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Polymerization of Phenylacetylenes. 8. Simultaneous Coordination and Cationic Polymerizations in the WCl_6-Catalyzed Copolymerization of Phenylacetylene with Styrene

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ABSTRACT: The WCl_6-catalyzed copolymerization of phenylacetylene with styrene was investigated. Chromatographic and spectroscopic analyses showed that the product was a mixture of poly(phenylacetylene) and a copolymer of styrene with phenylacetylene. The effects of solvent, reducing agent, and catalyst on the copolymerization were studied. It was concluded that poly(phenylacetylene) was produced by coordination polymerization and the copolymer of styrene with phenylacetylene was formed by cationic polymerization simultaneously in a homogeneous system. Either the coordination or cationic polymerization could selectively be brought about by choosing suitable reaction conditions.

In a previous paper it was reported that WCl_6 and $MoCl_5$ worked as effective catalysts for the polymerization of phenylacetylene.[1] The effects of solvent,[1] substituent,[2] reducing agent,[3] and chain transfer agent[4] were examined in detail for this polymerization. The results obtained showed that the WCl_6-catalyzed polymerization of phenylacetylene proceeded by a coordination mechanism. The polymerization behavior resembled in several aspects that of cycloolefin polymerization by tungsten-based catalysts. On the other hand, WCl_6 has been known as a Lewis acid. For example, it can catalyze the cationic polymerization of styrene[5] and 2,4-hexadiene,[6] as most metal halides do.

Thus, WCl_6 can catalyze two totally different kinds of polymerizations, that is, coordination or cationic polymerization depending on the kind of monomer present. It seems, therefore, of great interest to study the WCl_6-catalyzed copolymerization of phenylacetylene with styrene, associated with the following questions: What is the copolymerization product and what mechanism is governing this copolymerization?

This paper deals with monomer reactivities, products, and reaction mechanisms in the WCl_6-catalyzed copolymerization of phenylacetylene with styrene.

Experimental Section

Materials. Phenylacetylene was prepared by the bromination of styrene and the subsequent dehydrobromination. Tungsten hexachloride was commercially obtained (Mitsuwa Chem. Corp., purity >99%) and used without further purification. Styrene and other reagents for polymerization were purified by the usual methods. Spectroscopic grade reagents were used for measuring UV-vis and fluorescence spectra.

Polymerization. The polymerizations of phenylacetylene and styrene were carried out in a 30-mL Erlenmeyer flask equipped with a three-way stopcock under a dry nitrogen atmosphere. Unless otherwise stated, polymerization was performed at 30 °C with a catalyst concentration of 10 mM and a total monomer concentration of 1.0 M.

Water, half as much as WCl_6, was added to the WCl_6 catalyst; the catalyst system is denoted as $WCl_6{\cdot}{}^1/_2H_2O$. This amount of water enhances polymer yield yet hardly affects polymer molecular weight or polymer structure.[1] The $WCl_6{\cdot}Ph_4Sn$ catalyst was prepared by mixing equimolar amounts of WCl_6 and tetraphenyltin in a solvent and by aging for 15 min at 30 °C before use. The $SnCl_4{\cdot}CCl_3CO_2H$ catalyst is an equimolar mixture of $SnCl_4$ and CCl_3CO_2H in a solvent.

The conversion of each monomer was monitored by measuring the amount of residual monomer by gas chromatography in aliquots taken at given intervals. Polymer samples were isolated by pouring the reaction products into a large amount of methanol. When necessary, the products were washed with a mixture of methanol and concentrated hydrochloric acid (9:1 volume ratio) to remove the catalyst residue.

Polymer Characterization. The number-average molecular weight of polymers was determined by vapor pressure osmometry using a Hitachi 117 osmometer.

Thin-layer chromatography was performed as follows: A silica gel plate (E. Merck 60 F_{254}; layer thickness 0.25 mm) was used as a stationary phase. Immediately before use, ether was used for purification and the gel layer was activated for 1 h at 120 °C. Stock solutions were prepared by use of carbon tetrachloride as a solvent (2.0 g/dL for No. 1 and 3 and 5.0 g/dL for No. 2 and 4; see Table I for the numbers). A spot of each solution, containing 40 μg or 200 μg of polymers for No. 1 and 3 and Nos. 2 and 4, respectively, was formed on the gel layer. A mixture of carbon tetrachloride and benzene (50:50 volume ratio) was used as a developer. After developing, the positions of the polymers were visualized by exposing the plate to iodine vapor.

The gel permeation chromatograms of polymers were recorded on a Toyo Soda HLC801A (column: GMH, 4 ft) using tetrahydrofuran as a solvent (0.30 w/v %).

UV-vis spectra were observed in ethylene dichloride (concentration 2.0×10^{-4} M) on a Shimadzu UV210 spectrophotometer.

Fluorescence spectra were observed in tetrahydrofuran (concentration 5.0×10^{-5} M) using a Hitachi MPF4 fluorescence spectrophotometer. Emission spectra were measured by exciting at 270 nm (excitation band width 4 nm; emission band width 10 nm). The emission intensity was well corrected against wavelength dependence.

Differential thermal analysis was performed on a Shimadzu DT-20B analyzer. All runs were made at a heating rate of 10 °C/min in a temperature range of 30–270 °C under a helium stream (30 mL/min) with α-alumina as the reference. Temperature was corrected by measuring the melting point of indium (156.4 °C).

Results and Discussion

Copolymerization of Phenylacetylene with Styrene under Various Conditions. Figure 1 shows the time–

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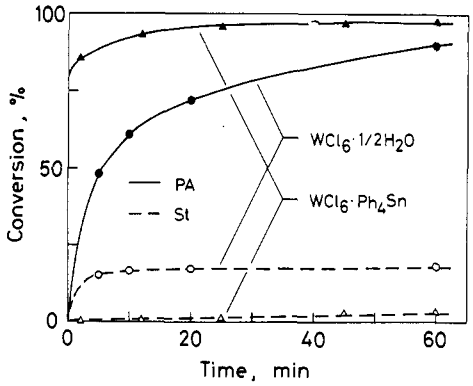


Figure 1. Copolymerizations of phenylacetylene (PA) with styrene (St) catalyzed by $WCl_6 \cdot {}^1/_2H_2O$ and $WCl_6 \cdot Ph_4Sn$ in benzene at 30 °C: $[WCl_6]_0$ = 10 mM, $[PA]_0 = [St]_0$ = 0.50 M.

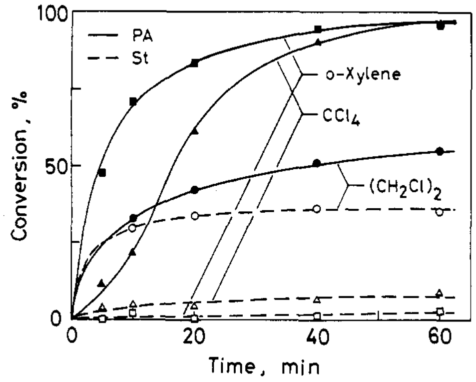


Figure 2. Solvent effect in the copolymerization of phenylacetylene with styrene at 30 °C: $[WCl_6 \cdot {}^1/_2H_2O]_0$ = 10 mM, $[PA]_0 = [St]_0$ = 0.50 M.

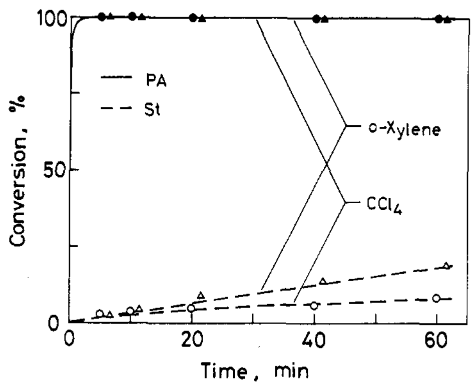


Figure 3. Eventual coordination polymerizations of phenylacetylene at 30 °C: $[WCl_6 \cdot 2Ph_4Sn]_0$ = 10 mM, $[PA]_0 = [St]_0$ = 0.50 M.

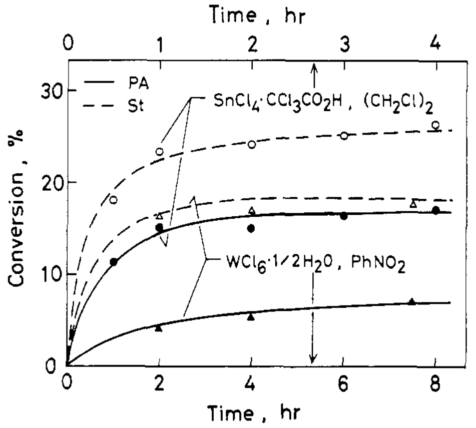


Figure 4. Cationic copolymerizations of phenylacetylene with styrene at 60 °C: $[Cat]_0$ = 20 mM, $[PA]_0 = [St]_0$ = 0.50 M.

conversion curves of each monomer in the copolymerizations of phenylacetylene with styrene catalyzed by $WCl_6 \cdot {}^1/_2H_2O$ and $WCl_6 \cdot Ph_4Sn$. In the $WCl_6 \cdot {}^1/_2H_2O$-catalyzed copolymerization, the conversion of phenylacetylene reached 90% in 60 min while that of styrene reached 18%. The conversion curve of styrene appears to level off at an early stage.

As seen in Figure 1, the $WCl_6 \cdot Ph_4Sn$ catalyst caused a large change in the reactivities of phenylacetylene and styrene; that is, the reactivity of phenylacetylene was remarkably enhanced but that of styrene was almost totally inhibited. A previous study has shown that tetraphenyltin extremely accelerates the WCl_6-catalyzed homopolymerization of phenylacetylene.[3] In the present study, it was further examined how tetraphenyltin would influence the WCl_6-catalyzed homopolymerization of styrene. As a result, WCl_6 whose concentration was as low as 1.0 mM effected a very rapid polymerization in benzene at 30 °C, $[St]_0$ = 1.0 M (100% conversion within 30 s), whereas the addition of small amounts of tetraphenyltin remarkably depressed the polymerization (e.g., 24% conversion after 5 min with 4.0 mM of tetraphenyltin). Thus, the addition of tetraphenyltin to the WCl_6 catalyst accelerated the polymerization of phenylacetylene and decelerated that of styrene both in homopolymerization and in copolymerization.

Figure 2 shows the solvent effect on the $WCl_6 \cdot {}^1/_2H_2O$-catalyzed copolymerization of phenylacetylene with styrene. Generally, *o*-xylene works as an effective retarder for the cationic polymerization of styrene.[4] In *o*-xylene as a solvent, phenylacetylene polymerized to a high conversion and styrene hardly polymerized. In carbon tetrachloride, which possesses a lower dielectric constant than benzene, the reactivity of phenylacetylene increased, while that of styrene decreased compared with those in benzene solution. On the other hand, ethylene dichloride, which is more polar than benzene, lowered the reactivity of phenylacetylene and enhanced that of styrene.

The effect of oxygen on the copolymerization of phenylacetylene with styrene was as follows: The polymerization of phenylacetylene was depressed in the presence of oxygen, whereas that of styrene was hardly affected. This is probable, provided that phenylacetylene is consumed by coordination polymerization and styrene by cationic polymerization (though a small quantity of phenylacetylene participates in cationic polymerization as will be clarified below).

On the basis of the above results, the reaction conditions were sought under which only phenylacetylene would be consumed in the copolymerization of phenylacetylene with styrene. The best results obtained to date are shown in Figure 3: When the copolymerization was performed by a mixture of WCl_6 and tetraphenyltin (1:2 mol ratio) in *o*-xylene or in carbon tetrachloride, then the polymerization of phenylacetylene was finished within 5 min whereas styrene gradually polymerized to yield only a low conversion after 1 h. If the reaction is terminated after 5 min, a product which consists almost only of phenylacetylene will be quantitatively obtained. Therefore it is possible to polymerize only phenylacetylene in the present copolymerization.

The cationic copolymerization of phenylacetylene with styrene was performed under two different reaction conditions (Figure 4). First, copolymerization was carried out with $SnCl_4 \cdot CCl_3CO_2H$ as a catalyst in ethylene dichloride. In this case styrene possessed a higher reactivity than phenylacetylene. This is consistent with the fact that

Table I
Homo- and Copolymerizations of Phenylacetylene and Styrene[a]

	run no.			
	1	2	3	4
monomer (s)	PA	St	PA-St (1.0:1.0)	PA-St (1.0:1.0)
catalyst	$WCl_6\cdot{}^1/_2H_2O$	$SnCl_4\cdot CCl_3CO_2H$	$WCl_6\cdot{}^1/_2H_2O$	$SnCl_4\cdot CCl_3CO_2H$
$[Cat]_0$, mM	10	5.0	10	20
conv., %	38	100	PA 55 St 36	PA 17 St 26
polymer mol wt	7400	5800	4400	2200
polymer color	tan	white	tan	white

[a] Polymerized in ethylene dichloride at 30 °C, $[M]_{total}$ = 1.0 M for 1.0 h (at 60 °C for 4.0 h with no. 4).

styrene is easily polymerized by $SnCl_4\cdot CCl_3CO_2H$ but phenylacetylene is hardly polymerized by this catalyst. The product of the copolymerization was white in contrast to the product from the WCl_6-catalyzed copolymerization (tan to dark red). The second cationic copolymerization was performed with $WCl_6\cdot{}^1/_2H_2O$ in nitrobenzene,[1] which is a good solvent for the cationic polymerization of styrene. As shown in Figure 4, phenylacetylene was less reactive than styrene as observed in the cationic copolymerization by $SnCl_4\cdot CCl_3CO_2H$ in ethylene dichloride. The product was white in this copolymerization as well.

Analyses of Copolymerization Products. As listed in Table I, four polymer samples were prepared for product analysis. Samples 1 and 2 are poly(phenylacetylene) prepared by $WCl_6\cdot{}^1/_2H_2O$ and polystyrene obtained by cationic polymerization, respectively. Sample 3 is the product in the $WCl_6\cdot{}^1/_2H_2O$-catalyzed copolymerization of phenylacetylene with styrene. Sample 4 is the product in the $SnCl_4\cdot CCl_3CO_2H$-catalyzed cationic copolymerization of phenylacetylene with styrene. Samples 1 and 3 were tan and samples 2 and 4 were white.

The thin-layer chromatography of the four polymer samples was studied. A mixture of carbon tetrachloride and benzene (50:50 vol ratio) was used as a developer. Poly(phenylacetylene) was hardly developed, whereas the R_f value of polystyrene was close to unity. Sample 3 (the product in the $WCl_6\cdot{}^1/_2H_2O$-catalyzed copolymerization of phenylacetylene with styrene) showed two spots. One of them was located at the same position as poly(phenylacetylene) and was colored tan just like poly(phenylacetylene). The other spot was colorless and its R_f value was almost unity. This finding demonstrates that sample 3 consists of two different polymers, one of which is poly(phenylacetylene). Sample 4 showed only one spot at a similar position to that of polystyrene. Therefore, sample 4 is composed of a single kind of polymer and does not contain poly(phenylacetylene).

The results of gel permeation chromatography confirmed the above findings on thin-layer chromatography (see Figure 5). Among the four polymer samples, only sample 3 showed a bimodal molecular weight distribution. Only the faster eluting fraction in sample 3 was colored tan. This infers that sample 3 is a mixture of poly(phenylacetylene) and the product in cationic copolymerization of phenylacetylene with styrene. The values of molecular weight, which are shown in Figure 5, were obtained by calibrating with polystyrene.

UV-vis spectra showed that sample 3 involved poly(phenylacetylene) and that sample 4 was not polystyrene but a copolymer of styrene with phenylacetylene (see Figure 6): A broad absorption ranging from the UV to the visible region was observed in the spectrum of poly(phenylacetylene).[7] As is known, polystyrene showed only a small absorption around 260 nm. The spectrum of sample 3 was very similar to that of poly(phenylacetylene), which means that sample 3 contains poly(phenylacetylene). The spectrum observed with the product obtained by cationic copolymerization (sample 4) was different from that of polystyrene. Therefore, a copolymer should have been formed by the cationic copolymerization of phenylacetylene with styrene.

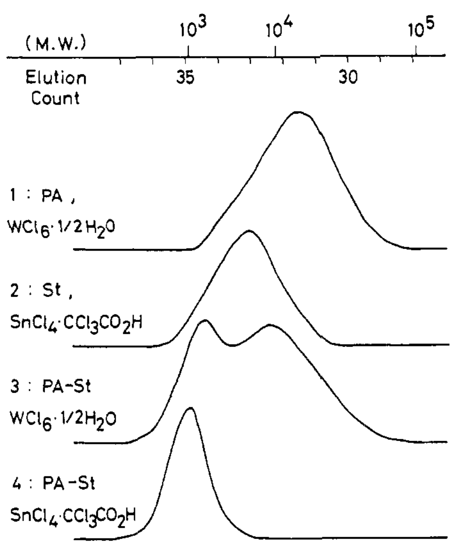


Figure 5. Gel permeation chromatograms of polymers.

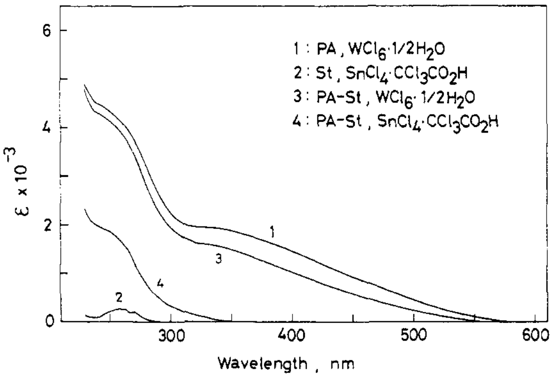


Figure 6. UV-vis spectra of polymers: in ethylene dichloride, concentration 2.0×10^{-4} M.

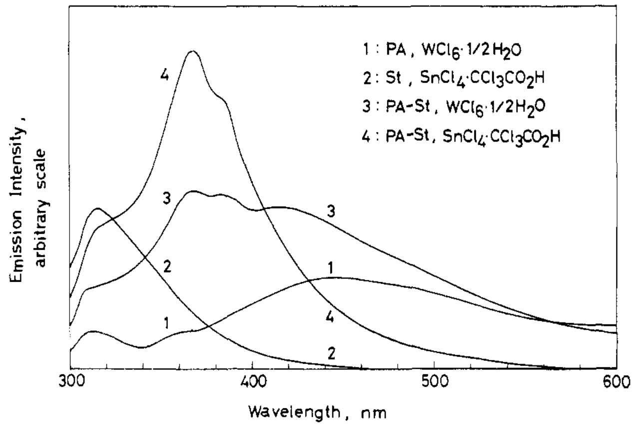
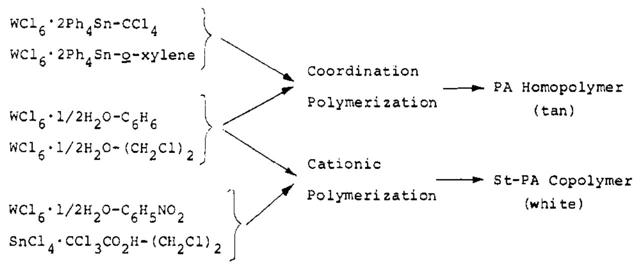


Figure 7. Fluorescence spectra of polymers: in tetrahydrofuran, concentration 5.0×10^{-5} M, excited at 270 nm.

Scheme I



The fluorescence spectra of the polymers are shown in Figure 7. The spectrum of poly(phenylacetylene) is broad, dependent on the exciting-light wavelength, and more or less irreproducible probably because of the instability of the polymer solution to the exciting light.[7] Polystyrene showed an emission centered at 320 nm. The spectrum of sample 4 was characterized by a strong emission centered at 367 nm which disappeared around 560 nm; it was clearly different from that of polystyrene. This result again indicates that sample 4 is a copolymer of styrene with phenylacetylene. Sample 3 is regarded as a mixture of poly(phenylacetylene) and the product from cationic copolymerization, based on the four fluorescence spectra.

In differential thermal analysis, samples 2 and 4 exhibited no obvious exo- or endothermic peak between 30 and 270 °C, while samples 1 and 3 showed an exothermic peak at temperatures a little higher than 200 °C. This kind of exotherm has been observed also with polyacetylene and has been accounted for by cis-to-trans isomerization occurring in the main chain.[8] It should be noted that sample 4, which also contains the phenylacetylene unit, shows no such exotherm; this is expected if an isolated carbon–carbon double bond will not isomerize in this temperature region. Consequently, the exotherm in sample 3 indicates the presence of poly(phenylacetylene) in the product.

Copolymerization Mechanism. In the WCl_6-catalyzed copolymerization, the reactivities of phenylacetylene and styrene depended very much on the reaction conditions. The polymerization of phenylacetylene was promoted in nonpolar solvents and by the addition of tetraphenyltin as a reducing agent and was depressed in the presence of oxygen. Polar solvents favored the polymerization of styrene.

Thin-layer and gel permeation chromatographies showed that the product from $WCl_6 \cdot {}^1/_2H_2O$-catalyzed copolymerization is a mixture of two kinds of polymers. Thin-layer chromatography, UV–vis spectroscopy, and differential thermal analysis showed that one component of the mixture was poly(phenylacetylene). It is not clear, however, whether a small amount of styrene unit was included or not. According to the UV–vis and fluorescence spectra, the other component was shown to be a copolymer of styrene with phenylacetylene obtained by the cationic mechanism.

On the basis of the above results and considerations, the present copolymerization can be depicted as in Scheme I. When the copolymerization of phenylacetylene with styrene is carried out by $WCl_6 \cdot {}^1/_2H_2O$ in benzene or in ethylene dichloride, coordination and cationic polymerizations proceed simultaneously. The former polymerization produces poly(phenylacetylene) and the latter gives a copolymer of styrene with phenylacetylene. This copolymerization is one of the rare cases where two kinds of polymerizations are simultaneously induced by a single catalyst, which seems very interesting. Further, the $WCl_6 \cdot 2Ph_4Sn$-catalyzed polymerization in carbon tetrachloride or in *o*-xylene brings about coordination polymerization selectively. On the other hand, the $WCl_6 \cdot {}^1/_2H_2O$–nitrobenzene and $SnCl_4 \cdot CCl_3CO_2H$–ethylene dichloride systems give rise only to cationic polymerization.

In conclusion, the present study revealed that coordination and cationic polymerizations proceed simultaneously in the WCl_6-catalyzed copolymerization of phenylacetylene with styrene and that the former polymerization gives poly(phenylacetylene) and the latter a copolymer of styrene with phenylacetylene.

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