

A Study of the Thermal and Photochemical Reactions of the Group 6 Metal Carbonyls with Organic Polymer Supports

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Abstract

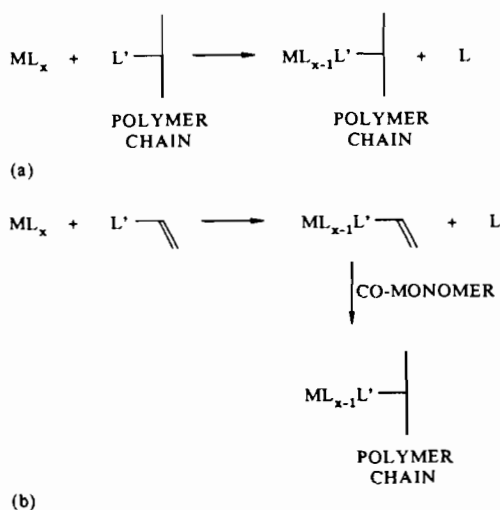
The synthesis of organic polymers containing metal carbonyl moieties is described. The reaction of $[\text{Mo}(\text{CO})_4(\text{bipy})]$ with poly-4-vinylpyridine proceeds smoothly to give $[\text{Mo}(\text{CO})_3(\text{bipy})(\text{poly-4-vinylpyridine})]$ which has a *fac* configuration. The thermal chemistry of a variety of polymer-bound metal carbonyl compounds is also presented, as is evidence for the formation of $[\text{W}(\text{CO})_4(\text{poly-4-vinylpyridine-styrene})]$ from $[\text{W}(\text{CO})_5(\text{poly-4-vinylpyridine-styrene})]$. Included is evidence for the decarbonylation of polymer-bound metal compounds resulting in polymers which contain fully decarbonylated metal centres. Preliminary photochemical investigations indicate the generation of active coordinatively unsaturated metal carbonyl species in polymer matrices at low temperatures.

Introduction

The generation of coordinatively unsaturated metal complexes is now known to play a fundamental role in many organometallic and catalytic systems [1]. Coordinatively unsaturated materials have been shown to react with species which normally would be considered inert, for example dinitrogen [2], xenon [3], and alkanes [4]. We have been interested in the generation of coordinatively unsaturated compounds by both thermal and photochemical means [4a, 5], and our research has concentrated on the chemistry of the Group 6 carbonyls. This is because of the large data base available for these systems and also the wide variety of spectroscopic and physical techniques which can be used in their study. In particular we wish to examine the effect of polymer-binding on the chemistry of metal carbonyls, with a view to the synthesis of polymers in which active coordinatively

unsaturated species could be generated, either by thermal, photochemical [6], or electrochemical means. This work follows the general thrust for the development of hybrid phase catalysts in which the active site maintains the stereochemistry, which occurs in homogeneous solution, while the bulk solubility of the material can be controlled by varying the nature of the polymer backbone [7].

The polymers of interest in this work contain pendant donor atoms [8], in particular nitrogen. The synthesis of polymer-bound metal carbonyl compounds of this type can be achieved by two routes. The first route involves the preparation of the polymer and a subsequent complex forming reaction to bind the metal moiety to it (Scheme 1a). The second pathway involves the preparation of the metal complex containing a group capable of polymerisation which could later be co-polymerised with suitable co-monomers producing the desired polymer-bound complex (Scheme 1b). Both of these routes were utilised in this work, depending on the particular properties required of the polymer.



Scheme 1.

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We have divided the work into two parts. The first is concerned with the thermal reactions of metal carbonyl complexes with poly-4-vinylpyridine. This investigation seeks to determine whether the polymer chain can influence the stereochemistry of the products formed. The second part is an investigation of the thermal and photochemical reactions of metal carbonyl complexes when bound to polymer supports and cast as films.

Experimental

Materials

4-Vinylpyridine which was distilled under vacuum prior to use, was obtained from Riedel-de Haën, as was tungsten and molybdenum carbonyls (used as supplied). Styrene and n-butyllithium (Merck) were used as obtained from the suppliers. 2-Vinylpyridine was obtained from Aldrich and was distilled under vacuum before use. Tetrahydrofuran, and toluene were reagent grade and were purified by fractional distillation.

Equipment

Infrared spectra were recorded on a Perkin-Elmer 983G ratio recording instrument, using an internal polystyrene spectrum as calibration. This machine is fitted with pre-sample chopping, and therefore can compensate for sample emission. Peak maxima are accurate to $\pm 3 \text{ cm}^{-1}$. A Specac Model 21.000 variable temperature solids sample holder; and a variable temperature 10 cm gas cell, fitted with a 20100 automatic temperature control unit was utilised, and sample temperatures are estimated to be accurate to $\pm 5^\circ \text{C}$. Ultraviolet/visible spectra were recorded either on a Shimadzu UV240 or a Hewlett-Packard 8452A spectrophotometer. Differential scanning calorimetry experiments were conducted on a Stanton Redcroft series 700 instrument. Photolyses were carried out using a medium pressure mercury vapour lamp obtained from Applied Photophysics. Preparative photolyses were carried out in a quartz immersion well using a medium pressure mercury vapour lamp as the source (Applied Photophysics). All preparative photolyses were conducted at room temperature under a nitrogen atmosphere.

Synthesis of [$W(\text{CO})_4(4\text{-vinyl-4'-methyl-2,2'-bipyridyl})$]

4-Vinyl-4'-methyl-2,2'-bipyridyl was prepared by the method of Abruña and co-workers [9]. [$W(\text{CO})_6$] (0.5 g) was dissolved in freshly distilled tetrahydrofuran (thf; 150 cm^3), and the solution was exposed to broad-band radiation from a medium pressure mercury lamp. After two hours photolysis, the 4-vinyl-4'-methyl-2,2'-bipyridyl (one mole equivalent) was added to the solution. The thf was then removed

under reduced pressure. The crude product was recrystallised from toluene. Infrared spectroscopy was used to confirm the product as [$W(\text{CO})_4(4\text{-vinyl-4'-methyl-2,2'-bipyridyl})$] (carbonyl stretching bands at $2001(\text{w})$, $1875(\text{s})$, $1963(\text{m})$, and $1823(\text{m}) \text{ cm}^{-1}$).

Synthesis of [$W(\text{CO})_5(4\text{-vinylpyridine})$]

[$W(\text{CO})_5(4\text{-vinylpyridine})$] was prepared as previously described [8]. A typical preparation involved dissolving [$W(\text{CO})_6$] (0.5 g) in freshly distilled thf (150 cm^3). The solution was then exposed to broad-band radiation from a medium pressure mercury lamp. Following two hours of photolysis the yellow-green solution of [$W(\text{CO})_5(\text{thf})$] was added to freshly distilled 4-vinylpyridine (0.1 cm^3). The solvent was then removed under reduced pressure, and the crude product was recrystallised from methanol.

Polymer Nomenclature

In this work the polymers have been assigned numbers e.g. polymer 1, 2, etc., whether they be homopolymers, copolymers, or terpolymers. Polymers containing metal moieties are given the suffix M to indicate this, *i.e.* polymer 1-M, 2-M etc.

Preparation of Polymers 1, 2 and 4

The polymers were prepared by free radical polymerisation of a mixture of the comonomers. The weights of the various components are given in Table I. The mixtures were heated to $80\text{--}90^\circ \text{C}$ for two hours under a nitrogen atmosphere. The crude polymers were purified by precipitation from chloroform solution by n-hexane.

TABLE I. The Weights of the Various Components (g) Used in the Syntheses of the Polymers, Copolymers and Terpolymers

Polymer no.	Styrene	2-Vp	4-Vp	$W(\text{CO})_4\text{Vbp}$	Vbp	AIBN
1	4.5		0.23			0.1
2	4.5				0.4240	0.1
3-M	2.0		0.1	0.4318		0.05
4		4.5				0.1
5	4.5	0.23				0.1

^a2-Vp = 2-vinylpyridine; 4-Vp = 4-vinylpyridine; Vbp = 4-vinyl-4'-methyl-2,2'-bipyridyl. Glass transition temperatures for polymers 1–5 were measured by differential scanning calorimetry and were found to be below 100°C in all cases.

Preparation of Polymer 3-M

A terpolymer of 4-vinylpyridine (0.1 g), styrene (2.0 g) and [$W(\text{CO})_4(4\text{-vinyl-4'-methyl-2,2'-bipyridyl})$] (0.43 g) was prepared by free radical polymerisation of a mixture of the monomers in the absence of any

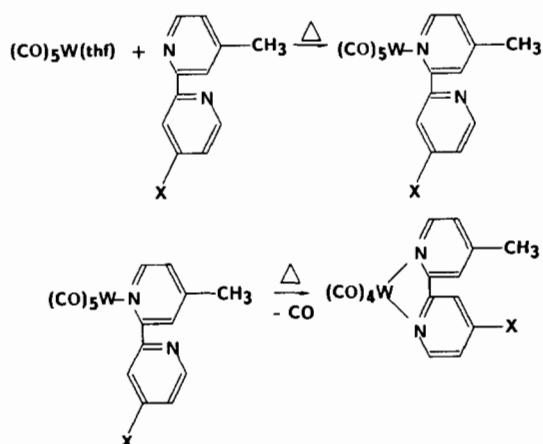
solvent; azoisobutyronitrile (aibn; 0.05 g) was used as the radical initiator. The mixture was heated to 70–80 °C for two hours and the crude polymer was purified by precipitation from chloroform solution by n-hexane.

Polymer 5. A Copolymer of Styrene and Pyridylmethane

A copolymer of styrene and 2-vinylpyridine (20:1 mole ratio) was prepared by free radical polymerisation as indicated above. The polymer was isolated by precipitation from chloroform in n-hexane. The lithium salt of 2-methylpyridine was prepared by treating 2-methylpyridine (0.3 cm³) with n-butyl-lithium (15% solution in n-hexane; 1.65 cm³) at room temperature under a nitrogen atmosphere. A solution (0.75 g in 2 cm³ of toluene) of the polymer was then added and the resulting mixture was stirred for 8 h. Following this, ice (10 cm³) was added and the solution was extracted with dichloromethane (40 cm³). The organic fraction was then concentrated by rotary evaporation and the polymer was precipitated by addition to n-hexane.

The Binding of Metal Complexes to Polymers

The polymers (except polymer 3-M), prepared as indicated above, were added to a solution of [W(CO)₅(thf)] in thf at the appropriate concentration (1:1 molar ratio of binding sites to [W(CO)₅(thf)]). The [W(CO)₅(thf)] was generated by the photolysis of [W(CO)₆] in thf [8]. Ethanol was sometimes used as the solvent for this photolysis, for polymers which are insoluble in thf. The solvent was then removed under reduced pressure, the thf being displaced from the metal complex by the pendant pyridine moieties to form the polymer-bound metal carbonyl species. In the case of polymers containing bipyridyl binding sites a further decarbonylation occurred during the preparation, forming the metal tetracarbonyl derivative (Scheme 2). The resulting polymers were purified by



Scheme 2.

precipitation from dichloromethane solution by n-hexane, filtered and dried in air. All polymer-bound complexes were found to be air stable and no precautions were made to protect them from atmospheric oxygen.

The presence of metal carbonyl fragments on the polymers was verified by both IR and UV–Vis spectroscopy. The carbonyl stretching frequencies are given in Table II, while UV–Vis data are presented in Table III.

Results and Discussion

Thermal Reactions of Poly-4-vinylpyridine with Complexes of Molybdenum Tetracarbonyl

The 2,2'-bipyridyl (bipy) and 1,10-phenanthroline (phen) complexes [Mo(CO)₄(bipy)] and [Mo(CO)₄(phen)] react readily with pyridine (py) to form the *fac*-tricarbonyl products [Mo(CO)₃(bipy)(py)] and [Mo(CO)₃(phen)(py)] respectively, characterised by CO stretching bands near 1900(A₁) and 1780(E) cm⁻¹ in the infrared spectrum [10]. The reactions of

TABLE II. The Infrared Stretching Frequencies of the Carbonyl Ligands in the Polymer-bound Compounds along with some Monomeric Complexes

Compound	$\nu(\text{CO})$ (cm ⁻¹) ^b					
Polymer 1-M	2068(w)	1921(s)	1895(m)			
Polymer 2-M	2073(w)	2002(w)	1931(s)	1881(s)	1885(sh)	1825(m)
Polymer 3-M	2001(w)	1883(s)	1872(sh)	1832(m)		
Polymer 4-M	2072(w)	1934(s)	1890(sh)			
Polymer 5-M	2067(w)	1927(s)	1895(sh)			
Polymer 6-M	2068(w)	1925(s)	1893(m)			
[Mo(CO) ₃ (bipy)(py)] ^a	1908(s)	1777(s,br)				
[Mo(CO) ₃ (phen)(py)] ^a	1902(s)	1782(s,br)				
[Mo(CO) ₃ (bipy)(poly-4-vinylpyridine)]	1898(s)	1769(s,br)				
[Mo(CO) ₃ (phen)(poly-4-vinylpyridine)]	1895(s)	1770(s,br)				

^aRef. 15. ^bs = strong, m = medium, w = weak, sh = shoulder, br = broad.

TABLE III. The Wavelengths of Maximum Absorbance of some of the Polymer-bound Compounds in a Variety of Solvents

Solvent	λ_{\max} (nm)		
	Polymer 1-M	Polymer 2-M	Polymer 4-M
Chloroform	336	376	378
thf	332	366	364
Dichloromethane	333	375	375
Dimethylformamide	316	387	380
Et ₂ O	335	370	
Acetone	326	370	
Ethyl acetate	332	376	
Benzene	339	380	
Toluene	338	385	
CCl ₄	343		
Ethanol			375
Methanol			380

these tetracarbonyl complexes with poly-4-vinylpyridine in boiling toluene yields products whose infrared spectra are virtually identical (in the CO stretching region) with those of the monomeric pyridine complexes, and clearly again have *fac*-octahedral coordination geometry at the metal atom (Table II).

The physical properties of the polymeric tricarbonyl complexes depend on the metal content of the polymer. The reaction of $[\text{Mo}(\text{CO})_4(\text{bipy})]$ with poly-4-vinylpyridine in 1:20 ratio based on 4-vinylpyridine monomer units, yields a red, soluble, tractable polymer which can be cast into films. The solubility of the polymer decreases as the metal content is increased, until, at a 1:5 metal to ligand ratio the product is effectively insoluble. Attempts to prepare products with a higher metal content than this were unsuccessful, the products always containing unreacted $[\text{Mo}(\text{CO})_4(\text{bipy})]$: the 1:5 ratio appears to represent an upper limit for the incorporation of the metal complex into the polymer.

The thermal reaction of poly-4-vinylpyridine with the dipyridylamine compound $[\text{Mo}(\text{CO})_4(\text{dipyam})]$ ($\text{dipyam} = (\text{C}_5\text{H}_4\text{N})_2\text{NH}$) showed some evidence of incorporation of the metal complex into the polymer chain but failed to yield reproducible products. In most cases, the materials extracted from the reaction mixtures contained much unreacted $[\text{Mo}(\text{CO})_4(\text{dipyam})]$ and in general this tetracarbonyl complex appears to react less readily with the polymeric pyridine than it does with monomeric heterocyclic amines [10].

The Thermal Properties of the Polymer Bound Metal Carbonyl Complexes when Cast as Films

The polymers were cast as films on a sapphire support from chloroform solution. The thickness of

the polymer film could be varied by changing the volume or concentration of the solution, thus the intensity of the carbonyl stretching bands in the infrared spectrum could be adjusted. A sapphire support was chosen because of its robustness and resistance to thermal shock. The window was then mounted in a variable temperature IR cell. All variable temperature experiments were carried out *in vacuo*.

Polymer 1-M

On heating this polymer to temperatures above 140 °C, the bands characteristic of a pentacarbonyl species disappeared and were replaced by bands which can be assigned to a *cis*-disubstituted tetracarbonyl species (Fig. 1) [11]. This could be explained by the occurrence of either of two reactions. In the first instance (Scheme 3a), it is possible that not every pendant pyridine on the polymer had coordinated to metal centres during the synthesis (although a 1:1 ratio of pendant pyridines to $\text{W}(\text{CO})_5$ moieties was used). Thus, uncoordinated pyridines could be available to take part in an associative carbonyl displacement reaction. In the second instance (Scheme 3b), a dissociative process, involving the formation of free metal pentacarbonyl might occur. This free pentacarbonyl could react with another pentacarbonyl moiety producing metal hexacarbonyl and a metal tetracarbonyl centre, which would then coordinate two pendant pyridine groups. This latter reaction is known to occur in the thermal conversion of $[\text{W}(\text{CO})_5(\text{dipyam})]$ to $[\text{W}(\text{CO})_4(\text{dipyam})]$ in the solid state [12].

In order to clarify which of these mechanisms was more probable, a copolymer of $[\text{W}(\text{CO})_5(4\text{-vinylpyridine})]$ and styrene (polymer 6-M) was prepared (see Table I). In this instance, all the binding sites on the polymer were coordinated to a metal carbonyl moiety. Upon heating this polymer, the spectral

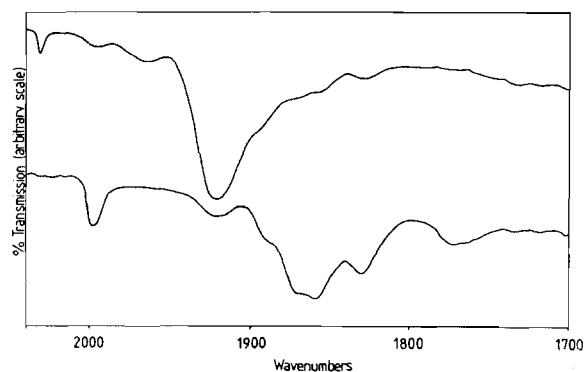
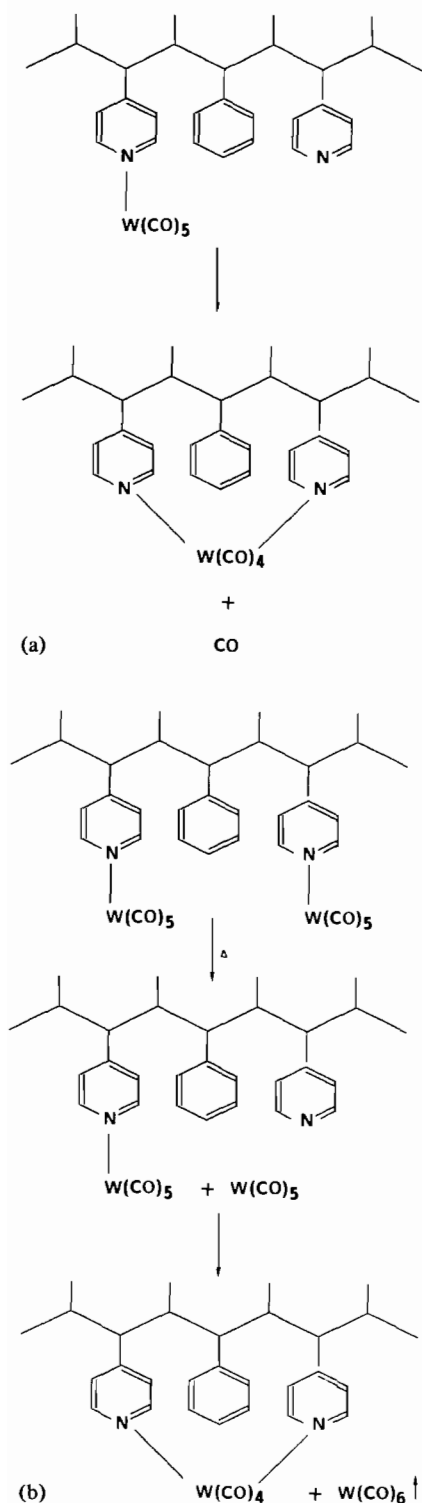


Fig. 1. Changes observed in the 2100–1700 cm^{-1} region of the infrared spectrum, upon heating polymer 1-M. These changes are consistent with the formation of a *cis*-disubstituted tetracarbonyl complex.



Scheme 3.

changes were found to be identical with those obtained in the case above. This is evidence for the occurrence of the disproportionation process, indicat-

ing the production of free metal pentacarbonyl species in the polymer matrix.

Further spectroscopic evidence for this process was obtained by investigating the volatile components produced on heating polymer 1-M. These experiments were performed using a variable temperature infrared gas cell (10 cm path length). The solid polymer was introduced into the cell and the cell was carefully evacuated and then sealed. The gases evolved upon heating the solid polymer were then determined by infrared spectroscopy at various temperatures. These results confirm the formation of the metal hexacarbonyl complex at temperatures above 110 °C ($[\text{W}(\text{CO})_6]$ has a carbonyl stretching band at 1988 cm^{-1}) along with free carbon monoxide. These products would be expected if a disproportionation process occurs.

Polymer 2-M and polymer 3-M

The thermal reactions of a polymer containing chelating coordinating sites were also investigated. In the first instance, a co-polymer of 4-vinyl-4'-methyl-2,2'-bipyridyl and styrene (polymer 2-M) was used. The binding of the metal carbonyl complex to this polymer was achieved in a manner similar to that for polymer 1-M, but in this case the metal tetracarbonyl derivative was produced (see Table II) [3]. Upon heating polymer 2-M to 150 °C, the sole process observed in the infrared spectrum was the loss of all carbonyl stretching vibrations, indicating either complete decarbonylation or sublimation of the metal carbonyl species from the polymer. Heating this polymer in a variable temperature infrared gas cell to 150 °C, and the subsequent examination of the gases produced, confirmed the presence of both the metal hexacarbonyl and free carbon monoxide. This suggests that the thermal reaction again involves a disproportionation process, which would result in some of the metal centres suffering decarbonylation, with concomitant formation of the metal hexacarbonyl.

A further polymer was prepared by the polymerisation of $[\text{W}(\text{CO})_4(4\text{-vinyl-4'-methyl-2,2'-bipyridyl})]$ with a mixture of styrene and 4-vinylpyridine (polymer 3-M). In this case the metal carbonyl is bound to the polymer via the chelating bipyridyl ligand but free pendant pyridines are present on the polymer backbone. Heating this polymer to 150 °C, in a manner similar to polymer 2-M, afforded a carbonyl containing species with bands at 1888 and 1775 cm^{-1} (Fig. 2). These band positions are close to those reported for $[\text{W}(\text{CO})_3(\text{bipy})(\text{py})]$ (1892 and 1773 cm^{-1} in nujol mull) [14], which has a *fac*-configuration. It is therefore proposed that the carbonyl containing product observed here is the *fac*-tricarbonyl species. This suggests that, in the case of a metal tetracarbonyl derivative bound to a polymer and in the absence of excess binding sites,

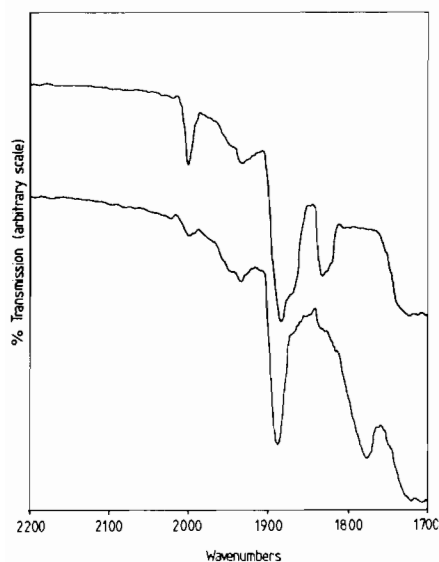


Fig. 2. Changes observed in the infrared spectrum (2200–1700 cm^{-1} region) upon heating polymer 3-M. These changes are consistent with the formation of the *fac*-tricarbonyl complex.

loss of a carbonyl ligand is an important route for its thermal reactions. This type of reaction is also observed in homogeneous solution [10]. An examination of the volatile components produced in this reaction, failed to detect significant amounts of the metal hexacarbonyl, while carbon monoxide was observed.

The tricarbonyl complex obtained by heating polymer 3-M is clearly closely related to the product obtained from the reaction of $[\text{Mo}(\text{CO})_4(\text{bipy})]$ with poly-4-vinylpyridine. The main difference apart from the nature of the transition metal involved is that in the former complex the metal is bound to the polymer backbone through three coordination sites, whereas in the latter the attachment is through only one vinylpyridine unit.

Polymer 4-M and polymer 5-M

The heating of a homopolymer of 2-vinylpyridine with pendant $\text{W}(\text{CO})_5$ groups (polymer 4-M) to 125 $^\circ\text{C}$, resulted in the loss of all bands in the carbonyl region of the infrared spectrum. However, treatment of a copolymer of poly-2-vinylpyridine and styrene with lithiated 2-picoline [15] yielded a polymer with pendant dipyridylmethane moieties (polymer 5). Reaction of this polymer with the photochemically produced $[\text{W}(\text{CO})_5(\text{thf})]$ produced a polymer with metal pentacarbonyl species bound to it (polymer 5-M). Upon heating this polymer to 140 $^\circ\text{C}$ spectral changes consistent with the production of a tetracarbonyl fragment were observed. It is known that dipyridylmethane has the ability to act both as a monodentate and a bidentate ligand, and

we have recently found independent evidence to demonstrate that the related di-2-pyridylamine complex $[\text{W}(\text{CO})_5(\text{dipyam})]$ can undergo a conversion from monodentate to bidentate coordination in the solid state.

Preliminary Photochemical Studies of the Polymer-bound Materials

In these experiments the polymer films were again cast on a sapphire support. The temperature of the films was reduced to -150 $^\circ\text{C}$ and the samples exposed to broad-band radiation from a medium pressure mercury lamp, filtered through the sodium chloride plates of the variable temperature IR cell. The low temperatures were utilised in order to 'freeze' any reactive photoproducts in the polymer matrix, in a manner similar to that developed by Hooker and Rest [16].

Polymer 1-M

In the case of polymer 1-M the principal spectral change following irradiation, is the formation of a new band at 2077 cm^{-1} which is characteristic of a metal pentacarbonyl species. The broadness of the remaining carbonyl bands precluded any significant spectral changes being observed below 2000 cm^{-1} . No free carbon monoxide could be detected in the infrared spectrum. The primary carbonyl containing photoproduct therefore appears to be a pentacarbonyl species, which is no longer bound to the polymer via the pendant nitrogen atoms (this is not surprising since the primary photoreaction of $[\text{W}(\text{CO})_5(\text{py})]$ is loss of the pyridine ligand [17]). However, on the basis of matrix isolation [18] and flash photolysis [4] experiments it is thought unlikely that this pentacarbonyl species is coordinatively unsaturated, but rather interacts with sites of electron density on the polymer, possibly the aromatic moieties. On warming this sample to room temperature, the spectral changes were found to reverse, indicating that on heating, the photoproducted pentacarbonyl again reacts with the nitrogen sites on the polymer backbone.

Polymer 4-M

Photolysis of a film of polymer 4-M at -150 $^\circ\text{C}$ resulted in the decrease of peaks characteristic of a pentacarbonyl species. Evidence for the formation of free carbon monoxide was obtained from the grow-in of a band at 2132 cm^{-1} . This reaction was not reversible on warming to room temperature. The reason for the differences in the photochemical behaviour of polymer 1-M and polymer 4-M, both of which initially contain metal pentacarbonyl fragments bound to the polymer through a metal to nitrogen bond, is uncertain at present, and further work is in progress to investigate this phenomenon.

Conclusions

Investigations of the thermal properties of these polymers have shown that the chemistry of metal complexes bound to copolymers of 2-vinylpyridine differs significantly from that of copolymers of 4-vinylpyridine. In the case of the copolymers and also the homopolymers of 2-vinylpyridine, loss of the metal carbonyl fragment appears to be the only thermal route available. This is probably the result of significant steric hindrance to the coordination of the pyridine moiety in these polymers. In the case of copolymers of 4-vinylpyridine, the thermal chemistry involves the formation of the *cis*-disubstituted tetracarbonyl complex. Polymers containing the good chelating bipyridyl ligand suffered the loss of the carbonyl stretching bands at temperatures above that observed for the loss of the metal carbonyl species in the polymers of 2-vinylpyridine, producing a fully decarbonylated material. However in the presence of additional binding sites on the polymer the metal tricarbonyl complex is formed.

The photolysis of the copolymers of 4-vinylpyridine resulted in the formation of a metal pentacarbonyl fragment, which was found to be thermally unstable. This result indicates the formation of a species which could exhibit catalytic activity. In the case of polymers of 2-vinylpyridine evidence for photodecarbonylation was obtained.

These experiments indicate the variety of chemistry exhibited by such materials and how the nature of the polymer can influence the direction of both thermal and photochemical reactions. Reactions in the solid state suggest that the stereochemistry of the thermal products are dictated by the metal centre and not by the physical restraints of the polymer, while reactions involving polymers in solution appear to differ significantly from reactions with monomeric ligands.

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