Articles

Living Polymerization of Phenylacetylene by Isolated Rhodium Complexes, Rh[C(C_6H_5)═C(C_6H_5)$_2$](nbd)(4-XC_6H_4)$_3$P (X = F, Cl)

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ABSTRACT: Novel Rh complexes, Rh[C(C_6H_5)═C(C_6H_5)$_2$](nbd)(4-XC_6H_4)$_3$P (**1a**: X = F; **1b**: X = Cl), were isolated from mixtures of [(nbd)RhCl]$_2$, (C_6H_5)$_2$C═C(C_6H_5)Li, and (4-XC_6H_4)$_3$P, and the polymerization of phenylacetylene thereby was investigated. The polymerization by **1a** in toluene at 30 °C in the presence of (4-FC_6H_4)$_3$P (5 equiv to Rh or more) proceeded with virtually quantitative initiation efficiency to give polymer with low polydispersity (M_w/M_n ∼1.05). The living character of this polymerization was confirmed by means of both the time profile of polymerization and the multistage polymerization. Toluene, benzene, and THF were particularly useful as polymerization solvents; the polydispersity remained 1.05−1.06, while the larger the dielectric constant of the solvent, the slower the polymerization. This polymerization smoothly proceeded in the temperature range 15−60 °C.

Introduction

It has been known that substituted acetylenes such as phenylacetylenes[1] and propiolic esters[2] polymerize with Rh catalysts. The rhodium catalysts produce polymers with stereoregular main chains, and the polymers have been attracting much attention for not only academic but practical values.[3] Further, Noyori et al. have reported that Rh[C≡C(C_6H_5)](nbd)(P(C_6H_5)$_3$)$_2$/4-(dimethylamino)pyridine[4] and [(nbd)Rh(OMe)]$_2$/(C_6H_5)$_3$P/4-(dimethylamino)pyridine[5] systems (nbd = bicyclo-[2,2,1]hepta-2,5-diene) induce the living polymerization of phenylacetylene to provide polymer with low polydispersity (M_w/M_n = 1.11). However, these systems require the addition of 4-(dimethylamino)pyridine to prevent the formation of a less active dinuclear rhodium complex.[6] The polymerization of phenylacetylene by Rh catalyst is inferred to proceed via an insertion mechanism, which means that the propagating species is a vinylrhodium. We assumed that appropriate vinylrhodium species are able to initiate the living polymerization of phenylacetylene and examined various systems that generate vinylrhodium species to eventually develop a ternary [(nbd)RhCl]$_2$/(C_6H_5)$_2$C═C(C_6H_5)Li/(C_6H_5)$_3$P system.[7] This catalyst system initiates the polymerization of phenylacetylene quantitatively, and the resulting polymer possesses exclusively a triphenylvinyl group at the initiating chain end.

In the present study, we isolated novel Rh complexes Rh[C(C_6H_5)═C(C_6H_5)$_2$](nbd)(4-XC_6H_4)$_3$P (**1**) (**a**: X = F; **b**: X = Cl) from a reaction mixture of [(nbd)RhCl]$_2$, (C_6H_5)$_2$C═C(C_6H_5)Li, and (4-XC_6H_4)$_3$P in benzene and investigated the polymerization of phenylacetylene by these complexes. They induced living polymerization in the presence of (4-XC_6H_4)$_3$P. This polymerization showed the following characteristics: (1) the polymer formed with **1a** possessed a lower polydispersity than that with the [(nbd)RhCl]$_2$/(C_6H_5)$_2$C═C(C_6H_5)Li/(C_6H_5)$_3$P system, (2) the polymerization proceeded with virtually quantitative initiation efficiency (∼100%), and (3) the polymerization by **1a** was tolerant to water.

Experimental Section

Materials. Phenylacetylene (Aldrich, 98%) was distilled twice under reduced pressure. The polymerization solvents were purified by the standard methods. [(nbd)RhCl]$_2$ (Aldrich), (4-FC_6H_4)$_3$P (Aldrich, 99%), (4-ClC_6H_4)$_3$P (Aldrich, 97%), and (C_6H_5)$_3$P (Wako, 97%) were used without further purification.

Rhodium Complexes 1. A (C_6H_5)$_2$C═C(C_6H_5)Li (50 mM, 20.0 mL) solution was prepared by the reaction of Li (13.9 mg, 2.0 mmol) with (C_6H_5)$_2$C═C(C_6H_5)Br (335 mg, 1.0 mmol) in diethyl ether (20 mL) at low temperature (0−10 °C) under dry nitrogen.[7] To a solution of [(nbd)RhCl]$_2$ (69.2 mg, 0.15 mmol) and either (4-FC_6H_4)$_3$P (95.0 mg, 0.30 mmol) or (4-ClC_6H_4)$_3$P (110 mg, 0.30 mmol) in benzene (12 mL) was added the solution of (C_6H_5)$_2$C═C(C_6H_5)Li (0.050 M, 6.0 mL, 0.30 mmol) at room temperature. After stirring for 15 min, the reaction mixture was subjected to column chromatography (neutral activated alumina 90 (activity I), Merck). The orange-colored fraction was collected, from which the Rh complex Rh-[C(C_6H_5)═C(C_6H_5)$_2$](nbd)(4-FC_6H_4)$_3$P (**1a**) or Rh[C(C_6H_5)═C(C_6H_5)$_2$](nbd)(4-ClC_6H_4)$_3$P (**1b**) was isolated by recrystallization from *n*-hexane (yield: **1a**, 65%; **1b**, 32%). **1a**: Anal. Calcd for $C_{45}H_{35}F_3PRh$: C, 70.50; H, 4.60. Found: C, 70.23; H, 4.87. ^{1}H NMR ($CDCl_3$): δ 7.80−6.40 (m, 27H), 3.90−3.10 (m, 6H) and 1.70−1.30 (m, 2H). IR (KBr): 1590, 1495, 1392, 1304, 1233, 1159, 1090, 1015, 830, 700, 527, and 463 cm^{-1}. **1b**: Anal. Calcd for $C_{45}H_{35}Cl_3PRh$: C, 66.24; H, 4.32. Found: C, 66.01; H, 4.60. ^{1}H NMR ($CDCl_3$): δ 7.80−6.40 (m, 27H), 3.90−3.10 (m, 6H), and 1.70−1.30 (m, 2H). IR (KBr): 1480, 1385, 1304, 1176, 1080, 1012, 819, 698, 497, and 428 cm^{-1}.

X-ray Structure of 1b. X-ray-quality crystals (0.6 × 0.3 × 0.1 mm) of **1b** were obtained by slow diffusion of a benzene solution of the complex into methanol. Cell parameters were obtained from a least-squares refinement using the setting angles of 25 reflections in the range of 29.73° < 2θ < 30.02°.

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Data were collected ($6° \leq 2\theta \leq 55°$) on a Rigaku AFC7R diffractometer (296 K) with graphite-monochromated Mo Kα radiation ($\lambda = 0.710\ 69$ Å) using the ω scan technique. A total of 8785 reflections were collected, of which 8510 were unique. The structure was solved by the direct method[8] and expanded using Fourier techniques. Refinement was done by full-matrix least-squares procedures. Crystal and refinement data: $C_{45}H_{35}PCl_3Rh$, fw = 816.01, monoclinic, $P2_1/n$, $a = 11.032(3)$ Å, $b = 19.531(3)$ Å, $c = 17.253(4)$ Å, $\beta = 95.87(2)°$, $V = 3698(1)$ Å^3, $Z = 4$, $d_{calc} = 1.466$ g/cm^3, with 486 parameters refined based on 5755 data with $I > 3\sigma(I)$, $R = 0.037$ and $R_w = 0.037$, GOF = 1.06.

Polymerization. Polymerizations were initiated by adding a monomer solution to a solution of **1a** and phosphine under dry nitrogen and quenched with a small quantity of acetic acid. The standard polymerization conditions were as follows: the **1a**/(4-$FC_6H_4)_3$P catalyst system, in toluene, 30 °C, 1 h, $[M]_0 = 0.50$ M, [**1a**] = 2.0 mM, [(4-$FC_6H_4)_3$P] = 10.0 mM. Polymers formed were precipitated in a large amount of methanol, filtered, and dried to constant weight.

Measurements. The molecular weights and polydispersity indices (M_w/M_n) of polymers were measured by GPC with a Jasco PU-980/RI-930 chromatograph; eluent THF, columns KF-805 (Shodex) ×3, calibrated with polystyrene standards. ^{1}H NMR spectra were observed on a JEOL EX-400 spectrometer at room temperature. IR spectra were recorded with a Shimadzu FTIR-8100 spectrophotometer.

Results and Discussion

Synthesis and Identification of Rh Complexes 1. We attempted the isolation of a Rh complex from the ternary [(nbd)RhCl]$_2$/($C_6H_5)_2$C=C(C_6H_5)Li/($C_6H_5)_3$P system that was employed in the polymerization of phenylacetylene in a previous study.[7] The reaction mixture was subjected to column chromatography to give an orange powder, which was dissolved in hexane and cooled to provide a vitrified solid. This solid occluded *n*-hexane, and the isolation of a complex with a definite composition was unsuccessful. Because the ternary [(nbd)RhCl]$_2$/($C_6H_5)_2$C=C(C_6H_5)Li/(4-R$C_6H_4)_3$P (R = F, Cl, CH_3, CH_3O) systems also induce the living polymerization of phenylacetylene,[9] the isolation of Rh complexes was examined by using triphenylphosphine derivatives. When (4-$FC_6H_4)_3$P and (4-$ClC_6H_4)_3$P were utilized, the complexes Rh[C(C_6H_5)=C($C_6H_5)_2$](nbd)(4-X$C_6H_4)_3$P (**1**) (**1a**: X = F; **1b**: X = Cl) were isolated. Although the phosphines were employed in 2 equiv to Rh, the complexes contained only one phosphine molecule according to elemental analysis. Complex **1b** provided X-ray quality single crystals, and hence its structure was determined by X-ray single-crystal structure analysis (Figure 1). The Rh atom assumes a distorted square-planar coordination structure. The α carbon atom of the vinyl group is located on the plane formed by the Rh atom and the centers of the two double bonds of norbornadiene. However, the phosphorus atom lies aside the plane. On the other hand, the X-ray single-crystal structure analysis of **1a** was impossible because X-ray quality crystals could not be obtained. Nevertheless, **1a** is inferred to have a structure close to that of **1b** because the spectroscopic data of these complexes are virtually identical. Kishimoto et al. revealed that Rh[C≡C(C_6H_5)](nbd)(P($C_6H_5)_3)_2$, an 18-electoron ethynylrhodium complex, has a trigonal-bipyramidal structure.[4] It is assumed that, in **1**, a second phosphine ligand cannot coordinate to the Rh atom because of the presence of the bulky triphenylvinyl group.

Polymerization of Phenylacetylene by 1. Polymerization of phenylacetylene by **1a** alone produced poly(phenylacetylene) having a somewhat broad molecular weight distribution (MWD) ($M_w/M_n \sim 1.50$). On the basis of this finding, we assumed that **1** may be more or less unstable in solution and examined the effect of addition of (4-$FC_6H_4)_3$P on the polymerization (Figure 2). Interestingly, the polydispersity ratio of the formed polymer decreased with increasing amount of the phosphine to become as small as ca. 1.05 at [P]/[Rh] = 5. The initiation efficiencies of all the polymerizations in the presence of the phosphine were nearly 100%. The added phosphine decelerated the polymerization; e.g., the polymerization was finished within 30 min at [P]/[Rh] = 5, while it took about 1 h at [P]/[Rh] = 20. In the following experiments, 5 equiv of phosphine was usually employed. Like the case of **1a**, the Rh complex **1b** polymerized phenylacetylene with a quantitative initiation efficiency to give polymer having a low polydispersity ($M_w/M_n \sim 1.06$) in the presence of (4-$ClC_6H_4)_3$P ([P]/[Rh] = 5). On the other hand, the initiation efficiency was lower (~73%), and the MWD was broader ($M_w/M_n \sim 1.15$) in the polymerization catalyzed by the [(nbd)-RhCl]$_2$/($C_6H_5)_2$C=C(C_6H_5)Li/($C_6H_5)_3$P ternary system ([Rh]:[Li]:[P] = 1:5:5) under practically the same conditions. These results show that the isolated Rh complex

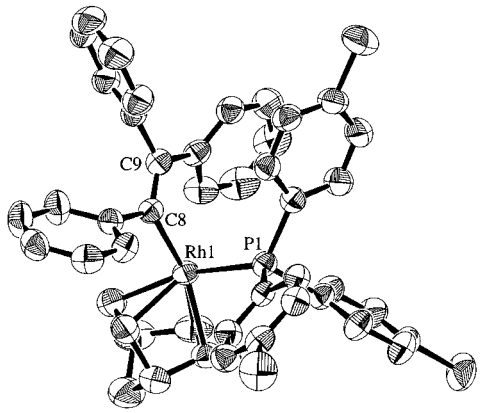

Figure 1. ORTEP drawing of the molecular structure of Rh[C(C_6H_5)=C($C_6H_5)_2$](nbd)(4-$ClC_6H_4)_3$P (**1b**). The hydrogen atoms are omitted for simplicity. Selected bond lengths (Å): Rh(1)−C(8), 2.058(4); Rh(1)−P(1), 2.318(1); C(8)−C(9), 1.332(5). Selected bond angles (deg): Rh(1)−C(8)−C(9), 120.0(3); P(1)−Rh(1)−C(8), 93.8(1).

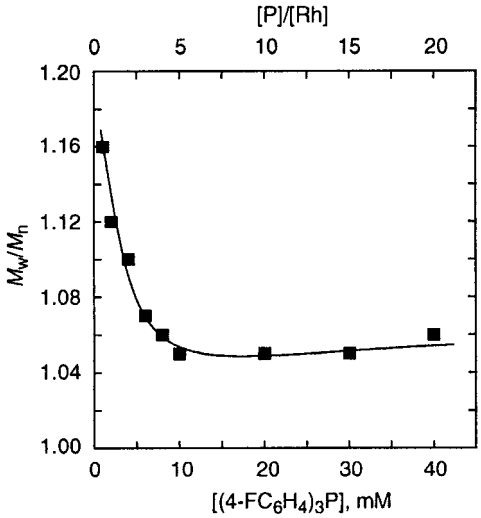

Figure 2. Dependence of M_w/M_n on the (4-$FC_6H_4)_3$P concentration in the polymerization of phenylacetylene by **1a** (in toluene, 30 °C, 1 h; $[M]_0 = 0.50$ M, [**1a**] = 2.0 mM, all the conversions ~100%, $M_n = 2.4 \times 10^4$−2.6×10^4).

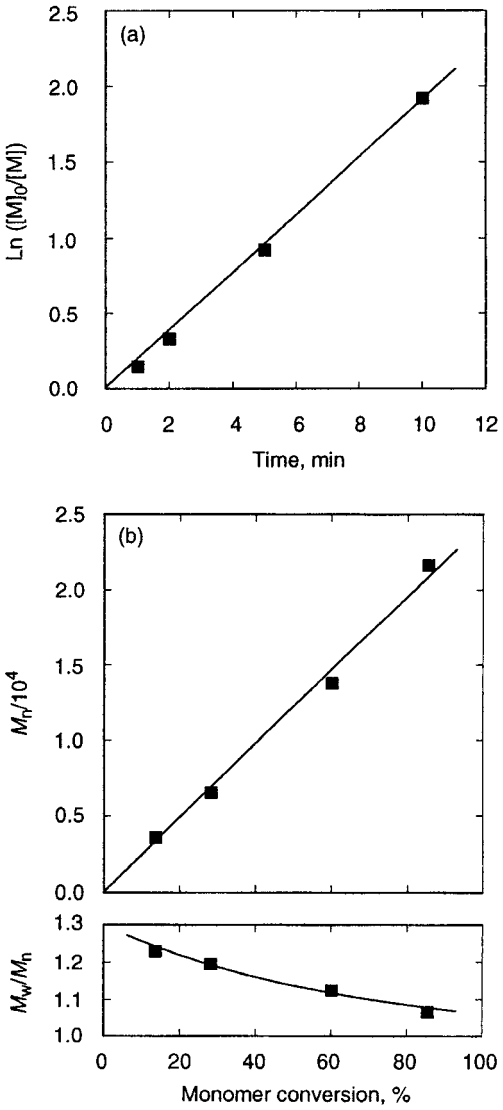

Figure 3. (a) First-order plot and (b) monomer conversion−M_n, $-M_w/M_n$ plots in the polymerization of phenylacetylene by **1a** (in toluene, 30 °C; $[M]_0 = 0.50$ M, [**1a**] = 2.0 mM, [(4-$FC_6H_4)_3P$] = 10.0 mM).

1 is more efficient than the ternary catalyst system to achieve living polymerization.

Proof of Living Character of the Polymerization by 1a. The time profile of the polymerization of phenylacetylene by **1a** was examined (Figure 3). The first-order plot with respect to the monomer gave a good linear relationship, which supports the idea that the concentration of the propagating species does not change during the polymerization and the propagation reaction is a bimolecular reaction of the propagating species and the monomer. The M_n value of the polymer increased in proportion to the monomer conversion, indicating that neither chain-transfer reaction nor chain termination occurred. The initiation efficiency calculated from the monomer conversion and the M_n of the polymer was 100%.

Multistage polymerization was carried out under conditions similar to those for the polymerization in Figure 3, by supplying the monomer feed three times at intervals of 1 h (Figure 4). The monomer was completely consumed within 1 h in each stage, and the M_n value of the polymer increased in direct proportion to the monomer consumption, while the polydispersity

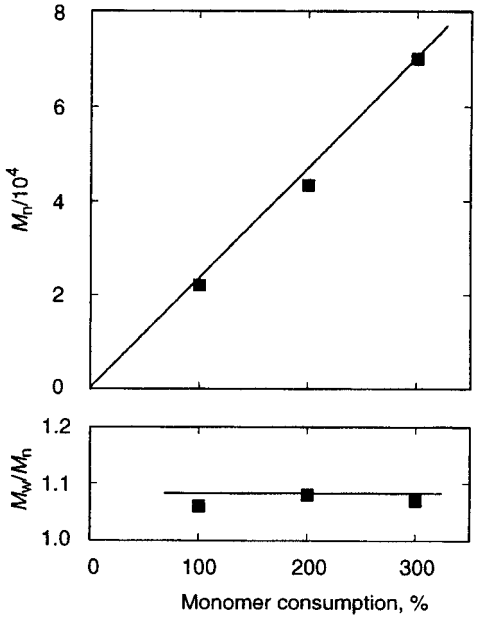

Figure 4. Multistage polymerization of phenylacetylene by **1a** (in toluene, 30 °C, 1 h each; $[M]_0 = [M]_{added} = 0.50$ M, [**1a**] = 2.0 mM, [(4-$FC_6H_4)_3P$] = 10.0 mM).

Table 1. Effect of Various Solvents on the Polymerization of Phenylacetylene by 1a[a]

	polymer		
solvent	M_n	M_w/M_n	[P*]/[Rh], %[b]
toluene	25 000	1.05	100
benzene	25 000	1.06	100
o-dichlorobenzene	26 000	1.10	97
anisole	28 000	1.06	92
THF	24 000	1.07	100

[a] Polymerized at 30 °C for 1 h; $[M]_0 = 0.50$ M, [**1a**] = 2.0 mM, [(4-$FC_6H_4)_3P$] = 10.0 mM; all the conversions 100%. [b] Initiation efficiency.

ratio remained as small as ca. 1.1. These results manifest that this polymerization is a living polymerization.

Effect of Polymerization Conditions. The polymerization by **1a** was carried out in several solvents. Not only toluene but also benzene, anisole, *o*-dichlorobenzene, and tetrahydrofuran were useful. The polymerizations proceeded with high initiation efficiencies (∼100%) to give polymers with low polydispersity ($M_w/M_n < 1.10$) in all these solvents (Table 1). The higher the dielectric constant of the solvents employed, the slower the polymerization (Figure 5). This seems to be a general tendency in coordination polymerizations. On the other hand, when *n*-hexane, acetone, ethanol, diethyl ether, and triethylamine were employed as polymerization solvents, the formed polymers precipitated during polymerization and showed broad MWDs. When tetrahydrofuran containing 1.0 wt % of water was employed as polymerization solvent, the polymerization proceeded with high initiation efficiency (∼100%) to give polymer with low polydispersity ($M_w/M_n = 1.06$) under the same conditions as in Table 1. This tolerance of the polymerization by **1a** for water is interesting because the ternary catalyst $[(nbd)RhCl]_2/(C_6H_5)_2C{=}C(C_6H_5)Li/(C_6H_5)_3P$ is unavailable in the presence of water due to the hydrolysis of the vinyllithium.

The effect of temperature was examined in the range 0−60 °C (Table 2). In the range 30−60 °C, the polymerization was accomplished within 1 h and featured

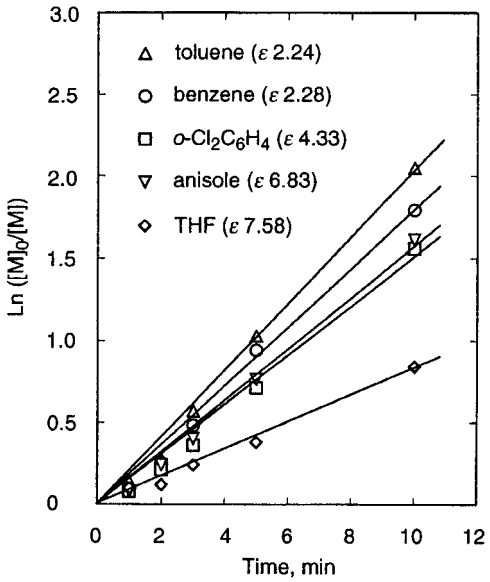

Figure 5. First-order plots in the polymerization of phenylacetylene by **1a** in several solvents (30 °C; $[M]_0 = 0.50$ M, [**1a**] = 2.0 mM, $[(4\text{-}FC_6H_4)_3P] = 10.0$ mM).

Table 2. Effect of Temperature on the Polymerization of Phenylacetylene by 1a[a]

		polymer		
temp,°C	conv, %	M_n	M_w/M_n	[P*]/[Rh], %[b]
0	8	2 000	1.24	
15	79	20 000	1.10	100
30	100	25 000	1.05	100
45	100	25 000	1.06	100
60	100	24 000	1.05	100

[a] Polymerized in toluene for 1 h; $[M]_0 = 0.50$ M, [**1a**] = 2.0 mM, $[(4\text{-}FC_6H_4)_3P] = 10.0$ mM. [b] Initiation efficiency.

virtually quantitative initiation efficiencies and narrow MWD of the resulting polymer. On the other hand, the polymerization was not finished within 1 h at 15 °C, although the MWD of the polymer was still narrow. The polymerization was sluggish at 0 °C and resulted in a broader MWD.

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Supporting Information Available: Tables giving atomic coordinates, anisotropic displacement parameters, and bond lengths and angles for **1b**. This material is available free of charge via the Internet at http://pubs.acs.org.

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