

**Development of Rhodium Complexes
for the Polymerization of Substituted Acetylenes,
and Their Application to Synthesis of Helical Polymers**

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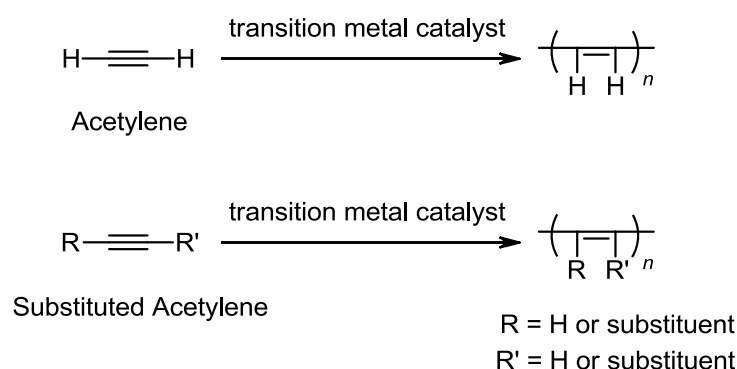
General Introduction

Research Background

Our life is supported by various functional materials including metals, ceramics and polymers, all of which are indispensable to modern civilization. Vinyl polymers such as polyethylene, polypropylene and polystyrene are synthesized by radical,¹ cationic,² anionic³ and transition metal catalyzed polymerizations.⁴ Since the discovery of Ziegler-Natta catalyst in the 1950's,⁵ enormous efforts have been made to develop highly active transition metal catalysts for olefin polymerization. Kaminsky catalyst developed in the 1980's is the most famous single site catalyst in the post Ziegler-Natta era.⁶ It has contributed to the remarkable progress of catalytic activity and selectivity based on ligand design. Transition metal catalysts enable precise control over stereoregularity, regioselectivity and tacticity of formed polymers. Especially, late transition metal catalysts are tolerant to polar groups, and therefore applicable to synthesis of various functional polymers.

Acetylene and its derivatives are polymerized by transition metal catalysts to afford polyacetylenes bearing conjugated main chains consisting of alternating double bonds (Scheme 1). Due to the main chain conjugation, the formed polymers show photoelectric properties such as electroluminescence, photoluminescence and photoconductivity. Substituted polyacetylenes are highly gas permeable and adopt helical conformation based on the rigid backbone.⁷

Scheme 1. Polymerization of Acetylene Compound Catalyzed by Transition Metal Catalyst



Various transition metal complexes are used as catalysts for acetylene polymerization (Chart 1).⁸ The polymerization mechanisms are categorized into two types, coordination-insertion and metathesis (Scheme

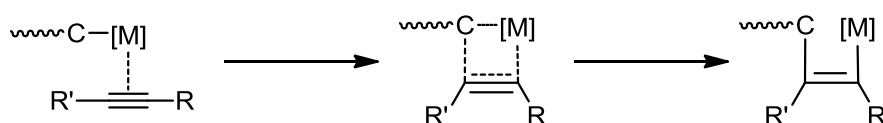
Chart 1. Transition Metal Catalysts for Acetylene Polymerization

Ti(O- <i>n</i> -Pr) ₄ /Et ₃ Al	Fe(acac) ₃
NbCl ₅ -cocatalyst	[(nbd)RhCl] ₂ -cocatalyst
TaCl ₅ -cocatalyst	(cocatalyst: Et ₃ N, Et ₃ Al, PrOH, etc)
(cocatalyst: Bu ₄ Sn, Ph ₃ Bi, etc)	[(nbd)Rh(η^6 -Ph)BPh ₃]
MoCl ₅ -cocatalyst	[(dppf)PdBr(Me)]-cocatalyst
WCl ₆ -cocatalyst	(cocatalyst: AgBF ₄ , AgOTf)
(cocatalyst: Bu ₄ Sn, Ph ₄ Sn, etc)	
Mo(CO) ₆ -CCl ₄ -h ν	
W(CO) ₆ -CCl ₄ -h ν	

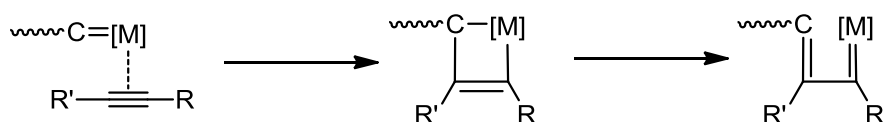
2). Ziegler-Natta catalysts polymerize acetylene monomers via the former mechanism, while carbene type catalysts including Grubbs and Schrock catalysts polymerize acetylenes via the latter mechanism.

Scheme 2. Acetylene Polymerization Mechanism

a) coordination-insertion mechanism



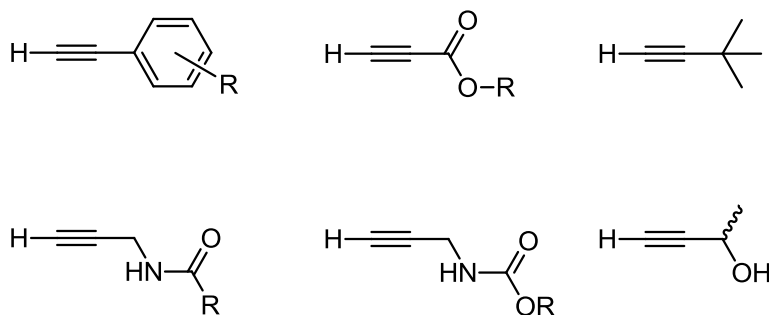
b) metathesis mechanism



In 1958, Natta and coworkers discovered Ti-catalyzed polymerization of acetylene for the first time.⁹ In 1974, Shirakawa and coworkers synthesized polyacetylene films by using a Ziegler-Natta catalyst, $\text{Ti}(\text{O}-n\text{-Bu})_4\text{-Et}_3\text{Al}$.¹⁰ Although the formed polyacetylene film found limited applications due to its insolubility in solvents and instability in air, it showed metallic conductivity upon doping with iodine. This finding stimulated the researches on the polymerization of substituted acetylenes, since the formed polymers are more stable than non-substituted one.

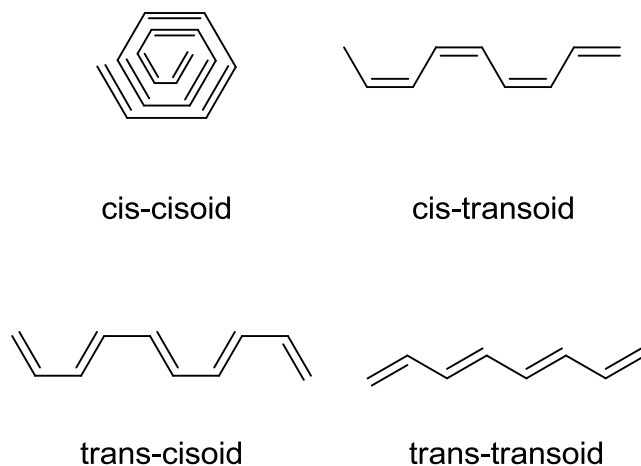
Until now, many kinds of transition metal catalysts have been developed for the polymerization of substituted acetylenes.⁸ Among them, rhodium (Rh) catalysts are especially effective for the polymerization of

Chart 2. Exaples of Acetylene Monomers Polymerizable with Rh Catalysts



monosubstituted acetylene monomers such as phenylacetylene,¹¹ *tert*-butylacetylene,¹² propiolic esters,¹³ *N*-propargylamides,¹⁴ *N*-propargylcarbamates¹⁵ and propargylalcohol derivatives¹⁶ (Chart 2). Rh catalysts are low oxophilic nature and applicable to the polymerization of a wide variety of monomers bearing ester, amide, carbamate and hydroxy groups. They are active in polar solvents including water¹⁷ as well as in nonpolar hydrocarbon solvents due to their high tolerance toward heteroatoms, unlike early transition metal catalysts that are inactivated by air, water and hetero-atom containing functional groups. Four stereoregulated structures are possible for substituted polyacetylenes, cis-cisoid, cis-transoid, trans-cisoid and trans-transoid as depicted in Chart 3. Rh catalysts selectively give cis-stereoregular polymers.^{11a, 11b, 18} Both cis-cisoidal and cis-transoidal are possible, because these two are conformational isomers and transformable each other.

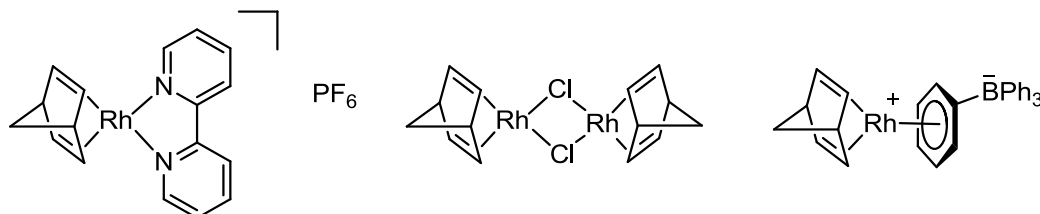
Chart 3. Possible Four Regulated Structure of Substituted Polyacetylenes



Kern and coworkers disclosed the Rh catalyzed polymerization of a substituted acetylene in 1969.¹⁹ They discovered that Wilkinson catalyst, $(PPh_3)_3RhCl$ polymerized phenylacetylene to afford the corresponding polymer with a low molecular weight ($M_n = 1100$). After that, Furlani and coworkers reported the polymerization of phenylacetylene by cationic Rh(I) complex, $[(nbd)Rh^+(2,2\text{-bipyridine})]PF_6^-$ ($nbd = 2,5\text{-norbornadiene}$) (Chart 4).^{11a, 11b, 18} They obtained cis-stereoregular poly(phenylacetylene) with a relatively high M_n in a high yield.

Tabata and coworkers discovered a Rh dimeric catalyst that is very usable for acetylene polymerization, i.e., $[(nbd)RhCl]_2$ (Chart 4).²⁰ This catalyst efficiently polymerizes phenylacetylene in the presence of triethylamine as a cocatalyst to afford the corresponding polymer with a high molecular weight quantitatively. Later, Masuda and coworkers improved the polymerization activity by employing alkali metal amides

Chart 4. Rh Catalysts of Acetylene Polymerization



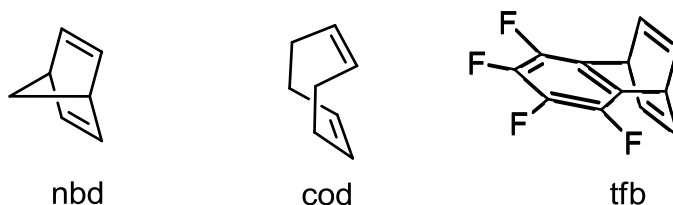
such as sodium amide instead of triethylamine.²¹ Noyori and coworkers synthesized zwitterionic Rh catalyst, $[(\text{nbd})\text{Rh}^+(\eta^6\text{-Ph})\text{B}^-\text{Ph}_3]$ which efficiently polymerized phenylacetylene.²² Zwitterionic type catalysts are often employed to polymerize monosubstituted acetylene compounds as well as dimer type catalysts.²³

Furlani and Feast reported that Rh-based substituted polyacetylenes possessed cis-rich alternating double bonds in the main chains, which were characterized by ^1H NMR spectroscopy.^{11a} They mentioned that the signal of cis-vinylene protons appeared around 5.8 ppm. Noyori and coworkers examined the reaction of $(\text{nbd})\text{Rh}(\text{PPh}_3)_2(-\text{C}\equiv\text{CPh})$ with fifty equivalents of phenylacetylene having deuterated ethynyl proton, and concluded that the Rh-catalyzed polymerization of phenylacetylene proceeded in 2,1-insertion mechanism.²⁴

Rh catalysts are commonly liganded by a diene, which is notably affective to the activity (Chart 5). Noyori and coworkers pointed out that nbd ligand is more effective than 1,5-cyclooctadiene (cod) for Rh catalysts.²² Masuda and coworkers demonstrated that π -acidity of a ligand was important to improve the catalytic activity.²⁵

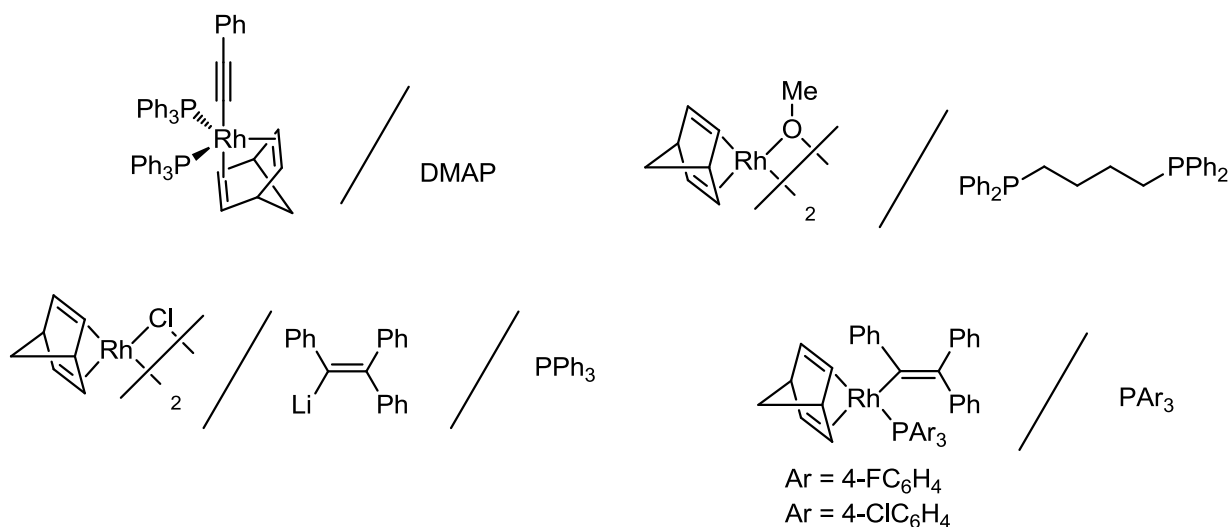
Tetrafluorobenzobarrelene (tfb) was proved to be π -acidic more than nbd by the PM3 calculation. Actually, [(tfb)RhCl]₂ consumed phenylacetylene much faster than [(nbd)RhCl]₂.

Chart 5. Diene Ligands



Some Rh catalysts polymerize monosubstituted acetylenes in a living fashion. Noyori and coworkers achieved the living polymerization of phenylacetylene in 1994.²⁶ They demonstrated that a phenylethynyl Rh complex, (nbd)Rh(PPh₃)₂(-C≡CPh) polymerized phenylacetylene in the presence of *N,N*-dimethylaminopyridine (DMAP) to afford the polymers with small PDIs in high yields.²⁷ This catalyst system was effective to synthesize a living poly(phenylacetylene), although the initiation efficiency was about 70%. They researched the polymerization mechanism in detail, and emerged that the initiation did not proceed via a direct insertion of a monomer into the Rh complex but via the formation of Rh-H complex by the reaction of the Rh complex with a monomer, followed by the insertion of another monomer. The initiation efficiency of this polymerization remained 33–56%. They also found the living polymerization of phenylacetylene using a ternary catalyst system, [(nbd)Rh(μ-OMe)]₂/PPh₃/DMAP with 70% initiation efficiency.²⁸ Falcon

Chart 6. Rh Catalysts for Living Polymerization



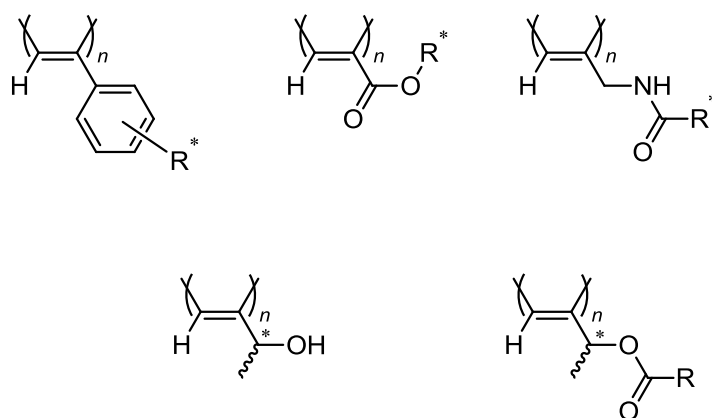
and coworkers succeeded in the living polymerization of phenylacetylene with $[(\text{nbd})\text{Rh}(\mu\text{-OMe})_2/\text{dppb}]$ [$\text{dppb} = 1,4\text{-bis(diphenylphosphino)butane}$] (Chart 6) to obtain poly(phenylacetylene) with small PDIs ($M_w/M_n < 1.1$). However, the initiation efficiency was as small as 1%.²⁹

Masuda and coworkers reported that ternary catalyst system composed of $[(\text{nbd})\text{RhCl}]_2/\text{Ph}_2\text{C}=(\text{Ph})\text{Li}/\text{PPh}_3$ induced the living polymerization of phenylacetylene to provide polymers with very small PDIs (~ 1.1) quantitatively (Chart 6).³⁰ They experimented multistage polymerization to demonstrate the living nature. This catalyst system enabled the synthesis of star polymers and star block copolymers composed of poly(phenylacetylene) and poly[(*p*-methylphenyl)acetylene] using 1,4-diethynylbenzene as a linking agent.³¹ They isolated $\text{Rh}[\text{C}(\text{Ph})=\text{CPh}_2](\text{nbd})[(4\text{-FC}_6\text{H}_4)_3\text{P}]$ from the reaction mixture of $[(\text{nbd})\text{RhCl}]_2$, $\text{Ph}_2\text{C}=(\text{Ph})\text{Li}$ and $(4\text{-XC}_6\text{H}_4)_3\text{P}$, with the aim of refining this catalyst system.³² The isolated complex was fully characterized by X-ray analysis, and induced the living polymerization of phenylacetylene. This

catalyst system was applicable to the polymerization of *N*-propargylamides as well, and the presence of a long-lived active species was confirmed.³³ An improved Rh(I) vinyl complex bearing tfb as a diene ligand provided a high molecular weight polymer with a PDI of 1.12 even at an extremely high monomer-to-catalyst ratio ($[M]_0/[Rh] = 4000$).³⁴

Helix is a fundamental higher order structure of synthetic polymers such as peptides,³⁵ polymethacrylates,³⁶ polysilanes,³⁷ and polyisocyanides.³⁸ *cis*-Stereoregular polyacetylenes are also typical helical polymers exhibiting useful photoelectric functions based on their π -conjugated backbones. Ciardelli and coworkers demonstrated a pioneering work regarding helical polyacetylenes, i.e., synthesis of optically active poly(1-alkyne) by use of $Fe(acac)_3$ as a polymerization catalyst in 1974.³⁹ Okamoto and coworkers firstly synthesized helical polyacetylenes using Rh catalyst.⁴⁰ They polymerized phenylacetylene derivatives bearing a chiral substituent at the *para*-position to obtain the

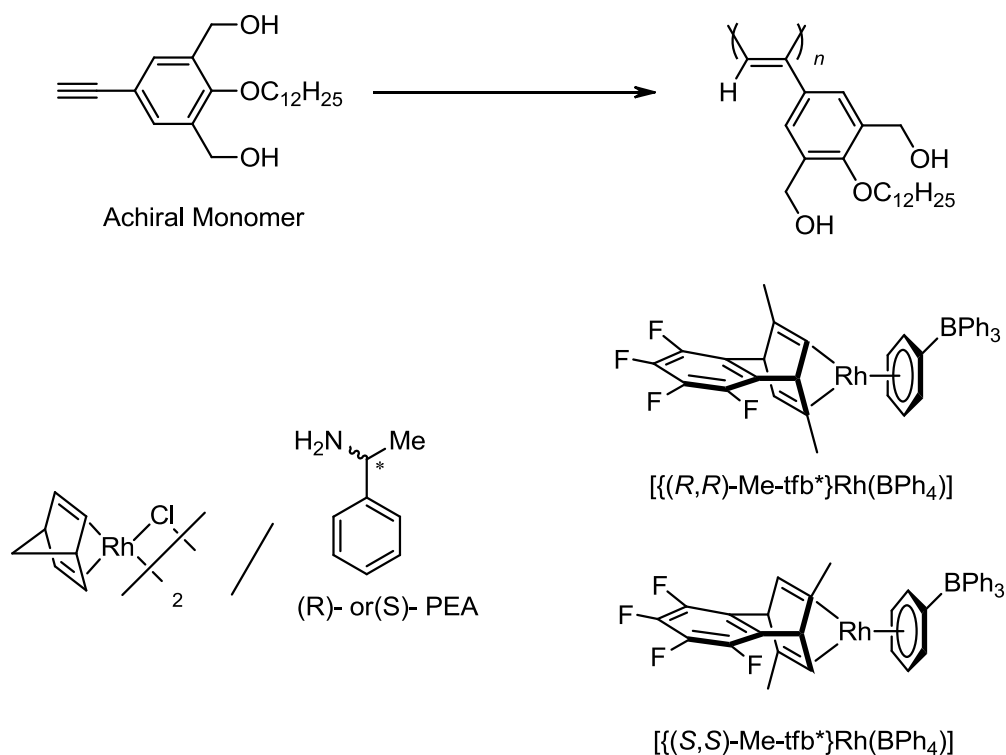
Chart 7. Helical Substituted Acetylenes



corresponding polymers adopting predominantly one-handed helical conformations (Chart 7). Masuda and coworkers polymerized propiolates,¹³ *N*-propargylamides,¹⁴ propargyl alcohols and esters¹⁶ (Chart 7) to obtain highly cis-stereoregular helical polymers. Poly(*N*-propargylamide)s formed intramolecular hydrogen-bonding strands between the amide groups at the side chains, which effectively stabilized the helical conformation in addition to the steric repulsion between the side chains. On the other hand, poly(propiolate)s, poly(1-methylpropargylalcohol)s and poly(1-methylpropargyl esters)s induce helical structures simply based on the steric repulsion.

Recently, chiral Rh catalyst systems were developed to synthesize predominantly one-handed helical polyacetylenes consisting of achiral acetylene monomer units. Aoki and coworkers polymerized an achiral acetylene monomer with [(nbd)RhCl]₂ in the presence of (*R*)-/(*S*)-phenylethylamine to obtain polymers showing intense CD signals (Scheme 3).⁴¹ After that finding, Hayashi and coworkers conceived chiral Rh zwitterionic catalysts bearing (*S,S*)-Me-tfb and (*R,R*)-Me-tfb as diene ligands, which enabled the helix-sense polymerization (Scheme 3).⁴²

Scheme 3. Helix-sense Selective Polymerization

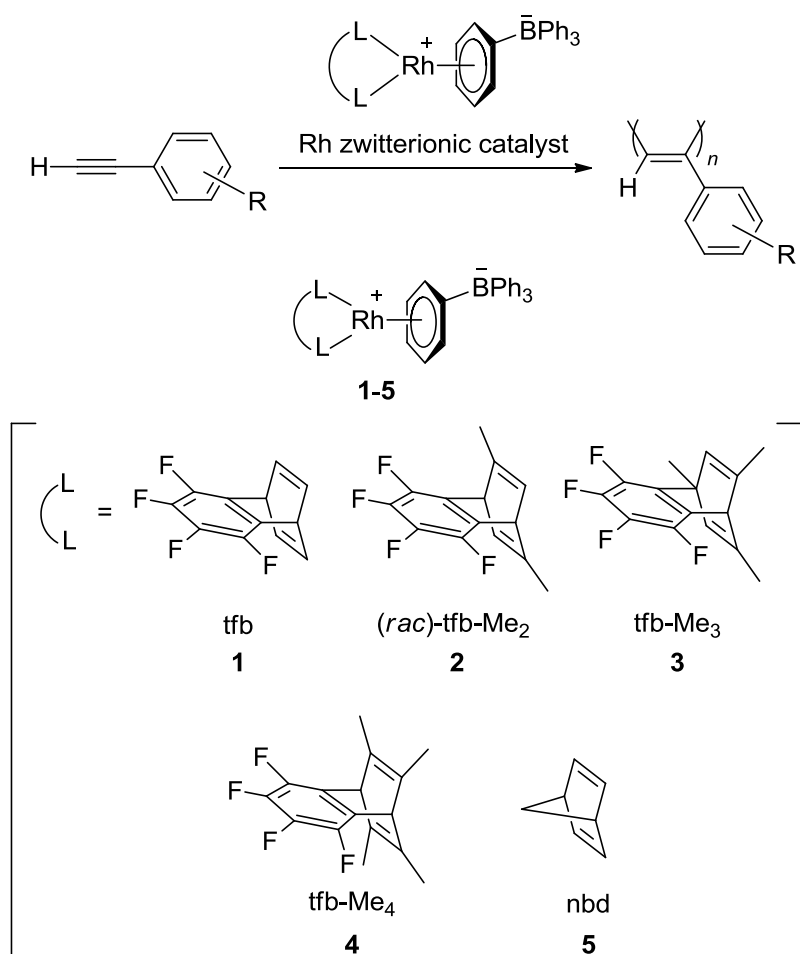


Outline of This Thesis

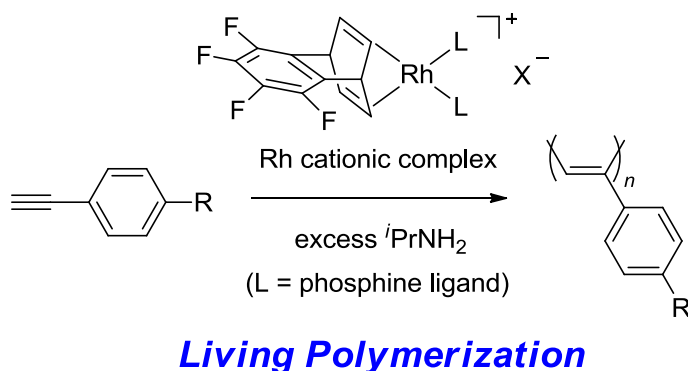
This thesis is composed of two parts. **Part I** (Chapters 1–3) deals with the development of novel Rh catalyst systems for the polymerization of substituted acetylenes, and activity control of the catalytic systems. **Part II** (Chapters 4 and 5) deals with the synthesis of helical polyacetylenes by Rh catalyst systems.

Chapter 1 discusses the synthesis of a novel zwitterionic Rh catalyst bearing tfb ligand, [(tfb)Rh(η^6 -Ph)] (**1**), and polymerization of

various mono- and disubstituted acetylenes with catalyst **1**. The author also demonstrates the polymerization using zwitterionic Rh catalysts **2–4** [**2**: tfb-Me₂, **3**: tfb-Me₃, **4**: tfb-Me₄] bearing a series of tfb ligands to produce polymers with molecular weights higher than those obtained from the conventional nbd analogue, (nbd)Rh⁺[(η⁶-Ph)B⁻Ph₃] (**5**). The catalytic activity tends to decrease with increasing the number of incorporated methyl groups. Catalyst **1** shows high activity in the polymerization of phenylacetylene derivatives irrespective of electron-donating or -withdrawing nature of ring-substituents of the monomers.

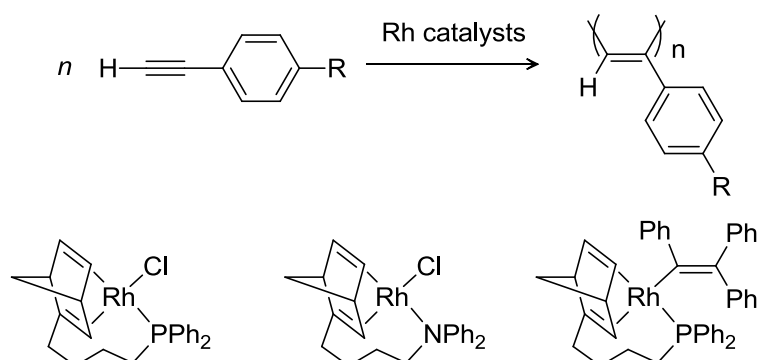


Chapter 2 describes the living polymerization of phenylacetylenes derivatives by novel binary Rh catalyst system composed of cationic Rh complexes, $[(\text{tfb})\text{Rh}(\text{L})_2]\text{X}$ (L: phosphine ligand, X: counter anion) and $i\text{PrNH}_2$. For instance, $[(\text{tfb})\text{Rh}(\text{PPh}_3)_2]\text{BPh}_4$ in conjunction with $i\text{PrNH}_2$ polymerizes phenylacetylene in a living fashion to give poly(phenylacetylene) with a small PDI ($M_w/M_n = 1.09$) quantitatively. The living nature is confirmed by the kinetic plots of the polymerization. Block copolymers are synthesized by the sequential polymerization of various phenylacetylenes.

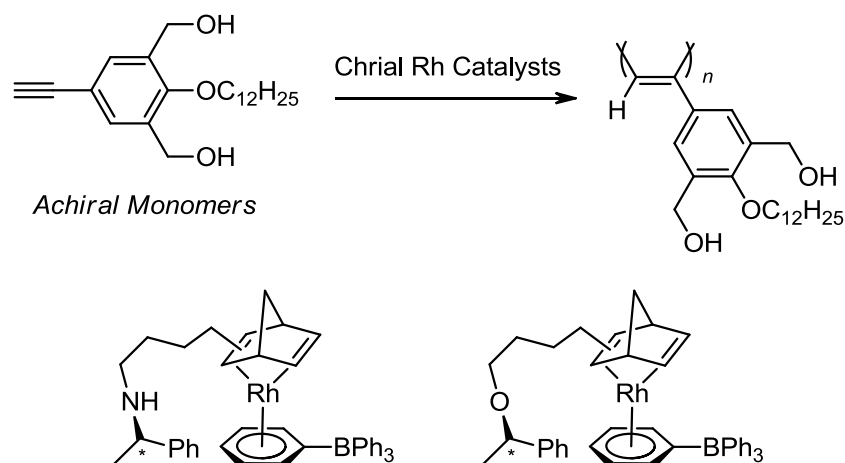


Chapter 3 describes the development of novel Rh catalysts bearing tridentate ligands, nbd derivatives tethering a chain containing a hetero atom. In the cases of chloride type catalysts, a nitrogen-containing Rh catalyst shows a catalytic activity for phenylacetylene polymerization higher than that of the phosphorous-containing counterpart. A vinyl type catalyst also shows high catalytic activity and affords polymers with

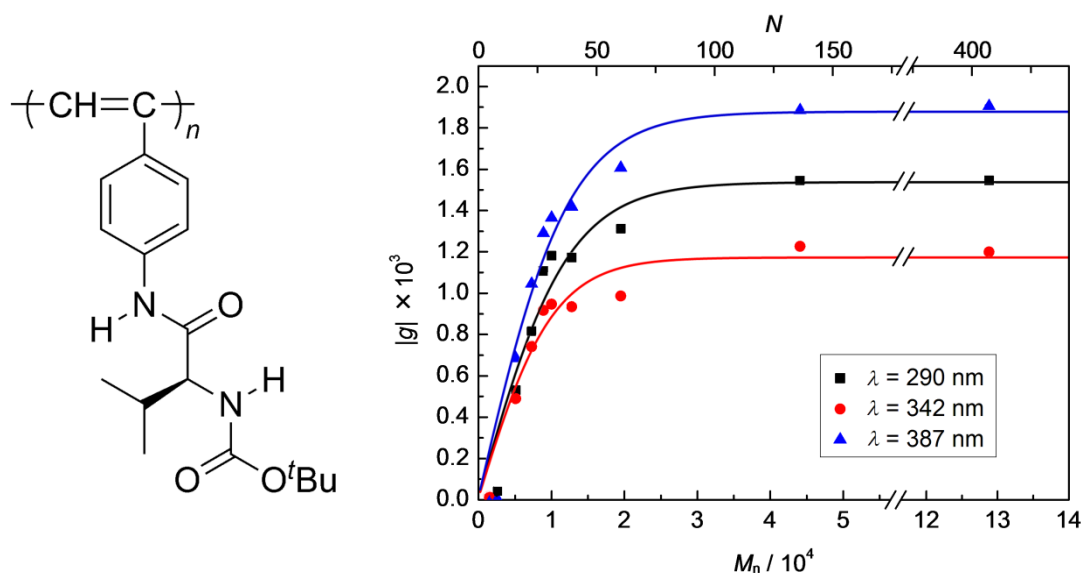
relatively small PDIs.



Chapter 4 describes the helix-sense selective polymerization of an achiral acetylene monomer catalyzed by chiral Rh catalysts. The Rh zwitterionic catalysts coordinated by chiral tridentate ligands polymerize the achiral acetylene monomer to afford polymers showing intense CD signals, which indicates that the polymers adopt predominantly one-handed helical conformations.



Chapter 5 describes the molecular weight effect on the helix conformation of the substituted acetylenes. A well-defined living polymerization catalyst, [(nbd)Rh{C(Ph)=CPh₂}(PPh₃)]/PPh₃, produces a series of amino acid based poly(phenylacetylene) derivatives with a wide range of molecular weights ($M_n = 1,500\text{--}128,800$) and small PDIs. The chiroptical properties of the polymers strongly depend on their molecular weights, which are analyzed by CD and UV-vis spectroscopies.



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Part I

Development of Novel Rhodium Catalyst System for the Polymerization of Substituted Acetylenes

Chapter 1

Polymerization of Phenylacetylenes with Rh Zwitterionic Complexes: Enhanced Catalytic Activity by π -Acidic Diene Ligand

Abstract: Zwitterionic Rh catalysts bearing a series of tetrafluorobenzobarrelene (tfb) ligands proved to be highly active in the polymerization of phenylacetylenes. The highest catalytic activity for the polymerization of phenylacetylene was observed with $(\text{tfb})\text{Rh}^+[(\eta^6\text{-Ph})\text{B}^-\text{Ph}_3]$ (**1**). Catalyst **1** displayed higher activity to produce higher molecular weight polymer than the conventional nbd analogue, $(\text{nbd})\text{Rh}^+[(\eta^6\text{-Ph})\text{B}^-\text{Ph}_3]$ (**5**, nbd = 2,5-norbornadiene). In the case of other zwitterionic Rh catalysts bearing polymethylated tfb ligands [tfb-Me_2 : **2**, tfb-Me_3 : **3**, tfb-Me_4 : **4**], the catalytic activity tended to decrease with increasing number of the incorporated methyl groups. Catalyst **1** also showed high activity in the polymerization of phenylacetylene derivatives irrespective of electron-donating or -withdrawing nature of ring-substituents of the monomers.

Introduction

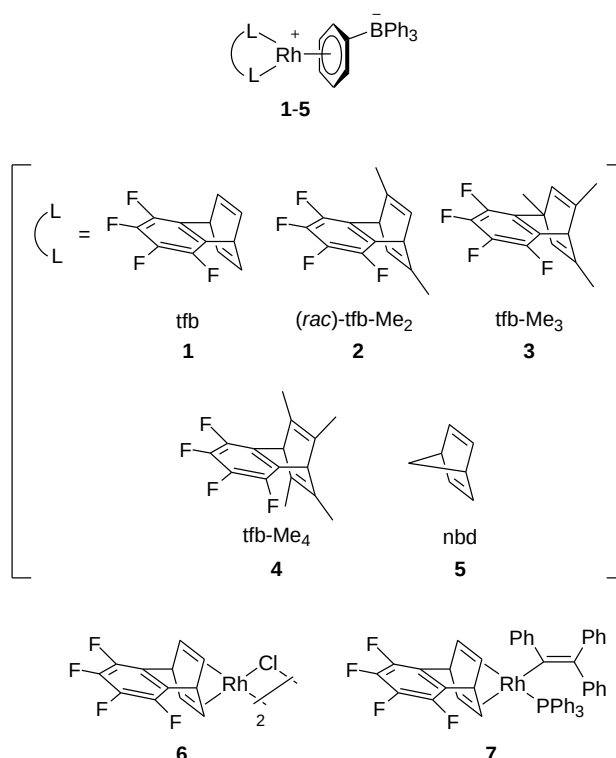
Substituted polyacetylenes are now recognized as interesting materials that exhibit functions such as non-linear optics, photo- and electroluminescence, high gas permeability, and helical conformation.¹⁻³ These unique features are mainly based on their stiff polyene main chain and can be tuned by the kind of side groups. These polymers can be obtained by the polymerization of corresponding acetylenic monomers using group 4–10 transition metal catalysts.^{1,2} Rh complexes are one of the most effective catalysts,^{2,4} particularly for the polymerization of monosubstituted acetylenes including phenylacetylene,⁵⁻⁹ *tert*-butylacetylene,^{10,11} *N*-propargylamide,¹²⁻¹⁶ and propiolic esters.¹⁷⁻²² Polymerization with Rh catalysts proceeds smoothly even in polar solvents²⁰⁻³¹ in addition to their high tolerance toward polar functional groups in the monomer.²³⁻²⁸ Further, Rh catalysts generally produce highly stereoregular polymers with cis-transoidal main-chain conformation.^{5,6}

Two types of complexes, $[(\text{diene})\text{RhCl}]_2$ ⁷ and $(\text{diene})\text{Rh}^+[(\eta^6\text{-Ph})\text{B}^-\text{Ph}_3]$,^{11,32} have often been used as highly active catalysts for the polymerization of monosubstituted acetylenes. These catalysts are categorized as ill-defined ones, because the initiation and propagation mechanisms of the polymerization thereby are not simple and have not been completely elucidated. However, even after the development of well-defined Rh catalysts such as $[(\text{nbd})\text{Rh}(\text{C}\equiv\text{CPh})(\text{PPh}_3)_2]/\text{DMAP}$ [nbd = 2,5-norbornadiene, DMAP =

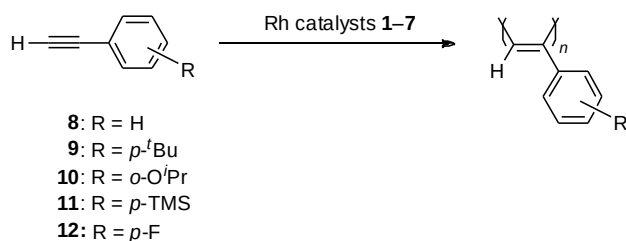
4-(dimethylamino)pyridine],^{33,34} [(nbd)Rh(OMe)]₂/PPh₃/DMAP,³⁵ and [(nbd)RhCl]₂/LiC(Ph)=CPh₂/PPh₃,^{36–40} which accomplish living polymerization, the ill-defined catalysts have an advantage of easy access. All the catalysts discussed above possess a bidentate diene ligand, which are in most cases nbd or 1,5-cyclooctadiene. Our group has recently reported that a highly π -acidic diene, tetrafluorobenzobarrelene (tfb), forms analogous complexes in place of the conventional nbd ligand and remarkably enhances the catalytic activity of Rh complexes in the polymerization of substituted acetylenes.^{41,42} For instance, [(tfb)RhCl]₂ affords a quantitative yield of poly(phenylacetylene) with even higher molecular weight than the nbd analogue.⁴¹ Further, a well-defined vinyl Rh complex, [(tfb)Rh{C(Ph)=CPh₂}(PPh₃)], has proved to achieve both high catalytic activity and the smallest polydispersity of 1.03 in the polymerization of phenylacetylene,⁴² whereas the corresponding nbd vinyl complex, [(nbd)Rh{C(Ph)=CPh₂}(PAr₃)] (Ar = *p*-XC₆H₄), does not.^{43,44}

One of the conventional Rh catalysts, (nbd)Rh⁺[(η^6 -Ph)B⁻Ph₃], show different catalytic behavior from that of [(nbd)RhCl]₂.¹⁰ Although this zwitterionic catalyst is active for a wider range of acetylenic monomers, there have been only limited examples¹¹ of replacing the diene ligand to examine the catalyst activity. These facts prompted us to examine a series of π -acidic tfb ligands in the zwitterionic Rh catalyst in order to enhance their activity. In the present paper, we report highly active zwitterion-type Rh catalysts containing tfb for the polymerization of phenylacetylene derivatives.

Chart 1. Structures of Rh Catalysts **1–7**



Scheme 1. Polymerization of Phenylacetylene and its Derivatives **8–12** with Rh Catalysts **1–7**



Experimental Section

Instruments. Monomer conversions were determined by GC [Shimadzu GC-14B, capillary column (CBP10-M25-025)]; column temperature: 125 °C (monomers **8**, **10**, and **12**) or 170 °C (monomers **9** and **11**); injection temperature 250 °C; internal standard *tert*-butylbenzene. 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 with a JASCO PU-980/ RI-930 chromatograph; 40 °C, eluent THF, columns KF-805 (Shodex) $\times$ 3, molecular weight limit up to 4×10^6 , flow rate 1 mL/min; calibrated with polystyrene standards. ^1H NMR spectra (400 MHz) were recorded on a JEOL EX-400 spectrometer with chemical shifts referenced to an internal standard, CD_2Cl_2 (5.32 ppm). ^{13}C NMR spectra (100 MHz) were observed on a JEOL ECX-400 spectrometer with chemical shifts referenced to the solvent used [CD_2Cl_2 , 53.8 ppm]. In the ^{13}C NMR of complexes **1**, **3**, and **4** shown below, a few peaks could not be clearly detected because of their multiplicity caused by F, B, and Rh atoms, which are to be assigned to the bridging aromatic carbons of tfb ligand and ipso carbon of $\eta^6\text{-C}_6\text{H}_5\text{B}$ moiety. Thus partial data of ^{13}C NMR spectra except for these unclear parts are listed for each complex. ^{19}F NMR spectra (373 MHz) were observed on a JEOL ECX-400 spectrometer with CFCl_3 as an external standard (0 ppm). Elemental analyses were performed at the Microanalytical Center of Kyoto University.

Materials. Monomer **8** was purchased (Aldrich) and distilled over CaH_2 under reduced pressure before use. The metal complexes of $(\text{nbd})\text{Rh}^+[(\eta^6\text{-Ph})\text{B}^-\text{Ph}_3]$ (**5**),^{11,33} $[(\text{tfb})\text{RhCl}]_2$ (**6**),⁴¹ $[(\text{tfb})\text{Rh}\{\text{C}(\text{Ph})=\text{CPh}_2\}(\text{PPh}_3)]$ (**7**),⁴² $[(\text{C}_2\text{H}_4)\text{RhCl}]_2$,⁴⁵ $[(\text{tfb-Me}_3)\text{RhCl}]_2$,⁴⁶ and $[(\text{tfb-Me}_4)\text{RhCl}]_2$ ⁴⁶ were prepared according to the reported methods. $(\text{rac})\text{-Tfb-Me}_2$,⁴⁷ and monomer **10**⁴⁸ were also prepared following the methods reported in the literature. Monomers **9** (Wako), **11** (NOF), **12** (Wako) and NaBPh_4 (Aldrich) were purchased and used without further

purification. Solvents were distilled by standard procedures.

(tfb)Rh⁺[(η^6 -Ph)B⁻Ph₃] (1). A Schlenk tube was charged with [(tfb)RhCl]₂ (54.0 mg, 0.074 mmol) and NaBPh₄ (66.2 mg, 0.193 mmol) and filled with the argon gas, to which CH₂Cl₂ (7.5 mL) was added. The mixture was stirred at room temperature for 1 h. Then the solvent was removed in *vacuo*, and the formed white residue was washed with methanol (3 mL $\times$ 3 times). The resulting grayish white solid was dried in *vacuo*. Yield: 57.6 mg (60%). ¹H NMR (CD₂Cl₂) δ : 7.38 [d, 6H, ³J = 7.3 Hz, BPh₃ (*ortho*)], 7.18 [vt, 6H, J = 7.3 Hz, BPh₃ (*meta*)], 7.04 [t, 3H, ³J = 7.3 Hz, BPh₃ (*para*)], 6.80 [d, 2H, ³J = 6.1 Hz, η^6 -Ph (*ortho*)], 6.74 [t, 1H, ³J = 6.2 Hz, η^6 -Ph (*para*)], 6.30 [vt, 2H, J = 6.3 Hz, η^6 -Ph (*meta*)], 4.89 (brs, 2H, bridgehead CH), 3.62 (m, 4H, *sp*²-CH). ¹³C NMR (partial data, in CD₂Cl₂) δ : 159.8 (m, *ipso* C of Ph₃B), 140.6 (dm, J = 246 Hz, C-F of tfb), 139.6 (dm, J = 250 Hz, C-F of tfb), 135.8 (BPh₃), 126.7 (BPh₃), 123.8 [BPh₃ (*para*)], 109.7 (d, ¹J_{C-Rh} = 3.8 Hz, η^6 -Ph), 101.4 (d, ¹J_{C-Rh} = 2.9 Hz, η^6 -Ph), 101.0 [d, ¹J_{C-Rh} = 2.9 Hz η^6 -Ph (*para*)], 43.3 (d, ¹J_{C-Rh} = 9.5 Hz, *sp*²-C of tfb), 36.2 (d, ²J_{C-Rh} = 1.9 Hz, bridgehead). ¹⁹F NMR (CDCl₃) δ : -146.5 (d, 2F, J_{F-Rh} = 22.8 Hz), -158.9 (s, 2F). Anal. Calcd. for C₃₆H₂₆BF₄Rh: C, 66.70%; H, 4.04%. Found: C, 66.93%; H, 3.95%.

((rac)-tfb-Me₂)Rh⁺[(η^6 -Ph)B⁻Ph₃] (2). The precursor, [((rac)-tfb-Me₂)RhCl]₂, of complex 2 was synthesized according to the following procedure: a solution of (*rac*)-tfb-Me₂ (166 mg, 0.65 mmol) and [(C₂H₄)₂RhCl]₂ (118 mg, 0.30 mmol) in CH₂Cl₂ (21 mL) was stirred at room temperature for 3 h. After removing the solvent in *vacuo*, the yellow

residue was washed with Et₂O (4.0 mL x 3). The resulting yellow solid was dried in vacuo. Yield 211 mg (89%). The ¹H NMR spectrum of an isolated mixture of diastereomers (CDCl₃) δ: 5.27 (brs, 4H, bridgehead CH), 3.38 (m, 4H, *sp*²-CH), 1.54 (s, 6H, CH₃), 1.45, (s, 6H, CH₃). Anal. Calcd. for C₂₈H₂₀Cl₂F₈Rh₂: C, 42.83%; H, 2.57%. Found: C, 42.69%; H, 2.71%. When a solution of NaBPh₄ (68.4 mg, 0.20 mmol) in methanol (7.0 mL) was added to a solution of [((*rac*)-tfb-Me₂)RhCl]₂ (71.3 mg, 0.09 mmol) in CH₂Cl₂ (2.0 mL), an off-white solid immediately precipitated. After 1 h, the solvent was removed in *vacuo*, and the white residue was washed with methanol (3 mL × 3 times). The resulting off-white solid was dried in *vacuo* to afford product **2**. Yield: 120 mg (98%). ¹H NMR (CD₂Cl₂) δ: 7.43 [d, 6H, ³*J* = 7.1 Hz, BPh₃ (*ortho*)], 7.20 [vt, 6H, *J* = 7.4 Hz, BPh₃ (*meta*)], 7.05 [t, 3H, ³*J* = 7.2 Hz, BPh₃ (*para*)], 6.95 (d, 1H, ³*J* = 6.6 Hz, *η*⁶-Ph), 6.91 (t, 1H, ³*J* = 6.3 Hz, *η*⁶-Ph), 6.57 (t, 1H, ³*J* = 6.4 Hz, *η*⁶-Ph), 6.26 (d, 1H, ³*J* = 6.4 Hz, *η*⁶-Ph), 5.59 (t, 1H, ³*J* = 6.3 Hz, *η*⁶-Ph), 4.65 (d, 2H, *J* = 5.8 Hz, bridgehead CH), 3.44 (m, 2H, *sp*²-CH), 1.42 (s, 6H, Me). ¹³C NMR (partial data, in CD₂Cl₂) δ: 159.6 (m, *ipso* C of Ph₃B), 135.9 (BPh₃), 126.7 (BPh₃), 126.3 (m, bridging C_{Ar} of tfb), 123.8 [BPh₃ (*para*)], 115.6 (*η*⁶-Ph), 108.8 (*η*⁶-Ph), 104.0 (*η*⁶-Ph), 102.3 (*η*⁶-Ph), 96.3 (*η*⁶-Ph), 62.5 (¹*J*_{Rh-C} = 9.53 Hz, C=C-H of tfb), 44.5 (¹*J*_{Rh-C} = 10.5 Hz, C=C-CH₃), 42.9 (bridgehead), 22.8 (CH₃). ¹⁹F NMR (CDCl₃) δ: -145.6 (d, 2F, *J*_{F-Rh} = 22.7 Hz), -157.0 (d, 2F, *J*_{F-Rh} = 22.8 Hz). Anal. Calcd. for C₃₈H₃₀BF₄Rh: C, 67.48%; H, 4.47%. Found: C, 67.27%; H, 4.55%.

(tfb-Me₃)Rh⁺[(*η*⁶-Ph)B⁻Ph₃] (3). Complex **3** was synthesized

according to the same method as that of **2** except for a prolonged reaction time of 4 h. Yield: 57.8mg (83%). The NMR spectral data agreed with the one reported before.⁴⁹

(tfb-Me₄)Rh⁺[(η^6 -Ph)B⁻Ph₃] (4**).** Complex **4** was synthesized according to the same method as for **2** except the reaction time of 13 h. Yield: 54.5 mg (79%). ¹H NMR (CD₂Cl₂) δ : 7.32 [d, 6H, ³J = 6.8 Hz, BPh₃ (*ortho*)], 7.18 [vt, 6H, J = 6.9 Hz, BPh₃ (*meta*)], 7.05 [t, 3H, ³J = 6.9 Hz, BPh₃ (*para*)], 6.85 [t, 1H, ³J = 6.0 Hz, η^6 -Ph (*para*)], 6.53 [d, 2H, ³J = 6.1 Hz, η^6 -Ph (*ortho*)], 6.00 [vt, 2H, J = 6.0 Hz, η^6 -Ph (*meta*)], 4.61 (s, 2H, bridgehead CH), 1.43 (s, 12H, Me). ¹³C NMR (partial data, in CD₂Cl₂) δ : 159.6 (m, *ipso* C of Ph₃B), 140.0 (dm, J = 251 Hz, C-F of tfb), 139.6 (dm, J = 259 Hz, C-F of tfb), 136.2 (BPh₃), 126.6 (BPh₃), 125.3 (m, bridging C_{Ar} of tfb), 123.8 [BPh₃ (*para*)], 109.3 (br s, η^6 -Ph), 105.7 [br s, η^6 -Ph (*para*)], 103.1 (br s, η^6 -Ph), 59.7 (d, ¹J_{C-Rh} = 11.4 Hz, *sp*²-C), 50.8 (d, ¹J_{C-Rh} = 2.9 Hz, bridgehead), 20.3 (CH₃). ¹⁹F NMR (CDCl₃) δ : -145.9 (s, 2F), -156.5 (d, 2F, J_{F-Rh} = 22.7 Hz). Anal. Calcd. for C₄₀H₃₄BF₄Rh: C, 68.20%; H, 4.87%. Found: C, 68.14%; H, 4.92%.

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 was as follows: A THF solution of phenylacetylene (**8**) (*c* = 1.0 M) was added to a catalyst solution ([Rh] = 2.0 mM). Polymerization was carried out at 30 °C for 24 h, and the formed polymer was isolated by precipitation in a large amount of methanol including a drop of acetic acid, filtered with a PTFE membrane filter, and

dried under vacuum to constant weight.

Supplementary information

Table S1. Crystallographic Data and Collection Parameters for **1–5**

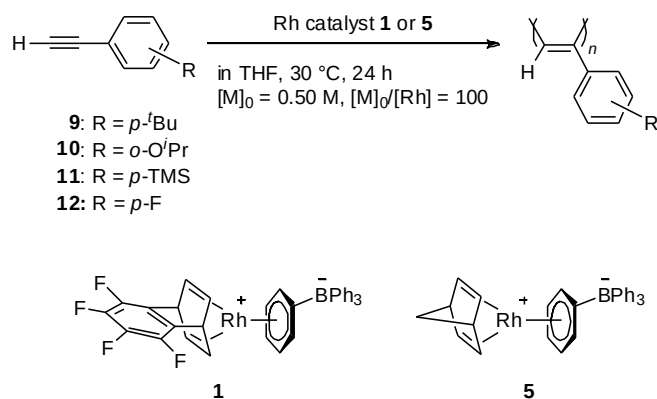
	1	3	4	5
Formula	C ₃₆ H ₂₆ BF ₄ Rh·C 4H ₈ O	(C ₃₉ H ₃₂ BF ₄ Rh) ₂ ·C H ₂ Cl ₂	C ₄₀ H ₃₄ BF ₄ Rh	C ₃₁ H ₂₈ BRh·CH ₂ Cl ₂
mol wt.	720.42	1465.71	704.42	599.21
crystal system	triclinic	triclinic	triclinic	monoclinic
space group	P-1	P-1	P-1	P2 ₁ /n
<i>a</i> , Å	10.066(6)	10.738(3)	10.267(6)	10.3734(8)
<i>b</i> , Å	11.586(6)	17.678(5)	11.174(7)	9.5048(7)
<i>c</i> , Å	13.911(8)	18.571(5)	15.202(10)	27.270(3)
α , deg	73.261(15)	70.184(7)	101.382(5)	90.0000
β , deg	85.706(19)	80.176(11)	106.071(8)	93.498(5)
γ , deg	89.60(2)	81.192(11)	97.165(7)	90.0000
<i>V</i> , Å ³	1549.0(15)	3250.4(16)	1612.8(18)	2683.7(4)
<i>Z</i>	2	2	2	4
<i>D</i> _{calc} , g cm ⁻³	1.544	1.497	1.450	1.483
<i>F</i> (000)	736.00	1492.00	720.00	1224.00
cryst dimens, mm	0.20 × 0.20 × 0.20	0.20 × 0.05 × 0.05	0.20 × 0.05 × 0.05	0.20 × 0.10 × 0.05
temp, °C	-130	-130	-130	-130
radiation	Mo K α (0.71070)	Mo K α (0.71070)	Mo K α (0.71070)	Mo K α (0.71070)
theta range, deg	3.1 to 27.6	3.1 to 27.5	3.0 to 27.4	3.0 to 27.5
μ , mm ⁻¹	0.608	0.658	0.580	0.854
reflections	11380	23833	11766	19419
independent reflections	11380 (R(int) = 0.031)	23833 (R(int) = 0.043)	11766 (R(int) = 0.050)	19419 (R(int) = 0.059)
<i>R</i> _f	0.0340	0.0570	0.0663	0.0732
<i>R</i> _w	0.0398	0.0498	0.0720	0.0798
GOF	1.062	1.134	1.039	1.090

Table S2. Selected Bond Distances (Å) for Rh Complexes of **1**, **3**, **4**, and **5**

	1	3^a	4	5
Rh(1)-C(1)	2.3801(19)	2.405(3)	2.425(4)	2.365(3)
Rh(1)-C(2)	2.244(2)	2.280(2)	2.288(4)	2.226(3)
Rh(1)-C(3)	2.285(2)	2.302(3)	2.309(5)	2.293(4)
Rh(1)-C(4)	2.294(2)	2.301(3)	2.323(5)	2.306(3)
Rh(1)-C(5)	2.238(2)	2.292(2)	2.262(4)	2.249(3)
Rh(1)-C(6)	2.3048(19)	2.358(3)	2.311(3)	2.311(3)
Rh(1)-Ctr(1-6) ^b	1.805	1.844	1.842	1.807
Rh(1)-C(25)	2.1325(18)	2.138(2)	2.134(4)	2.112(4)
Rh(1)-C(26)	2.124(2)	2.133(2)	2.149(5)	2.112(3)
Rh(1)-Ctr(25,26) ^c	2.010	2.016	2.021	1.993
Rh(1)-C(28)	2.128(2)	2.134(2)	2.130(5)	2.119(4)
Rh(1)-C(29)	2.130(2)	2.134(3)	2.132(5)	2.149(4)
Rh(1)-Ctr(28,29) ^d	2.011	2.013	2.012	2.017

^a selected among two molecules of **3** in a cell. ^b center of a benzene ring composed of C(1)-C(6). ^c center of C(25) and C(26). ^d center of C(28) and C(29).

Table S3. Polymerization of Phenylacetylene Derivatives **9–12** with Rh Catalysts **1** and **5**^a



entry	monomer	catalyst	conv. ^b (%)	polymer		
				yield ^c (%)	M_n^d	M_w/M_n^d
1	9	1	100	93	58,000	1.8
2	9	5	100	89	35,000	2.8
3	10	1	100	93	8,100	1.9
4	10	5	100	53	3,500	2.0
5	11	1	100	81	150,000	1.2
6	11	5	100	88	193,000	1.6
7	12	1	100	94	40,000	2.0
8	12	5	100	84	29,000	2.0

^a Conditions: for 24 h, in THF, 30 °C, $[M]_0 = 0.50 \text{ M}$, $[M]_0/[Rh] = 100$. ^b Determined by GC (*tert*-butylbenzene] = 50 mM as an internal standard of GC). ^c MeOH-insoluble part. ^d Estimated by GPC (PSt standard).

Results

Structures of 1-4. Rh zwitterionic complexes, **1**, **2**, and **4**, bearing a series of tfb ligands were newly synthesized by the reaction of [(diene)RhCl]₂ complexes with NaBPh₄. A longer reaction time was required in the case of the tetra-methylated tfb ligand (tfb-Me₄). All the formed complexes including the reported **3** were stable in the solid state even under air, but gradually decomposed in solutions. Chlorination of these catalysts regenerated the starting Cl-bridging dimers, [(diene)RhCl]₂ in CDCl₃ solution. The solid-state structures of **1**, **3**, **4**, and **5** were confirmed by single crystal X-ray analysis (Figures 1–4 and Tables S1 and S2 in Experimental Section). All the complexes possessed basically the same structure where the Rh(I) atom is ligated by a chelating diene and η^6 -Ph of BPh₄. Because the ¹H NMR spectra of **1–4** displayed symmetric olefinic and methyl protons of tfb ligands, the coordinating phenyl group of BPh₄ is assumed to rotate around the center of the phenyl ring when the complexes are in solution. Unfortunately, the formation of high quality crystals of **2** was unsuccessful. However, its structure was reasonably identified by the ¹H and ¹⁹F NMR spectra under comparison with those of the other complexes. The precursor, [((*rac*)-tfb-Me₂)RhCl]₂, of **2**, should consist of diastereomers, namely, a mixture of (*R,R*)- and (*R,R*)-tfb-Me₂, (*S,S*)- and (*S,S*)-tfb-Me₂, and (*R,R*)- and (*S,S*)-tfb-Me₂. The ¹H NMR spectrum of **2** showed only a singlet peak assigned to two of symmetric methyl groups, indicating that **2** was obtained in a racemic form.

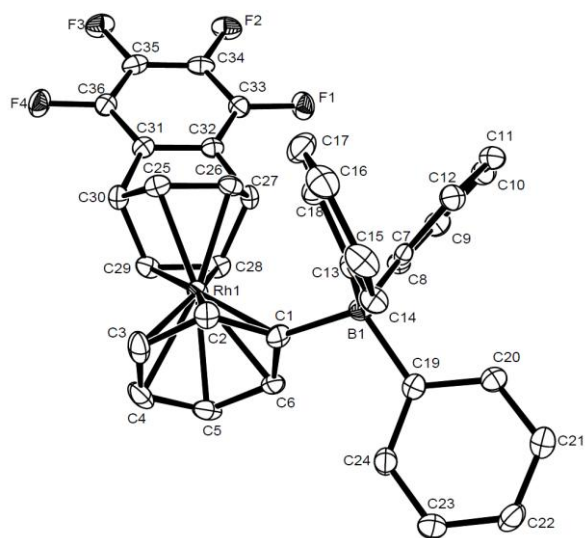


Figure 1. ORTEP view of **1** (50% probability ellipsoids).

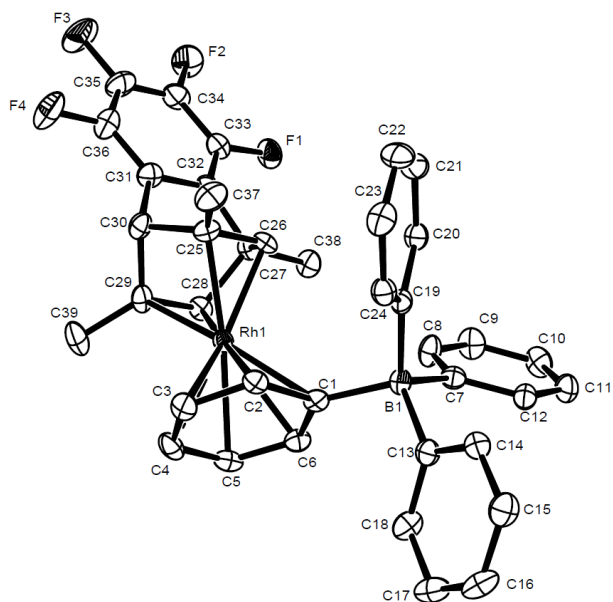


Figure 2. ORTEP view of **3** (50% probability ellipsoids).

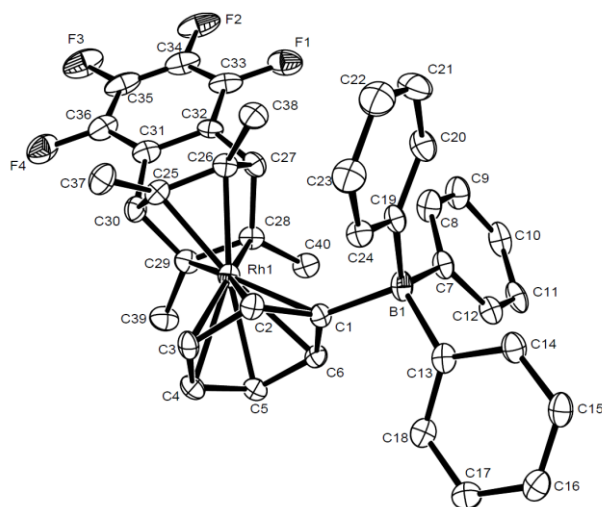


Figure 3. ORTEP view of **4** (50% probability ellipsoids).

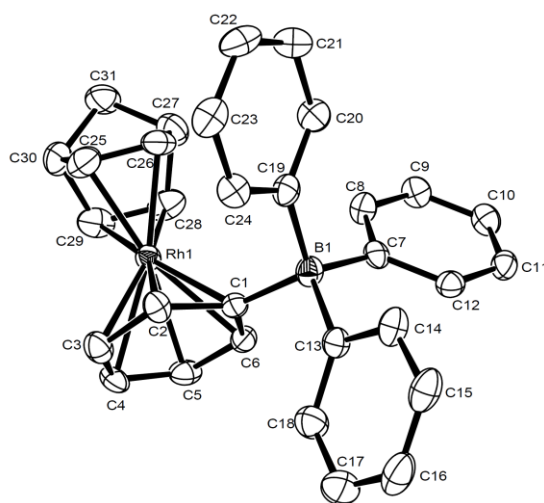


Figure 4. ORTEP view of **5** (50% probability ellipsoids).

Catalytic Activity of 1–4 in the Polymerization of 8. The polymerization of **8** was carried out using catalysts **1–4** in THF at 30 °C for 24 h. Table 1 summarizes the results along with those of previously reported catalysts, namely (nbd)Rh⁺[(η^6 -Ph)B⁻Ph₃] (**5**), [(tfb)RhCl]₂ (**6**),

and [(tfb)Rh{C(Ph)=CPh₂}(PPh₃)] (**7**) for comparison. Among **1–4**, catalyst **1** displayed the highest activity to quantitatively provide poly(**8**) with the highest molecular weight ($M_n = 180,000$). As the number of methyl groups on tfb increased, the catalytic activity tended to decrease with respect to both polymer yield and molecular weight. Thus, di- and trimethyl tfb catalysts, **2** and **3**, exhibited diminished polymerization rate and relatively lower molecular weights, and further tetra-methylated tfb catalyst **4** showed a quite low activity. These results suggest that the presence of methyl groups in tfb ligand sterically depress the coordination of monomer to the Rh active center. Further, the electron-donating effect of methyl groups is not negligible, and increases the electron density of the Rh atom to reduce the opportunity of monomer coordination.

While the conventional zwitterionic nbd catalyst **5** is one of the most active catalysts in the polymerization of **8**, it is noteworthy that the new tfb catalyst **1** displayed even higher performance with respect to both yield and molecular weight of polymer. Catalyst **1** also achieved a higher polymer yield than did the dimer-type Rh complex having tfb, **6**, although catalyst **6** had been reported to show very high activity in the polymerization of **8**.⁴² This finding agrees with the previous result that the zwitterionic Rh nbd complex is catalytically more active than the Rh dimer counterpart.¹⁰ As compared to the vinyl bearing catalyst **7**,⁴¹ catalyst **1** has produced a higher molecular weight polymer. This can be explained by the living nature and higher initiation efficiency of **7**.

Table 1. Polymerization of **8** with Rh Catalysts **1–7**^a

catalyst	conversion ^b	polymer		
		yield ^c (%)	M_n^d	M_w/M_n^d
1	100	100	180,000	1.8
2	100	91	56,000	2.7
3	100	85	55,000	1.7
4 ^e	22	5	2,600	1.3
5	100	79	158,000	1.8
6 ^f	100	79	205,000	1.9
7	100	100	41,000	1.1

^a In THF, 30 °C, 24 h, $[M]_0 = 0.50$ M, $[M]_0/[Rh] = 500$. ^b Determined by GC (*tert*-butylbenzene] = 50 mM as an internal standard of GC). ^c MeOH-insoluble part. ^d Estimated by GPC (PSt standard). ^e For 4 days. ^f $[NEt_3]/[Rh] = 10$.

Time Profiles of Polymerization of 8 with 1 and 5–7. To further study the catalytic behavior of new zwitterionic tfb catalyst **1**, the time courses of polymerization of **8** with **1** and conventional catalysts **5–7** were monitored by GC. Comparison of monomer consumption rates clearly displays the difference of activity of catalysts shown above. Here we define a catalyst that requires less time for quantitative consumption of monomer as a highly active one. The same polymerization conditions were employed as for Table 1 except for the temperature of 0 °C; the low

temperature was adopted to observe the polymerization rate clearly (Figure 5). Tfb catalyst **1** needed ca. 40 min to completely polymerize **8**, while nbd catalyst **5** took approximately 110 min, which indicates that the former catalyst is more active than the latter. This should be due to the strong back-donation of a tfb ligand as discussed in previous papers.^{41,42} Catalyst **6** could not achieve quantitative consumption of the monomer under the given conditions; i.e., 12% of monomer **8** remained even after 120 min. Thus the tfb zwitterionic catalyst **1** displayed higher catalytic activity than the tfb dimer catalyst **6**. With living polymerization catalyst **7**, polymerization proceeded rapidly at an early stage of polymerization, but it sharply slowed down, and consequently the complete monomer consumption took a longer time than with **1**.

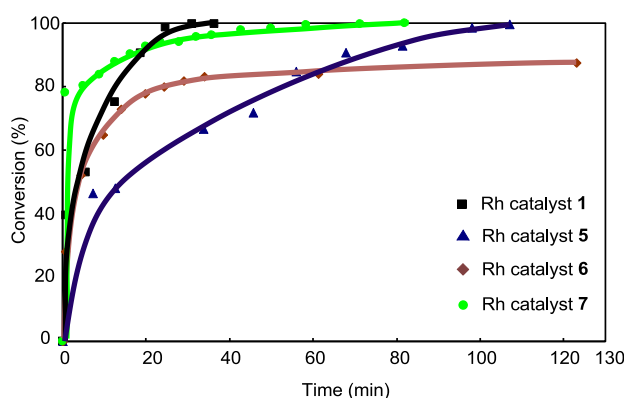


Figure 5. Time-conversion curves for the polymerization of monomer **8** with Rh catalysts **1** and **5–7** (conditions: in THF, 0 °C, $[M]_0 = 0.50$ M, $[M]_0/[Rh] = 500$).

Polymerization of Phenylacetylene Derivatives. Catalyst **1** also demonstrated excellent activity for the polymerization of ring-substituted phenylacetylenes, **9–12**, as shown in Figure 6. Monomers **9** and **10**, containing electron-donating *p*-*tert*-butyl and *o*-isopropoxy groups respectively, polymerized faster with **1** than with conventional **5**. Another electron-donating substituent, trimethylsilyl group (TMS), dramatically enhanced the polymerizability of monomer, as seen from the finding that the polymerization of **11** was completed in less than 1 min with both **1** and **5** and too fast to follow. Catalyst **1** displayed high activity also for monomer **12**, bearing an electron-withdrawing fluorine atom. These results show that catalyst **1** is applicable to a wide range of phenylacetylene monomers.

After completion of the polymerization judged from the time-conversion curve (Figure 6), the polymers produced from monomers **9–12** were isolated by precipitation from a large amount of methanol. The formed polymers were subjected to GPC measurements, and the data obtained are summarized in Table 2 (see also Table S3 in the Experimental Section, where polymerizations of monomers **9–12** were carried out without GC measurements to obtain the data of polymer yield). The polymers obtained with **1** tended to have higher molecular weights and the polymerizations were completed in shorter times compared to the case of catalyst **5** except for monomer **11**. This suggests that the propagation reaction is basically accelerated by the coordination of a strong π -acid, tfb, to the Rh metal. Monomer **11** did not follow this tendency, but catalyst **5**

is still quite active to complete the monomer conversion in less than 1 minute to give a result comparable to catalyst **1**.

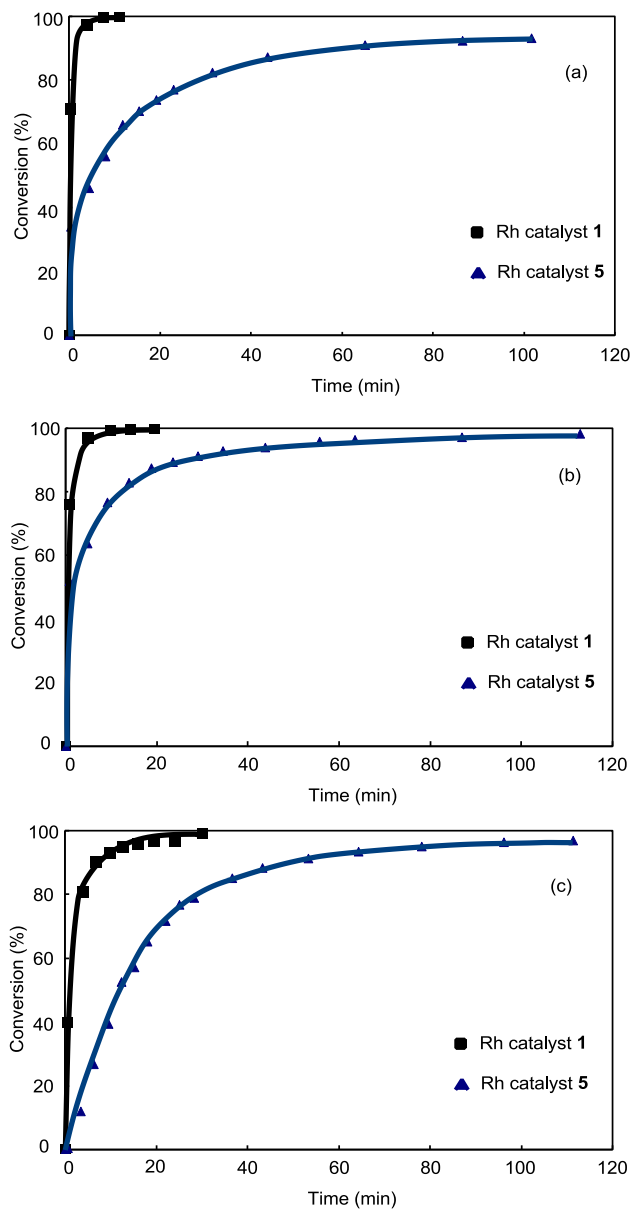


Figure 6. Time-conversion curves for the polymerization of monomers **9**, **10**, and **12** with Rh catalysts **1** and **5** (conditions; (a): monomer **9**, $[M]_0 = 0.50$ M, $[M]_0/[Rh] = 500$, 30 °C. (b): monomer **10**, $[M]_0 = 0.50$ M, $[M]_0/[Rh] = 100$, 30 °C. (c): monomer **12**, $[M]_0 = 0.50$ M, $[M]_0/[Rh] = 500$, 30 °C.)

Table 2. Polymerization of Phenylacetylene Derivatives **9–12** with Rh Catalysts **1** and **5**^a

entry	catalyst	monomer	time (min)	conv. ^c (%)	polymer ^b	
					M_n	M_w/M_n
1	1	9	16	100	63,000	3.1
2	5	9	126	94	41,000	2.8
3 ^d	1	10	24	100	13,000	2.4
4 ^d	5	10	180	99	7,000	2.2
5	1	11	5	100	74,000	3.1
6	5	11	5	100	121,000	4.4
7	1	12	35	100	31,000	2.4
8	5	12	116	96	26,000	2.4

^a Conditions: in THF, 30 °C, $[M]_0 = 0.50$ M, $[M]_0/[Rh] = 500$. ^b Estimated by GPC (PSt standard) with the isolated polymer after the completion of polymerization confirmed by GC. ^c Determined by GC (*tert*-butylbenzene] = 50 mM as an internal standard of GC). ^d Conditions: in THF, 30 °C, $[M]_0 = 0.50$ M, $[M]_0/[Rh] = 100$.

Discussion

The effect of tfb ligand has already been discussed in our recent papers for the polymerization of **8** using $[(\text{tfb})\text{RhCl}]_2$ ⁴¹ and $[(\text{tfb})\text{Rh}\{\text{C}(\text{Ph})=\text{CPh}_2\}(\text{PPh}_3)]$ ⁴² as catalysts. The very low energy level of LUMO of tfb has proved to lead to its strong π -acidity. This makes the

metal center of active species more electrophilic and, in turn, the monomer coordination easier. No significant difference in the solid-state structures of **1** and **5** was found according to X-ray analysis, suggesting that even a slight difference of electron density of Rh center is sufficient to enhance the catalyst activity.

Introduction of methyl groups on tfb apparently diminished the catalytic activity. The X-ray analysis of **3** and **4** showed the elongated coordination bonds between the Rh center and the olefins (Rh1–C25, –C26, –C28, and –C29 in Figures 1–4; see also Table S1 in the Experimental Section) and between the Rh center and η^6 -Ph (Rh1–C1~C6 in Figures 1–4; see also Table S1 in Experimental Section). Further, the BPh₃ moiety got more repelled as the number of methyl groups increased (Rh1-C1-B1 angles: 136.75° for **3** (Figure 2), 137.73° for **4** (Figure 3), while 135.60° for **1** (Figure 1) and 136.60° for **5** (Figure 4); see also Table S1 in Experimental Section). This steric repulsion seems to accelerate the dissociation of a coordinating η^6 -Ph group of borate to produce an active propagating species, which is supported by calculated initiation efficiencies (IEs) of catalysts. It appears that more methyl groups introduced in tfb ligand will lead to the increase of catalyst IE. For instance, the IE of non-methylated tfb complex **1** was calculated to be only 28%, while those of the other catalysts, **2-4**, were in a range of 83 to 98%.⁵⁰ Thus the sterically bulkier tfb should accelerate the dissociation of a coordinating aromatic ring of borate, leading to efficient formation of the propagating species.

It is also apparent that the propagation rate is also considerably affected by the numbers of methyl groups on tfb. As seen in Table 1, non-methylated catalyst **1** achieves larger molecular weight and higher yield of the polymer than methylated catalysts, **2–4**, in the same polymerization time. This indicates that the presence of methyls will suppress coordination of monomer to the Rh center and/or insertion of monomer to the Rh-C bond. The difference of propagation rates between tfb complex **1** and nbd complex **5** is explicable in terms of the inductive effect, because the X-ray structures of both complexes do not have any significant differences. Although it has not been revealed which rates of monomer coordination and insertion will be more affected by the inductive effect, further investigation of mechanistic aspects will elucidate the details of this catalytic system in the polymerization of acetylenic compounds.

In conclusion, we have developed a very active catalyst for the polymerization of phenylacetylenes by ligating a strong π -acid, tfb, to a zwitterionic Rh complex. Compared to conventional catalysts $[(\text{tfb})\text{RhCl}]_2$ (**6**) and $[(\text{nbd})\text{Rh}^+(\eta^6\text{-Ph})\text{B}^-\text{Ph}_3]$ (**5**), the new zwitterionic catalyst **1** features high activity and unnecessary of additional cocatalysts.

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50. $IE = M_{\text{theor}}/M_n$, where $M_{\text{theor}} = [\text{monomer}]_0/[\text{catalyst}] \times$
 $MW_{\text{phenylacetylene}} \times \text{polymer yield (using the data in Table 1)}$

Chapter 2

Living Polymerization of Phenylacetylenes Catalyzed by Cationic Rhodium Complexes Bearing Tetrafluorobenzobarrelene

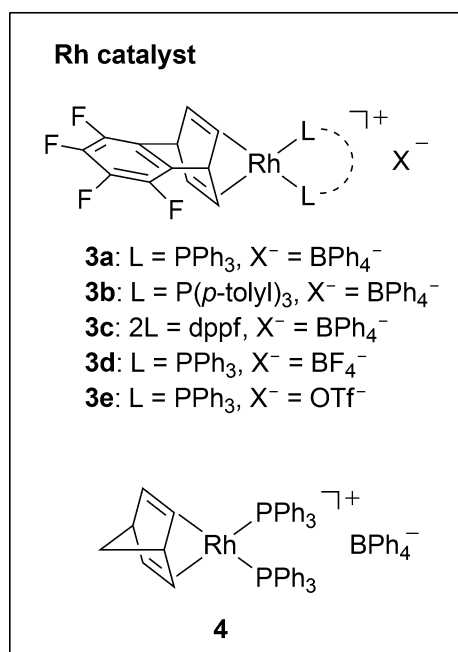
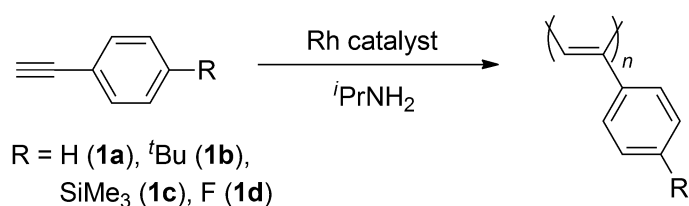
Abstract: Binary catalysts composed of cationic Rh complexes, $[(\text{tfb})\text{Rh}(\text{L})_2]\text{X}$ (tfb: tetrafluorobenzobarrelene, L: phosphine ligand, X: counter anion), and $^i\text{PrNH}_2$ induced living polymerization of phenylacetylene and its ring-substituted derivatives. For instance, $[(\text{tfb})\text{Rh}(\text{PPh}_3)_2]\text{BPh}_4$ in conjunction with $^i\text{PrNH}_2$ polymerized phenylacetylene in a living fashion to give poly(phenylacetylene) with narrow molecular weight distribution (M_w/M_n 1.09) quantitatively. The living nature was confirmed by kinetic plots of the polymerization. NMR studies revealed that $^i\text{PrNH}_2$ serves to dissociate the coordinating PPh_3 ligand of $[(\text{tfb})\text{Rh}(\text{L})_2]\text{X}$ to form an initiating species. Block copolymers were synthesized by the sequential polymerization of different phenylacetylenes using the present catalyst.

Introduction

Substituted polyacetylenes exhibit interesting properties and functions including photoconductivity, electroluminescence, stimuli responsiveness, gas permeability, and helical conformation,¹⁻⁵ which are mainly based on their conjugated and stiff main chain structure. A great deal of effort has been made to develop new active catalysts effective to a wide range of acetylenic monomers and precisely controlled polymerization. In the last decade, rhodium (Rh) catalysts have been commonly used for the synthesis of stereoregular polymers from monosubstituted acetylenes such as phenylacetylene (**1a**),⁶⁻⁷ propiolic esters,⁸ and *N*-propargylamides.⁹ Some of Rh catalysts have been found to achieve living polymerization of monosubstituted acetylenes. The first example of Rh-catalyzed living polymerization of **1a** was reported by Kishimoto et al., using two catalyst systems, namely $[(nbd)Rh(C\equiv CPh)(PPh_3)_2]/DMAP$ (nbd: 2,5-norbornadiene, DMAP: 4-dimethylaminopyridine)^{10,11} and $[(nbd)Rh(\mu-OMe)]_2/PPh_3/DMAP$.¹² Another catalyst system for living polymerization, $[(nbd)Rh(\mu-OMe)]_2/1,4\text{-bis(diphenylphosphino)butane}$, was proposed by Falcon et al.¹³ Our group reported a ternary catalyst, $[(nbd)RhCl]_2/PPh_3/LiC(Ph)=CPh_2$.¹⁴ A presumed active initiator, $[(nbd)Rh\{C(Ph)=CPh_2\}\{P(C_6H_4\text{-}p\text{-}F)_3\}]$, can be isolated from the ternary system and accomplish living polymerization of **1a** with virtually quantitative initiation efficiency (IE). The living catalyst is also applicable to the living-like polymerization of *N*-propargylamides.^{15,16} Thus far we have exploited a new class of active Rh catalysts bearing a

highly π -acidic diene ligand, tetrafluorobenzobarrelene (tfb).¹⁷⁻²¹ These tfb-bearing Rh catalysts feature higher activity in the polymerization of phenylacetylene-type monomers than the conventional Rh catalysts bearing nbd. For instance, the polymerization of **1a** catalyzed by a zwitterionic tfb-Rh complex, (tfb)Rh⁺[(η^6 -Ph)B⁻Ph₃] (**2**), proceeds much faster than that with the corresponding nbd analogue, (nbd)Rh⁺[(η^6 -Ph)B⁻Ph₃].¹⁹ In the course of further study on the tfb-Rh catalysts, we have recently found that a cationic Rh complex having two triphenylphosphine ligands, [(tfb)Rh(PPh₃)₂]BPh₄ (**3a**), in conjunction with amines polymerizes monomer **1a** in a living manner, as briefly reported in a communication.²⁹

Scheme 1. Polymerization of **1a–d** with Rh catalysts/*i*PrNH₂.



The present article is a full paper dealing with detailed investigation of the living polymerization of **1a** and its ring-substituted derivatives with cationic tfb-Rh catalysts including **3a** (Scheme 1).

Experimental

Instruments. Monomer conversions were determined by GC [Shimadzu GC-14B, capillary column (CBP10-M25-025)]; column temperature 125 °C, injection temperature 250 °C, internal standard *tert*-butylbenzene. The number- and weight-average molecular weights (M_n and M_w , respectively) and molecular weight distribution (MWD, M_w/M_n) of polymers were measured by GPC with a JASCO PU-980/RI-930 chromatograph; 40 °C, eluent THF, columns KF-805 (Shodex) $\times$ 3, molecular weight limit up to 4×10^6 , flow rate 1 mL/min; calibrated with polystyrene standards. ^1H (400 MHz), ^{13}C (100 MHz), ^{19}F (373 MHz), ^{31}P (160 MHz) NMR spectra were all recorded on a JEOL ECX-400 spectrometer with chemical shifts referenced to an internal standards CH_2Cl_2 (5.32 ppm, for ^1H NMR), CD_2Cl_2 (53.0 ppm, for ^{13}C NMR), and external standards $\text{P}(\text{OMe})_3$ (140 ppm, for ^{31}P NMR), CFCl_3 (0 ppm for, ^{19}F NMR). High resolution mass spectra were measured on a JEOL JMS-HX110A mass spectrometer (cationic complexes **3c–e** exhibited mass peaks consistent with their cationic moieties). Elemental analyses were performed at the Microanalytical Center of Kyoto University.

Materials. Phenylacetylene (**1a**) was purchased (Aldrich) and distilled over CaH_2 under reduced pressure before use. The metal complexes of

$(\text{tfb})\text{Rh}^+[(\eta^6\text{-Ph})\text{B}^-\text{Ph}_3]$ (**2**),¹⁹ $[(\text{tfb})\text{Rh}(\text{PPh}_3)_2]\text{BPh}_4$ (**3a**),²⁰
 $[(\text{tfb})\text{Rh}\{\text{P}(p\text{-tolyl})_3\}_2]\text{BPh}_4$ (**3b**),²² and $[(\text{nbd})\text{Rh}(\text{PPh}_3)_2]\text{BPh}_4$ (**4**)²³ were
 synthesized according to the literature. NaBPh_4 (Aldrich), PPh_3 (Aldrich),
 AgBF_4 (Wako), AgOTf (Wako), **1b** (Wako), **1c** (NOF), and **1d** (Wako) were
 purchased and used without further purification. Solvents were distilled
 by the standard procedures. $i\text{PrNH}_2$ and
 N,N,N',N' -tetramethylethylenediamine were purified by distillation over
 CaH_2 .

$[(\text{tfb})\text{Rh}(\text{dppf})]\text{BPh}_4$ (3c**).** A Schlenk tube equipped with a three-way
 stopcock was charged with $(\text{tfb})\text{Rh}^+[(\eta^6\text{-Ph})\text{B}^-\text{Ph}_3]$ (50 mg, 0.077 mmol)
 and dppf [1,1'-bis(diphenylphosphino)ferrocene, 45 mg, 0.080 mmol] and
 filled with argon gas, to which CH_2Cl_2 (7.5 mL) was added. After the
 mixture was stirred at room temperature overnight, the solvent was
 removed under reduced pressure, and the formed orange powder was
 purified by recrystallization from $\text{CH}_2\text{Cl}_2/\text{Et}_2\text{O}$. The obtained solid was
 dried in *vacuo*. Yield: 71 mg (77%). ^1H NMR (CD_2Cl_2) δ : 7.72 (m, 8H),
 7.59 (m, 12H), 7.32 (m, 8H), 7.01 (m, 8H), 6.86 (m, 4H), 5.65 (brs, 2H,
 bridgehead CH), 4.44 (br, 4H, Cp), 4.37 (brs, 4H, Cp), 4.18 (m, 4H,
 $sp^2\text{-CH}$). ^{13}C NMR (CD_2Cl_2) δ : 164.1 (q, $^1J_{\text{C-B}} = 49.6$ Hz, *ipso* C of BPh_4),
 140.6 (dm, $J = 256$ Hz, C-F of tfb), 139.0 (dm, $J = 248$ Hz, C-F of tfb),
 136.0 (Ph), 133.4 (Ph), 132.1 (Ph), 130.6 (Ph), 129.6 (Ph), 126.9 (m, *ipso* C
 of tfb), 125.6 (Ph), 121.7 (Ph), 83.2 (s, $sp^2\text{-C}$ of tfb), 75.6 (m, $\alpha\text{-C}$ of Cp),
 74.4 (s, $\beta\text{-C}$ of Cp), 72.2 (m, *ipso* C of Cp), 42.8 (s, bridgehead of tfb). ^{19}F
 NMR (CD_2Cl_2) δ : -145.8 (d, 2F, $J = 21.2$ Hz C-F of tfb), -158.0 (d, 2F, $J =$

21.6 Hz, C-F of tfb). ^{31}P NMR (CD_2Cl_2) δ : 27.7 (d, $J_{\text{Rh-P}} = 163$ Hz). HRMS (FAB) Calcd for $\text{C}_{46}\text{H}_{34}\text{F}_4\text{FeP}_2\text{Rh}$ (m/z): 883.0476, Found: 883.0474.

[(tfb)Rh(PPh₃)₂]BF₄ (3d). A Schlenk tube equipped with a three-way stopcock was charged with [(tfb)RhCl]₂ (30 mg, 0.041 mmol), PPh₃ (45 mg, 0.17 mmol), and AgBF₄ (18 mg, 0.092 mmol) and filled with argon gas, to which CH₂Cl₂ (4.0 mL) was added. After the mixture was stirred at room temperature for 5 h, the produced silver salt was removed by filtration. The solvent was removed from the filtrate under reduced pressure to afford orange powder. The formed solid was washed with Et₂O (2 mL $\times$ 3 times) and then dried in *vacuo*. Yield: 73.5 mg (95%). ^1H NMR (CD_2Cl_2) δ : 7.58–7.31 (m, 30H), 5.87 (brs, 2H, bridgehead CH), 4.32 (m, 4H, sp^2 -CH). ^{13}C NMR (CD_2Cl_2) δ : 140.5 (dm, $J = 241$ Hz, C-F of tfb), 138.9 (dm, $J = 254$ Hz, C-F of tfb), 133.8 [PPh₃(*ortho*)], 131.4 [PPh₃(*para*)], 129.6 [PPh₃(*ipso*)], 129.2 [PPh₃(*meta*)], 126.9 (m, bridging C_{Ar} of tfb), 83.0 (s, sp^2 -C of tfb), 42.6 (s, bridgehead CH of tfb). ^{19}F NMR (CD_2Cl_2) δ : –145.6 (d, 2F, $J = 22.7$ Hz, C-F of tfb), –152.3 (s, 4F, BF₄), –158.2 (d, 2F, $J = 22.7$ Hz, C-F of tfb). ^{31}P NMR (CD_2Cl_2) δ : 28.7 (d, $J_{\text{Rh-P}} = 156$ Hz). HRMS (FAB) Calcd for $\text{C}_{48}\text{H}_{36}\text{F}_4\text{P}_2\text{Rh}$ (m/z): 853.1283, Found: 853.1270.

[(tfb)Rh(PPh₃)₂]OTf (3e). Catalyst **3e** was prepared by the same method as for **3d** by using AgOTf (23 mg, 0.090 mmol) instead of AgBF₄. Yield: 80 mg (97%). ^1H NMR (CD_2Cl_2) δ : 7.43–7.31 (m, 30H), 5.86 (brs, 2H, bridgehead CH), 4.31 (brs, 4H, sp^2 -CH). ^{13}C NMR (CD_2Cl_2) δ : 140.5 (dm, $J = 245$ Hz, C-F of tfb), 138.9 (dm, $J = 257$ Hz, C-F of tfb), 133.8

[PPh₃(*ortho*)], 131.4 [PPh₃(*para*)], 129.4 [PPh₃(*ipso*)], 129.2 [PPh₃(*meta*)], 127.0 (m, bridging C_{Ar} of tfb), 121.2 (q, ¹J_{C-F} = 321.2 Hz, CF₃), 83.0 (s, sp²-C of tfb), 42.6 (s, bridgehead CH of tfb). ¹⁹F NMR (CD₂Cl₂) δ: 78.3 (s, 3F, OTf), -145.6 (d, 2F, J = 22.7 Hz, C-F of tfb), -158.2 (d, 2F, J = 22.7 Hz, C-F of tfb). ³¹P NMR (CD₂Cl₂) δ: 28.6 (d, J_{Rh-P} = 157 Hz). HRMS (FAB) Calcd for C₄₈H₃₆F₄P₂Rh (m/z): 853.1283, Found: 853.1274. Anal. Calcd. for C₄₉H₃₆F₇O₃P₂RhS: C, 58.69%; H, 3.62%. Found C, 58.43%; H, 4.03%.

Polymerization. All the polymerizations of **1a–d** were carried out under an argon atmosphere in a Schlenk tube equipped with a three-way stopcock (for polymerization conditions, see, e.g., caption *a* in Table 1). A THF solution of **1a–d** was added to an Rh catalyst solution of the same volume in the Schlenk tube. The polymerization solution was stirred at 30 °C for 24 h, and the formed polymer was isolated by precipitation in a large amount of methanol including a drop of acetic acid, filtered with a PTFE membrane, and dried under vacuum to constant weight.

Multistage Polymerization. Three stage polymerization of **1a** with catalyst **3a** and ^{*i*}PrNH₂ were performed in the following experiment. The first stage polymerization was started by the addition of a **1a** (0.22 mL, 2.0 mmol) solution in THF (2.0 mL) to a solution of Rh catalyst **3a** (9.4 mg, 8.0 μmol) with ^{*i*}PrNH₂ (6.9 μL, 80 μmol) in THF (2.0 mL), which was kept at 30 °C during polymerization. After confirming the completion of the first-stage by GC, a part (1.0 mL) of the polymerization solution was taken out and poured into methanol to precipitate the polymer as orange solid.

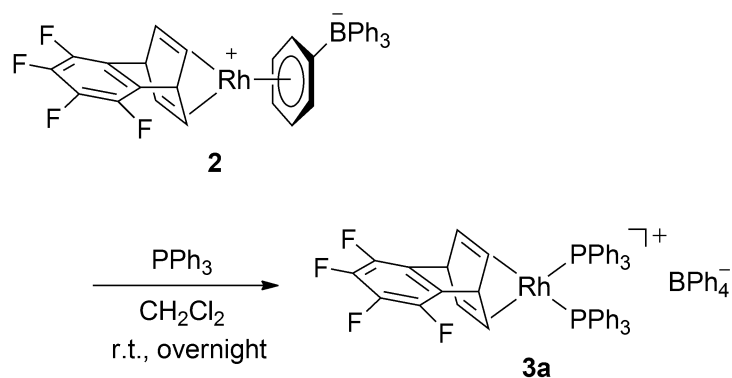
Then the second feed of **1a** (0.16 mL, 1.5 mmol) was added to the remaining polymerization solution. After complete consumption of **1a** in the second stage, an aliquot of the polymerization solution (1.0 mL) was taken out and poured into a large amount of methanol to isolate the polymer. To the remaining polymerization solution, the third feed of **1a** (0.11 mL, 1.0 mmol) was added and monitored by GC until the end of polymerization. Then the polymerization solution was poured into methanol to isolate the polymer formed at the last stage. Each of the obtained poly(**1a**)s were subjected to GPC measurement to give their M_n and M_w/M_n .

Block Copolymerization. Monomer **1a** was firstly polymerized in THF for 60 min using catalyst **3a** and $i\text{PrNH}_2$. After the completion of monomer consumption was confirmed by GC, an aliquot was taken out to isolate the formed poly(**1a**) from excess MeOH, which is subjected to GPC measurement. Then, an equimolar amount of monomer **1b** or **1c** to monomer **1a** was added to the remaining polymerization solution, and the resulting solution was further stirred for 60 min (polymerization conditions: in THF, 30 °C; $[\text{monomer}]_0 = [\text{monomer}]_{\text{added}} = 0.50 \text{ M}$, $[\text{monomer}]_0/[\text{Rh}] = 250$, $[i\text{PrNH}_2]/[\text{Rh}] = 10$). The formed block copolymers were isolated in a manner similar to the homopolymer of **1a**.

Results and Discussion

Our recent paper demonstrated that a zwitterionic Rh catalyst **2** is very active for polymerization of **1a** to give poly(**1a**) with high molecular weight (M_n 180,000) (conditions: in THF, 30 °C, 24 h, $[\mathbf{1a}]_0 = 0.50$ M, $[\mathbf{1a}]_0/[\mathbf{2}] = 500$).¹⁹ However, the obtained polymer showed rather broad MWD (M_w/M_n 1.80), suggesting non-living character of the catalytic system. Relatively well-controlled polymerization was achieved by a cationic complex **3a**, derived from **2** (Scheme 2), which afforded poly(**1a**) with lower molecular weight (M_n 54,000) and somewhat narrower MWD (M_w/M_n 1.40) under the same polymerization conditions (Table 1, Entry 1). Besides, the addition of amines such as Et_3N , Et_2NH , $n\text{BuNH}_2$, $i\text{PrNH}_2$, and pyridine to the polymerization system with **3a** was found to reduce the MWD of the formed poly(**1a**) ($M_w/M_n < 1.23$). The narrowest MWD (M_w/M_n 1.09) with M_n of 100,000 of poly(**1a**) was accomplished by the combination of **3a** and 10 equivalents of $i\text{PrNH}_2$ (Table 1, Entry 2).²⁰ The ^1H NMR confirmed that the formed poly(**1a**) with M_w/M_n of 1.09 possessed highly stereoregular cis-transoidal structure (cis content = 97%) in the main

Scheme 2. Synthesis of the cationic Rh catalyst **3a** by the reaction of **2** with PPh_3 .



chain as the case of other Rh catalysts.⁷

The monomer consumption rate in the polymerization of **1a** with catalyst **3a** and *i*PrNH₂ was monitored (Figure 1). The polymerization proceeded in first order with respect to monomer concentration, indicating a bimolecular reaction between monomer **1a** and the propagating end. The line was found not to pass the origin, implying that some complicated steps requiring monomer **1a** may be included in the formation of initiating species at early stage of the polymerization.

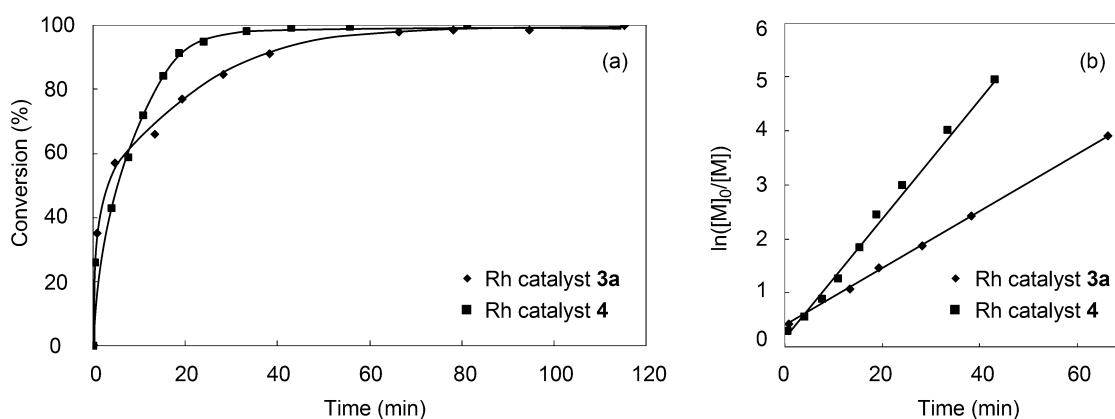


Figure 1. (a) Time-conversion curves and (b) first-order plots for the polymerization of **1a** with Rh catalyst **3a** (♦) or **4** (■) in conjunction with *i*PrNH₂ (conditions: in THF, 30 °C, [**1a**]₀ = 0.50 M, [**1a**]₀/[Rh] = 500, [*i*PrNH₂]/[Rh] = 10).

The living nature of the polymerization of **1a** by the current binary catalyst, **3a**/*i*PrNH₂, was also confirmed by the multistage polymerization. In the employed three stage polymerization of **1a** (conditions, in THF, 30 °C, [*i*PrNH₂]/[Rh] = 10, [**1a**]₀/[Rh] = 250, and [**1a**]₀ = [**1a**]_{add} = 0.50 M), monomer **1a** was completely consumed at the end of each stage, confirmed

by GC analyses. The second and third stages were then started by supplying **1a** to the polymerization solution. The M_n of the produced polymers increased in proportion to the consumption of monomer [M_n = 55,000 (1st stage), 119,000 (2nd), and 168,000 (3rd)], while MWDs

Table 1. Polymerization of **1a** with a series of cationic Rh catalysts **3a–e** and **4**.^a

Entry	Cat	[ⁱ PrNH ₂]/[Rh]	Conv. ^b (%)	Polymer			
				Yield ^c (%)	M_n^d	M_w/M_n^d	IE ^e (%)
1	3a	0	100	95	54,000	1.40	90
2	3a	10	100	100	100,000	1.09	51
3	4	0	100	96	146,000	1.72	34
4	4	10	100	98	116,000	1.30	43
5	3b	0	100	100	202,000	1.31	25
6	3b	10	100	100	210,000	1.15	24
7	3c	0	100	100	996,000	1.58	5
8	3c	10	100	100	961,000	1.59	5
9	3d	0	100	100	600,000	2.07	9
10	3d	10	100	100	195,000	1.14	26
11	3e	0	100	100	550,000	2.22	9
12	3e	10	100	100	174,000	1.10	29

^a In THF, 30 °C, 24 h, [**1a**]₀ = 0.50 M, [**1a**]₀/[Rh] = 500. ^b Determined by GC ([*tert*-butylbenzene] = 50 mM as an internal standard of GC). ^c MeOH-insoluble part. ^d Estimated by GPC (PSt standard). ^e Catalyst initiation efficiency.¹⁹

remained in a range of small value [$M_w/M_n = 1.23$ (1st stage), 1.13 (2nd), 1.17 (3rd)].

It is of interest to compare the catalytic activity of **3a** with that of an analogous cationic complex bearing nbd, **4** (Scheme 1). It has been reported that the highly π -acidic tfb ligand is preferable for high turnover in the propagation reaction of **1a**^{17,19} and even for the synthesis of high molecular weight living poly(**1a**).¹⁸ Results for the polymerization of **1a** with **3a** and **4** are displayed in Figure 1 and Table 1, Entries 1–4. Both **3a** and **4** were active for the polymerization of **1a** irrespective of the presence and absence of *i*PrNH₂. Interestingly, the rate of monomer consumption with nbd-Rh catalyst **4** was faster than that with tfb-Rh catalyst **3a**. It is the opposite tendency to the results using the other type of catalysts such as [(diene)RhCl]₂ and zwitterionic Rh complexes.^{17,19} The MWDs of the polymers obtained with **3a** were narrower than those with **4** regardless of the presence or absence of *i*PrNH₂.

A series of cationic Rh catalysts **3b–e** (Scheme 1) were investigated for the polymerization of **1a** (Entries 5–12, Table 1). For seeing effect of phosphine ligand, the Rh catalysts, **3b** and **3c**, bearing more electron donative bulky monophosphine, P(*p*-tolyl)₃, and bidentate phosphine, dppf, were examined. Either with or without addition of *i*PrNH₂, catalyst **3b** gave similar results to those of **3a** with respect to the MWD of the formed polymers, although the molecular weights appreciably increased (Entries 5, 6). It suggests that the number of active species derived from **3b** is

smaller than that from **3a**. It is supported by the polymerization results using catalyst **3c** bearing a dppf ligand. The polymerization with catalyst **3c** resulted in even higher molecular weights of poly(**1a**)s regardless addition of $i\text{PrNH}_2$ (Entries 7, 8), probably because slow dissociation of the bidentate dppf led the formation of small number of active propagation species. With addition of $i\text{PrNH}_2$ to catalyst **3c**, no effect on the MWD of the obtained poly(**1a**) could be observed, suggesting that $i\text{PrNH}_2$ did not accelerate the dissociation of dppf from an Rh center by ligand exchange. These tendencies are consistent with the results of the calculated initiation efficiencies described in Table 1.

The effect of counter anion of the cationic Rh catalyst was investigated with catalysts **3d** and **3e**, having tetrafluoroborate and triflate as a counter anion, respectively. Both catalysts **3d** and **3e** without amine afforded poly(**1a**)s with much higher molecular weights and broad MWDs, more than 2.0 (Entries 9, 11). In both cases of **3d** and **3e**, addition of $i\text{PrNH}_2$ remarkably decreased the MWDs of the produced polymers (Entries 10, 12). However, the molecular weights of the polymers did not decrease as much as those of the **3a**-based polymer probably due to insufficient formation of active species from **3d** and **3e**. Thus, it can be said that the catalyst composed of **3a** and $i\text{PrNH}_2$ is the most appropriate for precise control of the polymerization among the catalyst examined.

Table 2. Effect of monomer/Rh and amine/Rh ratios on the polymerization of **1a** with **3a**/ⁱPrNH₂ catalyst.^a

Entry	[1a] ₀ /[Rh]	[ⁱ PrNH ₂]/[Rh]	Conv. ^b	Polymer			IE ^e
				Yield ^c	<i>M</i> _n ^d	<i>M</i> _w / <i>M</i> _n ^d	
1 ^f	500	10	100	100	100,00	1.09	51
2	250	10	100	100	60,000	1.11	43
3	500	10	100	98	110,00	1.10	45
4	1000	10	100	100	170,00	1.10	60
5	2000	10	100	100	310,00	1.19	66
6	4000	10	100	100	500,00	1.47	82
7	1000	1	100	100	200,00	1.15	51
8	1000	100	100	100	200,00	1.12	51
9	1000	250	100	100	200,00	1.19	51
10	1000	500	100	100	192,00	1.23	53

^a In THF, 30 °C, 24 h. ^b Determined by GC ([*tert*-butylbenzene] = 50 mM as an internal standard of GC). ^c MeOH-insoluble part. ^d Estimated by GPC (PSt standard). ^e Catalyst initiation efficiency.^{19 f} [**1a**]₀ = 0.50 M.

The effect of monomer/Rh ratio ([**1a**]₀/[Rh]) on the polymerization was investigated by changing the catalyst concentration and keeping the monomer concentration at 0.25 M (Table 2). A monomer concentration of 0.25 M instead of 0.50 M was adopted to avoid the formation of insoluble high molecular weight polymers. It is noteworthy that the polymer molecular weight increased with higher monomer/Rh ratio, while the monomer conversion was invariably quantitative. The MWD remained smaller than 1.2 in the range of [**1a**]₀/[Rh] = 250–2,000, supporting the living nature of polymerization. Apparent catalyst initiation efficiencies

were calculated based on the molecular weights (M_n), monomer/Rh ratios, and yields of the formed polymers, which are displayed in Table 2. Admittedly, the IE tends to be improved with higher monomer/Rh ratio: the highest IE of 82% was achieved in the case of $[1a]_0/[Rh] = 4000$, although MWD went broad to 1.47. It suggests that the formation of active initiator requires incorporation of **1a** and the rate of the initiation reaction is slower than that of propagation.

The effect of amine/Rh ratio was also examined by changing the $[iPrNH_2]/[Rh]$ ratio from 1 to 500. As seen in Table 2, the M_w/M_n remained below 1.20 in a wide range of amine/Rh = 1–250. It is noted that even one equivalent of $iPrNH_2$ to the Rh catalyst is effective to some extent. On the other hand, a large excess of $iPrNH_2$ like 500 equivalents showed a slight adverse effect. Thus it is concluded that ten equivalents of amine is optimal to suppress the polydispersity.

In the specific polymerizations in Entries 4 and 5 of Table 2, the monomer conversion was again monitored by GC (Figure 2). It was confirmed that the polymerizations proceeded in first order with respect to monomer concentration at either $[1a]_0/[Rh]$ ratios of 1,000 or 2,000. Furthermore, these first order plots exactly passed the origin unlike the cases of Figure 1. This is probably because the amount of monomer **1a** required for the formation of initiating species is negligible at such high monomer/Rh ratios. Reducing the catalyst ratio to half (from 0.25 mM to 0.125 mM of $[Rh]$, Figure 2(a) and 2(b), respectively) did not result in the half rate of monomer consumption: only slightly lower rate was observed with the half

of catalyst concentration of 0.125 mM. It indicates that the IE increases with lower catalyst concentration, consistent with the results in Table 2, Entries 4 and 5.

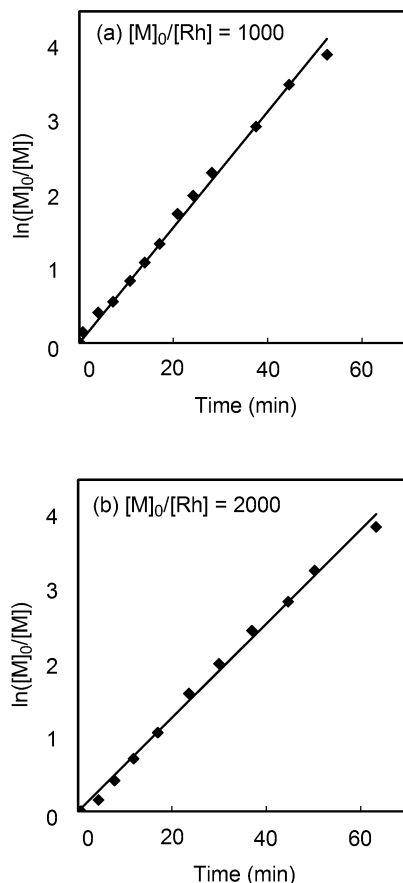


Figure 2. First-order plots for the polymerization of **1a** with **3a**/*i*PrNH₂ catalyst (conditions: (a) $[1a]_0 = 0.25$ M, $[1a]_0/[Rh] = 1000$, $[iPrNH_2]/[Rh] = 10$. (b) $[1a]_0 = 0.25$ M, $[1a]_0/[Rh] = 2000$, $[iPrNH_2]/[Rh] = 10$).

The present catalyst consisting of **3a** and *i*PrNH₂ also showed activity in other polymerization solvents than THF. For example, when the polymerization of **1a** was carried out in toluene under the same conditions as those of Entry 4, Table 2, practically the same results were obtained (in toluene: polymer yield 100%, M_n 170,000, M_w/M_n 1.10). On the other

hand, CH₂Cl₂ affected the polymerization in a different way; i.e., although the polymerization proceeded quantitatively, the polymer showed higher molecular weight (M_n 300,000) and a larger MWD (M_w/M_n 1.32), suggesting a lower IE.

The following NMR experiments elucidated a part of the roles of *i*PrNH₂ in the current living polymerization. In ³¹P NMR, complex **3a** showed a doublet at 29.6 ppm in CD₂Cl₂ [Figure 3(a)]. This doublet kept its narrow shape even in the presence of PPh₃ (1.1 equivalents) [Figure 3(b)], indicating slow ligand exchange between the coordinating and free PPh₃ in NMR time scale. With addition of *i*PrNH₂ (3 equivalents), however, both of the signals apparently became broad [Figure 3(c)]. With 10 equivalents of *i*PrNH₂, the two peaks almost coalesced [Figure 3(d)]. These results show that *i*PrNH₂ accelerates the ligands exchange between the coordinating and free PPh₃. A mixture of **3a** and *i*PrNH₂ (3 equivalents) with no addition of PPh₃ gave one broad peak at ca. 26 ppm and did not show any signal assignable to free PPh₃ [Figure 3(e)]. This is explained by fast exchanging between major coordinating PPh₃ of **3a** and minor dissociated PPh₃. Another supportive experimental results were given by mixing **3a** with a bidentate amine ligand, *N,N,N',N'*-tetramethylethylenediamine (TMEDA), which shows a broad peak at ca. -4 ppm assignable to free PPh₃ [Figure 3(f)].

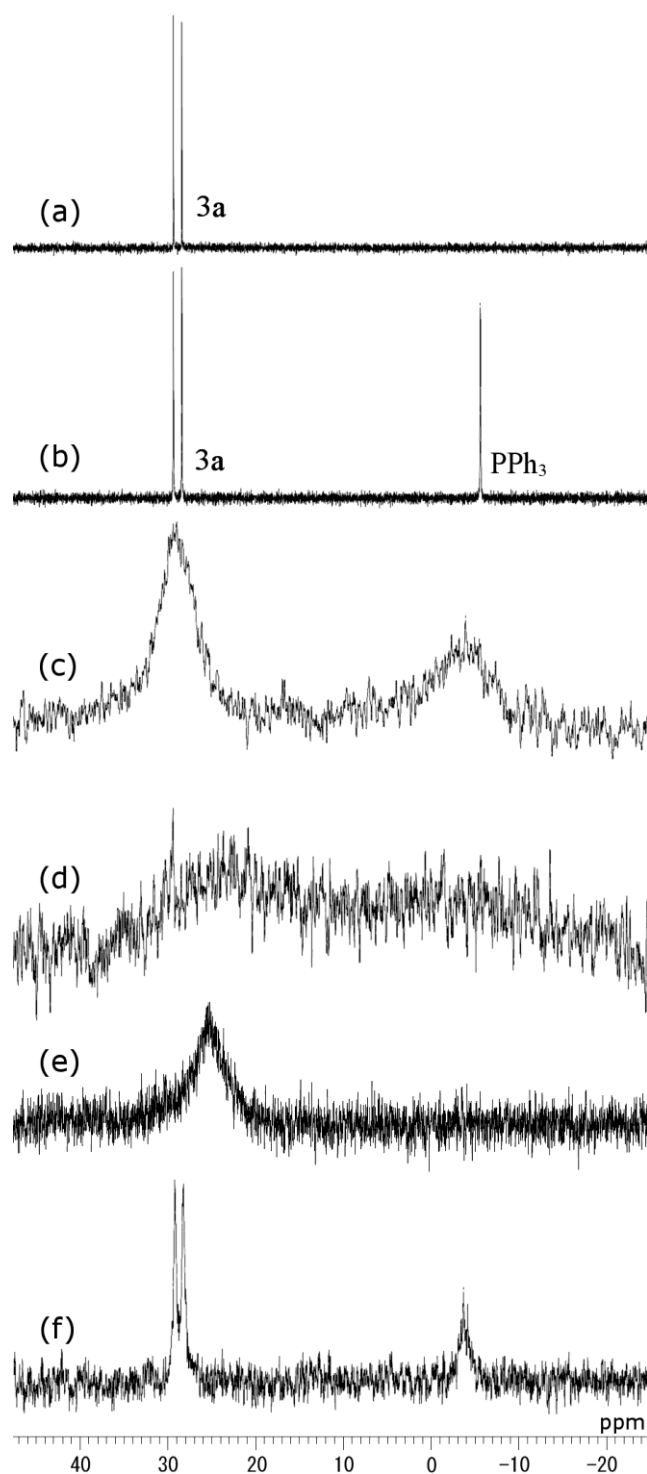
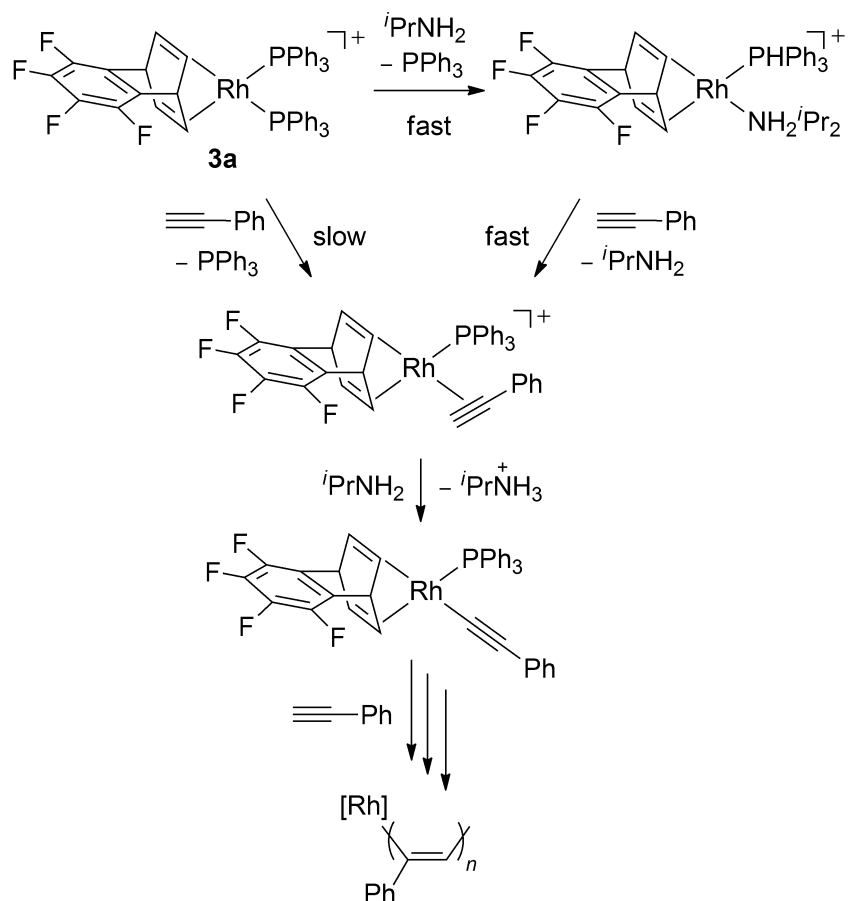


Figure 3. ^{31}P NMR spectra of (a) **3a**, (b) **3a** with PPh_3 (1.1 equiv), (c) **3a** with PPh_3 (1.1 equiv) and $i\text{PrNH}_2$ (3 equiv), (d) **3a** with PPh_3 (1.1 equiv) and $i\text{PrNH}_2$ (10 equiv), (e) **3a** with $i\text{PrNH}_2$ (3 equiv), and (f) **3a** with TMEDA (2 equiv) in CD_2Cl_2 .

Unfortunately, it was unable to identify the newly formed complex in the reaction of **3a** with $i\text{PrNH}_2$. The ^1H and ^{31}P NMR of the mixture of **3a** and $i\text{PrNH}_2$ in CD_2Cl_2 even at $-85\text{ }^\circ\text{C}$ did not give clear results to prove the formation of new Rh species, because the observed spectra at the low temperature remained almost unchanged from to the one at room temperature. From the mixture of **3a** and $i\text{PrNH}_2$ in CD_2Cl_2 , evaporation of all volatiles perfectly reproduced **3a**. A CD_2Cl_2 solution of the residue showed no other signal assignable to new species.

The results shown above indicate that $i\text{PrNH}_2$ promotes the dissociation of PPh_3 from **3a** with its weak coordination. Thus a certain amine complex like $[(\text{tfb})\text{Rh}(\text{PPh}_3)(\text{H}_2\text{N}^i\text{Pr})]^+$ may presumably be formed for a short time in the mixture of **3a** and $i\text{PrNH}_2$. Jimenéz et al. recently demonstrated that a cationic Rh complex bearing a phosphine-amine bidentate ligand, namely, $[\text{Rh}(\text{cod})\{\text{Ph}_2\text{P}(\text{CH}_2)_3\text{NMe}_2\}][\text{BF}_4]$, is active for polymerization of **1a**.²⁵ This complex forms a phenylethynyl-Rh initiating species by reaction with **1a** along with the formation of an ammonium moiety on the bidentate ligand. In the present living polymerization, the same experiment could not give the sufficient evidence for the formation of a similar alkynyl-Rh complex because of the instability of the new amine complex. Assuming the formation of the analogous amine-phosphine complex, $[(\text{tfb})\text{Rh}(\text{PPh}_3)(\text{H}_2\text{N}^i\text{Pr})]^+$, a possible mechanism of the polymerization was depicted in Scheme 3.

Scheme 3. Possible mechanism of the polymerization of **1a** with **3a**/*i*PrNH₂. The counter anions of the cationic Rh complexes were omitted for clarity.



To survey further application of **3a**/*i*PrNH₂ system, polymerizations of monomer **1b-d** (Scheme 1) were experimented and the polymerization results are summarized in Table 3. In the polymerization of **1b** bearing a *tert*-butyl group, the catalyst **3a** with *i*PrNH₂ showed excellent activity to afford the corresponding polymer in quantitative yield with high molecular weight of 190,000, but it exhibited relatively broad MWD (M_w/M_n 1.40) (Entry 2). Monomer **1c** bearing a trimethylsilyl group also polymerized

with the current living catalyst to give poly(**1c**) in excellent yield with high molecular weight of 200,000 (Entry 3). It is noteworthy that the produced poly(**1c**) showed even smaller MWD (M_w/M_n 1.13) than that of the poly(**1b**). It implies that even slight difference of electron donativity between *tert*-butyl and trimethylsilyl affect the control of polymerization with the current catalytic system and the trimethylsilyl-substituted **1c** is rather favored for well-controlling of the MWD. In the polymerization of **1d** having an electron withdrawing fluoro group, the monomer was unable to be sufficiently consumed in the given condition to afford only 37% yield of the corresponding polymer with broad MWD (M_w/M_n 1.70) (Entry 4). It appears that the electron-withdrawing substituent lowers the monomer reactivity and renders living polymerization difficult.

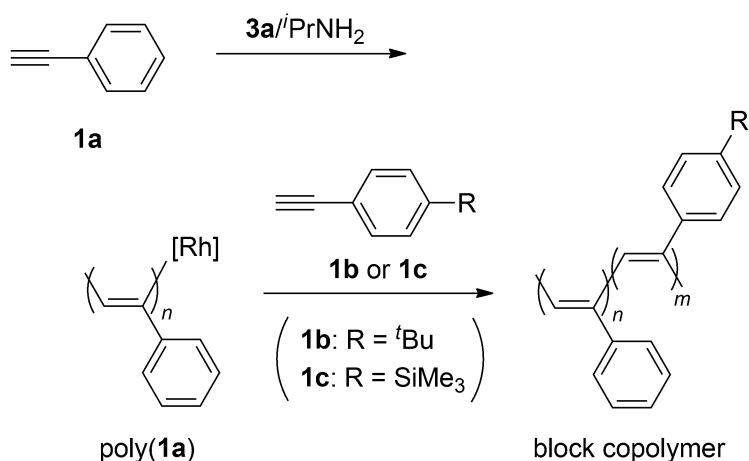
Table 3. Polymerization of monomers **1a–d** with **3a**/^{*i*}PrNH₂ catalyst.^a

Entry	Monomer	Conv. ^b (%)	Polymer		
			Yield ^c (%)	M_n^d	M_w/M_n^d
1	1a	100	100	100,000	1.09
2	1b	100	100	190,000	1.40
3	1c	100	100	200,000	1.13
4	1d	40	37	20,000	1.70

^a In THF, 30 °C, 24 h, [monomer]₀ = 0.50 M, [monomer]₀/[Rh] = 500, [^{*i*}PrNH₂]/[Rh] = 10. ^b Determined by GC ([*tert*-butylbenzene] = 50 mM as an internal standard of GC) ^c MeOH-insoluble part. ^d Estimated by GPC (PSt standard).

Block Copolymer Synthesis. The present catalyst, $3a/iPrNH_2$, was applied to the block copolymer synthesis by the sequential polymerization of **1a** and its derivative **1b** or **1c** (Scheme 4), which gave the corresponding block copolymers almost quantitatively. Figure 4(a) shows the GPC profiles of the first-stage homopolymer, poly(**1a**), and the second-stage block copolymer, poly(**1a**)-*block*-poly(**1b**). The first-stage polymer showed a unimodal GPC curve (M_n 69,000, M_w/M_n 1.10). The second-stage polymer also exhibited a unimodal peak in a higher molecular weight region (M_n 161,000, M_w/M_n 1.18), which is indicative of selective formation of the block copolymer. Poly(**1a**)-*block*-poly(**1c**) showed a GPC peak similar to that of poly(**1a**)-*block*-poly(**1b**), although a small shoulder was observed at the position of the first-stage poly(**1a**) [Figure 4(b)]. The ratios of the monomer units in the block copolymers were calculated from the peak area ratios of aromatic and either *tert*-butyl or trimethylsilyl protons in their 1H NMR spectra to be 1:1.14 (**1a:1b**) and 1:1.07 (**1a:1c**), respectively. These ratios are close to the supplied monomer ratio of 1:1.

Scheme 4. Synthesis of block copolymers with $3a/iPrNH_2$ catalyst.



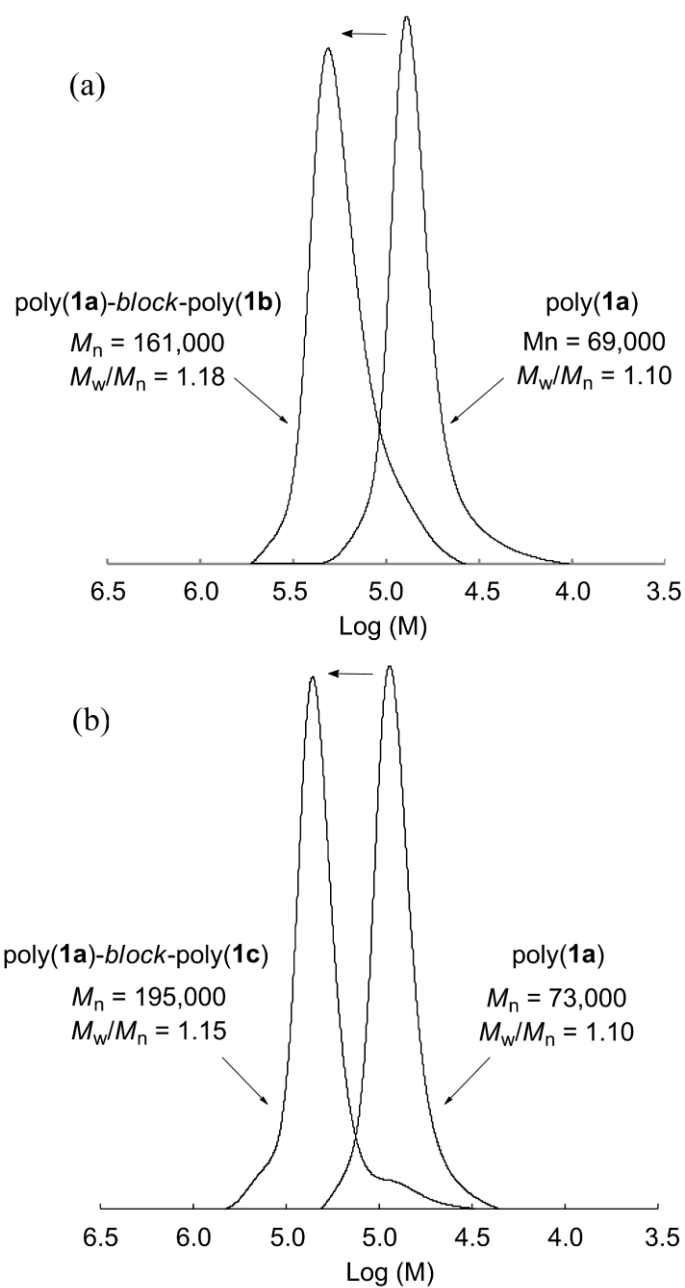


Figure 4. GPC charts (a) poly(**1a**) and poly(**1a**)-*block*-poly(**1b**) and (b) poly(**1a**) and poly(**1a**)-*block*-poly(**1c**).

Conclusions

A new binary catalyst consisting of $[(\text{tfb})\text{Rh}(\text{PPh}_3)_2]\text{BPh}_4$ (**3a**) and $i\text{PrNH}_2$ proved to achieve living polymerization of phenylacetylene-type monomers.

The present living polymerization is applicable to the syntheses of block copolymers composed of two types of phenylacetylene monomers. Further studies of the present Rh catalyst and living polymerization, especially the polymerization mechanism, are now in progress.

Acknowledgements

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Chapter 3

Polymerization of Phenylacetylenes by Novel Rhodium Catalyst Containing Norbornadiene Tethering Functional Group

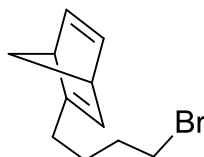
Abstract: Novel Rh catalysts, [nbd-(CH₂)₄-X]RhR, **1**: X = PPh₂, R = Cl; **2**: X = NPh₂, R = Cl; **3**: X = PPh₂, R = C(Ph)=CPh₂ (nbd = 2,5-norbornadiene) were synthesized, and the catalytic activity was examined for the polymerization of phenylacetylene and the derivatives (HC≡CC₆H₄-*p*-TMS, HC≡CC₆H₄-*p*-^tBu, HC≡CC₆H₄-*p*-F). Catalyst **1** was inactive in the absence of triethylamine, while active in the presence of the amine. Catalysts **2** and **3** were active without triethylamine to afford the corresponding polymers in good yields. Catalyst **3** induced living polymerization of phenylacetylene in the late stage of the polymerization. The yields of the polymers obtained from HC≡CC₆H₄-*p*-TMS and HC≡CC₆H₄-*p*-^tBu were higher than that of the polymer from HC≡CC₆H₄-*p*-F.

Introduction

Substituted polyacetylenes gather much attention due to the useful functions including photoconductivity, electroluminescence and gas permeability.¹⁻⁷ They are commonly synthesized by the polymerization of the corresponding monomers catalyzed with transition metal complexes.^{8,9} Rhodium (Rh) catalysts are most widely used due to the high functional group tolerance and cis-stereoregularity of main chains of the formed polymers.¹⁰⁻²⁰ Most Rh catalysts for acetylene polymerization contain bicyclic diene ligands such as 2,5-norbornadiene (nbd), because of high stability of the rigidly chelated structures. Masuda and coworkers have reported that the π -acidity of bicyclic diene ligands largely affects the catalytic activity of Rh catalysts.²¹ For example, Rh catalysts bearing highly π -acidic tetrafluorobenzobarrelene (tfb) ligand polymerize acetylene monomers much faster than the nbd-counterparts. It is expected that design of bicyclic diene ligands leads to improvement of catalytic activity. However, introduction of functional groups on such bicyclic diene ligands is not easy because they are synthesized by the Diels-Alder reaction, which is largely disturbed by incorporation of substituents on the starting dienes and/or dienophiles.

In the present study, we disclose the synthesis of novel nbd derivatives tethering phosphine and amine moieties as tridentate ligands for Rh complexes, and demonstrate the catalytic activity for the polymerization of phenylacetylene derivatives. The tridentate nbd ligands are synthesized from nbd-(CH₂)₄-Br (Chart 1),²² which is prepared by the reaction of nbd

and $\text{Br}-(\text{CH}_2)_4-\text{Br}$. This synthetic method allows introduction of functional groups on nbd by the substitution of the bromide group with nucleophiles, leading to easy synthesis of nbd derivatives tethering various functional groups.



nbd- $(\text{CH}_2)_4-\text{Br}$

Chart 1.

Experimental Section

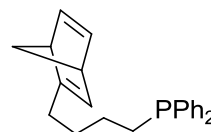
Instruments. Monomer conversions were determined by GC [Shimadzu GC-14B, capillary column (CBP10-M25-025)]; column temperature: 125 °C; injection temperature 250 °C; internal standard *tert*-butylbenzene. Number- and weight-average molecular weights (M_n and M_w , respectively) and polydispersity indices (M_w/M_n) of polymers were measured by GPC with a JASCO PU-980/ RI-930 chromatograph; 40 °C, eluent THF, columns KF-805 (Shodex) $\times$ 3, molecular weight limit up to 4×10^6 , flow rate 1 mL/min; calibrated with polystyrene standards. ^1H NMR spectra (400 MHz), ^{13}C NMR (100 MHz), ^{31}P NMR (161 MHz) were recorded on a JEOL ECX-400 spectrometer. Elemental analyses were performed at the Microanalytical Center of Kyoto University.

Materials. Phenylacetylene and its derivatives were purchased (Aldrich) and distilled over CaH_2 under reduced pressure before use.

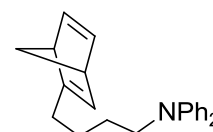
KPPh₂ (0.5 M in THF, Aldrich), HNPh₂ (TCI) were purchased and used without further purification. All solvents were distilled by standard procedures. nbd-(CH₂)₄-Br,²² Rh complex, [(C₂H₄)₂RhCl]₂²⁶ were synthesized according to the literature.

Ligand synthesis

nbd-(CH₂)₄-PPh₂. KPPh₂ (0.5 M in THF, 12 mL, 6.0 mmol) was added dropwise to a solution of nbd-(CH₂)₄-Br (1.30 g, 5.72 mmol) in THF (2.0 mL) under Ar at 0 °C. Then, the mixture was warmed up to room temperature and stirred for 1.5 h. Water (0.5 mL) was added to the reaction mixture to quench the reaction, and the resulting mixture was evaporated under vacuum. The residual yellow oil was purified by silica gel column chromatography eluted with hexane under Ar to obtain nbd-(CH₂)₄-PPh₂ as a colorless oil (1.41 g, 79%). ¹H NMR (CDCl₃) δ: 7.42–7.25 (m, 10H), 6.70 (s, 2H), 6.07 (s, 1H), 3.45 (s, 1H), 3.23 (s, 1H), 2.20–2.16 (m, 2H), 2.07–2.02 (m, 2H), 1.92–1.89 (brs, 2H), 1.57–1.49 (m, 2H), 1.44–1.36 (m, 2H). ¹³C NMR (CDCl₃) δ: 158.3, 143.7, 142.3, 139.0, 138.9, 133.5, 132.7, 132.5, 128.3, 73.4, 53.3, 49.9, 31.0, 28.8, 27.8, 25.4. ³¹P NMR (CDCl₃) δ: –15.5. Anal. Calcd. for C₂₃H₂₅P: C, 83.10%; H, 7.58%. Found: C, 83.11%; H, 7.58%.

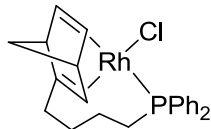


nbd-(CH₂)₄-NPh₂. NaH (540 mg, 22.5 mmol) was added to a solution of nbd-Br (520 mg, 2.29 mmol) and HNPh₂ (1.37 g, 8.09 mmol) in CH₃CN (10 mL). The resulting mixture was



heated at 50 °C for 20 h. The reaction mixture was cooled to room temperature, and then quenched with water (20 mL) and extracted with CHCl₃ (20 mL × 3 times). The combined organic phase was dried over anhydrous sodium sulfate. After filtration, the filtrate was concentrated in vacuo. The residue was purified by silica gel column chromatography eluted with hexane/EtOAc = 100/1 (v/v) to obtain nbd-(CH₂)₄-NPh₂ as a colorless oil (570 mg, 79%). ¹H NMR (CDCl₃) δ: 7.25–7.15 (m, 10H), 6.71 (s, 2H), 6.10 (s, 1H), 3.68 (m, 2H), 3.47 (s, 1H), 3.24 (s, 1H), 2.20–2.18 (m, 2H), 1.92 (brs, 2H), 1.63–1.42 (m, 4H). ¹³C NMR (CDCl₃) δ: 158.6, 145.8, 143.8, 142.3, 133.3, 128.3, 126.7, 126.5, 73.4, 58.3, 53.4, 50.0, 31.3, 30.0, 25.0. Anal. Calcd. for C₂₃H₂₅N: C, 87.57%; H, 7.99%; N, 4.44%. Found: C, 87.41%; H, 7.75%; N, 4.36%.

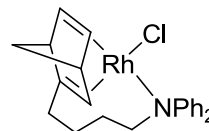
Catalyst Synthesis

[nbd-(CH₂)₄-PPh₂]RhCl (1). A solution of  (103 mg, 0.31 mmol) in CH₂Cl₂ (3.0 mL) was added to a solution of [(C₂H₄)₂RhCl]₂ (55 mg, 0.14 mmol) in CH₂Cl₂ (4.0 mL) under Ar at room temperature, and the resulting mixture was stirred for 3 h. After removing the solvent in vacuo, the resulting orange solid was purified by recrystallization from CH₂Cl₂/Et₂O. Yield 95 mg (83%). ¹H NMR (CDCl₃) δ: 7.79–7.77 (m, 2H), 7.69–7.66 (m, 2H), 7.38 (m, 6H), 5.33 (s, 1H), 5.22 (s, 1H), 3.78 (s, 1H), 3.56 (s, 1H), 3.36 (s, 1H), 2.37–2.07 (m, 4H), 1.76–1.42 (m, 4H), 1.25–1.10 (m, 2H). ³¹P NMR (CDCl₃) δ: 23.7 (d, J_{Rh-P} = 172 Hz). Anal. Calcd. for C₂₃H₂₅ClPRh: C,

58.68%; H, 5.35%. Found: C, 58.73%; H, 5.36%.

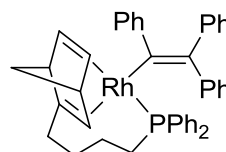
[nbd-(CH₂)₄-NPh₂]RhCl (2).

A solution of nbd-(CH₂)₄-NPh₂ (457 mg, 1.45 mmol) in CH₂Cl₂ (5.0 mL) was added to a solution of [(C₂H₄)₂RhCl]₂ (264 mg, 0.68 mmol) in CH₂Cl₂ (8.0 mL) under Ar at room temperature, and the resulting mixture was stirred overnight. After removing the solvent in vacuo, the orange residue was purified by column chromatography (Al₂O₃) using toluene as the eluent. The resulting yellow oil was dried in vacuo. Yield 365 mg (60%). ¹H NMR (CDCl₃) δ: 7.26-7.21 (m, 4H), 6.99-6.90 (m, 6H), 3.96 (s, 1H), 3.90 (s, 1H), 3.84 (brs, 1H), 3.81 (s, 1H), 3.75-3.69 (m, 3H), 3.51-3.49 (m, 2H), 2.17-2.03 (m, 2H), 1.74-1.55 (m, 4H). Anal. Calcd. for C₂₃H₂₅NClRh: C, 60.87%; H, 5.55%, N, 3.09%. Found: C, 60.86%; H, 5.54%, N, 3.03%.



[nbd-(CH₂)₄-PPh₂]Rh(Ph)C=CPh₂ (3).

BrMg{C(Ph)=CPh₂} (0.58 M in THF), was prepared from Mg (0.60 g, 24.7 mmol) with triphenylvinyl bromide (4.19 g, 12.5 mmol) in THF (12 mL), and the portion (0.65 mL, 0.38 mmol) was added to a solution of Rh complex **1** (60 mg, 0.13 mmol) in THF (1.0 mL) under Ar. The resulting mixture was stirred at 50 °C for 24 h. It was concentrated and the residue was purified by Al₂O₃ column chromatography eluted with Et₂O, followed by recrystallization from CH₂Cl₂/pentane to obtain a yellow solid. Yield 45 mg (51%). ¹H NMR



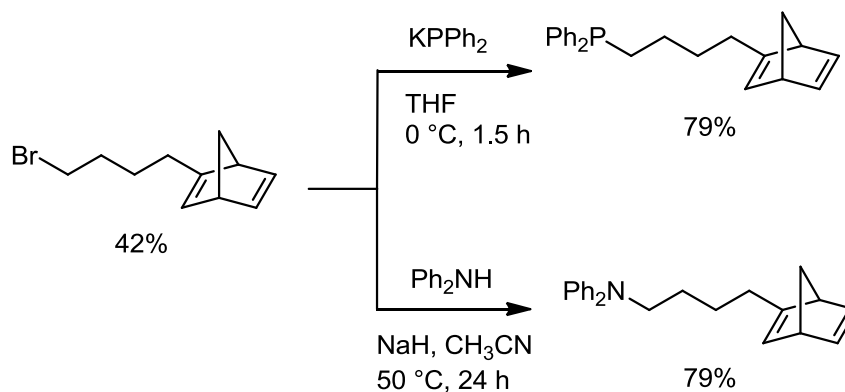
(CD₂Cl₂) δ : 8.01-7.97 (m, 2H), 7.52-6.47 (m, 23H), 4.37 (s, 1H), 4.00-3.59 (m, 4H), 3.08-3.01 (m, 2H), 2.48-2.28 (m, 2H), 1.90 (m, 2H), 1.67-1.25 (m, 4H), 1.76-1.42 (m, 4H), 1.25-1.10 (m, 2H). ³¹P NMR (CD₂Cl₂) δ : 26.3. Anal. Calcd. for C₄₃H₄₀PRh: C, 74.78%; H, 5.84%. Found: C, 74.65%; H, 5.91%.

Polymerization. All the polymerizations were carried out in a Schlenk tube equipped with a three-way stopcock under Ar. A THF solution of phenylacetylene (c = 1.0 M) was added to a catalyst solution ([Rh] = 2.0 mM). The resulting mixture was stirred at 30 °C for a set time, and poured into a large amount of methanol containing a drop of acetic acid to precipitate a polymer. It was isolated by filtration with a PTFE membrane (pore size = 0.2 μ m), and dried under vacuum to constant weight.

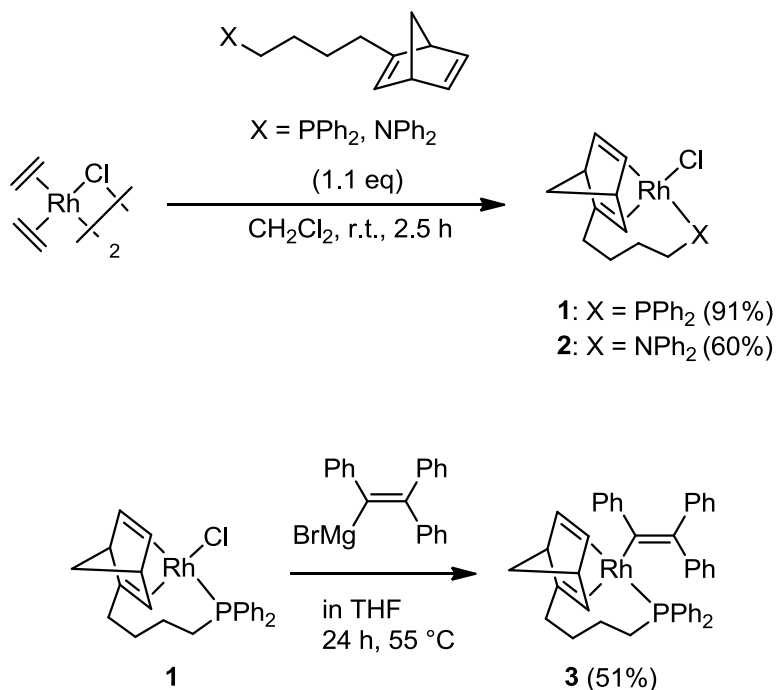
Results and Discussion

Synthesis of Novel Rh Complexes 1–3. Tridentate ligands containing phosphorous and amino groups were synthesized by the reaction of nbd-(CH₂)₄-Br with the corresponding phosphine and amine derivatives in moderate yields (Scheme 1). The structures were confirmed by ¹H and ¹³C NMR spectroscopies and elemental analysis. The resulting compounds were reacted with [(C₂H₄)₂RhCl]₂ in CH₂Cl₂ to afford chloride type complexes **1** and **2** (Scheme 2).²³ In the ¹H NMR spectra, olefin proton signals assignable to the olefin moieties appeared around 6.7 and 6.0 ppm, which were shifted 3–4 ppm toward high electric field compared with those of the dienes before the reaction, due to the coordination to the Rh center. Complex **1** was converted into **3** bearing –C(Ph)=CPh₂ group by the reaction with BrMg{C(Ph)=CPh₂}. It is expected that **3** enables living polymerization of phenylacetylene because the structure is analogous to the propagation species of acetylene polymerization.^{24, 25}

Scheme 1. Synthesis of Novel Tridentate Ligands..



Scheme 2. Synthesis of Novel Rh Complexes **1–3**.



Polymerization. The polymerization of phenylacetylene was carried out with catalysts **1–3** (Scheme 3). Catalyst **1** tethering a phosphine ligand converted the monomer less than 1% (Table 1, run 1). The catalytic activity was very low. The monomer conversion increased to 11% when triethylamine was added as a cocatalyst (run 2). Extension of polymerization time from 24 to 72 h was effective in enhancing the monomer conversion to afford the polymer with the M_n of 69,000 in a moderate yield (67%) (run 3).

Scheme 3. Polymerization of Phenylacetylene with Rh Catalysts **1–3**.

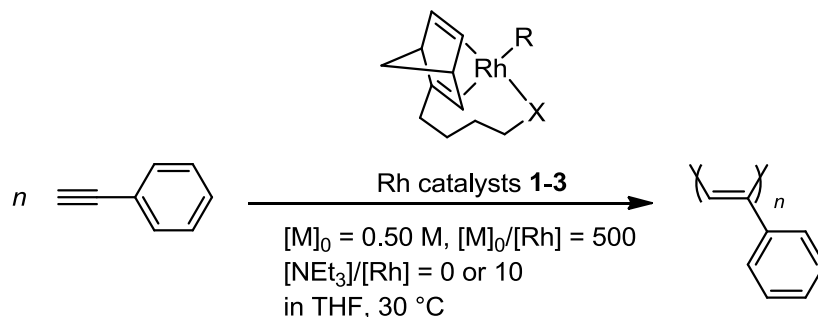


Table 1. Polymerization of Phenylacetylene with Rh catalysts **1–3**.^a

Run	Catalyst	Additive	Time (h)	Conv. ^b (%)	Polymer		
					Yield ^c (%)	M_n^d	M_w/M_n^d
1	1	None	24	<1	—	—	—
2	1	NEt ₃	24	11	—	—	—
3	1	NEt ₃	72	70	67	69,000	1.7
4	2	None	24	100	83	240,000	1.7
5	3	None	24	100	94	85,000	1.3

^a $[M]_0 = 0.50 \text{ M}$, $[M]_0/[Rh] = 500$ in THF, 30 °C. ^b Determined by GC ([*tert*-butylbenzene] = 50 mM as an internal standard). ^c MeOH-insoluble part. ^d Estimated by GPC (PSt standard).

On the other hand, catalyst **2** tethering an amine ligand polymerized phenylacetylene smoothly under the conditions same as those as run 1 to afford the polymer quantitatively (run 4). The difference of catalytic activity between **1** and **2** is explainable from the coordination ability. It is likely that the amine ligand of **2** coordinating to the Rh center is exchangeable with an incoming acetylene monomer more easily than the

phosphine ligand of **1**, resulting in the higher activity.

Next, vinyl type complex **3** was subjected to the polymerization of phenylacetylene. It converted phenylacetylene quantitatively to give the polymer in 94% yield (run 5). The molecular weight distribution was narrow ($M_w/M_n = 1.3$) compared with the polymers obtained by the polymerization using **1** and **2** ($M_w/M_n = 1.7$).

The monomer conversion was monitored by GC in order to examine the feature of vinyl catalyst **3**. It reached 100% at 180 min under the conditions of Figure 1. The first order plot was non-linear at the early stage, indicating the incomplete livingness of the polymerization. On the other hand, two-stage polymerization satisfactorily took place to convert the second fed monomer quantitatively as depicted in Figure 2a. Interestingly, the first-order plot became almost linear in the second stage of the polymerization as depicted in Figure 2b. It is assumed that the induction period at the initial stage is caused by the bulkiness around the monomer coordination site consisting of a tethering phosphine ligand and triphenylvinyl group. The initiation seems to be slow due to the unfavorable monomer approach to the Rh center. Once the monomer insertion takes place, the coordination site becomes less bulky because Rh–triphenylvinyl species turns into Rh–monophenylvinylene. As the result, propagation proceeds smoothly in the late stage of the polymerization and the second stage of the polymerization.

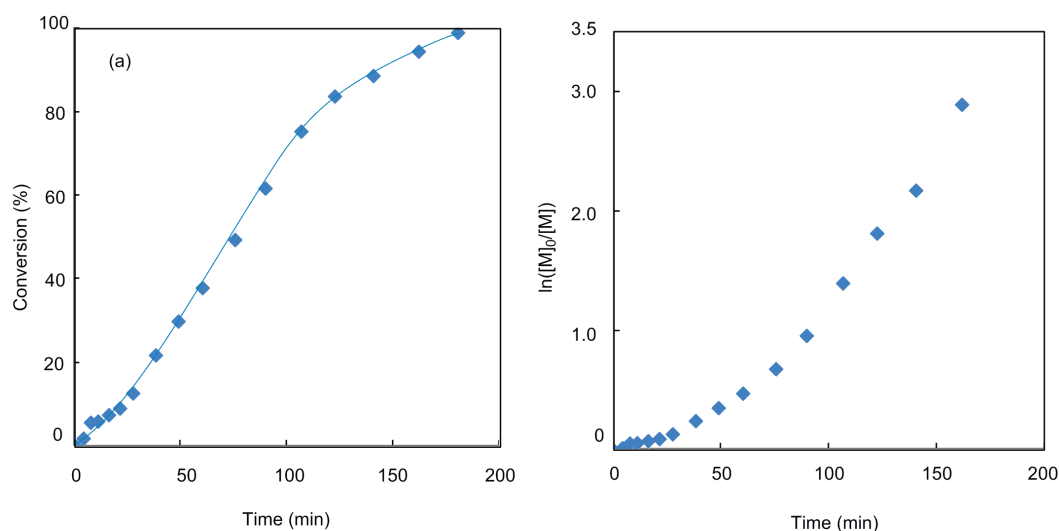


Figure 1. (a) Time-conversion curve for the polymerization of phenylacetylene with Rh catalyst **3**. (b) $\ln([M]_0/[M])$ vs. time for the polymerization of phenylacetylene with Rh catalyst **3**: (conditions: $[M]_0 = 0.50$ M, $[M]_0/[Rh] = 500$ in THF, 30 °C)

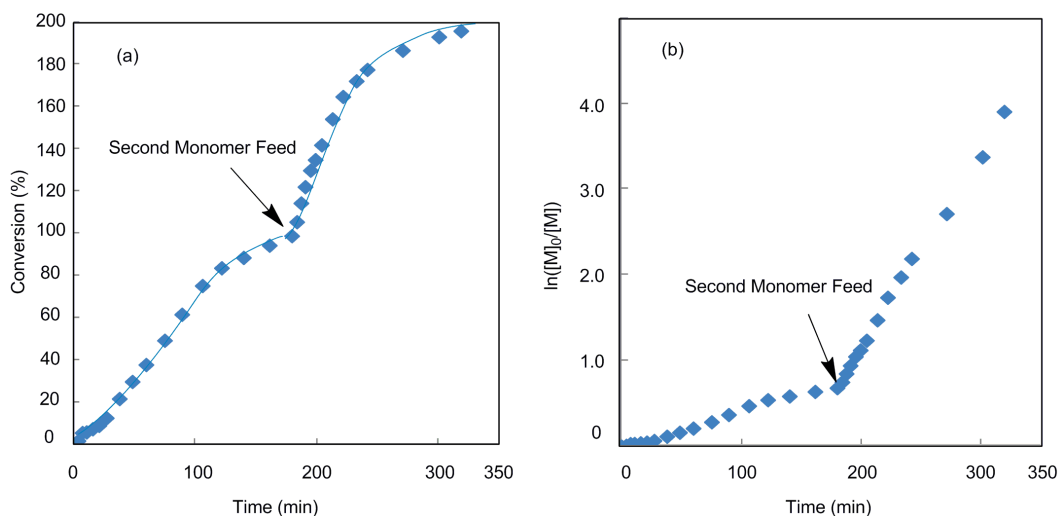


Figure 2. (a) Time-conversion curve for the two-stage polymerization of phenylacetylene with Rh catalyst **3**. (b) $\ln([M]_0/[M])$ vs. time for the two-stage polymerization of phenylacetylene with Rh catalyst **3**: (conditions: $[M]_0 = [M]_{add} = 0.50$ M, $[M]_0/[Rh] = 500$ in THF, 30 °C).

Scheme 4. Polymerization of Phenylacetylene Derivatives with Rh Catalyst **3**.

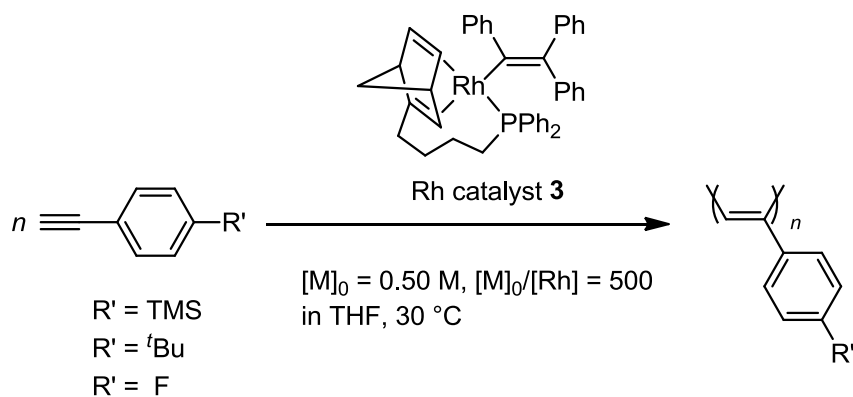


Table 2. Polymerization of Phenylacetylene Derivatives with Rh catalyst **3**.^a

R'	Conv. ^b (%)	Polymer		
		Yield ^c (%)	<i>M</i> _n ^d	<i>M</i> _w / <i>M</i> _n ^d
TMS	92	91	75,000	2.2
<i>t</i> Bu	76	74	45,000	1.6
F	44	40	35,000	1.7

^a [M]₀ = 0.50 M, [M]₀/[Rh] = 500 in THF, 30 °C, 24 h. ^b Determined by GC ([*tert*-butylbenzene] = 50 mM as an internal standard). ^c MeOH-insoluble part. ^d Estimated by GPC (PSt standard).

Polymerization of Phenylacetylene Derivatives. Vinyl catalyst **3** was also subjected to the polymerization of phenylacetylenes substituted with TMS, *t*Bu and F (Scheme 4). As listed in Table 2, monomers bearing *p*-TMS and *p*-*t*Bu groups underwent polymerization to give the corresponding polymers in good yields (91 and 74%), while the monomer bearing *p*-F gave the polymer in a low yield (40%). It is considered that the low monomer reactivity of the latter monomer is caused by the low coordination ability of the triple bond due to the electron-withdrawing

character of F.

Conclusion. We have developed novel Rh complexes bearing tridentate ligands. They showed catalytic activity for the polymerization of phenylacetylene and its derivatives. Triethylamine was necessary for chloride catalyst **1** tethering a phosphine ligand. On the other hand, catalysts **2** tethering an amine ligand polymerized phenylacetylene without the assistance of triethylamine, presumably due to the rapid exchange between the amine ligand and an incoming monomer. Vinyl catalyst **3** polymerized phenylacetylene in a living fashion in the late stage, and achieved complete consumption of the second fed monomer. We are investigating the block copolymerization of various phenylacetylene derivatives using **3** as a catalyst.

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Part II

Synthesis of Helical Polyacetylenes by Rhodium Catalyst

Chapter 4

Helix-Sense Selective Polymerization of Achiral Acetylene Monomer Catalyzed by Chiral Rh Complex

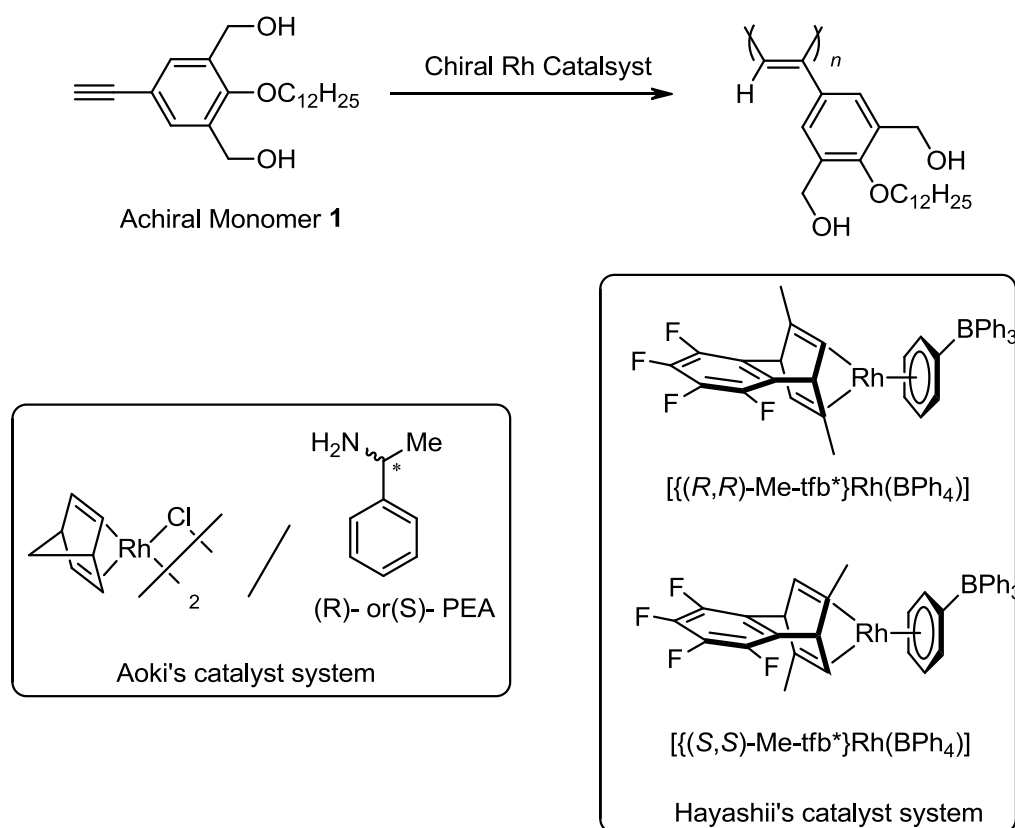
Abstract: Novel chiral zwitterionic Rh complexes were synthesized by the reaction of $[(C_2H_4)_2RhCl]_2$ and 2,5-norbornadiene $-(CH_2)_4-R$ [$R = (R)-NH(CH_3)CHPh$, $(R)-O(CH_3)CHPh$], followed by the reaction with $NaBPh_4$. The complexes catalyzed the polymerization of 3,5-bis(hydroxymethyl)-4-dodecyloxyphenylacetylene (**1**) to afford the polymers [poly(**1**)s] with number-average molecular weights of 16,000 and 82,000. Poly(**1**)s showed clear CD signals based on the polyacetylene backbone, indicating the formation of predominantly one-handed helical structures.

Introduction

Substituted cis-stereoregular polyacetylenes commonly adopt helical conformations due to the rigid backbone and steric repulsion between the side chains.¹⁻¹² The population of right- and left-handed helices deviates from 1:1 when the substituents are chiral, because the steric repulsion is chirally biased. Meanwhile, polyacetylenes substituted with achiral groups induce predominantly one-handed helical structures by the addition of chiral compounds due to the formation of pseudo chirality around the side chains. Intermolecular hydrogen bonding, van der Waals and ionic interactions between the polymers and the chiral compounds play important roles for helix induction.¹³⁻¹⁹ Aoki et al. have reported helix-sense-selective polymerization of achirally substituted polyacetylenes, another methodology for induction of one-handedness in achiral polyacetylenes.²⁰⁻²⁴ For example, achiral phenylacetylene derivative **1** substituted with two hydroxymethyl groups undergoes polymerization with [(nbd)RhCl]₂ (nbd = 2,5-norbornadiene) catalyst in the presence of (*R*)-/(*S*)-phenylethylamine to give the corresponding polymer [poly(**1**)] with predominantly one-handed screw sense (Scheme 1). Intramolecular hydrogen bonding between the hydroxy groups is indispensable for poly(**1**) to adopt a chirally biased helical conformation. On the other hands, Hayashi and coworkers conceived that chiral Rh zwitterionic catalysts bearing (*S,S*)-Me-tfb and (*R,R*)-Me-tfb (tfb = tetrafluorobenzobarrelene) as a diene ligand also achieve the helix-sense-selective polymerization of monomer **1** (Scheme 1).²⁵ This one-component catalytic system is

simple and the active species is clear compared to $[(\text{nbd})\text{RhCl}]_2-(R)\text{-}/(S)\text{-phenylethylamine}$ system, but the drawbacks are difficult synthesis of the chiral ligands. It is necessary to separate the enantiomers by chiral HPLC, which makes the catalysts inversatile. It is desirable to develop easily synthesizable catalyst systems for helix-sense-selective polymerization of achiral acetylenes. In this article, we report the synthesis of novel Rh catalysts bearing a chiral tridentate ligand, and demonstrate the helix-sense-selective polymerization of **1** with the catalysts.

Scheme 1. Helix-sense Selective Polymerization



Experimental Section

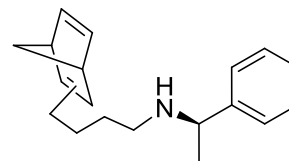
Instruments. The number- and weight-average molecular weights (M_n and M_w) and polydispersity indices (PDI) of the polymers were estimated by GPC on a JASCO PU-980/ RI-930 chromatograph; 40 °C, eluent THF, columns KF-805 (Shodex) $\times$ 3, molecular weight limit up to 4×10^6 , flow rate 1 mL/min; calibrated with polystyrene standards. ^1H NMR spectra (400 MHz) were recorded on a JEOL ECX-400 spectrometer with chemical shifts referenced to an internal standard, CHDCl_2 (5.32 ppm).

Materials. Monomer **1**,²⁰ nbd-(CH₂)₄-Br²⁶ and [(C₂H₄)₂RhCl]₂²⁹ were synthesized according to the literature. (*R*)-phenylethylamine (Aldrich), (*R*)-1-phenylethanol (Aldrich), and NaBPh₄ (Aldrich) were purchased and used without further purification. Solvents were distilled by the standard procedures.

Ligand Synthesis.

nbd-(CH₂)₄-{(*R*)-NH(CH₃)CHPh} (II).

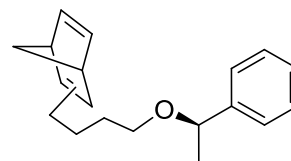
(*R*)-1-Phenylethylamine (0.500 mL, 3.92 mmol) was added to a solution of nbd-(CH₂)₄-Br (300 mg,



1.32 mmol) in CH₃CN (10 mL). The mixture was stirred at 110 °C with refluxing for 10 h. After cooling to room temperature, the reaction mixture was concentrated under reduced pressure. The resulting residue was dissolved in EtOAc (40 mL) and then washed with saturated NaHCO₃ aq (40 mL) and H₂O (40 mL $\times$ 3). The organic layer was dried over

anhydrous sodium sulfate. The solids were removed by filtration, and the filtrate was concentrated in vacuo. The residue was purified by silica gel column chromatography eluted with hexane/EtOAc = 9/1 (v/v) to obtain **II** as colorless oil (315 mg, 89%). ^1H NMR (CDCl_3) δ : 7.27–7.15 (m, 5H), 6.66 (s, 2H), 6.02 (s, 1H), 3.68 (q, 1H, J = 6.8 Hz), 3.41 (s, 1H), 3.18 (s, 1H), 2.45–2.40 (m, 2H), 2.15–1.93 (m, 5H), 1.42–1.38 (m, 4H), 1.33 (d, 3H, J = 6.8 Hz), 1.15 (broad s, 1H). ^{13}C NMR (CDCl_3) δ : 158.6, 145.8, 143.8, 142.3, 133.3, 128.3, 126.7, 126.5, 73.4, 58.3, 53.4, 50.0, 47.7, 31.3, 30.0, 25.0, 24.4. Anal. Calcd. for $\text{C}_{19}\text{H}_{25}\text{N}$: C, 85.34%; H, 9.42%; N, 5.24%. Found: C, 85.46%; H, 9.42%; N, 5.02%.

nbd-(CH₂)₄-{(R)-O(CH₃)CHPh} (III). NaH (50% assay, 185 mg, 5.54 mmol) was added to a solution of nbd-(CH₂)₄-Br (677 mg, 2.98 mmol) and (R)-1-phenylethanol (364 mg, 2.98 mmol) in DMF (8.0 mL). The

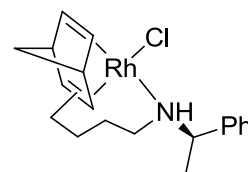


The solution was heated under Ar at 60 °C for 6 h. The reaction mixture was cooled to room temperature, and then poured into saturated Na_2CO_3 aq (50 mL) and extracted with Et_2O (50 mL $\times$ 3 times). The combined organic phase was dried over anhydrous sodium sulfate. The solids were removed by filtration, and the filtrate was concentrated in vacuo. The residue was purified by preparative HPLC eluted with CHCl_3 to obtain **III** as colorless oil (302 mg, 38%). ^1H NMR (CDCl_3) δ : 7.33–7.30 (m, 5H), 6.73 (s, 2H), 6.09 (s, 1H), 4.38 (q, 1H, J = 6.4 Hz), 3.48 (s, 1H), 3.27 (m, 3H), 2.16 (m, 2H), 1.94 (m, 2H), 1.52 (m, 4H), 1.42 (d, 3H, J = 6.0 Hz). ^{13}C NMR

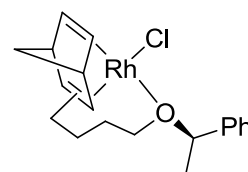
(CDCl₃) δ : 158.7, 144.3, 143.8, 142.4, 133.5, 128.4, 127.3, 126.1, 77.9, 73.4, 68.5, 53.4, 50.0, 31.2, 29.6, 24.2, 23.8. Anal. Calcd. for C₁₉H₂₄O: C, 85.03%; H, 9.01%. Found: C, 84.99%; H, 8.72%.

Catalyst Synthesis

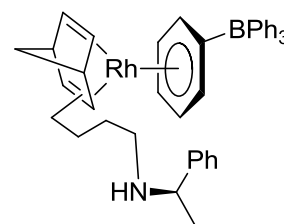
nbd-(CH₂)₄-{(R)-NH(CH₃)CHPh}RhCl (II'). A solution of **II** (280 mg, 1.09 mmol) in CH₂Cl₂ (4.0 mL) was added to a solution of [(C₂H₄)₂RhCl]₂ (185 mg, 0.480 mmol) in CH₂Cl₂ (4.0 mL), and the resulting mixture was stirred under Ar at room temperature for 15 h. After removing the solvent in vacuo, the orange residue was purified by recrystallization from CH₂Cl₂/pentane. The resulting yellow solid was dried in vacuo. Yield 320 mg (83%). Anal. Calcd. for C₁₉H₂₅NClRh: C, 56.24%; H, 6.21%; N, 3.45%. Found: C, 56.31; H, 6.39%; N, 3.35%.



nbd-(CH₂)₄-{(R)-O(CH₃)CHPh}RhCl (III'). This compound was synthesized from **III** and [(C₂H₄)₂RhCl]₂ in a fashion similar to **II'**, and purified by recrystallization from Et₂O/pentane at -78 °C. The resulting orange residue was dried in vacuo. Yield 221 mg (66%).



nbd-(CH₂)₄-{(R)-NH(CH₃)CHPh}Rh[(η^6 -Ph)BPh₃] (2**).** **II'** (60.0 mg, 0.148 mmol), NaBPh₄ (55.8 mg, 0.163 mmol) and CH₂Cl₂ (5.5 mL) were fed into a Schlenk

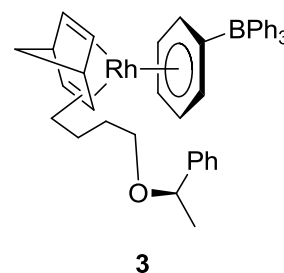


2

tube filled with Ar. The resulting mixture was stirred at room temperature overnight. After removing excess NaBPh₄ by filtration, the solvent was removed from the filtrate in *vacuo*, and the formed white residue was purified by recrystallization from CH₂Cl₂/pentane. The resulting grayish white solid was dried in *vacuo*. Yield 90.1 mg (89%). ¹H NMR (CDCl₃) δ: 7.37–7.00 (m, 20H), 6.60 (m, 2H), 6.38 (m, 1H), 6.25 (m, 1H), 5.84 (m, 1H), 3.80 (s, 1H), 3.71 (m, 1H), 3.66 (m, 1H), 3.46 (m, 1H), 3.31 (m, 1H), 3.14 (m, 1H), 2.42 (broad s, 1H), 2.31 (broad s, 1H), 2.06 (m, 1H), 1.38–1.29 (m, 7H), 1.09–1.00 (m, 4H). Anal. Calcd. for C₄₃H₄₅BNRh: C, 74.90%; H, 6.58%; N, 2.03%. Found: C, 74.60%; H, 6.31%; N, 1.94%.

nbd-(CH₂)₄-{(R)-O(CH₃)CHPh}Rh[(η⁶-Ph)BPh₃] (3).

This compound was synthesized from **III'** and [(C₂H₄)₂RhCl]₂ in a fashion similar to **2**. Yield 40.1 mg (79%). ¹H NMR (CDCl₃) δ: 7.41–7.03 (m, 20H), 6.67 (m, 1H), 6.50 (m, 1H), 6.43 (m, 1H), 6.20 (m, 1H), 5.79



(m, 1H), 4.35 (q, 1H, *J* = 6.8 Hz), 3.77 (broad s, 1H), 3.63 (broad s, 1H), 3.46 (broad s, 1H), 3.33 (brs, 1H), 3.21 (m, 2H), 3.15 (broad s, 1H), 2.07 (m, 2H), 1.43–1.01 (m, 9H). Anal. Calcd. for C₄₃H₄₄BORh: C, 74.79%; H, 6.42%. Found: C, 73.17%; H, 6.16%.

Polymerization. A THF solution of monomer **1** (*c* = 0.20 M) was added to the same volume of catalyst solution ([Rh] = 2.0 mM) in a Schlenk tube equipped with a three-way stopcock under Ar atmosphere. The

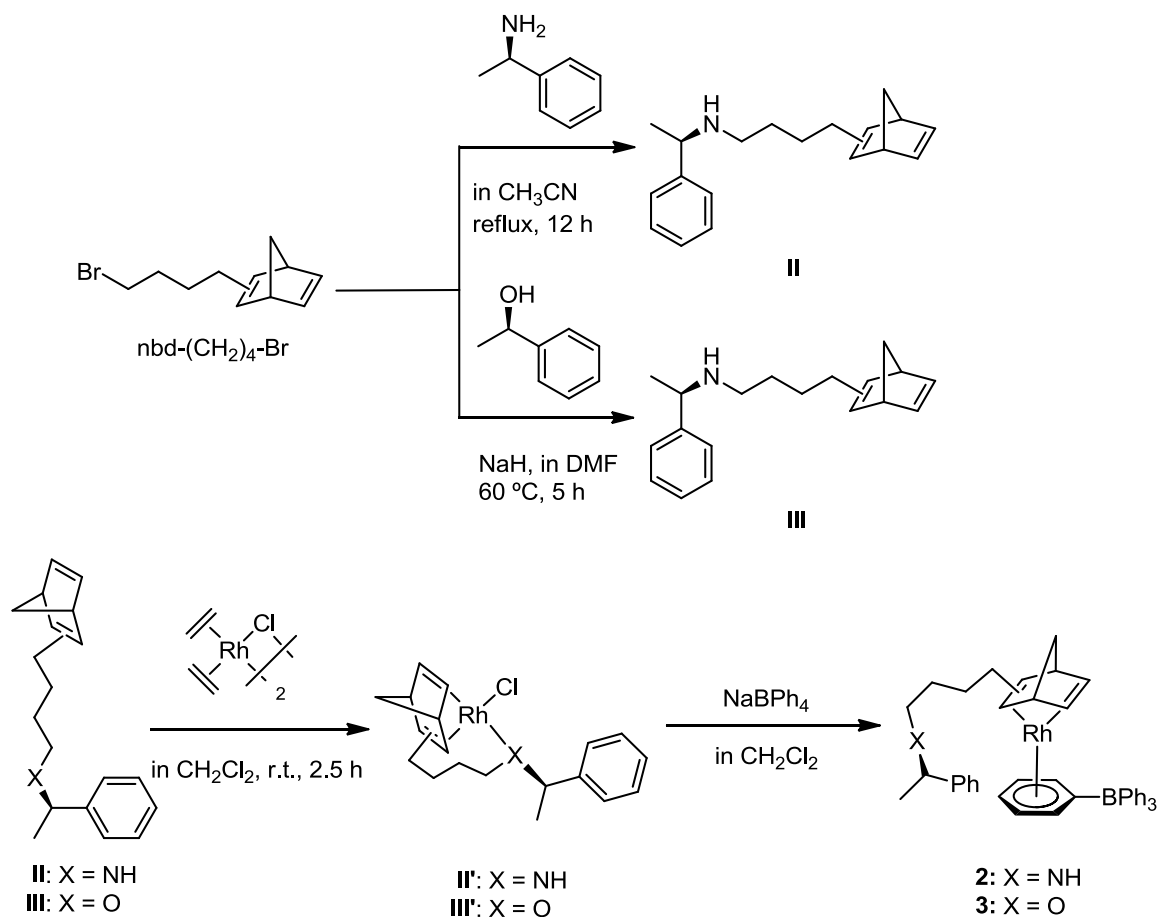
polymerization solution was kept at 30 °C for 24 h, and poured into a large amount of MeOH to precipitate a polymer. It was filtered with a PTFE membrane, and dried under vacuum to constant weight.

Acknowledgement. This research was supported by the Grant-in-Aid for Young Scientists (B) (22750108) and the Kyoto University Global COE Program “International Center for Integrated Research and Advanced Education in Materials Science” from the Ministry of Education, Culture, Sports, Science, and Technology, Japan, and Nippon Chemical Industrial Co., Ltd

Results and Discussion

Catalyst Synthesis. nbd-(CH₂)₄-Br,²⁶ an nbd derivative tethering 4-bromobutyl group was employed in order to synthesize the novel chiral Rh catalysts. The bromide group was convertible into novel chiral tridentate ligands **II** and **III** by nucleophilic substitution reactions with (*R*)-1-phenylethylamine and (*R*)-1-phenylethanol as illustrated in Scheme 2. It is considered that **II** and **III** are diastereomer mixtures, because nbd-(CH₂)₄-Br is a racemic mixture [(1*R*,4*S*) and (1*S*,4*R*)]. HPLC analysis revealed that the ratios of diastereomers were almost 1:1 in the both cases. We attempted to separate the enantiomers of nbd-(CH₂)₄-Br, and the diastereomers of the **II** and **III**, but failed due to the close elution times in all cases. We therefore used **II** and **III** as mixtures of diastereomers. Chiral Rh catalysts **II'** and **III'** were synthesized by the

Scheme 2. Synthesis of Chiral Rh Catalysts **2** and **3**.



reaction of $[(\text{C}_2\text{H}_4)_2\text{RhCl}]_2$ with **II** and **III** (Scheme 2).²⁷ Zwitterionic type catalysts **2** and **3** were synthesized by the reaction of **II'** and **III'** with NaBPh_4 .²⁸

Polymerization. Table 1 lists the results of polymerization of achiral monomer **1** with novel zwitterionic chiral catalysts **2** and **3**. Amino group containing catalyst **2** gave poly(**1**) with a high molecular weight ($M_n = 82,000$) almost quantitatively. On the other hand, ether group containing catalyst **3** gave poly(**1**) with a low molecular weight ($M_n = 16,000$) in a

Scheme 3. Polymerization Achiral Monomer **1** with Chiral Rh Catalysts **2** or **3**.

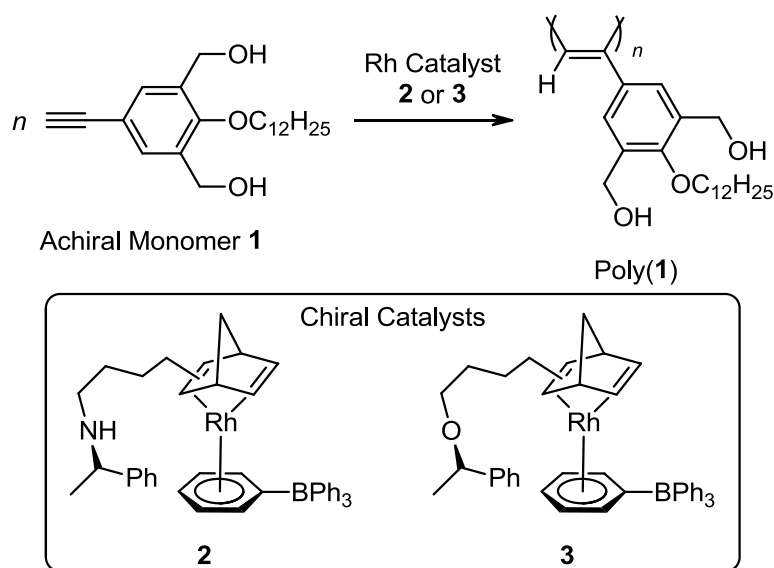


Table 1. Polymerization of **1** with Rh catalysts **2** and **3**.^a

Catalyst	Polymer		
	Yield ^b (%)	Mn	PDI ^c
2	97	82,000	5.7
3	25	16,000	1.3

^a [M]₀ = 0.10 M, [M]₀/[Rh] = 100 in THF at 30 °C. ^b MeOH-insoluble part. ^c Estimated by GPC (PSt standard).

poor yield (25%). The catalytic activity of **2** was higher than that of **3**. It is likely that the coordination ability of **2** higher than that of **3** causes the higher activity but the concrete reason is unclear.

The secondary structure of poly(**1**) was analyzed by CD and UV-vis spectroscopies. Poly(**1**) synthesized by Rh catalyst **2** exhibited a broad negative CD signal around 430 nm, and bisignated positive and negative

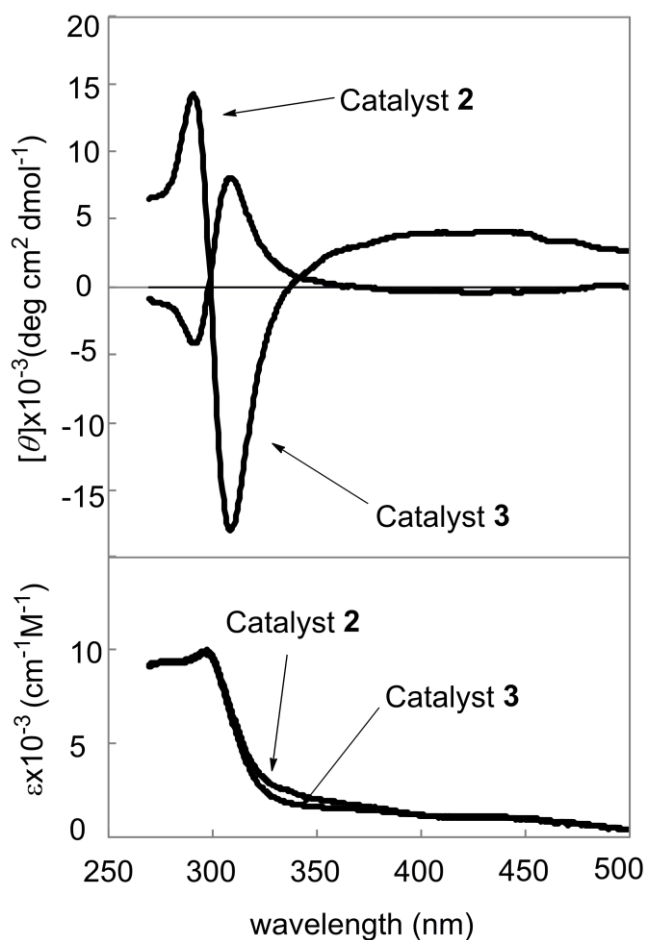


Figure 1. CD and UV-vis spectra of poly(**1**) measured in CHCl₃ at 20 °C (*c* = 0.10 mM).

signals at 310 and 280 nm, respectively, as shown in Figure 1. It is considered that **2**-based poly(**1**) adopts a predominantly one-handed helical conformation in a fashion similar to the previous reports. Catalyst **3**-based poly(**1**) also showed Cotton effects with intensities smaller than those of **2**-based poly(**1**) at the same wavelengths. The total helix contents of the both polymers seem to be the same, because the difference of intensities of the UV-vis spectra is negligibly small between the polymers. Interestingly, the signs of the CD signals of the two polymers

were completely opposite, indicating the opposite predominant screw sense.

Conclusion

We have demonstrated the synthesis of novel chiral zwitterionic catalysts **2** and **3**, and the polymerization of achiral acetylene monomer **1** with the catalysts. The formed polymers showed Cotton effects originating from the conjugated backbone, indicating the formation of predominantly one-handed helical structures. We are investigating the application of the present catalysts to helix-sense-selective polymerization of the other acetylene monomers.

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Chapter 5

Molecular Weight Dependence of Helical Conformation of Amino Acid-Based Polyphenylacetylene

Abstract. A well-defined living polymerization catalyst, [(nbd)Rh{C(Ph)=CPh₂}(PPh₃)]/PPh₃, produced a series of amino acid based polyphenylacetylene derivatives having a wide range of molecular weights (M_n : 1,500–128,800) with relatively narrow polydispersity. Based on the CD and UV-vis spectra of the obtained polymers measured in DMF, plotting the $[\theta]$ and Kuhn dissymmetry factor, g , against the molecular weight revealed that their predominantly one-handed helical conformation strongly depended on their molecular weights.

Introduction.

Dynamic helical polymers such as polyisocyanates,¹ polysilanes,² and polyacetylenes³⁻⁷ readily invert the helical sense owing to relatively low energy barriers for the helix reversal.⁸ Thus they can transform their higher order structures, e.g., from helix to coil and/or from right- to left-handed helices, offering their potential application to chiral sensors, molecular memory, and so on. Lifson, Green, Teramoto, Sato and co-workers proposed the statistical mechanical theory for helix inversion of polyisocyanates, in which a polymer chain of optically active polyisocyanates is composed of biased right- and left-handed long helical sequences separated by the reversal points.^{1,9-13} This theory expects that the chiroptical properties of the polymers considerably depend on their molecular weights, because the molecular weight and the average length of the one-handed helical sequence determine the number of helix reversal per molecule. It was actually proven by the experiments using poly[(*R*)-2-deuterio-1-hexyl isocyanate], for example; the specific rotation $[\alpha]$ at a wavelength of 300 nm rapidly increases with the degree of polymerization (*N*) below ca. 1,000, but tends to level off to be limited to an apparent constant value in a higher molecular weight region.¹¹

Helical polyacetylenes are amenable to the same theory,⁸ as experimentally demonstrated by circular dichroism (CD) spectroscopy along with atomic force microscopy,¹⁴ variable temperature NMR spectroscopy,¹⁵ thermodynamic calculations,¹⁶ etc. However, there has been no systematic study directly showing the dependence of optical properties of

the polymers on their molecular weights, to the best of our knowledge. The present study deals with the chiroptical behavior of predominantly one-handed helical amino acid based polyphenylacetylene derivatives depending on the molecular weights.

Experimental

Instruments. Polymers were purified by preparative high performance liquid chromatography (HPLC) on JAIGEL-1H and JAIGEL-2H. ^1H (400 MHz) and ^{13}C NMR (100 MHz) spectra were recorded on JEOL EX-400 and JEOL AL-400 spectrometers. Elemental analyses were performed at the Microanalytical Center of Kyoto University. IR spectra were measured on a JASCO FT/IR-4100 spectrophotometer. Melting points (mp) were measured on a Yanaco micro melting point apparatus. Number and weight-average molecular weights (M_n and M_w) of polymers were determined by size-exclusion chromatography (SEC) on TSK gel α -M and TSK gel GMH_{XL}, using a solution of LiBr (10 mM) in DMF as an eluent at a flow rate of 1.0 mL/min, calibrated by polystyrene standards at 40 °C. CD and UV-vis spectra were measured in a quartz cell (optical distance: 1 cm) using a JASCO J-820 spectropolarimeter. Specific rotations ($[\alpha]_D$) were measured on a JASCO DIP-100 digital polarimeter with a sodium lamp as a light source. Absolute M_w 's²⁷ of polymers were determined by multi-angle laser light scattering (MALLS) equipped with SEC on a Dawn E instrument (Wyatt Technology; Ga-As laser, λ = 690 nm). The SEC was performed on three linear-type polystyrene gel columns (Shodex

KF-805L), using a solution of LiBr (10 mM) in DMF as an eluent at a flow rate of 1.0 mL/min at 40 °C. The refractive index increment (dn/dc) was measured in DMF at 40 °C on an Optilab DSP refractometer (Wyatt Technology; $\lambda = 690$ nm, $c < 2.5$ mg/mL).

Materials. TRIAZIMOH [4-(4,6-dimethoxy-1,3,5-triazin-2-yl)-4-methyl-morpholinium chloride] was offered by Tokuyama Co. and used without further purification. DMAP [4-(*N,N*-dimethylamino)pyridine] (Wako), *p*-ethynylaniline (Wako), Boc-Val-OH [*N*-(*tert*-butoxycarbonyl)-L-valine] (Kokusan Chemical Co.), Boc-*N*-Me-Val-OH [*N*-(*tert*-butoxycarbonyl)-*N*-methyl-L-valine] (Watanabe Chemical Industries), triphenylphosphine (Aldrich) were purchased and used as received. [(nbd)Rh{C(Ph)=CPh₂(PPh₃)}] (nbd = 2,5-norbornadiene) was prepared by the reported method.¹⁷ DMF and CH₂Cl₂ for polymerization were purified by distillation over CaH₂.

Monomer Synthesis

***N*-*tert*-Butoxycarbonyl-L-Valine 4-Ethynylanilide (1a).** TRIAZIMOH (water content: 14.7%, 7.81 g, 24.1 mmol) and DMAP (293 mg, 2.40 mmol) were added to a stirred solution of 4-ethynylaniline (2.34 g, 20.0 mmol) and Boc-Val-OH (5.21 g, 24.0 mmol) in THF (50 mL) at 0 °C, and the reaction mixture was kept for stirring at room temperature overnight. Ethyl acetate (50 mL) was added to the mixture, and the organic phase was sequentially washed with 0.5 M HCl aq (50 mL), saturated NaHCO₃ aq (50 mL), and saturated NaCl aq (50 mL). The organic phase was dried over

anhydrous MgSO_4 , filtered, and concentrated under reduced pressure. The residue was purified by column chromatography (SiO_2 , hexane/ethyl acetate = 4/1 v/v). Yield: 67% (yellow powder). $[\alpha]_{\text{D}}^{23}$: +8.1° (in DMF, $c = 0.10$ g/dL), -55.1° (in CHCl_3 , $c = 0.10$ g/dL). ^1H NMR (CDCl_3): $\delta = 8.60$ (br s, 1H, ArNHCO), 7.43 (d, $J = 8.4$ Hz, 2H, H_{Ar}), 7.38 (d, $J = 8.4$ Hz, 2H, H_{Ar}), 5.32 (br m, 1H, NHCOO), 4.07 (br m, 1H, $\text{CHCH}(\text{CH}_3)_2$), 3.03 (s, 1H, $\text{C}\equiv\text{CH}$), 2.21 (br m, 1H, $\text{CH}(\text{CH}_3)_2$), 1.44 (s, 9H, $\text{C}(\text{CH}_3)_3$), 1.02 (d, $J = 6.8$ Hz, 3H, CH_3), 1.00 (d, $J = 6.8$ Hz, 3H, CH_3). ^{13}C NMR (CDCl_3): $\delta = 170.5$ (ArNHCO), 156.5 (NHCOO), 138.1 (C_{Ar}), 132.8 (C_{Ar}), 119.4 (C_{Ar}), 117.7 (C_{Ar}), 83.4 ($\text{C}\equiv\text{CH}$), 80.5 ($\text{C}\equiv\text{CH}$), 76.7 ($\text{C}(\text{CH}_3)_3$), 61.0 (CHNH), 30.6 ($\text{CH}(\text{CH}_3)_2$), 28.3 ($\text{C}(\text{CH}_3)_3$), 19.4 and 18.2 (CH_3 s of *i*Pr). IR (cm^{-1} , KBr): 3306, 2967, 2109 ($\text{C}\equiv\text{C}$), 1671, 1599, 1527, 1406, 1368, 1287, 1249, 1172, 840. Mp: 133 °C. Anal. Calcd. for $\text{C}_{18}\text{H}_{24}\text{N}_2\text{O}_3$: C 68.33, H 7.65. Found: C 68.40, H 7.57.

***N*-tert-Butoxycarbonyl-*N*-Methyl-L-Valine 4-Ethynylanilide (1b).** The title compound was synthesized from Boc-*N*-Me-Val-OH and 4-ethynylaniline in a manner similar to *N*-tert-butoxycarbonyl-L-valine 4-ethynylanilide. Yield: 36% (white powder). $[\alpha]_{\text{D}}^{23}$: -86.5° (in DMF, $c = 0.10$ g/dL), -161.4° (in CHCl_3 , $c = 0.10$ g/dL). ^1H NMR (CDCl_3): $\delta = 8.47$ (s, 1H, ArNHCO), 7.49 (d, $J = 8.4$ Hz, 2H, H_{Ar}), 7.44 (d, $J = 8.8$ Hz, 2H, H_{Ar}), 4.10 (d, $J = 11.0$ Hz, 1H, $\text{CHCH}(\text{CH}_3)_2$), 3.03 (s, 1H, $\text{C}\equiv\text{CH}$), 2.83 (s, 3H, NCH_3), 2.38 (br m, 1H, $\text{CH}(\text{CH}_3)_2$), 1.49 (s, 9H, $\text{C}(\text{CH}_3)_3$), 1.03 (d, $J = 6.4$ Hz, 3H, CH_3), 0.93 (d, $J = 6.4$ Hz, 3H, CH_3). ^{13}C NMR

(CDCl₃): δ = 171.1 (ArNHCO), 157.6 (N(CH₃)COO), 138.5 (C_{Ar}), 132.9 (C_{Ar}), 119.2 (C_{Ar}), 117.4 (C_{Ar}), 83.4 (C $\equiv$ CH), 80.9 (C $\equiv$ CH), 76.6 (CH(CH₃)₃), 66.5 (CHNCH₃), 30.8 (CH(CH₃)₂), 28.3 (CH(CH₃)₃), 26.0 (NCH₃), 19.9 and 18.7 (CH₃s of *i*Pr). IR (cm⁻¹, KBr): 3322, 2974, 2109 (C $\equiv$ C), 1689, 1656, 1597, 1399, 1361, 1310, 1244, 1156, 838. Mp: 103 °C. Anal. Calcd. for C₁₉H₂₆N₂O₃: C 69.06, H 7.93. Found: C 69.06, H 7.90.

Polymerization. The polymerization of **1a** and **1b** was carried out under the conditions described in each entry of Table 1. A solution of [(nbd)Rh{C(Ph)=CPh₂}(PPh₃)] and PPh₃ in DMF/CH₂Cl₂ (3/1 v/v) was added to a solution of a monomer in DMF/CH₂Cl₂ (3/1 v/v) in a glass tube equipped with a three-way stopcock under argon. The resulting mixture was stirred at 30 °C for 24 h. After confirming the formation of a polymer with a target molecular weight by GPC, the polymer was isolated by preparative HPLC (see the details in the Instruments shown above). The polymer samples were finally freeze-dried from their benzene solution for complete removal of solvent.

Supplementary Information

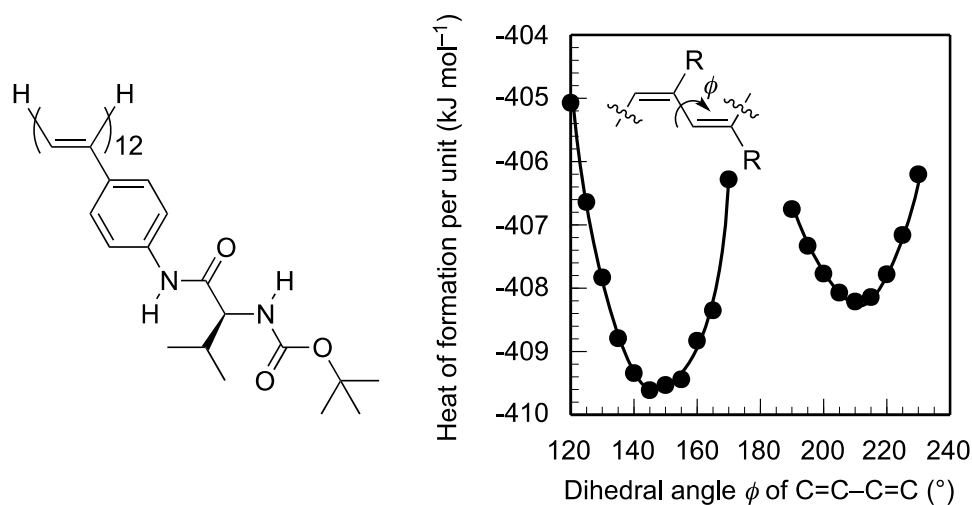


Figure S1. Relationship between the dihedral angle ϕ at the single bond in the main chain of *cis*-stereoregular poly(**1a**) (12-mer, the both chain ends are terminated with hydrogen) and heat of formation calculated by MOPAC2006 version 1.0.2²⁸ using the AM1 hamiltonian with a keyword of MMOK for correction of amide-bond barrier. The MOZYME method was used to save CPU time.

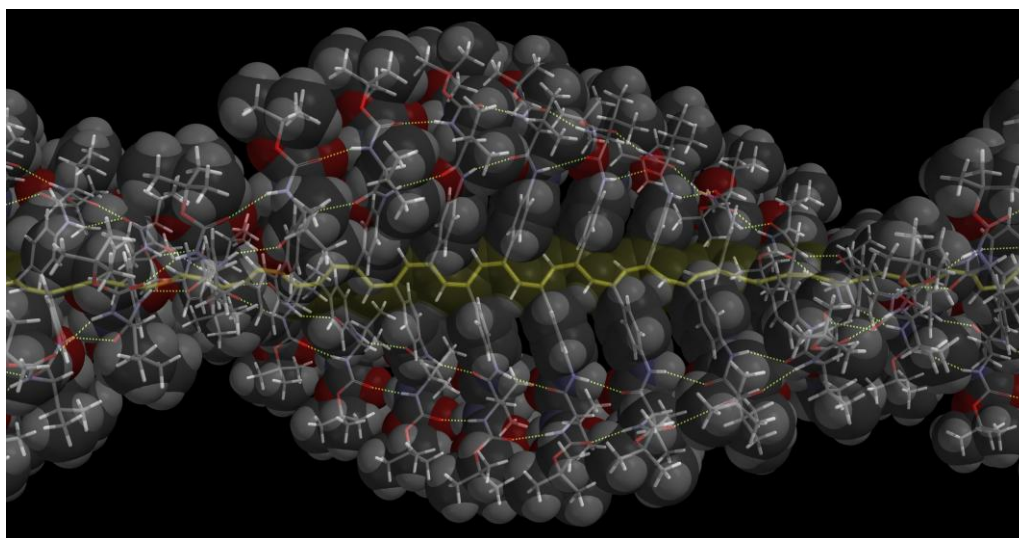


Figure S2. A possible conformer of *cis*-stereoregular poly(**1a**) assembled based on the MOPAC2006/AM1 analysis (Figure S1). The dihedral angle ϕ at the single bond in the main chain is fixed at 145°. The green dotted lines represent hydrogen bonds ($>\text{C}=\text{O} \cdots \text{H}-\text{N}<$) between the amide groups and carbamate groups at *i* th and (*i*+2) th monomer units. The polyacetylene backbone (colored in yellow) forms a right-handed helix, and the side chains form two left-handed helical arrays.

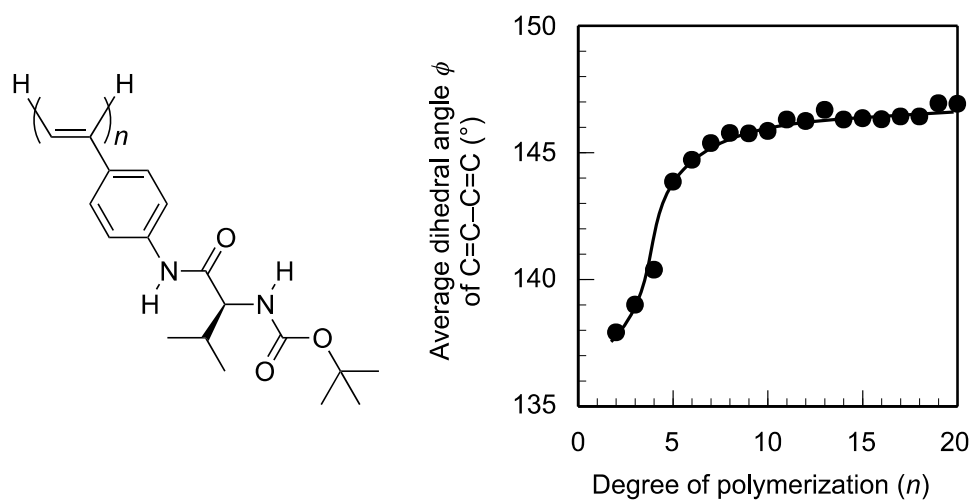


Figure S3. Relationship between the degree of polymerization and average dihedral angle ϕ at the single bond in the main chain of *cis*-stereoregular poly(**1a**) (2–20-mers, the both chain ends are terminated with hydrogen) calculated by MOPAC2006/AM1. The geometries were fully optimized started from the conformers with $\phi = 145^\circ$. The data of ϕ of one end unit were excluded from the calculation of average because of large deviations (ca. 20°).

Results and Discussion

We chose the binary Rh catalyst system consisting of $[(\text{nbd})\text{Rh}\{\text{C}(\text{Ph})=\text{CPh}_2\}(\text{PPh}_3)]^{17}$ and PPh_3 to the polymerization of monomers **1a** and **1b** (Scheme 1). This kind of catalyst promotes *cis*-stereoregulated living polymerization of phenylacetylene-type monomers and *N*-propargylamides as reported in the literature.¹⁸⁻²⁰ The corresponding polymers with relatively small molecular weight distribution were successfully obtained (Table 1). The polymers were isolated by preparative HPLC (eluent: CHCl_3) for complete removal of the catalyst residue and undesired oligomers. The ranges of number-average molecular weights (M_n 's) of poly(**1a**) and poly(**1b**) were 1,500–128,800 and 2,700–70,300, respectively, which correspond to *N*'s of 5–407 for poly(**1a**) and 8–213 for poly(**1b**).

Scheme 1. Polymerization of Amino Acid Based Phenylacetylene Derivatives **1a** and **1b** with the Well-Defined Catalyst, $[(\text{nbd})\text{Rh}\{\text{C}(\text{Ph})=\text{CPh}_2\}(\text{PPh}_3)]/\text{PPh}_3$

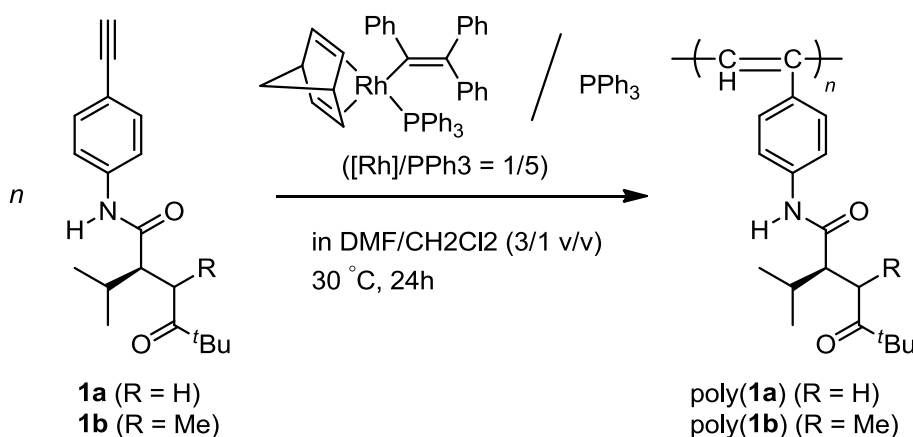


Table 1. Polymerization of **1a** and **1b**.^a

entry	monomer	[M] ₀ (M)	[M] ₀ / [Rh]	yield ^b (%)	<i>M</i> _n ^c	<i>M</i> _w / <i>M</i> _n ^c	<i>N</i> ^d
1	1a	0.20	75	66	128,800	1.11	407
2	1a	0.20	60	74	44,100 ^e	1.32	139
3	1a	0.20	50	95	19,500	1.24	62
4	1a	0.20	25	92	12,800	1.21	40
5	1a	0.20	20	59	10,000	1.24	32
6	1a	0.20	15	>99	8,900	1.21	28
7	1a	0.10	10	>99	7,300	1.25	23
8	1a	0.05	5	48	5,100	1.24	16
9	1a	0.01	1	49	2,600	1.28	8
10	1a	0.001	0.5	>99	1,500	1.64	5
11	1b	0.20	150	82	70,300	1.14	213
12	1b	0.20	100	79	50,300 ^f	1.13	152
13	1b	0.20	60	58	18,700	1.19	57
14	1b	0.20	50	65	16,000	1.22	48
15	1b	0.20	70	37	15,300	1.23	46
16	1b	0.20	25	64	7,100	1.41	21
17	1b	0.20	20	67	6,100	1.45	18
18	1b	0.20	15	66	5,800	1.34	18
19	1b	0.10	10	57	5,700	1.18	17
20	1b	0.05	5	42	3,800	1.17	12
21	1b	0.01	1	85	2,700	1.14	8

^a In DMF/CH₂Cl₂ (3/1 v/v), 30 °C, for 24 h. ^b Isolated yield. ^c Estimated by GPC (PSt Standard). ^d Degree of polymerization calculated by dividing the *M*_n by the formula weight of the monomer unit [316.39 for poly(**1a**), 330.42 for poly(**1b**)]. ^e *M*_w (SEC) = 58,200, *M*_w (MALLS) = 67,200 (*dn/dc* = 0.147 mL/g). ^f *M*_w (SEC) = 56,800, *M*_w (MALLS) = 93,100 (*dn/dc* = 0.142 mL/g).

The CD and UV-vis spectra of the obtained polymers were measured in DMF at room temperature (Figure 1). Poly(**1a**)s with *M*_n's of 5,100–128,800 showed split-type intense Cotton effects in the conjugated

polyene chromophore region, while poly(**1a**)s with the lowest class of molecular weight ($M_n \leq 2,600$) did not show any Cotton effect [Figure 1(a)]. It suggests that poly(**1a**)s with the mid-range M_n formed predominantly one-handed helical structures in DMF. The Cotton effects tended to become larger with increase of M_n of poly(**1a**) in the mid-range M_n . However, its trend obviously decelerated in the higher M_n region more than 10,000 of M_n . Finally the intensity increase of the Cotton effect seemed to achieve saturation at the highest M_n region. Analogous poly(**1b**), having a Me group on the carbamate nitrogen, showed almost identical tendencies to poly(**1a**), although the lowest molecular weight poly(**1b**) ($M_n = 2,700$) still showed slight Cotton effect in its CD spectrum [Figure 1(b)]. The similar tendencies of this molecular weight dependence for both poly(**1a**) and (**1b**) were also seen in the CD spectra with their CHCl_3 solutions.

The optical properties of poly(**1a**) and poly(**1b**) were further investigated with the Kuhn dissymmetry factor, g ($g = \Delta\epsilon/\epsilon$, in which $\Delta\epsilon = [\theta]/3298$), which gives quantitative information of the degree of preferential screw sense.²¹ Plotting M_n (and degree of polymerization N calculated based on M_n and the formula weight of the monomer units) versus g values at the wavelengths of ca. 290, 340, and 390 nm clearly shows the molecular weight dependence of the optical properties of poly(**1a**) and poly(**1b**) [Figures 1(c) and 1(d), respectively]. The g values of poly(**1a**) greatly extended with increase of M_n , but the development abruptly turned dull at M_n of ca. 10,000 and the g value appeared to become saturated. Poly(**1b**) showed the almost same tendency as displayed in Figure 1(d), although the

turning point was slightly shifted to a lower molecular weight region.

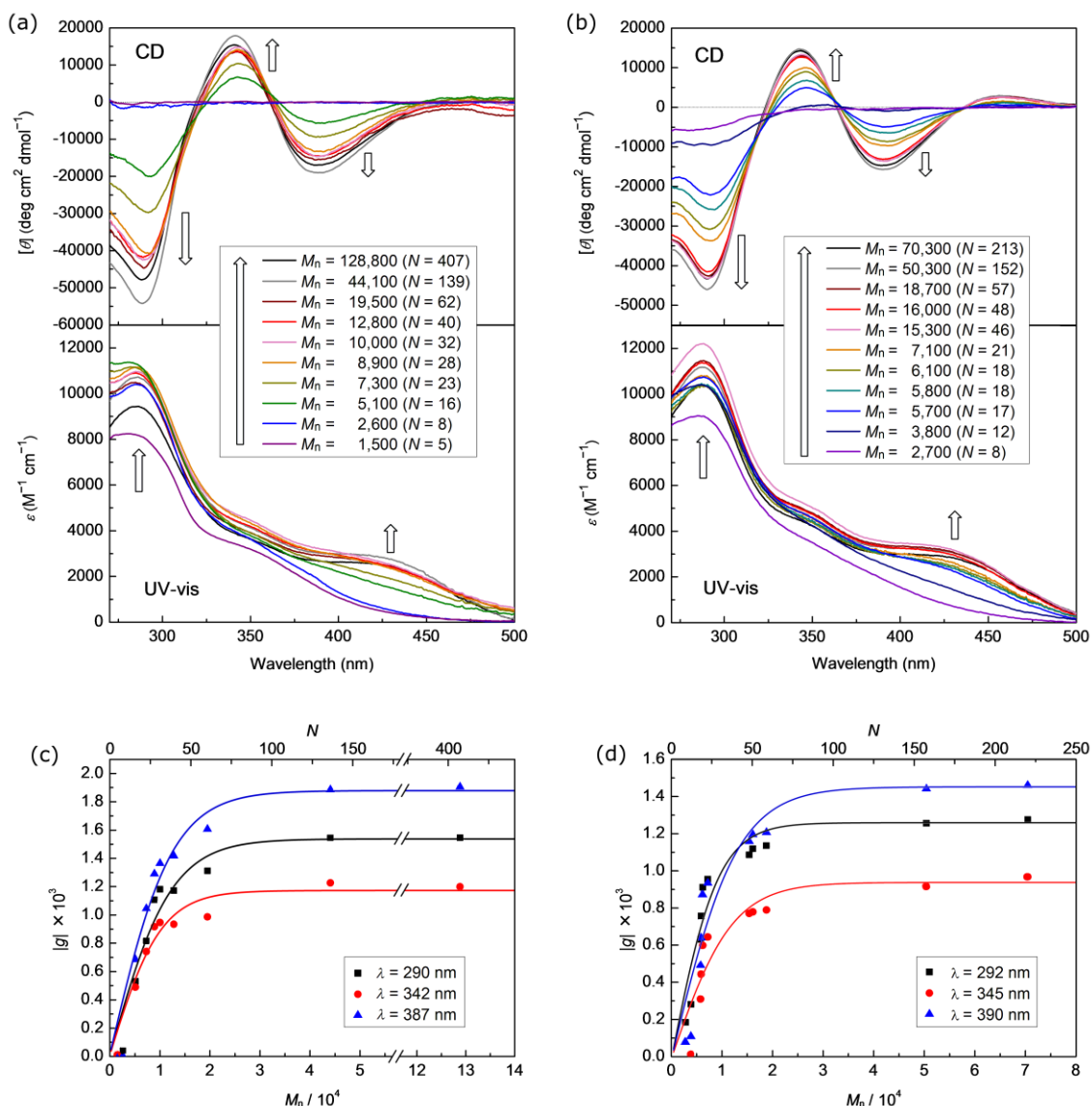


Figure 1 CD and UV-vis spectra of series of poly(**1a**)s and poly(**1b**)s [(a) and (b)] and M_n - g value plots for poly(**1a**)s and poly(**1b**)s [(c) and (d)]. The solid curves in (c) and (d) were the theoretical lines calculated with the equations based on reference 22.

The helical conformation of substituted polyacetylenes is stabilized by the intramolecular hydrogen bonding between the side chains having

appropriate substituents such as amide²³ and carbamate²⁴ moieties. In CHCl₃, monomer **1a** (*c* = 20 mM) and poly(**1a**) (*M_n* = 12,800, *c* of the monomer unit = 20 mM) displayed C=O stretching absorption peaks at 1692 and 1669 cm⁻¹, respectively, both of which rationally consist of the overlapped two carbonyl absorption peaks of the carbamate and amide. The observed shift by 23 cm⁻¹ between **1a** and poly(**1a**) suggests the formation of intramolecular hydrogen bonding in poly(**1a**).²⁵ It is noted that the poly(**1a**)s with lower *M_n*'s exhibited smaller shifts of C=O absorption in the IR spectra (Table 2), corresponding with the relationship between the molecular weight of poly(**1a**) and its CD intensity. Methylated monomer **1b** displayed separated two C=O stretching peaks at 1696 and 1665 cm⁻¹ assignable to amide and carbamate moieties. Poly(**1b**)s showed a single broad peak with an apparent peak top at 1684–1685 cm⁻¹ (Table 2). Although the peak shift for poly(**1b**) was not as large as that for poly(**1a**), the result supports the presence of intramolecular hydrogen bonding.

Table 2 Solution-State IR Spectroscopic Data of Monomers **1a** and **1b**, Poly(**1a**), and Poly(**1b**)^a

compound	wavenumber (cm ⁻¹)	
	C=O	N–H
1a	1692 ^c	1508
1a ^b	1694 ^c	1508
poly(1a) (<i>M_n</i> = 12,800)	1669 ^c	1505
poly(1a) (<i>M_n</i> = 7,300)	1672 ^c	1511
poly(1a) (<i>M_n</i> = 1,500)	1689 ^c	1511
1b	1696, 1665 (amide, carbamate)	1515
1b ^b	1697, 1668 (amide, carbamate)	1517
poly(1b) (<i>M_n</i> = 50,300)	1684 ^c	1518
poly(1b) (<i>M_n</i> = 5,800)	1684 ^c	1518
poly(1b) (<i>M_n</i> = 2,700)	1685 ^c	1519

^a Measured in CHCl₃ (*c* = 20 mM). ^b *c* = 10 mM. ^c Two carbonyl peaks of the carbamate and amide were overlapped.

Each result displayed in Figures 1(c) and 1(d) consists of three different regions along their abscissa axes. In the lowest molecular weight region, there is no significant excess formation of one-handed helices because the Cotton effect was not clearly observed in this region and the IR spectra did not show any significant shift of C=O stretching peaks. It suggests that

helix formation requires a certain level of polymer chain length.²⁶ The mid-range molecular weight region showed the strongly rising up of the g value with increasing molecular weight of the polymer, corresponding to the constant formation of helices and relatively low frequency of helix reversals. This tendency considerably changed at the molecular weight region with M_n higher than 10,000. The growth of g value tended to be slower compared to that in the second region and also appears to be almost saturated. These behaviors appear fitting to the statistical mechanical theory proposed by Lifson, Green, Teramoto, Sato and co-workers,^{1,9-13} as previously displayed by the variable temperature CD spectra and the thermodynamic calculations.¹⁶ In this theory, the numbers of helix reversal in one polymer chain is the key importance; a short polymer chain (in the mid-range molecular weight region) does not tend to have a number of reversal points and thus the $\Delta\epsilon$ rise directly reflects the molecular weight of the polymer. On the contrary, a longer polymer chain can have more helix reversal points, which results in the apparent saturation on helix bias and eventually slow growth of the g value against molecular weight increase.

Conclusion

The current work revealed that the chiroptical properties of the amino acid based polyacetylenes strongly depended on their molecular weights, which is applicable to the thermodynamic calculation estimating the free energy

difference between the right- and left-handed helical states, the energy of the helix reversal state. Further investigation including these calculations is now under progress.

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- 25 The conformational analysis by the molecular orbital (MO) calculation supported the formation of a helical structure stabilized by intramolecular hydrogen bonding between the amide and carbamate groups at the side chains of poly(**1a**) (See Figures S1 and S2 in the Experimental Section).
- 26 The MO calculation of poly(**1a**) (2–20-mers) supported that a certain degree of polymerization is necessary for the polymer to adopt a regulated helical conformation. Otherwise, the torsional angles of the single bonds at the main chain deviate from the most stable value (ca. 145°) (See Figure S3 in the Experimental Section).

27 As shown in Table 1, SEC-MALLS revealed the absolute molecular weights of poly(**1a**) and poly(**1b**) somewhat larger than estimated by SEC [115% for poly(**1a**) (Entry 2), 163% for poly(**1b**) (Entry12)]. This is probably because both of the polymers adopt a helical conformation that is more packed than randomly coiled polystyrenes used for SEC calibration. The result also suggests that poly(**1b**) is more ‘packed’ than poly(**1a**).

28 MOPAC 2006 Version 1.0.2, J. J. P. Stewart, Fujitsu Limited, Tokyo, Japan.

List of Publications

Chapter 1

“Polymerization of Phenylacetylenes with Rh complexes: Enhanced Catalytic Activity by π -Acidic Diene”

Naoya Onishi, Masashi Shiotsuki, Fumio Sanda, Toshio Masuda
Macromolecules **2009**, 42, 4071–4076.

Chapter 2

“Living Polymerization of Phenylacetylene Catalyzed by a Cationic Rh Complex Bearing Tetrafluorobenzobarrelene”

Masashi Shiotsuki, Naoya Onishi, Fumio Sanda, Toshio Masuda
Chem. Lett., **2010**, 39, 244–245.

“Living Polymerization of Phenylacetylenes Catalyzed by a Cationic Rhodium Complexes Bearing Tetrafluorobenzobarrelene”

Masashi Shiotsuki, Naoya Onishi, Fumio Sanda, Toshio Masuda
Polym. J., **2011**, 43, 51–57.

Chapter 3

“Polymerization of Phenylacetylenes by Novel Rhodium Catalyst Containing Norbornadiene Tethering Functional Group”

Naoya Onishi, Masashi Shiotsuki, Fumio Sanda, Toshio Masuda
under preparation

Chapter 4

“Helix-Sense Selective Polymerization of Achiral Acetylene Monomer Catalyzed by Chiral Rh Complex”

Naoya Onishi, Masashi Shiotsuki, Fumio Sanda, Takashi Kaneko, Masahiro Teraguchi, Toshiki Aoki, Toshio Masuda
under preparation

Chapter 5

“Molecular Weight Dependence of Helical Conformation of Amino Acid-Based Polyphenylacetylene”

Masashi Shiotsuki, Shohei Kumazawa, Naoya Onishi, Fumio Sanda

J. Polym. Sci., Part A: Polym. Chem. in press (DOI: 10.1002/pola.24941).

Other Publications Not Included in This Thesis

“Asymmetric Polymerization of Achiral Arylacetylenes Giving Helical Polyacetylenes in the Presence of a Rhodium Catalyst with a C₂-Symmetric Tetrafluorobenzobarrelene Ligand”

Takahiro Nishimura, Yoshitaka Ichikawa, Tamio Hayashi, Naoya Onishi, Masashi Shiotsuki, Toshio Masuda

Organometallics, **2009**, 28, 4890–4893.

"Amino Acid-Functionalized Ethyl Cellulose: Synthesis, Characterization, and Gas Permeation Properties"

Yoshitaka Ikeuchi, Fareha Zafar Khan, Naoya Onishi, Masashi Shiotsuki, Toshio Masuda, Yoshiyuki Nishio, Fumio Sanda

J. Polym. Sci., Part A: Polym. Chem., **2010**, 48, 3986–3993.

“Synthesis of End-functionalized Poly(phenylacetylene)s with Well-characterized Palladium Catalysts”

Masashi Shiotsuki, Atsushi Nakagawa, Jesus Rodriguez Castanon, Naoya Onishi, Tatsurou Kobayashi, Fumio Sanda, Toshio Masuda

J. Polym. Sci., Part A: Polym. Chem., **2010**, 48, 5549–5556.

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