Polymerization of Phenylacetylenes. 4. Effects of Tetraphenyltin and Initiation Mechanism in the WCl_6-Catalyzed Polymerization

Toshio Masuda,* Kim-Quan Thieu, Noriaki Sasaki, and Toshinobu Higashimura

Department of Polymer Chemistry, Kyoto University, Kyoto 606, Japan.

Received April 28, 1976

ABSTRACT: A small amount of tetraphenyltin (Ph_4Sn) accelerated markedly the polymerization of phenylacetylene by WCl_6 in benzene at 30 °C under nitrogen. Polymers having molecular weights greater than 10 000 were produced. This catalyst system was so active that even at 0 °C a high polymerization rate and a high polymer yield were observed. The acceleration of reaction was observed only when a mixture of WCl_6 and Ph_4Sn was aged for a given time before addition to the monomer solution. The polymerization was depressed in the presence of oxygen or by use of more polar solvents. These results indicated that the polymerization of phenylacetylene by WCl_6 proceeded by a coordination mechanism. The initiation mechanism was inferred.

In a previous paper, we reported that WCl_6 and $MoCl_5$ work as effective catalysts for the polymerization of phenylacetylene.[1] The results on solvent effect,[1] ring-substituent effect,[2] and chain-transfer reaction[3] in the polymerization suggested that the polymerization proceeded rather by a coordination mechanism than by a conventional cationic one.

WCl_6 and $MoCl_5$ are well known as catalyst components of the olefin metathesis reaction. Usually these metal halides need organometallics such as alkylaluminum chlorides and alkyllithiums to catalyze the metathesis reaction.[4]

In order to elucidate the mechanism of the polymerization of phenylacetylene by WCl_6, and to search for active catalysts, phenylacetylene was polymerized by using several organometallic compounds. In the course of the investigation on the effects of organometallics, tetraphenyltin (Ph_4Sn) was found to have a great activity. That is, the addition of Ph_4Sn increased not only the final conversion but also greatly increased the initial rate. This paper deals with the Ph_4Sn acceleration of the WCl_6-catalyzed polymerization of phenylacetylene, and also with the initiation mechanism.

Experimental Section

Materials. Phenylacetylene, WCl_6, and solvents were purified by the same method as described in a previous paper.[1] Commercial Ph_4Sn was purified by recrystallizing twice from carbon tetrachloride (mp 288.8 °C, lit.[5] 228–229 °C). All other commercial organometallics were used without further purification.

Procedures. Polymerizations were performed in a dilatometer under a dry nitrogen atmosphere. Unless otherwise noted, Ph_4Sn was added into a WCl_6 solution. This catalyst solution was aged under a given condition and was added to monomer solution to start polymerization. The polymerization rate was determined by use of dilatometry and gas chromatography as described previously.[1] The polymer produced was purified by precipitating into methanol, filtering, and drying to constant weight. Polymer molecular weights were measured by use of a Hitachi 117 vapor pressure osmometer. Infrared spectra were measured in KBr disks on a Shimadzu IR-27G spectrophotometer.

The average oxidation state of tungsten in the catalyst solution was determined as follows.[6] Dilute sulfuric acid (100 ml) (1 N) was added to the aged catalyst solution to decompose organometallic compounds. After 30 min an excess of ferric ammonium sulfate solution (1 N) was added and the mixture was stirred for 30 min at 20 °C to oxidize tungsten to the VI state. The ferrous ion formed was titrated with 0.1 N $KMnO_4$ by use of tri-*o*-phenanthroline ferrous sulfate as indicator.

Results

Acceleration of the Polymerization by Ph_4Sn. A small amount of Ph_4Sn was found to greatly increase the initial polymerization rate of phenylacetylene by WCl_6 in benzene. Figure 1 shows the time–conversion curves in the presence of various concentrations of Ph_4Sn. When the molar ratio of Ph_4Sn to WCl_6 was in the range of 1 to 2, the polymerization rate reached the maximum. When the ratio of Ph_4Sn to WCl_6 was greater than 2, the catalyst solution became a slurry and both the reaction rate and the polymer yield decreased. In the polymerization shown in Figure 1, the catalyst solution was aged for 10 min at 30 °C. As Table I shows, the polymer molecular weights scarcely changed when the Ph_4Sn to WCl_6 ratio was less than 1. However, an excess of Ph_4Sn over WCl_6 decreased the polymer molecular weight. Thus, the equimolar mixture of WCl_6 and Ph_4Sn was optimal to maximize both the polymerization rate and the polymer molecular weight. Therefore, the equimolar mixture was employed in further experiments.

When WCl_6 and Ph_4Sn are mixed together in benzene, the color of the solution gradually changed from dark blue to brown and the catalyst activity also varied with the change of color. Figure 2 shows the effect of aging time on the reaction course. When Ph_4Sn was added to the monomer solution beforehand and the reaction was started by adding WCl_6 solution, the polymerization rate was almost the same as that of the polymerization in the absence of Ph_4Sn. That is, the effect of Ph_4Sn was not observed. The polymerization rate increased with an increase in aging time, and reached the maximum when the aging time was 10–30 min. With a longer aging time the catalyst solution tended to be a fine suspension and the polymerization rate decreased. The polymer molecular weight was almost unaffected by the aging time. The catalyst solutions in the following experiments were aged for 10 min at 30 °C before use.

Several organometallics were employed to examine whether such an acceleration was observed. When n-Bu_4Sn several times as much as WCl_6 was added to the WCl_6 solution, the polymerization was slightly accelerated. The acceleration, however, was not so large as with Ph_4Sn. The polymerization was decelerated when triethylaluminum, diethylaluminum chloride, ethylaluminum dichloride, or butyllithium (each equimolar to WCl_6) were added to the WCl_6 solution. The latter catalyst solutions were inhomogeneous. Thus, an evident acceleration was observed only with Ph_4Sn as organometallic compounds.

As Figure 3 shows, the reaction product of WCl_6 and a catalytic amount of phenylacetylene (PA) promoted the polymerization, though the extent was not so great as that for the $WCl_6 \cdot Ph_4Sn$ catalyst. In curve b, the catalyst solution was prepared by mixing equimolar WCl_6 and phenylacetylene at −70 °C in toluene and thereafter keeping it at 30 °C for 20 min. This solution was brown like the $WCl_6 \cdot Ph_4Sn$ solution (cf. the WCl_6 solution was dark blue).

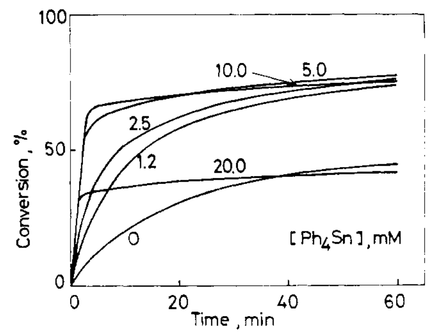

Figure 1. Effect of Ph_4Sn concentration on the polymerization of phenylacetylene by WCl_6 in benzene at 30 °C: $[M]_0 = 1.0$ M, $[WCl_6] = 5.0$ mM, aging time 10 min at 30 °C.

Table I
Effect of Ph_4Sn Concentration on the Molecular Weight of Poly(phenylacetylene)[a]

[Ph_4Sn]4, mM	Conversion, %	$\bar{M}_n$
0	46.1	10 600
1.2	74.5	10 000
2.5	76.0	11 000
5.0	77.1	12 000
10.0	74.7	5 300
20.0	42.5	4 800

[a] Polymerized in benzene at 30 °C for 1 h under nitrogen: $[M]_0 = 1.0$ M; $[WCl_6] = 5.0$ mM; catalyst aged for 10 min at 30 °C.

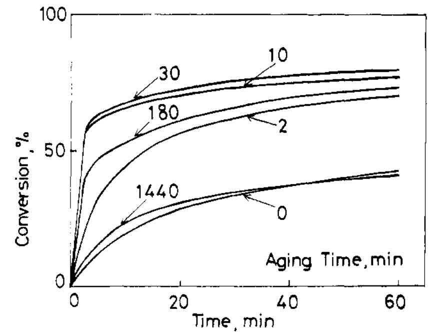

Figure 2. Effect of aging time of $WCl_6 \cdot Ph_4Sn$ on the polymerization of phenylacetylene in benzene at 30 °C: $[M]_0 = 1.0$ M, $[WCl_6 \cdot Ph_4Sn] = 5.0$ mM.

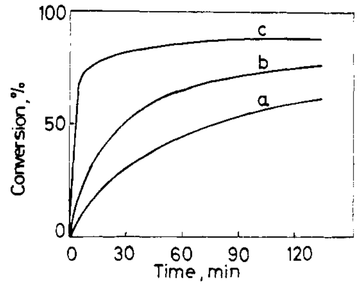

Figure 3. Effect of phenylacetylene as a catalyst component on the polymerization of phenylacetylene by WCl_6 in toluene at 30 °C: $[M]_0 = 1.0$ M; (a) $[WCl_6] = 5.0$ mM; (b) $[WCl_6 \cdot PA\ (1{:}1)] = 5.0$ mM; (c) $[WCl_6 \cdot Ph_4Sn] = 5.0$ mM.

Characteristics of the Polymerization by $WCl_6 \cdot Ph_4Sn$. To investigate the behavior of this polymerization, the influence of solvent polarity was investigated at first. Phenylacetylene was polymerized by use of carbon tetrachloride, toluene, and ethylene dichloride under the same conditions as shown in Figure 1. With the same catalyst concentration, the polymerization rate and final conversion decreased in the following order:

$$CCl_4 > C_6H_5CH_3 \simeq C_6H_6 > (CH_2Cl)_2$$

This sequence is the same as that of the polymerization of phenylacetylene by WCl_6,[1] and is just opposite to that observed in the cationic polymerization of styrene by WCl_6.[7] This solvent effect suggests a mechanism other than a cationic one.

As described below, a significant effect of oxygen on the polymerization provides another evidence of a noncationic mechanism. As is clear from Figure 4, when the polymerization of phenylacetylene was carried out under a dry oxygen atmosphere the polymerization rate markedly decreased regardless of the presence of Ph_4Sn. The molecular weight of the polymer was not influenced by oxygen. For the sake of comparison, the influence of Ph_4Sn on the polymerization of styrene by WCl_6 was examined under a nitrogen atmosphere and also under an oxygen atmosphere. The polymerization of styrene catalyzed by WCl_6 in benzene at 30 °C proceeded very fast until all the monomer was consumed. The polymerization rate decreased with the addition of Ph_4Sn. Furthermore, oxygen did not depress the polymerization of styrene catalyzed either by WCl_6 with or without Ph_4Sn.

The effects of catalyst ($WCl_6 \cdot Ph_4Sn$ (1:1)) and monomer concentrations on the conversion in benzene solution were examined. At any catalyst concentration in the range of 1.5–10.0 mM a rapid polymerization took place (within the first 3 min), and the polymerization proceeded slowly thereafter. The final conversion increased with increasing catalyst concentration. Figure 5 shows the time–conversion curves obtained at various monomer concentrations. The final conversion decreased with increasing monomer concentration. In Table II are listed the molecular weights of polymers obtained at various catalyst and monomer concentrations. The molecular weight increased with the decrease of catalyst concentration and with the increase of monomer concentration.

Figure 6 shows the effect of temperature on polymerization. The polymerization took place fast within a few minutes at temperatures from 0 to 60 °C and it was difficult to evaluate the rate accurately. However, the rate seemed to be almost independent of the polymerization temperature. It is of interest that even at 0 °C the polymerization proceeded rapidly. The final conversion decreased as the polymerization temperature was raised. This observation suggests the active species is more easily deactivated at higher temperatures. The molecular weights of the polymers produced after 1 h of polymerization are shown in parentheses in Figure 6. The molecular weight slightly decreased with the increase of polymerization temperature.

Oxidation State of Tungsten in the $WCl_6 \cdot Ph_4Sn$ Catalyst. WCl_6 is anticipated to be reduced when a reducing agent such as Ph_4Sn is added. The average oxidation state of tungsten in the present catalyst system was examined. As seen from Figure 7, tungsten was reduced to the IV state in average by the addition of equimolar Ph_4Sn and was not reduced further with an excess of Ph_4Sn. This result corresponds with the finding that the polymerization rate reaches the maximum at the Ph_4Sn/WCl_6 ratio of unity. WCl_6 was also reduced by phenylacetylene. The average oxidation number of the tungsten was five even with an excess of phenylacetylene.

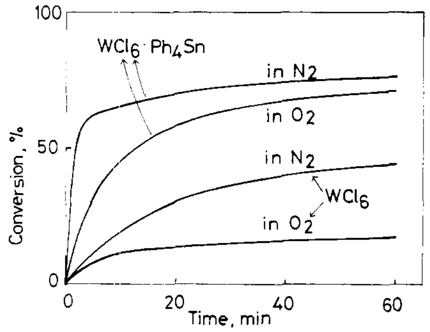

Figure 4. Effect of oxygen on the polymerization of phenylacetylene by WCl_6 and $WCl_6 \cdot Ph_4Sn$ in benzene at 30 °C: $[M]_0 = 1.0$ M, $[WCl_6]$ and $[WCl_6 \cdot Ph_4Sn] = 5.0$ mM.

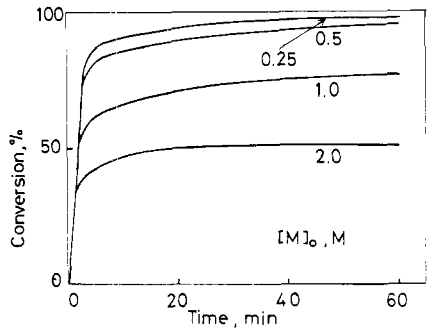

Figure 5. Effect of monomer concentration on the polymerization of phenylacetylene by $WCl_6 \cdot Ph_4Sn$ in benzene at 30 °C: $[WCl_6 \cdot Ph_4Sn] = 5.0$ mM.

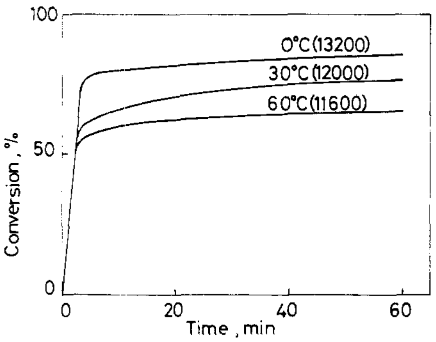

Figure 6. Effect of polymerization temperature on the polymerization of phenylacetylene by $WCl_6 \cdot Ph_4Sn$ in benzene: $[M]_0 = 1.0$ M, $[WCl_6 \cdot Ph_4Sn] = 5.0$ mM. The numbers in parentheses indicate polymer molecular weights.

Thus, it is obvious that the acceleration of polymerization is closely correlated with the reduction of WCl_6.

Structure of Poly(phenylacetylene) Obtained by $WCl_6 \cdot Ph_4Sn$. The polymers produced by $WCl_6 \cdot Ph_4Sn$ in benzene were dark red powders, and appeared similar to those obtained by WCl_6 alone. Furthermore, the infrared spectra of polymers in this study were identical with those obtained using WCl_6.[8] The polymers had trans-rich structure, and their softening point were about 220 °C. These were the same tendencies as in the polymers obtained by WCl_6.[8] There were no differences between the infrared spectra of the polymers produced at an initial stage (~10 s, 5% conversion) and those produced after a long time. These facts indicate that the polymer structure is unaffected by Ph_4Sn, which suggests that the same intermediate was generated during the polymerization. Oxygen did not influence the polymer structure.

Table II
Effects of $WCl_6 \cdot Ph_4Sn$ and Monomer Concentration on the Molecular Weight of Poly(phenylacetylene)[a]

$[WCl_6 \cdot Ph_4Sn]$, mM	$[M]_0$, M	Conversion, %	$\bar{M}_n$
1.5	1.0	32.7	12 500
5.0	1.0	77.1	12 000
10.0	1.0	100.0	7 700
5.0	0.25	97.7	8 100
5.0	0.50	95.0	10 400
5.0	2.0	50.7	13 300

[a] Polymerized in benzene at 30 °C for 1 h under nitrogen; catalyst aged for 10 min at 30 °C.

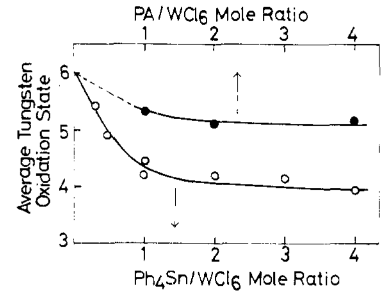

Figure 7. Relationships between the average tungsten oxidation state and the ratios of Ph_4Sn/WCl_6 or PA/WCl_6 in catalyst solutions.

Discussion

WCl_6 and $MoCl_5$ were found to be specifically effective catalysts for this polymerization.[1] Moreover, the present catalyst system ($WCl_6 \cdot Ph_4Sn$) was found to bring about a very rapid polymerization of phenylacetylene giving a high molecular weight polymer.

The following results all support the idea that the polymerization of phenylacetylene by WCl_6 proceeds by a coordination mechanism: (i) nonpolar solvents favor the polymerization,[1] (ii) the σ–ρ relationship denies a cationic species as propagating end,[2] (iii) reducing agents such as Ph_4Sn accelerate the polymerization, and (iv) oxygen depresses the polymerization. On the other hand, the polymerization of styrene by WCl_6 is cationic, as proved by the following observations: (i) the ρ value is a large negative,[2] (ii) alkylbenzenes function as chain transfer agent,[3] (iii) the addition of Ph_4Sn decelerates the polymerization, and (iv) oxygen does not affect the polymerization at all. Thus, the reaction mechanisms of polymerizations of phenylacetylene and styrene by WCl_6 are fundamentally different regardless of using the same catalyst.

The present study revealed that Ph_4Sn markedly accelerated the polymerization of phenylacetylene by WCl_6. It has been known that combinations of either WCl_6 or $MoCl_5$ and organometallic compounds serve as effective catalysts in olefin metathesis.[4] There are reports which claim that the active intermediate in the metathesis reactions catalyzed by $WCl_6 \cdot SnR_4$[9] or $WCl_6 \cdot RLi$[10] is $WCl_4 \cdot 2$(olefin). There is another report describing that the chlorine atom of WCl_6 is easily substituted by phenylacetylene.[4] A similar reaction should be taking place in the present polymerization. The active complex (complex I) formed by the reaction of WCl_6 with Ph_4Sn probably comprises W(IV). A mixture of WCl_6 and phenylacetylene also gives a pretty active initiating species (complex II). The three catalysts, WCl_6, $WCl_6 \cdot Ph_4Sn$, and $WCl_6 \cdot PA$ (PA, phenylacetylene), produce polymers whose structures and molecular weights are very similar to each other. Therefore, the three catalysts seem to be different only in the feasibility of producing the same propagating end. From these considerations, the following scheme is assumed:

$$\begin{tikzcd}
 & \text{complex I} \arrow[dr, "PA"] & & \\
WCl_6 \arrow[ur, "Ph_4Sn"] \arrow[dr, "PA"'] & & \text{propagating species} \arrow[r, "PA"] & \text{polymer} \\
 & \text{complex II} \arrow[ur, "PA"'] & &
\end{tikzcd}$$

The structures of complexes I and II are not known yet. However, the results on the tungsten oxidation state suggest that the complexes and the propagating end consist of species less oxidized than W(VI). It is presumed that complex I is $WCl_4 \cdot 2Ph$ or simply WCl_4, and complex II is $WCl_4 \cdot nPA$ (a σ complex, π complex, or metal-carben complex). The propagating species may be a metal–carben complex or a four-membered metalocycle on the basis of the polymerization behavior.[1,2,8]

In conclusion, it is found that Ph_4Sn accelerates remarkably the polymerization of phenylacetylene and that oxygen decelerates the polymerization. The reaction mechanism of initiation is proposed. However, the structures of the active complexes are not identified. Further investigation is being performed to determine the structures of complexes I and II.

References and Notes

(1) T. Masuda, K. Hasegawa, and T. Higashimura, *Macromolecules*, **7**, 728 (1974).
(2) K. Hasegawa, T. Masuda, and T. Higashimura, *Macromolecules*, **8**, 255 (1975).
(3) K. Hasegawa, T. Masuda, and T. Higashimura, *J. Polym. Sci., Polym. Chem. Ed.*, in press.
(4) E.g., as a recent review, G. Dall'Asta, *IUPAC Additional Publication*, **1**, 133 (1974).
(5) L. A. Rothman and E. I. Becker, *J. Org. Chem.*, **24**, 294 (1959).
(6) E. J. Arlman and J. R. De Jong, *Recl. Trav. Chim. Pays-Bas*, **79**, 910 (1960).
(7) T. Masuda, T. Miura, M. Mizuno, and T. Higashiumra, unpublished data.
(8) T. Masuda, N. Sasaki, and T. Higashimura, *Macromolecules*, **8**, 717 (1975).
(9) G. Lehnert, D. Maertens, G. Pampus, and M. Zimmermann, *Makromol. Chem.*, **175**, 2617 (1974).
(10) J. L. Wang and H. R. Menapace, *J. Org. Chem.*, **33**, 3794 (1968).

Polymerization of Phenylacetylenes. 5. Polymerization of Phenylpropyne Catalyzed by Tungsten Hexachloride–Tetraphenyltin

Noriaki Sasaki, Toshio Masuda,* and Toshinobu Higashimura

Department of Polymer Chemistry, Kyoto University, Kyoto 606, Japan.

Received April 28, 1976

ABSTRACT: *Phenylpropyne was found to polymerize easily with an equimolar mixture of* WCl_6 *and tetraphenyltin* as catalyst. Polymers having a molecular weight of 3000–6000 were produced in hydrocarbons and halogenated hydrocarbons as solvents. At temperatures higher than 60 °C the polymerization proceeded at a high initial rate but stopped before all monomer was consumed. On the other hand, in a range of 0–30 °C no saturation phenomenon was observed. The poly(phenylpropyne) formed was a white powder and soluble in aromatic and chlorinated hydrocarbons. The softening point was in a range of 230–240 °C. Ir, ^1H NMR, ^{13}C NMR, and uv spectroscopies showed that the polymer possesses a polyene structure having phenyl and methyl side groups. The phenomenon that the polymer is white in spite of having a polyene structure was explained in terms that the polyene does not take a planar conformation due to the steric effect of the two bulky groups.

We found that phenylacetylene was polymerized easily by WCl_6 at room temperature and formed a polymer having a molecular weight of 10 000–15 000.[1] Further, we reported in the preceding paper[2] that a catalytic amount of tetraphenyltin (Ph_4Sn) accelerates the polymerization of phenylacetylene by WCl_6 to a great extent without changing the molecular weight of the polymer. Therefore, it will be interesting to see if this catalyst system, which is very effective in the polymerization of phenylacetylene, is effective also in the polymerization of other acetylenic compounds.

In general, α,β-disubstituted olefins and acetylenes are expected to be less reactive than monosubstituted ones in polymerization. This is probably due to the steric effect. Although there are many studies on the cyclic trimerization of internal acetylenes,[3,4] very few have been reported with regard to the polymerization of internal acetylenes. To our knowledge, there has been only one report on the polymerization of phenylpropyne; recently Woon and Farona have reported that phenylpropyne is polymerized by Mo complexes to a polymer with a molecular weight of ca. 1500.[5]

The present paper describes the reactivity of phenylpropyne in the polymerization by $WCl_6 \cdot Ph_4Sn$ and the structure of poly(phenylpropyne) produced. The $WCl_6 \cdot Ph_4Sn$ catalyst was found to be very effective for polymerization of phenylpropyne. No cyclic trimer was observed during polymerization. The polymer was white due to little conjugation of the main chain.

Experimental Section

Materials. phenylpropyne was synthesized from α-methylcinnamic acid by reported methods.[6] α-Methylcinnamic acid was prepared by the Perkin reaction.[7] The purity of the phenylpropyne was greater than 99% according to gas chromatography. Solvents, WCl_6, and Ph_4Sn were purified by the same methods as described in previous papers.[1,2]

Procedures. Polymerization was carried out under the same conditions as the polymerization of phenylacetylene.[2] An equivalent amount of Ph_4Sn was added to a WCl_6 solution and this catalyst solution was aged at 60 °C for 15 min just before polymerization. Polymerization was started by adding the catalyst solution to the monomer solution. Monomer consumption was determined by measuring residual monomer concentration by gas chromatography. The number-average molecular weight of the polymer was measured by use of a Hitachi 117 vapor pressure osmometer. Ir spectra of the polymers were measured with KBr disks. ^1H NMR spectra of the polymers were measured in a 20% carbon tetrachloride solution (JEOL MH60). ^{13}C