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Molybdenum tetracarbonyl complexes with linear chain polyether-containing Schiff base ligands and their reactivity in the polymerization of methyl methacrylate

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$Mo(CO)_6$ was reacted with the Schiff base ligand obtained by condensation reaction of 2-acetyl- or benzoylpyridine with poly(propylene glycol)bis(2-aminopropyl ether) to obtain polymeric, dinuclear metal tetracarbonyl compounds. The long-chain Schiff base complexes are highly soluble even in non-polar solvents such as petroleum ether, diethyl ether and *n*-hexane. These complexes, as free-radical initiators, afforded methyl methacrylate polymerization in chlorinated solvents. Copyright © 2004 John Wiley & Sons, Ltd.

KEYWORDS: metal–polymer complexes; heteroatom-containing polymers; polyether; poly(methyl methacrylate); transition metal chemistry; propylene glycol; organometallic catalysts

INTRODUCTION

Transition metal carbonyl complexes are widely used in synthetic organic chemistry. Some transition metal carbonyls are known to promote the activation of carbon–halogen and related covalent bonds to generate radical species, and the resulting radicals can add to multiple bonds. Among such reactions are the Kharasch or atom-transfer and addition reactions.[1,2] Metals Rh(II), Ru(II), Co(II), Fe(II), Ni(II), Mn(0), Re(0) and Mo(0), among others, interact with halogen atoms in organic halides via redox reactions of the metal centre. These metal complexes are employed for redox initiation of free-radical polymerization, where the metal complexes interact with polyhalogen compounds such as CCl_4 to generate the initiation radicals but polymerization proceeds by conventional, poorly controlled radical mechanisms.[3,4] Homogeneous, late-metal catalysts with chelating α-diimine ligands that catalyse olefin polymerization have received much attention recently.[5] The ease with which the ligands can be synthesized enables steric, electronic and solubility parameters of the catalyst to be varied and optimized. Also, ligand modifications can result in desirable changes in the properties of the resulting polymers.

Zero-valent transition metal carbonyl compounds with chelating α-diimine ligands such as 2,2′-bipyridyl (bipy), 1,10-phenanthroline (phen) and 1,4-diazabutadiene (DAB), and the pyridylamine Schiff base, have been well studied and their reactivity has been determined.[5–12]

Nitrogen donor ligands for metal binding units introduced into polyester, poly(2-R-2-oxazolines), polystyrenes, poly(methyl methacrylates), poly(ε-caprolactones), poly(ethylene glycol) and poly(lactic acid) and their complexes have been reported.[13,14]

We reported previously the preparation of *cis*-$[Mo(CO)_4L_2]$ ($L_2 = \alpha$-diimine) compounds by treating *cis*-$[Mo(CO)_4(pip)_2]$ (pip = piperidine) with appropriate α-diimine ligands in refluxing *i*-PrOH.[8,9]

In this paper we report the preparation of macroligands by treatment of equivalent amounts of 2-acetylpyridine (ap) or 2-benzoylpyridine (bp) with linear chain polyethers containing the diamine poly(propylene glycol)bis(2-amino-propylether) (PPG-Am_2, $H_2NCH(CH_3)CH_2[OCH_2CH(CH_3)]_nNH_2$) having number-average molecular weights of $M_n \sim 400\ g\ mol^{-1}$ ($n_{av} \sim 6$) and $M_n \sim 2000\ g\ mol^{-1}$ ($n_{av} \sim 33$). Molybdenum complexes **3a**, **3b**, **4a** and **4b** were obtained by treating $[Mo(CO)_6]$ with the appropriate α-diimine ligands in refluxing *i*-PrOH (Fig. 1). These complexes can be used

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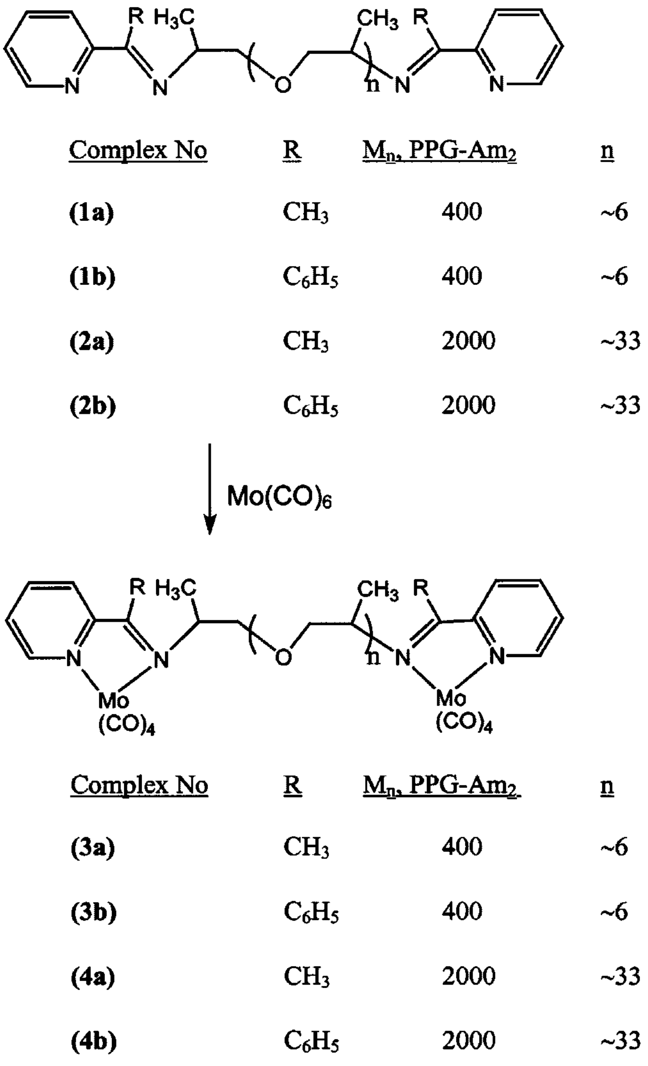

Complex No	R	M_n, PPG-Am$_2$	n
(1a)	CH$_3$	400	~6
(1b)	C$_6$H$_5$	400	~6
(2a)	CH$_3$	2000	~33
(2b)	C$_6$H$_5$	2000	~33

Complex No	R	M_n, PPG-Am$_2$	n
(3a)	CH$_3$	400	~6
(3b)	C$_6$H$_5$	400	~6
(4a)	CH$_3$	2000	~33
(4b)	C$_6$H$_5$	2000	~33

Figure 1. Ligands and their molybdenum complexes.

as radical initiators for the polymerization of methyl methacrylate.

EXPERIMENTAL

All reactions were performed under a dry, oxygen-free nitrogen atmosphere. Fast atom bombardment mass spectroscopy (FAB-MS) measurements of the liquid complexes were obtained on a GC–MS Zapspec spectrometer. The ^{1}H NMR spectra were recorded at room temperature in CDCl$_3$ on a Bruker 200 AC spectrometer operating at 200 MHz with SiMe$_4$ (0.0 ppm) as internal reference. Infrared spectra were recorded on a Perkin-Elmer J77 spectrophotometer in CHCl$_3$ over the 4000–600 cm^{-1} range. Molecular weights and molecular weight distributions were determined using a Waters 6000 A gel permeation chromatograph with THF as eluent, and calibration was conducted using polystyrene standards.

Molecular weights of polymers were determined using an Ubbelohde viscosimeter with CHCl$_3$ as solvent at 20 °C.

Mo(CO)$_6$, toluene, methanol, tetrahydrofuran, chloroform, *i*-propanol, 2-acetylpyridine, 2-benzoylpyridine and poly(propylene glycol)bis(2-aminopropyl ether) (PPG-Am$_2$, $H_2NCH(CH_3)CH_2[OCH_2CH(CH_3)]_nNH_2$, $M_n \sim$ 400 and ~2000 g mol^{-1}) were used as supplied from Aldrich Chemical Company. Methyl methacrylate (MMA) was dried over calcium hydride and distilled under vacuum at 35 mmHg.

General methods of preparation

Compounds **3a**, **3b**, **4a** and **4b** were prepared by refluxing [Mo(CO)$_6$] with the diimine ligand components in stochiometric quantities in *i*-PrOH under N$_2$. The reactions are completed in <4 h in all cases. Dark maroon viscous liquids were obtained when the reaction mixtures were evaporated to dryness. All the compounds are very soluble in petroleum ether, diethyl ether and dichloromethane to give deep maroon solutions.

Preparations of Schiff base ligands

*Poly(propylene glycol)$_{400}$bis(2-iminoethylpyridine-*N,N′*)* ***(1a)***. 2-Acetylpyridine (1.21 g, 10 mmol) and PPG-Am$_2$ ($M_n \sim$ 400 g mol^{-1}, 2 g, 5 mmol) were heated at 50 °C in *i*-PrOH (10 ml) for 3 h. Evaporations to dryness gave a deep-maroon viscous liquid, yield 1.9 g (33%). ^{1}H NMR: δ = 0.93–1.11 (brd, H^{2,6}, J = 5 Hz, –CH_3); 2.31 (s, 6H, N=C-CH_3); 3.32 (br, 21H^{1,5,3,4},–CH_2, –CH); 7.15–8.61 (m, 8H, *Arom.*). IR: 1700 s ν(C=N). FAB-MS: 606.

*Poly(propylene glycol)$_{400}$bis(2-iminophenylmethylpyridine-*N,N′*)* ***(1b)***. 2-Benzoylpyridine (2.32 g, 12.7 mmol) and PPG-Am$_2$ ($M_n \sim$ 400 g mol^{-1}, 2.54 g, 6.35 mmol) were heated at 50 °C in *i*-PrOH (10 ml) for 3 h. Evaporation to dryness gave a yellow viscous liquid, yield 3.28 g (74%). ^{1}H NMR: δ = 1.03 (d, 3H^2, J = 5 Hz, –CH_3); 1.12 (d, 18H^6, J = 5 Hz, –CH_3); 3.45–3.55 (br, 14H^{3,4}, –CH_2); 3.12 (br, 7H^{1,5}, –CH); 7.23–8.72 (m, 18H, *Arom.*). IR: 1660 s ν(C=N). FAB-MS: 730.

*Poly(propylene glycol)$_{2000}$bis(2-iminoethylpyridine-*N,N′*)* ***(2a)***. Prepared as for ligand **1a** except PPG-Am$_2$ ($M_n \sim$ 2000 g mol^{-1}) was used, yield 3.18 g (29%). ^{1}H NMR: δ = 1.03 (d, 3H^2, J = 5 Hz, –CH_3); 1.12 (d, 18H^6, J = 5 Hz, –CH_3); 3.45–3.55 (br, 14H^{3,4}, –CH_2); 3.12 (br, 7H^{1,5}, –CH); 7.23–8.72 (m, 8H, *Arom.*). IR: 1701 s ν(C=N).

*Poly(propylene glycol)$_{2000}$bis(2-iminophenylmethylpyridine-*N,N′*)* ***(2b)***. Prepared as for ligand **1b** except PPG-Am$_2$ ($M_n \sim$ 2000 g mol^{-1}) was used, yield 4.5g (75%). ^{1}H NMR: δ = 1.12 (d, 102H^{1,6}, J = 5 Hz, –CH_3); 3.49–3.59 (br, 68H^{3,4}, –CH_2); 3.35–3.46 (br, 34H^{1,5}, –CH); 7.23–8.72 (m, 18H, *Arom.*). IR: 1660 s ν(C=N).

Preparation of metal complexes

*{$Mo(CO)_4$bis[poly(propylene glycol)$_{400}$bis(2-imino-ethyl-pyridine-*N,N′*)]$Mo(CO)_4$}* ***(3a).*** $Mo(CO)_6$ (0.1 g, 0.38 mmol) and ligand **1a** (0.1 g, 0.19 mmol) were added to *i*-PrOH (10 ml) under N_2. The reaction mixture was refluxed for 3 h to give a deep-maroon liquid **(3a)**, yield 0.16 g (77%). ^1H NMR: $\delta = 1.03$ (d, $3H^2$, $J = 5$ Hz, $-CH_3$); 1.12 (d, $18H^6$, $J = 5$ Hz, $-CH_3$); 3.45–3.55 (br, $14H^{3,4}$, $-CH_2$); 3.12 (br, $7H^{1,5}$, $-CH$); 7.23–8.72 (m, 8H, *Arom.*). IR: 1692 s ν(C=N); 2010 s, 1899 s, 1872 sh, 1827 s ν(C≡O).

*{$Mo(CO)_4$bis[poly(propylene glycol)$_{400}$bis(2-iminophenylmethylpyridine-*N,N′*)]$Mo(CO)_4$}* ***(3b).*** $Mo(CO)_6$ (0.20 g, 0.76 mmol) and ligand **1b** (0.28 g, 0.38 mmol) were added to *i*-PrOH (10 ml) under N_2. The reaction mixture was refluxed for 3 h to give complex **3b**, yield 0.39 g (71%). ^1H NMR: $\delta = 1.10$ (d, $21H^{2,6}$, $J = 3.8$ Hz, $-CH_3$); 3.48–3.80 (br, 21 $H^{1,5,3,4}$, $-CH_2$, $-CH$); 7.21–9.23 (m, 18H, *Arom.*). IR: 1660 s ν(C=N); 2000 s, 1900 s, 1880 sh, 1825 s ν(C≡O).

*{$Mo(CO)_4$bis[poly(propylene glycol)$_{2000}$bis(2-imino-ethylpyridine-*N,N′*)]$Mo(CO)_4$}* ***(4a).*** $Mo(CO)_6$ (0.1 g, 0.378 mmol) and ligand **2a** (0.4 g, 0.183 mmol) were added to *i*-PrOH (10 ml) under N_2. The reaction mixture was refluxed for 3 h to give complex **4a**, yield 0.130 g (28%). ^1H NMR: $\delta = 0.92$ (d, $102H^{2,6}$, $J = 5$ Hz, $-CH_3$); 3.16 (br, $68H^{3,4}$, $-CH_2$); 4.38 (br, $34H^{1,5}$, $-CH$); 7.23–8.72 (m, 8H, *Arom.*). IR: 1698 s ν(C=N); 2003 s, 1888 s, 1870 s, 1827 s ν(C≡O).

*{$Mo(CO)_4$bis[poly(propylene glycol)$_{2000}$bis(2-imino-phenylmethylpyridine-*N,N′*)] $Mo(CO)_4$}* ***(4b).*** $Mo(CO)_6$ (0.20 g, 0.76 mmol) and ligand **2b** (0.88, 0.38 mmol) were added to *i*-PrOH (10 ml) under N_2. The reaction mixture was refluxed for 3 h to give complex **4b**, yield 1.33 g (75%). ^1H NMR: 1.13 (d, $102H^{2,6}$, $J = 5.5$ Hz, $-CH_3$); 3.45–3.52 (br, $68H^{3,4}$, $-CH_2$); 3.39 (br, $34H^{1,5}$, $-CH$); 7.25–8.73 (m, 18H, *Arom.*). IR: 1660 s ν(C=N); 2010 m, 1950 w, 1900 s, 1830 s ν(C≡O).

Polymerization of methyl methacrylate (MMA)

The complexes were dissolved in 5 ml of toluene/chloroform (4:1) in a test tube. Nitrogen was bubbled through the solution for 3–5 min to expel the air. Freshly distilled MMA was added under nitrogen. The reaction mixture was heated at 80 °C for about 24 h. The maroon colour of the solution turned to colourless. Addition of MeOH gave a dirty-white solid that was washed with H_2O, diethyl ether and dried in *vacuo*. The solid was redissolved in a small amount of chloroform and filtered to remove metal residue. Addition of MeOH to the filtrate gave poly(methyl methacrylate), which was dried in *vacuo* and characterized by ^1H NMR, infrared spectroscopy, thermal gravimetric analysis, differential scanning calorimetry and gel permeation chromatography. IR: 1728 s ν(C=O), 1300–1100 s ν(C–O–O). ^1H NMR (250 MHz) $\delta = 0.88$ (br, $-CH_3$), 1.80 (br, $-CH_2$), 3.58 (s, COO-CH_3). Thermal gravimetric analysis (weight loss in parentheses): 310 °C (45%), 410 °C (92%). Differential scanning calorimetry: $T_g = 70$ °C. The gel permeation chromatography results are shown in Fig. 3.

RESULTS AND DISCUSSION

Macroligands containing poly(propylene glycol) (**1a**, **1b**, **2a**, **2b**) and macrocomplexes (**3a**, **3b**, **4a**, **4b**) have been prepared, as shown in Fig. 1. All the compounds were isolated as viscous liquids. The macroligands have been characterized by ^1H NMR and infrared spectroscopy. The macrocomplexes were characterized by ^1H NMR, infrared spectroscopy and gel permeation chromatography. Although the metal complexes are stable in the dark at room temperature, they give deep-violet solutions in most organic solvents such as chloroform, dichloromethane, toluene, diethyl ether and ethanol. Metal–imine bond cleavage can be observed when solutions of the complexes are exposed to sunlight.

The ^1H NMR spectra of the Schiff base ligands (numbering scheme shown in Fig. 2) were obtained. The aromatic protons of the pyridylamine Schiff base molybdenum complexes all have multiplets between 7.19 and 8.73 ppm in the aromatic region.

The infrared spectra of the compounds have characteristic signals. The complexes have C_{2v} symmetry and show four stretching frequencies assignable to the carbonyl ligands ($2A_1 + B_1 + B_2$) in the carbonyl region of 1825–2010 cm^{-1}. These frequencies for the complexes of unsymmetrical ligands derived from 2-acetylpyridine or 2-benzoylpyridine are assigned as follows: the higher frequency A_1 and B_1 bands are assigned to the *trans*-carbonyl ligands and the lower frequency A_1 and B_2 bands are assigned to the *cis*-carbonyls. The N=C stretching frequency is observed at 1660–1700 cm^{-1}.

The FAB mass spectra of ligands **1a** and **1b** showed fragmentation due to loss of propyl glycol groups.

Gel permeation chromatography of complexes **3b** and **4b** gave their weight-average molecular weight (M_w), number-average molecular weight (M_n) and molecular weight distribution (M_w/M_n), as shown in Table 1. These complexes have a narrow MWD range (Fig. 3).

During the course of our syntheses we found that these long-chain Schiff base complexes are highly soluble even in non-polar solvents such as diethyl ether, petroleum ether and

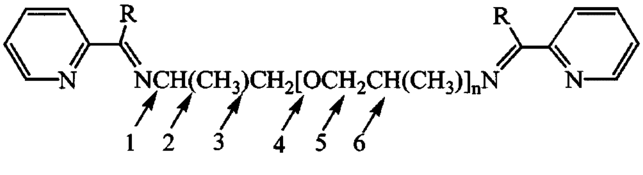

Figure 2. Numbering scheme for ^1H NMR of ligands **1a**, **1b**, **2a** and **2b** and complexes **3a**, **3b**, **4a** and **4b** (R = CH_3 or C_6H_5, $n = \sim 6$ or ~ 33).

Table 1. Gel permeation chromatography (GPC) result of long-chain Schiff base–ligand complexes

Complex	M_n (calculated)	M_n (GPC)	MWD[a]
3b	1146	1159	1.02
4b	2750	2890	1.12

[a] MWD = molecular weight distribution = M_w/M_n.

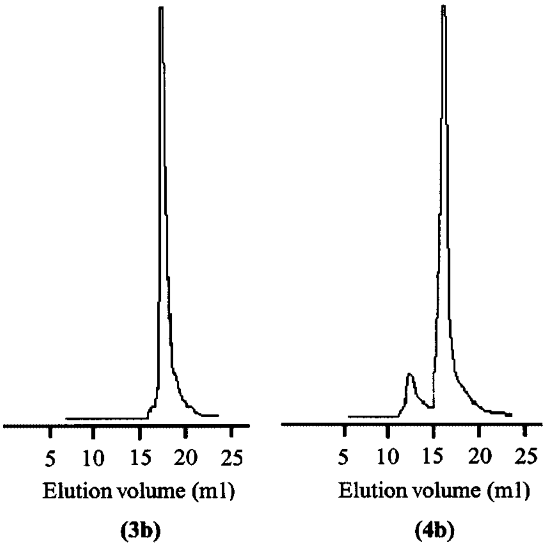

Figure 3. Gel permeation chromatograms of macrocomplexes **3b** and **4b**.

n-hexane. When solutions of the complexes are exposed to sunlight they decomposed in ~3 h. The deep-maroon colour of the solutions in petroleum ether turned to colourless under sunlight, whereas on keeping the solution in the dark for a few days no changes were observed. In previous studies of hydrocarbon solutions of *cis*-[Mo(CO)$_4$(bpmi)] (bpmi = benzoylpyridine-methyl imine), which were deep-maroon in colour, there was no sign of discoloration to the yellow Schiff base even after prolonged periods of exposure to sunlight under ambient conditions.[8] It is envisaged that the complex is stable with respect to either dissociation of the Schiff base ligands or any oxidative addition to the metal.

Our result for the synthesis of the first macroligand–Schiff base complexes with molybdenum(0) tetracarbonyl demonstrated that the nature of the alkyl group dramatically affects the solubility of the metal complexes in a range of solvents, especially at ambient temperatures: as the length of the alkyl group increased, the system becomes more soluble in non-polar solvents. The effect of the long-chain alkyl groups on the α-diimine–metal bond cleavage were also investigated and M–N bonds were cleaved easily. This behaviour, together with homolytic cleavage of the metal carbonyl,[2] may be the reason for the polymerization reactions designed in Fig. 4. Preliminary results of these polymerizations (Table 2)

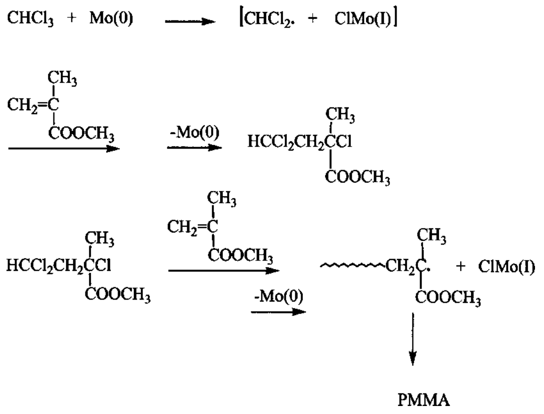

Figure 4. Proposed reaction mechanism for the polymerization of methyl methacrylate (MMA).

Table 2. Results and conditions for the polymerization of methyl methacrylate (MMA)[a]

Initiator		Amount of MMA (ml)	Total polymer yield (g)	$M^b \times 10^4$
Type	Amount (g)			
3a	0.100	2	0.864	7.8
3a	0.100	3	1.286	20.5
3a	0.075	2	0.131	7.1
3a	0.150	2	2.561	7.5
4b	0.100	2	0.577	25.4
3b	0.200	2	0.675	20.6
3b	0.300	2	1.211	15.8
3b	0.400	2	1.350	16.7

[a] Polymerization condition: toluene/chloroform (volume ratio, 4 : 1) at 80 °C for 24 h.

[b] Determined by Ubbelohde viscosimeter. The relationship between intrinsic viscosity (η) and molecular weight was used: $\eta = 5.5 \times 10^{-5} \times M^{0.79}$ in CHCl$_3$.

showed that the Schiff base complexes of molybdenum have decomposed in chlorinated solvents to give a radical that leads to free-radical polymerization of MMA. Table 2 indicates the result and conditions of the polymerization of MMA with macroligand complexes. This interesting behaviour is still under investigation.

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