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Synthesis and Electronic Behavior of a Ternary, Networked Alternating Cerium-Phenylene-Holmium Hybrid Copolymer

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Hybrid copolymers having cerium-phenylene-holmium frameworks were prepared by reacting 4-hydroxythiophenol with cerium ethoxymethoxide, holmium chloride. The UV-VIS and ESR spectral analyses indicate that an electron transfer takes place from a phenylene group to the cerium atom via the holmium atom in the framework.

Keywords cerium, holmium, alternating hybrid copolymer, electron transfer

Introduction

New types of materials having magnetic, optical, and electronic functions have been expected to be practically realized, and the hybridization technique has been expected to provide such highly functionalized materials (1–8). We have recently reported the syntheses of networked organic-metal hybrid copolymers with covalent bond by reacting such metal alkoxides as titanium isopropoxide (9), zirconium 2-methyl-2-buthoxide (10), and yttrium isopropoxide (11) with organic diols. An electron transfer was shown to take place from the organic aryl groups to the metal atoms in the networked frameworks.

Here, we have assumed that the ability/or degree of the electron transfer will be altered when an aryl group is sandwiched with two different kinds of metal atoms. In this work, we wish to report the synthesis of a novel ternary hybrid copolymer with an alternating cerium-phenylene-holmium unit linked by covalent bond. The cerium atom is known to have a high redox ability, while a holmium atom shows a high magnetic behavior due to 10 electrons in its 4f orbital. Therefore, it is expected that, the ability and/or degree of the electron transfer may be affected by the combination of the cerium and holmium atoms.

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Experimental

Reagents

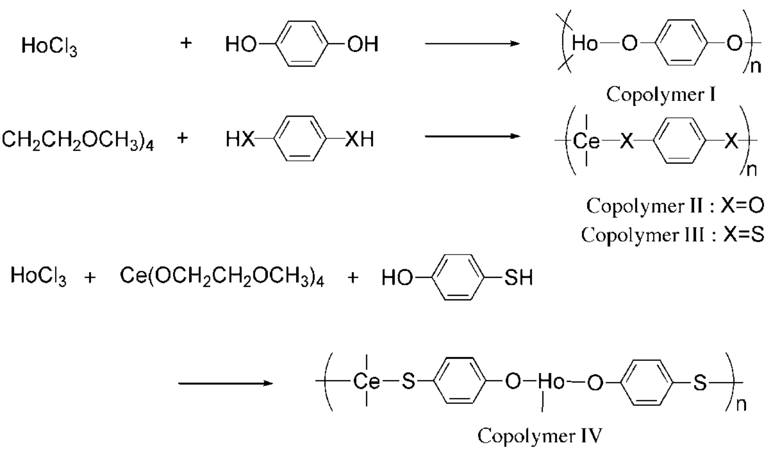
Commercially available cerium ethoxymethoxide and holmium chloride were used. Other reagents and solvents were purified by standard procedures.

Syntheses of the Copolymers

In order to determine the procedure for synthesizing the ternary hybrid copolymer IV, the reactivities of holmium chloride and/or cerium ethoxymethoxide with 1,4-hydroquinone and/or 1,4-benzeneithiol were examined (Scheme 1). Holmium chloride (0.6 mmol) was found to react with 1,4-hydroquinone (0.9 mmol) in anhydrous ethanol (10 ml) in the presence of a proton sponge (2.4 mmol), N,N,N′,N′-tetramethyl-1,8-naphtalenediamine, at 80° for 3 h to give the binary copolymer I (brown-colored), while no reaction took place with 1,4-benzenedithiol. On the other hand, it was found that cerium ethoxymethoxide (0.45 mmol) reacted with both 1,4-hydroquinone (0.9 mmol) and 1,4-benzenedithiol (0.9 mmol) in anhydrous THF (10 ml) at 80° for 3 h to give the corresponding binary copolymers II (brown-colored) and III (flesh-colored), respectively. Thus, the ternary hybrid copolymer IV was synthesized in the following way. A solution of proton-sponge (2.4 mmol) in 10 ml of anhydrous chloroform was added dropwise into a solution of 4-hydroxythiophenol (2.4 mmol) and holmium chloride (0.8 mmol) in 10 ml of anhydrous chloroform, and the mixture was stirred at 80° for 3 h. Then, into the reaction mixture obtained was added a solution of cerium ethoxymethoxide (0.6 mmol) in 10 ml of anhydrous chloroform, dropwise, and the mixture was stirred at 80° for 3 h to give the copolymer IV (brown-colored). The precipitates formed above were collected, washed with anhydrous ethanol by using a Soxhlet extractor, and dried by heating under vacuum to obtain the copolymers.

Apparatus

UV-VIS spectra were taken by using a Hitachi U-4000 unit, ESR spectra were taken by using a JEOL TE-200 instrument, XPS spectra were taken by using a Shimadzu



Scheme 1. Syntheses of copolymers.

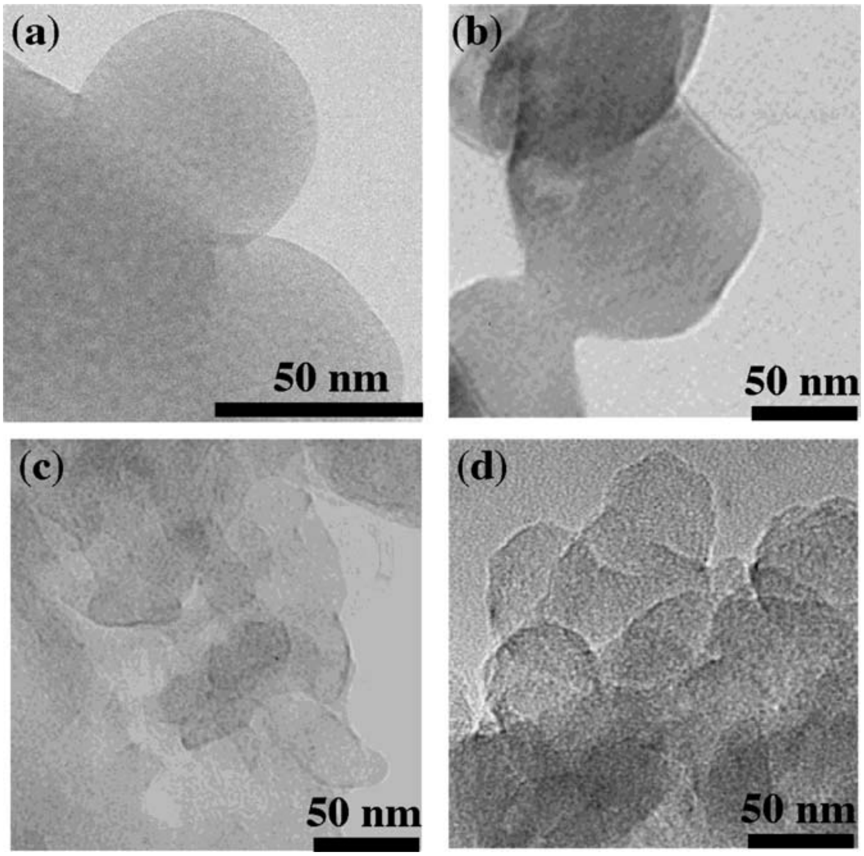


Figure 1. TEM images of the hybrid copolymers. (a) copolymer I, (b) copolymer II, (c) copolymer III, (d) copolymer IV, Measurement condition: AcV, 300 kV; magn, 300 K.

ESCA-850, and TEM images were taken by using a JEOL JEM-3010 instrument. Carbon and hydrogen analyses were carried out with a Yanaco MT-6 CHN analysis unit. Whereas, sulfur analyses were carried out with a Yanaco YS-10 apparatus. Cerium and holmium analyses were carried out with a Rigaku RIX 2000 apparatus. FT-IR spectra were taken by using a Perkin-Elmer FT-IR 1760-X.

Results and Discussion

The elemental analyses of the copolymers showed that the observed values of the carbon and/or sulfur atoms were lower than the calculated values[1], which is considered to be due to the incomplete combustion of the samples during the elemental analyses, because partly black-colored residues were yielded after elemental analysis operations, and the SEM-EDX

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[1] I: Anal. found Ho 43.01%, C 25.52%: Anal. calcd. Ho 50.43%, C 33.05%. II: Anal. found Ce 39.44%, C 18.24%: Anal. calcd. Ce 39.32%, C 40.45%. III: Anal. found Ce 37.30%, C 15.39 %, S 15.38%.: Anal. calcd. Ce 33.32%, C 34.27%, S 30.55%. IV: Anal. found Ce 17.79%, Ho 24.64 %, C 28.18%, S 11.37%.: Anal. calcd. Ce 16.39%, Ho 25.67 %, C 33.65%, S 14.97%.

measurements of the residues were thus performed to reveal the presence of carbon and sulfur atoms. Thus, the accurate contents of the metal-phenylene units in the copolymers were unable to be determined. The contents of metals in the copolymers were determined by XRF analyses (see footnote 1) and the value of the ratio of the holmium content against the cerium content in the copolymer IV was determined to be 1.18. As the value of the ideal ratio is 1.5, the content of an ideal ternary unit in IV was calculated to be 78.7%. The IR spectra of the copolymer IV showed peaks due to the phenylene group at $820\,\mathrm{cm}^{-1}$ ($\upsilon_{C=C}$) and $1508\,\mathrm{cm}^{-1}$ ($\delta_{C=C}$), and the sulfide group at $643\,\mathrm{cm}^{-1}$ (υ_{C-S}). These results suggest that the greater part of the copolymer IV consists of a nearly alternative ternary hybrid structure.

In order to see the sizes and forms of the copolymers, their TEM images were taken and shown in Figure 1, indicating that their forms were amorphous particles with the diameter of ca. 20–200 nm. Another interesting finding is that an electron beam from an electron microscope penetrated through the particles, and the overlapped parts of the particles become dim, suggesting that the particles are half-transparent, as reported in a previous paper (10).

Interestingly, the colors of the copolymers were found to vary by changing the metals, and their UV-VIS spectra were thus taken (Figure 2), indicating that the absorption bands of the ternary hybrid copolymer IV was observed over the whole wavelengths with the highest intensity in comparison with other binary copolymers I, II, and III. Our opinion is that an electron transfer takes place from the phenylene group to either the cerium atom or the holmium atom to produce the cation radical on the phenylene group. In order to verify their cause, the ESR spectra of the copolymers were taken. As shown in Figure 3, a peak at 337 mT (g = 2.0032) due to an organic free electron was observed for every copolymer, suggesting that the electron transfer takes place, as expected

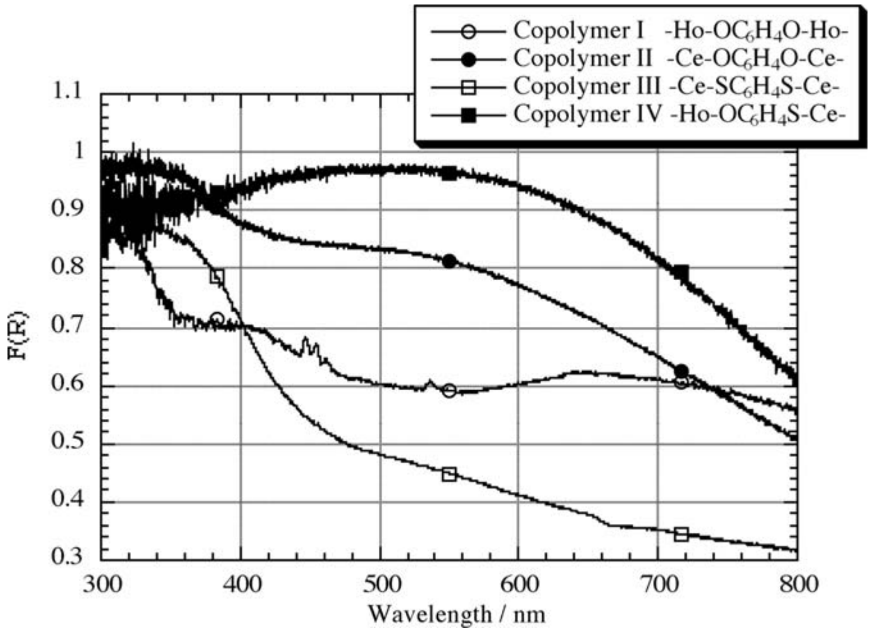


Figure 2. UV-VIS spectra of the hybrid copolymers. The spectra were taken by using the diffusion reflecting method. F(R) is a coefficient of diffusion reflecting which is calculated by the following equation: $F(R) = \{1 - R(1)\}^2/2R(1)$, R(1): reflection rate of the sample.

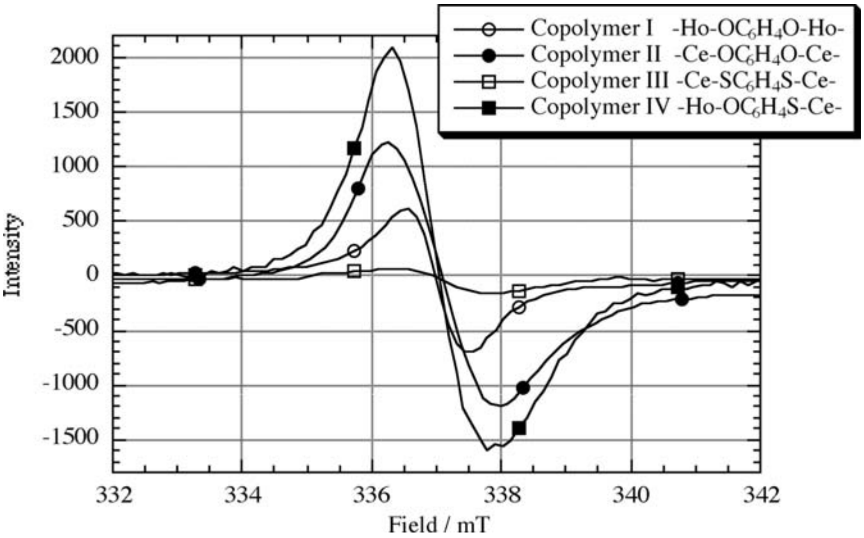


Figure 3. ESR spectra of the hybrid copolymers. The spectra were taken by using 30 mg of sample. Measurement condition: C.field, 337.00 mT; power, 1.00 mW; sweep width, 10 mT; modulation width, 0.5 mT; time constant, 0.1 s; temp., room temperature.

above. It is noteworthy that the peak intensity of the ternary copolymer IV was higher than those of the binary copolymers I, II, and III.

In order to examine the electronic state on metals, the XPS measurements of the copolymers were performed (Figure 4). A peak at 883.3 eV, due to the 3d 5/2 orbital of

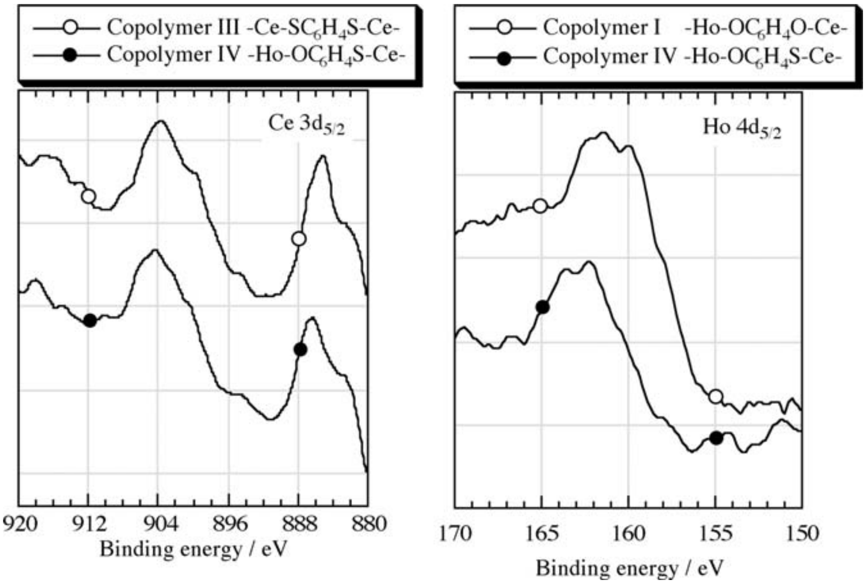
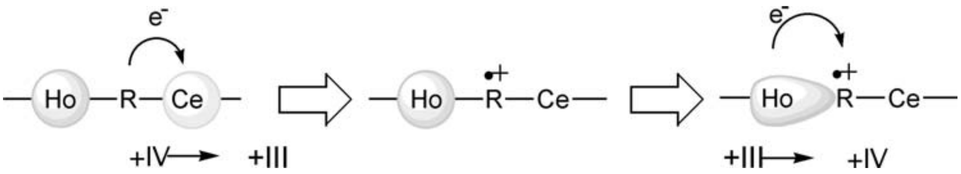


Figure 4. X-ray photoelectron spectrometer of the hybrid copolymers. Non-monochromatic Mg-Ka(1253.6 eV) radiation was sourced from an X-ray gun operated at 8 kV and 30 mA.



Scheme 2. Plausible mechanism of electron transfer.

the cerium atom in III was found to shift to 882.2 eV in IV, indicating that the electron density of the cerium atom in IV was higher than that in III. On the other hand, peaks due to the 4d 5/2 orbital of the holmium atom in I and IV were observed at 159.9 eV and 162.1 eV, respectively, indicating that the electron density on the holmium atom in IV was lower than that in I. One possible explanation is that the electron transfer takes place from the phenylene group to the redox-active cerium atom and is accelerated by the adjacent holmium atom through possibly 4f electron assistance (Scheme 2).

Conclusions

In this work, we described the synthesis and property of a novel ternary, alternating cerium-phenylene-holmium hybrid copolymer with covalent bonding. UV-VIS and ESR spectra of the copolymer revealed that the electron transfer from the phenylene group to the cerium atom via the holmium atom took place in the alternating framework.

We believe that such a multi-stage electron transfer will be achieved by various combinations of organic moieties and different kinds of metal, which will provide many useful materials, for example, optical, magnetic, and electronic devices.

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