# Remarkable Cocatalytic Effect of Organometallics and Rate Control by Triphenylphosphine in the Rh-Catalyzed Polymerization of Phenylacetylene

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## Introduction

Group 5 and 6 transition metal catalysts and Rh catalysts are known to be effective for the polymerization of substituted acetylenes.[1] While group 5 and 6 transition metal catalysts polymerize various mono- and disubstituted acetylenes, Rh catalysts polymerize only monosubstituted ones, especially phenylacetylenes (PAs). There are two major features with the Rh catalysts: First, they selectively produce stereoregular poly(PAs) with cis−transoid structure,[2,3] which gives rise to selective screw-sense, helical conformations on either introduction of chiral ring substituents[4] or complexation with optically active compounds.[5] Second, the polymerization readily occurs in protic solvents such as amines,[6] alcohols,[3,7] and even water.[8]

While the polymerization of PA is very sluggish and hardly proceeds with $[(nbd)RhCl]_2$ alone in aromatic solvents, the polymerization is appreciably accelerated by addition of catalytic amounts of NaOH[3] and $Et_3N$.[6] The polymerization of PA by $[(nbd)RhCl]_2/Et_3N$ is so fast that the polymerization behavior has not been studied in detail. Cationic complexes[9,10] and zwitterionic complexes[11,12] of Rh also work as catalysts for the polymerization of PA. Further, Noyori et al. have reported that PA polymerizes in a living fashion with Rh catalysts, $Rh(C{\equiv}CC_6H_5)(nbd)(PPh_3)_2$[13] and $[(nbd)Rh(OMe)]_2-Ph_3P$[14] in the presence of 4-(dimethylamino)pyridine.

In the present study, we examined the effect of various organometallics (RLi, $R_2Zn$, $R_3Al$, or $R_3B$, etc.) as cocatalysts in the polymerization of PA by $[(nbd)RhCl]_2$, aiming at the developments of highly active catalysts and the elucidation of polymerization mechanism. Consequently, suitable organometallic cocatalysts induced virtually instantaneous polymerization to give polymers with high molecular weight in high yields, while no polymerization occurred without the cocatalysts. Further, it was found that the addition of $Ph_3P$ retarded the polymerization to enable the control of the polymerization rate.

## Experimental Section

PA was distilled twice from $CaH_2$ at reduced pressure. Toluene was washed by the standard method, dried, and distilled twice from $CaH_2$. $[(nbd)RhCl]_2$ (Aldrich) and organometallic cocatalysts (Aldrich or Kanto Chemicals) were used as purchased.

Polymerizations were carried out under dry nitrogen in a Schlenk tube equipped with a three-way stopcock. Unless otherwise specified, the reaction conditions were as follows: in toluene, 30 °C, 1 h; $[M]_0 = 0.50$ M, $[[(nbd)RhCl]_2] = 1.0$ mM, [cocatalyst] = 2.0 mM. The monomer conversions were determined by GC using bromobenzene as an internal standard. Polymers were isolated by precipitation in a large amount of methanol, and polymer yields were determined by gravimetry. The molecular weights of polymers were evaluated by GPC: eluent THF, columns Shodex KF-806L × 2, polystyrene calibration. The NMR spectra were measured on a JEOL GSX-270 spectrometer.

**Table 1. Effect of Cocatalysts on the Polymerization of Phenylacetylene by $[(nbd)RhCl]_2$ Catalyst**[a]

| cocatalyst | monomer conv, % | polymer yield, % | polymer $M_n/10^3$ | polymer $M_w/M_n$ |
|---|---|---|---|---|
| none | 0 | 0 | | |
| $Et_3N$ | 100 | 79 | 118 | 2.68 |
| *n*-BuLi | 100 | 75 | 336 | 2.31 |
| MeLi | 100 | 85 | 135 | 1.95 |
| *t*-BuLi | 100 | 90 | 257 | 2.34 |
| PhLi | 96 | 87 | 482 | 2.06 |
| *n*-BuMgBr | 0 | 0 | | |
| $Ch_2{=}CHMgBr$ | 0 | 0 | | |
| $Et_2Zn$ | 89 | 70 | 159 | 3.30 |
| $Et_3B$ | 80 | 71 | 237 | 2.71 |
| $Et_3Al$ | 95 | 75 | 296 | 2.51 |
| $Et_2AlCl$ | 7 | 0 | | |
| $EtAlCl_2$ | 19 | 0 | | |
| *n*-$Bu_4Sn$ | 8 | 3 | | |

[a] In toluene, 30 °C, 1 h; $[[(nbd)RhCl]_2] = 1.0$ mM, [Cocat] = 2.0 mM, $[M]_0 = 0.50$ M.

## Results and Discussion

**Effects of Various Organometallic Cocatalysts.** Table 1 shows the results of the polymerization of PA by $[(nbd)RhCl]_2$ in conjunction with various organometallic cocatalysts. When hexane solution of a cocatalyst was added to $[(nbd)RhCl]_2$ in toluene, the solution turned red from yellow in the polymerization systems that showed remarkable acceleration. This suggests that the Rh complex has been alkylated. When a toluene solution of PA was added to the catalyst solution composed of $[(nbd)RhCl]_2$ and *n*-BuLi, polymerization proceeded virtually instantaneously to give a methanol-insoluble yellow polymer in high yield up to 75%. The $M_n$ of the formed polymer was larger than the value with $Et_3N$ as cocatalyst (*n*-BuLi, 336 000; $Et_3N$, 118 000). The $^1H$ NMR spectrum of the polymer showed a sharp peak due to the vinyl protons of the main chain with cis−transoid structure (in $C_6D_6$, $\delta$ 6.2 ppm, singlet). The cis content was virtually 100% according to the ratio of the vinyl to aromatic protons.

Other organolithiums were also effective and produced polymers with large $M_n$ values (130 000−480 000). Further, $Et_2Zn$, $Et_3Al$, and $Et_3B$ also induced fast polymerization of PA to give polymers in relatively high yields. On the other hand, in the presence of organoaluminum chlorides, Grignard reagents, and *n*-$Bu_4Sn$ as cocatalysts, polymerization did not occur at all or hardly occurred. The polydispersity ratios ($M_w/M_n$) were all about 2−3. These results lead to a conclusion that strong alkylating agents (*n*-BuLi, $Et_2Zn$, $Et_3Al$, $Et_3B$, etc.) are useful as cocatalysts, whereas halogen-containing organometallics (*n*-BuMgBr, $Et_2AlCl$, etc.) and weak alkylating agents (e.g., *n*-$Bu_4Sn$) are ineffective.

The effect of cocatalyst concentration was examined using *n*-BuLi, $Et_2Zn$, and $Et_3Al$ as cocatalysts (Figure 1). Even though their concentration was varied in a wide range of [Cocat]/[Rh] = 0.25−4, the monomer was consumed quantitatively after 1 h. With increasing

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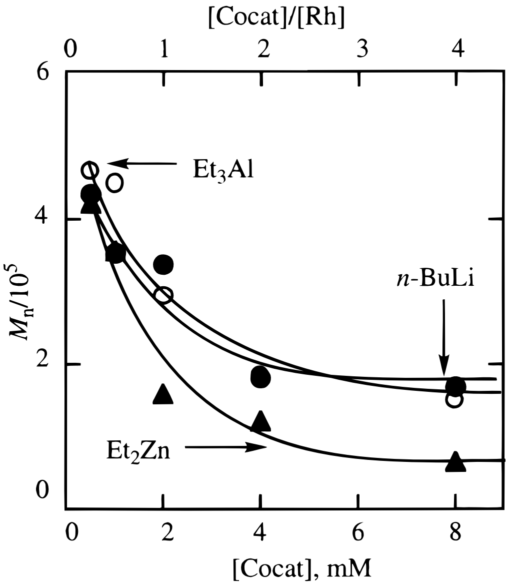
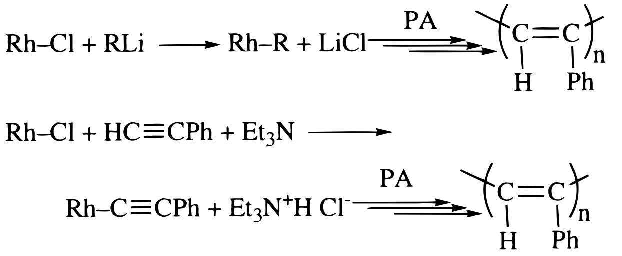


**Figure 1.** Effect of cocatalyst concentration on the polymerization of phenylacetylene (in toluene, 30 °C, 1 h; $[[(nbd)RhCl]_2]$ = 1.0 mM, $[M]_0$ = 0.50 M).

**Scheme 1**



cocatalyst concentration, the molecular weight of the formed polymer decreased and then leveled off when 2 equiv or more of cocatalysts was employed. This suggests that the concentration of propagating species becomes fairly high in the presence of catalytic amounts of these organometallic cocatalysts. No large differences were observed in the molecular weight distribution of polymer even though the cocatalyst concentration was changed ($M_w/M_n$ ca. 2–3 in all the cases).

The formation of initiating species in the presence of an organolithium cocatalyst can be depicted as in Scheme 1; i.e., the Rh complex and an organolithium react to form a Rh-alkyl species, to which PA monomers insert successively. On the other hand, $Et_3N$ seems to work as a scavenger of HCl in the reaction of the Rh complex with PA.

**Effect of Triphenylphosphine.** As shown above, the polymerization in the presence of suitable organometallic cocatalysts is so fast that it is rather difficult to investigate its kinetics. It is very probable that triphenylphosphine ($Ph_3P$), a typical soft base, coordinates to the Rh propagating species. Thus, the effect of $Ph_3P$ was examined. When $Ph_3P$ was added to $[(nbd)RhCl]_2$ in toluene, the color of the solution remained yellow. When hexane solution of $n$-BuLi was further added after 15 min aging, the solution changed from yellow to red.

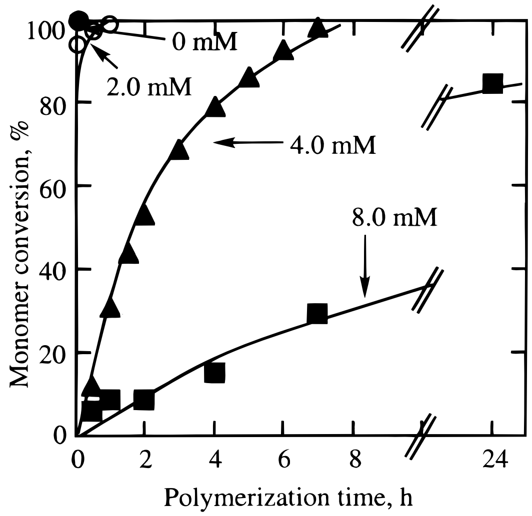


**Figure 2.** Effect of $Ph_3P$ concentration on the polymerization of phenylacetylene (in toluene, 30 °C; $[[(nbd)RhCl]_2]$ = 1.0 mM, [$n$-BuLi] = 2.0 mM, $[M]_0$ = 0.50 M).

**Scheme 2**

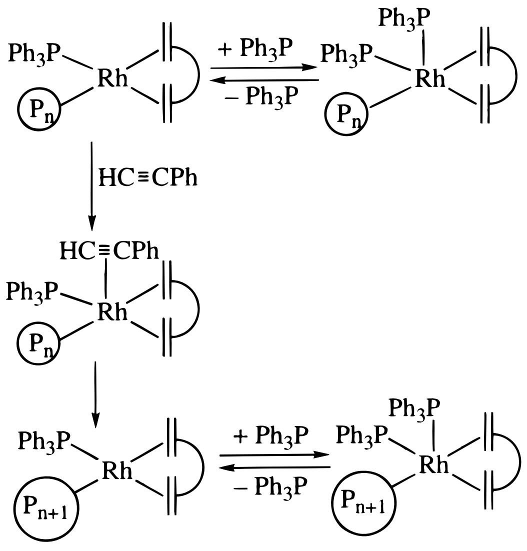


Figure 2 shows time courses of the polymerizations in the absence and presence of $Ph_3P$. The polymerization without $Ph_3P$ proceeded virtually instantaneously. In contrast, with increasing $Ph_3P$ concentration, the polymerization was retarded progressively; i.e., the polymerization was finished after 1 and 8 h at $[Ph_3P]$ = 2 and 4 mM, respectively, while it was not completed even after 24 h at $[Ph_3P]$ = 8 mM. The molecular weight of the formed polymer decreased with increasing $Ph_3P$ concentration; $M_n = 34 \times 10^4$, $28 \times 10^4$, $22 \times 10^4$, and $8 \times 10^4$ at $[Ph_3P]$ = 0, 2.0, 4.0, and 8.0 mM, respectively (at 100% conversion except for $[Ph_3P]$ = 8.0 mM (at 85%)). The molecular weight distributions changed from 2.3 without $Ph_3P$ to 1.5 by addition of $Ph_3P$ (8.0 mM).

The effect of $Ph_3P$ is explained as follows: As shown in Scheme 2, the propagating species in the presence of $Ph_3P$ is assumed to be a tetracoordinate 16-electron Rh complex. Whereas the coordination of monomer leads to propagation, the competitive coordination of $Ph_3P$ generates a stable dormant species, which results in the retardation of polymerization. The decrease of polymer molecular weight by addition of $Ph_3P$ suggests the formation of a fairly stable, in other words, long-lived propagating species in a large quantity. In contrast, the propagating species in the absence of $Ph_3P$ should be quite different and may be a dinuclear complex.

## Conclusions

Use of various organometallic cocatalysts in conjunction with $[(nbd)RhCl]_2$ induced virtually instantaneous polymerization of PA in toluene to give yellow polymers with high molecular weight in high yields. Alkyl compounds of Li, Zn, B, and Al were effective, whereas Grignard reagents and organoaluminum chlorides, which contain halogen atoms, were not. It seems that the Rh complex and organometallic cocatalysts react to form Rh−alkyl species, which initiate the polymerization. The molecular weight of polymer decreased with increasing cocatalyst concentration, suggesting the increase in the concentration of the active species. Addition of $Ph_3P$ as the third component decelerated the polymerization and enabled the control of its rate.

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