

Living polymerization of several substituted acetylenes by CpMoCl₄-based catalysts

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Dedicated to Professor Imanishi on the occasion of his retirement

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Abstract

[(*o*-Trifluoromethyl)phenyl]acetylene polymerized in a living fashion in the presence of CpMoCl₄-cocatalyst–EtOH catalysts (Cp: cyclopentadienyl; cocatalyst: EtMgBr, Et₃Al, *n*-BuLi). The CpMoCl₄–EtMgBr–EtOH (1:2:2) catalyst was particularly effective, with which the M_w/M_n of the formed polymer and the initiation efficiency, $[P^*]/[Cat]$, were 1.06 and 7.6%, respectively. Further, $[P^*]/[Cat]$ increased up to 10–13% at low temperatures (e.g. 0 °C) of catalyst aging and monomer addition. [(*o*-Trimethylsilyl)phenyl]acetylene also provided polymer having narrow molecular weight distributions with CpMoCl₄–EtMgBr–EtOH (1:2:2). CpMoCl₄ was more stable to air and moisture than MoOCl₄ owing to the steric and electronic effects of the Cp ligand, while the activity of the CpMoCl₄-based catalysts were lower than that of the MoOCl₄-based counterparts. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Substituted acetylene; Molybdenum catalyst; Living polymerization

1. Introduction

Polymerization of substituted acetylenes with group 5, 6 transition metal (Mo, W, Ta, Nb) catalysts is known to proceed by metathesis mechanism, whereas that with Rh catalysts is explained in terms of the insertion mechanism [1–4]. Living polymerization of several substituted acetylenes has been achieved, examples of which include (monomer/catalyst): 2-butyne/Schrock's Ta carbene [5], ethynylferrocene [6], α,ω -diyne [7] and *ortho*-substituted phenylacetylenes [8]/Schrock's Mo carbenes, and phenylacetylene/Rh catalysts [9–12].

We have found that MoOCl₄-cocatalyst–EtOH (cocatalyst: *n*-Bu₄Sn [13], Et₃Al [14], Et₂Zn [15], *n*-BuLi [16], etc.) systems serve as living polymerization catalysts for a number of substituted acetylenes such as *ortho*-substituted phenylacetylenes [17], 1-chloro-1-alkynes [17], 1-chloro-2-phenylacetylene [18], *t*-butylacetylene [19], and linear internal alkynes [20]. As shown before, many organometallic cocatalysts have been developed for this MoOCl₄-based catalyst. On the other hand, only MoOCl₄ and WOCl₄ [21] have been known as the main catalyst components.

In this study, we investigated the development of novel

living polymerization catalysts using CpMoCl₄ (Cp: cyclopentadienyl) as main catalyst component. It is very interesting to examine how CpMoCl₄ behaves as a main catalyst component compared to MoOCl₄. [(*o*-Trifluoromethyl)phenyl]acetylene (*o*-CF₃PA) and other substituted acetylenes were used as monomers. Steric and electronic effects of Cp ligand on polymerization were examined.

2. Experimental

o-CF₃PA [22,23], [(*o*-trimethylsilyl)phenyl]acetylene (*o*-Me₃SiPA) [22,23], (*o*-methylphenyl)acetylene (*o*-MePA) [22,23], 1-chloro-2-phenylacetylene [22,24], 1-chloro-1-octyne [24] and *t*-butylacetylene [25] were prepared as described in the literature and distilled twice from CaH₂ at reduced pressure before use. 2-Nonyne (Lancaster) was distilled twice from CaH₂ at reduced pressure. CpMoCl₄ (Strem) and cocatalysts (Kanto Chemical) were commercially obtained and used without further purification. Anisole as polymerization solvent was washed with aqueous sodium hydroxide solution (5%) and water successively, dried over anhydrous calcium chloride, and distilled twice from sodium metal [purity > 99.9% by gas chromatography (GC)]. Oxygen- or nitrogen-containing compounds as third catalyst components were distilled and stored as anisole solution. All the procedures of catalyst preparation and

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Table 1

Effect of cocatalysts on the polymerization of *o*-CF₃PA by CpMoCl₄-based catalysts (polymerized in anisole at 30 °C for 24 h; [CpMoCl₄] = 10 mM, [M]₀ = 100 mM)

Catalyst (mole ratio)	Conversion ^a (%)	M_n^b	M_w/M_n^b	[P*]/[Cat] (%)
CpMoCl ₄	58	428,000	1.84	–
CpMoCl ₄ - <i>n</i> -Bu ₄ Sn (1:1)	100	176,000	2.45	–
CpMoCl ₄ -Et ₂ Zn-EtOH (1:1:3)	60	92,000	1.33	–
CpMoCl ₄ -EtMgBr-EtOH (1:2:2) ^c	99	22,000	1.06	7.6
CpMoCl ₄ -Et ₃ Al-EtOH (1:1:4)	99	104,000	1.05	1.6
CpMoCl ₄ - <i>n</i> -BuLi-EtOH (1:1:1)	100	207,000	1.04	0.8

^a Determined by GC.

^b Determined by GPC using a polystyrene calibration.

^c Polymerized for 100 h.

polymerization were carried out under dry nitrogen. Unless otherwise stated, catalyst solutions were prepared as follows: an anisole solution of CpMoCl₄ and an anisole solution of cocatalyst were mixed, and the mixture was aged at room temperature for 15 min. When necessary, an anisole solution of third catalyst component was further added to the CpMoCl₄-cocatalyst solution, and the mixture was aged at room temperature for an additional 15 min. Polymerizations were carried out in a pre-baked Schlenk tube equipped with a three-way stopcock; the concentrations of CpMoCl₄ and monomer were 10 and 100 mM, respectively. Polymerizations were quenched by adding EtOH. Monomer conversions were determined by GC. The polymerization mixture was washed with 5% hydrochloric acid and then with water, and subsequent evaporation of volatile materials afforded the polymer. Polymer yields were determined by gravimetry. The monomer conversion and the polymer yield agreed well. The molecular weight distributions (MWD) of polymers were recorded on a gel permeation chromatograph (GPC) (Jasco PU930; eluent chloroform; Shodex K805, 804, 803 polystyrene gel columns; RI detector). The number- and weight-average molecular weights (M_n and M_w , respectively) of polymers were determined by using a polystyrene calibration. Initiation efficiencies ([P*]/[Cat]; where [P*] and [Cat] are the concentrations of the propagating species and CpMoCl₄, respectively) were calculated from the polymer yield and the degree of polymerization of polymers.

3. Results and discussion

Effects of cocatalysts and third catalyst components on the polymerization of *o*-CF₃PA by CpMoCl₄-based catalysts were examined (Table 1). When EtMgBr, Et₃Al and *n*-BuLi were used as cocatalysts, the MWDs of the formed polymers narrowed. In contrast, narrow MWD ($M_w/M_n \leq 1.1$) was not attained with *n*-Bu₄Sn and Et₂Zn, which are useful cocatalysts in the case of MoOCl₄-based catalysts [13,15]. Since the Cp ligand is bulky and electron-donating, it seems that CpMoCl₄ requires stronger alkylating agents as compared to MoOCl₄. Among EtMgBr, Et₃Al and *n*-BuLi,

which proved effective as cocatalysts of CpMoCl₄-based catalysts, EtMgBr achieved the highest initiation efficiency (7.6%) in the present system, although it is ineffective as cocatalyst of MoOCl₄-based catalyst [13].

The effect of EtMgBr concentration was examined (Fig. 1). When EtOH as third catalyst component was not added, the initiation efficiency was 6.1% and the highest at [EtMgBr]/[CpMoCl₄] = 2, i.e. [EtMgBr] = 20 mM, while the M_w/M_n was smaller and 1.04 at [EtMgBr]/[CpMoCl₄] = 1. The effect of EtOH was next examined with a fixed ratio of [EtMgBr]/[CpMoCl₄] = 2 (Fig. 2). The initiation efficiency took a maximum around [EtOH]/[CpMoCl₄] = 1–4, while the M_w/M_n gradually decreased with increasing

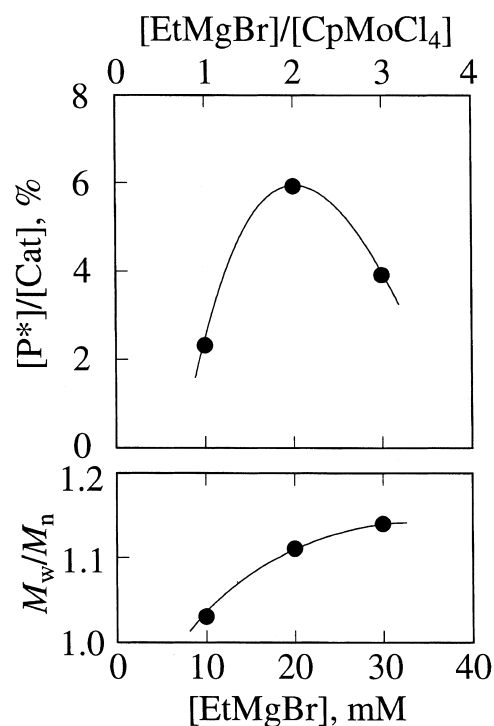


Fig. 1. Effect of [EtMgBr] on the polymerization of *o*-CF₃PA by CpMoCl₄-EtMgBr (1:*X*) (polymerized in anisole at 30 °C; [CpMoCl₄] = 10 mM, [M]₀ = 100 mM).

Table 2

Effect of the third catalyst components (X) on the polymerization of *o*-CF₃PA by CpMoCl₄-EtMgBr-X (1:2:2) (polymerized in anisole at 30 °C; [CpMoCl₄] = 10 mM, [M]₀ = 100 mM)

X	Time (h)	Conversion ^a (%)	M_n^b	M_w/M_n^b	[P*]/[Cat] (%)
None	100	97	23,100	1.11	6.1
MeOH	48	72	16,300	1.06	7.5
EtOH	100	99	22,000	1.06	7.6
CF ₃ CH ₂ OH	100	96	37,100	1.08	4.4
<i>i</i> -PrOH	48	41	300	–	–
<i>t</i> -BuOH	48	37	400	–	–
C ₂ H ₅ CHO	48	48	18,600	1.07	4.3
CH ₃ COOH	48	86	44,200	1.05	3.3
Pyridine	100	9	300	–	–

^a Determined by GC.

^b Determined by GPC using a polystyrene calibration.

[EtOH] to become ca. 1.05 at [EtOH]/[CpMoCl₄] = 2–5. As seen in Table 2, not only EtOH but also sterically uncrowded alcohols (MeOH, CF₃CH₂OH) and some carbonyl compounds (propanal, acetic acid) tend to decrease the M_w/M_n value to 1.05–1.07 (cf. 1.11 without a third catalyst component). However, the initiation efficiencies remained ca. 3–7% irrespective of the presence or absence of these third catalyst components. In contrast, use of sterically crowded alcohols (*i*-PrOH, *t*-BuOH) and amines (pyridine, aliphatic amines) remarkably retarded or completely inhibited the present polymerization. Thus it can be said that the CpMoCl₄-EtMgBr-EtOH (1:2:2) system is particularly effective to achieve narrow MWD in the polymerization of *o*-CF₃PA.

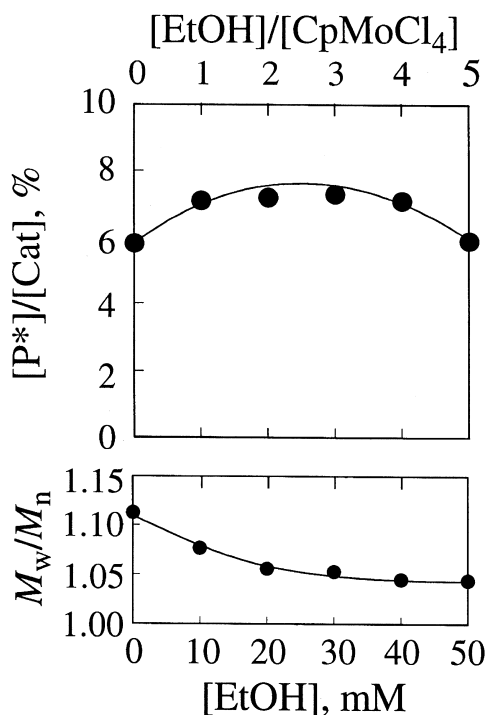


Fig. 2. Effect of [EtOH] on the polymerization of *o*-CF₃PA by CpMoCl₄-EtMgBr-EtOH (1:2:X) (polymerized in anisole at 30 °C; [CpMoCl₄] = 10 mM, [M]₀ = 100 mM).

The living nature of the present polymerization system was examined. As seen in Fig. 3, the logarithmic [M]₀/[M] increases in direct proportion to the polymerization time. This indicates that the polymerization is of first order with respect to the monomer concentration, while the concentration of the propagating species remains constant. Fig. 4 shows that, in multistage polymerization, the M_n of polymer increases in proportion to the monomer consumptions, while the polydispersity remains about 1.06. These results verify that this polymerization is a living polymerization.

The effect of temperature was examined (Table 3). T_1 , T_2 and T_3 denote the temperatures of catalyst aging, monomer addition (for the period from 10 min before and 5 min after the monomer addition), and polymerization (for the period of 5 min after the monomer addition and until quenching), respectively. When only either T_1 or T_2 was 0 °C, the initiation efficiency was similar to that for room temperature (runs 1–3). In contrast, when both T_1 and T_2 were 0 °C, the initiation efficiency increased up to 10–13% (runs 4–6). This is probably because the deactivation of active species is restrained at low temperature. The polydispersity ratio did not depend on T_3 very much.

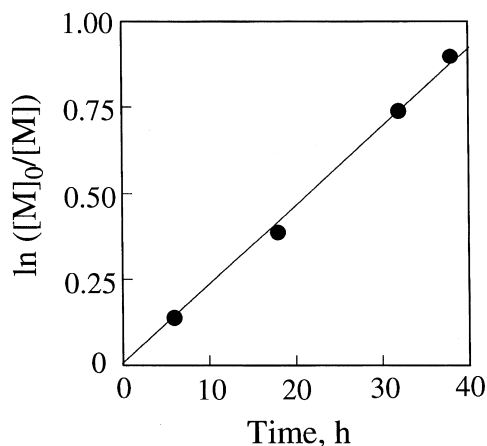


Fig. 3. First-order plot for the polymerization of *o*-CF₃PA by CpMoCl₄-EtMgBr-EtOH (1:2:2) (polymerized in anisole at 30 °C; [CpMoCl₄] = 10 mM, [M]₀ = 100 mM).

Table 3

Effect of temperature on the polymerization of *o*-CF₃PA by CpMoCl₄-EtMgBr-EtOH (1:2:2) (polymerized in anisole; [CpMoCl₄] = 10 mM, [M]₀ = 100 mM; all conversions were 100%)

Run	T ₁ ^a (°C)	T ₂ ^a (°C)	T ₃ ^a (°C)	Time (h)	M _n ^b	M _w /M _n ^b	[P*]/[Cat] (%)
1	r.t.	r.t.	30	100	22,000	1.06	7.6
2	r.t.	0	60	20	25,000	1.09	6.8
3	0	60	60	20	26,000	1.07	6.5
4	0	0	30	95	16,000	1.06	10.6
5	0	0	60	20	16,000	1.09	10.6
6	0	0	0	30 × 24	13,000	1.12	13.1

^a T₁, T₂ and T₃ denote the temperatures of catalyst aging, monomer addition and polymerization, respectively.

^b Determined by GPC using a polystyrene calibration.

Table 4

Polymerization of several substituted acetylenes by CpMoCl₄-EtMgBr-EtOH (1:2:2) (polymerized in anisole at 30 °C; [CpMoCl₄] = 10 mM, [M]₀ = 100 mM)

Monomer	Time (h)	Conversion ^a (%)	M _n ^b	M _w /M _n ^b	[P*]/[Cat] %
<i>o</i> -CF ₃ PA	100	100	22,000	1.06	7.6
<i>o</i> -Me ₃ SiPA	96	100	34,000	1.07	5.1
<i>o</i> -MePA	24	100	28,000	1.30	–
1-Chloro-1-octyne	72	15	–	–	–
1-Chloro-2-phenylacetylene	72	10	–	–	–
<i>t</i> -Butylacetylene	72	98	194,000	4.19	–
2-Nonyne	100	90	95,000	1.95	–

^a Determined by GC.

^b Determined by GPC using a polystyrene calibration.

Polymerization of several substituted acetylenes was examined by using CpMoCl₄-EtMgBr-EtOH (1:2:2) (Table 4). When *o*-Me₃SiPA, another phenylacetylene with a bulky *ortho* substituent, was employed, polymer

having narrow MWD was obtained. However, none of *o*-MePA, *t*-butylacetylene and 2-nonyne provided polymers with narrow MWD. Further, 1-chloro-1-octyne and 1-chloro-2-phenylacetylene formed no methanol-insoluble polymer, which is attributable to rather low activity of the present catalyst.

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References

- [1] Harrell KJS, Nguyen ST. *Handb Adv Electron Photonic Mater Devices* 2001;8:131.
- [2] Choi S-K, Gal Y-S, Jin S-H, Kim HK. *Chem Rev* 2000; 100:1645.
- [3] Tabata M, Sone T, Sadahiro Y. *Macromol Chem Phys* 1999;200:265.
- [4] Shirakawa H, Masuda T, Takeda K. In: Patai S, editor. *The chemistry of triple-bonded functional groups*, Suppl. C2. Chichester: Wiley, 1994. p. 945.
- [5] Wallace LC, Liu AH, Davis WM, Schrock RR. *Organometallics* 1989;8:644.
- [6] Buchmeiser M, Schrock RR. *Macromolecules* 1995;28:6642.

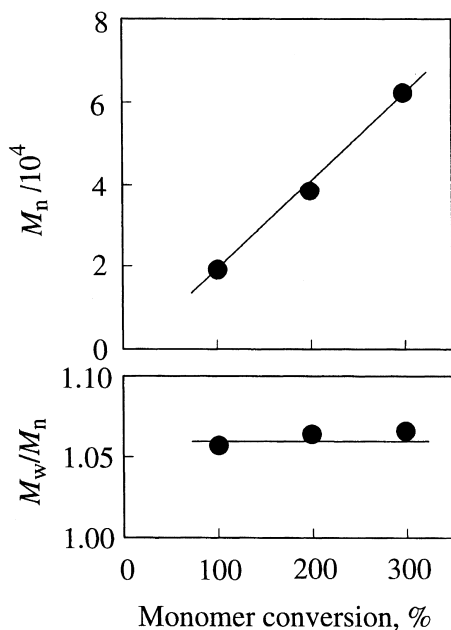


Fig. 4. Multistage polymerization of *o*-CF₃PA by CpMoCl₄-EtMgBr-EtOH (1:2:2) (polymerized in anisole at 30 °C; [CpMoCl₄] = 10 mM, [M]₀ = [M]_{added} = 100 mM).

- [7] Fox HH, Wolf MO, O'Dell R, Lin BL, Schrock RR, Wrighton MS. *J Am Chem Soc* 1994;116:2827.
- [8] Schrock RR, Luo S, Lee JC, Zanetti N, Davis WM. *J Am Chem Soc* 1996;118:3883.
- [9] Kishimoto Y, Eckerle P, Miyatake T, Ikariya T, Noyori R. *J Am Chem Soc* 1994;116:12131.
- [10] Kishimoto Y, Miyatake T, Ikariya T, Noyori R. *Macromolecules* 1996;29:5054.
- [11] Misumi Y, Masuda T. *Macromolecules* 1998;31:7572.
- [12] Miyake M, Misumi Y, Masuda T. *Macromolecules* 2000;33:6636.
- [13] Hayano S, Itoh T, Masuda T. *Polymer* 1999;40:4071.
- [14] Kaneshiro H, Hayano S, Masuda T. *Polym J* 1999;31(4):348.
- [15] Hayano S, Masuda T. *Macromol Chem Phys* 1997;198:3041.
- [16] Hayano S, Masuda T. *Macromolecules* 1998;31:3170.
- [17] Hayano S, Masuda T, Iwawaki E, Nomura R. *J Mol Cat A Chem* 1998;133:213.
- [18] Hayano S, Masuda T. *J Macromol Sci, Pure Appl Chem* 2000;A37(8):853.
- [19] Nakano M, Masuda T, Higashimura T. *Macromolecules* 1994;27:1344.
- [20] Kubo H, Hayano S, Masuda T. *J Polym Sci, Part A Polym Chem* 2000;38:2697.
- [21] Hayano S, Masuda T. *Macromolecules* 1999;32:7344.
- [22] Brandsma L, Hommes H, de Jong RLP, Verkrujisse HD. *Recl Trav Chim Pays-Bas* 1985;104:226.
- [23] Sonogashira K, Tohda Y, Hagihara N. *Tetrahedron Lett* 1975;50:4467.
- [24] Brown HC. *Organic syntheses via boranes*. New York: Wiley/Interscience, 1975. p. 184.
- [25] Okano Y, Masuda T, Higashimura T. *J Polym Sci, Part A Polym Chem* 1987;25:1181.