

## Polymerization of Phenylacetylenes. VII. Effect of Oxygen-Containing Compounds on the $WCl_6$ -Catalyzed Polymerization of Phenylacetylene\*

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**ABSTRACT:** The effects of oxygen-containing compounds was investigated for the  $WCl_6$ -catalyzed polymerization of phenylacetylene. A catalyst composed of  $WCl_6$ , phenylacetylene (as a reducing agent) and 1,4-dioxane (as modifier) (1:1:0.1 in molar ratio) was found to be very effective. Catalysts consisting of two out of the above three components were not so effective. The addition of a larger amount of 1,4-dioxane brought about an induction period. A variety of oxygen-containing compounds such as ethers (1,4-dioxane, tetrahydropyran, 1,2-dimethoxyethane, dibutyl ether, anisole, phenetole), ketones (acetone, 2-butanone), ethanol, and water served as modifiers. Tungsten (VI) was reduced by the addition of phenylacetylene, but not reduced by 1,4-dioxane. The functions of modifiers were discussed.

**KEY WORDS** Phenylacetylene / Tungsten Hexachloride / Coordination Polymerization / Catalyst / Modifier / Oxygen-Containing Compound / 1,4-Dioxane /

We reported that the  $WCl_6$ -catalyzed polymerization of phenylacetylene is appreciably accelerated by a small amount of tetraphenyltin ( $Ph_4Sn$ ) which is a mild reducing agent.<sup>2</sup> From this result, the active species for the polymerization was assumed to involve tungsten having a lower valency than six. In fact,  $WCl_6$  is reduced with various kinds of compounds ( $Ph_4Sn$ ,<sup>3</sup>  $(CH_3)_2Zn$ ,<sup>4</sup>  $(C_2H_5)_4Sn$ ,<sup>4</sup> nitriles,<sup>5</sup> alkenes,<sup>6</sup> and so on) and the products have been identified.  $WCl_6$  is also reduced with organoaluminums and organolithiums, the products of which can be effective catalyst species for olefin metathesis, though the structures of active species are not clear.

A number of catalysts based on W(VI) have been developed for olefin metathesis. Among these the effective catalysts appear to be composed of three components:  $WCl_6$ , a reducing agent and a modifier. A variety of oxygen-containing compounds can be the modifier. For instance, Calderon, *et al.*, have found that a mixture of  $WCl_6$ , ethanol, and ethylaluminum

dichloride (atomic ratio of 4:1:1 for Al:W:O) serves as a good catalyst for olefin metathesis, while this catalyst is less active in the absence of ethanol.<sup>7</sup> It has been reported that in  $WCl_6$ -( $n-C_4H_9$ )<sub>4</sub>Sn catalyzed metathesis, the addition of a small amount of esters or ethers enhances its reactivity and selectivity.<sup>8</sup> Muetterties and coworkers have claimed that both chlorine and oxygen ligand atoms are essential in W(VI)-based catalysts for the high metathesis activity.<sup>9</sup>

The  $WCl_6$  or  $MoCl_5$  catalyzed polymerization of phenylacetylene and the metathesis of olefins have many features in common (*e.g.*, the relationship between product *cis/trans* ratio and catalyst<sup>10,11</sup>). In the  $WCl_6$ -catalyzed polymerization of phenylacetylene, phenylacetylene itself is considered to work as a reducing agent.<sup>2</sup> It is not known, however, whether a modifier accelerates this polymerization or not. Therefore, it is of great interest to investigate the influences of oxygen-containing compounds. In this study, the effects of ethers, ketones, ethanol, and water on the  $WCl_6$ -catalyzed polymerization of phenylacetylene have been examined.

\* For Part VI of this series, see ref 1.

## EXPERIMENTAL

Commercial phenylacetylene (guaranteed reagent) was purified by distilling twice over calcium hydride. The purity was more than 99.9% according to gas chromatography. 1,4-Dioxane was fractionally distilled over sodium. Other reagents were purified as described in previous papers.<sup>1,2</sup>

Unless otherwise stated, catalyst solutions were prepared as follows. Under a dry nitrogen atmosphere, given amounts of  $WCl_6$ , benzene, and phenylacetylene (the same amount as  $WCl_6$ , as reducing agent) were mixed in this order and aged for 30 min at 30°C. Following this, a benzene solution of 1,4-dioxane was added and further aged for 10 min at 30°C. The catalyst solutions thus prepared were used immediately. In a similar way, two-component catalyst were prepared by aging solution for 30 min at 30°C.

Polymerization was initiated by the addition of a catalyst solution to a monomer solution and was terminated by the addition of ammoniacal methanol. Time—conversion curves were obtained by dilatometry and through determination of the amount of residual monomer following polymerization by gas chromatography (column, poly(ethylene glycol) 6000/celite 545 2 m; temp, 110°C; internal standard, chlorobenzene).

The polymer produced was precipitated in a large amount of methanol, filtered, washed with methanol and dried to a constant weight. The number-average molecular weight of the polymer was measured by vapor-pressure osmometry using a Hitachi-117 osmometer (in benzene at 40°C).

The average oxidation-state of tungsten was determined by oxidation—reduction titration with a potassium permanganate solution.<sup>2</sup>

## RESULTS

*Effect of Ethers as Modifiers*

An examination was made of the effects of phenylacetylene as reducing agent and 1,4-dioxane as modifier in the polymerization of phenylacetylene by  $WCl_6$  in benzene at 30°C. 1,4-Dioxane 1/10, as much as  $WCl_6$ , was used so that no induction period would appear (*vide infra*). As Figure 1 shows, the catalyst activities

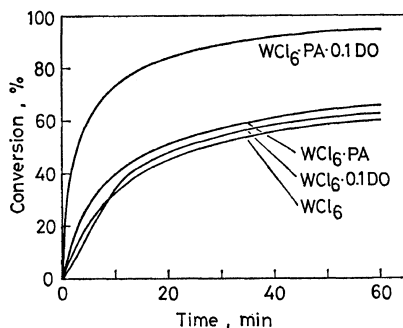


Figure 1. Effectiveness of  $WCl_6 \cdot PA \cdot 0.1DO$  as catalyst in the polymerization of phenylacetylene in benzene at 30°C:  $[M]_0 = 1.0M$ ;  $[WCl_6]_0 = 5.0mM$ .

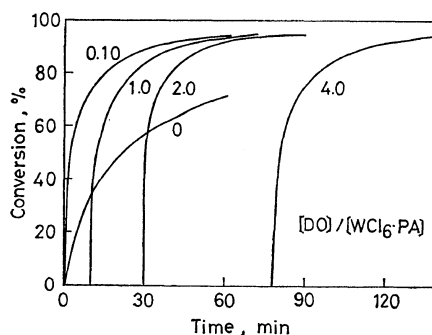


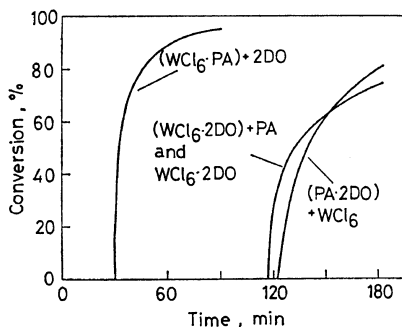
Figure 2. Effect of 1,4-dioxane concentration on the polymerization of phenylacetylene by  $WCl_6 \cdot PA$  in benzene at 30°C:  $[M]_0 = 1.0M$ ;  $[WCl_6 \cdot PA]_0 = 5.0mM$ .

of mixtures of  $WCl_6$  and either phenylacetylene or 1,4-dioxane were similar to that of  $WCl_6$  itself. On the contrary, the mixture of  $WCl_6$ , phenylacetylene and 1,4-dioxane in a molar ratio of 1 : 1 : 0.1 (denoted as  $WCl_6 \cdot PA \cdot 0.1DO$  in Figure 1) was clearly more active than the other catalysts.

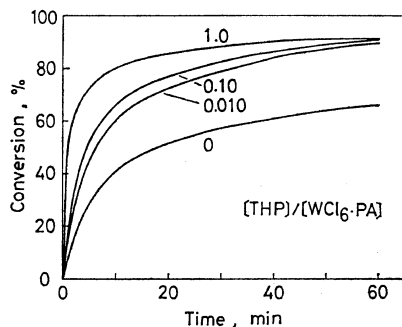
Figure 2 shows the effect of 1,4-dioxane concentration on time—conversion curve in the polymerizations catalyzed by the  $WCl_6 \cdot PA$  catalyst. When the ratio of 1,4-dioxane to  $WCl_6$  was 1 : 10, no induction period was observed. By increasing the DO amount, an induction period was observed and it increased. It should be noted that the final conversions are about 95% independent of the length of induction period.

It is supposed that in a multi-component catalyst system, both the addition order and aging times have considerable influence on the formation of active species. When a catalyst

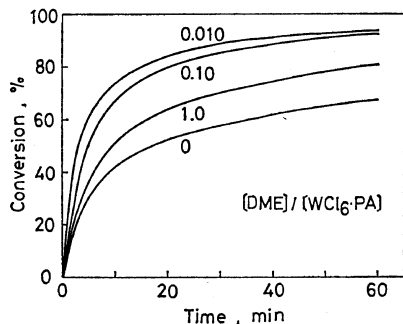
was prepared by aging a mixture of  $\text{WCl}_6$  and phenylacetylene in benzene for 30 min, adding a twofold excess of 1,4-dioxane, and aging additional 10 min (denoted as  $(\text{WCl}_6 \cdot \text{PA}) + 2\text{DO}$ ),



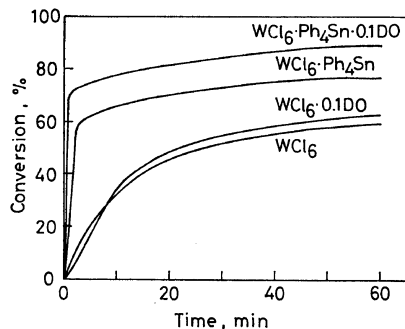
**Figure 3.** Effect of addition order of catalyst components on the polymerization of phenylacetylene in benzene 30°C:  $[\text{M}]_0 = 1.0\text{M}$ ;  $[\text{WCl}_6]_0 = 5\text{mM}$ .



**Figure 4.** Effect of tetrahydropyran concentration on the polymerization of phenylacetylene by  $\text{WCl}_6 \cdot \text{PA}$  in benzene at 30°C:  $[\text{M}]_0 = 1.0\text{M}$ ;  $[\text{WCl}_6 \cdot \text{PA}]_0 = 5.0\text{mM}$ .



**Figure 5.** Effect of 1,2-dimethoxyethane concentration in the polymerization of phenylacetylene by  $\text{WCl}_6 \cdot \text{PA}$  on benzene at 30°C:  $[\text{M}]_0 = 1.0\text{M}$ ;  $[\text{WCl}_6 \cdot \text{PA}]_0 = 5.0\text{mM}$ .



**Figure 6.** Effectiveness of  $\text{WCl}_6 \cdot \text{Ph}_4\text{Sn} \cdot 0.1\text{DO}$  as catalyst in the polymerization of phenylacetylene in benzene at 30°C:  $[\text{M}]_0 = 1.0\text{M}$ ;  $[\text{WCl}_6]_0 = 5.0\text{mM}$ .

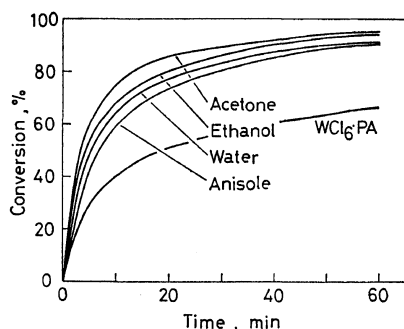
the induction period was relatively short (about 30 min) and the yield after 1-hr polymerization was high (see Figure 3). On the other hand, when the addition order of catalyst components was  $(\text{WCl}_6 \cdot 2\text{DO}) + \text{PA}$  or  $(\text{PA} \cdot 2\text{DO}) + \text{WCl}_6$ , the induction period was longer (about 2 hr) and the reaction was slower. The time—conversion curves with the  $(\text{WCl}_6 \cdot 2\text{DO}) + \text{PA}$  and  $\text{WCl}_6 \cdot 2\text{DO}$  catalysts coincided with each other.

The effect of modifier concentration was examined using two other ethers, tetrahydropyran (THP), and 1,2-dimethoxyethane (DME) (Figures 4 and 5, respectively). In both cases, the presence of an ether accelerated the  $\text{WCl}_6 \cdot \text{PA}$ -catalyzed polymerization of phenylacetylene. The addition of tetrahydropyran in amount equal to the  $\text{WCl}_6$  (5.0 mM) brought about no induction period or decrease in the final conversion. With an increase in concentration of 1,2-dimethoxyethane, the polymerization rate decreased but no induction period appeared. In this way, the manner of influence of the modifier depends on the individual ethers.

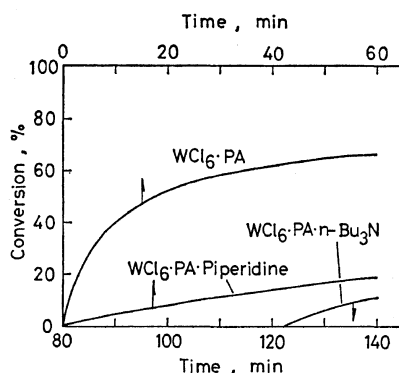
The effect of 1,4-dioxane was examined in the system where tetraphenyltin was used as reducing agent instead of phenylacetylene. Figure 6 shows that the final yield has increased by the addition of a small amount of 1,4-dioxane, though not as much as when the  $\text{WCl}_6 \cdot \text{PA} \cdot 0.1\text{DO}$  catalyst was used.

#### *Effect of Other Oxygen- and Nitrogen-Containing Compounds*

Figure 7 and Table I show the results with other oxygen-containing compounds. It is clear that different kinds of oxygen-containing com-



**Figure 7.** Influence of various oxygen-containing compounds (Z) on the polymerization of phenylacetylene in benzene at 30°C:  $[M]_0=1.0M$ ;  $[WCl_6 \cdot PA \cdot 0.1Z]_0=5.0mM$ .



**Figure 8.** Influence of amines (Z) on the polymerization of phenylacetylene in benzene at 30°C:  $[M]_0=1.0M$ ;  $[WCl_6 \cdot PA \cdot Z]_0=5.0mM$ .

**Table I.** Polymerization of phenylacetylene initiated by  $WCl_6 \cdot PA \cdot 0.1Z^{a,b,c}$

Z <sup>c</sup>	Conversion, %	$\bar{M}_n$
1,4-Dioxane	95.5	10300
Tetrahydropyran	90.5	13000
1,2-Dimethoxyethane	92.5	11300
Dibutyl ether	92.0	10800
Anisole	90.5	—
Phenetole	94.0	—
Acetone	96.0	11300
2-Butanone	94.0	—
Ethanol	94.0	—
Water	92.0	—
$WCl_6$ (as catalyst)	61.0	11600
$WCl_6 \cdot PA$ (as catalyst)	66.0	13900

<sup>a</sup> Polymerized in benzene at 30°C for 1 hr under nitrogen;  $[M]_0=1.0M$ ,  $[WCl_6 \cdot PA \cdot 0.1Z]=5.0mM$ .

<sup>b</sup> PA, phenylacetylene as a catalyst component.

<sup>c</sup> Z, oxygen- or nitrogen-containing compound as a third catalyst component.

pounds are unexpectedly effective: ethers (1,4-dioxane, tetrahydropyran, 1,2-dimethoxyethane, dibutyl ether, anisole, phenetole), ketones (acetone, 2-butanone), ethanol and water. The last two compounds possess a proton which can be released while the other compounds do not. With any of the oxygen-containing compounds examined, the yields after 1 hr polymerization were 90–96%, which are greater than the yields with  $WCl_6$  or  $WCl_6 \cdot PA$  (61.0 and 66.0%, respectively). The polymer molecular weights

were all slightly over 10,000 and do not seem to be affected by oxygen-containing compounds. No difference was observed in the IR spectra of the polymers obtained in the presence or absence of oxygen-containing compounds, indicating that the geometric structure of polymer is not affected by the presence of oxygen-containing compounds (see ref 10 for the relationship between the IR spectrum and geometric structure of poly(phenylacetylene)).

The effect of nitrogen-containing compounds was examined (Figure 8). Contrary to oxygen-containing compounds, addition of amines (tributylamine and piperidine) reduced the reaction rate and/or brought about an induction period.

#### *Tungsten Valency in the Catalyst and Polymerization Systems*

The influence of phenylacetylene and 1,4-dioxane on the oxidation state of tungsten in the catalyst solution were investigated (Figure 9). The sample solutions for determining the oxidation state of tungsten were prepared in the same way as the catalyst solutions. Even if a twofold excess of 1,4-dioxane was added to the  $WCl_6$  solution, the valency of tungsten was scarcely reduced from 6. On the other hand, the addition of an equivalent amount of phenylacetylene to the  $WCl_6$  solution reduced the valency of the tungsten to 5.5. A twofold excess of phenylacetylene reduced the valency of tungsten to 5. 1,4-Dioxane did not affect the valency of tungsten in the  $WCl_6 \cdot PA$  (1:1) solution. Thus, phenylacetylene was capable of reducing W(VI) but

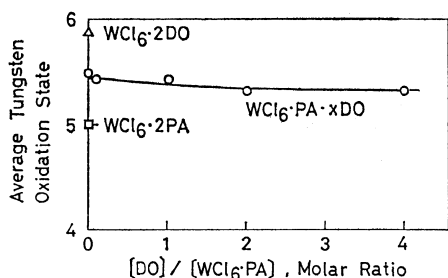


Figure 9. Relationship between the oxidation state of tungsten and 1,4-dioxane content in catalyst solution:  $[WCl_6]_0 = 5.0 \text{ mM}$ .

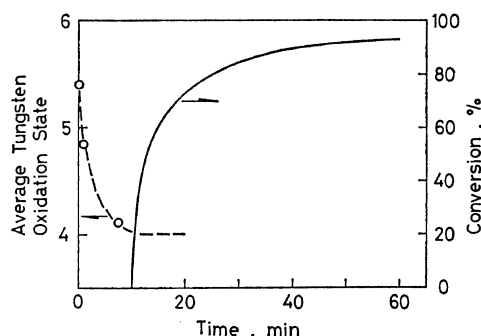


Figure 10. Oxidation state of tungsten in the polymerization system of phenylacetylene by  $WCl_6 \cdot PA \cdot DO$  in benzene at  $30^\circ C$ :  $[M]_0 = 1.0 M$ ;  $[WCl_6 \cdot PA \cdot DO]_0 = 5.0 \text{ mM}$ .

1,4-dioxane was not.

The change in tungsten valency with time was examined for the polymerization with the  $WCl_6 \cdot PA \cdot DO$  (1 : 1 : 1) catalyst (Figure 10). An induction period of 10 min was observed in this polymerization. Tungsten was reduced from 5.5 to 4 during the induction period. Therefore, the active species in the present polymerization presumably involves W(IV).

## DISCUSSION

As is clear from the above results, the addition of a reducing agent is not necessary in the  $WCl_6$ -catalyzed polymerization of phenylacetylene, because phenylacetylene reduces the tungsten of  $WCl_6$  to give an active species (Figure 9). This is different from the case of olefin metathesis, in which a reducing agent is indispensable. The reducing power of phenylacetylene, however, does not seem very strong. There-

fore, the addition of an appropriate reducing agent such as tetraphenyltin increases the catalyst activity in the polymerization of phenylacetylene (Figure 6).

It has become clear that a variety of oxygen-containing compounds are effective as modifiers. The oxygen-containing compounds consist of two kinds: those which easily release proton (*e.g.*, water) and the ones which do not (*e.g.*, 1,4-dioxane). Therefore, no chemical reaction may take place between tungsten and oxygen-containing compounds, but only the coordination of the oxygen atom in these compounds on tungsten seems to take place.

The molecular weight and the geometric structure of polymer were unaffected by the presence of modifiers (Table I). This suggests that modifiers did not produce a different, more active propagating species but only increased the number of propagating species.

A probable explanation for the function of modifiers is as follows. The active species seems to be W(IV) according to the results described above (Figure 10).  $WCl_4$  is reportedly insoluble in most organic solvents, and  $WCl_4 \cdot 2C_2H_5CN$ <sup>5</sup> and  $WCl_4 \cdot 2$  tetrahydrothiophene<sup>12</sup> are soluble. Thus, it is supposed that a modifier makes the transient W(IV) species soluble which exists while  $WCl_6$  changes into a propagating species. Another possible explanation is that an oxygen-containing compound coordinatively bound to tungsten weakens the Lewis acidity of the active species, resulting in the enhancement of activity.

In conclusion, the catalysts composed of  $WCl_6$ , a reducing agent (phenylacetylene or tetraphenyltin) and a modifier (various oxygen-containing compounds) were found to be very effective for the polymerization of phenylacetylene.

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