

acetonitrile solution of sulfenamide derivatives, which were determined by analysis of Cole-Cole plot (Figure 5) and Bode plot (Figure 6). As mentioned in figure captions, Figures 5 and 6 are the CBTS cases. As shown in Table 3, the charge transfer resistance of CBTS ( $275.21 \text{ k}\Omega \cdot \text{cm}^2$ ) is larger than DCBS ( $14.24 \text{ k}\Omega \cdot \text{cm}^2$ ), TBBS ( $54.15 \text{ k}\Omega \cdot \text{cm}^2$ ) than TABS ( $0.96 \text{ k}\Omega \cdot \text{cm}^2$ ). Here,  $R_{ct}$  is the characteristic of the corrosion resistance of electrode material in given solution.<sup>18</sup> That is, the larger  $R_{ct}$  is, the better a corrosion resistance is. On the other hand, the double layer capacitance of CBTS ( $7.0 \mu\text{F} \cdot \text{cm}^{-2}$ ) is smaller than DCBS ( $26 \mu\text{F} \cdot \text{cm}^{-2}$ ), TBBS ( $16 \mu\text{F} \cdot \text{cm}^{-2}$ ) than TABS ( $83 \mu\text{F} \cdot \text{cm}^{-2}$ ).  $C_{dl}$  is the characteristic of the corrosion area. That is, the decrease of a double layer capacitance is due to the decrease in the corrosive area.<sup>18</sup> As a result, the weaker the electron donating inductive effect of derivatives is and the smaller the effect of steric hindrance is, the larger  $R_{ct}$  is and the smaller  $C_{dl}$  is, thus, the more a corrosion is prevented. If we compare the results of corrosion current density and corrosion rate in Table 2 with the results of charge transfer resistance and double layer capacitance in Table 3, there are some differences in the corrosion effect of sulfenamide derivatives containing different functional group. That is because a charge transfer resistance at a applied constant potential is said to represent only cathodic current and not the corrosion rate itself.<sup>15,19</sup> That is, when we consider the corrosion effect of sulfenamide derivatives by comparing charge transfer resistances, we can explain the corrosion effect just for the case in which sulfenamide derivatives have the similar functional groups.

## References

1. Altmayer, F. *Met. Fin.* **1987**, *83*, 57.

2. Schueller, G. R. T.; Taylor, S. R. *J. Electrochem. Soc.* **1992**, *139*, 3120.
3. Dobbelaar, J. A. L.; de Wit, J. H. W. *J. Electrochem. Soc.* **1990**, *137*, 2038.
4. Milosev, I.; Metikosi-Huković, M. *Corrosion* **1992**, *48*, 185.
5. Sekine, I.; Sangbongi, M.; Hagiuda, H.; Oshibe, T.; Yuasa, M.; Imahama, T.; Shibata, Y.; Wake, T. *J. Electrochem. Soc.* **1992**, *139*, 3167.
6. Bonnel, A.; Dabosi, F.; Deslouis, C.; Duprat, M.; Keddam, M.; Tribollet, B. *J. Electrochem. Soc.* **1983**, *130*, 753.
7. Hedayat, A.; Postlethwaite, J.; Yannacopoulos, S. *Corrosion* **1992**, *48*, 1027.
8. Kelly, R. G.; Moran, P. J. *J. Electrochem. Soc.* **1987**, *134*, 31.
9. Downey, S. B.; Devereux, O. F. *J. Electrochem. Soc.* **1992**, *139*, 3129.
10. Van Ooij, W. J. V. *Surf. Sci.* **1977**, *68*, 1.
11. Ishikawa, Y.; Kawakami, S. *Rubber Chem. Technol.* **1985**, *59*, 1.
12. Natarajan, R.; Angelo, P.; Gerge, N.; Tamhankar, R. *Corrosion* **1975**, *31*, 302.
13. Walker, G. D. *Corrosion* **1977**, *33*, 262.
14. Zaucker, E.; Bogemann, M. U.S. Patent **1934**, 19286.
15. Rajagopal, V.; Iwasaki, I. *Corrosion* **1992**, *48*, 124.
16. EG & G PARC Application Note 148.
17. Murray, J. N.; Hack, H. P. *Corrosion* **1992**, *48*, 671.
18. Sekine, I.; Kohara, K.; Sugiyama, T.; Yuasa, M. *J. Electrochem. Soc.* **1992**, *139*, 3090.
19. Thompson, N. G.; Lawson, K. M.; Beavers, J. A. *NACE* **1988**, *44*, 585.

## The Chemistry of Rhodium in Polysulfone: Reactions with Various Small Gas Molecules

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$\text{RhCl}[\text{P}(\text{C}_6\text{H}_5)_2]_3$  complexes have been incorporated in polysulfone (PS) as a dispersion medium using cosolvent (THF). The interactions between Rh(I) complexes and polysulfone polymer molecules are examined by infrared spectroscopy and thermal analysis. The chemical reactivity of Rh in PS films has been investigated by reacting Rh sites with CO, H<sub>2</sub>, D<sub>2</sub>, O<sub>2</sub>, NO, C<sub>2</sub>H<sub>2</sub> and C<sub>2</sub>H<sub>4</sub> in the temperature range 25-200°C. Various Rh-carbonyl, -hydride and -nitrosyl species formed in PS films are characterized by their infrared spectra. Rh complexes in PS film show interesting catalytic reactivities in the reactions such as hydrogenation of C<sub>2</sub>H<sub>2</sub> and C<sub>2</sub>H<sub>4</sub>, oxidation of CO, and reduction of NO by CO or H<sub>2</sub> gas under relatively mild conditions.

## Introduction

Metal-containing polymeric materials have been a topic

of considerable interest in recent years because of the burgeoning interests in search for new high-performance materials.<sup>1-6</sup> In addition, these materials have received much at-

tention for the development of the so-called reactive membrane that can function as both catalytic system and separation medium.<sup>7</sup>

It has been reported that some of the typical transition metal complexes can easily be incorporated into ion-exchange resins or neutral organic polymers without introducing typical ligand groups.<sup>8-12</sup> The metal complexes in the polymer matrices showed interesting chemical reactivities toward various small gaseous molecules under relatively mild conditions that are different from those of the corresponding ordinary transition metal complexes. Also, it was surprisingly found that essentially pure H<sub>2</sub> gas could be recovered from a 1:1 mixture of H<sub>2</sub> and CO gases using ruthenium-containing cellulose acetate membrane.<sup>9</sup> This result suggests that the chemical alteration of permeation selectivity could be realized by the incorporation of transition metal complexes into organic polymer membrane. However, little has been reported in the literature on the fundamental reaction chemistry of transition metal complexes in various polymer matrices which is believed to be of great importance for the development of the reactive membrane.<sup>7</sup>

As a part of the continuing focus on this field, RhCl[P(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>]<sub>3</sub> complexes have been incorporated into polysulfone (PS) which is well characterized and known to have good membrane properties.<sup>13,14</sup> The resulting homogeneous Rh-containing polysulfone films are investigated to understand the interactions between the Rh complex and PS polymer molecules, the effect of the metal complex on the thermal property of PS and the chemical reactivities of Rh complex in the polymer matrix. These results are reported in this paper.

## Experimental

Transparent thin films of polysulfone (PS) (Aldrich CO., average M.W.: 30,000) were prepared by dissolving PS resin in tetrahydrofuran (Hayasi Pure Chem. Ind. Ltd.) and casting the thick solution (PS concentration *ca.* 12 wt.%) on a glass plate by a scalpel at room temperature. After slow evaporation of solvent in air, resulting pure PS films were annealed at 110°C overnight. The thickness of the films was controlled to 10-20 μm range, which is convenient for transmission infrared spectroscopic study.

RhCl[P(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>]<sub>3</sub>-containing PS films were made in a similar manner. For a typical preparation of 10 wt.% Rh-containing PS film, 3.6 g of PS and 0.4 g of RhCl[P(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>]<sub>3</sub> (Aldrich Co.) were dissolved in about 100 ml of THF and the resulting mixture was boiled gently in the open for 10 min. Then the solution was warmed to 40-50°C and the solvent was evaporated until the concentration of the solution reached *ca.* 12 wt.%. After 3 hr in air, the yellow-colored homogeneous Rh-containing PS films (designated as [PS-Rh]) were annealed at 110°C overnight. Other PS films containing 5-40 wt.% Rh complexes were prepared in an analogous manner. These films become deformed at about 250°C, but stable below 200°C even for a long period of heating at the temperature range.

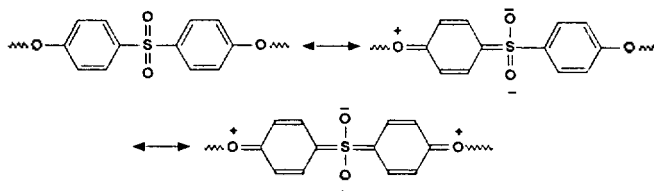
Infrared spectra in 4000-600 cm<sup>-1</sup> or 4000-250 cm<sup>-1</sup> region were recorded on Hitachi 260-10, I-3001, and Nicolet MX-5 spectrometers. UV/Vis spectra for elution tests were recorded on Shimadzu UV-240 spectrometer. A series of measurements for glass transition temperature (*T*<sub>g</sub>) were carried out

by using Dupont Model 910 and General V4.1C thermal analyzer. In a typical DSC scan sequence, *dq/dt* was measured on heating the film by 20°C/min from 30°C to 240°C with 20 mV/cm range. Several DSC scans were made on the cycles of heating at these conditions to remove the effect of thermal history for each sample.

The gases used in this work, carbon-monoxide, hydrogen, oxygen, nitric oxide, deuterium, ethylene and acetylene (Matheson, high purity) were dried by passing them through Drierite gas-drying units before they were added for reactions and most of the gas-phase reactions were monitored and analyzed by infrared spectroscopy. In gas chromatography (Shimadzu GC-R14) for hydrogen and butane gas analyses, we used helium as a carrier gas and a 6ft copper column, containing molecular sieve 5 Å with TCD detector. The transmission electron microscopy was performed on JEM-200CX microscope at 100 kV by direct observation to investigate the films after reduction reaction with H<sub>2</sub> gas. The samples were prepared by embedding the films in epoxy resin and microtoming them.

## Results and Discussion

**Interactions between Rh complex and PS.** It was reported that when a solution of Cu(NO<sub>3</sub>)<sub>2</sub> treated on anionic polymer containing sulfone, the Cu(II) ions were coordinated to oxygen atom of sulfone and nitrogen atoms of amine of the polymer backbone, resulting in the formation of a six membered ring.<sup>15</sup> Quite similar interactions are presumed to occur between Rh(I) ion and PS molecules on the basis of following electronic resonances<sup>13-15</sup>;



These resonances would increase negative charge on the oxygen atoms of sulfone group in PS to a certain extent and correspondingly increase positive charge on the ethereal oxygen atoms. Accordingly, the electron rich oxygen atoms of sulfone groups are likely to be the most probable ligating atoms in PS toward electropositive Rh(I) cations.

This presumed coordination of Rh(I) ions to PS polymer molecules can be evidenced from infrared spectral study; as the oxygen atoms of sulfone group coordinate to Rh(I) ions, the S=O stretching bands shift to lower frequency and the ethereal C-O stretching band to higher frequency.<sup>15,16</sup> As expected, the bands at 1328 and 1112 cm<sup>-1</sup> due to  $\nu_{as(S=O)}$  and  $\nu_{s(S=O)}$  shift to 1320 and 1101 cm<sup>-1</sup>, respectively. Also, the  $\nu_{(C-O)}$  stretching band at 1241 cm<sup>-1</sup> broadens to higher frequency at about 1248 cm<sup>-1</sup>. Accordingly the Rh(I) ions are concluded to interact, at least partially, to oxygen atoms of sulfone groups of PS. In addition, such interactions would occur on intermolecular level and the PS polymer molecules are thought to be cross-linked through such coordination, resulting in the increase of glass transition temperature (*T*<sub>g</sub>) of PS polymer.<sup>17</sup>

The glass transition temperature of 10 wt.% [PS-Rh] film

**Table 1.** Summary of Known *cis*-Rh(CO)<sub>2</sub> Species

Assignment	$\nu(\text{CO})(\text{cm}^{-1})$	Reference
<i>cis</i> -Rh(CO) <sub>2</sub> (A21) <sup>a</sup> Cl	2083, 2022	19
<i>cis</i> -Rh(CO) <sub>2</sub> (PVPy) <sup>b</sup> Cl	2085, 2010	19
<i>cis</i> -Rh(CO) <sub>2</sub> (PBCN) <sup>c</sup> Cl	2088, 2018	19
<i>cis</i> -Rh(CO) <sub>2</sub> (Sil) <sup>d</sup> Cl	2085, 2015	20
<i>cis</i> -Rh(CO) <sub>2</sub> (PSSA) <sup>e</sup> Cl	2095, 2023	21
<i>cis</i> -Rh(CO) <sub>2</sub> (CA) <sup>f</sup> Cl	2085, 2010	10
<i>cis</i> -Rh(CO) <sub>2</sub> (Al <sub>2</sub> O <sub>3</sub> ) <sup>g</sup>	2107, 2042	22

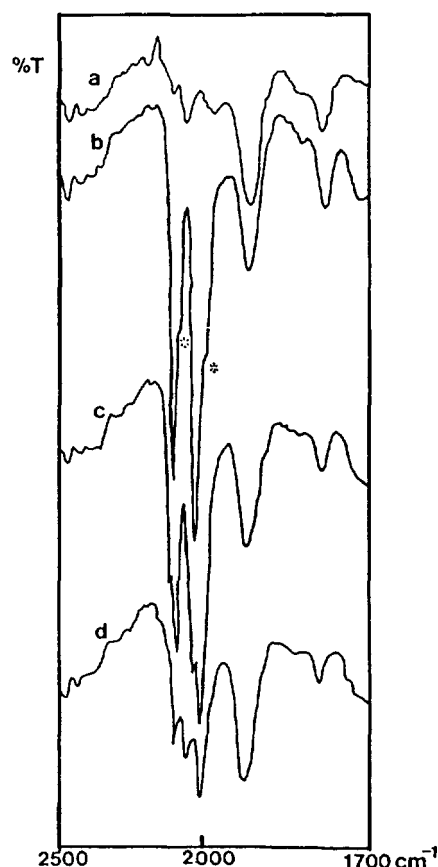
<sup>a</sup>A21 : Poly-N,N-dimethylvinylbenzylamine, <sup>b</sup>PVPy : Poly-2-vinylpyridine, <sup>c</sup>PBCN : Polyvinylbenzylcyanide, <sup>d</sup>Sil : Phosphine ligand bound on the surface of silica, <sup>e</sup>PSSA : Sulfonated linear polystyrene, <sup>f</sup>CA : Cellulose acetate.

increase by 25°C in comparison to that of pure PS ( $T_g$ : 190°C) as expected. But in the cases of 20 and 30 wt.% [PS-Rh] films, they show slight decreases to 210 and 202°C, respectively. This result is quite analogous to those of Ru<sup>12</sup>, Rh<sup>10</sup>, or Pd<sup>11</sup>-containing cellulose acetate films and are explained by assuming that at these high metal concentrations, the metal complexes do not act as cross-linking agents any more but rather cause an increase in the mobility of polymer molecules, leading to the decrease of  $T_g$ . Similar result was reported in the study of sulfonated polysulfone ionomers.<sup>18</sup>

In order to understand further the interactions between Rh metal ion and PS polymer molecules in the point of solution chemistry, the films are immersed in methanol at room temperature for 24 hr and then dried to remove solvent molecules at 110°C in vacuum for 24 hr. The yellow color of the film remains unchanged. Upon treatment of these films with CO (600 torr) at 200°C for 2 days, four  $\nu_{\text{CO}}$  bands at 2090, 2070 (sh), 2010, and 1990 (sh)  $\text{cm}^{-1}$  (see later section) appear in their infrared spectra. The intensities of these bands are weaker by about 20%, compared with those of corresponding [PS-Ru] films without dipping in methanol solution. This result indicates that there is some elution of Rh metal complexes from PS polymer matrix to the same extent and is confirmed by UV/Vis spectroscopy study. It is interesting to note that in the case of cellulose acetate films containing same Rh complexes, only phosphine ligands are removed from the polymer matrix under the same conditions.<sup>10</sup>

**Reaction of Rh in PS with CO.** When 10 wt.% [PS-Rh] films, dried at 120°C in vacuum for 12 hr, are treated with CO (600 torr) at 200°C for 24 hr, four strong bands at 2090, 2070 (sh), 2010, 1990 (sh)  $\text{cm}^{-1}$  are observed in their infrared spectra. In the similar reactions as a function of CO gas pressure or reaction temperature, the two bands at 2090 and 2010  $\text{cm}^{-1}$  always show up simultaneously with equal intensities and are quite similar in shape to those of other polymer- or inorganic oxide- supported Rh-carbonyl species which are characteristically assigned to *cis*-Rh(I)(CO)<sub>2</sub>. Listings of the examples are given in Table 1 (see Figure 1).

Two shoulder bands at 2070 and 1990  $\text{cm}^{-1}$  with equal intensity are quite weak in their intensities when the thickness of the film is less than about 12  $\mu\text{m}$ , but they are strong

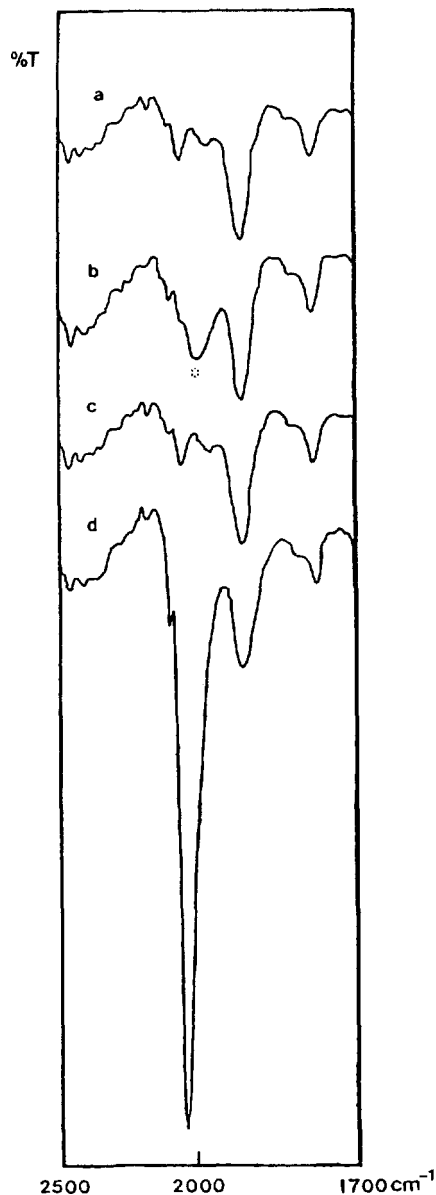


**Figure 1.** IR spectra for the formation of Rh-carbonyl species and their reactions in polysulfone a. 20 wt.% [PS-Sh] film, b. after reaction with CO (600 torr), c, d. after reaction with H<sub>2</sub> (600 torr).

when the films are thick or Rh metal complex concentration is over 20 wt.%. Also, these bands do not appear when the film is reexposed to CO gas after consecutive reactions with H<sub>2</sub> and O<sub>2</sub> gases (see Figure 3).

Considering the effects of film thickness and metal concentration on the intensities of the shoulder bands, some of Rh complexes introduced into PS are believed to exist as only additives without the aforementioned direct interaction with PS and to form *cis*-Rh(CO)<sub>2</sub> species by the reaction with CO. At this stage, it is not clear why the bands in question do not reappear after consecutive reactions with H<sub>2</sub> and O<sub>2</sub> gases. But it is thought that after such treatments its interactions with PS are increased; as a result, the Rh complexes do not exist as additives any more.

Thus, the two bands at 2900 and 2010  $\text{cm}^{-1}$  are assigned to *cis*-Rh(CO)<sub>2</sub> formed in PS and the two shoulder bands at 2070 and 1990  $\text{cm}^{-1}$  to similar *cis*-Rh(CO)<sub>2</sub> species, but without direct interactions with PS molecules. The two shoulder bands remain almost unchanged upon reaction with H<sub>2</sub> gas or upon desorption at 150°C under vacuum, but the intensities of the other bands at 2090 and 2010  $\text{cm}^{-1}$  are significantly reduced upon the reactions under the same conditions, revealing that these Rh-carbonyls are quite reactive. These results are quite interesting in contrast with the reaction chemistry of the same Rh complex without polymer sup-

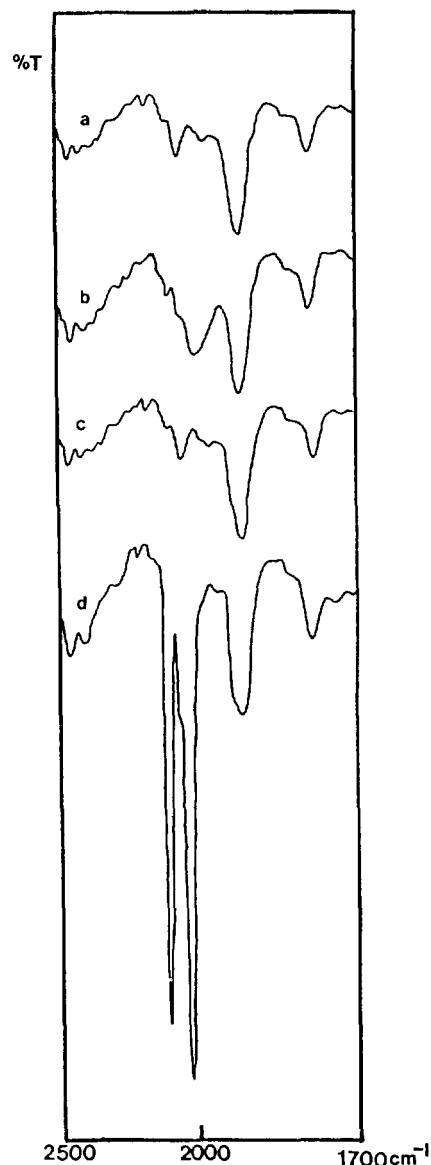


**Figure 2.** IR spectra showing the formations of Rh-hydride and Rh(0)-CO species in polysulfone a. 20 wt% [PS-Rh] film, b. after reaction with H<sub>2</sub> (600 torr), c. from b, after 3 hr in air, d. after reaction with CO (600 torr).

port, in which only Rh[(CO)Cl[P(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>]<sub>2</sub>] is formed and resulting Rh-carbonyl is not reactive to H<sub>2</sub> or O<sub>2</sub> gases under the similar conditions.<sup>23</sup>

**Reactions of Rh in PS with H<sub>2</sub> and CO.** When 10 wt.% [PS-Rh] films are exposed to H<sub>2</sub> (600 torr) at 200°C, the light yellow color of the film changes to dark brown. This color change is typical of metal-particle formation in polymer matrices.<sup>20,21</sup>

In infrared spectra of the resulting films, a weak band at 1995 cm<sup>-1</sup> is observed, which can be attributed to rhodium monohydride. After 3 hr in air, the band disappears and this result is consistently observed in repeated experiments. This rhodium hydride is confirmed by finding corresponding rhodium-deuteride (ν(Rh-D): 1440 cm<sup>-1</sup>) (see Figure 2).



**Figure 3.** IR spectra for the cyclic reaction in PS with H<sub>2</sub>, O<sub>2</sub>, and CO consecutively a. 20 wt% [PS-Sh] film, b. after reaction with H<sub>2</sub>, c. after reaction with O<sub>2</sub>, d. after reaction with CO (gas P: 600 torr).

Compared to known Rh(I) and Rh(III) hydride complexes<sup>24-26</sup>, usually stable in air at room temperature, the Rh-hydride species formed in PS is quite active in air at the ambient temperature and is believed to be Rh(0)-monohydride. It is interesting to point out that the gas phase reduction reaction of free RhCl[P(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>]<sub>3</sub> in solid state with H<sub>2</sub> produced RhH<sub>2</sub>Cl[P(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>]<sub>3</sub> (ν(Rh-H): 2078, 2013 cm<sup>-1</sup>)<sup>27</sup>. In ethanol solution, the same Rh complex was reported to be transformed to RhH[P(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>]<sub>3</sub> (ν(Rh-H): 2020 cm<sup>-1</sup>) upon reduction reaction with NaBH<sub>4</sub> in the presence of P(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>.<sup>28</sup>

In transmission electron microscopy study of the [PS-Rh] films after reduction reaction with H<sub>2</sub> gas, a wide range of Rh metal particles from ca. 50 Å upto 400 Å in diameter are observed and this result suggests that there is very active Brownian motion-type behavior of the produced Rh me-

tal atoms in PS, giving various metal particles in different sizes<sup>29</sup>. It is noteworthy that there was no Rh metal particle formation in case of silica supported  $\text{RhCl}[\text{P}(\text{C}_6\text{H}_5)_3]_3$  under hydrogen for 1 month.<sup>20</sup>

When the [PS-Rh] films are subsequently treated with CO (600 torr) at 200°C for 24 hr after reduction reaction with H<sub>2</sub> gas, a strong band at 2040 cm<sup>-1</sup> appears in their infrared spectra (see Figure 2). This band is easily assigned to Rh(0)-monocarbonyl since corresponding  $\nu(\text{CO})$  bands appear characteristically in the 2010-2080 cm<sup>-1</sup> region.<sup>21,30-32</sup> Besides, it should be noted that the described reduction conditions is relatively mild because typical reduction temperature of Rh(I) supported in inorganic-oxide is over 300°C. Accordingly almost all Rh(I) complexes are concluded to be reduced to Rh(0) at the described conditions. But it should be mentioned that partial reduction reaction of Rh(I) complexes is also possible by controlling the reaction conditions. The band at 2040 cm<sup>-1</sup> remains unchanged upon reaction with H<sub>2</sub> gas (700 torr) at 200°C, but decreases significantly in its intensity upon reaction with O<sub>2</sub> gas under the same conditions. The product of the latter case is found to be CO<sub>2</sub>.

**Reaction of Rh in PS with O<sub>2</sub>.** When the [PS-Rh] films are exposed to O<sub>2</sub> (600 torr) at 200°C for 3 days, there are no appreciable changes in color of the films and in their infrared spectra except the effect of dehydration. When the same films are treated with CO at the same conditions, only four  $\nu(\text{CO})$  bands at 2090, 2070 (sh), 2010, and 1990 (sh) cm<sup>-1</sup> as noted above appear, indicating that there is no oxidation of Rh(I) to Rh(III), nor formation Rh=O at all. The two bands at 2090 and 2010 cm<sup>-1</sup> decrease gradually in their intensities when reacted with O<sub>2</sub> (600 torr) at 180°C, but are not removed completely even after 3 day reaction under the same conditions. This result is consistently obtained when the [PS-Rh] films are treated with CO, O<sub>2</sub>, CO, and O<sub>2</sub> gases in a cyclic manner. The product of these reactions is easily identified as CO<sub>2</sub> by gas phase infrared spectroscopy.

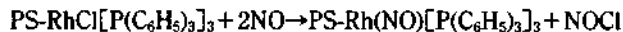
When the [PS-Rh] films, after complete reduction by H<sub>2</sub> gas, are left at ambient condition for 5 days, and then are reexposed to CO (660 torr) at 200°C for 1 day, there is no 2040 cm<sup>-1</sup> band due to Rh(0)-CO species but the four bands at 2090, and 2010 cm<sup>-1</sup> appear in strong intensity, indicating that almost all Rh(0) atoms are oxidized to Rh(I) (see Figure 3). The same result is obtained when the reduced [PS-Rh] film with H<sub>2</sub> gas is treated with O<sub>2</sub> and CO gases consecutively under the same conditions as above. Accordingly, it is imagined that during the reaction process, the Rh(I)-O<sub>2</sub> species be formed in PS film, and several attempts to find any evidence for that are tried but fail. However, such oxidation from Rh(0) to Rh(I) is not believed unusual at the described conditions.

**Reaction of Rh in PS with NO.** The gas phase of reaction of  $\text{RhCl}[\text{P}(\text{C}_6\text{H}_5)_3]_3$  with NO in solid state was reported to produce  $\text{Rh}(\text{NO})(\text{NO}_2)\text{Cl}[\text{P}(\text{C}_6\text{H}_5)_3]_3$ .<sup>33</sup> But when the same Rh complexes in PS film are treated with NO gas (200 torr) at room temperature, there is a weak NO adsorption band at 1640 cm<sup>-1</sup> in the infrared spectra, which can be assigned to Rh-mononitrosyl with bent geometry on the base of various reported Rh-nitrosyl complexes.<sup>34,35</sup> Analogous reaction with prior reduction of the film by H<sub>2</sub> (600 torr) gas at 200°C for 1 day gives exactly same result. This result

**Table 2.** Summary of Rh-Carbonyl, Hydride and Nitrosyl Species formed in PS

$\nu(\text{cm}^{-1})$	Assignment
2090, 2010	<i>cis</i> -PS-Rh(I)(CO) <sub>2</sub>
2040	PS-Rh(0)CO
1995	PS-Rh(0)H
1640	PS-Rh(NO)

leads us to believe that there is reductive nitrosylation in the direct reaction of [PS-Rh] film with NO gas without prior reduction treatment<sup>34</sup> as below:



The band at 1640 cm<sup>-1</sup> is 30 cm<sup>-1</sup> higher than that of the free  $\text{Rh}(\text{NO})[\text{P}(\text{C}_6\text{H}_5)_3]_3$  complex<sup>35</sup>, but the interaction of Rh with PS polymer molecules is believed to result in such shift. The band in question almost disappears in the spectrum when the films are left in air for 1 day but reappears upon reaction with NO.

The types of PS-Rh carbonyls, hydride and nitrosyl discussed and their frequencies are listed in Table 2.

**Catalytic reactivities of Rh in PS.** Several cyclic reactions of [PS-Rh] films with hydrogen, carbon monoxide, and oxygen give rise to the same results as above without any decrease in reactivities of rhodium under the described conditions. Also small rhodium metal particles are observed to be formed in PS upon the reduction reaction with hydrogen, which are expected to be active catalyst or catalytic precursor. Therefore, a few simple catalytic reactions in static state are carried out using the [PS-Rh] films after reduction reaction with H<sub>2</sub> gas at 200°C for 1 day to test their catalytic potentials in a preliminary way.

**Hydrogenation of ethylene and acetylene.** When a 1:1 mixture of ethylene and hydrogen (total pressure: 1 atm) in about 500 ml flask is reacted at 150°C with 0.05 g of [PS-Rh] film, after 5 days complete conversion of ethylene to ethane is easily identified by the infrared spectroscopic analysis for the reaction gas mixture. There is no appreciable decrease in catalytic activity of [PS-Rh] film after repeated hydrogenation reactions. The analogous reactions in high pressure (total P.: 100 psi) give the same results as above. A 1:2 mixture of acetylene and hydrogen gases (total P.: 150 psi) reacted in the same manner as above and, after 5 day reaction, complete hydrogenation of acetylene to ethane is observed. Such conversion is easily identified by gas phase infrared spectra.

**Reaction of acetylene with hydrogen at low pressure.** As noted above, simple hydrogenation reaction of acetylene with H<sub>2</sub> gas is expected even at low gas pressure. But surprisingly, butane is found to be the major product from the 5 day reaction between acetylene (200 torr) and hydrogen (400 torr) at 150°C. Of course, very small amount of ethane is also identified. The major product is easily confirmed and distinguished from other gas molecules because of its characteristic infrared adsorption bands, arising from the C-H stretching and the C-H stretching and the C-H deformation of -CH<sub>2</sub>- groups. However, there are no olefins in the product nor any evidence for coordinated unsaturated

species to Rh metals.

**Oxidation of carbon monoxide by oxygen gas.** A 2:1 mixture of CO and O<sub>2</sub> (total P.: 600 torr) is reacted as above and complete conversion of CO to CO<sub>2</sub> is observed after 5 day reaction. After the reaction, the used [PS-Rh] films are examined by infrared spectroscopy but there are no noticeable changes except the adsorption bands due to the rhodium-carbonyls as previously discussed.

**Water-gas shift reaction.** CO (1 atm) and slightly excess of equivalent H<sub>2</sub>O are reacted in the same flask at 150 °C; but in this case the reaction flask is insulated to avoid condensation of water, and the reaction mixture is frequently monitored by infrared spectroscopy. During the reaction, the intensity of the band due to ν(CO) at 2143 cm<sup>-1</sup> gradually decreases and those of the bands due to CO<sub>2</sub> increase correspondingly. After 7 days, the conversion is completed.

**NO reduction reactions.** It is well known that NO gas is catalytically reduced by CO or H<sub>2</sub> gas. Also, we reported that RhCl[P(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>]<sub>3</sub> complexes incorporated into neutral cellulose acetate film completely convert NO to N<sub>2</sub>O and CO<sub>2</sub> by reaction with CO, and to N<sub>2</sub>O and H<sub>2</sub>O by reaction with H<sub>2</sub> under the relatively mild condition.<sup>36</sup> Interestingly, there were no typical surface intermediates such as metal-cyanide or metal-isocyanate during the catalytic reactions.<sup>36-39</sup>

In this study, analogous NO reduction reactions by CO or H<sub>2</sub> gas at 150°C (total P.: 70 torr) are carried out using 0.1 g of [PS-Rh] films but, conversion of NO to N<sub>2</sub>O is only about 50-60% even though they are reacted over 7 days. At this stage, it is not clear how the polymer matrix affects the reaction chemistry of a transition metal complex. Further comparative study should be followed to find the reasons.

## Conclusions

RhCl[P(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>]<sub>3</sub> complexes have been incorporated into polysulfone without introduction of any typical pendant ligand groups to polymer backbone and the resulting yellow-colored transparent films with 10-20 wt% Rh complex loading are found to be stable upto 200°C. On the basis of infrared spectral and thermal analysis data, the rhodium metal cations are supposed to interact with the oxygen atoms of the sulfone groups of PS and to act as cross-linking agents for PS molecules. The reaction of 10 wt.% [PS-Rh] films with CO and/or H<sub>2</sub> gas at about 200°C results in two different Rh-carbonyl species which are assigned to *cis*-PS-Rh(I)(CO)<sub>2</sub>[ν(CO): 2090 and 2010 cm<sup>-1</sup>] and PS-Rh(0)[ν(CO): 2040 cm<sup>-1</sup>]. Treatment of the [PS-Rh] films with H<sub>2</sub> at 200°C produced a wide range of small Rh metal particles from 50 Å to 400 Å in diameter and active rhodium hydride [ν(Rh-H): 1995 cm<sup>-1</sup>] species, indicating that the Rh(I) complexes are reduced to Rh(0). These Rh(0) species are found to be reoxidized by reaction with O<sub>2</sub> or by standing them in air. But there is no spectroscopic evidence for the interactions between rhodium metal and oxygen molecules.

The Rh complexes supported by polysulfone show interesting catalytic reactivities in the temperature range of 150-200 °C in the hydrogenation of ethylene and acetylene, oxidation of carbon monoxide, and water-gas shift reactions. These catalytic activities under relatively mild conditions are believed to arise from the small Rh metal particles formed in PS polymer matrix. Further comparative studies on the reac-

tion chemistry of polysulfone-supported transition metals and their catalytic activities are in progress in our laboratory.

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## References

1. Mark, J. E.; Allcock, H. R.; West, R. *Inorganic Polymer*; Prentice-Hall Inc.: 1992.
2. Ro, K. S.; Woo, S. I. *J. Mol. Catal.* 1990, 61, 27.
3. Costa, G.; Piaggio, P. *J. Mol. Catal.* 1990, 59, 39.
4. Nichida, M.; Ishiyama, I.; Kurokawa, Y. *Reactive Polymers* 1991, 14, 207.
5. Feldman, J.; Orchin, M. *J. Mol. Catal.* 1990, 63, 213.
6. Grunewald, G. C.; Drago, K. D.; Clank, J. L.; Livesey, A. B. *J. Mol. Catal.* 1990, 60, 239.
7. See special issue on *Catalytic Membranes; Applied Catalysis* 1993, 96, 1-98.
8. Shim, I. W.; Mattera, Jr., V. D.; Risen, Jr., W. M. *J. Catal.* 1985, 94, 531.
9. Lee, K. I.; Hwang, S. T.; Shim, I. W. *J. Membrane Sci.* 1991, 60, 207.
10. Park, K. M.; Shim, I. W. *J. Appl. Polym. Sci.* 1991, 42, 1361.
11. Hwang, S. T.; Shim, I. W. *J. Appl. Polym. Sci.* 1992, 46, 603.
12. Chu, J. W.; Shim, I. W. *J. Mol. Catal.* 1993, 78, 189.
13. Mark, H. F.; Gaylord, N. G. *Polysulfones, Encyc. Polym. Sci. & Tch.* 1964, 11, 447.
14. Sada, E.; Kumazawa, H.; Xu, P.; Inoue, H. *J. Appl. Polym. Sci.* 1990, 41, 2427.
15. Barbucci, R.; Casolaro, M.; Corezzi, S.; Reginato, G. *Polymer*, 1986, 27, 1986.
16. Barnard, D.; Fabian, J. M.; Koch, H. P. *J. Chem. Soc.* 1949, 2442.
17. Andrady, A. L.; Sefcik, M. O. *J. Appl. Polym. Sci.* 1984, 29, 3561.
18. Drzewinski, M.; Macknight, W. J. *J. Appl. Polym. Sci.* 1985, 30, 4753.
19. Rollmann, L. D. *Inorg. Chem. Acta*, 1972, 6, 137.
20. Bartolin, M.; Graillat, C. H.; Guyot, A.; Condurier, G.; Brandiera, J.; Naccahe, C. *J. Mol. Catal.* 1977/8, 3, 17.
21. Mattera, Jr., V. D.; Squattrito, P. J.; Risen, Jr., W. M. *Inorg. Chem.* 1984, 23, 3587.
22. Basu, P.; Panayotov, D.; Yates, J. T. *J. Am. Chem. Soc.* 1988, 110, 2074.
23. Wilkinson, G. (Ed.), *Comprehensive Organometallic Chemistry*; Pergamon: New York, 1982, 5, 277-540.
24. Thomas, K.; Osborn, J. A.; Powell, A. R.; Wilkinson, G. *J. Chem. Soc.* 1968, (A), 1801.
25. Ito, T.; Kitazume, S.; Yamamoto, A.; Ikeda, S. *J. Am. Chem. Soc.* 1970, 92, 3011.
26. Kingston, J. V.; Scollary, G. R. *J. Chem. Soc. Chem. Comm.* 1970, 670.
27. Osborn, J. A.; Jardine, F. H.; Wilkinson, G.; Young, J. F. *J. Chem. Soc.* 1966, (A), 1711.
28. Holah, L. G.; Hughes, A. N.; Hui, B. C. *Can. J. Chem.* 1975, 53, 3669.
29. Masson, A.; Metois, J. J.; Kern, R. *Surf. Sci.* 1971, 27, 463.

30. Brown, M. F.; Gonzalez, R. D. *J. Phys. Chem.* 1976, 80, 1731.
31. Betta, D. *J. Phys. Chem.* 1975, 79, 2519.
32. Bell, A. T.; Kuznetsov, V. L.; Yermakov, Y. I. *J. Catal.* 1980, 65, 374.
33. Ahmad, N.; Levison, J. J.; Robinson, S. D.; Uttley, M. F. *Inorg. Synth.* 1974, 15, 45.
34. Lee, I. M. *Progress in Chem. & Chem. Engineering Industry, Korean Chem. Soc.* 1991, 31, 498.
35. Wilkinson, G. Ed.; *Comprehensive Coordination Chemistry*; Pergamon Press: New York, 1987, 4, 1066-1074.
36. Kim, S. J.; Shim, I. W. submitted to *J. Mol. Catal.* 1992.
37. McCabe, R. W.; Wong, C. *J. Catal.* 1990, 121, 422.
38. Novak, E.; Solymosi, F. *J. Catal.* 1990, 125, 112.
39. Liang, J.; Wang, H. P.; Spicer, L. D. *J. Phys. Chem.* 1985, 89, 5840.

## Reaction of Bis(diethylamino)aluminum Hydride in Tetrahydrofuran with Selected Organic Compounds Containing Representative Functional Groups

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Bis(diethylamino)aluminum hydride was utilized in a systematic study of the approximate rates and stoichiometry of the reaction of excess reagent with 55 selected organic compounds containing representative functional groups under standardized conditions (THF, 0°C, reagent to compound=4:1) in order to define the characteristics of the reagent for selective reductions. The reducing action of BEAH was also compared with that of the parent aluminum hydride. The reducing action of the reagent is quite similar to that of aluminum hydride, but the reducing power is much weaker. Aldehydes and ketones were readily reduced in 1-3 h to the corresponding alcohols. However, unexpectedly, a ready involvement of the double bond in cinnamaldehyde was realized to afford hydrocinnamyl alcohol. The introduction of diethylamino group to the parent aluminum hydride appears not to be appreciably influential in stereoselectivity on the reduction of cyclic ketones. Both *p*-benzoquinone and anthraquinone utilized 2 equiv of hydride readily without evolution of hydrogen, proceeded cleanly to the 1,4-reduction products. Carboxylic acids and acid chlorides underwent reduction to alcohols slowly, whereas cyclic anhydrides utilized only 2 equiv of hydride slowly to the corresponding hydroxylacids. Especially, benzoic acid with a limiting amount of hydride was reduced to benzaldehyde in a yield of 80%. Esters and lactones were also readily reduced to alcohols. Epoxides examined all reacted slowly to give the ring-opened products. Primary and tertiary amides utilized 1 equiv of hydride fast and further hydride utilization was quite slow. The examination for possibility of achieving a partial reduction to aldehydes was also performed. Among them, benzamide and *N,N*-dimethylbenzamide gave *ca.* 90% yields of benzaldehyde. Both the nitriles examined were also slowly reduced to the amines. Unexpectedly, both aliphatic and aromatic nitro compounds proved to be relatively reactive to the reagent. On the other hand, azo- and azoxybenzenes were quite inert to BEAH. Cyclohexanone oxime liberated 1 equiv of hydrogen and utilized 1 equiv of hydride for reduction, corresponding to *N*-hydroxycyclohexylamine. Pyridine ring compounds were also slowly attacked. Disulfides were readily reduced with hydrogen evolution to the thiols, and dimethyl sulfoxide and diphenyl sulfone were also rapidly reduced to the sulfides.

### Introduction

The dialkylamino-substituted derivatives of lithium aluminum hydride have appeared to exhibit reducing properties significantly different from those of the parent reagent.<sup>1</sup> For example, lithium tris(diethylamino)aluminum hydride (LT-DEA) has proven to be a valuable selective reducing agent for transformation of carboxylic acids,<sup>2</sup> esters,<sup>3,4</sup> primary carboxamides,<sup>4,5</sup> tertiary carboxamides<sup>4,6</sup> and aromatic nitriles<sup>4,7</sup> to the corresponding aldehydes.

Similarly, the dialkylaminoaluminum hydrides are expected to exhibit reducing properties different from those of the parent reagent. In fact, as Mukaiyama and coworker first reported in 1970s, the dialkylaminoaluminum hydrides were

shown to reduce carboxylic acids and esters to aldehydes in good yields.<sup>8,9</sup> Accordingly, it appeared desirable to undertake a systematic exploration of the reaction of bis(diethylamino)aluminum hydride (BEAH), one of the class of dialkylamino derivatives, with organic compounds containing representative functional groups, under standardized conditions in order to define its reducing characteristics. The reducing properties of BEAH are also compared to those of the parent aluminum hydride.

### Results and Discussion

The usual laboratory procedure for preparation of dialkylaminoaluminum hydrides involves the reaction of lithium alu-