Polymerization of phenylacetylene induced by u.v. irradiation of group 6 transition metal carbonyls*

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(*Received* 26 *September* 1981; *revised* 11 *November* 1981)

The polymerization of phenylacetylene induced by u.v. irradiation of $W(CO)_6$ in carbon tetrachloride provided a polymer, in a virtually quantitative yield, whose molecular weight reached $\sim 1 \times 10^5$. The polymerization did not occur without u.v. irradiation or in the absence of a halide such as carbon tetrachloride. The influence of reaction conditions was examined. The corresponding $Mo(CO)_6$–CCl_4–$h\nu$ catalyst was less active, and the polymer molecular weight was $\sim 1 \times 10^4$. $Cr(CO)_6$, $Mn_2(CO)_{10}$ and $Re_2(CO)_{10}$ were found to be ineffective. The polymers formed were dark brown to yellow solids, and had the structure, $\text{-(}CH{=}CPh\text{)-}_n$. The polymerization mechanism was discussed in comparison with olefin metathesis.

Keywords Polymerization; phenylacetylene; tungsten hexacarbonyl; ultra violet irradiation; metal carbene; high polymer

INTRODUCTION

The polymerization of phenylacetylene has been investigated by use of various initiators[2] and most of the products were oligomers with molecular weights of a few thousand. This has been attributed to low reactivity of both the monomer and its propagating end in conventional radical and ionic polymerizations. Thus the synthesis of high molecular weight poly(phenylacetylene) is an unsolved and intriguing subject, and the polymer formed might be expected to show various functionalities such as photoconductivity and gas separation.

We have reported that WCl_6 and $MoCl_5$ work as very effective catalysts in the polymerization of phenylacetylene and that the resulting highest polymer molecular weight was about 15 000[3]. Recently we briefly reported[4] that phenylacetylene is polymerized by the catalyst obtained from the u.v. irradiation of $W(CO)_6$ in carbon tetrachloride and that the polymer formed has higher molecular weight than does the polymer obtained with WCl_6.

The two main purposes of the present paper are to clarify the behaviour of phenylacetylene polymerization induced by u.v. irradiation of group 6 transition metal carbonyls and to establish the reaction conditions which make the resulting polymer molecular weight as high as possible. In addition, this polymerization is compared with olefin metathesis with respect to similarities in catalyst and in reaction mechanism.

EXPERIMENTAL

Phenylacetylene was prepared from styrene by bromination and dehydrobromination[5], and distilled twice from calcium hydride at reduced pressure. Metal carbonyls were purchased from Strem Chemical Inc. and used without further purification. Solvents were washed with acid and/or alkali solutions and distilled twice from calcium hydride before use.

All the irradiation and polymerization procedures were conducted under a dry nitrogen atmosphere unless otherwise stated. U.v. irradiation was performed with a 200 W high-pressure mercury lamp (Fuji Glass Work, Japan) at a distance of 5 cm. Catalyst solutions and polymerization solutions were kept in the dark whenever u.v. irradiation was not applied. A general polymerization procedure is as follows: a solution (5 ml) of $W(CO)_6$ (0.10 mmol) was irradiated with u.v. light at 30°C for 1 h, to the solution was added a solution of phenylacetylene (10 mmol, 1.10 ml) and chlorobenzene (0.50 ml, as internal standard for gas chromatography) in the same solvent (3.4 ml) as for $W(CO)_6$, and the mixture was kept in the dark at a constant temperature for a given time. Polymerization was terminated with methanol, and monomer consumption was determined by gas chromatography. The polymer formed was precipitated in methanol, filtered off, washed with methanol, and dried to a constant weight.

Number average molecular weights ($\bar{M}_n$) of polymers were measured by the membrane osmotic-pressure method (Mechrolab 502 osmometer; toluene, 20°C) for high polymers ($\bar{M}_n > 3 \times 10^4$) and by vapour pressure osmometry (Hitachi 117 MW Apparatus, Japan; benzene, 45°C) for low polymers ($\bar{M}_n < 3 \times 10^4$). I.r., u.v. and n.m.r. spectra of polymers were recorded on Shimadzu IR27G, Shimadzu UV190, and JEOL FX90Q spectrometers, respectively.

RESULTS

Studies on the catalyst system

The catalytic activities of group 6 and 7 transition metal carbonyls ($Cr(CO)_6$, $Mo(CO)_6$, $W(CO)_6$, $Mn_2(CO)_{10}$ and

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* Part 12 of 'Polymerization of phenylacetylenes'. For part 11 see ref 1.

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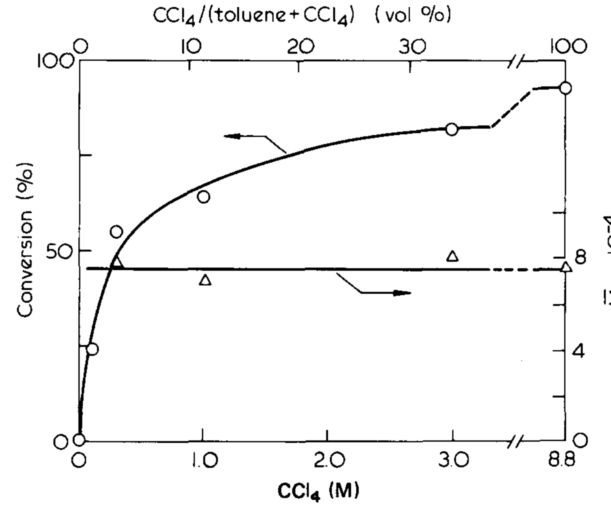


Figure 1 Polymerization of phenylacetylene with $W(CO)_6$–hν in mixtures of carbon tetrachloride and toluene: 30°C, 24 h, $[M]_0 = 1.0$ M, $[W(CO)_6] = 10$ mM

$Re_2(CO)_{10}$) for the polymerization of phenylacetylene were investigated.

Polymerizations were attempted in carbon tetrachloride at 30°C for 24 h after solutions of these metal carbonyls in carbon tetrachloride were irradiated at 30°C for 1 h. Among the metal carbonyls, $W(CO)_6$ showed a very high activity (conversion 93%, $\bar{M}_n$ 77000). The monomer consumed in the presence of the $W(CO)_6$–CCl_4-hν catalyst was quantitatively recovered as a methanol-insoluble polymer. Therefore, the formation of cyclotrimers, which are soluble in methanol, is denied. The molecular weight of the polymer formed was much higher by far, than those molecular weights reported before. $Mo(CO)_6$ was much less active (conversion 8%, $\bar{M}_n$ 13000), and the other metal carbonyls were completely inactive.

The polymerization with the $W(CO)_6$–hν catalyst was attempted with halides, hydrocarbons and ethers as solvents. Polymerization conditions were the same as stated above. Conversions were as follows: CCl_4 93%; $CBrCl_3$ 42%;$CHCl_3$ 33%;CH_2Cl_2 5%; $(CH_2Cl)_2$, toluene, 1,4-dioxane and PCl_3 all 0%. Thus, the highest conversion was in carbon tetrachloride among the solvents examined. Polymerization did not proceed in toluene and 1,4-dioxane, although these solvents are excellent for polymerization with WCl_6[3,6].

Furthermore, polymerization did proceed in toluene solution in the presence of organic halides (1.0 M), these halides being analogous to carbon tetrachloride. Polymerization was carried out as described before, except for irradiation of a mixture of $W(CO)_6$ (0.10 mmol) and a halide (10 mmol) in toluene solution (5 ml in total). Monomer conversions were as follows: CBr_4 34%; $CHCl_2CCl_3$ 18%; Ph_2CCl_2 14%; $PhCCl_3$ 12%; CCl_3CN 0% compared with CCl_4 67%.

Figure 1 shows the dependences of monomer conversion and polymer molecular weight on carbon tetrachloride concentration for the polymerization in toluene solution. At concentrations of carbon tetrachloride lower than 1 M, conversion decreased abruptly with decreasing carbon tetrachloride concentration, indicating that catalytic amounts of carbon tetrachloride are insufficient for the formation of active species. However, the polymer molecular weight was unaffected by the ratio of carbon tetrachloride to toluene.

The above findings concerning the effect of halides, show that an appropriate halide is essential to the present catalyst system and that carbon tetrachloride is eminently suitable as both catalyst component and polymerization solvent.

The effect of irradiation was then investigated. No monomer was converted without u.v. irradiation, which makes the presence of light an indispensable catalyst component. In the near u.v. region, $W(CO)_6$ and $Mo(CO)_6$ showed absorptions having a maximum at 288 nm and continuing as far as ~380 nm. The same high conversion (93%) was observed with Pyrex glassware and with 'hard' glassware. A quartz vessel also gave a similar conversion value. These results indicate that light, of wavelength shorter than 300 nm, is not responsible for the formation of active species. A comparable conversion (69%) was attained through a Toshiba UV-35 glass filter (light <325 nm completely cut off), whereas no polymerization took place when the irradiation was made through a Toshiba L-42 glass filter (light <390 nm completely cut off). Consequently it is concluded that the u.v. light at 334 and 365 nm from the high-pressure mercury lamp are useful in producing active species.

The catalyst solution, prepared by u.v. irradiation of $W(CO)_6$ in carbon tetrachloride for 1 h, was a greenish colour with fine black particles. No absorption characteristic of WCl_6 was observed in the u.v. visible spectrum, suggesting that the active species is not formed *via* WCl_6.

Influence of reaction conditions

The effect of irradiation time and temperature on the polymerization with the $W(CO)_6$–CCl_4-hν catalyst were investigated (see *Table 1*). The polymerization was run at 30°C for 24 h. As described above, no monomer was converted without u.v. irradiation. Though even a short-time irradiation such as 10 min brought about an appreciably high conversion, the longer the irradiation time (e.g., 1 h) the higher the conversion. Irradiation at lower temperatures favoured the conversion, suggesting the decomposition of active species at high temperatures. When the irradiation was carried out in the presence of monomer, the conversion remained low; and this may be attributed to the absorption of u.v. light by the polymer

Table 1 Effect of irradiation time and temperature on the polymerization of phenylacetylene with $W(CO)_6$–CCl_4–hν catalyst[a]

No.	Irradiation: Time (min)	Irradiation: Temperature (°C)	Conversion[b] (%)	$\bar{M}_n$
1	0	30	0	–
2	10	30	83	76000
3	30	30	91	79000
4	60	30	93	77000
5	120	30	96	77000
6	60	0	96	68000
7	60	60	28	–
8[c]	60	30	35	–

[a] Polymerized in CCl_4 after u.v. irradiation of catalyst solutions: $[M]_0 = 1.0$ M, $[W(CO)_6] = 10$ mM
[b] Conversions after polymerization at 30°C for 24 h
[c] Polymerization solution irradiated

Table 2 Effect of polymerization conditions on the polymerization of phenylacetylene with $W(CO)_6$–CCl_4–hν catalyst[a]

No.	Polymerization temperature (°C)	$[M]_0$ (M)	$[W(CO)_6]$ (mM)	Conversion (%)	$\bar{M}_n$
1	0	1.0	10	54	45000
2	30	1.0	10	93	77000
3	60	1.0	10	100	31000
4	30	0.125	10	77	33000
5	30	0.25	10	77	56000
6	30	0.50	10	85	78000
7	30	2.0	10	73	88000
8	30	3.0	10	76	101000
9	30	4.0	10	65	70000
10	30	5.0	10	54	71000
11	30	1.0	2.5	73	59000
12	30	1.0	5.0	89	65000
13	30	1.0	20	93	70000

[a] Polymerized in CCl_4 for 24 h after catalyst solutions were irradiated at 30°C for 1 h

formed. The polymer molecular weights were 7×10^4–8×10^4, being independent of irradiation time and temperature.

Table 2 shows results for the effect of polymerization temperature and effect of monomer and metal carbonyl concentrations. The catalyst solution was prepared by the u.v. irradiation of $W(CO)_6$ in carbon tetrachloride at 30°C for 1 h. As polymerization temperature was raised conversion increased, while polymer molecular weight reached a maximum at 30°C. Regarding the effect of monomer concentration, the highest conversion and polymer molecular weight were observed at $[M]_0=1.0$ and 3.0 M, respectively. The polymer molecular weight obtained at $[M]_0=3.0$ M reached $\sim1\times10^5$. An increase in $W(CO)_6$ concentration enhanced conversion when the concentration was lower than 10 mM. Conversion, however, did not increase above 10 mM since the solubility of $W(CO)_6$ in carbon tetrachloride at 30°C was about 10 mM.

Figure 2 shows the time dependences of monomer conversion and polymer molecular weight. The reaction was fast at the initial stage and slowed down, suggesting that some termination reaction gradually takes place. The polymer molecular weight was virtually independent of conversion. This can be explained by the propagation reaction being a chain reaction accompanied with a transfer.

The influences of oxygen and methanol were investigated under the reaction conditions identical to those for *Table 1*, No. 4. When polymerization was attempted under a dry oxygen atmosphere instead of dry nitrogen, no monomer was consumed at all. Addition of small amounts of methanol depressed both conversion and polymer molecular weight: [MeOH] = 10 mM, conversion 95%, $\bar{M}_n$ 9400; [MeOH] = 30 mM, conversion 5%; [MeOH] = 100 mM, conversion 0%. Thus exclusions of air and oxygen-containing impurities is required in the present polymerization.

As stated above, $Mo(CO)_6$ was much less active than $W(CO)_6$. To accomplish an efficient polymerization with the $Mo(CO)_6$–CCl_4–hν catalyst, the polymerization was run at 60°C with higher catalyst concentrations. Other reaction conditions are the same as for *Table 1*, No. 4. The results are: conversion 49%, $\bar{M}_n$ 5900 at $[Mo(CO)_6]=20$ mM; conversion 63%, $\bar{M}_n$ 7100 at $[Mo(CO)_6]=30$ mM, and thus fairly high conversions were realized. The yields of the methanol-insoluble polymer were somewhat lower than the corresponding monomer conversions, suggesting the formation of a methanol-soluble oligomer. The polymer molecular weights were low as compared with those of the polymers obtained with the $W(CO)_6$-based catalyst.

Polymer characterization

The polymer obtained with the $W(CO)_6$-based catalyst was a dark brown solid. The elemental composition of the polymer agreed well with the composition calculated for $(C_8H_6)_n$. No carbonyl group was observed in the i.r. spectrum of the polymer. The i.r., u.v., ^1H and ^{13}C n.m.r. data and solubility of the polymer were similar to those of the polymer obtained with WCl_6[7], which indicates that the polymer obtained with $W(CO)_6$ also has a *trans*-rich conjugated double bond structure.

The polymer produced with the $Mo(CO)_6$-based catalyst was a yellow solid, and showed similar spectral and solubility properties to those of the polymer prepared with $MoCl_5$[7]; thus the polymer produced with $Mo(CO)_6$ is concluded to have a *cis*-rich structure.

DISCUSSION

The present polymerization possesses the following features: (i) $W(CO)_6$ and $Mo(CO)_6$ are air- and heat-stable unlike most metal carbonyls and the air- and moisture-sensitive active species is prepared *in situ*, so that the polymerization procedure is facile, and (ii) poly(phenylacetylene) having a high molecular weight of 1×10^5 has been obtained by a judicious choice of catalyst system and reaction conditions; this molecular weight value is higher than any values previously reported for poly(phenylacetylene).

Polymerization mechanism

A probable polymerization mechanism is illustrated in Scheme I, based on the knowledge that a metal carbene is formed by u.v. irradiation of $W(CO)_6$ in carbon tetrachloride[8].

The initiation reaction is thought to be the formation of phenylacetylene-coordinating metal carbene. Initially a

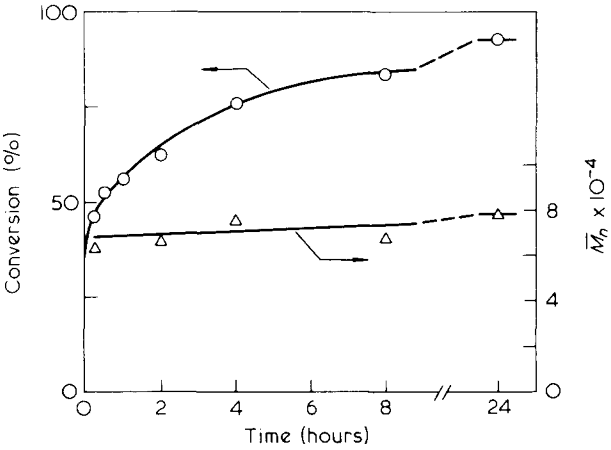
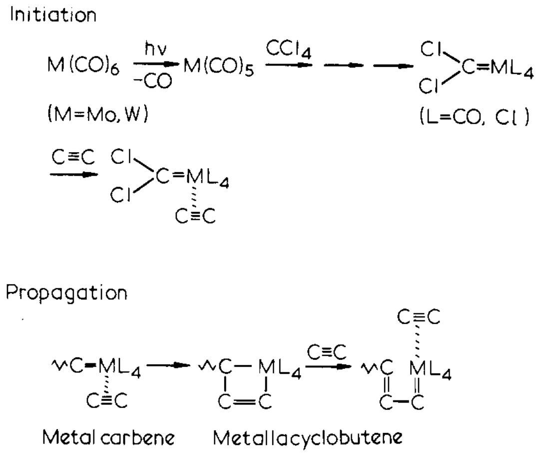


Figure 2 Time dependences of conversion and polymer molecular weight for the polymerization of phenylacetylene with $W(CO)_6$–CCl_4–hν: in CCl_4, 30°C, $[M]_0$ = 1.0 M, $[W(CO)_6]$ = 10 mM



Scheme I

metal hexacarbonyl releases one molecule of carbon monoxide on u.v. irradiation[9]. The reaction of the CO-deficient metal pentacarbonyl with carbon tetrachloride should eventually lead to the formation of a metal carbene through several steps. This has been verified by the isolation and identification of products in the reaction of the postulated metal carbene with olefins[8]. One molecule of phenylacetylene coordinates onto the metal carbene, thus the initiating species is formed.

The propagation reaction proceeds *via* metal carbenes and metalacyclobutenes, as depicted in Scheme I[7,10].

An apparently similar catalyst system (various combinations of metal carbonyls and organic halides) is known to effect radical polymerization of vinyl monomers[11-13]. Most metal carbonyls work as a catalyst component in this vinyl polymerization. However, $W(CO)_6$ and $Mo(CO)_6$ were effective specifically in the polymerization of phenylacetylene, which rules out the radical mechanism for acetylene polymerization.

Relationship to olefin metathesis

Two types of catalysts have been reported to be effective for both polymerization of acetylene derivatives and olefin metathesis (including metathesis polymerization of cyclo-olefins in the latter): (i) an equimolar mixture of WCl_6 and Ph_4Sn[14,15], and (ii) isolated tungsten carbenes $[Ph(MeO)C=W(CO)_5$ and $Ph_2C=W(CO)_5]$[10,16,17]. Furthermore, the present study revealed that phenylacetylene was polymerized by the $W(CO)_6$–CCl_4–$h\nu$ catalyst which is also a catalyst for olefin metathesis[8,18,19]. Such effectiveness of identical catalysts may lead one to think that both reactions might have a common reaction mechanism. It is now generally accepted that olefin metathesis and cyclo-olefin polymerization proceed *via* metal carbenes. Therefore, it seems reasonable to consider metal carbenes as intermediates in acetylene polymerization by Mo- and W-based catalysts. It is possible and interesting to regard an acetylene as an extreme example of a cyclo-olefin, that is, a 'two-membered one' where both monomers can be polymerized by the above-described identical catalysts and apparently by the same mechanism. We claim that the acetylene polymerization exploited in our series of studies is, following olefin metathesis and cyclo-olefin polymerization, the third important reaction that is catalyzed by W and Mo and mediated by metal carbenes.

ACKNOWLEDGEMENT

The authors would like to thank Dr Toshiro Masuda for kindly permitting us to use a Mechrolab 502 osmometer. This investigation was partly supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science and Culture (No. 56550646) Japan.

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