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Polymerization of substituted acetylenes by (mesitylene)M(CO)$_3$ (M=W, Mo)

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Summary

Phenylacetylene could be polymerized by (mesitylene)W(CO)$_3$ in CCl$_4$ to give a polymer with $\overline{M}_n$ 12,000 in ca. 80% yield. UV irradiation was unnecessary unlike the W(CO)$_6$–CCl$_4$–hν catalyst. The present polymerization did not proceed in toluene. The (mesitylene)W(CO)$_3$ catalyst afforded high molecular weight polymers ($\overline{M}_n$ 3x10^5–4x10^5) from phenylacetylenes bearing bulky substituents (e.g., Me$_3$Si and CF$_3$) at the ortho position. The Mo counterpart, (mesitylene)Mo(CO)$_3$, catalyzed the polymerization of 1-chloro-2-phenylacetylene and 1-chloro-1-octyne to provide high molecular weight polymers ($\overline{M}_n$ ca. 4x10^5). Catalytic amounts of Lewis acids accelerated the polymerization of phenylacetylene by (mesitylene)W(CO)$_3$, but decreased the polymer molecular weight; this polymerization proceeded not only in CCl$_4$ but also in toluene.

Introduction

We have found that acetylenes bearing various substituents can be polymerized with WCl$_6$ and MoCl$_5$ (1). It is also known that the M(CO)$_6$–CCl$_4$–hν (M = W, Mo) catalyst systems are less active than WCl$_6$ and MoCl$_5$, but yield polymers with higher molecular weights (1). The (arene)M(CO)$_3$ (M = W, Mo) catalysts induce olefin metathesis without light (2, 3). However, there have been very few attempts on the polymerization of substituted acetylenes catalyzed by this type of transition metal complexes (4, 5).

The polymerization of substituted acetylenes catalyzed by (arene)-M(CO)$_3$ is expected to show the following features: (i) Polymerization proceeds without light. (ii) Owing to low Lewis acidity of the central metal, acid-catalyzed side reactions such as molecular-weight decrease are restrained.

Here we report on the polymerization of various acetylenes by (mesitylene)M(CO)$_3$ [(mes)M(CO)$_3$; M = W, Mo] and catalytic properties of these complexes.

Experimental

Materials

(Mesitylene)W$(CO)_3$ (Strem Chemicals, Inc.) was used as received. (Mesitylene)Mo$(CO)_3$ was prepared with reference to the method of Nicholls (6): The crude product was dissolved in diethyl ether and was filtered through celite 545 (Nachalai tesque). The product was precipitated by adding petroleum ether, and filtered off. The concomitant $Mo(CO)_6$ was removed by sublimation. Anal. Calcd. for $C_{12}H_{12}O_3Mo$: C, 48.02 ; H, 4.03. Obsd. : C, 47.76 ; H, 3.97. Phenylacetylene and (*p*-methylphenyl)acetylene were commercially obtained. Other acetylenes were prepared according to the literature methods (1,7). All the monomers were distilled twice from CaH_2; purities >99% by gas chromatography (GC). Lewis acids (Aldrich Chem. Co., Inc.) were used as received.

Polymerization

A standard polymerization procedure is as follows: A CCl_4 solution (2.5 mL) of (mesitylene)M$(CO)_3$ (M = W, Mo) (0.050 mmol) was stirred in the dark at 60°C for 1 h. To this was added a CCl_4 solution (2.5 mL) of a monomer (2.5 mmol) and an internal standard of GC (e.g. chlorobenzene) (0.2 mL), and the mixture was kept in the dark. Polymerization was quenched with methanol (0.5 mL). In a few cases, the catalyst solution was irradiated with a 200-W high-pressure mercury lamp (Fuji Glass Work) from a distance of 5 cm at 60°C for 1 h before monomer was added. All the polymerization procedures were carried out under dry nitrogen.

Monomer conversions were determined by GC and the number-average molecular weights ($\overline{M}_n$) of polymers were determined by gel-permeation chromatography (GPC ; eluent $CHCl_3$, polystyrene calibration).

Results and Discussion

Polymerization of Phenylacetylene by (Mesitylene)W(CO)$_3$

Table I shows results of the polymerization of phenylacetylene catalyzed by (mesitylene)W$(CO)_3$. The monomer was quantitatively consumed in CCl_4 at 60°C in the dark to give a polymer with $\overline{M}_n$ ca. 1×10^4. UV irradiation hardly affected the monomer conversion and polymer yield, which indicates that this catalyst system does not need UV irradiation. This gives a contrast to $W(CO)_6$ which requires UV irradiation (8,9). Consequently, all the following polymerizations were performed in the dark. When toluene and cyclohexane were employed as polymerization solvents, no

Table I. Polymerization of Phenylacetylene by (Mes)W(CO)$_3$ [a]

Polymn	Polymn	Monomer	Polymer [b]	
solvent	temp, °C	convn, %	Yield, %	$\overline{M}_n/10^3$ [c]
CCl_4	60	100	82	12
CCl_4	60 [d]	100	85	6.8
toluene	60	0	0	–
cyclohexane	60	0	0	–
CCl_4	30	24	24	68
CCl_4	45	61	54	51
CCl_4	75	100	57	3.2

[a] Polymerized for 24 h; $[M]_0 = 0.50$ M, [Cat] = 10 mM (dark). [b] Methanol-insoluble product. [c] Determined by GPC. [d] Catalyst solution irradiated with UV light at 60°C for 1 h.

polymerization occurred at all. This suggests that CCl_4 is indispensable for the formation of the propagating species as in the W(CO)$_6$-catalyzed polymerization.

Whereas the polymerization by W(CO)$_6$–CCl_4–hν at 30°C proceeds virtually quantitatively after 24 h (8), the monomer conversion was no more than 24% with (mesitylene)-W(CO)$_3$–CCl_4 under the same conditions. As the polymerization temperature was raised, however, the polymerization was accelerated. The $\overline{M}_n$ (68,000) of the polymer obtained with (mesitylene)W(CO)$_3$–CCl_4 at 30°C is comparable to the value (79,000) with the W(CO)$_6$–CCl_4–hν (8). However, the molecular weight of polymer decreased with increasing temperature of polymerization.

Polymerization of phenylacetylene by (mesitylene)W(CO)$_3$ was examined in mixtures of CCl_4 and toluene (Figure 2). The polymerization in a 1:1 (vol)

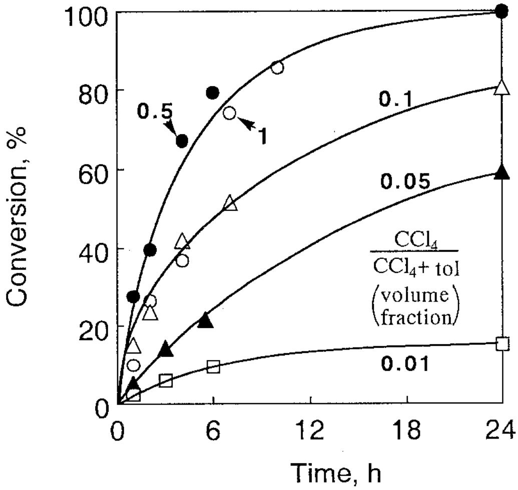


Figure 1. Polymerization of phenylacetylene by (mes)W(CO)$_3$ in mixtures of CCl_4 and toluene (30°C, $[M]_0 = 0.50$ M, [Cat] = 10 mM (dark)).

toluene/CCl_4 mixture proceeded similarly to the one in CCl_4 solution. The polymerization rate, however, decreased as the toluene fraction was further increased. This suggests that a large excess of CCl_4 against the catalyst is necessary for phenylacetylene to polymerize quantitatively.

Polymerization of Other Acetylenes by (Mesitylene)W(CO)$_3$

Table II shows results of the polymerization of various substituted acetylenes catalyzed by (mesitylene)W(CO)$_3$ in CCl_4. Phenylacetylenes having bulky substitutents at the ortho position polymerized virtually quantitatively within 2 h to give polymers with $\overline{M}_n$ up to a few hundred thousand. The polymerizations of the meta- or para-substituted phenylacetylenes were slower (completed after 24 h), and the $\overline{M}_n$ values of the formed polymers stayed several tens of thousand. As an exception, *p*-CF_3-phenylacetylene gave only methanol-soluble oligomers.

These results show that the present catalyst is useful for the synthesis of high polymers from phenylacetylenes with bulky ortho-substituents, but that it is not the case with meta- and para-substituted phenylacetylenes irrespective of the electronic nature of substituents.

Table II. Polymerization of Ring-Substituted Phenylacetylenes (PAs) by (Mes)W(CO)$_3$ [a]

Monomer	Polymn time, h	Monomer convn, %	Polymer [b] Yield, %	$\overline{M}_n/10^3$ [c]
o-Me_3SiPA	2	100	95	390
o-CF_3PA	2	100	100	290
o-ClPA	24	31	21	76
o-CH_3PA	24	100	98	150
m-CF_3PA	8	100	94	31
m-ClPA	4	100	100	66
m-CH_3PA	24	84	77	11
p-CF_3PA	24	100	0	–
p-ClPA	24	98	38	12
p-CH_3PA	24	99	88	15

[a] Polymerized in CCl_4 at 60°C; $[M]_0 = 0.50$ M, [Cat] = 10 mM (dark). [b] Methanol-insoluble product. [c] Determined by GPC.

Table III. Polymerization of Substituted Acetylenes by (Mes)Mo(CO)$_3$ [a]

Monomer	Monomer convn, %	Polymer [b] Yield, %	Polymer [b] $\overline{M}_n/10^3$ [c]
PhC≡CH (PA)	52	4	–
o-Me$_3$SiPA	55	34	36
o-CF$_3$PA	100	83	110
t-BuC≡CH [d]	95	89	– [e]
PhC≡CCl	95	77	410
n-C$_6$H$_{13}$C≡CCl	92	70	300

[a] Polymerized in CCl$_4$ at 60°C for 24 h; $[M]_0 = 0.50$ M, [Cat] = 10 mM (dark). [b] Methanol-insoluble product. [c] Determined by GPC. [d] Polymerized at 30°C. [e] Partly insoluble in CHCl$_3$.

Polymerization of Substituted Acetylenes by (Mesitylene)Mo(CO)$_3$

Polymerization of substituted acetylenes was examined by use of (mesitylene)Mo(CO)$_3$ as catalyst (Table III). The polymerizations were performed in CCl$_4$ at 60°C for 24 h.

Neither phenylacetylene nor *o*-Me$_3$Si-phenylacetylene polymerized quantitatively with (mesitylene)Mo(CO)$_3$, which is in contrast to the results with the W counterpart. The $\overline{M}_n$ of the poly(*o*-Me$_3$Si-phenylacetylene) formed was only one tenth that of the polymer obtained with the W counterpart.

On the other hand, acetylenes bearing electron-withdrawing groups such as 1-chloro-2-phenylacetylene and 1-cloro-1-octyne could be polymerized in high yields by (mesitylene)Mo(CO)$_3$ in CCl$_4$. *tert*-Butylacetylene also provided a polymer almost quantitatively in the presence of this catalyst.

Thus, (mesitylene)Mo(CO)$_3$ proves to be effective especially to acetylenes bearing electron-withdrawing groups and *tert*-butylacetylene. This tendency is the same as with other Mo-based catalysts such as MoCl$_5$ and Mo(CO)$_6$–CCl$_4$–hv.

Effect of Lewis Acids

The Lewis acidity of the present complexes should be weaker than that of WCl$_6$ and MoCl$_5$, and there is a possibility that the difference in the Lewis acidity brings about differences in the property of catalyst. Thus, we studied

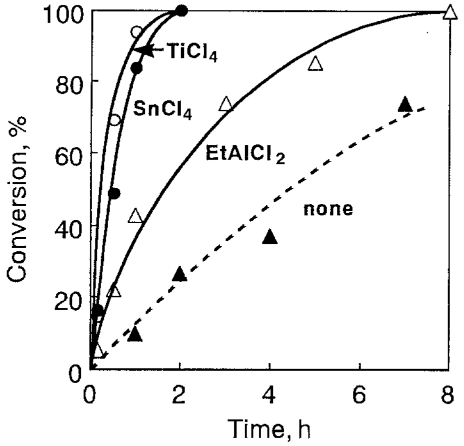


Figure 2. Polymerization of phenylacetylene by (mes)W(CO)$_3$–Lewis acid (in CCl$_4$, 60°C, $[M]_0$ = 0.50 M, [Cat] = 10 mM, [Acid] = 20 mM (dark)).

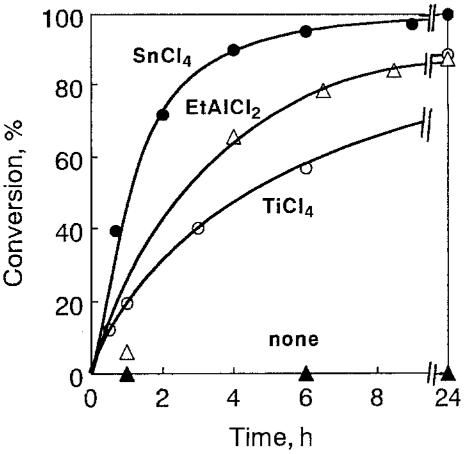


Figure 3. Polymerization of phenylacetylene by (mes)W(CO)$_3$–Lewis acid (in toluene, 60°C, $[M]_0$ = 0.50 M, [Cat] = 10 mM, [Acid] = 20 mM (dark)).

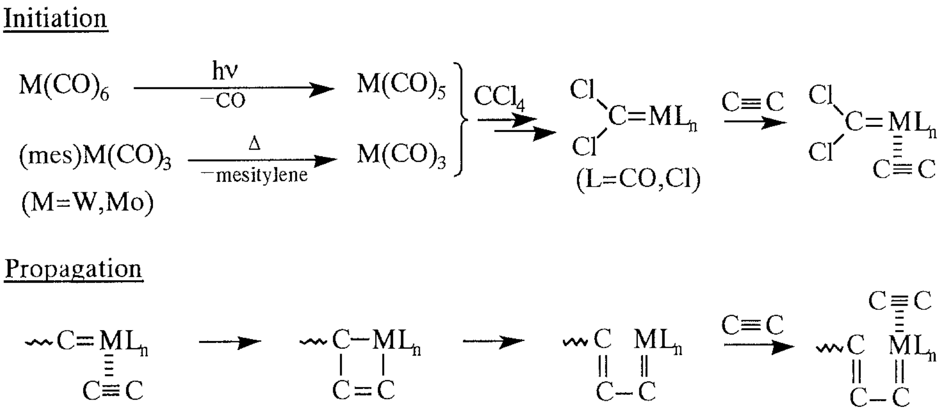
the effect of Lewis acids on the polymerization of phenylacetylene by (mesitylene)W(CO)$_3$. (Mesitylene)W(CO)$_3$ and a Lewis acid (mole ratio 1:2) were dissolved in CCl$_4$, and the solution was stirred in the dark at 60°C for 1 h before use.

Figure 2 shows time profiles of the polymerization in CCl$_4$. Addition of Lewis acids considerably accelerated the polymerization. Thus the monomer conversion reached 100% within 2 h in the presence of TiCl$_4$ and SnCl$_4$. The $\overline{M}_n$'s of the formed polymers were, however, decreased by addition of Lewis acids; e.g. $\overline{M}_n$ (after 2-h polymerization) 6,200 (TiCl$_4$), 9,600 (SnCl$_4$), cf. 42,000 (no Lewis acid).

As described above, the polymerization of phenylacetylene by (mesitylene)W(CO)$_3$ dose not proceed in toluene. In contrast, polymerization took place in high yields when Lewis acids (20 mM) were added to this system (Figure 3). The $\overline{M}_n$'s after 24-h polymerization were: 12,000 (TiCl$_4$), 8,500 (SnCl$_4$), and 8,200 (EtAlCl$_2$).

On the Polymerization Mechanism

The polymerization of phenylacetylene by (mesitylene)M(CO)$_3$ (M = W, Mo) proceeded without UV irradiation, but required a large excess of CCl$_4$ against the catalyst. The reaction mechanism as shown in Scheme I seems plausible for this polymerization, when the polymerization mechanism previously proposed for the W(CO)$_6$–CCl$_4$–hν system is taken into account



Scheme I

(8). The point is that (mesitylene)M(CO)$_3$ releases the ligating mesitylene in solution without the aid of UV light, and then reacts with CCl$_4$ to form a metal carbene which is the initiating species.

The polymerization by (mesitylene)W(CO)$_3$ in CCl$_4$ was fairly accelerated by Lewis acids. This should be caused by the coordination of the Lewis acids to the propagating end, which enhances the electrophilicity of the metal and, in turn, facilitates coordination of the monomer to the propagating end. As another function of Lewis acids, they may attack the double bond of the polymer chain to bring about the decrease of polymer molecular weight.

The polymerization of phenylacetylene by (mesitylene)W(CO)$_3$ did not occur in toluene, but did occur when a catalytic amount of Lewis acids were added. It has been reported that UV irradiation of a hexane solution of W(CO)$_6$ and phenylacetylene leads to the formation of a metal carbene complex (10). In a similar way, a toluene solution of (mesitylene)W(CO)$_3$ and phenylacetylene will produce a metal carbene without UV irradiation. This metal carbene, however, contains no chlorine ligand, which should be responsible for the result that the polymerization by (mesitylene)W(CO)$_3$ in toluene does not take place. Chauvin et al. (11) have reported that the Fischer carbene, i.e., Ph(CH$_3$O)C=W(CO)$_5$, can hardly polymerize cycloolefins by itself, but can polymerize them when combined with Lewis acids. By analogy, it is assumed that, in the present polymerization, Lewis acids activate the metal carbene formed from (mesitylene)W(CO)$_3$ and phenylacetylene to effect polymerization.

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