New catalyst systems for the polymerization of substituted acetylenes: M(CO)₆—Lewis acid—hν (M=W, Mo)

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SUMMARY

A new catalyst system prepared by UV irradiation of a toluene solution of $W(CO)_6$ and a Lewis acid polymerized phenylacetylene (e.g., polymer yield 50%, $\overline{M}_n$ 5.0x10^4 with $SnCl_4$ (0.5 equivalent to $W(CO)_6$) as Lewis acid). This catalyst afforded high molecular weight polymers ($\overline{M}_n$ 4x10^5–5x10^5) from phenylacetylenes with ortho-substituents (e.g., o-Me₃Si and o-CF₃). The $Mo(CO)_6$-based counterpart was rather effective to acetylenes having electron-withdrawing groups (e.g., ClC≡CPh). Polymerization of phenylacetylene occurred as well when $SnCl_4$ was added after UV irradiation of a toluene solution of $W(CO)_6$ and the monomer; this suggests that the polymerization proceeds via metal carbenes having coordinated $SnCl_4$.

INTRODUCTION

Olefin metathesis takes place in the presence of catalyst systems prepared by UV irradiation of CCl_4 solution of $M(CO)_6$ (M = W, Mo) (1–3). The same catalyst systems induce various substituted acetylenes to polymerize (4,5). Thus olefin metathesis and polymerization of substituted acetylenes share many features. Further, it is known that the above-stated olefin metathesis occurs even in benzene when a catalytic amount of Lewis acid (e.g., $TiCl_4$) is added (6). We have recently found that the polymerization of substituted acetylenes by (mesitylene)M(CO)₃ (M = W, Mo) proceeds even without CCl_4 when Lewis acids are added (7). These findings suggest that, in the $M(CO)_6$-catalyzed polymerization of substituted acetylenes, Lewis acids in catalytic amounts can play a role similar to that of CCl_4 solvent in generating the propagating species.

Here we report that the $M(CO)_6$–Lewis acid–hν systems (M = W, Mo) serve as effective catalysts in the polymerization of various acetylenes in toluene solution. Further, the role of Lewis acids on this polymerization is discussed.

EXPERIMENTAL

A standard polymerization procedure is as follows: A toluene solution (5.0 mL) of $M(CO)_6$ (M = W or Mo) (0.10 mmol) and a Lewis acid (0.050 mmol) was irradiated with a 200-W high-pressure mercury lamp (Fuji Glass Work, Japan) at 30°C for 1 h. To this was added a toluene solution (5.0 mL) of a monomer (5.0 mmol) and an internal standard (0.30 mL; e.g., chlorobenzene for phenylacetylene) of gas chromatography (GC). The mixture was kept in the dark for a given time, and then the polymerization was quenched with methanol (0.50 mL). 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 W(CO)₆–Lewis acid–hv catalyst

Table I. Polymerization of Phenylacetylene by
W(CO)₆–Lewis Acid–hv[a]

Lewis	Monomer	Polymer [b]	
acid	convn, %	Yield, %	$\overline{M}_n$[c]
none	0	—	—
$SiCl_4$	6	5	18,000
$GeCl_4$	16	16	54,000
$SnCl_4$	53	48	17,000
$TiCl_4$	3	3	17,000
$ZrCl_4$	8	7	33,000
$EtAlCl_2$	58	0	—
$FeCl_3$	6	5	12,000

[a] Polymerized in toluene at 30°C for 24 h after UV irradiation of catalyst solution at 30°C for 1 h; $[M]_0$ = 0.50 M, $[W(CO)_6]$ = 10 mM, [Acid] = 20 mM. [b] Methanol-insoluble part. [c] Determined by GPC.

   Polymerization of phenylacetylene was examined by using catalyst systems prepared by UV irradiation of mixtures of $W(CO)_6$ and Lewis acids at a mole ratio of 1:2 ($W(CO)_6$–Lewis acid–hv catalyst) in toluene solution (Table I). No polymerization occurred without a Lewis acid. When $SnCl_4$ was added, a polymer with $\overline{M}_n$ 17,000 was formed in 48% yield (cf. the yield of methanol-soluble oligomers <5%). The polymers obtained with $GeCl_4$ and $ZrCl_4$ have higher molecular weights ($\overline{M}_n > 3 \times 10^4$), although their yields are only about 10%. Though the monomer conversion is the highest (ca. 60%) with $EtAlCl_2$ as Lewis acid, the product was exclusively a mixture of methanol-soluble oligomers. Thus $SnCl_4$ proved the most effective as catalyst component, and hence it was exclusively used in further experiments.

   The effect of $SnCl_4$ concentration on the polymerization by $W(CO)_6$–$SnCl_4$–hv catalyst was studied (Figure 1). In the range Sn/W $\leq$ 0.5, the monomer conversion increases with increasing concentration of $SnCl_4$ to reach 50% at [$SnCl_4$] = 5 mM. Larger amounts of $SnCl_4$ hardly affect the monomer conversion, but decrease the polymer molecular weight. Presumably $SnCl_4$ coordinates to the propagating end, which will enhance the electrophilicity of the metal to induce polymerization. An excess of $SnCl_4$, however, will not coordinate to the propagating end, but will act as Lewis acid
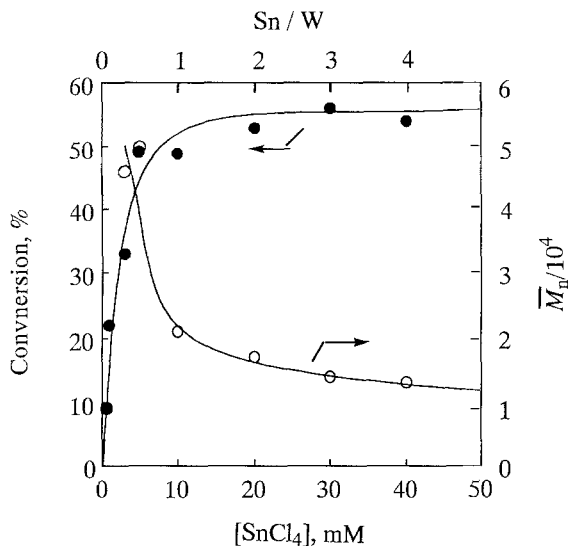

Figure 1. Effect of [$SnCl_4$] on the polymerization of phenylacetylene by $W(CO)_6$–$SnCl_4$–hv (in toluene, 30°C, 24 h; [M]$_0$ = 0.50 M, [$W(CO)_6$] = 10 mM).

Table II. Effect of UV Irradiation on the Polymerization of Phenylacetylene by $W(CO)_6$–$SnCl_4$–hv[a]

Irradiation		Monomer	Polymer [b]	
Time, min	Temp, °C	convn, %	Yield, %	$\bar{M}_n$[c]
0	—	0	—	—
10	30	37	27	32,000
30	30	50	41	41,000
60	30	50	46	50,000
120	30	19	12	55,000
60	0	38	38	51,000
60	30	50	46	50,000
60	60	33	25	96,000

[a] Polymerized in toluene at 30°C for 24 h after UV irradiation of catalyst solution; $[M]_0$ = 0.50 M, $[W(CO)_6]$ = 10 mM, $[SnCl_4]$ = 5 mM. [b] Methanol-insoluble part. [c] Determined by GPC.

by itself to cause the degradation of the formed polymer. On the basis of above-described results, the $SnCl_4$ concentration was fixed at 5 mM in further experiments.

Table II shows effects of UV irradiation on the polymerization by $W(CO)_6$–$SnCl_4$–hv catalyst. Polymerization did not proceed without UV irradiation, which indicates that UV irradiation is indispensable to this polymerization. When the irradiation temperature was fixed at 30°C, the monomer conversion took a maximum value at an irradiation time in the range 30–60 min. The molecular weight of the formed polymer increased with increasing irradiation time. Regarding the temperature of UV irradiation, the monomer conversion was the highest at 30°C, while the polymer molecular weight increased with raising temperature. It is assumed that the active species is partly inactivated under severe irradiation conditions (i.e., a long time or a high temperature), which seems to lead to low monomer conversions and high molecular weights of polymer. The optimal irradiation conditions, consequently, are 1 h and 30°C.

Figure 2 shows a time profile for the polymerization of phenylacetylene by $W(CO)_6$–$SnCl_4$–hv catalyst. Based on the above-stated results, the polymerization was carried out at $[SnCl_4]$ = 5 mM after UV irradiation at 30°C for 1 h. The monomer conversion increases to 50% after 24 h and then levels off. The molecular weight of polymer reaches ca. 50,000 after 3 h and
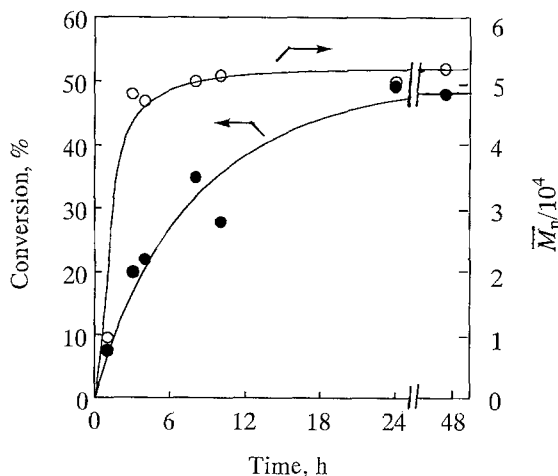
Figure 2. Polymerization of phenylacetylene by $W(CO)_6$–$SnCl_4$–hv (in toluene, 30°C; $[M]_0$ = 0.50 M, $[W(CO)_6]$ = 10 mM, $[SnCl_4]$ = 5 mM).

remains constant thereafter. It is worth noting that this molecular weight is larger than that (13,000) with WCl_6–Ph_4Sn catalyst (7), and fairly close to the value (79,000) with $W(CO)_6$–CCl_4–hv catalyst (4).

Effects of temperature and solvents on the polymerization by $W(CO)_6$–$SnCl_4$–hv catalyst were studied (Table III). This polymerization hardly proceeds at 0°C. When the temperature was raised from 30 to 80°C, the monomer conversion somewhat increased while the $\overline{M}_n$ decreased. Unlike the case of the $M(CO)_6$–CCl_4–hv systems, one can employ various solvents other than CCl_4 for the present catalysts. As seen in Table III, cyclohexane accomplished a very high molecular weight ($\overline{M}_n$ 86,000) while retaining a good polymer yield. In CCl_4, $SnCl_4$ gave rise to rather adverse effects; i.e., the monomer conversion was hardly affected, while the $\overline{M}_n$ of polymer lowered owing to the action of $SnCl_4$ as Lewis acid. Basic solvents such as 1,4 -dioxane and anisole reduced both yield and $\overline{M}_n$ of polymer. It is expected that these solvents coordinate to $SnCl_4$ as well as to the propagating end, which will decelerate the polymerization.

Polymerization of substituted acetylenes by $M(CO)_6$–$SnCl_4$–hv catalysts (M = W, Mo)

The polymerization of substituted acetylenes, which have proved to yield high molecular weight polymers in previous studies, were examined

Table III. Effects of Temperature and Solvents on the Polymerization of Phenylacetylene by W(CO)$_6$–SnCl$_4$–hv[a]

Polymn solvent	Polymn temp, °C	Monomer convn, %	Polymer[b]	
			Yield, %	$\overline{M}_n$[c]
toluene	0	5	2	9,000
toluene	30	50	46	50,000
toluene	60	67	55	31,000
toluene	80	72	55	23,000
cyclohexane	30	64	52	86,000
CCl$_4$ [d]	30	87	80	67,000
CCl$_4$	30	88	69	26,000
1,4-dioxane	30	19	17	16,000
anisole	30	14	12	18,000

[a] Polymerized for 24 h after UV irradiation of catalyst solution at 30°C for 1 h; [M]$_0$ = 0.50 M, [W(CO)$_6$] = 10 mM, [SnCl$_4$] = 5 mM. [b] Methanol-insoluble part. [c] Determined by GPC. [d] [SnCl$_4$] = 0 mM.

using M(CO)$_6$–SnCl$_4$–hv catalysts (M = W, Mo) (Table IV).

The W(CO)$_6$–SnCl$_4$–hv catalyst affords high molecular weight polymers ($\overline{M}_n$ 4x10^5–5x10^5) from phenylacetylenes bearing bulky ortho-substituents (e.g., Me$_3$Si and CF$_3$) in good yields. *tert*-Butylacetylene provides a polymer in high yield, which is, however, partly insoluble in any organic solvent. The Mo(CO)$_6$-based counterpart gives high molecular weight polymers ($\overline{M}_n$ ~10^4) from acetylenes bearing electron-withdrawing groups (e.g., *o*-[(trifluoromethyl)phenyl]acetylene and 1-chloro-2-phenylacetylene), although the polymer yields are rather low. *tert*-Butylacetylene polymerizes quantitatively to give again an insoluble polymer.

These tendencies are similar to those for other metal carbonyl-based catalysts such as M(CO)$_6$–CCl$_4$–hv (5) and (mesitylene)M(CO)$_3$–CCl$_4$ (7) (M = W, Mo).

Polymerization of phenylacetylene by W(CO)$_6$–SnCl$_4$–hv catalyst: effect of the order of adding the catalyst components

The polymerization of phenylacetylene by W(CO)$_6$–SnCl$_4$–hv catalyst

Table IV. Polymerization of Substituted Acetylenes by
M(CO)$_6$–SnCl$_4$–hv[a]

| Monomer	Monomer	Polymer[b]	
	convn, %	Yield, %	$\overline{M}_n$/10^3 [c]
M(CO)$_6$: W(CO)$_6$			
o-Me$_3$SiPA	57	34	470
o-CF$_3$PA	92	90	440
t-BuC≡CH	94	83	—[d]
M(CO)$_6$: Mo(CO)$_6$			
o-CF$_3$PA	21	12	340
PhC≡CCl	13	7	490
n-C$_6$H$_{13}$C≡CCl	17	3	150
t-BuC≡CH	100	94	—[d]

[a] Polymerized in toluene at 30°C for 24 h after UV irradiation of catalyst solution at 30°C for 1 h; [M]$_0$ = 0.50 M, [W(CO)$_6$] = 10 mM, [SnCl$_4$] = 5 mM. [b] Methanol-insoluble part. [c] Determined by GPC. [d] Partly insoluble in any solvent.

was carried out in various procedures. Common polymerization conditions were: 30°C, 24 h, in the dark, [SnCl$_4$] = 20 mM, and UV irradiation at 30°C for 1 h. In the above-stated polymerization, phenylacetylene had been added after UV irradiation of a toluene solution of W(CO)$_6$ and SnCl$_4$ leading to the formation of a polymer having an $\overline{M}_n$ of 17,000 in 48% yield. In contrast, the polymerization did not proceed when SnCl$_4$ was added after UV irradiation along with phenylacetylene. On the other hand, addition of SnCl$_4$ after UV irradiation of a toluene solution of W(CO)$_6$ and phenylacetylene effected polymerization to give a polymer with $\overline{M}_n$ 22,000 in 44% yield. Both SnCl$_4$ and UV irradiation were indispensable also in this catalyst system.

On the polymerization mechanism
     Probable initiation mechanisms for the present catalyst systems are shown in Scheme I. In the system where a mixture of M(CO)$_6$ and SnCl$_4$ is UV-irradiated, SnCl$_4$ coordinates to the M(CO)$_5$ generated by UV irradiation to form a complex, which will react with a monomer to yield a metal carbene (metal vinylidene) activated by SnCl$_4$ (route 1). On the other hand, in the

system where a mixture of $M(CO)_6$ and an acetylene is UV-irradiated, the $M(CO)_5$ formed reacts with the acetylene to give a metal carbene, which, however, shows only a negligible catalytic activity (9). This metal carbene is activated (the central metal becomes more electrophilic) by coordination of $SnCl_4$ (route 2). In both cases, the propagating species is inferred to be an identical metal carbene (1) activated by the coordination of $SnCl_4$ probably through a carbonyl ligand.
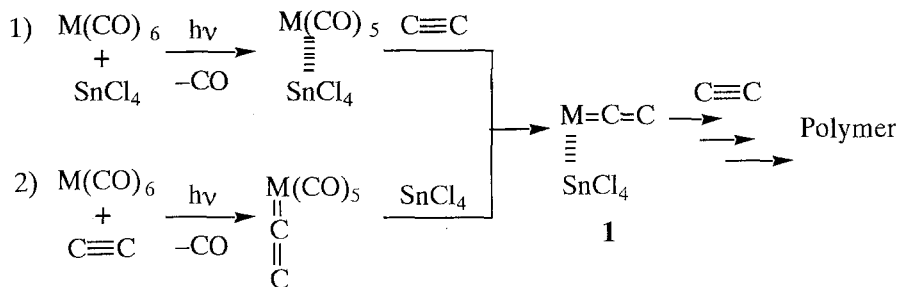
Scheme I. Plausible initiation mechanisms for $M(CO)_6$–$SnCl_4$–hν (M =W, Mo)

ACKNOWLEDGEMENT

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