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Complexes in polymers: FT-IR spectra and photochemistry of some monomeric organometallic carbonyl complexes in polystyrene, poly(methyl methacrylate), polystyrene–poly(methyl methacrylate) and polystyrene–polyacrylonitrile copolymers

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A convenient method for embedding organometallic complexes in polymer films has been developed and the FT-IR spectra of these films have been investigated at room temperature. Infrared data in the ν(CO) stretching region are reported for $M(CO)_6$ (M = Cr, Mo, W), $CpMn(CO)_3$ ($Cp = \eta^5\text{-}C_5H_5$), $\eta\text{-}C_6H_6Cr(CO)_2L$ [L = CO, $P(n\text{-}Bu)_3$], $(\eta^6\text{-}C_6H_5NH_2)Cr(CO)_3$, $[\eta^6\text{-}o\text{-}C_6H_4(NH_2)MeCr(CO)_3]$, CpFe(CO)LR [L = CO, PPh_3; R = Me, C(O)Me] embedded in poly(methyl methacrylate) (PMMA), polystyrene (PS), polystyrene–poly(methyl methacrylate) (PS–PMMA), and polystyrene–polyacrylonitrile (PS–AN) plastic films. These matrices appear to approximate the common solvents ethyl acetate, toluene, toluene–ethyl acetate, and toluene–acetonitrile, respectively, with respect to ν(CO) vibrational band behavior. Several of the films have been subjected to UV irradiation and the photoproducts formed have been identified by FT-IR spectroscopy. PS–AN effectively traps photogenerated coordinatively unsaturated species via coordination of its pendant nitrile groups.

Keywords: Organometallic compounds, polymer matrices, FT-IR spectroscopy

INTRODUCTION

Metal-containing polymers are of continuing practical and theoretical interest. They are potentially useful in applications ranging from electronics, solar power, nuclear fusion and catalysis.[1] Of particular relevance here is the development of near-IR radiation absorbing lenses via decomposition of $W(CO)_6$ in polycarbonate-type polymers.[2] Organometallics such as $\eta\text{-}C_6H_6Cr(CO)_3$ have also been studied as photo-initiators for styrene polymerization.[3] Moreover, $Cr(CO)_6$ embedded in polystyrene (PS) is a useful calibrant for IR spectra[4] and ferrocene in poly(methyl methacrylate) (PMMA) is the light-absorbing layer in an improved imaging device.[5]

Our interest in this area arose from studies of the mechanical spectroscopy of PS strips containing organometallic complexes dispersed as a solid solution throughout the polymer.[6] It was shown that the barriers to rotation of π-bonded $C_5H_5^-$ and C_6H_6 rings about the ring–metal axis are significantly greater in the matrix than in solution or in the crystal. Polystyrene and other polymers have a 'window' of low absorbtivity in the region of the IR spectrum where bands due to terminal CO stretching vibrations of metal carbonyls are detected. Therefore, it is reasonable to probe the environment of such complexes in polymers using IR spectroscopy.

The practice of embedding organometallic compounds into polymer matrices in order to study their photochemistry dates from the early 1960s when Massey and Orgel[7] examined the photochemistry of the Group VIB metal hexacarbonyls, $M(CO)_6$ (M = Cr, Mo, W), in PMMA

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films at room temperature. Over the next 15 years, little additional work[8] was done until Galembeck, De Paoli and coworkers reported the results of the effect of UV light on polytetrafluoroethylene and polyethylene films in the absence and presence of such ligands as olefins, dienes and acrylic acid.[9–14] More recently, Rest and his colleagues have studied the photochemistry of complexes in polymers throughout the temperature range 12–300 K.[15] This group used poly(vinyl chloride) (PVC),[16,17] poly(vinyl alcohol),[18] paraffin wax,[16] and Nujol mull.[19] Stufkens, Oskam and colleagues have examined the photochemistry of metal–metal bonded species such as $(CO)_5ReMn(CO)_3$(i-Pr-DAB) (DAB = 1,4-diaza-1,3-butadiene) in PVC films.[20]

Embedding organometallic complexes in polymers has been accomplished in the past either by soaking the polymer film in liquid complexes [9–14] such as $Fe(CO)_5$ or by solvent casting.[15–18] The latter procedure is the most commonly used and involves dissolving a mixture of the polymer and complex in a volatile solvent and then allowing the solvent to evaporate to leave a thin film of the polymer with the complex embedded in it. The embedding process employed in our work involves freeze-drying a benzene solution of the polymer and complex and then pressing the resulting fluffy product in a die at about 120°C and 3000 psi (21×10^3 kPa). Clear, mechanically robust films are produced in this way. The technique is quite general and is suitable for a wide range of complexes and polymers.

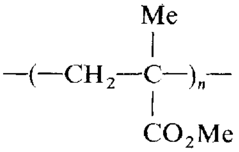
In this paper, we report the FT-IR spectra of $M(CO)_6$ (M = Cr, Mo, W), $CpMn(CO)_3$, η-$C_6H_6Cr(CO)_2L$ [L = CO, P(n-Bu)$_3$], (η^6-$C_6H_5NH_2$)$Cr(CO)_3$, [η^6-*o*-$C_6H_4(NH_2)MeCr(CO)_3$], CpFe(CO)LR [L = CO, PPh_3; R = Me, C(O)Me] in PS, PMMA, polystyrene–poly(methyl methacrylate) copolymer (PS–PMMA) and polystyrene–polyacrylonitrile (PS–AN) copolymer matrices, and the behavior of several of them under UV irradiation. Our objectives in this work were: (1) to extend our efforts[6] to characterize the environments imposed on complexes by these plastics and (2) to investigate the photochemistry of metal carbonyls in donor (PS–AN) and non-donor (PS) polymers.

EXPERIMENTAL

The organometallic compounds were either purchased from Strem Chemicals or synthesized by the literature methods indicated: η-$C_6H_6Cr(CO)_2$-[(n-Bu)$_3$P],[21] (η^6-$C_6H_5NH_2$)$Cr(CO)_3$, [η^6-*o*-$C_6H_4(NH_2)Me$]$Cr(CO)_3$,[22] CpFe(CO)LR [L = CO, PPh_3; R = Me, C(O)Me].[23] The PMMA, PS, PS–PMMA (70:30%), and PS–AN (75:25%) polymers were supplied by Polysciences.

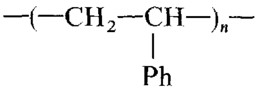
The polymer films embedded with organometallic compounds were prepared as follows. Polymer (1 g) was added to benzene (70 cm^3) in a 500 cm^3 round-bottomed flask. The mixture was left stirring overnight to ensure that the polymer had completely dissolved. The solution was then degassed by bubbling nitrogen through it for 4–5 min. While stirring and bubbling were continued, enough organometallic complex was added to produce a 1–2 mol% solution (approximately 0.05 g). After the complex had dissolved completely, the solution was rapidly frozen by immersing the flask in a liquid nitrogen bath and then quickly transferred to a vacuum line. The liquid nitrogen bath was replaced with an ice bath and the benzene was pumped off over at least a 24 h period. The resulting fluffy material was stored under nitrogen and kept in a freezer prior to further use. To make the films, a sample

PMMA



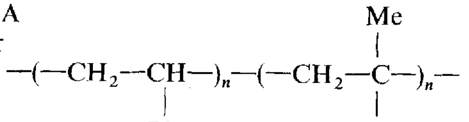
$$-(-CH_2-\underset{CO_2Me}{\overset{Me}{C}}-)_n-$$

PS



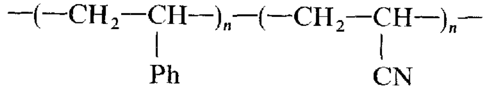
$$-(-CH_2-\underset{Ph}{CH}-)_n-$$

PS–PMMA
copolymer



$$-(-CH_2-\underset{Ph}{CH}-)_n-(-CH_2-\underset{CO_2Me}{\overset{Me}{C}}-)_n-$$

PS–AN
copolymer



$$-(-CH_2-\underset{Ph}{CH}-)_n-(-CH_2-\underset{CN}{CH}-)_n-$$

of the fluffy material was pressed between two aluminum foil-covered, flat metal plates at 120°C for 30 min at 3000 psi (21×10^3 kPa). The plates were allowed to cool to 65°C at 3000 psi, then the pressure was released, and the films were removed when ambient temperature was reached. Films produced in this manner always had absorbances below 2.0 in the ν(CO) region and were of reasonably uniform thickness. The pressed films were stored in a nitrogen-filled bottle and kept in a freezer.

FR-IR spectra were recorded on a Nicolet model 6000 spectrometer at 1 cm^{-1} resolution using a liquid-nitrogen-cooled mercury–cadmium–telluride detector. The band positions were reproducible to within at least ± 1 cm^{-1}. There were no polymer peaks of significant intensity in the ν(CO) region examined.

The photolysis experiments were performed in a closed box (16 in × 26 in × 24 in; 39.6 cm × 65 cm × 60 cm) lined with aluminum foil using a water-cooled 100 W Hanovia lamp as the irradiation source. The films were mounted on an IR sample-holder located about 5 cm from the lamp. Irradiation into specific wavelength regions was achieved using filters: $H_2NC(S)C(S)NH_2$ in ethanol (250–270 nm);[24] Pyrex (> 310 nm).

RESULTS AND DISCUSSION

The films produced by the hot-pressing technique are approximately 0.1 mm thick, and similar in stiffness to PS films used to calibrate IR spectrometers. The color of each film depends on the nature and the concentration of the organometallic complex embedded in it. The films are usually transparent and transmit IR and UV radiation easily.

IR spectra

The IR-active ν(CO) peaks observed observed for the organometallic compounds embedded in various polymer matrices are given in Table 1. There are slight differences in the peak positions and intensities with changes in polymer film and, in several cases, there is some evidence of breakdown in formal IR selection rules.

The Group VIB $M(CO)_6$ complexes formally have O_h symmetry for which only one strong IR-active ν(CO) mode (t_{1u}) is expected. However, in all four polymer matrices, there are additional peaks observed. In most cases there are two extra peaks above the t_{1u} mode. Under rigorous O_h selection rules, the a_{1g} and e_g modes are Raman-active only but, if the $M(CO)_6$ molecules are slightly distorted in the polymer matrices, the molecular symmetry will be reduced. Therefore, it is quite reasonable for the a_{1g} and e_g ν(CO) modes to gain some weak IR activity. Hooker and Rest[16] have noted the same effect for the metal hexacarbonyls in PVC matrices. The band positions in the various polymers considered here are close to those reported for the $M(CO)_6$ complexes in the solid state.[25] The position of the t_{1u} ν(CO) mode decreases by about 2 cm^{-1} in going from PS (Cr, 1980; Mo, 1981 cm^{-1}) to PS–PAN (Cr, 1978; Mo, 1980 cm^{-1}). These peak positions match closely those for the $M(CO)_6$ complexes in toluene (Cr, 1981.5; Mo, 1982.8 cm^{-1}) and acetonitrile (Cr, 1980.2; Mo, 1981.2 cm^{-1}) (Table 2). In these solvents, the shift in going from toluene to acetonitrile is about 1.5 cm^{-1}. In the non-polar solvent benzene, the t_{1u} modes are at significantly higher wavenumbers: $Cr(CO)_6$, 1985.9; $Mo(CO)_6$, 1987.6 cm^{-1}. The observed shift in ν(CO) to lower wavenumber in the polymers reflects the increasing polarity/polarizability of the environment of the metal carbonyl complexes in the films. Such shifts are well documented in studies of the effects of solvents on the positions of ν(CO) bands.[26,27]

Several of the other monomeric metal carbonyl complexes also exhibit breakdown in selection rules in the polymer films, e.g. the e ν(CO) modes of the tricarbonyl complexes are usually split into several components. Such splittings have been observed[28] and are attributed to isotropic solvation of the complexes by the polymer. Some of the complexes have amine groups on an aromatic ring, i.e. $(\eta^6\text{-}C_6H_5NH_2)Cr(CO)_3$ and $[\eta^6\text{-}o\text{-}C_6H_4(NH_2)Me]Cr(CO)_3$. IR data for the NH stretching region in PS and PMMA, and in the closely related solvents toluene and ethyl acetate, are listed in Table 3. Once again, these vibrations show the similarity of the polymer environments to those of the free solvents. Both complexes exhibit bands in the regions typical of primary amines: 3550–3330 cm^{-1} [$\nu(NH)_{asym}$]; 3450–3250 cm^{-1} [$\nu(NH)_{sym}$] and the peaks observed in the polymer matrices satisfy the usual relationship (Eqn [1]) for normal NH_2 groups.[29] The values predicted for $\nu(NH)_{sym}$ using this equation are all 4–12 cm^{-1} higher than those actually observed.

$$\nu(NH)_{sym} = 345.5 + 0.876\nu(NH)_{asym} \qquad [1]$$

Table 1 Observed carbonyl stretching modes of the monomeric metal carbonyl complexes in polymer film matrices (cm^{-1})

	Polymer film				Assignments
Complex	PMMA	PS	PS–PMMA	PS–PAN	ν(CO)
$Cr(CO)_6$	2113vw	2113vw		2113vw	a_{1g}
	2020w	2019w	2022w	2021w	e_g
	1980s	1980s	1980s	1978s	t_{1u}
$Mo(CO)_6$	2117vw			2117vw	a_{1g}
	2022w	2021w	2022w	2023vw	e_g
	1982s	1981s	1982s	1980s	t_{1u}
$W(CO)_6$	2118w	2118w		2118vw	a_{1g}
	2018w	2016w		2016w	e_g
	1977s	1977s		1974s	t_{1u}
η-$C_6H_6Cr(CO)_3$	1964s	1970s	1969s	1965s	a_1
	1902s	1896s	1892s	1934sh	e
	1887s			1887s	
	1879s				
$CpMn(CO)_3$	2016s	2018s	2018s	2017s	a_1
	1945s	1949ms	1943sh	1940sh	e
	1932s	1921s	1921s	1929sh	
	1919s	1902sh		1918s	
η-$C_6H_6Cr(CO)_2PPh_3$	2063vvw	2064vvw	2062vvw	2062vvw	
				2012vvw	
	1965s	1968s	1965s	1967s	a'
	1908sh			1959s	
		1937vw	1938w		
				1919m	
	1897s	1901s	1900s	1897s	a''
	1890s		1885s	1873s	
	1885sh				
	1879sh				
η-$C_6H_6Cr(CO)_2PBu_3$		1888s	1884s	1879s	
		1833s	1828s	1822s	
$CpFe(CO)_2Me$	2004s	2004s	2004s	2002s	a'
	1944s	1946s	1945s	1942s	a''
		1919vvw	1914vvw		
$CpFe(CO)Me(PPh_3)$	2008vw	2006vw	2004vw	2002vw	
	1907s	1910s	1907s	1905s	
$CpFe(CO)[C(O)Me](PPh_3)$		2005vw			
		1915s			
		1615w			ν(C=0)
$CpFe(CO)_2[C(O)Me]$		2013s			
		1954s			
		1919vw			
		1657m			ν(C=0)
η-$C_6H_5NH_2Cr(CO)_3$	1980sh				
	1950s	1960s			a_1
	1878s	1892sh			e ν(CO)
	1862s	1884s			
		1861s			
		1814vw			
η-o-$C_6H_4(NH_2)MeCr$ $(CO)_3$	1976vw	1979sh			
	1948s	1956s			a_1
	1876sh	1888s			e
	1864s	1880sh			
		1859s			

Table 2 Observed carbonyl stretching modes of some of the monomeric metal carbonyl complexes in various solvents (cm^{-1})

Complex	Solvent				Assignments
	PhMe	MeCN	$MeCO_2Et$	C_6H_6	$\nu(CO)$
$Cr(CO)_6$	1981.5s	1980.2s	1981.3s	1985.9s	t_{1u}
				1953.3vw	(^{13}CO)
$Mo(CO)_6$	2021.2vw		2022.3vw		
	1982.8s	1981.2s	1982.5s	1987.6s	t_{1u}
	1942.6vw			1955.9vw	(^{13}CO)
η-$C_6H_6Cr(CO)_3$	1972.7s	1966.8s	1970.4s	1982.5s	a_1
				1973.4sh	(^{13}CO)
	1897.9s	1884.8s	1892.9s	1914.7s	e
				1879.7vw	
$CpMn(CO)_3$	2022.2m	2021.3ms	2022.0m	2027.1ms	a_1
	1936.5s	1931.7s	1934.1s	1945.0s	e
			1890.4vw	1911.2vw	
η-$C_6H_6Cr(CO)_2PPh_3$	1972.6s	1966.6s	1970.1s		a'
	1942.1vw				
	1897.7s	1884.8s	1892.2s		a''
	1855.7vw				
$C_6H_5NH_2Cr(CO)_3$			2021.2vw		
	1961.1s		1956.1s		a_1
			1934.4sh		
	1880.7s		1873.4s		e
η-o-$C_6H_4(NH_2)MeCr(CO)_3$	1957.1s		1953.0s		a_1
	1947.3sh				
	1875.8s		1869.9s		e

Table 3 Observed NH stretching modes of the amine complexes investigated (cm^{-1})[a]

Complex	PS	PMMA	$MeCO_2Et$	PhMe	Assignment
η-$C_6H_5NH_2Cr(CO)_3$	3492.8w	3461.6w	3463.4ms	3488.8s	$\nu(NH)_{asym}$
	3393.9m	3370.1m	3366.7m	3389.7s	$\nu(NH)_{sym}$
	3384.6sh			3376.2sh	
	(3405.2)	(3377.9)	(3379.4)	(3401.7)	
	3225.6vw	3249.3w	3248.5vw	3232.6vw	
η-$C_6H_4NH_2MeCr(CO)_3$	3482.0w	3471.9w	3460.1vw	3477.4w	$\nu(NH)_{asym}$
	3388.1m	3376.4m	3372.1s	3387.4m	$\nu(NH)_{sym}$
	(3395.5)	(3386.9)	(3376.6)	(3391.2)	
	~3222vw	3253.8w	3254.5w	3222.4vw	

[a] Values calculated for ν_{sym} are given in parentheses (see text).

The initial IR spectra of $M(CO)_6$ in PS and PS–AN are of interest since the termperature employed to prepare the films (120°C) is similar to that required to attach $Cr(CO)_3$ residues to the phenyl side groups of PS[30] and to prepare derivatives of the type $M(CO)_{6-x}(CH_3CN)_x$, where $x = 1,2,3$.[31] No peaks attributable to (phenyl)$M(CO)_3$ were detected in films of $M(CO)_6$ in PS. However, for $M(CO)_6$ in PS–AN, extra peaks were observed which are assigned to $M(CO)_5$(PS–AN) on the basis of the subsequent photolysis studies described below. These bands were very weak for M = Cr, and weak for M = Mo and W. Similarly, bands of moderate intensity due to $CpMn(CO)_2$(PS–AN) were observed in freshly prepared films of $CpMn(CO)_3$

in PS–AN. Weak bands due to $Cr(CO)_6$ were observed in the spectra of η^6-$C_6H_6Cr(CO)_3$ embedded in PMMA and PS–AN.

Complexes of the type $CpFe(CO)(L)[C(O)Me]$ are prepared by heating $CpFe(CO)_2Me$ in the presence of a ligand (L) which drives the equilibrium in Eqn [2] to the acyl product.[32,33] No peaks were detected due to the presence of such acyl species where the donor atoms of PMMA or PS–AN acted as L. The results are consistent with a minimum of chemical reaction between the complexes and the polymers during the embedding procedure, except in the case of PS–AN. Attempts to embed $Fe(CO)_5$ and $Co_2(CO)_8$ failed due to their volatility and temperature sensitivity, respectively.

$$CpFe(CO)_2Me \rightleftharpoons CpFe(CO)[C(O)Me] \xrightarrow{L} CpFe(CO)L[C(O)Me] \qquad [2]$$

Photolysis experiments

The $M(CO)_6$ complexes in PS, PMMA and PS–AN were irradiated in the region 250–270 nm. In the case of the PS films, the ν(CO) bands due to the hexacarbonyls decrease in intensity and no new peaks appear. For $Cr(CO)_6$, the clear, colorless PS film becomes green, presumably as a result of the formation of chromium oxides.[34]

The PMMA samples show similar behavior upon irradiation in that the parent hexacarbonyl ν(CO) bands decrease in intensity. However, as observed by Massey and Orgel[7] (but not tabulated), new peaks appear in the spectra at lower wavenumbers (Table 4). These are very similar in frequency to those reported by Hooker and Rest[16] for $M(CO)_5(THF)$, which is consistent with an oxygen atom of PMMA acting as a ligand. This result confirms the proposal[16] that the product of room-temperature irradiation of the metal hexacarbonyls in PMMA is the complex $M(CO)_5(PMMA)$ and not $M(CO)_5$, although such species may be the initial short-lived products. The intensities of the ν(CO) bands due to the $M(CO)_5(PMMA)$ derivatives relative to that of the starting hexacarbonyl are: strong for $M = W$, moderate for $M = Mo$ and quite weak for $M = Cr$. These observations are consistent with the stability of the appropriate $M(CO)_5$ species. The longer-lived $W(CO)_5$ species is more likely to be trapped by a pendant oxygen atom before it decomposes than the shorter-lived Cr and Mo analogs.

The ν(CO) bands of the hexacarbonyls decrease in intensity upon irradiation in PS–AN and new bands appear (Table 4). At first, the spectra are very similar to those reported for the complexes $M(CO)_5(NCMe)$.[35] As the irradiation reaction continues, additional bands appear which are similar to those reported for the disubstituted complexes *cis*-$M(CO)_4(NCMe)_2$.[35] The intensities of the bands due to $M(CO)_5$(PS–AN) are very strong relative to that of the

Table 4 Assignment of the CO stretching modes of the species generated by UV irradiation of the monomeric metal carbonyl complexes embedded in polymer film matrices

Species	Local symmetry of metal carbonyl moiety	ν(CO) (cm^{-1})[a]			
$Cr(CO)_5$(PMMA)	C_{4v}		1932sh(e)	1884w(a_1)	
$Cr(CO)_5$(PS–AN)	C_{4v}	2074vw(a_1^{eq})	1936s(e)	1914sh(a_1^{ax})	
$Mo(CO)_5$(PMMA)	C_{4v}		1932sh(e)	1884w(a_1)	
$Mo(CO)_5$(PS–AN)	C_{4v}	2076mw(a_1^{eq})	1941s(e)	1903mw(a_1^{ax})	
cis-$Mo(CO)_4$(PS–AN)$_2$	C_{2v}	2020mw(a_1)	1918s(a_1)	1911s(b_1)	1850m(b_2)
$W(CO)_5$[b]	C_{4v}	2084(a_1^{eq})	1946(e)	1918(a_1^{ax})	
$W(CO)_5$(PS–AN)	C_{4v}	2075vw(a_1^{eq})	1938s(e)	?(a_1^{ax})	
cis-$W(CO)_4$(PS–AN)$_2$	C_{2v}	2015mw(a_1)	1901s(a_1)	1885s(b_1)	1851m(b_2)
$W(CO)_5$(PMMA)	C_{4v}	2074w(a_1^{eq})	1930s(e)	1884m(a_1^{ax})	
$W(CO)_5$(PS)	C_{4v}	2074vw(a_1^{eq})	1931s(e)	1897m(a_1^{ax})	
$CpMn(CO)_2$(PS–AN)	C_s	1934s(a')	1864s(a'')		
$CpMn(CO)_2$[c]	C_{2v}	1953s(a_1)	1896s(b_2)		
η-$C_6H_6Cr(CO)_2$(PS–AN)	C_s	1891s(a')	1835s(a'')		

[a] Proposed assignments are given in parentheses, [b] In PVC film, 12–200 K (from Ref. 16), [c] In PS at room temperature.

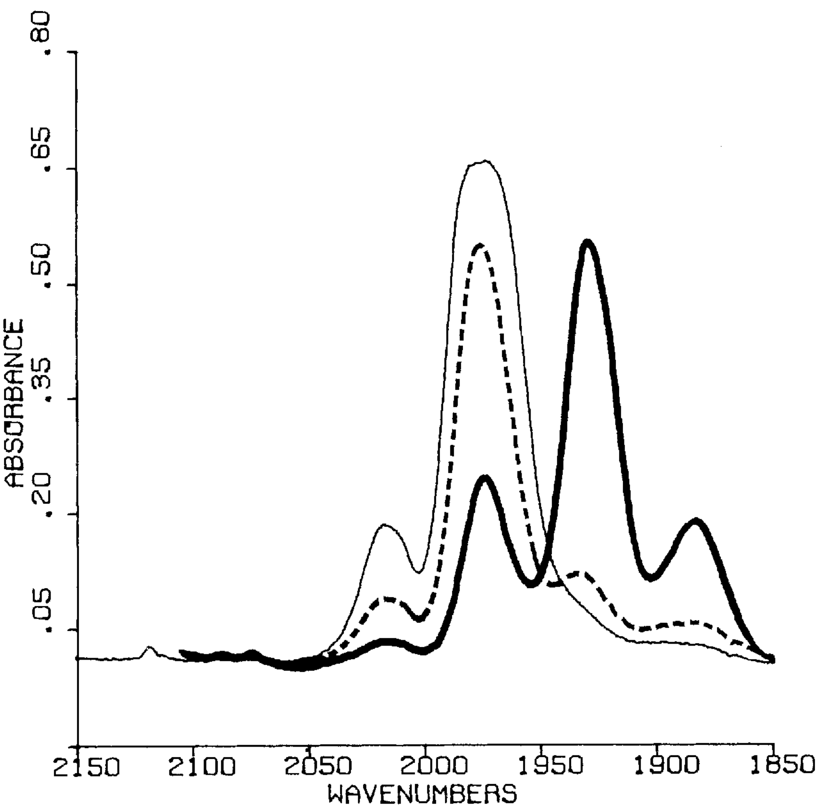


Figure 1 The infrared spectrum in the carbonyl region of $W(CO)_6$ in PMMA (————) before irradiation, after irradiation (Pyrex filter) for 10 min (▬▬▬▬) and after allowing the latter sample to stand for 8 h (-----).

starting hexacarbonyls indicating that PS–AN is an efficient trapping agent. The bands due to $M(CO)_4(PS\text{–}AN)_2$ are less intense than those of the monosubstituted species, but still strong for M = W, moderate for M = Mo and weak for M = Cr. For M = W, the film is no longer soluble in toluene following the irradiation, presumably because *cis*-$W(CO)_4(PS\text{–}AN)_2$ functions as a crosslinking agent. For M = Mo, the irradiated film dissolves with some difficulty in toluene, possibly because $Mo(CO)_4(PS\text{–}AN)_2$ is unstable. Slow addition of the toluene solution to a large excess of methanol causes the polymer to precipitate. In one experiment, the precipitate was collected on a fritte, washed well with methanol and pumped on. The resulting fluffy material was then redissolved in toluene and allowed to evaporate at room temperature leaving a thin film. The IR spectrum of this cast film showed strong $\nu(CO)$ bands due to $Mo(CO)_5(PS\text{–}AN)$ only. This result further suggests attachment of the complex to the polymer since bands due to unreacted $Mo(CO)_6$ present in the irradiated film were not detected.

Films containing $W(CO)_6$ in PS, PMMA and PS–AN were also irradiated at room temperature through quartz with no filter and their IR spectra were monitored upon standing. In all cases, the $\nu(CO)$ bands due to $W(CO)_6$ decreased in intensity much more rapidly than when the filter was used. In PS, very weak peaks at 2074, 1931 and 1897 cm^{-1} were detected by measuring the spectrum immediatiately after irradiation. However, these peaks rapidly decreased in intensity upon standing while the intensities of bands due to $W(CO)_6$ increased slightly. The frequencies of these weak bands do not correspond to those of $W(CO)_5$,[16] $W(CO)_5$(cyclohexane)[36] or $W(CO)_5$(benzene).[36] However, they do correspond well to those reported for $W(CO)_5(THF)$[16] and somewhat less well to those reported for $W(CO)_5(OH_2)$.[37] A more precise assignment awaits further study. In PMMA, the strong new bands due to $W(CO)_5$(PMMA) decreased in intensity upon standing (8 h) and the bands due to $W(CO)_6$ were substantially regenerated[16] (Fig. 1). The CO ligands needed are presumably produced

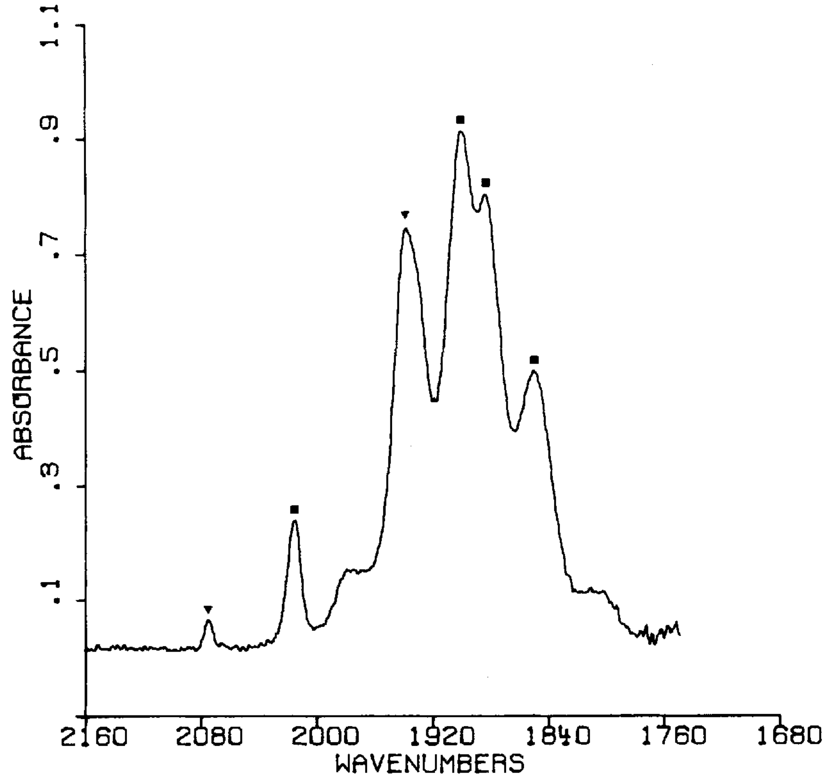


Figure 2 The infrared spectrum in the carbonyl region of $W(CO)_5PS$–AN (▼) and *cis*-$W(CO)_4(PS–AN)_2$ (■) prepared by irradiating $W(CO)_6$ in PS–AN (Pyrex filter, 10 min).

by decomposition of $W(CO)_5(PMMA)$ although free CO is not detected in the matrix at room temperature.[38] Irradiation of $W(CO)_6$ in PMMA at −150°C did afford evidence of free CO, however. In PS–AN, bands due to $W(CO)_5(PS–AN)$ and *cis*-$W(CO)_4(PS–AN)_2$ soon appeared (Fig. 2), and, upon standing (8 h), those due to the former continued to intensify at the expense of the latter. No bands due to $W(CO)_6$ were detected.

Room-temperature irradiation of η-$C_6H_6Cr(CO)_3$ in PS, PMMA or PS–AN using a Pyrex filter (>310 nm) led to the parent ν(CO) bands decreasing in intensity. In PS and PMMA, new bands due to $Cr(CO)_6$ appeared. This is consistent with earlier studies which indicate that, while the initial product of photolysis at low temperature in an inert matrix is η-$C_6H_6Cr(CO)_2$,[39] the final product at room temperature in methyl methacrylate[40] and other solvents[41] is $Cr(CO)_6$. In addition, new bands at 2062 and 1930 cm^{-1} are observed. These bands are very weak in PS and moderate in PMMA. They vanished upon standing (one day) with a concomitant slight increase in intensity of the band due to $Cr(CO)_6$. The assignment of these additional bands is not readily apparent. Their frequencies are similar to those reported[16] for species of the type $Cr(CO)_5X$ and are not in the range appropriate to those expected for η-$C_6H_6Cr(CO)_2(PMMA)$.[40,42] It is worth noting that the proposed mechanism for the photoproduction of $Cr(CO)_6$ from η-$C_6H_6Cr(CO)_3$ in solution involves aggregation of two or more chromium species.[40,43] However, non-volatile metal complexes, at the concentration used here, are assumed to be well isolated in polymer films[44] and unable to aggregate. Therefore it is reasonable to assume that $Cr(CO)_6$ results from the scavenging of CO molecules generated by decomposition of η-$C_6H_6Cr(CO)_2$.

In PS–AN, new bands of a major product appeared at 1891 and 1835 cm^{-1}, but $Cr(CO)_6$ was not detected. In addition, weak bands due to $Cr(CO)_5(PS–AN)$ were observed. The bands due to the major product largely disappeared upon standing for a few days with no concomitant increase in intensity of any other bands. η-$C_6H_6Cr(CO)_2(NCMe)$ is apparently rather unstable,[45] and its $\nu(CO)$ bands in the IR in hexane solvent are reported to be 1915 and 1814 cm^{-1}. Nevertheless, the new bands in PS–AN are in the appropriate range and are tentatively assigned to η-$C_6H_6Cr(CO)_2$(PS–AN).

Irradiation of $CpMn(CO)_3$ in PS, PMMA and PS–AN at room temperature through Pyrex leads to a decrease in intensity of the parent bands. In PS, two new $\nu(CO)$ bands appear at 1953 and 1896 cm^{-1}. These bands are also detected, although with lower relative intensities, in PMMA. The new bands are stable upon standing, even for several days. Their positions are in agreement with those reported[39,42] for $CpMn(CO)_2$ and are assigned accordingly. In PS–AN, the parent bands disappear after only 30 min irradiation and are replaced by two new strong bands attributable to $CpMn(CO)_2$(PS–AN)[46] (Fig. 3).

The CpFe(CO)(L)[C(O)Me] complexes undergo photochemical decarbonylation in solution to give CpFe(CO)(L)Me. Irradiation of $CpFe(CO)_2$[C(O)Me] in PS led to the immediate (10 min) disappearance of the acyl peak at 1657 cm^{-1} and a shift of the dicarbonyl bands to frequencies corresponding to those of $CpFe(CO)_2Me$. A similar, though slower, change occurred upon irradiation of the film containing $CpFe(CO)(PPh_3)$[C(O)Me]. In this case, the peak due to the acyl is very close to the characteristic band of PS at 1601 cm^{-1}. A band at 1604 cm^{-1}, detected using a deconvolution procedure, decreased in intensity (40 min) and is tentatively assigned as the acyl band. The single metal–carbonyl band shifted to 1911 cm^{-1}, close to the value measured for $CpFe(CO)(PPh_3)Me$. These results are consistent with the photochemically induced decarbonylation of the acyl complexes (Eqn [3]) consistent with a similar study in PVC.[47]

$$\mathrm{CpFe(CO)(L)[C(O)Me]} \xrightarrow{h\nu} \mathrm{CpFe(CO)(L)Me + CO} \qquad [3]$$

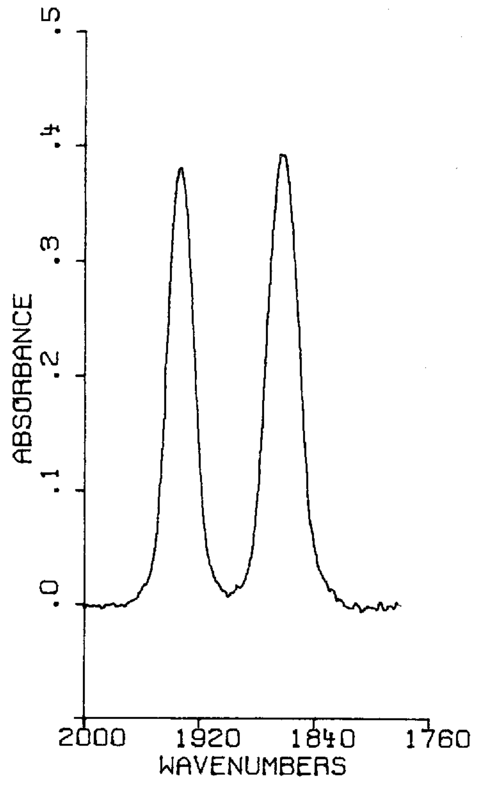


Figure 3 Infrared spectrum in the carbonyl region of $CpMn(CO)_2$PS–AN produced by UV irradiation (Pyrex filter) of $CpMn(CO)_3$ in PS–AN for 30 min.

CONCLUSIONS

The method described here for embedding organometallic complexes in polymers is very flexible, fairly general and non-destructive. The polymers PS, PMMA and PS–AN approximate the solvents toluene, ethyl acetate and acetonitrile, respectively, in their influence on the shapes and positions of the infrared bands of metal carbonyls. As expected,[16] these polymers do not function as 'room-temperature inert matrices', and photogenerated 'naked' species such as $M(CO)_5$ where M = Cr, Mo, and W are not observed. However, PS–AN and to a lesser extent PMMA stabilize coordinatively unsaturated intermediates via coordination of a pendant donor atom. Since these useful plastics can be pressed into any shape desired it should be possible to photochemically transform embedded complexes after fabrication.

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