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Syntheses and Electronic Behaviors of Novel Networked Alternating Organic Moiety-Ruthenium Hybrid Copolymers

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The reaction of ruthenium chloride with organic dithiols gave ruthenium-organic moiety hybrid copolymers. ESR and XPS spectral examinations showed that an electron transfer from the organic moiety to the ruthenium atom took place.

Keywords ruthenium, hybrid copolymer, electron transfer

Introduction

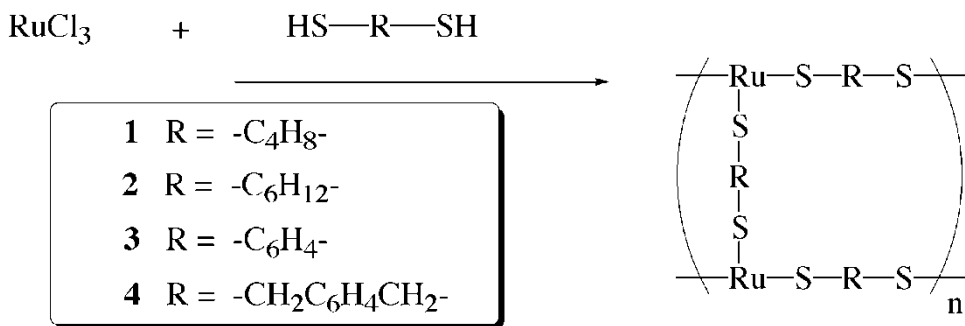
Recently, advanced technology has provided highly functional materials, and a hybridization technique has been expected to supply such novel functions (1, 2). Coordinated organic-inorganic composite materials have thus been developed (3–7), however, a coordination bond in the metal complexes will not have an electronic interaction enough to exhibit the original characteristic of metal because an electron supply to metal from a ligand is considered to be limited to a coordination bond.

We considered that alternating organic-inorganic composite materials with covalent bonding will provide new types of hybrid materials. In previous papers on networked hybrid copolymers with covalent organic-metal units, an electron transfer was shown to take place from the organic moieties to such metal atoms as Ti, Zr, Ta, Y, and Yb, and further, an electron transfer in copolymers depended on the kinds of organic moieties, where the higher degree of the electron transfer was observed in the case using an aryl group as the organic moiety (8–12). In this work, we wish to report the syntheses and electronic properties of alternating hybrid copolymers with organic-ruthenium units (Scheme 1).

Ruthenium is known to have high redox ability with several valences. Therefore, an organic-ruthenium hybrid copolymer is expected to promote the electron transfer ability

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Scheme 1. Syntheses of hybrid copolymers.

between the organic group and ruthenium, and the charge-separation state may be stabilized in the composite framework.

Experimental

Reagents

Commercially available ruthenium chloride, 1,4-butanedithiol, 1,6-hexanedithiol, 1,4-benzenedithiol, and 1,4-benzenedimethanedithiol were used.

Syntheses of Copolymers

A solution of ruthenium chloride (0.6 mmol) in 20 mL of anhydrous ethanol was added into a solution of 1,4-butanedithiol (0.9 mmol) in 20 mL of anhydrous ethanol, and the mixture was stirred with the use of alumina as a base in a cylindrical filter at 80°C for 12 h. The precipitate formed was collected, washed with anhydrous ethanol using a Soxhlet extractor, and dried by heating under vacuum to obtain copolymer 1. Similar treatments of ruthenium chloride with 1,6-hexanedithiol, 1,4-benzenedithiol, and 1,4-benzenedimethanedithiol gave copolymers 2, 3, and 4, respectively.

Apparatus

Elemental analyses were performed for C using a Yanaco MT-6, for S using a Yanaco YS-10, and for Ru by inductively coupled plasma atomic emission spectrometry (ICP-AES)

Table 1
Elemental analyses of copolymers

| Copolymer | Found (%) | | | Color of copolymer |
|-----------|-----------|-------|-------|--------------------|
| | Ru | C | S | |
| 1 | 23.08 | 21.41 | 26.91 | Brown |
| 2 | 28.36 | 28.84 | 22.48 | Brown |
| 3 | 21.26 | 27.78 | 23.48 | Dark brown |
| 4 | 16.46 | 37.46 | 24.47 | Gray |

Table 2
IR spectra of copolymers

| Copolymer | Frequency (cm^{-1}) |
|-----------|--|
| 1 | 2926 (C-H), 663 (C-S) |
| 2 | 2941 (C-H), 655 (C-S) |
| 3 | 1581 (C_6H_4), 677 (C-S) |
| 4 | 1564 (C_6H_4), 668 (C-S) |

using a Shimadzu ICPS-7500. Transmission electron microscopy (TEM) measurements were done using a Jeol TEM-3010 microscope. UV-VIS spectra were measured using a Hitachi U-4000 spectrometer. Electron spin resonance (ESR) spectra were taken using a Jeol JES-TE200 spectrometer. X-ray photoelectron spectra (XPS) measurements were carried out using a Shimadzu ESCA-850 spectrometer.

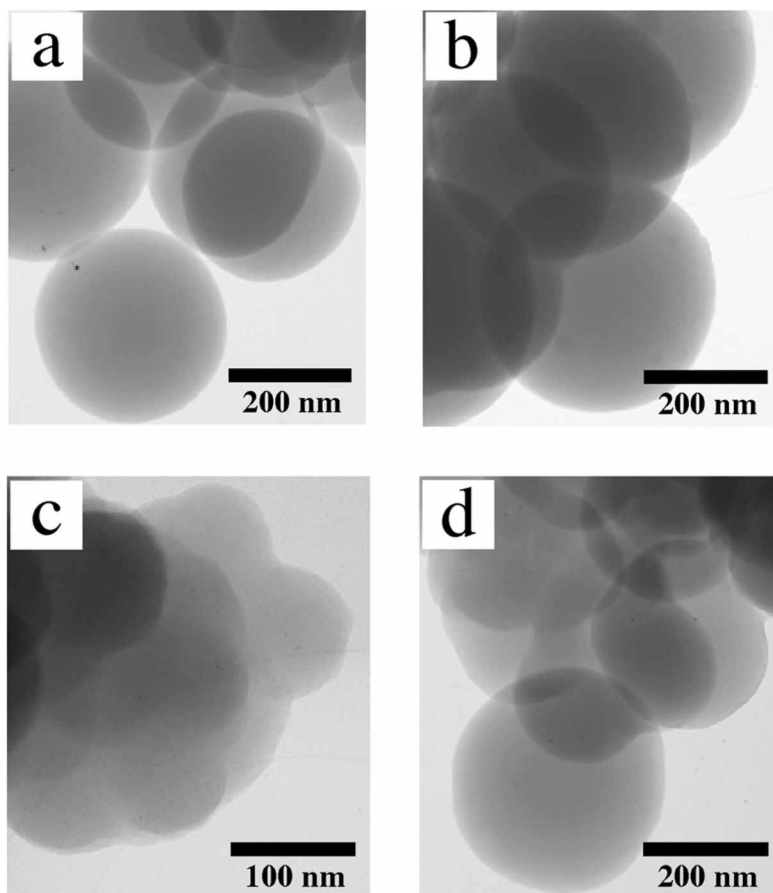


Figure 1. TEM images of hybrid copolymers. (a) Copolymer 1 ($-\text{C}_4\text{H}_8-$ system), (b) copolymer 2 ($-\text{C}_6\text{H}_{12}-$ system), (c) Copolymer 3 ($-\text{C}_6\text{H}_4-$ system), (d) Copolymer 4 ($-\text{CH}_2\text{C}_6\text{H}_4\text{CH}_2-$ system). Measurement condition: AcV: 300 KV.

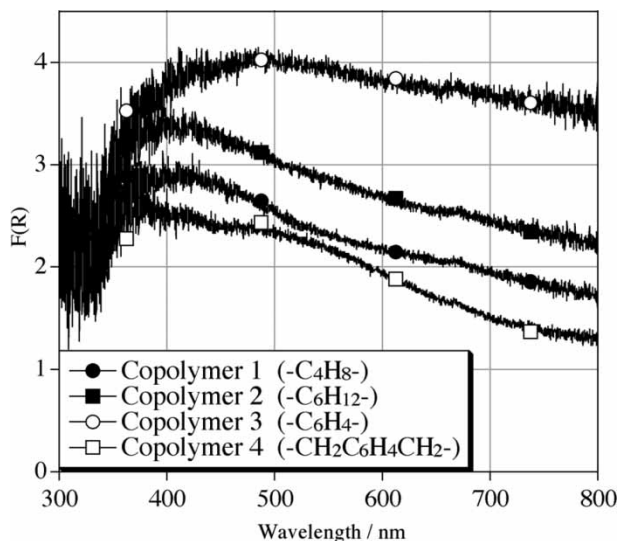


Figure 2. UV-vis spectra of hybrid copolymers. (Spectra were taken by Hitachi U-4000 with the diffusion reflecting method.) $F(R)$ is a coefficient of diffusion reflecting, which is calculated by the following equation: $F(R) = \{1 - R(\lambda)\}^2 / 2R(\lambda)$, $R(\lambda)$: reflection rate of sample.

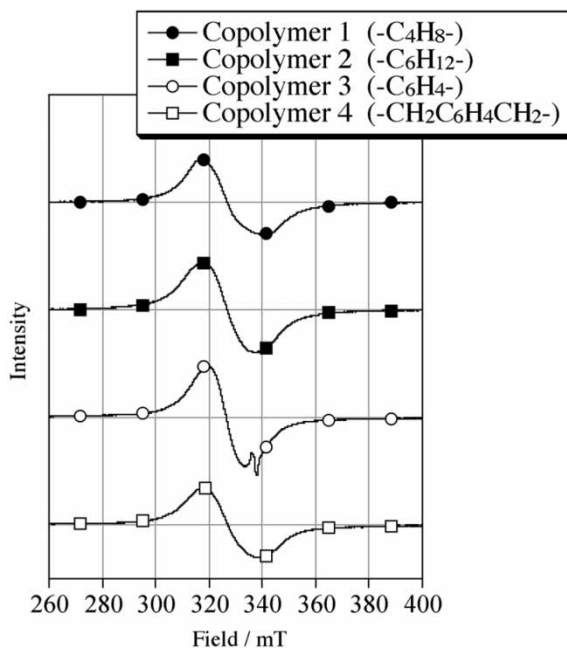


Figure 3. ESR spectra of hybrid copolymers. Spectra were taken by using 5 mg of sample. Measurement conditions: C. Field; 337.00 mT, power; 1.00 mW, sweep width; 100 mT, modulation width; 0.5 mT, time constant; 0.1 s, temp; room temp.

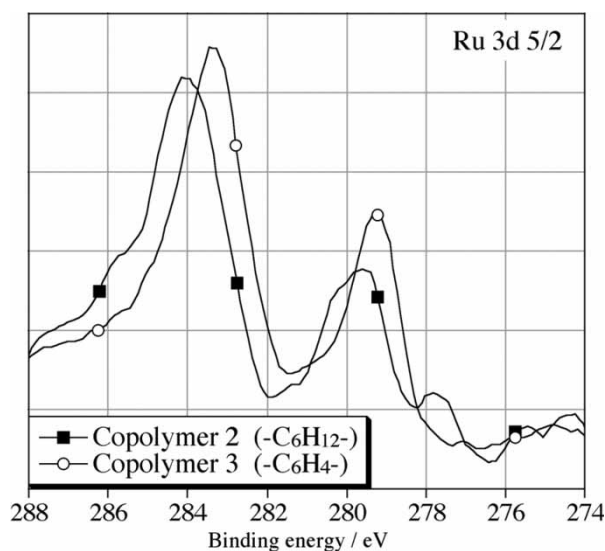


Figure 4. XPS spectra of hybrid copolymers. Non-monochromatic Mg-K α (1253.6 eV) radiation was sourced from an X-ray gun operated at 8 kV and 30 mA.

Results and Discussion

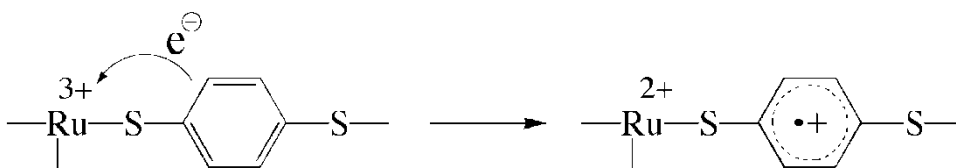
The reaction of ruthenium chloride with organic dithiols proceeded smoothly to give the corresponding hybrid copolymers. The elemental analyses of the copolymers were carried out (Table 1). The percentages of organic moieties included in the copolymers were calculated from the observed carbon contents to be 84% for 1, 86% for 2, 80% for 3, and 92% for 4, respectively. The IR spectra of the copolymers (Table 2) showed frequencies due to organic groups and C–S bond. These results indicate that ruthenium-organic units were involved in the copolymers.

To see the sizes and forms of the copolymers, their TEM images were taken and shown in Figure 1. The forms of copolymers 1, 2 and 4 were found to be spherical particles with diameters of ca. 250 nm, and copolymer 3 had a spherical particle with diameters of ca. 100 nm.

Interestingly, the colors of the copolymers were found to vary by changing the organic moieties; namely, brown for 1 and 2, dark brown for 3, and gray for 4. Thus, their UV-Vis spectra were taken (Figure 2), indicating that strong absorption bands were observed over the entire range of wavelength with high intensities for all copolymers.

The ESR spectra of the copolymers were taken (Figure 3). All copolymers showed a peak at $g = \text{ca. } 2.07$ which is ascribed to a free electron on the trivalent ruthenium atom and a rather small peak area was observed for 3. It is noteworthy that copolymer 3 showed another peak at $g = \text{ca. } 2.003$, which is ascribed to a free electron formed on the organic moiety. Our understanding is that, as reported in the previous works (8–12), an electron transfer took place between an organic group and a metal, and the electronic states on the Ru atom in the copolymers are considered to vary.

The XPS measurements of copolymers 2 and 3 were thus performed to investigate the electronic state of the ruthenium atom in the copolymers (Figure 4). A peak due to a 3d 5/2 orbital of ruthenium atom in copolymer 2 was observed at 279.69 eV, whereas copolymer 3 showed a peak at ca 279.22 eV, indicating an increase of electron density



Scheme 2. Plausible of electron transfer.

for 3. One possible explanation is that the reduction of ruthenium atom through the electron transfer in 3 took place, as shown in Scheme 2.

We believe that such an electron transfer will be achieved by various combinations of the organic moieties and the metals with different electronegativities, and our findings will provide many useful materials, for example, optical, magnetic, and electronic devices.

References

- Burch, R. (1990) Oxidation-reductions for preparation of $[\text{Ti}(\text{OC}_6\text{H}_4\text{O}_2)]_n$ and related metalloquinone polymers: Hybrid inorganic-organic metal oxides. *Chem. Mater.*, 2: 633–635.
- Fukuoka, A., Sakamoto, Y., Guan, S., Inagaki, S., Sugimoto, N., Fukushima, Y., Hirahara, K., Iijima, S., and Ichikawa, M. (2001) Novel templating synthesis of necklace-shaped mono- and bimetallic nanowires in hybrid organic-inorganic mesoporous material. *J. Am. Chem. Soc.*, 123: 3373–3374.
- Rauchfuss, T.B., Damian, P., Rodgers, S., and Wilson, S.R. (1986) Synthesis of a new type of metal dithiolene complex via an induced reaction of acetylenes with a ruthenium sulfide. *J. Am. Chem. Soc.*, 108: 3114–3115.
- Motoyama, Y., Tanaka, M., and Mikami, K. (1997) Synthesis, structure, and high catalytic activity of cationic alkoxytitanium(IV) complexes in the Diels-Alder reaction. *Inorg. Chem. Acta*, 256: 161–163.
- Hagrman, D. and Zubieta, J. (1998) Organic-inorganic composite oxide phase: one-dimensional molybdenum oxide chains entrained within a three-dimensional coordination complex cationic framework in $[\{\text{Cu}_2(\text{triazolate})_2(\text{H}_2\text{O})_2\}\text{Mo}_4\text{O}_{13}]$. *J. Chem. Soc., Chem. Commun.*, 2005–2006.
- Kepert, C.J. and Rosseinsky, M.J. (1998) A porous chiral framework of coordinated 135-benzenetricarboxylate: quadruple interpenetration of the (10, 3)-A network. *J. Chem. Soc., Chem. Commun.*, 31–32.
- Jung, O. and Pierpont, G.C. (1994) Photomechanical polymers. Synthesis and characterization of a polymeric pyrazine-bridged cobalt semiquinone-catecholate complex. *J. Am. Chem. Soc.*, 116: 2229–2230.
- Yoshihara, M., Okada, A., and Matsui, H. (2001) Syntheses of novel networked alternative titanium-organic hybrid copolymers. *J. Mater. Sci. Lett.*, 20: 1151–1153.
- Yoshihara, M., Takeuchi, T., Matsui, H., and Ito, S. (2001) Synthesis of novel particles with alternative organic-zirconium hybrid structures. *J. Jpn Soc. Colour Mater.*, 74: 229–231.
- Yoshihara, M., Kudo, R., and Matsui, H. (2002) Syntheses of novel networked hybrid copolymers with alternative tantalum-organic moieties. *J. Chem. Soc. Jpn.*, 3: 371–375.
- Yoshihara, M., Oie, H., Okada, A., Matsui, H., and Ohshiro, S. (2002) Synthesis of yttrium-organic hybrid networks. *Macromolecules*, 35: 2435–2436.
- Yoshihara, M., Shino, T., Matsui, H., and Ohshiro, S. (2002) Syntheses of novel networked alternative ytterbium-organic moieties hybrid copolymers. *J. Mater. Sci. Lett.*, 21: 1051–1053.