Polymerization of Phenylacetylenes. I. Polymerization of Phenylacetylene Catalyzed by WCl_6 and $MoCl_5$

Toshio Masuda, Kan-ichi Hasegawa, and Toshinobu Higashimura*

Department of Polymer Chemistry, Kyoto University, Kyoto 606, Japan. *Received April 30, 1974*

ABSTRACT: WCl_6 and $MoCl_5$ were found to be effective initiators for the polymerization of phenylacetylene. The catalytic activity of WCl_6 was larger than that of $MoCl_5$. Poly(phenylacetylene) was produced from phenylacetylene without formation of a cyclic trimer by using these metal halides in benzene and ethylene chloride at 30°. The polymerization of phenylacetylene by WCl_6 in benzene proceeded at a high initial rate which was proportional to monomer and WCl_6 concentrations. Addition of a small amount of water increased both the polymerization rate and the number-average molecular weight of the polymer which reached about 15,000 under suitable conditions. On the other hand, in the polymerization by WCl_6, trichloroacetic acid decreased both the polymerization rate and the molecular weight of the polymer. The more polar the solvent, the smaller the polymerization rate. No polymer was produced in a nitrobenzene solution. The deteriorating effects of trichloroacetic acid and a polar solvent in the polymerization of phenylacetylene by WCl_6 are not explained in terms of a conventional cationic mechanism.

This paper is concerned with the formation of poly(phenylacetylene) having high molecular weight (5,000–15,000). Phenylacetylene was found to form the polymer in a high yield by using WCl_6 and $MoCl_5$ as catalysts.

Polymerization of phenylacetylene has been attempted under various conditions, for example, by radical (thermal initiation,[1,2] high-energy radiation,[3,4] and peroxide[5]), cationic (protonic acids[6,7] and metal halides[8–10]), and coordination[11–20] mechanisms. However, the polymerizations in the previous papers have often been accompanied with some of the following problems: (i) the molecular weight of the poly(phenylacetylene) is low (usually less than 3000), (ii) the product involves a methanol-soluble oligomer and/or a benzene-insoluble fraction, (iii) a cyclic trimer (1,3,5-triphenylbenzene) is formed as a by-product, and (iv) the reaction needs a long time and/or a high temperature.

The low molecular weight of the polymer produced from phenylacetylene by a cationic mechanism has been explained in terms of either a low reactivity of phenylacetylene for electrophiles[21] or a high stability of the propagating end due to the conjugation of double bonds.[22,23]

The present authors have investigated the reactivity of phenylacetylene in the polymerization by Lewis acids and attempted to compare it with that of styrene derivatives. In this study, it was found that WCl_6 and $MoCl_5$ were effective initiators to obtain poly(phenylacetylene) in a high yield. Therefore, the effect of reaction conditions on the polymerization of phenylacetylene was studied to clarify the nature of the polymerization of phenylacetylene by these metal halides.

Experimental Section

Materials. Commercial phenylacetylene (guaranteed reagent) was purified by distillation from CaH_2. The purity was more than 99.9% by gas chromatography. Solvents (benzene, ethylene chloride, and nitrobenzene) were purified by the usual methods. The monomer and the solvents were distilled from CaH_2 or Na in a vacuum line to remove traces of water and stored in an ampoule equipped with a break-seal. WCl_6, $MoCl_5$, and trichloroacetic acid (TCA) were sublimed under vacuum and stored in an ampoule equipped with a break-seal.

Procedures. All manipulations, except for the polymerization in ethylene chloride by $MoCl_5$, were carried out under vacuum (10^{-5} mm). Initiator was added to the monomer solution which contained ethylbenzene as an internal standard for gas chromatography, and the mixture was transferred to a dilatometer to follow the polymerization by volume contraction. After a given time, methanol containing a small amount of ammonia was added to stop the polymerization. A portion of the solution was sampled to determine the residual monomer by gas chromatography. The solution was then poured into a large amount of methanol. The methanol-insoluble product was recovered and weighed to determine the yield of polymer. The consumption of the monomer determined by gas chromatography was in agreement with the polymer yield determined by gravimetry. During the polymerization of phenylacetylene, 23.1% was taken for the volume contraction. This was the observed value on the basis of the densities of benzene solutions of the monomer and the polymer.

The molecular weights of the polymers were determined in benzene solutions using a vapor pressure osmometer Hitachi 115. Infrared spectra of the polymers were recorded in a KBr disk. Proton nmr spectra (100 MHz) of the polymer were measured in a 10% tetrachloroethylene solution.

Results

Formation of Poly(phenylacetylene) by WCl_6. Phenylacetylene was found to polymerize easily by WCl_6 in benzene. As seen in Figure 1, the polymerization proceeded at a high initial rate and produced a polymer in a high yield. The polymerization was very rapid at the initial stage but soon slowed down and then stopped before all monomer was consumed. The polymerization rate and the final yield in polymer depended on the concentration of water. Both increased with increasing the concentration of water until the molar ratio $[H_2O]/[WCl_6]$ reached *ca.* 2 and decreased at the ratio more than 2. It should be noted that the polymerization proceeded without the addition of water.

The mixture became pale green immediately after the blue-purple solution of WCl_6 in benzene was added to the monomer solution in benzene. Then 0.5 to 2 min later the solution changed into dark red as the polymer formed. No cyclic trimer was found in the polymerization solution. Polymers produced in benzene by WCl_6 were dark red powders and were amorphous according to X-ray analysis. Infrared spectra of the polymers were identical with those obtained by a thermal polymerization[2] or by aluminum chloride,[9] which have been proved to be linear polymers. In the nmr spectra, only signals for phenyl and olefinic protons were observed. These findings suggest that the polymers obtained here are linear poly(phenylacetylene).

Number-average molecular weights of the polymers formed with reaction rates as in Figure 1 are shown in Figure 2. The polymer molecular weight reached the maximum value (*ca.* 10,000) when the molar ratio $[H_2O]/[WCl_6]$ was in the range of 0.5–1.0. Thus, the addition of a suitable amount of water increased both the polymerization rate and the polymer molecular weight.

As TCA is an effective cocatalyst for the cationic polymerization of styrene by metal halides, the effect of TCA on the polymerization of phenylacetylene by WCl_6 was investigated. As shown in Figure 3, addition of TCA decreased both the initial polymerization rate and the poly-

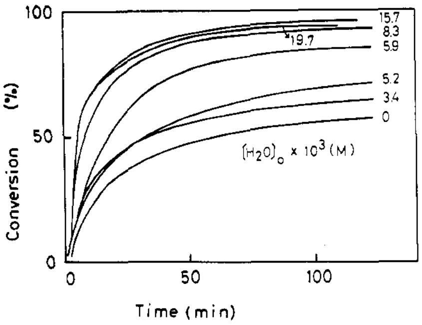

Figure 1. Effect of H_2O on time-conversion curves for the polymerization of phenylacetylene by WCl_6 in benzene at 30°: $[M]_0 = 1.0\ M$, $[WCl_6]_0 = 9.5 \times 10^{-3}\ M$.

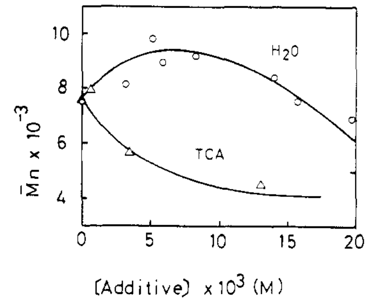

Figure 2. Effect of H_2O and TCA on $\bar{M}_n$ of poly(phenylacetylene) obtained by WCl_6 in benzene at 30°: $[M]_0 = 1.0\ M$, $[WCl_6]_0 = 9.5 \times 10^{-3}\ M$.

Table I
Number-Average Molecular Weight of Poly(phenylacetylene) Obtained by WCl_6 at 30°

Solvent	$[M]_0$, M	$[WCl_6]_0 \times 10^3$, M	$\bar{M}_n$
Benzene[a]	1.0	8.2	8,300
	1.0	6.6	8,400
	1.0	5.0	14,500
	1.0	4.0	9,200
	1.0	2.5	15,400
Benzene[a]	2.3	5.0	8,200
	1.7	5.0	12,600
	0.51	5.0	11,000
Ethylene[b] chloride	1.0	9.1 (none)	3,500
	1.0	9.1 (4.7×10^{-3})	7,800
	1.0	9.1 (16.8×10^{-3})	7,300

[a] $[WCl_6]/[H_2O] = 2{:}1$ molar ratio. [b] Added water concentrations are shown in parentheses.

mer yield. TCA decreased the molecular weight of polymer as well, which is seen in Figure 2.

Next, the effect of solvent polarity was investigated. As shown in Figure 4, the polymerization rate in the more polar ethylene chloride was lower than that in the less polar benzene. Furthermore, the molecular weight of polymers produced in ethylene chloride was lower than that in benzene (Table I). The use of much more polar nitrobenzene as solvent prohibited the formation of polymer, regardless of the amount of water. On the other hand, the cationic polymerization of styrene by WCl_6 is accelerated in more polar solvents.[24] Thus, the effect of solvent polarity in the polymerization of phenylacetylene is quite different from that for styrene.

Kinetics in the Polymerization of Phenylacetylene by WCl_6. Since WCl_6 was found to be an effective initiator for the polymerization of phenylacetylene, the kinetics of the polymerization in benzene was investigated. At a constant $[WCl_6]/[H_2O]$ (1:0.5), the effect of the initiator concentration on the polymerization was investigated. As shown in Figure 5, both the initial polymerization rate and the final polymer yield increased with increasing initiator concentration. On the other hand, the change of the monomer concentration in the range of 0.5–2.3 M affected the time–conversion curves of the polymerization only a little; both the polymerization rate and the final polymer yield decreased slightly with increasing monomer concentration.

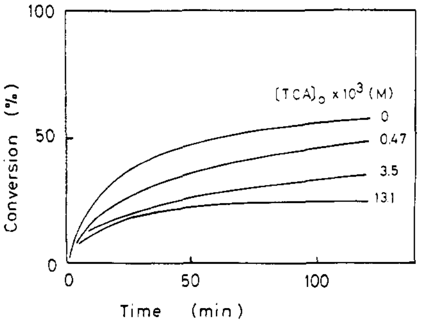

Figure 3. Effect of TCA on time-conversion curves for the polymerization of phenylacetylene by WCl_6 in benzene at 30°: $[M]_0 = 1.0\ M$, $[WCl_6]_0 = 9.5 \times 10^{-3}\ M$.

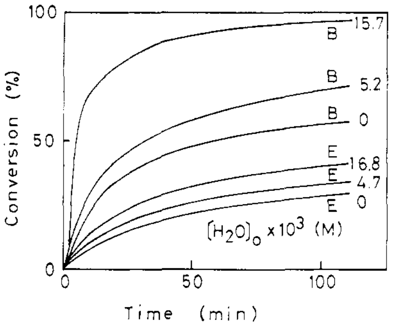

Figure 4. Effect of solvents on time-conversion curves for the polymerization of phenylacetylene by WCl_6 at 30°. $[M]_0 = 1.0\ M$; B, benzene, $[C]_0 = 9.5 \times 10^{-3}\ M$; E, ethylene chloride, $[C]_0 = 9.1 \times 10^{-3}\ M$.

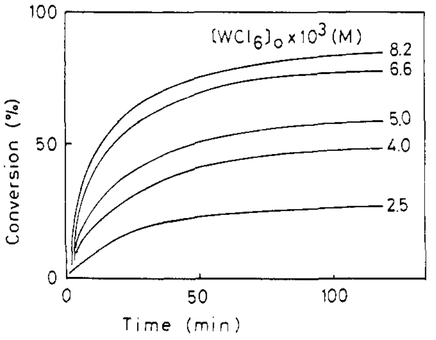

Figure 5. Effect of catalyst concentration on time–conversion curves for the polymerization of phenylacetylene by WCl_6 in benzene at 30°: $[M]_0 = 1.0\ M$, $[WCl_6]_0/[H_2O]_0 = 2{:}1$ molar ratio.

Figure 6 shows the relationships between the initial polymerization rate and the concentrations of initiator and monomer. The initial polymerization rate is approximately proportional to the concentrations of the initiator and the monomer.

In Table I are summarized the effects of the concentrations of initiator and monomer on the polymer molecular weight. The molecular weights shown are those of the polymers at the final conversion. At a constant monomer concentration, the polymer molecular weight increased with decreasing the initiator concentration. At a constant initiator concentration, the polymer molecular weight seems to reach a maximum near a monomer concentration of 1 M. It

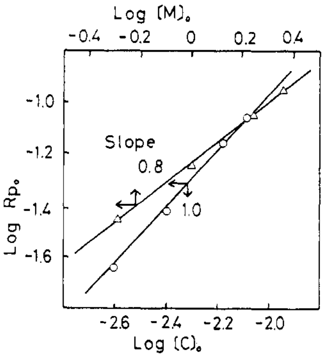

Figure 6. Dependence of the initial polymerization rate on monomer and WCl_6 concentration in benzene at 30°. $[WCl_6]_0/[H_2O]_0$ = 2:1 molar ratio: (a) $[M]_0 = 1.0\ M$, (b) $[WCl_6]_0 = 5.0 \times 10^{-3}\ M$.

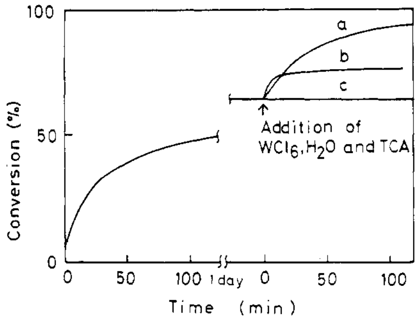

Figure 7. Effect of the addition of WCl_6, H_2O, and TCA on the polymerization of phenylacetylene by WCl_6 in benzene at 30°. $[M]_0 = 1.0\ M$, $[WCl_6 \cdot H_2O\ (1{:}0.5)]_0 = 4 \times 10^{-3}\ M$: (a) WCl_6 ($9.1 \times 10^{-3}\ M$), (b) H_2O ($6.0 \times 10^{-3}\ M$), (c) TCA ($3.3 \times 10^{-3}\ M$).

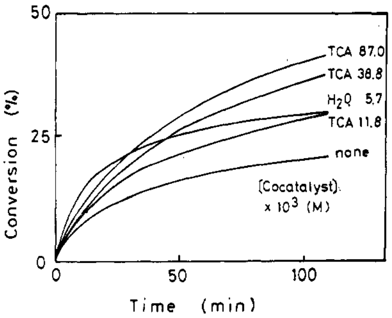

Figure 8. Effect of H_2O and TCA on time–conversion curves for the polymerization of phenylacetylene by $MoCl_5$ in benzene at 30°: $[M]_0 = 1.0\ M$, $[MoCl_5]_0 = 7.8 \times 10^{-3}\ M$.

Table II
Effect of Cocatalyst Concentration on Number-Average Molecular Weight of Poly(phenylacetylene) Obtained by $MoCl_5$ in Benzene at 30°[a]

Additive	[Additive] × 10^3, *M*	$\bar{M}_n$
None		6900
H_2O	5.7	6900
TCA	3.2	5700
TCA	11.8	5700
TCA	38.8	4000
TCA	87.0	5000

[a] $[M]_0 = 1.0\ M$, $[MoCl_5]_0 = 7.8 \times 10^{-3}\ M$.

is clear from Table I that poly(phenylacetylenes) having large molecular weights of *ca.* 15,000 were formed by WCl_6 under proper conditions.

WCl_6, H_2O, or TCA was added to the dormant system and the effect of this addition on the polymerization was investigated. As seen in Figure 7, addition of WCl_6 reinitiated the polymerization at the same rate as before, while addition of H_2O led to a smaller increase in conversion. Addition of TCA did not bring about repolymerization at all.

Polymerization of Phenylacetylene by $MoCl_5$. WCl_6 was found to be an effective initiator for the polymerization of phenylacetylene. Accordingly $MoCl_5$ was tested next since Mo belongs to the same VIb group as W in the periodical table. As shown in Figure 8, $MoCl_5$ in benzene induced a slower polymerization and gave a lower yield than WCl_6. Effects of the additions of H_2O and TCA are also shown in Figure 8. Both H_2O and TCA were effective cocatalysts for the polymerization by $MoCl_5$, that is, the additions increased the polymerization rate. This differs from the polymerization behavior by WCl_6. It is noted that a large excess of TCA over the initiator is necessary to accelerate the polymerization by $MoCl_5$.

Infrared and nmr spectra of the polymers produced by $MoCl_5$ were similar to those produced by WCl_6. Nevertheless, the polymers produced by $MoCl_5$ were orange powders. This may be due to a different microstructure of the polymer and/or a low molecular weight. This point is being investigated. As shown in Table II, the molecular weights of the polymers produced by $MoCl_5$ were lower than those produced by WCl_6. Neither H_2O nor TCA affected greatly the molecular weight in the polymerization by $MoCl_5$.

To investigate the solvent effect the polymerization by $MoCl_5$ was carried out in ethylene chloride. The polymerization was conducted in a dry nitrogen atmosphere. From comparison of Figure 9 with Figure 8, it is seen that the polymerization without TCA was faster in benzene than in ethylene chloride but *vice versa* in the presence of TCA as cocatalyst.

Discussion

It was found in this investigation that phenylacetylene produced polymers in high yields and the polymer molecular weights ranged between 7,000 and 15,000 when polymerized by WCl_6.

Acetylenes are less reactive than corresponding olefins in most electrophilic reactions.[21] Furthermore, the propagating species in the cationic polymerization of acetylenes are stabilized by the delocalization of the charge and hence are deactivated.[22,23] Thus, the cationic polymerization of acetylenes is less favored than that of the corresponding olefins in view of both the monomer reactivity and the propagating end reactivity.

We attempted the cationic polymerization of phenylacetylene using metal halides ($TiCl_4$, $SnCl_4$, BF_3OEt_2), H_2SO_4, and acetyl perchlorate which are all effective in the polymerization of styrene, but no polymer was obtained in the polymerization of phenylacetylene. This agrees with previous papers[6,7,10] reporting that the cationic polymerization of phenylacetylene has been unsuccessful. On the other hand, WCl_6 and $MoCl_5$ catalyzed the polymerization of phenylacetylene very effectively without the formation of a cyclic trimer. Especially, WCl_6 produced the polymers having molecular weights higher than 10,000. Accordingly, it is concluded that WCl_6 is the most effective initiator for the polymerization of phenylacetylene among the radical, cationic, anionic, and coordination catalysts used so far.

WCl_6 acts as a conventional cationic catalyst in the polymerization of styrene and is more active than most cationic catalysts such as $SnCl_4$ and BF_3OEt_2.[24] On the other hand, WCl_6 is a well-known catalyst component effective for the metathesis of olefins and the metathesis polymerization of cycloolefins. As to the present polymerization, it is not conclusive at this stage whether the polymerization of phenylacetylene by WCl_6 proceeds with a conventional cation-

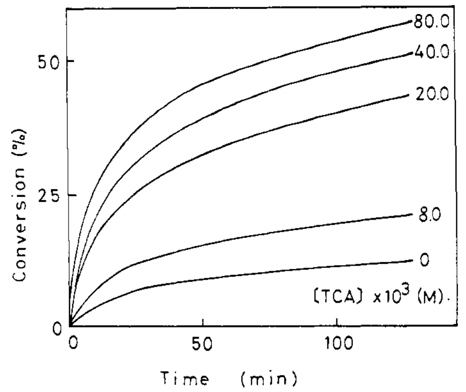

Figure 9. Effect of TCA on time–conversion curves for the polymerization of phenylacetylene by $MoCl_5$ in ethylene chloride at 30°: $[M]_0 = 1.0\ M$, $[MoCl_5]_0 = 8.0 \times 10^{-3}\ M$.

ic mechanism or with a different mechanism such as a coordination one. The results obtained in this study showed several features attributable to either cationic or coordination mechanism.

In the polymerization of phenylacetylene by WCl_6 in benzene, (i) a trace of water accelerated the polymerization, (ii) further additions of water diminished the molecular weight of the polymer obtained, and (iii) the initial rate of polymerization was proportional to the concentrations of initiator and monomer. These results are the same as in the cationic polymerization of styrene by most metal halides and suggest that phenylacetylene polymerized under a conventional cationic mechanism.

Some observations are not explainable by the conventional cationic mechanism: (i) the presence of TCA decreased both the polymerization rate of phenylacetylene and the molecular weight of the polymer, although TCA works as a good cocatalyst in the polymerization of styrene by metal halides; (ii) the more polar the solvent, the smaller the polymerization rate and the molecular weight of the polymer; and (iii) phenylacetylene polymerized at a considerable rate without water. The polymerization without water may be possible if phenylacetylene acts as a cocatalyst using its acidic proton. Therefore, iii is not incompatible with a conventional cationic mechanism. However, i and ii are not explained in terms of this mechanism.

TCA did not inhibit but accelerated the polymerization of phenylacetylene by $MoCl_5$. Therefore, the deteriorating effect of TCA in the polymerization by WCl_6 is not due to the scavenging by TCA of the propagating end of phenylacetylene. TCA may have diminished the reactivity of the propagating end by a complexation with the counterion produced from WCl_6.

The decreased polymerizability in a more polar solvent is explained as well in terms of a stabilization of the propagating end due to the dissociation of the counterion. That is to say, the polymerization of phenylacetylene by WCl_6 may proceed well when the interaction between the propagating end and the counterion produced from WCl_6 is strong; this is reminiscent of a coordination polymerization. The solvent effect contrasts to that observed in the cationic polymerization of styrene by WCl_6, in which the polymerization was accelerated in a more polar solvent.[24] We investigated the reaction mechanism of the polymerization of phenylacetylene in more detail through the effect of ring substituents, and the results will be reported in a subsequent paper.

The catalytic activity of $MoCl_5$ for the polymerization of phenylacetylene was smaller than that of WCl_6. This was the case also for the cationic polymerization of styrene[24] and the metathesis polymerization of cycloolefins.[25] The polymerization of phenylacetylene by $MoCl_5$ was accelerated not only by water but also by TCA and was not greatly affected by the solvent polarity. Thus, the polymerization by $MoCl_5$ differs from that by WCl_6 in several aspects. Further investigations are necessary for a conclusion to be drawn to this problem.

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