Living metathesis polymerization of (*p-n*-butyl-*o,o,m,m*-tetrafluorophenyl)acetylene by MoOCl₄–*n*-Bu₄Sn–EtOH (1:1:1)

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SUMMARY

Possibility of living metathesis polymerization by Mo catalysts was examined for (*p-n*-butyl-*o,o,m,m*-tetrafluorophenyl)acetylene, which has two fluorine atoms at both ortho positions. The MoOCl₄–*n*-Bu₄Sn–EtOH (1:1:1) catalyst yielded a polymer with narrow molecular weight distribution ($\bar{M}_w/\bar{M}_n$ = 1.12), but the corresponding MoCl₅-based catalyst did not formed such a polymer. With the former catalyst, the number-average molecular weight of polymer increased in direct proportion to monomer conversion, while the molecular weight distribution remained narrow; this proves the livingness of the polymerization. The optimal conditions for the living polymerization were [*n*-Bu₄Sn]/[MoOCl₄] = ~1.0, [EtOH]/[MoOCl₄] = 0.5–1.5, and temperature ≤ 30 °C. *n*-Butyl acetate and acetone as well as EtOH were effective as third catalyst components.

INTRODUCTION

It is known that phenylacetylene (PA) which has no substituent at the ortho position does not form a high molecular weight polymer in the presence of W and Mo catalysts (1). In contrast, PAs with bulky *ortho*-substituents (e.g., *o*-CF₃PA, *o*-Me₃SiPA, and *o*-Me₃GePA) yield high molecular weight polymers ($\bar{M}_w$ > 1x10⁶) (2-4). (*p-n*-Butyl-*o,o,m,m*-tetrafluorophenyl)-acetylene (*p*-BuF₄PA), which carries two electron-withdrawing fluorine atoms at both ortho positions, also forms a high molecular weight polymer (5).

Thus far only a few reports have appeared regarding living polymerization of substituted acetylenes (6-9). In our previous papers, we have clarified that the MoOCl₄(or MoCl₅)–*n*-Bu₄Sn–EtOH catalysts induce the living polymerization of *o*-CF₃PA (8), *o*-Me₃SiPA (9), and *o*-Me₃GePA (4). In contrast, PA itself does not polymerize in a living fashion with this catalyst. It suggests that side reactions such as chain transfer readily occur if there is no *ortho*-substituent. In the present

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study, we investigated whether *p*-BuF4PA, an *ortho*-substituted PA, would polymerize in a living manner with the Mo-based ternary catalysts.

EXPERIMENTAL

Materials

The main catalysts (MoOCl4 and MoCl5; from Strem; purities >99%) and organometallic cocatalysts were commercially obtained and used without further purification. Toluene as polymerization solvent and oxygen-containing compounds were purified according to standard methods (10). The monomer was synthesized as follows (11, 12):
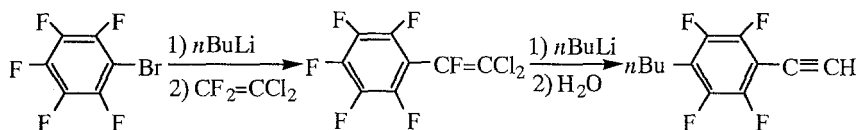
Polymerization

Binary catalysts (MoOCl4–*n*-Bu4Sn and MoCl5–*n*-Bu4Sn) were prepared under a dry nitrogen atmosphere by mixing the two components at a 1:1 ratio in toluene followed by aging at 30 °C for 15 min. Ternary catalysts (MoOCl4–*n*-Bu4Sn–EtOH and MoCl5–*n*-Bu4Sn–EtOH) were obtained by addition of an equimolar amount of third component (oxygen-containing compound) to the above-stated mixtures followed by aging at 30 °C for another 15 min. Polymerizations were initiated by adding the monomer solution to the catalyst solution, and quenched by adding a small amount of methanol to the polymerizing system. The formed polymers were isolated by precipitation into methanol, and their yields were determined by gravimetry.

Monomer conversions were determined by gas chromatography, and number- and weight-average molecular weights ($\bar{M}_n$ and $\bar{M}_w$, respectively) of the polymers were determined by gel permeation chromatography (GPC; polystyrene calibration). The initiator efficiency was evaluated by the mole ratios of the propagating species to molybdenum chlorides ([P*]/[Cat]).

RESULTS AND DISCUSSION

Polymerization by MoOCl4- and MoCl5-based catalysts

Figure 1 shows GPC charts and polydispersity ratios ($\bar{M}_w/\bar{M}_n$) for the poly(*p*-BuF4PA)s obtained with MoOCl4- and MoCl5-based catalysts. The polymers formed with MoOCl4 alone and MoOCl4–*n*-Bu4Sn catalysts exhibited broad molecular-weight distributions (MWDs) (1.6 – 1.9). In contrast, the polymer produced with MoOCl4–*n*-Bu4Sn–EtOH ($\bar{M}_n$ =
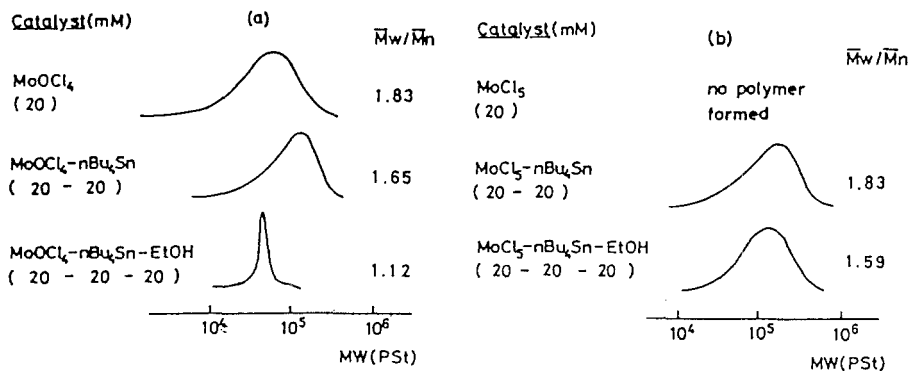
Catalyst(mM) (a) $\overline{M}_w/\overline{M}_n$ Catalyst(mM) (b) $\overline{M}_w/\overline{M}_n$

MoOCl$_4$ (20)   1.83   MoCl$_5$ (20)   no polymer formed

MoOCl$_4$-nBu$_4$Sn (20 - 20)   1.65   MoCl$_5$-nBu$_4$Sn (20 - 20)   1.83

MoOCl$_4$-nBu$_4$Sn-EtOH (20 - 20 - 20)   1.12   MoCl$_5$-nBu$_4$Sn-EtOH (20 - 20 - 20)   1.59

10^4 10^5 10^6 10^4 10^5 10^6

MW(PSt)   MW(PSt)

Figure 1. MWD curves of the poly(p-BuF$_4$PA)s obtained with Mo catalysts (polymerized in toluene at 30 oC for 4 h; $[M]_0 = 0.50$ M).

6.39×10^4) showed a narrow MWD ($\overline{M}_w/\overline{M}_n = 1.12$), which suggests a living polymerization. No polymer was formed with MoCl$_5$ catalyst alone. MoCl$_5$–n-Bu$_4$Sn and MoCl$_5$–n-Bu$_4$Sn–EtOH yielded polymers whose MWDs were broader than those with the MoOCl$_4$–based counterparts. Consequently, only the MoOCl$_4$–n-Bu$_4$Sn–EtOH catalyst appears to effect living polymerization of the present monomer.

In order to see whether the polymerization by MoOCl$_4$–n-Bu$_4$Sn–EtOH is living or not, the dependences of $\overline{M}_n$ and $\overline{M}_w/\overline{M}_n$ on monomer conversion were examined. Figure 2 manifests that $\overline{M}_n$ increases in direct proportion to the monomer conversion and that the $\overline{M}_w/\overline{M}_n$ invariably remains ca. 1.1. It can, therefore, be concluded that the polymerization by MoOCl$_4$–n-Bu$_4$Sn–EtOH is living. This living polymerization should have been caused by the steric effect and not by the electronic effect of the two ortho fluorines, since both
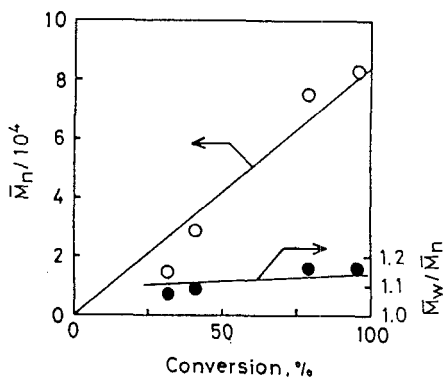
Figure 2. $\overline{M}_n$ and $\overline{M}_w/\overline{M}_n$ of poly (p-BuF$_4$PA) as a function of monomer conversion (polymerized in toluene at 30 oC; $[M]_0 = 0.50$ M, $[MoOCl_4] = [n\text{-}Bu_4Sn] = [EtOH] = 20$ mM).

electron-donating and -withdrawing *ortho*-substituents are effective for living polymerization (4, 8, 9).

Effect of n-Bu4Sn concentration

Figure 3 shows the effect of n-Bu$_4$Sn concentration on the polymerization of p-BuF$_4$PA by MoOCl$_4$–n-Bu$_4$Sn–EtOH. The polymer yield showed a maximum value when n-Bu$_4$Sn was equivalent to MoOCl$_4$ (20 mM). Although the $\overline{M}_w/\overline{M}_n$ took a large value of 2.23 in the absence of n-Bu$_4$Sn, the $\overline{M}_w/\overline{M}_n$ decreased with increasing [n-Bu$_4$Sn] to become around 1.1 at n-Bu$_4$Sn = 20 mM and above. Thus, the amount of n-Bu$_4$Sn should be equivalent to or more than that of MoOCl$_4$ for the formation of species effective in the living polymerization. The initiator efficiencies gradually increased with increasing [n-Bu$_4$Sn], but remained lower than 10%. It is known that the reaction of MoOCl$_4$ with n-Bu$_4$Sn forms metal carbenes faster than does the reaction with an acetylene monomer. Hence an adequate amount of n-Bu$_4$Sn will accelerate the initiation reaction, leading to narrow MWD of the formed polymer. Use of excess amounts of n-Bu$_4$Sn, however, reduced the catalyst activity.
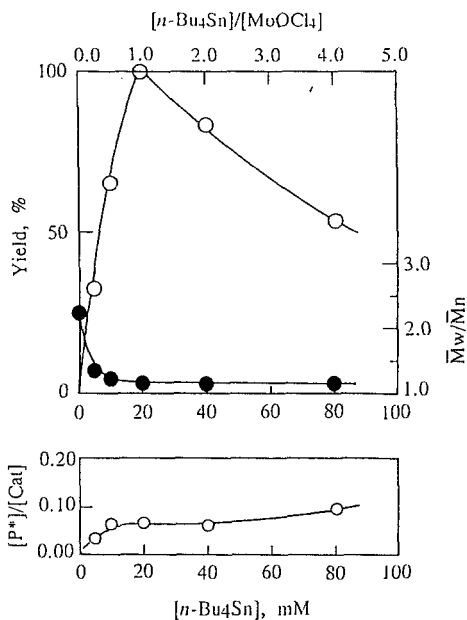

Figure 3. Effect of n-Bu$_4$Sn concentration on the polymerization of p-BuF$_4$PA by MoOCl$_4$–n-Bu$_4$Sn–EtOH (polymerized in toluene at 30 °C for 4 h; [M]$_0$ = 0.50 M, [MoOCl$_4$] = [EtOH] = 20 mM).

Effect of third catalyst components

The effect of various oxygen-containing compounds (O-compounds) as third components was examined in the MoOCl$_4$–n-Bu$_4$Sn–O-compound system (Table I). The MWD of the polymer obtained without a third component was broad ($\overline{M}_w/\overline{M}_n$ =1.65). Ethanol, n-butyl acetate and acetone made the $\overline{M}_w/\overline{M}_n$ values smaller than 1.20, indicating their effectiveness as third components in the living polymerization. Phenol showed an adverse effect.

Table I. Effects of O-compounds on the polymerization of BTFPA by $MoOCl_4$–n-Bu_4Sn–EtOH (1:1:1) [a]

	Polymer [b]			
O-compound	Yield, %	$\bar{M}_n/10^4$ [c]	$\bar{M}_w/\bar{M}_n$	[P*]/[Cat]
None	100	6.85	1.65	0.084
EtOH	100	6.39	1.12	0.090
CH_3COOnBu	100	7.43	1.13	0.077
Acetone	100	8.20	1.18	0.070
CH_3COOtBu	86	6.98	1.34	0.071
CH_3COOH	100	6.08	1.30	0.094
Phenol	78	6.85	1.93	0.066

[a] In toluene, 30 oC, 4 h, $[M]_0 = 0.50$ M, $[MoOCl_4] = 20$ mM.
[b] MeOH–insoluble product. [c] Determined by GPC.

Figure 4 depicts variations of polymer yield, $\bar{M}_w/\bar{M}_n$ and initiator efficiency with ethanol (a third component) concentration. The initiator efficiency was roughly 0.10 irrespective of ethanol concentration. The narrowest MWDs were achieved at the $[EtOH]/[MoOCl_4]$ ratio from 0.5 to 1.5. This implies that there is an optimal region of ethanol concentration. The polymer yield was quantitative up to [EtOH] = 20 mM and then decreased.

In a previous paper (8), we discussed the function of the third component in living polymerization and pointed out a possible reaction of ethanol with metal carbene as follows;
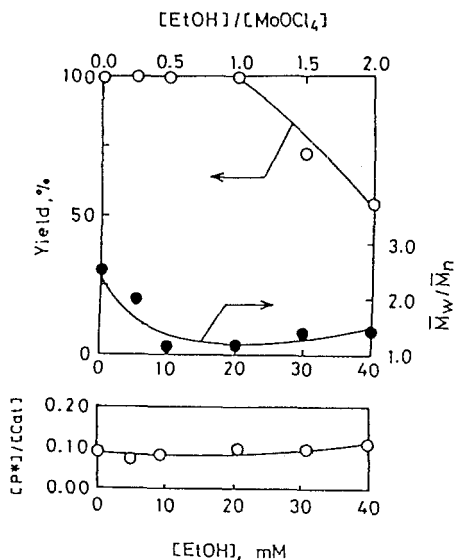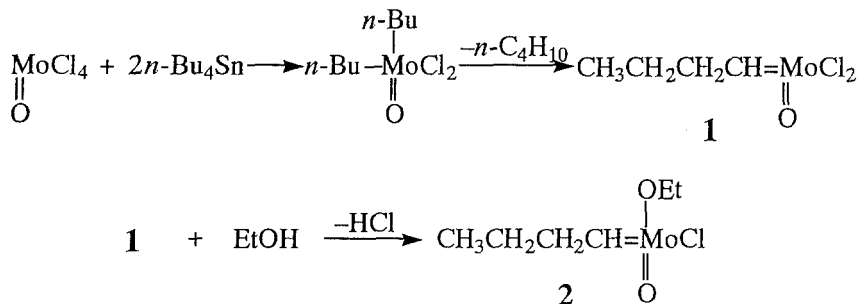

Figure 4. Effect of EtOH concentration on the polymerization of p-BuF_4PA by $MoOCl_4$–n-Bu_4Sn–EtOH (polymerized in toluene at 30 oC for 4 h; $[M]_0 = 0.50$ M, $[MoOCl_4] = [n$-$Bu_4Sn] = 20$ mM).

$$n\text{-Bu}$$
$$MoCl_4 + 2n\text{-Bu}_4Sn \longrightarrow n\text{-Bu}-\overset{|}{\underset{\overset{\|}{O}}{MoCl_2}} \xrightarrow{-n\text{-}C_4H_{10}} CH_3CH_2CH_2CH=\underset{\overset{\|}{O}}{MoCl_2}$$

with $\overset{\|}{\underset{O}{MoCl_4}}$ at left.

$$\mathbf{1} \quad + \quad EtOH \xrightarrow{-HCl} CH_3CH_2CH_2CH=\overset{OEt}{\underset{\overset{\|}{O}}{MoCl}}$$

1

2

The role of ethanol, for example, is considered to replace a chlorine ligand of metal carbene **1** by an ethoxy ligand, forming metal carbene **2**. Metal carbene **2** should be less active but more stable than **1** since the ethoxy ligand is less electron-withdrawing than the chlorine ligand. This is one of the reasons why the $MoOCl_4$–n-Bu_4Sn–EtOH system works as a living polymerization catalyst. The decrease of polymer yield in the presence of excessive ethanol is interpretable in terms of the formation of a metal carbene having two ethoxy ligands, which is even less active than **2**.

Effect of temperature

As seen in Figure 5, the $\bar{M}_w/\bar{M}_n$ was small (< 1.20) at 0 and 30 °C, while it became as large as 1.7 at 60 °C. The initiator efficiency at 60 °C took a very small value, and the monomer conversion did not reach 100%. These findings suggest that the propagating species is unstable at high temperatures like 60 °C to suffer termination and/or transfer reactions.
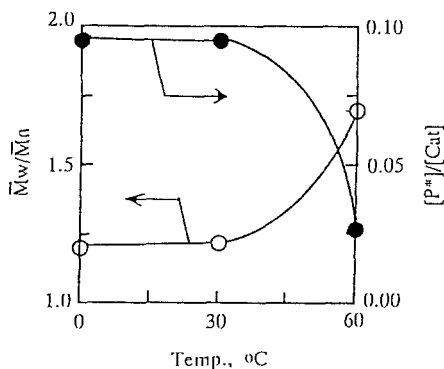

Figure 5. Effect of temperature on the polymerization of p-BuF$_4$PA by $MoOCl_4$–n-Bu_4Sn–EtOH (1:1:1) (polymerized in toluene for 24 h; $[M]_0 = 0.50$ M, $[MoOCl_4] = 20$ mM).

REFERENCES

1. G. Costa, in *Comprehensive Polymer Science* (Ed. G. Allen), Vol. 4, Pergamon, Oxford, 1989, Chap. 9.
2. T. Masuda, T. Hamano, T. Higashimura, T. Ueda, and H. Muramatsu, *Macromolecules*, **21**, 281 (1988).

3. T. Masuda, T. Hamano, K. Tsuchihara, and T. Higashimura, *Macromolecules*, **23**, 1374 (1990).
4. T. Mizumoto, T. Masuda, and T. Higashimura, *J. Polym. Sci., Part A, Polym. Chem.*, **31**, 2555 (1993).

5. T. Yoshimura, T. Masuda, T. Higashimura, K. Okuhara, and T.Ueda, *Macromolecules*, **24**, 6053 (1991).
6   K. C. Wallace, A. H. Liu, W. M. Davis, and R. R. Schrock, *Organometallics*, **8**, 644 (1989).
7. H. H. Fox and R. R. Schrock, *Organometallics*, **11**, 2763 (1992).
8. T. Masuda, K. Mishima, J. Fujimori, M. Nishida, H. Muramatsu, and T. Higashimura, *Macromolecules*, **25**, 1401 (1992).
9. T. Masuda, J. Fujimori, M. Z. A. Rahman, and T. Higashimura, *Polym. J.,* **25**, 535 (1993).
10. D. D. Perrin, W. L. F. Armarego, and D. R. Perrin, *Purification of Laboratory Chemicals,* 2nd ed., Pergamon, Oxford, 1980.
11. K. Okuhara, *Bull. Chem. Soc. Jpn.*, **61**, 1625 (1988).
12. K. Okuhara, *J. Org. Chem.*, **41**, 1487 (1976).