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### Novel Catalyst Systems for the Polymerization of Substituted Acetylenes

Toshio Masuda<sup>a</sup>; Hisayasu Kaneshiro<sup>a</sup>; Shigetaka Hayano<sup>a</sup>; Yoshihiko Misumi<sup>a</sup>; Lajos Bencze<sup>b</sup>

<sup>a</sup> Department of Polymer Chemistry, Kyoto University, Kyoto, Japan <sup>b</sup> Department of Organic Chemistry, University of Veszprem, Veszprem, Hungary

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## NOVEL CATALYST SYSTEMS FOR THE POLYMERIZATION OF SUBSTITUTED ACETYLENES

**Toshio Masuda,\* Hisayasu Kaneshiro,  
Shigetaka Hayano, and Yoshihiko Misumi**  
Department of Polymer Chemistry  
Kyoto University  
Kyoto 606-01, Japan

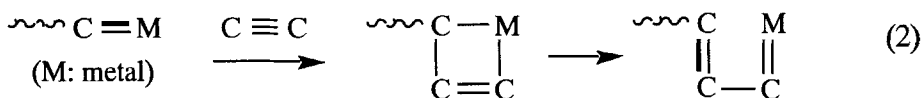
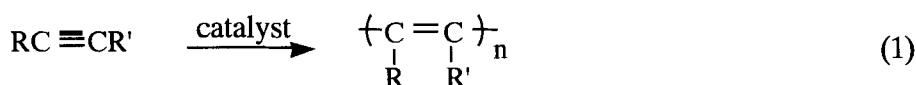
**Lajos Bencze**  
Department of Organic Chemistry  
University of Veszprem  
Veszprem H-8201, Hungary

### ABSTRACT

This article reviews two types of novel catalyst systems for the polymerization of substituted acetylenes; i.e., i)  $\text{MoOCl}_4$ -based catalysts and ii) metal carbonyl-based catalysts. The  $\text{MoOCl}_4$ - $n$ - $\text{Bu}_4\text{Sn}$ - $\text{EtOH}$ (1:1:1) catalyst achieves living polymerization of 1-chloro-1-octyne, *tert*-butylacetylene, and phenylacetylenes having bulky ortho substituents. The initiator efficiency for the polymerization of *o*- $\text{CF}_3$ -phenylacetylene reaches about 40% in anisole.  $\text{Et}_3\text{Al}$ ,  $\text{Et}_2\text{Zn}$ , and  $n$ - $\text{BuLi}$  also work as useful cocatalysts in the  $\text{MoOCl}_4$ -based system; the polydispersity ratios of poly(*o*- $\text{CF}_3$ -phenylacetylene) are as small as 1.06 to 1.02. The binary  $\text{MoOCl}_4$ - $n$ - $\text{BuLi}$  system serves without ethanol. Block copolymers of *o*- $\text{CF}_3$ - and *o*- $\text{Me}_3\text{Si}$ -phenylacetylenes can be obtained by using  $\text{MoOCl}_4$ - $\text{Et}_3\text{Al}$ - $\text{EtOH}$ (1:1:4). Whereas  $\text{CCl}_4$  is used as solvent in the polymerization of phenylacetylene by  $\text{W}(\text{CO})_6$ - $\text{CCl}_4$ - $h\nu$ , only a few equivalents of  $\text{Ph}_2\text{CCl}_2$  to tungsten is needed in the  $\text{W}(\text{CO})_6$ - $\text{Ph}_2\text{CCl}_2$ - $h\nu$  system. A tungsten complex,  $\text{WCl}_2(\text{CO})_3^-$  ( $\text{AsPh}_3$ )<sub>2</sub> by itself induces the polymerization of phenylacetylenes.

## INTRODUCTION

Substituted acetylenes can be polymerized by suitable transition-metal catalysts [1–3] (Equation 1). The polymerization of substituted acetylenes by group 5 and 6 transition metal catalysts proceeds via metal carbenes; i.e., a metal carbene reacts with an acetylene to give a metallacyclobutene, ring opening of which regenerates a metal carbene (Equation 2). This mechanism is essentially the same as that of ring-opening metathesis polymerization (ROMP) of cycloolefins [4–6]. Thus, this polymerization of substituted acetylenes is a metathesis addition polymerization.

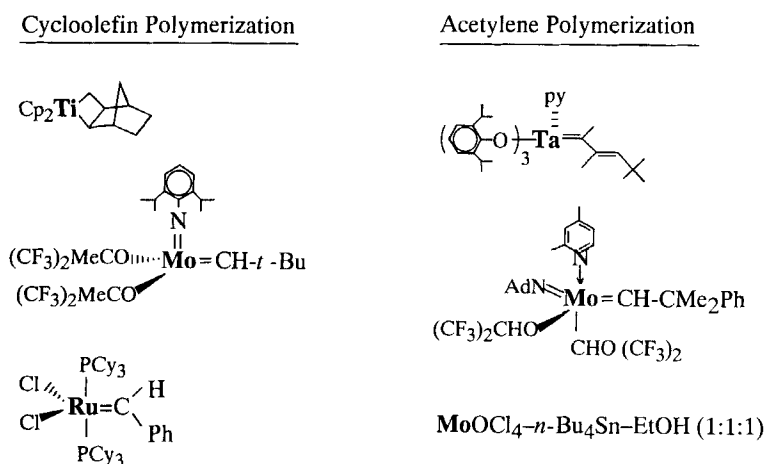


The produced polymers have alternating double bonds along the main chain and various groups as the side chains. Based on their unique structure, development of various functions are under intensive research. As a typical function of substituted polyacetylenes, one can point out gas-separation membrane due to their high gas permeability [7,8]. Other examples of functions include separation of ethanol/water mixture by pervaporation [9], electrochromism [10], third-order nonlinear optical properties [11], and electroluminescence [12].

Herein, we survey our recent studies concerning two types of catalysts for the polymerization of substituted acetylenes: i.e., MoOCl<sub>4</sub>-based catalysts and metal carbonyl-based catalysts.

### Polymerization of Substituted Acetylenes by MoOCl<sub>4</sub>-Based Catalysts

Living polymerization is one of the most useful means to control both molecular weight and molecular weight distribution (MWD) of polymers. Many living processes have been developed in not only anionic but also various types of polymerizations [13, 14], and the study on the living ROMP of cycloolefins has made great progress in the last decade [4, 5] (Scheme 1). The living ROMP was first achieved by use of titanacyclobutanes, though their activity was not very high [15]. Schrock's molybdenum carbenes polymerize not only norbornene but its derivatives with polar groups in a living fashion [4], and recently living ROMP has



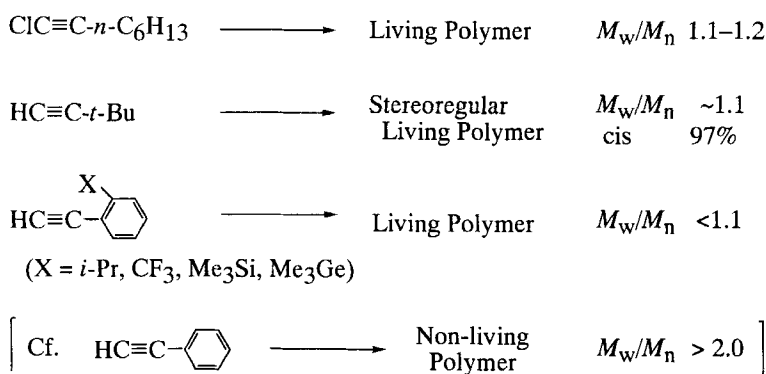
**Scheme 1.** Catalysts for living metathesis polymerization.

been accomplished in protic solvents including water by use of Grubbs' ruthenium carbenes [16].

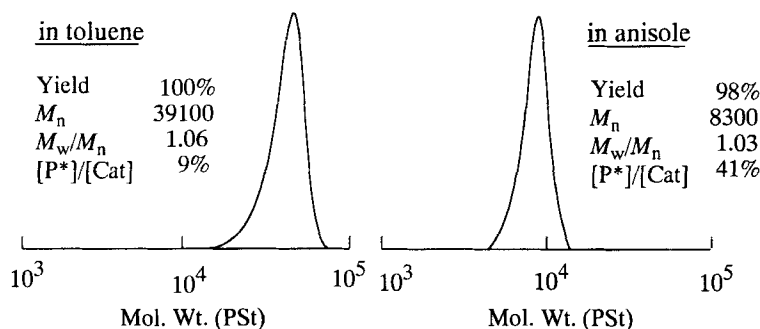
Recently, the examples of the living polymerization of substituted acetylenes have been gradually increasing (Scheme 1). For instance, Schrock carbenes induce excellent living polymerization of several acetylenes (e.g., MeC≡CMe [17], (HC≡C)<sub>2</sub>C(CO<sub>2</sub>Et)<sub>2</sub> [18], HC≡CFC [19], HC≡CC<sub>6</sub>H<sub>4</sub>-*o*-SiMe<sub>3</sub> [20]; polydispersity ratio ( $M_w/M_n$ ) 1.03–1.05 in every case). Tabata, *et al.* have reported the presence of long-lived species in the Rh-catalyzed polymerization of phenylacetylene [21]. A Rh-alkyl complex, reportedly, effects stereospecific and virtually living polymerization of phenylacetylene (*cis* 100%,  $M_w/M_n$  1.17) [22].

Scheme 2 shows acetylenic monomers that undergo living polymerization in cocatalyst. 1-Chloro-1-octyne provides a living polymer whose  $M_w/M_n$  is 1.1–1.2 [23]. Interestingly, *tert*-butylacetylene produces a stereoregular living polymer, that is, a polymer having 97% *cis* and a  $M_w/M_n$  of 1.1 [24]. Such stereospecific living polymerizations are rare, even though all the polymerization mechanisms are considered. Further, phenylacetylenes having ortho substituents such as *o*-*i*-Pr, *o*-CF<sub>3</sub>, *o*-Me<sub>3</sub>Si, and *o*-Me<sub>3</sub>Ge groups also polymerize in a living fashion [25, 26]. This finding is noteworthy because phenylacetylene itself does not give a living polymer with this catalyst.

Figure 1 shows solvent effects on the polymerization of *o*-CF<sub>3</sub>-phenylacetylene by MoOCl<sub>4</sub>-*n*-Bu<sub>4</sub>Sn-EtOH [27]. Polymerizations have been carried out at 30°C for 1 hour. In toluene, the  $M_w/M_n$  ratio is 1.06 and the initiator efficiency



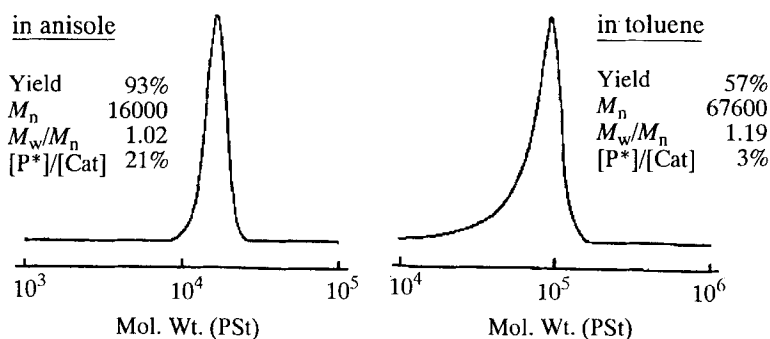
**Scheme 2.** Living polymerization of various substituted acetylenes by  $\text{MoOCl}_4$ -*n*-Bu<sub>4</sub>Sn-EtOH (1:1:1) (in toluene, 0–30°C).



**Figure 1.** Solvent effect on the polymerization of *o*-CF<sub>3</sub>-phenylacetylene by  $\text{MoOCl}_4$ -*n*-Bu<sub>4</sub>Sn-EtOH(1:1:1) (30°C, 1 hour,  $[\text{M}]_0 = 0.20$  M,  $[\text{MoOCl}_4] = 10$  mM).

( $[\text{P}^*]/[\text{Cat}]$ ), i.e., the ratio of the propagating species to catalyst, is no more than 9%. On the other hand, when anisole is used as polymerization solvent, the  $M_w/M_n$  becomes as small as 1.03 and, more importantly, the  $[\text{P}^*]/[\text{Cat}]$  increases up to about 40%. The effect of ethanol concentration was examined for this *n*-Bu<sub>4</sub>Sn/ani-sole system. The  $M_w/M_n$  is 1.05 and the  $[\text{P}^*]/[\text{Cat}]$  is 29% without ethanol. On the other hand, when the  $[\text{EtOH}]/[\text{MoOCl}_4]$  is unity or larger, the  $M_w/M_n$  stays about 1.03 and the  $[\text{P}^*]/[\text{Cat}]$  invariably as high as about 40%.

To develop a new catalyst system, Et<sub>3</sub>Al was examined as a cocatalyst in the polymerization of *o*-CF<sub>3</sub>-phenylacetylene by the  $\text{MoOCl}_4$ -based ternary catalyst. Toluene as polymerization solvent results in a larger  $M_w/M_n$  and a smaller



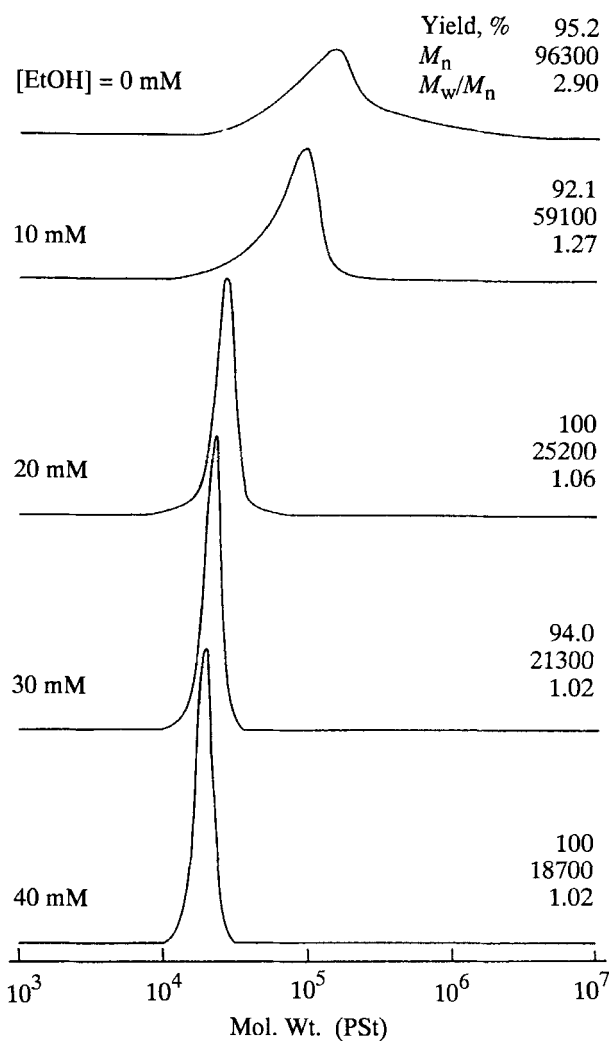
**Figure 2.** Polymerizations of *o*-CF<sub>3</sub>-phenylacetylene by MoOCl<sub>4</sub>-Et<sub>3</sub>Al-EtOH(1:1:4) in anisole and in toluene (30°C, 1 hour, [M]<sub>0</sub> = 0.20 M, [MoOCl<sub>4</sub>] = 10 mM).

$[P^*]/[Cat]$ , indicating that anisole is preferable to toluene. The reason for this is probably due to the strong reducing ability of Et<sub>3</sub>Al. Eventually, the Et<sub>3</sub>Al/anisole combination gives an even smaller  $M_w/M_n$  value than does the *n*-Bu<sub>4</sub>Sn/toluene version.

The effect of ethanol concentration was examined for the MoOCl<sub>4</sub>-Et<sub>3</sub>Al-EtOH catalyst system (Figure 3). Without ethanol, the MWD of the polymer is rather broad. The MWD narrows with increasing ethanol concentration, and the  $M_w/M_n$  becomes 1.02 at 30 and 40 mM. Meanwhile, the molecular weight decreases, and the  $[P^*]/[Cat]$  goes up to about 20%. Consequently, it is concluded that an [EtOH] of 40 mM, i.e., MoOCl<sub>4</sub>:Et<sub>3</sub>Al:EtOH = 1:1:4, is favorable to achieve the narrow MWD.

Figure 4 shows results for the multistage polymerization by use of the Et<sub>3</sub>Al-the presence of MoOCl<sub>4</sub>-*n*-Bu<sub>4</sub>Sn-EtOH catalyst. When all the monomer had been consumed, new monomer feeds were supplied two more times repeatedly. The polymer molecular weight increases in direct proportion to the polymer yield even after repeated monomer additions. Meanwhile, the  $M_w/M_n$  decreases to become as small as 1.02 finally. These results manifest that this Et<sub>3</sub>Al-containing catalyst is a living polymerization catalyst.

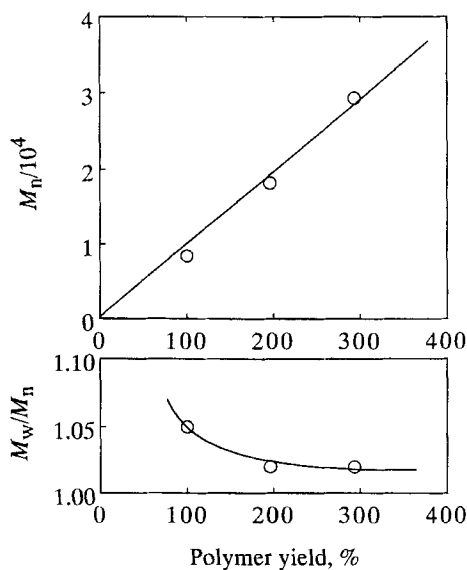
The temperature effect was examined in the Et<sub>3</sub>Al system. Figure 5 shows the first-order plots with respect to monomer concentration. Good linear relationships are observed in the temperature range 0-30°C. The plots of  $M_n$  versus polymer yield at various temperatures give a single straight line passing through the



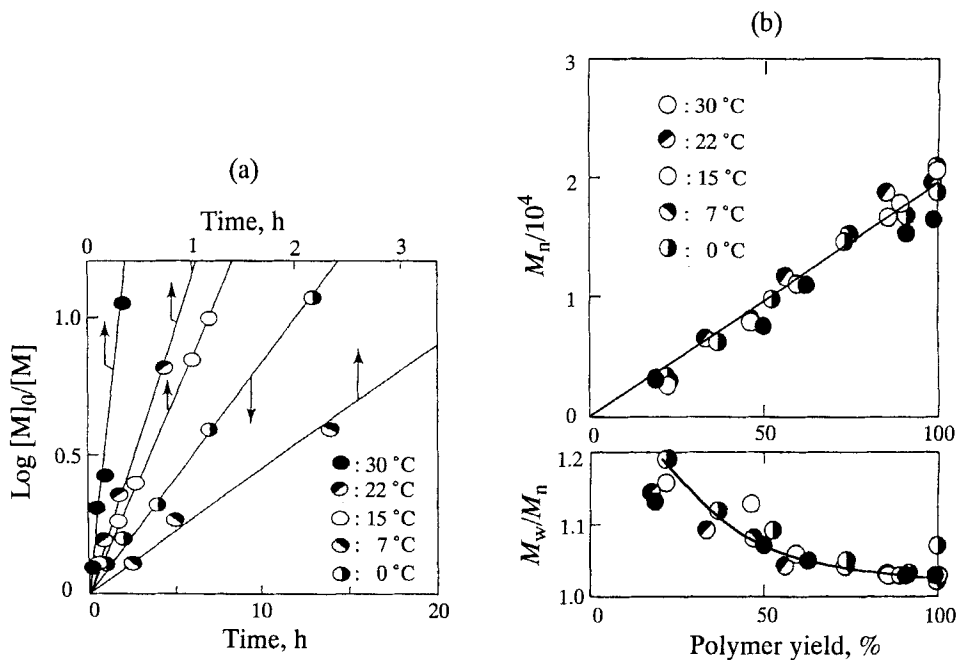
**Figure 3.** Effect of ethanol concentration on the polymerization of *o*-CF<sub>3</sub>-phenylacetylene by MoOCl<sub>4</sub>-Et<sub>3</sub>Al-EtOH (in anisole, 30°C, 1 hour, [M]<sub>0</sub> = 0.20 M, [MoOCl<sub>4</sub>] = [Et<sub>3</sub>Al] = 10 mM).

origin. The  $M_w/M_n$  diminishes to about 1.02 at high conversions. Thus, the living nature of the polymerization is maintained in the temperature range 0-30°C.

Not only Et<sub>3</sub>Al, but also Et<sub>2</sub>Zn has been found to be effective in the living polymerization of *o*-CF<sub>3</sub>-phenylacetylene by the MoOCl<sub>4</sub>-cocatalyst-EtOH system [29]. In this case, the smallest  $M_w/M_n$  is 1.03, which is achieved at [EtOH] = 30

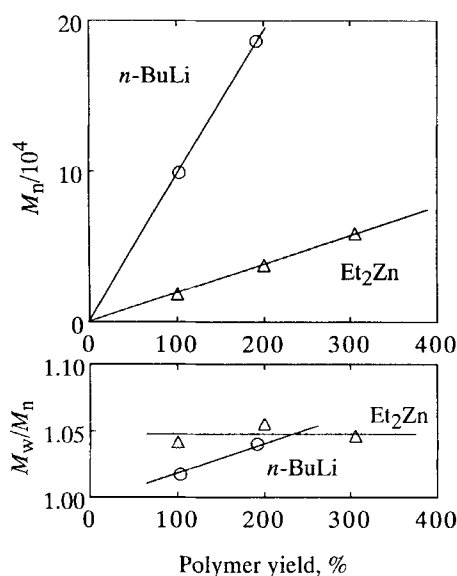


**Figure 4.** Multistage polymerization of *o*-CF<sub>3</sub>-phenylacetylene by MoOCl<sub>4</sub>-Et<sub>3</sub>Al-EtOH(1:1:4) (in anisole, 30°C, 1 hour, [M]<sub>0</sub> = [M]<sub>added</sub> = 0.10 M, [MoOCl<sub>4</sub>] = 10 mM).



**Figure 5.** Effect of temperature on the polymerization of *o*-CF<sub>3</sub>-phenylacetylene by MoOCl<sub>4</sub>-Et<sub>3</sub>Al-EtOH(1:1:4) (in anisole, [M]<sub>0</sub> = 0.20 M, [MoOCl<sub>4</sub>] = 10 mM).



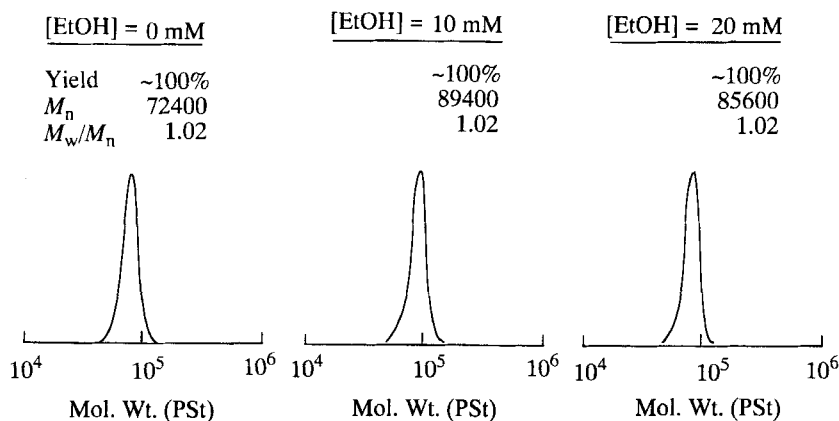


**Figure 6.** Multistage polymerizations of *o*-CF<sub>3</sub>-phenylacetylene by MoOCl<sub>4</sub>-Et<sub>2</sub>Zn-EtOH(1:1:3) and MoOCl<sub>4</sub>-*n*-BuLi-EtOH(1:1:2) (in anisole, 30°C, [M]<sub>o</sub> = [M]<sub>added</sub> = 0.10 M, [MoOCl<sub>4</sub>] = 10 mM).

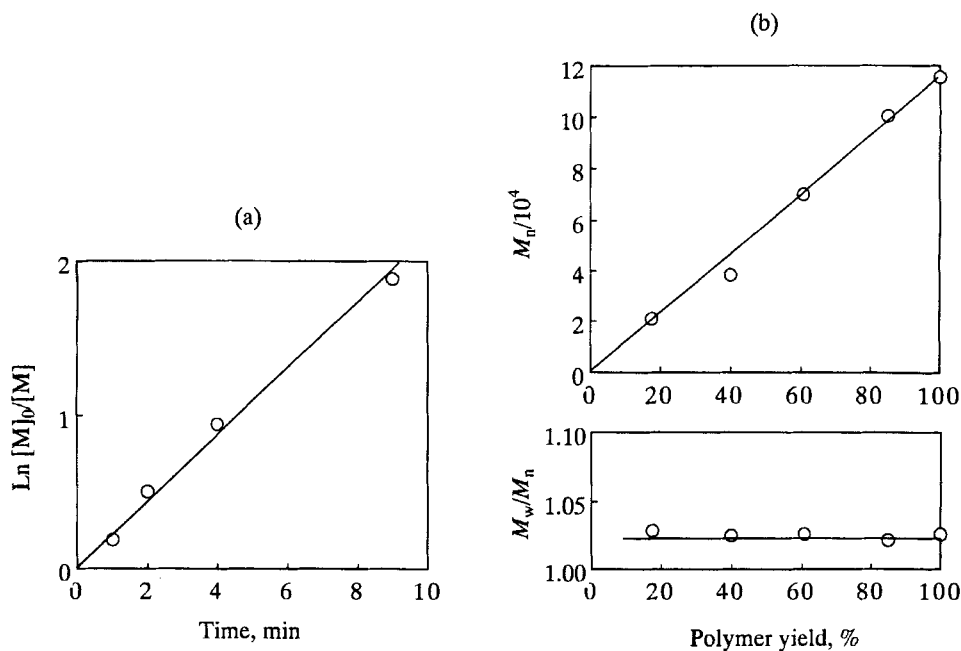
mM (MoOCl<sub>4</sub>:*n*-BuLi:EtOH = 1:1:3). Further, *n*-BuLi is also useful as cocatalyst; i.e., the  $M_w/M_n$  is 1.02 at MoOCl<sub>4</sub>:*n*-BuLi:EtOH = 1:1:2. Figure 6 shows results for the multistage polymerization using Et<sub>2</sub>Zn and *n*-BuLi as cocatalysts. When new monomer feeds are repeatedly supplied, the molecular weight increases in proportion to polymer yield. Meanwhile, the  $M_w/M_n$  ratios are maintained below 1.05. These results manifest the polymerization systems are all living. These living polymerizations occur in the temperature range 0–30°C.

The polymerization by the *n*-BuLi-containing catalyst showed an interesting effect of ethanol concentration [29]. That is, even though the ethanol concentration is changed from 0 to 10 and 20 mM, the  $M_w/M_n$  remains about 1.02 and barely changes (Figure 7). Thus, the binary system composed of MoOCl<sub>4</sub> and *n*-BuLi provides a polymer with very narrow MWD despite the absence of ethanol.

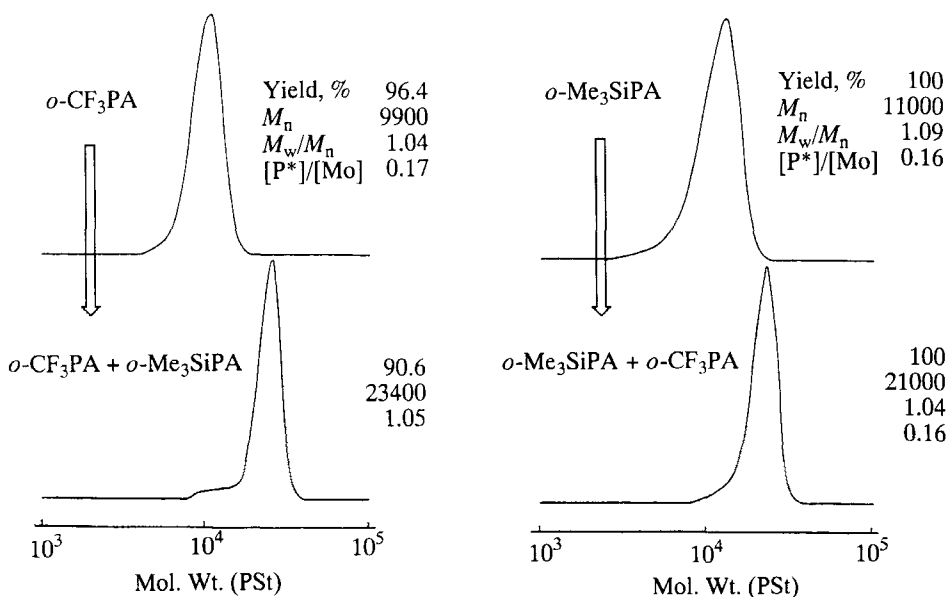
It was examined whether the polymerization by the MoOCl<sub>4</sub>-*n*-BuLi catalyst is living or not. As seen in Figure 8a, the polymerization proceeds in the first order of monomer concentration. Figure 8b shows that the polymer molecular weight is proportional to the polymer yield, while the  $M_w/M_n$  is invariably as small as about 1.02. All these findings support that the binary MoOCl<sub>4</sub>-*n*-BuLi catalyst serves as a living polymerization catalyst.



**Figure 7.** Effect of ethanol concentration on the polymerization of *o*-CF<sub>3</sub>-phenylacetylene by MoOCl<sub>4</sub>-*n*-BuLi-EtOH (in anisole, 30°C, 3 hours, [M]<sub>0</sub> = 0.10 M, [MoOCl<sub>4</sub>] = [*n*-BuLi] = 10 mM).



**Figure 8.** Polymerization of *o*-CF<sub>3</sub>-phenylacetylene by MoOCl<sub>4</sub>-*n*-BuLi(1:1) (in anisole, 30°C, [M]<sub>0</sub> = 0.10 M, [MoOCl<sub>4</sub>] = 10 mM).



**Figure 9.** Block copolymerization of *o*-CF<sub>3</sub>- and *o*-Me<sub>3</sub>Si-phenylacetylenes by MoOCl<sub>4</sub>-Et<sub>3</sub>Al-EtOH(1:1:4) (in anisole, 30°C, 1 hour,  $[M]_0 = [M]_{added} = 0.10$  M,  $[MoOCl_4] = 10$  mM).

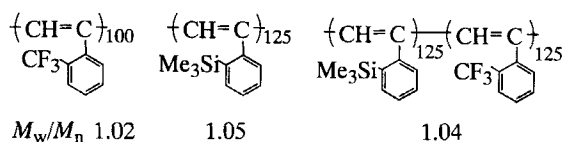
Not only *o*-CF<sub>3</sub>-phenylacetylene (*o*-CF<sub>3</sub>PA) but also *o*-Me<sub>3</sub>Si-phenylacetylene (*o*-Me<sub>3</sub>SiPA) provides a living polymer with the MoOCl<sub>4</sub>-Et<sub>3</sub>Al-EtOH catalyst. Hence, block copolymerizations of *o*-CF<sub>3</sub>PA and *o*-Me<sub>3</sub>SiPA have been tried (Figure 9). When living poly(*o*-CF<sub>3</sub>PA) is prepared and *o*-Me<sub>3</sub>SiPA is added to it, the GPC peak shifts to the high molecular weight side, indicating the formation of a block copolymer. However, a small amount of homopolymer of *o*-CF<sub>3</sub>PA also forms. In contrast, when the monomers are polymerized in the order of *o*-Me<sub>3</sub>SiPA and then *o*-CF<sub>3</sub>PA, a block copolymer is exclusively formed.

TEM pictures of a block copolymer of *o*-CF<sub>3</sub>PA and *o*-Me<sub>3</sub>SiPA were taken by an electron energy loss spectroscopy (EELS) type of electron micrograph, which is capable of measuring images for particular elements [30]. Consequently, a picture for fluorine indicated a microdomain structure, and a picture for silicon also showed the same structure. These findings support the existence of a microdomain structure and, in turn, prove the formation of a block copolymer.

Scheme 3 shows main conclusions regarding MoOCl<sub>4</sub>-based catalysts. Initially, it was found that all the MoOCl<sub>4</sub>-based catalysts in the Scheme work as excellent living polymerization catalysts in anisole as solvent. The *n*-Bu<sub>4</sub>Sn system

New Living Polymerization Catalysts (in anisole)

MoOCl <sub>4</sub> - <i>n</i> -Bu <sub>4</sub> Sn-EtOH	(high [P*]/[Cat] up to ~40%)
MoOCl <sub>4</sub> -Et <sub>3</sub> Al-EtOH	(small <i>M<sub>w</sub></i> / <i>M<sub>n</sub></i> of ~1.02)
MoOCl <sub>4</sub> -Et <sub>2</sub> Zn-EtOH	( " )
MoOCl <sub>4</sub> - <i>n</i> -BuLi	(binary system)

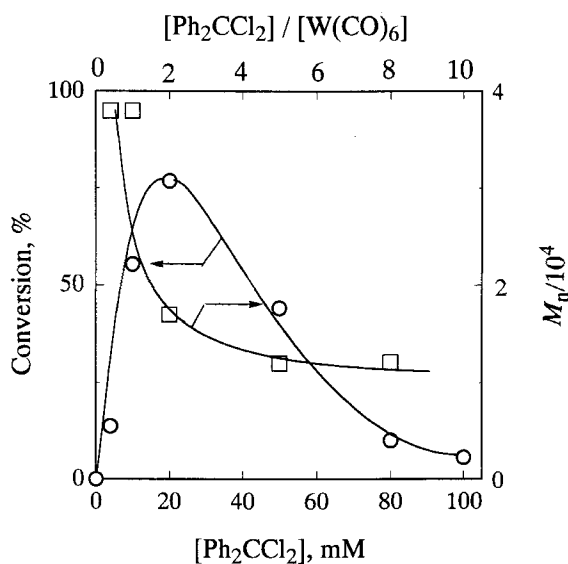
Synthesis of Living Polymers and Block Copolymers**Scheme 3.** New catalysts and precision polymer syntheses.

features high initiator efficiency. The Et<sub>3</sub>Al and Et<sub>2</sub>Zn systems give polymers with very narrow MWDs, and the *n*-BuLi system does not need ethanol. Secondly, the syntheses of living polymers with narrow MWDs and a block copolymer from *o*-CF<sub>3</sub>- and *o*-Me<sub>3</sub>Si-phenylacetylenes were achieved.

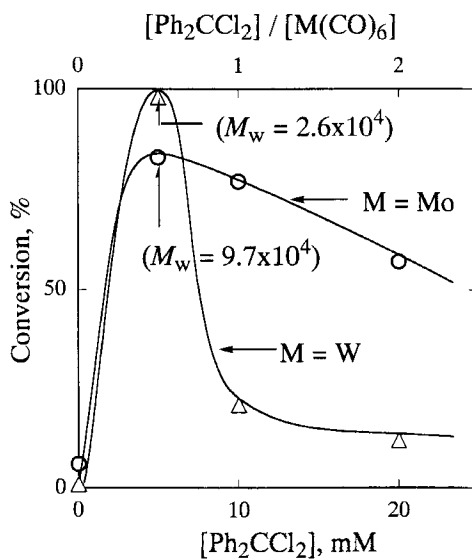
**Polymerization of Substituted Acetylenes by Metal Carbonyl-Based Catalysts**

Group 6 transition metal carbonyl-based catalysts such as M(CO)<sub>6</sub>-CCl<sub>4</sub>-*hν* [31], M(CO)<sub>6</sub>-SnCl<sub>4</sub>-*hν* [32], and M(CO)<sub>3</sub>(mesitylene)-CCl<sub>4</sub> [33] (M = W, Mo) are known to induce the polymerization of substituted acetylenes. These metal carbonyl-based catalysts are characterized by both the formation of high molecular weight poly(phenylacetylene) and the stability of the metal carbonyls to air and moisture. The M(CO)<sub>6</sub>-CCl<sub>4</sub>-*hν* catalysts require CCl<sub>4</sub> not only as catalyst component, but also as solvent and further require UV irradiation. Recently, various organic chlorides have been examined in place of CCl<sub>4</sub>, leading to a finding that Ph<sub>2</sub>CCl<sub>2</sub> works in a catalytic amount [34].

Figure 10 shows the effect of Ph<sub>2</sub>CCl<sub>2</sub> concentration on the polymerization of phenylacetylene by W(CO)<sub>6</sub>-Ph<sub>2</sub>CCl<sub>2</sub>-*hν* [35]. The catalyst was prepared by UV irradiation of the solution of W(CO)<sub>6</sub>-Ph<sub>2</sub>CCl<sub>2</sub> in toluene at 30°C. No polymerization proceeds without Ph<sub>2</sub>CCl<sub>2</sub>. The monomer conversion shows a maximum of ca. 75% at [Ph<sub>2</sub>CCl<sub>2</sub>]/[W(CO)<sub>6</sub>] = 2, and gradually decreases on addition of more than two equivalents of Ph<sub>2</sub>CCl<sub>2</sub>. The *M<sub>n</sub>* of the formed polymer is high (ca. 4 × 10<sup>4</sup>) at [Ph<sub>2</sub>CCl<sub>2</sub>]/[W(CO)<sub>6</sub>] = 1 and below, but decreases monotonously with






**Figure 10.** Effect of Ph<sub>2</sub>CCl<sub>2</sub> concentration on the polymerization of phenylacetylene by W(CO)<sub>6</sub>-Ph<sub>2</sub>CCl<sub>2</sub>-hν (catalyst solution UV-irradiated at 30°C for 1 hour; polymerized in toluene at 30°C for 18 hours; [M]<sub>0</sub> = 0.50 M, [W(CO)<sub>6</sub>] = 10 mM).



**Figure 11.** Effect of Ph<sub>2</sub>CCl<sub>2</sub> concentration on the polymerization of norbornene by M(CO)<sub>6</sub>-Ph<sub>2</sub>CCl<sub>2</sub>-hν (catalyst solution UV-irradiated at 60°C for 1 hour; polymerized in toluene at 60°C for 24 hours; [M]<sub>0</sub> = 0.10 M, [M(CO)<sub>6</sub>] = 10 mM).

TABLE 1. Polymerization of Various Substituted Acetylenes by  $M(\text{CO})_6\text{-Ph}_2\text{CCl}_2\text{-hv}^a$ 

Monomer	$M(\text{CO})_6$	Polymer	
		Yield, %	$M_w$
$\text{HC}\equiv\text{C}$ - 	$\text{W}(\text{CO})_6$	70	30,000
$\text{HC}\equiv\text{C}$ - 	$\text{W}(\text{CO})_6$	55	230,000
$\text{HC}\equiv\text{C}$ - <i>t</i> -Bu	$\text{W}(\text{CO})_6$	71	630,000
-----			
$\text{HC}\equiv\text{C}$ - 	$\text{Mo}(\text{CO})_6$	8	380,000
$\text{HC}\equiv\text{C}$ - <i>t</i> -Bu	$\text{Mo}(\text{CO})_6$	70	240,000
$\text{ClC}\equiv\text{C}$ - <i>n</i> - $\text{C}_6\text{H}_{13}$	$\text{Mo}(\text{CO})_6$	4	780,000

<sup>a</sup> Polymerized in toluene at 30 °C for 24 h;  $[\text{M}]_0 = 0.50$   
 $\text{M}$ ,  $[\text{M}(\text{CO})_6] = 10 \text{ mM}$ ,  $[\text{Ph}_2\text{CCl}_2] = 20 \text{ mM}$ .

increasing  $[\text{Ph}_2\text{CCl}_2]$ . Thus, it proves that a catalytic amount of  $\text{Ph}_2\text{CCl}_2$  is sufficient in this catalyst system unlike  $\text{W}(\text{CO})_6\text{-CCl}_4\text{-hv}$  which needs  $\text{CCl}_4$  in a large excess over  $\text{W}(\text{CO})_6$  and preferably as solvent. Since a catalytic amount of  $\text{Ph}_2\text{CCl}_2$  is effective, various polymerization solvents can be employed in this catalyst system. The  $\text{Mo}(\text{CO})_6$ -based counterpart is much less active in the polymerization of phenylacetylene.

The effect of  $\text{Ph}_2\text{CCl}_2$  concentration was studied in the polymerizations of norbornene by  $\text{W}(\text{CO})_6\text{-Ph}_2\text{CCl}_2\text{-hn}$  and  $\text{Mo}(\text{CO})_6\text{-Ph}_2\text{CCl}_2\text{-hn}$  (Figure 11). The catalysts were prepared by UV irradiation of the toluene solution of an  $\text{M}(\text{CO})_6$  and  $\text{Ph}_2\text{CCl}_2$  at 60°C. No polymerization proceeds without  $\text{Ph}_2\text{CCl}_2$  as in the case of phenylacetylene. The monomer conversion shows a sharp maximum of ca. 100% at  $[\text{Ph}_2\text{CCl}_2]/[\text{W}(\text{CO})_6] = 0.5$ , and steeply decreases in the presence of larger amounts of  $\text{Ph}_2\text{CCl}_2$ . With  $\text{Mo}(\text{CO})_6$  as well, a maximum (ca. 80%) is seen in conversion at  $[\text{Ph}_2\text{CCl}_2]/[\text{Mo}(\text{CO})_6] = 0.5$ . The  $M_n$  values of the polymer obtained at  $[\text{Ph}_2\text{CCl}_2]/[\text{M}(\text{CO})_6] = 0.5$  are ca.  $3 \times 10^4$ – $10 \times 10^4$ . The polynorbornenes formed are partly insoluble in toluene and chloroform.

TABLE 2. Effects of Solvents and UV Irradiation on the Polymerization of Phenylacetylene by  $WCl_2(CO)_3(AsPh_3)_2$ <sup>a</sup>

Solvent	Irradn time <sup>b</sup> , h	Monomer convn, %	Polymer	
			Yield, %	$M_n$
toluene	0	85	66	33,000
toluene	1	84	65	34,000
CCl <sub>4</sub>	0	98	82	12,000
CCl <sub>4</sub>	1	99	72	14,000

<sup>a</sup> Polymerized at 60 °C for 24 h;  $[M]_0 = 0.50$  M,  $[Cat] = 2.0$  mM.

<sup>b</sup> Catalyst solution UV-irradiated at 60 °C for 1 h.

Polymerization of various substituted acetylenes by  $M(CO)_6-Ph_2CCl_2-h\nu$  was examined (Table 1). Phenylacetylene, *o*-Me<sub>3</sub>Si-phenylacetylene, and *tert*-butylacetylene polymerize with the W catalyst in high yields. *o*-CF<sub>3</sub>-phenylacetylene, *tert*-butylacetylene, and 1-chloro-1-octyne polymerize with the Mo catalyst, but the yields are rather low except for *tert*-butylacetylene. The polymer molecular weights for sterically crowded monosubstituted acetylenes and 1-chloro-1-octyne tend to be very high. Thus, the  $M(CO)_6-Ph_2CCl_2-h\nu$  catalysts polymerize various substituted acetylenes, and the kind of polymerizable monomers depends on the metal hexacarbonyl employed.

It has been reported that metal dichlorocarbenes are the initiating species for the  $M(CO)_6-CCl_4-h\nu$  systems [36]. By analogy, it is assumed that the initiating species for the present catalysts be metal diphenylcarbenes.

Bencze, *et al.* have reported that group 6 transition metal complexes  $MCl_2(CO)_3(AsPh_3)_2$  ( $M = W, Mo$ ) effect olefin metathesis and metathesis polymerization of norbornene [37]. Since the active species for the polymerization of substituted acetylenes by group 5 and 6 transition metals are also metal carbenes, it is interesting to examine the polymerization of substituted acetylenes by these catalysts.

TABLE 3. Effects of Additives on the Polymerization of Phenylacetylene by  $WCl_2(CO)_3(AsPh_3)_2$ <sup>a</sup>

Additive	Monomer convn, %	Polymer	
		Yield, %	$M_n$
none	85	66	33,000
TiCl <sub>4</sub>	45	22	33,300
AlBr <sub>3</sub>	22	9	8,400
EtAlCl <sub>2</sub>	36	3	30,000
<i>n</i> -Bu <sub>4</sub> Sn	76	65	40,000
Et <sub>3</sub> Al	38	32	26,000
Et <sub>2</sub> Zn	39	31	38,500

<sup>a</sup> Polymerized in toluene at 60 °C for 24 h;  $[M]_0 = 0.50$  M,  $[Cat] = 2.0$  mM,  $[Additive] = 2.0$  mM.





The polymerization of phenylacetylene by  $WCl_2(CO)_3(AsPh_3)_2$  proceeds in toluene to yield a polymer of  $M_n 33 \times 10^3$  (Table 2) [38]. UV irradiation on preparation of the catalyst does not affect the polymerization. The polymerization proceeds also in CCl<sub>4</sub>, and UV irradiation again hardly affects. Thus, in contrast to the above-stated  $M(CO)_6$ -based catalysts, neither organic chlorides nor UV irradiation is necessary for this catalyst.

It is known that Lewis acids and organometallic alkylating agents activate the  $M(CO)_6$ - and  $MCl_n$ -based catalysts, respectively [39]. Table 3 shows the effects of Lewis acids and organometallics for  $WCl_2(CO)_3(AsPh_3)_2$ . Addition of Lewis acids such as TiCl<sub>4</sub>, AlBr<sub>3</sub>, and EtAlCl<sub>2</sub> rather decreases the polymer yield. Addition of an organometal, *n*-Bu<sub>4</sub>Sn does not greatly affect the polymerization, while Et<sub>3</sub>Al and Et<sub>2</sub>Zn reduce the polymer yields. Thus, these additives show only adverse effects to the present catalyst.

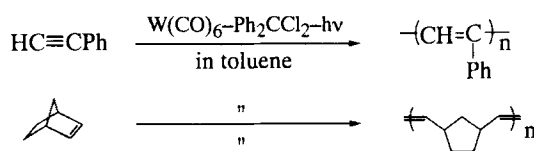
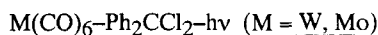
Table 4 shows the polymerizations of various substituted acetylenes by  $WCl_2(CO)_3(AsPh_3)_2$ . The polymer yields for phenylacetylenes are good, and the polymer molecular weights for ortho-substituted phenylacetylenes are considerably high. In contrast, aliphatic acetylenes are less reactive, and disubstituted acetylenes such as 1-phenyl-1-propyne and 1-chloro-1-octyne scarcely polymerize.



TABLE 4. Polymerization of Various Substituted Acetylenes by  $WCl_2(CO)_3(AsPh_3)_2$ <sup>a</sup>

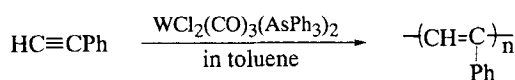
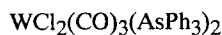
Monomer	Monomer convn, %	Polymer <sup>a</sup>	
		Yield, %	$M_n$
$HC\equiv C$ - 	100	95	390,000
$HC\equiv C$ - 	100	93	380,000
$HC\equiv C$ - 	72	45	27,400
$HC\equiv C$ - 	72	72	35,200
$HC\equiv C$ - <i>t</i> -Bu	33	20	47,800
$HC\equiv C$ - <i>n</i> -C <sub>8</sub> H <sub>17</sub>	45	13	—

<sup>a</sup> Polymerized in toluene at 60 °C for 24 h;  $[M]_0 = 0.50$  M,  $[Cat] = 2.0$  mM.



\*  $Ph_2CCl_2$  : catalytic amount

\* Various solvents are available.



\*  $RCl_n$  and  $h\nu$ : not needed

**Scheme 4.** Polymerization by metal carbonyl-based catalysts.

The initiation mechanism for the polymerization of norbornene by  $WCl_2(CO)_3(AsPh_3)_2$  is thought to be the 2,3-hydrogen shift of the coordinating norbornene to form a metal carbene species [40]. It is postulated in a similar way that 1,2-hydrogen shift will form the initiating species, a metal vinylidene, in the polymerization of substituted acetylenes.

## CONCLUSION

Group 6 transition metal carbonyl-based catalysts,  $M(CO)_6-Ph_2CCl_2-h\nu$  induce metathesis polymerization of phenylacetylenes and norbornene (Scheme 4). A catalytic amount of  $Ph_2CCl_2$  is enough, and various solvents can be used.  $WCl_2(CO)_3(AsPh_3)_2$  induces the polymerization of substituted acetylenes. It does not require either  $RCl_n$  or UV irradiation.

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