Metathesis Polymerization of Substituted Acetylenes and Norbornene by $M(CO)_6$-Ph_2CCl_2-hv (M = Mo, W) Catalysts

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ABSTRACT: The $M(CO)_6$-Ph_2CCl_2-hv (M = W, Mo) systems worked as effective catalysts in the metathesis polymerization of substituted acetylenes and norbornene. Thus, $W(CO)_6$-Ph_2CCl_2-hv polymerized phenylacetylene in toluene at 30°C for 24 h to provide a polymer with M_w 30000 in 70% yield, and polymerized norbornene at 60°C to give a polymer with M_w 26000 quantitatively. Ph_2CCl_2 and ultraviolet (UV) irradiation were essential for the catalytic activity. However, Ph_2CCl_2 was sufficient in catalytic amounts unlike the $M(CO)_6$-CCl_4-hv systems which require CCl_4 as solvent. A maximum was seen in catalytic activity at $[Ph_2CCl_2]/[M] = 0.5$—2. The molecular weight of the poly(phenylacetylene) was higher than those for MCl_n-based catalysts.

KEY WORDS   Metathesis Polymerization / Substituted Acetylene / Norbornene / Diphenyldichloromethane / Ultraviolet Irradiation /

It is well known that ring-opening metathesis polymerization of cycloolefins is effected by various transition metal catalysts.[1-3] Such catalysts include transition metal chloride–organometallic cocatalyst systems,[1-3] metallacyclobutanes,[4-6] Schrock-type metal carbenes,[7] ruthenium carbenes developed by Grubbs et al.[8] Groups 5 and 6 transition metal chloride-based catalysts,[9] Schrock-type metal carbenes,[10,11] etc. are effective in metathesis polymerization of substituted acetylenes as well. Polymerization of phenylacetylene readily proceeds in the presence of metal chloride-based catalysts, but the molecular weight of the formed polymer is around 5000 at highest probably due to the Lewis acidity of the catalysts.[9]

Group 6 transition metal hexacarbonyl-based catalysts, $M(CO)_6$-CCl_4-hv (M = W, Mo), induce metathesis polymerization of both cycloolefins[12,13] and substituted acetylenes.[14,15] The Lewis acidity of these catalysts is lower than those of metal chlorides, and consequently the molecular weight of the poly(phenylacetylene) produced by the $W(CO)_6$-based catalyst reaches almost a hundred thousand. A requirement for the $M(CO)_6$-based catalysts is that CCl_4 must be used as solvent; otherwise sufficient catalytic activity is not attained.

It is assumed that a metal carbene, which serves as active species, is generated by CO elimination from $M(CO)_6$ by ultraviolet (UV) irradiation and subsequent reactions of $M(CO)_5$ with CCl_4, and so forth.[16] Further, generation of tungsten diphenylcarbene as an intermediate in the $W(CO)_6$-Ph_2CCl_2-hv system was suggested on the basis of a finding that the presence of 2-ethoxynorbornene in this system leads to the formation of a diphenylcarbene adduct.[17] Taking this into account, we examined Ph_2CCl_2 in place of CCl_4 in the $W(CO)_6$-CCl_4-hv system to find that the $W(CO)_6$-Ph_2CCl_2-hv system polymerizes phenylacetylene.[18] In the present study, we investigated the polymerization of substituted acetylenes and norbornene by the $M(CO)_6$-Ph_2CCl_2-hv (M = W, Mo) systems in detail to clarify the effectiveness of Ph_2CCl_2 as second catalyst component

and differences of the present catalyst systems, $M(CO)_6$-CCl_4-hv, and metal chloride-based catalysts.

EXPERIMENTAL

Materials

Phenylacetylene (Aldrich) was distilled twice from CaH_2 before use. [(o-Trimethylsilyl)phenyl]acetylene,[19] tert-butylacetylene,[20,21] and 1-chloro-1-octyne[22] were synthesized according to the literature methods and purified by distillation. Norbornene was distilled from CaH_2 and stored as toluene solution. Ph_2CCl_2 was distilled under reduced pressure and stored as toluene solution. $W(CO)_6$ and $Mo(CO)_6$ (Strem) were used as received. Toluene was purified by the standard method.

Procedure

UV irradiation and polymerizations were carried out under dry nitrogen. The catalyst solution was UV irradiated with a high-pressure Hg lamp (200 W) at a distance of 5 cm and kept in the dark. The colorless toluene solution of $M(CO)_6$ and Ph_2CCl_2 turned green on UV irradiation. To this catalyst solution was added a monomer solution, and the polymerization solution was kept at a constant temperature. The polymerization was quenched by addition of methanol, and monomer conversion was determined by GC. The formed polymer was isolated by precipitation in a large amount of methanol. The molecular weights of polymers were determined by GPC ($CHCl_3$ eluent, polystyrene calibration). Poly(phenylacetylene) was totally soluble in toluene and $CHCl_3$, whereas poly(norbornene) was partly insoluble in these solvents.
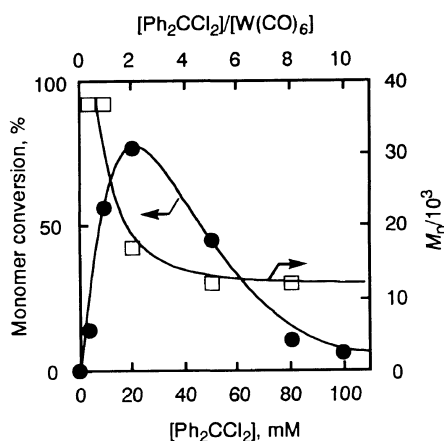
RESULTS AND DISCUSSION

Polymerization of Phenylacetylene

Since preliminary experiments revealed that $Mo(CO)_6$-Ph_2CCl_2-hv hardly polymerized phenylacetylene, the polymerization of phenylacetylene by $W(CO)_6$-Ph_2CCl_2-hv was investigated in detail.

Figure 1 shows the effect of Ph_2CCl_2 concentration in

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Figure 1. Effect of $[Ph_2CCl_2]$ on the polymerization of phenylacetylene by $W(CO)_6$–Ph_2CCl_2–$h\nu$ (in toluene, 30°C, UV irradiation 1 h, polymerization 18 h; $[Monomer]_0 = 0.50$ M; $[W(CO)_6] = 10$ mM).
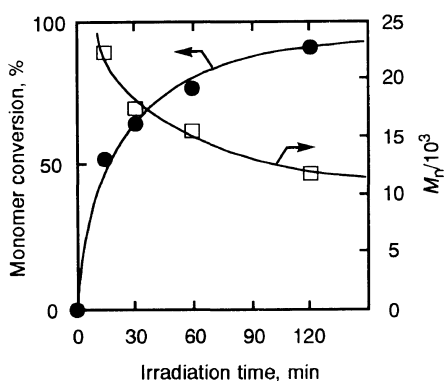
Figure 2. Effect of UV irradiation time on the polymerization of phenylacetylene by $W(CO)_6$–Ph_2CCl_2–$h\nu$ (in toluene, 30°C, polymerization 18 h; $[Monomer]_0 = 0.50$ M; $[W(CO)_6] = 10$ mM; $[Ph_2$-$CCl_2] = 20$ mM).

the range 0 to 10 equivalents to tungsten at a fixed $[W(CO)_6]$ of 10 mM. No polymerization proceeded in the absence of Ph_2CCl_2. The monomer conversion showed a maximum when $[Ph_2CCl_2]$ was 20 mM, i.e., 2 equivalents to tungsten, and excess Ph_2CCl_2 lowered the catalytic activity. The molecular weight of polymer decreased with increasing Ph_2CCl_2 concentration. The effect of UV irradiation time in preparation of the catalyst at 30°C is shown in Figure 2. No polymerization proceeded without UV irradiation. The monomer conversion increased with increasing irradiation time, while the molecular weight of polymer tended to decrease. From these results, it is concluded that both Ph_2CCl_2 and UV irradiation are essential for activation of the present system. A feature is that the amount of Ph_2CCl_2 required for polymerization is a catalytic amount, whereas the $W(CO)_6$–CCl_4–$h\nu$ system needs CCl_4 as solvent.

Figure 3 shows time profiles of the polymerization at $[W(CO)_6] = 10$ mM and $[Ph_2CCl_2] = 20$ mM (a) and 10 mM (b). The monomer conversion exceeded 95% after 48 h in case (a). The molecular weight of polymer showed a maximum of 20000 at 4 h, and decreased at longer polymerization times. In case (b), the monomer conversion was no more than 75% after 48 h, but the molecular weight was over 30000.

Figure 4 shows the effect of $W(CO)_6$ concentration for
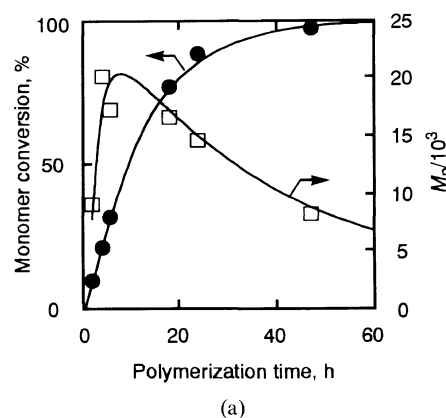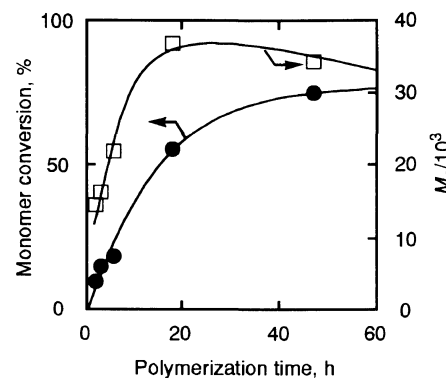
Figure 3. Time profiles of the polymerization of phenylacetylene by $W(CO)_6$–Ph_2CCl_2–$h\nu$ (a) $[Ph_2CCl_2] = 20$ mM and (b) $[Ph_2CCl_2] = 10$ mM (in toluene, 30°C, UV irradiation 1 h; $[Monomer]_0 = 0.50$ M; $[W(CO)_6] = 10$ mM).

cases (a) $[W] : [Ph_2CCl_2] = 1 : 2$ and (b) $[W] : [Ph_2$-$CCl_2] = 1 : 1$. The monomer conversion showed a maximum at $[W(CO)_6] = 10$ mM in case (a), whereas the monomer conversion increased monotonously in the range of $[W(CO)_6] = 0$—30 mM in case (b). The molecular weight decreased with increasing $W(CO)_6$ concentration in both cases. These results indicate that Ph_2CCl_2 not only works as catalyst component but exhibits adverse effects if it remains unreacted. From Figure 5, one can see that, while the monomer conversion shows a maximum at $[Monomer]_0 = 0.5$ M, the molecular weight increases with increasing monomer concentration to reach 50000 at $[Monomer]_0 = 1.0$ M.

From the above-stated data, one can point out the following features for the $W(CO)_6$–Ph_2CCl_2–$h\nu$ system: (i) the catalytic activity is low and the molecular weight of the poly(phenylacetylene) is high compared with MCl_n-based catalysts probably due to the low Lewis acidity of the catalysts, and (ii) the behavior is similar to that of the $W(CO)_6$–CCl_4–$h\nu$ system except for the Ph_2CCl_2 concentration.

Table I shows results for the polymerization of various substituted acetylenes. The $W(CO)_6$–Ph_2CCl_2–$h\nu$ system was effective in the polymerization of phenylacetylene, its ring-substituted derivatives, and tert-butylacetylene. Interestingly, the molecular weights of poly([(o-trimethylsilyl)phenyl]acetylene) and poly(tert-butylacetylene) reached several hundred thousand. On the other hand, the $Mo(CO)_6$-based counterpart polymerized only tert-butylacetylene in high yield, and the polymer yields

(a)

(b)
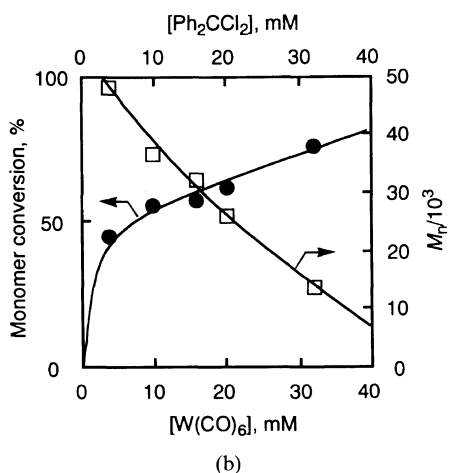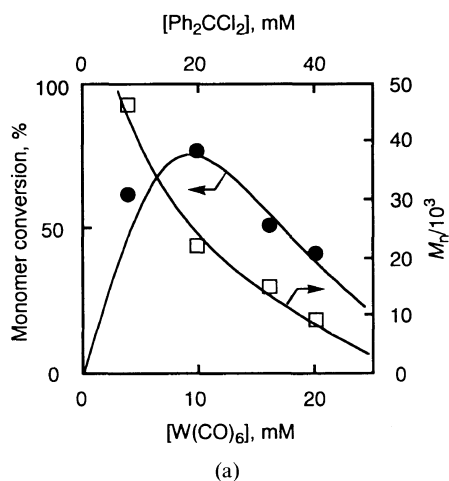
Figure 4. Effect of [$W(CO)_6$] on the polymerization of phenylacetylene by $W(CO)_6-Ph_2CCl_2-h\nu$ (a) [$W(CO)_6$]/[Ph_2CCl_2] = 1/2 and (b) [$W(CO)_6$]/[Ph_2CCl_2] = 1 (in toluene, 30°C, UV irradiation 1 h; [Monomer]$_0$ = 0.50 M).
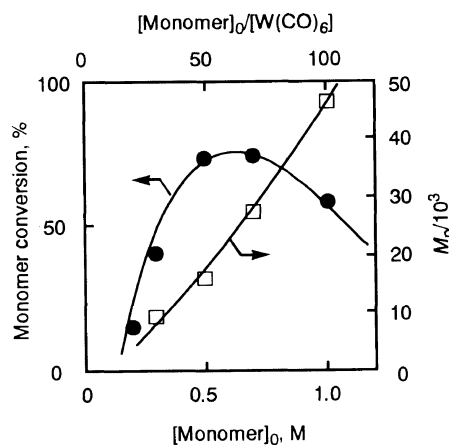
Figure 5. Effect of [Monomer]$_0$ on the polymerization of phenylacetylene by $W(CO)_6-Ph_2CCl_2-h\nu$ (in toluene, 30°C, UV irradiation 1 h; polymerization 18 h; [$W(CO)_6$] = 10 mM; [Ph_2CCl_2] = 20 mM).

for o-Me$_3$Si-phenylacetylene and 1-chloro-1-octyne were rather low. Thus the kind of polymerizable monomers greatly depended on which of tungsten and molybdenum is the central metal.
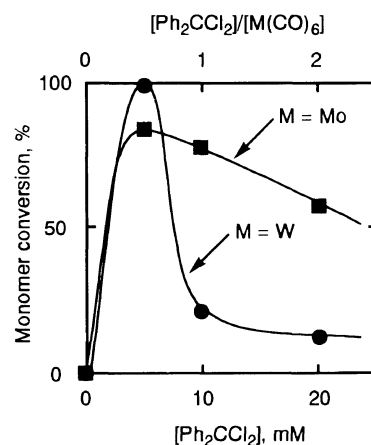
Polymerization of Norbornene
It was examined whether the present catalyst systems

Table I. Polymerization of Substituted Acetylenes by $M(CO)_6-Ph_2CCl_2-h\nu$[a]

Monomer	$M(CO)_6$	Polymer[b]	
		Yield/%	$M_w/10^3$
Phenylacetylene	$W(CO)_6$	70	30
(o-Me$_3$Si)Phenylacetylene	$W(CO)_6$	55	230
$tert$-Butylacetylene	$W(CO)_6$	71	630
(o-Me$_3$Si)Phenylacetylene	$Mo(CO)_6$	8	380
$tert$-Butylacetylene	$Mo(CO)_6$	70	240
1-Chloro-1-octyne	$Mo(CO)_6$	4	780

[a] In toluene, 30°C, 24 h; [$M(CO)_6$] = 10 mM; [Ph_2CCl_2] = 20 mM; [M]$_0$ = 0.50 M. [b] Methanol-insoluble product.

Figure 6. Effect of [Ph_2CCl_2] on the polymerization of norbornene by $M(CO)_6-Ph_2CCl_2-h\nu$ (in toluene, 60°C, UV irradiation 1 h, polymerization 24 h; [Monomer]$_0$ = 0.10 M; [$M(CO)_6$] = 10 mM).
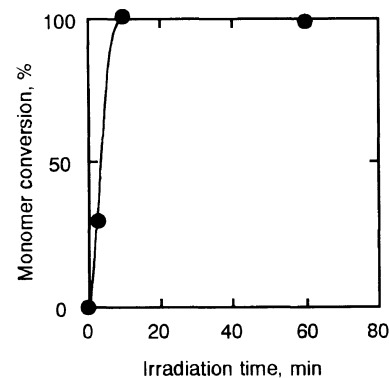
Figure 7. Effect of UV irradiation time on the polymerization of norbornene by $W(CO)_6-Ph_2CCl_2-h\nu$ (in toluene, 60°C, polymerization 24 h; [Monomer]$_0$ = 0.10 M; [$W(CO)_6$] = 10 mM; [Ph_2CCl_2] = 5.0 mM).

induce the ring-opening metathesis polymerization of norbornene or not. Since norbornene turned out to be less reactive than phenylacetylene, both the preparation of catalyst and the polymerization were performed at 60°C.

Figure 6 shows the effect of Ph_2CCl_2 concentration. No polymerization of norbornene proceeded in the absence of Ph_2CCl_2 like the case of phenylacetylene. The
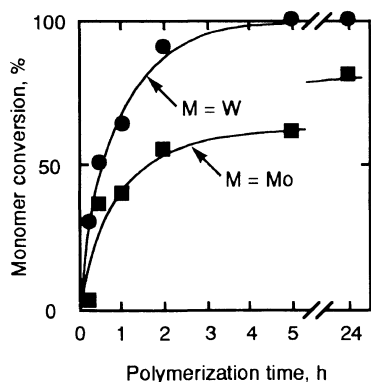
Figure 8. Time profiles of the polymerization of norbornene by $M(CO)_6-Ph_2CCl_2-h\nu$ (in toluene, 60°C, UV irradiation 1 h; [Monomer]$_0$ = 0.10 M; [M(CO)$_6$] = 10 mM; [Ph$_2$CCl$_2$] = 5.0 mM).
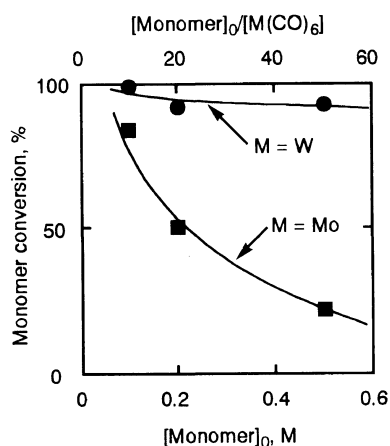
Figure 9. Effect of [Monomer]$_0$ on the polymerization of norbornene by $M(CO)_6-Ph_2CCl_2-h\nu$ (in toluene, 60°C, UV irradiation 1 h; polymerization 24 h; [M(CO)$_6$] = 10 mM; [Ph$_2$CCl$_2$] = 5.0 mM).

monomer conversion showed a maximum at [Ph$_2$CCl$_2$]/[M(CO)$_6$] = 0.5 with both tungsten and molybdenum. The molecular weights of polymers by tungsten and molybdenum at [Ph$_2$CCl$_2$]/[M(CO)$_6$] = 0.5 were 26000 and 97000, respectively. As the quantity of Ph$_2$CCl$_2$ was increased further, the catalytic activity gradually lowered with Mo(CO)$_6$, whereas it sharply decreased with W(CO)$_6$. Thus a half equivalent of Ph$_2$CCl$_2$ to M(CO)$_6$ was used in further experiments. As seen in Figure 7, UV irradiation is essential for catalyst activation, which is in agreement with the polymerization of phenylacetylene. The monomer conversion reached 100% at 10 min and longer irradiations.

Figure 8 shows time profiles of the polymerization of norbornene by tungsten and molybdenum catalysts. The polymerization proceeded without an induction phase with both catalysts. The monomer conversion reached 100% after 5 h by the tungsten catalyst, whereas the

polymerization leveled off at 80% conversion after 24 h by the molybdenum counterpart. The effect of initial monomer concentration is shown in Figure 9. The monomer conversion hardly decreased in the tungsten-catalyzed polymerization up to a [monomer]/[metal] of 50, whereas it decreased progressively with the molybdenum catalyst.

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