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Synthesis and Electronic Behavior of a Ternary, Alternating Zirconium-Phenylene-Tin Hybrid Copolymer

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A ternary, networked zirconium-phenylene-tin hybrid copolymer was synthesized by initially reacting zirconium n-butoxide with 4-hydroxythiophenol followed by a reaction with tin t-butoxide, and its electronic behavior was examined by UV-VIS and ESR spectral analyses and ab-initio calculation of copolymer models. It was shown that an electron transfer takes place initially from the phenylene moiety to LUMO of tin atom followed by the second electron transfer to LUMO + 1 of zirconium atom.

Keywords zirconium, tin, hybrid copolymer, electron transfer

Introduction

Organic-inorganic hybrid materials have attracted much attention because they have been expected to exhibit unique properties by a combination of both organic and inorganic characteristics (1). Many studies on the syntheses of multi-dimensional polymers via coordination polymerization have thus been reported (2–4). We have considered that an alternative organic-inorganic hybrid copolymer with covalent bonding can constitute new types of composite materials, which may show novel properties in comparison with coordination polymer, because a covalent bonding electron is considered to be expanded beyond a metal-organic part, while a coordination bonding electron may be localized on a metal-ligand part. In previous papers on networked hybrid copolymers having covalent bonded metal-organic units, (5–8) an electron transfer was shown to take place from organic moieties to metal atoms, and a higher degree of the electron transfer was observed when using an aryl group as the organic moiety.

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We have assumed that, when the aryl group is sandwiched by two different kinds of metal atoms, the electron transfer will be affected and multi-step electron transfer may be involved. In the present study, we wish to report the synthesis and the electronic behavior of a ternary, alternative zirconium-phenylene-tin hybrid copolymer IV (Scheme 1). Zirconium has a rather high electron reception ability and tin has a rather low ionic potential, therefore, the ability and degree of the electron transfer of copolymer IV will be different with those of corresponding binary metal-phenylene hybrid copolymers I, II, and III.

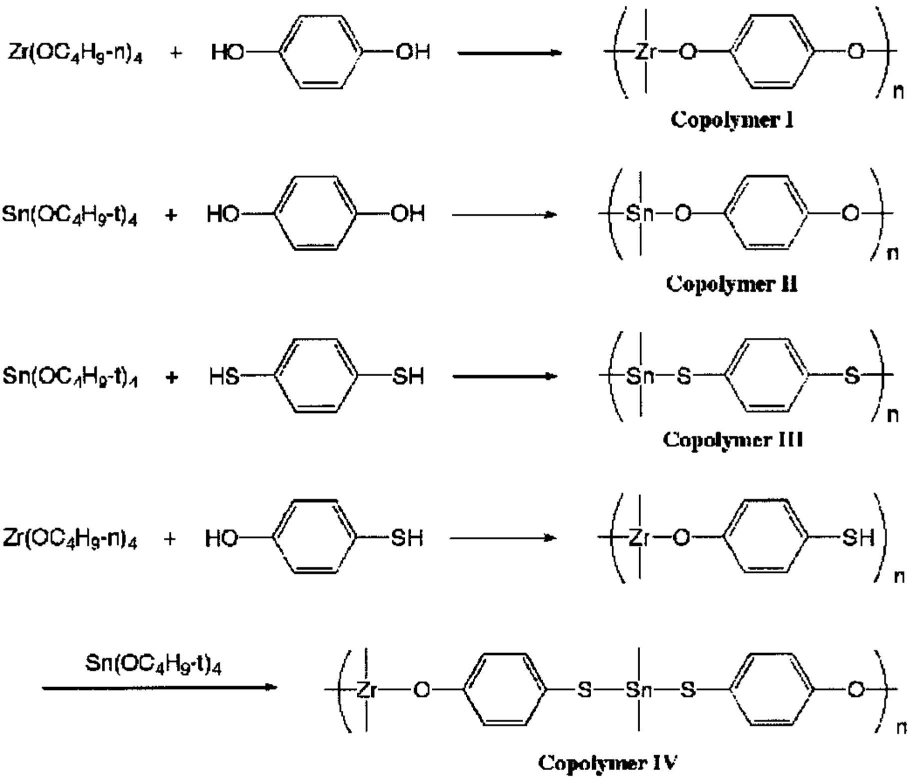
Experimental

Reagents

Commercially available zirconium *n*-butoxide, tin *t*-butoxide, 1,4-hydroquinone, 1,4-benzenedithiol, and 4-hydroxythiophenol were used. Other reagents and solvent were purified by the usual procedures.

Syntheses of Copolymers

A solution of 1,4-hydroquinone (1 mmol) in anhydrous THF (10 mL) was added to a solution of zirconium *n*-butoxide (0.5 mmol) in anhydrous THF (10 mL), and the



Scheme 1. Syntheses of hybrid copolymers.

mixture was refluxed for 3 h. The precipitate formed was washed with anhydrous THF by using a Soxhlet extractor and dried at 60°C under *vacuo* to obtain a binary zirconium-O-phenylene hybrid copolymer I (white-colored). Similar treatment of tin *t*-butoxide (0.5 mmol) with either 1,4-hydroquinone or 1,4-benzenedithiol gave a binary tin-O-phenylene hybrid copolymer II (dark green-colored) or a binary tin-S-phenylene hybrid copolymer III (yellow-colored).

A solution of 4-hydroxythiophenol (2 mmol) in anhydrous THF (10 mL) was added to a solution of zirconium *n*-butoxide (0.5 mmol) in anhydrous THF (10 mL), and the mixture was refluxed for 30 min. A solution of tin *t*-butoxide (0.5 mmol) in anhydrous THF (10 mL) was added to the reaction mixture, and the mixture was refluxed for 3 h. The precipitate formed was washed with anhydrous THF by using a Soxhlet extractor and dried at 60°C under *vacuo* to obtain a ternary hybrid copolymer IV (dark yellow-colored).

Apparatus

UV-VIS spectra of copolymers were taken using a Hitachi U-4000 apparatus. ESR spectra were taken using a JEOL TE-200 unit. TEM images were taken using a JEOL JEM-3010 unit. Carbon analyses were performed with a Yanako MT-6 CHN recorder. Sulfur analyses were carried out with a Yanako YS-10 apparatus. Metal analyses were performed with a Shimadzu ICPS-1000IV analyzer. FT-IR spectra were taken using a Perkin-Elmer FT-IR 1760-x unit.

Results and Discussion

In order to determine the procedure for synthesizing ternary hybrid copolymer IV, the reactivities of zirconium *n*-butoxide and/or tin *t*-butoxide with 1,4-hydroquinone and/or 1,4-benzenedithiol were examined. Zirconium *n*-butoxide did not react with 1,4-benzenedithiol but reacted with 1,4-hydroquinone to give copolymer I. On the other hand, tin *t*-butoxide was found to react with either 1,4-hydroquinone or 1,4-benzenedithiol, to give copolymer II or III. Thus, copolymer IV was prepared in the following way. Initially, Zirconium *n*-butoxide was allowed to react with 4-hydroxythiophenol followed by a reaction with tin *t*-butoxide for obtaining IV.

The formation and composition of the copolymers were examined. First, FT-IR spectra analyses showed frequencies due to the phenylene group for all the copolymers, the C–O bond for I, II, and IV, and C–S bond for III and IV (Table 1). Copolymer II

Table 1
IR spectra of hybrid copolymers

Copolymer	Wavenumber (cm^{-1})
I	1503 (C_6H_4), 1093 (C–O), 843 (C_6H_4)
II	1514 (C_6H_4), 1098 (C–O), 833 (C_6H_4), 573 (Sn═O), 524 (Sn═O)
III	1469 (C_6H_4), 813 (C_6H_4), 702 (C–S)
IV	2879 (CH_3), 2803 (CH_2), 1484 (C_6H_4), 1365 (CH_3, CH_2), 1093 (C–O), 829 (C_6H_4), 686 (C–S)

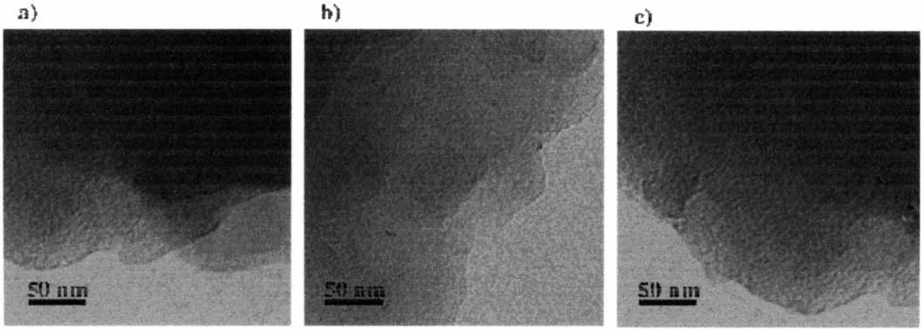


Figure 1. TEM images of copolymers: a) Copolymer I (Zr-O-phenylene system), b) Copolymer III (Sn-S-phenylene system), c) Copolymer IV (Zr-Sn system). The measurement condition: AcV: 300 kV.

showed frequencies due to SnO_2, which may be formed by a reaction with a small amount of water contained in the solvent during either the reaction process or the after-treatment. TEM measurements (Figure 1) revealed that II had highly-condensed cores of a few nm which must be a SnO_2 particle, while such a core was not detected for I, III, and IV. The frequencies of CH_3 and CH_2 groups were observed for copolymer IV, indicating an incomplete substitution reaction of alkoxide with 4-hydroxythiophenol. Incomplete reaction in IV was also shown by CP/MAS ^{13}C-NMR spectral analysis of IV, in which peaks due to the n-C_4H_9 group of the starting zirconium *t*-butoxide at 18 and 38 ppm and the t-C_4H_9 group of tin *t*-butoxide at 25 and 70 ppm were detected. Thus, accurate metal-phenylene units were unable to be determined. Incidentally, with the use of observed sulfur and/or metal contents (Table 2), percentage of phenylene moiety in III and IV were calculated to be 46 and 81 %, respectively, and further, the ratio of Sn:C_6H_4 in III was 1:1.11 (an ideal ratio, 1:1) and that of Sn:Zr:C_6H_4 in IV was 1:1.51:2.14 (an ideal ratio, 1:1:2).

The copolymers colors were found to vary with the metal atoms, and their UV-VIS spectra were thus taken (Figure 2). The absorption bands beyond 300 nm appeared for I, III, and IV, and the intensities beyond ca 500 nm were in the order of I > IV > III. Our opinion is that an electron transfer will take place between the phenylene group and metal, and its degree may be affected by metal. Therefore, in order to verify this cause, the ESR spectra of copolymers I, III, and IV were obtained (Figure 3). All the copolymers were found to have a peak at 337 mT ($g = 2.0038$) due to an organic free electron

Table 2
ICP and elemental analyses of hybrid copolymers

	Found (%)/calcd. (%)					
Copolymer	Zr	Sn	C	H	S	Color of copolymer
I	20.6/29.7	—	34.5/46.9	3.7/2.6	—	White
II	—	40.4/35.5	21.1/43.0	2.9/2.4	—	Dark green
III	—	24.9/29.7	31.1/36.1	2.0/2.0	14.9/32.1	Yellow
IV	14.7/12.9	12.7/16.8	33.6/40.8	2.8/2.3	14.7/18.2	Dark yellow

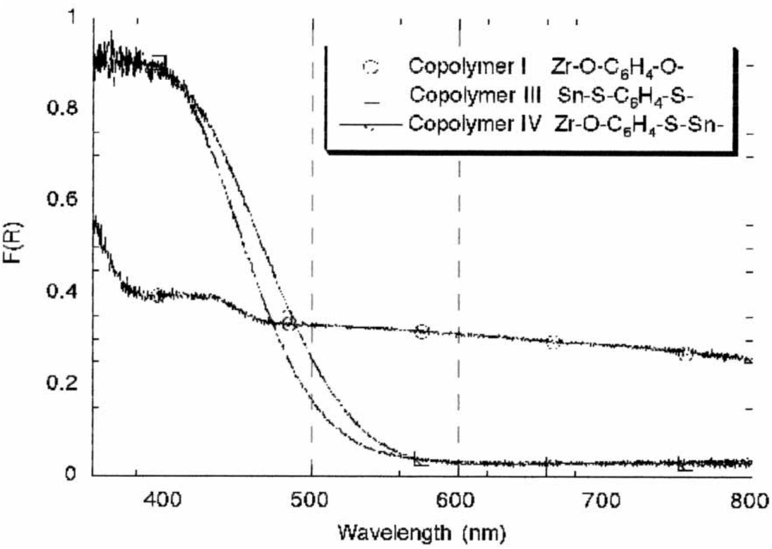


Figure 2. UV-VIS spectra of hybrid copolymers. The spectra were taken by using diffusion reflecting method. F(R) is a coefficient of diffusion reflecting which is calculated by the following equation: $F(R) = \{1 - R(\lambda)\}^2/2R(\lambda)$, $R(\lambda)$: reflection rate of sample.

and their intensities were in the order of I > IV > III, which was the same as the order of the intensities of the UV-VIS spectra.

To evaluate electron transfer process theoretically, *ab-initio* calculations were performed by using copolymer models. In the models of I and III (Figures 4 and 5), HOMO is delocalized on the phenylene moiety and LUMO uses metals atoms, suggesting

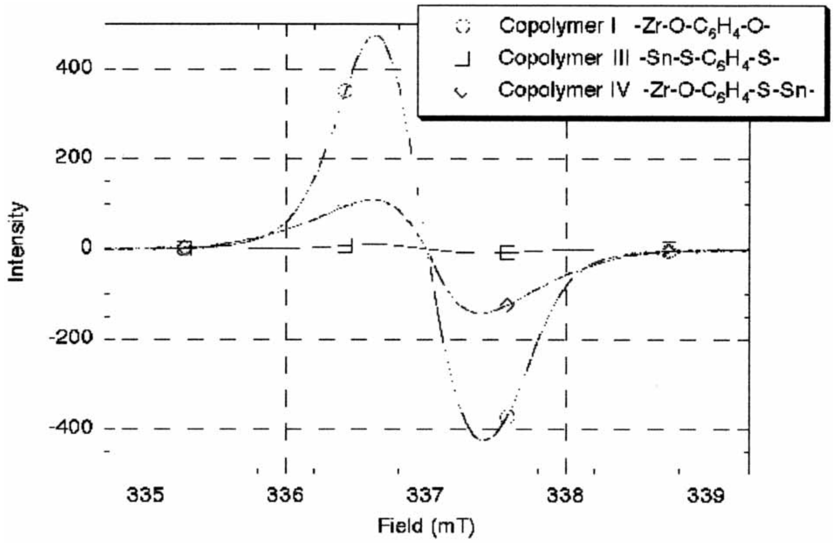


Figure 3. ESR spectra of hybrid copolymers. The spectra were taken by using 5 mg of sample. The measurement conditions: C. Field, 337.00 mT, power, 1.00 mW, sweep width, 2.5 mT, modulation width, 0.5 mT, time constant, 0.1 s, temp, room temp.

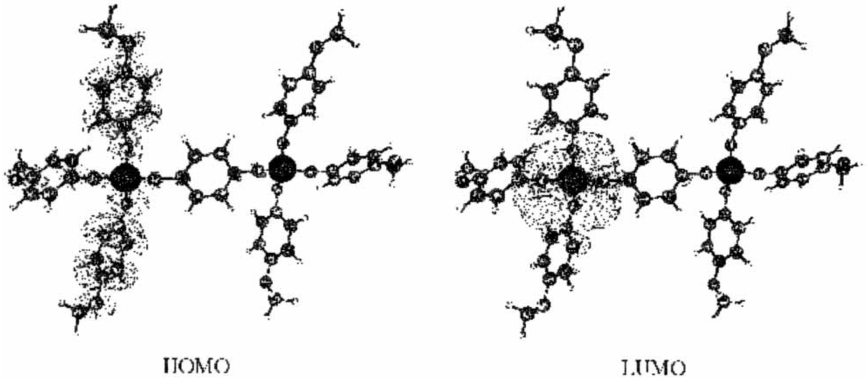


Figure 4. HOMO and LUMO in the model of I.

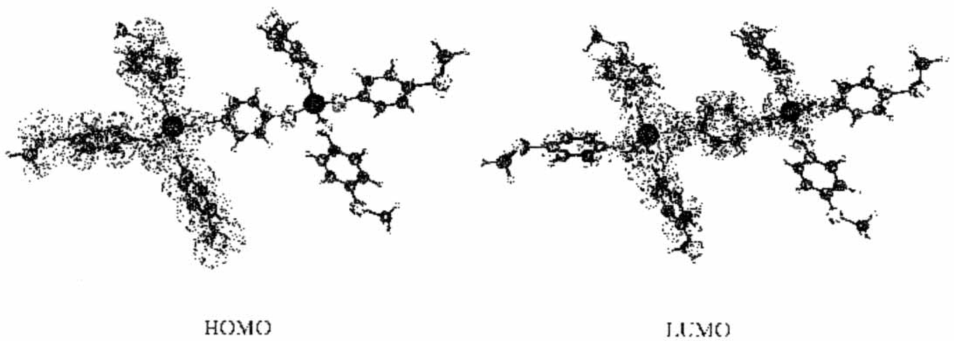


Figure 5. HOMO and LUMO in the model of III.

that an electron transfer takes place from the phenylene moiety to the metal atoms. The value of HOMO/LUMO energy difference (ΔE) of copolymer I model was found to be lower than that of copolymer III model (Table 3), indicating that the degree of the electron transfer in I is higher than that in III, possibly due to the higher electron reception ability of Zr^{4+} with a $4d^0$ orbital in comparison with Sn^{4+} with a $4d^{10}$ orbital. On the other hand, the ΔE value of copolymer IV model was found to be the highest, however, the degree of the electron transfer in IV was higher than in III, as seen in UV-VIS and ESR spectra. Here, it was found that, in the model of IV (Figure 6),

Table 3
HOMO and LUMO energy levels of copolymer models (hartree)

Copolymer	HOMO	LUMO	LUMO + 1	HOMO-LUMO	LUMO-LUMO + 1
I	−0.211	0.142		0.353	
III	−0.243	0.188		0.431	
IV	−0.226	0.219	0.230	0.445	0.011

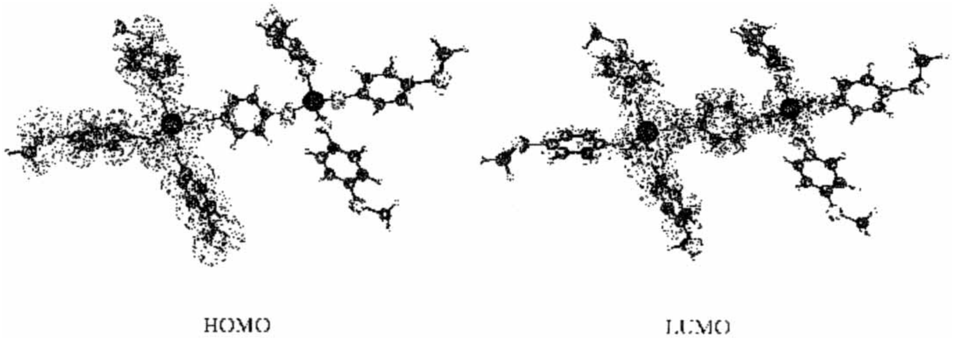


Figure 6. HOMO and LUMO in the model of IV.

HOMO uses the phenylene moiety and LUMO is delocalized on both tin and the phenylene moiety, and further, LUMO + 1 is localized on the tin atom. Moreover, HOMO/LUMO + 1 energy difference in IV is quite small (0.010 hartree), suggesting that an electron transfer from LUMO to LUMO + 1 takes place easily. From these findings, we wish to assume that, in copolymer IV, the electron transfer takes place initially from the phenylene moiety to LUMO of tin followed by the second transfer to LUMO + 1 of zirconium. In other words, a two-step electron transportation process of phenylene → Tn → Zr is presumed to take place in IV.

Conclusion

We have reported the synthesis of a ternary, zirconium-phenylene-tin hybrid copolymer having covalent organic-inorganic structure. The UV-VIS and ESR spectral of copolymer and *ab-initio* calculation of copolymer model indicated that a two-step electron transportation process of phenylene → Tn → Zr was presumed to take place. We believe that such a multi-step electron transfer, as seen in the photosynthesis of plants, will occur various types of hybrid copolymers composed of aryl group and two different kinds of metals, and such copolymers will be useful as magnetic, electronic, and photochemical materials.

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