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Living polymerization of substituted acetylenes by $MoOCl_4$–*n*-Bu_4Sn–EtOH in anisole which features high initiator efficiency

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Abstract

Various solvents and cocatalysts were examined for the purpose of achieving high initiator efficiency in the living polymerization of substituted acetylenes catalyzed by $MoOCl_4$-based catalysts. Eventually, anisole and *n*-Bu_4Sn were found to be very useful as solvent and cocatalyst, respectively. The initiator efficiency of the $MoOCl_4$–*n*-Bu_4Sn–EtOH (1:1:2)/anisole system was as high as 40% in the polymerization of *o*-CF_3-phenylacetylene, whereas the value for the corresponding toluene system was no more than 10%. *o*-Me_3Si-phenylacetylene, 1-chloro-1-octyne, 2-octyne, and 1-chloro-2-phenylacetylene and a few other monomers were also polymerized in a living manner by the present catalyst/solvent system, the initiator efficiencies being 20–40% and larger than those of the previous systems. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Living metathesis polymerization; Molybdenum catalyst; Substituted acetylene

1. Introduction

A variety of substituted acetylenes polymerize in the presence of transition-metal catalysts to produce polymers having alternating double bonds in the main chain [1,2]. The polymerization of substituted acetylenes occurs by either the metathesis or insertion mechanism. Living polymerization of substituted acetylenes has also been investigated intensively in the last decade. Thus, it has been revealed that Schrock carbenes [3–6], $MoOCl_4$-based catalysts [7–14] and rhodium-based catalysts [15,16] induce the living polymerizations of substituted acetylenes. So far, we have achieved the living polymerization of many substituted acetylenes such as 1-chloro-1-alkynes [7], *o*-CF_3-phenylacetylene [8], *o*-Me_3Si-phenylacetylene [9], *t*-butylacetylene [11,12], and other monomers [13] by using the $MoOCl_4$–*n*-Bu_4Sn–EtOH catalyst in toluene solution.

When employed in toluene, the $MoOCl_4$–*n*-Bu_4Sn–EtOH catalyst exhibits rather poor reproducibility and its initiator efficiency is appreciably low (~10% for *o*-CF_3-phenylacetylene) [13]. One reason for this seems to be the low solubility of $MoOCl_4$ in toluene. For the past few years, we have examined various organometallics as cocatalysts (second catalyst component) to develop novel $MoOCl_4$-based catalysts which show improved living nature [17–19]. Eventually, it was found that in addition to *n*-Bu_4Sn, three organometallics, i.e., Et_3Al, Et_2Zn, and *n*-BuLi, work as effective cocatalysts in the $MoOCl_4$-based systems. The data for the polymerization of *o*-CF_3-phenylacetylene catalyzed by the $MoOCl_4$-based systems were as follows: $M_w/M_n = 1.02$, [P*]/[Cat] = 20% with $MoOCl_4$–Et_3Al–EtOH (1:1:4) [17]; $M_w/M_n = 1.03$, [P*]/Cat] = 8% with $MoOCl_4$–Et_2Zn–EtOH (1:1:3) [18]; $M_w/M_n = 1.02$, [P*]/Cat] = 2% with $MoOCl_4$–*n*-BuLi (1:1) [19]. Interestingly, the $MoOCl_4$–*n*-BuLi system did not require ethanol as the third catalyst component to achieve living polymerization. A common feature of these novel systems is very narrow molecular weight distribution ($M_w/M_n \sim 1.03$) of the poly(*o*-CF_3-phenylacetylene). However, their initiator efficiencies were invariably as low as 2–20%.

In the present paper, we report on novel $MoOCl_4$-based living polymerization catalysts which are characterized by high initiator efficiency. To be more specific, we examined the following three points in detail: (1) effect of various solvents, (2) effect of cocatalysts, (3) polymerization of various monomers using the catalyst that features high initiator efficiency. *o*-CF_3-phenylacetylene, which shows excellent living nature, was mainly used as monomer. Eventually, it was found that the initiator efficiency in the polymerization of *o*-CF_3-phenylacetylene by the $MoOCl_4$–*n*-Bu_4Sn–EtOH (1:1:2)/anisole system reaches 40%.

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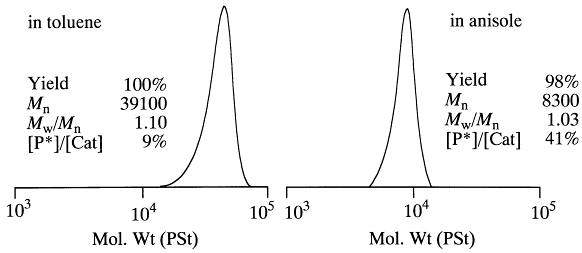

Fig. 1. Effect of solvents on the polymerization of *o*-CF_3-phenylacetylene by $MoOCl_4$–*n*-Bu_4Sn–EtOH (1:1:2) (polymerized at 30°C for 1 h; $[MoOCl_4] = 10$ mM, $[M]_0 = 0.20$ M).

2. Experimental

2.1. Materials

o-CF_3-phenylacetylene was prepared with reference to the literature methods [20,21]. $MoOCl_4$ (Strem), Grignard reagents (Kanto Chemical) and Et_3B (Kanto Chemical) were commercially obtained and used without further purification. Organosilicon, -germanium, and -tin compounds (Wako Chemical or Aldrich) were purchased and distilled twice at reduced pressure before use. However, Ph_4Sn was purified by recrystallization from methanol. Anisole as polymerization solvent was successively washed with aqueous sodium hydroxide solution (5%) and water, dried over anhydrous calcium chloride, and distilled twice from sodium metal (purity $>$ 99.9% by GC). Other solvents were purified by the standard methods. Ethanol (Wako Chemical) was distilled twice from $Mg(OEt)_2$ (purity $>$ 99.9% by GC).

2.2. Polymerization

All the procedures were carried out under dry nitrogen. Unless otherwise stated, catalyst solutions were prepared as follows: an anisole solution of $MoOCl_4$ and an anisole solution of *n*-Bu_4Sn were mixed, and the mixture was aged at room temperature for 15 min. A solution of ethanol was then added to the $MoOCl_4$–*n*-Bu_4Sn solution and the mixture was aged at room temperature for an additional 15 min. Polymerizations were carried out at 30°C in a pre-baked Schlenk tube equipped with a three-way stopcock; the concentrations of $MoOCl_4$ and monomer were 10 mM and 0.20 M, respectively. Polymerizations were initiated by the addition of monomer solution to the catalyst solution and quenched with an anisole/methanol mixture (volume ratio 1:1). Polymer yields were determined by gravimetry.

Table 1
Effect of solvents on the polymerization of *o*-CF_3-phenylacetylene by $MoOCl_4$–*n*-Bu_4Sn–EtOH (1:1:2)[a]

Solvent	Catalyst solubility	M_w/M_n	[P*]/[Cat], %
Toluene	Partly soluble	1.10	9
Chlorobenzene	Soluble	1.04	13
Anisole	Soluble	1.03	40
Phenetole	Soluble	1.03	40
p-Chloroanisole	Soluble	1.05	45
p-Methylanisole	Soluble	1.04	38
t-Butyl methyl ether	Insoluble	No polymer	–
Acetophenone	Soluble	No polymer	–
Ethyl benzoate	Soluble	No polymer	–

[a] Polymerized at 30°C for 1 h; $[MoOCl_4] = 10$ mM, $[M]_0 = 0.20$ M.

2.3. Polymer characterization

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. The initiator efficiencies ([P*]/[Cat]) were calculated from the yield and the degree of polymerization of a polymer (unless otherwise specified, the initiator efficiencies were based on the relative M_n values from GPC).

3. Results and discussion

3.1. Effect of solvents

Toluene and anisole as polymerization solvents were compared in the polymerization of *o*-CF_3-phenylacetylene by the previously developed $MoOCl_4$–*n*-Bu_4Sn–EtOH (1:1:2) catalyst (Fig. 1). In toluene solution, the initiator efficiency of the $MoOCl_4$–*n*-Bu_4Sn–EtOH (1:1:2) was no more than 9% and the polydispersity ratio (M_w/M_n) of the formed polymer was 1.10. In contrast, in anisole, the initiator efficiency increased up to 41% and the MWD narrowed further, as evidenced by the M_w/M_n value of 1.03. Thus, anisole is obviously preferable to toluene as a solvent for the living polymerization by the $MoOCl_4$-based catalyst. The main reason for this seems to be that anisole completely dissolves $MoOCl_4$ and possesses a moderate basicity.

The initiator efficiencies described above were estimated directly from the relative M_n values based on GPC measurements and a polystyrene calibration, and hence are relative values. In order to obtain accurate initiator efficiencies, the following relationship was used: $M_n(\text{VPO}) = 1.48 \times M_n(\text{GPC})$ [8]. The accurate values were determined to be 28% for the $MoOCl_4$–*n*-Bu_4Sn–EtOH (1:1:2)/anisole system and 6% for the $MoOCl_4$–*n*-Bu_4Sn–EtOH (1:1:2)/toluene system.

On the basis of the above-stated findings, several other solvents were examined to attempt further increase in the initiator efficiency (Table 1). In toluene and chlorobenzene, which are often used in the metathesis polymerizations by Mo and W catalysts, the initiator efficiencies were around 10%. In contrast, when anisole derivatives and phenetole were employed, high initiator efficiencies of ca. 40% were attained, which were comparable with the value of anisole. On the other hand, *t*-butyl methyl ether, acetophenone, and ethyl benzoate were not effective. Thus, one can see that

Table 2
Effect of anisole on the polymerization of *o*-CF_3-phenylacetylene by $MoOCl_4$–*n*-Bu_4Sn–EtOH (1:1:2)[a]

[anisole]	M_n	M_w/M_n	[P*]/[Cat], %
0	25600	1.04	13
10 mM	11700	1.05	29
20 mM	11000	1.05	31
30 mM	9300	1.04	37
100 vol%	7800	1.03	44

[a] Polymerized in chlorobenzene at 30°C for 2 h (anisole was added to the $MoOCl_4$ solution).

aromatic ethers are most favorable as polymerization solvents.

It was examined how much anisole was necessary for the above-stated polymerization in chlorobenzene, which dissolves $MoOCl_4$ completely (Table 2). Even one equivalent of anisole to $MoOCl_4$ remarkably increased the initiator efficiency. Anisole with a several-fold excess over $MoOCl_4$ seems sufficient to accomplish a high initiator efficiency and small polydispersity ratio. These results suggest that anisole selectively solvates or coordinates to $MoOCl_4$-based species to stabilize it. Anisole was exclusively employed as polymerization solvent in further experiments.

3.2. Effect of cocatalysts

It has been clarified that several cocatalysts such as *n*-Bu_4Sn, Et_3Al, Et_2Zn, and *n*-BuLi are useful for the $MoOCl_4$-based living polymerization catalysts. Here, various alkylating agents were examined as cocatalysts from the viewpoint of which catalyst systems achieve high initiator efficiencies. Table 3 shows the results of the polymerization of *o*-CF_3-phenylacetylene by use of several $MoOCl_4$–R_4M–EtOH (1:1:2; M = group IV A element) systems. No polymerization proceeded in the presence of Et_4Si, Me_4Ge and *n*-Bu_4Ge, i.e., these organometallics did not work as cocatalysts. Me_4Sn behaved similarly to *n*-Bu_4Sn to some extent, but the initiator efficiency remained at 20% and not as large as the case of *n*-Bu_4Sn. *i*-Bu_4Sn and *i*-Pr_4Sn gave inferior results, which appears to be associated with their larger steric effects. The ineffectiveness of Ph_4Sn is attributable to its inability to alkylate. *n*-Bu_4Pb gave a result comparable with results from *n*-Bu_4Sn and Me_4Sn. These results imply that the alkylating ability is important for cocatalysts to work.

Table 3
Effect of group IV A organometallic cocatalysts on the polymerization of *o*-CF_3-phenylacetylene by $MoOCl_4$–R_4M–EtOH (1:1:2)[a]

Cocatalyst	Polymer yield, %	M_n	M_w/M_n	[P*]/[Cat], %
None	No polymer	–	–	–
Et_4Si	No polymer	–	–	–
Me_4Ge	No polymer	–	–	–
n-Bu_4Ge	No polymer	–	–	–
n-Bu_4Sn	100	8100	1.03	41
Me_4Sn	100	16600	1.05	20
i-Bu_4Sn	44	25900[b]	1.14	–
i-Pr_4Sn	7	34100	1.54	–
Ph_4Sn	No polymer	–	–	–
n-Bu_4Pb	100	22300	1.02	15

[a] polymerized in anisole at 30°C for 1 h; [$MoOCl_4$] = 10 mM, $[M]_0$ = 0.20 M.[b] A bimodal MWD.

It was further examined whether organo-Mg and -B compounds are useful or not (Table 4). The MWDs of the formed polymers were not narrow when Grignard reagents were used as cocatalysts. $MoOCl_4$–Et_3B (1:1) induced rapid polymerization, but the MWD of the polymer was similar to that with $MoOCl_4$ alone. When ethanol was added as a third component to this catalyst system, the monomer was hardly consumed. It is known that many of the organometallics in Tables 3 and 4 serve as cocatalysts in the Mo- and W-based binary systems; i.e., such catalyst systems induce fast polymerization of substituted acetylenes. The present results, in contrast, indicate that only cocatalysts having sufficient alkylating ability are useful in the $MoOCl_4$-based ternary system.

3.3. Polymerization of other monomers

The results described above indicate that the $MoOCl_4$–*n*-Bu_4Sn–EtOH/anisole system induces excellent living polymerization of *o*-CF_3-phenylacetylene. In order to clarify how general the effectiveness of the present catalyst system is, other acetylenic monomers were examined (Table 5). For comparison, Table 5 includes the results using not only anisole but also toluene as solvent.

As was known before, sterically crowded phenylacetylenes such as *o*-CF_3-, *o*-Me_3Si-, *o*-Me-, and *p*-*n*-Bu-*o*,*o*,*m*,*m*,-F_4-phenylacetylenes polymerize in a living fashion even in toluene [9–11]. However, the MWDs of the formed polymers are not very narrow (M_w/M_n 1.11–1.35) and their initiator efficiencies are rather low (9–15%). In contrast, when anisole was employed as solvent, the polydispersity ratios of the polymers diminished (M_w/M_n 1.03–1.15) and the initiator efficiencies increased up to 25–44%. However, phenylacetylene itself did not polymerize in a living fashion, irrespective of the kind of solvents used.

1-Chloro-1-octyne underwent living polymerization both in toluene and in anisole. In the latter solvent, the MWD somewhat broadened, but the initiator efficiency increased up to ca. 20%. It is worth noting that several acetylenic monomers, which do not show living nature in toluene, gave living polymers in anisole. For instance, 1-chloro-2-phenylacetylene polymerized in a living manner with the $MoOCl_4$–*n*-Bu_4Sn–EtOH/anisole (1:1:2) to give a polymer of $M_w/M_n \sim 1.1$ [22]. Further, 2-octyne and other aliphatic internal acetylenes also afforded living polymers of $M_w/M_n \sim 1.1$ by using anisole solvent [23].

As demonstrated so far, narrow MWDs and high initiator efficiencies can be achieved for many acetylenes including

Table 4
Effect of organo-Mg and -B cocatalysts on the polymerization of *o*-CF_3-phenylacetylene by $MoOCl_4$-based catalysts[a]

Catalyst	Mole ratio	Polymerization time, h	Polymer yield, %	M_n	M_w/M_n
$MoOCl_4$–EtMgBr	1:1	3	100	30×10^4	~ 1.6
$MoOCl_4$–EtMgBr–EtOH	1:1:2	3	50	30×10^4	~ 1.6
$MoOCl_4$–VinylMgBr	1:1	24	80	40×10^4	~ 1.6
$MoOCl_4$–Et_3B	1:1	0.5	100	10×10^4	1.1
$MoOCl_4$–Et_3B–EtOH	1:1:2	24	No polymer	–	–

[a] Polymerized in anisole at 30°C.

Table 5
Polymerization of substituted acetylenes by $MoOCl_4$–*n*-Bu_4Sn–EtOH

Monomer	$MoOCl_4$–*n*-Bu_4Sn–EtOH (1:1:2) in anisole[a]		$MoOCl_4$–*n*-Bu_4Sn–EtOH (1:1:1) in toluene[b]	
	M_w/M_n	[P*]/[Cat], %	M_w/M_n	[P*]/[Cat], %
$HC{\equiv}CC_6H_4$–*o*-CF_3	1.03	42	1.11	13
$HC{\equiv}CC_6H4$–*o*-$SiMe_3$	1.15	37	1.12	17
$HC{\equiv}CC_6F_4$–*p*-*n*-Bu	1.04	44	1.35	9
$HC{\equiv}CC_6H_4$–*o*-Me	1.12[c]	25	1.30	15
$HC{\equiv}CC_6H_5$	1.42	–	1.65	–
$ClC{\equiv}C$–*n*-C_6H_{13}	1.27	22	1.16	11
$ClC{\equiv}C$–C_6H_5	1.13[c]	28	1.36	10
$MeC{\equiv}C$–*n*-C_5H_{11}	1.07[c]	3	–	–

[a] Polymerized in anisole at 30°C; $[MoOCl_4] = 10$ mM, $[M]_0 = 0.20$ M.
[b] From Refs. [13,14]; polymerized in toluene at 30°C; $[MoOCl_4] = 10$ mM, $[M]_0 = 0.10$ M.
[c] Polymerized at 0°C.

some new monomers by use of the $MoOCl_4$–*n*-Bu_4Sn–EtOH/anisole system. These features seem to originate from the good stability of the propagating species in this system.

3.4. Detailed examination of the *o*-CF_3-phenylacetylene system

At first, the effect of ethanol concentration was examined for the $MoOCl_4$–*n*-Bu_4Sn–EtOH (1:1:x) system (Fig. 2). In the presence of $MoOCl_4$–*n*-Bu_4Sn (1:1), *o*-CF_3-phenylacetylene was consumed instantaneously to form a living polymer (M_w/M_n 1.05). The initiator efficiency was fairly large (~30%), but the polymerization was too fast for its conversion to be controlled. In contrast, when ethanol was added in catalytic amounts, polymerization proceeded not instantaneously, but smoothly. Further, the initiator efficiency increased to 40% and the polydispersity ratio diminished to 1.03. Next, the effect of *n*-Bu_4Sn concentration was examined. $MoOCl_4$–EtOH (1:2) did not induce polymerization. Though polymerization took place with $MoOCl_4$–*n*-Bu_4Sn–EtOH (1:2:2), the initiator efficiency was no more than 7%. Thus, the catalyst composition of $MoOCl_4$:*n*-Bu_4Sn:EtOH = 1:1:1–2 turned out to be favorable.

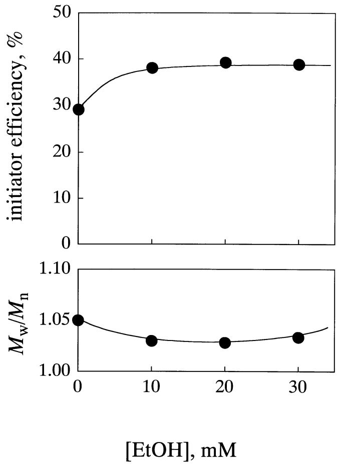

Fig. 2. Effect of [EtOH] on the polymerization of *o*-CF_3-phenylacetylene by $MoOCl_4$–*n*-Bu_4Sn–EtOH (1:1:x) (polymerized in anisole at 30°C for 1 h; $[MoOCl_4] = 10$ mM, $[M]_0 = 0.20$ M).

To confirm the living nature of the $MoOCl_4$–*n*-Bu_4Sn–EtOH/anisole system, we carried out multistage polymerization (Fig. 3). When monomer feeds were supplied three times repeatedly, the M_n of the polymer increased in direct proportion to the polymer yield. Meanwhile, the polydispersity ratios remained at 1.05 or smaller. This indicates that this polymerization is a living polymerization.

4. Concluding remarks

The present study has revealed that the $MoOCl_4$–*n*-Bu_4Sn–EtOH/anisole system achieves high initiator

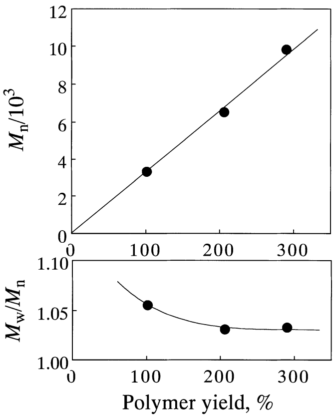

Fig. 3. Multistage polymerization of *o*-CF_3-phenylacetylene by $MoOCl_4$–*n*-Bu_4Sn–EtOH (1:1:2) (polymerized in anisole at 0°C; $[MoOCl_4] = 10$ mM, $[M]_0 = [M]_{add} = 0.076$ M).

efficiencies and narrow MWDs in the polymerization of various substituted acetylenes. In anisole, one can use not only *n*-Bu_4Sn but also Et_3Al, Et_2Zn and *n*-BuLi as cocatalysts in the polymerization of *o*-CF_3-phenylacetylene by the $MoOCl_4$–cocatalyst–EtOH system. All these systems achieve very narrow MWDs whose M_w/M_n values are as small as 1.02–1.03, whereas the initiator efficiency varies over a wide range of ca. 2–40% depending on the catalyst systems. Such a large variation in initiator efficiencies enables the synthesis of living polymers with a wide range of molecular weights. Further, it is expected that the large initiator efficiency of the present system leads to the direct observation of the propagating species and high-efficiency end functionalization.

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