Well-Controlled Polymerization of Phenylacetylenes with Organorhodium(I) Complexes: Mechanism and Structure of the Polyenes

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Abstract: A tetracoordinate rhodium complex, $Rh(C{\equiv}CC_6H_5)(nbd)[P(C_6H_5)_3]$ (nbd = 2,5-norbornadiene), combined with 4-(dimethylamino)pyridine (DMAP) is an excellent initiator for the stereospecific living polymerization of phenylacetylene and its *m*- and *p*-substituted derivatives. The rhodium initiator can be generated efficiently by dissociation of triphenylphosphine from isolable $Rh(C{\equiv}CC_6H_5)(nbd)[P(C_6H_5)_3]_2$ or by reacting $Rh(CH_3)(nbd)[P(C_6H_5)_3]_2$ or $[Rh(OCH_3)(nbd)]_2/P(C_6H_5)_3$ with one equivalent of phenylacetylene. The use of a phenylethynyl group, triphenylphosphine, and NBD ligand attached to the rhodium center is crucial for the well-controlled polymerization of phenylacetylenes. An additive, DMAP, is necessary to attain low polydispersities of the polymer products. An active rhodium(I) complex bearing a growing polymer chain, NBD, and $P(C_6H_5)_3$ was isolated from a reaction mixture and was characterized by NMR, GC−MS, XPS, and elemental analyses. The isolated active polymer initiates the further polymerization of the same monomer or substituted ones with an almost 100% initiation efficiency to give higher molecular weight homopolymers or block copolymers, respectively. Detailed NMR structural analysis of the products indicated that the polymerization with the rhodium(I) complexes proceeds via a 2,1-insertion mechanism to provide stereoregular poly(phenylacetylene)s with cis−transoidal backbone structure.

Introduction

Transition metal-mediated polymerization of substituted acetylenes generates polyenes with π-conjugated backbones. The products might lead to new synthetic materials with unique physical properties such as photoconductivity, optical nonlinear susceptibility, and magnetic susceptibility.[1,2] To tune the properties of the polyenes, the molecular weight, polyene geometry, degree of conjugation, polymer end groups, and molecular-weight distribution should be controllable. Stereospecific living polymerization promises the preparation of such well-designed polyenes as block copolymers and end-functionalized polymers.

The first transition metal-promoted living polymerization of acetylenes[3] was reported in 1987 by Masuda and Higashimura who used a $MoCl_5$- or $MoOCl_4$-based three-component system as an initiator. A variety of *o*-substituted phenylacetylenes,[4] *tert*-butylacetylene,[5] and 1-chloro-1-octyne[3a] are usable with this initiating system. Recently, Schrock found well-characterized molybdenum−alkylidene complexes that effect the living polymerization of (*o*-trimethylsilylphenyl)acetylene[6] and ethynylmetallocenes[7] and the living cyclopolymerization of 1,6-

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heptadiyne derivatives.[8] Tantalum−carbene complexes with 2,6-diisopropylphenoxide ligands are also effective for living polymerization of 2-butyne.[9] Nakamura found tungsten complexes with bulky phenoxide ligands initiating polymerization of *tert*-butylacetylene to give a polymer with relatively low polydispersity.[10]

Rhodium(I) complexes exhibit various kinds of reactivities[11−13] toward aromatic substituted acetylenes including dimerization,[11] cyclization, and oligomerization,[12] depending on the structure of the acetylenes and the reaction conditions. In the presence of NaOH or triethylamine, cationic rhodium(I) complexes of the general formula [Rh(diene)(L−L)]X (diene = 1,5-cyclooctadiene (COD) and 2,5-norbornadiene (NBD); L−L = 2,2′-bipyridine or 1,10-phenanthroline; X = PF_6, ClO_4, $B(C_6H_5)_4$)[13a] or $[RhCl(diene)]_2$[13d] initiate stereospecific polymerization of phenylacetylenes (**PA**s), albeit in a nonliving manner. Without any additives the rhodium(I) complexes, Rh(cod)(N−P−Z)[13e] (N−P−Z = C_5H_4N-2-$(CH_2)_2P(C_6H_5)(CH_2)_3ZR$, ZR = OC_2H_5, OC_6H_5, $NH(C_6H_5)$, NH(*cyclo*-C_6H_{11})) and Rh(diene)[(η^6-C_6H_5)B-$(C_6H_5)_3$] (diene = COD,[13f] NBD[14]) also give stereoregular high-molecular-weight polymers.

Although the structures of poly(substituted acetylene)s obtained with early transition metal and group 9 transition metal complexes have been investigated by NMR and IR spectroscopies, there is little information concerning the details of the structure of the polyene backbone. For example, the metathesis polymerization of *tert*-butylacetylene using group 6 metal catalysts gave an 88−97% cis polymer as judged by the chemical shift and line shape of the side chain's methyl carbons in the $^{13}C\{^1H\}$ NMR spectra.[5,10] The poly(phenylacetylene)s (poly**PA**s) prepared with group 9 transition metal complexes were believed to have a cis−transoidal structure based on the chemical shift and shape of the olefinic proton signals in the ^1H NMR spectra.[13a] A very sharp peak at δ 5.83 (in $CDCl_3$) has been tentatively assigned to the olefinic protons on the cis−transoidal main-chain polyene backbone, and the stereoregularity was determined by their peak-line analysis. These structural characterizations are still unsatisfactory. A soluble stereoregular polymer with a narrow molecular-weight distribution is a crucial tool for the mechanistic study of the polymerization and full analysis of the structure of the polyenes as well as its potential characteristics.

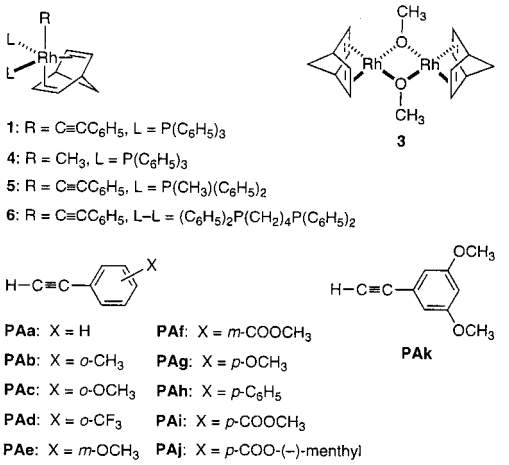

Figure 1. Rhodium(I) initiators and substituted acetylene monomers.

We have recently demonstrated the well-controlled polymerization of phenylacetylene and its *p*-substituted derivatives by using a newly developed organorhodium(I) complex, Rh(C≡CC_6H_5)(nbd)[$P(C_6H_5)_3$]$_2$ (**1**)[15] as well as a tetracoordinate initiator, Rh(C≡CC_6H_5)(nbd)[$P(C_6H_5)_3$] (**2**), generated in situ by mixing $[Rh(OCH_3)(nbd)]_2$[16] (**3**) and $P(C_6H_5)_3$ in a 1:2 molar ratio.[17] Noticeably, an active tetracoordinate rhodium(I) complex bearing a growing polymer chain was isolated from the reaction mixture. The isolable polymer in fact initiated further polymerization almost quantitatively.[18] The preliminary mechanistic investigations showed that the reaction proceeds via an insertion mechanism, consistent with the formation of cis structured polyenes. Here, we disclose the details of our investigation of the mechanism of polymerization of **PA**s with the organorhodium(I) complexes (Figure 1) and the first precise structural analysis of the polyene product.

Results and Discussion

Polymerization of Phenylacetylene and Ring-Substituted Phenylacetylenes with Organorhodium(I) Complexes. Polymerization of phenylacetylene (**PAa**) in the presence of complex **1** and 4-(dimethylamino)pyridine (DMAP) (**1**:DMAP:**PAa** = 1:10:50) in ether proceeded rapidly at room temperature, resulting in the formation of a red-brown precipitate (Scheme 1). Treatment of the reaction mixture with acetic acid[19] afforded poly(phenylacetylene) (poly**PAa**) in an almost quantitative yield. The reaction product is soluble in most common aprotic solvents such as toluene, dichloromethane, and THF, but only slightly soluble in ether. The polymer was purified, when necessary, by dissolution in THF and precipitation with methanol to give a fine yellow powder. In THF, under otherwise identical conditions, the polymerization proceeded homogeneously to give products similar to those obtained in ether. The reaction in ether was slower than that in THF probably because of the hetero-

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Scheme 1

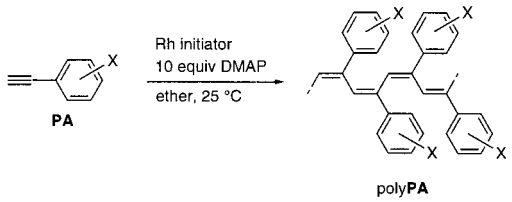

Table 1. Polymerization of Phenylacetylene Initiated by Rh Complexes[a] [15,17]

entry	initiator	[**PAa**]$_o$/[Rh]$_o$	time (min)	conv (%)	poly**PAa** M_n[b]	poly**PAa** M_w/M_n[b]
1	**1**	25	90	94	7700	1.17
2	**1**	50	6	33	4900	1.06
3	**1**	50	10	39	7600	1.09
4	**1**	50	15	70	10 100	1.11
5	**1**	50	35	84	14 200	1.14
6	**1**	50	117	97	14 900	1.15
7	**1**	150	150	97	48 900	1.21
8	**3** + $P(C_6H_5)_3$[c]	25	8	97	4200	1.11
9	**3** + $P(C_6H_5)_3$[c]	50	10	100	7100	1.17
10	**3** + $P(C_6H_5)_3$[c]	150	20	94	23 200	1.13
11	**3** + $P(C_6H_5)_3$[c]	250	8	98	34 900	1.13

[a] Conditions: [**PAa**]$_o$ = 150 mM, [DMAP]$_o$/[Rh]$_o$ = 10, at 25 °C in ether (entries 1−7) or in THF (entry 8−11). [b] Determined by GPC based on monodisperse polystyrene standards. [c] Rh:$P(C_6H_5)_3$ = 1:1.2.

Table 2. Polymerization of Phenylacetylenes Initiated with Rh Complexes[a]

entry	monomer[b]	initiator	time (min)	conv (%)	poly **PA** M_n[c]	poly **PA** M_w/M_n[c]
1	**PAa**	**1**	117	97	14 900	1.15
2	**PAa**	**3**+$P(C_6H_5)_3$[d]	10	90	6900	1.11
3	**PAa**	**4**	240	82	29 000	1.28
4	**PAb**	**1**	240	19	insoluble	
5	**PAc**	**1**	240	76	insoluble	
6	**PAd**	**1**	240	9	insoluble	
7	**PAe**	**1**	120	97	19 200	1.28
8	**PAf**	**1**	90	97	18 900	1.21
9	**PAg**	**1**	120	95	17 100	1.25
10	**PAh**	**1**	120	61	insoluble	
11	**PAi**	**1**	90	86	12 300	1.38
12	**PAj**	**1**	240	100	24 300	1.25
13	**PAj**	**1**[e]	60	74	5300	1.11
14	**PAk**	**1**	80	91	insoluble	

[a] Conditions: [**PA**]$_o$ = 150 mM, [**PA**]$_o$/[Rh]$_o$ = 50, [DMAP]$_o$ = 30 mM, in ether at 25 °C. [b] See Figure 1 for monomer identification. [c] Determined by GPC based on monodisperse polystyrene standards. [d] In THF, Rh:$P(C_6H_5)_3$ = 1:1. [e] [**PA**]$_o$ = 30 mM, [**1**]$_o$ = 3 mM, [DMAP]$_o$ = 30 mM.

geneity of the reaction system, but it gave a lower polydispersity of the products. Tables 1 and 2 show the representative results of reactions of **PAa** and its derivatives using **1** or related rhodium(I) complexes as initiators. As shown in Table 1, M_n values of the poly**PAa** obtained with **1** appeared to increase proportionally to the conversion of **PAa** and the polydispersity, M_w/M_n, remained within a narrow range throughout the polymerization. The molecular weights of the polymers are controllable by varying the initial feed ratio of **PAa**/Rh, and a polymer with a higher M_n, up to 2×10^5 could be obtained.[15] The presence of DMAP is crucial to maintaining a narrow molecular-weight distribution (vide infra).

A 1:2 mixture of **3** and $P(C_6H_5)_3$ is an excellent initiator, which gave the same yellow product, poly**PAa** with an M_n of 8100 and an M_w/M_n of 1.15 in THF.[17] The reaction is 3−4 times faster than with the isolated initiator **1** (Table 2), and its initiation efficiency increases to 70% from 35% obtained with the complex **1** (Table 1 and Table 2).[15,17] The reaction of **PAa** in the presence of a methylrhodium complex, $Rh(CH_3)(nbd)[P(C_6H_5)_3]_2$ (**4**)[20] and DMAP in ether at 19 °C for 4 h gave a brown poly**PAa** with an M_n of 29 000 and an M_w/M_n of 1.21 in 82% yield (entry 3 in Table 2). However, the initiation efficiency of **4** was much lower (16%) than those of **1** and the **3**/$P(C_6H_5)_3$ system.

Under identical conditions, *p*- and *m*-substituted **PA**s (**PAe**−**g**, **PAi**, **PAj**) reacted with **1** at a similar rate to **PAa** to give brown to yellow polymers with a narrow molecular-weight distribution. The linear dependence of the M_n values of these products on the monomer conversions was also observed in the reaction of these monomers. Reaction of (*p*-menthoxycarbonylphenyl)acetylene (**PAj**) with **1** gave a polymer with a polydispersity as low as 1.1. The reaction of (*p*-phenylphenyl)acetylene (**PAh**) and (3,5-dimethoxyphenyl)acetylene (**PAk**) with **1**, however, gave sparingly soluble yellow polymers.

Reactions of *o*-substituted **PA**s (**PAb**−**d**) under the conditions in Table 2 were slow. The resulting polymers were scarcely soluble in common organic solvents such as toluene, THF, ether, dichloromethane, and chloroform. This is the most distinguishing characteristic, compared to molybdenum-based initiating systems which give soluble polymers.[4,6]

The initiators **1** or **3**/$P(C_6H_5)_3$ showed low activity for *tert*-butylacetylene, which gave a white polymer with an M_n of 23 500 and an M_w/M_n of 2.05 in a 17% yield.

Initiators of the Controlled Polymerization. Well-characterized rhodium(I) complexes bearing a phenylethynyl, norbornadiene, and triphenylphosphine ligands effect the well-controlled polymerization of **PA**s. All of the ligands attached to the rhodium metal were crucial components for the reaction, producing stereoregular polymers with predicted molecular weight and low polydispersity.

1. Phenylethynyl Group. The phenylethynyl group on the rhodium center is the key starter of the polymerization when **3**/$P(C_6H_5)_3$ or $[RhCl(nbd)]_2$/$NaOCH_3$/$P(C_6H_5)_3$ is employed as an initiator precursor. NMR analysis showed that a mixture of **3**, $P(C_6H_5)_3$, and **PAa** in a 1:2:10 molar ratio in THF-d_8 at −30 °C formed a tetracoordinate rhodium complex **2**, while no polymerization occurred at this temperature (eq 1). When 2 equiv of $P(C_6H_5)_3$ to rhodium were employed, quantitative formation of the isolable pentacoordinate complex **1** was observed in the spectrum (eq 2). The same initiator **2** can be conveniently generated in situ by mixing a methanol solution of $NaOCH_3$, $[RhCl(nbd)]_2$, and $P(C_6H_5)_3$ in a 2:1:2 molar ratio (eq 3).[17]

$$[Rh(OCH_3)(nbd)]_2 + 2\ P(C_6H_5)_3 + 2\ HC{\equiv}CC_6H_5 \rightarrow 2Rh(C{\equiv}CC_6H_5)(nbd)[P(C_6H_5)_3] + 2\ CH_3OH \quad (1)$$

$$[Rh(OCH_3)(nbd)]_2 + 4\ P(C_6H_5)_3 + 2\ HC{\equiv}CC_6H_5 \rightarrow 2Rh(C{\equiv}CC_6H_5)(nbd)[P(C_6H_5)_3]_2 + 2\ CH_3OH \quad (2)$$

$$[RhCl(nbd)]_2 + 2\ NaOCH_3 + 2\ P(C_6H_5)_3 + 2\ HC{\equiv}CC_6H_5 \rightarrow 2Rh(C{\equiv}CC_6H_5)(nbd)[P(C_6H_5)_3] + 2\ CH_3OH + 2\ NaCl \quad (3)$$

The methylrhodium complex **4** has a fairly good reactivity for the controlled polymerization of **PA**s as shown in Table 2. A ^1H NMR spectrum of a mixture of **4** and **PAa** in a 1:1 molar

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ratio in THF at −20 °C showed that **4** converts rapidly to **1** with a release of methane even at low temperature. Interestingly, these initiator precursors including **1**, **4**, or combined initiators **3** + $P(C_6H_5)_3$ or $[RhCl(nbd)]_2$ + $NaOCH_3$ + $P(C_6H_5)_3$, gave the same tetracoordinate phenylethynylrhodium(I) complex **2** at the initial stage of the reaction. Contrary to these, an analogous cationic rhodium(I) complex without a phenylethynyl group, $\{Rh(nbd)[P(C_6H_5)_3]_2\}[B(C_6H_5)_4]$,[21] has low reactivity when it is reacted with **PAa** in THF giving a product with an M_n of 24 100 and an M_w/M_n of 3.77 at a 27% conversion after 4 h at room temperature. These results indicate that the phenylethynyl group plays an important role in efficiently generating a real initiator, although no direct evidence for phenylacetylene insertion into the rhodium−alkynyl bond[22] could be obtained by NMR studies. Furthermore, the result shown in eq 3 suggests that the role of sodium alkoxide as an additive in the $[RhCl(diene)]_2$-promoted polymerization,[23] can be explained by the formation of the alkynylrhodium species via alkoxyrhodium species.

2. 2,5-Norbornadiene. In terms of activity and stability, NBD, which has stronger σ-donating and π-back-bonding acceptor capabilities than COD,[24] is the best diene ligand to achieve excellent initiator performance. Steric and electronic effects of the NBD ligand might affect the stability and reactivity of the intermediary rhodium complexes. The COD version of **1** could not be isolated, since it was easily replaced by $P(C_6H_5)_3$. Reaction of $[RhCl(cod)]_2$, $P(C_6H_5)_3$, and $LiC{\equiv}CC_6H_5$ only generated $Rh(C{\equiv}CC_6H_5)[P(C_6H_5)_3]_3$.[25] Thus, the reaction of **PAa** with the initiator generated in situ from $[Rh(OCH_3)(cod)]_2$[26] and $P(C_6H_5)_3$ in a 1:2 molar ratio proceeded to give a high molecular-weight poly**PAa** (M_n = 96 000) with a broader molecular-weight distribution (M_w/M_n = 2.10).

3. Triphenylphosphine. The nature of the phosphine ligand significantly influences the initiator performance. The single-crystal X-ray-analysis of **1** indicates that it has a pentacoordinate trigonal bipyramidal geometry with two phosphine ligands located in the equatorial plane.[15a] An analogous methyldiphenylphosphine complex, $Rh(C{\equiv}CC_6H_5)(nbd)[P(CH_3)(C_6H_5)_2]_2$ (**5**), afforded poly**PAa** in <3% yield, if any, after a 5 h reaction in THF containing DMAP. Use of a bidentate phosphine complex, $Rh(C{\equiv}CC_6H_5)(nbd)(dppb)$ (**6**, dppb = 1,4-bis(diphenylphosphino)butane) resulted in no consumption of **PAa** after 3 h under the identical conditions. The marked difference in reactivity between complexes **1** and **5** or **6** can be explained by their solution behavior. The $^{31}P\{^1H\}$ NMR study of **1** in THF showed that a singlet at δ 20.48 (85% H_3PO_4 as the external standard) became a doublet coupled to rhodium with J_{P-Rh} = 119.3 Hz when the temperature was lowered from room temperature to −50 °C. Thus, **1** has two magnetically equivalent phosphorus nuclei in solution and at room temperature, a rapid dissociative equilibrium is set up between **1** and a tetracoordinate rhodium complex **2** plus free $P(C_6H_5)_3$ (eq 4).[27]

$$Rh(C{\equiv}CC_6H_5)(nbd)[P(C_6H_5)_3]_2 \rightleftharpoons Rh(C{\equiv}CC_6H_5)(nbd)[P(C_6H_5)_3] + P(C_6H_5)_3 \quad (4)$$

The structure assignment is consistent with its crystalline structure. Addition of 1 equiv of $P(C_6H_5)_3$ to **1** retarded the dissociation of the phosphine ligand from **1**, thereby resulting in a significant decrease in the rate of the polymerization. However, addition of 1 equiv of NBD to **1** caused no significant retardation. The spectra of **5** and **6** in THF-d_8 gave a doublet even at room temperature at δ 6.82 with J_{P-Rh} = 122.6 Hz and δ 17.75 with J_{P-Rh} = 120.5 Hz, respectively. This suggests that $P(CH_3)(C_6H_5)_2$ and dppb ligands are bound strongly to the rhodium center and that these ligands are reluctant to dissociate to give a coordinatively unsaturated species. Relevant phenylethynylrhodium complexes having a more rigid tridentate phosphine ligand are known to be inert to the polymerization.[22] These facts imply that a labile $P(C_6H_5)_3$ ligand is responsible for the initiator having an excellent performance for the controlled polymerization.

The effect of phosphine ligand(s) on the reactivity was further examined in the combined system of **3** and phosphines. In contrast to the reaction with the pentacoordinate complex **5** giving almost no conversion of **PAa** mentioned above, the use of $P(CH_3)(C_6H_5)_2$ in the combined system under otherwise the identical conditions resulted in a slow reaction to give moderately regulated poly**PAa** with an M_n = 50 100 and an M_w/M_n = 1.70. The phosphine ligand in the **3**/$P(CH_3)(C_6H_5)_2$ combined initiator has a similar effect to that of $P(C_6H_5)_3$ on the chain propagation reaction. In this way the effect of the phosphine ligands on the initiation and propagation steps can be predicted.

4. 4-(Dimethylamino)pyridine (DMAP). With or without DMAP, **PA**s polymerize at similar rates by way of a long-lived species. The presence of DMAP, however, improves the polydispersity of poly**PAa** from 1.31 without DMAP to 1.15 with 10 equiv of DMAP per **1** under the conditions in Table 2. The GPC profile of the product obtained in the absence of DMAP gave a small new peak which was observed due to the minor polymer fraction, whose molecular weight was twice as large as that of the major poly**PA** product. The use of DMAP removed the minor product.

The role of DMAP was clarified by a separate stoichiometric reaction. Reaction of the complex **1** with 1.2 equiv of **PAa** in ether without DMAP gave a red binuclear rhodacyclopentadiene complex **7** (vide infra) in about 30% yield based on **1**. Complex **7** has moderate activity for the polymerization of **PAa** regardless of the presence or absence of DMAP. Under conditions similar to those listed in Table 1, a 4 h reaction of **PAa** with **7** gave a poly**PAa** with an M_n of 175 000 and an M_w/M_n of 2.45 with a 30% conversion of the monomer. Thus, the complex **7** is not a real active initiator for the controlled polymerization. The presence of DMAP completely prevented this formation of **7**, as judged by ^1H and $^{31}P\{^1H\}$ NMR spectra of the reaction mixture. As a consequence, polymerization in the presence of DMAP leads to stereoregular polymers with a narrow molecular-weight distribution.

Isolation and Characterization of Living Rh(polyPAa)(nbd)[$P(C_6H_5)_3$]. Direct evidence for the livingness of this polymerization was obtained by isolating a polymer with an active end,[28] Rh(poly**PAa**)(nbd)[$P(C_6H_5)_3$] (**8**), from the reaction mixture. Reaction of complex **1** with 30−50 equiv of **PAa** under

(21) Schrock, R. R.; Osborn, J. A. *J. Am. Chem. Soc.* **1971**, *93*, 2398−2407.

(22) Bianchini, C.; Meli, A.; Peruzzini, M.; Vizza, F.; Frediani, P. *Organometallics* **1990**, *9*, 1146−1155.

(23) (a) Cataldo, F. *Polym. Int.* **1992**, *30*, 375−379. (b) Cataldo, F. *Polym. Commun.* **1992**, *33*, 3073−3075.

(24) (a) Volger, H. C.; Gaasbeek, M. M. P.; Hogeveen, H.; Vrieze, K. *Inorg. Chim. Acta* **1969**, *3*, 145−150. (b) Green, M.; Kuc, T. A. *J. Chem. Soc., Dalton Trans.* **1972**, 832−839.

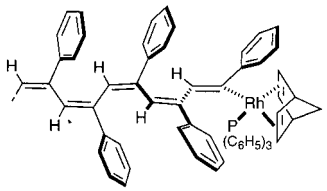
(25) $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 85% phosphoric acid as external standard) δ (ppm) 36.4 (td, J_{P-P} = 33.2 Hz, J_{P-Rh} = 139 Hz, $P(C_6H_5)_3$ trans to $C{\equiv}CC_6H_5$), 33.2 (dd, J_{P-P} = 33.2 Hz, J_{P-Rh} = 152 Hz, $P(C_6H_5)_3$ cis to $C{\equiv}CC_6H_5$).

(26) Uson, R.; Oro, L. A.; Cabeza, J. A. *Inorg. Synth.* **1985**, *23*, 126−130.

(27) For related methylrhodium complexes, see: Rice, D. P.; Osborn, J. A. *J. Organomet. Chem.* **1971**, *30*, C84−C88.

(28) For examples of the isolation of living organometallic polymers, see: (a) Reference 1h. (b) Safir, A. L.; Novak, B. M. *J. Am. Chem. Soc.* **1998**, *120*, 643−650.

Scheme 2



8

the standard polymerization conditions in ether led to a red-brown precipitate which was isolated under an argon atmosphere (M_n = 9700, M_w/M_n = 1.14) (eq 5).

$$Rh(C{\equiv}CC_6H_5))(nbd)[P(C_6H_5)_3] + n\ HC{\equiv}CC_6H_5 \rightarrow Rh(poly\mathbf{PAa})(nbd)[P(C_6H_5)_3] \quad (5)$$

Elemental analysis of **8** revealed that rhodium and phosphorus were present in a 1:1 ratio. Its $^{31}P\{^1H\}$ NMR spectrum showed a doublet at δ 21.9 with J_{P-Rh} = 179 Hz. ^1H NMR spectrum suggested the presence of the $P(C_6H_5)_3$ and NBD ligand in a 1:1 molar ratio in addition to olefinic protons of the main chain of the polymer. Thus, **8** was proved to contain $P(C_6H_5)_3$, NBD, and rhodium metal in a 1:1:1 ratio. The oxidation state of the rhodium atom was confirmed to be +1 by comparing an Auger parameter of 307.9 eV for complex **8** to those measured for some rhodium(I) complexes in the literature.[29] The value is close to 308.1 eV for the complex **1** measured under identical conditions, and 308.9 eV for $Rh^+(nbd)[(\eta^6\text{-}C_6H_5)B^-(C_6H_5)_3]$. The treatment of a reaction mixture containing **8** and $P(C_6H_5)_3$ with excess acetic acid (eq 6)[19] gave $Rh(OCOCH_3)(nbd)[P(C_6H_5)_3]_2$ and poly**PAa**. The rhodium acetate complex did not promote the polymerization of **PAa**. These results are consistent with **8** having a tetracoordinate-structure around the rhodium center similar to complex **2** (see Scheme 2).

$$Rh(poly\mathbf{PAa})(nbd)[P(C_6H_5)_3] + CH_3COOH + P(C_6H_5)_3 \rightarrow Rh(OCOCH_3)(nbd)[P(C_6H_5)_3]_2 + poly\mathbf{PAa} \quad (6)$$

The isolated complex **8** (M_n = 9100, M_w/M_n = 1.11) initiated the polymerization of **PAa** in the presence of a small amount (0.4−1.0 equiv) of $P(C_6H_5)_3$ giving almost quantitatively poly**PAa** with M_n and M_w/M_n values of 33 000 and 1.14, respectively. The second reaction proceeded at the same rate as the first reaction. The clean shift of the GPC peak to the higher-molecular-weight region as shown in Figure 2 indicated clearly that the complex **8** promotes the second polymerization with an almost 100% initiation efficiency. Without extra $P(C_6H_5)_3$, the active polymer **8** (M_n = 8100, M_w/M_n = 1.09) did polymerize **PA**s, but the resulting poly**PA**s had a broader molecular-weight distribution (M_n = 24 100, M_w/M_n = 2.19) (Figure 2). $^{31}P\{^1H\}$ NMR spectrum of a mixture of **8** and $P(C_6H_5)_3$ (1 equiv of Rh) in THF-d_8 at 27 °C showed a doublet at δ 21.8 due to $P(C_6H_5)_3$ attached to rhodium and a sharp singlet due to the added free $P(C_6H_5)_3$, indicating that the exchange between the attached phosphine and the free one is slow within the NMR time scale at this temperature. In the absence of added $P(C_6H_5)_3$, **8** decomposed gradually at room temperature but quickly in refluxing THF to an unidentifiable species, which had no activity for polymerization of **PA**s. Thus, an addition of a small amount of $P(C_6H_5)_3$ in the second polymerization using **8** is necessary to prevent the decomposition of the living active species.

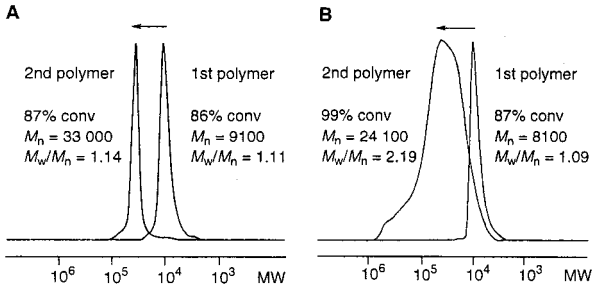


Figure 2. GPC traces of poly**PAa**s obtained by the polymerization of **PAa** using **8** (A) with $P(C_6H_5)_3$ ($P(C_6H_5)_3$/Rh = 1) and (B) without $P(C_6H_5)_3$.

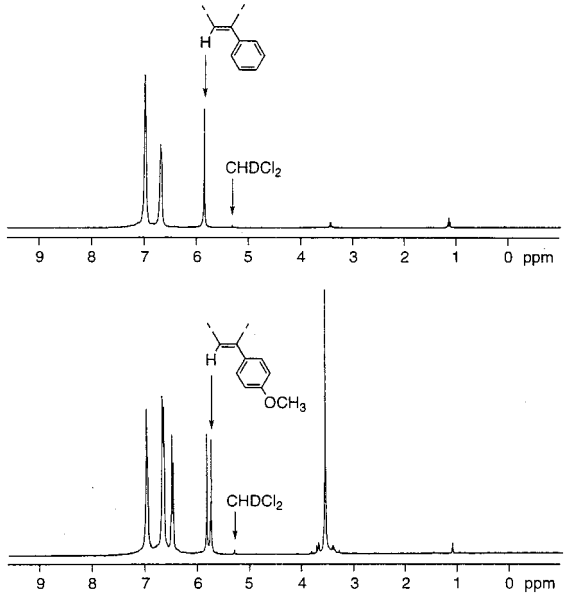


Figure 3. ^1H NMR spectra of poly**PAa** (top) and poly**PAa**−**PAg** (bottom) taken in CD_2Cl_2 at 25 °C. Peaks at δ 1.07 and 3.34 are due to the polymerization solvent.

The living nature of this reaction allows the synthesis of AB type block copolymers from different **PA**s. For example, a copolymer possessing an M_n of 15 300 and an M_w/M_n value of 1.16 was obtained almost quantitatively by reacting a solid poly**PAa** with an M_n of 7300 and an M_w/M_n of 1.09 and 50 molar equiv of **PAg** in ether.[15] When **PAi** was used as the second monomer, a stereoregular poly**PAa**−**PAi** with an M_n of 20 800 and an M_w/M_n of 1.20 was obtained. The clean shift of the GPC peak of poly**PAa** to higher-molecular-weight region due to poly**PAa**−**PAg** was also observed. The ^1H NMR spectrum of the poly**PAa**−**PAg** gave two sharp singlet at δ 5.83 and 5.75 due to the vinylic protons in the unsubstituted and *p*-methoxy-substituted poly**PA** units, respectivly as shown in Figure 3.

Polyene Backbone Structure. With regard to the structures of stereoregular poly**PA**s, four stereoisomers are possible in terms of the configuration of the C═C bond and the conformation of the C−C single bond of the polymer main chain as shown in Figure 4. The ^1H NMR spectrum of poly**PAa** in $CDCl_3$ displays a sharp singlet due to olefinic protons at δ 5.83 in addition to other protons on the substituents (Figure 3). The NBD moiety in **1** was not incorporated in the polymer. Table 3 lists chemical shifts of the olefinic protons of the polymers

(29) (a) Mason, R.; Mingos, D. M. P.; Rucci, G.; Connor, J. A. *J. Chem. Soc., Dalton Trans.* **1972**, 1729−1731. (b) Nefedov, V. I.; Shubochikina, E. F.; Kukolev, V. P.; Kolomnikov, I. S.; Baranovski, I. B.; Shubochkin, L. K. *Zh. Neorg. Khim.*, **1973**, *18*, 845−848. (c) Nefedov, V. I. *J. Electron Spectrosc. Relat. Phenom.* **1977**, *12*, 459−476.

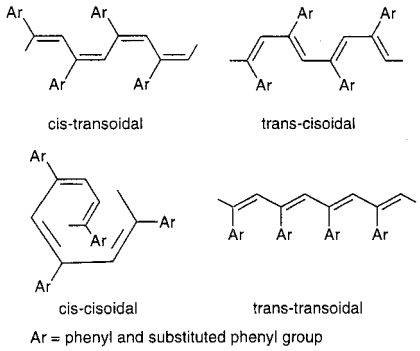


Figure 4. Four possible stereoisomers of poly(phenylacetylene)s.

Table 3. ^{1}H NMR Data of Poly(phenylacetylene)s[a]

	polymer, chemical shift in δ (multiplicity, intensity)	
monomer	vinyl proton	other protons
PAa	5.84 (br s, 1H)	6.94 (m, 3H), 6.63 (d, 2H)
PAb[b]	5.40 (br s, 1H)	6.81 (t, 1H), 6.69 (m, 2H), 6.22 (d, 1H), 1.79 (br s, 3H)
PAc[b]	5.51 (br s, 1H)	6.81 (t, 1H), 6.42 (m, 2H), 6.22 (d, 1H), 3.42 (br s, 3H)
PAe	5.85 (br s, 1H)	6.83 (t, 1H), 6.52 (d, 1H), 6.27 (m, 2H), 3.55 (br s, 3H)
PAf	5.71 (br s, 1H)	7.66 (d, 1H), 7.41 (br s, 1H), 7.01 (t, 1H), 6.76 (d, 1H), 3.76 (br s, 3H)
PAg	5.76 (br s, 1H)	6.63 (d, 2H), 6.46 (d, 2H), 3.58 (s, 3H)
PAi	5.79 (br s, 1H)	7.90 (d, 2H), 6.68 (d, 2H), 3.84 (br s, 3H)
PAj	5.82 (br s, 1H)	7.70 (d, 2H), 6.63 (d, 2H), 4.83 (br s, 1H) 2.00, 1.81, 1.65, 1.49 (set of br s, 6H), 1.06, 0.88, 0.83, 0.69 (set of br s, 12H)

[a] In $CDCl_3$ at 27 °C. [b] In $CDCl_3$ at 50 °C.

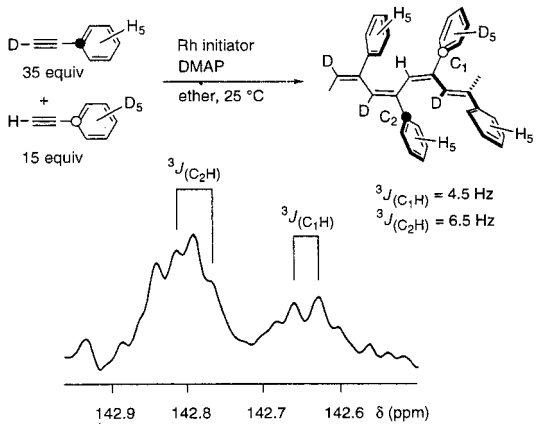


Figure 5. ^{13}C NMR spectrum of poly(**PAa**-d_1-*co*-**PAa**-d_5) in CD_2Cl_2 at 25 °C. A unit mol ratio of **PAa**-d_1/**PAa**-d_5 in the polymer is 7:3.

obtained from *m*- and *p*-substituted **PA**s and **1** in the range between δ 5.71 and 5.85. Although no direct structural characterization has been achieved so far, these signals could probably be correlated to the regular head-to-tail cis−transoidal structure analogous to parent poly**PAa**.[13]

Isotope labeling experiments provide us with more information concerning the details of the structure. The synthesis of isotope-labeled stereoregular poly**PA**s in which the starting labeled monomers distributed statistically is easily attainable. As shown in Figure 5, the proton-coupled ^{13}C NMR analyses of the polymer obtained from a 7:3 mixture of DC≡CC_6H_5 and HC≡CC_6D_5 revealed that signals due to the *ipso* carbons of the phenyl ring and the perdeuterated phenyl ring are observed separately at 142.6 and 142.8 ppm, respectively.[30] The coupling constant between the *ipso* carbon of the perdeuterated phenyl group and vinyl proton through the C=C double bond is 4.5 Hz,[31] while the coupling constant between the *ipso* carbon of the phenyl group and vinyl proton through the C−C single bond is 6.5 Hz.[31] Taking into account the insertion mechanism of this polymerization as discussed later, these results are consistent with the C1 carbon being cis to the vinyl proton and C2 occupying a transoidal position. Thus, the polymer backbone has a cis−transoidal structure.

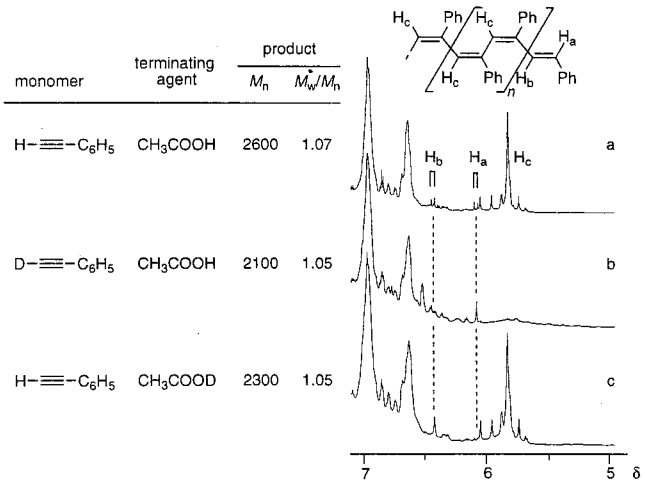


Figure 6. ^{1}H NMR spectra of unlabeled and deuterium-labeled oligo**PAa**s taken in CD_2Cl_2 at 25 °C.

Since the isolated living polymer **8** reacts with CH_3COOH to provide a rhodium-free organic polymer and a rhodium acetate complex (eq 6), the terminal end can be determined by isotope-labeling experiments. Figure 6a shows the ^{1}H NMR spectrum of oligo**PAa** prepared by the reaction of HC≡CC_6H_5 followed by treatment with CH_3COOH. In addition to a sharp singlet at δ 5.83 due to olefinic protons of the main chain,[13a] several small peaks were observed in the δ 5.6−6.5 region. On the other hand, the ^{1}H NMR spectrum of the oligo**PAa** obtained by the reaction of DC≡CC_6H_5 followed by CH_3COOH treatment gave only one broad peak at δ 6.11, which could be assigned to the Ha proton on the carbon atom originally attached to the rhodium center (eq 6 and Figure 6b). Moreover, in the ^{1}H NMR spectrum of the oligo**PAa** obtained from the reaction of HC≡CC_6H_5 followed by CH_3COOD treatment, the peak at δ 6.11 disappeared, while the Hb peak at δ 6.45 became a singlet (Figure 6c). The Ha and Hb protons were coupled with J = 16 Hz. These results suggest that these two protons have the trans relationship and that the propagating rhodium atom in the vinylrhodium complex **8** should be connected to the α carbon of the HC≡CC_6H_5 monomer. The comparison of the intensity of the main peak at δ 5.83 and the Ha peak revealed that the number-average degree of polymerization of oligo**PAa** can be estimated to be ca. 22, which is in a fair agreement with the number, 25.5, measured by GPC analysis. On the basis of these NMR studies as well as analytical data discussed above, a possible structure of the propagating site of the living poly**PAa** can be written as shown in Scheme 2.

Polymerization Mechanism. 1. Initiation. Although attempts to identify the initiation end group by MS, NMR, and IR

(30) The proton-decoupled ^{13}C NMR studies indicate that because of deuterium isotope effect on ^{13}C chemical shifts, four possible singlet peaks due to *ipso* carbons of the phenyl ring and the perdeuterated phenyl ring, −CH=C(C_6D_5)−CD=C(C_6H_5)−, −CH=C(C_6D_5)−CH=C(C_6D_5)−, −CD=C(C_6H_5)−CD=C(C_6H_5)−, and −CD=C(C_6H_5)−CH=C(C_6D_5)− unit, were observed at δ 142.62, 142.65, 142.80, and 142.84, respectively.

(31) J values of cis olefins falls in the range of 2.5−7.1 Hz. See; Marshall, J. L. In *Carbon−carbon and Carbon-proton NMR Couplings*; Verlag Chemie International, Inc.: Deerfield Beach, 1983; pp 33−64.

spectroscopies were unsuccessful, several lines of experimental results concerning the initiation step were obtained. When an isotope-labeled complex, $Rh(^{13}C{\equiv}^{13}CC_6H_5)(nbd)[P(C_6H_5)_3]_2$, was employed as an initiator, no ^{13}C-enriched polymeric products were obtained. This result indicates that the polymerization does not start via a direct insertion of **PA**s into either the rhodium−phenylethynyl bond or a vinylidenecarbene rhodium complex derived from **2**.[32] The ^1H NMR spectrum of the oligomer (M_n = 2600, M_w/M_n = 1.10) obtained by polymerization of $DC{\equiv}CC_6H_5$ with **1** and DMAP in ether/methanol (2 equiv to $DC{\equiv}CC_6H_5$) gave no peaks due to olefinic protons at around δ 5.8, indicating methanol did not participate in the initiation step.

Valuable information for the initiation step was provided by detection of 1,4-diphenyl-1,3-butadiyne from a mixture of **1** and **PAa**. This diyne was obtained in about 30% yield based on the amount of the propagating rhodium center. The formation of $C_6H_5C{\equiv}C-{}^{13}C{\equiv}{}^{13}CC_6H_5$ by reaction of **1** and $H^{13}C{\equiv}{}^{13}CC_6H_5$ in a 1:6 molar ratio is possibly explained by oxidative addition of **PAa** to the tetracoordinate alkynylrhodium complex and the subsequent reductive coupling of two alkynyl groups of dialkynyl complex.[22,33,34] The reaction, in turn, generates probably a rhodium hydride species which could act as an initiator for the polymerization. Unfortunately, attempts to isolate the rhodium−hydride complex analogous to **1** were unsuccessful. On the other hand, in the absence of DMAP, this diyne product probably further reacts with the rhodium−hydride complex and **PAa** to give the binuclear rhodacyclopentadiene complex **7** (see next section).

2. Formation of Binuclear Rhodacyclopentadiene Complex 7. The $^{31}P\{^1H\}$ NMR spectrum of a 1:1.2 mixture of **1** and **PAa** (no DMAP) in CD_2Cl_2 revealed the formation of 30% of complex **7**, 4% of the active polymer **8**, 15% of free $P(C_6H_5)_3$, and 60% of unreacted **1**, in addition to a small amount of $Rh(C{\equiv}CC_6H_5)[P(C_6H_5)_3]_3$. An increase in the initial **PAa**:**1** molar ratio actually led to the controlled polymerization of **PAa**, where the active polymer **8** became the major product while **7** was a minor product in the NMR spectrum.

Complex **7** was obtained from the above reaction mixture as red crystals. Single-crystal X-ray analysis of **7** showed that **7** was a binuclear rhodium complex in which one rhodium atom forms a metallacyclopentadiene structure and the other interacts with it (Figure 7). The complex has three **PAa** units, two of which participate to form the cyclopentadiene framework in a head−tail fashion. The Rh1 atom has one $P(C_6H_5)_3$ and one NBD ligand, while the Rh2 has a NBD ligand. These two rhodium atoms are directly linked to form a metal−metal bond, whose length, 2.70 Å, is within a range of those observed in the literature.[35] The coordination geometry might be best described as a distorted octahedral configuration around the Rh1, C1, and C4 of the metallacycle and NBD occupy the equatorial positions, and the phosphine and Rh2 the axial positions. The Rh2 atom is a part of a distorted square-pyramid configuration

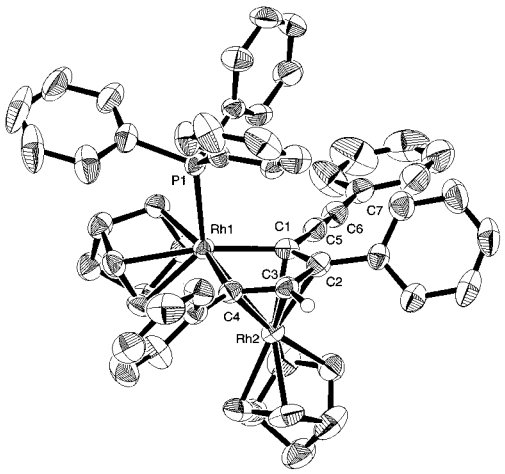
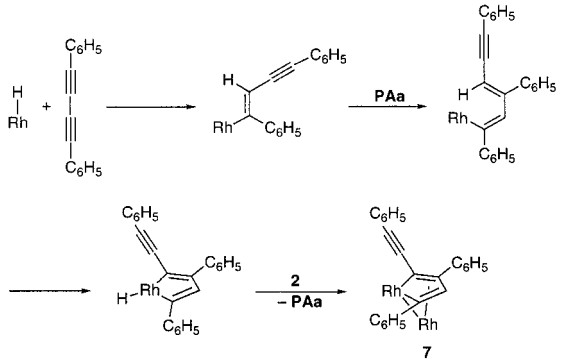


Figure 7. ORTEP view (50% probability ellipsoids) of **7**. The hydrogen atoms except for those of metallacyclopentadiene are omitted for clarity. Bond lengths (Å): Rh(1)−Rh(2), 2.7124(8); Rh(1)−C(1), 2.072(6); Rh(1)−C(4), 2.046(6); Rh(2)−C(1), 2.135(6); Rh(2)−C(2), 2.240(7); Rh(2)−C(3), 2.247(6); Rh(2)−C(4), 2.210(6); C(1)−C(2), 1.432(8); C(2)−C(3), 1.401(9); C(3)−C(4), 1.409(8); C(1)−C(5), 1.444(8); C(5)−C(6), 1.193(9); C(6)−C(7), 1.437(9). Bond angles (deg): Rh(2)−Rh(1)−P(1), 138.88(5); P(1)−Rh(1)−C(1), 98.7(2); P(1)−Rh(1)−C(4), 98.3(2); C(1)−Rh(1)−C(4), 77.3(2); Rh(1)−C(1)−C(5), 125.5(5); C(1)−C(5)−C(6), 175.6(8); C(5)−C(7)−C(6), 174.8(8).

Scheme 3



with NBD and the C=C bonds of the metallacycle in equatorial and the Rh1 atom in axial position. The carbon−carbon bond distances in the metallacycle show leveling, suggesting that a strong back-donation from Rh2 into the rhodacyclopentadiene unit can be postulated. This has been observed in analogous iron complexes.[36]

The formation of the metallacyclopentadiene complex is possibly explained by Scheme 3. We believe that the stepwise insertion mechanism is more plausible in this case, based on the 2,1-insertion polymerization mechanism as discussed in the above section. When **PAa** concentration is low, 1,4-diphenyl-1,3-butadiyne rivals **PAa** in the reaction with a rhodium hydride species. It can be assumed that the 2,1-insertion of the diyne triple bond to the rhodium−hydride bond followed by insertion of **PAa** to the rhodium−vinyl bond provides the metallacycle precursor, which is consistent with the trans relationship of the substituents on the C1 and C2 carbons of this complex. The η^4-coordination of the second molecule of **2** to the metallacycle should assist the oxidative cyclization because of the formation of a metal−metal bond which gives a closed-shell structure with two rhodium metal centers.[37]

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(33) (a) Reitsma, D. A.; Keene, F. R. *Organometallics* **1994**, *13*, 1351−1354. (b) Pedersen, A.; Tilset, M.; Folting, K.; Caulton, K. G. *Organometallics* **1995**, *14*, 875−888.

(34) Unfortunately, some analyses such as monitoring of the polymerization reaction from −20 to 0 °C by ^1H NMR spectroscopy and isomerization of 1- or 2-hexene under the polymerization conditions did not confirm the presence of a rhodium hydride species in the initial stage of the polymerization.

(35) Bateman, L. R.; Maitlis, P. M.; Dahl, L. F. *J. Am. Chem. Soc.* **1969**, *91*, 7292−7300.

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(37) Bruce, M. I. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 73−86.

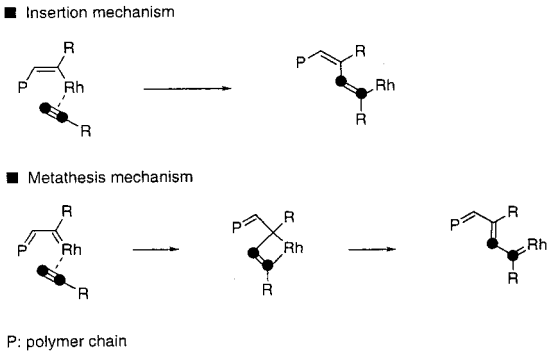

Figure 8. Two possible propagation mechanisms for the transition-metal-mediated polymerization of acetylenes.

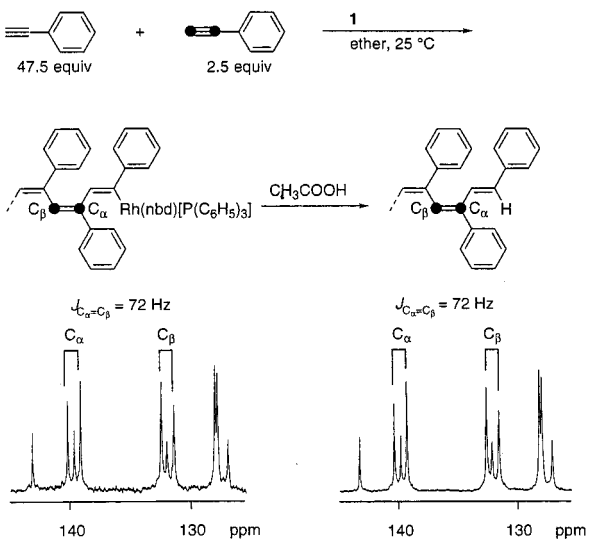

Figure 9. $^{13}C\{^1H\}$ NMR spectra of ^{13}C-labeled poly**PAa** before and after the treatment with excess amount of acetic acid.

3. Propagation. For the propagation of acetylene polymerization, two possible mechanisms have been proposed: a metathesis mechanism via a metal−carbene complex and an insertion mechanism via a metal−vinyl complex.[38] ^{13}C-labeling experiments[14] can easily distinguish both mechanisms, in which the triple bond changes to a single bond in the metathesis mechanism, while it becomes a double bond in the insertion mechanism. Both mechanisms are illustrated in Figure 8. The former case can allow the formation of the polymers containing a mixture of cis and trans configurated double bonds, while the latter case should provide only cis polymer based on the cis-insertion of acetylenes into the rhodium−carbon bond. The $^{13}C\{^1H\}$ NMR spectrum of poly**PAa** obtained from a 95:5 mixture of $HC{\equiv}CC_6H_5$ and $H^{13}C{\equiv}^{13}CC_6H_5$ displayed two doublets at δ 132.2 and 139.9 with a coupling constant of $J_{^{13}C-^{13}C} = 72$ Hz, in accordance with the presence of a $^{13}C{=}^{13}C$ bond in the polymer chain (Figure 9).[39] Treatment of the rhodium-containing polymer **8** with an excess amount of acetic acid caused no shift of the double bond in the polymer backbone. The solid-state NMR analysis of the same polymer indicates the bond distance between these labeled carbons as 1.386 ± 0.009 Å.[40] It is clear that this $^{13}C-^{13}C$-labeled bond has a double bond character both in solution and in solid state. These facts, in combination with the analysis of the growing end (see above), are consistent with our proposed mechanism that the polymerization of **PA**s with **1** and related rhodium(I) complexes proceeds via a cis-insertion mechanism in which the incoming monomer reacts with the rhodium−vinyl bond[18] in a 2,1-manner.

Concluding Remarks

Newly developed $Rh(C{\equiv}CC_6H_5)(nbd)[P(C_6H_5)_3]$ in combination with DMAP is an excellent initiator for the living polymerization of *m*- and *p*-substituted phenylacetylenes as well as the parent phenylacetylene. The tetracoordinated initiator precursor can be generated in situ from the isolable $Rh(C{\equiv}CC_6H_5)(nbd)[P(C_6H_5)_3]_2$ or by reacting $Rh(CH_3)(nbd)[P(C_6H_5)_3]_2$ or $[Rh(OCH_3)(nbd)]_2/P(C_6H_5)_3$ with one equivalent of phenylacetylene. The use of a phenylethynylrhodium complex with a labile triphenylphosphine ligand is crucial for producing well-defined poly**PA**s from **PA**s, and DMAP suppresses the formation of a binuclear rhodacyclopentadiene complex and consequently causes low polydispersity of the product polymers.

A tetracoordinate active rhodium(I) complex bearing a growing polymer chain, a norbornadiene and a triphenylphosphine can be isolated from the reaction mixture, and has been characterized by NMR, GC−MS, XPS, and elemental analysis. A detailed structure analysis using NMR spectroscopy revealed that the polymerization with these rhodium(I) complexes proceeds via a 2,1-insertion mechanism, not via a metathesis pathway to provide the polymers with a cis−transoidal backbone structure. Although direct evidence for an initiation step has not been obtained yet, a plausible mechanism for this polymerization system is shown in Scheme 4.

Experimental Section

The preparation of the initiators and the polymerization were carried out in Schlenk tubes under an argon atmosphere. $[Rh(OCH_3)(nbd)]_2$ (**3**),[16] $Rh(CH_3)(nbd)[P(C_6H_5)_3]_2$ (**4**),[20] $\{Rh(nbd)[P(C_6H_5)_3]_2\}[B(C_6H_5)_4]$,[21] and $[Rh(OCH_3)(cod)]_2$[26] were prepared according to literature procedure. (*o*-Methylphenyl)-(**PAb**),[41] (*o*-methoxyphenyl)-(**PAc**),[41] (*o*-trifluoromethylphenyl)-(**PAd**),[41] (*m*-methoxyphenyl)-(**PAe**),[41] (*m*-methoxycarbonylphenyl)-(**PAf**),[41] (*p*-methoxyphenyl)-(**PAg**),[41] (*p*-phenylphenyl)-(**PAh**),[42] (*p*-methoxycarbonylphenyl)-(**PAi**),[42] [*p*-(L)−(−)-menthoxycarbonylphenyl] (**PAj**),[41] and (3,5-dimethoxyphenyl)-acetylene (**PAk**)[42] were prepared by literature methods and stored under an argon atmosphere. Commercially available phenylacetylene (**PAa**), 1-phenyl-1-propyne, and *tert*-butylacetylene were dried over CaH_2 and then distilled over CaH_2. THF and diethyl ether were distilled over sodium benzophenone ketyl just before use. Triphenylphosphine and 4-(dimethylamino)pyridine (DMAP) were purified by recrystallization from hexane and toluene, respectively.

Preparation of $Rh(C{\equiv}CC_6H_5)(nbd)[P(C_6H_5)_3]_2$ (1). An ether solution of $LiC{\equiv}CC_6H_5$ (4.0 mmol) was added by syringe to an ether solution of $[RhCl(nbd)]_2$ (1.6 mmol) and triphenylphosphine (7.2 mmol) which had been cooled to −20 °C. The reaction mixture was stirred at 0 °C for 2 h before quenching with methanol. After removal of the solvent by vacuum

(38) Although radical polymerization of **PAa** is also possible, it can be ruled out because the polymers obtained by radical reaction are known to contain cyclohexadiene and polyphenylene structure sequences. (a) Amdur, S.; Cheng, A. T. Y.; Wong, C. J.; Ehrlich, P.; Allendoerfer, R. D. *J. Polym. Sci., Part A: Polym. Chem.* **1978**, *16*, 407−414. (b) Chauser, M. G.; Rodionov, Y. M.; Cherkashin, M. I. *J. Macromol. Sci., Chem.* **1978**, *A11*, 1113−1135.

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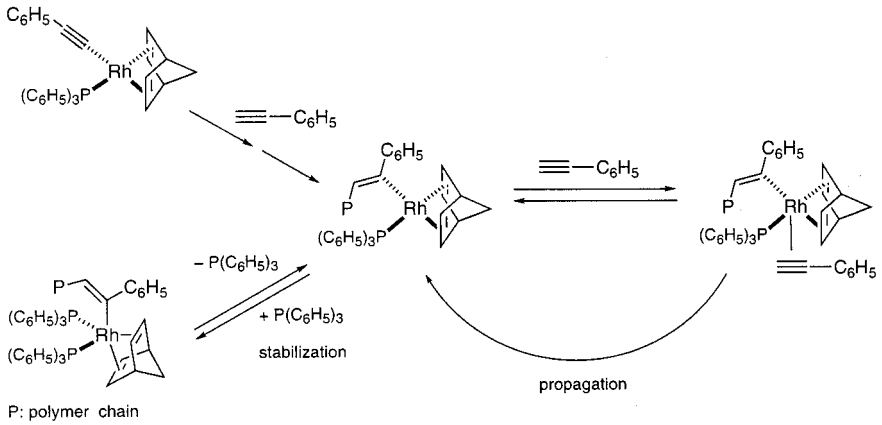
Scheme 4



distillation, the product was washed with ethanol, and dried under vacuum at room temperature. Yellow crystals were obtained by recrystallization from ether. Yield: 77%. ^{1}H NMR (CD_2Cl_2, tetramethylsilane as internal standard) δ 7.51 (t, $P(C_6H_5)_3$, 12H), 7.34−7.19 (m, $P(C_6H_5)_3$, 18H), 7.06 (t, $C\equiv CC_6H_5$, 2H), 6.95 (t, $C\equiv CC_6H_5$, 1H), 6.80 (d, $C\equiv CC_6H_5$, 2H), 3.51 (br s, nbd-olefin, 4H), 3.07 (br s, nbd-CH, 2H), 1.03 (br s, nbd-CH_2, 2H); ^{13}C{^{1}H} NMR (CD_2Cl_2, tetramethylsilane as internal standard) δ 138.47 (d, J_{C-P} = 24.4 Hz, $P(C_6H_5)_3$), 134.27 (d, J_{C-P} = 12.2 Hz, $P(C_6H_5)_3$), 130.60 (s, $C\equiv CC_6H_5$), 129.75 (s, $C\equiv CC_6H_5$), 128.93 (s, $P(C_6H_5)_3$), 128.06 (d, J_{C-P} = 7.3 Hz, $P(C_6H_5)_3$), 127.81 (s, $C\equiv CC_6H_5$), 124.05 (s, $C\equiv CC_6H_5$), 114.05 (d, J_{C-Rh} = 49 Hz, $C\equiv CC_6H_5$), 109.85 (d, J_{C-Rh} = 10 Hz, $C\equiv CC_6H_5$), 61.71 (d, J_{C-Rh} = 4 Hz, nbd), 47.57 (s, nbd), 15.66 (s, nbd); ^{31}P{^{1}H} NMR (THF-d_8, 85% phosphoric acid as external standard, downfield being positive) δ (ppm) 20.48 (s); IR (CH_2Cl_2) 2095 cm^{-1} (C≡C). Elemental analysis: Calcd for $C_{51}H_{43}P_2Rh$ C, 74.63; H, 5.28. Found C, 74.33; H, 5.18.

Preparation of Rh(C≡CC$_6$H$_5$)(nbd)[P(CH$_3$)(C$_6$H$_5$)$_2$]$_2$ (5). $Rh(C\equiv CC_6H_5)(nbd)[P(CH_3)(C_6H_5)_2]_2$ (**4**) was prepared using a procedure similar to that used to make **1**: ^{1}H NMR (CD_2Cl_2) δ 7.63 (br s, $P(C_6H_5)_2$, 4H), 7.33 (br s, $P(C_6H_5)_2$, 16H), 7.12−6.94 (m, $C\equiv CC_6H_5$, 5H), 3.22 (br s, nbd-olefin, 4H), 2.99 (br s, nbd-CH, 2H), 1.91 (br s, PCH_3, 6H), 0.93 (br s, nbd-CH_2, 2H); ^{13}C{^{1}H} NMR (CD_2Cl_2) δ 140.27 (br s, $P(C_6H_5)_2$), 133.5−132.0 (m, $P(C_6H_5)_2$), 130.69 (s, $C\equiv CC_6H_5$), 129.99 (s, $C\equiv CC_6H_5$), 129.5−128.5 (m, $P(C_6H_5)_2$), 128.21 (br s, $P(C_6H_5)_2$), 128.08 (s, $C\equiv CC_6H_5$), 124.14 (s, $C\equiv CC_6H_5$), 114.18 (d, J_{C-Rh} = 51 Hz, $C\equiv CC_6H_5$), 105.73 (br s, $C\equiv CC_6H_5$), 60.80 (s, nbd), 47.48 (br s, PCH_3), 46.75 (s, nbd), 17.43 (br s, nbd); ^{31}P{^{1}H} NMR (THF-d_8, 85% phosphoric acid as external standard) δ (ppm) 6.82 (d, J_{P-Rh} = 122.6 Hz); IR (CH_2Cl_2) 2095 cm^{-1} (C≡C). Elemental analysis: Calcd for $C_{41}H_{39}P_2Rh$ C, 70.04; H, 5.48. Found C, 70.31; H, 5.52.

Preparation of Rh(C≡CC$_6$H$_5$)(nbd)(dppb) (6). $Rh(C\equiv CC_6H_5)(nbd)(dppb)$ (**5**, dppb = 1,4-bis(diphenylphosphino)-butane) was prepared using a procedure similar to that used for **1**: ^{1}H NMR (CD_2Cl_2) δ 7.92 (br s, $P(C_6H_5)_2$, 4H), 7.38, 7.30 (br s, $P(C_6H_5)_2$, 16H), 7.09−6.86 (m, $C\equiv CC_6H_5$, 5H), 3.22, 2.02, 1.29 (br, $P(CH_2)_4$, 8H) 3.02 (br s, nbd-olefin, 4H), 2.99 (br s, nbd-CH, 2H), 0.87 (br s, nbd-CH_2, 2H); ^{13}C{^{1}H} NMR (CD_2Cl_2) δ 140.27 (br s, $P(C_6H_5)_2$), 133.5−132.0 (m, $P(C_6H_5)_2$), 130.69 (s, $C\equiv CC_6H_5$), 129.99 (s, $C\equiv CC_6H_5$), 129.5−128.5 (m, $P(C_6H_5)_2$), 128.21 (br s, $P(C_6H_5)_2$), 128.08 (s, $C\equiv CC_6H_5$), 124.14 (s, $C\equiv CC_6H_5$), 114.18 (d, J_{C-Rh} = 51 Hz, $C\equiv CC_6H_5$), 105.73 (br s, $C\equiv CC_6H_5$), 60.80 (s, nbd), 47.48 (br s, PCH_3), 46.75 (s, nbd), 17.43 (br s, nbd); ^{31}P{^{1}H} NMR (THF-d_8, 85% phosphoric acid as external standard) δ (ppm) 17.75 (d, J_{P-Rh} = 120.5 Hz); IR (CH_2Cl_2) 2094 cm^{-1} (C≡C). Elemental analysis: Calcd for $C_{43}H_{41}P_2Rh$ C, 71.47; H, 5.72; Found C, 71.08; H, 5.60.

Typical Procedure of Polymerization of Phenylacetylenes with 1 in Ether. Polymerization was conducted by adding an ether solution (4 mL) of **PAa** (1.5 mmol) to an ether solution (6 mL) of **1** (0.03 mmol) and DMAP (0.3 mmol) at room temperature. A red-brown polymer precipitated from the reaction mixture during the reaction. After 120 min, acetic acid (100 equiv of **1**) was added, and this mixture was stirred for 10 min at room temperature. The red-brown precipitate was filtered, and this crude polymer was then purified, when necessary, by dissolving it in THF and precipitating it with methanol to give a fine yellow powder. In both cases, the precipitate was filtered and dried under vacuum at room temperature for several hours. The monomer conversion was determined by analyzing the reaction mixture by GC.

Typical Procedure of Polymerization of Phenylacetylenes with 1 in THF. Polymerization was initiated by adding of a THF solution (4 mL) of **PAa** (1.5 mmol) to an THF solution (1 mL) of **1** (0.03 mmol) and DMAP (0.3 mmol) at room temperature. The polymerization proceeded homogeneously to completion, and the reaction mixture gradually turned to dark brown. After 40 min, acetic acid (100 equiv of **1**) was added, and this mixture was stirred for 10 min at room temperature. The resulting solution was poured into methanol (100 mL) to precipitate a polymer. The yellow precipitate was filtered and dried under vacuum at room temperature for several hours.

Synthesis of Living Poly(phenylacetylene), Rh(polyPAa)-(nbd)[P(C$_6$H$_5$)$_3$] (8). An ether solution (7 mL) of **PAa** (2.7 mmol) was added to an ether solution (18 mL) of **1** (0.091 mmol) and DMAP (0.90 mmol) at room temperature to initiate the polymerization. After 5 min, a red-brown polymer deposited on the inner wall of the vessel. The red-brown precipitate was filtered, washed with ether (10 mL × 2), and then dried under vacuum at room temperature for a few hours. Yield: 238 mg (86% yield). M_n = 9700, M_w/M_n = 1.14. ^{31}P{^{1}H} NMR (CD_2Cl_2, 85% phosphoric acid as external standard) δ (ppm) 21.9 (d, J_{P-Rh} = 179 Hz). Elemental analysis: Calcd for Rh-(poly**PAa**)(nbd)[$P(C_6H_5)_3$] P, 0.32; Rh, 1.06, P/Rh = 1.00. Found P, 0.30; Rh, 0.97, P/Rh = 1.01. XPS analysis: Auger parameter of Rh, 307.9 eV.

Typical Procedure of Polymerization of Phenylacetylenes with Isolated Rh(polyPAa)(nbd)[P(C$_6$H$_5$)$_3$] (8). An ether solution (2.4 mL) of **PAa** (0.6 mmol) was added to an ether solution (4 mL) of **1** (0.02 mmol) and DMAP (0.20 mmol) at room temperature. After 60 min, the red-brown precipitate (**8**) was filtered, washed with ether (5 mL × 2), and dried under

vacuum at room temperature. Then, to an ether suspension (4 mL) containing the isolated polymer **8** (M_n = 9100, M_w/M_n = 1.11) and triphenylphosphine (0.008 mmol) was added an ether solution (2.4 mL) of **PAa** (0.60 mmol) at room temperature. After the mixture stirred for 120 min, acetic acid (100 equiv of active end) was added, and this mixture was stirred for 10 min at room temperature. The red-brown precipitate was filtered, washed with methanol, and dried under vacuum at room temperature for several hours. Yield: 264 mg. M_n = 33 000, M_w/M_n = 1.14.

Characterization of Polymer. The molecular-weight distribution of the polymers was determined using size-exclusion chromatography (SEC) in THF at 40 °C on a Waters 510 system equipped with three polystyrene gel columns (Shodex KF-802, 803 and 804; 8 mm i.d. × 300 mm). The number-average molecular weight (M_n) and the polydispersity (M_w/M_n) of the polymers were calculated from SEC eluograms based on polystyrene calibration. The ^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR spectra were recorded on a JEOL JNM-270 spectrometer. GC−MS analysis was carried out on a Shimadzu QP-1100EX equipped with a capillary column (Shimadzu DB-1).

Synthesis of Binuclear Rhodacyclopentadiene Complex 7. An ether solution of **PAa** (109 mmol) was added dropwise to an ether solution of **1** (67.4 mg, 82 mmol) at room temperature for 0.5 h. The reaction mixture was then stirred for 10 min before treatment with acetic acid (0.15 mL). The resulting ether solution was washed with aqueous sodium bicarbonate, and was concentrated under reduced pressure. When acetone was added to the solution, red crystals precipitated. Yield: 11.8 mg (12 mmol; 30% based on rhodium). Pure **7** can be obtained as red crystals by recrystallization from acetone: ^{1}H NMR (CD_2Cl_2) δ 7.25 (m, P(C_6H_5)$_3$ and phenyl groups on metallacycle, 25H), 6.92 (m, C═CC_6H_5, 3H) and 6.18 (m, C═CC_6H_5, 2H); 6.08 (m, H at C3, 1H); 4.89 (nbd-olefinic H at Rh1, 1H), 4.73 (nbd-olefinic H at Rh1, 1H), 3.99 (nbd-olefinic H at Rh1, 1H), 3.72 (nbd-olefinic H at Rh1, 1H), 3.60 (nbd-olefinic H at Rh2, 2H), 3.46 (nbd-olefinic H at Rh2, 2H), 2.96 (nbd-CH at Rh1, 1H), 2.83 (nbd-CH at Rh2, 2H), 2.61 (nbd-CH at Rh1, 1H) and 1.1 (m, nbd-CH_2 at Rh1 and Rh2, 4H). All NBD signals appear as broad multiplets from which no coupling constant could be determined. ^{31}P{^{1}H} NMR (CD_2Cl_2, 85% phosphoric acid as external standard) δ (ppm) 26.5 (dd, $^1J_{P-Rh1}$ = 145.8 Hz, $^2J_{P-Rh2}$ = 6.5 Hz). X-ray crystallographic analysis of **7** was carried out on a Rigaku AFC7R diffractometer, with graphite-monochromated Cu Kα radiation, λ = 0.154 178 Å (μ = 69.48 cm^{-1}), using the w-2θ scan technique. Crystal data for **7**: $C_{56}H_{47}PRh_2$, M_r = 956.77, red crystal (0.10 × 0.10 × 0.10 mm), monoclinic, space group $P2_1/c$, a = 11.278(4) Å, b = 10.927-(3) Å, c = 34.446(2) Å, β = 94.22(1)°, V = 4233(1) Å^3, Z = 4, D_{calcd} = 1.501 (g/cm^3), T = 293 K. 8067 reflections were observed, 7649 of which were unique. The structure was solved by direct methods[43] and expanded using Fourier techniques.[44] The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. The final cycle of full-matrix least-squares refinement was based on 5039 observed reflections ($I > 3.00\sigma(I)$) and 533 variable parameters and converged with R = 0.045 and R_w = 0.054. The maximum and minimum peaks on the final difference Fourier map corresponded to 0.86 and −0.84 e$^-$/Å^3, respectively.

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Supporting Information Available: Tables of positional parameters, thermal parameters, bond distances, and bond angles for **7** (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

JA991903Z

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