Electronic and magnetic behaviors of calcined material from a neodymium-O-phenylene-O-ytterbium hybrid copolymer

Hideo Matsui*, Hirokazu Miyazaki*, Keigo Otsuki*, Emi Kunimitsu*, Yasuhiro Seguchi*, Tetsuro Kawahara** and Masakuni Yoshihara*,***◆

A networked neodymium-O-phenylene-O-ytterbium ternary hybrid copolymer was calcined under vacuum at 400, 500, 600, and 700 °C to obtain black-colored materials composed of carbon clusters and nano-sized Yb₂O₃ and Nd compound particles. ESR spectral examinations showed that the calcined materials have a free electron on carbon clusters via electron transfer between carbon clusters and metal compounds. From the changes of ESR signal intensity of the calcined materials under magnetic field impression, spin relaxation in the neodymium atom is presumed to be controlled by a spin interaction with the ytterbium atom.

KEYWORDS : Nd compound, Yb₂O₃, Electron transfer, Magnetic field-response characteristic

1. Introduction

Hybrid materials composed of organic and inorganic units have been attracting much attention, because the properties of the materials are expected to be controlled by changing the natures and/or ratios of organic and inorganic components^{1), 2)}. Many studies focused on metal-organic coordination polymerization have been reported for building up multi-dimensional networks³⁾⁻⁷⁾. We have considered that alternating organic-metal hybrid copolymers with covalent bonding can constitute new types of multi-aggregated composite materials⁸⁾⁻¹²⁾, which are expected to exhibit unique electronic, magnetic, and optical properties.

We have recently reported the synthesis of a ternary neodymium-O-phenylene-O-ytterbium hybrid copolymer I (Scheme 1), in which an electron transfer between the phenylene moiety and the ytterbium atom through the neodymium atom takes place to form a

stable free electron on the phenylene moiety¹³⁾. Here, we consider that the calcination of copolymer I under reducing atmosphere will give a new type of a composite material composed of carbon clusters and each metal oxide, possibly neodymium oxide and ytterbium oxide, and such a material will show unique electronic, magnetic, and/or photochemical natures. In the present study, we describe the electronic and magnetic behaviors of the material obtained by calcinating copolymer I under vacuum.

2. Experimental

2.1 Reagents

Commercially available neodymium chloride, ytterbium chloride, 1,4-hydroquinone, and 1,8-bis(dimethylamino)naphthalene (proton sponge) were used. Other reagents and solvents were purified by standard procedures.

2.2 Syntheses of copolymers I, II, and III

Copolymers I, II, and III (Scheme 1) were synthesized according to the previously reported procedures¹¹⁾⁻¹³⁾.

Copolymer I was synthesized by the first reaction of 1,4-hydroquinone (3.0 mmol, 0.34 g) with neodymium chloride (1.0 mmol, 0.25 g) at -70 °C followed by the second reaction with ytterbium chloride (1.0 mmol, 0.28 g) at -30 °C in the presence of proton sponge (6.0 mmol, 1.28 g). Copolymers II and III were synthesized by the reaction of 1,4-hydroquinone (1.5 mmol, 0.17 g) with neodymium chloride (1.0 mmol, 0.25 g) or ytterbium chloride

Scheme 1 Syntheses of copolymers I, II, and III.

◆ Corresponding Author, E-mail: m-yoshi@apch.kindai.ac.jp

(Received December 19, 2005, Accepted August 7, 2006)

* Department of Applied Chemistry, Faculty of Science and Engineering, Kinki University : 3-4-1 Kowakae, Higashiosaka, Osaka 577-8502, Japan

** Nippon Sheet Glass Co. Ltd. : 2-1-7 Kaigan, Minato-Ku, Tokyo 105-8552, Japan

***Molecular Engineering Institute, Kinki University : 11-6 Kayanomori, Iizuka, Fukuoka 820-8555, Japan

(1.0 mmol, 0.28 g), respectively, at room temperature in the presence of proton sponge (3.0 mmol, 0.64 g).

2.3 Calcination of copolymers

0.2 g of copolymer I in a porcelain crucible was calcined under vacuum with a heating rate of 5 °C/min and kept for 1 hr at 400, 500, 600, and 700 °C, respectively, using an electric furnace, Denken KDF-75. Copolymers II and III were calcined by the same procedure at 500 °C.

2.4 Measurements

TG-DTA analysis of copolymer I (1.0 mg) was performed in nitrogen atmosphere using Rigaku TG-DTA-MS 8010. C and H contents were analyzed by coulometric titration using Yanaco CHN corder MT-6. Nd and Yb contents were analyzed using Shimadzu ICP-7500. X-ray diffraction (XRD) spectra were measured using Rigaku Mini Flex with Cu-K α source (30 kV, 15 mA). Transmission electron microscopy (TEM) observations were done using Jeol JEM-3010 microscope (accelerating voltage : 300 kV). UV-VIS spectra were measured using Hitachi U-4000. Electron spin resonance (ESR) spectra were taken using Jeol JES-TE 200 spectrometer (sample weight : 5 mg, c. field ; 337.00 mT, power ; 1.00 mW, sweep width ; ± 5 mT, modulation width ; 0.5 mT, time constant ; 0.1 sec, temp. ; room temp.). X-ray photoelectron spectra (XPS) measurements were carried out using Shimadzu ESCA-850 spectrometer.

3. Results and discussion

TG-DTA measurement of copolymer I under a nitrogen atmosphere with a heating rate of 5 °C/min (Fig.1) showed weight decrease with an endothermic reaction of 25 ~ 150 °C due to evaporation of volatile components and an exothermic reaction of 300 ~ 700 °C due to possibly carbonization of copolymer.

Copolymer I was calcined under vacuum with a heating rate of 5 °C/min and kept for 1 hour at 400, 500, 600, and 700 °C, respectively, to obtain calcined materials Ic-400, Ic-500, Ic-600, and Ic-700, respectively.

In order to check the calcination process of copolymer I and to determine the compositions of the materials, ICP and elemental analyses were performed (Table 1). The observed hydrogen contents in the calcined materials decreased with increasing calcination temperature, indicating that the carbonization of copolymer I proceeded. The molar ratios of neodymium to ytterbium contents in the calcined materials were in the range of 0.84 ~ 0.87 (Table 1). XRD pattern of the Ic-700 showed clear peaks due to ytterbium oxide (Yb₂O₃) at $2\theta = 29.3^\circ$, 34.3° , 49.4° , and 58.6° , and those of Ic-400, Ic-500, Ic-600 showed broad peak at 29.3° (Fig.2). On the other hand, although the ICP analyses showed the presence of Nd atom (Table 1), clear peak due to elemental neodymium or any of its compounds could not be observed. It can be supposed

Fig.1 TG-DTA analysis of copolymer I.

Fig.2 X-ray diffraction patterns of calcined materials Ic.

Table 1 ICP and elemental analyses of copolymer and calcined materials.

Material	Found / %				Molar ratio of Nd/Yb
	Nd	Yb	C	H	
I	18.60	20.49	13.77	2.82	1.09
Ic-400	19.80	27.46	14.63	2.31	0.87
Ic-500	21.07	29.01	12.26	1.31	0.87
Ic-600	23.30	33.29	11.23	1.01	0.84
Ic-700	26.11	36.11	10.16	0.67	0.87

that neodymium exist as oxide (Nd₂O₃). TEM images (Fig.3) showed the presence of ultra-fine particles with diameters of 1 ~ 5 nm, possibly ytterbium oxide and neodymium compound, in the matrix of amorphous carbon clusters with diameters of 100 ~ 500 nm. Thus, the calcined materials are considered to be composed of carbon clusters and nano-sized ytterbium oxide (Yb₂O₃) and neodymium compound particles.

The electronic behaviors of the calcined materials were examined. UV-VIS spectral measurements of copolymer I and calcined materials Ic's showed absorption bands with high intensities over the entire range of wavelength (Fig.4), indicating that the electron transfer excitation takes place easily. In order to verify these findings, ESR spectra of I and Ic's were measured to show the signal due to a free electron at 337 mT ($g = 2.003$) (Fig.5). The radical spin quantities (rsq) of the materials were determined by a double

Fig.3 TEM images of calcined materials Ic.

Fig.4 UV-VIS spectra of copolymer I and calcined materials Ic.

Fig.5 ESR spectra of copolymer I and calcined materials Ic.

integrating calculation of the differential absorption line with the use of DPPH (Table 2). The rsq values were larger in the order of $Ic-500 > Ic-600 > Ic-400 > Ic-700 > \text{copolymer I}$, and the rsq

Table 2 Radical spin quantities (rsq) of copolymer and calcined materials.

Material	Radical spin quantity (rsq)/spins $\cdot g^{-1}$	Ratio (Ic/I)
I	5.62×10^{18}	1
Ic-400	8.32×10^{19}	15
Ic-500	5.25×10^{20}	93
Ic-600	1.77×10^{20}	31
Ic-700	1.32×10^{19}	2

Fig.6 ESR spectra of 500 °C-calcined material (Ic-500) in the presence of reductant or oxidant.

value of Ic-500 was about 93 times as large as that of copolymer I. Our opinion is that the electron transfer between carbon clusters and metal oxides takes place to form a stable radical on carbon clusters, and that although the calcination treatment is indispensable for the electron transfer, there exist an optimal structure or degree of crystallization which could be obtained by calcination at ca. 500 °C with the condition of this study. As shown in Fig.6, the addition of an oxidant (benzoquinone) to Ic-500 decreased slightly the signal intensity at 337 mT, but the signal intensity increased with the addition of a reductant (pyrogallol), suggesting that the signal is due to an anion radical formed on the carbon clusters. In other words, an electron transfer from the metal oxide to the carbon clusters may take place. In order to examine the electron transfer feature in Ic-500, individual binary hybrid copolymers, i.e. phenylene-O-ytterbium hybrid copolymer II and phenylene-O-neodymium hybrid copolymer III (Scheme 1), were synthesized, and the copolymers were calcined at 500 °C under vacuum for 1 hr to obtain calcined materials IIc-500 and IIIc-500, respectively (Table 3). Table 4 summarizes the results of XPS analyses of calcined materials and metal oxide. The values of $4d\ 5/2$ of Nd in the calcined materials Ic and IIIc-500 were considerably higher than that in Nd_2O_3 , and those of $4d\ 5/2$ of Yb in the calcined materials were slightly higher than that in Yb_2O_3 , suggesting that the electron density of Nd atom in the calcined materials decreased in comparison with that of Yb atom. Therefore, an electron transfer in Ic-500 is considered to take place in the process of Nd compound $\rightarrow$ carbon clusters $\rightarrow Yb_2O_3$

Table 3 Elemental analyses of copolymers II and III and calcined materials IIc-500 and IIIC-500.

Table 4 Binding energies (eV) of metal oxides and calcined materials.

Fig.8 ESR spectra of 500 t -calcined material (IIc-500) under magnetic field impression.

Fig.9 ESR spectra of 500 t -calcined material (IIIC-500) under magnetic field impression.

Scheme 2 A proposed electron transfer process.

Fig.7 ESR spectra of 500 t-calcined material (Ic-500) under magnetic field impression.

carbon clusters(Scheme 2).

Both ytterbium and neodymium atoms have an odd electron in the 4f orbital, and thus, the calcined material is expected to show a unique magnetic characteristic. As shown in Fig.7, the impression of strong magnetic field (magnetic field strength ; 5 G) to Ic-500 increased the ESR signal intensity, which, after eliminating magnetic-field, gradually increased, then decreased, and finally

returned to the original intensity, indicating that hysteresis phenomena appeared in the demagnetization process of Ic-500. ESR spectra of IIc-500 and IIIC-500 under magnetic field impression (Figs.8 and 9) showed hysteresis phenomena similar to Ic-500. From the results given in Figs.7, 8 and 9, the decrease in signal intensity during 24 h after eliminating magnetic field was relatively larger for IIIC-500 (Nd system) and smaller for IIc-500 (Yb system) . It suggests that, in Ic-500 (Nd-Yb system) , a rather fast spin relaxation in the neodymium atom may be controlled by the ytterbium atom ; thus, a spin interaction between ytterbium and neodymium atoms may take place. In other words, a spin transport in Ic-500 is considered to be brought by an electron transfer between neodymium and ytterbium atoms. It should be noted that the signal intensities in Ic-500 and IIIC-500 at 24 h after eliminating magnetic field were lower than those before magnetic field application, and its reason is not yet cleared. We have found that the neodymium compound-ytterbium oxide-carbon cluster composite material has a magnetic field-response characteristic. We believe that similar functions can be achieved by the combination of carbon clusters and semiconductors having an odd electron in f-orbital of metals, and the materials will be useful as magnetic devices.

References

- 1) J. Cho and K. Sul, *Polymer* **42** (2001) 727.
- 2) Z. Huang and K. Qiu, *Polymer* **38** (1997) 521.
- 3) H. Bonneman and N. Waldofner, *Chem. Mater.* **14** (2002) 1115.
- 4) D. M. Young, U. Geiser, A. J. Schultz and Z. Wang, *J. Am. Chem. Soc.* **120** (1998) 1331.
- 5) B. F. Hoskins, R. Robson and D. A. Slizys, *J. Am. Chem. Soc.* **119** (1997) 2952.
- 6) D. Hagrman and J. Zubieta, *J. Chem. Soc. Chem. Commun.* **1998** 2005-2006.
- 7) C. J. Kepert and M. J. Rosseinsky, *J. Chem. Soc. Chem. Commun.* **1998** 31-32.
- 8) H. Matsui, A. Okada and M. Yoshihara, *J. Mater. Sci. Lett.* **20** (2001) 1151-1153.
- 9) M. Yoshihara, H. Oie, A. Okada, H. Matsui and S. Ohshiro, *Macromolecules* **35** (2002) 2435-2436.
- 10) H. Matsui, A. Okada, T. Takeuchi and M. Yoshihara, *Electrochemistry* **11** (2002) 842.
- 11) M. Yoshihara, T. Shino, K. Otsuki, H. Matsui and S. Ohshiro, *J. Mater. Sci. Lett.* **21** (2002) 1051-1053.
- 12) H. Matsui, K. Otsuki and M. Yoshihara, *J. Macr. Sci. Part A-Appl. Chem.* **42** (2005) 633.
- 13) H. Matsui, K. Otsuki and M. Yoshihara, *J. Jpn. Soc. Colour Mater.* **78** (2005) 122 (in Japanese).