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Living Polymerization of Phenylacetylene with Tetrafluorobenzobarrelene Ligand-Containing Rhodium Catalyst Systems Featuring the Synthesis of High Molecular Weight Polymer

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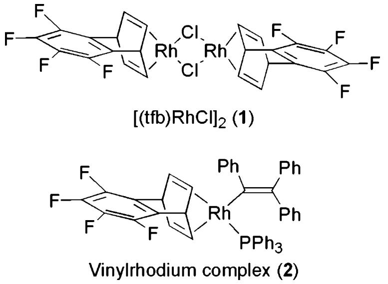
ABSTRACT: Highly active Rh-based living polymerization catalysts were developed, which enabled the synthesis of poly(phenylacetylene) with high molecular weight and narrow molecular weight distributions (e.g., M_n = 195 000, M_w/M_n = 1.06). For instance, a Rh-based ternary catalyst system composed of $[(tfb)RhCl]_2$ (**1**) (tfb, tetrafluorobenzobarrelene), $Ph_2C{=}C(Ph)Li$, and Ph_3P (1:5:10) mediated the living polymerization of phenylacetylene (PA) with virtually 100% initiation efficiency. Furthermore, a well-defined vinylrhodium complex $[(tfb)Rh\{-C(Ph){=}CPh_2\}(Ph_3P)]$ (**2**) also polymerized PA in a living fashion with quantitative initiation efficiency in the presence of at least 5 equiv of Ph_3P to Rh. The livingness of these polymerizations was confirmed by multistage polymerization, first-order linear plot, and effect of initial monomer concentration on molecular weight and MWD, and their initiation efficiencies were practically quantitative. A salient feature of catalyst **2** is its high activity even at a very low concentration ($[M]_0/[Rh]$ = 4000, [Rh] = 0.125 mM) to quantitatively afford a high molecular weight polymer (M_n = 401 000) having very narrow MWD (M_w/M_n = 1.12). The formed polymers possessed highly stereoregular cis-transoidal main chain (cis contents ≥99%).

Introduction

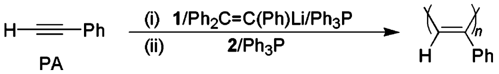
Design and development of novel catalyst systems for the polymerization of substituted acetylenes have been an active area of research in the past several years, and various transition metal catalysts from group 4 to 10 have been developed for this purpose.[1−5] Research in this field is being motivated by the multidimensional significance of the resulting polymers in a wide array of applications such as photonics, nonlinear optics, electrical conductors, gas separation membranes, stimuli-responsive materials, liquid crystals, and organic light-emitting diodes.[6] Rh catalysts efficiently polymerize monosubstituted acetylenes[4,5] such as phenylacetylene (PA) and its ring-substituted derivatives,[7−9] propiolic esters,[10,11] and *N*-propargylamides.[12] Owing to their low oxophilicity, Rh catalysts feature excellent tolerance toward various polar functional groups.[13] Moreover, the Rh-catalyzed polymerization can be carried out in highly polar solvents such as alcohols,[7a,8b] amines,[8c] and even in water[9b] and ionic liquids[9a] to selectively produce stereoregular polymers with cis-transoidal main chain structure.[7a,b,8a]

The first example of living polymerization of PA was reported by Kishimoto et al. using two catalyst systems, i.e., $[(nbd)Rh(-C{\equiv}CPh)(Ph_3P)_2]$/DMAP[14] (DMAP, 4-(dimethylamino)pyridine; nbd, 2,5-norbornadiene) and $[(nbd)Rh(OMe)]_2/Ph_3P/$DMAP,[15] displaying initiation efficiencies of 37% and 73%, respectively. Falcon et al. have observed that the polymerization of PA with $[(nbd)Rh(OCH_3)]_2$/dppb (dppb = $Ph_2P(CH_2)_4PPh_2$) proceeds in a living fashion to give poly(PA) with narrow molecular weight distribution (MWD M_w/M_n < 1.1).[16] However, the initiation efficiency is less than 1% due to the formation of various species from the mixture of $[(nbd)Rh(OCH_3)]_2$ and dppb. Our research group has reported that the $[(nbd)RhCl]_2/Ph_2C{=}C(Ph)Li/Ph_3P$ ternary catalyst system polymerizes PA and its ring-substituted derivatives in a living manner with quantitative initiation efficiency, and this system was successfully used for the synthesis of various block copolymers, star polymers, and star block copolymers.[17] Furthermore, a well-defined isolated Rh complex, $[(nbd)Rh\{-C(Ph){=}CPh_2\}(4\text{-}FC_6H_4)_3P]$, also mediated the living polymerization of PA with virtually quantitative initiation efficiency in the presence of 5 equiv of $(4\text{-}FC_6H_4)_3P$,[18a] and induced the living-like polymerization of *N*-propargylamides as well, for the first time.[18b]

Chart 1. Structures of Catalysts 1 and 2



Scheme 1. Polymerization of PA with (i) 1/Ph$_2$C═C(Ph)Li/Ph$_3$P and (ii) 2/Ph$_3$P



All the known Rh-based catalysts that induce living polymerization contain exclusively the nbd ligand, and their 1,5-cyclooctadiene (cod) counterparts have never been found to affect the living polymerization.[14,15,17] Rh catalysts possessing nbd ligand show higher activity than cod analogues.[7,8c,9c] We have recently found that the tetrafluorobenzobarrelene (tfb) coordinated Rh complex, $[(tfb)RhCl]_2$ (**1**), is more active than its nbd counterpart.[19] In the present study, we found that both the ternary catalyst system, **1**/$Ph_2C{=}CPh(Li)/Ph_3P$, and the vinylrhodium complex, $[(tfb)Rh\{-C(Ph){=}CPh_2\}(Ph_3P)]$ (**2**), mediate the living polymerization of PA in the presence of Ph_3P (Chart 1 and Scheme 1). This polymerization displays virtually quantitative initiation efficiency and leads to the formation of

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a very high molecular weight polymer ($M_n = 401\,000$) with narrow MWD ($M_w/M_n = 1.12$).

Experimental Section

Instruments. Monomer conversions were determined by GC (Shimadzu GC-8A; Silicone SE30 (5% on Chromosorb W(AW-DMCS), 80−100 mesh); injection and column temperatures were 200 and 180 °C, respectively) using bromobenzene as an internal standard. The number- and weight-average molecular weights (M_n and M_w, respectively) and polydispersity indices (M_w/M_n) of polymers were measured by GPC at 40 °C with a Jasco PU-980/RI-930 chromatograph; eluent THF, columns KF-805 (Shodex) × 3, molecular weight limit up to 4×10^6, flow rate 1 mL/min, calibrated with polystyrene standards. ^{1}H, ^{13}C, and ^{31}P NMR spectra were recorded on a JEOL EX-400 spectrometer, and the ^{19}F NMR spectrum was observed on a Varian Mercury-200 spectrometer with chemical shifts referenced to internal standards Me_4Si (0 ppm, ^{1}H), $CDCl_3$ (77.0, ppm ^{13}C), and $CFCl_3$ (0 ppm, ^{19}F) and to external standard $P(OMe)_3$ (140 ppm, ^{31}P). IR spectra were measured on a Jasco FTIR-4100 spectrophotometer. Elemental analyses were performed at the Microanalytical Center of Kyoto University. Melting points were determined with a Yanaco MP-50859 melting point apparatus.

Materials. PA (Aldrich) was purchased and distilled over CaH_2 under reduced pressure before use. Toluene (Wako, Japan) as polymerization solvent was purified before use by the standard procedure. 1-Bromo-1,2,2-triphenylethene (TCI, Japan), *n*-BuLi (1.6 mol/L in hexane solution; Kanto Kagaku, Japan), and other reagents were purchased and employed without further purification. Catalyst **1** was synthesized according to our previous report.[19] Triphenylvinyllithium [$Ph_2C{=}C(Ph)Li$] (in situ) and catalyst **2** were synthesized according to the procedures described below.

Triphenylvinyllithium [$Ph_2C{=}C(Ph)Li$]. The reported procedure was modified to synthesize this compound.[17a] 1-Bromo-1,2,2-triphenylethene (67 mg, 0.2 mmol) was dissolved in toluene (1.0 mL), and the resulting solution was cooled to 0 °C in an ice bath. *n*-BuLi (0.127 mL, 0.2 mmol) was added dropwise, resulting in the immediate formation of a yellow solution. Total volume was made up to 2.0 mL by adding toluene (0.87 mL) to give a 0.1 M solution of triphenylvinyllithium [$Ph_2C{=}C(Ph)Li$], which was used without elimination of the formed LiBr.

Vinylrhodium Complex [(tfb)Rh{−C(Ph)═CPh$_2$}(Ph$_3$P)] (2). The reported procedure for the corresponding nbd complex was slightly modified to synthesize catalyst **2**,[18a] as follows: a $Ph_2C{=}C(Ph)Li$ (50 mM, 16 mL) solution was prepared by the reaction of *n*-BuLi (0.5 mL, 0.8 mmol) with $Ph_2C{=}C(Ph)Br$ (268 mg, 0.8 mmol) in diethyl ether (16 mL) at low temperature (0 °C) under dry argon. To a solution of [(tfb)RhCl]$_2$ (146 mg, 0.20 mmol) and Ph_3P (210 mg, 0.80 mmol) in benzene (15 mL) was added the solution of $Ph_2C{=}C(Ph)Li$ (50 mM, 8.0 mL, 0.40 mmol) at 0 °C. The reaction mixture was slowly warmed to 25 °C, and after stirring for 3 h at this temperature, it was subjected to column chromatography (neutral activated alumina 90 (activity I), Merck) using toluene as the eluent. The orange-colored fraction was collected, and toluene was evaporated to dryness. The Rh complex [(tfb)Rh{−C(Ph)═CPh$_2$}(Ph$_3$P)] (**2**) was isolated by recrystallization from CH_2Cl_2/*n*-pentane. Yield 84%, mp 161.0−162.0 °C. IR (KBr): 3032, 3010, 2917, 1611, 1595, 1527, 1461, 1301, 1190, 1131, 965, 801, 761, 705. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ: 7.40−6.90 (m, 22H, Ar), 6.85−6.78 (m, 4H, Ar), 6.62 (d, 4H, $J = 7.6$ Hz, Ar), 5.51−5.19 (m, 2H, bridgehead CH), 3.75−3.20 (m, 4H, ═CH). The ^{13}C NMR spectrum of **2** showed extensive splitting of the signals caused by the coupling of the carbon atoms with Rh, P, and F, which did not allow the complete assignment. ^{31}P {^{1}H} NMR (162 MHz, $CDCl_3$, 25 °C) δ: 26.25 (d, $J_{Rh-P} = 189.0$ Hz). ^{19}F NMR (282 MHz, $CDCl_3$, 25 °C) δ: −148.2 to −148.8 (m, 2F), −161.1 to −161.5 (m, 2F). Anal. Calcd for $C_{50}H_{36}F_4PRh$: C, 70.93%; H, 4.29%. Found: C, 70.75%; H, 4.50%.

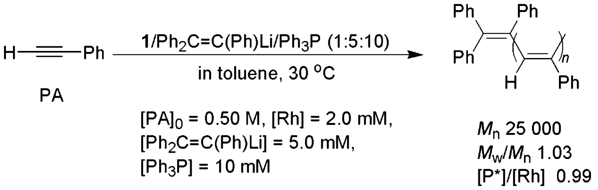
Polymerization. All the polymerizations were carried out under an argon atmosphere in a Schlenk tube equipped with a three-way stopcock. A typical polymerization procedure with the ternary catalyst system is as follows: The catalyst solution was prepared by dissolving **1** (5.0 μmol) in toluene (3.0 mL) followed by the addition of the toluene solution of triphenylvinyllithium (50 μL, 25 μmol). Although 2.0 equiv of triphenylvinyllithium is required theoretically, an excess amount, i.e., 5.0 equiv, was employed to compensate the loss caused by reaction with the moisture in the system. A toluene solution (2.0 mL) of PA (2.5 mmol) was added to the catalyst solution (3.0 mL) with/without Ph_3P. Polymerization was carried out at 30 °C for 1 h, and the formed polymer was isolated by precipitation in a large amount of methanol, filtered with a glass filter, and dried under vacuum to constant weight.

In the case of isolated catalyst **2**, a toluene solution (2.0 mL) of PA (2.5 mmol) was added to a toluene solution (3.0 mL) of **2** (10 μmol) with/without Ph_3P, and the polymerization was carried out at 30 °C for 1 h. The formed polymer was isolated by precipitation in a large amount of methanol, filtered with a glass filter, and dried under vacuum to constant weight.

Results and Discussion

Living Polymerization of PA with a Ternary Catalyst System. The polymerization of PA by the catalyst, prepared in situ from **1**, $Ph_2C{=}C(Ph)Li$, and Ph_3P (1:5:10), smoothly proceeded in toluene to afford a methanol-insoluble yellow polymer in quantitative yield (Scheme 2). According to GPC analysis, the number-average molecular weight (M_n) of the polymer was 25 000 with a remarkably narrow MWD ($M_w/M_n = 1.03$), while the corresponding nbd system also affects the living polymerization of PA with an M_w/M_n of 1.14, under the same coditions.[17a] It is noteworthy that the polydispersity of 1.03 achieved with the present ternary catalyst system is the smallest reported so far in the polymerization of PA with Rh catalysts. In the case of nbd-based ternary system, it was revealed that triphenylvinyl moiety is quantitatively introduced at the initiating end of the polymer chain.[17a] The initiation efficiency ([P*]/[Rh]) of the present ternary system calculated from the M_n value (25 000), by assuming that each polymer chain possesses a triphenylvinyl group at the initiating chain end, was virtually quantitative.

Scheme 2. Living Polymerization of PA Catalyzed by 1/Ph$_2$C═C(Ph)Li/Ph$_3$P (1:5:10) in Toluene at 30 °C; [PA]$_0$ = 0.50 M, [1] = 1.0 mM, [Rh] = 2.0 mM



The living nature of this polymerization was confirmed by means of a multistage polymerization experiment; quantitative formation of the polymer was observed each of the three times, upon addition of PA to catalyst solution at intervals of 1 h. As shown in Figure 1, the M_n values of the polymer increased in direct proportion to the polymer yield, while the MWDs remained as narrow as ca. 1.05. This observation implies that all the propagating species are active even after the complete consumption of monomer. A close agreement between the observed M_n values (25 000, 53 000, 75 000) and the theoretical ones (26 000, 51 000, 77 000) indicates an approximately quantitative initiation efficiency ([P*]/[Rh] > 0.96). According to the previously reported examples of Rh-based living polymerization catalysts, only nbd ligand is known to be capable of mediating the living polymerization of PA and its ring-substituted derivatives.[13,15,17] To the best of our knowledge, this

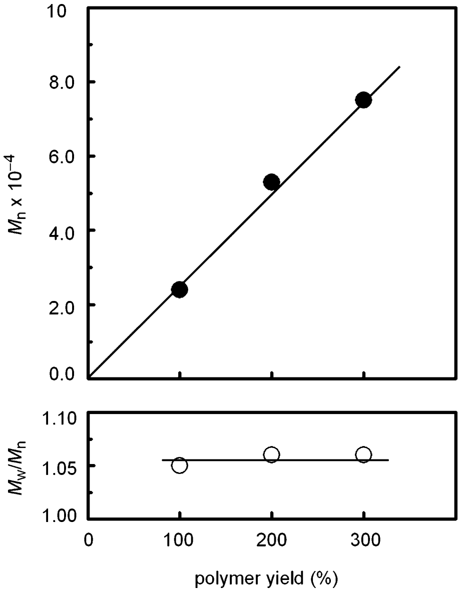


Figure 1. Multistage polymerization of PA catalyzed by **1**/$Ph_2C{=}C(Ph)Li/Ph_3P$ in toluene at 30 °C. The monomer feeds were supplied three times at intervals of 1 h; [Rh] = 2.0 mM, [$Ph_2C{=}C(Ph)Li$] = 5.0 mM, [Ph_3P] = 10.0 mM, $[PA]_0 = [PA]_{added} = 0.50$ M.

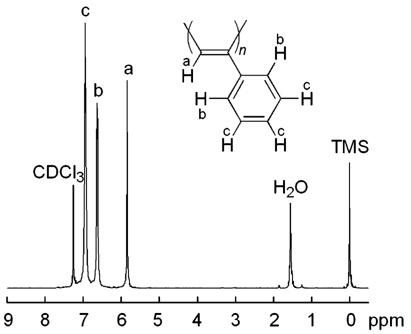


Figure 2. ^{1}H NMR spectrum of poly(PA) obtained with the **1**/$Ph_2C{=}C(Ph)Li/Ph_3P$ in toluene at 30 °C; $[PA]_0 = 0.50$ M, [Rh] = 2.0 mM, [$Ph_2C{=}C(Ph)Li$] = 5.0 mM, [Ph_3P] = 10 mM.

is the first example of any diene ligand except nbd, which is capable of inducing the living polymerization of PA with quantitative initiation efficiency.

Rh catalysts usually polymerize monosubstituted acetylenes in a stereospecific fashion to produce polymers with cis-transoidal main chain structure.[7−12] The ^{1}H NMR spectra of the poly(PA) obtained with the ternary catalyst system displayed a sharp peak at 5.84 ppm due to the olefinic proton of the main chain (Figure 2). The cis contents, calculated from the integration ratio of olefinic protons to aromatic protons, were almost quantitative (cis contents ≥99%), manifesting a high level of stereoregularity. This observation implies that the ternary catalyst system is capable of inducing the highly stereospecific living polymerization. This result is of considerable significance as highly stereospecific living polymerization still remains a subject difficult to achieve.[20]

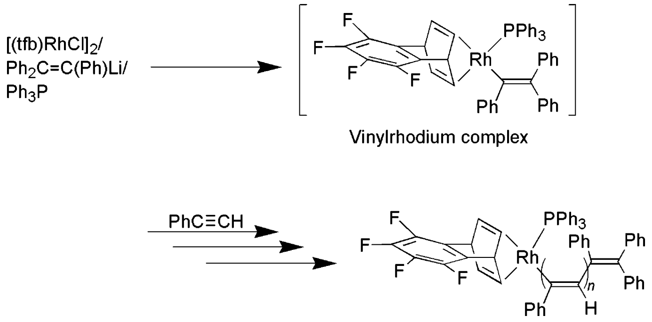
The effects of the components of the ternary catalyst system were examined. A combination of catalyst **1** and Ph_3P ([P]/[Rh] = 5) produced only a trace amount of the polymer (run 1; Table 1), while that of **1** and $Ph_2C{=}C(Ph)Li$ resulted in the formation of a high molecular weight polymer (M_n = 479 000) in quantitative yield (run 2); however, the M_w/M_n of the polymer was 1.60, which denies living polymerization. In another attempt, a three-component catalyst system, consisting of **1**, $Ph_2C{=}C(Ph)Li$, and Ph_3P, was employed to polymerize PA, and the initiation efficiency was observed to increase (as indicated by the decrement in M_n) while MWD went on narrowing with the increase in the phosphine concentration. For instance, in the presence of 5 equiv or more of Ph_3P to Rh, the initiation efficiency was almost quantitative and MWD became as narrow as $M_w/M_n = 1.04$ (runs 5 and 6).[21] On the other hand, when *n*-BuLi was employed along with Ph_3P, a polymer with molecular weight (M_n = 80 000) higher than the theoretical value (26 000) and a broad MWD ($M_w/M_n = 1.49$) was observed (run 8). Thus, both the $Ph_2C{=}C(Ph)Li$ ([Li]/[Rh] > 1) and Ph_3P ([P]/[Rh] ≥ 5) are prerequisites for this catalyst system to exhibit an excellent living nature, and this behavior is practically the same as the previously reported results for the nbd-based ternary catalyst system.[17a] The reaction of **1**, $Ph_2C{=}C(Ph)Li$, and Ph_3P presumably results in the in-situ generation of a vinylrhodium complex which acts as an initiating species, and the polymerization takes place by the insertion of PA into the Rh−vinyl bond (Scheme 3). The structural resemblance of the triphenylvinylrhodium initiating species with the propagating end is probably responsible for the smooth initiation, which results in the quantitative initiation efficiency.

Table 1. Effect of Alkylating Agents and Ph_3P on the Polymerization of PA with Catalyst 1[a]

			polymer[b]			
run	alkylating agent	[Ph_3P]/[Rh]	yield (%)	M_n[c]	M_w/M_n[c]	[P*]/[Rh]
1		5.0	trace			
2	$Ph_2C{=}C(Ph)Li$	0.0	100	479 000	1.60	0.05
3	$Ph_2C{=}C(Ph)Li$	1.0	100	276 000	1.45	0.09
4	$Ph_2C{=}C(Ph)Li$	3.0	100	71 000	1.18	0.35
5	$Ph_2C{=}C(Ph)Li$	5.0	100	25 000	1.04	1.00
6	$Ph_2C{=}C(Ph)Li$	10	100	25 000	1.04	1.00
7	*n*-BuLi	0.0	100	398 000	2.32	0.06
8	*n*-BuLi	5.0	100	80 000	1.49	0.32

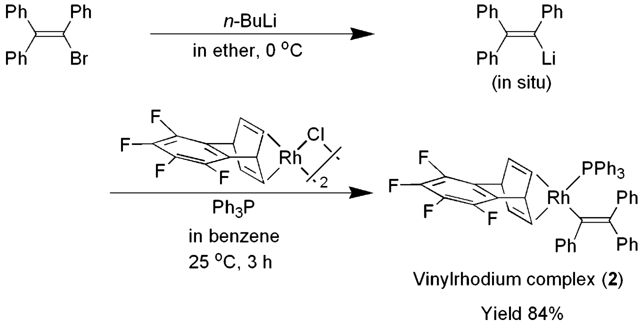
[a] In toluene, 30 °C, 1 h; $[PA]_0 = 0.50$ M, [Rh] = 2.0 mM, [$Ph_2C{=}C(Ph)Li$] = 5.0 mM, [*n*-BuLi] = 5.0 mM. [b] Methanol-insoluble product. [c] Determined by GPC (THF, PSt).

Scheme 3. Mechanism of Polymerization of PA by the Ternary Catalyst System 1/$Ph_2C{=}C(Ph)Li/Ph_3P$



Synthesis and Identification of Rh Complex 2. The isolation of vinylrhodium complex (**2**) was attempted by subjecting the solution of the ternary catalyst, **1**/$Ph_2C{=}C(Ph)Li/Ph_3P$, to column chromatography using toluene as an eluent, followed by the solvent evaporation and recrystallization from CH_2Cl_2/*n*-pentane to obtain complex **2** in high yield (84%). Failure to obtain the single crystal of the complex did not allow the X-ray structure analysis to be carried out. However, the spectroscopic data and elemental analysis (see Experimental Section) suggested that complex **2** has the structure shown in Scheme 4, and further evidence was furnished by a recent report on the isolation of a series of arylrhodium complexes having a structure similar to that of **2**.[22] It has been revealed by X-ray structure analysis of a vinylrhodium complex [(nbd)Rh{−C(Ph)=CPh$_2$}-

Scheme 4. Synthesis of Vinylrhodium Complex (2)



$\{(4\text{-}FC_6H_4)_3P\}]$[18a] and arylrhodium complexes $[(nbd)Rh(Ar)(Ph_3P)]$ (Ar: 2,6-$Me_2C_6H_3$, 2-methyl-1-naphthyl, 9-anthracenyl)[22] that they adopt a square-planar geometry around the Rh atom. Since **2** is structurally similar to the above complexes, it also presumably possesses a square-planar coordination structure. Our assumption is compatible with the ^1H NMR spectrum of **2**, in which signals arising due to bridgehead methine protons (5.51−5.19 ppm) and olefinic protons (3.75−3.20 ppm) appeared as multiplets, indicative of the unsymmetrical nature of the tfb ligand in **2**. The ^{31}P NMR spectrum of **2** showed a doublet at 26.25 ppm with $J_{Rh-P} = 189$ Hz. Although Ph_3P was employed in 2 equiv to Rh, the elemental analysis indicated the presence of only one phosphine ligand in complex **2**. Catalyst **2** in the solid state was fairly stable in air, and no change in its ^1H and ^{31}P NMR spectra was observed even after a 24 h exposure to air.

Polymerization of PA by Isolated Catalyst 2. Although the polymerization of PA by catalyst **2** afforded the polymer in quantitative yield, the M_n of the resulting polymer was 262 000, corresponding to an initiation efficiency of only 10% along with a broad MWD ($M_w/M_n = 1.45$). As discussed above, the ternary catalyst system requires 5 equiv of Ph_3P to Rh to accomplish the perfect living polymerization (Table 1), and this finding prompted us to examine the effect of addition of Ph_3P on the polymerization of PA catalyzed by **2** (Figure 3). Interestingly, the MWD of the formed polymer exhibited a tendency to become narrow with an increase in the amount of the phosphine and became as narrow as ca. 1.05 at [P]/[Rh] = 5, as illustrated in Figure 3a. Beyond this concentration, no discernible change was observed in the MWD of poly(PA). The initiation efficiency also showed a large dependence on the concentration of added phosphine (Figure 3b). For instance, catalyst **2** exhibited an initiation efficiency of only ca. 10% in the absence of phosphine, which was observed to become almost quantitative upon the addition of 5 equiv of phosphine to Rh. The added phosphine exerted a decelerating effect on the polymerization; e.g., the polymerization was very rapid and finished in about 1 min at [P]/[Rh] = 5, while it required about 15 min at [P]/[Rh] = 20 to reach completion. The role of Ph_3P is assumed to be the formation of a stable dormant species, due to its coordination with Rh in competition with the monomer, as depicted in Scheme 5.[23] Since the active species are isoelectronic with complex **2** (16 electron), a square-planar configuration seems to be the most probable for active species.

The polymerization was too fast to monitor the monomer conversion in the presence of 5 equiv of Ph_3P at $[PA]_0 = 0.5$ M and [Rh] = 2.0 mM; hence, the time profile of the polymerization of PA by **2** was examined at a lower concentration of catalyst ([Rh] = 1.0 mM) in the presence of 20 equiv of Ph_3P to Rh, which appreciably decelerated the rate of polymerization (Figure 4). The first-order plot with respect to the monomer conversion showed a linear relationship, thus supporting the idea that the concentration of the propagating species does not change in the course of polymerization and that the propagation reaction is a bimolecular reaction involving the propagating species and the monomer. The M_n value of the polymer increased in direct proportion to the monomer conversion, ruling out the possibility of any chain transfer or chain termination reaction. The initiation efficiency calculated from the monomer conversion and the M_n of the polymer was again confirmed to be 100%.[24]

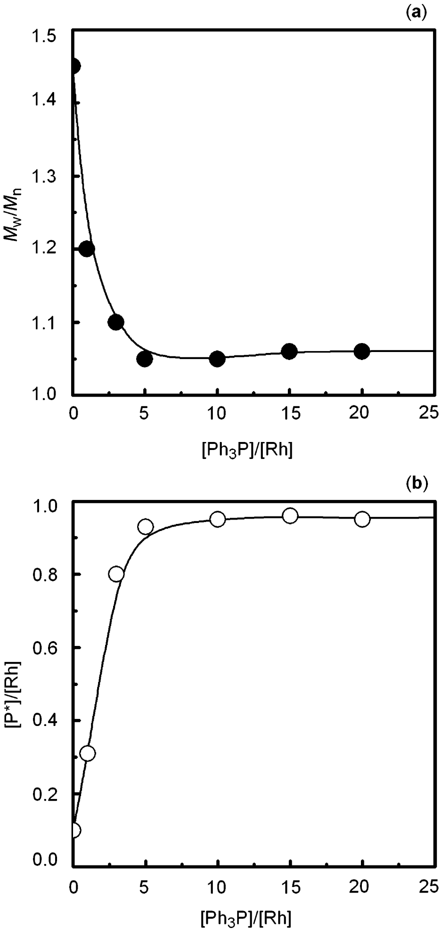
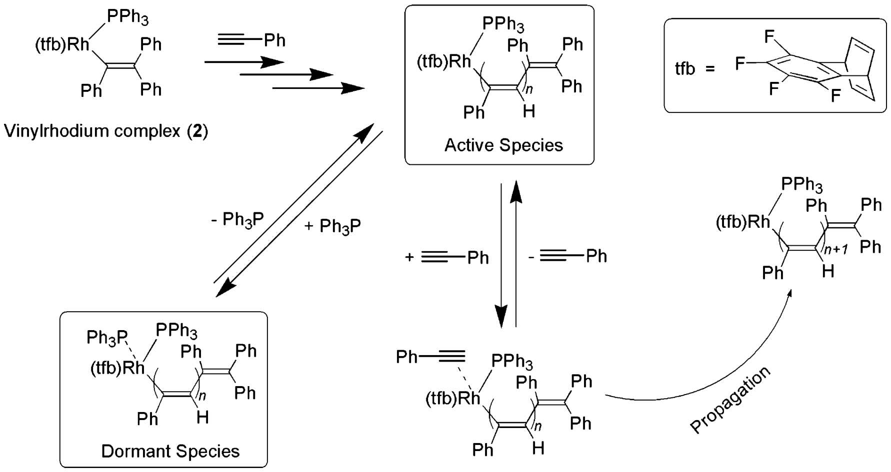


Figure 3. Effect of Ph_3P concentration on (a) molecular weight distribution and (b) initiation efficiency in the polymerization of PA with catalyst **2** in toluene at 30 °C; $[PA]_0 = 0.50$ M, [Rh] = 2.0 mM.

Further evidence for the living nature of the polymerization was obtained by the multistage polymerization of PA with **2**/Ph_3P (1:5), in which the stepwise addition of the monomer was carried out three times at regular intervals of 1 h (Figure 5). As observed in the case of ternary catalyst system, the monomer consumption was complete within 1 h in each stage, and the M_n value of the polymer increased linearly with the polymer yield, while the MWD remained as narrow as ca. 1.05. The initiation efficiency was virtually quantitative as indicated by the close agreement of the M_n values with the theoretical ones. These observations imply that all the propagating species remain active even after the complete consumption of the monomer, hence confirming the excellent living nature of the polymerization.

Figure 6 shows the effect of initial monomer concentration on the polymerization of PA by catalyst **2**/Ph_3P. Use of initial monomer concentrations in the range of 0.5−2.0 M led to the quantitative formation of the polymers, possessing narrow MWDs ($M_w/M_n = 1.04-1.10$). The M_n values were observed to undergo an increase in direct proportion to the initial

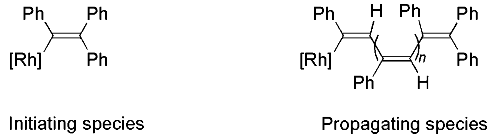
Scheme 5. Formation of Active Species in the Polymerization of PA with Catalyst 2



monomer concentration (Figure 6) while indicating an initiation efficiency of 100%, thus furnishing the evidence for the living mode of the polymerization.[25]

The effect of monomer-to-rhodium ratio ($[M]_0/[Rh]$) was examined by decreasing the concentration of catalyst **2**, as shown in Table 2. When $[M]_0/[Rh]$ was increased in the range of 250−2000 (runs 1−4), the M_n of the resulting polymer increased in direct proportion to it, while MWD remained very narrow ($M_w/M_n = 1.04-1.06$), and initiation efficiencies in all these cases were almost quantitative. More remarkably, a high molecular weight poly(PA) ($M_n = 401\,000$) was obtained with narrow M_w/M_n of 1.12 (run 5), in a quantitative yield at $[M]_0/[Rh]$ of 4000, which indicates that catalyst **2** is highly active even at very low concentration ($[\mathbf{2}] = 0.125$ mM). To the best of our knowledge, synthesis of such a high molecular weight poly(PA) having narrow MWD with quantitative initiation efficiency has never been reported so far. When $[M]_0/[Rh]$ was increased to 8000, a very high molecular weight polymer ($M_n = 742\,000$) was obtained with a somewhat broad MWD ($M_w/M_n = 1.42$) in

Chart 2



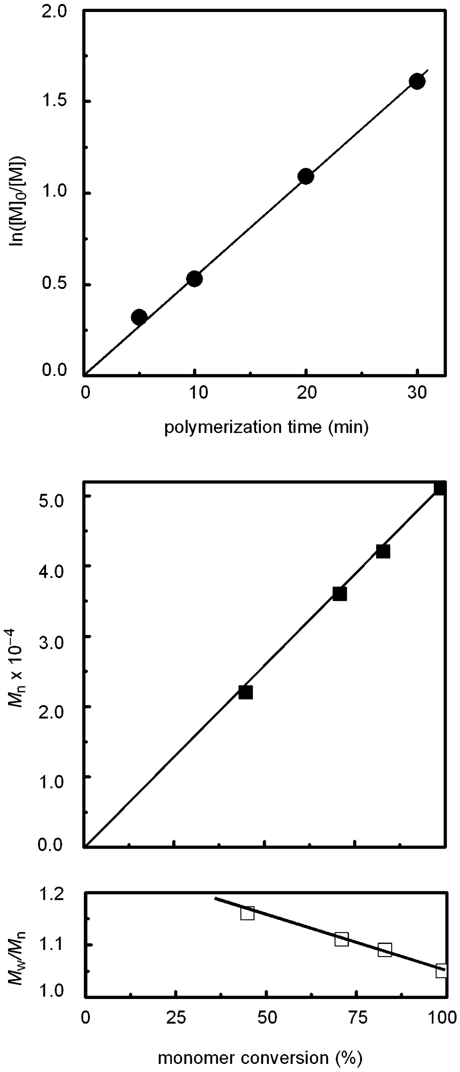


Figure 4. (a) First-order plot and (b) monomer conversion−M_n and monomer conversion−M_w/M_n plots in the polymerization of PA by **2** in toluene at 30 °C; $[PA]_0 = 0.50$ M, $[Rh] = 1.0$ mM, $[Ph_3P] = 20.0$ mM.

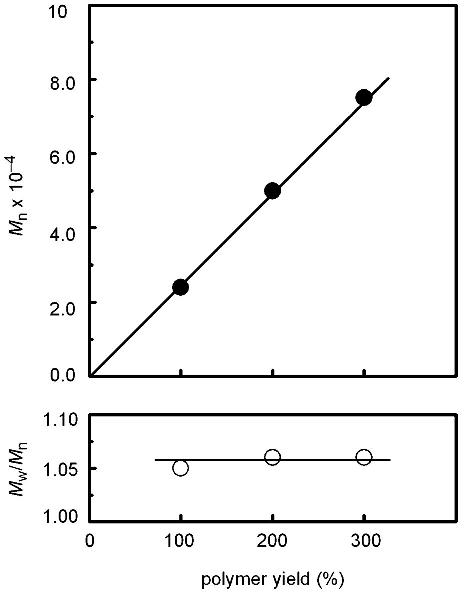


Figure 5. Multistage polymerization of PA catalyzed by **2**/Ph_3P in toluene at 30 °C; the monomer feeds were supplied three times at intervals of 1 h; $[PA]_0 = [PA]_{added} = 0.5$ M, $[Rh] = 2.0$ mM, $[Ph_3P] = 10.0$ mM.

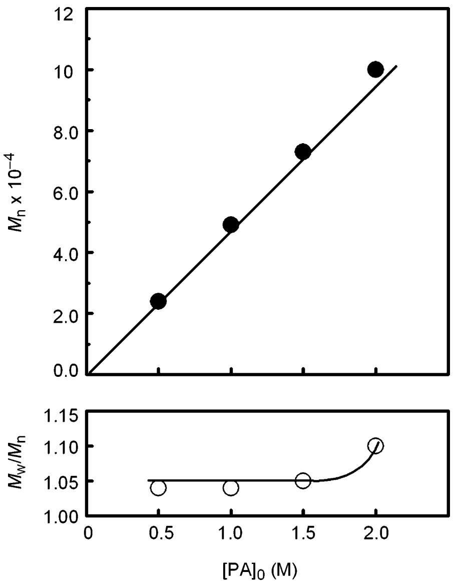


Figure 6. Effect of initial monomer concentration on the polymerization of PA catalyzed by **2**/Ph_3P in toluene at 30 °C for 1 h; [Rh] = 2.0 mM, [Ph_3P] = 10.0 mM.

Table 2. Effect of Monomer-to-Rhodium Ratio ($[M]_0$/[Rh]) on the Polymerization of PA with Catalyst 2[a]

			polymer[b]			
run	$[M]_0$/[Rh]	[Rh] (mM)	yield (%)	M_n[c]	M_w/M_n[c]	[P*]/[Rh]
1	250	2.00	100	25 000	1.04	0.98
2	500	1.00	100	52 000	1.05	0.98
3	1000	0.500	100	99 000	1.06	0.97
4	2000	0.250	100	195 000	1.06	0.95
5	4000	0.125	100	401 000	1.12	0.98
6	8000	0.063	96	742 000	1.42	0.96

[a] In toluene, 30 °C, 1 h; $[PA]_0$ = 0.50 M, [Ph_3P]/[Rh] = 5.0. [b] Methanol-insoluble product. [c] Determined by GPC (THF, PSt).

approximately quantitative yield (96%), which indicates the highly active nature of catalyst **2** in the polymerization of PA.

Conclusions

This study has revealed that both the ternary **1**/$Ph_2C{=}C(Ph)$-Li/Ph_3P catalyst system and well-defined vinylrhodium complex **2** mediate the living polymerization of PA with nearly quantitative initiation efficiency. These catalyst systems represent the first example of any diene ligand other than nbd capable of mediating the living polymerization of PA. The role of Ph_3P is very important in both systems as the polymerization behavior of PA is hardly close to living in its absence. The optimum concentration of Ph_3P required for an excellent living polymerization system is 5 equiv of Rh. A salient feature of catalyst **2** in combination with Ph_3P is its capability to provide high molecular weight polymer (M_n = 401 000) with very narrow MWD (M_w/M_n = 1.12).

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(21) The effect of other phosphorus ligands was also examined in the polymerization of PA. As observed with the nbd-based ternary system,[17f] the presence of electron-withdrawing groups at the para position of Ph_3P (e.g., $(4\text{-}FC_6H_4)_3P$) enhances the rate of the polymerization and vice versa. Triphenyl phosphite was also equally effective in the present catalyst system.[18b]

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(24) As shown in Figure 4, the MWD is somewhat broad ($M_w/M_n = 1.16$) in the initial stage of polymerization and then becomes narrow as the polymerization progresses. This observation is attributed to a slightly slower initiation than propagation (i.e., $k_i \leq k_p$) probably due to different steric environments in the initiating and propagating species. The trisubstituted vinylrhodium moiety in the initiating species is sterically more demanding than the disubstituted vinylrhodium moiety in the propagating species. Hence, coordination of PA to the propagating species should be more facile than to the initiating species, causing broadening of MWD in the initial stage of polymerization (see Chart 2).

(25) Catalyst **2** was also employed for the polymerization of *N*-propargylheptanamide (**3a**), *tert*-butylacetylene (**3b**), and *n*-hexyl propiolate (**3c**). In the presence of 5 equiv of Ph_3P to Rh, catalyst **2** polymerized **3a** with somewhat broad MWD ($M_w/M_n = 1.40$), and further increase of Ph_3P did not narrow the MWD. Despite the broad MWD, the M_n of the formed polymer increased in direct proportion to polymer yield, while the M_w/M_n practically remained unchanged in the multistage polymerization of **3a**, thus indicating a living-like nature of this polymerization. The larger M_w/M_n values are probably an outcome of an unfavorably large ratio of propagation and initiation rates (k_p/k_i) in accordance with our previous results.[18b] The catalyst system **2**/Ph_3P (1:5) polymerized **3b**, resulting in the quantitative formation of a polymer with M_w/M_n of 1.33. We anticipated a living-like nature of this polymerization like the case of monomer **3a**; however, the MWD underwent a significant broadening upon addition of the second monomer feed ($M_w/M_n = 1.71$) in the multistage polymerization of **3b**. Furthermore, the relationship between M_n and polymer yield was far from linear ruling out the possibility of living polymerization. Monomer **3c** afforded polymer only in low yield ($\leq$20%) with bimodal GPC curve, suggesting a nonliving polymerization.

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