polymer obtained by the reaction of **1** with piperadine and model compounds are also reported.

The reactions of **1** with DA18C6 and piperadine caused ring-opening of the pyridyl ring of **1** to provide polymers **polymer-1** and **polymer-2** in 43 and 93% yields, respectively (Scheme 1a). The lower yield of **polymer-1** than **polymer-2** seems to be ascribed to formation of low molecular weight products that were removed by repeated reprecipitations. Model compounds **model-1** and **model-2** were synthesized by the reactions of **1** with 1-aza-18-crown 6-ether and piperidine, respectively (Scheme 1b). Results of the reactions are summarized in Table I. The obtained polymers and model compounds were soluble in water and polar organic solvents such as methanol, dimethyl sulfoxide, and *N*-methyl-2-pyrrolidinone. Their structures were determined by ¹H and ¹³C NMR spectroscopy.

Figure 1 depicts ¹H NMR spectra of **polymer-1** and **model-1** in DMSO-*d*₆. As seen in Figure 1, peaks due to hydrogen atoms H^a, H^b, and H^c of **polymer-1** and **model-1** appear at approximately δ 7.8, 7.4, and 5.9 in a 2:1:2 integral ratio, respectively. The observation of these three signals indicates that the π -electrons are delocalized along the aminopenta-2,4-dienylidene group. ¹³C NMR data also supported this view, showing three signals due to the aminopenta-2,4-dienylidene group at approximately δ 163, 162, and 104. On the other hand, the ¹H NMR peaks assignable to H^a and H^b of the aminopenta-2,4-dienylidene group of **polymer-2** and **model-2** were duplicated with a 3:2 integral ratio between H^a + H^b and H^c. The ¹³C NMR spectra of **polymer-2** and **model-**

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**Scheme 1.** Synthesis of the polymers and the model compounds.**Table I.** Synthesis results and optical and electrochemical properties

	Yield (%)	M_n^a	M_w^a	η_{sp}/c^c , dLg ⁻¹	λ_{max}^d /nm	E_{pa}^e /V
polymer-1	43	1760	6320	0.20	429	0.79
polymer-2	93	— ^b	— ^b	0.25	471	0.70
model-1	99	—	—	—	420	0.78
model-2	37	—	—	—	422	0.93

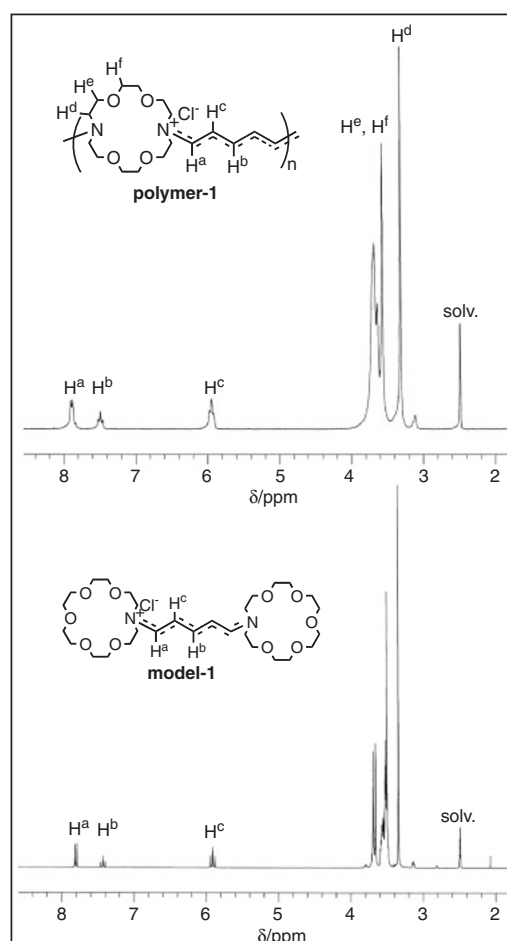
^aMeasured by GPC. Eluent = CHCl₃. ^bNot measured due to poor solubility in the eluent. ^c η_{sp}/c : Reduced viscosity. Measured at the concentration of 0.06 g dL⁻¹ in DMSO at 30 °C. ^d λ_{max} : Absorption maximum in DMSO. ^e E_{pa} : Oxidation potential vs. Ag⁺/Ag. Measured in an acetonitrile solution of [Et₄N]BF₄ (0.1 M). Sweep rate was 50 mVs⁻¹.

2 showed three signals due to the aminopenta-2,4-dienylidene group. These NMR data suggest that the π -electrons in **polymer-2** and **model-2** are also delocalized along the aminopenta-2,4-dienylidene group.

IR spectra of the polymers and the model compounds showed absorptions due to $\nu(C=C)$ and $\nu(C=N)$ of the aminopenta-2,4-dienylidene group at approximately 1550 cm⁻¹ and 1440 cm⁻¹, respectively.

As shown in Figure 1, peaks ascribed to the terminal groups of the **polymer-1** are not observed in the ¹H NMR spectrum. However, the molecular weights of the polymer determined by the GPC measurement were not high ($M_n = 1760$ and $M_w = 6320$). The somewhat low molecular weights of **polymer-1** were presumably due to a strong interaction of the polymer with polystyrene gel in the GPC column. The molecular weight of **polymer-2** was not able to be determined by GPC due to poor solubility in the eluent. However, the reduced viscosity (η_{sp}/c) value of **polymer-2** was 0.25 dLg⁻¹ at the concentration of 0.06 g dL⁻¹ in DMSO at 30 °C, whose value was comparable to that of **polymer-1** ($\eta_{sp}/c = 0.20$ dLg⁻¹ in a 0.06 g dL⁻¹ DMSO solution at 30 °C).

Formation of an adduct between **polymer-1** and the metal ion was investigated by monitoring of electric conductivity of aqueous solutions of the polymer when the metal ion in limited amounts were added

**Figure 1.** ¹H NMR spectra of **polymer-1** and **model-1** in DMSO-*d*₆.

to the polymer solutions. Ag⁺ and K⁺ were selected as the metal ions since the two ions had a suitable size to be included into DA18C6.^{8,9} Figure 2 depicts electric conductivity (σ) changes of the aqueous solution of **polymer-1** by adding AgClO₄ or KClO₄ to the solutions. When the metal perchlorates were added to the polymer solutions, no precipitate was formed from the solutions. As shown in Figure 2a, the conductivities of the polymer solutions are slightly decreased by adding AgClO₄ to the equivalence point and increase in proportion to the amounts of AgClO₄ after the

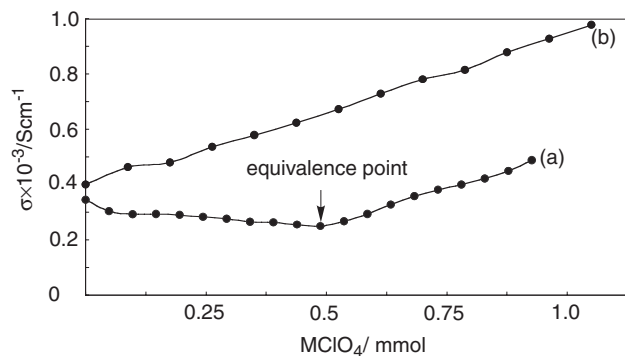


Figure 2. Conductivity changes of an aqueous solution of **polymer-1** (0.5 mmol/L) by addition of MClO_4 ($M = \text{Ag}$; (a), K ; (b)).

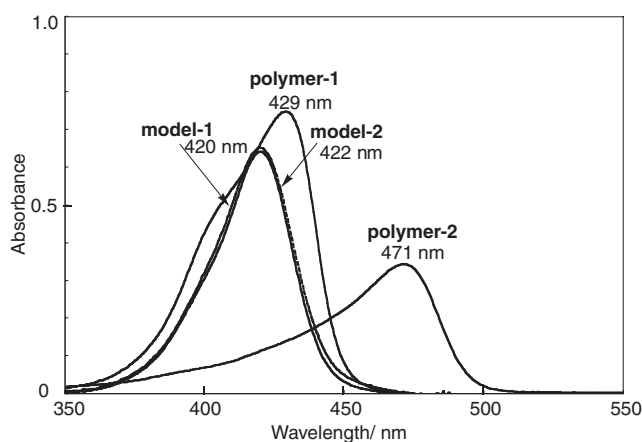


Figure 3. UV-vis spectra of **polymer-1**, **polymer-2**, **model-1**, and **model-2** in DMSO.

equivalence point. Whereas the conductivities of the **polymer-2** solutions increased in proportion to the amounts of AgClO_4 added. These data suggest that Ag^+ was included into DA18C6 in the polymer chain until the equivalence point. Whereas the electric conductivities of the **polymer-1** solution increase in proportion to the amounts of KClO_4 added, suggesting that K^+ is not included into DA18C6 in the polymer chain, as depicted in Figure 2b. It is known that diaza-crown ethers bearing neutral nitrogen atom classified as soft atoms tend to include transition metal ions classified as a soft ion rather than alkaline metal ions classified as a hard ion.^{8,9} Although the nitrogen atoms of DA18C6 of **polymer-1** have a positive charge, the difference of inclusion behavior between Ag^+ and K^+ seems to be scribed to a soft basic property of the nitrogen atoms.

Figure 3 depicts UV-vis spectra of **polymer-1**, **polymer-2**, **model-1**, and **model-2** in DMSO. The absorption data are summarized in Table I. **Model-1** and **model-2** show absorption maxima (λ_{max}) at essentially the same position. The λ_{max} of **polymer-1** appears at a wavelength slightly longer than that of **model-1**.

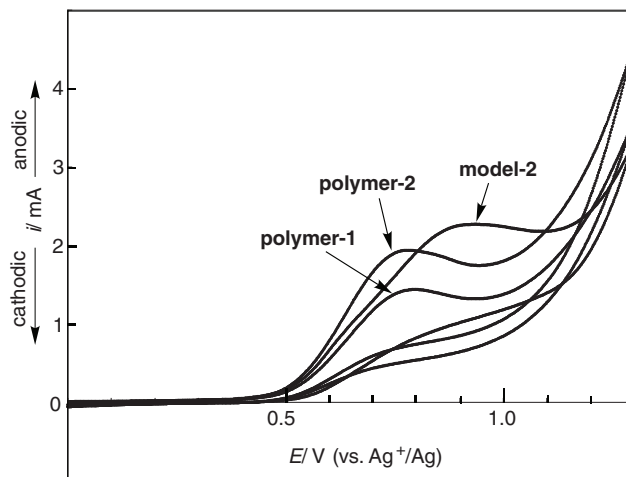


Figure 4. Cyclic voltammograms of **polymer-1**, **polymer-2**, and **model-2** in a DMSO solution of $[\text{Et}_4\text{N}]\text{BF}_4$ (0.1 M). The scan rate was 50 mVs^{-1} .

Whereas **polymer-2** shows λ_{max} at a wavelength considerably longer as compared to **model-2** and **polymer-1**, probably due to transfer of a positive charge on the iminium group between the aminopenta-2,4-dienylidene groups beyond the piperadinium ring. It has been reported that nonconjugated polymers such as *cis*-poly-1,4-isoprene cause bathochromic shift of an absorption peak by p-doping with iodine that leads generation of a positive charge on the double-bond site.^{10–12} For **polymer-1**, such a charge transfer between the aminopenta-2,4-dienylidene groups can not take place since the aminopenta-2,4-dienylidene groups are separated by the larger DA18C6 ring. The UV-vis spectrum of **polymer-1** in DMSO solution was essentially the same to that in the presence of Ag^+ , indicating that the inclusion of Ag^+ into DA18C6 brought about no effect on the π -conjugation system of the aminopenta-2,4-dienylidene group.

The polymers and model compounds were electrochemically active in a DMSO solution of $[\text{Et}_4\text{N}]\text{BF}_4$ (0.1 M). Cyclic voltammetry (CV) measurements suggested that the polymers underwent an electrochemical oxidation in the DMSO solution including $[\text{Et}_4\text{N}]\text{BF}_4$. The CV data are summarized in Table I. The cyclic voltammogram of **polymer-1** was resemble to that of **model-1**. Whereas the oxidation potential of **polymer-2** is lower than that of **model-2**, which corresponds to the observation of λ_{max} of **polymer-2** at a longer wavelength as compared to **model-2**. As shown in Figure 4, the corresponding reduction peak does not appear in the cyclic voltammograms, probably due to formation of a stable adduct between iminium cations of the polymers and model compounds and BF_4^- to prevent electrochemical reduction (p-undoping).

In conclusion, the reactions of **1** with DA18C6 and piperadine gave **polymer-1** and **polymer-2** that were

consisted of the 5-alkane-penta-2,4-dienylideneammonium chloride unit. The corresponding model compounds were also obtained. The ^1H NMR spectra suggested that the π -electrons of the penta-2,4-dienylideneammonium group of the polymers and model compounds were delocalized. The electric conductivity measurements indicated that the DA18C6 of **polymer-1** was able to include Ag^+ in solution. The polymers and the model compounds are electrochemically active in solutions, as revealed by cyclic voltammetry.

Electronic Supporting Information Available. General, Synthesis and Reference. These materials are available *via* the Internet at <http://www.spsj.or.jp/c5/pj/pj.htm>.

REFERENCES

1. U. Tunca and Y. Yabci, *Prog. Polym. Sci.*, **19**, 233 (1994).
2. B. Fabre and J. Simonet, *Coord. Chem. Rev.*, **178–180**, 1211 (1998).
3. J. M. G. Cowie, *Polym. Int.*, **47**, 20 (1998).
4. D. Spiro, S. D. Alexandratosa, and C. L. Stine, *React. Funct. Polym.*, **60**, 3 (2004).
5. W. M. Feigenbaum and R. H. Michel, *J. Polym. Sci., A-1*, **9**, 817 (1971).
6. S. H. Chan, W. T. Wong, and W. K. Chan, *Chem. Mater.*, **13**, 4635 (2001).
7. I. Yamaguchi, Y. Gobara, and M. Sato, *J. Polym. Sci., Part A: Polym. Chem.*, **45**, 1507 (2007).
8. R. M. Izatt, L. D. Hansen, D. J. Eatough, J. S. Bradshaw, and J. J. Christensen, "Metal-Ligand Interactions in Organic Chemistry and Biochemistry, Part 1", Reidel, Dordrecht, 1977, p337.
9. F. Vögtle and E. Weber, "The Chemistry of the Ether Linkage, Suppl. E, Part 1", Wiley, Chichester, 1981, p59.
10. M. Thakur, *Macromolecules*, **21**, 661 (1988).
11. M. Thakur and B. S. Elman, *J. Chem. Phys.*, **90**, 2042 (1989).
12. M. Thakur, R. Swamy, and J. Titus, *Macromolecules*, **37**, 2677 (2004).