Note

A study of molybdenum catalysts in the polymerization of 2,5-didodecyl-1,4-dipropynylbenzene

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Abstract

The reaction of 2,5-didodecyl-1,4-dipropynylbenzene with different molybdenum sources ($Mo(CO)_6$, norbornadiene-$Mo(CO)_4$, cyclooctadiene-$Mo(CO)_4$, cycloheptatriene-$Mo(CO)_3$, $(PhC\equiv CPh)_3Mo(CO)$, $(acac)_2MoO_2/AlEt_3$) was investigated in the presence of 4-chlorophenol or 2-fluorophenol. Upon heating to 105–130 °C, the formation of didodecyl-PPE resulted. The degree of polymerization of the PPE is dependent on the used phenol and to the utilized molybdenum precursor. The most active catalyst forms from $(acac)_2MoO_2$, $AlEt_3$ and 2-fluorophenol. This catalyst combination gives high molecular weight PPEs after 6 h at 105 °C.
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1. Introduction

Homogeneous metathesis of disubstituted alkynes has been studied for a number of years [1] and acyclic diyne metathesis (ADIMET) is now a route to high molecular weight polymers [2]. In 1998 [2a], $Mo(CO)_6$/*p*-chlorophenol was reported to produce poly(*p*-phenyleneethynylene)s (PPEs, **2**). Other molybdenum complexes perform alkyne metathesis [3] as well, but there have been no systematic investigations in the effectiveness of these catalysts to form **2**. We compare the polymerization of 2,5-didodecyl-1,4-dipropynylbenzene (**1**) using: (a) $(\rangle C=C\langle)_n Mo(CO)_{6-n}$ (**3–5**) [3], (b) $MoO_2(acac)_2$/*n*$AlEt_3$ (**6**) [3] and (c) $Mo(CO)(tolane)_3$ (**7**) [4,5] (See Scheme 1).

2. Results and discussion

(a) The reactions of **1** with **3–5** [4,5] were carried out in *o*-dichlorobenzene with 4-chlorophenol as co-catalyst [2]. As the polymer formation progressed, samples were withdrawn and analyzed by NMR spectroscopy. The degree of polymerization (P_n) was calculated as the ratio of the integrated area of the methyl protons of the dodecyl substituents ($\delta = 0.92$) to the area of the methyl protons of the terminal propynyl groups ($\delta = 2.11$). This method of determining P_n is limited to the early stages of the reaction ($P_n < 500$) because in the larger chains the area under the terminal methyl groups cannot be measured with any degree of accuracy. A plot of P_n vs. time of representative runs with **3–5** respective is shown in Fig. 1. All three catalyst precursors show similar activity and produce PPEs **2** of similar P_n. How do **3–5** compare with $Mo(CO)_6$ [2]? When using small amounts of reactants (~0.5 mmol of **1** and co-catalyst, 5–10 mol% of catalyst), polymer formation was slower when using $Mo(CO)_6$ instead of **3–5**, and it was difficult

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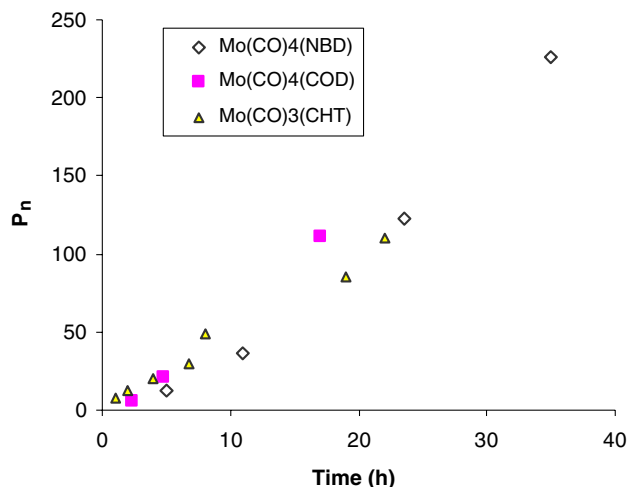*E-mail address:* uwe.bunz@chemistry.gatech.edu (U.H.F. Bunz).
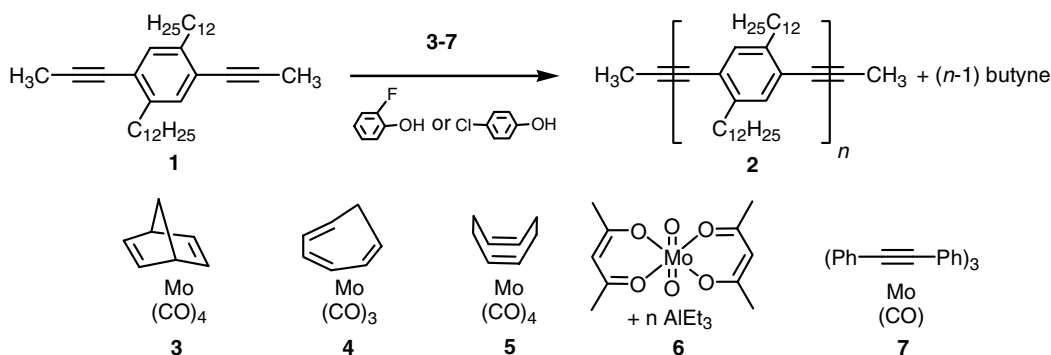
Scheme 1.

Fig. 1. Comparison of catalytic activity of **3**–**5** by degree of polymerization (P_n) of **2** vs. time. Reactants: monomer **1** (245 mg, 0.499 mmol); 4-chlorophenol (70 mg, 0.544 mmol); catalyst (15 mg, each of either **3**, **4** or **5**). Solvent: *o*-dichlorobenzene (4 mL).
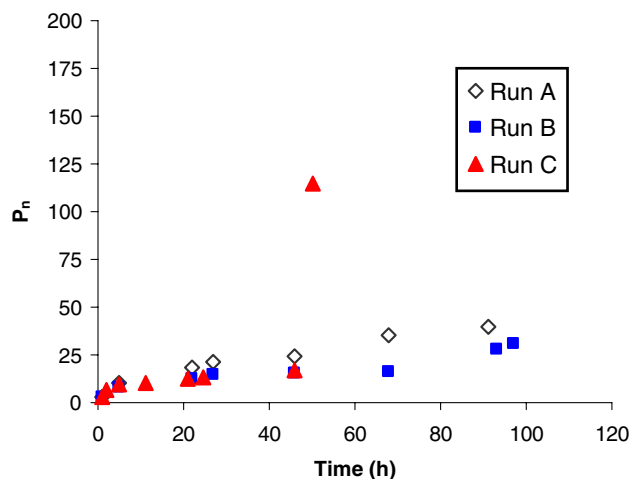

Fig. 2. Catalytic activity of $Mo(CO)_6$: degree of polymerization (P_n) vs. time. Reactants: monomer 1 (245 mg, 0.499 mmol), 4-chlorophenol (70 mg, 0.544 mmol), solvent: *o*-dichlorobenzene (4 mL). In run C additional $Mo(CO)_6$ was added after 40 h of reaction.

to obtain reproducible results. The cause for these inconsistencies may be the high volatility of the molybdenum hexacarbonyl. When nitrogen is passed over the heated reaction mixture to remove the formed butyne, much of the $Mo(CO)_6$ is swept into the condenser before the start of polymer formation (Fig. 2). Runs A and B were allowed to proceed for >90 h using 0.5 mmol of **1** plus co-catalyst and 10 mol% of $Mo(CO)_6$. In Run A, all of the components were combined prior to heating, while in Run B the catalyst was added after reaching the final reaction temperature. Run C was started using only 5 mol% of catalyst at ambient temperature and another 5 mol% was added after 46 h. The rate of polymerization increases dramatically if fresh catalyst is added partway through the reaction. It is not clear why polymer formation is more favorable if catalyst is added to the heated mixture in portions (C) instead of all at once (B).

Decrease in the rate of polymerization was less of a problem with **3**–**5**, but occasionally, in the later stages, rate decreases were observed and the reactions had to

be "revitalized" by adding more catalyst. Why did the slowdown occur with these much less volatile catalysts? A reason appears to be ligand exchange. Molybdenum hexacarbonyl as well as free olefins could be detected by NMR when heating d^4-*o*-dichlorobenzene solutions of **3**–**5** to above 115 °C. Volatile materials could be recovered from the condenser.

Another comparison of catalytic activity is shown in Fig. 3. Here reactions using 1 mmol of **1** with 1.1 mmol of 4-chlorophenol and a 10 mol% of either $Mo(CO)_6$ or **4**, were carried out in chlorobenzene at reflux (instead of *o*-dichlorobenzene at 135°) *without* the sweep of nitrogen. The rate of polymer formation is increased and the activity of $Mo(CO)_6$ is identical to that of **3**–**5**. The complexes **3**–**5** and $Mo(CO)_6$ are reservoirs for the catalytically active species. The lower volatility of **3**–**5** gives them an advantage when working in *o*-dichlorobenzene, but this advantage disappears when working in the lower boiling chlorobenzene under reflux.

(b) The $MoO_2(acac)_2/(1-10)AlEt_3$ combination **6** is a non-carbonyl-based alkyne metathesis system [3], much
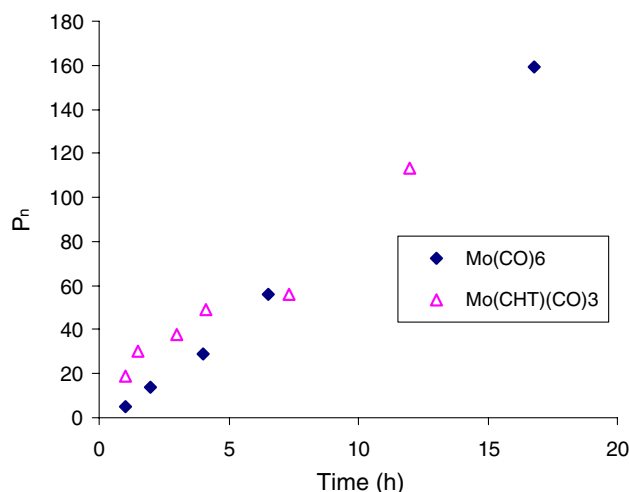
Fig. 3. Comparison of catalytic activity measured as degree of polymerization (P_n) vs. time. Reactants: monomer **1**, (490 mg 1.00 mmol); *p*-chlorophenol, (140 mg, 1.09 mmol); catalyst (Mo(CO)$_6$: 26 mg, 0.100 mmol; **4**: 27 mg, 0.100 mmol), solvent: chlorobenzene (5 mL).

more active than molybdenum hexacarbonyl or **3–5** in the presence of phenol. We evaluated the effectiveness of **6** in the formation of **2** in toluene solutions that were 0.1 M in monomer, 0.1 M in phenol and contained 1 mol % of catalyst with a 1/7 Mo/Al ratio. After ~24 h at 30° only **1** could be detected. A second portion of freshly made catalyst solution was added to the refluxing reaction mixture. Samples withdrawn and analyzed after three one-hour intervals showed P_n values of only 3.9, 5.1 and 6.1. Changing the co-catalyst from phenol to *p*-chlorophenol or *o*-fluorophenol [6] *caused a dramatic increase in the rate of polymer formation.* Table 1 shows a comparison in activity of the three co-catalysts that were used.

To obtain a direct comparison of **6** with **3–5**, we carried out the polymerization of **1** in concentrations comparable to those used in our earlier experiments. We found that when adding 10 mol% of **6** and a 1:2 ratio of **1** to *o*-fluorophenol [7] in refluxing toluene, PPE **2** with a $P_n > 400$ resulted.

(c) The third catalyst type, **7**, promotes the formation of oligomers from **1** ($P_n < 33$) but it is less effective than

3–6. Like **3–5**, **7** loses carbon monoxide when heated to 100–120 °C in the absence of monomer, but unlike **3–5**, it does not generate detectable amounts of molybdenum hexacarbonyl. We could not identify individual components of the complex mixture that **7** generates upon heating.

3. Summary and conclusions

The catalytic activity of **3–7** is summarized in Table 2. The three examined types of Mo-catalysts exhibit a wide range of activity in the formation of **2**. Catalysts **3–5** and Mo(CO)$_6$ are of about equal activity [2]. In view of the observed ligand exchange reactions (vide supra), we presume that the active ingredient(s) is (are) the same in these four catalysts. The non-carbonyl-based catalyst **6** is the most active one. When carrying out the polymerization with a 10 mol% of **6**, **2** of $P_n = \sim 420$ was isolated after 6 h in refluxing toluene, compared to $P_n = \sim 30$ with catalysts **3–5** after 6 h at 135° in *o*-dichlorobenzene. However, even with this catalyst, a higher temperature was required to polymerize **1** (~110 °C) than was used by Mortreux [3] to carry out the metathesis of nonyne (30 °C). Dialkyldipropynylbenzenes are sluggish substrates and require heating even with Schrock tungsten carbynes [9,10]. An advantage of **6**, compared to that of the molybdenum carbonyl complexes, is its lack of volatility, making it possible to remove butyne without the loss of catalyst. A disadvantage of catalyst **6** is its lack of stability. Unlike catalysts **3–5**, which could be stored for several months in the refrigerator, MoO$_2$(acac)$_2$/7AlEt$_3$/toluene deteriorates quickly. Of the investigated catalysts, **7** is the least active and it does not have any advantage over **3–6**. The most active and promising catalyst is the combination of acac$_2$MoO$_2$ (**6**) with Grela's 2-fluorophenol [6].

In conclusion, we have found **6** in combination with 2-fluorophenol effectively generates PPEs from **1**. Our findings will add some insight to the, as yet unresolved, question regarding the exact mechanism of these reactions. The increased activity of **6**/2-fluorophenol is promising.

Table 1
Polymerization of **1** with O$_2$Mo(acac)$_2$/7 equivalents AlEt$_3$ as catalyst in toluene as solvent

Temperature (°C)	Time (h)	P_n		
		Phenol[a]	*p*-Chlorophenol[a]	*o*-Fluorophenol[a]
30	~24	1	1	1
Reflux, 105 °C	1[b]	1.2	2.3	2.4
Reflux, 105 °C	2	3.9	26	23
Reflux, 105 °C	3	5.1	52	69
Reflux, 105 °C	4	6.1	65	127

A comparison of the activity of different co-catalysts.
[a] Co-catalyst.
[b] Fresh catalyst was added after the first hour.

Table 2
The polymerization of 2,5-didodecyl-1,4-dipropynylbenzene 1

Catalyst	Wt Monomer (mg)	Conc. Monomer (mmol/mL)	Conc. Cocat. (mmol/mL)	Mol% Cat.	Time (h)	Temp. (°C)	P_n	Solvent
3	245	0.125	0.137	10	20	135	120[a]	$o\text{-}C_6H_4Cl_2$
5	245	0.125	0.137	10	20	135	120[a]	$o\text{-}C_6H_4Cl_2$
4	245	0.125	0.137	10	20	135	120[a]	$o\text{-}C_6H_4Cl_2$
4[c]	490	0.2	0.22	10	15	132	130[c]	C_6H_5Cl
$Mo(CO)_6$[b]	490	0.2	0.22	10	15	132	140[c]	$o\text{-}C_6H_4Cl_2$
$MoO_2(acac)_2$ 7AlEt_3	245	0.125	0.274	10	6	110	420	$C_6H_5CH_3$
7	470	0.12	0.125	5	20	140	33	$o\text{-}C_6H_4Cl_2$

[a] These values were read off the combined plots in Fig. 1.
[b] These runs were carried out at reflux without N_2 being passed over the solution.
[c] These values were read off the plots in Fig. 3.

4. Experimental section

4.1. Catalysts

Catalysts **3**–**5** and **7** were prepared as reported [3,4,8]. $MoO_2(acac)_2/7Al(Et)_3$ (**6**) [3] was prepared by adding a 1.9 M toluene solution of triethylaluminum (Aldrich) to a stirred solution of $MoO_2(acac)_2$ (Acros Organics) in freshly distilled toluene. All operations were carried out under a nitrogen atmosphere; **6** deteriorates at ambient temperature but remains active for ~3–4 h at 0 °C.

4.2. Polymerization of 1 with catalysts 3–5 in o-dichlorobenzene solution

Stirred solutions of 245 mg (0.500 mmol) **1**, 70 mg (0.544 mmol) of 4-chlorophenol and 15 mg of **3**, **4** or **5** and 4 mL of o-dichlorobenzene were heated under a slow stream of nitrogen at 135 °C in 50-mL side-arm flasks. Small samples (~0.1 mL) were periodically withdrawn by syringe, under a back flush of nitrogen, combined with 0.5 mL of $CDCl_3$ in a 5-mm tube and analyzed by ^1H NMR on a Bruker AM 300 MHz or a Varian Mercury 400 MHz spectrometer. The number of monomeric units incorporated in the polymer chain was calculated as the ratio of the integrated areas of the methyl protons of the dodecyl substituents to the methyl protons of the terminal propynyl groups. In the later stages of the reactions, special care had to be taken to measure the area of the methyl end groups with any degree of accuracy. Spectra were recorded after 64 scans, with a one-second pulse delay. The area of the terminal methyl signals was taken as one tenth of the measured (not printed) value of the integral step with the amplitude set to 10 times higher than was used to measure the area of the dodecyl methyls. The values recorded in Table 2 are accurate within ~10%.

Reactions were discontinued when **2** began to separate from the solution. A 5–10 mL portion of solvent was added to the reaction mixture, heated to dissolve **2** and filtered through a plug of cotton. The filtrate was stirred consecutively with 5 mL of 10% aqueous sodium hydroxide for 7 h, washed with water and stirred with 10 mL of 25% HCl. Precipitation into methanol, filtration and drying furnished **2** [2b].

4.3. Polymerization of 1 with 4 and 5 in chlorobenzene solution

Stirred solutions of 490 mg (0.998 mmol) of **1**, 140 mg (1.09 mmol) of p-chlorophenol and 28 mg (0.104 mmol) of **4** or 26 mg (0.0828 mmol) of **5** in 5 mL of chlorobenzene (50-mL side-arm flasks) were flushed with nitrogen and heated to reflux. Samples of **2** were withdrawn, analyzed by ^1H NMR and **2** was isolated (see Section 4.2).

4.4. Polymerization of 1 with catalyst 6 in toluene solution

To stirred solutions of 245 mg (0.500 mmol) of **1** and ~0.55 mmol of co-catalyst (phenol, p-chlorophenol or o-fluorophenol) in 4.5 mL of toluene (freshly distilled from calcium hydride) was added to 0.5 mL of a toluene solution containing 0.005 mmol of **6**. The mixtures were kept overnight at 30 °C under a steady stream of nitrogen. Small samples (~0.1 mL) were withdrawn from each, combined with ~2 mL of methanol and the product was extracted with chloroform and dried under vacuum. The reaction temperature was next increased to reflux. Samples were removed after 1 h and worked up (see Section 4.2). Freshly prepared catalyst (0.5 mL, 0.005 mmol) was added to each solution and samples were withdrawn after three additional one-hour periods (Table 1). In a second experiment, a mixture of 245 mg (0.499 mmol) of **1**, 140 mg (1.09 mmol) of o-fluorophenol and 1 mL of toluene was combined with 3 mL of **6** (0.05 mmol) and heated to reflux under nitrogen. Intermittently samples were withdrawn and **2** was isolated and analyzed.

4.5. Polymerization of 1 with 7 in o-dichlorobenzene

This reaction was carried out at 140 °C, under a stream of nitrogen, using 470 mg (0.957 mmol) of **1**,

128 mg (1.00 mmol) of *p*-chlorophenol and 33 mg (0.0501 mmol) of **7**. After 20 h, the reaction mixture was worked up (Section 4.2) to yield 370 mg (86%) of **2**, P_n = 33 (^{1}H NMR).

4.6. Thermal stability of catalysts 3–5

Solutions containing 25–30 mg of **3–5** in 0.8 mL of d^4-*o*-dichlorobenzene each were analyzed by ^{13}C NMR with the probe temperature gradually being raised, in 20° increments, from 25–105 °C, and finally maintained at 115–120° for 2.5–3 h. Spectra were recorded (256 scans, 3-s pulse delay) after each temperature increase and at ambient temperature after the completion of a run. Ligand exchange was detected by the appearance of signals that could be assigned to molybdenum hexacarbonyl (δ = 201.4 ppm) and to decomplexed alkenes; **5** was found to be the most stable. When heating **5**, traces of Mo(CO)$_6$ appeared only after 2.5 h at 120°, while **3** and **4** started decomplexation at temperatures as low as 65–85°.

Acknowledgments

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