A STUDY OF THE THERMAL AND PHOTOCHEMICAL REACTIONS OF GROUP 6 METAL CARBONYL COMPOUNDS WHEN BOUND TO ORGANIC POLYMER SUPPORTS

Ph.D THESIS

DUBLIN CITY UNIVERSITY

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Declaration

I declare that the work presented in this thesis is based entirely on my research carried out at Dublin City University from October 1987 to August 1990 under the supervision of Dr. Conor Long.

Graham Russell

Graham Russell

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Abstract

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. In particular, we wish to examine the effect of polymer binding on the chemistry of group 6 metal carbonyls, with a view to the synthesis of polymers in which active coordinatively unsaturated species could be generated, either by thermal or photochemical means.

The polymers of interest contain pendant donor atoms, in particular nitrogen or phosphorus, to which metal carbonyls of the type $[M(CO)_{6-n}L_n]$ (M = Cr, Mo, or W; L = vinylpyridine, 2,2'-bipyridyl, or p-styryldiphenylphosphine) are anchored. The preparation and characterisation of these materials is discussed. The synthesis of the polymer-bound metal carbonyls can be achieved by two routes. The first involves the preparation of the polymer and subsequent complex forming reaction to bind the metal carbonyl moiety to it. The second pathway involves the synthesis of the metal carbonyl complex containing a polymerisable group which can later be copolymerised with suitable comonomers. The polymer-bound systems were characterised by UV/visible and infrared spectroscopy. The polymer materials exhibit similar spectroscopic behaviour to their monomeric analogues. The position of the metal-to-ligand charge transfer (MLCT) bands in the UV/visible was found to depend on the nature of the polymer backbone. Laser flash photolysis studies investigating the mechanism and kinetics of binding of the metal carbonyl fragment to the polymer is reported.

The thermal reactions of a variety of the polymer-bound metal carbonyl compounds when cast as films is also presented, as is evidence for the thermal decarbonylation of these materials 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.

AGGJ

To my parents.

CHAPTER 1

AN INTRODUCTION TO POLYMER-BOUND GROUP 6 METAL CARBONYLS

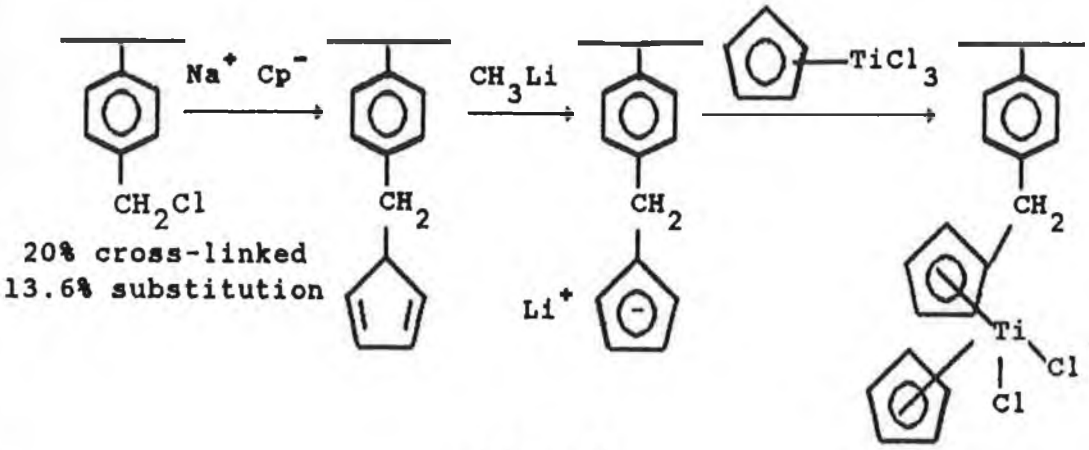
1.1 Introduction

In recent years organometallic polymers have attracted considerable attention and this interest has resulted in the publication of several reviews in this area[1-5]. The majority of this research has been concentrated on the attachment of organometallic catalysts to organic polymer supports, and indeed a look at the literature dealing with organometallic catalysis reveals the enormous synthetic utility of homogeneous catalysts bound to polymeric matrices.

Anchoring a homogeneous catalyst to a polymer backbone effectively "heterogenises" it, allowing it to function mechanistically as if it were in solution, but physically it would operate as a separate immobile phase. These systems display many of the desirable characteristics indigenous to homogeneous systems, such as catalyst recovery and re-use and high selectivity even under mild conditions. One basic requirement for organometallic catalysis by a transition metal complex, is the presence of an open coordination site[6]. Binding a catalyst, which potentially could contain a vacant coordination site to a rigid polymer might permit this molecule to be isolated, thus avoiding non-productive self-aggregation reactions and so affording high concentrations of unsaturated complexes. In this way it is envisioned that the lifetime of highly reactive intermediates could be increased by attaching them to polymeric supports.

The concept of binding known homogeneous catalysts to solid phase supports was first introduced by the work of Haag and Whitehurst[7], of Mobil Oil, who demonstrated the catalytic use of salts of $Pt(NH_3)_4^{+2}$ with polymeric sulfonate counterions and later the catalytic applications of heterogeneous species obtained by the coordination of $RhCl_3$ to polymers containing pendant phosphine units[8]. Since then, work in this area advanced due to the continued efforts of several groups. Further advantages, in addition to ease of catalyst recovery, have been reported for polymer-bound systems. These include enhanced hydrogenation activity of immobilised titanocene[10a] and $[Ir(CO)Cl(PPh_3)_2]$[10b], greater positional selectivity in both hydrogenations[10] and hydroformylations[1-5], as well as increased selectivity based on substrate size considerations[10c].

Grubbs *et al.*[2,10a] anchored titanocene dichloride to a 20% cross-linked styrene-divinylbenzene (DVB) resin and reduced this with two equivalents of butyllithium in an attempt to produce a "matrix-isolated" titanocene (Scheme 1). The resulting polymer was 6.7 times more active a hydrogenation catalyst than reduced benzyltitanocene dichloride. These workers also demonstrated the olefin hydrogenation selectivity as a function of substrate molecular bulk afforded by a form of the Wilkinson's catalyst [i.e., $ClRh(PPh_3)_3$], when bonded to a rigid polymer matrix[10c]. They concluded that the catalyst demonstrated many of the best properties of both homogeneous and heterogeneous catalysts and in addition, were capable of selecting olefins from solution on



Scheme 1

the basis of their size, the rate of reduction being dependant on the molecular size of olefin. In a similar work[11], Grubbs et *al.* showed that polymers may exert polar selectivities as well as those based on size. Polystyrenes (1-2% DVB) swell less in polar solvents so that ethanol decreases pore size and increases diffusional restrictions, thus the rate of cyclohexene reduction increased upon changing the solvent from benzene to 1:1 benzene-ethanol. Despite a reduction in swelling, a polar gradient is established which favours a higher concentration of the alkene within the resin when ethanol was used. These findings had not only demonstrated that these heterogenised anchored systems could perform as well as their homogeneous counterparts, but also that the polymer matrix could play an important role in determining the outcome of catalysis.

Polymer-supported catalysts also exhibit selectivities when used as hydroformylation catalysts[1-5,12-16]. Phosphinated polystyrene (PS) cobalt catalysts of the type $[PS\text{-}PPh_2Co(CO)_3]_2$ gave complete conversion of 1-pentene to the appropriate aldehyde in 96% selectivity (4% pentane) at 150°C and 68 atm H_2/CO[16]. Compared with the homogeneous catalyst, the normal to branched ratio (n/b) was 2, close to that of the unbound analogue. More alcohols were produced over 150°C and the n/b ratio dropped to 1.4. This is lower than that of the unbound catalyst (n/b=3), $Co_2(CO)_2(PPh_3)_2$.

Pittman and Smith[12] put forward the first examples of sequential multistep organic reactions in which two catalysts, $[(PPh_3)_2Ni(CO)_2]$ and $[(PPh_3)_3RhCl]$, were bound to the same crosslinked polystyrene backbone. They described the sequential cyclooligomerisation-hydroformylation of butadiene in which the product of the first reaction (vinylcyclohexene) is "fished out" by the second very selective hydroformylation of a terminal double bond. The aldehydes are readily separated from the remaining products. Butadiene was first cyclooligomerised quantitatively to cyclooctadiene, 1,5,9-cyclododecatriene and vinylcyclohexene by the supported nickel carbonyl. The supported rhodium catalyst was highly selective in catalysing the hydroformylation of the only terminal double bond in the products (vinylcyclohexene). The two catalysts can be attached to the same resin, or to two separate resins which may be subsequently mixed in the reactor. These experiments illustrated that the two bound catalysts behaved as they do individually, and that reaction of the two mixed catalysts with each other was avoided because contact between them was prevented by anchoring to the rigid supports.

While having enormous utility in the field of organometallic catalysis, the number of potential applications in which the use of metal-containing polymers can be considered is wide. Areas of application[4] currently under investigation include a) catalysis, b) thermally stable materials applications, c) biological applications (antifungal agents and insecticides), d) biomedical applications (antibacterial, controlled release, antiviral, antitumoral), e) additives (coatings, paper, plastics), f) electrical applications (conductors, semiconductors), g) photoactive materials (xeroxing type applications), h) analytical applications, i) flame retardants, j) nonlinear optical devices, and k) preparation of ceramics. These examples illustrate the applications and importance of the many and varied metal-containing polymer systems. An excellent and comprehensive review on the above applications has been published by Pittman and Carraher[4].

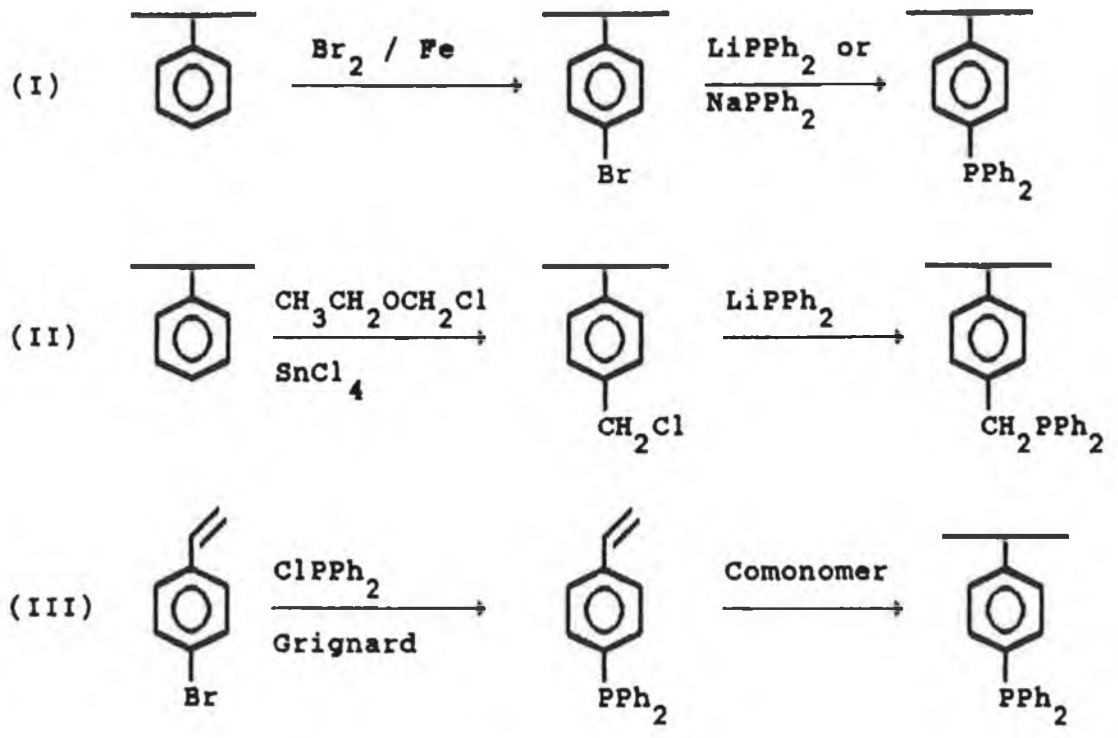
A number of organometallic metal carbonyl containing polymers have been investigated. Many metal carbonyl complexes of group 6 and 7 metals have been reported to catalyse well known reactions such as isomerisations[17], hydrogen shift reactions[17], hydrogenations[17,19], dimerisations[17], oligomerisations[20], alkylations and acylations[21], and olefin metathesis[22,23]. As a result, many of their polymer-bound analogues have been reported.

Metal carbonyl complexes undergo many photochemical[17,24,25] and thermal[24,26] reactions. Indeed, metal carbonyls are among the most thermally and photochemically labile range of compounds so far investigated. Hence, thermal and photochemical reactions of metal carbonyls have found wide applications for synthetic purposes. Thermolysis or photolysis can result in the production of coordinatively unsaturated species and so consequently, the generation of these reactive species in polymer-anchored systems is of particular interest. The high extinction coefficients of metal carbonyl complexes in the ultraviolet and infrared regions of the spectrum facilitate their study, and polymer supports can be chosen to be transparent in the region needed for spectral examination. The availability of a large data base for the systems makes them ideal for further investigation.

Many transition metal carbonyl containing organic polymers have been prepared. Example classes include polymers where the metal is (a) bound by phosphine or nitrogen ligands[1-3,16,27-31], (b) π-bonded to aryl ligands[52-56], (c) chelated as coordination complexes[30,32], or (d) attached to the matrix by a carbon-to-metal σ-bond[62,63]. These methods of bonding the metal carbonyl complexes to polymers provide convenient routes to the incorporation of transition metal carbonyl moieties into polymers. Some examples of each class will be discussed.

Phosphine ligands have received the most attention as modes of attaching transition metal complexes to polymer supports[2]. As a result of the wide variety of known transition metal organometallic species containing coordinated phosphines, a vast array of polymer-bound catalysts may be envisioned in which the active metal is directly coordinated to a polymeric phosphine ligand. In many catalytic reactions loss of a phosphine ligand is an important step, and so has important consequences in hybrid system design for these complexes. Numerous metal carbonyl derivatives have been formed from phosphine ligands[32]. Group 6 carbonyl complexes with phosphine ligands are usually synthesised using standard substitution reactions; (1) displacement of CO from $M(CO)_6$ aided by heat and/or UV light, (2) displacement of one or more weakly bonded ligands from carbonyl derivatives, also usually aided by heat and/or UV light and (3) direct combination of the phosphine ligand and $M(CO)_6$ in a sealed tube. These methods can be employed in the preparation of polymer-anchored systems.

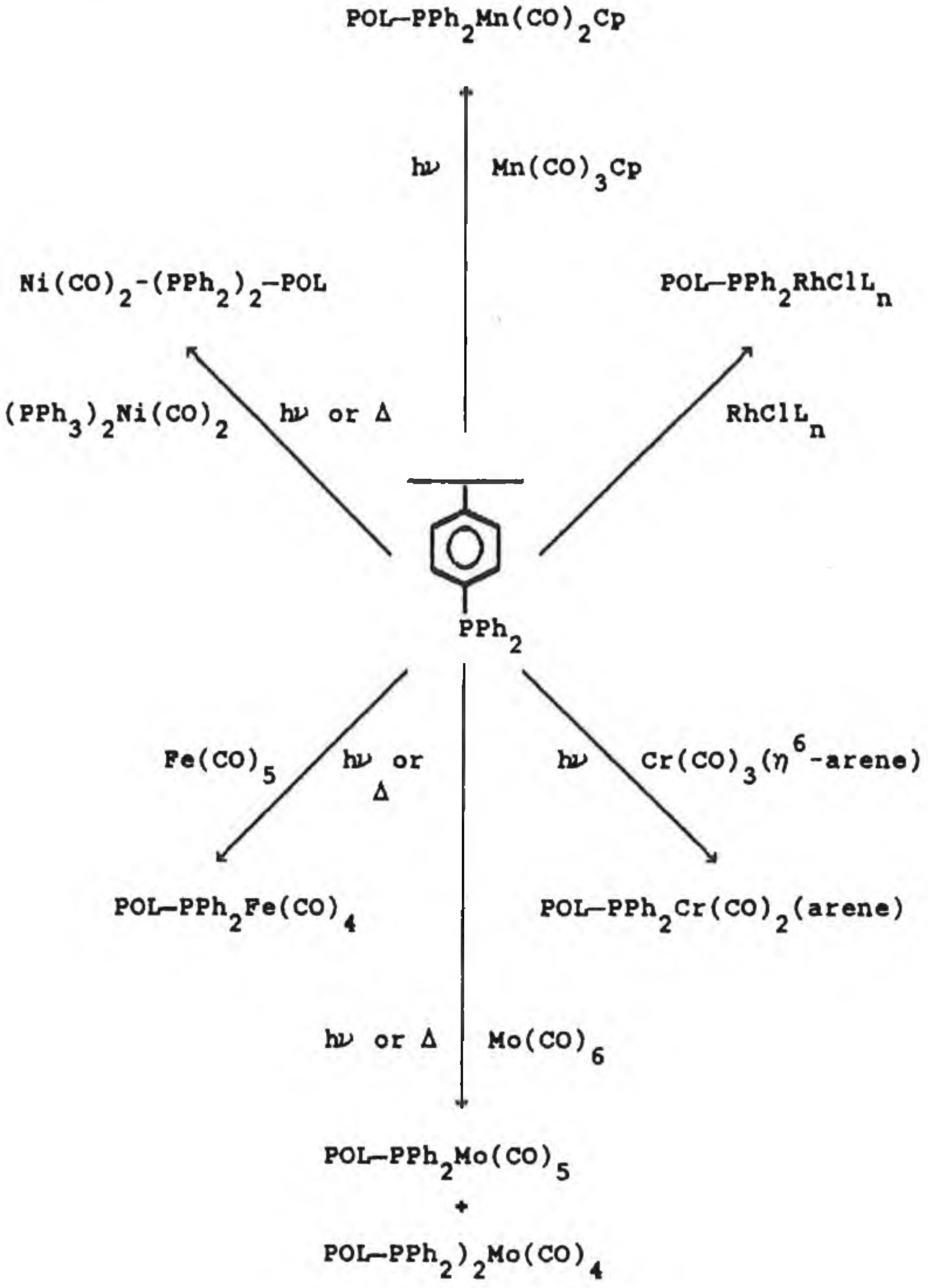
Polymeric phosphine ligands have have been synthesised in most reports by functionalisation of a preformed polymer. Examples include the preparation of the polymeric analogue of triphenylphosphine by the lithium diphenylphosphide-bromine route[33-35](I), and the preparation of polymeric analogues of benzyldiphenylphosphine by the reaction of lithium diphenylphosphide ($LiPPh_2$) with the corresponding chloromethylated polystyrene (II)[8,36,37]. Alternatively, the phosphine containing monomer may be prepared and then copolymerised[38-44] (III) (see Scheme 2). The method used will depend on the desired properties of the polymer, but because of the availability of polystyrenes with a wide range of crosslink densities, narrow molecular weight distributions, and surface areas and porosities, methods I and II have received most attention.



Scheme 2

Pittman[16] examined a large number of reactions of metal carbonyls with polymeric analogues of both benzyldiphenylphosphine and triphenylphosphine in terms of the extent of metal incorporation onto linear and cross-linked polymers and the properties of several of these species as catalysts in organic reactions. The compounds $M(CO)_6$ (M = Cr, Mo, or W), cyclopentadienylmanganese tricarbonyl ($CpMn(CO)_3$) and $Mn_2(CO)_{10}$ were reacted with the polymeric ligands to produce the bound metal carbonyls via carbonyl substitution reactions. The two metal phosphines compounds, $[(PPh_3)_2Ni(CO)_2]$ and $[(PPh_3)_3RhCl]$, were bound to the cross-linked polymeric ligands by phosphine exchange reactions. These and other phosphine bound metal carbonyls investigated are illustrated in Scheme 3.

In all the systems studied the reactions of the metal carbonyls with the polymeric ligands were found to proceed smoothly in a manner not unlike the reactions between the metal carbonyls and monomeric phosphines. Both the linear and the cross-linked resins were found to be reactive and a high percentage of metal was incorporated onto the polymers based upon the available phosphine present. Reactions of $M(CO)_6$ (M = Cr, Mo, or W) with polymer-bound benzyldiphenylphosphine were carried out both thermally and photochemically, both proving to be equally efficient in incorporating the metal carbonyl. The polymers were characterised by their infrared spectra and the CO stretching frequencies were similar to the


POL–PPh2Mn(CO)2Cp
hν
Mn(CO)3Cp
Ni(CO)2-(PPh2)2–POL
POL–PPh2RhClLn
(PPh3)2Ni(CO)2
hν or Δ
RhClLn
PPh2
Fe(CO)5
hν or Δ
hν
Cr(CO)3(η6-arene)
POL–PPh2Fe(CO)4
POL–PPh2Cr(CO)2(arene)
hν or Δ
Mo(CO)6
POL–PPh2Mo(CO)5
+
POL–PPh2)2Mo(CO)4

Scheme 3

related monomeric derivatives. Although the reactions were carried out using a molar excess of the metal carbonyl compound, the CO stretching spectra of the resin-bound derivatives of the group 6 hexacarbonyls indicated that significant amounts of trans-disubstituted derivatives had formed. This observation indicates a high degree of mobility of the coordination sites within the matrices containing a low degree of crosslinking.

Cais et al.[27] treated chloromethylated styrene-divinylbenzene resins with lithium diphenylphosphide to produce resins containing bound PPh_2 groups. A photochemical substitution reaction with phenanthrenechromium tricarbonyl yielded polymer attached phenanthrenechromium dicarbonyl units (see Scheme 3). They investigated the catalytic activity of this system in the hydrogenation of dienes. Mechanistic studies indicated that if the $Cr(CO)_3$ groups were attached directly to the phenyl rings the group would be leached into solution by coordinating solvents used in the reaction. Anchoring of arenechromium carbonyl complexes by a phosphine ligand covalently bound to the polymer would prevent leaching of the chromium moiety into solution in the course of the reaction. Scanning electron microscopy (SEM) showed that chloromethylation proceeded uniformly throughout the polymer beads, while phosphination and the photochemical reactions behaved differently, depending on the macrostructure and morphology of the polymer beads. It was discovered that polymers with large pores (1300Å) allowed the reagents (phosphine and chromium complex) to react throughout the polymer beads, while in polymers with small pores (<50A), penetration was limited.

In another study, Sanner and coworkers described the preparation and photocatalytic activity of a $Fe(CO)_n$ (n = 3 or 4) species bound to a styrene-divinylbenzene resin via a triarylphosphine anchor[45]. A key question concerning the use of polymer-anchored catalyst precursors concerns the photostability of the anchoring bond. In this instance the question posed was whether photoexcitation of $[POL\text{-}PPh_2]_{5-n}Fe(CO)_n$ will break Fe-P bonds or result in CO expulsion. Results for photocatalysed alkene isomerisation and alkene reaction with trialkylsilane using the polymer-anchored system were very similar to results found by using $[Fe(CO)_4PPh_3]$ and $[Fe(CO)_3(PPh_3)_2]$ in homogeneous solution. The photocatalytic activity was attributable to the photogeneration of coordinatively unsaturated iron carbonyl species which then follow a mechanism similar to that of $Fe(CO)_5$[46], with the perturbation of having triarylphosphine in the coordination sphere. Thus, irradiation of $[Fe(CO)_3(PPh_3)_{5-n}]$ (n = 4) resulted in loss of CO not PPh_3, suggesting a photoinert anchor to the $Fe(CO)_n$ groups in the polymer matrix. These experiments established the viability of photogenerating catalysts anchored to polymer supports without destruction of the anchor bond in the photogeneration procedure.

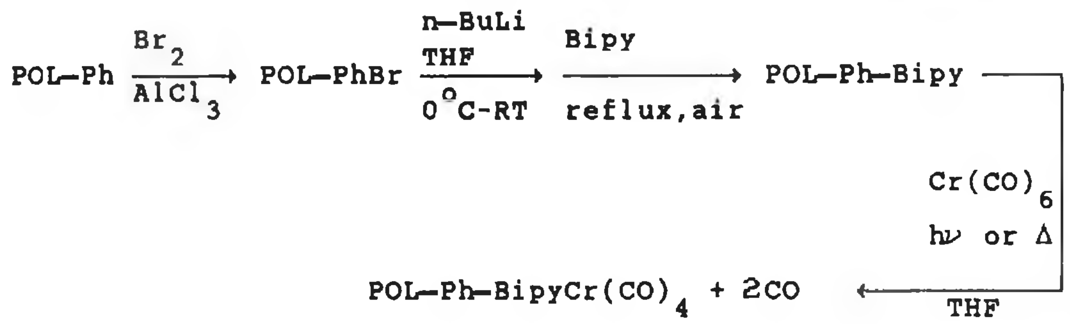
Polyvinylpyridines have been complexed with a large number of metal salts and complexes. Examples[3] include $Cu(OAc)_2$

complexes used as H_2O_2 decomposition catalysts, Mn(II) phthalocyanine complexes and other Cu(II) salts. Metal carbonyl complexes of pyridine and substituted pyridine are easily prepared by substitution reactions by thermal or photolytic means, and have been the subjects of many studies[32]. The synthesis of anchored group 6 metal carbonyls has been achieved by reaction with polymer-bound pyridine. Biedermann[48] first studied the substitution reactions of chromium and tungsten hexacarbonyls with poly-4-vinylpyridine. He reported that heating $M(CO)_6$ (M = Cr or W) and 4-vinylpyridine (L) in an evacuated autoclave gave $[ML_5CO]_n$, $[ML_6]_n$, $[ML_3(CO)_3]_n$, and $[ML_4(CO)_2]_n$. The complexes were characterised by their infrared spectra. Simultaneous polymerisation of L occurred during the reaction.

Moffat[47] reported the use of poly-2-vinylpyridine to support cobalt carbonyls. Since cobalt carbonyls attached to pyridine, triphenylphosphine, and other coordinating groups catalyse hydroformylations, Moffat proposed that polymers containing these groups might also do so. He found that poly-2-vinylpyridine can be used, but its behaviour is not quite what one would expect. Polymers of little or no crosslinking may be soluble under hydroformylation conditions but at high crosslinking the solubility is very low. At intermediate levels the polymer swells, but does not dissolve. With 4 to 8% DVB crosslinking, some of the catalytic portion of the molecule escapes into the solution and carries the reaction forward. The concentration of cobalt in the reaction medium under reaction conditions in Moffat's experiment was 100-300 ppm. Upon cooling and admission of H_2 and CO, the concentration fell to less than 10 ppm. He found that the cobalt carbonyl species are released from the the solid polymer phase, depending on the presence or absence of hydrogen. Thus surprisingly, the polymer acted as a catalyst reservoir.

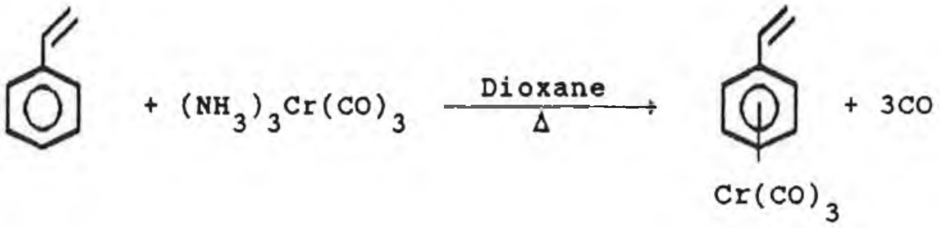
The synthesis, spectroscopic, chemical and photochemical properties of $M(CO)_5$ (M = Cr, Mo, or W) complexes of 2- and 4-vinylpyridine (4-VP) and their copolymers with vinylpyridines, styrene and methylmethacrylate have been studied[29]. It has been known that the efficiency of an organometallic catalyst can be greatly enhanced by UV irradiation and that the possibility exists for both generation and regeneration of the catalyst by this means. The $[W(CO)_5$(substituted pyridine)] was a particularly well characterised system[17,24,25]. It seemed therefore, that a study of $M(CO)_5$ complexes of polyvinylpyridine might prove useful in determining how the photoprocesses of a substituted metal carbonyl are affected by binding to a polymer and in seeing whether the photochemical properties of the complex can be "tuned" by systematic variation in the polymer backbone. The metal carbonyl containing polymers were synthesised either by reaction of photochemically generated $[M(CO)_5$(ethanol)] with a preformed well characterised homopolymer or copolymer of vinylpyridines (VP) or alternatively, by preparing the $[M(CO)_5$(VP)] complex and copolymerising it with other vinyl monomers. The results reported indicated that $M(CO)_5(4\text{-}VP)$ complexes have properties similar to those of other pyridine substituted metal pentacarbonyl species. However, 2-vinylpyridine complexes were unstable and this instability was probably attributable to the steric interaction of the $M(CO)_5$ group and the vinyl group. It was found that $M(CO)_5(4\text{-}VP)$ readily copolymerised with other vinyl monomers. Preliminary results indicated that the energy of the metal-to-ligand charge transfer band in the UV/visible is sensitive to the nature of the polymer backbone, shifting to lower energy when vinylpyridine replaces styrene in the polymer chain. Photocleavage of the W-N bond was found when $W(CO)_5(VP)$-copolymers were irradiated at $\lambda = 436$ nm and the relative quantum yield for photodissociation in styrene-4-vinylpyridine-$W(CO)_5(4\text{-}VP)$ terpolymers was dependent on the nature of the polymer backbone and in particular, on the proportion of uncoordinated vinylpyridine groups on the chain. These observations confirmed the view that it should be possible to "tune" the photochemical properties of organometallic compounds by binding them to polymers and so develop more effective photocatalysts.

The chelating ligand 2,2'-bipyridine (bipy) has been used to attach metal carbonyls to polymer matrices[49]. Card and Neckers reported the synthesis of a crosslinked polystyrene-based bipyridine system and discussed some of it's physical, chemical and catalytic properties. One of the potential advantages of a polymer-bound chelating ligand is the expected decreased lability due to the chelation effect[6]. The ligand was attached to the polymer backbone by reaction with the lithiated phenyl residues (see Scheme 4). Zerovalent metal carbonyl complexes such as [*POL*-Ph-bipy-M(CO)$_4$] (M = Cr, Mo, or W) were readily prepared by refluxing with the parent hexacarbonyl.



Scheme 4

A number of research groups have investigated transition metal carbonyl π-complexes bound to polymers. The preparation of vinyl monomers containing π-bonded metal carbonyls has received considerable attention. Rausch and Moser were the first to report the successful synthesis of η^6-(styrene)chromiumtricarbonyl (III)[50]. They reported that the reaction of styrene and triamminechromiumtricarbonyl in refluxing dioxane gives the desired vinyl metal carbonyl in 50-60% yield, while synthesis *via* a Wittig reaction involving benzaldehydechromiumtricarbonyl gives an improved yield of 83% (Scheme 5). Synthesis from chromium hexacarbonyl and styrene by methods analogous to those of Nicholls and Whiting[51] was unsuccessful producing only polystyrene and green chromium

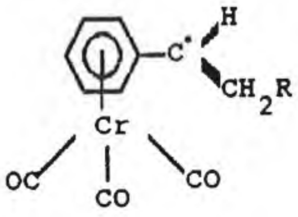


(III)

Scheme 5

salts. Studies suggested that (III) undergoes polymerisation less readily than does styrene itself. Attempts to polymerise (III) in degassed toluene at 60-80°C using azobisisobutyronitrile (AIBN) as the initiator failed. Under these same conditions styrene polymerises readily. However, thermal copolymerisation of styrene and (III) afforded the desired copolymer, identified by IR spectroscopy.

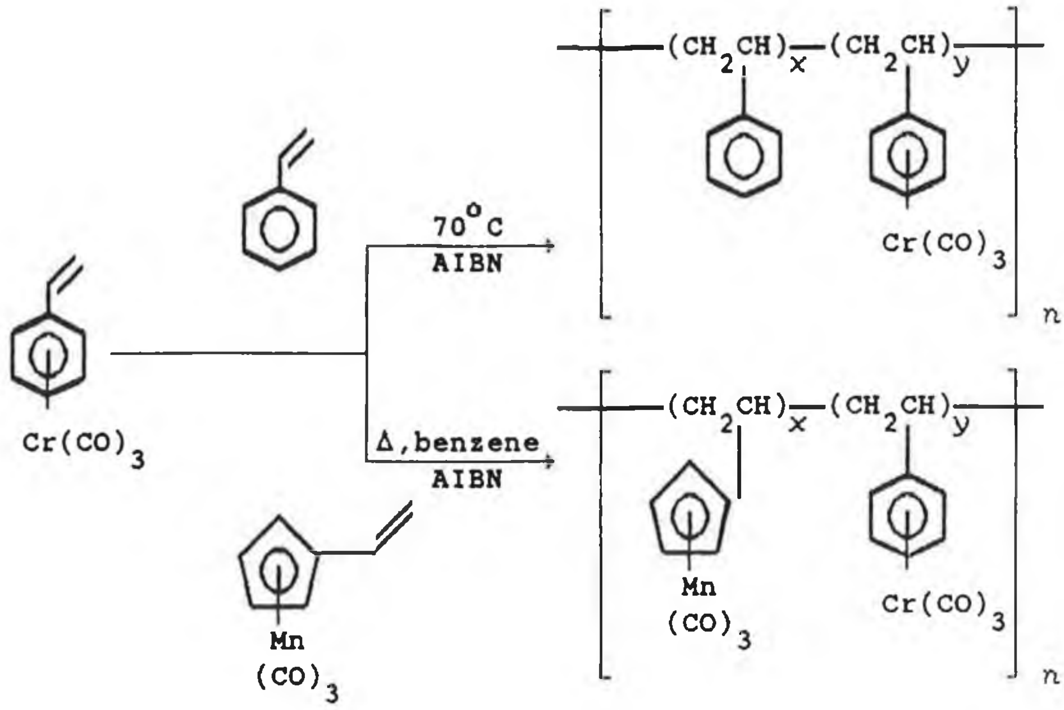
Pittman[52], in the first of his many detailed investigations into the reactivity of vinyl metal carbonyl monomers, probed the reactivity of the radical (IV) in copolymerisations with styrene and methyl acrylate. The values for the reactivities were found to be small, indicating that radical (IV) does not add (if at all) to (styrene)chromium tricarbonyl. This agreed well with the observed inability to homopolymerise this monomer. Radical (IV) readily adds to styrene and methyl acrylate, and also styryl and



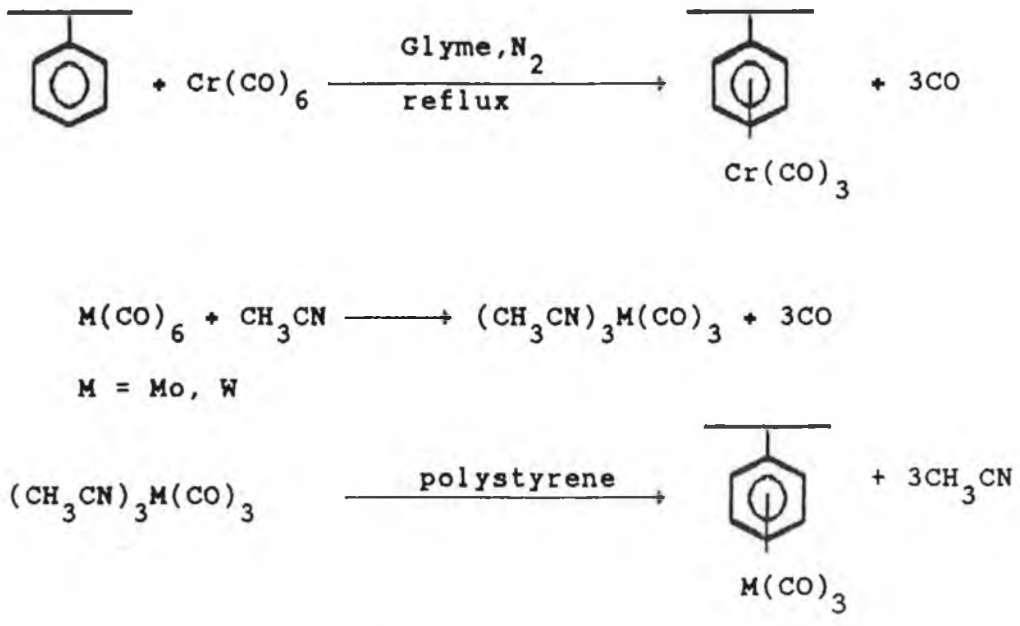
(IV)

methyl acrylate radicals readily add to (III). The π-$Cr(CO)_3$ moiety has a strong electron withdrawing effect, but it supplies electron density to adjacent centres of electron deficiency by resonance or a direct interaction mechanism. The ability of (IV) to add readily to both styrene and methyl acrylate, suggests that a steric effect might be preventing the addition of (IV) to (III). (Styrene)chromium tricarbonyl (III) was successfully copolymerised with styrene and methyl acrylate and with η^5-(vinylcyclopentadienyl)manganese tricarbonyl (Scheme 6)[52]. The copolymers were characterised by infrared spectroscopy.

An alternative route to (styrene)chromiumtricarbonyl polymers is the reaction of polystyrene with chromium hexacarbonyl by refluxing in dimethoxyethane according to scheme 7. Pittman et al. used this polystyrene-anchored chromium tricarbonyl in the hydrogenation of methyl sorbate[52c]. They found that the product distribution was different from that of a known homogeneous hydrogenation catalyst for methyl sorbate. They assigned this difference to diffusion into the polymer beads being a rate-limiting factor. Similar molybdenum and tungsten tricarbonyl polymers were synthesised by reacting the prepared tris-acetonitrile tricarbonyl complexes with polystyrene since the rate at which $Mo(CO)_6$ and $W(CO)_6$ react with aryl rings to give the respective π-complexes is much slower than that with $Cr(CO)_6$.

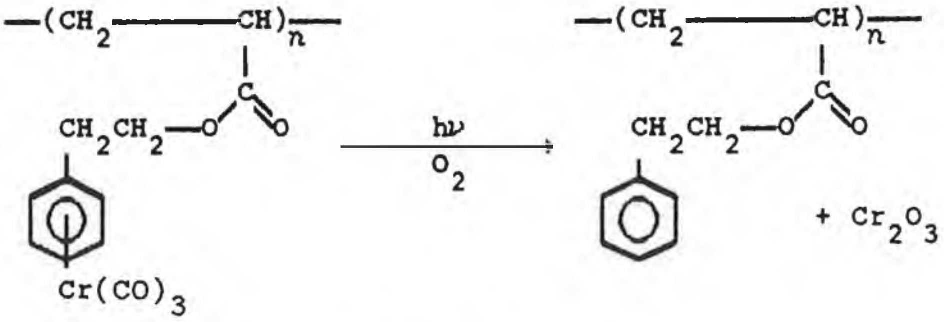


Scheme 6



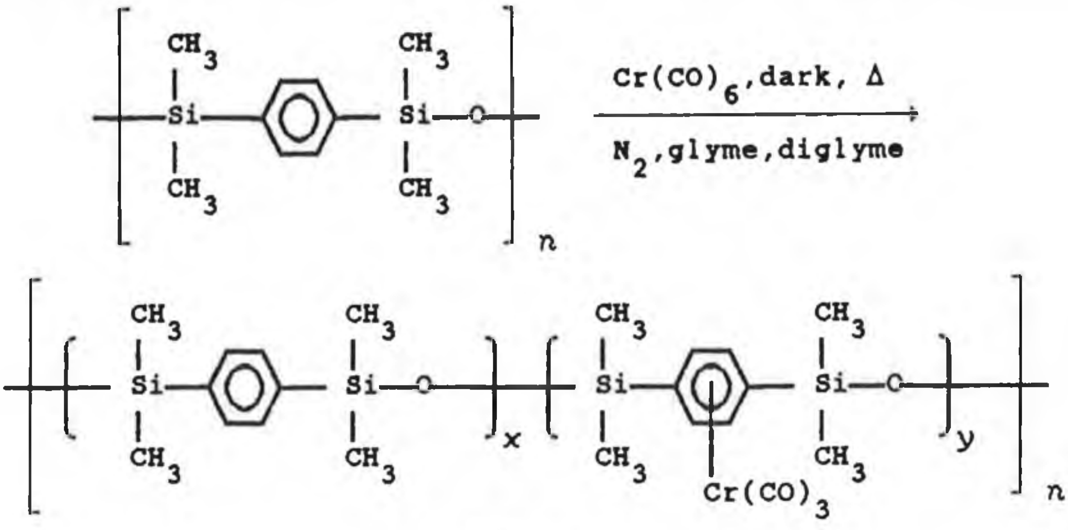
Scheme 7

Pittman and coworkers investigated other η^6-metal carbonyl vinyl monomers. The monomers η^6-(2-phenylethyl acrylate)chromium tricarbonyl (V)[53] and η^6-(benzyl acrylate)chromium tricarbonyl (VI)[54] were synthesised and copolymerised in solution at 70°C with styrene, methyl acrylate, acrylonitrile and 2-phenylethyl acrylate in ethyl acetate, AIBN being used as the radical initiator. A homopolymer of (V) and copolymer of (V) with styrene were decomposed under the influence of UV and visible light. The CO stretching bands in the infrared disappeared with continued exposure to light. The polymers were found to contain Cr_2O_3 (Scheme 8). Thermal decompositions were also conducted. These also resulted in decomposition of η^6-(aryl)$Cr(CO)_3$ units to produce mixed oxides embedded in the highly crosslinked polymers.



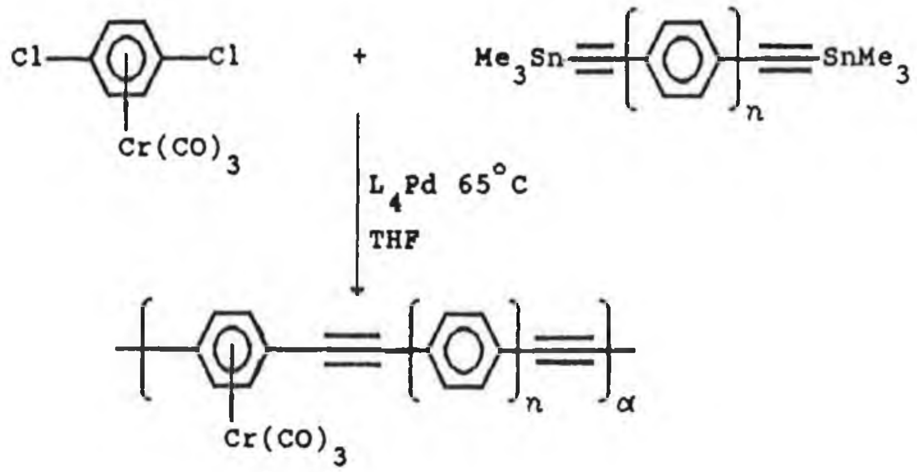
Scheme 8

In a succeeding paper, Pittman reported decomposition experiments of siloxane polymers to which transition metal carbonyls had been π-bonded to the aryl rings[55]. Two siloxane polymers were chosen for complexation with $Cr(CO)_6$. One of the siloxane polymers prepared, containing an in-chain phenyl substituent, is illustrated in Scheme 9. Thermal analysis indicated the loss of CO at 200°C and subsequent freeing of tiny chromium oxide particles within the polymer matrix.



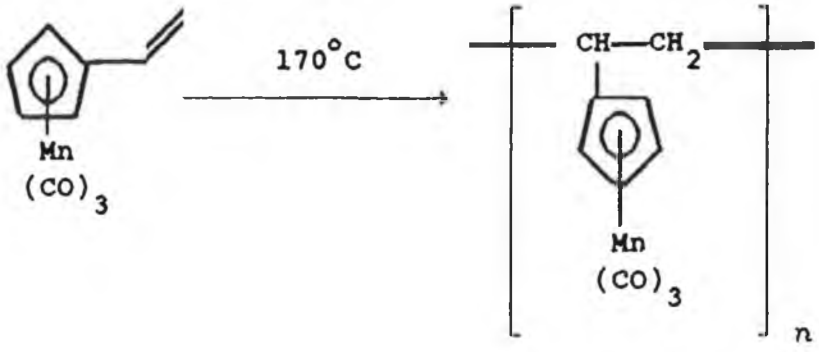
Scheme 9

In a more recent publication[56], Wright synthesised conjugated organic polymers having chromium carbonyls coordinated to the polymer backbone. He reported an efficient means of preparing conjugated polymers via the palladium-catalysed polycondensation of group 6 arene complexes with organostannane compounds (Scheme 10). Thermolysis of these polymers resulted in weight loss and changes in the infrared spectrum due to CO loss. Combustion analysis data and differential scanning calorimetry were consistent with carbon monoxide loss at the chromium metal centres followed by some form of cross-linking. A similar change in the infrared spectrum can be obtained by irradiating the polymer. Thermogravimetric analysis in air shows a break point of 381°C and rapid weight loss to give Cr_2O_3.



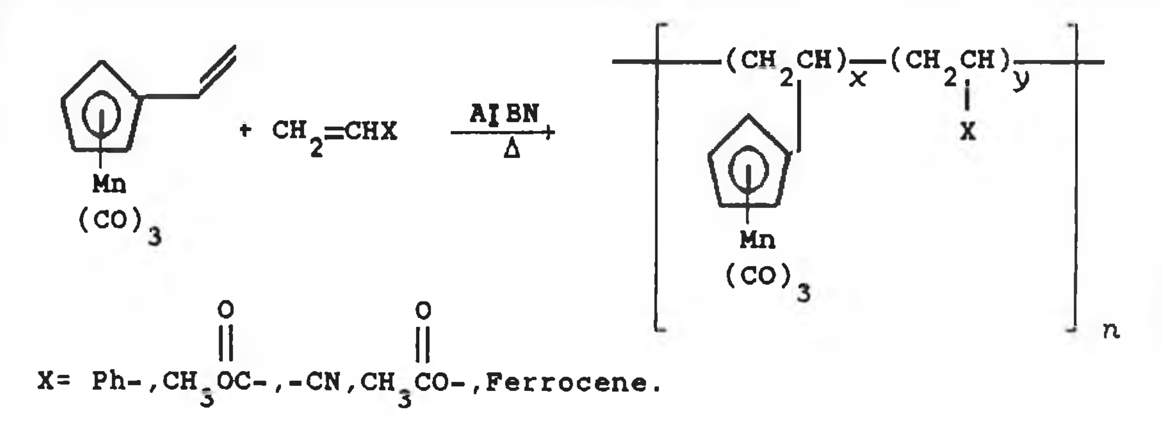
Scheme 10

One of the first organometallic carbonyl polymers prepared was reported by Cais[57], and involved the thermal polymerisation of η^5-(cyclopentadienyl)manganese tricarbonyl (VII) during the dehydration of (1-hydroxyethyl)cyclopentadienylmanganese tricarbonyl over $KHSO_4$ (Scheme 11). The polymerisation proceeded easily at 170°C to give an orange glassy polymer which softened at 80°C. This polymer was recommended as an additive to liquid and solid fuels as a combustion catalyst.



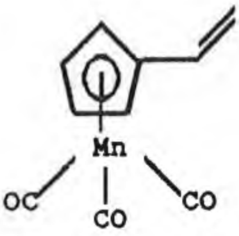
Scheme 11

Following this brief report, Pittman's group became the first to conduct a detailed study of η^5-CpM(CO)$_3$ containing polymer systems. Vinylcyclopentadienylmanganese tricarbonyl (VII) has been readily copolymerised with styrene, methyl acrylate, acrylonitrile, vinyl acetate and vinylferrocene in benzene or ethyl acetate at 70°C using azobisisobutyronitrile (AIBN) radical initiation (Scheme 12)[58]. The polymers were characterised by gel permeation chromatography (GPC) and infrared spectroscopy. The reactivity ratios were determined. It was found that transition metal carbonyl functions, when attached to a vinyl group, exert large effects on the addition polymerisation reactivity. These organometallic monomers exhibit very electron-rich vinyl groups in radical polymerisations. In another study, the same group synthesised η^5-(vinylcyclopentadienyl)dicarbonylnitrosyl chromium (VIII) and copolymerised it in solution with styrene and N-vinyl-2-pyrrolidone[59]. They demonstrated that changing the metallic fragment from Mn(CO)$_3$ to Cr(CO)$_2$NO did not effect the

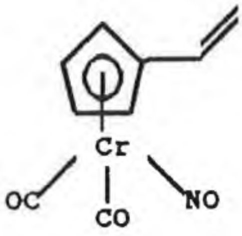


Scheme 12

reactivity of the vinyl group. Copolymers of (VIII) were shown to catalyse the selective 1,4-hydrogenation of methyl sorbate. The potential biological activity which monomer (VII) might impart to polymer coatings was investigated and the films formed were found to exhibit fungal resistance in accelerated growth tests.



(VII)

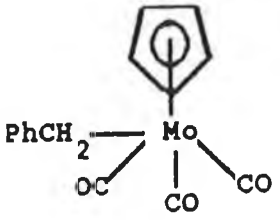


(VIII)

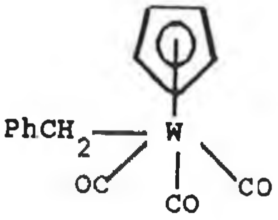
N-vinyl-2-pyrrolidone is a versatile monomer with useful adhesive properties. It's homopolymer is water soluble and forms hard, transparent films which are strongly adhesive to smooth surfaces. These properties, and the added advantage that it is inert toxicologically, mean that it finds great utility in the formulation of paints. With these properties in mind, Pittman copolymerised N-vinyl-2-pyrrolidone with (VII) to investigate if the presence of manganese and it's polar carbonyl groups might lead to useful adhesive properties[60]. The resulting copolymers were readily soluble and exhibited excellent adhesive properties. Thermal decompositions were carried on the copolymers and upon heating, carbon monoxide evolution was noted with corresponding weight loss, until at 280°C a dark insoluble polymer with no CO bands in the infrared remained. The decrease in solubility, it was suggested, resulted from crosslinking by cyclopentadienyl dimerisation. Also free manganese oxide distributed throughout the polymer would result in decreased solubility and darkening.

Tricarbonyl hydride derivatives of cyclopentadienyl chromium, molybdenum and tungsten compounds were covalently linked to highly crosslinked polystyrene (PS) supports by Brintzinger and Gubitosa[61]. Treatment of polystyrene-attached cyclopentadienyl anions with the respective metal hexacarbonyl and subsequent acidification gave $(PS)\text{-}CH_2\text{-}C_5H_4M(CO)_3H$ (M = Cr, Mo or W). The thermal stabilities of the polymer-supported cyclopentadienyl tricarbonyl hydrides, particularly those of chromium and molybdenum, up to temperatures close to the melting point of the polymer matrix contrasts sharply with the thermal instability of $C_5H_5Cr(CO)_3H$ and $C_2H_5Mo(CO)_3H$. These compounds are known to lose H_2 at temperatures of about 50°C with formation the binuclear species $[C_5H_5Cr(CO)_3]_2$, while the polymeric materials undergo decompositions with loss of H_2 and CO at much higher temperatures of about 200-210°C.

The use of metal carbonyl anions give particularly convenient routes to incorporate transition metal carbonyl moieties into polymers. Metal carbonyl anion chemistry provides facile routes to polymers where the organometallic group is fixed to the polymer via pendant σ carbon-metal bonds. Treating chloromethylated polystyrene resins with $NaMn(CO)_5$, introduced pendant [*POL*-$C_6H_4CH_2Mn(CO)_5$] functions in polymers[62]. Thermal decomposition at 140°C released $Mn_2(CO)_{10}$ within the matrix. In another paper the synthesis and thermal decomposition of η^1-benzyl-η^5-cyclopentadienylmolybdenum tricarbonyl (IX) (and tungsten (X)), and their linear and crosslinked polymers [*POL*-$C_6H_4CH_2M(CO)_3(C_5H_5)$] to which (IX) and (X) have been affixed were discussed[63].

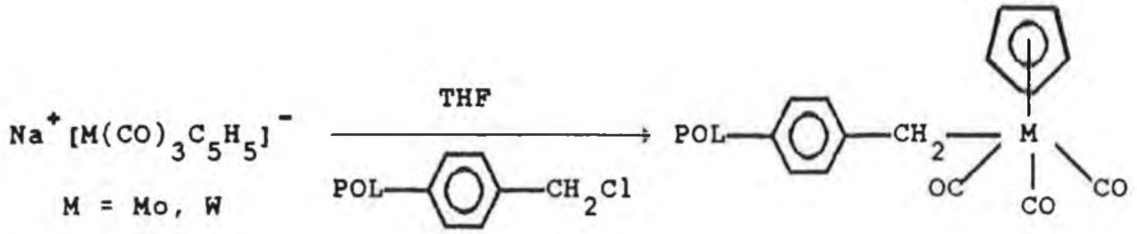


(IX)



(X)

The metal carbonyls, (IX) and (X), were attached to the polymer by reacting the chloromethylated polystyrene with either excess $Na^+[Mo(CO)_3C_5H_5]^-$ or $Na^+[W(CO)_3C_5H_5]^-$ to generate the desired polymer (see Scheme 13). Thermal studies of (IX) and (X) were carried out in solution and neat. Carbon-metal bond cleavage was followed by collapse to dimer. Large amounts of benzyl migration to the cyclopentadienyl rings occurred. The polymers decomposed more rapidly in solution than neat as larger amounts of dimer were recovered in solution decompositions. It was proposed that in the absence of solvent, carbon-metal recombination would be more efficient since the polymers were solid and radicals would be expected to have lower mobility. In solution, the $[C_5H_5M(CO)_3]^{\cdot}$ radical would have sufficient mobility to allow radical combination reactions to produce dimeric species. The tungsten polymers decomposed more slowly than their molybdenum analogues in agreement with the well established increase in metal-carbon bond strengths moving from Cr to Mo to W.



Scheme 13

The main growth in the research of attaching an organometallic transition complex to an organic polymer backbone arose from the greatly improved and easy separation of expensive anchored catalysts from reaction mixtures. It later became clear that the support could play an even more important role other than improving catalyst separation. Not only was it found that these "heterogenised" systems could perform as well as their homogeneous analogues, but by varying the composition of the polymer backbone one could introduce selectivities based on the properties of the support. So the outcome of a catalytic reaction can depend as much on the polymeric support, as on the bound catalyst. Selectivities have been induced in polymer-bound systems simply by changing the crosslink density. The number of polymers available which can be used to attach transition metal complexes is enormous and the different inherent properties of these polymers can be used and chosen to ones advantage. The vast majority of work in this area has been involved in the area of organometallic catalysis and because of the interest this topic generates, numerous comparisons with the known homogeneous systems have been conducted. Organometallic catalysis is not the only area these materials find applications. Reports have appeared acknowledging their use in a wide variety of applications including uses in electronic and biomedical applications.

Transition metal carbonyls can be easily attached to polymer supports with high degrees of metal incorporation. Many vinyl containing metal carbonyl complexes have been synthesised and both homopolymerised and copolymerised with widely available comonomers. The intense absorptions of metal carbonyls in the infrared make them easily characterisable. The ease with which metal carbonyls undergo photochemical and thermal reaction make them ideal for investigation due to the wide number of photochemical, spectroscopic and thermal techniques available for their study. A great deal of research is performed in the field of metal carbonyl chemistry every year, so the potential number of analogous polymer-bound related experiments is enormous. Metal carbonyl incorporation into polymer backbones is achieved relatively easily, in one step reactions in most instances. However, a look at the literature illustrates just how little work has been done into this area. Much of the research concentrates on their use, not surprisingly, as polymer-bound catalysts. Another area of interest is the thermal decomposition of metal carbonyl moieties to free metals, metal oxides or organometallic carbonyl groups within polymeric matrices.

This thesis is concerned with the preparation of a series of polymer-bound group 6 metal carbonyl compounds and the examination of the effect of polymer-binding on the chemistry of the metal carbonyl moieties. This work has as it's general aim the synthesis of polymers in which active coordinatively unsaturated species could be generated, either by thermal or photochemical means. The 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.

CHAPTER 2

THE SYNTHESIS AND CHARACTERISATION OF POLYMER-BOUND GROUP 6 METAL CARBONYLS

and tetracarbonyls are rare. The photochemistry of these metal carbonyls, and to a lesser extent the thermal chemistry, of these metal carbonyls is well known and documented. It seemed likely then, that the polymer bound analogues would be photochemically and thermally reactive also, but the effect the polymer backbone might have on these reaction routes was of interest.

The syntheses of suitable polymerisable ligands and metal carbonyl containing systems and the polymerisation, identification and characterisation of appropriate copolymers will be discussed in this section. Laser flash photolysis studies investigating the mechanism and kinetics of binding of the metal carbonyl fragment to the polymer backbone will also be presented. The experimental details of syntheses and procedures employed are presented collectively in section 5.

2.2 Preparation of Polymer-Bound Metal Carbonyls

The polymers of interest contain contain pendant donor atoms, in particular nitrogen or phosphorus. The synthesis of polymer-bound metal carbonyls of this type can be achieved by two routes. The first route involves the preparation of the polymer and subsequent complex forming reaction to bind the metal carbonyl moiety to it (Scheme 14a). The second pathway involves the preparation of the metal complex containing a polymerisable group which can later be copolymerised with suitable comonomers producing the desired polymer-bound complex

(Scheme 14b). Advantages and disadvantages exist for both routes. Using the first route (Scheme 14a), the polymer can be fully characterised before complex binding. However, during the complex forming reaction it is possible that not every site on the polymer backbone will coordinate to a metal centre (even though a 1:1 ratio of $W(CO)_5$ moieties to pendant sites on the polymer is used). In the latter case (Scheme 14b), every pendant site is coordinated to a metal centre because the metal carbonyl was reacted with a polymerisable ligand, purified and then copolymerised so that the loading of metal carbonyl complex in the polymer backbone is known. Unfortunately these polymer systems are difficult to characterise. Both of these methods were utilised in this work, depending on the particular properties required of the polymer.

The metal carbonyl complexes were bound to the polymer supports by reaction with $[M(CO)_5(\text{tetrahydrofuran})]$ (M = Cr, Mo, or W) in tetrahydrofuran (THF) at the required concentration. The $[M(CO)_5(THF)]$ species is generated by photolysis of the parent hexacarbonyl, $M(CO)_6$, in THF[17,24,25].

$$M(CO)_6 + S \xrightarrow[N_2]{h\nu} M(CO)_5S + CO$$

$$M(CO)_5S + L \longrightarrow M(CO)_5L + S$$

M = Cr, Mo or W
S = Solvent
L = Monomer or polymer containing a pendant donor atom.

Scheme 15

Irradiation of $M(CO)_6$ in a weakly coordinating solvent such as THF in the presence of an incoming ligand, proceeds by a stabilised transition state to give an observable $[M(CO)_5S]$ intermediate. The addition of L then gives the product by facile replacement of the coordinated solvent molecule.

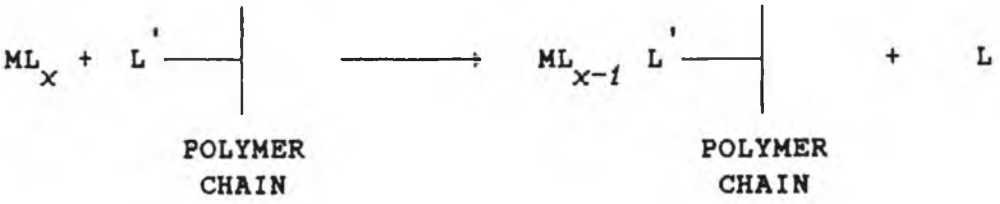
In this study, all the monomer and polymer metal carbonyl complexes were prepared by the same above route involving reaction with $[M(CO)_5(THF)]$. The solvent adduct $[M(CO)_5(THF)]$ is generated as a clear yellow solution by photolysis of $M(CO)_6$ in freshly distilled THF under a continuous nitrogen purge, and added to a solution of the monomer or polymer in THF. The solvent is then removed under reduced pressure, the THF being displaced from the metal complex by the pendant moieties on the polymer backbone to form the desired metal carbonyl system. In the instance of polymer or monomers containing bipyridyl (bipy) binding sites, an additional thermal decarbonylation occurs during the preparation to give the tetracarbonyl species.

$$W(CO)_5S \quad + \quad \text{bipy} \quad \xrightarrow{\Delta} \quad W(CO)_5(\text{bipy}) \quad + \quad S$$

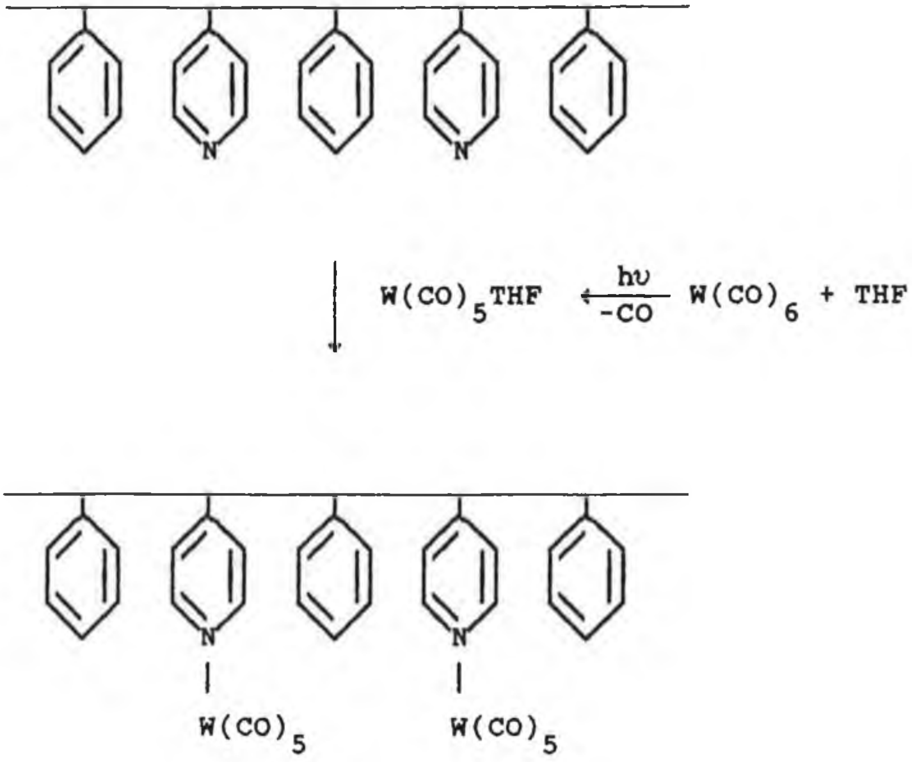
$$W(CO)_5(\text{bipy}) \quad \xrightarrow{\Delta} \quad W(CO)_4(\text{bipy}) \quad + \quad CO$$

ROUTE 1

Direct reaction of the metal carbonyl complex with a polymer containing pendant binding sites.



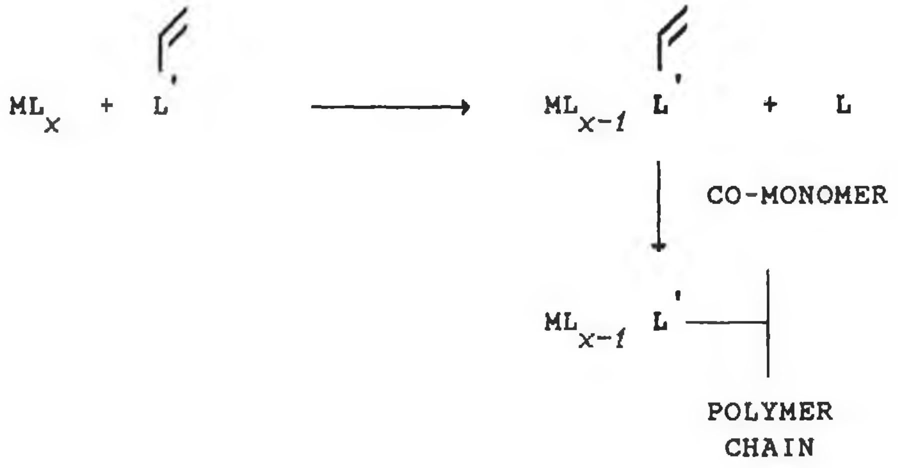
FOR EXAMPLE :



Scheme 14a

ROUTE 2

Formation of the metal carbonyl complex containing a polymerisable group followed by copolymerisation of complex with suitable comonomers.

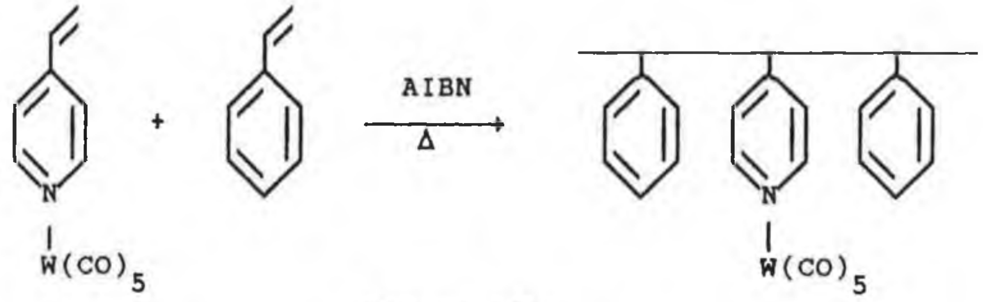


FOR EXAMPLE :

$$W(CO)_6 + THF \xrightarrow{h\nu} W(CO)_5THF + CO$$

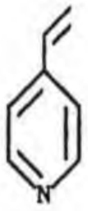
$$W(CO)_5THF + 4\text{-}VP \longrightarrow W(CO)\ (4\text{-}VP) + THF$$

VP = vinylpyridine

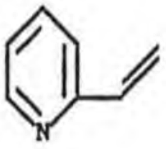


Scheme 14b

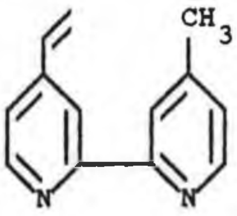
The ligands/monomers of interest 4-vinylpyridine (XI), 2-vinylpyridine (XII), 4-vinyl-4'-methyl-2,2'-bipyridyl (XIII), and p-styryldiphenylphosphine (XIV) are illustrated below. The vinylpyridines (XI) and (XII) are commercially available, (XIII) was synthesised according to the method of Ghosh and Spiro[32b], while (XIV) was prepared by Grignard synthesis from p-bromostyrene and chlorodiphenylphosphine[38]. Each monomeric ligand contains a donor atom (nitrogen or phosphorus) and a polymerisable vinyl group. These ligands readily replace carbon monoxide from metal carbonyl complexes (see Scheme 15 above) and yield stable complexes which survive polymerisation reactions using AIBN as the radical initiator.



(XI)



(XII)



(XIII)

(XIV)

Complexes of the type $[W(CO)_5(Xpy)]$, where Xpy represents a substituted pyridine, are particularly well characterised and have been the subject of many photochemical investigations[16,24,25]. Pyridine is a ligand with good donor ability, and it and it's substituted derivatives are the most common type of σ-donor nitrogen ligands found in metal carbonyl compounds, although reports of similar polymer-bound systems are rare. Homopolymers and copolymers of vinylpyridines containing bound $M(CO)_5$ moieties have been previously investigated as potential photocatalysts, and the effects of the polymer backbone composition on the observed photochemistry discussed[29]. The bidentate nitrogen ligand 2,2'-bipyridyl, has been the topic of many studies[64]. Potentially bidentate nitrogen ligands (L-L) can act as chelating ligands or as bridging ligands if geometrical constraints preclude chelation. Many of the studies of chelation reactions have been carried out with α-diimine ligands such as 2,2'-bipyridyl. The chelation processes of such ligands at metal hexacarbonyl centres, particularly $Cr(CO)_6$, have been investigated. The efficiency of bipyridyl and other diimine ligands is due to both their chelating ability and a balance between their σ-donor and π-acceptor properties. The ligand 4-vinyl-4'-methyl-2,2'-bipyridyl (XIII) and similar vinyl monomers have been copolymerised and used to anchor ruthenium complexes and tungsten tetracarbonyl complexes for use as electrode coatings[67]. In other papers, 2,2'-bipyridyl has been attached directly to polystyrene polymers from the reaction of lithiated polystyrene with bipyridyl in THF and used to complex chromium tetracarbonyl and palladium complexes[30].

Group 6 carbonyl complexes with monodentate phosphorus ligands are usually synthesised using standard substitution reactions. The phosphorus atom has a lone pair of electrons available for σ-donation, as well as an empty $3d\pi$ orbital of the appropriate symmetry and energy to accept electron density from the metal in a π-bonding interaction. Although amines are better σ-donors than trivalent phosphorus compounds, the π-acceptor capability of the phosphorus ligands makes them effective as ligands in complexes of metals in low oxidation states. In general, the greater the electronegativity of the substituent on the phosphorus atom, the poorer the basicity of the lone pair, and the poorer the σ-donation. Many monomeric phosphines of the type $[M(CO)_5(PPh_3)]$ have been synthesised and characterised[65]. Phosphine ligands have received most attention in the area of polymer-bound organometallic complexes and have been widely used as anchors to attach organometallic transition metal complexes to polymeric supports[33-37]. Polymers containing phosphine ligands have been prepared either by functionalisation of preformed polystyrenes or by copolymerising p-styryldiphenylphosphine (XIV) with suitable comonomers, followed by subsequent complex forming reaction. Pittman et al.[16] attached group 6 metal carbonyls to a crosslinked polystyrene support containing diphenylphosphino ligands by both thermal and photochemical means. Polymer-bound phosphines have also found utility as polymeric reagents in Wittig olefin synthesis[66].

The monomers of interest were either copolymerised with suitable comonomers (Scheme 14a) and then reacted with $[M(CO)_5(THF)]$ to give the polymer-bound metal carbonyl or, firstly reacted with $[M(CO)_5(THF)]$ to give the functionalised monomer and then copolymerised (Scheme 14b). Copolymerisations were carried out by free-radical polymerisation at 70-80^{0}C in the absence of solvent under a nitrogen atmosphere, using azobisisobutyronitrile (AIBN) initiation. The polymerisations all proceeded in good yield, and the polymers were readily purified by repeated precipitation from chloroform by petroleum ether.

2.3 Characterisation of Polymer-Bound Metal Carbonyl Systems

A number of techniques are available for the study and characterisation of these materials. Spectroscopic techniques have been invaluable in the study of group 6 metal carbonyls and their derivatives, but in these systems one can utilise techniques employed for the analyses of polymers also, and apply them to the polymer-bound metal carbonyl materials. In the following sections, infrared and UV/vis spectroscopy, elemental analysis and gel permeation chromatography (GPC) are discussed with particular regard to the characterisation of these polymeric materials.

2.3.1 *Vibrational Spectra of Metal Carbonyls.*

Infrared spectroscopy is widely used in the study of metal carbonyls since the CO stretching frequencies give very strong sharp bands (ε up to 10,000) well separated from other vibrational modes of any other ligands that may also be present. CO is a very weak electron donor and the principal process which holds the CO onto the metal is back-bonding[6]. Thus the bonding in metal carbonyl compounds involves a dative overlap of filled carbon σ-orbital and 3d σ-orbitals of the metal, and a dative overlap of a filled 3dπ metal orbitals with empty pπ^* orbitals of the CO. As CO "pushes" electrons onto the metal atom, the metal can off-load the increased electron density into the π^* orbital in CO. So the π^* antibonding orbital in CO is partially populated. The effect of this back-bonding is to increase the M-C bond strength while reducing the strength of the C-O bond. Therefore, the carbonyl stretching frequency (ν_{CO}) of CO decreases on binding to the metal. The CO molecule has a stretching frequency of 2143 cm^{-1} in the gas phase, while terminal CO groups in neutral metal carbonyl molecules are found in the range 2100 to 1800 cm^{-1}, showing the reduction in CO bond orders. Moreover, when changes are made that should increase the extent of M-C back-bonding, the CO frequencies are shifted to even lower values. Thus, if some CO groups are replaced by ligands with low or negligible back-accepting ability, those CO groups that remain must accept more dπ electrons from the metal to prevent the accumulation of negative charge on the metal atom. Hence, the frequency of $Cr(CO)_6$ is *ca.* 2000 cm^{-1} whereas, when three CO's are replaced by amine groups which have essentially no ability to back-accept, as in $Cr(CO)_3$(dien), dien = $NH(CH_2CH_2NH_2)_2$, two CO stretching absorptions are observed at *ca.* 1900 and *ca.* 1760 cm^{-1}.

The most important use of infrared spectra of metal carbonyl compounds is in structural diagnosis, whereby bridging and terminal CO groups can be recognised. For terminal M-CO the frequencies of C-O stretches range 1800-2100 cm^{-1} but for bridging CO groups the range is 1700-1800 cm^{-1}. These facts may be used to infer structures. In general, we can also state that every unique CO in the molecule will give one stretching frequency while every group of equivalent CO's will give two stretching frequencies. In this way we can tell the molecular conformation formed from the number of CO stretching frequencies in the infrared. Symmetry elements can be used to determine the number of infrared active modes. A point group is assigned and symmetry operations performed on the molecule. The active modes can then be determined from character tables.

2.3.2 Infrared Spectroscopic Properties of Monomer Complexes.

The metal carbonyl containing monomers were prepared as described earlier by reaction with photogenerated $[M(CO)_5(THF)]$. Metal carbonyl complexes of 2- and 4-vinylpyridine (vp), $[M(CO)_5(vp)]$ (M = Cr, Mo, or W), were obtained as bright yellow crystalline solids and were purified by recrystallisation from degassed ethanol. All the complexes were handled as air sensitive and in general the stability of the complexes is in the order W > Cr >> Mo and 4-vp > 2-vp). The decreased stability of the 2-vinylpyridine may be attributed to steric interaction of the $M(CO)_5$ group and the vinyl group[29]. The infrared absorption spectra of these complexes show three strong bands due to the C-O stretch of the carbonyl groups (2100-1700 cm^{-1}) (Table 2.1). The spectra of each pentacarbonyl are identical in all qualitative features (see Fig. 2.1). The pattern and position of the ν_{CO} vibrations are those expected for a $M(CO)_5$ metal carbonyl moiety and are consistent with a C_{4V}

local symmetry and importantly, the similarity of all the complexes is consistent with bonding of the pyridine through the pyridine ring nitrogen atom[68,69]. No evidence was found for other complexes such as $(\eta^2\text{-vp})M(CO)_5$, $M(CO)_5(\mu\text{-vp})M(CO)_5$, or $M(CO)_4(vp)_2$, indicating that these must be at very best minor products.

Assignments of the spectral bands can be made from symmetry operations, and these systems are well characterised and data is available for comparison[68-71]. In Figure 2.1, band 1 is assigned to the A_1 mode. This band occurring *ca.* 2065-2075 cm^{-1} is characteristic of a pentacarbonyl species. Kraihanzel and Cotton[70] have assigned band 2 to the B_1 mode. This band is Raman active only, but they suggest that it gains some infrared intensity because the structure of the ligand makes it impossible for the molecule to have true C_{4v} symmetry. The T_{1u} mode of the hexacarbonyls appears around the frequency of the B_1 mode also, so the band could be due to hexacarbonyl impurity. Bands 3 and 4 are assigned to the E and A_1 modes respectively, the bands being just resolved, the A_1 mode appearing as a shoulder.

Reaction of photogenerated $[M(CO)_5(THF)]$ with p-styryldiphenylphosphine (XIV) yields the pentacarbonyl species. The spectral features of the phosphine complex are similar to those of the $[M(CO)_5(vp)]$ metal carbonyls. However, Kraihanzel and Cotton[65] stated that in complexes of the type

$[M(CO)_5(PPh_3)]$, the E and A_1 modes are accidentally degenerate, or so nearly so that the bands are entirely unresolved. Lowering the π-acceptor strength of the substituent (from phosphine to amine) would lower the frequency of the A_1 mode relative to the E mode and so the bands are resolved in amine complexes. In all spectra of the pentacarbonyl species however, the assignment of the E and A_1 modes are difficult due to the broadness of the bands.

Figure 2 shows the spectrum of the tungsten tetracarbonyl complex of 4-vinyl-4'-methyl-2,2'-bipyridyl (XIII) and the frequencies of all compounds are listed in **Table 2.1**. The four non-degenerate CO stretching frequencies are consistent with a C_{2v} *cis*-disubstituted symmetry at the metal centre[70,72,73]. The assignments of these bands are shown in **Figure 2.2**[70]. The high frequency band at *ca*. 2000 cm^{-1} is indicative of a tetracarbonyl species. The stretching frequencies are close to those previously reported for *cis*-disubstituted tetracarbonyl 2,2'-bipyridyl complexes[72].

Table 2.1. The CO stretching frequencies for monomer complexes.

Complex	ν_{CO} (cm^{-1})[a]
$W(CO)_5$(4-vp)	2068 (m), 1931 (s), 1904 (sh)
$Cr(CO)_5$(4-vp)	2063 (m), 1938 (s), 1907 (sh)
$Mo(CO)_5$(4-vp)	2070 (m), 1944 (s), 1904 (sh)
$W(CO)_5$(2-vp)	2067 (m), 1927 (s), 1910 (sh)
$Cr(CO)_5$(2-vp)	2065 (m), 1935 (s), 1918 (sh)
$W(CO)_4$(Vbipy)	2001 (m), 1883 (sh), 1861 (m), 1808 (s)
$Cr(CO)_4$(Vbipy)	2003 (m), 1890 (s), 1860 (sh), 1807 (s)
$Mo(CO)_4$(Vbipy)	2007 (m), 1887 (s), 1861 (sh), 1810 (s)
$W(CO)_5$(p-SDPP)	2069 (m), 1936 (s)

[a] In Nujol mulls beteen sodium chloride windows.

vp = vinylpyridine Vbipy = 4-vinyl-4'-methyl-2,2'-bipyridyl,

p-SDPP = *para*-styrldiphenylphosphine.

m = moderate intenity, s = strong, sh = shoulder.

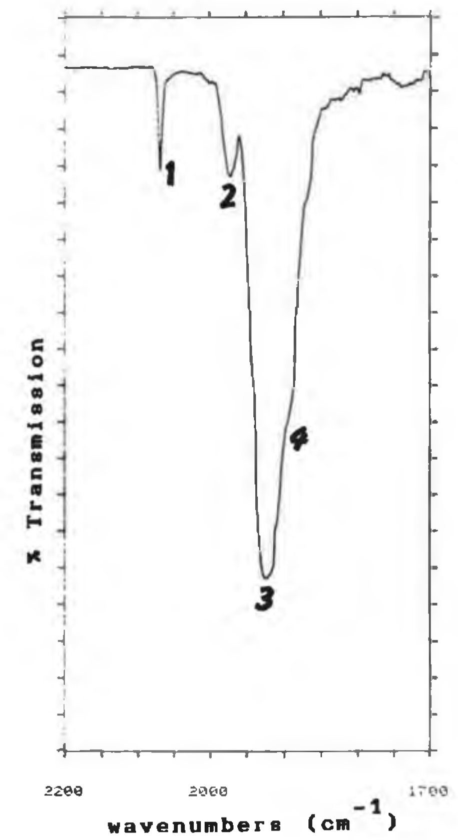
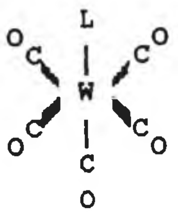


Fig.2.1. The CO stretching region of $[W(CO)_5(4\text{-vp})]$ in nujol. The spectra of analogous Cr and Mo complexes are virtually identical.

Band 1: A_1 2068 cm^{-1}
Band 3: E 1931 cm^{-1}
Band 4: A_1 1904 cm^{-1}

monodentate pentacarbonyl



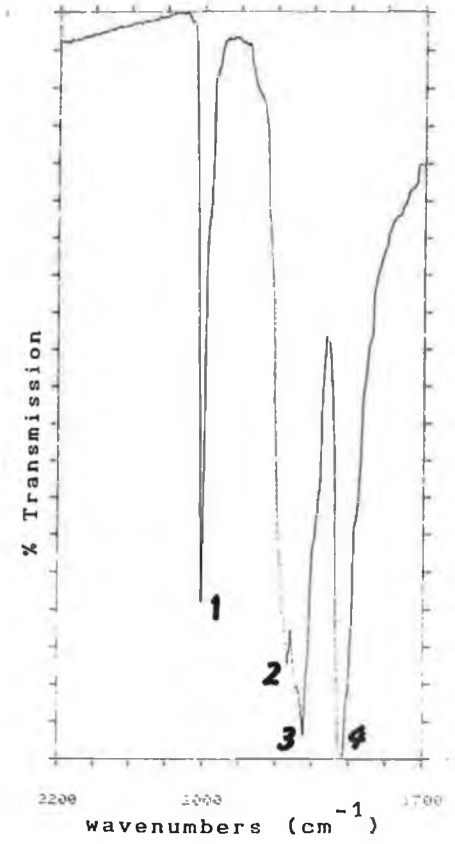
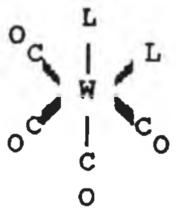


Fig.2.2. The CO stretching region of *cis*-$[W(CO)_4(Vbipy)]$ in nujol. Cr and Mo complexes have similar spectra.

Band 1: A_1 2001 cm^{-1}
Band 2: B_1 1883 cm^{-1}
Band 3: A_1 1861 cm^{-1}
Band 4: B_2 1807 cm^{-1}

cis-disubstituted tetracarbonyl



2.3.3 *Infrared Spectroscopic Properties of Polymer Complexes.*

The incorporation of the metal carbonyl fragment into the polymers can be confirmed easily from the strong bands exhibited by the polymer-bound metal carbonyls in the carbonyl stretching frequency region of the infrared spectrum. These bands are well separated from interfering polymer bands. From the number and position of the carbonyl bands the coordination about the metal can be easily determined. The spectra are essentially identical in appearance to those of the analogous monomers. The frequencies of the CO stretching modes are shown in Table 2.2.

……

Notes on Table 2.2

[a] All the copolymers were prepared so that the mole ratio of metal carbonyl to monomer was 20/1.

[b] Chloroform film on sodium chloride window.

Copolymers represented thus, P[comonomers]-M(CO)$_x$, were prepared using Route 1, while those written P[comonomers-M(CO)$_x$] were pepared by Route 2.

P = copolymer, EA = ethyl acrylate, MA = methyl acrylate

MMA = methylmethacrylate

vp = vinylpyridine, p-SDPP = p-styrldiphenylphosphine

Vbipy = 4-vinyl-4'-methyl-2,2'-bipyridyl.

[*] Pentacarbonyl and tetracarbonyl species both present.

Peak assignments are accurate to +/- 3cm^{-1}.

w = weak intensity, m = moderate, s = strong, sh = shoulder.

[†] Bands due to C=O stretch of acrylate polymer backbone.

……

Table 2.2. Infrared Spectral Data in the Carbonyl Stretching Region for Polymer Complexes.

Complex[a]	ν_{CO} (cm^{-1})[b]
P[styrene-W(CO)$_5$(4-vp)]	2068(m), 1926(s), 1892(sh)
P[styrene-Cr(CO)$_5$(4-vp)]	2064(m), 1929(s), 1900(sh)
P[styrene-Mo(CO)$_5$(4-vp)]	2070(m), 1935(s), 1905(sh)
P[styrene-(4-vp)]W(CO)$_5$	2068(m), 1926(s), 1890(sh)
P[styrene-(4-vp)]Cr(CO)$_5$	2064(m), 1929(s), 1900(sh)
P[styrene-(4-vp)]Mo(CO)$_5$	2070(m), 1935(s), 1900(sh)
*P[styrene-(Vbipy)]W(CO)$_4$	2072(w), 2002(m), 1931(s), 1881(s) 1865(sh), 1825(s)
P[styrene-W(CO)$_4$(Vbipy)]	2003(m), 1890(s), 1876(sh), 1830(s)
*P[styrene-(Vbipy)]Cr(CO)$_4$	2070(vw), 2003(m), 1930(w), 1892(s) 1870(sh), 1826(s)
P[styrene-Cr(CO)$_4$(Vbipy)]	2001(m), 1890(s), 1878(sh), 1830(s)
P[styrene-(Vbipy)]Mo(CO)$_4$	2008(m), 1898(s), 1876(sh), 1831(s)
P[EA-W(CO)$_5$(4-vp)]	2069(m), 1926(s), 1890(sh), †1724(s)
P[EA-Cr(CO)$_5$(4-vp)]	2065(m), 1934(s), 1898(sh), †1727(s)
P[EA-W(CO)$_4$(Vbipy)]	2001(m), 1883(s), 1858(sh), 1830(m) †1726(s)
P[MA-W(CO)$_5$(4-vp)]	2069(s), 1914(s), 1885(sh), †1727(s)
P[MMA-W(CO)$_5$(4-vp)]	2068(m), 1933(s), 1900(sh), †1723(s)
P[MMA-Cr(CO)$_5$(4-vp)]	2065(m), 1935(s), 1895(sh), †1723(s)
P[MMA-Mo(CO)$_5$(4-vp)]	2071(m), 1936(s), 1898(sh), †1723(s)
*P[styrene-(p-SDPP)]W(CO)$_5$	2068(m), 2012(m), 1935(s), 1888(sh)
*P[styrene-(p-SDPP)]Cr(CO)$_5$	2069(m), 2004(m), 1936(s), 1883(sh)
*P[styrene-(p-SDPP)]Mo(CO)$_5$	2069(m), 2017(m), 1942(s), 1903(sh)
P[styrene-W(CO)$_5$(p-SDPP)]	2072(m), 1935(s), 1910(sh)
P[(4-vp)-W(CO)$_5$(4-vp)]	2069(w), 1924(s), 1895(sh)
P[(2-vp)-W(CO)$_5$(2-vp)]	2069(w), 1931(s), 1905(sh)

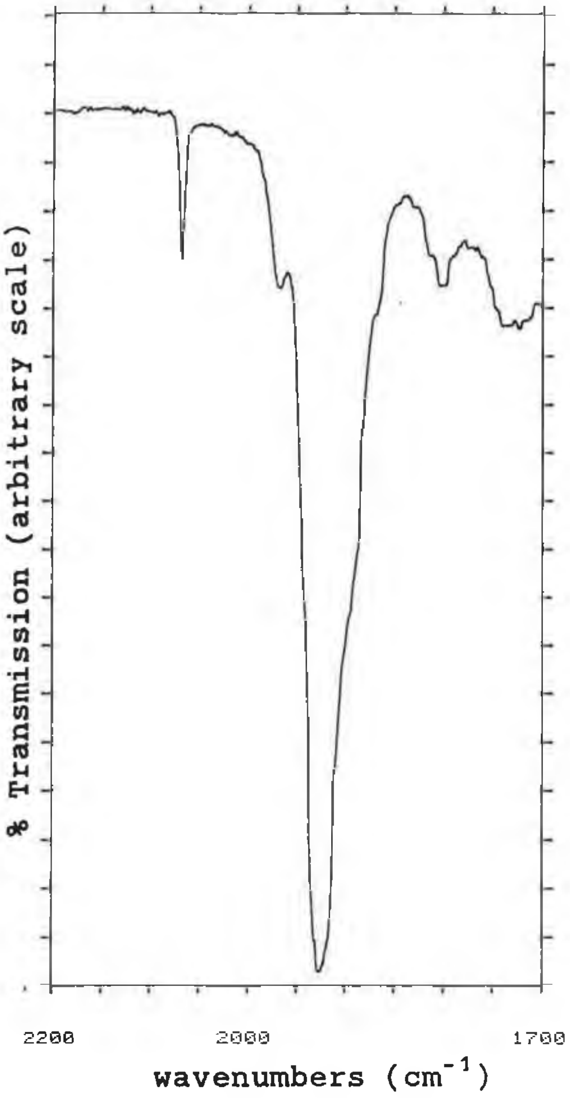


Fig. 2.3. The CO stretching frequency region of a copolymer of styrene and [W(CO)$_5$(4-vp)]. The spectra of the Cr and Mo copolymers are very similar.

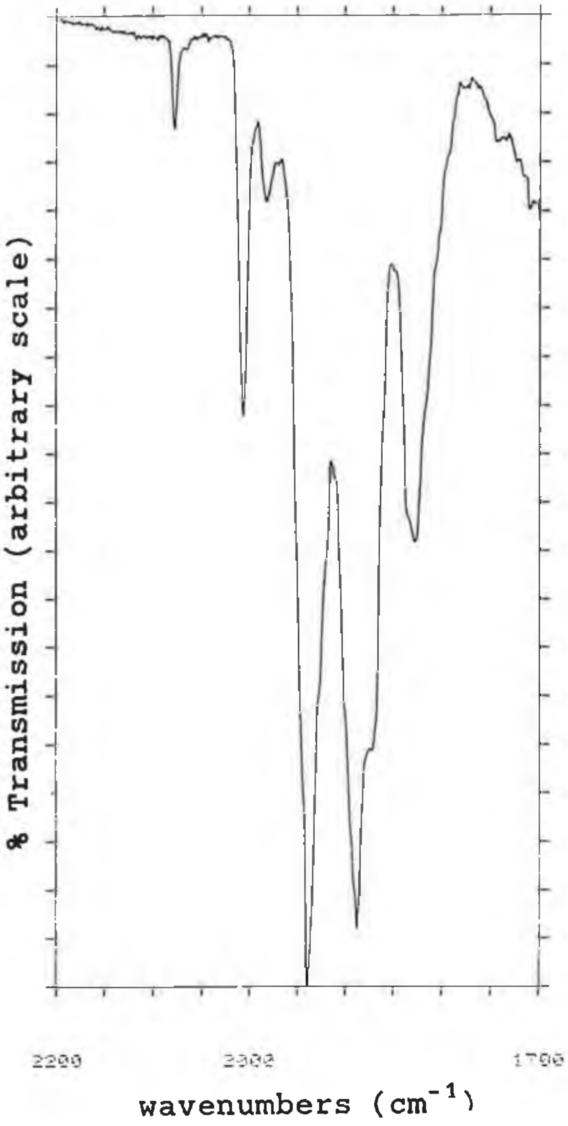


Fig. 2.4. The CO stretching frequency region of a copolymer of styrene and Vbipy which when reacted with [W(CO)$_5$(THF)], produced a species containing both bound *cis*-tetracarbonyl moieties and pentacarbonyl moieties.

The number and position of the bands are almost identical to those of their monomeric analogues indicating that the symmetry at the metal centre is unchanged upon polymer-binding. Comparing both methods of synthesising the polymer-bound metal carbonyls, preformed copolymers of styrene and vinylpyridine to which the metal carbonyl fragment was reacted (Route 1) exhibit similar bands to those of a copolymer of styrene and $[W(CO)_5(vp)]$ (vp = 2- or 4- vinylpyridine) (Route 2). The band at *ca.* 2068 cm^{-1} is the characteristic high energy pentacarbonyl band. However, preformed copolymers of styrene and 4-vinyl-4'-methyl-2,2'-bipyridyl which were reacted with $[M(CO)_5(THF)]$ (M = Cr or W) have CO stretching bands assignable to both the expected *cis*-tetracarbonyl species (A_1: 2002, B_1: 1881, A_1: 1865 and B_2: 1825 cm^{-1}) and the pentacarbonyl species (A_1: 2072, E: 1931 cm^{-1}) (Figure 2.3). This observation was of interest as the isolation of monodentate monomeric α-diimine ligands has proven difficult, because the chelation reactions of these complexes occur on fast timescales, and as a result, flash photolysis techniques must be used for their study[64c]. In one study, Oshi investigated the flash photolysis of $Cr(CO)_6$ in the presence of phenanthroline, and concluded that the rate of formation of $[Cr(CO)_5(phenanthroline)]$ depended on the substituents on phenanthroline[64d]. In addition studies have shown that 2,2'-bipyridyl exists in solution in an s-trans conformation. Such a conformation would require rotation about the C-C bond to form the bidentate product. The presence of the polymer chain may hinder the formation of the tetracarbonyl species by restricting rotation of the bound bipyridyl. No evidence for the [$(M(CO)_5)_2$(bipy)] was found. Those copolymers of styrene and [$M(CO)_4$(Vbipy)] show bands only due to the metal tetracarbonyl species.

Disubstituted derivatives were also formed on reaction of [$W(CO)_5$(THF)] with copolymers of styrene and p-styryldiphenylphosphine. Bands arising form the *cis*-disubstituted metal carbonyl species were observed, as well as the expected pentacarbonyl bands[65]. Pittman[16], in his study of group 6 metal carbonyls attached to polymers containing phosphine units, found similar spectroscopic evidence for the formation of the trans-disubstituted derivative. He stated that this observation attested to the high degree of mobility of the coordination sites within these matrices. Collman and coworkers[74] earlier emphasised this mobility and general tendency toward chelation in the reactions of resin-substituted triphenylphosphine with [$IrCl(CO)(PPh_3)_2$] and [$RhCl(CO)(PPh_3)_2$].

2.3.4 UV/Visible Spectroscopic Properties of Metal Carbonyls.

Considerable effort has been directed toward understanding the electronic structure of carbonyl complexes of Cr, Mo, and W. The band position, intensity, and likely assignments for the electronic transitions of a large number of metal carbonyls and their derivatives have been determined, and many of the results have proved valuable in a number of photochemical systems. Generally, the complexes exhibit a number of intense ($\varepsilon > 10^2$) transitions in the UV-visible region which are associated with ligand field (LF) and M ⟶ L and L ⟶ M charge-transfer (CT) absorptions[17,25,32].

The UV spectra of $M(CO)_6$ (M = Cr, Mo, or W) compounds are dominated by two intense ($\varepsilon > 10^4$) metal-to-ligand charge transfer (M ⟶ LCT) bands at *ca.* 280 nm and *ca.* 230 nm. Also seen as shoulders on these large peaks are two strong ($\varepsilon > 10^3$) ligand field (LF) transitions at *ca.* 320 nm and *ca.* 260 nm assigned as $^1A_{1g} \longrightarrow {}^1T_{1g}$ and $^1A_{1g} \longrightarrow {}^1T_{2g}$, respectively. Each observed LF transition weakens both the π and σ components of the M-CO bond making $M(CO)_6$ (and metal carbonyls in general) among the most photoreactive metal complexes known. The dominant photoreaction for $M(CO)_6$, therefore, is dissociation of CO.

In absorption spectra for C_{4v} $[M(CO)_5L]$ (L << CO in ligand field strength), the lowest energy absorption corresponds to a ligand field $^1A_1(e^4b_2^2) \longrightarrow {}^1E(e^3b_2^2a_1^1)$ transition around 400 nm, for ligands L having no low-lying π^* levels (e.g. piperidine)[69] (see Figure 2.6). This is at lower energy than the corresponding $M(CO)_6$ transition. For M = W the spin-forbidden $^1A_1(e^4b_2^2) \longrightarrow {}^3E(e^3b_2^2a_1^1)$ transition has significant intensity. If the ligand L has low lying π^* orbitals, a MLCT absorption can be the lowest energy transition. When L = 4-formylpyridine the complex has a low-lying MLCT absorption, while exhibiting all of the low-lying LF bands present when L = piperidine. Variation in the pyridine substituents results in variation in the CT band position[69]. The more electron-releasing substituents give a higher energy CT. MLCT bands are very sensitive to solvent polarity; more polar solvents give blue-shifted CT band maxima, while LF bands are little affected. Consequently, when LF and MLCT bands are overlapping, it is possible to resolve them by varying the polarity of the solvent.

The electronic spectra of C_{2V} disubstituted complexes *cis*-$[M(CO)_4L_2]$ or $[M(CO)_4(L\text{-}L)]$ are basically similar to the monosubstituted complexes. For σ-donor only ligands the lowest transition is a ligand field transition ($^1A_1 \longrightarrow {}^1A_{1g}\,{}^1B_2$) around 420 nm (slightly lower than for $[M(CO)_5L]$). If the ligand can function as a π-acceptor, MLCT and intraligand transitions are often observed as the lowest energy transitions. Among metal carbonyls, the only mononuclear complexes which have been investigated which unequivocally have a MLCT lowest excited state are $[M(CO)_4L]$[64,75]. For these complexes the M ⟶ LCT transition yielded no detectable CO substitution.

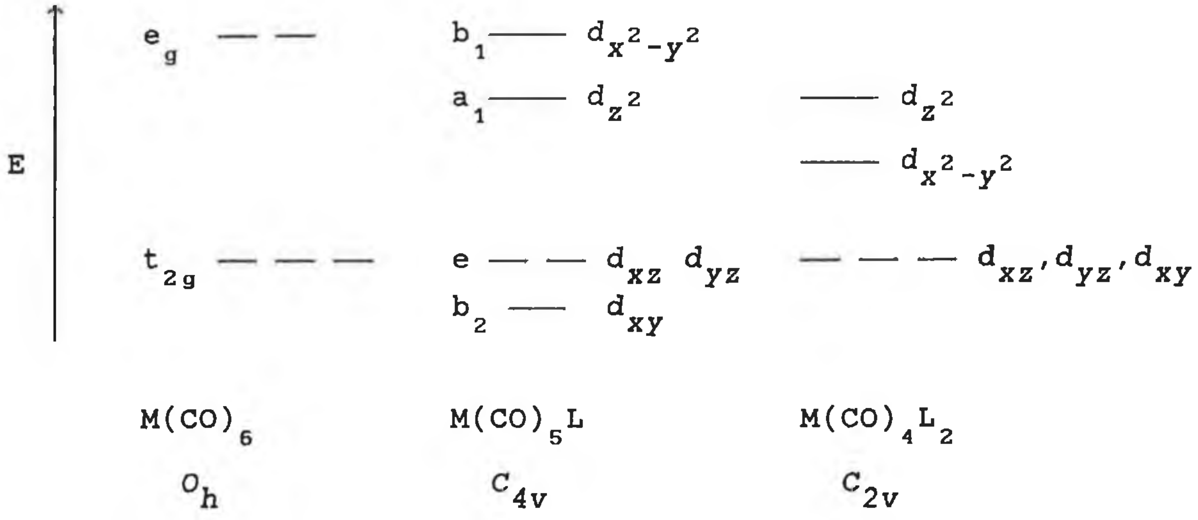


Fig. 2.6 The one electron diagram for O_h, C_{4v} and C_{2v} *complexes.*

2.3.5 *UV/Visible Spectroscopic Properties of Polymer Systems*

A comparison of the UV/vis spectra (270-500 nm) of a copolymer of styrene and 4-vinylpyridine and the tungsten carbonyl analogue in chloroform solution is shown in **Figure 2.7.** Low-lying LF transitions and MLCT are observed. The electronic spectrum and position of the bands are very similar to those of $[W(CO)_5(pyridine)]$ in the region 300-500 nm (see **Figure 2.8**).

Three distinct transitions can be observed. Each $[W(CO)_5(4\text{-vp})]$ polymer exhibits a low energy band near 440 nm, which is the one previously associated[17,69,71,75] with the spin-forbidden LF $^1A_1(e^4b_2^2) \longrightarrow {}^3E(e^3b_2^2a_1^1)$ transition. The corresponding singlet-singlet LF transition is associated with

Fig. 2.7. UV/Visible spectrum of poly[styrene-(4-vp)] (———) and poly[styrene-$W(CO)_5$(4-vp)] (---) in chloroform solution.

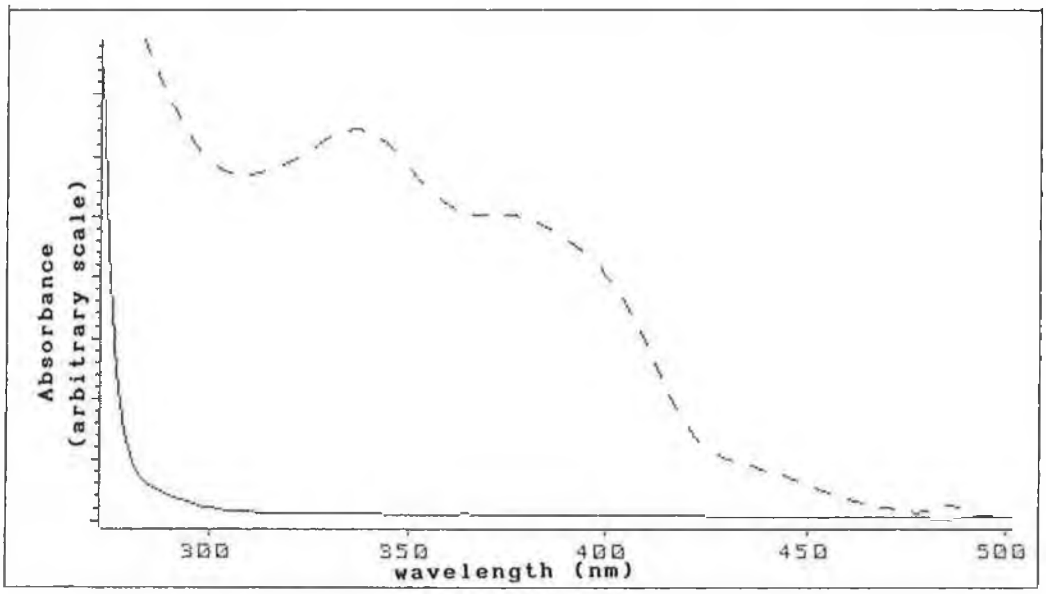
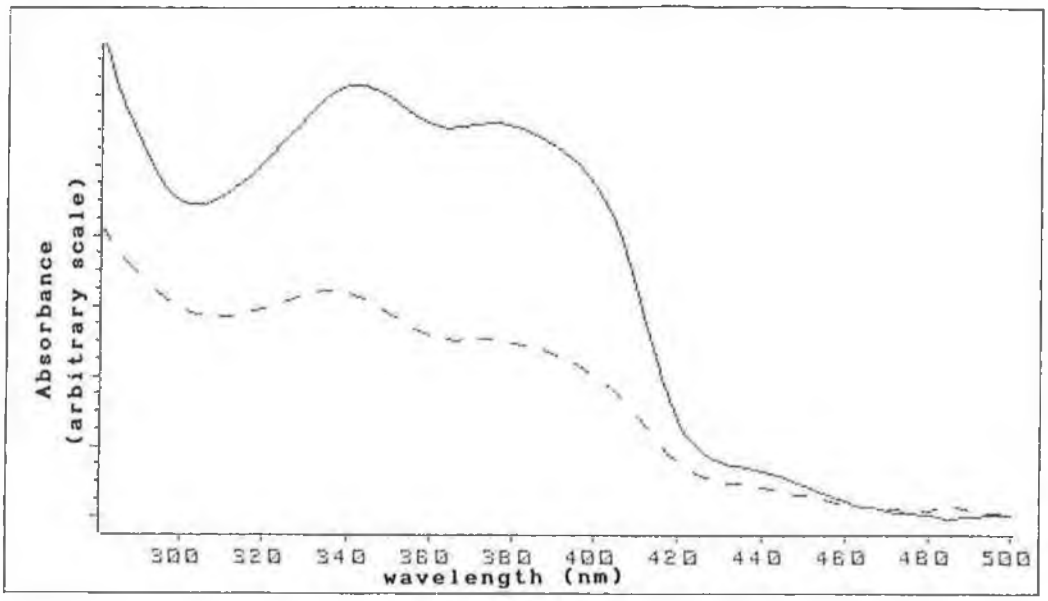


Fig.2.8. Comparison of the UV/vis spectra of [$W(CO)_5$(py)] (——) and P[styrene-$W(CO)_5$(4-vp)] (---) in chloroform solution.



the absorption band near 380 nm. The band at around 340 nm has been assigned to a MLCT band in $[W(CO)_5(Xpy)]$ complexes where Xpy is pyridine or a substituted pyridine. The position of the MLCT band is very sensitive to the solvent, while LF bands are unaffected by solvent polarity. The effect of the solvent on the electronic absorption spectrum of a copolymer of styrene and $[W(CO)_5(4\text{-}vp)]$ was investigated (although the solvent polarity range is severely restricted due to the insolubility of the polymer in many non-polar and polar solvents). A marked solvent dependence was found for the λ_{max} of the band at around 335 nm. This absorption band can then be assigned to a W ⟶ LCT transition of the polymer-bound $[W(CO)_5(py\text{-}\overset{|}{C}H\text{-}CH_2\text{-})]$ group. While the MLCT band blue shifts as the solvent polarity increases, the LF transitions at around 376 and 440 nm remain relatively unaffected. The affect of solvent is shown in Table 2.4 and illustrated in Figure 2.9.

Figure 2.9 Effect of solvent on the MLCT band of polymer-bound $[W(CO)_5(py\text{-}\overset{|}{C}H\text{-}CH_2\text{-})]$.

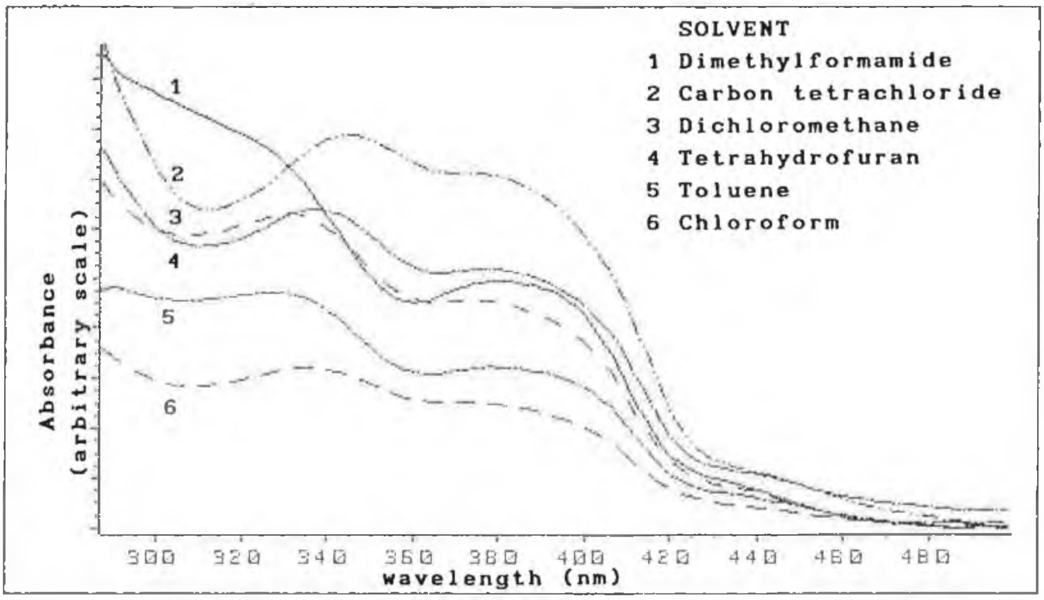


Table 2.4 Spectral Band Maxima and Assignments for polymer-bound $[W(CO)_5(py\text{-}\overset{|}{C}H\text{-}CH_2\text{-})]$.

Solvent	$^1A_1(e^4b_2^2) \longrightarrow {}^3E(e^3b_2^2a_1^1)$ nm	$^1A_1(e^4b_2^2) \longrightarrow {}^3E(e^3b_2^2a_1^1)$ nm	$W \longrightarrow LCT$ nm
DMF	438	378	318
Dichloromethane	440	374	330
Benzene	440	375	335
Tetrahydrofuran	442	378	332
Chloroform	442	376	334
Toluene	442	375	338
CCl_4	436	380	342

Absorption spectra of a copolymer of styrene and $[W(CO)_4$(4-vinyl-4'-methyl-2,2'-bipyridyl)] were recorded in a number of solvents. A spectrum of the copolymer is shown in Figure 2.10. The spectrum shows two well resolved bands in the region 320-500 nm in contrast to those spectra of $[M(CO)_5$(4-vp)], where considerable overlap of LF and MLCT bands occurs in copolymers of $[M(CO)_5$(4-vp)]. In the case of M = Cr or Mo the MLCT bands cannot be distinguished. The broad and intense long wavelength absorption band near 500 nm has been assigned to a lowest energy MLCT absorption in complexes of the type $[M(CO)_4(L)]$, where L denotes a bidentate diimine such as 2,2'-bipyridyl[77,78]. The impressive solvochromatic behaviour of these complexes with solvent-dependent shifts of the low energy band gives additional support for the MLCT assignment. Table 2.5

shows the effect of solvent polarity on the tetracarbonyl copolymer.

Figure 2.10 Absorption spectrum of a copolymer of styrene and [W(CO)$_4$(4-vinyl-4'-methyl-2,2'-bipyridyl)] in CH$_3$Cl.

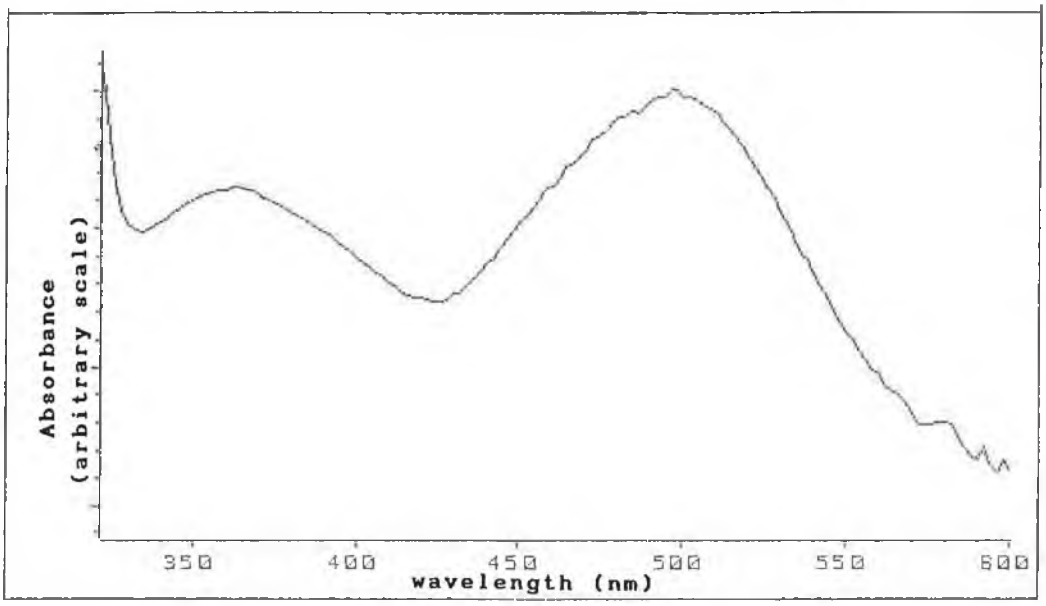


Table 2.5 Band Maxima and Assignments for a Copolymer of Styrene and [W(CO)$_4$(4-vinyl-4'-methyl-2,2'-bipyridyl)] in a variety of solvents.

Solvent	LF ($^1A_1 \longrightarrow {}^1A_{1g}\,{}^1B_2$) nm	W $\longrightarrow$ LCT nm
DMF	385	445
Dichloromethane	376	470
Benzene	380	477
Tetrahydrofuran	377	485
Chloroform	376	492
Toluene	373	500

The band centered around 490 nm ($CHCl_3$ solution) shows marked solvent dependence. On the basis of previously published work on complexes of the type *cis*-$[W(CO)_4(bipy)]$, this band can be assigned to a MLCT transition, as the absorption blue shifts in progressively more polar solvent media. The LF band at around 380 nm is relatively unaffected. There has been much interest in metal carbonyls of the type $[M(CO)_4(L)]$, where L is 2,2'-bipyridine, because their low-lying MLCT states are so well resolved from higher LF states that they offer an opportunity to study the photophysical and photochemical properties of the MLCT excited states exclusively[77].

In $[W(CO)_5(Xpy)]$ complexes, where Xpy is a substituted pyridine, the MLCT band was found to depend on the electronic nature of the substituent X[69]. The position of the MLCT can be changed rather dramatically by tampering with the electronic nature of the substituent X. As the pyridine substituent becomes more electron withdrawing, the MLCT transition shifts to longer wavelength. The position of the MLCT band in copolymers of $[M(CO)_5(4\text{-}vp)]$ is also sensitive to the composition of the polymer backbone. (Table 2.6 gives some data for copolymers in chloroform solution). It should be noted that for the styrene-4-vinylpyridine-$[M(CO)_5(4\text{-}vp)]$ terpolymers the position of the MLCT band shifts to longer wavelength as the proportion of vinylpyridine in the copolymer is increased. Surprisingly the shift is in the direction expected for an increasingly less-polar environment of the bound $[W(CO)_5(py\text{-}\overset{|}{C}H\text{-}CH_2\text{-})]$.

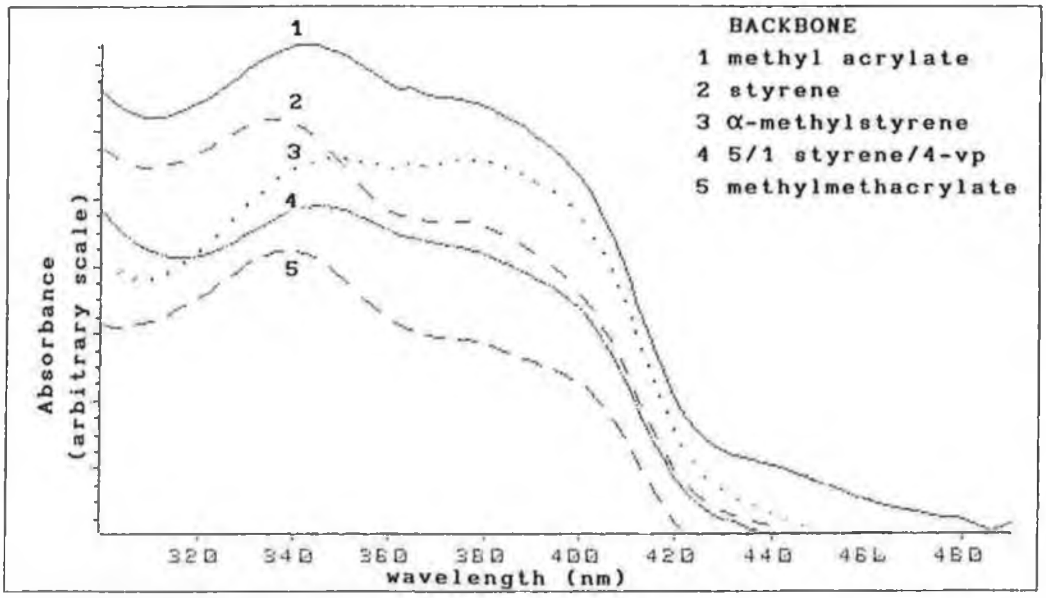
Presumably the environment of the complex is determined both by the solvent and by the presence of the other polymer chains, the extent of each being controlled by the tightness of the polymer coil in the solvent[29]. The position of the MLCT bands in these polymer systems are sensitive to both solvent and polymer backbone composition. These observations confirm the view that it should be possible to "tune" the photochemical properties of organometallic compounds by binding them to polymers and hopefully it may be possible in this way to develop more effective photocatalysts.

Table 2.6 Variation with Polymer Backbone Composition of the Absorption bands of [W(CO)$_5$(4-vp)] copolymers in chloroform solution.

Backbone[a]	LF ($^1A_1 \longrightarrow {}^3E$) nm	LF ($^1A_1 \longrightarrow {}^1E$) nm	MLCT nm
Styrene	442	376	336
Styrene/4-vp (5/1)	438	376	338
4-vp	440	375	344
Methyl acrylate	438	378	342
Methylmethacrylate	438	378	346
Ethyl acrylate	440	380	340
α-methylstyrene	440	376	348

[a] All the copolymers were prepared using a 20/1 mole ratio of monomer to [W(CO)$_5$(4-vp)] unless indicated otherwise.

Figure 2.11 The Variation of the Absorption Bands of Copolymers of $[W(CO)_5(4\text{-}vp)]$ in Chloroform Solution.



2.3.6 Gel Permeation Chromatography (GPC).

Gel permeation chromatography[76] is a widely used technique employed in the characterisation of polymer materials. The separation in GPC is based on molecular size, the molecule being restricted by it's ability (depending on it's size) to penetrate the pore structure of the gel separation media. In molecular weight determinations, calibration curves are prepared by running polystyrene standards of known molecular weight, and preparing a plot of log molecular weight versus retention volume. This plot is usually linear over a wide range of molecular weights. However, the true nature of the separation in GPC is based on hydrodynamic volume and not molecular weight. So, a calibration made with narrow distribution linear polystyrene will not apply to a polymer of another composition. The availability of narrow distribution polymers is restricted to only a few polymers and so standards are not available to give a true indication of the molecular weight. An approximate correction (Q-factor) is often applied which takes into account the differences in molecular weight per unit chain length. However, in this instance comparisons between various samples only is required so the use of a calibration curve is adequate.

GPC has been previously used to characterise polymer-bound metal carbonyls. Pittman characterised polystyrene polymers to which he attached $M(CO)_3$ moieties[52]. GPC showed that the narrow molecular distribution of the polystyrene was maintained following complexation to the phenyl residues, and that no decomposition of the polymer occurred during reaction. He found an increase in the number average molecular weight ($\overline{M}_n$) on anchoring of the metal tricarbonyl. He used the $\overline{M}_n$ to calculate the percentage complexation and results agreed well with elemental analyses. In another study, Pittman used GPC to fractionate a wide molecular weight distribution formed on the bulk homopolymerisation of (η^5-vinylcyclopentadienyl)-dicarbonylnitrosylchromium (see VIII section 1). From these fractions a GPC calibration curve was constructed for a polymer of VIII.

In this work, molecular weight studies were performed by gel permeation chromatography in THF. A calibration curve was constructed using narrow distribution polystyrene standards. Several styrene copolymers were examined and shown to be true polymers of a relatively narrow molecular weight distribution in each case. On attaching the metal carbonyl complexes to these copolymers, GPC data demonstrated that the narrow molecular weight distribution was maintained (see **Figure 2.12**). No low molecular weight polymer was observed, indicating that the copolymers did not degrade during reaction. Similar copolymers prepared by the polymerisation of styrene with the metal carbonyl monomer produced polymers of comparable distributions. The data is shown in Table 2.4.

Figure 2.12 GPC chromatogram of Poly[styrene-(4-vp)] (——) and Poly[styrene-(4-vp)]$W(CO)_5$ (·········) in THF.

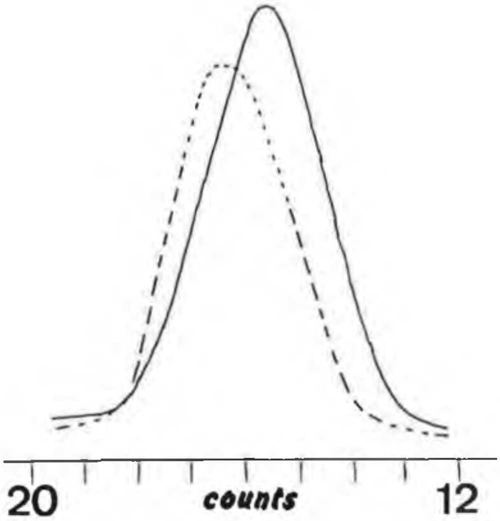


Table 2.7. GPC Molecular Weight Determinations for a Representative Series of Copolymers.

Polymer[a]	$\bar{M}_n$	$\bar{M}_w$	$\bar{M}_w / \bar{M}_n$
P[styrene-(4-vp)]	8180	17200	2.11
P[styrene-(4-vp)]$W(CO)_5$	10100	27500	2.72
P[styrene-(Vbipy)]	14900	36800	2.46
P[styrene-(Vbipy)]$W(CO)_4$	20200	58100	2.87
P[styrene-$W(CO)_5$(4-vp)]	12870	39150	3.04

[a] Each copolymer was prepared so that the mole ratio of metal carbonyl to monomer was 1/20 .

$\bar{M}_n$ = number average molecular weight (a.m.u).

$\bar{M}_w$ = weight average molecular weight (a.m.u).

2.3.7 Determination of Metal Incorporation.

Atomic absorption spectroscopy was used to determine the extent of metal incorporation in the polymer-bound materials. The data for different polymer types is presented in **Table 2.5**. In general, a high percentage of metal was incorporated onto the polymers, but the important thing to note is the difference in percentage metal incorporation found on comparing the two methods of syntheses. Those polymers prepared via the copolymerisation of the functionalised monomer containing the metal carbonyl and comonomer (Route 2) contained a higher percentage metal than those preformed copolymers which were then reacted with the $[M(CO)_5(THF)]$ (M = Cr, Mo, or W) species.

Table 2.8. Metal Analyses of Polymer-Bound Metal Carbonyls.

Polymer	% Metal Incorporation	
	Theory	Found
$P[styrene-(4-vp)]W(CO)_5$	7.32	5.42
$P[styrene-W(CO)_5(4-vp)]$	7.32	6.35
$P[styrene-(Vbipy)]W(CO)_4$	7.14	5.28
$P[styrene-W(CO)_4(Vbipy)]$	7.14	6.07
$P[styrene-(4-vp)]Cr(CO)_5$	2.19	1.69
$P[styrene-Cr(CO)_5(4-vp)]$	2.19	1.91
$P[styrene-(4-vp)]Mo(CO)_5$	3.96	2.49
$P[styrene-Mo(CO)_5(4-vp)]$	3.96	3.27
$P[styrene-(2-vp)]W(CO)_5$	7.32	5.41
$P[styrene-W(CO)_5(2-vp)]$	7.32	6.22
$P[MA-W(CO)_5(4-vp)]$	8.55	7.29
$P[(4-vp)-W(CO)_5(4-vp)]$	7.26	6.12
$P[styrene-W(CO)_5(p-SDPP)]$	6.82	5.79
$P[styrene-(p-SDPP)]W(CO)_5$	6.82	4.64
$P[styrene-(p-SDPP)]Cr(CO)_5$	2.03	1.50
$P[styrene-(p-SDPP)]Mo(CO)_5$	3.68	2.28

2.4. Investigation of the Interaction of Metal Carbonyls with Polymeric Supports.

The reaction of the metal carbonyl fragments with polymeric supports was studied using laser flash photolysis. In effect we were investigating the synthesis routes used in the preparation of these polymer-bound materials. The first method of synthesising these polymer materials discussed involved the formation of the solvent adduct and it's subsequent reaction with the polymer backbone containing pendant sites (Route 1). Laser flash photolysis allows us to detect the short-lived primary photoproduct, $M(CO)_5S$ (S = solvent), and to determine it's rate of reaction with the polymer support. The observation of an intermediate following the photolysis of $M(CO)_6$ in toluene solvent at room temperature is reported and the kinetics of it's subsequent reactions with monomeric pyridine and polymer-bound pyridine are determined. Toluene was chosen because it is a good solvent for copolymers of styrene and 4-vinylpyridine, and because of the insolubility of the copolymers in many of the popularly used solvents. In addition, little work in this area using toluene has been reported. However, the choice of toluene as the solvent causes experimental problems. Because toluene absorbs below 290 nm it restricts the region of the spectrum we can investigate, and the laser frequency we can use (λ = 355 nm). The flash photolysis experiment is one of monitoring absorbance changes, following pulsed-laser photolysis. The experimental procedures and laser equipment are discussed in greater detail in section 5.

2.4.1 Photochemistry of Group 6 Metal Carbonyls.

Following initial studies by Strohmeier and coworkers[24] the photochemical behaviour of group 6 metal carbonyls have been the subject of numerous investigations. Intermediates produced in the photolysis of group 6 hexacarbonyls have been studied in low-temperature glasses and matrices, in the liquid phase, and in the gas phase, and have been widely reviewed[17,24,25]. In more recent studies, conventional flash photolysis techniques have provided information about intermediates produced in these photolyses[79-84]. The primary photoreaction in solution is one of efficient CO dissociation to form the coordinatively unsaturated pentacarbonyl species. This highly reactive species coordinates to the solvent to produce an observable $M(CO)_5S$ intermediate. In the presence of coordinating ligand L, the substitution product $M(CO)_5L$ is formed with near unitary quantum efficiency.

$$M(CO)_6 + h\nu \longrightarrow M(CO)_5 + CO$$

$$M(CO)_5 + S \longrightarrow M(CO)_5S$$

$$M(CO)_5S + L \longrightarrow M(CO)_5L + S$$

It is the structure, the solvation, and the reaction kinetics of the $M(CO)_5$ species that has been of much interest. Extensive studies in low-temperature matrices supported the presence of an intermediate with a C_{4v} square-pyramidal structure and one which could undergo thermal reaction with the photoproduced or added CO[85,86]. Direct comparison with visible absorption bands of matrix-isolated $M(CO)_5$ is difficult because of wavelength shifts produced by $M(CO)_5$ matrix interactions. $M(CO)_5$ interacts with solvent molecules and in solution the $M(CO)_5$ species cannot be considered as "naked". These highly reactive coordinatively unsaturated species have been shown to react with materials which would normally be considered inert, such as dinitrogen[84] and alkanes[86], and their formation and reactions in the liquid phase has been reported to be very fast. Simon and Xie[84] reported a rise time of less than 0.8 ps for the formation of $Cr(CO)_5$(cyclohexane) in cyclohexane solution.

2.4.2 Laser Flash Photolysis with UV/vis Monitoring

Using laser flash photolysis techniques intermediates can be detected on a timescale comparable to the fastest chemical processes in solution, and the technique provides information about primary photochemical processes in organometallic compounds. Detection of short lived primary photoproducts and the determination of the rates of coordination, and especially the influence of the solvent on these rates is of particular interest.

In principle, flash photolysis involves the generation of a high concentration of a short-lived intermediate using a high intensity pulse of radiation of very short duration. At a short time interval after the generating pulse the system is analysed by observing the intermediates emission or absorption characteristics. The process can be followed by photographing the emission spectrum using a spectrograph, or the absorption spectrum can be measured by triggering an analytical beam passing through the reaction cell to flash at a predetermined time interval after the initial flash. Alternatively, the process may be followed kinetically by monitoring the emission or absorption at a particular wavelength using a detector coupled to an oscilloscope with a time-based sweep. The polychromatic nature of the radiation from conventional discharge tubes increases the possibility of generating more than one emitting or absorbing species. Lasers overcome this problem because their radiation is monochromatic. Other advantages of lasers are that the pulse is of very short duration (Q-switching) and highly reproducible. Frequency doubling and mixing can be used to increase the range of the laser source from it's fundamental harmonic. Oscilloscope traces of the transient are recorded using a high intensity monitoring beam which helps to overcome problems caused by background noise with lower intensity sources. UV/vis spectra of the transient are obtained point by point by changing the monitoring wavelength on the monochromator and recording a series of readings at a fixed time interval after the flash.

2.4.3 Laser Flash Photolysis Studies of $W(CO)_6$ Toluene Solutions Containing a Polymer-Bound Pyridine Ligand.

The aim of this study was to compare the reaction kinetics of intermediates produced in the photolysis of $W(CO)_6$ in toluene solutions containing a poly(styrene-*co*-4-vinylpyridine) copolymer of various compositions with those of monomeric pyridine.

Laser pulse photolysis at 355 nm of $W(CO)_6$ in room temperature toluene produces an intermediate proposed to be $W(CO)_5$(toluene), with an absorption maximum at 415 nm (see Figure 2.4.3). The position of the maximum is within the range of wavelengths reported for tungsten pentacarbonyl species generated in low-temperature matrices [SF_6 (461 nm), Ar (437 nm), Xe (417 nm), and CH_4 (413 nm)]^{85}. In the presence of added pyridine (monomeric or polymeric) the intermediate reacts to form $W(CO)_5$(pyridine), having a absorption maximum at around 390 nm.

$$W(CO)_6 \quad + \quad \text{toluene} \quad \xrightarrow[355\text{nm}]{h\nu} \quad W(CO)_5(\text{toluene}) \quad + \quad CO$$

$$W(CO)_5(\text{toluene}) \quad + L \quad \xrightarrow{k_2} \quad W(CO)_5L \quad + \quad \text{toluene}$$

The $W(CO)_5$(pyridine) species is stable and it's UV/vis absorption spectrum exhibits bands at around 395 and 440 nm attributable to LF transitions of $W(CO)_5$(pyridine) previously reported^{69}. Typical transients obtained are shown in Figures 2.4.1 and 2.4.2. The oscilloscope is set with a delay to enable the initial absorbance to be recorded, and the trace shows the rate of change in absorbance of the transient species with time. All reactions were found to follow first order kinetics. The traces were analysed kinetically to determine the observed rate constants for the reactions. The $W(CO)_5$(toluene) species is formed immediately in the flash and it's formation is too rapid to be detected with the equipment available. **Figure 2.4.1** shows the formation of the intermediate in the laser pulse at 310 nm, followed by it's decay as it reacts with the added ligand. The formation of $W(CO)_5L$ is shown in **Figure 2.4.2** at 390 nm. The $W(CO)_5$(toluene) is formed in the pulse as before and the ligand species "grows-in" at a rate equal to the rate of decay of the $W(CO)_5$(toluene) species. A transient absorption difference spectrum is shown in **Figure 2.4.3.** Absorbance readings were recorded at different monitoring wavelengths immediately after the laser pulse and after the decay of the transient.

Fig. 2.4.1 Transient data recorded at 310 nm following photolysis of $W(CO)_6$ ($1X10^{-7}M$) and $2X10^{-2}M$ pyridine in a 5/1 copolymer of styrene and 4-vinylpyridine in toluene. (Timebase = 200μs/channel; k_{obs} = 78.22 s^{-1}).

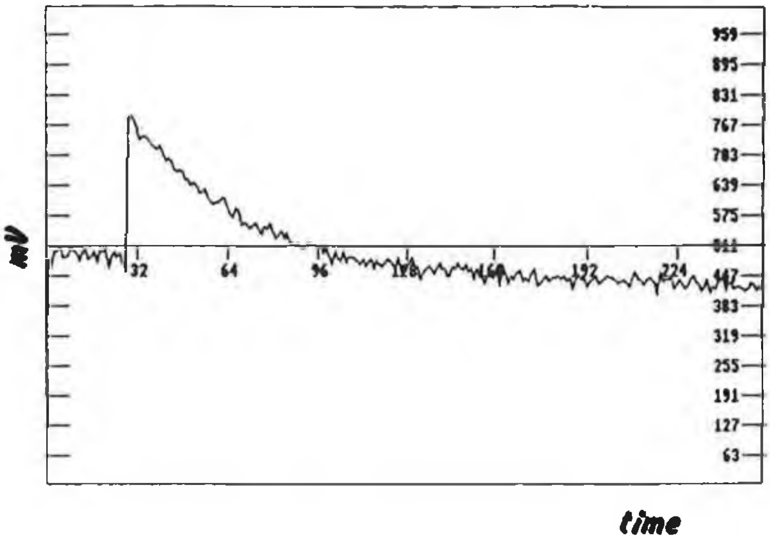


Fig. 2.2.2 Transient data recorded at 390 nm following photolysis of $W(CO)_6$ ($1X10^{-7}M$) and $2X10^{-2}M$ pyridine in a 5/1 copolymer of styrene and 4-vinylpyridine in toluene. (Timebase = 200μs/channel; k_{obs} = 69.01 s^{-1}).

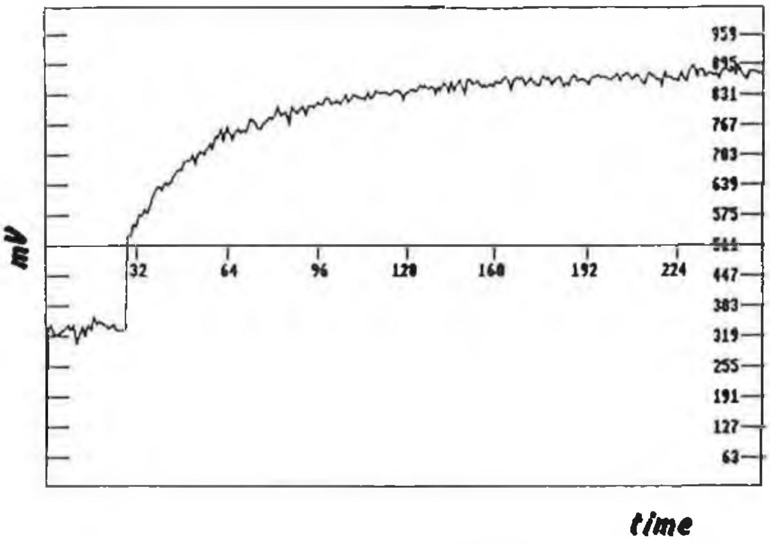
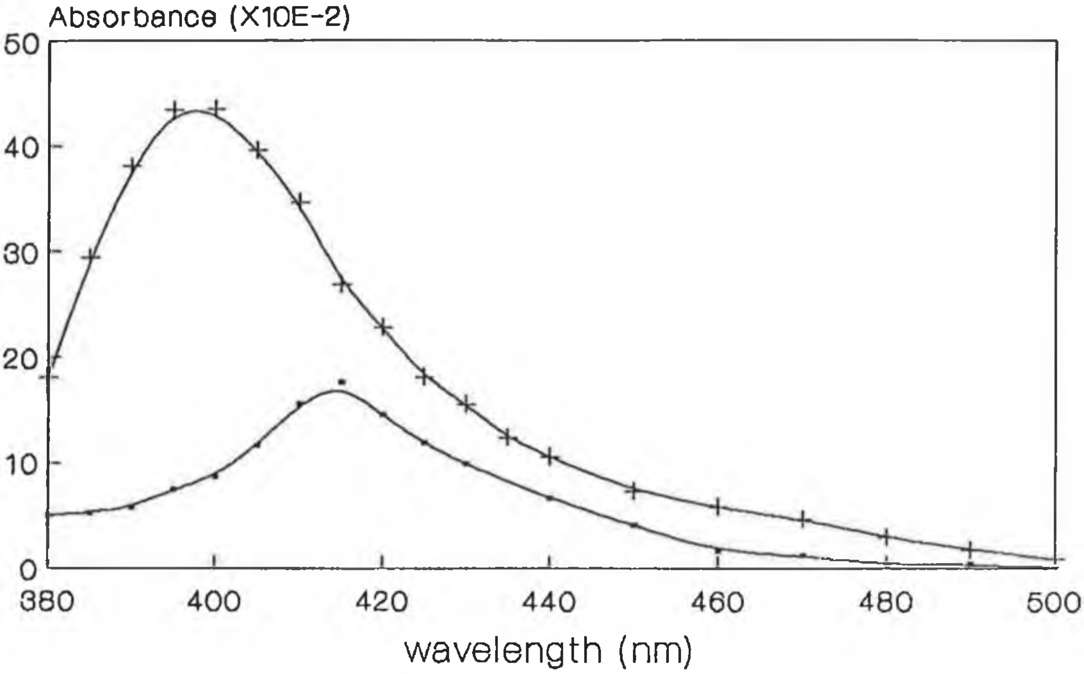


Fig. 2.4.3 Transient UV/vis difference spectrum recorded immediately after laser pulse and after decay of transient.



The rate of disappearance of the intermediate follows pseudo first order kinetics. A plot of k_{obs} versus pyridine concentration gives the second order rate constant, k_2 as the slope.

$$W(CO)_5(toluene) + L \xrightarrow{k_2} W(CO)_5L + toluene$$

To determine the effect of the polymer backbone, the k_2 of monomeric pyridine in toluene solution was compared to that of the k_2 obtained for the same concentration of pyridine in copolymers of different loading of styrene to 4-vinylpyridine (loading determined by % N microanalysis). The variation of k_{obs} with pyridine concentration is shown in Figure 2.4.4, and the values of k_2 are given in Table 2.4.1.

Fig. 2.4.4 Plot of k_{obs} versus [pyridine].

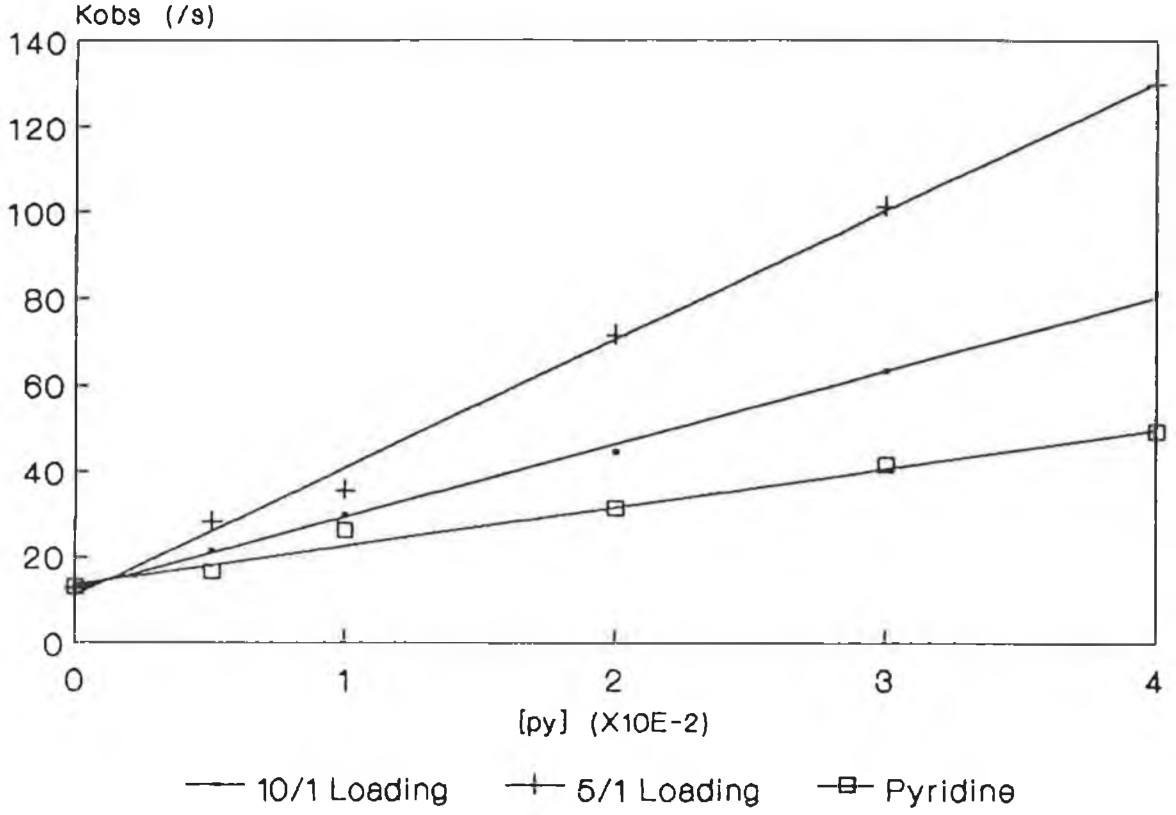


Table 2.4.1 Second order rate constants.

Sample	k_2 ($dm^3mol^{-1}s^{-1}$)
Pyridine	0.9×10^3
5/1[a] Copolymer	3.2×10^3
10/1 Copolymer	1.4×10^3

[a] Refers to the mole ratio of styrene to 4-vinylpyridine.

Surprisingly, the second order rate constants for the copolymers are higher than those for free pyridine in toluene solution. One may have expected a difference in second order rates because perhaps of diffusion constraints posed by the polymer coils in solution, but then we would expect k_2 to be higher for monomeric pyridine. The copolymers have different k_2 values from one another, the higher loading (5/1) polymer having the higher rate constant. The effect could perhaps be thermodynamic in origin. The difference in rates could be attributable to a difference in the spontaneity of the reactions, i.e., a difference in the free energy change of activation, $\Delta G^{\ddagger}$.

The activation parameters were calculated from the Arrhenius and Eyring equations[87]. The Arrhenius equation is given by:

$$\ln k = \ln A - \frac{E_a^{\ddagger}}{RT} \qquad (1)$$

where A is the frequency factor, and $E_a^{\ddagger}$ is the activation energy of the activated complex. The rate constant is dependent on the energy of activation. A plot of $\ln k_{obs}$ versus $1/T$ should give a straight line of slope of $-E_a^{\ddagger}/R$. From transition-state theory in thermodynamics we obtain the Eyring equation:

$$k_2 = \frac{kT}{h}\left(e^{-\Delta G^{\ddagger}/RT}\right) \qquad (2)$$

so that $k_2 \ \alpha \ \Delta G^{\ddagger}$ and if $\Delta G^{\ddagger} = \Delta H^{\ddagger} - T\Delta S^{\ddagger}$ then

$$k_2 = \frac{kT}{h}\left(e^{\Delta S^{\ddagger}/R}.e^{-\Delta H^{\ddagger}/RT}\right) \qquad (3)$$

where $\Delta G^{\ddagger}$, $\Delta H^{\ddagger}$, and $\Delta S^{\ddagger}$ are called the Gibbs free energy change of activation, the enthalpy change of activation, and the entropy change of activation (k is the Boltzmann constant and h the Planck constant). It follows from (3) then that:

$$\ln\frac{k}{T} = \ln\frac{k}{h} + \frac{\Delta S^{\ddagger}}{R} + \left(\frac{-\Delta H^{\ddagger}}{RT}\right) \qquad (4)$$

From a plot of ln (k_{obs}/T) *versus* 1/T we can find $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$.

$$\text{Slope} = \frac{-\Delta H^{\ddagger}}{R} \quad \text{and} \quad \text{Intercept} = \ln\frac{k}{h} + \frac{\Delta S^{\ddagger}}{R}.$$

The samples containing the hexacarbonyl ($1X10^{-7}$M) and $2X10^{-2}$M pyridine in toluene were heated in increments of 5 K, and the transient recorded at a monitoring wavelength of 395 nm. The observed rate constants were calculated at each temperature. The experimental results are tabulated in Tables 2.4.3 to 2.4.5, and corresponding plots shown in Figures 2.4.5 to 2.4.10. The activation parameters are shown in Table 2.4.2.

Table 2.4.2 Activation parameters for the formation of $W(CO)_5$(pyridine) on flash photolysis of $W(CO)_6$ in toluene in the presence of a pyridine ligand.

Sample	$E_a^{\ddagger}$ ($KJmol^{-1}$)	$\Delta H^{\ddagger}$ ($KJmol^{-1}$)	$\Delta S^{\ddagger}$ ($JK^{-1}mol^{-1}$)	$\Delta G^{\ddagger}$ ($KJmol^{-1}$)
Pyridine	32.4	29.7	-115.8	61.3
Polymer 5/1	22.7	21.1	-137.69	59.8
Polymer 10/1	20.2	20.8	-131.96	60.1

The activation energies of the pyridine containing polymers, while lower than the value for monomeric pyridine, are essentially the same regardless of the loading. When two reactions of similar activation energies are studied at the same temperature and found to proceed at different rates, there must be a difference in their entropy of activation. However, the entropies are all within experimental error of each other. The negative value of $\Delta S^{\ddagger}$ indicates the associative nature of the transition state. The values of the Gibbs free energy of activation are the same also, so there is no difference in the spontaneity of the processes regardless of whether the pyridine is polymeric or monomeric in nature.

The variation in k_{obs} with pyridine concentration does not therefore result from a thermodynamic effect. A different $\Delta G^{\ddagger}$ for these processes was expected, but surprisingly, they were all within experimental error. As k_2 is proportional to $\Delta G^{\ddagger}$ and

k_{obs} = [pyridine]k_2, it is proposed that this variation is a reflection of effective pyridine concentration as opposed to calculated pyridine concentration. One possibility is that the tungsten hexacarbonyl diffuses into the polymer coils in solution where the effective pyridine is higher than that of free pyridine in solution, and as a result the local pyridine concentration in the vicinity of the reaction centre may be high because of polymer coiling. At higher pyridine loading a proximity effect may exist where a high frequency factor could operate for pyridine-tungsten carbonyl encounters. The effective concentration would be greater in a polymer of higher loading of bound pyridine, and as a result the second order rate constant would be larger.

Pittman put forward a similar explanation to explain the decreased catalytic activity of a polystyrene anchored rhodium hydroformylation catalyst[13]. He found that the activity decreased as the bound PPh_2 to Rh ratio increased. He suggested that the effective concentration of the bound phosphine units is greater in the anchored system relative to dissolved PPh_3, and consequently excess bound phosphine can contact the catalytic sites decreasing the concentration of coordinatively unsaturated rhodium intermediates available for catalysis.

This study provides important information on the reaction kinetics of metal carbonyls with polymeric supports containing pendant sites. To our knowledge this is the first of such investigations.

Table 2.4.3 Experimental data for the determination of the activation parameters for the formation of $W(CO)_5$(pyridine) for $2X10^{-2}M$ pyridine in toluene.

Temp (K)	1/T (K^{-1}) ($X10^{-3}$)	k_{obs} (s^{-1})	ln k_{obs}	ln k_{obs}/T
285	3.51	20.06	2.99	-2.65
288	3.47	21.56	3.07	-2.59
293	3.41	27.73	3.32	-2.36
298	3.36	29.36	3.38	-2.32
303	3.30	44.62	3.80	-1.92
308	3.25	52.29	3.96	-1.77
313	3.19	59.85	4.09	-1.65
318	3.14	88.43	4.48	-1.28
323	3.10	89.04	4.49	-1.29

Arrhenius Plot

Slope = -3891 ± 196.07
Intercept = 16.59 ± 8.06E-2
Correlation = 0.99

$E_a^{\ddagger}$ = 32.35 ± 1.63 KJ mol^{-1}

Eyring Plot

Slope = -3574.4 ± 199.41
Intercept = 9.83 ± 8.20E-2
Correlation = 0.99

$\Delta H^{\ddagger}$ = 29.72 ± 1.66 $KJmol^{-1}$
$\Delta S^{\ddagger}$ =-115.84 ± 25 $JK^{-1}mol^{-1}$

Fig.2.4.5 Arrhenius plot for the formation of $W(CO)_5$(pyridine) on the photolysis of $W(CO)_6$ in toluene in the presence of $2X10^{-2}M$ pyridine.

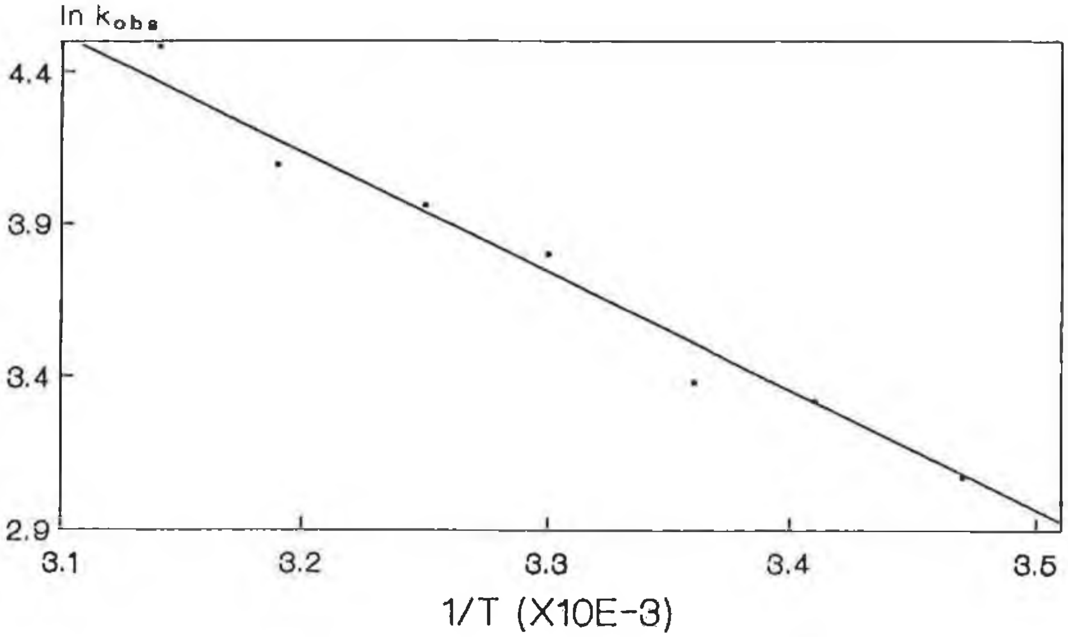


Fig. 2.4.6 Eyring plot for the formation of $W(CO)_5$(pyridine) on the photolysis of $W(CO)_6$ in toluene in the presence of $2X10^{-2}M$ pyridine.

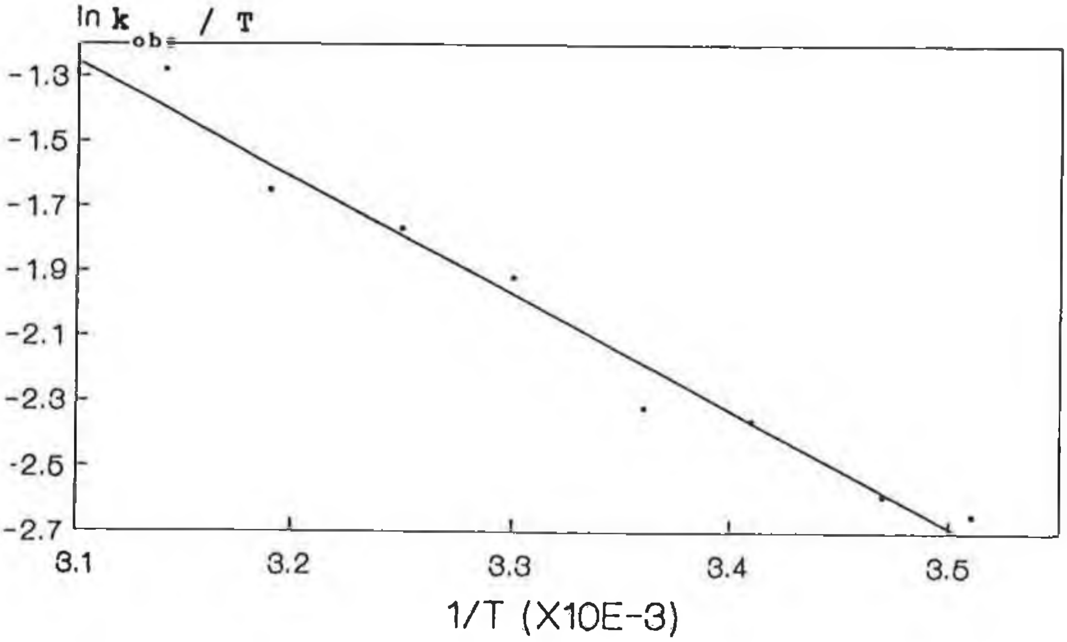


Table 2.4.4 Experimental data for the determination of activation parameters for the formation of $W(CO)_5$(pyridine) for $2X10^{-2}M$ pyridine in a 5/1 copolymer of styrene and 4-vinylpyridine.

Temp (K)	1/T (K^{-1}) ($X10^{-3}$)	k_{obs} (s^{-1})	ln k_{obs}	ln k_{obs}/T
290	3.45	58.65	4.07	-1.60
295	3.39	71.76	4.27	-1.41
298	3.36	86.74	4.46	-1.23
303	3.30	95.67	4.56	-1.15
308	3.25	107.27	4.67	-1.05
313	3.19	122.73	4.81	-0.94
318	3.14	145.47	4.98	-0.78
323	3.10	156.62	5.05	-0.73

Arrhenius Plot

Slope = -2734.9 ± 181.8
Intercept = 13.56 ± 5.77E-2
Correlation = 0.99

$E_a^{\ddagger} = 22.74 \pm 1.51$ KJ mol^{-1}

Eyring Plot

Slope = -2532.2 ± 231.51
Intercept = 7.20 ± 6.05E-2
Correlation = 0.99

$\Delta H^{\ddagger} = 21.06 \pm 1.92$ $KJmol^{-1}$
$\Delta S^{\ddagger} = -137.69 \pm 25$ $JK^{-1}mol^{-1}$

Fig. 2.4.7 Arrhenius plot for the formation of $W(CO)_5$(pyridine) on the photolysis of $W(CO)_6$ in toluene in the presence of $2X10^{-2}M$ pyridine in a 5/1 copolymer of styrene and 4-vinylpyridine.

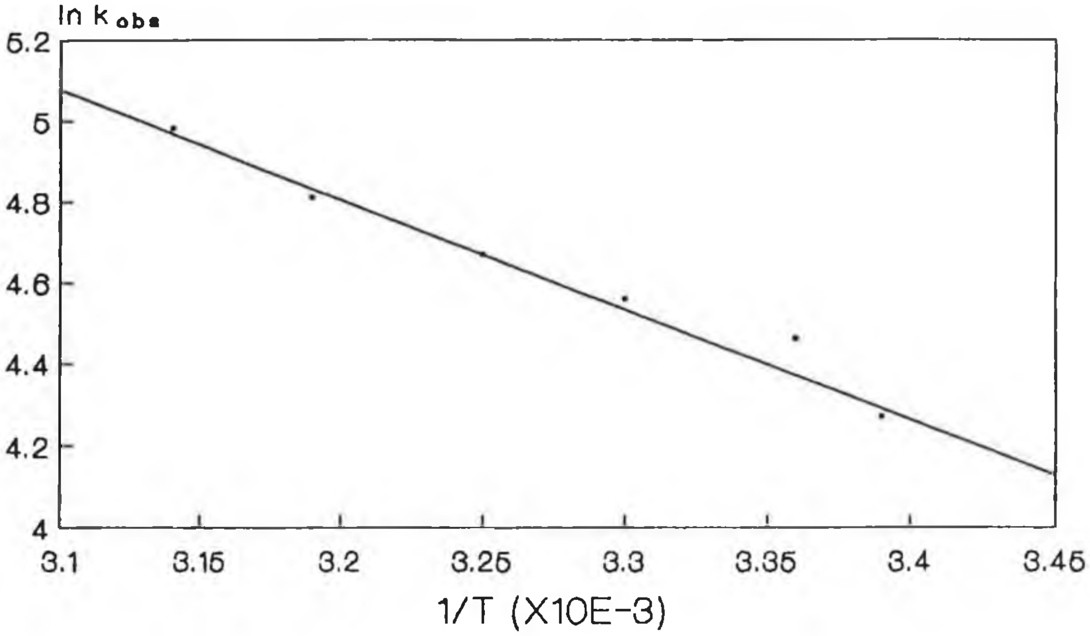


Fig. 2.4.8 Eyring plot for the formation of $W(CO)_5$(pyridine) on the photolysis of $W(CO)_6$ in toluene in the presence of $2X10^{-2}M$ pyridine in a 5/1 copolymer of styrene and 4-vinylpyridine.

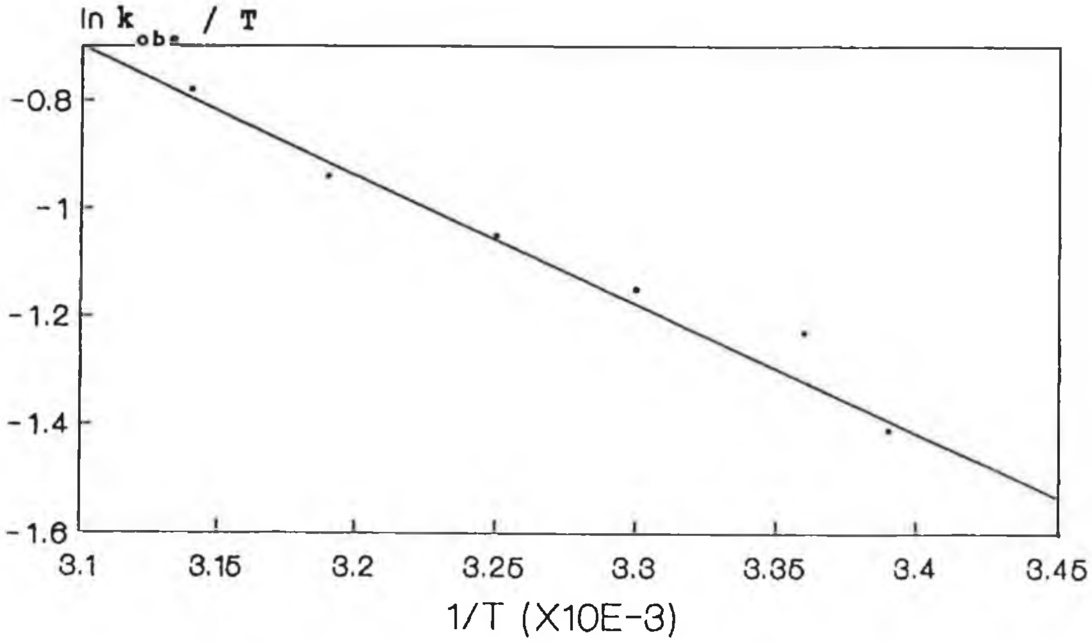


Table 2.4.5 Experimental data for the determination of the activation parameters for the formation of $W(CO)_5$(pyridine) for $2X10^{-2}M$ pyridine in a 10/1 copolymer of styrene and 4-vinylpyridine.

Temp (K)	1/T (K^{-1}) ($X10^{-3}$)	k_{obs} (s^{-1})	ln k_{obs}	ln k_{obs}/T
323	3.10	354.25	5.87	0.09
318	3.14	281.46	5.64	-0.12
313	3.19	265.07	5.58	-0.17
308	3.25	221.41	5.40	-0.33
303	3.30	184.93	5.22	-0.48
298	3.36	175.91	5.17	-0.53
293	3.41	148.41	5.00	-0.68
289	3.46	125.21	4.83	-0.84

Arrhenius Plot

Slope = -2431.9 ± 186.8
Intercept = 13.28 ± 4.62E-2
Correlation = 0.99

$E_a^{\ddagger}$ = 20.22 ± 1.55 KJ mol^{-1}

Eyring Plot

Slope = -2475.9 ± 217.28
Intercept = 7.74 ± 7.09E-2
Correlation = 0.99

$\Delta H^{\ddagger}$ = 20.77 ± 1.81 $KJmol^{-1}$
$\Delta S^{\ddagger}$ =-131.96 ± 25 $JK^{-1}mol^{-1}$

Fig.2.4.9 Arrhenius plot for the formation of $W(CO)_5$(pyridine) on the photolysis of $W(CO)_6$ in toluene in the presence of $2X10^{-2}M$ pyridine in a 10/1 copolymer of styrene and 4-vinylpyridine.

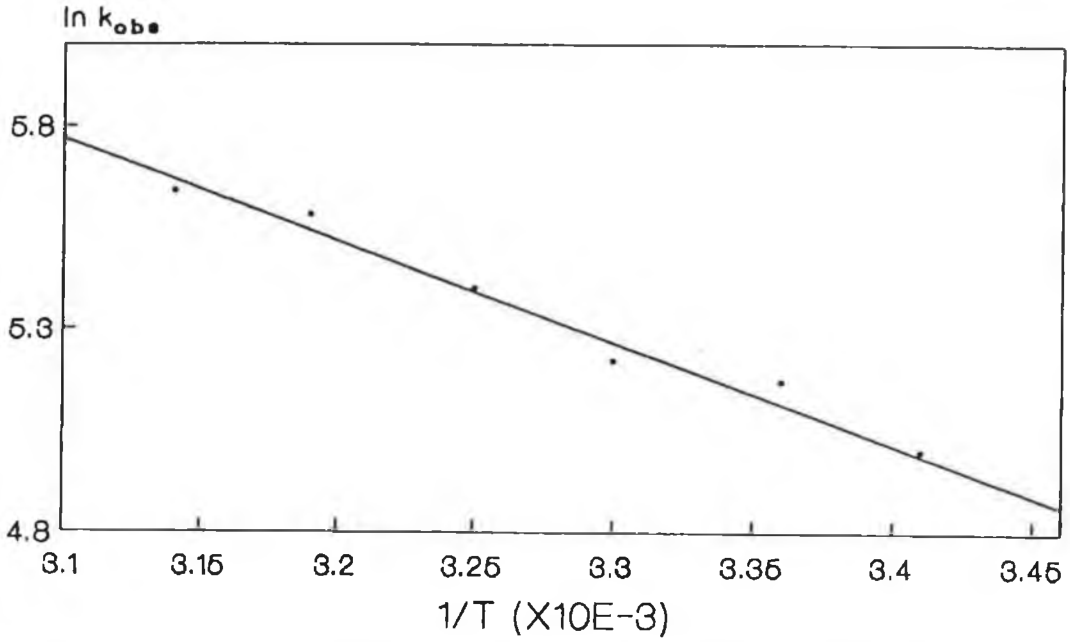
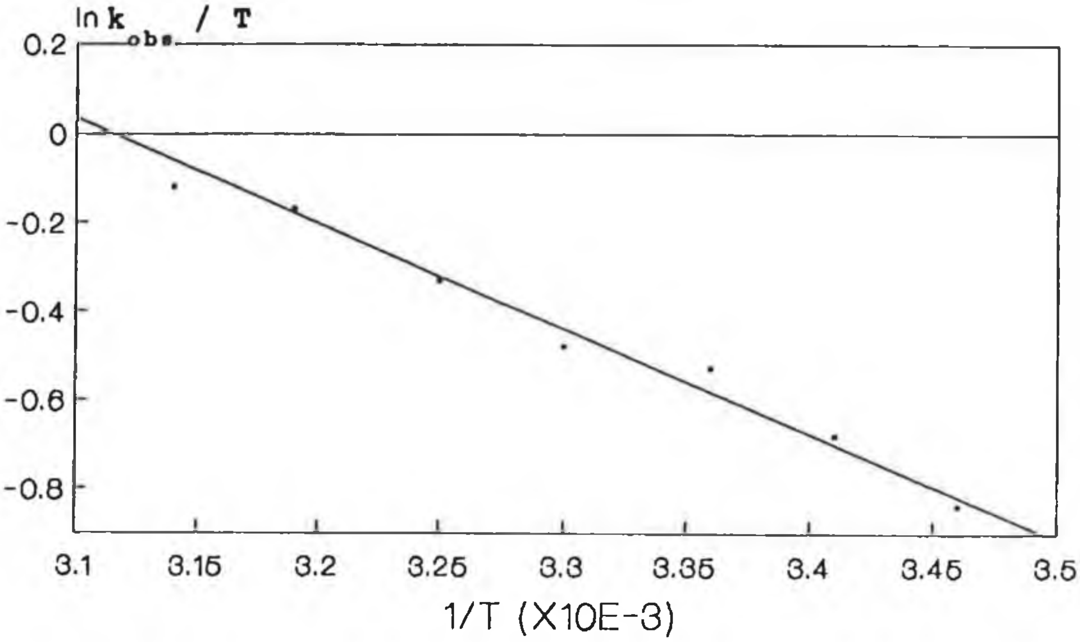


Fig.2.4.10 Eyring plot for the formation of $W(CO)_5$(pyridine) on the photolysis of $W(CO)_6$ in toluene in the presence of $2X10^{-2}M$ pyridine in a 10/1 copolymer of styrene and 4-vinylpyridine.



2.5 Conclusions

The syntheses of suitable polymerisable ligands and metal carbonyl containing polymer systems was discussed. Polymer-bound metal carbonyls are conveniently prepared by one of two methods: the first involving the preparation of a metal carbonyl containing monomer by reaction with photogenerated [W(CO)$_5$(THF)] followed by subsequent copolymerisation, and the second involving direct reaction of photogenerated [W(CO)$_5$(THF)] with a preformed copolymer. Polymerisations were carried out by free-radical polymerisations in the absence of solvent to give narrow molecular weight distribution polymers with high metal incorporation.

The presence of the metal carbonyl moiety was confirmed by infrared and UV/vis absorption spectroscopy. The polymer anchored metal carbonyls exhibited strong bands in the carbonyl stretching frequency of the infrared spectrum, and the bound species were readily characterised on the basis of the position and number of the stretching frequencies. The spectra were found to be similar to those of their monomeric analogues. Those copolymers formed by reaction of [W(CO)$_5$(THF)] with a copolymer of styrene and 4-vinyl-4'-methyl-2,2'-bipyridyl (Vbipy) exhibited infrared bands of the expected *cis*-tetracarbonyl species, and also bands attributable to the pentacarbonyl, while a copolymer of styrene and [W(CO)$_4$Vbipy] shows only carbonyl stretching bands due to the tetracarbonyl species. The MLCT electronic absorption bands of a copolymers of

$[W(CO)_5(4\text{-vinylpyridine})]$ were sensitive to both the solvent and the composition of the polymer backbone. Those copolymers of styrene and $[W(CO)_4(Vbipy)]$ exhibit low energy MLCT transitions which showed marked solvent dependence.

The interaction of tungsten carbonyl with copolymers of styrene and 4-vinylpyridine in toluene was investigated using laser flash photolysis. The rates of coordination of photogenerated $[W(CO)_5(toluene)]$ were found to be higher for polymer-bound pyridine as opposed to monomeric pyridine in toluene. The rates were dependent on the loading of the copolymers, the rate being higher for copolymers of higher loading of 4-vinylpyridine to styrene. This difference in rates was thought to be a reflection of effective pyridine concentration, the effective pyridine concentration being higher in the polymer coils in solution than that of monomeric pyridine.

CHAPTER 3

THERMAL REACTIONS OF POLYMER-BOUND GROUP 6 METAL CARBONYLS WHEN CAST AS FILMS.

3.1 Thermal Reactions of Polymer-Bound Group 6 Metal Carbonyls when Cast as Films

The thermal reactions of the polymer-bound metal carbonyl compounds when cast as films and the effect of the polymer backbone on the thermal reaction routes available are investigated using variable temperature infrared spectroscopy. The influence of physical properties such as the molar mass and the glass transition temperature, T_g, were investigated. The importance of the T_g on the observed thermal reactions and the effect of binding the metal complexes to the polymer backbone is examined using differential scanning calorimetry (DSC). The provision of free pendant binding sites on the polymer backbone, the importance of metal loading, and in particular the effect of different polymer backbones is also investigated. Included is evidence for the decarbonylation of the polymer anchored metal carbonyl complexes resulting in polymers which contain fully decarbonylated metal centres. The nature of the thermal products are also examined.

3.1.1 Thermal Substitution Reactions of Group 6 Metal Carbonyls.

In general, metal carbonyls and metal carbonyl compounds can undergo substitution reactions under either thermal and/or photochemical conditions. Thermal substitution reactions of group 6 carbonyls and derivatives often follow kinetics similar to those of their photochemical substitution reactions. The hexacarbonyls of Cr, Mo, and W undergo measurable substitution and CO exchange at relatively high temperatures (100-170°C)[25a]. The substitution reactions of $[M(CO)_5(L)]$ usually proceed by loss of L or CO:

$$[M(CO)_5(L)] \xrightarrow{k_1} [M(CO)_5] + L \qquad (1)$$

$$[M(CO)_5(L)] + L' \xrightarrow{k_2} [M(CO)_4(L)(L')] + CO \qquad (2)$$

$$\text{Rate} = k_1[M(CO)_5(L)] + k_2[M(CO)_5(L)].[(L')]$$

The ligand independent first order path described by k_1 is consistent with ligand dissociation to form a five-coordinate intermediate as the rate determining step. The ligand dependent path described by k_2 could involve attack of the ligand at either the carbonyl carbon or metal. In addition, however, the nature of the ligand L in $[M(CO)_5(L)]$ complexes greatly influences the reaction rate, especially the magnitude of k_1, the rate constant for the ligand independent term. In virtually all cases the rate of the substitution reaction is greater when L is any ligand other than CO. The ligands with good σ-donor ability but poor π-acceptor ability show significantly faster rates than those ligands closer to CO in bonding - the π-acceptor ligands[26,32]. The order of labilising ability is $Cl^- > NCO^- > Br^- > py > I^- > PPh_3 > CO$. Thus, if L is a halide or pyridine the rate of CO dissociation from $[M(CO)_5(L)]$ is much greater than that for $M(CO)_6$.

The labilising of $[M(CO)_5(L)]$ by L is invariably of carbonyl ligands *cis* to L, thus the incoming ligand is initially in the *cis* position. The *cis* labilisation could be because of the strengthened M-CO bond *trans* to L, especially for poor π-acceptor ligands. Alternatively, the five-coordinate intermediate species $[M(CO)_4(L)]$ could be stabilised by poor π-acceptors occupying a basal position in a square pyramidal intermediate, thereby facilitating the reaction.

Reactions of $[M(CO)_4(L-L)]$ with a ligand, L, result in one of three complexes namely *fac-* or *mer-* $[M(CO)_3(L-L)(L)]$, $[M(CO)_4(L_2)]$, or $[M(CO)_3(L_3)]$[25]. Which of these compounds is formed depends on the nature of the chelate ligand (L-L) as the stronger ligands, such as 2,2'-bipyridyl or 1,10-phenanthroline, tend to be retained and $[M(CO)_3(L-L)(L)]$ complexes formed while weaker ligands are displaced and $[M(CO)_4(L_2)]$ formed. But the N donor ligands appear to greatly labilise CO groups in the complex. For α-diimine complexes such as those of 2,2'-bipyridyl, the dissociation of CO forms a five-coordinate complex which reacts with L to form the product. Evidence strongly suggests that dissociation occurs from carbonyl positions *cis* to the 2,2'-bipyridyl ligand.

The thermal chemistry of group 6 metal carbonyls is particularly important in synthetic applications and in the understanding of their substitution reaction kinetics. However, more recently much greater attention has been paid to their photochemical reactivity. Photochemical substitution reactions are used more widely in the preparation of metal carbonyl derivatives because of their high quantum yields , and because the high temperatures and long reaction times employed in thermal syntheses often give rise to decomposition of complexes. The advancements and development in photochemical procedures and equipment have meant that more attention has been concentrated in this area. In this study of the thermal reactions of polymer-bound metal carbonyls, we were interested in the thermal generation of coordinatively unsaturated species in solid samples and were curious to investigate the influence of the polymer matrix on the observed thermal reactions.

3.1.2 Colloidal Metal Dispersions in Polymers.

Organic polymers containing metal carbonyl functions are of particular interest because their decomposition could free metals or metal oxides within the polymer. Such a decomposition is applicable to the synthesis of a "solution of metal or mixed oxide" within the polymer mass. Mixing metal oxides into polymers results only in heterogeneous composite materials since the particle size of the metal oxides cannot be infinitely reduced. Since these compositions are mechanically blended, it is a major technological problem to control the uniformity of the dispersion and the size of the metallic aggregates. As a result, thermal decompositions of polymer anchored transition metal carbonyls offers a complementary method to generate metal oxide particles that are homogeneously dispersed at the molecular level.

Metallic species created by UV photolysis, thermal or electron beam decomposition in a polymer matrix should be highly reactive[88]. There are two major pathways for chemical reaction available for these species: (i) metal ions/radicals can attack the polymer, a process that can lead to various polymer degradation, crosslinking, or metal attachment processes, and (ii) metal species can aggregate to form very small clusters 10-100 Å in diameter. Both processes may occur and may be significantly influenced by reducing or oxidative atmospheres. The chemistry of the system, the relative importance of the two processes, is determined by the structure of the solid polymer matrix and by the rate of decomposition process as compared to the diffusion time of the active metal species in the solid polymer matrix.

The interest in this area is because colloidal metals have proved very efficient in many catalytic processes and find other applications in magnetic media storage, conducting and semi-insulating polymers, and polymers with special mechanical properties. The vast majority of studies of the thermal reactions of metal carbonyl complexes bound to polymer supports have been concerned with dispersing metals in polymeric materials. It seems a convenient route to the production of these dispersions by relatively simple and inexpensive means. Dispersions of a variety of metals within a number of different polymer systems have been reported.

Polymers containing attached η^6-(arene)Cr(CO)$_3$ moieties have been thermally decomposed to produce chromium oxide particles within the polymer matrix[53-56,60]. Pittman et al.[53] demonstrated that thermal decomposition of η^6-(aryl)-Cr(CO)$_3$ units produced mixed oxides imbedded in highly crosslinked polystyrene polymers, and that similar siloxane containing π-complexed chromium tricarbonyl polymers liberated CO between 100 and 200°C to give Cr_2O_3[55]. In thermal decompositions of (η^1-benzyl)-(η^5-cyclopentadienyl)tricarbonylmolybdenum and it's tungsten analogue attached to the matrix by a carbon-to-metal σ-bond, decompositions were found to proceed more efficiently in solution than in the absence of solvent because of decreased mobility of radicals when samples were neat[63]. Heating samples of copolymers of vinylcyclopentadienylmanganese tricarbonyl resulted in CO evolution to produce crosslinked polymers containing free manganese[60].

The above examples involve thermal decompositions studies of polymer-bound metal carbonyl complexes. In an extensive study, Tannenbaum *et al.*[88] investigated the decomposition of iron carbonyls in solid polymer matrices in an attempt to prepare novel metal-polymer composites. In his approach he prepared dispersions of metals by *in situ* phase-separation in a solid polymer matrix under controlled conditions. The organometallic complexes were dissolved in polymer solutions to form homogeneous mixtures. These solutions were then cast and the resulting films exposed to thermal, photolytic or electron beam energy. These treatments decomposed the organometallic complex to form fine uniform dispersions of metal or metal oxide particles (50-500 Å) in the polymer matrix. It was suggested that these materials may be designed to exhibit novel catalytic activity and also that the technique described could be of value for development of novel solid matrix isolation methods to substitute for conventional gas matrices for infrared matrix isolation studies of excited atomic or molecular species.

Thermolysis of transition metal carbonyls in solvents under an inert atmosphere is a well known technique for the preparation of pure metal powders. Smith et *al.*[89] successfully applied this method to the formation of stable colloidal dispersions (50-150 Å) of zerovalent iron by thermolysis of $Fe(CO)_5$ in dilute polymer solutions. Smith, in a later report, developed a method for the preparation of a homogeneous, physically stable colloidal elemental transition metal dispersion comprising of metal particles having a particle size within the range of 10-200 Å dispersed in an inert liquid and stabilised by the presence of a functional polymer to the reactive sites of which the metal particles are bound[90]. The method involved preparing a solution of a functional polymer in an inert solvent, and incrementally adding a group 6 metal hexacarbonyl precursor, at a temperature of 100-200°C at which the metal carbonyl precursor becomes bound to the polymer and thermally decomposes to produce elemental transition metal particles, the process being carried out in an inert atmosphere.

The functional polymers used included copolymers of styrene with a comonomer containing a binding moiety such as butadiene, para-styryldiphenylphosphine, and 4-vinylpyridine. Such dispersions, it was proposed, could be used as catalysts, or may be used for the preparation of supported colloidal transition metal catalysts. The dispersions may also be used for the preparation of ablative optical recording media.

In our investigation of polymer-bound metal carbonyls one may envision that thermal decomposition of these materials could free group 6 metals, metal oxides, or organometallic groups within the polymer matrix.

3.2 Thermal Reactions of Metal Carbonyl Containing Polymers.

The polymers were cast as films on a sapphire support from chloroform solution and mounted in a variable temperature cell fitted with sodium chloride windows. The temperature of the cell was raised slowly from room temperature and the changes in the carbonyl stretching frequency region of the infrared (2200-1700 cm^{-1}) were monitored. The thickness of the polymer film could be varied by changing the volume or concentration of the casting solution, thus the intensity of the carbonyl stretching bands in the infrared spectrum could be adjusted. A sapphire support was chosen because of it's robustness and resistance to thermal shock. All variable temperature experiments were carried out *in vacuo*. Syntheses of polymers and any procedures are explained in greater detail in section 5.

3.2.1 *Copolymers of Styrene and $M(CO)_5$(vinylpyridine).*

On heating a copolymer of styrene and $[W(CO)_5(4\text{-vp})]$ (20/1 mole ratio) to temperatures in excess of 100°C, the carbonyl stretching frequencies of the pentacarbonyl species decreased in intensity and were replaced by new bands (2000, 1883, 1861, and 1832 cm^{-1}) which can be assigned to *cis*-disubstituted tungsten tetracarbonyl species[68] (see Figures 3.2.1 and 3.2.2). Further heating the polymer resulted in loss of the tetracarbonyl bands to give a fully decarbonylated polymer at around 150°C. The bands assignable to the thermally formed *cis*-tetracarbonyl are close to those reported for *cis*-$[W(CO)_4(\text{pyridine})_2]$ (2002, 1885, 1868, and 1820 cm^{-1} in nujol mull)[73]. As there are no uncoordinated pyridine units available on the polymer backbone, a dissociative process involving the formation of free metal pentacarbonyl might occur. The free pentacarbonyl could react with another bound pentacarbonyl moiety producing metal hexacarbonyl and a metal tetracarbonyl centre, which could then coordinate two pendant bound pyridine groups (Scheme 3.1). A similar reaction has been observed in the thermal conversion of $[W(CO)_5(\text{dipyridylamine})]$ to $[W(CO)_4(\text{dipyridylamine})]$ in the solid state[28].

Such a thermal reaction involving the formation of $[M(CO)_5]$ is known to occur in metal carbonyls containing amine ligands in solution[32]. $[M(CO)_5(\text{amine})]$ complexes thermally decompose by loss of the amine and abstraction of CO by the reactive intermediate $[M(CO)_5]$ (equation 3).

$$[M(CO)_5(\text{amine})] \xrightarrow{\Delta} M(CO)_5 \xrightarrow{[M(CO)_5(\text{amine})]} M(CO)_6 + \text{degradation products}$$

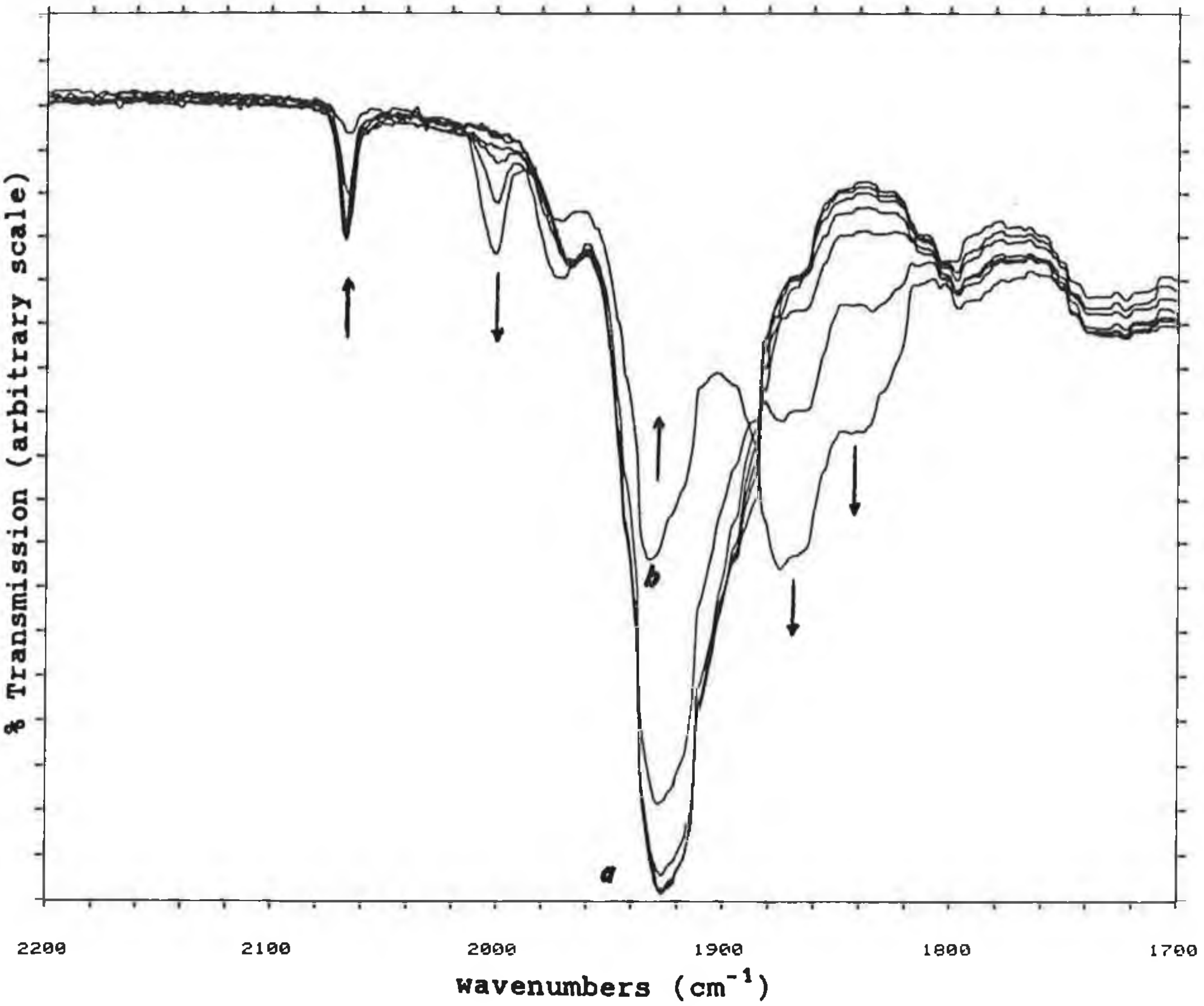
Equation 3

Further spectroscopic evidence for the occurrence of this disproportionation process was obtained by investigating the volatile components produced on heating the copolymer. These experiments were performed using a variable temperature infrared gas cell (10 cm pathlength). The solid was introduced into the cell and then the cell was evacuated and sealed. The gases evolved upon heating the solid polymer were then determined by infrared spectroscopy at various temperatures. On heating the sample to about 100°C, bands attributable to gaseous $W(CO)_6$ (T_{1u}: 1998 cm^{-1} in the gas phase[32]) and carbon monoxide (2143 cm^{-1}) were detected. These products would be expected if a disproportionation process was occurring.

Heating a similar copolymer of styrene and $[W(CO)_5(2\text{-vinylpyridine})]$ resulted only in the loss of all the carbonyl bands in the carbonyl region of the infrared at 130°C (Figure 3.2.3), with gaseous tungsten hexacarbonyl and CO being evolved. The difference in thermal behaviour between copolymers of 4-vinylpyridine and 2-vinylpyridine is probably a result of significant steric hindrance to the coordination of the pyridine in copolymers of 2-vinylpyridine. Consequently, loss of the metal carbonyl fragment appears to be the only thermal route available to copolymers of 2-vinylpyridine containing bound pentacarbonyl moieties. However, treatment of a copolymer of styrene and 2-vinylpyridine (20/1 mole ratio) with lithiated 2-picoline[91] yielded a copolymer with pendant dipyridylmethane moieties (Scheme 3.2). Reaction of this polymer with the photochemically generated $[W(CO)_5(THF)]$ produced a polymer with metal pentacarbonyl species bound to it. Upon heating this polymer to over 100°C, spectral changes consistent with the thermal production of the *cis*-tetracarbonyl fragment were observed. It is known that dipyridylmethane has the ability to act both as a monodentate and a bidentate ligand, and evidence has been reported which demonstrates that the related di-2-pyridylamine complex [W(CO)$_5$(dipyam)] can undergo a conversion from monodentate to bidentate coordination in the solid state[91].

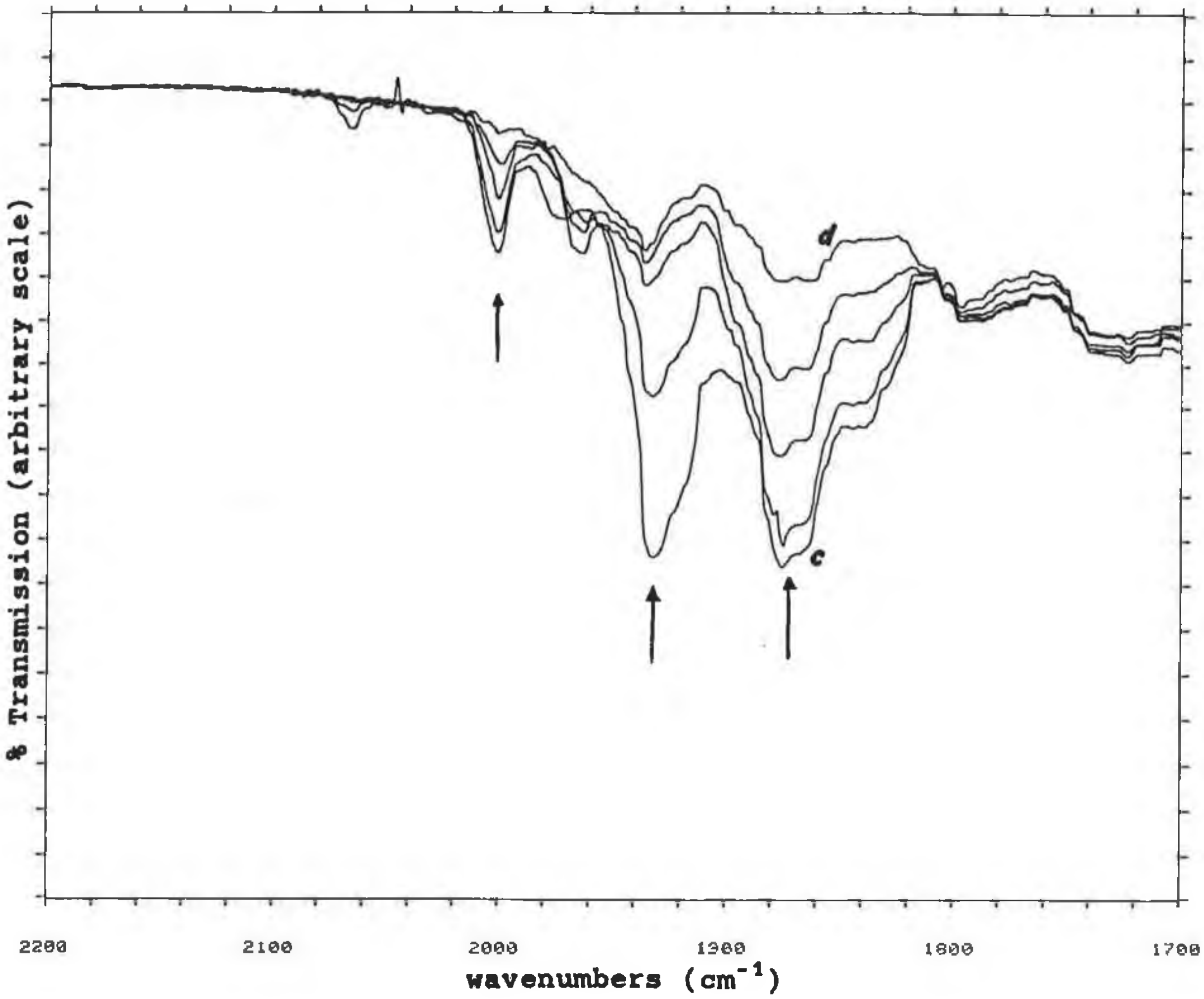
Heating copolymers of styrene and [Cr(CO)$_5$(4-vp)] (20/1 mole ratio) to temperatures of greater than 100°C, resulted only in a decarbonylated polymer, no tetracarbonyl being observed. Similar experiments with [Mo(CO)$_5$(4-vp)] copolymers when heated exhibited new bands at 2008, 1886, and 1835 cm^{-1} assignable to the *cis*-tetracarbonyl species (*cis*-[Mo(CO)$_5$(py)$_2$]: 2002, 1899, 1871, and 1828 cm^{-1} in nujol mull)[73]. This difference in thermal reactivity is probably because of the thermal instability of the chromium tetracarbonyl species in accordance with the sequence of stabilities of group 6 metal tetracarbonyls: Mo > W > Cr.

Fig. 3.2.1a Changes observed in the 2200-1700 cm^{-1} region of the infrared spectrum, upon heating a copolymer of styrene and $[M(CO)_5(4\text{-}vp)]$ (M = W or Mo). These changes are consistent with the formation of a *cis*-disubstituted tetracarbonyl complex.



The characteristic pentacarbonyl bands decrease in intensity at 100°C and are replaced those of the cis-tetracarbonyl species.
a = *20°C, b = 125°C.*

Fig. 3.2.1b Changes observed in the 2200-1700 cm^{-1} region of the infrared region on further heating. Complete decarbonylation of the metal centres occurs on raising the temperature to 165°C.



The bands of the cis-tetracarbonyl decrease in intensity to eventually leave a fully decarbonylated polymer.
c = 125°C, d = 165°C.

Scheme 3.1 Proposed mechanism for the thermal reaction routes of a copolymer of styrene and [$W(CO)_5$(4-vp)].

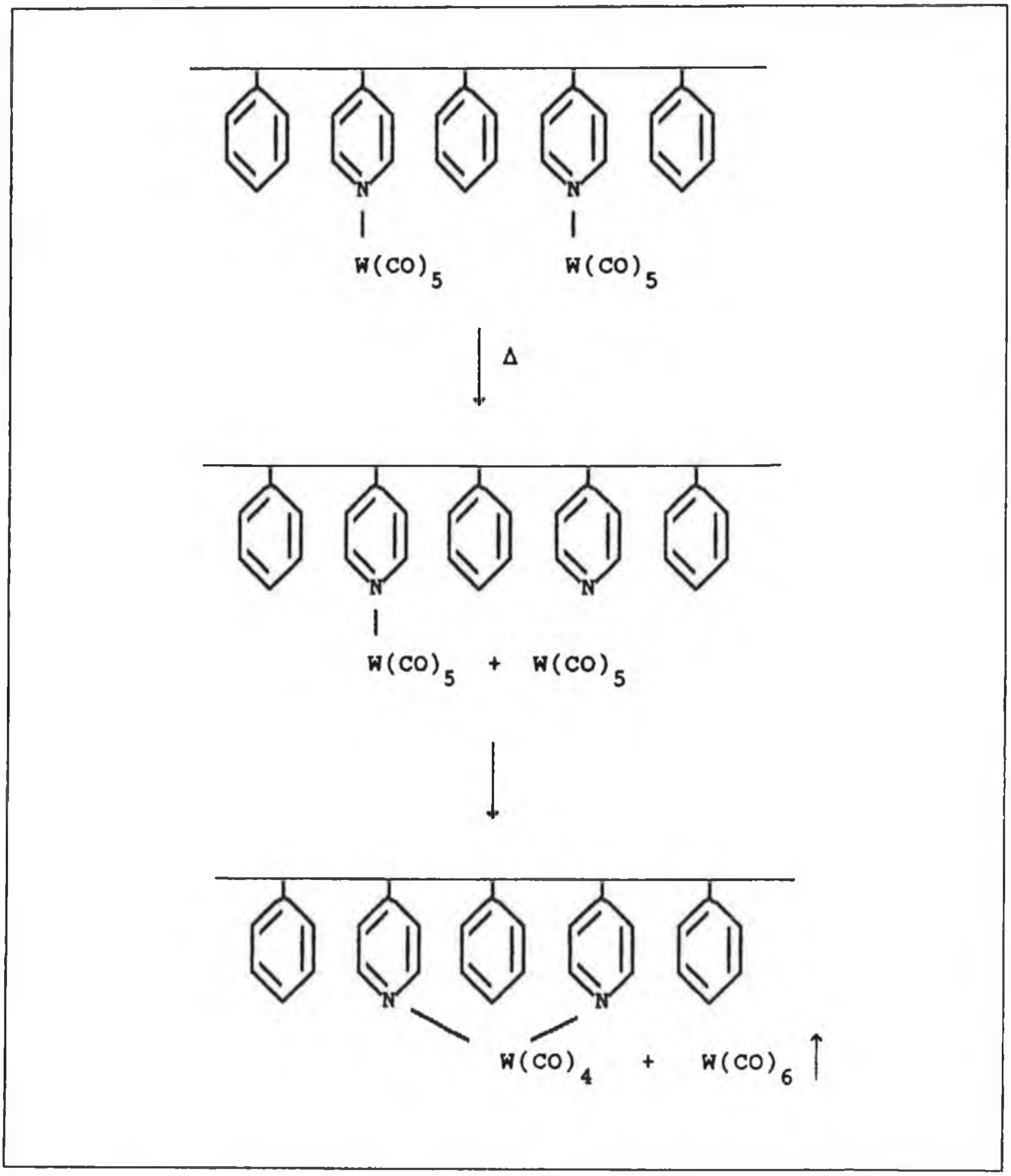
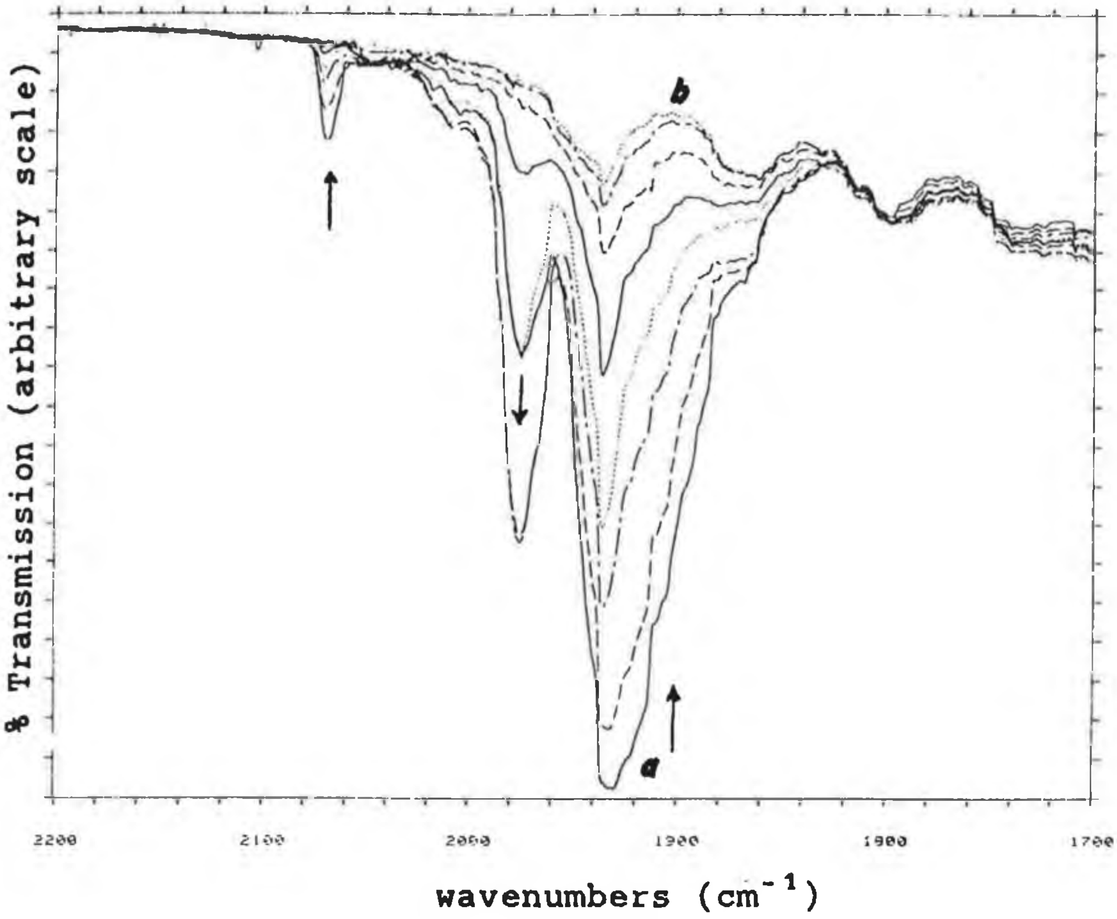


Fig. 3.2.2 The changes observed in the carbonyl stretching frequency region of the infrared on heating a copolymer of styrene and [$W(CO)_5$(2-vinylpyridine)]. Decarbonylation of the metal centres is the only thermal reaction route available.

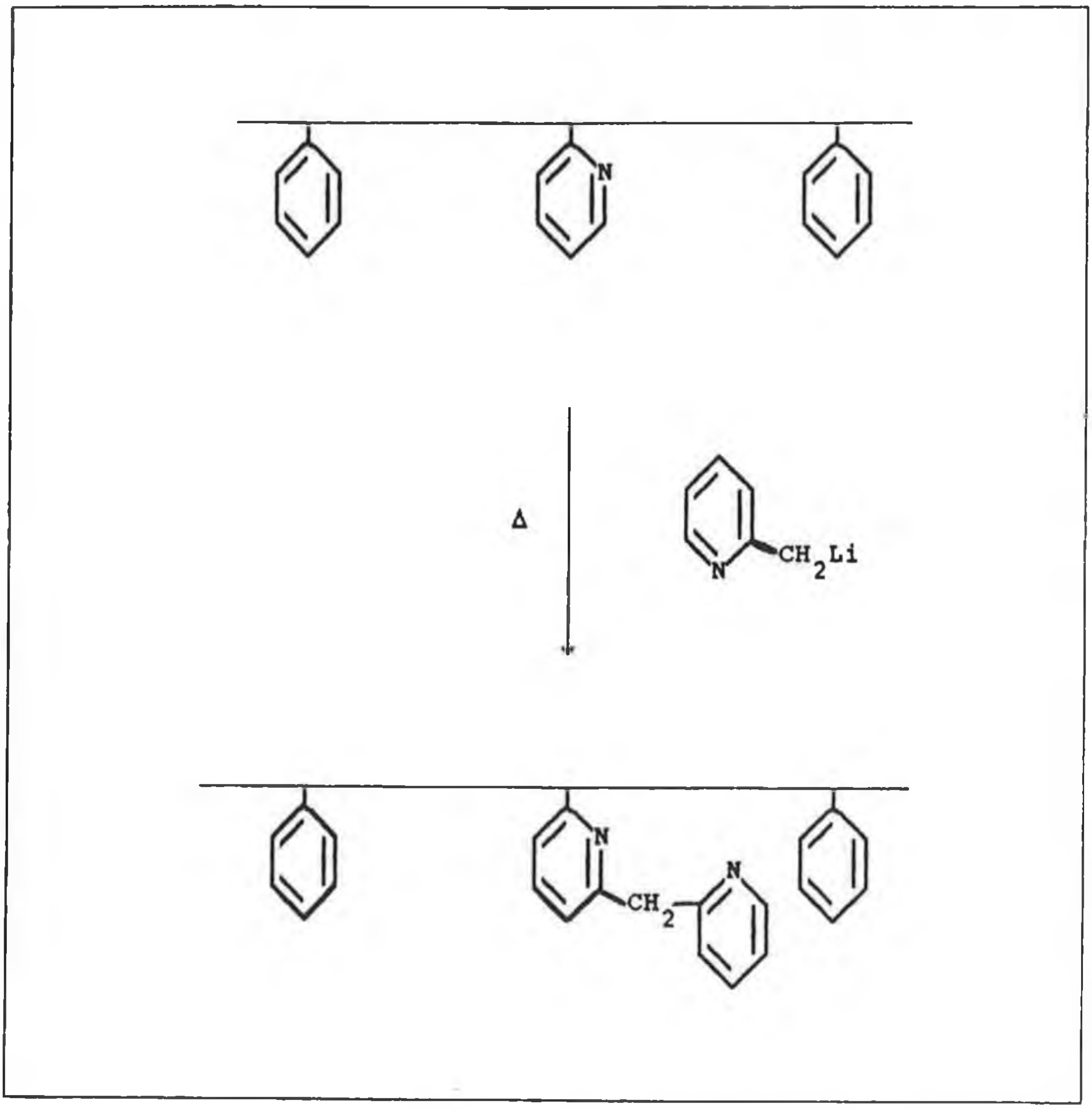


The difference in thermal behaviour of copolymers of 2- and 4-vinylpyridine is thought to due to steric effects imposed by the polymer backbone in those copolymers of 2-vinylpyridine.

a = 25°C, b = 175°C.

Note the production of $W(CO)_6$ *(ca. 1975* cm^{-1}*).*

Scheme 3.2 The derivatisation of a copolymer of styrene and 2-vinylpyridine using lithiated 2-picoline, resulting in a coordinating polymer in which the coordination mode may be varied.



3.2.2 *Polymers of Styrene and $M(CO)_4$(4-vinyl-4'-methyl-2,2'-bipy)*

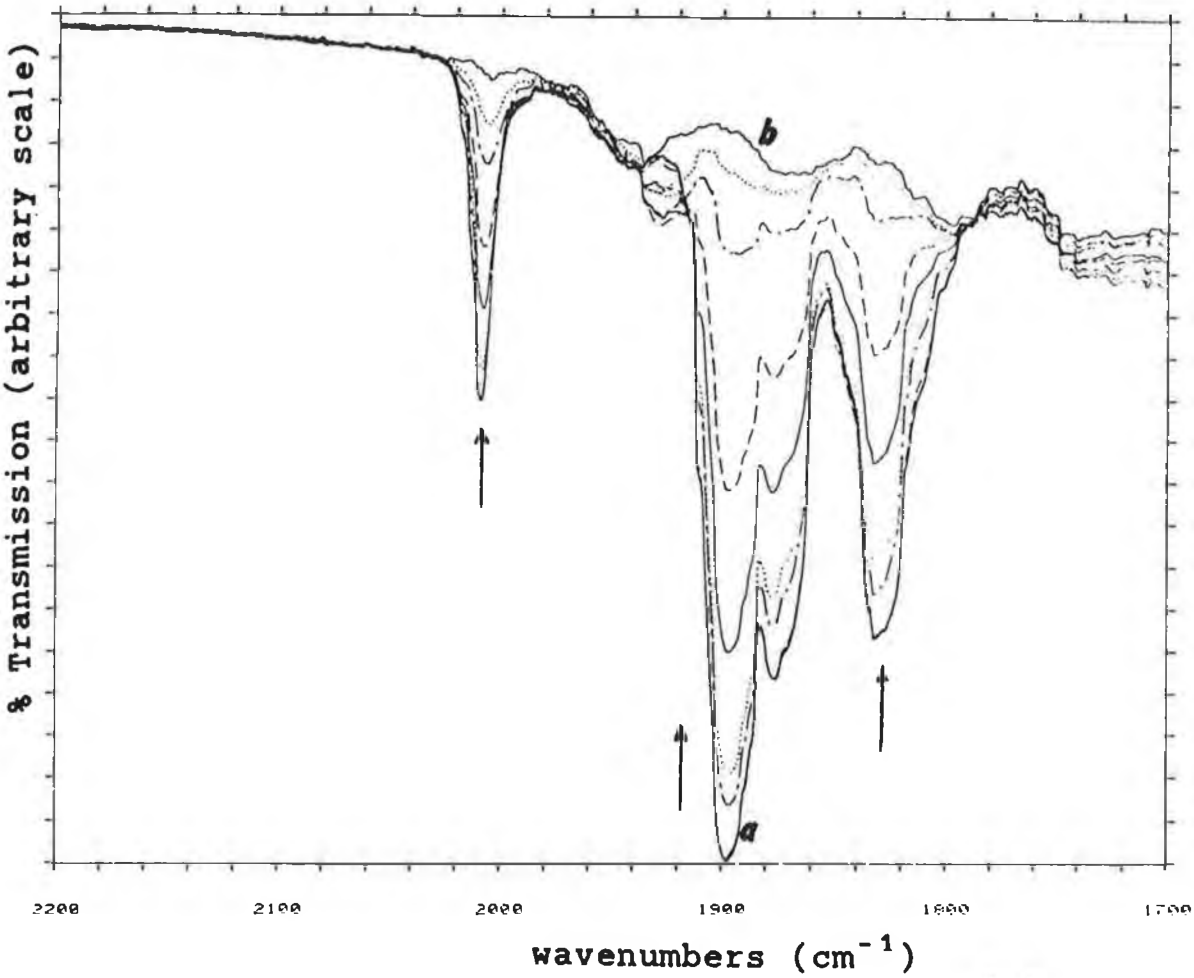
The thermal reactions of copolymers containing chelating coordinating sites were also investigated. Copolymers of styrene and $[M(CO)_4$(4-vinyl-4'-methyl-2,2'-bipyridyl)] (M = Cr, Mo, or W) were prepared as described earlier. On heating these polymers to elevated temperatures a decrease in the tetracarbonyl bands was observed until at 140°C, loss of all carbonyl stretching frequencies occurred, indicating complete decarbonylation of the metal carbonyl species from the polymer (see **Figure 3.2.3**). Heating this polymer in a variable temperature infrared gas cell to 140°C and the subsequent examination of the gases produced, confirmed the presence of both metal hexacarbonyl and free carbon monoxide. This suggested that the thermal reaction again involved a disproportionation process, which would result in some of the metal centres suffering decarbonylation, with concomitant formation of the metal hexacarbonyl.

3.2.3 *Thermal Reactions of Polymers of p-Styryldiphenylphosphine*

Copolymers of styrene and *para*-styryldiphenylphosphine were prepared and reacted with photochemically produced $[M(CO)_5(THF)]$. The resulting polymers displayed carbonyl bands of both the pentacarbonyl and *cis*-tetracarbonyl species in the infrared spectrum[92]. At elevated temperatures the pentacarbonyl frequencies decrease with an accompanying increase in intensity of the tetracarbonyl bands until only tetracarbonyl absorptions remain (**Figure 3.2.4**). Decarbonylation then takes place at about

200°C. In general, the thermally produced phosphine tetracarbonyls had greater thermal stability than those of the nitrogen containing polymers. This is probably a consequence of the better labilising ability of amines over phosphines[26,32]. Analysis of the volatiles of the thermal reaction showed the presence of the metal hexacarbonyl and CO. Monomeric phosphines of the type $[M(CO)_4(PPh_3)_2]$ usually favour the trans isomer, the trans disubstituted isomer being more thermodynamically stable[32,92]. Darensbourg[92b] in his study of $[Mo(CO)_4(PPh_3)_2]$ found that the *cis* isomer thermally rearranges completely to the trans isomer *via* a dissociative process involving Mo-P bond cleavage at 60-80°C in solution. In contrast, the *cis* isomer was formed thermally in the case of polymer anchored $[Mo(CO)_4(PPh_3)_2]$.

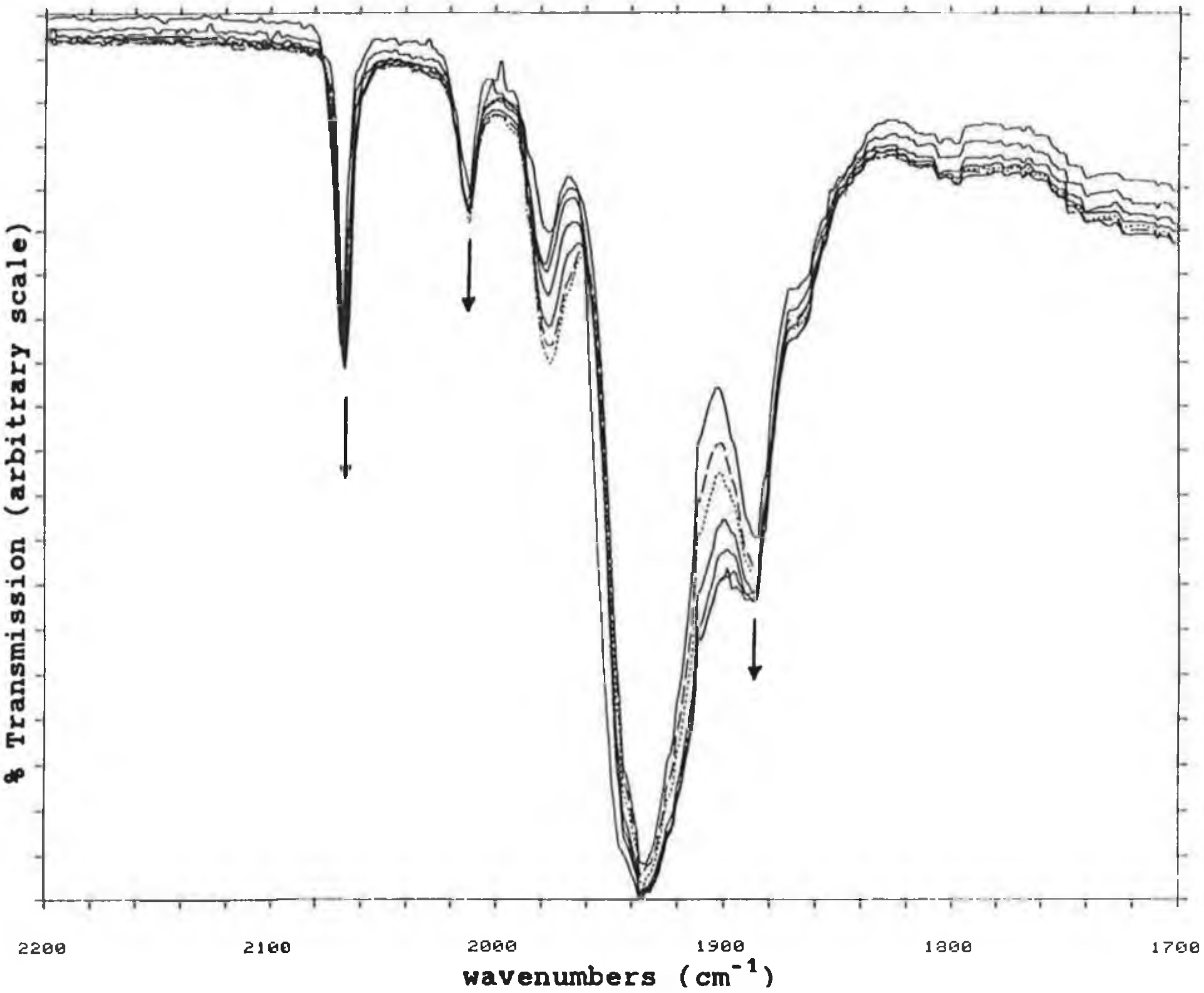
Fig. 3.2.3 Changes observed in the carbonyl stretching frequency region of the infrared on heating a copolymer of styrene and [W(CO)$_4$(4-vinyl-4'-methyl-2,2'-bipyridyl)] to 150°C.



Decarbonylation is the only available thermal route for copolymers of styrene containing the good chelating ligand 2,2'-bipyridyl (M = Cr, Mo, or W).

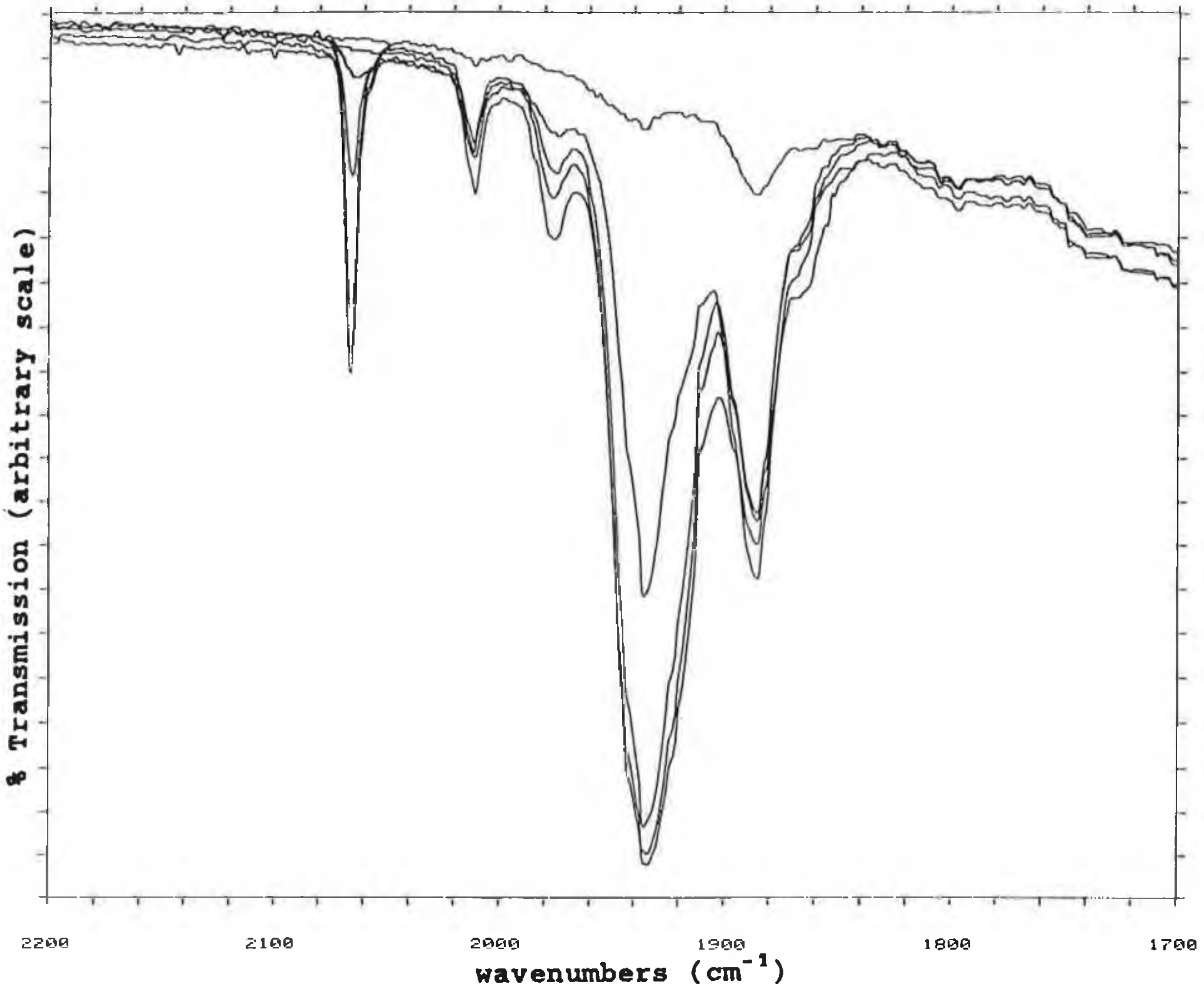
a=20°C,b=150°C.

Fig. 3.2.4a Changes observed in the infrared spectrum (2200-1700cm^{-1}) upon heating a tungsten carbonyl containing copolymer of styrene and p-styryldiphenylphosphine.



These polymers contained both bound pentacarbonyl (2069, 1936 cm^{-1}*) and cis-tetracarbonyl (2017, 1903 cm*$^{-1}$*, the band expected at around 1940 cm*$^{-1}$ [92c] *is masked by the intense pentacarbonyl fundamental absorption) species. On heating to 125°C the pentacarbonyl bands decrease with a concomitant increase in intensity in the tetracarbonyl absorptions.*

Fig. 3.2.4b Changes observed in the region 2200-1700 cm^{-1} on further raising the temperature to 200°C.



At 165°C the tetracarbonyl bands (2011, 1934, 1885, and 1867 (sh) cm^{-1}*) are resolved as the pentacarbonyl bands decrease. Further heating to 200°C results in decarbonylation of the metal centers.*

3.3 The Effect of the Chemical Composition of the Polymer Backbone on the Thermal Chemistry.

On heating copolymers of styrene containing bound group 6 metal penta- and tetra- carbonyl moieties bound *via* nitrogen or phosphorus metal bonds, the decarbonylation of the carbonyl species to yield a polymer containing fully decarbonylated metal centres was observed. It was of interest to determine whether chemical properties can influence the reactions observed on heating thin films of these polymers. Introducing excess binding sites, changing the metal loading, and examining the effects of different polymer backbone compositions may provide us with a clearer understanding of the thermal behaviour of these materials. It also of importance to examine the effect these parameters have on the nature of the final decarbonylated product.

3.3.1 The Effect of Changing the Polymer Backbone.

Alterations in the the chemistry of the comonomer would obviously result in copolymers with vastly differing chemical properties which in themselves may affect the thermal reactions of metal carbonyl moieties bound to them. For this reason copolymers of $[M(CO)_5(4\text{-vp})]$ and $[M(CO)_4(4\text{-vinyl-}4'\text{-methyl-}2,2'\text{-bipy})]$ with methylmethacrylate and ethyl acrylate were prepared. The resulting copolymers have oxygen sites on the polymer backbone. Oxygen, like other first row electronegative elements possessing lone pairs, functions as a σ-donor ligand in metal carbonyl complexes. The Lewis basicity of oxygen is less than that of nitrogen, and as a consequence ligands bonding through oxygen are less effective than those bonding through nitrogen and in most complexes the oxygen ligand is rather weakly bound[32]. However, oxygen sites may act by stabilising thermally produced intermediates.

Heating copolymers of $[M(CO)_5(4\text{-vp})]$ (M = Mo or W) with methylmethacrylate or ethyl acrylate to elevated temperatures resulted in the formation of the *cis*-tetracarbonyl species followed by decarbonylation at higher temperatures. In similar copolymers with M = Cr, decarbonylation was the only thermally observed event. Decarbonylation was the only route available for copolymers of $[M(CO)_4(4\text{-vinyl-}4'\text{-methyl-}2,2'\text{-bipy})]$ (M = Cr, Mo, or W) and methylmethacrylate or ethyl acrylate. Metal hexacarbonyl and carbon monoxide were detected in each instance on monitoring the volatiles above the samples at elevated temperatures. The thermal reactions of polymer films of methylmethacrylate and ethyl acrylate appear to be similar to the reactions of their analogous styrene copolymers. These findings indicate that donor oxygen sites on the polymer backbone do not play a significant role in stabilising the metal carbonyl fragments at these temperatures.

3.3.2 *Thermal Reactions of Polymers with Free Pendant Sites.*

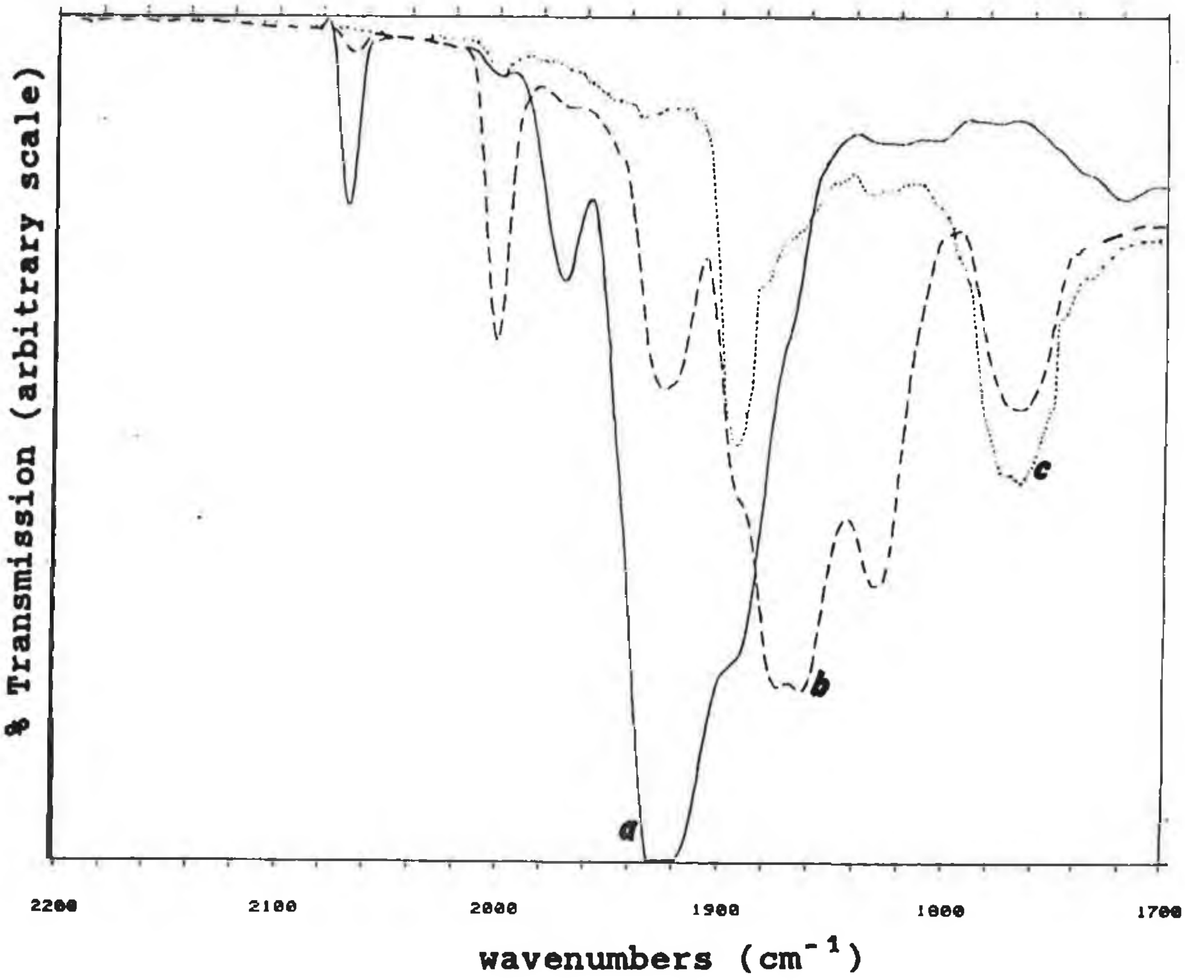
A series of terpolymers of styrene and $[W(CO)_5(4\text{-vp})]$ (20/1 mole ratio) containing excess pendant pyridine were synthesised, and the effect of these additional binding sites on the observed thermal reactivity investigated. Heating polymers containing an excess of 4-vinylpyridine of 1/15 mole ratio of 4-vp/styrene or greater, resulted in the appearance of the *cis*-tetracarbonyl bands with accompanying decrease in the intensity of the pentacarbonyl frequencies at 100°C as before. However, these tetracarbonyl bands were replaced by new bands at 1892 and 1765 cm^{-1} on further heating to 150-175°C (see Figure 3.3.1). These carbonyl stretching frequencies are close to those reported for $[Mo(CO)_3(py)_3]$ (1888, 1746 cm^{-1} in nujol mull)[93], which has a *fac*-configuration. These new bands can be assigned to the thermally produced *fac*-tricarbonyl compound, bound *via* three polymer anchored pyridine coordination sites. Further raising the temperature resulted in loss of the carbonyl bands. Those polymers containing lower concentrations of excess pyridine behaved as before with production of the tetracarbonyl and eventual decarbonylation of the metal centres.

An identical experiment was conducted with copolymers of styrene and $[W(CO)_5(4\text{-vp})]$ incorporating free pendant 2-vinylpyridine onto the polymer backbone. The additional 2-vinylpyridine residues had no effect on the thermal chemistry. A copolymer of 2-vinylpyridine (20/1 mole ratio) and $[W(CO)_5(4\text{-vp})]$ displays the same thermal reactivity as a copolymer of styrene and $[W(CO)_5(4\text{-vp})]$, that is tetracarbonyl formation followed by decarbonylation, no evidence of tricarbonyl formation being found. Copolymers of 2-vinylpyridine and $[W(CO)_5(2\text{-vp})]$ (20/1 mole ratio) form the *cis*-disubstituted tetracarbonyl at over 100°C, but no tricarbonyl formation was observed. For those polymers of lower loading of free 2-vinylpyridine no tetracarbonyl formation was noted. The observed reactions of these materials is in sharp contrast to the observed thermal reaction routes available to similar polymers of 4-vinylpyridine. Both contain a tungsten pentacarbonyl moiety bound *via* a nitrogen ligand, and were prepared by the same procedures. The difference in thermal behaviour between copolymers of 4-vinylpyridine and 2-vinylpyridine must be a result of steric hindrance to coordination in 2-vinylpyridine systems.

Further polymers were prepared of styrene and [$W(CO)_4$(4-vinyl-4'-methyl-2,2'-bipy)] incorporating excess 4-vinylpyridine. Heating a polymer with a 1/30 mole ratio of 4-vp/styrene, or higher, yielded bands at 1888 and 1775 cm^{-1} (see Figure 3.3.2). These band positions are close to those of *fac*-[$W(CO)_3$(bipy)(py)] (1892 and 1773 cm^{-1} in nujol mull) previously reported[94]. It is therefore proposed that the carbonyl containing product observed here is the *fac*-tricarbonyl species. Heating further leads to complete decarbonylation (Scheme 3.3).

These findings suggest that the loss of a CO ligand is an important route for the thermal reactions of these systems in the absence of excess binding sites. The concentration of pendant sites on the backbone is also important in these reactions.

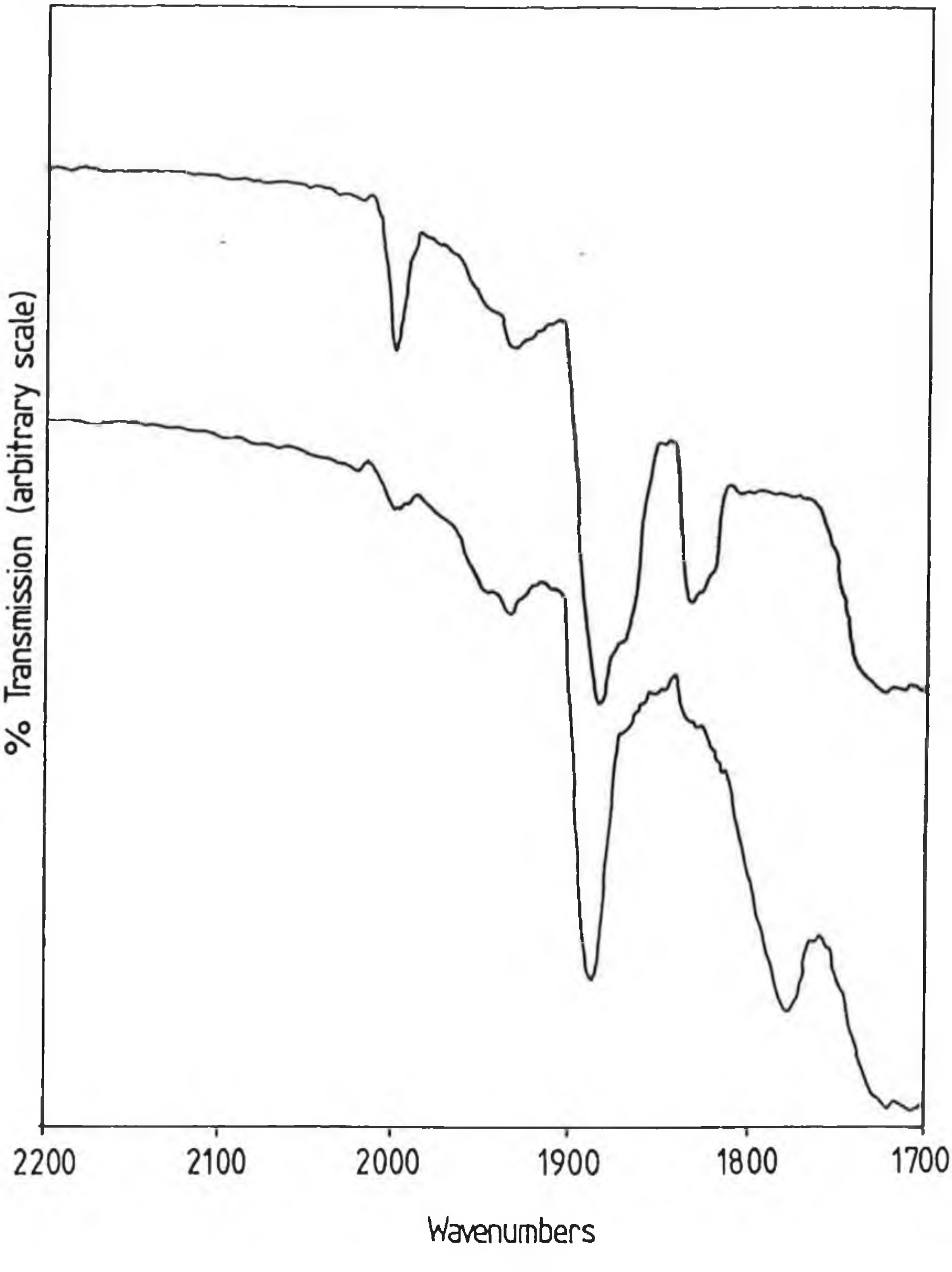
Fig. 3.3.1 Changes observed in the carbonyl stretching frequency region of the infrared on heating a polymer of styrene and $[W(CO)_5(4\text{-}vp)]$ (20/1 mole ratio) containing excess 4-vinylpyridine binding sites (5/1 mole ratio of styrene to free 4-vinylpyridine).



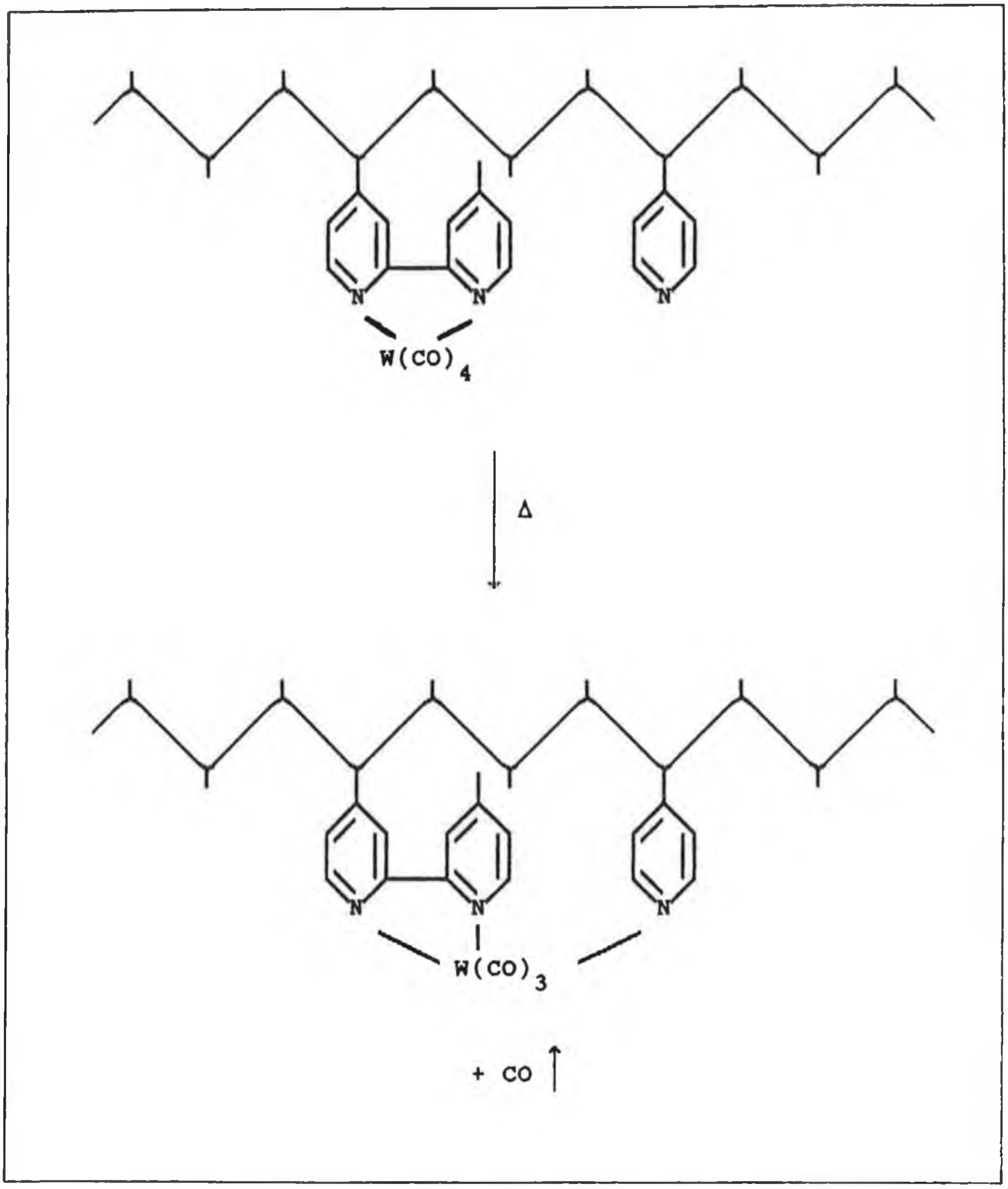
In the presence of excess binding sites, the fac-tricarbonyl species is formed.

a = *20°C*, b = *135°C*, *c* = *175°C*.

Fig. 3.3.2 Changes observed in the infrared spectrum (2200-1700 cm^{-1}) upon heating a terpolymer of styrene and $[W(CO)_4$(4-vinyl-4'-methyl-2,2'-bipy)] (20/1 mole ratio) with 4-vinylpyridine (10/1 mole ratio of styrene/4-vp). These changes are consistent with the formation of fac-tricarbonyl complex.



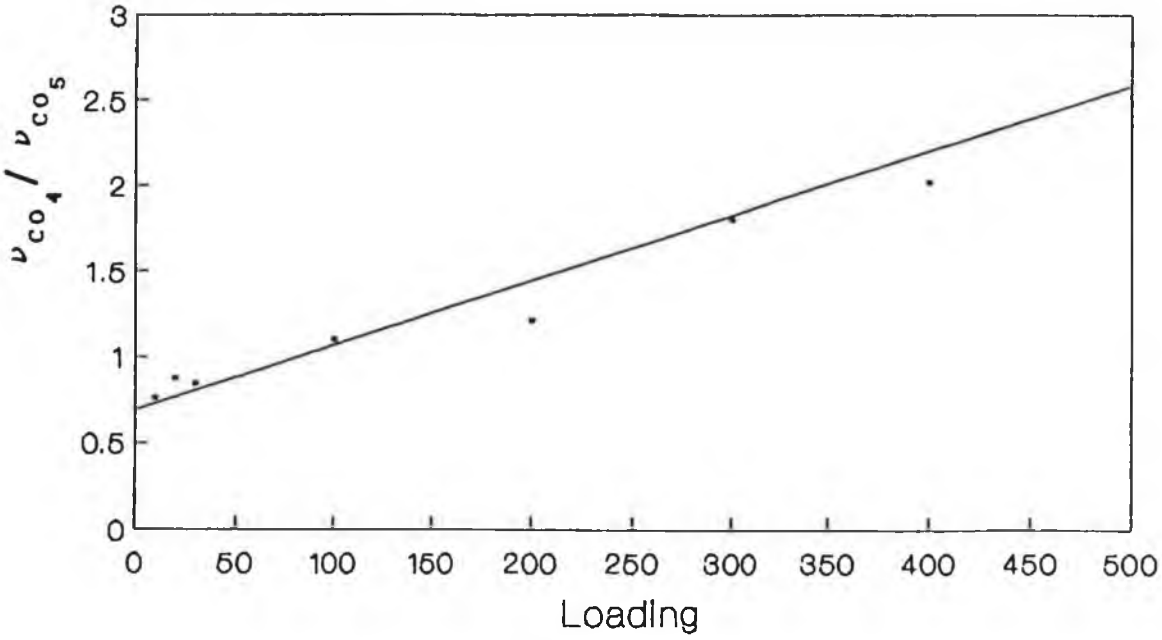
Scheme 3.3 The effect of free binding sites on the observed thermal chemistry of a copolymer of styrene and [$W(CO)_4$(4-vinyl-4'-methyl-2,2'-bipy)]. In the presence of additional binding sites the fac-tricarbonyl species is formed.



3.3.3 *Effect of Metal Loading*

A series of copolymers of different metal loading were prepared. At loadings on styrene to [$W(CO)_5$(4-vp)] of greater than 5:1 the polymers become insoluble. The polymers were heated as before and the changes in the carbonyl stretching frequency range monitored. At higher loadings the metal tetracarbonyl species was produced until at loadings of 1:600 and lower, no tetracarbonyl species was observed. The amount of thermally produced *cis*-tetracarbonyl decreased as the loading of the metal carbonyl species in the polymer was decreased. Figure 3.3.3 shows the change in the ratio of the percent transmission of tetracarbonyl species (measured at the high frequency absorption at 2000 cm^{-1}) to pentacarbonyl (measured at 2068 cm^{-1}) with metal loading. No metal tricarbonyl was found even at higher loadings.

Fig. 3.3.3 Plot of the ratio of percent transmission of thermally produced metal tetracarbonyl to metal pentacarbonyl in the infrared for copolymers of styrene and [$W(CO)_5$(4-vp)] having different metal loadings.



These results suggested that the formation of the *cis*-tetracarbonyl species depends on the proximity of the pentacarbonyl units on the polymer chain. It also supports the mechanism involving the thermal cleavage of the W-N bond with generation of the pentacarbonyl and subsequent reaction of this fragment to produce a tetracarbonyl centre and metal hexacarbonyl, more metal hexacarbonyl being detected for higher loadings.

3.4 The Effect of the Physical Properties of the Polymer Backbone on the Thermal Chemistry

We were interested to investigate whether physical parameters were important in the thermal reactions of these systems. The influence of the molar mass and glass transition temperature (T_g) on the thermal chemistry were examined using variable temperature infrared studies and thermal methods of analysis. Differential scanning calorimetry (DSC) was employed to determine the effect of metal carbonyl binding on the polymer and to study the importance of the T_g on the thermal behaviour of these materials.

3.4.1 Effect of Relative Molar Mass on the Thermal Reactions of Polymer-Bound $W(CO)_5$ species.

A series of copolymers of styrene and 4-vinylpyridine (20/1 mole ratio) of a range of molar masses ($\bar{M}_w$ = 10,000-200,000 a.m.u) were synthesised by using different amounts of the initiator azobisisobutyronitrile (0.05-4% AIBN) in the polymerisation mixture. The molar masses were determined by gel permeation chromatography using polystyrene standards to construct a calibration curve over the expected molecular weight range. Each of these copolymers were then reacted with $[W(CO)_5(THF)]$, produced by the photolysis of the parent hexacarbonyl in THF. Sufficient $[W(CO)_5(THF)]$ was added to ensure that every vinylpyridine was coordinated to a $W(CO)_5$ unit. Examination of the spectral changes observed on heating these copolymers indicated that the same thermal reaction was occurring for all the polymers, i.e., initial decarbonylation of the $W(CO)_5$ moiety to produce the $M(CO)_4$ unit followed by complete decarbonylation of the metal centres. The T_g's of these polymers were determined and are given in Table 3.4.1 together with the molar mass data of the copolymers.

Table 3.4.1 Molar masses and glass transition temperatures of copolymers of styrene and 4-vinylpyridine prepared using varying amounts of AIBN.

% AIBN	T_g (°C)	$\overline{M}_w$ (a.m.u)	$\overline{M}_n$ (a.m.u)	$\overline{M}_w/\overline{M}_n$
4.00	108	10600	5650	1.88
2.00	113	17200	8180	2.11
1.00	120	26500	14880	1.78
0.66	122	38200	19150	2.00
0.50	115	47400	28200	1.88
0.40	122	51100	25800	1.98
0.33	126	67500	30100	2.24
0.25	122	70900	31400	2.25
0.20	125	99800	47200	2.11
0.10	128	162000	70200	2.31
0.05	132	204000	86700	2.36

The T_g values show the expected slight dependence on relative molar mass, increasing from 108°C to 132°C for a $\overline{M}_w$ of 10,600 to 204,000 a.m.u. A typical DSC thermogram of one of these copolymers is shown in **Figure 3.4.1**. The T_g is taken as the onset temperature of the heat capacity change. A DSC thermogram of the corresponding metal carbonyl containing polymer is illustrated in **Figure 3.4.2**. The latter thermogram is dominated by a large exothermic event representing formation of tetracarbonyl species, followed by complete decarbonylation (*vide infra*). Similar exotherms have been reported previously in DSC studies of polymer anchored metal carbonyls[56,95]. The thermal reaction is accompanied by a shift in baseline which implies a change in entropy/order within the system. Similar thermogram profiles were obtained for each of the above copolymers, and for those metal carbonyl containing polymers of 2-vinylpyridine and 4-vinyl-4'-methyl-2,2'-bipyridyl. From **Figure 3.4.2**, it is apparent that the initial monodecarbonylation of the $M(CO)_5$ moiety and the subsequent full decarbonylation are not resolved thermal events. It is important to note that in the case of DSC experiments the temperature is continually changing while in the variable temperature infrared experiments, the temperature is changed in a step-wise fashion.

A further transition was observed at 220-280°C (depending on the polymer) which may be the T_g of the polymer which now contains fully decarbonylated metal species. Thermogravimetric analysis (TGA) of this process confirmed that weight loss (caused by sublimation of $W(CO)_6$ or loss of CO) occurred only during the low temperature event (see Figure 3.4.3). This could confirm the assignment of the event following decarbonylation, to a glass transition. It also indicates that appreciable metal must remain within the polymer following complete decarbonylation, as in all polymer systems studied weight losses in the region 2-5% were found. (If a copolymer of styrene and $[W(CO)_5(4\text{-vp})]$ (20/1 mole ratio) suffered loss of all it's metal and CO, a weight loss of 13% would be expected). As a consequence, metal loss via metal hexacarbonyl formation must only be a minor route to the loss of the carbonyl moieties. One might expect the glass transition temperature of the polymer to increase because of the increase in energy required for rotation on attachment of the metal carbonyl fragment[76b]. An increase in the T_g's of copolymers on binding metal carbonyl complexes have previously been reported in studies of bound iron carbonyl complexes[95], and in thermal studies of polystyrene anchored chromium tricarbonyl[96]. Attempts to obtain the T_g of the decarbonylated polymer, proved to be unsuccessful.

These results confirm that the molar mass of the polymer backbone has little influence on the direction of reactions of the metal pentacarbonyls bound to the polymer. However, the physical properties of the polymer are significantly affected by the presence of the pentacarbonyl moieties as indicated by the appearance of a new glass transition temperature at a higher temperature than the T_g of the non-metallated polymer.

Fig. 3.4.1 DSC thermogram of a copolymer of styrene and 4-vinylpyridine ($\overline{M}_w$ = 10,600 a.m.u). (T_g onset = 110°C; Heating rate = 5°C/min, Atmosphere = N_2 at 30 cm^3/min).

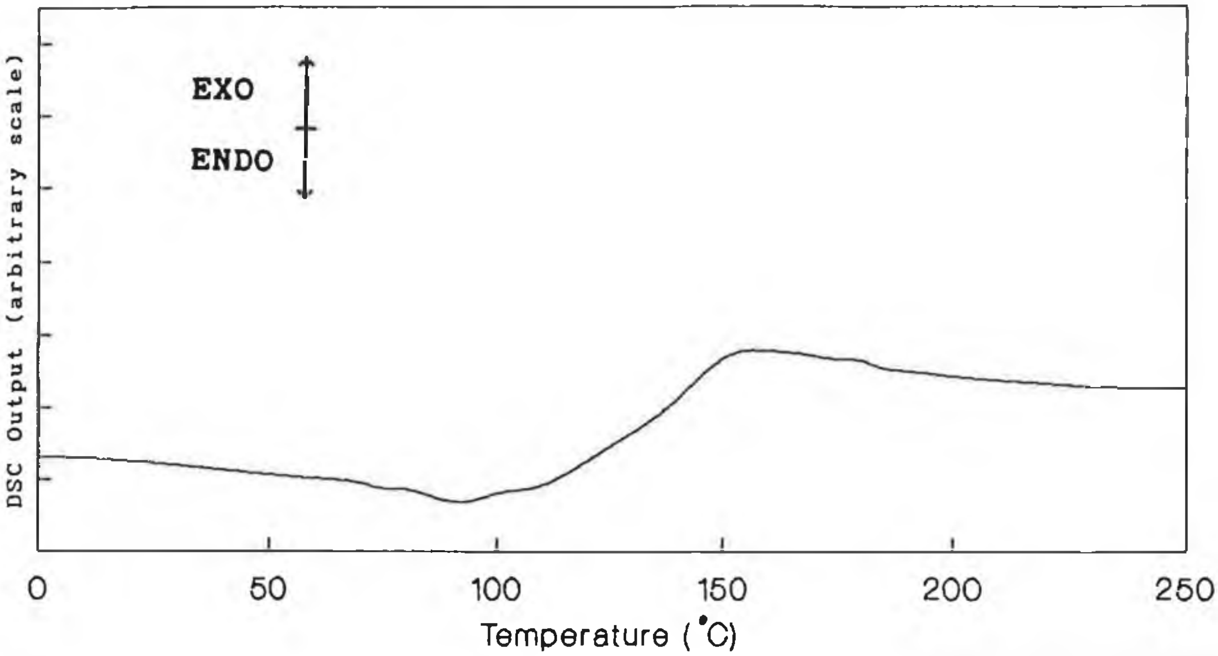


Fig. 3.4.2 DSC thermogram of a copolymer of styrene and [$W(CO)_5$(4-vp)]. (Heating rate = 5°C/min; Atmosphere = N_2 at 30 cm^3/min).

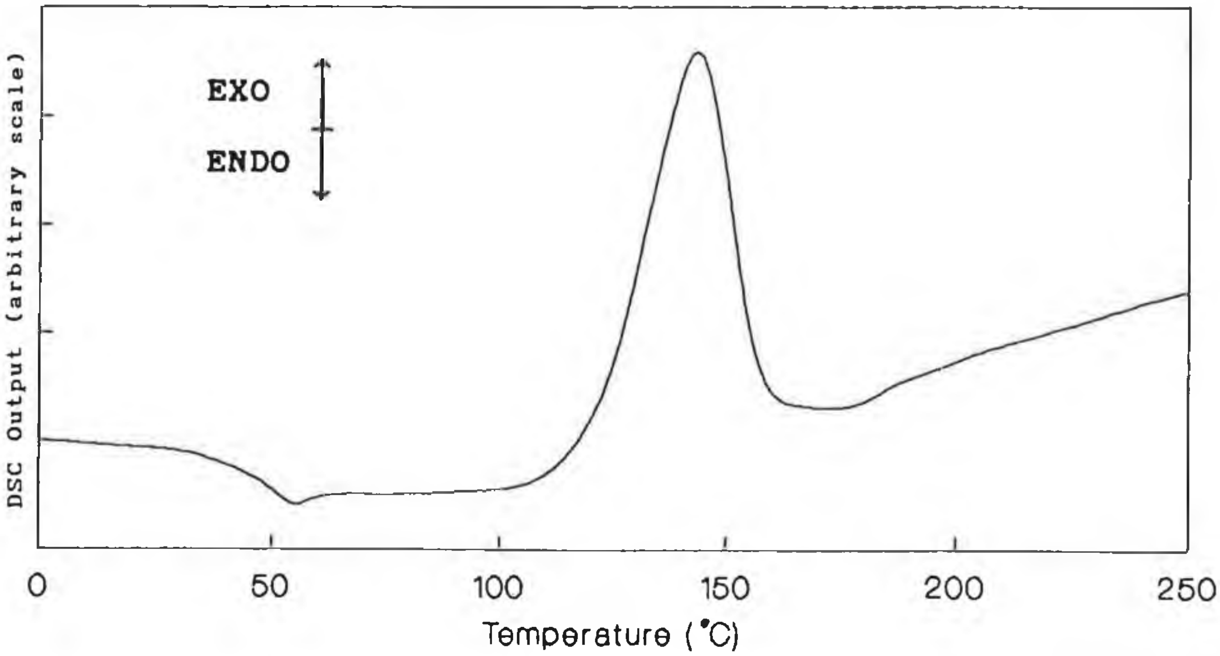
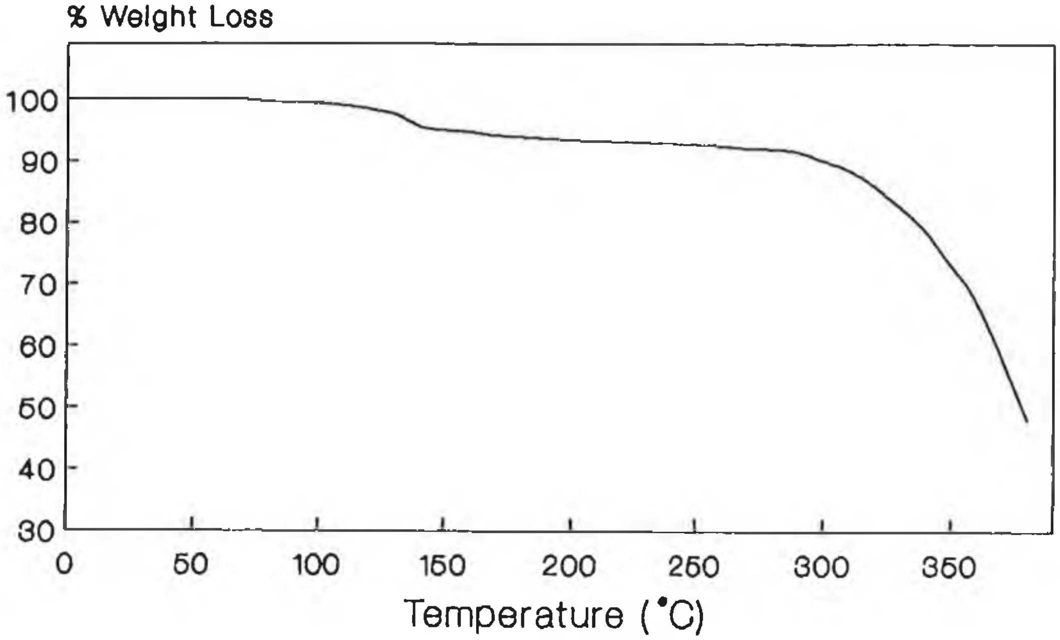


Fig. 3.4.3 TGA curve for a copolymer of styrene and $[W(CO)_5(4\text{-vp})]$. A 4% weight loss occurs between 110-165°C, with decomposition at 330°C. (Heating rate = 10°C/min; Atmosphere = N_2 at 10 cm^3/min).



3.4.2 *The Importance of the Glass Transition Temperature.*

In the DSC studies of these polymer-bound materials the decarbonylation reactions commenced at a temperature close to the T_g of the unmetallated polymer. This observation posed the question as to whether or not the extra chain mobility induced by exceeding the glass transition of the polymer was a prerequisite for the thermal reactions to occur.

In order to investigate the importance of the T_g on the observed thermal reactions, a series of copolymers of 4-vinylpyridine and various comonomers were synthesised. These comonomers were ethyl and methyl acrylate and α-methylstyrene and were chosen because their polymers exhibit a wide T_g range (literature values for homopolymers: polyethylacrylate = -24°C, polymethylacrylate = 0°C and poly-α-methylstyrene = 172°C)[76]. However, alterations in the chemistry of the comonomer would obviously result in copolymers of vastly differing chemical properties which in themselves may effect the thermal reactions of the bound metal carbonyls. For this reason, copolymers of 4-vinylpyridine and methylmethacrylate were prepared. These copolymers have a T_g (onset 110°C) similar to copolymers of styrene and 4-vinylpyridine, while the chemistry of the polymer backbone should resemble that of the 4-vinylpyridine-co-ethyl acrylate copolymer (the only difference being the presence of an α-CH_3 in methylmethacrylate polymers).

The T_g's of copolymers of 4-vinylpyridine with methyl and ethyl acrylate were determined to be -22°C and +9°C respectively. These materials were isolated as rubbery solids as opposed to those polymers of styrene and methylmethacrylate of higher T_g's which were obtained as powders. Metal carbonyl containing copolymers (20/1 mole ratio) of ethyl and methyl acrylate were prepared by copolymerisation of the acrylate with $[W(CO)_5(4\text{-vp})]$. The resulting polymer of ethyl acrylate was isolated as a rubbery solid (T_g < room temperature) while that of methyl acrylate was a powder (T_g > room temperature). Heating these polymers in the variable temperature cell resulted in changes in the infrared similar to those of metallated copolymers of methylmethacrylate and styrene, i.e., *cis*-tetracarbonyl formation followed by decarbonylation.

Examining the DSC trace of these acrylate copolymers (see **Figure 3.4.5**) it is apparent that the decarbonylation event is not well defined. The baseline slopes gradually until at about 110°C a shouldered exothermic event occurs. The sloping baseline, which is absent in the DSC of the non-metallated copolymer (**Figure 3.4.4**), suggested that the thermal reaction may be taking place after the glass transition temperature had been reached. Indeed, **Figure 3.4.5** shows the spectra obtained after maintaining a film of a copolymer of ethyl acrylate and $[W(CO)_5(4\text{-vp})]$ at 70°C and continuously scanning the carbonyl stretching frequency region of the infrared at fixed time intervals. The result was a gradual but steady decrease in intensity of the pentacarbonyl carbonyl bands with concomitant formation of bands which can be assigned to the tetracarbonyl species, followed eventually by total decarbonylation. A similar result was found for methyl acrylate copolymers containing bound metal pentacarbonyl or tetracarbonyl. For those copolymers of styrene and methylmethacrylate of higher glass transition temperatures, no change in the intensity of the carbonyl stretching frequencies was found on prolonged heating at 70°C. The fact that a copolymer of methylmethacrylate undergoes no reaction at 70°C rules out the possibility of oxygen donor sites acting as binding sites. Reaction of the acrylate was found to proceed at lower temperatures (50°C) but at slower rates.

temperature reaction proceeds anyway. If the T_g is below the threshold temperature the reaction will proceed above the T_g of the polymer, and if the T_g is above the threshold temperature the reaction proceeds at this threshold temperature.

Fig. 3.4.4 DSC thermogram of a copolymer of ethyl acrylate and 4-vinylpyridine (20/1 mole ratio). (T_g = -22°C, Heating rate = 5°C/min, Atmosphere = N_2 at 30 cm^3/min).

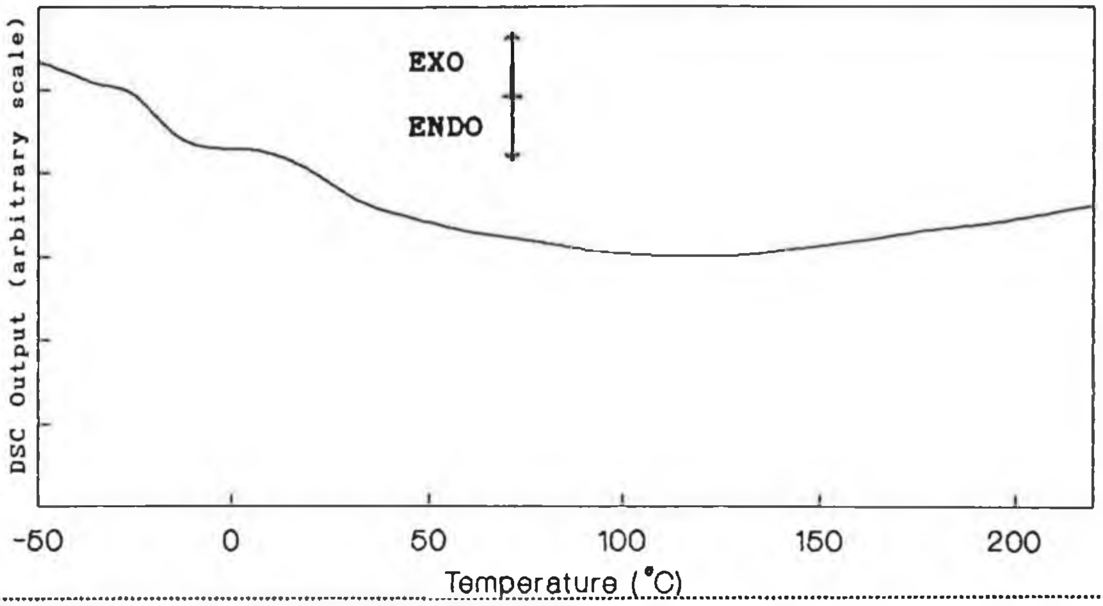


Fig. 3.4.4 DSC thermogram of a copolymer of ethyl acrylate and $[W(CO)_5(4\text{-}vp)]$. (Heating rate = 5°C/min, Atmosphere = N_2 at 30 cm^3/min).

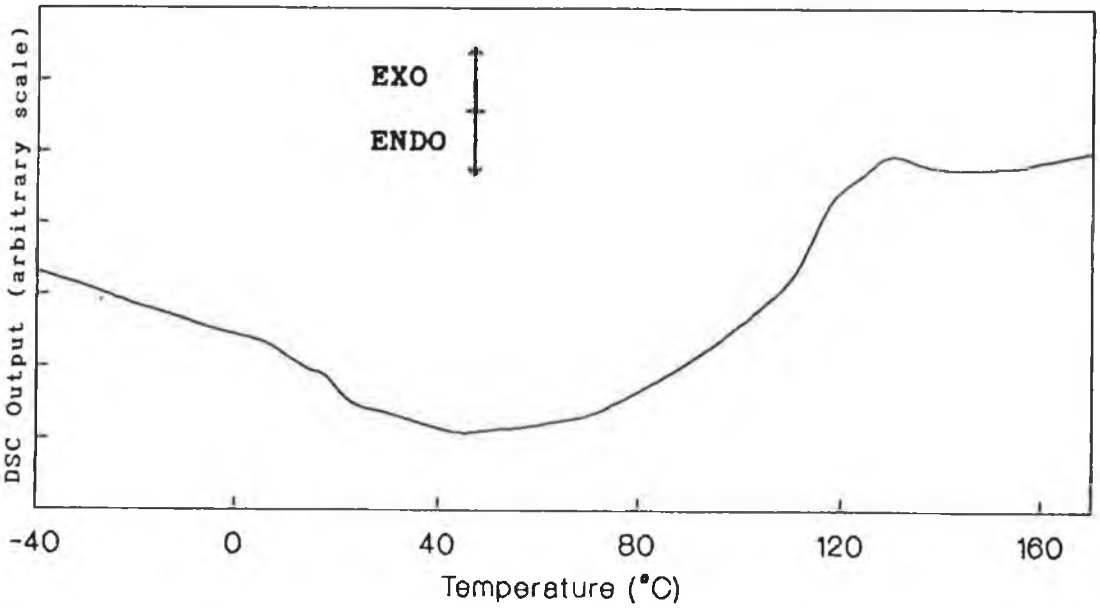
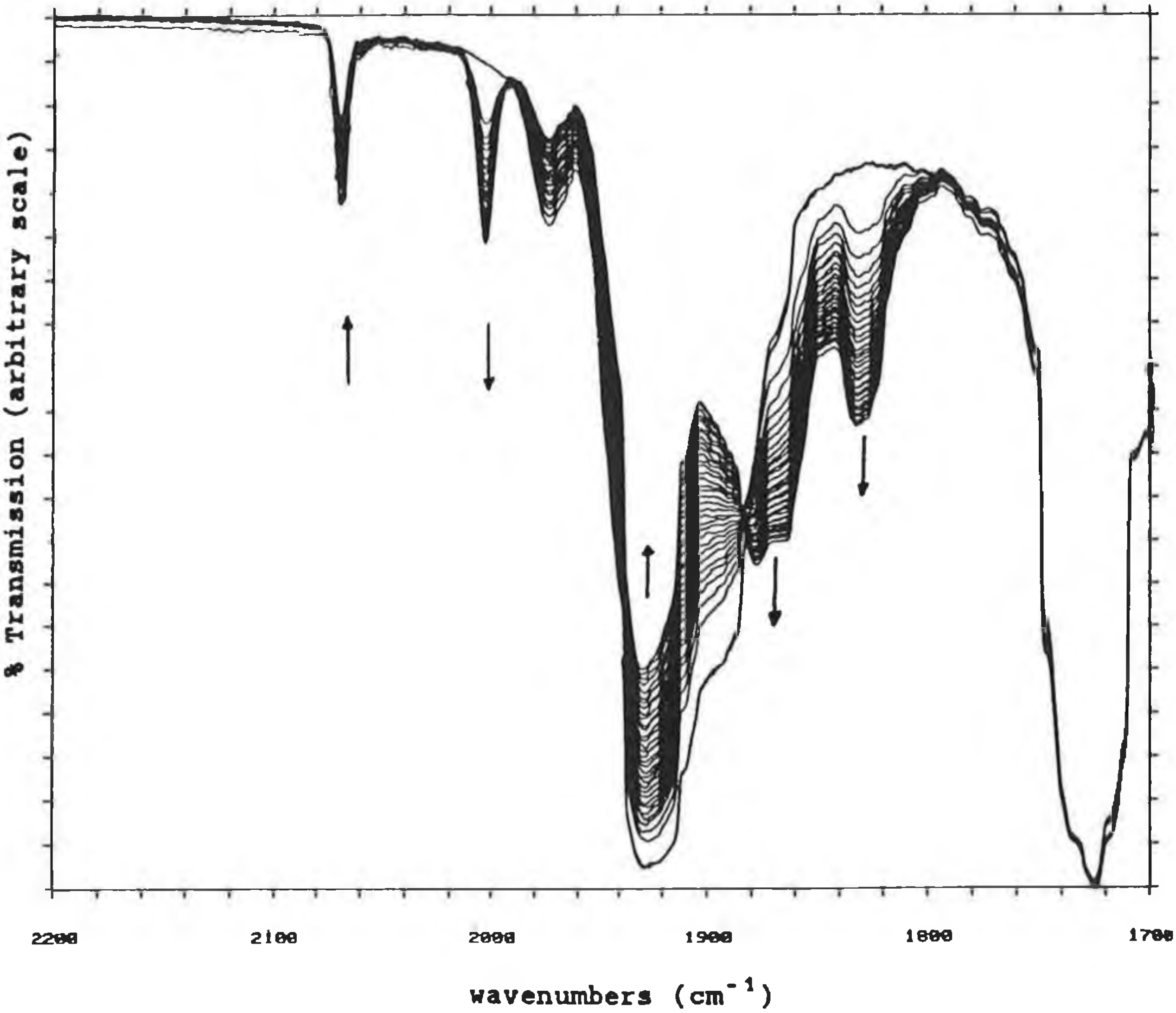
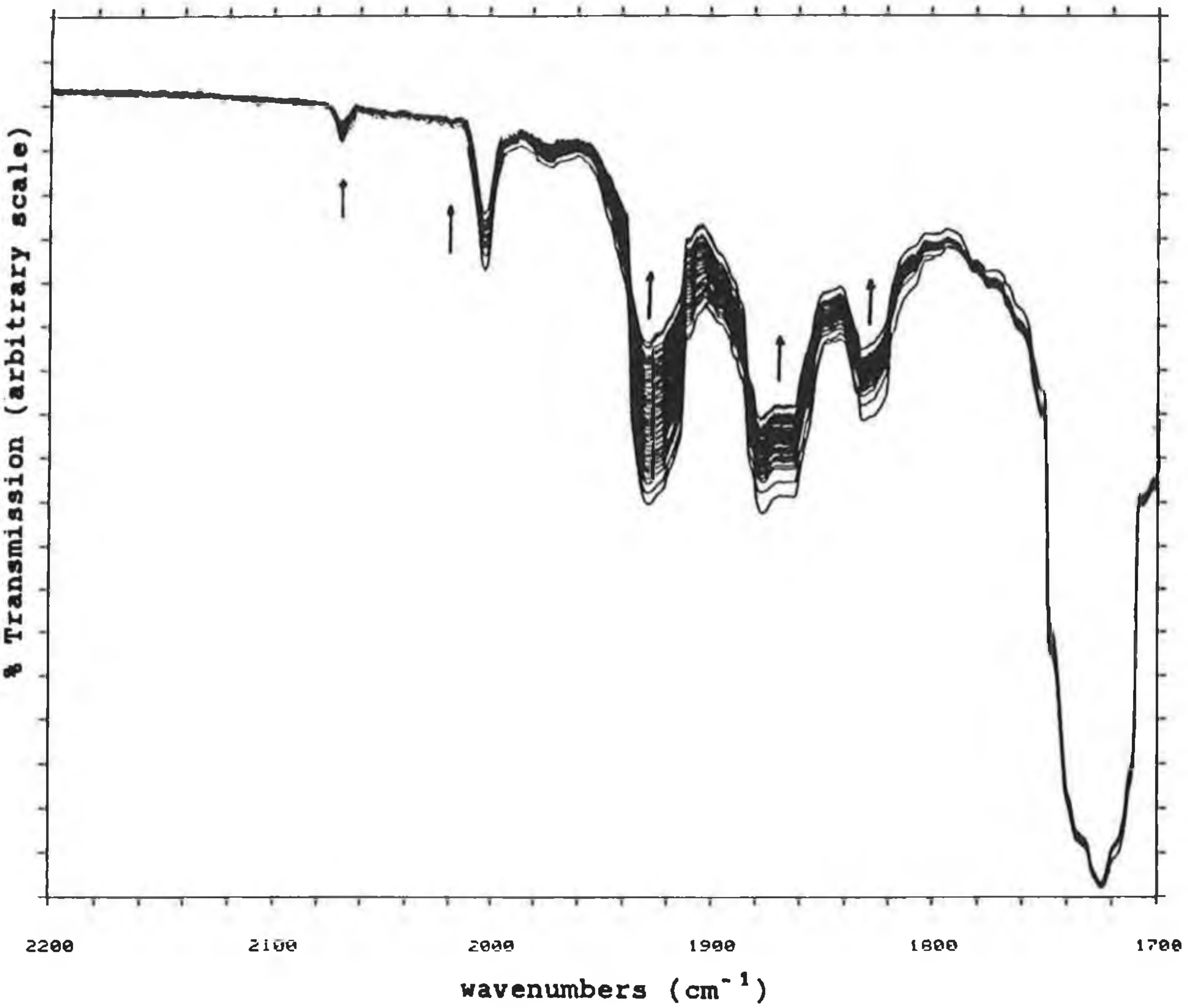


Fig. 3.4.5a Changes observed in the 2200-1700 cm^{-1} region of the infrared on heating a copolymer of ethyl acrylate and $[W(CO)_5(4\text{-vp})]$ to 70°C for 16h.



On continued heating, maintaining the temperature at 70°C, the pentacarbonyl bands decrease in intensity and are replaced by those of the cis-disubstituted tetracarbonyl bands.
The band at 1727 cm^{-1} *is due to the acrylate backbone.*

Fig. 3.4.5b Changes observed in the carbonyl stretching frequency region of the infrared on continued heating of a copolymer of ethyl acrylate and $[W(CO)_5(4\text{-vp})]$ for 30h.



Continued heating at 70°C results in eventual decarbonylation. No such reaction occurs for polymers of styrene or methylmethacrylate.

3.5 Analysis of the Thermal Product of the Decarbonylation.

Much of the interest in the thermal chemistry of metal carbonyls when bound to organic polymer supports has been concerned with the formation of colloidal metal dispersions within polymer matrices. Many of the studies have been performed by preparing homogeneous solutions of metal carbonyls and the polymer matrix and subsequent generation of the metal or metal oxide domains by thermal, photolytic or electron beam methods[88,90]. Other reports have dealt with the thermal decomposition of anchored metal carbonyl systems in solution[62,63,95,96]. It seemed likely that heating cast films of polymer attached group 6 metal carbonyls may afford polymers containing small metal clusters having catalytic activity.

Each of the thermal reactions of all the studied polymer systems produced fully decarbonylated metal centres (vide infrared spectroscopy) under relatively mild thermal conditions. The mechanism suggested was one of a dissociative process involving the formation of free metal pentacarbonyl fragments which react with other bound pentacarbonyl units producing the tetracarbonyl centre and metal hexacarbonyl (in the case of polymers of $[M(CO)_5(4\text{-vp})]$). The production of metal hexacarbonyl was confirmed by analysis of the products in the headspace above a heated sample. This process would result in appreciable metal loss because of sublimation of the hexacarbonyl from the polymer. Thermogravimetric analysis of the polymers however, revealed that little metal was lost upon decarbonylation. A more quantitative evaluation of the metal content following thermal reaction was required.

The amount of metal remaining following decarbonylation was determined by atomic absorption spectroscopy. One set of polymers were thermally reacted under vacuum at 200°C. The absence of carbonyl stretching frequencies in the reacted samples was confirmed by infrared spectroscopy. These samples were analysed for metal content and compared with a set of identical unreacted samples. Results showed that as much as 90% of the metal remained within the polymer matrix following thermal reaction. Of all the polymers studied there were no significant differences in the percentage metal remaining, regardless of the polymer composition.

Analysis of decarbonylated polymer films of styrene and [$M(CO)_5$(4-vp)] by X-ray photoelectron spectroscopy (XPS)[97], revealed the presence of WO_3 dispersions on the surface of the films. Decarbonylations were carried out under vacuum, so presumably highly reactive elemental metallic species produced react with oxygen to form the metal oxide on exposure to air.

This work suggests that high concentrations of metal or metal oxide dispersions can be produced under mild conditions (less than 70°C for ethyl acrylate copolymers). It is also very likely that metallic chromium and molybdenum dispersions are produced on thermal decomposition of polymers when M = Cr or Mo.

Further studies of these materials are necessary to investigate aspects of nucleation and growth of metal and metal oxide clusters in the solid state as well as the properties of such microparticles as a function of cluster size, concentration and environment.

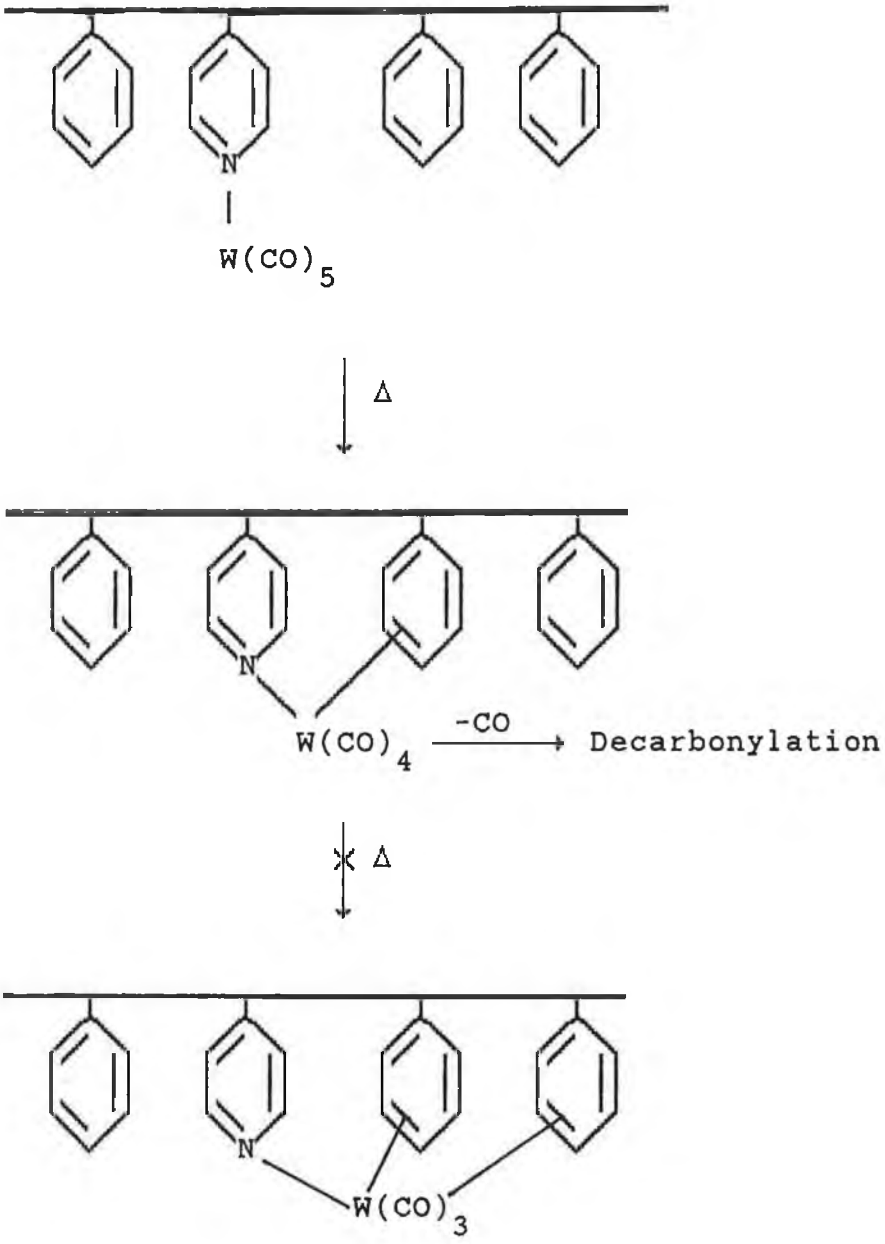
3.6 Conclusions

Investigations of the thermal properties of these polymers when cast as films 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 copolymers of 2-vinylpyridine loss of the metal carbonyl fragment appears to be the only thermal route available. This is probably a result of significant steric hindrance by the polymer to the coordination of the pyridine in these polymers. For those polymers of 4-vinylpyridine, the thermal chemistry involves the formation of the *cis*-disubstituted tetracarbonyl complex. This is in sharp contrast to that of monomeric [W(CO)$_5$(pyridine)], which sublimes on heating. Polymers containing 2,2'-bipyridyl metal tetracarbonyl complexes suffered the loss of the carbonyl stretching frequencies at elevated temperatures. In the presence of free binding sites on the polymer backbone, the *fac*-tricarbonyl species is formed. Polymers of ethyl and methyl acrylate were found to undergo thermal decarbonylations at lower temperatures than those copolymers of styrene, methylmethacrylate, and α-methylstyrene. This difference was attributed to a difference in glass transition temperatures. The lower T_g of the acrylate polymers lowered the reaction temperature because of the increased polymer chain mobility at temperatures above the T_g.

Studies of copolymers of styrene containing bound $[W(CO)_5(4\text{-vp})]$ units, suggested that a dissociative mechanism involving the formation of free pentacarbonyl fragments was taking place on heating these polymers. These highly reactive coordinatively unsaturated species could be stabilised by olefin interactions with the polymer backbone. The mechanism proposed suggested that reaction of these fragments with bound pentacarbonyl units produces a *cis*-tetracarbonyl centre and metal hexacarbonyl. The tetracarbonyl centre would then coordinate to the pyridine site on the polymer formed by the cleavage of $(CO)_5W\text{-}N$ bond producing a metal tetracarbonyl species bound through two pyridine coordination sites on the polymer backbone. Analysis of the volatiles of the reaction supported this process. However, results from atomic absorption spectroscopy (AAS) and thermogravimetric analysis (TGA) experiments showed that most of the metal remains after decarbonylation has occurred. It is thought then that the above mechanism is not the only one (see later). From experiments with polymers of different metal loadings, the proximity of two metal pentacarbonyl moieties was found to be important for the outcome of the reaction. In the presence of free pendant sites on the polymer backbone, the *fac*-tricarbonyl is formed. The *fac*-tricarbonyl is also produced on heating terpolymers of

$[W(CO)_4$(4-vinyl-4'-methyl- 2,2'-bipyridyl)] incorporating free pendant sites, suggesting that CO dissociation is an important thermal route for polymer anchored bipyridyl carbonyl complexes. No evidence of metal dicarbonyl or monocarbonyl was found indicating that decarbonylation occurs rapidly past the tricarbonyl stage.

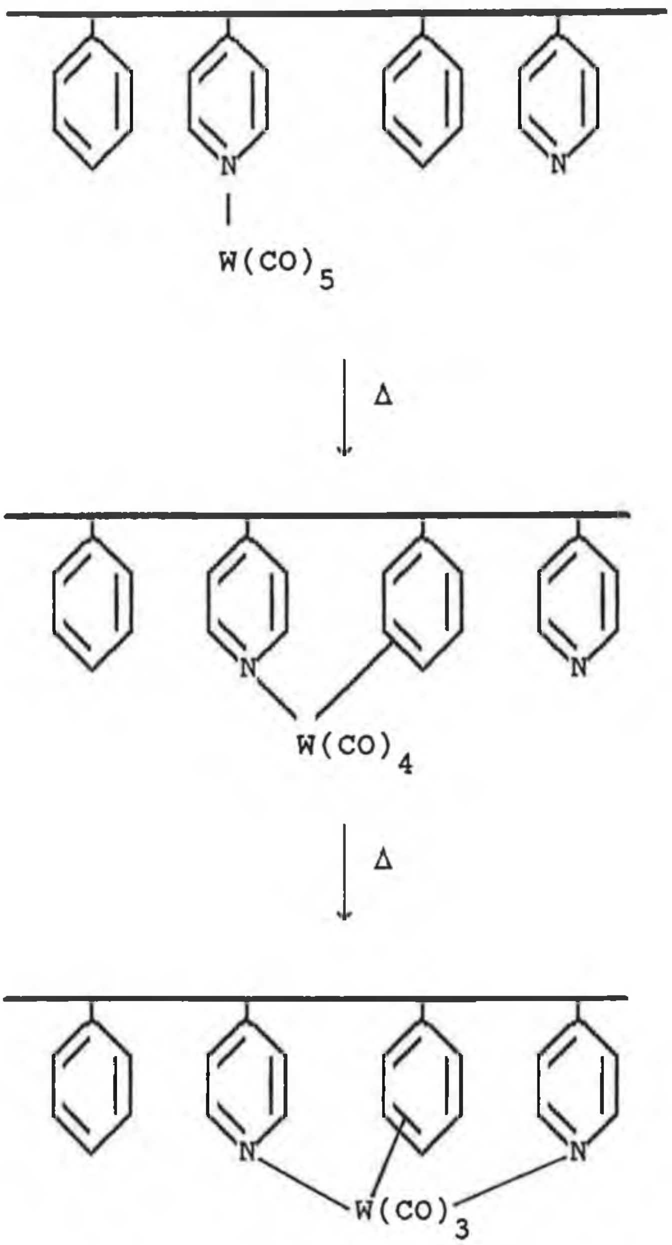
Thermogravimetric and atomic absorption spectroscopy experiments do not support the above mechanism. Following cleavage of the W —— N bond and the production of the metal hexacarbonyl, one would expect a much greater metal loss following thermal decarbonylation of the metal centres, because of sublimation of the metal hexacarbonyl. Data from TGA and AAS experiments indicated that almost all the metal remained within the polymer matrix following decarbonylation. Although gaseous metal hexacarbonyl was detected as a product of the decarbonylation, the extinction coefficient of gaseous hexacarbonyl in the infrared is probably very large, and as a result the metal hexacarbonyl may only be a very minor product. An alternative mechanism is thus proposed. The thermal reaction of a copolymer of styrene and $[W(CO)_5$(4-vp)] may involve CO dissociation to yield a metal tetracarbonyl centre stabilised by alkene interactions with the polymer backbone (Scheme 3.4). Such an interaction would not be expected to be stable in solution, but in the solid polymer matrix the metal centre is surrounded by potential alkenic ligands and so such an interaction may be favourable. Thermal dissociation of a CO ligand forms a metal



Scheme 3.4

tetracarbonyl centre, which could then coordinate an alkene group on the polystyrene backbone to produce a $[W(CO)_4(py)(\eta^2\text{-alkene})]$ species. Further heating results in decarbonylation of the metal centre as the tricarbonyl involving coordination to two alkene groups may not be thermally stable. A number of alkene complexes of the general formula $[M(CO)_{6-n}(L)_n]$ ($L = \eta^2$-alkene) have been reported[99]. These have been prepared by either heating together $M(CO)_6$ and the appropriate alkene or performing the reaction under UV irradiation.

In the presence of excess pyridine binding sites on the polymer backbone, the fac-$[W(CO)_3(py)_2(\eta^2$-alkene)] species could be formed (Scheme 3.5). The preparation of the complexes *cis*-$[W(CO)_4(L)(\eta^2$-alkene)] and *fac*-$[W(CO)_3(L)_2(\eta^2$-alkene)] have been previously described[99,100]. There are relatively few chromium η^2-alkenic complexes known[99,101], and in general the stability of the complexes is in the order W > Mo >> Cr[99]. This greater instability of the alkenic complexes of chromium would explain why no disubstituted tetracarbonyl species were observed on heating copolymers of $[Cr(CO)_5(4\text{-vp})]$. In the case of copolymers of methyl or ethyl acrylate and methylmethacrylate, oxygen sites on the polymer backbone could stabilise the tetracarbonyl centre. There is no firm experimental evidence for this mechanism, it is purely speculative. It is the most plausible explanation as such a mechanism would result in a large percentage of the metal remaining within the polymer matrix following thermal decarbonylation of the metal centres.



Scheme 3.5

Chain mobility is important in the thermal chemistry of these materials. Acrylate polymers were found to undergo decarbonylation at 70°C or lower, while those of higher T_g were thought to begin reaction at a threshold temperature around

100°C. Complete decarbonylation was achieved at around 160°C. Complete decarbonylation would not take place at around 100°C, however, in contrast to polymers of ethyl acrylate which could be fully decarbonylated at 70°C. At the glass transition, rotation about single bonds is no longer restricted and the onset of large-scale motion of chain molecular segments begins and so the polymer becomes more fluid. Above the T_g, the chain segments can undergo cooperative rotational, transitional, and diffusional motion and as the temperature is raised sufficiently (to, say T_g +100°C) the material behaves like a liquid, having of course very high viscosity. The average mobility of the chain segments increases dramatically and as a result, the lifetime of reactive species formed thermally will be decreased. Below the T_g, rotation about the single bonds of the polymer chain is restricted. In the case of ethyl acrylate copolymers, at 70°C the polymer is well above it's T_g and so the metal carbonyl complexes would have sufficient mobility to allow tetracarbonyl formation, and would be expected to have much greater mobility than the metal carbonyl complexes in polymers having higher T_g's. In many studies of polymer-bound organometallic catalysts, polymers of high crosslink densities have been constructed to decrease mobility to increase the lifetime of reactive species by preventing self-aggregation affording high concentrations of unsaturated complexes[2,3,10,74]. However, the formation of uniform metal dispersions at such mild conditions seems an attractive prospect.

These experiments have demonstrated that it is possible to produce metallic species in polymers by binding the metal carbonyl complex and subjecting cast films of these polymers to mild heating conditions. XPS confirmed the presence of WO_3 on the surface of a copolymer of styrene and $[W(CO)_5(4\text{-vp})]$ which had been thermally decarbonylated. Group 6 metal oxides are employed as catalysts for a variety of reactions[6], WO_3 being a well known catalyst for oxygen evolution and to some extent for hydrogen evolution[98]. Using this technique it is likely that elemental metal can be produced by excluding oxygen or by reducing the metal oxides *in situ* with H_2 to generate highly reactive metallic species. A wide variety of metal dispersions, or even mixed metal systems, could be produced by thermal decarbonylation of metal carbonyl compounds anchored to organic supports.

These experiments indicate the variety of chemistry exhibited by such materials and how the nature of the polymer can influence the direction of the thermal reactions. The chemical and physical properties of the polymer support are important in determining the thermal reaction routes available to these systems. By heating cast films of these polymers it is possible to produce high concentrations of metal dispersions which may have useful catalytic activity.

CHAPTER 4

PRELIMINARY PHOTOCHEMICAL STUDIES OF POLYMER-BOUND GROUP 6 METAL CARBONYLS WHEN CAST AS FILMS

4.1 Preliminary Photochemical Studies of Polymer-Bound Group 6 Metal Carbonyls when Cast as Films

Studies have demonstrated that solvent-cast polymer film matrices may be used to study organometallic photochemistry at a variety of temperatures and have some advantages over hydrocarbon glasses[85] and paraffin wax[102] matrices. The main attraction of such a polymer matrix is that it enables the isolation and study of unstable species at very low temperatures and allows the subsequent thermal reactions of such species to be monitored over a wide temperature range. While reports exist of the photolysis of metal hexacarbonyls and metal carbonyl compounds introduced into polymer films, we report the photolysis at low temperatures of solvent-cast organic polymers having metal carbonyl complexes bound to them.

The photochemistry of group 6 metal carbonyl complexes when cast as films at low temperatures has been investigated. Infrared spectroscopic evidence for the formation of a metal pentacarbonyl fragment formed on the photolysis of copolymers of styrene and [$W(CO)_5$(4-vp)] at 120 K is presented. The influence of the polymer backbone on the observed photoreactions is discussed. Photolysis of polymers of 2-vinylpyridine results in photodecarbonylation.

A brief introduction to the photochemistry of group 6 metal carbonyls and matrix isolation techniques using polymer films is given. Some aspects of group 6 metal carbonyl photochemistry have been previously discussed in section 2.

4.1.1 The Photochemistry of Metal Carbonyl Compounds.

In general, primary photoinduced reaction of metal carbonyls involves the monodecarbonylation process[17,24,25] :

$$M(CO)_x \xrightarrow{h\nu} M(CO)_{x-1} + CO \qquad (1)$$

The importance of these processes lie in the high quantum efficiency and also in the nature of the decarbonylated complex. The high quantum efficiency can be explained in simple terms by examining the nature of the bonding between the metal and the carbon monoxide ligand. From a simplified molecular orbital diagram the highest occupied orbital set are principally the metal based t_{2g} orbital sub-set, while the lowest unoccupied orbitals are strongly anti-bonding with respect to the σ-interaction of the carbonyls. The photoinduced promotion of an electron from the t_{2g} orbital sub-set to the σ^*-orbital removes electron density from those orbitals contributing to the backbonding interaction and populates an orbital which is strongly anti-bonding with respect to the carbonyl σ-interaction. The result of this is the labilisation of the metal carbonyl interaction.

Extensive studies of group 6 hexacarbonyls support very efficient generation of the coordinatively unsaturated intermediate $[M(CO)_5]$.

$$M(CO)_6 \xrightarrow{h\nu} M(CO)_5 + CO \qquad (2)$$

$$M(CO)_5 + L \longrightarrow M(CO)_5L \qquad (3)$$

It is the exceptional reactivity of the sixteen electron species which has been the subject of many investigations, and they have been shown to interact with many compounds considered inert[85,86]. Vibrational spectra of the $M(CO)_5$ species in low temperature matrices have confirmed that it's structure is square pyramidal[85].

The synthetic utility of the above sequence has had considerable impact on systematic studies of the $M(CO)_n(L)_{6-n}$ complexes. Derivatives of $M(CO)_6$ can be prepared by irradiation in the presence of almost any ligand. Photolysis of $M(CO)_5L$ could result in the loss of another CO molecule or loss of L. Loss of CO leads potentially to two isomers of $[M(CO)_4(L_2)]$, and loss of L leads simply to ligand exchange in the presence of added L.

$$M(CO)_5L \longrightarrow M(CO)_4L + CO \qquad (4)$$

$$M(CO)_5L \longrightarrow M(CO)_5 + L \qquad (5)$$

The relative efficiencies of processes (4) and (5) were found to be very sensitive to the nature of L. The relative importance of (4) was found to increase with increasing strength of the M — L bond. Generally when L resembles CO in it's bonding properties, sequential substitution of CO by L is possible until every CO has been replaced, e.g., $Mo(CO)_6$ can be converted to $Mo(P(OCH_3)_3)_6$[103]. The reaction quantum yield of (4) or (5) was also found to be sensitive to the wavelength of the exciting light. Higher energy irradiation yields more efficient loss of CO. The opposite wavelength dependency for the two processes (4) and (5) is rationalised by invoking two reactive LF excited states[17].

In the photochemistry of compounds of $M(CO)_5L$ (where L = pyridine or a substituted pyridine) the direction and efficiency of the photochemical processes depends on the electronic nature of any substituent on the pyridine ring system[69]. For substituents which do not affect the energy of the π^*-orbital on the pyridine ligand, the lowest energy transition is thought to be principally a metal centered LF transition. Population of the LF state tends to result in the efficient photoexpulsion of the unique ligand. In the case of substituents which lower the π^*-orbital energy, the lowest energy transition assumes some MLCT character. In general population of MLCT states in organometallic compounds results in photochemical reactions of low quantum efficiency. $W(CO)_5$(pyridine) shows wavelength dependent photochemistry in solution. At 366 nm, $W(CO)_5$ is generated, suggesting a dissociative mechanism for loss of L. At 254 nm, free CO is detectable. The results with the pyridine complexes, however, are somewhat ambiguous, owing to the established fact that such complexes exhibit M ⟶ py CT[69] in the wavelength region where the CO lability is observed[69b]. Loss of CO from $M(CO)_4L$ (L = 2,2'-bipyridine and related ligands) does occur upon photoexcitation into upper excited LF states[75]. The quantum efficiencies are small and wavelength-dependent, and the MLCT state is not reactive.

Interest in the photoactivation of transition metal carbonyls stems in part from their potential use as photocatalysts[17]. Wrighton and others, for example, have demonstrated the catalytic activity of products derived from the photolyses of $M(CO)_6$ (M = Cr, Mo, or W) complexes. Although the large majority of work has focused on photocatalytic behaviour in homogeneous solution, recent studies have begun to explore the photoactivation of metal carbonyls in polymeric matrices[102,106-111], and more recently on surfaced-confined metal carbonyls on porous glass[112], as an alternative route to hybrid catalysis. In this work, we follow the general thrust for the development of more efficient hybrid-phase catalysts. We were interested in the photochemical reactions of the well characterised $[W(CO)_5(pyridine)]$ and *cis*-$[W(CO)_4(bipy)]$ systems when bound to polymeric supports, and in particular the photogeneration of coordinatively unsaturated species which may be used as potential photocatalysts.

4.1.2 Matrix Isolation in Polymer Matrices.

The detection and characterisation of highly reactive metal carbonyl fragments have been the subject of many investigations in organometallic chemistry. Identification of the intermediates in a particular reaction, their structures, and how fast they react is of much interest. Understanding these processes can lead to a better knowledge of the mechanisms of organometallic reactions, and to the development of more efficient organometallic catalysts.

There have been major technical advances in the photochemical study of organometallic reaction intermediates. Laser flash photolysis studies are used widely for the detection of intermediates by UV/vis absorption on a timescale comparable to the fastest chemical processes in solution. There are limitations of UV/vis detection however, due to the general broadness and lack of resolvable fine structure in the electronic absorptions of most organometallic species. Thus, UV/vis spectra rarely provide much structural information about transition metal fragments. Such information can be provided by vibrational spectroscopy. Time-resolved infrared spectroscopy allows the IR spectra of short-lived intermediates in solution to be recorded on a microsecond timescale. Infrared spectra are particularly important in characterising organometallic intermediates as they can often provide quite detailed structural information. There have been some major advances in fast infrared spectroscopy. It is now possible to detect metal carbonyl intermediates at room temperature in both solution and gas phase reactions. The use of low temperature solutions to extend the lifetimes of some reaction intermediates produced in solution, has allowed these reactive species to be studied. The intermediate can be generated photochemically and trapped in a low-temperature solid matrix which permits examination of both vibrational and electronic spectra.

The technique of matrix isolation involves the isolation of a stable metal carbonyl species in a large excess of an inert solid, the matrix. Photolysis then generates the unstable fragments. The most common matrix materials are solid gases (e.g., noble gases or CH_4 at 10-30 K) or frozen hydrocarbons, or more recently polymer films. The great strength of matrix isolation is the wide range of spectroscopic techniques which can be brought to bear on a particular isolated metal fragment.

Infrared characterisation of the $M(CO)_5$ intermediate was first gained by Sheline and coworkers[86] who obtained infrared spectra after photolysis of $M(CO)_6$ at 77 K in methylcyclohexane glasses. The spectra supported assignment of the primary photoproduct as a C_{4v} $M(CO)_5$. In a later work Turner[85] carried out photolysis of group 6 hexacarbonyls in low-temperature matrices. Photolysis of $M(CO)_6$ in argon at 20 K yields $M(CO)_5$, having C_{4v} symmetry. Both infrared and UV/vis spectral changes were consistent with this assignment. The photogenerated $M(CO)_5$ then thermally reacts with photoreleased or added CO. For numerous UV/vis studies of photoproduced $M(CO)_5$ in many matrices, it became clear that the visible absorption of the pentacarbonyl is extremely sensitive to the matrix (SF_6 (460 nm), Ar (437 nm), Xe (417 nm), CH_4 (413 nm)). As a result, it became clear that $M(CO)_5$ interacts with the matrix, the matrix occupying the sixth coordination site.

The photochemistry of group 6 metal carbonyls in polymer films was first studied by Massey and Orgel[104]. They found that irradiating a methylmethacrylate polymer containing a small amount of metal hexacarbonyl at room temperature produced a deep yellow colour. They proposed that the $M(CO)_5$ fragment had been formed. The fragment was found to be stable at liquid nitrogen temperatures. On leaving the polymer in the dark the parent hexacarbonyl reformed. It was almost ten years later when McIntyre reported that the thermal back reaction upon photolysis of $Cr(CO)_6$ in a polystyrene film occurred at a much slower rate than in cyclohexane solution[105]. This he attributed to the greatly decreased mobility of CO in cyclohexane relative to polystyrene. Since McIntyre's experiment, the use of polymer matrices for studying metal carbonyl photochemistry had not been reported in ernest until Rest and coworkers produced a series of publications on the generation of metal carbonyl intermediates in polymer films over a wide range of temperatures.

In one such report, Hooker and Rest[102] studied the photochemistry of group 6 hexacarbonyls in PVC films. Room temperature UV irradiation ($\lambda < 350$ nm) of a film cast from THF, afforded bands at 2074, 1929 and 1887 cm^{-1} (M = W) with a reduction of the parent bands. The film, which had turned yellow, also exhibited a new absorption at 420 nm. A slow reversal of the reaction occurred on leaving the polymer in the dark for several days. Irradiation of $W(CO)_6$ under the same conditions in a PVC film cast from 1,2-dichloroethane solution also produced three new IR bands but at higher wavenumbers (2080, 1932 and 1887 cm^{-1}). In contrast, thermal reversal of the reaction occurred only after a few minutes. Rest assigned the complex formed in polymer films in which THF is present to $W(CO)_5(THF)$. UV irradiation of $M(CO)_6$ (M = Cr or Mo) in these films resulted in the formation of the species $M(CO)_5(THF)$. In photolysis of $W(CO)_6$ in films at 12 K new IR bands appeared at 2084, 1946 and 1918 (sh) cm^{-1}, together with a band for free CO at 2135 cm^{-1} with an accompanying decrease in the parent bands. The photoreaction reversed at 12 K on irradiation with visible light. On slow warming the product bands decreased with regeneration of the hexacarbonyl bands. The product bands were assigned to the $W(CO)_5$ fragment and was thought to be stabilised by interactions with the polymer matrix.

In another report, Rest *et al.* investigated the photochemical reactions of $CpMo(CO)_3(CH_3)$ ($Cp = \eta^5\text{-}C_5H_5$) in PVC films in the range 10-293 K[106]. On irradiation at 12 K, they observed changes in the carbonyl stretching frequency region of the IR consistent with the formation of $CpMo(CO)_2(CH_3)$ and

$CpMo(CO)_3^{\bullet}$. Further irradiation produced bands they assigned to $CpMo(CO)_3Cl$, formed from reaction of photochemically produced $CpMo(CO)_3^{\bullet}$ radicals with the PVC matrix. In similar studies in PVC at 12 K, photolysis of $CpM(CO)_3(C_2H_5)$ results in loss of CO[107]. The photoproduct rearranges thermally to form trans-$CpM(CO)_2(C_2H_4)H$.

De Paoli and coworkers[108] reported studies of the photochemical reactions of pentacarbonyliron with olefins in a PTFE room temperature matrix. The reactions of the dienes butadiene and isoprene in the matrix produced not only dienetricarbonyliron but also bis(diene)monocarbonyliron compounds. With ethylene and acetylene they observed the formation of ethylenetetracarbonyliron and acetylenetetracarbonyliron. Hooker and Rest[109] investigated the photolysis of acetyldicarbonyl(η^5-cyclopentadienyl)iron complexes in PVC matrices at 12-200 K. The photoinduced decarbonylation of $CpFe(CO)_2(COCH_3)$ was found to be thermally reversible. The decarbonylated species could not be generated in conventional frozen matrices even under vigorous irradiation conditions. They suggested that this failure was due to a rapid back reaction of the photogenerated fragments in the closely confined gas matrix environment. In contrast, the polymer film matrices are thought to provide a more cavernous medium[110] in which the "cage effect" is a less serious problem.

A number of studies have demonstrated the potential of polymer films for investigating the photoreactions of organometallic compounds. Reactive intermediates can be trapped and studied at cryogenic temperatures in a similar and complementary fashion to studies in in hydrocarbon glasses and frozen gas matrices. Using polymer films, stabilities of photoproduced intermediates can be studied over a far greater temperature range, and De Paoli[108] suggested that a polymer film at 293 K was a possible replacement for elaborate gas matrix isolation studies requiring expensive cryogenic equipment. Indeed, using polymer film matrices it is possible to trap at low-temperatures reactive species which cannot be formed by similar *in situ* photolysis of molecules in conventional frozen gas matrices[109]. In the case of low-temperature matrices the sorts of reactions that may occur photochemically are very limited by the restrictions of the so called "cage effect"[110]. It is generally difficult to produce a species by an *in situ* photolysis in low-temperature matrices by photoejection of a ligand because the molecule is too large to squeeze readily through lattice interstices and away from the newly formed unstable species. Thus, in the low-temperature matrices, the two fragments held together in the matrix cage recombine to reform the parent molecule. In room temperature polymer matrices the molecules held in the amorphous sites apparently have a much higher mobility, in such a way that a carbon monoxide ligand can diffuse away and the other ligand approaches the coordinatively unsaturated species formed.

In this research it was hoped that any reactive photoproducts could be "frozen" in the polymer matrix in a manner similar to that developed by Hooker and Rest[102]. In this instance, however, the parent metal carbonyl complexes are bound to the polymer matrix. This method provides the advantage of better metal carbonyl distribution in the polymer matrix, as soaking polymers very often results in high local concentrations of species and the presence of aggregates in these films. However, the number and broadness of the bands make the attainment of spectral information more difficult than those studies of metal hexacarbonyls whose spectra are less detailed. In this study, it was of interest not only to investigate the photochemistry of metal carbonyls bound to polymer supports, but importantly to examine the effect of the polymer backbone on the photochemical reaction routes.

4.2 Low-Temperature Photolysis of Polymer-Bound Group 6 Metal Carbonyls.

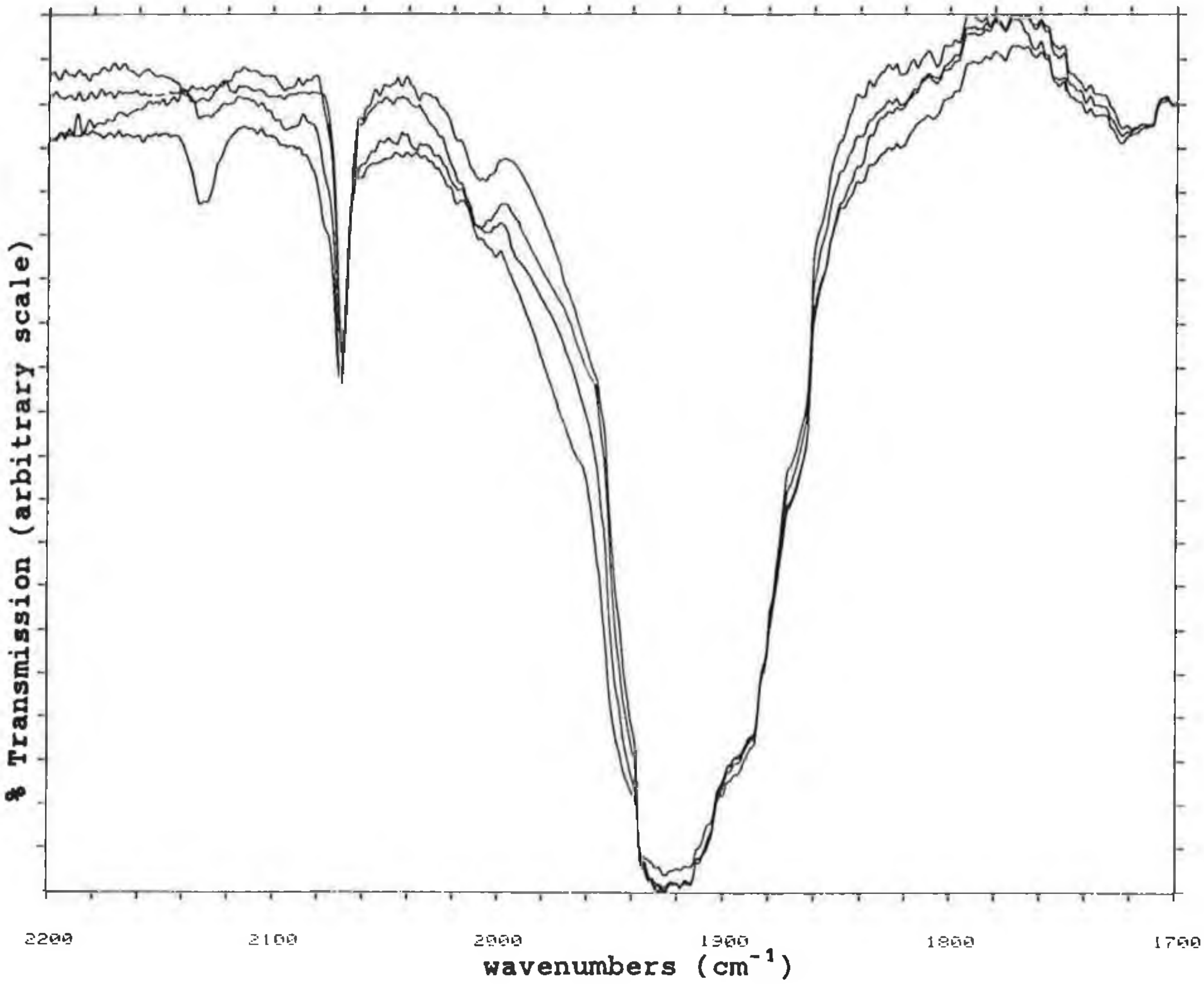
In these experiments the polymer films were cast as films on a sapphire support. The films were pumped under vacuum to remove any traces of solvent, and fitted in a variable temperature infrared cell and cooled to 120 K. The samples were then exposed to broad-band radiation from a low pressure mercury lamp, filtered through the sodium chloride windows of the variable temperature cell. Any spectral changes were monitored in the carbonyl stretching frequency region of the infrared (2200-1700 cm^{-1}). All photolysis experiments were carried out *in vacuo*.

4.2.1 *A Copolymer of Styrene and $W(CO)_5$(vinylpyridine).*

Irradiation of a copolymer of styrene and $[W(CO)_5(4\text{-vp})]$ at 120 K resulted in the appearance of a new IR band at 2077 cm^{-1} (shouldering the high frequency characteristic pentacarbonyl band) together with a band for free CO at 2139 cm^{-1}, at the expense of the parent bands (see **Figure 4.2.1**). The broadness of the remaining carbonyl bands precluded any significant spectral changes being observed below 2000 cm^{-1}. Thermal reversal of the reaction occurred on warming the film to 200 K. The primary photoproduct was assigned to that of a pentacarbonyl species which is no longer attached to the polymer backbone via the pendant nitrogen atom of a pyridine moiety. This is not surprising since the primary photoreaction of $[W(CO)_5(\text{pyridine})]$ is loss of the pyridine ligand[17]. Rest reported that the UV photolysis of $[W(CO)_5(\text{pyridine})]$ isolated at high dilution in methane matrices at 10 K, produces new IR absorptions associated with $W(CO)_5$ and free ligand[111]. However, on the basis of matrix isolation[85,102] and flash photolysis experiments[79-81], 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 photoproduced pentacarbonyl again reacts with the nitrogen sites on the polymer backbone. This reversal suggests that photoejected CO molecules and $W(CO)_5$ fragments do not diffuse away from the photolysis sites at very low temperatures. Polymer matrices are thought to provide a more cavernous medium so that problems of recombination on photolysis found in other low-temperature matrices do not occur[110]. The photoejected $W(CO)_5$ can "move" readily through the spaces in the polymer matrix away from the pendant sites on the polymer.

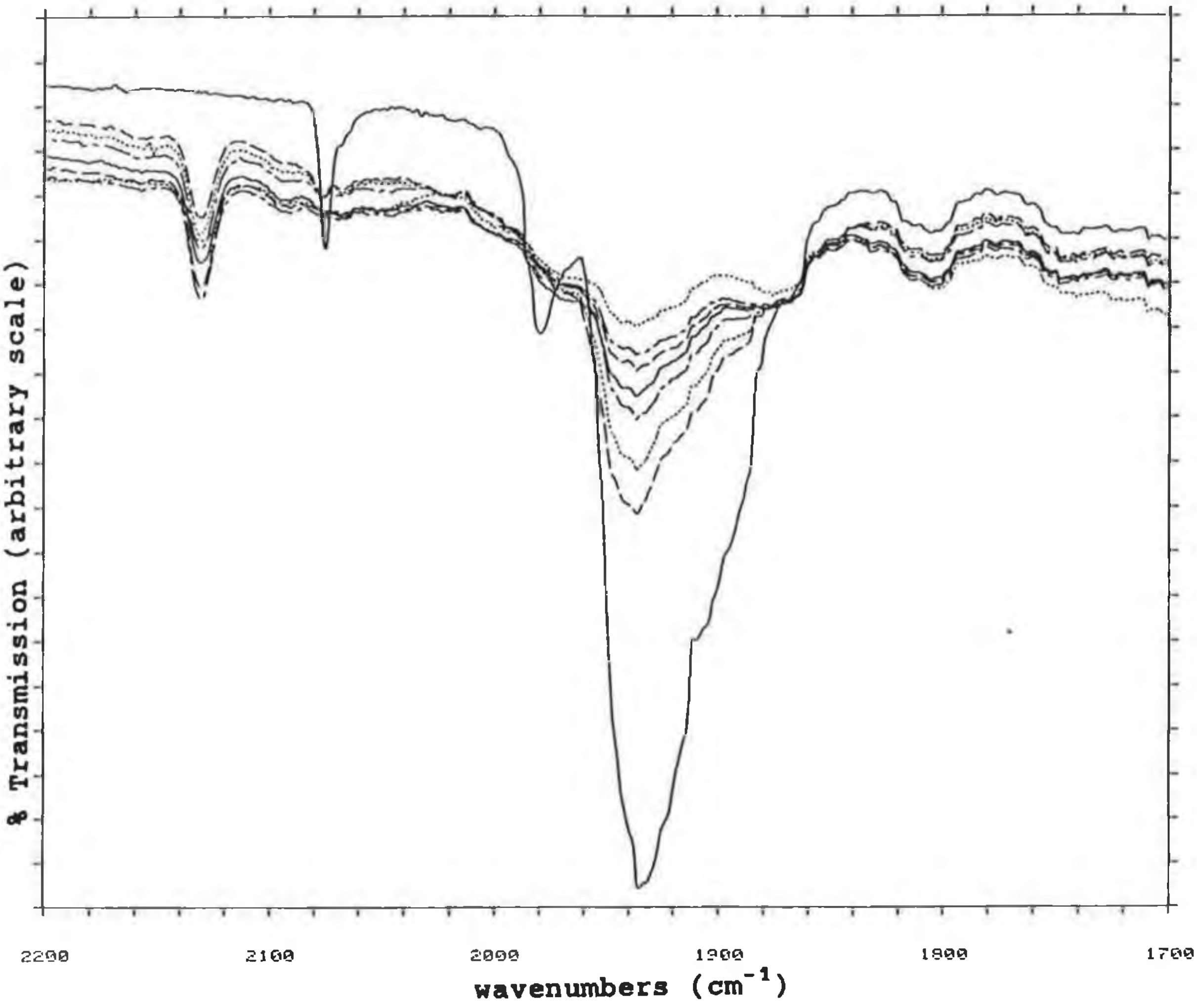
Photolysis of a film of a copolymer of styrene and $[W(CO)_5(2\text{-vp})]$ at 120 K, resulted in the decrease of the stretching frequencies of the characteristic of the pentacarbonyl species to give a photodecarbonylated polymer (see Figure 4.2.2). Evidence for the formation of free carbon monoxide was found from the production of a band at 2129 cm^{-1}. This reaction was not reversible on warming to room temperature. The reason for the differences in the photochemical behaviour of polymers of 2- and 4- vinylpyridine is uncertain. They both initially contain metal pentacarbonyl fragments bound to the polymer through a metal to nitrogen bond in identical environments.

Fig. 4.2.1 Changes observed in the carbonyl stretching region of the infrared on UV photolysis of a film of a copolymer of styrene and [W(CO)$_5$(4-vp)] at 120 K.



UV photolysis at 120 K results in the production a thermally unstable metal pentacarbonyl fragment (2077 cm^{-1}sh) with some metal centers suffering photodecarbonylation (free CO at 2139 cm^{-1}). Warming the sample gradually to room temperature results in the disappearance of the new bands with regeneration of the parent pentacarbonyl.

Fig. 4.2.2 UV photolysis of a cast film of a polymer of styrene and $[W(CO)_5(2\text{-vp})]$ at 120 K monitored by observing the changes in the infrared spectrum (2200-1770 cm^{-1}).



UV photolysis results in complete photodecarbonylation of the metal centers after one hour. The reaction is not reversible on warming to room temperature.

4.2.2 Photolysis of Metal Carbonyl Containing Acrylate Polymers.

Irradiating a copolymer of ethyl acrylate and [W(CO)$_5$(4-vp)] at low temperatures lead to the appearance of grow-in bands at 2010, 1866 (sh), and 1831 cm^{-1} (Figure 4.2.3). Some free CO was detected at 2131 cm^{-1}. The broadness of the parent pentacarbonyl bands prevented the attainment of further spectral information. On warming the sample to room temperature, the bands decreased in intensity together with an accompanying increase in the parent pentacarbonyl frequencies. Similar spectral changes were recorded on photolysis of a copolymer of methyl acrylate and [W(CO)$_5$(4-vp)].

It is proposed that the primary photoreaction is loss of a CO ligand to form the tetracarbonyl species, which then coordinates to an oxygen site on the acrylate backbone. Bonding through oxygen is less effective that through nitrogen, and coordination *via* two nitrogen donors would be expected to produce a more stable tetracarbonyl species. To investigate this further, a polymer of [W(CO)$_5$(4-vp)] and 4-vinylpyridine was photolysed at low-temperature. Figure 4.2.4 shows the changes observed in the carbonyl stretching region on photolysis of a film of this polymer. Bands at 2003, 1881(sh) and 1825 cm^{-1} and a band due to free CO (2132 cm^{-1}) are formed with a reduction in the intensity of the parent bands. On heating to 20°C, the band due to CO gradually decreased in intensity as the CO diffused out of the polymer matrix. However, no change in intensity of the photoproduced bands was observed. These bands are close to those reported for *cis*-$[W(CO)_4(py)_2]$[70], and so it is proposed that the disubstituted tetracarbonyl species is formed following photoejection of a CO ligand. The tetracarbonyl formed through coordination through two pyridine residues is thermally stable suggesting that in the case of the acrylate polymers, the photoproduced tetracarbonyl is stabilised by interactions with the oxygen sites on the polymer backbone.

Strohmeier[24b], upon irradiation of $[W(CO)_5(pyridine)]$ in the presence of excess pyridine, reported the formation of $[W(CO)_4(py)_2]$ in solution. He postulated that $[M(CO)_5(py)]$ photodissociates into $[M(CO)_4(py)]$ (following photoexpulsion of an equatorial CO ligand) and into $[M(CO)_5]$ (as a result of photocleavage of the metal to pyridine bond) simultaneously with an overall quantum yield of unity. While the first intermediate $[M(CO)_4(py)]$ yields the product $[M(CO)_4(py)_2]$, the second intermediate $[M(CO)_5]$ should react with additional pyridine to give back the starting complex and so does not contribute to the net reaction. In the case of the 4-vinylpyridine copolymer, the local concentration of uncoordinated pyridine in the vicinity of any photoproduced $[M(CO)_5]$ would be high so that the rate of recombination would be expected to be high also. Further evidence for this was found on irradiating a terpolymer of styrene and $[M(CO)_5(vp)]$ containing 4-vinylpyridine (10/1 mole ratio of styrene/4-vinylpyridine). Irradiation resulted in the appearance of a new band at 2077 cm^{-1} which disappeared on raising the temperature. Bands assignable to *cis*-$[W(CO)_4(py)_2]$[70]

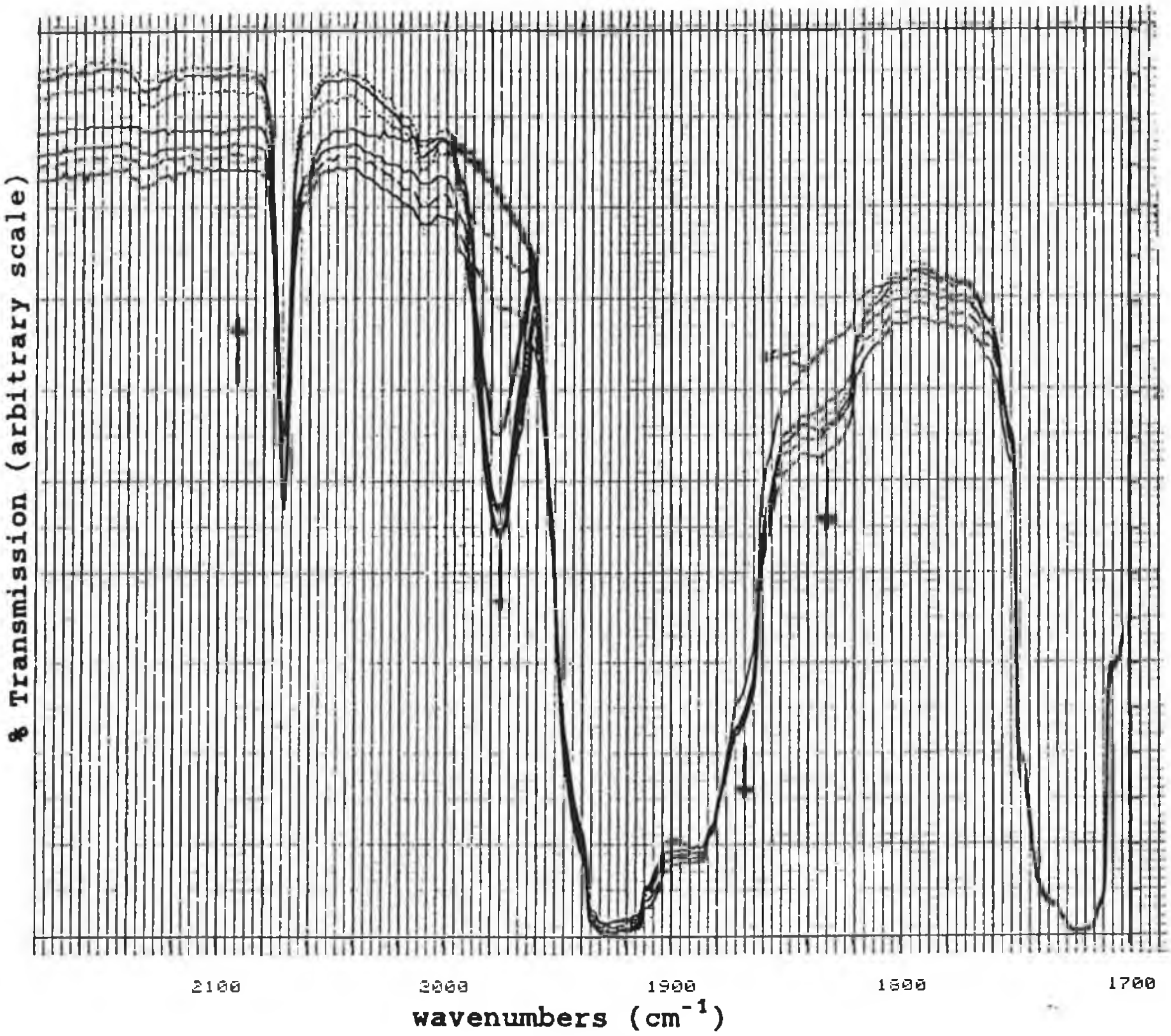
and free CO were also found. Thus, in the absence of a large excess of pyridine sites on the polymer backbone, matrix isolated $[W(CO)_5]$ is observed because the likelihood of encountering a recombination site is decreased. It has been previously reported that the quantum yield for photodissociation of the $[W(CO)_5(4\text{-vp})]$ complex in styrene-4-vinylpyridine-$[W(CO)_5(4\text{-vp})]$ terpolymers in solution is dependent on the nature of the polymer backbone, and in particular on the proportion of uncoordinated vinylpyridine groups on the chain[29]. Lower quantum yields were attributed to recombination of the initially formed $[W(CO)_5]$ with other uncoordinated pyridine groups of the polymer. The same can be stated for polymer films at low-temperatures.

In sharp contrast to those polymers of ethyl or methyl acrylate, irradiation of a copolymer of methylmethacrylate and $[W(CO)_5(4\text{-vp})]$ at low-temperature yielded a totally photodecarbonylated polymer. The difference in photoreactivity is not clear as both contain metal pentacarbonyls bound via a metal-nitrogen bond in polymer backbones of similar chemical composition. It is thought unlikely that the difference because of a difference in chain mobility of the two polymers. Motion of polymer chains probably ceases at low temperatures but the polymer matrix does not become too rigid to prevent the photoejection of the bulky ligand $[W(CO)_5]$.

4.2.3 Photolysis of Polymers Containing Metal Tetracarbonyl.

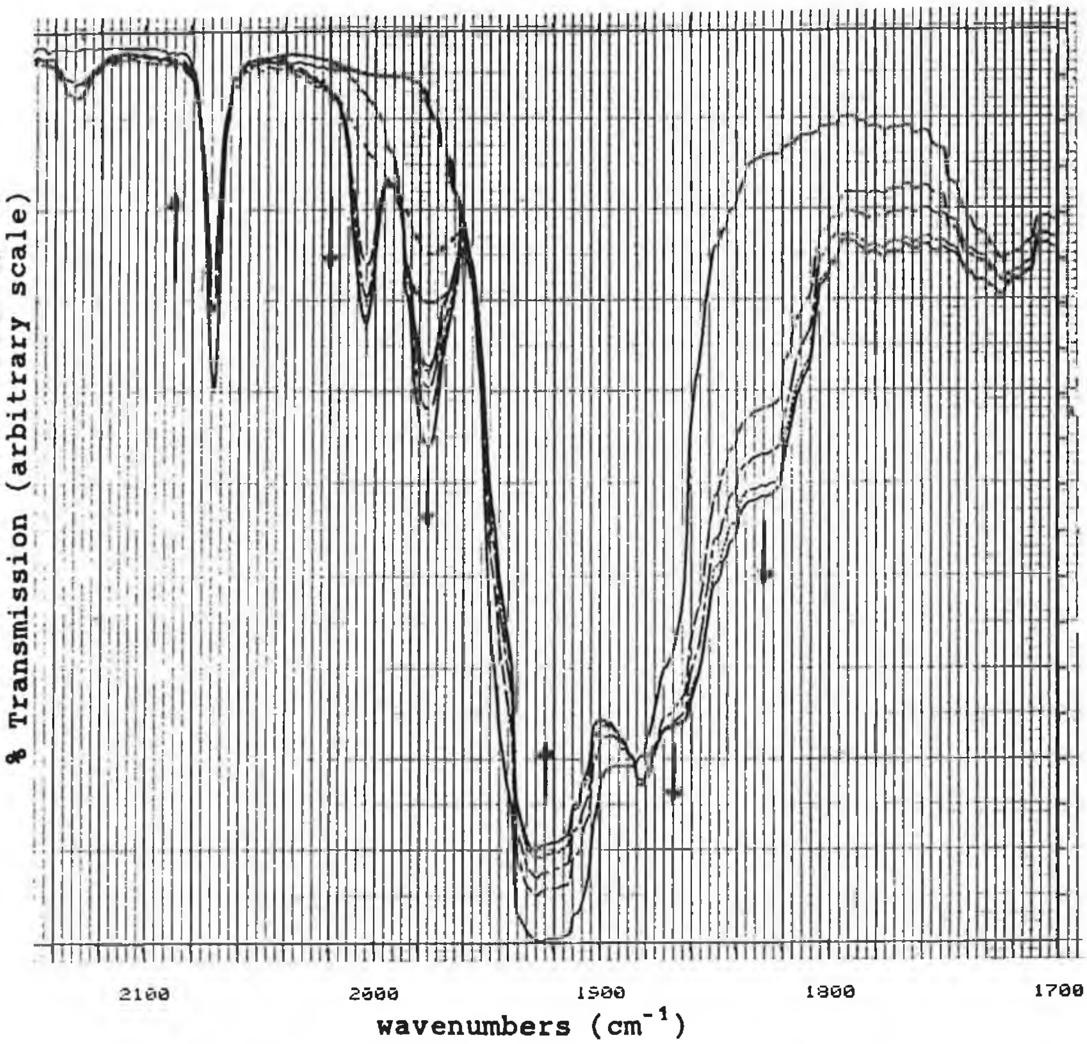
Copolymers of styrene, methylmethacrylate, and ethyl acrylate containing bound $[W(CO)_4(4\text{-vinyl-}4'\text{-methyl-}2,2'\text{-bipy})]$ did not exhibit any photoreactivity. Prolonged UV photolysis at low temperatures afforded no change in the tetracarbonyl bands in the infrared. Unlike complexes of the type $[W(CO)_5(\text{pyridine})]$ where the lowest excited state is a ligand field transition, the lowest energy transition of $[W(CO)_4(\text{bipy})]$ complexes assumes some metal-to-ligand charge transfer character (MLCT), and as previously stated population of MLCT states in organometallic compounds results in photochemical reactions of low quantum efficiency.

Fig. 4.2.3 Infrared spectral changes observed on UV photolysis of a cast film of a copolymer of ethyl acrylate and $[W(CO)_5(4\text{-vp})]$ at 120 K.



UV photolysis at 120 K results in the formation of a thermally unstable tetracarbonyl species thought to be formed through coordination through pyridine and oxygen on the polymer backbone.

Fig. 4.2.4 Changes observed in the infrared (2200-1700 cm^{-1}) on photolysis of a copolymer of 4-vinylpyridine and $[W(CO)_5(4\text{-}vp)]$ at 120 K.



On photolysis, a thermally stable cis-$[W(CO)_4(py)_2]$ tetracarbonyl species is produced.

4.3 Conclusions

The photolysis of styrene and [W(CO)$_5$(4-vp)] polymers generates an active coordinately unsaturated metal carbonyl species at low temperatures, 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. This could represent a simple and efficient means of incorporating metal dispersions in polymeric films by photolytic means. On the basis of reported experiments[53,88-90], it is likely that metal oxides or elemental metal could be generated in these films by photolysis of the bound metal pentacarbonyl. This method could overcome problems associated with conventional methods of preparing colloidal dispersions such as uniformity of dispersion and size of the aggregates. By preparing polymers containing metal carbonyls the distribution/loading of the metal complex can be controlled so that photolytic decomposition may produce dispersions of low diameter and of high uniformity. In this way metal dispersions could be prepared, without the need for elaborate equipment or procedures, at room temperature.

Photolysis of acrylate polymers results in the photogeneration of a thermally unstable tetracarbonyl species which is thought to be stabilised by oxygen interactions at low-temperatures. Those polymers of methylmethacrylate suffer complete photodecarbonylation. Experiments incorporating free uncoordinated pyridine into the polymer backbone indicate that the photochemical reaction routes of films of polymers containing [$W(CO)_5$(4-vp)], depend on the proportion of free pyridine on the polymer chain. In the presence of excess pyridine binding sites, the *cis*-tetracarbonyl species is formed. Low concentrations favour the formation of [$W(CO)_5$]. The photoexpulsion of a CO ligand from [$W(CO)_5$(4-vp)], produces a polymer-bound coordinatively unsaturated site. Suitable substrate molecules could be incorporated into the polymer matrix in a manner similar to that described by De Paoli and coworkers who studied the reactions of pentacarbonyliron with olefins in polymer matrices at room temperature[108]. On photoexpulsion of a CO ligand, a substrate molecule could be bound and so initiate catalysis.

Photolysis of thin films of these polymer-bound metal carbonyls at low-temperatures results in the production of species which could have catalytic potential. Evidence for full photodecarbonylated metal centers was also found suggesting that this technique could be utilised to produce metal deposits in polymer matrices. These experiments have shown that the polymer matrix is of particular importance in determining the available photochemical reaction routes.

CHAPTER 5

EXPERIMENTAL SECTION

5.1 Materials

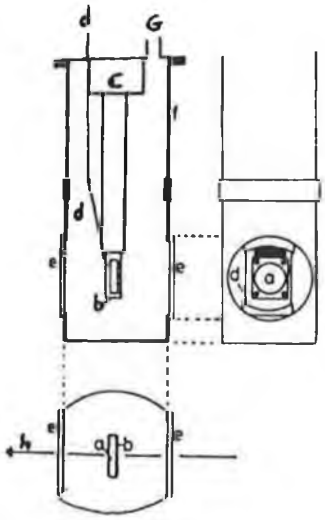
All monomers were washed to remove inhibitors according to the literature procedures[113] and distilled under vacuum before use. They were stored at -20°C under argon until required. Azobisisobutyronitrile (AIBN) (Merck) was recrystallised from anhydrous methanol and stored at 4°C. Metal hexacarbonyls (Riedel-de Haen or Strem) were used as supplied. Tetrahydrofuran and toluene were refluxed over lithium aluminium hydride or calcium hydride, distilled under argon, and stored over sodium wire. Solvents used for UV/vis measurements were analar grade. Nitrogen or argon gases were used as supplied from either Irish Industrial Gases Ltd. or Cryogas Ltd.

5.2 Equipment and Procedures

5.2.1 *Infrared and UV/visible Spectral Studies*

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 ± 3 cm^{-1}. All monomer complexes were recorded as Nujol mulls between sodium chloride plates. Polymer complex spectra were recorded as cast films from chloroform solution on sodium chloride plates. Polymer films were cast on a sapphire support for variable temperature and low-temperature photolysis experiments, the intensity of the carbonyl stretching frequencies could be altered by changing the thickness of the film. A Specac Model 21000 variable temperature solids sample and a variable temperature 10 cm pathlength gas cell, fitted with a Specac Model 20100 automatic control unit were utilised for variable temperature infrared work. A schematic diagram of the variable temperature is shown in **Figure 5.1**. The same cell was used for low-temperature photolysis experiments using liquid nitrogen as the coolant. Sample temperatures are estimated to be accurate to ± 5°C. Ultraviolet/visible spectra were recorded either on a Shimadzu UV240 grating spectrometer (peak positions accurate to ± 0.5 nm) or a Hewlett-Packard 8452A diode-array spectrophotometer (peak positions accurate to ± 2 nm) fitted with a Chemstation data station. Spectra were recorded immediately on dissolution of samples.

Fig. 5.1 Sample holder used for variable temperature and low-temperature photolysis experiments.



(a) sapphire disc
(b) disc support
(c) liquid nitrogen port
(d) thermocouple
(e) outer cell windows (NaCl)
(f) vacuum jacket
(g) to vacuum
(h) path of monitoring IR beam
or photolysis beam.

5.2.3 *Thermal Analysis*

Differential scanning calorimetry experiments were conducted on a Stanton Redcroft DSC-700 instrument. Thermograms were recorded using calcined α-alumina (BDH AnalaR) as the reference material. Sample crucibles were aluminium and typical sample weights were in the range 2-10 mg. Sub-ambient work was conducted using a liquid nitrogen cold finger attachment. All experiments were carried out under a nitrogen at a flow rate of 30 cm^3/min. A Linseis L6512 chart recorder was used to record the output. The performance of the instrument was assessed using standard samples of potassium nitrate and potassium sulphate. Temperatures were found to be accurate to ± 3°C. Glass transition temperatures were taken as the onset temperature of the heat capacity change. Thermogravimetric analysis was performed on a Stanton Redcroft TG-750. A platinum crucible was used. Typical sample weights were in the range 1-5 mg. All analyses were carried out under a nitrogen atmosphere at a flow rate of 20 cm^3/min.

5.2.4 *Gel Permeation Chromatography.*

Gel permeation chromatography (GPC) was carried out using a PL-GEL (10 μm MIXED 300 X 7.5 mm) column, and a PL-GEL (10 μm 100Å 50 X 7.5 mm) pre-column. A 20 μl injection loop was used. The detector was a Waters R401 Differential Refractometer. The method of Universal Calibration[76a] was used to determine the molecular weights of copolymers of styrene and 4-vinylpyridine (20/1 mole ratio of styrene to 4-vinylpyridine) using polystyrene standards (Polymer Laboratories Ltd.). Stabilised tetrahydrofuran (Riedel-de Haen) was used as the mobile phase (flow rate 0.4 cm^3/min), and toluene (BDH Analar) as the internal standard to correct for deviations in flow rate. The mobile phase was degassed by filtering through 0.5 μm Millipore filters under vacuum. Standards and samples were prepared in THF at concentrations of 0.4% w/v. The data from the detector was analysed using GPC software (Polymer Laboratories Ltd.) on a BBC microcomputer. Figure 5.2 shows the calibration curve obtained for the polystyrene standards with which the unknown samples were compared, and **Table 5.1** gives the corresponding experimental data.

Copolymers of varying molecular weights were synthesised by using different percentages of AIBN in the polymerisation mixture. The molecular masses calculated however, are not correct as the samples were compared with polystyrene standards rather than poly(styrene-co-4-vinylpyridine) standards. For relative work, however, this method proves quite satisfactory[76a]. GPC results indicated that molecular weight did change as the concentration of initiator was varied. The component weights of monomers used in the preparation of these copolymers and the calculated molecular weights and distributions are given in Table 5.2. Crosslinked copolymers were prepared using divinylbenzene (Aldrich), but the polymers were insoluble, only swelling in solvents, and so useless for our intended application.

Fig. 5.2 GPC calibration curve for polystyrene standards.

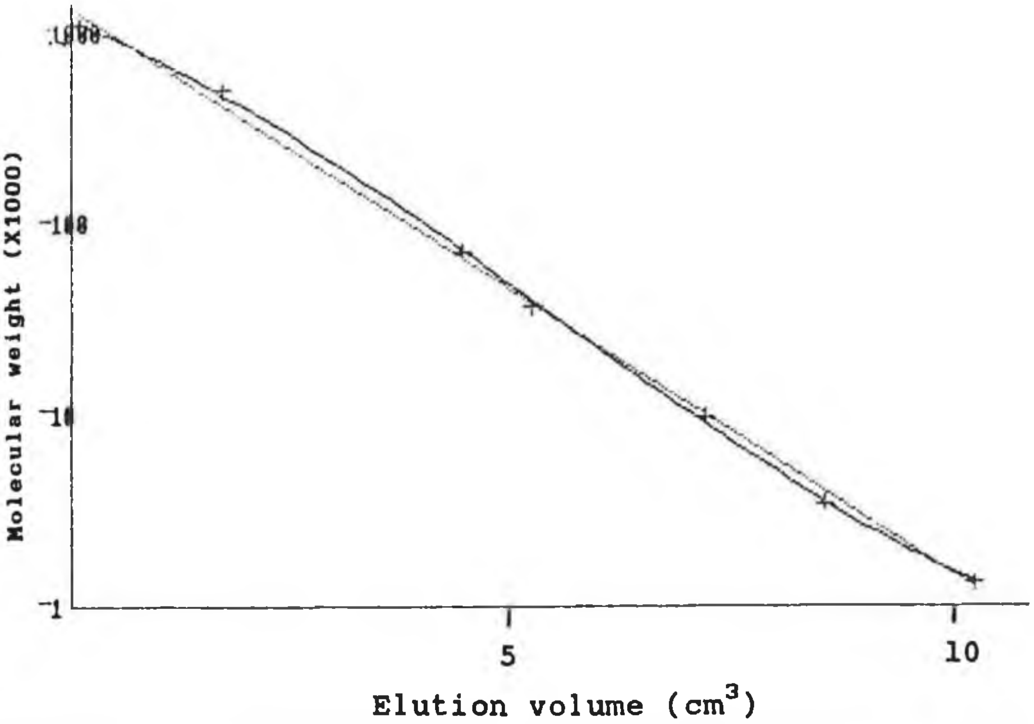


Table 5.1 Experimental data for a polystyrene calibration curve.

Elution volume (cm^3)	Molecular Weight (amu)		
	Standards	Linear Fit	
		Calculated	Ratio
10.09	1250	1145	1.09
9.57	3250	3740	0.87
9.16	9200	9510	0.97
8.56	34500	37266	0.93
8.32	68000	64353	1.06
7.60	470000	331368	1.42
7.00	1020000	1298466	0.79

* Toluene eluted after 13.95 cm^3.

Table 5.2 The weights (g) of the materials used in the syntheses of polymers of varying molecular weight.

% AIBN	Styrene	4-vp	AIBN	T_g^a (°C)	$\overline{M}_w$ (amu)	$\overline{M}_n$ (amu)	$\overline{M}_w/\overline{M}_n$
4.00	3.0000	.1515	.1260	108	10600	5650	1.88
2.00	3.0000	.1515	.0630	113	17200	8180	2.11
1.00	3.0000	.1515	.0320	120	26500	14880	1.78
0.66	3.0000	.1515	.0211	122	38300	19150	2.00
0.50	3.0000	.1515	.0157	115	47400	28200	1.88
0.40	3.0000	.1515	.0126	122	51100	25800	1.98
0.33	3.0000	.1515	.0105	126	67500	30100	2.24
0.25	3.0000	.1515	.0079	122	70900	31400	2.25
0.20	3.0000	.1515	.0064	125	99800	47200	2.11
0.10	5.0000	.2524	.0052	128	162000	70200	2.31
0.05	5.0000	.2524	.0026	132	204000	86700	2.36

T_g = glass transition temperature (^{a} Determined by DSC).

AIBN = azobisisobutyronitrile

4-vp = 4-vinylpyridine

$\overline{M}_w$ = weight average molecular weight

$\overline{M}_n$ = number average molecular weight

5.2.5 Atomic Absorption Spectroscopy (AAS).

An Instrumentation-Laboratories IL-AA/AE 357 instrument was utilised for metal determinations. Chromium, molybdenum and tungsten standards were prepared over the linear range stated in the Instrumentation-Laboratories manual by serial dilution of atomic absorptions standards (Spectrosol BDH). All of the solutions for atomic absorption measurements were prepared in distilled water which had been further purified using the Milli-Q water purification system. The glassware used was soaked in 1.6 M nitric acid and thoroughly rinsed with Milli-Q water prior to use. A fuel rich N_2O-Acetylene flame (cone 2 cm high) and an aspiration rate of 6 cm^3/minute was used. Other instrumental conditions are available in the IL-AA/AE 357 instrument manual. The experimental data and correlations for the standard solutions are given below in Tables 5.3a and 5.3b.

Table 5.3a Atomic Absorption Standards.

Metal	Linear Range (ppm)	Correlation	Intercept	Slope
Cr	0 - 5	0.996	-2.1E-3±4.8E-3	2.4E-2±1.7E-3
Mo	0 - 60	0.999	-1.3E-2±1.2E-2	1.1E-2±2.8E-4
W	0 - 500	0.999	-9.9E-4±2.8E-3	3.4E-4±5.5E-6

Table 5.3b Experimental results for atomic absorption standards.

Cr conc. (ppm)	Absorbance (377.9nm)	Mo conc. (ppm)	Absorbance (313.3nm)	W conc. (ppm)	Absorbance (255.1nm)
0.2	0.004	1.0	0.008	50	0.015
1.0	0.024	5.0	0.047	75	0.023
2.0	0.040	10	0.095	100	0.035
3.0	0.069	20	0.190	150	0.052
4.0	0.096	30	0.318	200	0.067
5.0	0.118	40	0.419	250	0.084
-	-	50	0.549	300	0.100
-	-	60	0.648	350	0.118
-	-	-	-	400	0.143
-	-	-	-	500	0.168

Readings were taken against a Milli-Q water blank (A=0.000).

Polymer samples were digested in 6 cm^3 concentrated sulphuric acid (May and Baker Analar Grade) with gentle heating. Following acid digestion, the samples were cooled and 3 cm^3 of hydrogen peroxide (Riedel-de Haen 70 % v/v) added carefully. After further heating, the clear solutions were cooled to room temperature and diluted to the 100 cm^3 volumetric mark with Milli-Q water. Another set of samples were heated under vacuum at 180 ^{0}C to produced the decarbonylated polymers. Infrared spectroscopy confirmed the absence of carbonyl stretching bands. These were then digested as described above. The absorbance of the polymer samples were read against a digested unmetallated polymer blank. Enough polymer sample was weighed to give an absorbance within the linear range for that metal, based on the theoretical metal content. Table 5.4 shows the results for the determination of the metal content following thermal decarbonylation.

Table 5.4 Determination of metal content of polymers after thermal decarbonylation by AAS.

Polymer Sample	Carbonylated			Decarbonylated			%M
	weight (g)	Abs.	M (ppm)	weight (g)	Abs.	M (ppm)	
P[styrene-$W(CO)_5$(4-vp)]	.2006	.043	127.0	.2013	.037	111.8	88
P[styrene-$Cr(CO)_5$(4-vp)]	.0253	.112	4.8	.0255	.097	4.1	86
P[styrene-$Mo(CO)_5$]	.1021	.347	32.7	.1038	.322	30.4	93
P[styrene-$W(CO)_5$(2-vp)]	.2011	.042	124.4	.2023	.038	112.0	90
P[styrene-$W(CO)_4$(Vbipy)]	.2009	.041	121.8	.2041	.039	116.9	96
P[styrene-$W(CO)_5$(4-vp)] (5/1 mol ratio)	.1002	.049	145.2	.0973	.041	123.4	82
P[4-vp-$W(CO)_5$(4-vp)]	.1021	.022	65.3	.1008	.019	59.4	91
P[MA-$W(CO)_5$(4-vp)]	.1592	.036	106.6	.1612	.032	94.9	89
P[styrene-p-SDPP]-$W(CO)_5$	.1242	.021	63.5	.1204	.020	59.7	94
P[styrene-p-SDPP]-$Cr(CO)_5$	.0125	.043	1.9	.0137	.039	1.7	90
P[styrene-p-SDPP]-$Mo(CO)_5$	.1012	.236	22.6	.0987	.216	20.8	92

Notes on Table 5.4

All copolymers contain 20/1 mole ratio of metal carbonyl to monomer unless otherwise stated.

All weigths of polymers are per 100 cm^3.

Abs = absorbance, M = metal, %M refers to the percentage metal remaining following thermal decarbonylation.

vp = vinylpyridine, MA = methyl acrylate,

p-SDPP = *para*-styryldiphenylphosphine

Vbipy = 4-vinyl-4'-methyl-2,2'-bipyridyl.

5.2.6 *Photolysis Experiments*

Preparative photolyses were performed using an Applied Photophysics 400 W medium pressure mercury vapour lamp. The lamp was housed in a double-walled quartz jacket through which water was circulated to prevent the lamp heating the photolysis solution. An Oriel 100 W short-arc mercury lamp was employed in low temperature photolyses experiments. The light was firstly collimated, passed through an infrared filter containing Milli-Q water, and finally through the sodium chloride windows of the variable temperature cell.

5.2.7 *Flash Photolysis of $W(CO)_6$ Toluene Solutions Containing Pyridine Ligands.*

Samples for flash photolysis experiments were prepared in anhydrous toluene (Aldrich Sureseal). Toluene solutions containing tungsten hexacarbonyl (1.14×10^{-7}M, $\varepsilon = 1.41 \times 10^6$ $mol^{-1}dm^3cm^{-1}$ at 355 nm) and pyridine (Aldrich Gold Label) were degassed by three freeze-pump-thaw cycles, followed by a liquid pumping phase, and then placed under one atmosphere of argon. Polymer samples containing the required concentration of pyridine (based on % N determined by microanalysis) and the desired amount of hexacarbonyl (1.14×10^{-7}M) were prepared in toluene and degassed as above. All polymers were dried under vacuum prior to use. **Table 5.5** gives the weights of monomeric and polymeric pyridine used in the study.

Table 5.5 Weights of samples used for flash photolysis studies.

		Weight (g) / 10 cm^3 Toluene				
		Concentrations (E-2 M)				
Sample	% N[a]	0.5	1.0	2.0	3.0	4.0
Pyridine	-	0.0036	0.0085	0.0172	0.0258	0.0324
Polymer 10/1	1.69	0.0412	0.0828	0.1657	0.2485	0.3314
Polymer 5/1	2.60	0.0269	0.0539	0.1076	0.1634	0.2152

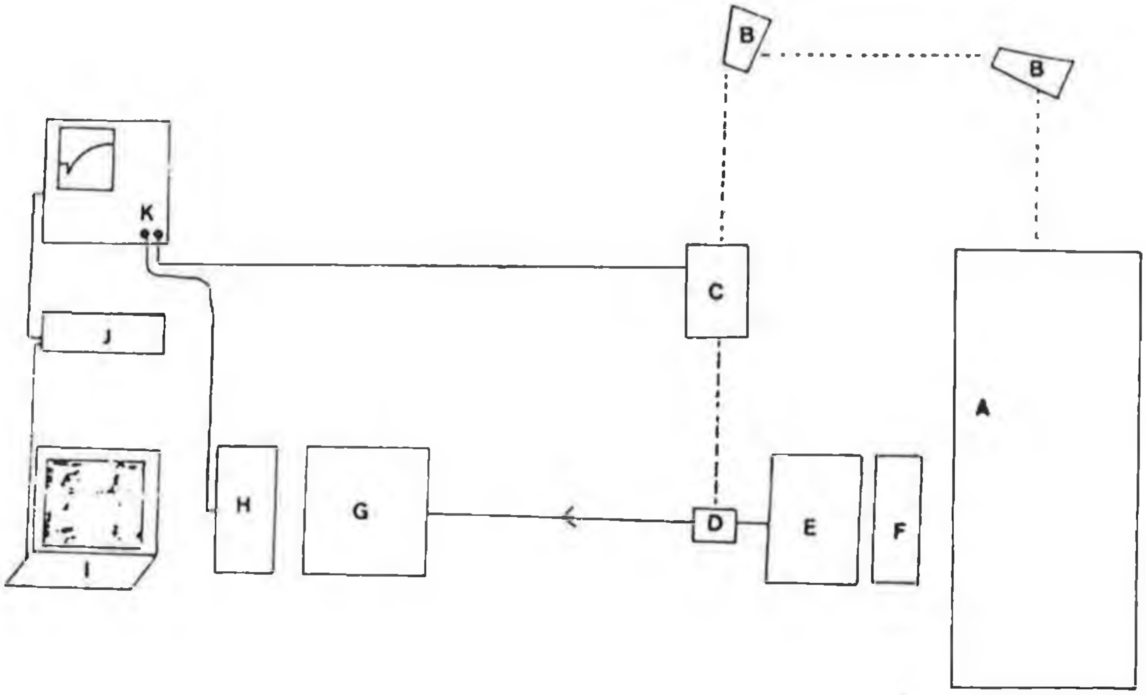
Determined by microanalysis, UCD Microanalytical Lab, Dublin.

A schematic diagram of the flash photolysis instrumentation is shown in **Figure 5.3**. The excitation source is a Q-switched Nd-YAG (neodynium doped yttrium aluminium garnet) laser (Spectron Laser Systems), which operates at 1064 nm but can be frequency doubled or tripled or quadrupled to generate a second, third, or fourth harmonic frequency at 532, 355, and 266 nm respectively. The power of the laser pulse can be varied by applying different voltages across the amplifier flash tube. At 355 nm, the power output was typically 30-40 mJ. The pulse time varies from 5 to 10 ns. The circular laser pulse (ca. 4 mm in diameter) is directed via two Pellin-Broca prisms onto the sample cuvette. A power meter, placed between the the second prism and sample holder, is used to trigger the oscilloscope and to measure pulse to pulse variation (this was estimated to be ± 5% at most in these experiments, and no correction was made for power variations. The monitoring light source was an Applied Photophysics 40804 air cooled 275 W Xenon arc lamp used at right angles to the laser beam. A UV filter ($\lambda > 400$ nm or $\lambda > 345$ nm) was placed between the monitoring source and the sample to prevent photolysis of the sample by the monitoring beam. The beam passes through the sample cell and is focused via a circular quartz lens onto the slit of a f/3.4 Applied Photophysics monochromator. The light detector is a Hamamatzu 5-stage photomultiplier which was operated at 850 volts. The signal output was connected via a variable load resistor to the transient analyser, a Phillips PM 3311 oscilloscope. The oscilloscope is partially controlled by a BBC microcomputer connected by an Acorn IEEE-488 computer interface.

An experiment is one of monitoring absorbance changes. Laser photolysis produces a transient species whose absorbance is recorded as a function of time. Initially I_o, the amount of monitoring light being transmitted through the solution before the laser flash is measured. This is achieved by recording the voltage corresponding to that light detected by the photomultiplier tube when the monitoring source shutter is open. I_o is directly proportional to this voltage. When recording transient data, the monitoring shutter is opened and the laser fired. The laser beam passes through the power meter, triggering the oscilloscope, and hits the sample cuvette producing a transient species. The monitoring beam traverses the region of the cuvette where the laser passed. The oscilloscope records the change in voltage with time from the photomultiplier tube, corresponding to a change in absorbance with time at the monitoring wavelength. The oscilloscope stores the trace and the transient data can be stored on floppy disc for analysis. The stored data can be used to calculate I_t, the amount of light being transmitted at any time t. An absorbance spectrum of the transient species is obtained by recording transient signals at different monitoring wavelengths. The absorbance readings can then be calculated at any time after the flash. The oscilloscope is set at a delay to enable the absorbance (corresponding to the absorbance of the parent material at that wavelength) to be recorded before the laser pulse. A transient difference spectrum is then obtained from a plot of absorbance versus wavelength.

For Arrhenius experiments, the sample cell was immersed in a thermostated water bath and allowed to equilibrated for 20 minutes. I_o was measured at the monitoring wavelength (λ = 395 nm) and the system readied for analysis prior to the sample being heated so that the transient data could be recorded immediately on removing the cell from the water bath. The sample was heated incrementally from room temperature to 50°C, a transient being recorded for analysis every 5°C.

Fig. 5.3 Schematic diagram of the laser flash photolysis system.



A	laser
B	prisms
C	power meter
D	sample cell housing
E	xenon arc lamp
F	Xenon lamp power supply
G	monochromator
H	photomultiplier
I	computer
J	IEEE interface
K	oscilloscope

5.3 Synthesis of Monomer Complexes

5.3.1 *Synthesis of $M(CO)_5$(vinylpyridine).*

The complexes were prepared via the corresponding tetrahydrofuran complex according to the literature procedures[17,24,69].

$$M(CO)_6 \xrightarrow[THF]{h\nu} M(CO)_5(THF) \xrightarrow[vp]{} M(CO)_5(vp) \qquad (1)$$

A typical preparation involved the photolysis of the parent hexacarbonyl (1.0 g) in freshly distilled THF (200 cm^3) at room temperature for about four hours. The photolysis solution was continuously purged with a stream of nitrogen to aid the removal of CO and maintain an inert atmosphere over the photolysis solution. Following the photolysis, the resulting clear yellow solution was added to a two molar excess of the desired vinylpyridine under nitrogen. The THF was removed by rotary evaporation. The crude product was recrystallised from degassed ethanol-chloroform to yield bright yellow crystals. Yields were typically 70 %. The complexes were pumped under vacuum to remove any traces of solvent and metal hexacarbonyl. The purity of the complexes was confirmed by infrared spectroscopy. The infrared and UV/vis data agreed with that already published[28,69]. The complexes are soluble in chlorinated solvents, alcohols, ether,and slightly soluble in hydrocarbons. Although all the complexes were handled as air sensitive, complexes of chromium and tungsten and 4-vinylpyridine show considerable stability even in aerated solution. Complexes of molybdenum are less stable and decompose in solution even when degassed. Those complexes of 2-vinylpyridine are much less stable, decomposing rapidly in solution even when degassed. [Mo$(CO)_5$(2-vp)] could not be isolated from reaction 1, presumably because of it's tendency to dissociate. In general, the stability of the complexes is in the order W > Cr >> Mo and 4-vp > 2-vp. The decreased stability of the 2-vinylpyridine complexes is attributed to steric interaction of the $M(CO)_5$ group and the vinyl group[29]. No evidence was found for other complexes such as $[M(CO)_4(vp)_2]$, $[M(CO)_5(\mu\text{-vp})M(CO)_5]$, or $[(\eta^2\text{-vp})M(CO)_5]$, indicating that these are minor products at the very best. ($W(CO)_5$(4-vp) Anal. Calcd.: C 33.59, H 1.64, N 3.26. Found: C 32.82, H 1.61, N 3.19. $W(CO)_5$(2-vp) Anal. Calcd.: C 33.59, H 1.64, N 3.26. Found: C 30.58, H 1.45, N 3.18). Infrared spectroscopic data were previously given in Table 2.1.

5.3.2 Preparation of $M(CO)_4$(4-vinyl-4'-methyl-2,2'-bipyridyl).

4-vinyl-4'-methyl-2,2'-bipyridyl was prepared according to the method of Ghosh and Spiro[67b]. [$M(CO)_5$(THF)] was prepared as described above and reacted with a molar equivalent of the bipyridyl in dry THF under nitrogen. A deep red solution was formed immediately. The THF was removed under vacuum and the crude product was recrystallised from a degassed acetone-toluene mixture to yield maroon crystals. The product was washed with hexane and dried under vacuum. Purity was confirmed by infrared spectroscopy. The spectroscopic data agreed well with previously reported studies on similar *cis*-[$M(CO)_4$(bipy)] complexes[72,73]. All complexes were treated as air sensitive and were stored under argon. The tetracarbonyls showed varying degrees of stability and readily decomposed on recrystallisation even in degassed solutions. In general the stabilities were in the order Mo > W > Cr. ($W(CO)_4$(Vbipy) Anal.Calcd.: C 41.48, H 2.46, N 5.68, Found: C 41.27, H 2.45, N 5.84).

Table 5.6 Component weights for synthesis of monomer complexes.

Complex	4-vp	2-vp	Vbipy	$M(CO)_6$		
				Cr	Mo	W
$Cr(CO)_5$(4-vp)	0.9560	-	-	1.0004	-	-
$Mo(CO)_5$(4-vp)	0.6790	-	-	-	0.8525	-
$W(CO)_5$(4-vp)	0.5980	-	-	-	-	1.0000
$Cr(CO)_5$(2-vp)	-	0.4870	-	0.5096	-	-
$W(CO)_5$(2-vp)	-	0.6010	-	-	-	1.0000
$Cr(CO)_4$(Vbipy)	-	-	0.1500	0.1682	-	-
$Mo(CO)_4$(Vbipy)	-	-	0.1250	-	0.1682	-
$W(CO)_4$(Vbipy)	-	-	0.2000	-	-	0.3587

All weights in grams.

5.3.3 *Synthesis of p-Styryldiphenylphosphine.*

The method of Rabinowitz and Marcus[38], with some slight modifications to the published procedure, was used to prepare p-styryldiphenylphosphine (p-SDPP) in good yield. The synthesis involved the reaction p-styrylmagnesium bromide with chlorodiphenylphosphine at 0°C using inverse addition. The organometalloid halide is prepared by Grignard synthesis and added to a solution of the phosphine. Direct addition of the phosphine to the Grignard reagent was reported to result in high degrees of polymerisation.

Materials

4-bromostyrene (Aldrich) was washed with aqueous 5% NaOH (3X) and then with distilled water (3X), and dried over magnesium sulphate. It was then distilled under reduced pressure, degassed under a stream of argon and stored at -20°C until required. Chlorodiphenylphosphine (Aldrich) was distilled under vacuum and stored under argon over type A4 molecular sieve at 4°C. Tetrahydrofuran was distilled under argon from lithium aluminium hydride and stored over sodium wire. Magnesium turnings (Riedel-de Haen) and ethyl bromide (BDH) were used as supplied.

Procedure

A dry 250 cm^3 three-necked round bottomed flask (rbf) was fitted with an argon inlet, thermometer, pressure equalising dropping funnel, and a Y-tube to which was attached a reflux condenser and $CaCl_2$ drying tube. The vessel was purged with a stream of argon for ten minutes and maintained at a positive argon pressure throughout the reaction. Magnesium turnings (5.0 g, 0.206 mole) were then added via a solids addition funnel under argon and the flask was charged with 40 cm^3 of freshly distilled THF. The suspension was stirred for 10 minutes while purging with a stream of argon. Ethyl bromide (0.5 cm^3) was added via a syringe to initiate the reaction. The temperature rose to 40°C. The flask was placed in an ice-bath and 4-bromostyrene (18.83 g, 0.103 mole) in 50 cm^3 of THF was added dropwise via the dropping funnel with stirring over 0.5 hour, the temperature never being allowed to exceed 40°C. The reaction was exothermic and proceeded vigorously, careful addition being needed to maintain the temperature at about 40°C. A further 20 cm^3 of THF was added and the resulting muddy Grignard reagent was stirred for a further 45 minutes at room temperature when addition was complete. Dropping an extract into methanol revealed that some polymer had formed at this stage. The reagent was filtered under argon using an on-line filter to remove any unreacted magnesium and precipitated magnesium bromide formed in the reaction.

A dry 250 cm^3 three-necked rbf was equipped with an argon inlet, thermometer, teflon coated magnetic stirring bar, and a rubber septum. The vessel was flushed with a stream of argon and chlorodiphenylphosphine (16.12 g, 0.073 mole) in 40 cm^3 THF was added via syringe. The solution was cooled to less than 0°C using an acetone slush bath. The phosphine was degassed under a stream of argon and allowed to equilibrate for 15 minutes with stirring. The Grignard reagent was added very gradually over 30 minutes via an air tight syringe, the temperature being maintained around 0°C. After addition of the Grignard was complete, the brown solution was allowed to warm to room temperature and stirred for a further 30 minutes. The solution was poured into 100 cm^3 of an aqueous solution of ammonium chloride (Riedel-de Haen) (15 g in 100 cm^3 distilled water) with stirring to decompose any unreacted Grignard reagent. This was then extracted with THF. The THF extracts were combined and filtered through a bed of silica gel (Merck) and dried over magnesium sulphate overnight. The solution was reduced to a volume of about 20 cm^3 by rotary evaporation and any polymer was precipitated (3X) in petroleum ether (600 cm^3). The ether was filtered through sintered glass and the solvent removed under vacuum to yield a yellow oil with some white solid. On addition of ethanol, the product dropped out of solution. The crude product was recrystallised from ethanol, and the resulting crystals were collected on sintered glass, washed with cold ethanol, and dried under vacuum to yield 14.91 g (70 % yield) of white crystals. The product could be further purified by chromatography on silica. Elution was first with chloroform:petroleum ether 40-60°C to remove polymer impurities, and then with petroleum ether. (Anal. Calcd.: P 10.74, Found: P 11.06; mp 76-77°C, Lit. value 77-78°C; IR (KBr): 1621 (C=C), 1428 (P-Ph), 837 (disub. aromatic), 745, 695 (monosub. aromatic) cm^{-1}. ^1H NMR ($CDCl_3$, 1% TMS, 60 MHz): chemical shifts (δ in ppm) and coupling constants (J in Hz) for vinylic H : H_1 6.38 (16.0, 9.8), H_2 5.16 (10.2, 1.8), H_3 5.60 (16.0, 1.8); aromatic H 7.1-7.5 ppm).

Attempts to prepare metal carbonyl complexes of p-SDPP via the photochemically produced $[M(CO)_5(THF)]$ as previously described in section 5.3.1, were unsuccessful. Low yields of the desired monomer metal carbonyl complexes could only be obtained, considerable amounts of polymer being formed in all cases.

5.4 Preparation of Polymers and Polymer-Bound Metal Carbonyls

The polymers were prepared by azobisisobutyronitrile (AIBN) initiated free-radical polymerisation in the absence of solvent. (Copolymers of α-methylstyrene were prepared by anionic polymerisation and are discussed later). Polymer-bound metal carbonyls were prepared either by reacting photogenerated $[M(CO)_5(THF)]$ with preformed copolymers containing pendant sites in a 1:1 mole ratio, or by copolymerisation of the metal carbonyl functionalised monomers with suitable comonomers.

Typically, the mixtures of monomers and initiator (2% w/w) were degassed by purging the solution with a stream of nitrogen for 10 minutes. Polymerisations were carried out by heating at 75-85°C for 1-2 hours under a nitrogen atmosphere. In the case of copolymers of styrene and methylmethacrylate, colourless glass-like polymers resulted while those of ethyl and methyl acrylate were rubbery in nature. The copolymers were purified by repeated precipitation from chloroform solution by petroleum ether 40-60°C (the minimum volume of chloroform required to dissolve the polymer was used and the resulting solution was added dropwise into a large volume of pet. ether (about 800 cm^3) with vigorous stirring). The polymers were collected on sintered glass and washed with petroleum ether of ethanol. Polymers of styrene and methylmethacrylate were isolated as floculent powders, while those of the acrylates were obtained as rubbery solids. All polymerisations proceeded in good yield (80-90%). They were dried under vacuum at 60°C for 24 hours. Those copolymers of the acrylates containing bound metal carbonyls were dried under vacuum at room temperature, due to the thermal reactivity of these polymers. The polymers are soluble in chlorinated solvents, toluene, benzene, ethyl acetate, THF and dimethylformamide but insoluble in diethyl ether, alcohols and hydrocarbons. The metalated polymers show decreased solubility when compared with their unmetallated analogues. The metal carbonyl containing polymers were treated as air and light sensitive, and stabilities were similar to those of their unbound monomeric analogues. Tables 5.7-5.12 show the weights of the various components used in the syntheses of the various polymer systems.

Table 5.7 Weights (g) of materials used in the synthesis of non-metallated copolymers (20/1 mole ratio).

Copolymer[1]	styrene	MMA	MA	EA	4-vp	2-vp	Vbipy
styrene-4-vp	5.0000	-	-	-	0.2524	-	-
styrene-2-vp	5.0000	-	-	-	-	0.2524	-
styrene-Vbipy	2.5000	-	-	-	-	-	0.2355
MMA-4-vp	-	5.0000	-	-	0.2625	-	-
MMA-Vbipy	-	2.0000	-	-	-	-	0.1960
MA-4-vp	-	-	5.0000	-	0.3053	-	-
EA-4-vp	-	-	-	5.0000	0.2625	-	-

[1] 2% AIBN used in all preparations.

Metal carbonyl complexes of the styrene copolymers were prepared by reaction with photogenerated $[M(CO)_5(THF)]$. Metallated copolymers of the acrylates and methylmethacrylate were not prepared by this route because of the likelihood of binding to the oxygen sites on the backbone. The polymer samples were dissolved in dry THF and reacted with a 1:1 molar ratio of pyridine binding sites to $[M(CO)_5(THF)]$. The THF was then removed by rotary evaporation at 30°C. The polymers were then precipitated into petroleum ether from chloroform, filtered on sintered glass, washed with ethanol, and dried under vacuum. In the case of those polymer prepared from the metal carbonyl containing monomers, the monomers and initiator were dissolved, degassed and heated under nitrogen in the manner described earlier.

Table 5.8 Weights (g) of monomers and metal carbonyl containing comonomers used in the synthesis of some of the polymer-bound metal carbonyls (20/1 mole ratio).

Polymer	Monomer	$M(CO)_5$(4-vp)	$M(CO)_5$(2-vp)	$M(CO)_4$(Vbipy)
styrene-$W(CO)_5$(4-vp)	2.0000	0.4120	-	-
styrene-$Cr(CO)_5$(4-vp)	2.0000	0.2854	-	-
styrene-$Mo(CO)_5$(4-vp)	2.0000	0.3280	-	-
styrene-$W(CO)_5$(2-vp)	2.0000	-	0.4120	-
styrene-$Cr(CO)_5$(2-vp)	2.0000	-	0.2858	-
styrene-$W(CO)_4$(Vbipy)	1.5000	-	-	0.3544
styrene-$Cr(CO)_4$(VBipy)	1.5000	-	-	0.2595
styrene-$Mo(CO)_4$(Vbipy)	1.5000	-	-	0.2911
MMA-$W(CO)_5$(4-vp)	2.5000	0.5360	-	-
MMA-$Cr(CO)_5$(4-vp)	2.5000	0.3710	-	-
MMA-$W(CO)_4$(Vbipy)	1.5000	-	-	0.3687
EA-$W(CO)_5$(4-vp)	2.5000	0.5357	-	-
EA-$Cr(CO)_5$(4-vp)	2.5000	0.3710	-	-
EA-$W(CO)_4$(Vbipy)	1.5000	-	-	0.3687
MA-$W(CO)_5$(4-vp)	2.5000	0.6230	-	-

vp = vinylpyridine, Vbipy = 4-vinyl-4'-methy-2,2'-bipyridyl
MMA = methylmethacrylate, EA = Ethyl acrylate,
MA = Methyl acrylate. 2% AIBN used in all cases.

Table 5.8 Polymers of styrene and [$W(CO)_5$(4-vp)] with free 4-vp.

Ratio of 4-vp/styrene	styrene	[$W(CO)_5$(4-vp)]	4-vp	AIBN
P[4-vp-$W(CO)_5$(4-vp)]	-	0.3060	1.5000	0.0361
1/5	1.2670	0.2610	0.2558	0.0357
1/10	1.2670	0.2610	0.1280	0.0332
1/20	1.2670	0.2610	0.0640	0.0318
1/40	1.2670	0.2610	0.0320	0.0312

Table 5.9 Polymers of [$W(CO)_5$(4-vp)] and styrene with free 2-vp.

Ratio of 2-vp/styrene	styrene	[$W(CO)_5$(4-vp)]	2-vp	AIBN
1/1	0.6068	0.1250	0.6125	0.0305
1/5	1.2136	0.2500	0.2425	0.0317
1/10	1.2136	0.2500	0.1225	0.0341
1/20	1.2136	0.2500	0.0613	0.0269

Table 5.10 Polymers of [W(CO)$_5$(2-vp)] and styrene (1/20 mole ratio) free 2-vp.

Ratio of 2-vp/styrene	styrene	[W(CO)$_5$(2-vp)]	2-vp	AIBN
1/5	0.9759	0.2018	0.2009	0.0279
1/10	0.9838	0.2032	0.1044	0.0247
1/20	0.9807	0.2038	0.0506	0.0241
P[(2-vp-W(CO)$_5$(2-vp)]	-	0.1996	1.0004	0.0250

All weights in grams.

Table 5.11 Polymers of [W(CO)$_4$(4-vinyl-4'-methyl-2,2'-bipy)] (1/20 mole ratio) and styrene with free 4-vp.

Ratio of 4-vp/styrene	styrene	[W(CO)$_4$(Vbipy)]	4-vp	AIBN
1/50	1.2000	0.2835	0.0242	0.0302
1/30	1.2000	0.2835	0.0404	0.0305
1/20	1.2000	0.2835	0.0606	0.0309
1/10	1.2000	0.2835	0.1212	0.0321

All weights in grams.

Table 5.12 Syntheses of copolymers of different metal loadings.

Loading	styrene	$[W(CO)_5(4\text{-vp})]$	AIBN
1:1000	5.0000	0.0206	0.1004
1:500	5.0000	0.0412	0.1008
1:200	3.0000	0.0618	0.0612
1:100	3.0000	0.1236	0.0620
1:40	3.0000	0.3089	0.0662
1:30	3.0000	0.4120	0.0682
1:10	1.5000	0.6068	0.0423
1:5[a]	1.0000	0.8240	0.0320

[a] Loadings greater 1:5 rendered the polymers insoluble.

5.4.1 Preparation of Polymer-Bound Dipyridylmethane.

A copolymer of styrene and 2-vinylpyridine (20/1 mole ratio) was prepared by free radical polymerisation as indicated earlier in section 5.4. The lithium salt of 2-methylpyridine was prepared by treating 2-methylpyridine (0.3 cm^3) with n-butyllithium (Merck, 1.65 cm^3 of a 15 % solution in hexane) at room temperature under a nitrogen atmosphere. A solution (0.75 g in 2 cm^3 of dry toluene) of the polymer was then added and the resulting mixture was stirred for 8 hours. Following this, ice (10 cm^3) was added carefully and the solution was extracted with dichloromethane (40 cm^3). The organic fraction was then concentrated by rotary evaporation and the polymer was precipitated by addition to petroleum ether.

5.4.2 Anionic Copolymerisation of α-methylstyrene.

Methylstyrene was copolymerised with 4-vinylpyridine and [$M(CO)_5$(4-vp)] by an anionic mechanism, using sodium naphthalide as the catalyst and THF as the solvent. Sodium naphthalide reacts rapidly with vinyl groups producing radical ions which quickly dimerise, destroying the radical activity and leaving a dianion capable of growth at both ends. This initiation process is quite rapid compared to propagation, and hence the growth of all the polymer chains is started almost at one time[76a]. Polymers with very narrow molecular distributions usually result. Both the catalyst and the growing chains are easily destroyed by oxygen, water, carbon dioxide, alcohols, and many other impurities. If these substances are rigorously eliminated, the chains are capable of further growth even if the supply of monomer is depleted; they constitute a "living" polymer system, defined as one in which there is no termination. Polymerisation can continue when more monomer of the same type or different is added.

Materials

Naphthalene (BDH) was sublimed under vacuum before use. Sodium (BDH) was reagent grade and was stored under paraffin oil. The outer tarnished crust was removed and the sodium cut into small pieces and washed with dry THF before use. THF and 4-vinylpyridine were purified as already described. α-Methylstyrene was washed with 10% NaOH (3X), distilled water (6X), and distilled under vacuum. It was then degassed with a stream of argon and stored over calcium hydride at 4°C until required. Methanol was reagent grade and used without further purification.

Preparation of sodium naphthalide

A two necked round-bottomed flask (rbf) was fitted with a nitrogen inlet, a reflux condenser, and a $CaCl_2$ guard tube. The flask was charged with naphthalene (1.5 g) in 50 cm^3 of dry degassed THF and freshly cut sodium (1.5 g), and the solution was stirred at room temperature under a continuous nitrogen purge. After 10 minutes dark green sodium naphthalide formed. The solution was stirred for a further 2 hours.

Procedure

A dry 250 cm^3 three-necked rbf was fitted with a rubber septum, gas inlet, and a $CaCl_2$ drying tube. The vessel was purged with argon for about 15 minutes. The monomers were dissolved in 50 cm^3 of THF and added to the flask. The solution was cooled to -80°C using a THF slurry bath, and allowed to equilibrate for about 15 minutes. The freshly prepared catalyst was added via syringe. A deep red colour appeared immediately as the styrene anions formed. After a few minutes, the chains were terminated by injecting methanol (4 cm^3). The red colour disappeared on addition of the methanol, a light green colour persisting. The flask was warmed to room temperature and the solution concentrated to about 15 cm^3. The polymer was precipitated in petroleum ether and dried under vacuum.

Table 5.12 Syntheses of α-methylstyrene copolymers (20/1 mole ratio).

α-methylstyrene	4-vp	$Cr(CO)_5(4\text{-vp})$	$W(CO)_5(4\text{-vp})$
4.5018	0.2023	-	-
2.0370	-	-	0.3652
2.0113	-	0.2512	-

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