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LIVING METATHESIS POLYMERIZATION OF 1-CHLORO-2-PHENYLACETYLENE BY MoOCl_4 -BASED CATALYSTS

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Key Words: Living Polymerization, Metathesis Polymerization, Substituted Acetylene, 1-Chloro-2-phenylacetylene, Transition Metal Catalyst

ABSTRACT

The living polymerization of 1-chloro-2-phenylacetylene was accomplished by use of the MoOCl_4 - $n\text{-Bu}_4\text{Sn}$ -EtOH/anisole catalyst/solvent system. The polydispersity ratio of the produced poly(1-chloro-2-phenylacetylene) was as small as 1.1. Living polymerization was verified by the multi-stage polymerization and the monomer-conversion dependence of the molecular weight. Only $n\text{-Bu}_4\text{Sn}$ was effective as cocatalyst of the MoOCl_4 -based catalyst, and Et_3Al , Et_2Zn , and $n\text{-BuLi}$ were not. Among 1-chloro-2-phenylacetylene analogues, only para-substituted derivatives appeared to polymerize in a living fashion.

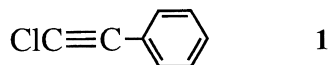
*Author to whom correspondence should be addressed.

INTRODUCTION

Recently, living polymerization of substituted acetylenes with various catalysts is under intensive research. Schrock carbenes (Mo carbenes) nicely induce the living polymerization of several acetylenes such as α,ω -diyne, ethynylferrocene and ortho-substituted phenylacetylenes [1]. Living polymerization of 2-butyne has been accomplished by using a Ta carbene [2]. Phenylacetylene and its meta- and para-substituted derivatives polymerize in a living manner with Rh complexes [3]. So far, we have found that MoOCl_4 -cocatalyst-EtOH systems (cocatalysts: *n*- Bu_4Sn , Et_3Al , Et_2Zn , and *n*-BuLi) and WOCl_4 -cocatalyst-*t*-BuOH systems (cocatalysts: *n*- Bu_4Sn , EtMgBr , and *n*-BuLi) enable living polymerization of various substituted acetylenes such as ortho-substituted phenylacetylenes, 1-chloro-1-*n*-alkynes, *t*-butylacetylene, and internal alkynes (Scheme 1) [4, 5].

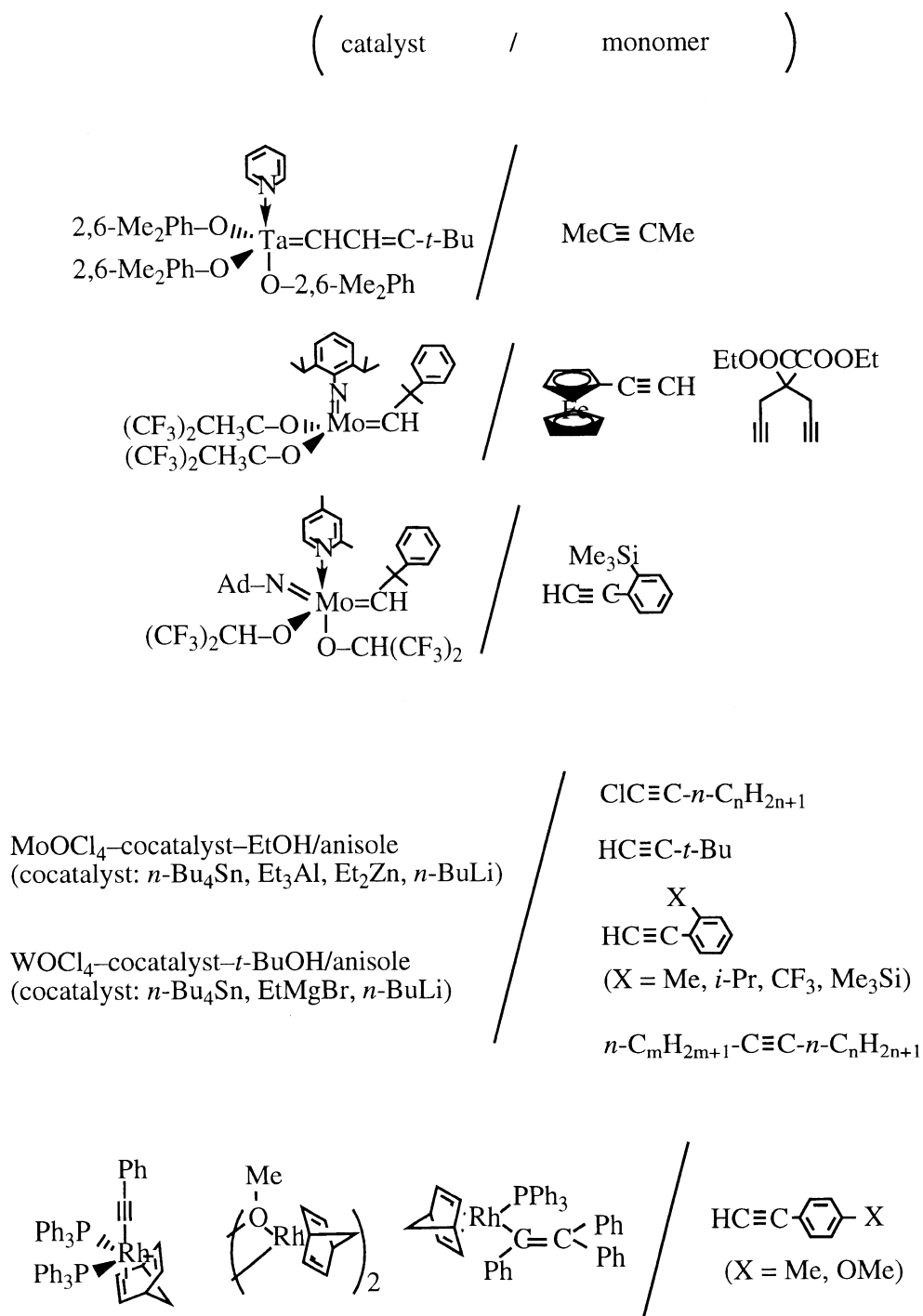
The characteristics of these living polymerization catalysts are summarized as follows: MoOCl_4 - and WOCl_4 -based catalysts are useful for monosubstituted acetylenes and sterically unhindered disubstituted acetylenes. Living polymerization induced by Schrock carbenes (Mo carbenes) are limited to only monosubstituted acetylenes. The Ta carbene is effective only for 2-butyne. Only phenylacetylenes polymerize in a living fashion with Rh complexes. In other words, the living polymerization of disubstituted acetylenes is rather difficult and only few studies have been reported. Thus, it is interesting to develop novel disubstituted acetylenes which polymerize in a living fashion.

In the present study, we investigated the polymerization of various disubstituted acetylenes having chlorine and/or phenyl group with the motivation to find monomers which undergo living polymerization. Consequently, the living polymerization of 1-chloro-2-phenylacetylene (**1**) was accomplished for the first time by use of the MoOCl_4 -*n*- Bu_4Sn -EtOH/anisole system, and the features of this living polymerization were clarified.



EXPERIMENTAL

1-Chloro-2-phenylacetylene was prepared with reference to the literature method [6]. MoOCl_4 (Strem), Et_3Al , Et_2Zn , and *n*-BuLi (Kanto Chemical) were



Scheme 1.

commercially obtained and used without further purification. $n\text{-Bu}_4\text{Sn}$ was distilled twice from CaH_2 under reduced pressure before use. 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 GC). Ethanol was distilled twice from $\text{Mg}(\text{OEt})_2$ and stored as anisole solution.

All the procedures were carried out under dry nitrogen. Catalyst solutions were prepared as follows: An anisole solution of MoOCl_4 and an anisole solution of $n\text{-Bu}_4\text{Sn}$ were mixed, and the mixture was aged at room temperature for 15 minutes. Then an anisole solution of EtOH was added to the MoOCl_4 - $n\text{-Bu}_4\text{Sn}$ solution, and the mixture was aged at room temperature for an additional 15 minutes. Polymerizations were initiated by adding monomer solution to the catalyst solution. Polymerizations were carried out usually at 0°C in a pre-baked Schlenk tube equipped with a three-way stopcock; the concentrations of MoOCl_4 and monomer were usually 10 mM and 0.20 M, respectively. Polymerizations were quenched with a large amount of methanol. Monomer conversions were determined by GC. Polymer yields were determined by gravimetry.

The molecular weight distributions (MWD) of polymers were measured by gel-permeation chromatography (GPC) [(Jasco, PU930; eluent; chloroform; Shodex K805, 804, 803 polystyrene gel columns (Showa Denko, Co.); RI and UV detector]. The number- and weight-average molecular weights (M_n and M_w , respectively) of polymers were determined by use of a polystyrene calibration. The initiation efficiency ($[\text{P}^*]/[\text{Cat}]$) was calculated from the monomer conversion and the degree of polymerization of polymers. The DP was estimated from the M_n obtained by GPC.

RESULTS AND DISCUSSION

Effect of Polymerization Conditions

Effects of solvents on the polymerization of 1-chloro-2-phenylacetylene by MoOCl_4 - $n\text{-Bu}_4\text{Sn}$ -EtOH(1:1:2) were examined (Figure 1). When toluene was used as solvent, the polymerization was finished instantaneously to yield the polymer having relatively broad MWD. In contrast, the polymerization in anisole proceeded slowly, and the MWD of the formed polymer was fairly narrow (M_n 10,700, M_w/M_n 1.13). The initiation efficiency was 25%. These results suggest that 1-chloro-2-phenylacetylene polymerize in a living manner with the MoOCl_4 - $n\text{-Bu}_4\text{Sn}$ -EtOH(1:1:2)/anisole catalyst/solvent system.

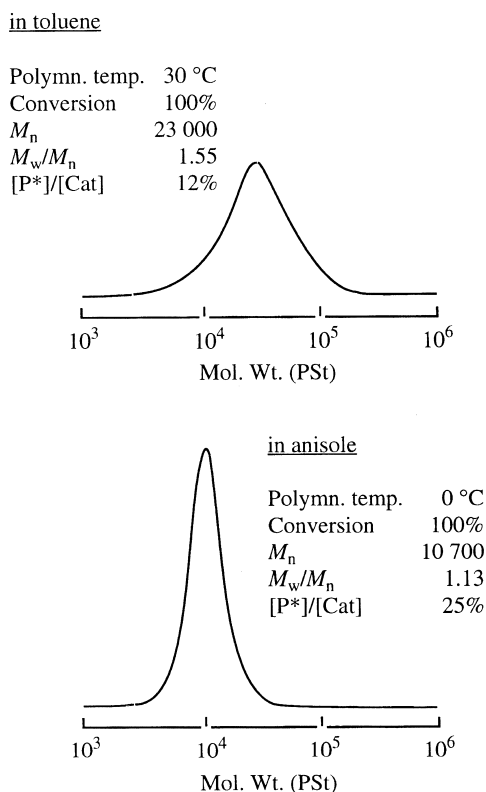


Figure 1. Effect of solvents on the polymerization of 1-chloro-2-phenylacetylene by $MoOCl_4$ - n - Bu_4Sn - $EtOH$ (1:1:2) (polymerized for 24 hours; $[MoOCl_4] = 10$ mM, $[M]_0 = 0.20$ M).

The effects of cocatalysts were examined, (see Table 1). The catalyst involving n - Bu_4Sn induced an excellent living polymerization; the initiation efficiency was high (25%), and the MWD of the obtained polymer was relatively narrow. In contrast, when Et_3Al , Et_2Zn , and n - $BuLi$ were employed, the MWD of the polymer became broad, indicating that these organometallics are rather useless.

In order to determine the appropriate catalyst composition of $MoOCl_4$ - n - Bu_4Sn - $EtOH$, the effect of ethanol concentration was investigated by changing its concentration in the range 0–20 mM. The monomer was completely consumed in 24 hours, irrespective of the ethanol concentration. Both M_n and M_w/M_n tended to decrease with an increasing amount of ethanol. The data of the formed polymers were as follows: M_n 16,300, M_w/M_n 1.28 with $MoOCl_4$ - n -

TABLE 1. Polymerization of 1-Chloro-2-phenylacetylene by MoOCl₄-Based Systems^{a)}

Catalyst	Conversion, %	M_n	M_w/M_n
MoOCl ₄ - <i>n</i> -Bu ₄ Sn-EtOH (1:1:1)	100	10,700	1.13
MoOCl ₄ -Et ₃ Al-EtOH (1:1:4)	50	54,800	1.62
MoOCl ₄ -Et ₂ Zn-EtOH (1:1:3)	52	98,600	1.48
MoOCl ₄ - <i>n</i> -BuLi (1:1)	32	65,100	1.39

^{a)} Polymerized in anisole at 0 °C for 2 days, [MoOCl₄] = 10 mM, [M]₀ = 0.20 M.

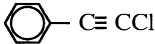
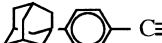
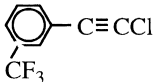
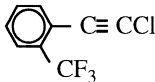
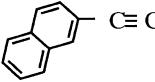
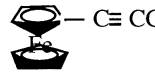
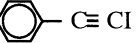
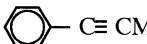
Bu₄Sn(1:1); M_n 10,700, M_w/M_n 1.14 with MoOCl₄-*n*-Bu₄Sn-EtOH(1:1:1); M_n 9,700, M_w/M_n 1.14 with MoOCl₄-*n*-Bu₄Sn-EtOH(1:1:2). Based on these results, the MoOCl₄-*n*-Bu₄Sn-EtOH(1:1:1-2)/anisole system was employed exclusively in the following experiments.

The effect of polymerization temperature was examined with the MoOCl₄-*n*-Bu₄Sn-EtOH(1:1:2)/anisole system. The polymerization at 30°C was finished instantaneously to produce a polymer having a rather broad MWD (M_n 11,800, M_w/M_n 1.30). The GPC curve narrowed with decreasing temperature; M_w/M_n = 1.10 at 0°C. Thus, it can be concluded that 0°C is preferable as polymerization temperature.

Polymerization of Other Monomers

Polymerization of several 1-chloro-2-phenylacetylene analogues was examined, the results of which are shown in Table 2. 1-Chloro-2-(*p*-adamantylphenyl)acetylene quantitatively produced a polymer having narrow MWD (Table 2, run 2). Polymerization of 1-chloro-2-(*m*-CF₃-phenyl)acetylene proceeded smoothly, but the MWD of the formed polymer was somewhat broad (run 3). 1-Chloro-2-phenylacetylene with *o*-CF₃ group did not polymerize with the present catalyst (run 4). These results indicate that the ring substituent of 1-chloro-2-phenylacetylene should be on the para position in order to form living polymer. 1-Chloro-2-β-naphthylacetylene yielded a polymer having rather broad MWD (run 5). 1-Chloro-2-ferrocenylacetylene gave no polymer irrespective of polymerization time and temperature (run 6). The polymerizations of

TABLE 2. Polymerization of Analogous of 1-Chloro-2-phenylacetylene by MoOCl_4 -*n*- Bu_4Sn - EtOH (1:1:1)^{a)}

Run	Monomer	Temp., °C	Time, h	Convsn., %	M_n	M_w/M_n
1	 $\text{C}\equiv\text{CCl}$	0	0.5	100	9,650	1.13
2	 $\text{C}\equiv\text{CCl}$	0	2	—	6,920	1.21
3	 $\text{C}\equiv\text{CCl}$	0	72	79	11,800	1.43
4	 $\text{C}\equiv\text{CCl}$	0	48	0	—	—
5	 $\text{C}\equiv\text{CCl}$	30	24	32	2,600	1.75
6	 $\text{C}\equiv\text{CCl}$	30	24	0	—	—
7	 $\text{C}\equiv\text{CI}$	0	24	36	2,450	1.34
8	 $\text{C}\equiv\text{CMe}$	0	72	16	6,710	1.55

^{a)} Polymerized in anisole, $[\text{MoOCl}_4] = 10 \text{ mM}$, $[\text{M}]_0 = 0.20 \text{ M}$.

both 1-iodo-2-phenylacetylene and 1-phenyl-1-propyne leveled off at low monomer conversions and were not living (runs 7, 8).

On Living Character of the Polymerization of 1-Chloro-2-phenylacetylene

Figure 2 shows the result of multistage polymerization. 1-Chloro-2-phenylacetylene was supplied three times repeatedly. The M_n of the polymer increased in proportion to the monomer conversion, while the polydispersity ratio was as small as about 1.2. This result clearly indicates that the present polymerization is a living polymerization.

Figure 3 (a) shows the first-order plots with respect to monomer concentration in the polymerization by MoOCl_4 -*n*- Bu_4Sn - EtOH (1:1:1 or 1:1:2)/anisole. While the polymerization rate sharply decreases with increasing ethanol concentration, logarithmic $[\text{M}]_0/[\text{M}]$ increases in direct proportion to the polymerization

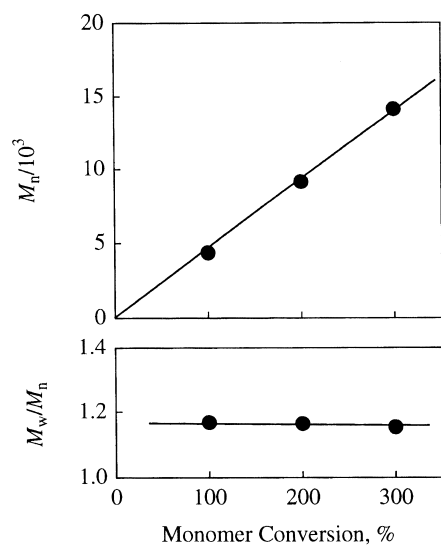


Figure 2. Multi-stage polymerization of 1-chloro-2-phenylacetylene by MoOCl_4 -*n*- Bu_4Sn - EtOH (1:1:1) (polymerized in anisole at 0°C for 20 minutes each; $[\text{MoOCl}_4] = 10 \text{ mM}$, $[\text{M}]_0 = [\text{M}]_{\text{add}} = 0.10 \text{ M}$).

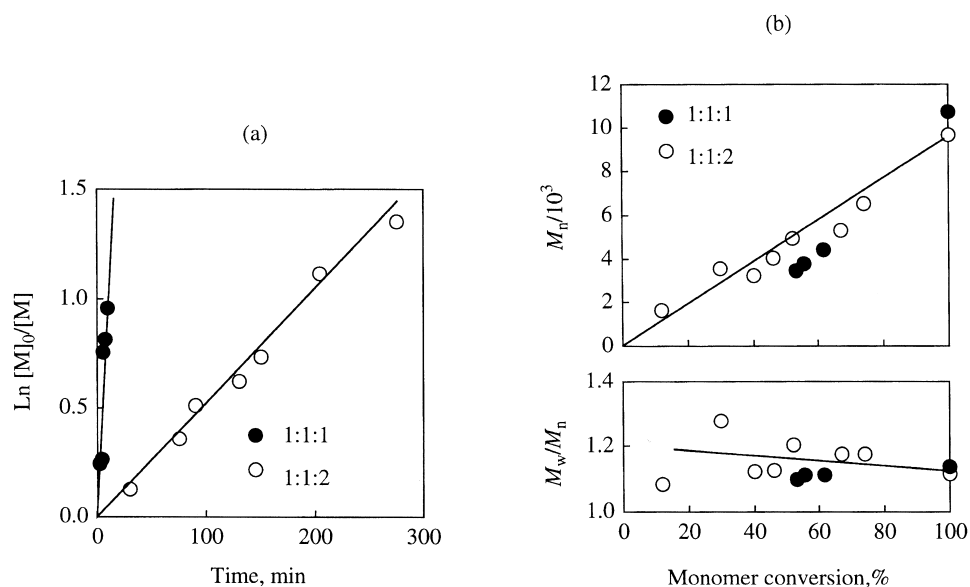


Figure 3. Polymerization of 1-chloro-2-phenylacetylene by MoOCl_4 -*n*- Bu_4Sn - EtOH (1:1:1-2); first-order plot (a) and conversion- M_n and $-M_w/M_n$ plots (b) (polymerized in anisole at 0°C ; $[\text{MoOCl}_4] = 10 \text{ mM}$, $[\text{M}]_0 = 0.20 \text{ M}$).

time irrespective of ethanol concentration. This indicates that the polymerization is of the first order with respect to the monomer concentration, while the concentration of the propagating species remains constant throughout the polymerizations. As seen in Figure 3 (b), the plots of M_n versus polymer yield give a single straight line passing the origin. The initiation efficiency determined from the slope of this line was 27%. The M_w/M_n diminishes to 1.2 at high polymer yields. This also confirms that the present system is a living polymerization irrespective of the concentration of ethanol.

Figure 4 shows the effect of initial monomer concentration on the polymerization of 1-chloro-2-phenylacetylene by MoOCl_4 -*n*- Bu_4Sn - EtOH (1:1:1)/anisole. In the range 0.05–0.20 M, 1-chloro-2-phenylacetylene quantitatively produced polymers with narrow MWD and the M_n increased in direct proportion to the initial monomer concentration. The initiation efficiency obtained from this plot was 30%. These results also support the conclusion that the present polymerization is living.

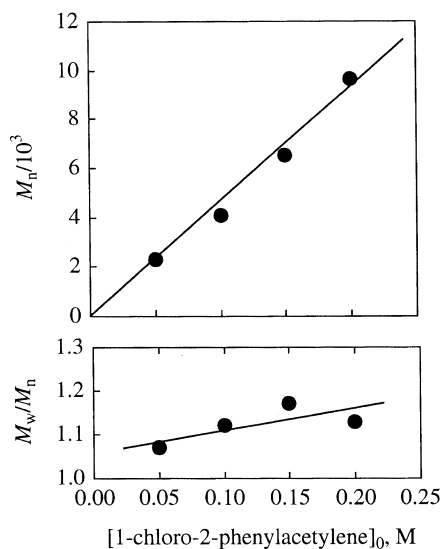


Figure 4. Effect of initial monomer concentration on the polymerization of 1-chloro-2-phenylacetylene by MoOCl_4 -*n*- Bu_4Sn - EtOH (1:1:1) (polymerized in anisole at 0°C for 2 hours; $[\text{MoOCl}_4] = 10 \text{ mM}$).

CONCLUSION

In the present article, the polymerization of 1-chloro-2-phenyl-acetylene and its various analogues was investigated by use of MoOCl_4 -based catalysts. Eventually, the following points have been revealed: (1) Living polymerization of 1-chloro-2-phenylacetylene was accomplished by use of the MoOCl_4 - n - Bu_4Sn - EtOH /anisole system. (2) Only n - Bu_4Sn was effective as cocatalyst of the MoOCl_4 -based catalyst, while Et_3Al , Et_2Zn and n - BuLi were not. (3) Para-substituted derivatives of 1-chloro-2-phenylacetylene appeared to polymerize in a living fashion

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