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

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Hybrid copolymers having neodymium-organic moiety frameworks were prepared by reacting neodymium isopropoxide with several organic diols. The colors of the copolymers varied by changing the organic moieties, and UV-VIS and ESR spectral analyses indicate that an electron transfer takes place from the organic moiety to the neodymium atom in the framework.

Keywords neodymium, hybrid copolymer, electron transfer

Introduction

Organic-inorganic hybrid materials have attracted much attention because the combination is expected to exhibit unique features (1–3), and many works on the syntheses of the coordinated metal-complex polymers have been reported (4–6). The systems of redox-active metal centers linked by a π-conjugated bidentate ligand have been expected to cause an electronic interaction between organic ligands and metal atoms. For example, Matsuda et al. reported the synthesis of binuclear molybdenum (V) porphyrins bridged by hydroquinone, and a reduction from Mo^{V} to Mo^{IV} by an intramolecular electron transfer from the bridging ligand to two Mo^{V} centers was shown to occur. An intramolecular electron transfer has thus attracted attention from viewpoints of molecular switches and molecular wires (7). However, the electronic motion of a coordinated metal-complex polymer is considered to be limited at a coordinated bond by an electron release from the ligand to the metal center. On the other hand, it is expected that an electronic motion in a covalent-bonded organic-inorganic polymer will be expanded beyond the covalent bond, possibly to the whole framework.

We have recently reported the electronic properties of covalent-bonded alternating metal-organic moiety hybrid copolymers having networked frameworks, in which an

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electron transfer took place from the aryl moieties to the metal atoms in the net-worked frameworks (8–10).

In this paper, we describe the syntheses of hybrid copolymers having alternating neodymium-organic moiety frameworks by the reaction of neodymium isopropoxide with several organic diols (Scheme 1). Neodymium(III) has an odd spin in its 4f orbital, and neodymium compounds are widely used as optical, electric, and/or magnetic devices, e.g., a permanent magnet for alloy. Therefore, neodymium-organic moiety hybrid copolymers are expected to show unique electronic and/or magnetic properties, the degree of which may be controlled by changing the organic moieties in the alternative framework.

Experimental

Reagents

Commercially available neodymium isopropoxide was used. Other reagents and solvents were purified by the standard procedures.

Reactions of Neodymium Isopropoxide with Organic Diols

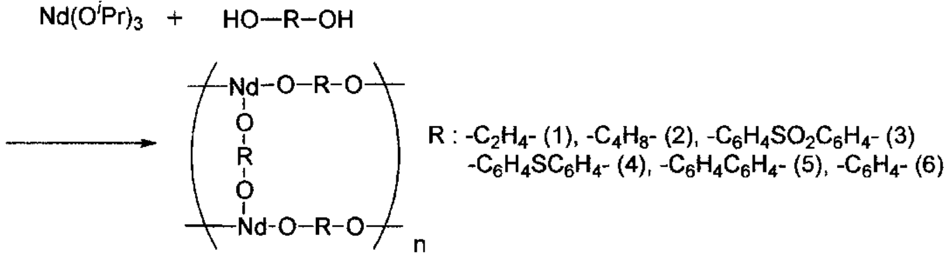
A solution of 0.75 mmol of organic diol in 10 cm^3 of anhydrous THF was added dropwise into a solution of 0.5 mmol of neodymium isopropoxide in 10 cm^3 of anhydrous THF, and the mixture was refluxed for 6 h. The precipitate was collected, washed with anhydrous THF by a Soxhlet extractor, and dried with heating under a vacuum.

Apparatus

UV-VIS spectra of the copolymers were taken using a Hitachi U-4000 spectrometer. ESR spectra were taken using a JEOL TE-200 spectrometer. TEM images were taken using a JEOL JEM-3010 unit. Carbon and hydrogen analyses were performed with a Yanako MT-6 CHN corder. Sulfur analyses were performed with a Yanako YS-10 unit. Neodymium analyses were performed with a Shimadzu ICPS-1000IV apparatus. FT-IR spectra were taken using a Perkin-Elmer FT-IR 1760-X spectrometer.

Results and Discussion

The reaction of neodymium isopropoxide with organic diols proceeded smoothly to give the precipitates. ICP and elemental analyses revealed that the carbon and/or sulfur contents of copolymers 1–6 were rather small in comparison with the calculated values



Scheme 1. Reactions of neodymium isopropoxide with diols.

Table 1
ICP and elemental analyses of the copolymers

Copolymer	R	% (Found/calcd.) Nd	C	H	S	Neodymium unit composition (%)[a]
1	$-C_2H_4-$	44.1/ 61.6	10.5/ 15.4	3.86/ 2.58	—	71.6
2	$-C_4H_8-$	44.5/ 52.2	12.0/ 26.1	3.05/ 4.38	—	85.2
3	$-C_6H_4SO_2C_6H_4-$	27.3/ 27.9	36.3/ 41.9	3.71/ 2.34	7.37/ 9.31	97.8
4	$-C_6H_4SC_6H_4-$	27.6/ 30.8	32.9/ 46.1	3.15/ 2.58	4.25/ 10.3	89.6
5	$-C_6H_4C_6H_4-$	30.0/ 34.3	39.5/ 51.4	3.07/ 2.88	—	87.5
6	$-C_6H_4-$	40.1/ 47.1	27.9/ 35.3	3.15/ 1.97	—	85.8

[a] Calculated by neodymium contents.

(Table 1). This may be caused by the incomplete combustion of the samples during the elemental analysis treatments, because partly black-colored residues were yielded after the elemental analysis operations. The SEM-EDX measurements of the residues were thus performed to show the presences of the carbon and/or sulfur atoms. The accurate ratios of metal against organic moiety in the copolymers were unable to be determined, however, the neodymium units involved in copolymers 1~6 were calculated to be 72~98%. The IR spectra of copolymers 3~6 were found to show frequencies due to the phenylene group at 1541–1599 cm^{-1}, and peaks due to the alkyl group were shown for copolymers 1 and 2 (Table 2). These results suggested that the neodymium-organic moiety units are involved in the copolymers.

In order to see the sizes and forms of the copolymers, the TEM images of the copolymers were taken (Figure 1), indicating that the forms of the particles differed with the

Table 2
IR spectra of the copolymers

Copolymer	R	Wave number (cm^{-1})
1	$-C_2H_4-$	2950 cm^{-1}, 2839 cm^{-1}($-CH_2-$)
2	$-C_2H_8-$	2940 cm^{-1}, 2873 cm^{-1}($-CH_2-$)
3	$-C_6H_4SO_2C_6H_4-$	1579 cm^{-1}, 1491 cm^{-1} ($-C_6H_4-$), 1139 cm^{-1}, 1291 cm^{-1} ($-SO_2-$)
4	$-C_6H_4SC_6H_4-$	1581 cm^{-1}, 1484 cm^{-1} ($-C_6H_4-$), 829 cm^{-1}, 669 cm^{-1} ($-C-S-$)
5	$-C_6H_4C_6H_4-$	1599 cm^{-1}, 1491 cm^{-1} ($-C_6H_4-$)
6	$-C_6H_4-$	1541 cm^{-1}, 1500 cm^{-1} ($-C_6H_4-$)

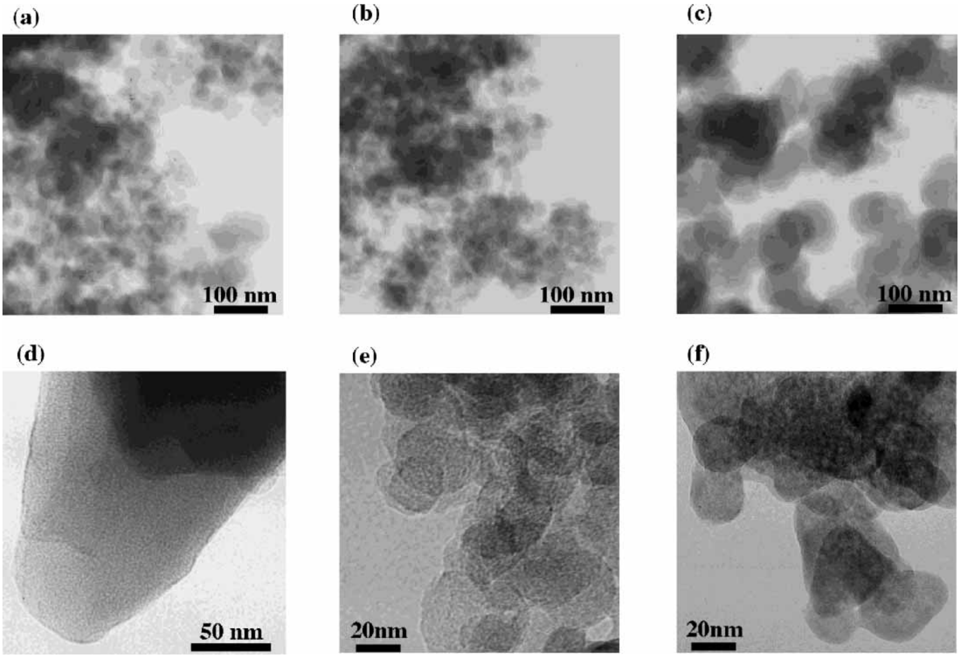


Figure 1. TEM images of the copolymers: (a) Copolymer 1 ($R = -C_2H_4-$), (b) Copolymer 2 ($R = -C_4H_8-$), (c) Copolymer 3 ($R = -C_6H_4SO_2C_6H_4-$), (d) Copolymer 4 ($R = -C_6H_4SC_6H_4-$), (e) Copolymer 5 ($R = -C_6H_4C_6H_4-$), (f) Copolymer 6 ($R = -C_6H_4-$). The measurement condition: AcV 300 kV.

organic moieties; namely, a spherical form with diameters of ca. 100 nm for copolymer 3, an ultra-fine particle with diameters of ca. 30–40 nm for copolymers 1, 2, 5, and 6, and a sheet form for copolymer 4. In addition, TEM electron beam was shown to penetrate through the particles of the copolymers, and the overlapped parts of the particles become dim, suggesting that the particles are half-transparent. This means that the particle has low density or hollow parts.

The colors of the hybrid copolymers were found to vary with organic moieties, and their UV-VIS spectra were thus taken (Figure 2). Copolymers 1($-C_2H_4-$ system) and 2 ($-C_4H_8-$ system) showed characteristic absorption bands due to Nd_2O_3, and copolymers 3 ($-C_6H_4SO_2C_6H_4-$ system) and 4 ($-C_6H_4SC_6H_4-$ system) showed absorption bands in longer wavelengths together with the bands due to Nd_2O_3. The formation of Nd_2O_3 is considered to be due to a reaction with a small amount of water contained in the solvent during either the reaction or the after treatment. On the other hand, the absorption bands over the whole wavelengths were observed for copolymers 5 ($-C_6H_4C_6H_4-$ system) and 6 ($-C_6H_4-$ system), and the intensities were in the order of $6 > 5 > 4 > 3 \approx 2 \approx 1$. Our opinion is that an electron transfer from the organic moiety to the neodymium atom in the framework will take place (Scheme 2).

In order to verify the electron transfer process in the framework, the ESR spectra of the copolymers were taken (Figure 3). A sharp peak at 337 mT ($g = 2.003$) due to an organic free electron was observed for copolymers 5 ($-C_6H_4C_6H_4-$ system) and 6 ($-C_6H_4-$ system), and the intensity of 6 was stronger than that of 5, suggesting that a larger amount of radical species is formed on the phenylene group of 6. It is noteworthy

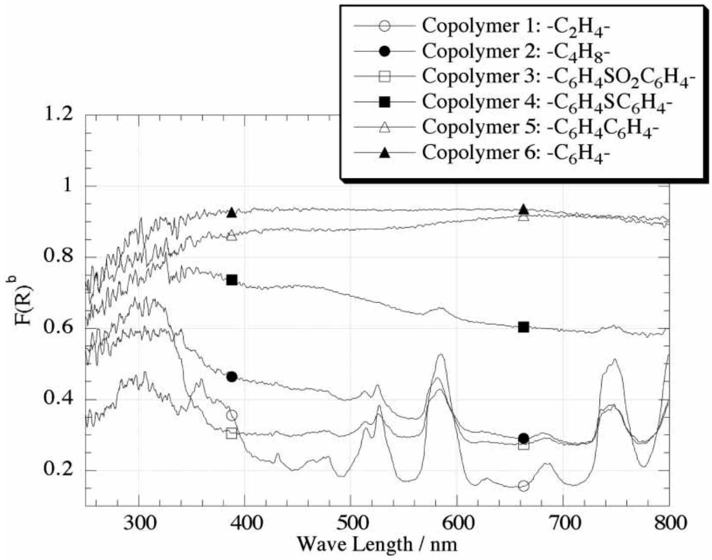


Figure 2. UV-VIS spectra of the copolymers. (i) The spectra were taken by using the diffusion reflecting method. (ii) F(R) is a coefficient of diffusion reflecting which is calculated by the following equation: $F(R) = \{1\text{-}R(\lambda)\}^2/2R(\lambda)$, $R(\lambda)$: reflection rate of sample.

that no peak at 337 mT was observed for copolymers 1($-C_2H_4-$ system), 2 ($-C_4H_8-$ system), and 3 ($-C_6H_4SO_2C_6H_4-$ system). These finding support the occurrence of the electron transfer from the aryl moieties to the neodymium atom in 5 and 6 to form a cation radical on the aryl moieties. In other words, a formation of a rather higher amount of radical species in 6 may be caused by a through-delocalization via a whole net-worked framework, and a rather smaller formation of the cation radical in 5 may be ascribed to a decrease of the delocalization by a torsion between two phenylene groups of a biphenylene moiety. Incidentally, a strong electron-withdrawing sulfonyl group in 3 is considered to inhibit the formation of the cation radical. Every copolymer was found to show a broad peak at 340 mT, which was ascribed to a radical species on the neodymium atom, because same broad peak was observed in the starting neodymium isopropoxide. It is noted that the intensity of the peak at 340 mT in 5 was higher than those in other copolymers and the starting alkoxide. An increase of the peak intensity at 340 mT means an increase of the number of an odd electron in the neodymium atom. In the case of 5, the electron transfer is considered to take place from the biphenyl group to the neodymium atom, possibly to a 4f orbital of the neodymium atom, to increase the number of an odd electron, and thus to form the cation radical on the biphenyl group, as shown in Scheme 2.

Scheme 2. Plausible mechanism of electron transfer.

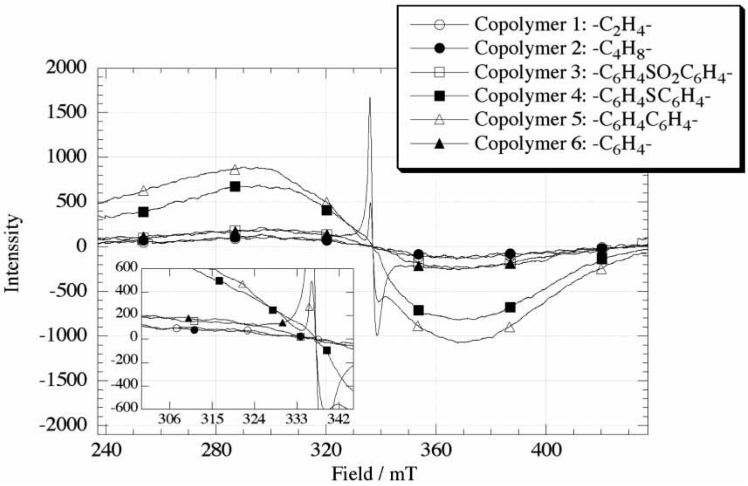


Figure 3. ESR spectra of the copolymers. The spectra were taken by using 1 mg of sample. The measurement conditions: C. Field 337.00 mT, Power: 1.00 mW, Sweep Width: 200 mT, Modulation Width: 0.5 mT, Time Constant: 0.1 s, Temp: room temp.

Conclusion

In this work, we reported the syntheses and properties of novel alternating neodymium-organic moiety hybrid copolymers with covalent bonding. The shapes of the copolymers varied by changing the organic moieties, and the copolymers having aryl moieties are colored. The UV-VIS and ESR spectra of the copolymers indicated that the electron transfer from the aryl moiety to the neodymium atom occurred in the alternating framework. We believe that such hybrid copolymers with novel electronic properties will be useful in many fields, for example, as electronic, magnetic, and optical devices.

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