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Syntheses of Novel Networked Alternating Samarium-Organic Moieties Hybrid Copolymers

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ABSTRACT

The reaction of samarium isopropoxide with several organic diols gave novel networked alternating hybrid copolymers of semi-transparent sheets or ultra-fine particles. Electron transfer from aryl groups to the samarium atom in the networked structures was shown by the results of UV–VIS and ESR spectra.

Key Words: Samarium-organic hybrid copolymer; Alternating structure; Electron transfer.

INTRODUCTION

Organic–inorganic hybrid copolymers have been studied successfully in the new materials fields, since the copolymers are expected to provide a variety of functions by combining both organic and inorganic characters.[1,2] One of the methods constructing the hybrid copolymers is the coordination polymerization and various multi-dimensionally

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coordinated hybrid copolymers were shown.[3–8] However, the hybrid materials with really useful properties do not seem to be given.

On the other hand, Burch showed the synthesis of a amorphous hybrid copolymer having porous structure with a high-surface-area by the reaction of $Ti(NMe_2)_4$ with hydroquinone,[9] and Wolczanski et al. reported that the treatment of $Ti(O^iPr)_4$ with hydroquinone gave the crystalline hybrid copolymer which was shown to have an alternating titanium–quinone structure with a covalent bonding.[10]

The copolymer with alternating covalent organic–inorganic structure is considered to provide novel composite materials having a unique electronic character in the alternating network, because the electronic interaction between the inorganic element and organic moiety is expected to be easily controlled by changing both organic moiety and metal.

Our previous report described the synthesis and the electronic behavior of covalent titanium-organic hybrid copolymers obtained by the reaction of titanium tetraisopropoxide with several organic diols.[11] This work, as one of a series of organic–inorganic hybrid copolymers, shows the preparation of novel networked samarium-organic hybrid copolymers with an alternating covalent organic–inorganic structure by reacting samarium isopropoxide with several organic diols. A permanent magnet made of a samarium–cobalt alloy is known to be one of the industrial uses of samarium. A samarium compound shows paramagnetism at the 3+ oxidation state because they have an odd electron in 4f orbital. Thus, electronic interaction between two samarium atoms linkaged with organic moieties by covalent bonding is expected to be stronger than that of the coordination bonding copolymers, and the spin information can also be controlled by changing the organic moieties.

EXPERIMENTAL

Reagents

Samarium isopropoxide was supplied from Sigma–Aldrich, Inc. Other reagents and solvents were purified by standard procedures.

Reactions of Samarium Isopropoxide with Diols

Into a solution of 0.4 mmol of samarium isopropoxide in 10 ml of anhydrous THF a solution of 0.6 mmol of organic diol in 10 ml of anhydrous THF was added dropwise, and the mixture was refluxed for 3 h (Fig. 1). The precipitate was collected, washed with anhydrous THF, and dried with heating at 60°C under vacuum.

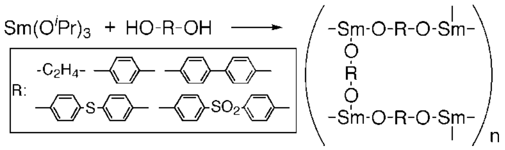

Figure 1. Reactions of Samarium isopropoxide with diols.

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Apparatus

UV–VIS spectra of the copolymers were taken by using Hitach U-4000. ESR spectra were taken by using JEOL TE-200. TEM images were taken by using JEOL JEM-3010. CP/MAS ^{13}C-NMR spectra were taken by using Bruker Avance-DSX400 (400 MHz). Carbon and hydrogen analyses were carried out with a Yanaco MT-6 CHN corder. Sulfur analyses were carried out with a Yanaco YS-10. Hafnium analyses were carried out with a Shimadzu ICPS-1000IV. FT-IR spectra were taken by using Perkin-Elmer FT-IR 1760-X.

RESULTS AND DISCUSSION

The Elemental Analyses and the Structure of the Products

The reaction of samarium isopropoxide with organic diols proceeded smoothly to give the precipitates.

To determine the components of the elements, the elemental analyses were done and the results were summarized in Table 1 . The contents of the samarium and the carbon in the products were small in comparison with the calculated values. The ratio of organic moiety against the samarium content in the precipitates was determined by using the result of the sulfur content of the product 5 (the diphenyl sulfone system) to obtain the value of 1.43 which is slightly small in comparison with the values of ideal ratio, 1.5. The IR spectra of product 5 showed peaks due to the phenyl and sulfonyl groups of bis(4-hydroxyphenyl) sulfone at 1581 and 1148 cm^{-1}, respectively. These results suggest that the samarium–diol hybrid copolymer had a nearly alternative structure and the smaller part would be composed of an extraneous substance, such as samarium oxide and/or unreacted residue. To inspect the details of the structures, CP/MAS ^{13}C-NMR spectra of product 2 (the phenyl system) and product 5 (the diphenyl sulfone system) were thus taken to reveal broad signals at 25 and 65 ppm due to the iso-propoxy group (Fig. 2). The results indicate that all of the isopropoxy groups in samarium isopropoxide do not react with the diols but unreacted isopropoxy groups partly remained in each of the products.

Table 1. Elemental analyses of the hybrid copolymers.

		Anal. found (%)			Anal. calcd (%)		
Product	R	C	H	Sm	C	H	Sm
1	$-C_2H_4-$	12.39	2.74	35.03	14.99	2.52	62.54
2	$-C_6H_4-$	24.35	2.49	34.95	34.59	1.94	48.11
3	$-C_6H_4C_6H_4-$	42.39	2.88	21.10	50.76	2.83	35.24
4	$-C_6H_4SC_6H_4-$	35.20	3.40	27.59	46.32	2.59	32.21
5	$-C_6H_4SO_2C_6H_4-$	35.80	3.23	21.36	41.36	2.31	28.70

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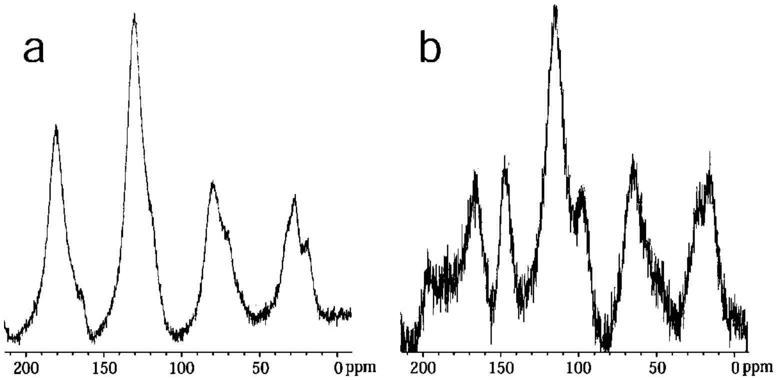

Figure 2. CP/MAS ^{13}C-NMR of the products. (a) Product 2 ($-C_6H_4-$ system), (b) product 5 ($-C_6H_4SO_2C_6H_4-$ system).

The Forms of the Products

To confirm the forms of the products, the TEM images of the copolymers were taken and the results are shown in Fig. 3. Interestingly, the forms of the products were found to differ with the organic moieties. Product 1 (the ethylene system) provided an ultra-fine particle with diameter of ca. 50 nm (Fig. 3a), however, product 5 (the diphenyl sulfone system) had a nearly square sheet form with the length of 500–1000 nm (Fig. 3b). An electron beam from an electron microscope seems to penetrate through the sheet of product 5 so that the overlapped part can be seen, suggesting that each sheet is transparent and thin.

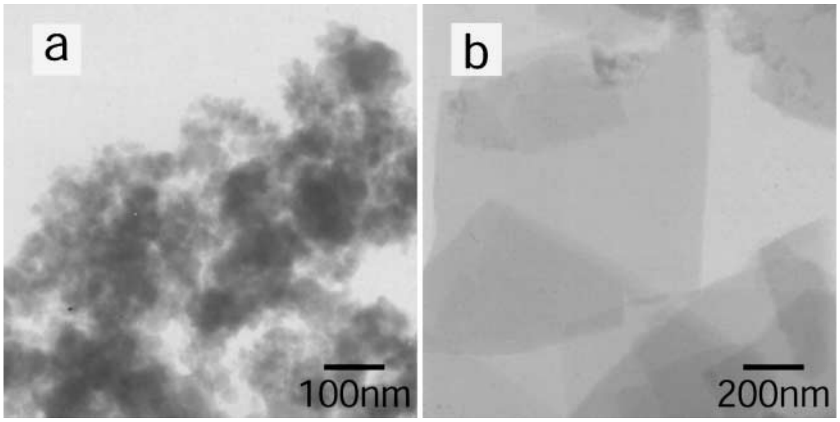

Figure 3. TEM images of the products. (a) Product 1 ($-C_2H_4-$ system), (b) product 5 ($-C_6H_4SO_2C_6H_4-$ system). The measurement condition: AcV 300 KV.

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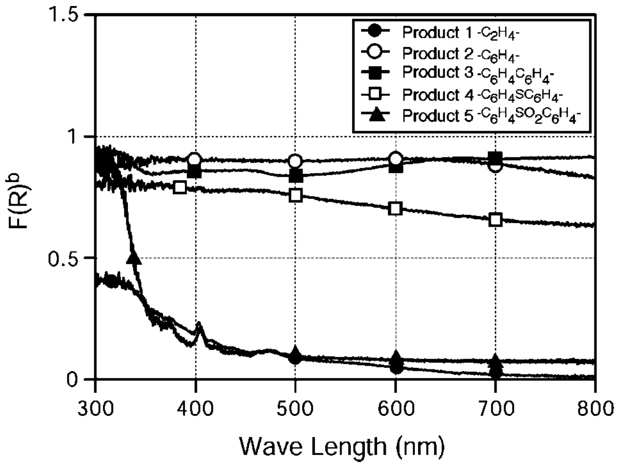

Figure 4. The UV–VIS spectra of the hybrid copolymers. (a) The spectra were taken by using the diffusion reflecting method. (b) F(R) is a coefficient of diffusion reflecting which is calculated by the following equation: $F(R) = \{1 - R(\lambda)\}^2/2R(\lambda)$, $R(\lambda)$: reflection rate of sample.

The Colors and Electronic Properties of the Products

Another interesting finding is that the colors of the products were different with organic moieties, and thus their UV–VIS spectra were taken (Fig. 4). The absorption bands of the copolymers obtained by the reaction with aromatic diols shifted to a longer wavelength and especially the absorption band of product 2 (the phenyl system) extended

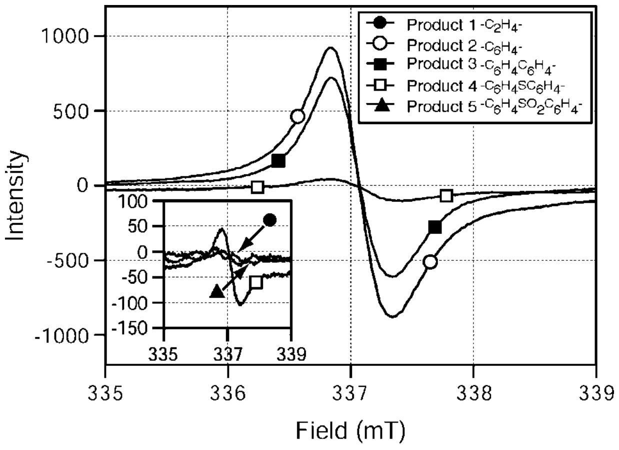

Figure 5. The ESR spectra of the hybrid copolymers. The spectra were taken by using 1 mg of sample. The measurement conditions: Field 337.00 mT, power 1.00 mW, sweep width 5 mT, modulation width 0.5 mT, time constant 0.1 s, temp. room temp.

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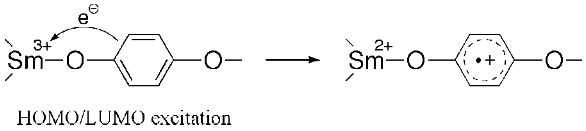

Figure 6. Plausible mechanism of electron transfer.

over a wide spectral range. The intensities of the absorbance increased in the order of $C_6H_4 > C_6H_4C_6H_4 > C_6H_4SC_6H_4 > C_6H_4SO_2C_6H_4 > CH_2CH_2$. One of the possible assumptions is an occurrence of an electron transfer from the aromatic moieties to the samarium atom. The ESR spectra of the copolymers were thus taken to investigate the assumption and the results are shown in Fig. 5. The spectra of the copolymers indicated a peak at $g = 2.0021$ due to a free electron and the order of their intensities were same as the intensities of UV–VIS spectra.

In the previous paper,[11] we observed similar tendencies in both UV–VIS and ESR spectra of the titanium–diol hybrid copolymer obtained by the reaction of titanium tetraisopropoxide with diols. The possibility of electron transfer was suggested by the ab initio calculation of copolymer model, where the HOMO/LUMO energy differences of the copolymer having aromatic moieties were lower than that of the copolymer having non-aromatic moiety, and the HOMO of the aromatic systems extended to the whole of the network but the LUMO of the copolymer was localized at the titanium atom.

We think that the same phenomena may occur in the present systems. In other words, the observed free electron is due to a radical cation formed at organic moiety by an electron transfer from the organic moiety to the samarium atom with reduction of the samarium atom from +3 to +2 (Fig. 6). The CP/MAS ^{13}C-NMR spectra measurement revealed the sharp and strong spectrum for product 2 in comparison with that for product 5. In general, a compound containing a paramagnetism species gives either a broad or no signal in the spectra, and the paramagnetism effect of the samarium in the oxidation state of +3 is stronger than that in the oxidation state of +2. The above findings suggest that the content of +2 in product 2 is much higher than that for product 5: this is caused by an easier electron transfer from organic moiety resulted in reduction of samarium atom in the product 2 in comparison with product 5. The electronic properties of the copolymer were thus found to be controlled by changing the organic moieties in the framework.

CONCLUSION

We have reported the syntheses of the novel organic-samarium hybrid copolymers with a nearly alternative covalent organic–inorganic structure. The colors of the products varied by changing the organic moieties in the copolymer networks. The UV–VIS and ESR spectra of the copolymers indicated that the electron transfer from aromatic group to samarium occurred with the reduction of the samarium atom from +3 to +2. We believe that such hybrid copolymers will be widely useful in many fields, for example, such as electronic, magnetic and optical devices and similar alternative organic–inorganic hybrid copolymers can be produced from the reactions of various metal alkoxides with diols

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and/or dithiols and also from the reactions of various metal halides with sodium and/or lithium salts of diols and/or dithiols.

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