

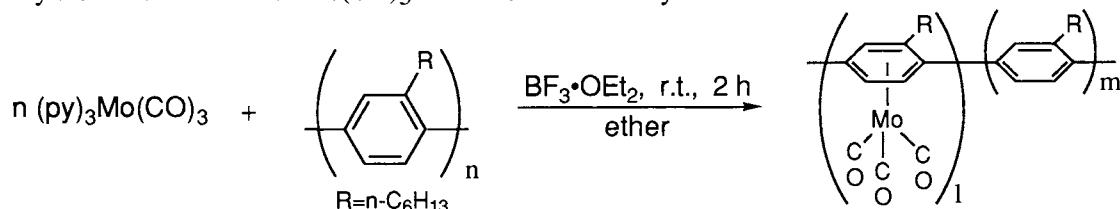
A Novel π -Conjugated Organometallic Polymer,
Molybdenum Tricarbonyl Modified Poly(n-hexylphenylene)

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Electrochemical and electrical properties of soluble poly(n-hexylphenylene) bound to $\text{Mo}(\text{CO})_3$ were investigated by cyclic voltammetry, spectro-electrochemistry and four-electrode voltammetry. Oxidation of the Mo complex polymer occurs at $E^0' = 0.51$ V vs. Ag/Ag^+ , which is less positive than that of free poly(n-hexylphenylene) by *ca.* 0.3 V. At this potential, conductivity of the Mo complex polymer increases. The band gap of the polyphenylene does not change significantly by coordinating to Mo.

Poly(*p*-phenylene) is a representative π -conjugated organic polymer consisting of only C and H,¹⁾ and its benzene ring unit can be a π -ligand.²⁾ It is interesting to see how the physical and chemical properties of π -conjugated systems by forming π -bonding with transition metals. Actually, preparation of chromium and molybdenum carbonyl complexes of poly(*p*-phenylene) and their ESCA, IR and conductivity analyses have been reported by Yaniger *et al.*³⁾ However, insolubility of poly(*p*-phenylene) and its complexes limits the kind of techniques available for their characterization. We have recently reported the synthesis of poly(n-alkylphenylene)s soluble in common organic solvents.⁴⁾ This good solubility enables the polyphenylenes utilizable in homogeneous reactions as ligating reagents. Characterization of the formed organometallic polymer can be made by regular analytical methods if the product is also soluble. We here presents the first example of soluble organometallic π -conjugated polymer, which is formed by the reaction of poly(n-hexylphenylene) (PHP) with tripyridinemolybdenum tricarbonyl. The degree of change in electrochemical properties of the π -conjugated system by the π -interaction with $\text{Mo}(\text{CO})_3$ is focused in this study.



The molybdenum tricarbonyl units were introduced to PHP by the reaction with $(\text{py})_3\text{Mo}(\text{CO})_3$ and $\text{BF}_3\cdot\text{OEt}_2$ in ethyl ether at room temperature for 2 h.^{5,6)} The formed complex polymer shows $\nu(\text{C}\equiv\text{O})$ bands at 1964, 1937, 1888 and 1829 cm^{-1} in the IR spectrum and a 290 nm peak assignable to intramolecular charge transfer band between the molybdenum and aromatic rings⁷⁾ overlapped with 270 nm band due to $\pi-\pi^*$ of polyphenylene in the UV-VIS spectrum, indicative of (arene) $\text{Mo}(\text{CO})_3$ -type structure⁸⁾ (thus the polymer is

abbreviated as PHP-Mo(CO)₃, hereafter). The PHP-Mo(CO)₃ is soluble in common organic solvents with low polarity such as dichloromethane or THF, but insoluble in polar solvents such as acetonitrile or methanol.

Figure 1 represents cyclic voltammograms of free PHP and PHP-Mo(CO)₃ in which the ratio of Mo(CO)₃ units to benzene rings estimated from elemental analysis and IR peak intensity analysis⁶⁾ is 1/4.8. The polymers were coated on indium-tin oxide (ITO)-coated glass electrodes by spin coating (film thickness was *ca.* 300 nm). A quasi-reversible redox wave appears at $E^{0'} = 0.51$ V vs. Ag/Ag⁺ (10 mmol dm⁻³ AgClO₄ in 0.1 mol dm⁻³ n-Bu₄NBF₄-MeCN) in the voltammogram of PHP-Mo(CO)₃ in 0.1 mol dm⁻³ KPF₆-propylene carbonate (Fig. 1b), which is not seen in the voltammogram of free PHP (Fig. 1a). On the other hand, the redox wave at 0.8-1.2 V vs. Ag/Ag⁺ characteristic of free PHP is scarcely seen in the voltammogram of PHP-Mo(CO)₃. The $E^{0'}$ value of PHP-Mo(CO)₃ is similar to the $E^{0'}$ values reported for (arene)M(CO)₃ (M = Cr, Mo).⁹⁾ The shift in oxidation potential should correspond to the decrease of HOMO energy of (arene)Mo(CO)₃ compared to free arene, as has been demonstrated by experimental¹⁰⁾ and theoretical studies.¹¹⁾

A question arose from the difference in electrochemical characteristics of PHP-Mo(CO)₃ from free PHP as noted above is whether the potential of polaronic state formation for the π -conjugated system and/or the conductivity increase also be shifted by interacting with Mo(CO)₃ moieties. Figure 2 displays the change in VIS spectra of PHP-Mo(CO)₃ coated on ITO with shifting the potential in the positive direction from 0 V vs. Ag/Ag⁺. The spectrum at 0.5 V shows only a little difference from that at 0 V, but significant absorption decreases at the short wavelength region (λ_{\min} in Fig. 2b is 420 nm) and increases in the long wavelength region (λ_{\max} in Fig. 2b is 620 nm) are observed from 0.6 V vs.

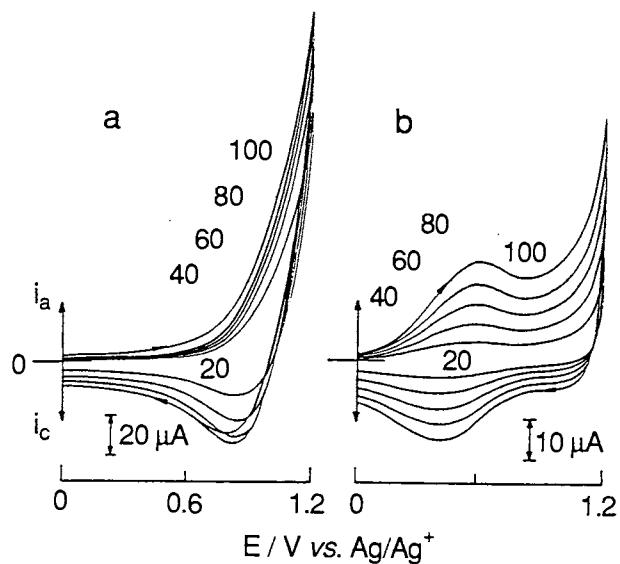


Fig. 1. Cyclic voltammograms of PHP / ITO (a) and PHP-Mo(CO)₃ / ITO (b) in 0.1 mol dm⁻³ KPF₆-propylene carbonate. Numbers in the figure denote the scan rate in mV s⁻¹.

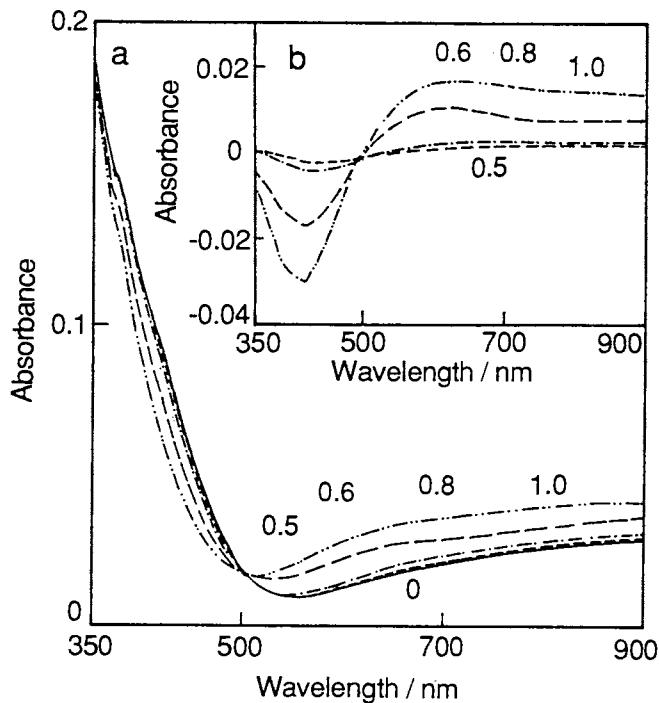


Fig. 2. VIS spectra of PHP-Mo(CO)₃ / ITO in 0.1 mol dm⁻³ n-Bu₄NClO₄-MeCN at the potentials given in V vs. Ag/Ag⁺ in the figure (a) and their differences from the spectrum at 0 V vs. Ag/Ag⁺ (b).

Ag/Ag^+ (Fig. 2b). These changes are almost consistent with those of free PHP.^{4,12} The band gap, E_g , estimated from the isobestic point in the spectra of PHP- $\text{Mo}(\text{CO})_3$ in Fig. 2b is 2.4 eV, and E_g estimated from $h\nu$ vs. $(\alpha h\nu)^2$ plots¹³ is 2.7 eV.

These values are a little smaller or same compared to those of free PHP, 2.6 or 2.7 eV obtained by the respective method. It is postulated from these results that the oxidation reaction of PHP- $\text{Mo}(\text{CO})_3$ at $E^0' = 0.51 \text{ V vs. Ag}/\text{Ag}^+$ does not cause the formation of the polaronic state in the π -conjugated chain of PHP- $\text{Mo}(\text{CO})_3$; that is, the positive charges generated by the oxidation are localized at the Mo complex sites.

Changes in conductivity of free PHP and PHP- $\text{Mo}(\text{CO})_3$ with the potential shift were measured by four electrode voltammetry using Pt interdigitated microarray (IDA) with 50 fingers with $10.0 \mu\text{m}$ width, 2.0 mm length, and $2.0 \mu\text{m}$ gap between the fingers as two working electrodes.¹⁴ Potentials of both working electrodes were scanned at 2 mV s^{-1} with holding the potential difference of 300 mV (W1 is more positive than W2) with a bipotentiostat and a function generator. The voltammograms obtained for the both electrodes are displayed in Fig. 3. The overall current contains two components; one is due to the redox reaction of the polymer mainly flowing between working and counter electrodes and the other due to electric conductivity of the polymer coating flowing between two working electrodes. At a slower scan rate, the former component is less significant and the voltammogram at both electrodes become more symmetrical. Thus, the current values in the opposite sign between W1 and W2 as shown in Fig. 3a for free PHP and at potentials of W1 between 0.5 and 0.8 V in Fig. 3b for PHP- $\text{Mo}(\text{CO})_3$ represent the increase in electrical conductivity of the polymers. A clear difference in the potential showing the conductivity increase is seen between free and Mo-bound PHP, and this corresponds to the discrepancy between their oxidation potentials shown in the cyclic voltammograms (Fig. 1). As the spectro-electrochemical behaviors shown in Fig. 2 do not indicate the polaronic state formation at $E^0' = 0.51 \text{ V vs. Ag}/\text{Ag}^+$ for PHP- $\text{Mo}(\text{CO})_3$, redox conduction ascribed to electron hopping between oxidation and reduction sites accompanying ionic motion¹⁵ should be dominant around this potential.

We are grateful to NTT Basic Research Laboratory for supplying high-quality IDA electrodes. This research was supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science and Culture, Japan (No. 04640585) and a Iketani Research Grant.

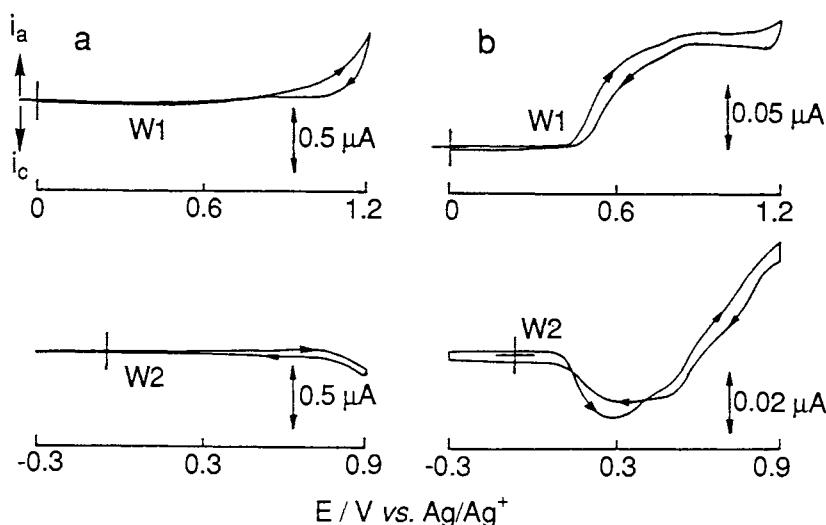


Fig. 3. Four-electrode cyclic voltammograms of PHP / IDA (a) and PHP- $\text{Mo}(\text{CO})_3$ / IDA (b). Potential difference between two working electrodes (W1, W2) was 0.3 V and the scan rate was 2 mV s^{-1} .

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(Received July 23, 1992)