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Syntheses and Electronic Behaviors of Several Phenylene-Chromium, -Molybdenum and/or -Tungsten Hybrid Copolymers

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Four binary hybrid copolymers having chromium-O-phenylene, chromium-S-phenylene, molybdenum-S-phenylene, and tungsten-S-phenylene units, two ternary hybrid copolymers having molybdenum-phenylene-chromium and chromium-phenylene-tungsten units, and further, a quartic hybrid copolymer having a molybdenum-phenylene-chromium-phenylene-tungsten framework were synthesized, and their electronic behaviors were examined. The results of UV-VIS, ESR, and XPS spectral analyses indicated that, in the ternary hybrid copolymers, an electron transfer takes place from chromium atom to either molybdenum or tungsten, and, in the quartic hybrid copolymer, an electron transfer takes place in the process of tungsten → molybdenum → chromium.

Keywords chromium, molybdenum, tungsten, hybrid copolymer, electron transfer

Introduction

Combinations of organic and inorganic species have been attracting much attention (1, 2), and many studies focusing on metal-organic coordination polymerization have been reported for strengthening multi-dimensional networks (3–7).

In previous papers on alternative metal-organic moiety binary hybrid copolymers with covalent bonding, an electron transfer was shown to take place from organic moieties to metal atoms such as Mg, Ti, Zr, and Y (8–11). When a phenylene group was sandwiched between vanadium and germanium atoms, a two-step electron-transfer was found to occur from the phenylene group to the vanadium atom through the germanium atom (12). Here, we have assumed that, if a phenylene group is covalent-bonded by three different kinds of metals, a material with a unique electronic property will be provided.

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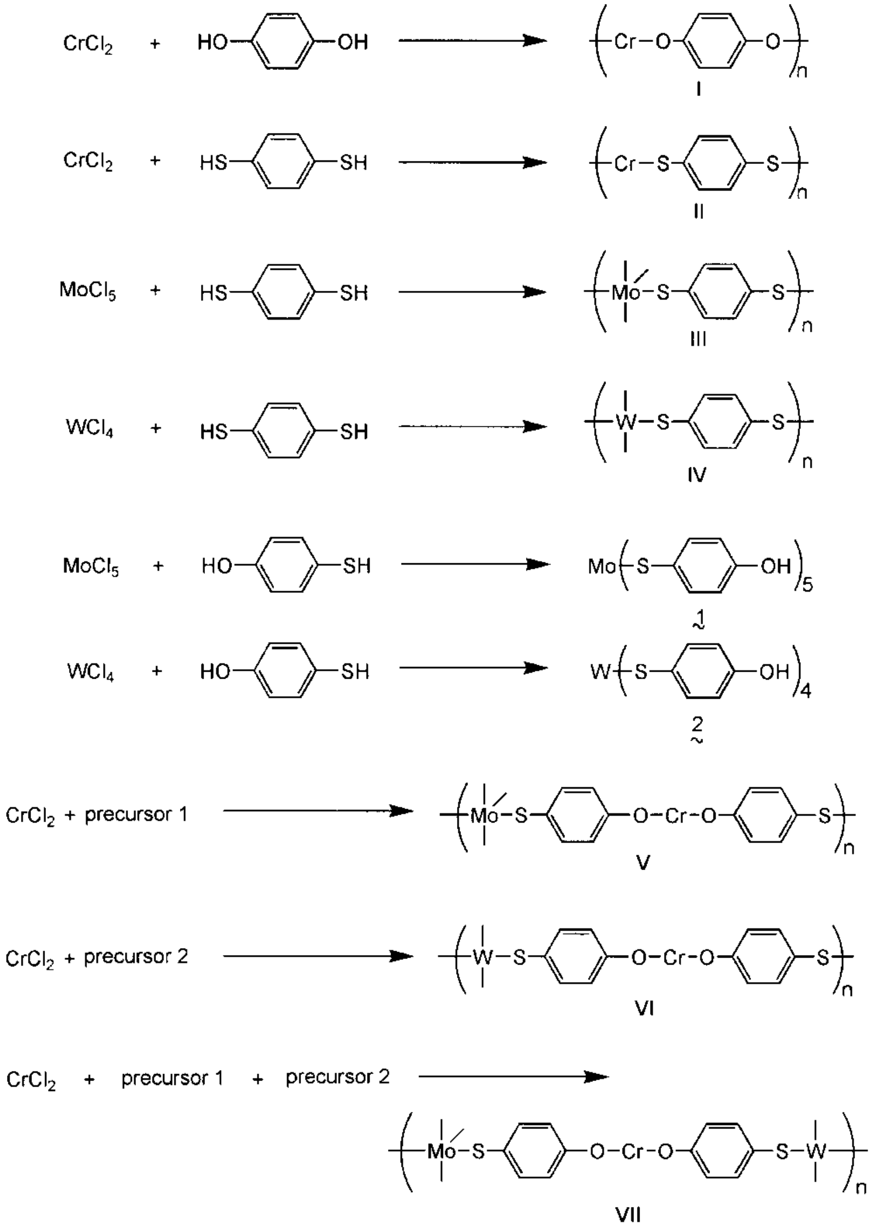
In this paper, we describe the results of the electronic natures of binary, ternary, and quartic hybrid copolymers composed of phenylene and chromium, molybdenum and/or tungsten atoms (Scheme 1). Chromium is known to vary the oxidation-reduction ability with changing the oxidation number, and both molybdenum and tungsten are known to exhibit photochemical activity, and, therefore, combinations of the phenylene group and these metals are expected to cause an electronically and/or photochemically unique property with a multi-electron transportation.



Scheme 1. Syntheses of hybrid copolymers.

Experimental

Reagents

Commercially available metallic chlorides, 1,4-hydroquinone, 1,4-benzenedithiol, 4-hydroxythiophenol, and proton sponge were used. Other reagents and solvents were purified by the usual procedures.

Apparatus

UV-VIS spectra were taken using a Hitachi U-4000 unit, ESR spectra were taken using a Jeol Jes-Te 200 ESR spectrometer, and XPS spectra were taken using a Shimadzu ESCA-850 apparatus.

Syntheses of Copolymers

A solution of 1,4-hydroquinone (1 mmol) in anhydrous ethanol (10 mL) was added to a solution of chromium chloride (1 mmol) and proton sponge (2 mmol) in anhydrous ethanol (30 mL), and the mixture was refluxed at 80°C for 3 h to obtain a binary copolymer I (green-colored). Similarly, copolymer II (ocher-colored) was given by the reaction of chromium chloride with 1,4-benzenedithiol. Refluxing a mixture of molybdenum chloride (1 mmol), 1,4-benzeneditihol (2.5 mmol), and proton sponge (5 mmol) in anhydrous ethanol (30 mL) gave a binary copolymer III (brown-colored). The reaction of tungsten chloride (1 mmol) and 1,4-benzenedithiol (2 mmol) in the presence of proton sponge (4 mmol) in anhydrous ethanol (30 mL) under refluxing for 3 hyielded a binary copolymer IV (ocher-colored).

A mixture of molybdenum chloride (1 mmol) and 4-hydroxythiophenol (5 mmol) in anhydrous ethanol (30 mL) was refluxed for 3 h to obtain a precursor **1** solution. Similarly, a precursor **2** solution was obtained by the reaction of tungsten chloride (1 mmol) and 4-hydroxythiophenol (4 mmol) in anhydrous ethanol (30 mL) under refluxing for 3 h. A mixture of chromium chloride (1 mmol) and proton sponge (7 mmol) in anhydrous ethanol (10 mL) was added into the precursor **1** solution, and the mixture was refluxed for 3 h to obtain a ternary copolymer V (brown-colored). A ternary copolymer VI (ocher-colored) was obtained by the reaction of the precursor **2** with chromium chloride (1 mmol) in the presence of proton sponge (6 mmol) in anhydrous ethanol (10 mL) under refluxing for 3 h.

A solution of chromium chloride (2 mmol) and proton sponge (13 mmol) in anhydrous ethanol (20 mL) was added into a mixture of the precursors **1** and **2**, and the mixture was refluxed for 3 h to obtain a quartic copolymer VII (brown-colored). All the copolymers obtained above were washed with anhydrous ethanol by using a Soxhlet extractor and dried by heating under *vacuo.*

Results and Discussion

In order to find the procedures for synthesizing ternary hybrid copolymers, V and VI, and quartic hybrid copolymer VII, the reactivities of chromium chloride, molybdenum chloride, and tungsten chloride with 1,4-hydroquinone and 1,4-benzenedithiol were examined. Chromium chloride was found to react with both 1,4-hydroquinone and 1,4-benzenedithiol in the presence of proton sponge for giving the corresponding binary copolymers I and II. Molybdenum chloride did not react with 1,4-hydroquinone, but reacted with 1,4-benzenedithiol in the presence of proton sponge to give the binary hybrid copolymer III. Tungsten chloride reacted with 1,4-benzendithiol in the presence of proton sponge to give the binary hybrid copolymer IV, while no reaction took place with 1,4-hydroquinone. Therefore, it is presumed that chromium chloride reacts with both hydroxyl and mercapto groups, while both molybdenum chloride and tungsten chloride do not react with a hydroxyl group but react with a mercapto group. Therefore, ternary hybrid copolymers V and VI were prepared in the following ways.

4-Hydroxylthiophenol was allowed to react with either molybdenum chloride or tungsten chloride for giving the corresponding precursor **1** or **2**. The reaction of the precursor 1 with chromium chloride, in the presence of proton sponge, gave the molybdenum -phenylene- chromium ternary hybrid copolymer V. The tungsten -phenylene- chromium ternary hybrid copolymer VI was prepared by the reaction of the precursor **2** with chromium chloride in the presence of proton sponge. The molybdenum – phenylene – chromium – phenylene – tungsten quartic hybrid copolymer VII was prepared by reacting chromium chloride with a mixture of the precursors **1** and **2** in the presence of proton sponge.

The formations of the copolymers were examined. First, the FT-IR spectra of the copolymers were found to show frequencies due to a phenylene group and a C–S bond (Table 1). Next, in order to determine the compositions of metal-phenylene units in the copolymers, ICP and elemental analyses measurements were performed, and the results are summarized in Table 2. The percentages of metal-phenylene units were found to be in the range of 51–91% by calculating with the observed metals and carbon contents. These results show that the metal-phenylene units are certainly involved in the copolymers.

The colors of the copolymers were found to vary by changing the metals and their combinations, and their UV-VIS spectra were thus taken (Figure 1). The most interesting finding is that the absorption bands of the quartic hybrid copolymer VII appeared at the longer wavelengths with the highest intensity. Our understanding is that such a red-shift is caused by an electron transfer in the networked frameworks. ESR spectral examinations were thus performed, and the results of the binary copolymers are shown in Figure 2. Copolymer I showed broad peak at 342 mT (g = 1.9812), which is credited to Cr^{2+} because the ESR spectra of $CrCl_2$ showed the same broad peak at 350 mT (g = 1.9462). Copolymer III had a hyperfine peak at 344 mT (g = 1.9799), which is

Table 1
FT-IR spectra of hybrid copolymers (cm^{-1})

Copolymer			C–S
I	1,494	817	—
II	1,470	808	739
III	1,470	811	767
IV	1,472	812	767
V	1,490	825	766
VI	1,490	830	766
VII	1,490	826	768

Table 2

ICP and elemental analyses of copolymers

	Content (%)				Ratio of unit			
Copolymer	Cr	Mo	W	C	Unit	Ideal	Found	Composition (%)
I	28.91	—	—	29.14	Cr:C_6H_4	1:1	1:0.73	73
II	18.51	—	—	35.35	Cr:C_6H_4	1:1	1:1.38	72
III	—	18.66	—	44.44	Mo:C_6H_4	1:2.5	1:3.17	79
IV	—	—	37.51	32.36	W:C_6H_4	1:2	1:2.20	91
V	8.90	15.25	—	34.50	Mo:Cr:C_6H_4	1:2.5:2.5	1:1.08:3.01	53
VI	7.44	—	27.94	24.86	W:Cr:C_6H_4	1:2:2	1:0.94:2.27	51
VII	7.60	9.21	14.28	23.03	Mo:Cr:W:C_6H_4	1:2.5:1.25:2.5	1:1.52:0.81:3.33	72

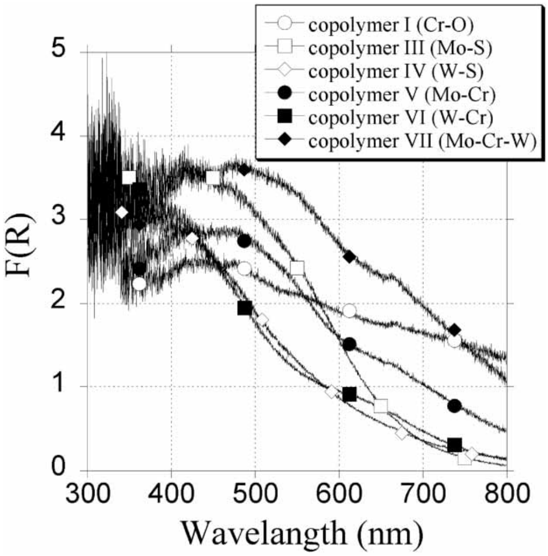


Figure 1. UV-vis spectra of hybrid copolymers. F(R) is a coefficient of diffusion reflecting which is calculated by the following equation: $F(R) = \{1 - R(\lambda)\}^2/2R(\lambda)$, $R(\lambda)$: reflection rate of sample.

due to Mo^{5+} because the same peak at 348 mT (g = 1.9533) was observed for $MoCl_5$. Copolymer IV showed a small peak at 348 mT (g = 1.9184), which is ascribed to W^{4+} because the same peak at 380 mT (g = 2.0057) was observed for WCl_4. Figure 3 shows the ESR spectra of the ternary copolymers, V and VI, and the quartic hybrid copolymer VII. In every case, a broad peak at 340 mT (g = 1.9462) due to Cr^{2+} was detected, and

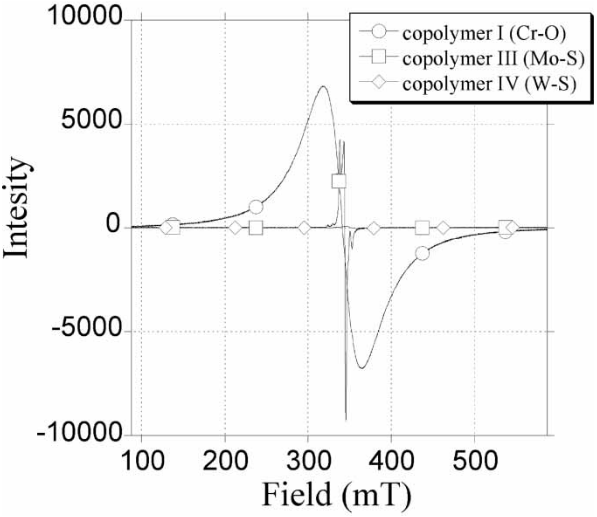


Figure 2. ESR spectra of binary hybrid copolymers. Spectrawere taken using 10 mg of sample. Measurement conditions: C Field 337.00 mT, power 1.00 mW, sweep width 250 mT, modulation width 0.5 mT, time constant 0.1 s, temp. room temp.

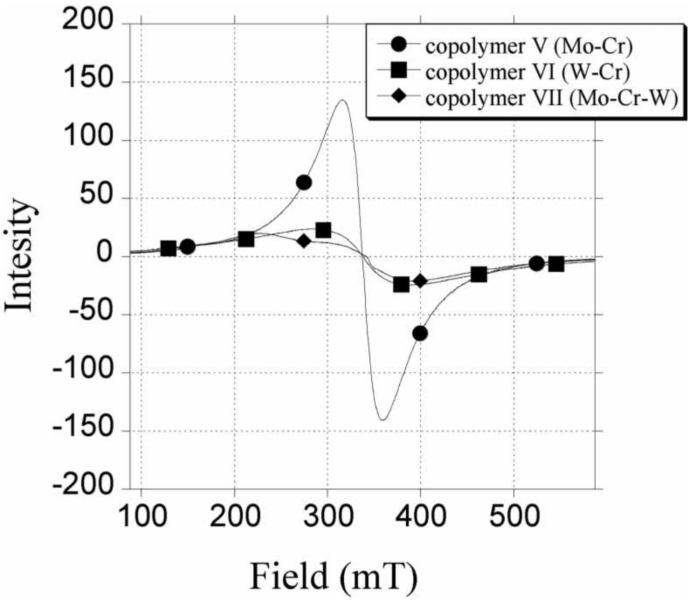


Figure 3. ESR spectra of ternary and quantic hybrid copolymers. Spectra were taken using 10 mg of sample. Measurement conditions: C. Field 337.00 mT, power 1.00 mW, sweep width 250 mT, modulation width 0.5 mT, time constant 0.1 s, temp. room temp.

the peak intensity was in the order of V $>$ VI$>$ VII. It is noted that the peak intensities of V-VII are significantly lower than that of copolymer I, suggesting that the electronic state of a metal varies by the combination of other metals.

Thus, in order to examine the electronic states of the metal atoms in the copolymers, XPS measurements were performed, and the results are summarized in Table 3. The values of a $2p_{3/2}$ of chromium atom in V, VI, and VII were obtained to be 575.16, 575.13, and 574.65 eV, respectively, whereas the value in I was 576.59 eV, indicating that a partial reduction of chromium atom in V, VI, and VII takes place and the chromium atom in VII is most highly reduced. The values of a $3d_{5/2}$ of molybdenum atom in V and VII were 227.66 and 227.62 eV, respectively, which were slightly small compared with that in III (227.78 eV), indicting that a slight reduction of molybdenum atom in V and VII

Table 3
Results of XPS spectra of copolymers

Copolymer		Cr 2p	Mo 3d	W 4f
I	Cr-O system	576.59	—	—
III	Mo-S system	—	227.78	—
IV	W-S system	—	—	30.81
V	Mo-Cr system	575.16	227.66	—
VI	W-Cr system	575.13	—	31.13
VII	Mo-Cr-W system	574.65	227.62	31.08

takes place. The values of a $4f_{7/2}$ of tungsten atom in VI and VII were obtained to be 31.13 and 31.08 eV, respectively, which were higher than that in IV (30.81 eV), indicating that a partial oxidation of the tungsten atom in VI and VII takes place. These findings suggest that an electron transfer from the tungsten atom to the chromium atom takes place, and, especially, an electron transfer process in VII is presumed to be $W \rightarrow Mo \rightarrow Cr$. A reduction of chromium atom by such an electron transfer may decrease the peak intensities in ESR spectra.

Conclusions

In this work, we have examined the effect of the combination of plural metals on the electronic natures of metal—organic moiety hybrid copolymers, and an electron transfer among plural metal atoms was shown to take place. We believe that similar phenomena will be observed in various modes of metal combinations, and our findings will provide a valuable source for new useful electronic and/or magnetic materials.

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