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REVERSIBLE COORDINATION OF MOLECULAR NITROGEN TO POLYMERIC BENZENECARBONYLCHROMIUM COMPLEXES

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ABSTRACT

Polymeric benzenetricarbonylchromium complexes were synthesized by radical copolymerization of benzyl acrylatetetracarboxylchromium with styrene and by reaction of (dimethylaminobenzene)tricarboxylchromium with poly(styrene-co-acrylic acid). The polymeric chromium complexes give transparent films and on UV irradiation under nitrogen lead to dinitrogen complexes of the corresponding polymeric dicarbonylchromium. The reversible coordination of dinitrogen was confirmed by IR and visible absorption spectroscopy. A predominant feature of the polymeric dinitrogen complexes is their extraordinarily high stability in air compared with the corresponding low molecular analogs. The effect of polymer matrices on dinitrogen coordination is discussed.

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INTRODUCTION

A large number of dinitrogen complexes of transition metals have been reported [1-3]. For example, benzenedicarbonyldinitrogenchromium complex is derived from the corresponding benzenetricarbonylchromium complex with UV irradiation under nitrogen. However, these dinitrogen-coordinated metal complexes are not stable and immediately degrade after exposure to air.

The authors previously reported the preparation and characteristic properties of dinitrogen complexes of triphenylphosphinecobalt [4] and cyclopentadienylmanganese [5, 6] bound to polymer matrices. Both polymeric dinitrogen complexes were fairly stable compared to the corresponding monomeric analogs. This paper describes the preparation of polymer-bound benzenetricarbonylchromium complexes (Schemes 1 and 2) and reversible coordination of molecular nitrogen to the chromium complexes.

EXPERIMENTAL

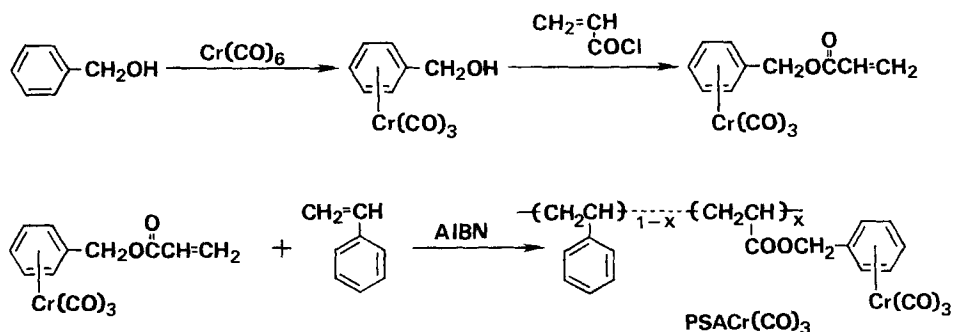
Chromium hexacarbonyl was purchased from Alfa Chemicals Co. and used after distillation *in vacuo*. Organic solvents were carefully dried by common methods before use. All reactions were carried out in an oxygen-free atmosphere. UV irradiation was carried out with a 32-W low-pressure mercury lamp (Riko-Kagaku Co., UV type L-32B).

Preparation of Poly(Styrenetricarbonylchromium) (PSCr(CO)₃)

Polystyrene (MW 54 000; 3.0 g, 29 mmol styrene unit) and chromium hexacarbonyl (6.0 g, 27 mmol) were reacted as in the literature [7]. The IR ν_{CO} peaks at 1860 and 1960 cm^{-1} supported the formation of styrenetricarbonylchromium residues. The chromium content of the polymer indicated that 29 mol% of the styrene residues in the polymer was complexed with tricarbonylchromium.

Preparation of Poly(Styrene-*co*-Benzyl Acrylatetricarbonylchromium) (PSACr(CO)₃) (Scheme 1)

Chromium hexacarbonyl (5.0 g, 20 mmol) was reacted with benzyl alcohol according to the literature procedure [8] to afford 3.5 g (yield 64%) of benzyl alcoholtricarbonylchromium as a light yellow crystal, mp 97°C. IR: 1870, 1960 cm^{-1} (ν_{CO}), 3280 cm^{-1} (ν_{OH}); ¹H NMR (CDCl₃): δ (ppm) = 2.3 (1H,



SCHEME 1.

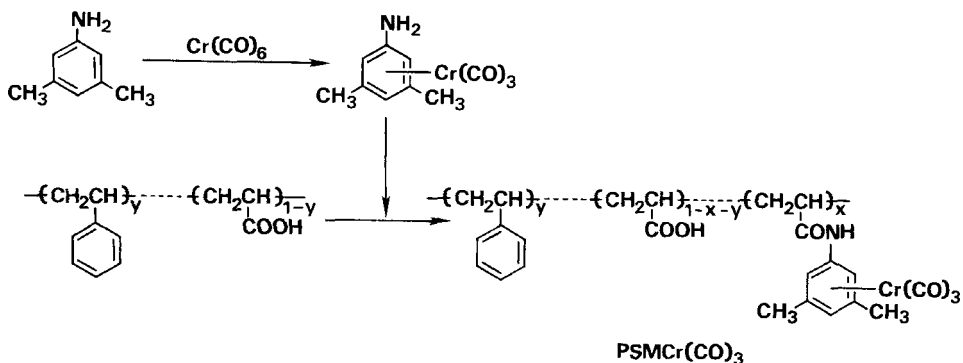
—OH), 4.6 (2H, —CH₂—), 5.6 (5H, —C₆H₅). Benzyl alcoholchromium (5.0 g, 20 mmol) was reacted with acrylic acid as in the literature [9] to yield 2.3 g (yield 40.1%) of (benzyl acrylate)tricarboxylchromium, mp 51.5°C. IR: 1720 (ν_{CO}), 1628 cm⁻¹ ($\nu_{\text{C}=\text{C}}$); ¹H NMR: δ (ppm) = 5.8–6.5 (3H, —CH=CH₂), 4.7 (2H, —CH₂—), 5.2 (5H, —C₆H₅).

Benzyl acrylate tetracarboxylchromium (1.3 g, 4.4 mmol) and styrene (4.1 g, 39 mmol) were copolymerized in ethyl acetate with azobisisobutyronitrile as an initiator at 60°C for 15 h. The copolymer was precipitated in diethyl ether and dried *in vacuo* to yield PSACr(CO)₃ as a yellow powder. Yield 1.2 g (19%). The content of chromium complex (x in Scheme 1) was determined as 0.19 by elemental analysis and atomic absorption spectrometry. Intrinsic viscosity in tetrahydrofuran (THF) at 25°C, $[\eta] = 0.067$ dL/g. IR: 1720 (ν_{CO}), 1601 cm⁻¹ ($\nu_{\text{C}=\text{C}}$, phenyl).

Preparation of Poly(Styrene-*co*-3,5-Dimethylacrylamidebenzene) Tricarboxylchromium (PSMCr(CO)₃) (Scheme 2)

Chromium hexacarbonyl (3.0 g, 14 mmol) and 3,5-dimethyl-1-aminobenzene (6.3 g, 52 mmol) were reacted as in the literature [10] to afford 1.8 g (yield 37%) of (3,5-aminodimethylbenzyl)tricarboxylchromium as yellow crystals. IR: 3290, 3440 cm⁻¹ (ν_{NH}), 1850, 1930 cm⁻¹ (ν_{CO}).

Poly(styrene-*co*-acrylic acid) (MW 25 000; acryl acid residue $1 - y$ in Scheme 2: 0.29; 0.6 g), (3,5-dimethylaminobenzyl)tricarboxylchromium (0.5 g, 1.8 mmol) and *N,N'*-dicyclohexylcarbodiimide (4.0 g, 19 mmol) were dissolved in 30 mL THF. The mixture was stirred at 0°C for 6 h under nitrogen. The reaction mixture was filtered to remove dicyclohexylurea,



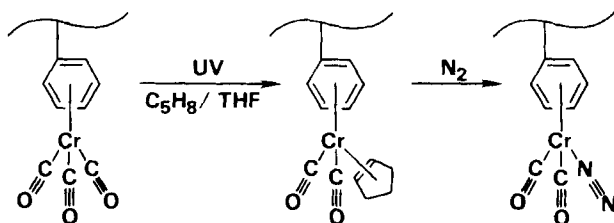
SCHEME 2.

and the filtrate was poured in diethyl ether. The precipitate was washed with diethyl ether and dried *in vacuo*. PSM Cr(CO)_3 was obtained as a yellow powder. x in Scheme 2: 0.07; IR: 1630 cm^{-1} (ν_{NH}).

RESULTS AND DISCUSSION

Polymeric benzenetricarbonylchromium complex PSM Cr(CO)_3 was obtained easily by the direct reaction of chromium hexacarbonyl with polystyrene, but it contained a trace of greenish chromium oxide and was excluded for the following reaction of dinitrogen coordination. On the other hand, the chromium complexes in the polymers were assigned to be benzenetricarbonylchromium(0) derivatives by visible absorption maxima at 316 and 313 nm, and its absorbance for PSAC Cr(CO)_3 and PSM Cr(CO)_3 prepared by Schemes 1 and 2, respectively. The polymeric chromium complexes gave transparent films by careful casting of their THF solutions.

A THF solution of PSAC Cr(CO)_3 and cyclopentene was irradiated with UV under argon at 0°C for 1 h (Scheme 3). The yellowish solution turned red. During the UV irradiation, UV and visible spectra changed from one with a maximum at 316 nm to one with maxima at 316 and 444 nm with isobestic points at 298, 396, and 500 nm. This spectral change corresponds to the reaction in which monocarbonyl is eliminated from the tricarbonylchromium complex and cyclopentene coordinates weakly to this, as previously reported for the monomeric benzenetricarbonylchromium complex [11, 12]. The



SCHEME 3.

solution turned from red to reddish brown with the absorption maximum at 380 nm after nitrogen gas bubbling for 1 h.

The solution was cast to prepare a brownish film. In the IR spectrum a new absorption band appeared at 2140 cm^{-1} . Sellmann [11] reported that the ν_{N_2} absorption peak was observed at 2140 cm^{-1} for $(\text{benzene})\text{Cr}(\text{CO})_2\text{N}_2$. Accordingly, an end-on type coordination of dinitrogen to the polymeric benzenedicarbonylchromium is strongly suggested here.

The degree of dinitrogen coordination to the chromium complex was calculated to be ~ 0.05 from the dinitrogen content obtained by elemental analysis. The intensity of the ν_{N_2} peak in air, shown in Fig. 1, decreases slowly with time, corresponding to decomposition of the dinitrogen complex to chromium oxide by air. Its degradation obeys first-order kinetics from which the lifetime (τ , half-life period) of the dinitrogen complex can be calculated, as in Table 1. It has been reported that the corresponding benzenedicarbonylnitrogenchromium complex is decomposed immediately after exposure to air [11, 12]. A polymeric matrix protects the dinitrogen chromium complex even in air, probably because the polystyrene matrix retards diffusion of oxygen and moisture to the complex to suppress irreversible oxidation of the chromium ion.

The solution turned from light yellow to red by UV irradiation of $\text{PSM}\text{Cr}(\text{CO})_3$ in THF under argon at 0°C . In the IR spectrum of this complex, ν_{CO} is reduced, which suggests that monocarbonyl is eliminated from $\text{PSM}\text{Cr}(\text{CO})_3$ and that THF coordinates weakly to the dicarbonylchromium complex. The color turned from red to orange while this solution was kept at 0°C under nitrogen for 20 min. The solution was then cast into a film. The IR data given in Table 1 support the formation of a dinitrogen complex. In comparison with the dinitrogen complex of $\text{PSA}\text{Cr}(\text{CO})_2$ (ν_{N_2} at 2140 cm^{-1}), the ν_{N_2} band (at 2120 cm^{-1}) of the dinitrogen complex of

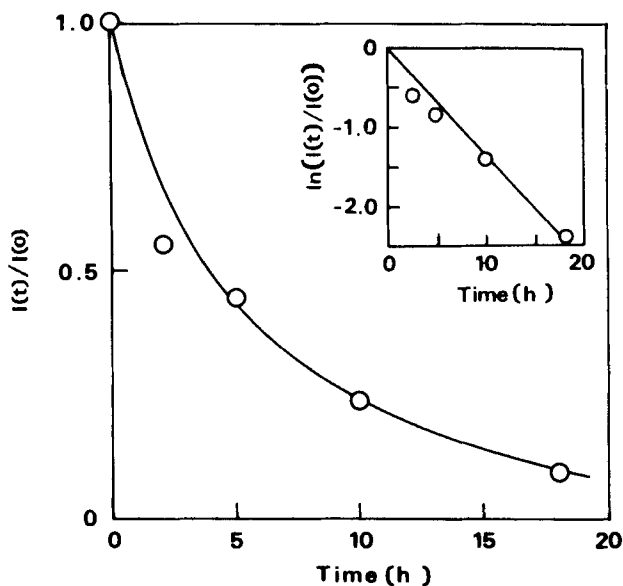


FIG. 1. Intensity (I) change of the ν_{N_2} peak at 2140 cm^{-1} with time and approximation to first-order kinetics for $\text{PSA}(\text{CO})_2\text{N}_2$ in air at 25°C .

TABLE 1. IR Absorption Peak and Lifetime of the Dicarbonyldinitrogen-chromium Complexes

Complex	ν, cm^{-1}		τ, h
	CO	N_2	
$\text{PSACr}(\text{CO})_2$	1970	2140	9.1
	1890		
$\text{PSMCr}(\text{CO})_2$	1940	2120	21
	1860		

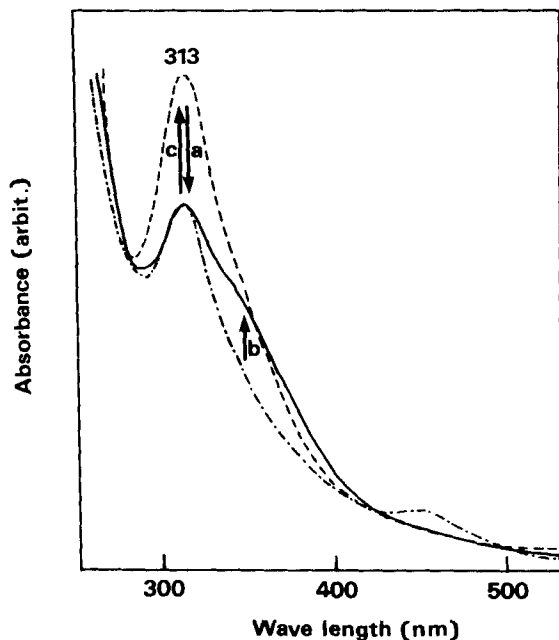
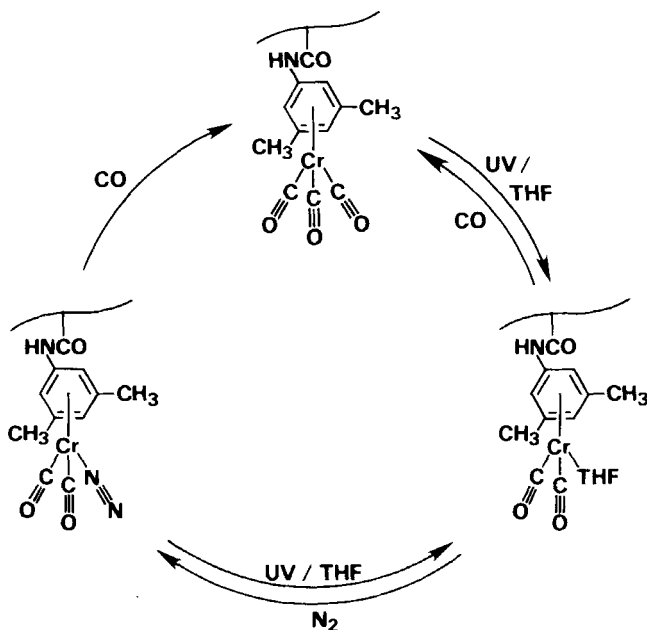


FIG. 2. UV and visible absorption spectra of the $\text{PSMCr}(\text{CO})_2$ at 0°C : (---) $\text{PSMCr}(\text{CO})_3$, (- · -) $\text{PSMCr}(\text{CO})_2$ THF, (—) $\text{PSMCr}(\text{CO})_2$ N_2 .

$\text{PSMCr}(\text{CO})_2$ was shifted to a lower wavenumber with a stronger intensity. The degree of dinitrogen coordination to the chromium complex was determined by elemental analysis to be 0.31. The results indicate that the dinitrogen complex of $\text{PSMCr}(\text{CO})_2$ was more stable than that of $\text{PSACr}(\text{CO})_2$, due to the $\text{Cr}-\text{N}_2$ bond being strong. This strong dinitrogen-bonding ability of $\text{PSMCr}(\text{CO})_2$ is probably based on higher electron density at the benzene ring, which is caused by the electron-donating property of the substituted methyl groups.

The visible absorption spectrum of $\text{PSMCr}(\text{CO})_3$ is shown in Fig. 2. The absorption spectrum changes with isosbestic points at 380, 422, and 500 nm from the spectrum with λ_{max} at 313 nm to that with λ_{max} at 445 nm on UV irradiation under argon (Fig. 2a), which corresponds to the formation of the THF complex from $\text{PSMCr}(\text{CO})_3$. When the THF complex was kept under nitrogen, the absorption at 445 nm decreased and that at 380 nm increased, indicating that the dinitrogen complex was formed by THF elimination and



SCHEME 4.

dinitrogen coordination (Fig. 2b). When carbon monoxide was bubbled through the dinitrogen complex solution, the absorption at 313 nm increased due to re-formation of tricarbonyl complex (Fig. 2c). On UV irradiation of the dinitrogen complex solution, the absorption at 445 nm increased, and the coordinated dinitrogen was substituted by THF. On carbon monoxide bubbling through this THF complex solution, the original $\text{PSMCr}(\text{CO})_3$ complex was regenerated. This cycle can be repeated several times, as shown in Scheme 4.

This reversible dinitrogen coordination was confirmed for $\text{PSMCr}(\text{CO})_2$ in a film by IR spectroscopy (Fig. 3). When the film of $\text{PSMCr}(\text{CO})_3$ was UV irradiated under nitrogen, the IR absorption at 2120 cm^{-1} assigned to the dinitrogen complex appeared (Fig. 3b). This absorption disappeared on UV irradiation under argon (Fig. 3c). The lifetime of the dinitrogen complex of $\text{PSMCr}(\text{CO})_2$, given in Table 1, was longer than that of $\text{PSACr}(\text{CO})_2$. This means that the polystyrene matrix of $\text{PSMCr}(\text{CO})_2$ protects the dinitrogen complex against air as it does in $\text{PSACr}(\text{CO})_2$ and that the stronger $\text{Cr}-\text{N}_2$ bond in $\text{PSMCr}(\text{CO})_2\text{N}_2$ reflects also on its lifetime.

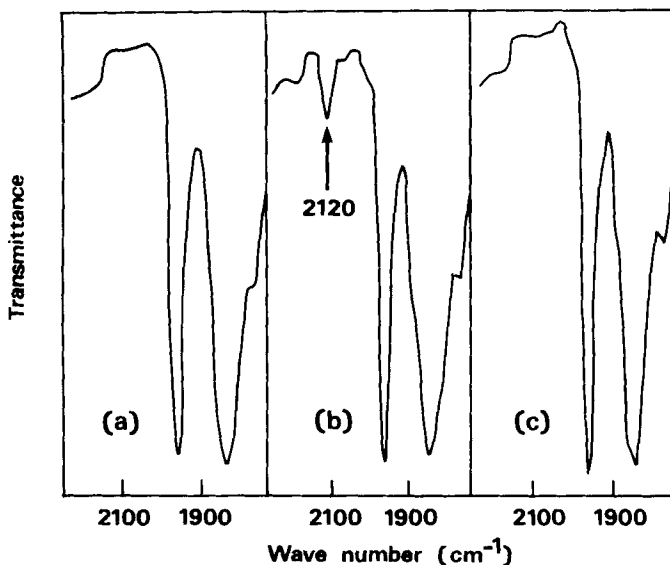


FIG. 3. IR spectra of the PSMCr(CO)₃ film (a), after UV irradiation under nitrogen (B), and after UV irradiation under argon (c).

It is concluded that the polymer-dinitrogen complex is stable even in air at room temperature due to the effect of the polystyrene matrix. Reversible coordination of molecular nitrogen can be observed directly by means of IR and visible absorption spectroscopy.

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