APPLIED ORGANOMETALLIC CHEMISTRY
Appl. Organometal. Chem. 2006; **20**: 754–757

(www.interscience.wiley.com) DOI:10.1002/aoc.1125

Free radical polymerization of methyl methacrylate initiated by the diphosphine Mo(0) complexes

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Received 13 February 2006; Accepted 13 May 2006

The polymerization of methyl methacrylate MMA catalyzed by [Mo(CO)$_4$L$_2$] [L$_2$ = diphenylphosphinomethane (dppm), diphenylphosphinoethane (dppe) or diphenylphosphinopropane (dppp)] has been studied. The activity of these single-component catalysts depends on the length of the (CH$_2$)$_n$ bridge of diphosphine ligand. Thus, the dppm derivative displays higher activity than dppe or dppp ligands. These complexes, as free radical initiators, afforded the methyl methacrylate polymerization in chlorinated solvents. The mechanism of the polymerization was discussed and a radical mechanism was proposed. Copyright © 2006 John Wiley & Sons, Ltd.

KEYWORDS: bidentatephosphine; carbonyl; molybdenum; poly(methyl methacrylate); transition metal chemistry; organometallic catalysts

INTRODUCTION

Over the past few years, successful applications of transition-metal complexes such as Ru, Cu, Ni, Fe, Rh, Pd, Re, Yb, W, Mo to polymerization have been explored.[1–9] Methyl methacrylate (MMA) can be polymerized by many methods, such as free radical, anionic, cationic, coordination, GTP (group transfer polymerization) and ATRP (atom transfer radical polymerization). Radical polymerizations of vinyl monomers and controlling radical polymerization with metal complex catalysts lies in the reversible activation of the carbon–halogen bonds (Fig. 1). During the polymerization, most of the polymer chains exist as the stable dormant species, which makes the radical concentration low enough to suppress the bimolecular termination reactions between the growing radical species.[3]

Bidentate phosphine complexes have been reported to be active catalysts for the polymerization of vinyls.[10–12] Reports on diphosphine-based Ni polymerization catalysts are scarce, despite the crucial role that the latter ligands play in homogenous catalysis. It has been demonstrated that, in CO–olefin coplymerization, both the steric properties and the bite angle of the associated diphosphine ligands exert a profound influence on the catalytic activity.[10] These factors could also be used to modify the catalyst activity from olefin polymerization.

Although [Mo(CO)$_4$L$_2$] (L$_2$ = bidentate phosphines) were synthesized long ago and their applications in organic synthesis are well known, this is the first time to the best of our knowledge that bidentate phosphine molybdenum tetracarbonyl complexes have been reported to be active for the polymerization of methyl methacrylate without using co-catalysts.[13]

In a previous paper, we reported that MMA can be polymerized by molybdenum tetracarbonyl complexes with linear chain polyether-containing Schiff base ligands.[7] In this paper, further work is described using [Mo(CO)$_4$L$_2$] [L$_2$ = diphenylphosphinomethane (dppm), **1**; diphenylphosphinoethane (dppe), **2**; diphenylphosphinopropane (dppp), **3**] complexes for MMA polymerization. We describe some of main features of this system, focusing on the influence of the diphosphine bite angle on the catalyst performance.

EXPERIMENTAL

Materials

All reactions were performed under a dry, oxygen-free, nitrogen atmosphere. ^{1}H NMR spectra were recorded at room temperature in CDCl$_3$ on a Bruker X-WIN spectrometer operating at 400 MHz with SiMe$_4$ (0.0 ppm) as internal reference. FT-IR spectra were recorded on a Jasco 300E spectrophotometer in CHCl$_3$ in the 4000–600 cm^{-1} range. Molecular weights and molecular weight distributions were determined by Knauer model gel permeation chromatograph (GPC) with CHCl$_3$ as eluents and calibration was conducted with polystyrene standards.

The compounds [Mo(CO)$_4$(dppm)], [Mo(CO)$_4$(dppe)] and [Mo(CO)$_4$(dppp)] were prepared using a procedure modified from the literature.[13] Solvents, carbontetrachloride, toluene,

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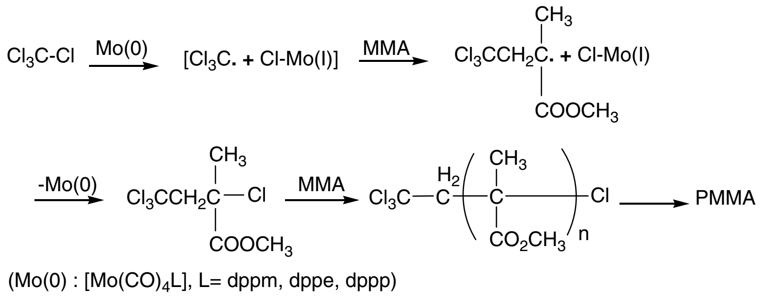

Figure 1. Transition metal-mediated radical polymerization of MMA with CCl_4 (initiator) and complexes **1, 2** and **3** (activator).

methanol and choloroform were used as supplied from Aldrich Chemical Company. MMA was dried over calcium hydride and distilled under vacuum at 35 mmHg.

Polymerization of MMA

The appropriate amount of complex were dissolved in carbontetrachloride–toluene (ratio as shown in Table 1) 5 ml in a Schlenk tube (50 ml) with a connection to a vacuum system. 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 pale yellow colour of the solution turned colourless. Addition of MeOH gave a dirty-white solid which was washed with H_2O, diethyl ether and dried *in vacuo*. The solid was redissolved in small amount of chloroform and filtered to remove metal residue. Addition of MeOH to filtrate gave poly(methyl methacrylate), which was dried in *vacuo* and characterized by ^1H NMR, FT-IR and GPC. IR: 1728 s $\nu(C{=}O)$, 1300–1100 s $\nu(C{-}O{-}O)$. ^1H NMR (400 MHz) $\delta = 0.78{-}1.15$ (br s, $-CH_3$), 1.75 (br s, $-CH_2$), 3.53 (s, $COO{-}CH_3$). The GPC results are shown in Table 1. To find the optimum values of polymerization conditions, the reaction was monitored by GPC.

Table 1. MMA polymerization[a] using **1–3** molybdenum complexes

Entry	Initiator	Solvent (CCl_4–toluene ratio, ml)	Complex (mol × 10^5)	Polymer yield (g)	($M_w{}^b$ ×10^{-3})	($M_n{}^b$ ×10^{-3})	$M_w/M_n{}^b$
1	**1**	1:4	6.8	45	36	21	1.7
2	**1**	1:4	13.6	52	55	38	1.5
3	**1**	1:4	20.4	63	72	45	1.6
4	**1**	1:4	27.2	78	85	53	1.6
5	**1**	2:3	6.8	51	82	48	1.7
6	**1**	2:3	13.6	64	33	17	1.9
7	**1**	2:3	20.4	75	30	14	2.1
8	**1**	3:2	6.8	63	98	78	1.3
9	**1**	3:2	13.6	75	37	23	1.6
10	**1**	3:2	20.4	84	43	28	1.5
11	**2**	1:4	6.8	36	29	14	2.1
12	**2**	1:4	13.6	44	35	60	1.7
13	**2**	1:4	20.4	55	63	36	1.8
14	**2**	1:4	27.2	60	81	45	1.8
15	**2**	2:3	6.8	37	35	16	2.2
16	**2**	3:2	6.8	45	49	26	1.9
17	**3**	1:4	6.8	7	23	15	1.5
18	**3**	1:4	13.6	13	25	15	1.7
19	**3**	1:4	20.4	19	32	19	1.7
20	**3**	1:4	27.2	24	35	22	1.6
21	**3**	2:3	6.8	9	28	17	1.7
22	**3**	3:2	6.8	11	28	19	1.5

[a] Polymerization conditions: [MMA] = 3.74 mol/l, at 80 °C for 24 h, N_2.
[b] Estimated by GPC on the basis of a polystyrene calibration.

DOI: 10.1002/aoc

RESULTS AND DISCUSSION

Preliminary experiments indicated that the single-component molybdenum tetracarbonyl bidentate phosphine complexes were completely inert to MMA. Then we used CCl_4 as initiator. CCl_4 alone was incapable of polymerizing MMA. Hence, our research was focused on the investigation of the polymerization of MMA. In the presence of CCl_4 the $[Mo(CO)_4(diphosphine)]$ compounds showed catalytic activity towards MMA polymerization. The highest yield of PMMA was lower than 90%.

The catalytic activity of complexes **1–3** was tested in CCl_4–toluene mixture in the absence of any cocatalyst. Table 1 summarizes the results of these reactions. After finding the optimum values of polymerization reactions, experiments were conducted for 24 h.

As can be seen in Table 1, the catalytic activities are strongly influenced by the size of the methylene spacer of the diphosphine ligands. Thus, in Fig. 2 the dppm complex **1** is significantly more active then dppe and dppp derivatives, **2** and **3**, respectively. This result is not entirely unexpected, as ligands with small bite angles have been found to give high activities in other polymerization systems.[10] The small bite angles as in complex **1** produce high M_w as determined by GPC, and complexes **2** and **3** produce low molecular weight polymer, as shown in Fig. 3.

The choice of solvent is very important. The polyhalogeno compounds such as CCl_4 are effective initiators because the electron withdrawing chlorine atoms activate the other C–X bonds by lowering the level of the lowest unoccupied molecular orbital, but there is the possibility that they may act as multifunctional initiators. The halogenated solvent gave best results.[1,8] This suggests that the metal carbonyl complexes are activated by the chlorine species provided by the CCl_4 solvent, as shown in Fig. 4.

The effect of the molar ratio [MMA]–[complex] is shown in Fig. 2; with the increase in catalyst amount, the monomer conversion rises gradually and reaches a peak value at [MMA] : [complex] 7.2×10^{-5} mol.

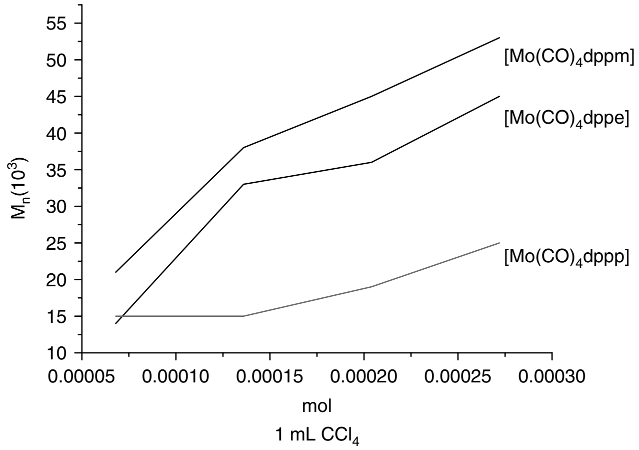

Figure 2. Effect of complex **1–3** and complex concentration on polymerization of MMA for entries 1–4, 11–14 and 17–20.

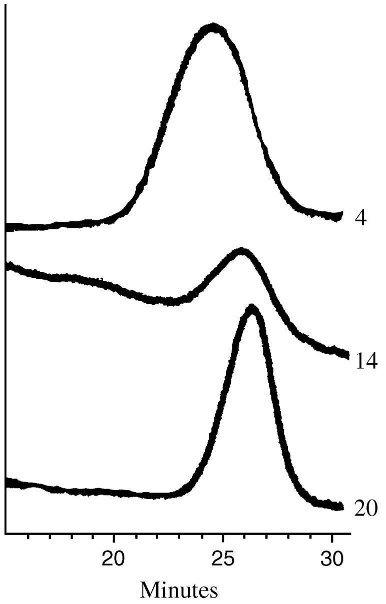

Figure 3. GPC spectra of PMMA for entries 4, 14 and 20.

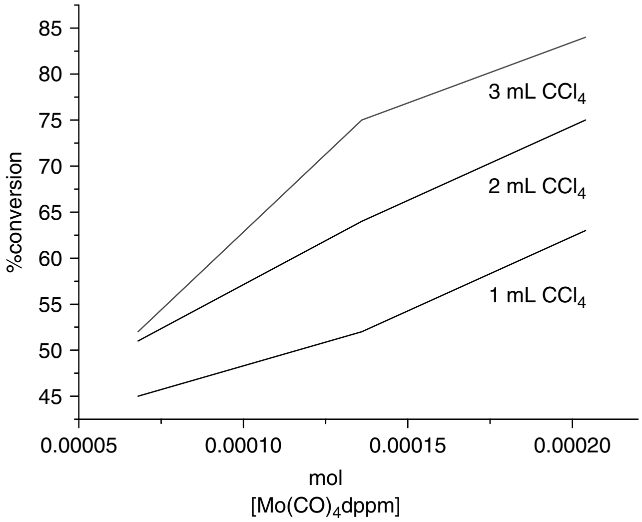

Figure 4. The effect of CCl_4 concentration on catalytic activity of compex **1** in MMA polymerization for entries 1–10. [MMA] = 3.74 mol/l, at 80 °C for 24 h, N_2, CCl_4–toluene, 5 ml.

The dependence of molecular weights of PMMA on polymerization time is shown in Fig. 5. Polymerization degrees (DP) of PMMA measured by GPC remained constant after about 10 h. GPC analysis of the PMMA showed that the polymer molecular weight distribution (MwD) was as narrow as 1.5 and the number-average molecular weights were 3.8×10^4 and 1.5×10^4 for entries 2 and 17 respectively.

The IR spectrum of PMMA showed strong peaks for C=O at 1729 cm^{-1} and C–O at 1147 cm^{-1} and medium

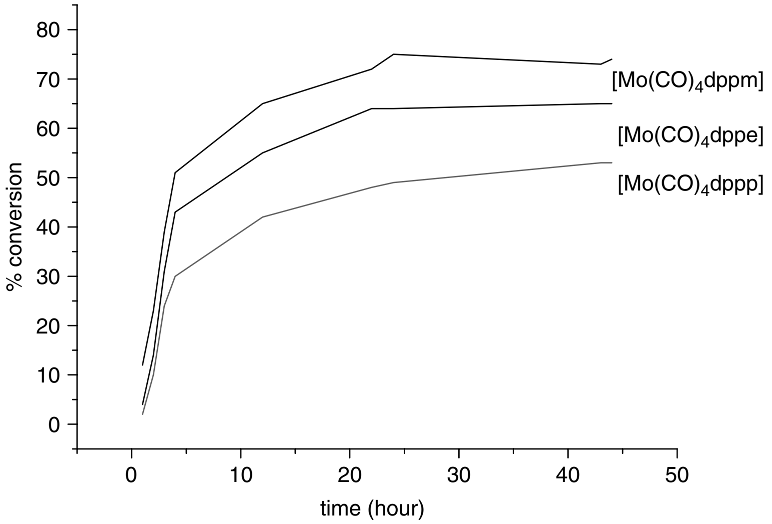

Figure 5. Plot of yields of PMMA versus reaction time. [Complex] = 6.8×10^{-5} mol, [MMA] = 3.74 mol/l, CCl_4–toluene (1 : 4) 5 ml, at 80 °C for 24 h, N_2.

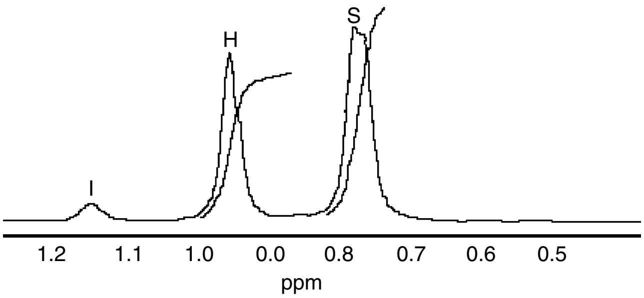

Figure 6. ^1H NMR spectrum of α-methyl protons region showing configuration-sensitive resonances of PMMA for entry 4.

peaks for C–H at 2952 cm^{-1}. A medium C=C peak at 1630 cm^{-1} was absent, indicating that the formation of polymer.

The ^1H NMR spectrum showed singlets at $\delta = 0.78–1.15$, $\delta = 1.75$ and $\delta = 3.53$ for methyl, ethylene and methoxy protons, respectively. PMMA has chiral centers which led to the formation of isotactic (I), syndiotactic (S) and atactic (H) stereoisomers that greatly influenced the mechanical properties. Therefore, the ^1H NMR spectrum was used for investigation of stereoregularity of the PMMA prepared.[14] The resonance peaks of CH_3 in Fig. 6 at 0.78, 0.95 and 1.15 ppm represent syndiotactic, atactic and isotactic polymers, respectively. The area under each of these peaks corresponds to the amount of each triad present in the polymer chain. This result shows that the content of syndiotactic PMMA was about 73%, which is in accordance with the results obtained from IR determination. GPC spectra, as shown in Fig. 3, indicated one peak. This suggests that the polymerization might be carried out with one active species.

CONCLUSIONS

Detailed study of factors such as the catalyst, catalyst concentration, the ratio of solvents, temperature and time influencing polymerization reaction indicated that the catalytic active species may be still somewhat stable at high temperature. Neither the blank experiment of CCl_4 nor the $[Mo(CO)_4(\text{dihosphine})]$ complexes (**1**–**3**) can initiate the MMA polymerization. The tacticity of PMMA can be calculated from the ^1H NMR spectrum of methylene region, showing about 73% syndiotactic content in the polymethyl methacrylate prepared.

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DOI: 10.1002/aoc