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Syntheses and electronic behaviors of net-worked, alternating hafnium-organic moiety hybrid copolymers

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Abstract Hafnium-organic moiety hybrid copolymers were prepared by reacting hafnium *n*-butoxide with organic diols. ESR spectral examinations of copolymers and *ab-initio* calculations of copolymer models suggest that an electron transfer from organic group to hafnium atom takes place.

Introduction

Hybrid materials having organic and inorganic units have been attracting an interest because of the possibilities to control the properties of the materials by changing the kind and ratios of organic and inorganic components [1, 2]. Among them, hybrid copolymers with alternating organic-inorganic structures are expected to show unique features resulting from the electronic interaction between the organic moieties and the metal atoms, and further, the interaction can be designed by choosing the kind of organic moieties and metal atoms. A number of researches on the syntheses of hybrid copolymers with multi-dimensional networks by coordination polymerization have been reported [3–6].

Wolczanski prepared a crystalline hybrid copolymer by reacting $Ti(Opr\text{-}i)_4$ with 1,4-hydroquinone and showed that the hybrid copolymer had a three-dimensional covalent titanium-quinone network [7]. Unique electronic, magnetic, and optical properties of alternating organic-metal copolymers with covalent bonding are caused by the electronic interaction between the organic and inorganic moieties in the covalent-bonded hybrid copolymer which extend in long range order.

In previous papers on networked hybrid copolymers having covalent metal-organic units, an electron transfer was shown to take place between the organic moieties and such metal atoms as Ti, Zr, Y, Ta, Yb, Si, and Nd [8–14]. In this work, we describe the syntheses and electronic behaviors of alternating hafnium-organic moiety hybrid copolymers I–V (Scheme 1). The outer-shell orbital of hafnium atom, 5 d, is expected to have an electron overlapping with the organic group larger than titanium atom having 3 d outer orbital or zirconium atom having 4 d outer orbital.

Experimental

Reagents

Commercially available hafnium *n*-butoxide, organic diols, and anhydrous THF were used.

Syntheses of copolymers

A mixture of hafnium *n*-butoxide (0.17 mL, 0.5 mmol) and ethylene glycol (0.08 g, 1.0 mmol) in anhydrous

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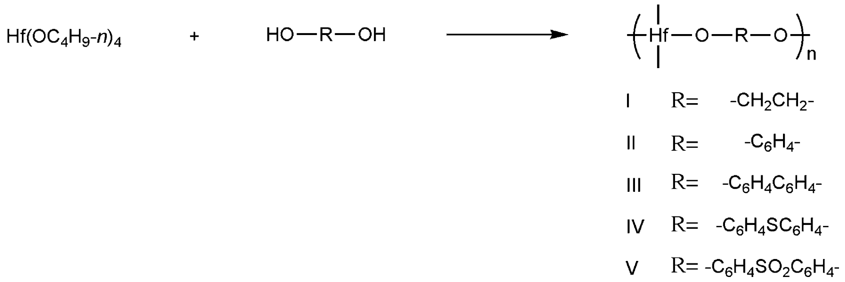
Scheme 1 Syntheses of copolymers



THF (20 mL) was refluxed under an argon atmosphere for 3 h. Precipitate formed was washed with anhydrous THF using a Soxhlet extractor and dried at 100 °C under vacuum to obtain copolymer I.

Similar treatments of hafnium *n*-butoxide (0.17 mL, 0.5 mmol) with 1,4-hydroquinone (0.11 g, 1.0 mmol), 4,4′-dihydroxybiphenyl (0.19 g, 1.0 mmol), bis (4-hydroxyphenyl)sulfide (0.22 g, 1.0 mmol), and bis(4-hydroxyphenyl)sulfone (0.25 g, 1.0 mmol) gave copolymers II, III, IV, and V, respectively.

Apparatus

Elemental analyses were performed for C and H using Yanaco CHN corder MT-6 and for Hf by inductively coupled plasma atomic emission spectroscopy (ICP-AES) using Shimadzu ICP-7500. FT-IR spectra were measured using Hitachi FT/IR-470. CP/MAS ^{13}C-NMR spectra were taken using Bruker AVANCE–DSX400. X-ray diffraction (XRD) spectra were measured using Rigaku MiniFlex. Transmission electron microscopy (TEM) observations were performed using Jeol TEM-3010 microscopy. UV–VIS spectra were measured using Hitachi U-4000. Electron spin resonance (ESR) spectra were measured using Jeol JES-TE200 spectrometer. ESCA observations were done using Shimadzu ESCA-850.

Results and discussion

The results of IR and ^{13}C-NMR spectral analyses of the copolymers are summarized in Table 1. Every copolymer was found to show characteristic IR absorption frequencies and NMR peaks due to organic groups. No NMR signal due to *n*-butyl group was dedected, suggesting that all the butoxy group of hafnium *n*-butoxide had reacted with diols. Table 2 summarizes the results of elemental analyses of the copolymers. The observed Hf and C compositions were lower than the calculated values assuming the reactions given in Scheme 1 have completed. However, the ratios of the observed to calculated values are in the range of 86–97%, thus it could be considered that the synthesized materials involve more than 86% of the hafnium-organic moiety units.

The TEM images of the copolymers are shown in Fig. 1. Copolymer I was amorphous particles with diameters of ca. 10 nm. Copolymers II–V having aromatic moieties, from the variation in contrast in

Table 1 IR and ^{13}C-NMR spectra of copolymers

Copolymer	IR spectra Wave number (cm^{-1})	^{13}C-NMR spectra Chemical shift (ppm)
I	2946 (C–H), 2887 (C–H)	70
II	1582 (C_6H_4), 1494 (C_6H_4)	120,150
III	1582 (C_6H_4), 1494 (C_6H_4)	118,129,130,160
IV	1582 (C_6H_4), 1492 (C_6H_4), 664 (C–S), 635 (C–S)	118,125,132,157
V	1582 (C_6H_4), 1494 (C_6H_4), 1343 (SO_2), 1141 (SO_2)	119,128,131,168

Table 2 Elemental analyses and colors of copolymers

Copolymer	Found/Calcd. (%)			Copolymer unit (%)[a]	Color of copolymer
	Hf (%)	C (%)	H (%)		
I	52.4/59.8	15.2/16.1	3.12/3.02	91	Light yellow
II	38.4/45.2	31.8/36.5	3.33/2.04	86	Dark green
III	26.5/32.6	49.8/52.7	4.44/2.95	88	Green
IV	28.2/29.2	45.6/47.2	3.95/2.64	97	Light brown
V	21.0/26.4	39.1/42.7	3.82/2.39	86	White

[a] Calculated by {Hf (Found)/Hf (Calcd.) × 100 + C (Found)/C (Calcd.) × 100}/2

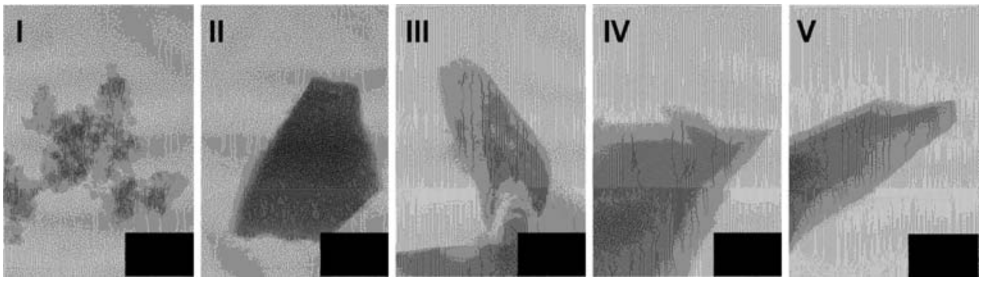


Fig. 1 TEM images of copolymers

Fig. 1, seem to have layered structure with the overlapped parts of the particles look dim. The XRD analyses of copolymers II–V (Fig. 2) showed peaks at $2\theta = 6.5$–9.5 deg, which correspond to the layer space of 10–15 Å.

The colors of the copolymers varied with the kind of organic moieties (Table 2), and the UV–VIS spectra of the copolymers were thus measured (Fig. 3). As shown in Fig. 3, absorption bands of the aromatic systems extend to longer wavelengths with stronger intensities compared with the non-aromatic system I, suggesting that aromatic moieties enhance the degree of an electron excitation. ESR spectra of the copolymers (Fig. 4) showed a free electron at 337 mT (g = 2.0032), and the intensities of the aromatic systems were stronger than that of I, which was the same as for UV–VIS spectra. Our understanding is that an electron transfer takes place between hafnium atom and organic moieties to form a free electron on organic moieties.

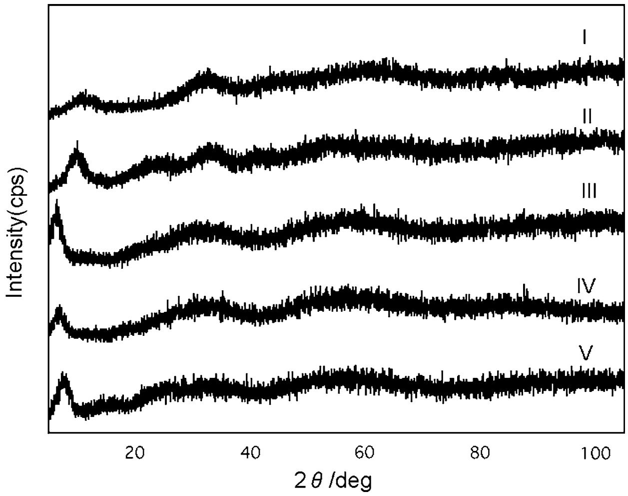


Fig. 2 X-ray diffraction spectra of copolymers

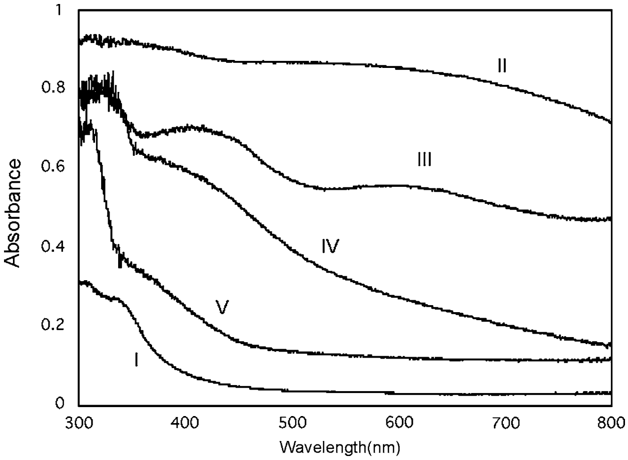


Fig. 3 UV–VIS spectra of copolymers

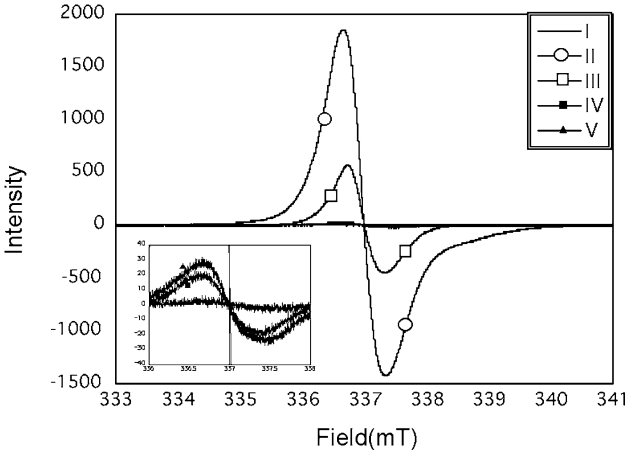


Fig. 4 ESR spectra of copolymers

In order to examine the electron transfer process theoretically, the HOMO/LUMO energy levels of the calculation models shown in Fig. 5 were determined by *ab-initio* calculation. Figure 6 shows the HOMO and LUMO distributions of model I_M corresponding to copolymer I and model II_M corresponding to copolymer II. In I_M, HOMO belongs to the ethylene group and LUMO belongs to the hafnium atom, and, in II_M, HOMO belongs to the phenylene group and LUMO belongs to the hafnium and O atoms. Therefore, HOMO–LUMO orbital combination is presumed to cause the electron transfer from the organic moieties to

$Hf(OROMe)_4$

I_M : R = $-CH_2CH_2-$
II_M : R = $-C_6H_4-$
III_M : R = $-C_6H_4C_6H_4-$
IV_M: R = $-C_6H_4SC_6H_4-$
V_M: R = $-C_6H_4SO_2C_6H_4-$

Fig. 5 Calculation models

Table 3 HOMO/LUMO energy levels (eV) of calculation models

Model	HOMO	LUMO	Δ E[a]
I_M	–9.47	5.01	14.48
II_M	–7.97	3.78	11.75
III_M	–7.56	3.57	11.13
IV_M	–8.05	3.27	11.32
V_M	–9.01	3.24	12.25

[a] ΔE = LUMO–HOMO

the hafnium atom, resulting in the formation of a stable radical cation on the organic groups. The radical cation thus formed is considered to be detectable by ESR spectrometer. Table 3 summarizes the results of RHF/STO-3G calculations. The HOMO/LUMO energy difference ΔE of model I_M (14.48 eV) is higher than those of other models (11.13–12.25 eV), suggesting that the electron transfer abilities of the aromatic systems are higher than that of the non-aromatic system.

The surface of copolymer II was modified with Pt vapor deposition by heating a Pt plate under vacuum to obtain Pt-loaded copolymer II. Figure 7 shows the ESCA spectrum of Pt-loaded copolymer II. Peaks due to $4f_{7/2}$ and $4f_{5/2}$ of Pt were found to split into two signals. Correction of the splitted peaks gave 69.12 eV for $4f_{7/2}$ and 72.59 eV for $4f_{5/2}$, respectively, whereas $4f_{7/2}$ and $4f_{5/2}$ of bulk Pt metal are known to appear at 70.90 and 74.25 eV, respectively. These findings suggest that the electron density on the Pt atom of the Pt–loaded II increased through electron transfer process of phenylene group → Hf → Pt.

In conclusion, we reported that, in hafnium-organic moiety hybrid copolymers, the electron transfer from

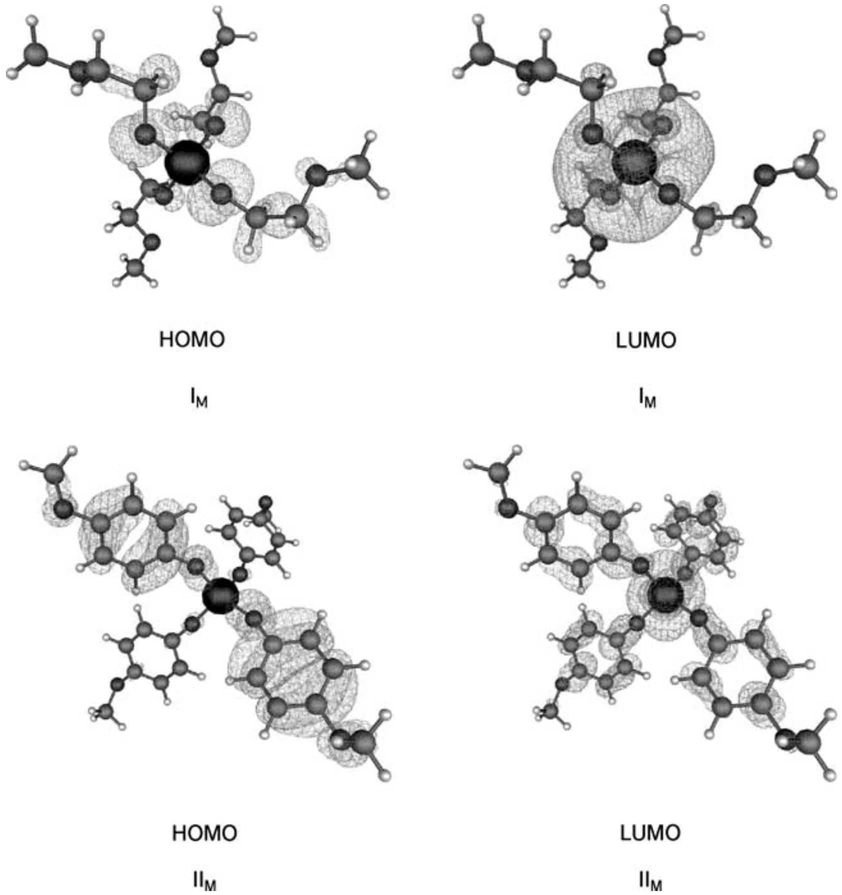


Fig. 6 HOMO/LUMO distribution of calculation models

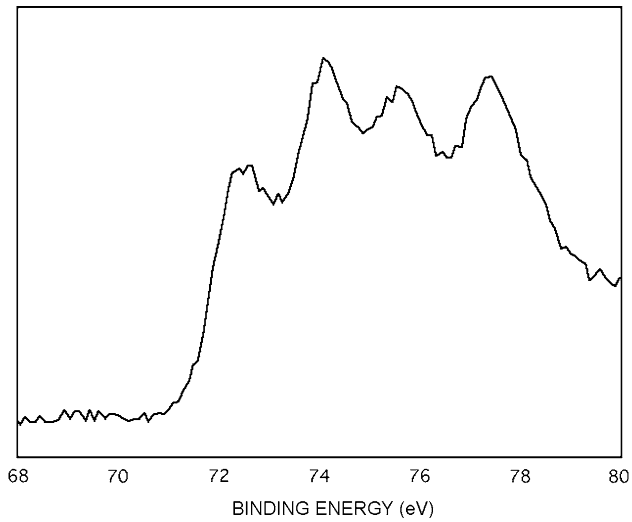


Fig. 7 ESCA spectra of Pt-loaded II

the organic moiety to the hafnium atom took place. We suggest that hybrid copolymers will be useful in many fields, for example, as electronic, magnetic, and optical devices.

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