Development of Pd and Rh Catalysts for the Controlled Synthesis of Substituted Polyacetylenes

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Contents

General Introduction

1. Background

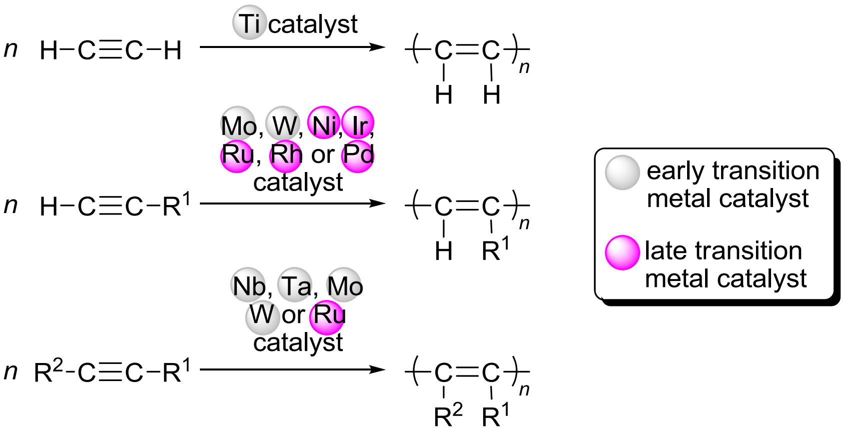
Transition metal catalysts are actively applied in the industry and academy for the polymerization of a vast amount of monomers. For instance, Ziegler-Natta[1] and Kaminsky catalysts[2] are remarkable examples of organometallic catalysts employed for the large-scale production of polyethylene and polypropylene, which are without doubt major products in the worldwide chemical industry.[1a,3] The ability to perform controlled polymerization reactions[2,3d,4] (controlled stereoregularity, regioregularity and tacticity) under mild conditions positions transition metal complexes as preferred catalysts for many polymerization reactions.

In more recent years, conjugated polymers have attracted academic and industrial interest due to their unparalleled semiconductivity and optoelectronic properties which make them potential materials for its application in next-generation optoelectronic devices.[5] Therefore, development of suitable transition metal catalysts for the synthesis of well-controlled conjugated polymers is fundamental for shedding light into the polymer structure-property relationship. Polyacetylene and its substituted derivatives triggered intense research in the area of conjugated polymers after the discovery of metallic conductivity in “doped” polyacetylene by Professors Heeger, MacDiarmid and Shirakawa, awarding them with the Nobel Prize in 2000.

2. Acetylene Polymers

The reports regarding the conductivity of polyacetylene importantly stimulated the research of acetylene polymers. Eventually, it was found that the introduction of substituents in polyacetylene main chain yielded materials featuring enhanced processability and singular outstanding properties such as nonlinear optical properties, magnetic properties, gas permeability, and photo- and electroluminescent properties.[6,7]

Scheme 1. Polymerization of acetylene and its substituted derivatives.



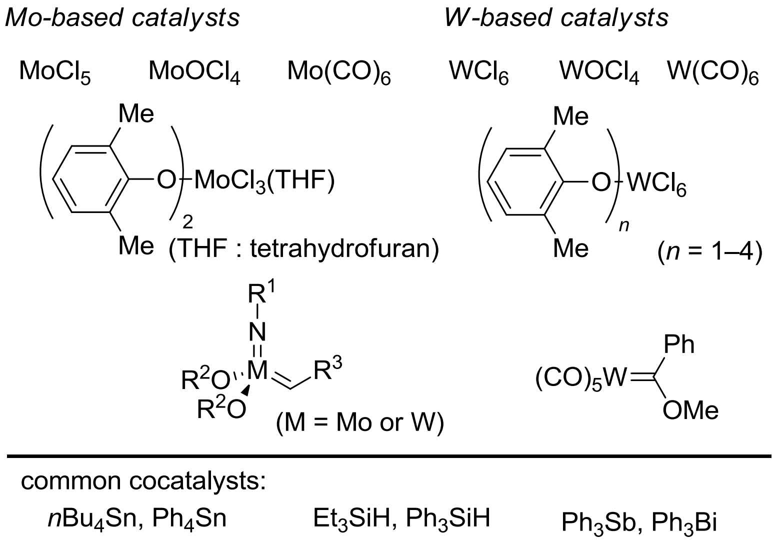
From the initial stages of the polymerization of acetylene monomers, transition metal catalysts have been employed (Scheme 1). The first report for the polymerization of acetylene was done by Natta and coworkers in 1958 employing a Ti-based catalyst.[8] However, the Ziegler catalyst could only polymerize steric unhindered monomers. Masuda and coworkers developed group 6 transition metal catalysts which made the polymerization of substituted acetylenes possible.[9] Posterior studies have been dealing with the development of new catalysts which feature high polymerization activities for a wide range of monomers as well as can control the polymer structure. Today, we count with a considerable amount of transition metal catalysts that roughly can be divided in early and late transition metal catalysts. The type of polymerizable monomers and the type attainable polymer structures vary from catalyst to catalyst. While the rest of the general introduction describes briefly the different type of catalysts and its characteristics, special attention is given to Pd and Rh catalysts, which are focused in the present work.

3. Transition Metal Catalysts Applied to the Polymerization of Substituted Acetylenes.

3.1 Early Transition Metal Catalysts.

The most common early transition metal catalysts that are employed for the polymerization of substituted acetylenes are Mo, W, Nb and Ta. In fact, the first report for the polymerization of a substituted acetylene in good yields was performed by group 6 catalysts (WCl_6 or $MoCl_5$).[9] At that time, poly(phenylacetylene) (PPA) was obtained in moderated to high yields featuring M_n's of approximately 15000. After this initial report, notable modifications have occurred to the early transition metal catalysts and nowadays high yields of polymers with molecular weights up to 2×10^6 can be obtained.[6,10] Common examples of early transition metal catalysts are displayed in Chart 1. Mo and W catalysts are effective for the polymerization of monosubstituted acetylenes (HC≡CR), particularly monosubstituted acetylenes with high steric hindrance (R = *tert*-butyl or *ortho*-substituted phenyl groups) afford polymers with high molecular weight (MW) while non-crowded monomers give low yields with unsatisfactory M_n.[6]

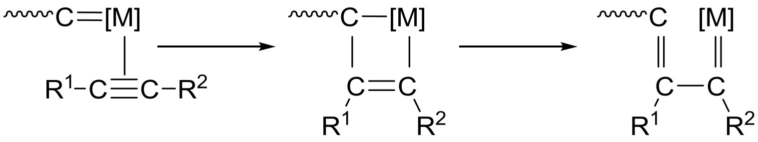
Chart 1. Common early transition metal catalysts



Nb and Ta catalysts (group 5) are very effective for the polymerization of bulky substituted acetylenes. Even nowadays, $NbCl_5$ and $TaCl_5$ are preferred catalysts for the polymerization of disubstituted acetylenes such as internal alkynes, 1-aryl-1-alkynes and diphenylacetylenes.[6,10a,10b] However, Nb and Ta catalysts majorly afford linear oligomers or tricyclization products when non-sterically hindered monomers are employed (such as 1-alkynes and phenylacetylenes).

The mechanism underlying the substituted acetylenes polymerization performed by Nb, Ta, Mo and W is metathesis (Scheme 2). In this mechanism the active species are alkylidene complex, namely species having a metal-*sp*^{2} carbon double bond.

Scheme 2. Metathesis mechanism for the polymerization of acetylene monomers.



3.2 Late Transition Metal Catalysts

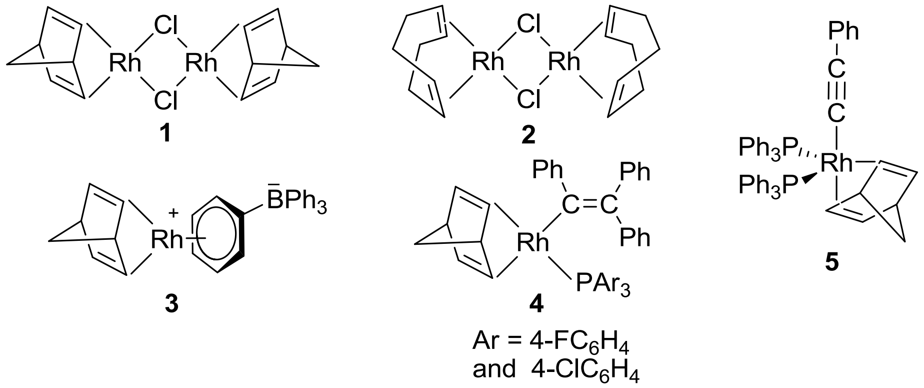
In more recent years, for the polymerization of monosubstituted acetylenes, late transition metal catalysts have been spotlighted because their lower oxophilicity allows them to polymerize monomers bearing polar substituents (such as hydroxy, amino, azo, and radical groups) which cannot be handled directly by early transition metal catalysts. In this work, Rh and Pd catalysts are the subjects of research and therefore in the following two sections the author describes the details regarding the employment of these two transition metals as catalysts.

3.2.1 Rh Catalysts

Rh-based catalysts have been extensively investigated due to their capacity to polymerize monosubstituted acetylenes in a stereoregular manner (head-to-tail and cis-transoidal), specially substituted arylacetylenes.[11]

Controlling the main chain stereoregularity of the acetylene polymers allows to modify their properties. As an example, the *cis*-transoidal stereoregularity of acetylene polymers is essential for the induction of a specific handedness in helical polyacetylenes which have given extreme popularity to the Rh catalysts for the synthesis of helical polyacetylenes.[12] The nature of the Rh catalysts for controlling the main chain-structure of the polyacetylenes have triggered numerous amount of research leading to the development of extremely sophisticated Rh-based catalytic systems that work efficiently even in water.[13] The most common Rh catalysts are ligated by a diene [commonly 2,5-norbornadiene (nbd) or 1,5-cyclooctadiene (cod)] while the rest of the coordination sites are occupied by the same or other ligands (Chart 2).

Chart 2. Common Rh catalysts employed for substituted acetylene polymerization.



Chloride bridging complexes **1** and **2**, as well as zwitter ionic complex **3** are well-employed for the polymerization of arylacetylenes. The high stability of these complexes towards oxygen and water allow us to handle them easily.

When chloride-bridged complexes **1** and **2** are employed together with an amine as a cocatalyst, the obtainted polymers feature controlled molecular weights, relatively narrow polydispersities (PDI = ~1.70) and almost quantitative *cis*-stereoregularity. The amine promotes the formation of a mononuclear Rh species that initiates the polymerization of acetylene monomers.[11c,11b,14]

Living polymerization is achieved when catalysts **4** and **5** are employed. Noyori and coworkers reported that catalyst **5** in combination with 4-(dimethylamino)pyridine (DMAP) yields a living catalytic system for the polymerization of *m*- and *p*-substituted phenylacetylenes.[11e,15] Moreover, isolation and characterization of an active Rh tetracoordinated complex from the polymerization reaction mixture provided concrete evidence for the 2,1-insertion mechanism. This mechanism was also concistent with the formation of the *cis*-transoidal polymer backbone as reported by Furlani and coworkers.[16] Masuda and coworkers developed well-defined vinyl rhodium catalyst **4** that can also perform the living polymerization of a numerous amount of monosubstiuted acetylenes with small PDIs.[17] The studies regarding catalyst **4** contributed to consolidate a clearer idea of the mechanism followed by Rh catalysts during the polymerization of monosubstitued acetylenes and in combination with DFT calculations,[18] today the mechanism in Scheme 3 has been proposed as the most probable one.

Masuda and coworkers demonstrated that Rh catalysts **6**–**8** bearing a highly π-acidic diene ligand, tetrafluorobenzobarrelene (tfb) (chart 3) show higher activity for the polymerization of monosubstituted acetylenes than the nbd-based counterparts.[19] Living polymerization of PA with a very small PDI (1.03) was achieved when catalyst **7** was employed.

Scheme 3. Proposed mechanism for the Rh-catalyzed polymerization of phenylacetylene (PA).

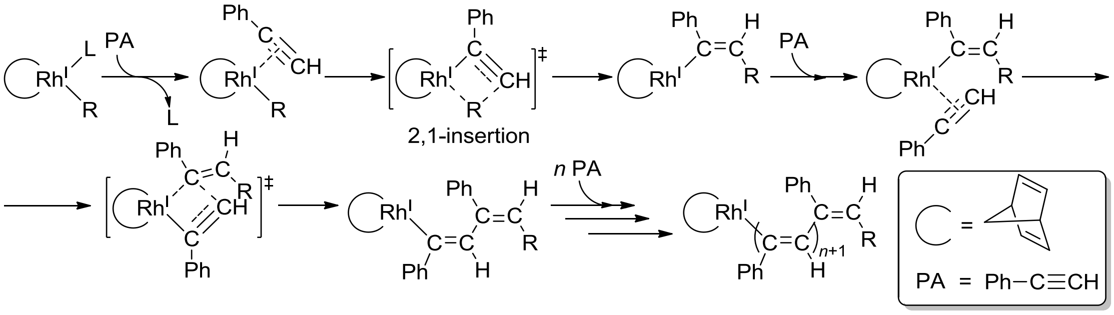
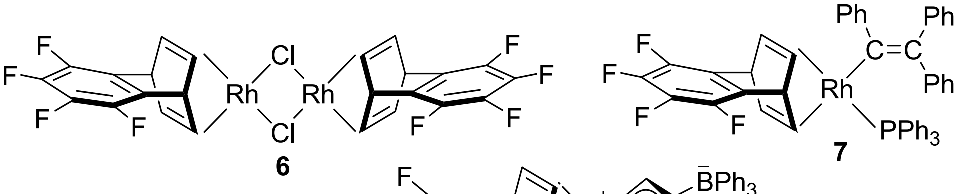


Chart 3. Tetrafluorobenzobarrelene-based Rh catalysts.



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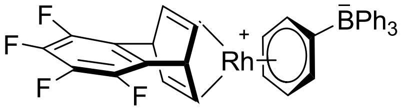

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In spite of the high activity and great accuracy that Rh catalysts offer for the polymerization of monosubstituted acetylenes, Rh catalysts have a considerable disadvantage. They can hardly polymerize disubstitued acetylenes. The inability of Rh catalysts to polymerize disubstitued acetylenes, excepting two reports,[20] is presumably due to the higher steric hindrance of these monomers compared to monosubstituted acetylenes.

3.2.2 Pd Catalysts

Pd catalysts have not been explored as exhaustively as Rh catalysts. Proper development of Pd catalysts for the polymerization of substituted acetylenes potentially allows us to combine this chemistry with that of olefin polymerization and chain polycondensation polymerization reactions employed for the synthesis of some conjugated polymers including polythiophene and polyfluorene.[4,5]

The application of Pd catalysts to the polymerization of substituted acetylenes originates with simple complexes such as $[(CH_3CN)_4Pd](BF_4)_2$ (**9**) and $[Pd(PPh_3)_2Cl_2]$ (**10**).[21] In spite of the simple structure, Pd catalyst **9** satisfactorily polymerized PA, methyl propiolate and olefins in yields ranging 30–90% with M_n's from 2000 to 9000.[21a] Catalyst **9** also polymerized cyanoacetylene to give polymers with M_w's lower than 8300 containing residual catalyst metals.[21d] Russo and coworkers developed [bis(triphenylphosphine)Pd(bisacetylide)] catalysts **11**–**15** (Chart 4)[21b,c,22] for the oligomerization/polymerization of polar monosubstituted acetylenes such as ethynylfluorenol (M_n < 2000),[21c] propargyl alcohol (M_n > 35000),[22a,d] and *N*,*N*-dimethylpropargylamine (M_n > 9300) (Chart 5).[22c] In addition, [bis(triphenylphosphine)Pd(bisacetylide)] catalysts **11** and **14** also successfully polymerized *p*-diethynylbenzene and trimethylsilylacetylene ($M_n \approx 20000$).[21b,22b] Catalysts **11** and **13** polymerized several polar and non-polar substitued acetylenes (HC≡CR where R = CH_2OH, CH_2OCOR', C_6H_4-*p*-C≡CH,

Chart 4. Pd catalysts employed for the polymerization of substituted acetylenes.

$[(CH_3CN)_4Pd]Cl_2$

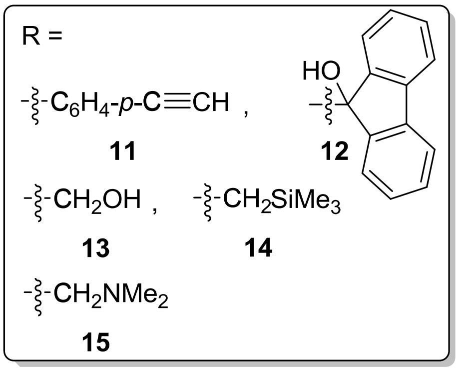
9

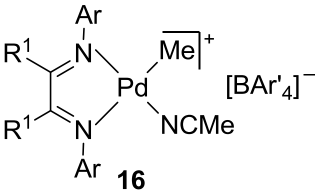
$[(Ph_3P)_2PdCl_2]$

10

$[(Ph_3P)_2Pd(C{\equiv}CR)_2]$

11–15





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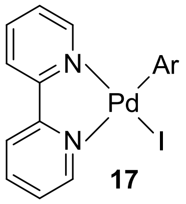

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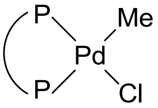

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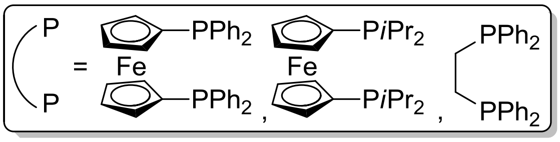
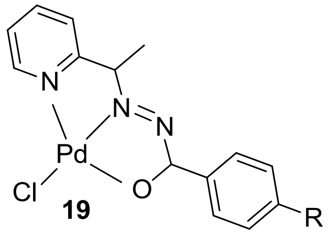
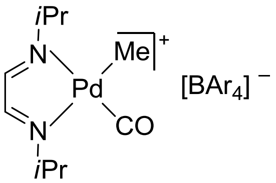




(R = Br, OMe, Me)



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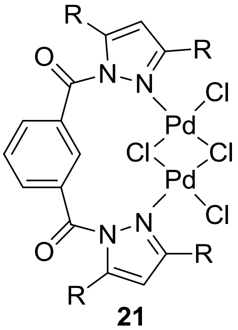

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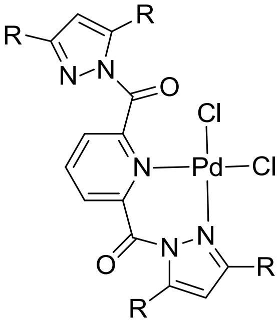
(R = *t*Bu, Ph, Me)



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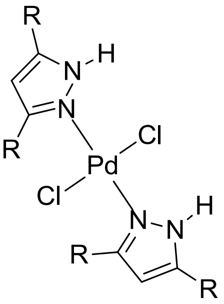
(R = *t*Bu, Me)



(R = H, Me, *t*Bu)

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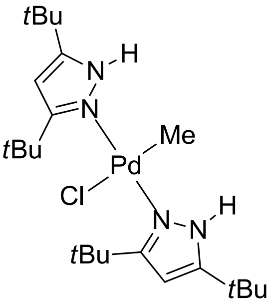

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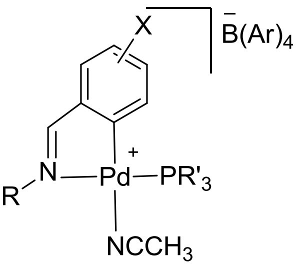

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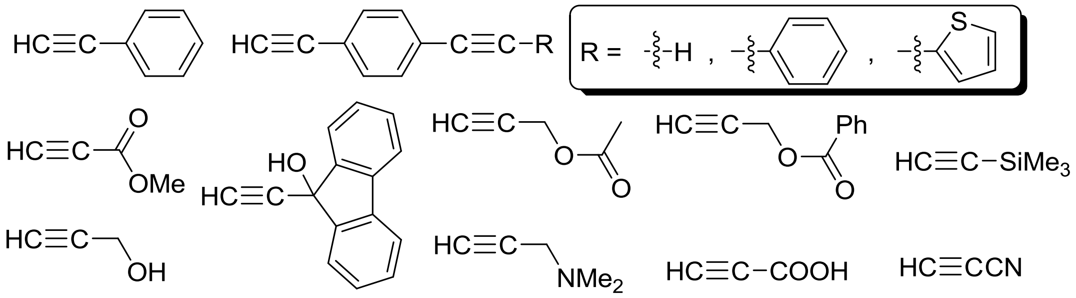
C_6H_4-*p*-C≡CC_6H_5) to give polymers with M_w's>4000 in yields higher than 61%.[22e] Yang and coworkers employed also bisacetylide Pd complexes to synthesize several copolymers such as poly(propargyl alcohol-*co*-*p*-diethynylbenzene), copolymers of propiolic acid with phenylacetylene, *p*-diethynylbenzene and propargyl alcohol, some of which were tested as humidity sensors.[22f,g]

Although the bisacetylide Pd catalysts represented a first approach to the employment of well-defined Pd precatalysts for the polymerization of monosubstituted acetylenes, the results were not fully consistent. The PDI's were large and metal coordinated residues remained at the polymer chain ends in some cases. Other efforts were done to develop active well-defined active Pd catalysts employing diimine ligands for the polymerization of monosubstituted acetylenes.[23] While (diimine)Pd catalysts are versatile for the polymerization of olefins,[24] they only yielded products of single to triple insertion of substituted acetylenes into the Pd-Me bond of **16**. Bipyridine coordinated Pd complex **17** similarly yielded products of single to multiple insertion of a substituted acetylene into the Pd-Ar bond.[25] In spite of the apparent failure to polymerize substituted acetylenes of well-defined Pd catalysts **16** and **17**, they provided evidence for Pd catalysts inserting acetylenes into the Pd–C bond of the starting Pd complexes.[23,25]

Darkwa and Pollack reported the generation of active Pd catalysts for the polymerization of PA from well-defined [(diphosphine)PdMeCl] (**18**) complexes upon cationitation with silver trifluoromethane sulfonate (AgOTf).[26] Remarkably, [(dppf)PdMe($NCCH_3$)]OTf [dppf = 1,1'-bis(diphenylphosphino)ferrocene] catalyzed the formation of poly(PA)s in very high yields (81–100%) featuring M_n's (4500–12000) close to the theoretical values ($[PA]_0/[Pd] = 50$). Moreover, ^{1}H and ^{13}C NMR spectra of the poly(PA)s exhibited weak methyl proton signals suggesting that the polymerization proceeded through the insertion mechanism but no further concrete evidence was presented.

A series of tricoordinated Pd complexes (**19,** R = Br, OMe, Me) were employed for the polymerization of PA in water, but high MW products were obtained only in low yields (<9%). The majority of the products were oligomers with low molecular weights (M_w<1400).[27] Diimine ligated Pd complex **20** polymerized PA but specific details were unclear.[28] Mecking and coworkers reported a series of papers involving the formation of poly(PA) nanoparticle dispersions by employing a Pd catalytic system $[Pd(OAc)_2]/t\mathrm{Bu}_2\mathrm{P(CH_2)_3P}t\mathrm{Bu}_2$ in water.[29] In addition, Darkwa employed pirazole and pyrazolyl ligated Pd complexes **21**–**24** for the polymerization of PA.[30] Ligands bearing bulky substituents (*t*Bu or Ph) yielded more active catalysts than ligands with low steric hindered groups (Me). The molecular weights of the polymers varied depending on the reaction conditions and typical M_w values ranged from 4000 to 12900 and the PDI's ranged from 2.29 to 2.99. A certain amount of CH_3CN as a coordinating solvent was essential for the smooth polymerization. The most recent paper regarding Pd catalysts employed for the polymerization of subsituted acetylenes concerned cationic palladacycles bearing imine and phosphine ligands (**25**) which yielded low molecular weight products (M_w < 2196) with variable monomer conversions. Only when trimethylphosphine was employed as a ligand, high molecular weight products (59000 > M_w > 45000) were obtained in very low yields.

Chart 5. Examples of substituted acetylenes polymerized by Pd catalysts.



4. Objectives of This Thesis

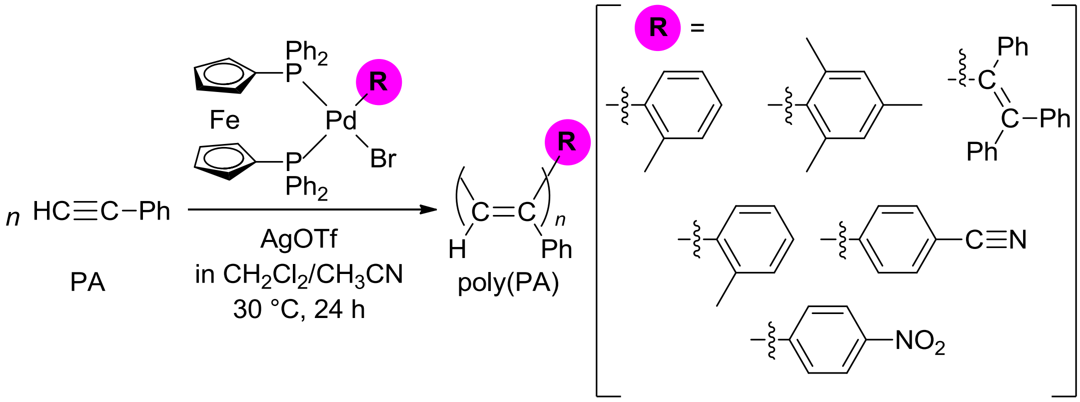
As described above, Pd catalysts polymerize polar and non-polar monosubstituted acetylenes (Chart 5), which proves the versatility of these catalysts. However, systematic study of the polymerization mechanism is still lacking. Moreover, there is no Pd catalyst capable of polymerizing disubstituted acetylenes. Polymers of disubstituted acetylenes are more stable and photoelectrically active than their monosubstituted analogues. The author focuses on the development and clarification of Pd catalysts for the polymerization of substituted acetylenes based on an enormous potential of Pd catalysts. In addition, the author also discusses the mechanistic aspects of PA polymerization by Rh catalysts.

5. Outline of This Thesis

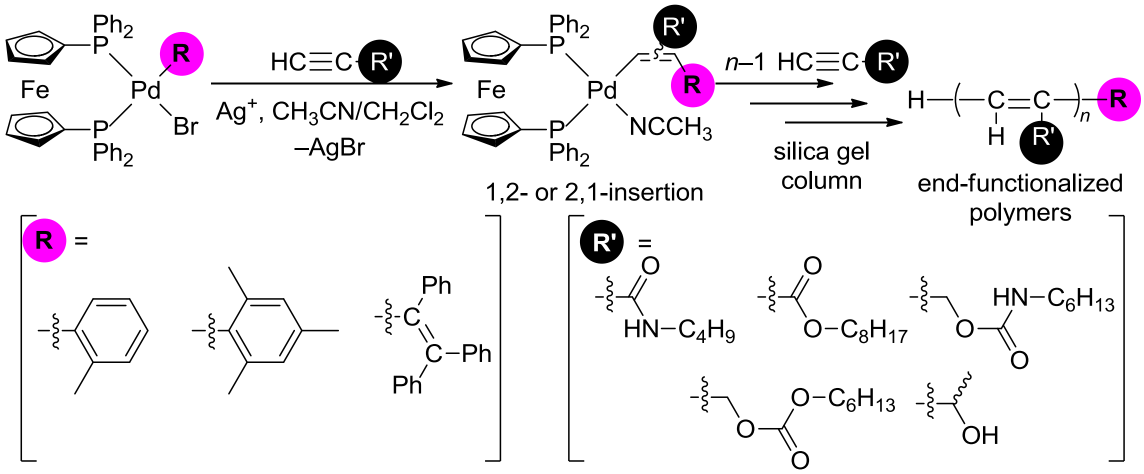
The present thesis consists of three parts: **Part I** (Chapters 1 and 2), **Part II** (Chapters 3 and 4) and **Part III** (Chapter 5). Every chapter has its own reference, compound, figure, scheme and table numbers; therefore may the author ask the reader to take care not to mix the numbers of one chapter with the others.

In **Part I**, the author synthesizes a series of [(dppf)PdRBr] complexes to obtain "R" end-funcitonalized polymers of polar and non-polar monosubstituted acetylene monomers. A stoichiometric reaction afforded concrete evidence demonstrating that the polymerization occurs through the insertion mechanism.

In **Chapter 1,** the author synthesized end-functionalized poly(phenylacetylene)s by the polymerization of PA using well-defined palladium catalysts [(dppf)PdBr(R)] in combination with AgOTf. The author detected the R groups, initially coordinated to the Pd center, at the polymer chain ends by IR and ^{1}H NMR spectroscopies as well as by MALDI-TOF mass analysis.

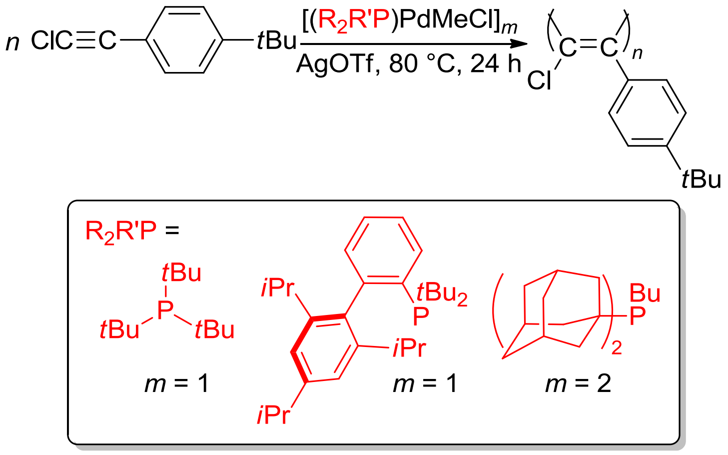


In **Chapter 2,** the author demonstrated that a series of [(dppf)PdBr(R)]-type complexes in conjunction with AgOTf were active for the polymerization of monosubstituted polar acetylene monomers. The author confirmed the incorporation of “R” and “H” groups at the polymer chain ends by MALDI-TOF analysis. The author identified the species formed by single, double and triple insertions of the monomers into the Pd–R bond by NMR and mass analyses, giving solid evidence of an insertion mechanism for the present system.

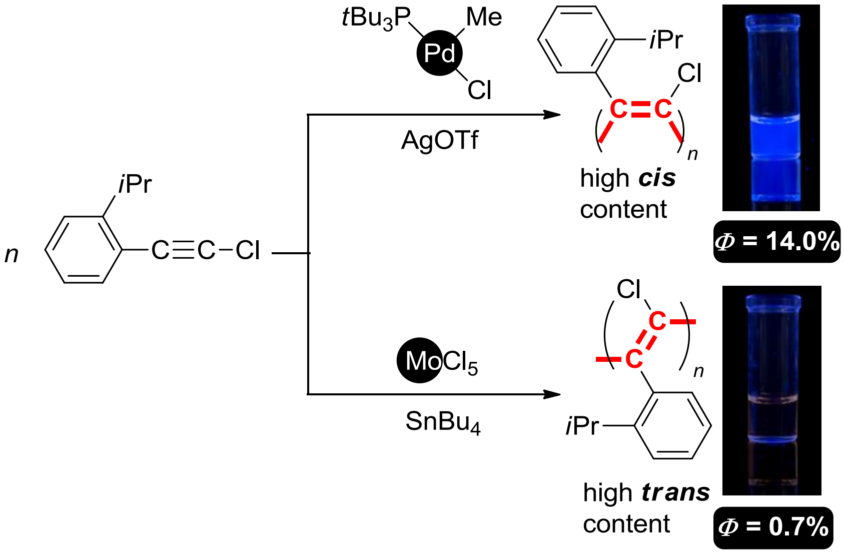


In **Part II**, the author demonstrated that a series of bulky monophosphine ligated Pd catalysts were active for the polymerization of 1-chloro-2-arylacetylenes. The author investigated the details regarding the structure-properties relation of the polymers as well as the mechanism of the polymerization.

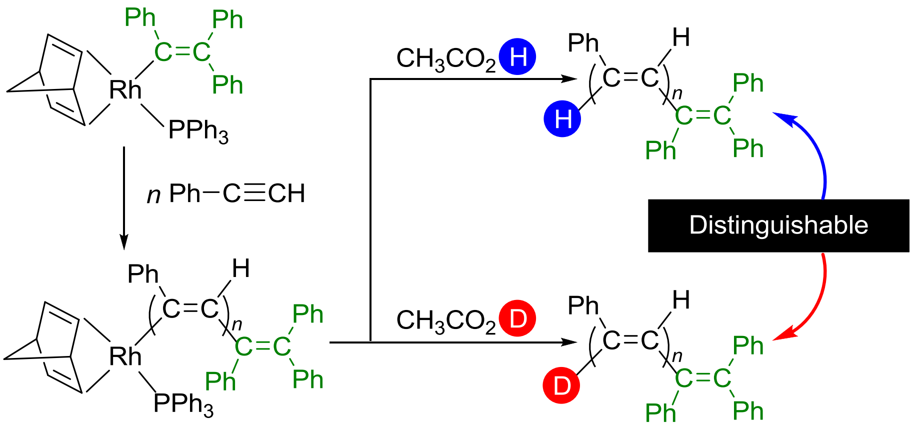
In **Chapter 3,** the author confirmed that bulky monophosphine-ligated Pd complexes served as unprecedented admirable catalysts for the polymerization of a disubstituted acetylene. The moderately high polymer yields and cis-content of the formed polyacetylene contrasted with those observed for traditional Mo catalyst-based polymer. These Pd catalysts are strong tools to promote the understanding of the structure-property relationships of disubstituted acetylene polymers.



In **Chapter 4,** the author synthesized a series of poly(1-chloro-2-arylacetylene)s [aryl = 4-isopropylphenyl, 4-isopropoxyphenyl and 2-isopropylphenyl] employing $t\mathrm{Bu_3PPdMeCl/AgOTf}$ and $\mathrm{MoCl_5/SnBu_4}$ catalysts. The author confirmed the higher *cis*-content and shorter main chain conjugation length for the Pd-based polymers than the Mo-based polymers by UV-vis spectroscopy. The polymers derived from the *ortho*-substituted monomer displayed intense emission spectra, in particular the case of a Pd-based polymer.



In **Part III**, Chapter 5, the author described a detail study of the termination mechanism for the polymerization of PA by $\mathrm{[(nbd)Rh\{C(Ph)=CPh_2\}]}$. The author elucidated the structures of $\mathrm{[(nbd)Rh\{C(Ph)=CPh_2\}]}$ (**Rh1**) and its reaction product with $\mathrm{CH_3CO_2H}$ were elucidated by $^1\mathrm{H}/^{13}\mathrm{C}/^{31}\mathrm{P}$ NMR spectroscopies, mass spectrometry, and single-crystal X-ray analysis. The author polymerized PA using **Rh1** as a catalyst with $[\mathrm{M}]_0/[\mathrm{Rh}] = 10$ and quenched with CH_3CO_2H and CH_3CO_2D to confirm the incorporation of H and D at the polymer ends by MALDI-TOF mass spectrometry and ^1H and ^1H–^{13}C HSQC NMR spectroscopy. The author calculated the polymerization degree to be 11 from the ^1H NMR spectrum, which agreed well with the theoretical value.



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Part I

Development of Pd Catalysts for the Synthesis of End-Functionalized Polymers of Monosubstituted Acetylenes

Chapter 1

Synthesis of End-Functionalized Poly(phenylacetylene)s with Well-Characterized Palladium Catalysts

Abstract

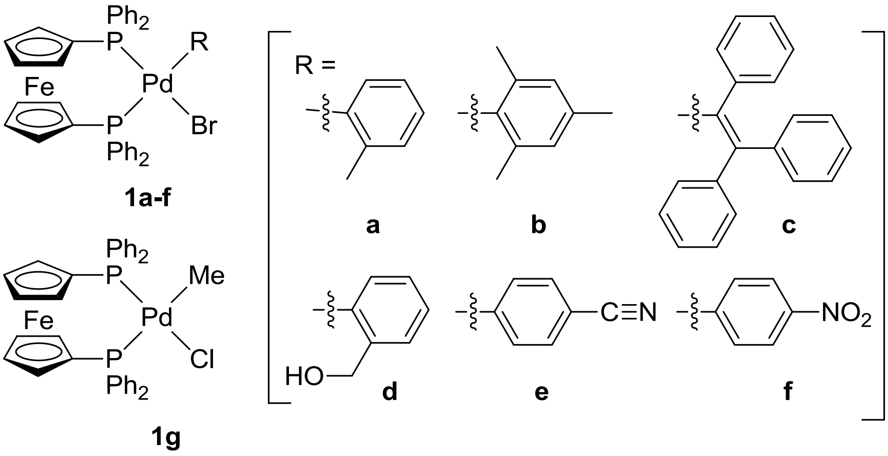
End-functionalized poly(phenylacetylene)s were synthesized by polymerization of phenylacetylene (PA) using the well-defined palladium catalysts represented as [(dppf)PdBr(R)] {dppf = 1,1'-bis(diphenylphosphino)ferrocene}. The Pd catalysts having a series of R groups such as o-tolyl, mesityl, C(Ph)=CPh_2, C_6H_4-*o*-CH_2OH, C_6H_4-*p*-CN, and C_6H_4-*p*-NO_2 in conjunction with silver triflate polymerized PA to give end-functionalized poly(PA)s bearing the corresponding R groups in high yields. The results of IR and NMR spectroscopies and MALDI-TOF mass analyses proved the introduction of these R groups at one end of each polymer chain. The poly(PA) bearing a hydroxy end group was applied as a macroinitiator to the synthesis of a block copolymer composed of poly(PA) and poly(β-propiolactone) moieties.

Introduction

Precise control of polymer structure is of key importance to access tailored polymeric materials. For the synthesis of substituted polyacetylenes, a great deal of effort has been made to develop well-controlled polymerization systems, because it contributes the investigation of their unique properties as polymeric materials derived from the stiff conjugated main-chain with a variety of pendant groups.[1–3] Fully characterized transition-metal catalysts composed of Ta,[4] Mo,[5–8] W,[9,10] Ru,[11–16] Rh,[17–22] and Pd[23,24] can provide fine control of polymer structure due to determined polymerization mechanism base on the structures of the catalysts. For instance, certain metal carbene complexes polymerize substituted acetylenes via the metathesis mechanism and even achieve living polymerization.[4–8] On the other hand, the catalysts having a metal-carbon single bond propagate a polymer chain by the insertion mechanism, which is often seen with late transition-metal catalysts, particularly groups 9 and 10.[17–24] Polymerizations using these catalysts generally start without any latent period for the formation of initiating species and smoothly proceed thanks to their identical structure to the propagating species.

Darkwa and Pollack's group reported the first well-characterized palladium complexes including [(dppf)PdCl(Me)] [**1g** (Chart 1), dppf: 1,1'-bis(diphenylphosphino)ferrocene] for the polymerization of phenylacetylene (PA).[23] Active cationic species are formed by reaction with silver triflate in the presence of CH_3CN, which polymerize PA via the insertion mechanism judging from the presence of a methyl group in the obtained polymer. Pd complexes are promising to serve as efficient and interesting catalysts in the polymerization of acetylenic monomers because of their potential activity in catalysis for various organic syntheses as well as high tolerance of polar functional groups. Indeed, a wide range of acetylenic monomers such as PA, propargyl alcohol, propiolic acid, and propiolic acid esters have been demonstrated to be polymerized by Pd catalysts.[23–33] However, the number of the papers studying the Pd catalysts is still limited.

Chart 1. Pd catalysts **1a**–**g** bearing a variety of R groups.



Introduction of a variety of functional groups into the [(dppf)PdCl(R)]-type complex is possible by virtue of the high tolerance toward polar functional groups. Besides, the “R” group of the Pd catalysts was proved eventually to be one chain end of the resulted polymers.[23] Thus we were inspired to apply the Pd catalysts to the synthesis of new end-functionalized polyacetylenes. Although some papers have discussed the related chemistry,[34–42] there have been no such examples achieved with well-defined Pd catalysts. In this chapter, we report the synthesis of end-functionalized poly(PA)s using a series of Pd catalysts (**1a**–**f**) shown in Chart 1 and its application to block copolymer synthesis. This article includes the first successful characterization of the end-functional groups of polyacetylenes by means of differential mass spectroscopy.

Results and Discussion

A series of new Pd complexes **1a**–**d** (Chart 1) were obtained by modified synthetic methods based on the reported procedures for **1e** and **1f**.[43,44] ^{1}H and ^{31}P NMR spectroscopies revealed that the new complexes **1a**–**d** are composed of a palladium(II) metal and coordinating dppf, Br, and various "R" ligands including polar and non-polar groups. The structure of complex **1c** was confirmed by X-ray analysis (Figure 1).

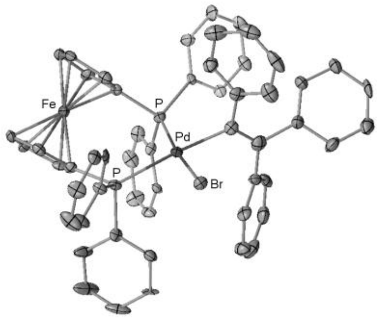
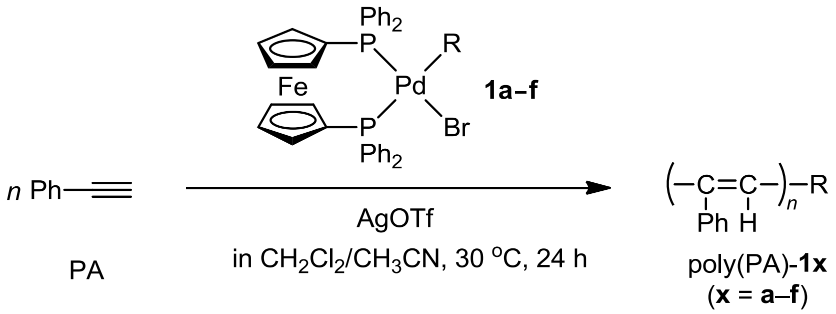


Figure 1. X-ray structure of **1c** (a selected molecule among two in the unit cell, described with 30% probability ellipsoids)

A series of R groups of **1a**–**f** directly connect to the Pd atom through a Pd–C single bond, which is considered as a key structure for monomer insertion step in coordination-insertion mechanism according to the case of Pd–Me catalyst **1g** reported by Darkwa and Pollack's group.[23]

Scheme 1. Polymerization of PA with Pd catalysts **1a**–**f**.



Polymerizations of PA were carried out using the well-characterized catalysts **1a**–**f** (Scheme 1). All the complexes were firstly reacted with silver triflate in CH_2Cl_2/CH_3CN to form Pd cationic active species. After filtering off the formed silver bromide, PA was added to the catalyst solution, which was kept at 30 °C for 24 h. With all the catalysts **1a**–**f**, the polymerizations proceeded to give poly(PA)s in high yields (Table 1). The M_n values of the obtained polymers were estimated by GPC to be 3700~5100 in the case of monomer/catalyst ratio of 50. In monomer/catalyst ratio of 500, a high molecular weight polymer (M_n = 26000) was obtained as seen in the representative result using **1e** (run 7). According to GPC, the PDI values did not become smaller than 1.65, which is comparable with the reported results using catalyst **1g**.[23] The ^{1}H NMR spectra of all the formed polymers show broad peaks in a range of 7.6 to 5.5 ppm with three peak tops at 6.94, 6.63, and 5.84 ppm [e.g., Figure 6 for poly(PA) based on **1d**]. It indicates that the main chain of the polymers formed with **1a**–**f** does not possess a highly regulated structure in terms of cis/trans configuration and head/tail regioselectivity, whereas the poly(PA) based on Pd–Me catalyst **1g** reportedly exhibits higher regularity.[23] According to the peak area ratio of the aromatic to vinylic protons in ^{1}H NMR,[19,45] the cis-transoidal stereoselectivity of the backbones of all the present poly(PA)s were approximately 50%. Although the stereoregularity and PDIs of the present polymers were not comparable than those of Rh- and **1g**-based poly(PA)s,[17,19,20,22] the polymerization of PA with any of **1a**–**f** readily undergoes to give the polymers with appropriate molecular weights for determining their end groups. In the following section, poly(PA)s obtained with Pd catalysts **1a**–**f** (runs 1–6, Table 1) and **1g** (see Experimental Section) will be abbreviated in such a way as “poly(PA)-**1a**” for simplicity.

Darkwa and Pollack’s group suggested that the poly(PA) produced by **1g** has Me-end group derived from the Me group of **1g**. Thus they concluded the polymerization proceeds in insertion mechanism (Scheme 2).[23] It is reasonable that analogous **1a**–**f** take the same mechanism for the polymerization of PA, which introduces the R groups of **1a**–**f** to terminal ends of the formed polymer chains. It is strongly supported by the following spectroscopic and spectrometric analyses.

Table 1. Polymerization of PA by well-characterized palladium complexes **1a**–**f**.[a]

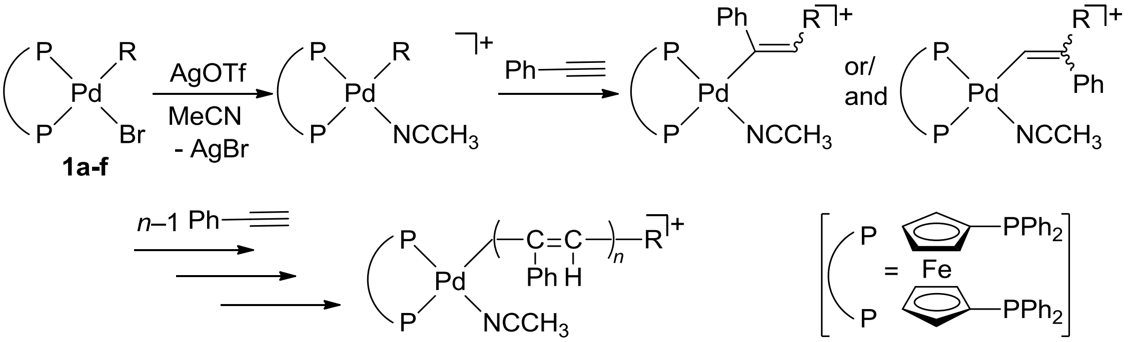
run	cat	R[b]	$[PA]_0$/[catalyst]	polymer			
				name	yield,[c] %	M_n[d]	PDI[d]
1	**1a**	*o*-tolyl	50	poly(PA)-**1a**	>99	3300	1.65
2	**1b**	mesityl	50	poly(PA)-**1b**	94	4200	1.78
3	**1c**	$C(Ph)=CPh_2$	50	poly(PA)-**1c**	>99	5100	2.26
4	**1d**	C_6H_4-*o*-CH_2OH	50	poly(PA)-**1d**	>99	3800	1.68
5	**1e**	C_6H_4-*p*-CN	50	poly(PA)-**1e**	94	3700	1.72
6	**1f**	C_6H_4-*p*-NO_2	50	poly(PA)-**1f**	>99	4300	1.79
7	**1e**	C_6H_4-*p*-CN	500	–	69	26000	1.74

[a] In CH_2Cl_2/CH_3CN = 3:1 (v/v), [Pd] = 3.5 mM, [AgOTf] = 4.2 mM, 30 °C, 24 h.

[b] The R group of [(dppf)PdBr(R)]-type catalysts (**1a**–**f**). [c] MeOH-insoluble part.

[d] Estimated by GPC (PSt standard).

Scheme 2. Possible mechanism of the polymerization of PA catalyzed by **1a**–**g**. The counter anions of the cationic Pd complexes are omitted for clarity.



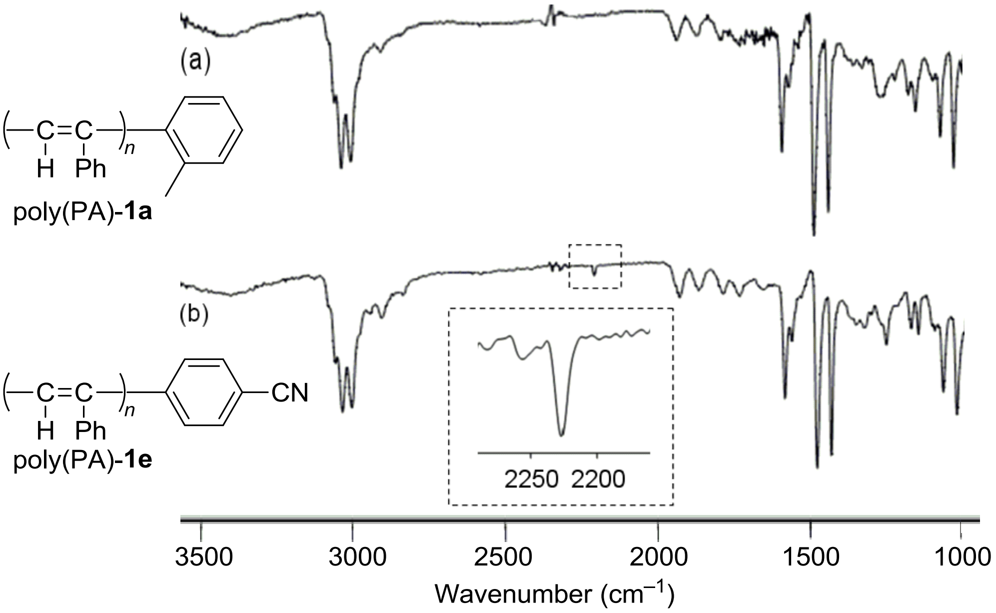


Figure 2. IR spectra of (a) poly(PA)-**1a** and (b) poly(PA)-**1e**.

The IR spectrum of poly(PA)-**1e** showed a small peak at 2232 cm^{-1} corresponding to CN stretching, while the other part of the spectrum were identical to those of poly(PA)s formed with other catalysts (Figure 2). In the ^{1}H NMR spectrum of poly(PA)-**1b**, multiple broad peaks (at least 5 peaks) were observed in a range of 2.4–1.6 ppm, which are assignable to the methyl protons of mesityl group. This result possibly reflects the lack of stereo- and regio-regularity in the first insertion of PA monomer in the Pd–C bond, leading to the generation of several magnetic circumstances around the R groups of the polymer.[46] Unfortunately, the other polymers obtained with catalysts **1a**, **1c**, **1d** and **1f** did not give sufficient evidences for identification of each R group in their ^{1}H NMR or IR results. However, another firm evidence for the presence of R groups in the series of the polymers was obtained by MALDI-TOF mass spectrometric analysis as shown below.

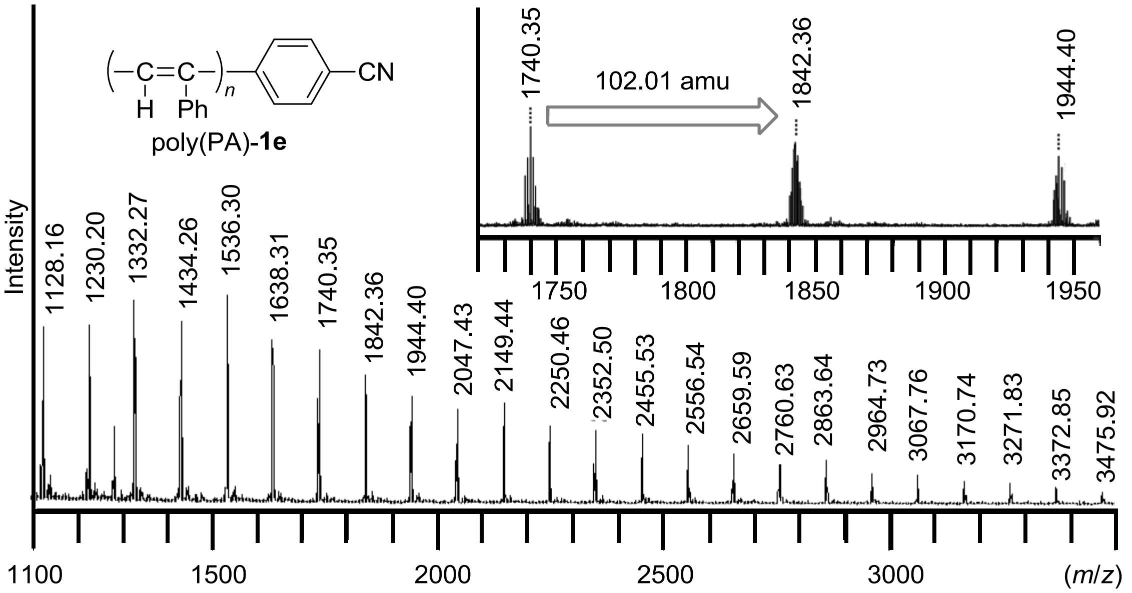


Figure 3. MALDI-TOF mass spectrum of poly(PA)-**1e** acquired with DCTB/AgTFA matrix.

Figure 3 shows the MALDI-TOF mass spectrum of poly(PA)-**1e**. A series of peaks are visible out to approximately 5000 Da with the progressive decrease of the peak intensity from the strongest peak at 1536.30 Da. There is a gap of 102.0 amu between adjacent two peaks, consistent with a PA repeating unit. No other major series with 102.0 amu mass differences are observed, suggesting that all the polymer chains are basically composed of one kind of structure. All the other polymers obtained with Pd catalysts **1a**–**d**, **1f**, and even **1g** show comparable peak profiles with a gap of 102.0 amu derived from the repeating PA unit (Figure 4). However, the absolute values of the peaks apparently do not match up between two different polymers. This finding should come from the difference of terminal groups of polymers obtained with

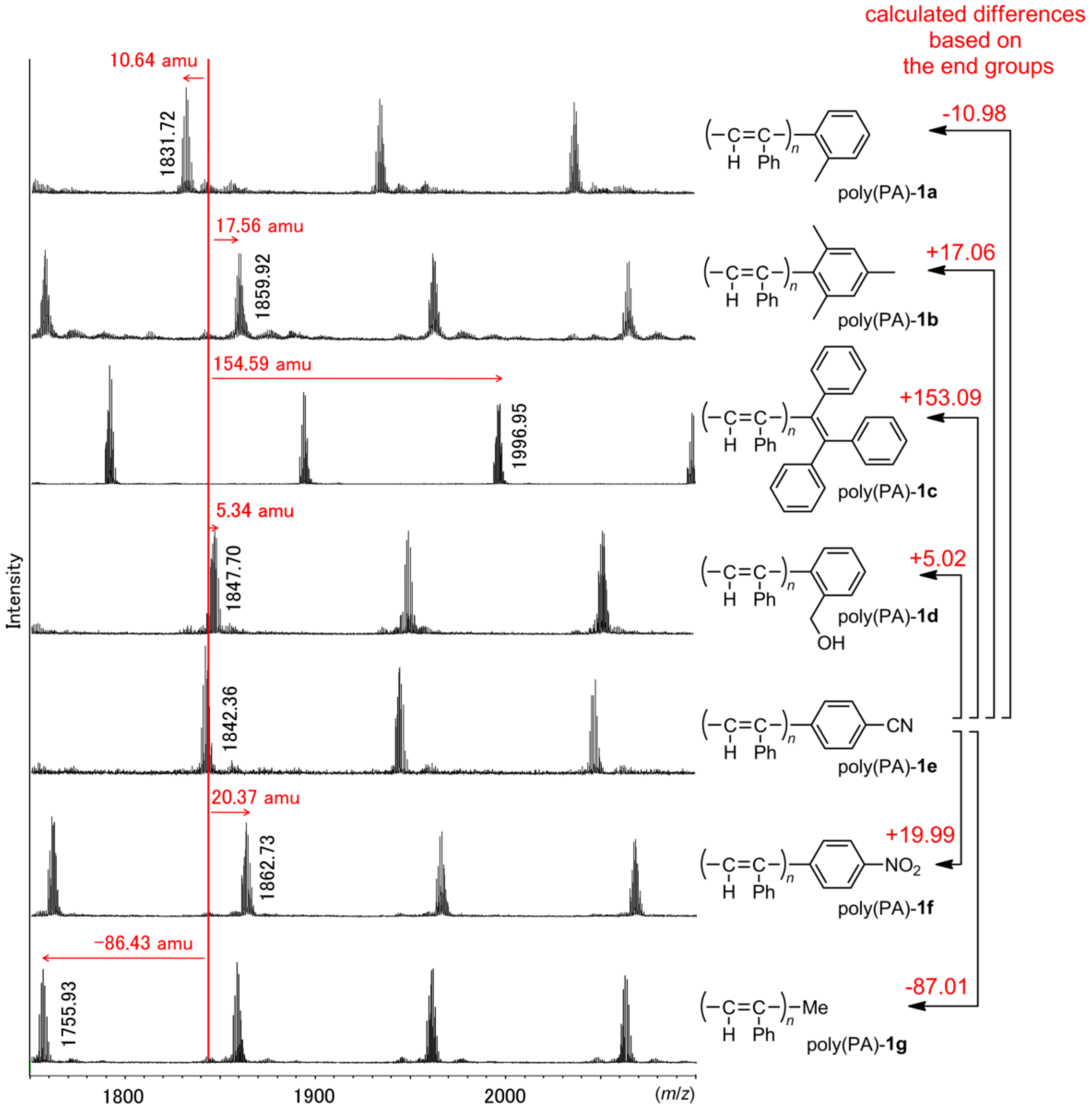
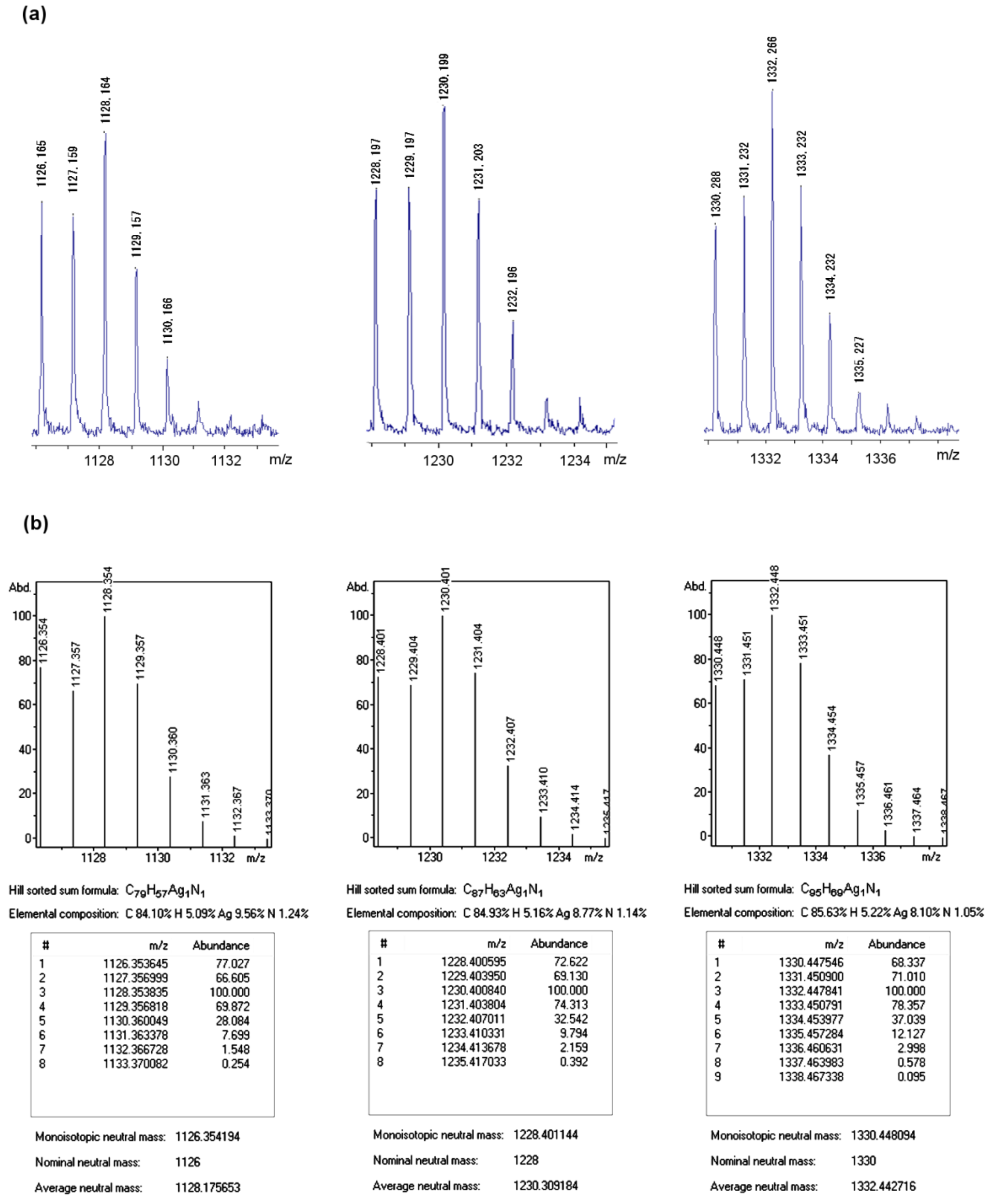


Figure 4. Relationship between mass peak differences and the end groups of the poly(PA)s in the MALDI-TOF mass spectra.

different catalysts. By determining a constant difference of these mass peaks between two polymers, it is possible to confirm the presence of the R groups in the polymer structures. For instance, all mass peaks of the poly(PA)-**1b** shift positively by 17.6 amu from those of poly(PA)-**1e**, which reasonably consist with the calculated mass difference between mesityl and cyanophenyl groups. In the same way, differences of 20.4 amu are observed between the spectra of poly(PA)-**1e** and poly(PA)-**1f**, which are quite close to the calculated mass difference between C_6H_4-CN and C_6H_4-NO_2. As shown in Figure 4, all the gaps of mass peaks between any two polymers almost perfectly coincide with the calculated differences based on the R groups.

These results also indicate that each of the obtained poly(PA)s is composed of only one type of the poly(PA) bearing one R group derived from the catalyst, **1a**–**g**, used for its synthesis; if two or more R groups have been incorporated in each polymer chain, the observed mass differences should not agree with the calculated differential values shown in Figure 4. On the same principle, the analogous polymer molecules having no R groups are also excluded.

There have been a quite limited number of papers reporting the successful mass spectrometric analysis of polyacetylenes, mainly because of difficulty of removing metal traces from the produced polymer: it leads complicated results on the mass analysis.[39,47–50] Fortunately, the measurements shown above sufficiently revealed the introduction of the R groups in each polymer chains in all the cases of using **1a**–**f**. However, the other terminating chain ends of the obtained poly(PA)s have not been completely revealed. According to the detected mass values, it is suggested that all the present polymers, poly(PA)-**1x** (x = **a**–**g**), have the same terminating chain end regardless



Hill sorted sum formula: $C_{79}H_{57}Ag_1N_1$

Elemental composition: C 84.10% H 5.09% Ag 9.56% N 1.24%

#	m/z	Abundance
1	1126.353645	77.027
2	1127.356999	66.605
3	1128.353835	100.000
4	1129.356818	69.872
5	1130.360049	28.084
6	1131.363378	7.699
7	1132.366728	1.548
8	1133.370082	0.254

Monoisotopic neutral mass: 1126.354194

Nominal neutral mass: 1126

Average neutral mass: 1128.175653

Hill sorted sum formula: $C_{87}H_{63}Ag_1N_1$

Elemental composition: C 84.93% H 5.16% Ag 8.77% N 1.14%

#	m/z	Abundance
1	1228.400595	72.622
2	1229.403950	69.130
3	1230.400840	100.000
4	1231.403804	74.313
5	1232.407011	32.542
6	1233.410331	9.794
7	1234.413678	2.159
8	1235.417033	0.392

Monoisotopic neutral mass: 1228.401144

Nominal neutral mass: 1228

Average neutral mass: 1230.309184

Hill sorted sum formula: $C_{95}H_{69}Ag_1N_1$

Elemental composition: C 85.63% H 5.22% Ag 8.10% N 1.05%

#	m/z	Abundance
1	1330.447546	68.337
2	1331.450900	71.010
3	1332.447841	100.000
4	1333.450791	78.357
5	1334.453977	37.039
6	1335.457284	12.127
7	1336.460631	2.998
8	1337.463983	0.578
9	1338.467338	0.095

Monoisotopic neutral mass: 1330.448094

Nominal neutral mass: 1330

Average neutral mass: 1332.442716

Figure 5. The results of (a) MALDI-TOF mass spectra of poly(PA)-**1e** and (b) the simulated isotope patterns of an Ag^+ adduct of poly(PA) terminated with a phenylethynyl and a *p*-cyanophenyl group at polymer chain ends [thus, PhC≡C-(-CH=CPh-)$_n$-C_6H_4-*p*-CN]. From left to right, the three sets of peaks correspond to the polymers with n = 8, 9, and 10, respectively. The simulated isotope patterns of the Ag^+ adducts appear fitting to the data actually measure

of types of the used catalyst for the polymerization, and that it could be a phenylethynyl group (Figure 5). Although further investigation for fully characterizing the terminating chain end is required, it can be concluded that each polymer chain of all the produced poly(PA)s bears one R group at the initiating chain end. Fortunately the undefined terminating end group does not affect the following experiment of block copolymer synthesis.

Synthesis of a block copolymer

Poly(PA)-**1d** was applied to the synthesis of a block copolymer composed of poly(PA) and polyester blocks (Scheme 3). For the polyester composition, poly(β-propiolactone) [poly(β-PL)] was chosen since a similar block copolymer consisting of Rh-based poly(PA) and poly(β-PL) had been reported.[38] At first, the terminal hydroxy group of poly(PA)-**1d** (M_n 3800, PDI 1.45) as a macroinitiator was reacted with NaH to provide a sodium benzyloxide moiety. Then β-PL was added to form the poly(β-PL) block. The GPC curve of the product displayed a unimodal profile, in which M_n = 5400 and PDI = 1.33. The formation of the block copolymer was confirmed by IR and ^{1}H NMR spectroscopies (Figures 6 and 7). The IR spectrum displayed a strong peak at 1737 cm^{-1} which is assignable to the C=O stretching of the ester group. The ^{1}H NMR spectrum of the polymer in $CDCl_3$ showed two broad peaks at 4.38 and

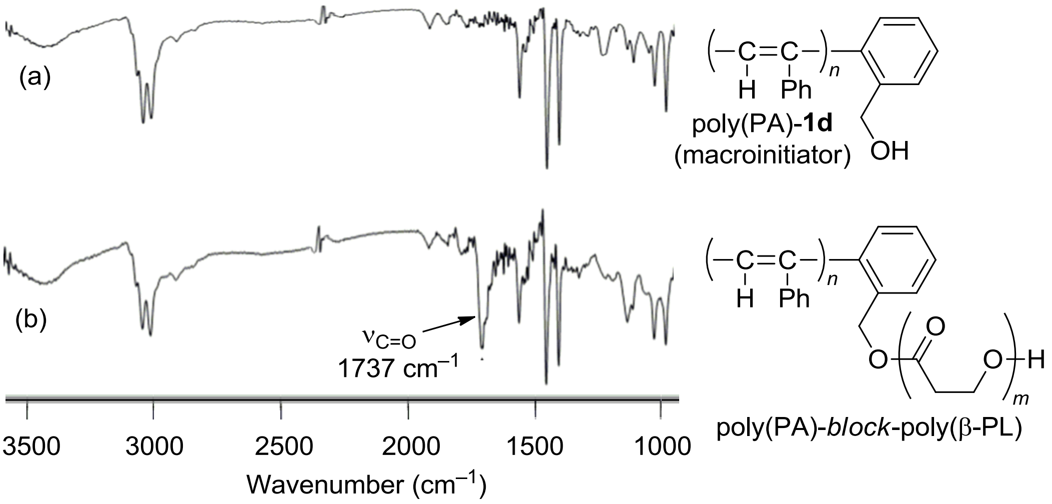


Figure 6. IR spectra of (a) macroinitiator, poly(PA)-**1d**, and (b) poly(PA)-block-poly(β-PL).

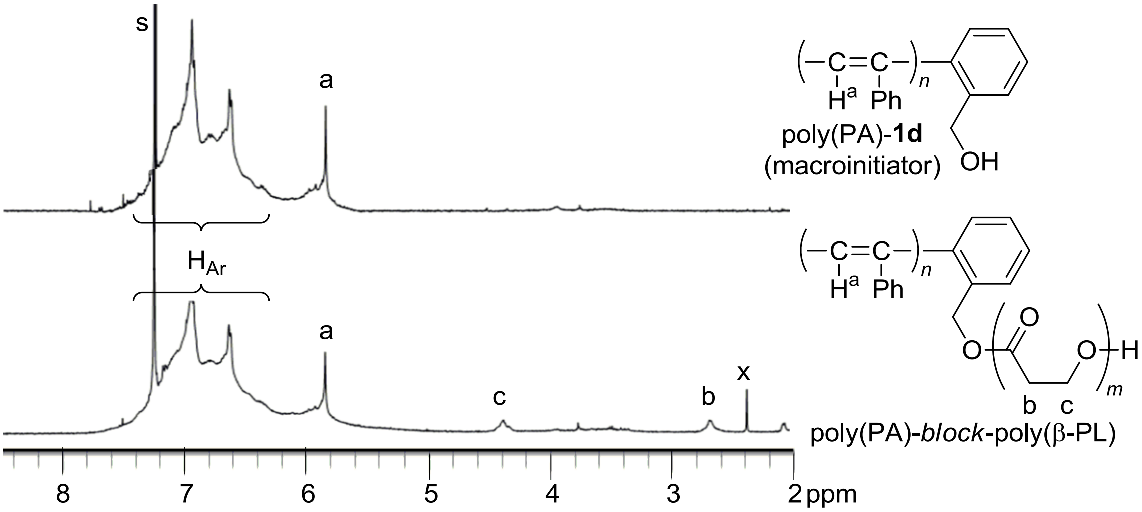


Figure 7. ^{1}H NMR spectra of macroinitiator, poly(PA)-**1d**, and poly(PA)-block-poly(β-PL) [in $CDCl_3$, s: solvent, x: impurity].

2.65 ppm corresponding to the methylene moieties of poly(β-PL) along with broad peaks derived from the poly(PA) block in the aromatic region. The degree of polymerization of the poly(β-PL) block was estimated from the integral ratio of poly(PA) and methylene moieties to be approximately 8, while that of poly(PA) block was calculated to be 37 based on the GPC data. Consequently, the ratio of the degree of polymerization turns out to be approximately 4.6:1 (n:m). This result is comparable with the report,[38] which supports that poly(PA)-**1d** contains a sufficient amount of hydroxy groups to achieve the end-functionalization of poly(PA).

Conclusions

The end-functionalization of poly(PA) using Pd complexes and its application to the synthesis of a block copolymer were demonstrated. Although a few examples discussing end-functionalization of polyacetylenes have been reported, the present polymerization system has an advantage of a wide range of introducible functional groups. It has been shown that the unprotected hydroxy group and even electrophilic cyano and nitro groups can be introduced into the initiating end of the formed polymer, which is technically impossible in the case of the Rh catalyst.[38] Further development of the Pd catalysts with wide range of functional groups is in progress.

Experimental Section

Instruments. The number- and weight-average molecular weights (M_n and M_w, respectively) and polydispersity indices (PDI) of polymers were estimated by GPC on a JASCO PU-980/RI-930 chromatograph; columns KF-805 (Shodex) × 3, molecular weight limit up to 4×10^6, eluent THF, column temperature 40 °C, flow rate 1 mL/min; calibrated with polystyrene standards. ^{1}H NMR spectra (400 MHz) were recorded on a JEOL ECX-400 (for all polymers and a part of Pd complexes) or EX-400 spectrometer (for the other Pd complexes) spectrometer with chemical shifts referenced to an internal standard, $CHDCl_2$ (5.32 ppm) or $CHCl_3$ (7.25 ppm). ^{31}P NMR spectra (162 MHz) were observed on a JEOL ECX-400 (for a part of Pd complexes) or EX-400 spectrometer (for the other Pd complexes) with $P(OMe)_3$ as an external standard (140 ppm). MALDI-TOF mass spectra were recorded on a Bruker ultraflex III equipped with a 355 nm YAG laser in reflectron and by using an acceleration voltage of 19 kV. Samples of MALDI-TOF mass spectrometry were prepared from a CH_2Cl_2 solution by mixing the sample (10 mg/mL using the polymers purified by column chromatography [silica gel, toluene as eluent] to remove a trace of Pd), DCTB (*trans*-2-[3-(4-*tert*-butylphenyl)-2-methyl-2-propenylidene]malononitrile, 20 mg/mL), and AgTFA (silver trifluoroacetate, 2 mg/mL) in a ratio of 2:1:1. All the mass differences discussed below were calculated by comparing mass values of two base peaks (the peak of most popular isotopomers). IR spectra were measured on a JASCO FTIR-4100 spectrophotometer using the KBr method. X-ray crystallographic analysis of complex **1c** was performed on a Rigaku Saturn with crystals obtained from CH_2Cl_2/Et_2O. Elemental analyses were performed at the Microanalytical Center of Kyoto University.

Materials. Phenylacetylene was purchased (Aldrich) and distilled over CaH_2 under reduced pressure before use. All aryl bromides (Aldrich), triphenylvinyl bromide (TCI) for the synthesis of Pd catalysts, dppf (Wako), AgOTf (Wako) and P(*o*-tolyl)$_3$ (Wako) were purchased and used as received. Solvents were purified by the standard procedures before use. $Pd_2(dba)_3$,[51] Pd[P(*o*-tolyl)$_3$]$_2$,[52] [(dppf)PdBr(C_6H_4-*p*-CN)] (**1e**),[43] [(dppf)PdBr(C_6H_4-*p*-NO_2)] (**1f**),[44] and [(dppf)PdCl(Me)] (**1g**)[23] were synthesized by the known methods. The poly(PA) based on catalyst **1g** was synthesized by the reported procedure.[23]

General procedures for the synthesis of palladium catalysts

Pd complexes **1a**, **1b**, and **1d** were synthesized by a modified method based on the report by Buchwald.[43] The detailed procedures are as follows: In a Schlenk tube were placed $Pd_2(dba)_3$ (200 mg, 0.218 mmol) and P(*o*-tolyl)$_3$ (400 mg, 1.31 mmol) under an Ar atmosphere. After benzene (6.0 mL) was added, the obtained suspension was stirred overnight at room temperature. To the suspension, an aryl bromide (e.g., *o*-tolyl bromide for complex **1a**: 263 μL, 2.19 mmol) was added [BrC(Ph)=CPh_2, which is a solid, was added as a benzene solution (1 mL)] and then the mixture was stirred at room temperature overnight. The precipitated powder was removed by filtration (PTFE membrane, 3.0 μm pore size) to give clear yellow filtrate, from which volatiles were removed under vacuum. The resulting yellow residue was washed with Et_2O to give light yellow powder, which could be confirmed by NMR to be practically pure $[(R)Pd\{P(o\text{-tolyl})_3\}(\mu\text{-Br})]_2$.[43] Subsequently, the formed $[(R)Pd\{P(o\text{-tolyl})_3\}(\mu\text{-Br})]_2$ and dppf (1.2 equiv) were placed in a Schlenk tube under an Ar atmosphere. All solids were dissolved in CH_2Cl_2 (10 mL) and the mixture was stirred at room temperature overnight. After removing solvents under reduced pressure, the produced [(dppf)PdBr(R)] was purified by washing with Et_2O several times. Following the previous studies of similar complexes.[43,44] all the complexes were identified by ^1H, ^{31}P NMR and elemental analysis (the ^{13}C NMR spectra did not provide useful information).[43,44]

[(dppf)PdBr(*o*-tolyl)] (1a). Yield 51%. ^1H NMR (on EX-400, $CDCl_3$) δ: 8.12 (m, 2H, ArH), 8.04 (m, 2H, ArH), 7.84 (m, 2H, ArH), 7.48 (br m, 4H, ArH), 7.46 (br, 4H, ArH), 7.29 (br, 2H, ArH), 7.12 (t, J = 7.6 Hz, 2H, ArH), 6.89 (dt, J = 7.6 Hz, 2H, ArH), 6.82 (vt, J = 7.6 Hz, 2H, ArH), 6.57 (t, J = 7.2 Hz, 1H, ArH), 6.48 (t, J = 7.2 Hz, 1H, ArH), 4.97 (br s, 1H, Cp), 4.59 (br s, 1H, Cp), 4.40 (br s, 2H, Cp), 4.13 (br s, 2H, Cp), 3.68 (br s, 1H, Cp), 3.52 (br s, 1H, Cp), 2.33 (s, 3H, Me). ^{31}P NMR (on EX-400, $CDCl_3$) δ: 29.2 (d, J = 34.8 Hz, 1P), 7.9 (d, J = 34.8 Hz, 1P). Anal. Calcd. for $C_{41}H_{35}BrFeP_2Pd$: C, 59.20%; H, 4.24%. Found: C 59.26%; H 4.14%.

[(dppf)PdBr(mesityl)] (1b). Yield 45%. ^1H NMR (on EX-400, $CDCl_3$) δ: 8.11 (br, 4H, ArH), 7.48 (br s, 8H, ArH), 7.25 (br, 4H, ArH), 7.00 (br, 4H, ArH), 6.17 (br, 2H, ArH of mesityl), 4.70 (very br, 2H, Cp), 4.52 (br, 2H, Cp), 4.09 (br s, 2H, Cp), 3.51 (br s, 2H, Cp), 2.43 (br s, 6H, *o*-Me), 1.95 (br s, 3H, *p*-Me). ^{31}P NMR (on EX-400, $CDCl_3$) δ: 29.0 (d, J = 36.7 Hz, 1P), 7.9 ((d, J = 36.7 Hz, 1P). Anal. Calcd. for $C_{43}H_{39}BrFeP_2Pd$: C, 60.06%; H, 4.57%. Found: C 60.33%; H 4.69%.

[(dppf)PdBr(C_6H_4-*o*-CH_2OH)] (1d). Yield 42%. ^{1}H NMR (on ECX-400, CD_2Cl_2) δ: 8.03 (br, 4H, ArH), 7.93 (br, 1H, ArH), 7.53 (br s, 8H, ArH), 7.53 (br, 2H, ArH), 7.22 (ddd, J = 6.7 Hz, J = 3.2 Hz, J = 1.6 Hz, 1H, ArH), 7.11 (br, 1H, ArH), 6.87 (br, 2H, ArH), 6.72 (br, 1H, ArH), 6.83 (tt, J = 7.5 Hz, J = 1.9 Hz, 2H, ArH), 6.62 (vt, J = 7.1 Hz, 1H, ArH), 6.65 (m, 1H, ArH), 5.08 (br, 1H, Cp), 4.72 (br, 1H, Cp), 4.65 (br, 1H, Cp), 4.42 (br, 1H, Cp), 4.40 (br, 1H, Cp), 4.18 (s, 2H, CH_2), 4.00 (br, 1H, Cp), 3.76 (br, 1H, Cp), 3.59 (br, 1H, Cp), 3.18 (vt, J = 6.3 Hz, 1H, OH). ^{31}P NMR (on ECX-400, CD_2Cl_2) δ: 30.5 (d, J = 30.6 Hz, 1P), 9.6 (d, J = 30.6 Hz, 1P). Anal. Calcd. for $C_{41}H_{35}BrFeOP_2Pd$: C, 58.08%; H, 4.16%. Found: C 57.78%; H 4.13%.

[(dppf)PdBr{C(Ph)=CPh_2}] (1c). To a benzene solution (2.2 mL) of Pd[P(*o*-tolyl)$_3$]$_2$, (51 mg, 0.071 mmol), a benzene solution (2.2 mL) of BrC(Ph)=CPh_2 (29 mg, 0.086 mmol) was added at room temperature. The mixture was stirred at room temperature for 2 h. Then dppf (47 mg, 0.085 mmol) dissolved in benzene (2.2 mL) was added to the mixture at room temperature, and stirring was continued for 30 min. The resulting mixture was concentrated and Et_2O (10 mL) was added to give yellow precipitation. After removing the supernatant by filtration, the yellow powder was washed with Et_2O

(2.5 mL, 2 times) and then dried under vacuum. Yield 50%. ^{1}H NMR (on ECX-400, C_6D_6, 70 °C) δ: 8.38 (d, J = 7.2 Hz, 2H, ArH), 8.27 (br, 2H, ArH), 8.11 (br, 2H, ArH), 7.63-7.48 (m, 6H, ArH), 7.34-6.77 (m, 23H, ArH), 4.57 (br, 1H, Cp), 4.31 (br, 1H, Cp), 4.02 (br s, 2H, Cp), 3.61 (br, 2H, Cp), 3.38 (br s, 1H, Cp), 3.34 (br s, 1H, Cp). ^{31}P NMR (on ECX-400, C_6D_6, 70 °C) δ: 26.3 (d, J = 39.1 Hz, 1P), 10.9 (d, J = 39.1 Hz, 1P). Anal. Calcd. for $C_{54}H_{43}BrFeP_2Pd$: C, 65.12%; H, 4.35%. Found: C 64.69%; H 4.37.

Polymerization of PA with Pd catalysts 1a–f. Polymerizations of PA with Pd catalysts **1a**–**f** were carried out by a modified method based on Darkwa and Pollack's report. The details are as follows: To a solution of one of Pd complexes **1a**–**f** (0.020 mmol) in CH_2Cl_2/CH_3CN (3:1 v/v, 2.85 mL), 2.85 mL of an AgOTf solution in CH_2Cl_2/CH_3CN (3:1 v/v, 8.4 mM of AgOTf, 0.024 mmol) was added to form a cationic Pd derivative and AgBr as white precipitate. After 5 min at room temperature, the silver salt was removed by filtration. After total 10 min from the addition of AgOTf solution, PA monomer (0.11 mL, 1.0 mmol) was added to the yellow filtrate to start the polymerization. The reaction mixture was kept at 30 °C for 24 h. Then all the volatiles were evaporated under reduced pressure to quench the polymerization. The residue was dissolved CH_2Cl_2 (0.3 mL) and then a large quantity of MeOH was added to isolate the produced polymer.

Polymerization of β-propiolactone with macroinitiator. Both the poly(PA) macroinitiator obtained with catalyst **1d** [M_n = 3700 (GPC), 86 mg;

theoretically 0.023 mmol of terminal OH group] and NaH (1.0 mg, 0.042 mmol) were placed in a Schlenk tube under an Ar atmosphere. Then CH_2Cl_2 (12.7 mL) was added and left for 15 min at room temperature to form the corresponding sodium alkoxide. β-Propiolactone [β-PL, 1.45 mL, 23 mmol (1000 equivalent of the ideal initiator)] was added to the obtained solution to start the reaction. The polymerization solution was stirred at 30 °C for 24 h and then 5 mL of MeOH was added to quench the polymerization of β-PL. After concentration of the obtained orange solution (to ~2 mL), 50 mL of hexane was added to precipitate the orange-colored product, and the product was washed with hexane 5 times. The product was dried under vacuum to constant weight. Yield 139.5 mg.

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Chapter 2

Synthesis of End-Functionalized Polyacetylenes Bearing Polar Groups Employing Well-Defined Pd Catalysts

Abstract

A series of [(dppf)PdBr(R)]-type complexes [dppf = 1,1’-bis(diphenylphosphino)ferrocene; R = *p*-cyanophenyl (**1a**), *o*-hydroxymethylphenyl (**1b**), triphenylvinyl (**1c**)] in combination with silver trifluoromethanesulfonate (AgOTf) were demonstrated to be active for the polymerization of monosubstituted polar acetylene monomers, $HC{\equiv}CCONHC_4H_9$ (**2**), $HC{\equiv}CCO_2C_8H_{17}$ (**3**), $HC{\equiv}CCH_2OCONHC_6H_{13}$ (**4**), $HC{\equiv}CCH_2OCO_2C_6H_{13}$ (**5**) and $HC{\equiv}CCH(CH_3)OH$ (**6**). The polymer yields and molecular weights depended upon the combination of the Pd catalyst and monomer employed. Matrix-assisted laser desorption/ionization-time of flight (MALDI-TOF) mass spectrometric analysis indicated the formation of polymers bearing “R” and “H” at the chain ends. IR spectroscopic analysis supported the “R” end-functionalization of the polymers. NMR and mass analyses identified the presence of species formed by single, double and triple insertions of monomers into the Pd–C_6H_4-*p*-CN bond, giving solid evidence of an insertion mechanism for the present system. Density functional theory (DFT)

calculations suggested the preferential occurrence of 1,2-insertion of the monomer compared to 2,1-insertion.

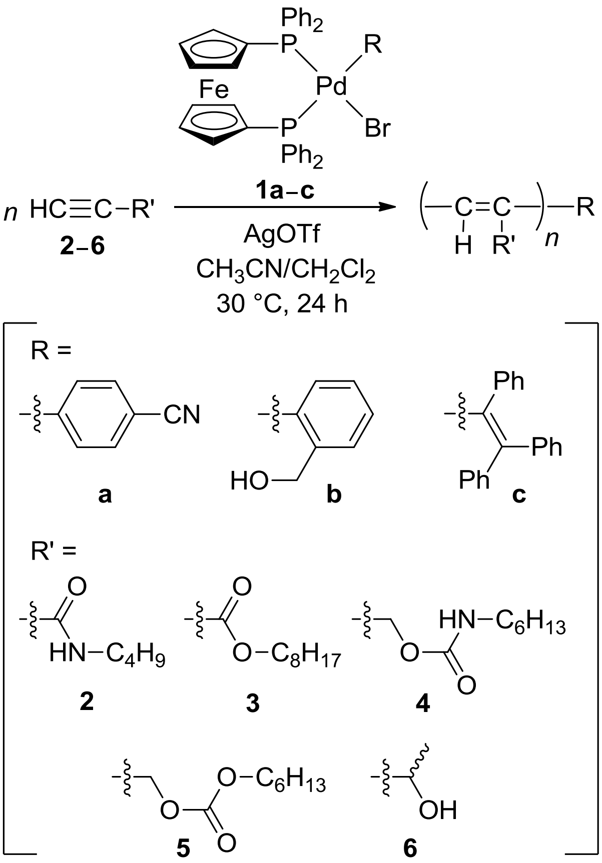
Introduction

Transition metal catalysts polymerize various acetylene monomers to yield substituted polyacetylenes featuring useful functions such as electro-active and photoluminescent properties as a result of the conjugated main chains, high gas permeability and helix-forming ability due to the rigid backbones.[1–5] Well-defined transition metal catalysts containing tantalum,[6] molybdenum,[7–9] ruthenium,[10–14] rhodium,[15–31] nickel[32] and palladium[33–40] are especially useful for acetylene polymerization, since they allow control over catalytic activity by ligand design, leading to achievement of living/controlled polymerization. As a result, precise modifications of polymer architectures are achieved, which enable the synthesis of block copolymers and star-shaped polymers.[41]

Among the transition metal catalysts for acetylene polymerization mentioned above, Rh- and Pd-based compounds catalyze the polymerization of acetylene monomers substituted with heteroatom-containing polar groups, as well as nonpolar hydrocarbon acetylene monomers, due to the low oxophilicity of late transition metals. Although Rh-based catalysts[15–31] are widely studied and utilized to obtain cis-stereoregular substituted polyacetylenes, Pd-based catalysts[32–40] have not been examined extensively for acetylene polymerization, presumably due to the lower activity compared with that of Rh-catalysts. Darkwa, Pollack and coworkers have developed well-defined [(diphosphine)Pd($NCCH_3$)(CH_3)]OTf-type catalysts, and successfully polymerized phenylacetylene (PA) to obtain poly(PA)s with moderate molecular weights in good yields.[36] The incorporation of a methyl group at the chain ends was confirmed by ^{1}H and ^{13}C NMR spectroscopic analysis of the synthesized poly(PA)s. This observation indicates that PA is polymerized via a coordination-insertion mechanism.

Inspired by this work, we have synthesized [(dppf)Pd(NCCH$_3$)(R)]OTf-type catalysts for the polymerization of PA.[38] We have proven that "R" groups are introduced at the chain ends of poly(PA), and have synthesized block copolymers utilizing the end-functionalized poly(PA) as macroinitiators. Thus far, only a couple of examples of Pd catalysts have been reported regarding the polymerization of non-PA type acetylene monomers bearing polar groups,[33–35] in spite of the encouraging results of PA polymerization with well-characterized Pd catalysts[36–38,40] and the many examples of Rh-catalyzed polymerization of non-PA monomers. Herein, we wish to report the polymerization of monosubstituted acetylenes (**2**–**6** in Scheme 1) bearing polar groups with well-defined [(dppf)PdBr(R)]-type complexes (**1a**–**c** in Scheme 1). Moreover, we report the mechanistic aspects of the polymerization based on NMR and IR spectroscopic analysis, mass spectrometric analysis, as well as DFT calculations.

Scheme 1. Polymerization of monosubstituted polar acetylene monomers **2**–**6** by well-defined Pd catalysts **1a**–**c**/AgOTf



Results and Discussion

Polymerization: The reaction of well-defined Pd complexes **1a**–**c** with AgOTf yields [(dppf)Pd(NCCH$_3$)(R)]OTf, **1aOTf** (R = –C$_6$H$_4$-*p*-CN), **1bOTf** (R = –C$_6$H$_4$-*o*-CH$_2$OH) and **1cOTf** [R = –C(Ph)=CPh$_2$], which catalyze the polymerization of phenylacetylene.[36,38] In the present study, the polymerization of monomers **2**–**6** bearing polar groups (amide, ester, carbamate, carbonate and hydroxy) was carried out under the conditions depicted in Scheme 1. As shown in Table 1, the polymer yields and molecular weights largely depended on the monomers and catalysts. Polymers poly(**2**) featuring weight-average molecular weight (M_w) values from 2000 to 2300 were obtained in 84–93% yields. Despite the analogous structure to monomer **2**, monomer **3** gave the polymers [poly(**3**)] in poor yields (21–29%) while the M_w's (5800–7400) were higher than those of poly(**2**). Under the same conditions, monomer **4** gave powdery polymers [poly(**4**)] insoluble in MeOH featuring M_w's from 4900 to 8700, while monomer **5** gave no solid, but rather liquid polymer [poly(**5**)] in spite of sharing a similar structure to poly(**4**). Poly(**5**) with M_w = 3700 was isolated by evaporating the solvent from the polymerization mixture. In addition to the main size exclusion chromatography (SEC) peaks (area ratios = 78–82%), broad peaks were observed at higher molecular weight regions for both samples, poly(**4**) and poly(**5**). Monomer **6** containing a hydroxy group also polymerized to afford poly(**6**) with M_w's of 10600–27300 in 22–55% yields. To the best of our knowledge, this is the first example of polymerization of a hydroxy group containing acetylene with Pd catalysts under ambient conditions.[42] The large polydispersity index (PDI) values of poly(**6**) may be due to the interaction between the hydroxy groups and the Pd active centers involved during the polymerization, leading to termination reactions. A model reaction supported this assumption. Namely, when **1cOTf** was left in C_6D_6 (0.5 mL) with 50 equivalents of MeOH at 55 °C for 24 h, triphenylethylene formed in 50% yield, which was confirmed by ^{1}H and ^{13}C NMR spectroscopy (Figure 1)

Table 1. Polymerization of monosubstituted acetylenes **2**–**6** bearing polar groups by (dppf)PdBr(R) (**1a**–**c**)/AgOTf.[a]

run	cat	monomer	polymer			
			sample[b]	yield,[c] %	M_w[d]	PDI[d]
1	**1a**	**2**	poly(**2**)-**1a**	84	2300	2.37
2	**1b**	**2**	poly(**2**)-**1b**	90	2000 (63%)[e]	1.26
3	**1c**	**2**	poly(**2**)-**1c**	93	2000 (56%)[e]	1.28
4	**1a**	**3**	poly(3)-**1a**	21	5800	1.45
5[f]	**1a**	**3**	poly(3)-**1a**	21	13000	2.89
6	**1b**	**3**	poly(**3**)-**1b**	29	7400	1.41
7	**1c**	**3**	poly(**3**)-**1c**	25	6600	1.28
8	**1a**	**4**	poly(**4**)-**1a**	28	7900 (80%)[g]	2.01
9	**1b**	**4**	poly(**4**)-**1b**	42	4900 (82%)[g]	1.61
10	**1c**	**4**	poly(**4**)-**1c**	8	8700 (78%)[g]	1.65
11	**1a**	**5**	poly(**5**)-**1a**	–[h]	3700 (81%)[i]	2.20
12	**1a**	**6**	poly(**6**)-**1a**	55	10600	5.52
13	**1b**	**6**	poly(**6**)-**1b**	47	15000	6.60
14	**1c**	**6**	poly(**6**)-**1c**	22	27300	8.60

[a] [Pd] = 10 mM, [AgOTf] = 12 mM, $[\text{monomer}]_0$ = 0.5 M in CH_3CN/CH_2Cl_2 = 1/3 (v/v), 30 °C, 24 h. [b] Defined by the combination of catalyst used and polymer obtained. [c] Poly(**2**): hexane-insoluble part; poly(**3**) and poly(**4**): MeOH-insoluble part; poly(**6**): Et_2O-insoluble part. [d] Estimated by SEC (PSt standards). Eluent: THF for poly(**2**) and poly(**3**); $CHCl_3$ for poly(**4**) and poly(**5**); DMF for poly(**6**). [e] Peak area ratio in SEC. The other part corresponded to low molecular weight oligomers. [f] $[\text{monomer}]_0/[\text{Pd}]$ = 100. [g] Peak area ratio in SEC. A broad high molecular weight signal was also observed (area ratio = ca. 15%). [h] Not determined because the polymer was not obtained as hexane, MeOH nor Et_2O-insoluble part but isolated by preparative HPLC. [i] Data for the residual mass after solvent removal from the reaction mixture.

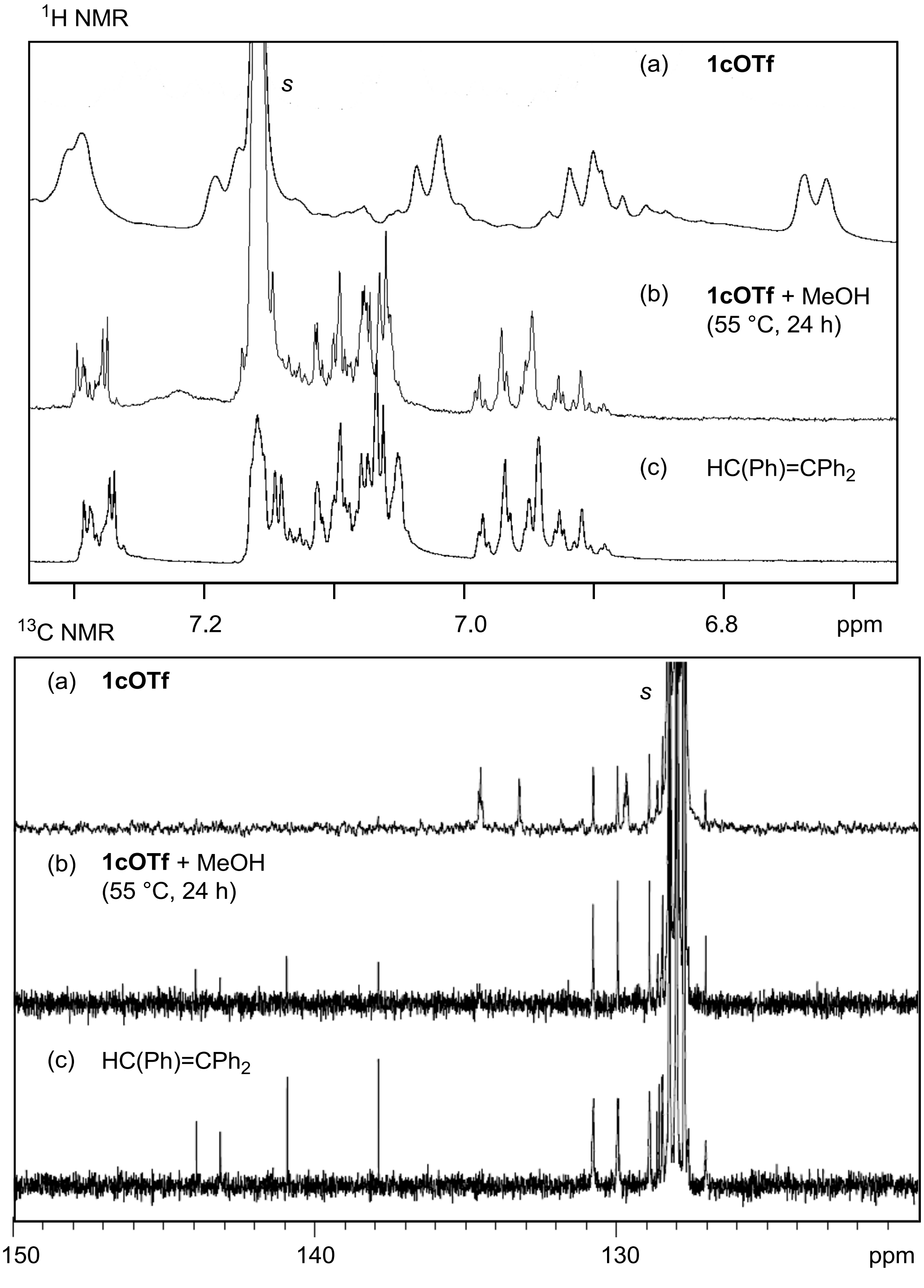


Figure 1. ^{1}H and ^{13}C NMR spectra of (a) **1cOTf**, (b) **1cOTf** + 50 equivalents of MeOH after heating at 55 °C for 24 h and (c) pure HC(Ph)=CPh$_2$ measured in CD$_3$CN/C$_6$D$_6$= 1/3 (v/v), [**1cOTf**]$_0$ = 25 mM at r.t. (s: solvent).

along with EI-mass spectrometry. The other products of the reaction could not be identified. Judging from this result, it is considered that termination occurs by the reaction of hydroxy groups of **6** and/or poly(**6**) with Pd–C=C–species, which should be formed from either insertion of the monomer between Pd and "R" or its subsequent insertion products (see below).[38,43] In fact when 50 equivalents of **6** were added to **1aOTf** stepwise (one equivalent each at every 5 minutes, total 50 steps), a polymer with M_w = 5600 and PDI = 3.14 was obtained in 32% yield. This result indicates that the termination reaction occurred less when the local monomer concentration was decreased (Table 2). The M_w of poly(**3**)**-1a** increased from 5800 to 13000 as the $[\text{monomer}]_0/[\text{Pd}]$ ratio was increased from 50 to 100. A similar behaviour is expected for the other monomers, but the $[\text{monomer}]_0/[\text{Pd}]$ was kept at 50 for the sake of easier polymer structure analysis.

Table 2. Polymerization of 3-butyn-2-ol (**6**) by **1a**.[a]

run	$[\text{monomer}]_0$, M	polymer		
		yield,[b] %	M_w[c]	PDI[c]
1	0.50	55	10600	5.52
2[d]	0.50[e]	32	5600(58%)[f]	3.14

[a] In CH_3CN/CH_2Cl_2 = 1/3 (v/v), [Pd] = 10 mM, $[\text{monomer}]_0$ = 0.5 M, [AgOTf] = 12 mM, 30 °C, 24 h. [b] Et_2O-insoluble part. [c] Estimated by SEC (PSt standards), DMF as eluent. [d] The monomer was added stepwise (one equivalent every 5 minutes, total 50 steps). [e] $[\text{monomer}]_{\text{final}}$. [f] Peak area ratio in the SEC. The other parts corresponded to low molecular weight oligomers.

Polymer characterization: First, the structures of the polymers were examined by ^{1}H NMR and IR spectroscopy. Poly(**2**) exhibited very broad signals at 6.0–8.3 ppm assignable to vinylene protons of the main chain (Figure 2). It was difficult to determine the cis content from the integration ratio due to the broadness. Since highly cis-stereoregular polyacetylenes commonly exhibit relatively sharp vinylene proton resonances, it seems that the cis-content of poly(**2**) is lower than those of the polymers obtained by the polymerization using Rh catalysts.[44–47]

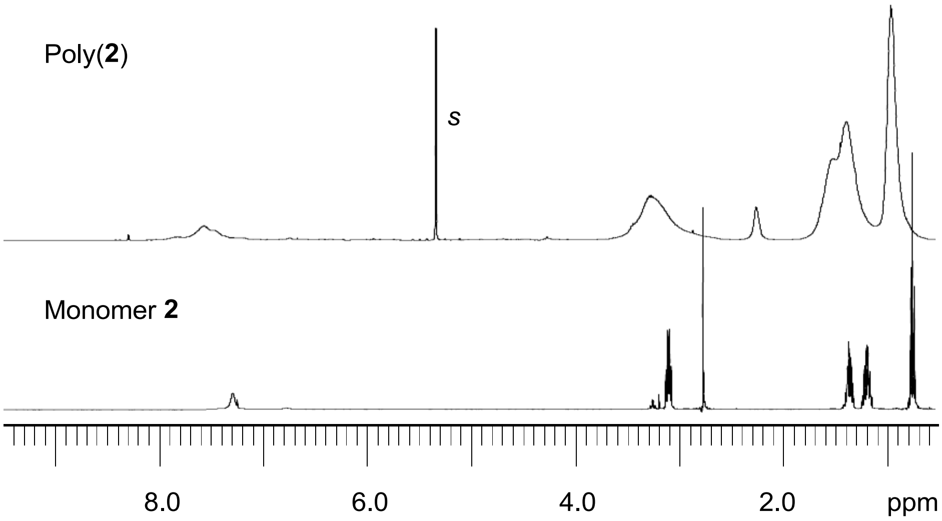


Figure 2. ^{1}H NMR spectra of poly(**2**) and monomer **2** measured in $CDCl_3$ at r.t. (s: solvent).

This was also supported by the presence of IR absorption peaks at 1276 (s) and 901 cm^{-1} (w) assignable to a trans structure, as well as a peak at 742 cm^{-1} (m) assignable to a cis structure (Figure 3).[48] Poly(**3**)–poly(**6**) showed trends of ^{1}H and IR spectra similar to those of poly(**2**).[49]

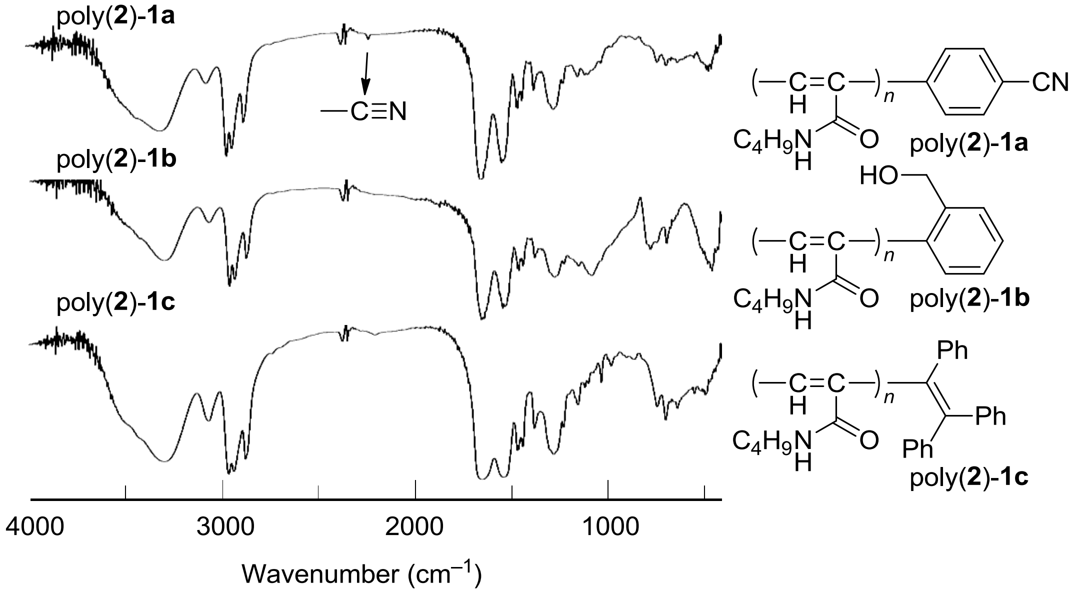


Figure 3. IR spectra of poly(**2**)-**1a**, poly(**2**)-**1b** and poly(**2**)-**1c** (KBr pellet).

The C_6H_4-*p*-CN end-functionalization of the polymers synthesized by **1aOTf** is indicated in the IR spectra, shown in Figure 3 for the poly(**2**) series obtained from initiators **1a**–**1c** as representatives. A C≡N stretching peak is observed at 2228 cm^{-1} in the IR spectrum of poly(**2**)-**1a**, while no peak is observed in this region in poly(**2**)-**1b** and poly(**2**)-**1c**. It is difficult to prove the introduction of the “R” groups into the later two polymers by IR spectroscopy due to the lack of such clear absorption peaks.

The structures of the poly(**3**) series and poly(**5**)-**1a** were also examined by MALDI-TOF mass spectrometry employing 2,5-dihydroxybenzoic acid (DHB).

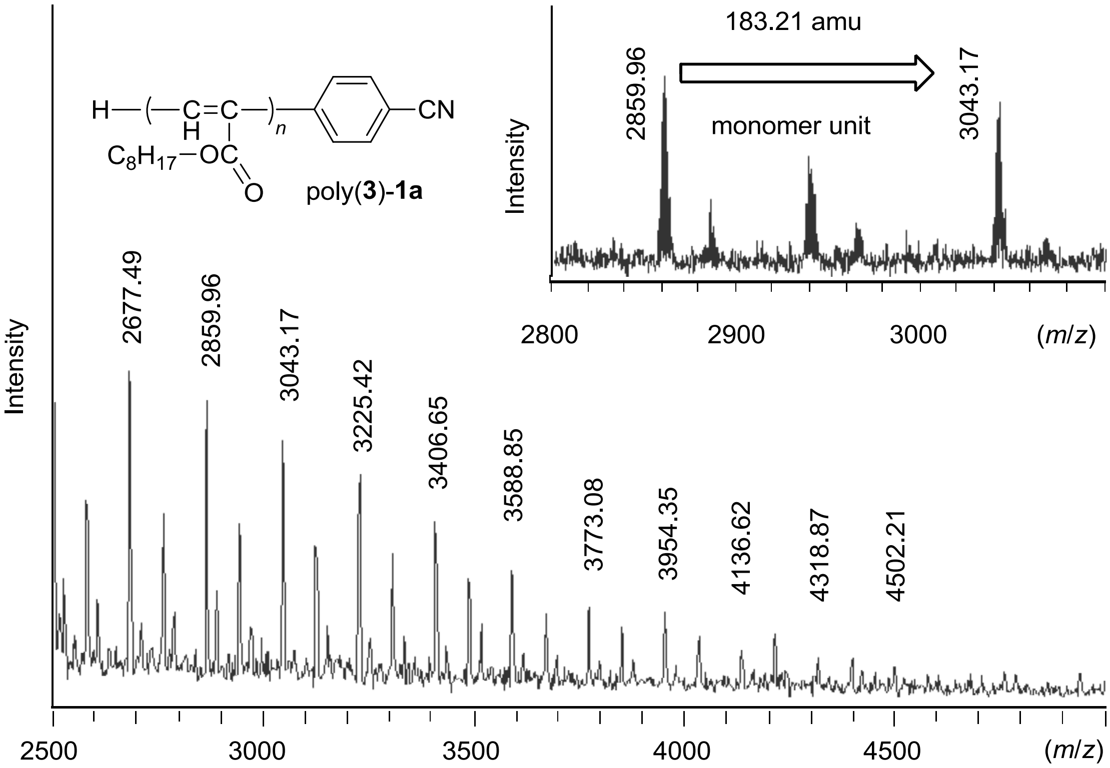


Figure 4. MALDI-TOF mass spectrum of poly(**3**)-**1a** acquired with DHB/NaTFA matrix. The inset shows a partial amplification.

as a matrix and sodium trifluoroacetate (NaTFA) as a cationizer, Figures 4 and 5 for poly(**3**) series. Two series of peaks are observed as shown in Figure 4. Either set of peaks features an interval of 183.21 amu, which is consistent with the calculated *m/z* (182.13) of a monomer unit. Noticeable differences of absolute values exist between the intense peak series of poly(**3**)-**1a**, poly(**3**)-**1b** and poly(**3**)-**1c**. The differences agree with those arising from the identical polymer chains bearing different chain ends. For instance, the difference between the signals of poly(**3**)-**1a** and poly(**3**)-**1c** is 152.77 amu, which matches

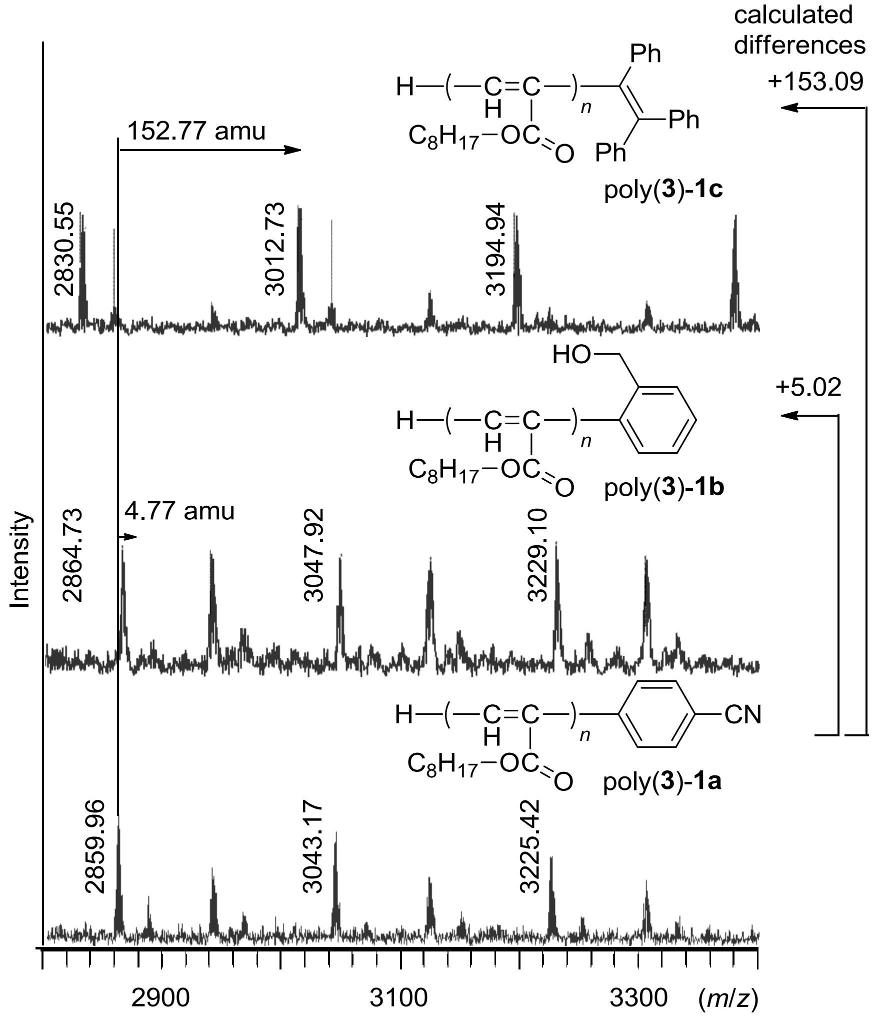


Figure 5. Comparison between the MALDI-TOF mass spectra of the poly(**3**) series obtained by the polymerizations initiated with **1a**, **1b** and **1c**.

reasonably with the calculated *m/z* difference (153.09) between C(Ph)=CPh_2 and C_6H_4-*p*-CN as chain end functional groups. Another chain end is assignable to –H from the calculated isotope patterns for the observed signals (Figure 6). The structure of poly(**5**)-**1a** is also suggested to correspond to a

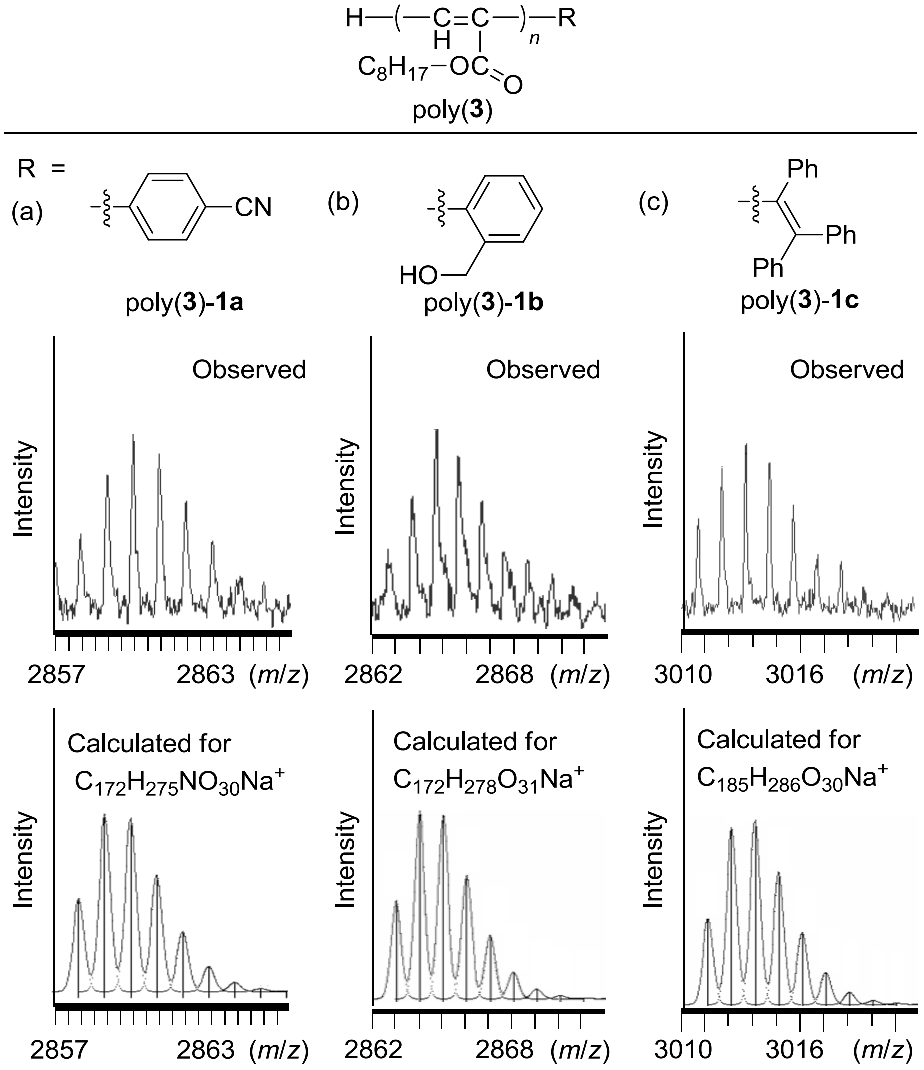


Figure 6. Selected isotope patterns in the MALDI-TOF mass spectra observed (enlarged view of the data presented in Figure 5) and calculated for (a) poly(**3**)-**1a**, (b) poly(**3**)-**1b** and (c) poly(**3**)-**1c**.

main chain with –H and –C_6H_4-*p*-CN chain ends according to similar results in the MALDI-TOF mass spectrometry to those shown for poly(**3**)-**1c**.

Stoichiometric reactions: Stoichiometric reactions of a catalyst with 1–3 equivalents of monomers were carried out to obtain further information on the end-functionalization. We examined the initial insertion of **5** into the Pd–C bond of **1aOTf**, which was formed *in situ* from **1a** and AgOTf, by NMR spectroscopy. Figure 7 presents the ^{1}H and ^{31}P NMR spectra of a sample solution of **1aOTf** in CD_3CN/CD_2Cl_2 upon stepwise addition of 1, 2 and 3 equivalents of **5** in an NMR sample tube. After the addition of 1 equivalent of **5**, vinylene proton signals appeared centered at 6.32 ppm (dd, J = 14.0 and 10.0 Hz). The peaks are assignable to vinylene protons accounting for 1,2-insertion products, considering the DFT calculations (see below).[50] The vinylene proton signals were intensified upon addition of the second and third portions of **5** (Figure 5, top). In the ^{31}P NMR spectra, the couple of doublet signals of **1aOTf** at 30.79 and 11.61 ppm ($^2J_{PP}$ = 27.5 Hz) were progressively reduced accompanying the growth of a new pair of doublets at 31.34 and 11.98 ppm ($^2J_{PP}$ = 29.4 Hz) (Figure 7, bottom) upon addition of 1–3 equivalents of **5**. The new doublet ^{31}P signals are assignable to the species formed by single insertion of **5** as illustrated in Scheme 2. This monomer insertion was supported by the observation of ESI-mass peaks corresponding to single, double, triple, quadruple and quintuple insertion products of **5** into the Pd–C bond of **1aOTf** as shown in Figure 8. Similar results were obtained when monomer **4** was used instead of **5**. These results demonstrate the end-functionalization of the present polymers by the Pd catalysts.

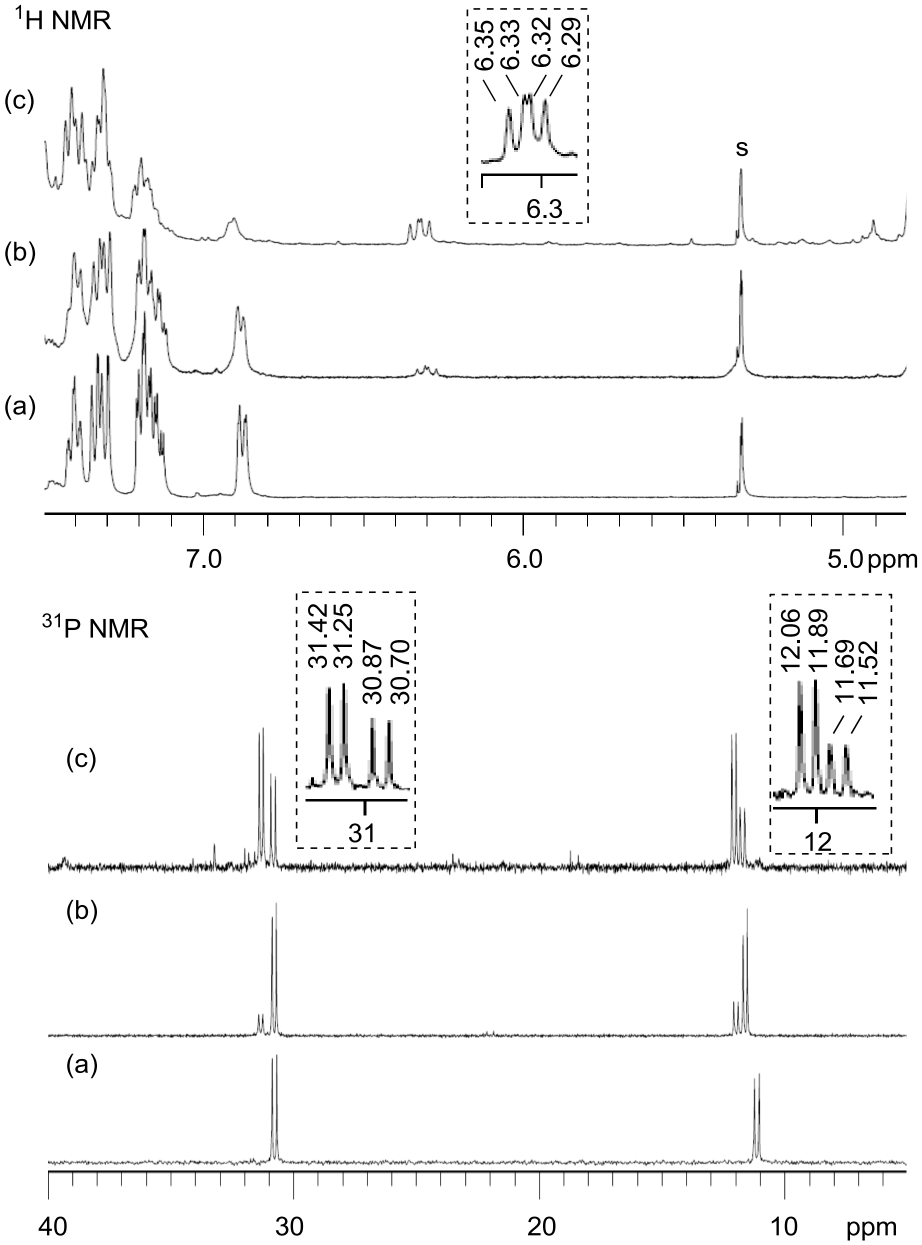


Figure 7. ^{1}H and ^{31}P NMR spectra of (a) **1aOTf**, (b) **1aOTf** + 1 equivalent of **5**, (c) **1aOTf** + 3 equivalents of **5** measured in CD_3CN/CD_2Cl_2 = 1/3 (v/v), [**1aOTf**]$_0$ = 34 mM at r.t. (s: solvent)

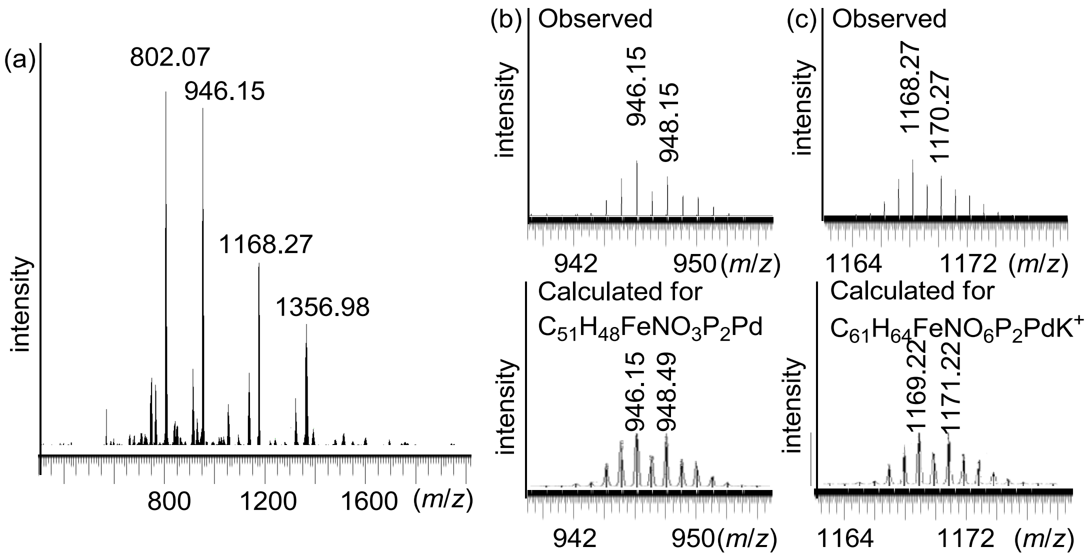
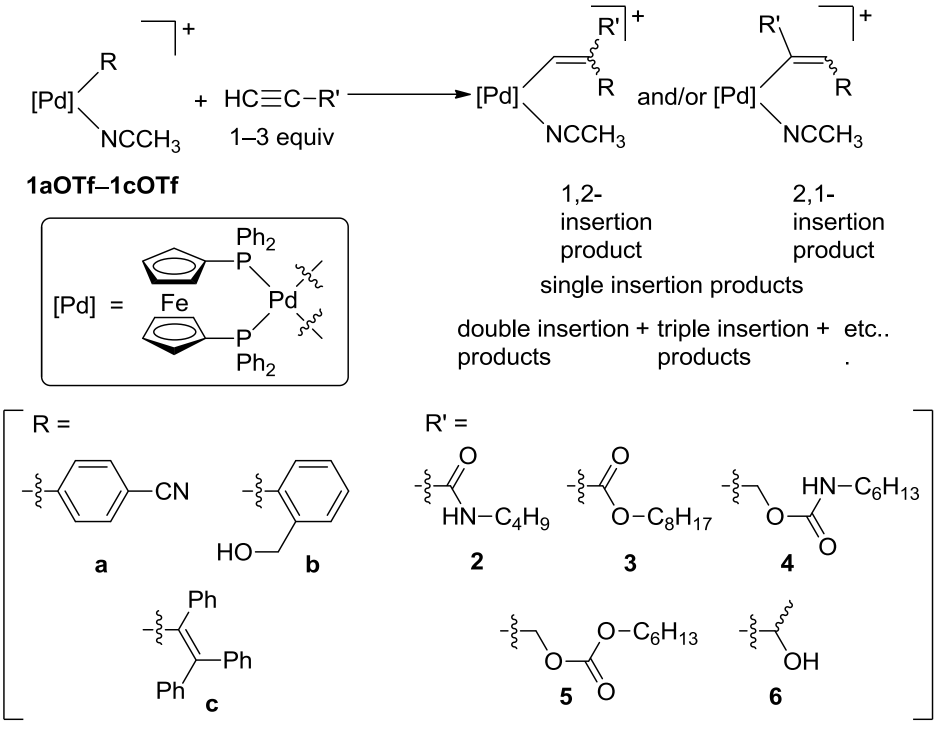


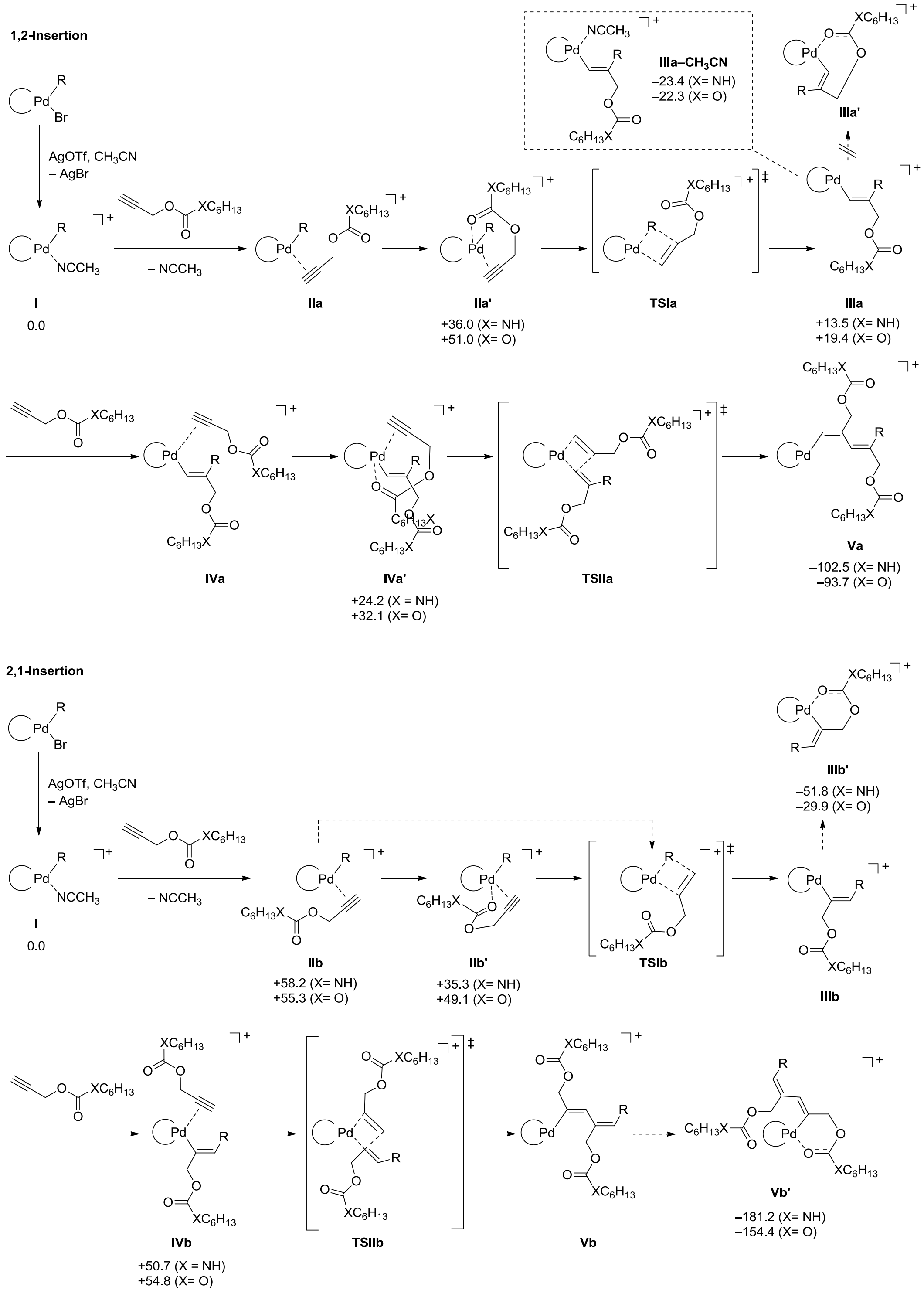
Figure 8. (a) ESI-mass spectrum of a mixture of **1aOTf** and 3 equivalents of **5**. (b) and (c): Isotope patterns in the ESI-mass spectra observed and calculated for single and double insertion products, respectively.

Scheme 2. Insertion of substituted acetylenes between the Pd and R of [(dppf)Pd(NCCH$_3$)(R)]OTf.



DFT calculations: The aforementioned results are consistent with the mechanism involving an insertion of acetylenes into a Pd-C bond.[43,51] DFT calculations were carried out to obtain detailed information on the polymerization mechanism. Monomers **4** and **5** were employed as representatives while [(dppf)Pd(C_6H_4-*p*-CN)Br] was the representative for the Pd complexes employed to catalyse the polymerizations. Scheme 3, top illustrates the reaction pathway for 1,2-insertion of the first and second monomers into cationic Pd(II) species **I**, which is formed by the reaction of a Pd(II) complex with square-planar geometry coordinated to dppf, *p*-cyanophenyl (R) and Br groups with AgOTf in CH_3CN/CH_2Cl_2. The first step is the replacement of CH_3CN of **I** with a monomer to form intermediate **IIa** coordinated by the triple bond of the monomer. After the geometry optimization of **IIa** with the distance between the Pd and carbonyl oxygen longer than 6 Å, it automatically converted to **IIa'** with Pd–O distances of 3.42 Å (X = NH) and 3.55 Å (X = O). This fact suggests that intermediate **IIa** easily turns into **IIa'**, which is stabilized by chelation with the carbonyl group of the monomer oriented perpendicular to the square-planar surface consisting of Pd, dppf, C_6H_4-*p*-CN (R) and the triple bond of the monomer. The next step is the insertion of a monomer between the Pd center and R via metallacyclobutane transition state **TSIa**. The monomer donates π-electrons of the triple bond to the Pd center to form a Pd–C bond.

Scheme 3. Reaction pathways for 1,2- and 2,1-insertions of $CH{\equiv}CH_2OCOXC_6H_{13}$ (X = NH, O) into $[(dppf)Pd(II)(NCCH_3)(C_6H_4\text{-}p\text{-}CN)]^+$. dppf and C_6H_4-*p*-CN are illustrated as an arc and R, respectively. The values below the compound numbers represent the relative ΔG (kJ mol^{-1}) based on **I**. The counter anion (TfO–) is omitted.



Simultaneously, the R group leaves from Pd and moves close to the monomer to form an R–C bond. The formation of 1,2-inserted product **IIIa** is endothermic (X = NH: +13.5 kJ mol^{-1}, X = O: +19.4 kJ mol^{-1}), while that of **IIIa–CH_3CN** is exothermic (X = NH: –23.4 kJ mol^{-1}, X = O: –22.3 kJ mol^{-1}) relative to **I**. It is likely that the CH_3CN coordinates to the Pd to stabilize the intermediate. The extension of conjugation from Pd–R of **I** to Pd–CH=C(R)$CH_2OCOXC_6H_{13}$ of **IIIa**–**CH_3CN** should be also effective to enhance the stability. Once **IIIa** and/or **IIIa**–**CH_3CN** are formed, the carbonyl group of the monomer unit cannot coordinate to Pd due to the geometric restriction, i.e., intermediate **IIIa'** does not exist due to the large strain.

The second monomer insertion starts with the coordination of another monomer to one square-planar site of Pd, resulting in the formation of **IVa**. In a fashion similar to the first monomer insertion, **IVa** is considered to turn into **IVa'** due to the stabilization based on the chelation of the carbonyl group.[52] The second monomer is inserted via a four-membered transition state **TSIIa** in a similar manner to **TSIa**. It is assumed that the activation energy for **TSIIa** is lower than those of **TSIa**, judging from the largely exothermic ΔG values from **IVa'** to **Va** (X = NH: –126.7 kJ mol^{-1}, X = O: –125.8 kJ mol^{-1}) compared to those from **IIa'** to **IIIa** (X = NH: –22.5 kJ mol^{-1}, X = O: –31.6 kJ mol^{-1}) and/or those from **IIa'** to **IIIa–CH_3CN** (X = NH: –59.4 kJ mol^{-1}, X = O: –73.3 kJ mol^{-1}). Further extension of conjugation seems to be effective for stabilizing **Va** even in the absence of CH_3CN.

Scheme 3, bottom illustrates the reaction pathway for 2,1-insertion of the first and second monomers into **I**. Upon optimizing the geometry, intermediate **IIb** does not automatically convert to its analogue **IIb’** (Pd–O distance, X = NH: 3.18 Å, X = O: 3.38 Å) that is chelated with the triple bond and the carbonyl group, differently compared to the **IIa→IIa’** transformation during the 1,2-insertion mentioned above. Although the ΔG’s of **IIb’** are smaller than those of **IIb**, the direct path from **IIb** to **TSIb** may exist. It seems that 2,1-insertion is unfavorable compared to 1,2-insertion judging from the ΔG’s of **IIb**, which are larger than those of **IIa’**, as predicted from the larger steric repulsion between the bulky dppf and $CH_2OCOXC_6H_{13}$ moieties. Interestingly, the 2,1-insertion product **IIIb** automatically converted to **IIIb’**, which is chelated by C=O with a square-planar geometry (Pd–O distance, X = NH: 2.16 Å, X = O: 2.18 Å). The formation of **IIIb’** is largely exothermic (X = NH: –51.8 kJ mol^{-1}, X = O: –29.9 kJ mol^{-1}) relative to **I**, while the formation of **IVb** is largely endothermic (X = NH: +50.7 kJ mol^{-1}, X = O: +54.8 kJ mol^{-1}). Once **IIIb’** is formed, the second monomer may no longer be able to coordinate to Pd at the square-planar site, resulting in the dead end of polymerization. The second monomer inserted intermediate **Vb**, formable from **IVb** via **TSIIb**, automatically turned into **Vb’** after optimizing geometry in a manner similar to **IIIb→IIIb’**.

Conclusions

We have demonstrated the polymerization of polar substituted acetylene monomers **2**–**6** catalyzed by well-defined Pd complexes **1a**–**c** in combination with AgOTf, forming [(dppf)Pd(NCCH$_3$)(R)]OTf as active catalytic species. The "R" groups of catalysts **1a**–**c** were introduced at the chain ends of poly(**2**)–poly(**6**), as confirmed by IR spectroscopy and MALDI TOF mass spectrometry. The incorporation was also confirmed by ^{1}H and ^{31}P NMR spectroscopic analysis of stoichiometric reactions of the catalyst and monomers. ESI-mass spectrometric analysis proved the production of compounds formed by single–quintuple insertions of monomers **4** and **5** between the Pd and R of **1aOTf**. The isotope patterns agreed well with those calculated for single and double insertion products. DFT calculations suggested that 1,2-insertion is preferable to 2,1-insertion, most likely due to steric repulsion between the bulky dppf ligand and an incoming monomer. Currently, we are investigating new Pd catalysts for acetylene polymerization, with the goal of improving the catalytic activity and cis-stereoregularity of the resulting polymers, especially compared to the capabilities of Rh catalysts.

Experimental Sections

Measurements. ^{1}H (400 MHz) and ^{13}C (100 MHz) NMR spectra were recorded on a JEOL EX-400 or an AL-400 spectrometer. Chemical shifts were referenced to $CHDCl_2$ (5.32 ppm), $CHCl_3$ (7.26 ppm) or C_6HD_5 (7.16 ppm) as an internal standard. ^{31}P NMR spectra (162 MHz) were observed on a JEOL ECX-400 or an EX-400 spectrometer with $P(OMe)_3$ as an external standard (140 ppm). IR spectra were measured on a JASCO FT/IR-4100 spectrophotometer using the KBr method. Elemental analyses were performed at the Microanalytical Center of Kyoto University. MALDI-TOF mass spectra were recorded on a Bruker Daltonics ultraflex III TOF/TOF equipped with a 355 nm YAG laser in the reflectron mode using an acceleration voltage of 25 kV. Samples for MALDI-TOF mass spectrometry were purified by silica gel column chromatography eluted with CH_2Cl_2/THF 1/1 (v/v) to remove residual Pd prior to measurement, and prepared by mixing CH_2Cl_2 solutions of the polymer (10 mg/mL), DHB (20 mg/mL) and NaTFA (2 mg/mL) in a ratio of 1:10:1. All the mass differences discussed below were calculated by comparing the mass values of two base peaks of the most abundant isotopomers. Weight-average molecular weights (M_w's) and polydispersity indices (PDI's) of polymers were determined by a JASCO system equipped with Shodex columns K803, K804 and K805 (molecular weight limit $\approx 4 \times 10^6$) eluted with $CHCl_3$, Shodex columns KF805 × 3 (molecular weight limit $\approx 4 \times 10^6$) eluted with THF, or Shodex columns K804, K805 and J806 (molecular weight limit $\approx 4 \times 10^8$) eluted with a solution of LiBr (10 mM) in DMF at 40 °C using polystyrene standards for calibration.

DFT calculations: All the calculations were performed with the GAUSSIAN 09 program[53] running on the supercomputer system, Academic Center for Computing and Media Studies, Kyoto University. The integrated molecular orbital and molecular mechanics method (ONIOM)[54,55] was used, in which the density functional theory (DFT)[56,57] method with the B3LYP/LANL2DZ and semiempirical method with the PM6 hamiltonian were employed for a higher layer (Pd, dppf moiety except phenyl groups, $CHCCH_2OCONH$ or $CHCCH_2OCOO$) and a lower layer (rest of the others), respectively.

Materials: Unless otherwise stated, reagents and solvents were used as received from commercial suppliers (Aldrich and Wako). [(dppf)PdBr(C_6H_4-*p*-CN)] (**1a**),[38] [(dppf)PdBr(C_6H_4-*o*-CH_2OH)] (**1b**),[38] {(dppf)PdBr[C(Ph)=CPh_2]} (**1c**),[38] *N*-butyl-2-propiolamide (**2**)[58] and octyl propiolate (**3**)[46,59] were synthesized by the methods reported in the literature. 3-Butyn-2-ol (**6**) (Aldrich) was distilled prior to use. Solvents for polymerization were purified by the standard procedures before use.

Synthesis of propargyl-*N*-hexylcarbamate (4): It was synthesized by a modified method reported in the literature.[60] The details are as follows: A solution of propargyl alcohol (1.6 g, 29 mmol) and pyridine (2.9 g, 37 mmol) in CH_2Cl_2 (40 mL) was added to a solution of *p*-nitrophenyl chloroformate (10.0 g, 50 mmol) in CH_2Cl_2 (60mL) dropwise at –50 °C, and the resulting mixture was kept stirring at –50 °C for 14 h. Then the mixture was washed with aqueous solutions of $NaHCO_3$ and NaCl successively. The organic phase was separated, dried over anhydrous $MgSO_4$, filtered, and then concentrated on a rotary evaporator. The residue was dissolved in DMF (100 mL), and pyridine (5.0 g, 63 mmol) was added to the solution. Hexylamine (3.1 g, 30 mmol) was added to the solution dropwise at 0 °C, and the mixture was allowed to warm to room temperature. After additional stirring overnight, water (160 mL) was added to the reaction mixture, and the solution was extracted with Et_2O. The organic phase was washed with 1 M NaOH (aq) until the aqueous phase became colorless. The organic phase was dried over $MgSO_4$, filtered, and then concentrated on a rotary evaporator. The residue was purified by column chromatography [SiO_2, hexane/ethyl acetate = 30/1 (v/v)] and then by distillation under reduced pressure to afford propargyl-*N*-hexylcarbamate as a colorless oil. Yield = 2.6 g (47%). ^1H NMR ($CDCl_3$, 25°C, TMS): δ 0.88 (t, J = 7.2 Hz, 3H; CH_3), 1.24–1.34 (m, 6H; $CH_2CH_2CH_2CH_3$), 1.43–1.49 (m, 2H; $NHCH_2CH_2$), 2.04 (s, 1H; $HC{\equiv}C$), 3.11–3.16 (m, 2H; $NHCH_2$), 4.68 (s, 2H; $\equiv CCH_2O$), 4.72 (broad, 1H; N*H*). ^{13}C NMR ($CDCl_3$, 25°C, TMS): δ 13.9, 22.5, 26.3, 29.8, 31.4, 41.2, 52.3, 74.4, 78.4, 155.4; HRMS (ESI): *m/z* calcd for $C_{10}H_{17}NO_2+H^+$: 184.1332 [M+H^+]; found 184.1331; elemental analysis calcd (%) for $C_{10}H_{17}NO_2$: C, 65.54; H, 9.35; N, 7.64; found: C, 65.29; H, 9.43; N, 7.47.

Synthesis of hexyl propargyl carbonate (5): This compound was synthesized using hexanol in place of hexylamine in a manner similar to propargyl-*N*-hexylcarbamate. Yield = 23% (colorless oil). ^1H NMR ($CDCl_3$, 25°C, TMS): δ 0.89 (t, J = 6.8 Hz, 3H; CH_2CH_3), 1.28–1.37 (m, 6H; $CH_2CH_2CH_2CH_3$), 1.64–1.71 (m, 2H; OCH_2CH_2), 2.52 (t, J = 2.4 Hz, 1H; $HC{\equiv}C$), 4.17 (t, J = 6.8 Hz, 2H; OCH_2), 4.73 (d, J = 2.4 Hz, 2H; $\equiv CCH_2O$); ^{13}C NMR ($CDCl_3$, 25°C, TMS): δ 13.9, 22.5, 25.3, 28.5, 31.3, 55.1, 68.8, 75.5, 77.1, 154.6; HRMS (ESI): m/z calcd for $C_{10}H_{16}O_3+H^+$: 185.1172 [$M+H^+$]; found 185.1171; elemental analysis calcd (%) for $C_{10}H_{16}O_3$: C, 65.19; H, 8.75; found: C, 65.26; H, 8.82.

Polymerization: All the polymerization procedures were performed under Ar atmosphere. A representative example is as follows: A solution of CH_3CN/CH_2Cl_2 [1/1 (v/v), 1 mL] was added to a mixture of Pd complex **1a** (18 mg, 2.0×10^{-2} mmol) and AgOTf (6.2 mg, 2.4×10^{-2} mmol) to form a cationic Pd derivative. After stirring the mixture at room temperature for 5 min, the white precipitate (AgBr) was removed by filtration. The catalyst solution was cooled to –78 °C, then CH_2Cl_2 (1 mL) and monomer (1.0 mmol) were added successively to the catalyst solution. The resulting solution was stirred at 30 °C for 24 h. Finally, the reaction mixture was concentrated and poured into hexane, MeOH or Et_2O (100 mL) to precipitate the polymer.

Stoichiometric reactions: The reactions were carried out under Ar atmosphere. The general procedure for a reaction is as follows: A solution of CD_3CN/CD_2Cl_2 [1/3 (v/v), 0.5 mL] was added to a mixture of **1a** (15 mg, 1.7×10^{-2} mmol) and AgOTf (5.2 mg, 2.0×10^{-2} mmol) in an NMR sample tube. Then **4** (3.1 mg, 1.7×10^{-2} mmol) or **5** (3.1 mg, 1.7×10^{-2} mmol) was added to the resulting mixture at –78 °C followed by vigorous shaking of the tube. Subsequent increments of monomer were added in a similar manner to the first addition. Every step of the reaction was monitored by NMR spectroscopy. The ESI-mass spectra were measured without purification.

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the terminal methyl proton signal in the hexyl group), IR 1258 cm^{-1} (trans), 725 cm^{-1} (cis). Poly(**5**): ^{1}H NMR 5.6–6.8 ppm, IR 913 cm^{-1} (trans), 750 cm^{-1} (cis). Poly(**6**): ^{1}H NMR 5.2–6.8 ppm, IR 1260 cm^{-1}, 937 cm^{-1} (trans), 749 cm^{-1} (cis). See references 13 and 48 regarding the presence of cis and trans structures in substituted polyacetylenes.

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Part II

Development of Bulky Monophosphine-Ligated Pd Catalysts for the Polymerization of 1-Chloro-2-Arylacetylenes

Chapter 3

A New Approach to the Polymerization of Disubstituted Acetylenes by Bulky Monophosphine-Ligated Palladium Catalysts

Abstract

Bulky monophosphine-ligated Pd complexes served as unprecedented admirable catalysts for the polymerization of a disubstituted acetylene. The moderately high polymer yields and cis-content of the formed polyacetylene contrasted with those observed for traditional Mo catalyst-based polymer. These Pd catalysts are strong tools to promote the understanding of the structure-property relationships of disubstituted acetylenes.

Introduction

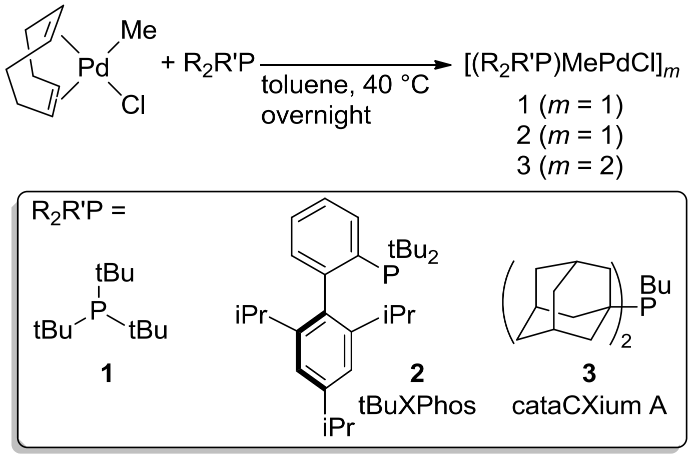
A Application of well-defined transition metal catalysts to polymerization reactions has contributed in numerous cases to develop controlled polymerization systems and in some cases to even gain some insight into the polymerization mechanism.[1–5] For the polymerization of substituted acetylenes, a great deal of effort has been devoted to develop controlled systems since the polymerization reaction directly impacts the unparalleled properties of these materials. Their higher stability, selective gas-permeability and superior luminescent properties make disubstituted polyacetylenes more suitable for practical applications than their monosubstituted counterparts. This has fostered the development of metal catalysts applicable to a wide range of monomers.[4–6] Although initial investigations of substituted polyacetylenes focused on early transition metal catalysts, in recent years the utilization of late transition metal catalysts has proven to be more attractive, because their lower oxophilicity allows them to polymerize acetylenes containing highly polar functional groups that cannot be handled by early transition metals.[4,5] However, late transition metal catalysts have not generally shown polymerization activity for disubstituted acetylenes, presumably due to the higher steric hindrance of these monomers compared to monosubstituted acetylenes.[5,6e]

In recent years, introduction of bulky alkyl monophosphines to palladium-catalyzed reactions has shown to yield high activities.[1,7] In particular, employment of bulky monophosphine-ligated Pd catalysts has allowed synthesis of polymers that are hardly accessible through other Pd catalysts.[1,8,9] Bulky monophosphine containing [(R_3P)PdR'X]-type complexes feature a T-shape tricoordinated Pd structure having a vacant site partially stabilized by weak interactions with the surrounding ligands.[7e,9–12] It is likely that the presence of a vacant site in the Pd structure favors reactions involving bulky substrates, since the vacant site potentially allows the sterically hindered substrate to be accommodated in the coordination sphere of the Pd center. Herein, we report the synthesis of bulky monophosphine-ligated [(R_2R'P)PdMeCl]-type complexes (**1**–**3**) to investigate the polymerization of a disubstituted acetylene, 1-chloro-2-(4-*tert*-butyl)phenylacetylene (**4**). Application of the bulky monophosphine-ligated Pd catalysts for the polymerization of disubstituted acetylenes is an exciting topic, since it potentially allows the synthesis of copolymers consisting of conjugated and non-conjugated blocks, i.e., polyacetylene and polyolefin blocks.

Results and Discussion

Bulky monophosphine ligated Pd complexes **2** and **3** were synthesized by replacing the 1,5-cyclooctadiene (cod) in [(cod)PdMeCl] with 2-di-*tert*-butylphosphino-2′,4′,6′-tri-isopropylbiphenyl (*t*BuXPhos) or di-1-adamantyl-*n*-butylphosphine (cataCXium A) in a similar manner to the reported synthetic method for **1** (Scheme 1).[9] The ^{1}H and ^{31}P NMR together with X-ray crystal structure analysis revealed a mononuclear structure for complex **2** and a dinuclear structure for **3**, both of which are in agreement with structures for other Pd complexes bearing adamantyl and biaryldialkylphosphine ligands (Figure 1).[11–13]

Scheme 1. Synthesis of bulky monophosphine-ligated palladium complexes



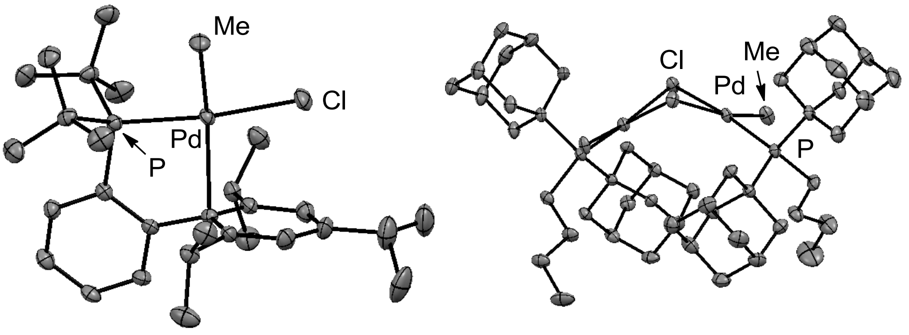
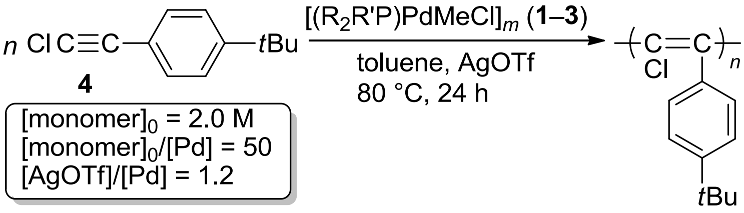


Figure 1. ORTEP drawing of **2** (left) and **3** (right). The thermal ellipsoids were set at 50% probability.

Scheme 2. Polymerization of 1-chloro-2-(4-*tert*-butyl)phenylacetylene (**4**) by ($R_2R'P$)PdMeCl (**1**–**3**)/AgOTf



Next, we examined the polymerization of acetylene monomer **4** using Pd complexes **1**–**3** (Scheme 2), wherein the complexes were dehalogenated with silver trifluoromethanesulfonate (AgOTf) in situ; the Cl atom was replaced by OTf, an anion having a weaker coordinating ability. Complexes **1**–**3** successfully polymerized **4** (Table 1, entries 1–3) to give the corresponding polymers in yields higher than 76%. In contrast, highly active Rh catalysts for

Table 1. Polymerization of **4** by **1**–**3**/AgOTf[a]

entry	catalyst	yield, %[b]	M_w[c]	PDI[c]	DP
1	**1**	77	37600	2.01	195
2	**2**	76	17000	3.51	88
3	**3**	76	24400	1.58	127
4[d]	$MoCl_5/SnBu_4$	58	350000	3.13	1816

[a] $[\mathbf{4}]_0$ = 2.0 M, $[\mathbf{4}]_0$/[Pd] = 50, [AgOTf]/[Pd] = 1.2. [b] MeOH-insoluble part. [c] Estimated by SEC of the THF-soluble part, THF as eluent (calibrated by polystyrene standards). [d] $[\mathbf{4}]_0$ = 1.0 M, $[\mathbf{4}]_0$/[Mo] = 50, $[SnBu_4]$/[Mo] = 1.0 in toluene at rt for 24 h.

the polymerization of monosubstituted acetylenes, [(nbd)Rh[(η^6-C_6H_5)B(C_6H_5)$_3$] (nbd = 1,5-norbornadiene) and [(nbd)RhCl]$_2$/NEt$_3$, only yielded products with M_w's < 800 from the analysis of the crude reaction mixture (Scheme 3 and Table 2).

Scheme 3. Polymerization of 1-chloro-2-(4-*tert*-butyl)phenylacetylene (**4**) by ($R_2R'P$)PdMeCl (**1**–**3**)/AgOTf

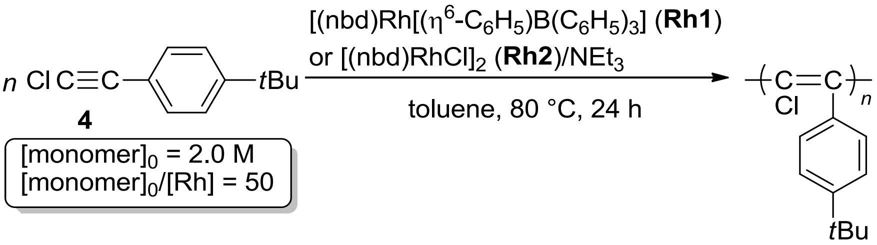


Table 2. Attempts to polymerize 1-chloro-2-(4-*tert*-butyl)phenylacetylene (**4**) by [(nbd)Rh[(η^6-C_6H_5)B(C_6H_5)$_3$] (**Rh1**) and [(nbd)RhCl]$_2$ (**Rh2**)/NEt$_3$[a]

catalyst	yield, %[b]	M_w[c]	PDI[c]	DP
Rh1	–	700	1.21	4
Rh2[d]	–	800	1.06	4

[a] [**4**]$_0$ = 2.0 M, [**4**]$_0$/[Rh] = 50. [b] No solid could be isolated from common solvents; therefore the reaction mixtures were analysed after evaporating the solvent. [c] Estimated by SEC, CHCl$_3$ as eluent (calibrated by polystyrene standards). [d] [NEt$_3$]/[monomer]$_0$ = 1.0

Approximately 60% of the **1**–**3**-based poly(**4**) (Table 1, entries 1–3) were insoluble in common organic solvents including CHCl$_3$, THF and DMF. It is reasonable to assume that the solvent-insoluble parts are high molecular weight fractions featuring high cis-contents as reported regarding cis-cisoidal stereoisomers of some other substituted polyacetylenes that are poorly soluble in common organic solvents.[5b,14] SEC analysis of the THF-soluble parts revealed that the M_w and PDI of **1**-based poly(**4**) [poly(**4**)-**1**] (Table 1, entry 1) were 37600 and 2.01. Catalysts **2** and **3** gave polymers [poly(**4**)-**2** and poly(**4**)-**3**] both in 76% yield. The comparatively low M_w and broad PDI of poly(**4**)-**2** may be explained by the occurrence of some termination reactions, which may be promoted by the presence of *t*BuXPhos ligand through dearomative rearrangement of Pd species, as reported for Pd-catalyzed reactions involving biaryldialkylphosphine ligands.[12a,15]

In order to compare the activity of the Pd catalysts presented in this work to the activities of the well-known Mo catalytic systems,[4c,16] we performed the polymerization of **4** by $MoCl_5/SnBu_4$ under conditions similar to those employed for the Pd catalytic systems ($[\mathbf{4}]_0$ = 2.0 M, $[\mathbf{4}]_0/[Pd]$ = 50). The yield of the Mo-based polymer [poly(**4**)-Mo] was lower than those featured by the Pd catalytic systems (58% *vs* 76–77%). Poly(**4**)-Mo was completely soluble in $CHCl_3$ and THF. We compared the structure of poly(**4**)-**Mo** with that of poly(**4**)-**1** to obtain further information about the differences of both catalytic systems. The IR spectroscopic analysis confirmed the complete transformation of the monomer to poly(**4**)-**1** and poly(**4**)-**Mo**, since the polymers displayed C=C stretching bands around 1608 cm^{-1}, but no C≡C stretching band around 2221 cm^{-1} (Figure 2). Moreover, no loss of Cl atoms was confirmed by the appearance of intense C–Cl stretching bands in the region of 828–834 cm^{-1}.[16d,e]

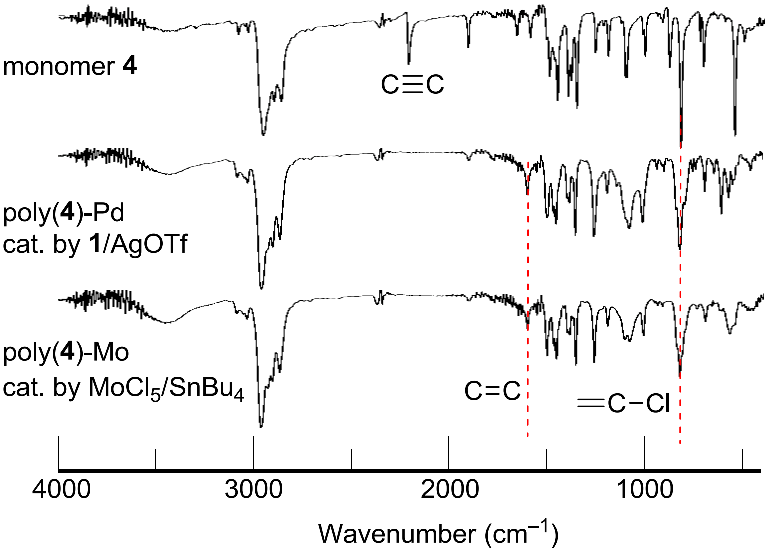


Figure 2. IR spectra of monomer **4**, poly(**4**) obtained by the 1/AgOTf catalytic system (Table 1, entry 1) and poly(**4**) obtained by the $MoCl_5/SnBu_4$ catalytic system (Table 1, entry 4).

Since the *cis*-/*trans*-geometries of main chains of substituted polyacetylenes significantly influence the properties,[4a,5b,17] it is important to develop polymerization methods that can yield substituted acetylene polymers containing highly *cis*- or *trans*-stereoregulated double bonds. The Raman spectra of poly(**4**)**-1** and poly(**4**)**-Mo** were measured to examine the stereoregularity.

As shown in Figure 3, poly(**4**)**-1** displayed Raman spectroscopic signals characteristic for both *trans*- (1573 and 1184 cm^{-1}) and *cis*-structures (1340 and 884 cm^{-1}) while poly(**4**)**-Mo** displayed only signals for the *trans*-structures around 1203 cm^{-1} (broad weak signal) and 1605 cm^{-1} (broad intense signal).[18]

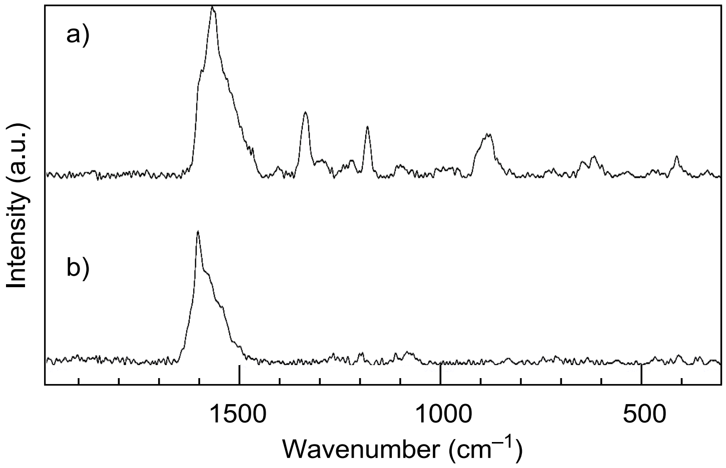


Figure 3. Raman spectra of: a) poly(**4**)-**1** (Table 1, entry 1) and b) poly(**4**)-Mo (Table 1, entry 4).

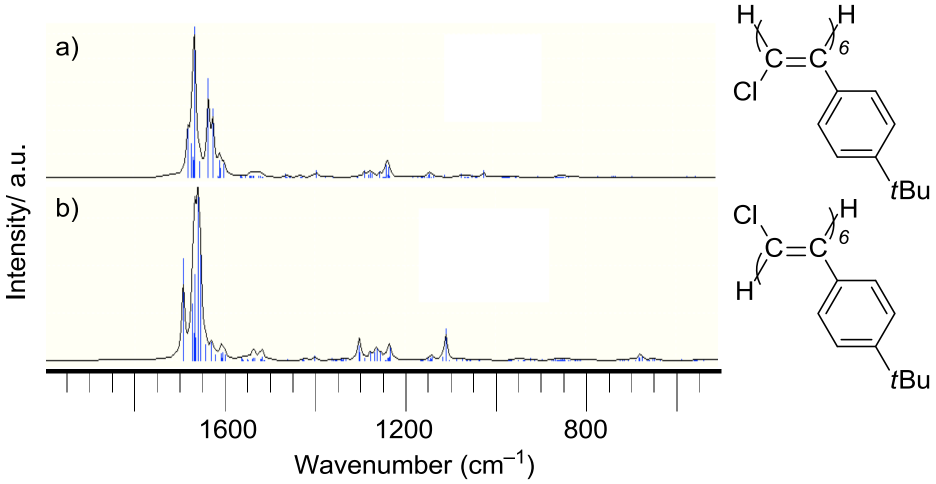


Figure 4. Raman spectra of a hexamer of **4** featuring: a) *cis*-stereochemistry and b) *trans*-stereochemistry simulated by the DFT (B3LYP/6-31G*) calculations.

The Raman spectra simulated for the *cis*- and *trans*-hexamers of **4** supported the above mentioned assignments (Figure 4). The calculation procedures were as follows. First, *cis*- and *trans*-stereoregular hexamers of monomer **4** were constructed, in which the main chains were twisted to release the steric repulsion between the side chains, i.e., the dihedral angles of C=C–C=C were set to 120.0°, forming right-handed helical structures. After full geometry optimization with the PM6 followed by the DFT calculations at the B3LYP/6-31G* level, the average dihedral angles of the *cis*- and *trans*-hexamer became 116.7° and 116.3°, respectively. The Raman spectra were simulated by force calculation. The order of appearance of the strong signals between 1570 and 1610 cm^{-1} for the

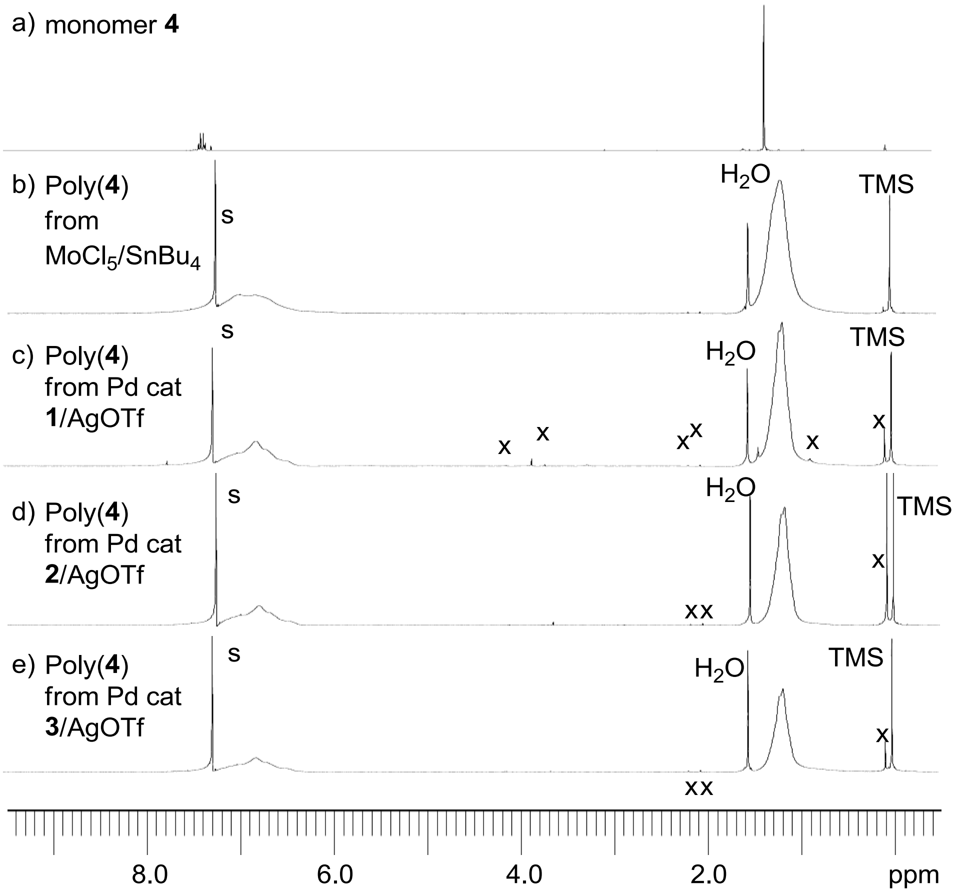


Figure 5. ^{1}H NMR spectra of: a) monomer **4**; b) poly(**4**) synthesized by $MoCl_5/SnBu_4$ (Table 1, entry 4); c) poly(**4**) synthesized by Pd catalyst **1**/AgOTf (Table 1, entry 1); d) poly(**4**) synthesized by Pd catalyst **2**/AgOTf (Table 1, entry 2) and e) poly(**4**) synthesized by Pd catalyst **3**/AgOTf (Table 1, entry 3). All spectra were measured in $CDCl_3$ at rt. (s: solvent, x: impurity).

Pd- and Mo-catalyzed poly(**4**)s in the experimental Raman spectra (Figure 3)matched the order of appearance that would arise for poly(**4**)-**1** having a higher *cis* content than poly(**4**)-**Mo** based on the calculated Raman spectra.

The ^{1}H and ^{13}C NMR spectra of poly(**4**)-**1** and poly(**4**)-Mo also confirmed the different structures for both polymers (Figures 5 and 6). The ^{1}H NMR spectroscopic analysis of the polymers (Figure 5) exhibited only broad signals assignable to the aromatic and *tert*-butyl protons at 6.4–7.5 ppm and 0.8–1.5 ppm, respectively. Pd-based poly(**4**) showed aromatic proton signals at 6.789 ppm with accompanying shoulders at 6.683 and 6.449 ppm, and *t*Bu proton signal at 1.167 ppm. Mo-based poly(**4**) showed two broad aromatic proton signals at 6.996 and 6.835 ppm, and the *t*Bu proton signal at 1.185 ppm. It was not possible to observe a Me-group signal at the chain-end due to considerable broadening despite the possible presence of oligomers formed by the insertion of one to three monomer units into the Pd-Me bond of **1OTf** (see below).

In the ^{13}C NMR spectra of all the poly(**4**)s we could confirm the disappearance of the C≡C signals at 67.14 and 69.48 ppm with the concomitant appearance of a new signal around 138.41 ppm (Figure 6). The signal at 138.41 ppm was hardly visible in the spectra of poly(**4**)-**Mo**, probably due to the disordered structure and a higher molecular weight compared to the Pd synthesized polymer. In particular, comparison of the experimental (Figure 7) and calculated (Chart 1) ^{13}C NMR spectra gave further support to the high *trans* content for poly(**4**)-Mo compared with that of poly(**4**)-**1**.

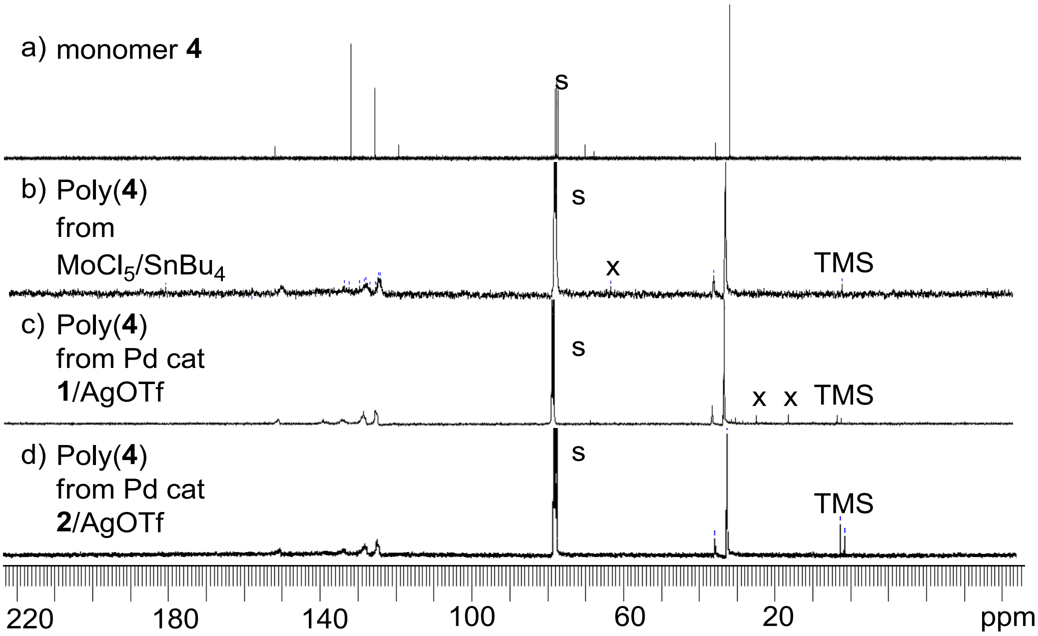


Figure 6. ^{13}C NMR spectra of: a) monomer **4**; b) poly(**4**) synthesized by $MoCl_5/SnBu_4$ (Table 1, entry 4); c) poly(**4**) synthesized by Pd catalyst **1**/AgOTf (Table 1, entry 1) and d) poly(**4**) synthesized by Pd catalyst **2**/AgOTf (Table 1, entry 2). All spectra were measured in $CDCl_3$ at rt. (s: solvent, x: impurity).

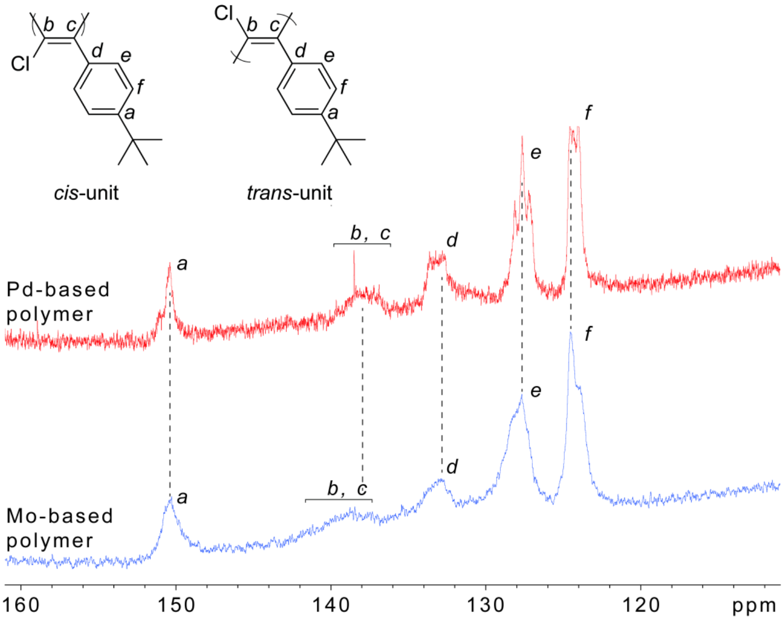
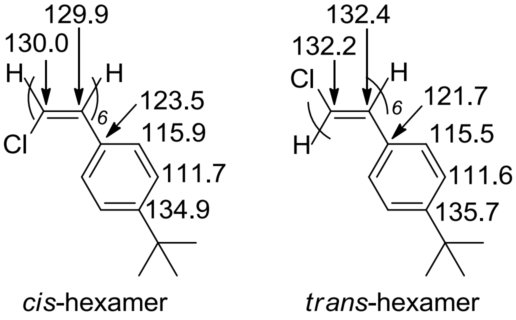


Figure 7. Expansion of ^{13}C NMR (150 MHz) spectra of poly(**4**)s synthesized by: upper) Pd catalyst **1**/AgOTf (entry 1 in Table 1) and lower) $MoCl_5/SnBu_4$ (entry 4 in Table 1). The spectra were measured in $CDCl_3$ at rt.

Chart 1. ^{13}C NMR chemical shifts (ppm) of *cis*- and *trans*-hexamers of **4** predicted by the DFT (B3LYP/6-31G*)–GIAO method.[a]

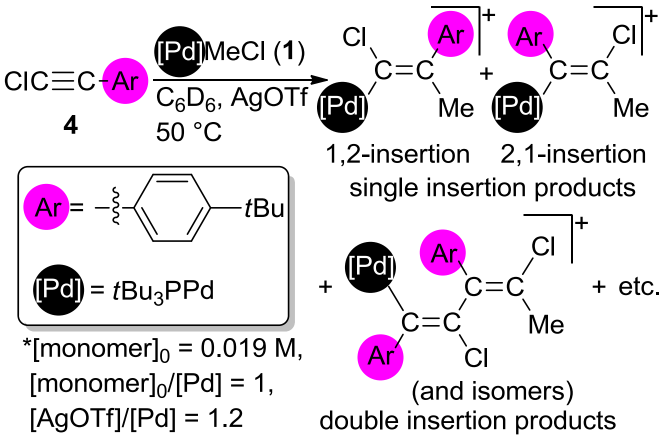


[a] Averages of the values for the carbon atoms, except for the terminal units, whose main chain carbon atoms are substituted with hydrogen atoms.

Figure 7 shows the ^{13}C NMR spectra of the polymers obtained by the polymerizations using (tBu$_3$P)PdMeCl/AgOTf and MoCl$_5$/SnBu$_4$ catalysts. The signals of the Pd-based polymer were sharp compared with those of the Mo-based polymer because of the lower molecular weight. In both cases, signals *b* and *c* assignable to carbon atoms of the main chain appeared broad compared with signals *a*, *d*, *e* and *f* assignable to the carbon atoms of phenyl ring (Chart 1), presumably due to the higher stiffness of the conjugated polyacetylene backbone. The NMR spectroscopic assignment was supported by the DFT calculations using the gauge independent atomic orbital (GIAO) method.[19] The calculation procedures were the same as those described for the calculation of the Raman spectrum. Chart 1 summarizes the average chemical shifts of the main chain and phenyl carbon atoms predicted by the GIAO method. The main chain carbon signals of the *cis*-hexamer were predicted to appear at a higher chemical shift region than the corresponding signals of the *trans*-hexamer by 2.2–2.5 ppm, in a fashion similar to (*Z*) and (*E*)–CH=CH– signals.[20] It should be noted that the signals assignable to the main chain carbon atoms of the Pd- and Mo-based polymers appeared differently in the ^{13}C NMR spectra shown in Figure 7, i.e., the centers of signals *b* and *c* of Pd-based polymer appeared at a higher chemical shifts compared to those of the Mo-based polymer. Judging from the trend of the chemical shifts of the main chain carbon atoms predicted by the DFT calculations, it is concluded that the cis content of the Pd-based polymer is higher than that of the Mo-counterpart. No apparent difference in the chemical shifts of the Pd- and Mo-based polymers was observed for signals other than those corresponding to the main chain carbons. It appears that the geometric difference of the main chain does not affect the chemical shifts of the *tert*-butylphenyl substituents.

Rh catalysts efficiently polymerize monosubstituted acetylenes to give the corresponding polymers featuring a high *cis*- double bond content, which is associated with the coordination-insertion mechanism.[4a–c,5a,5b,21] A large body of evidence demonstrates that Pd catalysts also yield *cis*-stereoregulated monosubstituted acetylene polymers through the coordination-insertion mechanism.[22] Together with the background for the polymerization of monosubstituted acetylenes by Pd and Rh catalysts, the high *cis*-content of poly(**4**)-**1** suggests that the Pd catalysts in the present work follow the coordination-insertion mechanism, in contrast to the metathesis mechanism featured representatively by Mo catalysts.[4a,5b] We attempted to give further support to this proposal by analyzing a mixture of a stoichiometric reaction between **4** and **1**/AgOTf using mass spectrometry, as well as ^{31}P and ^{1}H NMR spectroscopies (Scheme 4).

Scheme 4. Stoichiometric reaction between **1**/AgOTf and **4** (1:1). The counteranion (OTf^{-}) was omitted for clarity.



The ^{1}H and ^{31}P NMR spectra of the reaction mixture were measured at *t* = 25 min, 40 min and 12 h (Figures 8, 9 and 10). During the initial 40 min of the reaction, only a small amount of products was formed, as indicated by the appearance of small singlets at 2.57 and 2.17 ppm in the ^{1}H NMR, which potentially correspond to =CMe species formed from the insertion of a monomer into the Pd–Me bond (Scheme 4). New signals assignable to tBu$_3$P and tBu-p-C$_6$H$_4$ appeared between 1.19–1.26 ppm and 0.93–1.05 ppm after 25 min, and the intensities increased slightly after 40 min in the ^{1}H NMR spectra. After 12 h at 50 °C, the monomer was quantitatively consumed as indicated by the disappearance of an aromatic proton signal assignable to the unreacted monomer at 7.29 ppm, and concomitant appearance of new aromatic proton signals at 7.36,

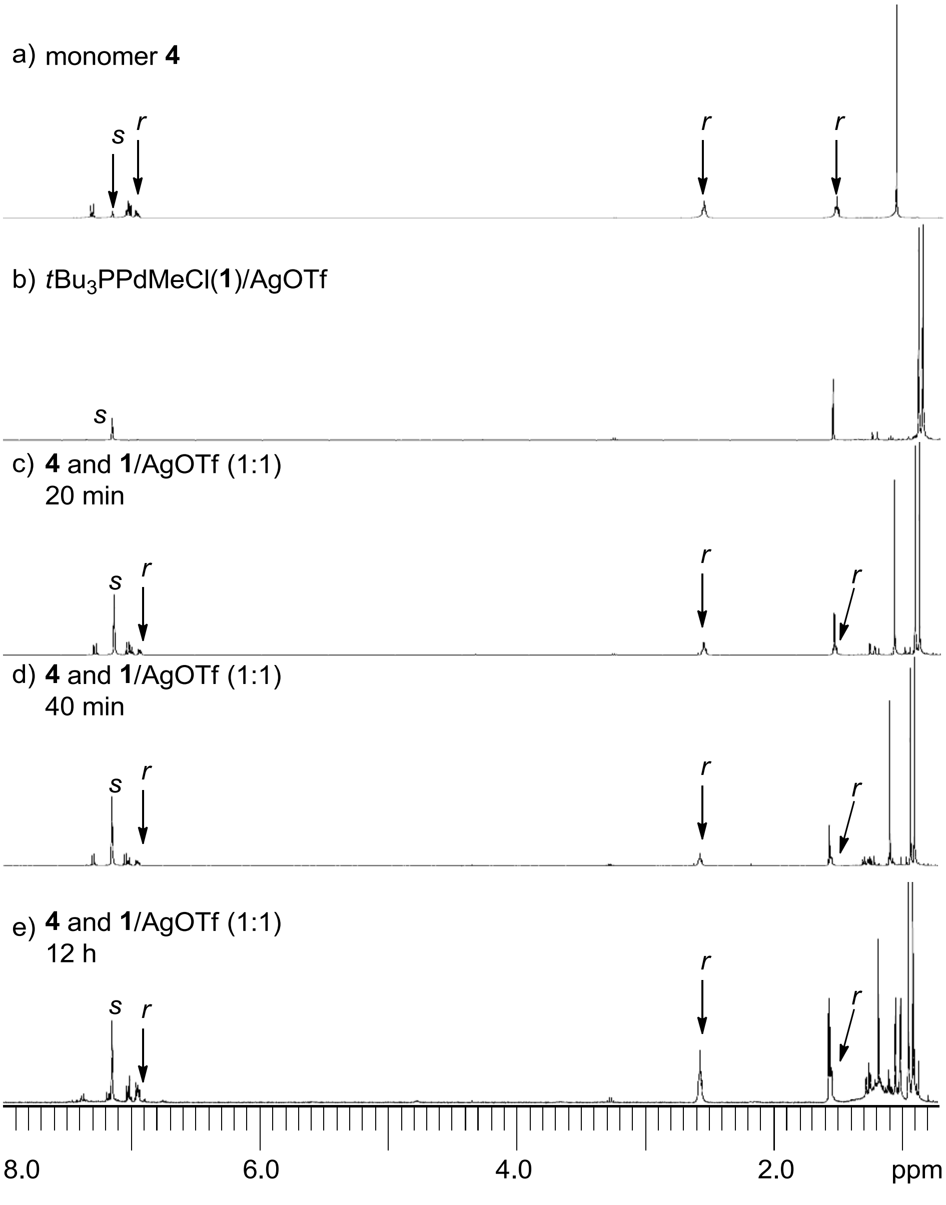


Figure 8. ^{1}H NMR spectra of: a) monomer **4** and 1,2,3,4-tetrahydronaphthalene (*r*); b) **1**/AgOTf; c) **1**/AgOTf and **4** (1:1) after 20 min of reaction; d) **1**/AgOTf and **4** (1:1) after 40 min of reaction; e) **1**/AgOTf and **4** (1:1) after 12 h of reaction. Detailed reaction conditions are described in Scheme 4 and the experimental section. The spectra were measured at 50°C in C_6D_6 (*s*: solvent).

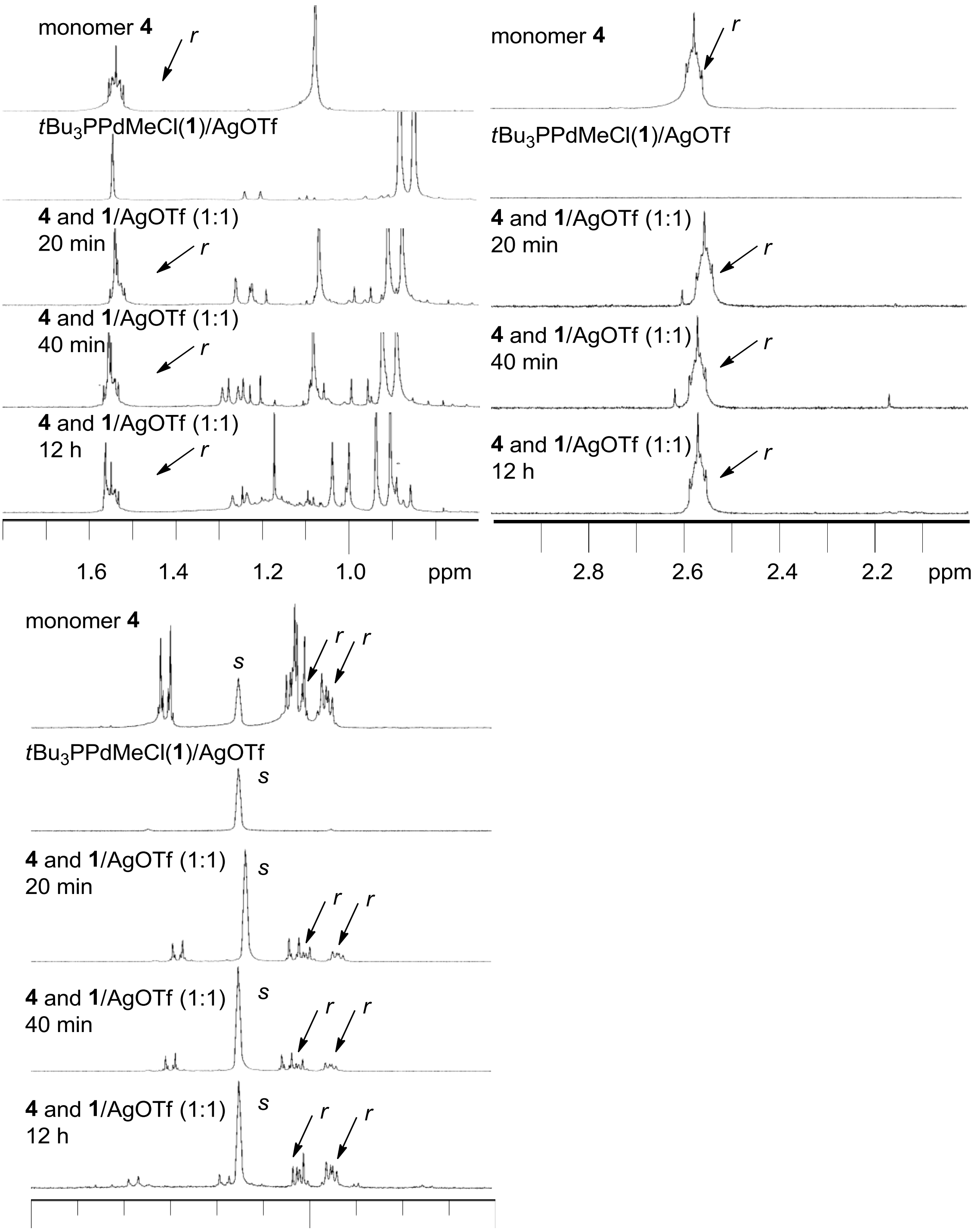


Figure 9. Expansion of key regions in the ^{1}H NMR spectra shown in Figure 8. Detailed reaction conditions are displayed in Scheme 4 and the experimental section. The spectra were measured at 50°C in C_6D_6 (*s*: solvent; *r*: 1,2,3,4-tetrahydronaphthalene).

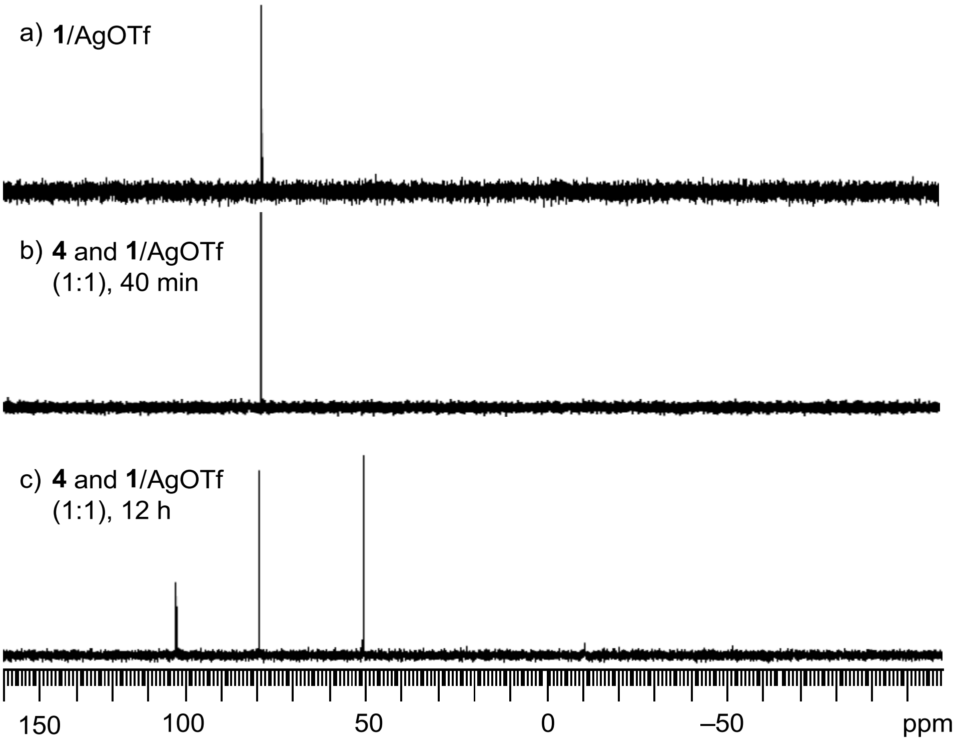


Figure 10. ^{31}P NMR spectra of: a) **1**/AgOTf, b) **1**/AgOTf and **4** (1:1) after 40 min of reaction; c) **1**/AgOTf and **4** (1:1) after 12 h of reaction. Detailed reaction conditions are described in Scheme 4 and the experimental section. The spectra were measured at 50 °C in C_6D_6.

7.19, 6.90 and 6.75 ppm (Figure 9). In addition, the =CMe signals at 2.15 ppm broadened and the number of signals for *t*Bu$_3$P and *t*Bu-*p*-C_6H_4 further increased (Figure 9). The ^{31}P NMR spectra of the stoichiometric reaction between **4** and **1**/AgOTf indicated that after 40 minutes of reaction almost all the starting Pd complex remained unreacted. After 12 h of reaction still some starting Pd catalyst **1**/AgOTf remained unreacted, but it was also possible to observe the formation of at least two new species containing phosphorous compounds. Precise assignment of the signals to certain structures was not possible.

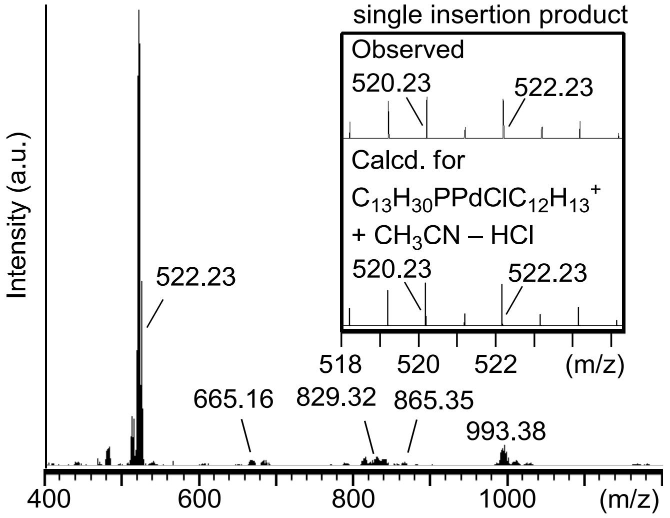


Figure 11. ESI-mass spectrum of a mixture of **1**/AgOTf and **4** (1:1). Inset: expanded experimental and calculated isotope patterns of a peak.

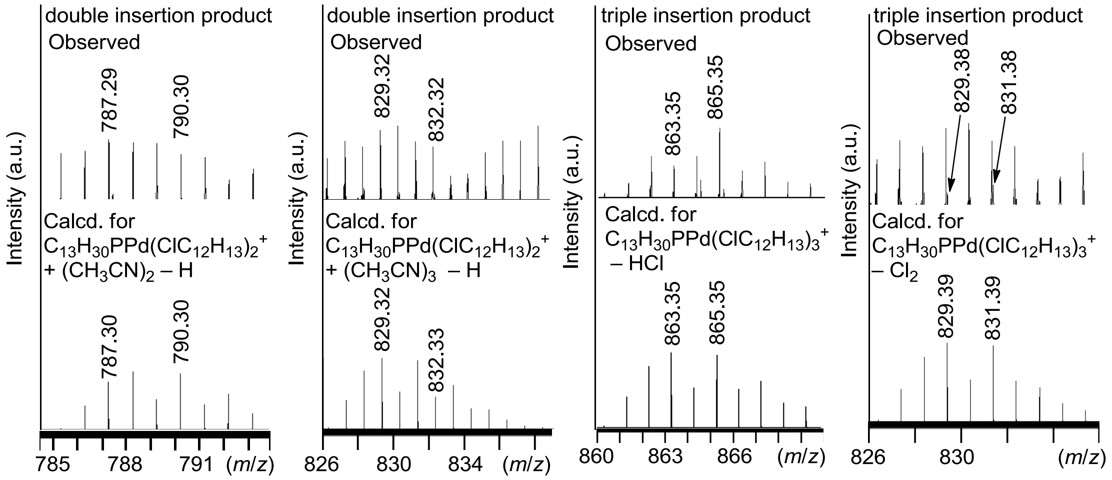


Figure 12. Amplification for some of the observed and calculated signals in the ESI-mass spectrum of a mixture of **1**/AgOTf and **4** (1:1) (Figure 11).

The final reaction mixture was analyzed by ESI-mass spectrometry as shown in Figures 11 and 12. We could observe signals corresponding to the products of single, double and triple insertion of monomer **4** into the Pd–Me bond of **1** as supported by comparison of the observed and calculated isotope patterns (Figure 12).[23] The low intensity of some signals made it difficult to match perfectly the height of the observed and calculated isotope patterns, but the remarkable agreement of the *m*/*z* values between the calculated and observed patterns together with the number of observed signals supported the above mentioned assignment. Therefore, the identification of the species in the mass spectrometry strongly supports the coordination-insertion mechanism featured by the Pd catalytic system **1**/AgOTf in the polymerization of disubstituted acetylene **4**. It is reasonable to conclude that the structure difference between the Pd- and Mo-based polymers arise from the different mechanisms in agreement with theoretical studies.[21]

Conclusion

In summary, we have presented the polymerization of a disubstituted acetylene **4** by Pd catalytic system **1**/AgOTf for the first time. The Pd-based disubstituted polyacetylenes featured *cis*-double bond content higher than the conventional Mo-based polymer according to the ^{13}C NMR and Raman spectroscopies. The stoichiometric reaction between **4** and **1**/AgOTf strongly supported the coordination-insertion mechanism for the polymerization. The Pd catalysts represent a key tool to understand the structure-property relation of disubstituted polyacetylenes. Even though the present research is limited to the polymerization of **4**, we are confident that bulky monophosphine-based Pd catalysts can be utilized for the polymerization of other disubstituted acetylenes, including monomers bearing polar groups, thereby expanding and simplifying the synthesis of a wide variety of disubstituted polyacetylenes. Moreover, due to the versatility of the Pd catalysts for the synthesis of many other polymers, we can foresee the combination of our method with already existing synthetic methodologies to yield new classes of materials. Research for the polymerization of other disubstituted monomers is ongoing.

Experimental Sections

Synthesis and Instrumentation: All air and moisture sensitive manipulations were performed under argon using standard Schlenk techniques. X-ray crystallographic analyses were recorded on a Rigaku Saturn with crystals obtained from CH_2Cl_2/pentane. ^1H NMR (400 MHz) and ^{13}C NMR spectra (100 MHz) were recorded on a JEOL EX-400 or an AL-400 spectrometer. Chemical shifts were referenced to $CHDCl_2$ (δ = 5.32 ppm), $CHCl_3$ (δ = 7.26 ppm), or C_6HD_5 (δ = 7.16 ppm) as an internal standard. ^{31}P NMR spectra (162 MHz) were recorded on a JEOL ECX-400 or an EX-400 spectrometer with $P(OMe)_3$ as an external standard (δ = 140 ppm). IR spectra were measured on a JASCO FT/IR-4100 spectrophotometer using the KBr method. Elemental analysis was performed at the Microanalytical Center of Kyoto University. High-resolution mass spectra were obtained with a JEOL JMS-MS700 (EI) or a

Thermo Fisher SCIENTIFIC EXACTIVE (ESI, APCI) spectrometer. The weight-average molecular weights (M_w) and the polydispersity indices (PDI) of the polymers were determined on a JASCO system equipped with Shodex columns KF805×3 (molecular weight limit $\approx 4\times10^6$, eluted with THF) at 40 °C by using polystyrene standards for calibration purposes. Laser Raman spectra were measured on a JASCO NRS-5100 spectrophotometer.

Materials: Unless otherwise stated, the reagents were used as received from commercial suppliers (Aldrich and Wako). $HC{\equiv}CC_6H_4$-*p*-*t*Bu was used as received from Aldrich. Phosphines 2-di-*tert*-butylphosphino-2′,4′,6′-tri-isopropylbiphenyl (*t*BuXPhos) and di-1-adamantyl-*n*-butylphosphine (cataCXium A) were received from Nippon Chemical Industrial and used without further purification. The solvents employed for the air and moisture sensitive procedures were purified using standard procedures. [(cod)PdMeCl] (cod = 1,5-cyclooctadiene) was synthesized according to the literature procedure.[24]

Synthesis of Monomer

1-Chloro-2-(substituted)phenylacetylene (**4**) employed for the polymerization was synthesized by a modified literature method.[16a] The detailed procedure is as follows. $HC{\equiv}CC_6H_4$-*p*-*t*Bu (5.4 mL, 30 mmol), potassium carbonate (4.1 g, 30 mmol) and CCl_4 (30 mL) were fed into a flask equipped with a three-way stopcock after flushing with nitrogen gas. Then, a solution of tetra-*n*-butylammonium fluoride in THF (1.0 mol/L, 1.6 mL, 1.6 mmol) was added to the mixture. After stirring the resulting mixture at 45 °C overnight, MeOH (5 mL) and $CHCl_3$ (40 mL) were added to the mixture. The resulting solution was washed with 1 M hydrochloric acid (2 × 50 mL) and then with water (50 mL). The organic phase was dried with anhydrous magnesium sulfate and the solvent was evaporated. The crude product was purified by preparative HPLC to yield the desired product (2.5 g, 55%) as a light yellow crystalline solid. Yield = 54%. ^{1}H NMR ($CDCl_3$, 25 °C, TMS): δ 1.31 (s, 9H; CH_3), 7.31–7.39 (m, 4H; Ar). ^{13}C NMR ($CDCl_3$, 25 °C, TMS): δ 31.2, 34.8, 67.1, 69.5, 119.1, 125.3, 131.6, 151.8; HR-MS (ESI): *m/z* calcd for $C_{12}H_{13}Cl$: 192.0706 [*M*]; found 192.0714; elemental analysis calcd (%) for $C_{12}H_{13}Cl$: C, 74.80; H, 6.80; Cl, 18.40; found: C, 74.53; H, 6.77; Cl, 18.16.

Synthesis of Pd Catalysts

Complexes **2** and **3** were synthesized by a modified literature method.[9] The details are as follows. [(cod)PdMeCl] (49.8 mg, 0.19 mmol) and phosphine (79.8 mg for *t*BuXPhos and 67.4 mg for cataCXium A, 0.19 mmol) were placed in a Schlenk flask under Ar inert atmosphere. Then, toluene (2 mL) was added to the mixture at room temperature and the reaction mixture was left at 45 °C overnight. The reaction mixture was filtrated through a PTFE filter to a Schlenk tube with pentane (8 mL) to precipitate the desired product. Finally, pure solid product was isolated after filtrating and washing the solid with pentane.

(2-Di-*tert*-butylphosphino-2′,4′,6′-triisopropylbiphenyl)PdMeCl (2). Yield: 43%. ^{1}H NMR (C_6D_6, 25 °C, 396 MHz): δ 0.95 (d, J = 6.7 Hz, 6H; ^{i}Pr), 1.21 (d, J = 13.5 Hz, 18H; ^{t}Bu), 1.61 (d, J = 7.1 Hz, 6H; ^{i}Pr), 1.68 (d, J = 6.7 Hz, 6H; ^{i}Pr), 1.88 (d, J = 2.7 Hz, 3H; Pd*Me*), 2.55 (m, 2H; C*H*$(CH_3)_2$ of ^{i}Pr), 3.23 (m, 1H; C*H*$(CH_3)_2$ of ^{i}Pr), 6.26 (m, 1H; Ar), 6.88 (m, 2H; Ar), 7.34 (s, 2H; Ar), 7.57 (m, 1H; Ar). ^{31}P{^{1}H} NMR (C_6D_6, 25°C, 160 MHz): δ 58.18; HRMS (ESI): *m/z* calcd for $C_{30}H_{48}PPd^+$: 545.2523 [*M*–Cl]$^+$; found 545.2533.

{[Di(1-adamantyl)-*n*-butylphosphine]PdMeCl}$_2$ (3). Yield: 47%. ^{1}H NMR ($CDCl_3$, 50 °C, 396 MHz): δ 0.77–0.88 (br, 8H), 1.20–1.32 (br, 4H), 1.61–1.74 (br, 12H), 1.91 (br, 6H), 2.24 (br, 12H). ^{31}P{^{1}H} NMR ($CDCl_3$, 50 °C, 160 MHz): δ 58.03; HRMS (ESI): *m/z* calcd for $C_{27}H_{45}PPdN^+$: 520.2319 [(*M*–Cl)+CH_3CN]$^+$; found 520.2325.

Polymerization

Monomer **4** was polymerized in a Schlenk tube equipped with a three-way stopcock employing standard Schlenk techniques. Unless otherwise specified, the polymerization was performed in toluene at 80 °C for 24h under the following conditions: $[\text{monomer}]_0$ = 2.0 M, $[\text{monomer}]_0/[\text{Pd}]$ = 50. A typical polymerization procedure is as follows. Monomer **4** (46.1 mg, 0.24 mmol) was fed into a Schlenk tube, and toluene (50 μL) was added to the monomer. In another Schlenk tube, a catalyst solution ([Pd] = 0.069 M) was prepared by stirring 1.0 equivalent of (phosphine)PdMeCl with 1.2 equivalents of silver trifluoromethanesulfonate (AgOTf) in toluene at 50 °C. After 30 min the catalyst solution was filtrated and a portion of the catalyst solution (70 μL) was added to the monomer solution. After stirring at 80 °C for 24h, the reaction mixture was poured into a large volume of MeOH to precipitate a solid polymer, which was filtered and dried under vacuum.

Stoichiometric Reaction

The stoichiometric reaction between **4** and **1**/AgOTf was performed as follows.* A solution of monomer **4** (9.4 mg, 48.6 μmol) and 1,2,3,4-tetrahydronaphthalene (6.6 μL, 0.049 mmol) in C_6D_6 (5 mL) was prepared. In a separate tube under Ar atmosphere, a solution of *t*Bu_3PPdMeCl (10.5 mg, 29.2 μmol) and AgOTf (9.0 mg, 35.0 μmol) in C_6D_6 (1.5 mL) was stirred at 50 °C for 30 min in an NMR sample tube. Then, 0.5 mL of the catalyst solution was added to 1 mL of the monomer solution, which was fed into an NMR tube under Ar atmosphere at –78 °C. The reaction was monitored by NMR spectroscopy just after the reaction was initiated and after stirring at 50 °C overnight. The sample was finally analyzed by mass spectrometry.

*1,2,3,4-Tetrahydronaphthelene was added to the reaction mixture as an internal standard ($[\text{monomer}]_0/[\text{standard}] = 1.0$) for the NMR measurements after drying over molecular sieves 3Å and freeze-pump-thaw degasification.

Computation

The DFT[25] calculations were performed with the GAUSSIAN 09 program,[26] EM64L-G09 Rev C.01 running on the supercomputer system at the Academic Center for Computing and Media Studies, Kyoto University.

Crystal Structures of 2 and 3

The X-ray diffraction experiments on both crystals **2** and **3** were carried out at 293.1 K on a Rigaku/Saturn70 CCD diffractometer using graphite-monochromated Mo-K□radiation (λ = 0.71070 Å) and processed using CrystalClear (Rigaku).[27] The crystal structures were solved by a direct method (SIR92 for **2** and SHELXS97 for **3**) and refined by full-matrix least-square refinement on F^2. The non-hydrogen atoms, except disordered atoms and solvated molecules, were refined anisotropically. All hydrogen atoms were located at the calculated positions and not refined. All calculations were performed using the CrystalStructure software package.[28] The results are presented in Table 3.

Table 3. X-ray crystallographic information for **2** and **3**

Compound	**2**	**3**
Colour, habit	Colorless prism	Colorless prism
Size/mm	0.20×0.20×0.20	0.20×0.20×0.20
Empirical formula	$C_{30}H_{48}ClPPd$	$(C_{25}H_{42}ClPPd)_2$
M	581.56	515.42 × 2
Crystal System	Tetragonal	Triclinic
Space group	$P\ 4_2/n$	P -1
a/Å	23.1123(4)	12.9304(12)
b/Å	23.1123(4)	15.4413(14)
c/Å	10.9451(3)	16.2376(16)
α/°	90.0000	87.520(4)
β/°	90.0000	87.956(4)
γ/°	90.0000	68.280(5)
$V/Å^3$	5846.6(2)	3008.4(5)
Z	8	2
μ/mm^{-1}	0.788	0.401
T/K	293.1	293.1
θ_{max}	27.47	27.49
Reflections: measured/independent	42742/6658	24056/13214
R_{int}	0.034	0.027
Final *R*1 and *wR*2	0.0406/0.1193	0.0581/0.1761
Largest peak, hole/e $Å^{-3}$	1.61, –0.59	3.19, –2.74
$\rho_{calcd}/g\ cm^{-3}$	1.144	0.738

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Chapter 4

Synthesis of Poly(1-chloro-2-arylacetylene)s with High cis-Content and Examination of Their Properties

Abstract

A series of 1-chloro-2-arylacetylenes [aryl = C_6H_5 (**1**), C_6H_4-*p*-*i*Pr (**2**), C_6H_4-*p*-O*i*Pr (**3**), C_6H_4-*p*-NHC(O)O*t*Bu (**4**) and C_6H_4-*o*-*i*Pr (**5**)] were polymerized using *t*Bu_3PPdMeCl (**6**)/silver trifluoromethanesulfonate (AgOTf) and $MoCl_5$ (**7**)/$SnBu_4$ catalysts. The corresponding polymers [poly(**1**)–poly(**6**)] with weight-average molecular weights of 5600–69000 were obtained in 10–91% yields. THF-insoluble parts, presumably high-molecular weight polymers, were formed together with THF-soluble polymers in the case of Pd-catalyzed polymerizations. Pd catalyst **6** polymerized nonpolar monomers **1** and **2** to give the polymers in yields lower than Mo catalyst **7**, while polymerized polar monomers **3** and **4** to give the corresponding polymers in higher yields. The ^{1}H NMR and UV-vis absorption spectra of the polymers indicated that the

cis-contents of Pd-based polymers were higher than those of Mo-based polymers, and the conjugation length of the Pd-based polymers was shorter than that of the Mo-based polymers. Poly(**5**)-Pd emitted the strongest fluorescence among poly(**1**)–poly(**5**).

Introduction

Polyacetylenes are a family of macromolecules that triggered intense research in the area of conjugated polymers after discovery of high conductivity in doped-polyacetylene films.[1] The most stable members of polyacetylene family are disubstituted acetylene derived polymers and therefore these polymers are the most suitable for industrial applications.[2] In addition to high stability, disubstituted acetylene polymers display other outstanding properties such as selective gas permeability, stimuli responsiveness, helix formation, electroluminescence (EL) and photoluminescence (PL).[3]

Numerous studies have been performed regarding PL of substituted polyacetylenes to constitute a base of knowledge that allow us to synthesize acetylene polymers featuring high emission efficiencies.[4,5] Monosubstituted acetylene polymers emit weak PL, while disubstituted acetylene polymers such as poly[(alkyl)C≡CAr] and poly[Ar'C≡CAr] emit intense blue–green PL.[4,5c] There are also various reports concerning the effect of alkyl chain length, bulkiness and electronic properties of substituents on the emission properties of the acetylene polymers.[4] The PL efficiency can also be further enhanced by introducing emissive groups such as silole, biaryl, and carbazolyl to the side chains of the sustituted polyacetylenes.[3,6] In spite of the great amount of research regarding the relationship between polymer structures and PL/EL properties of disubstituted acetylene polymers, there is no systematic study presenting the effect of geometry (variation of cis/trans content) of the main chain on the polymer properties, because disubstituted acetylene polymers were only synthesized by the early transition metal catalysts, wherein the stereoregularity is uncontrollable due to no cis/trans selectivity of the metathesis reaction.

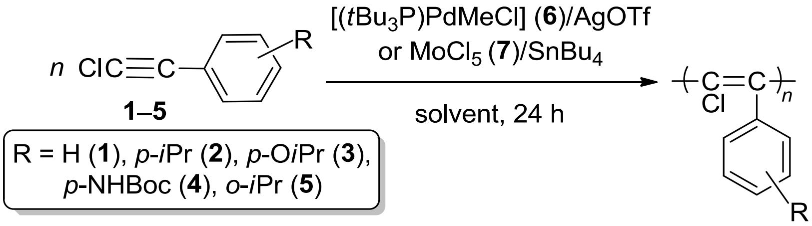
Recently, we presented a series of bulky monophosphine-ligated Pd catalysts that can polymerize 1-chloro-2-(4-*tert*-butyl)phenylacetylene to yield a polymer with a higher cis-content than that of the analogue polymer synthesized by a Mo catalyst.[7] No cis-stereoregulated disubstituted acetylene polymers had been synthesized previous to our study. Consequently, there was no paper analyzing the effect of the stereoregularity of disubstituted acetylene polymers on the properties. In this chapter, the author discloses the polymerization of 1-chloro-2-arylacetylenes [aryl = C_6H_5 (**1**), *p*-*i*PrC_6H_4 (**2**), *p*-O*i*PrC_6H_4 (**3**), *p*-NHC(O)O*t*BuC_6H_4 (**4**) and *o*-*i*PrC_6H_4 (**5**)] by employing (*t*Bu_3P)PdMeCl (**6**)/AgOTf and $MoCl_5$ (**7**)/$SnBu_4$ catalytic systems, and the influence of cis/trans contents on the properties of the polymers formed. The results for the polymerization of monomers **1**–**5** also serve to clarify the activity difference between the Pd catalyst **6** and Mo catalyst **7** towards substituents in the disubstituted acetylene monomers.

Results and Discussion

We explored the polymerization of 1-chloro-2-arylacetylenes [aryl =

C_6H_5 (**1**), C_6H_4-*p*-*i*Pr (**2**), C_6H_4-*p*-O*i*Pr (**3**), C_6H_4-*p*-NHC(O)O*t*Bu (**4**) and C_6H_4-*o*-*i*Pr (**5**)] employing two type of catalytic systems, $t\mathrm{Bu}_3\mathrm{PdMeCl}$ (**6**)/silver trifluoromethanesulfonate (AgOTf)[7] and MoCl_5 (**7**)/SnBu_4[3f,8] under the conditions shown in Scheme 1.

Scheme 1. Polymerization of 1-chloro-2-arylacetylenes (**1**–**5**) by [($t\mathrm{Bu}_3\mathrm{P}$)PdMeCl/AgOTf (**6**) and $\mathrm{MoCl}_5/\mathrm{SnBu}_4$ (**7**).



As summarized in Table 1, Pd catalyst **6** polymerized monomer **1** to yield a polymer [poly(**1**)-Pd] featuring a M_w of 5600 (entry 1) in 30% while Mo catalyst **7** yielded a polymer [poly(**1**)-Mo] featuring an M_w of 690000 in 91% (entry 2).[8d] Both the yield and M_w of poly(**1**)-Pd were lower than those of poly(**1**)-Mo. A similar trend was observed in the polymerization of monomer **2** bearing a *para*-isopropyl substituent (entries 3 and 4). On the other hand, Pd catalyst **6** polymerized monomer **3** bearing a *para*-isopropoxy substituent to give poly(**3**) with a higher M_w in a higher yield than Mo catalyst **7** (entries 5 and 6). The PDI of poly(**3**)-Pd was small (1.58), while that of poly(**3**)-Mo was large (3.13), indicating that the polymerization using the Pd catalyst proceeded in a more controlled manner. The low yield poly(**3**)-Mo is attributable to the

Table 1. Polymerization of **1**–**5** by [(tBu$_3$P)PdMeCl] (**6**)/AgOTf or MoCl$_5$ (**7**)/SnBu$_4$[a]

entry	monomer	catalyst[b]	yield,[c] %	content of insoluble fraction,[d] %	M_w[e]	PDI[e]
1	**1**	Pd	30	22	6500	1.62
2[f]	**1**	Mo	91	0	690000	–
3	**2**	Pd	31	18	20600	2.11
4	**2**	Mo	74	0	90500	2.31
5	**3**	Pd	34	24	42700	1.58
6	**3**	Mo	26	0	34500	3.13
7[g]	**4**	Pd	21	16	9100	1.91
8[g]	**4**	Mo	–	–	–	–
9	**5**	Pd	77	49	18300	1.99
10	**5**	Mo	10	0	13600	1.62

[a] Pd-catalyzed: [monomer]$_0$ = 2.0 M, [monomer]$_0$/[Pd] = 50, [AgOTf]/[Pd] = 1.2; Mo-catalyzed: [monomer]$_0$ = 1.0 M, [monomer]$_0$/[Mo] = 50, [Mo]/[Sn] = 1.0. [b] Catalyst, Pd: **6**/AgOTf and Mo: **7**/SnBu$_4$. [c] MeOH-insoluble part. For the Pd-synthesized polymers further purification was done by reprecipitation from a MeOH/Et$_2$O mixture (40/20). [d] Insoluble part in common organic solvents: THF, CHCl$_3$, CH$_2$Cl$_2$, benzene, toluene, MeOH, etc. [e] Estimated by SEC of the THF-soluble part, THF as eluent (calibrated by polystyrene standards). The quantities in parentheses are area ratios of the reported peaks, the rest corresponded to lower M_w products. [f] Data taken from reference 8d. [g] Polymerization was performed in CHCl$_3$ at 60 °C for 24 h using the next conditions for both catalysts: [monomer]$_0$ = 0.8 M, [monomer]$_0$/[cat] = 50, [cocatalyst]/[cat] = 1.2.

presence of the ether oxygen in **3**, which possibly coordinates to Mo resulting in decrease of catalytic activity. The yield of poly(**3**)-Pd was not low compared with those of poly(**1**)-Pd and poly(**2**)-Pd presumably due to the low oxophilicty of Pd compared with Mo. The difference of sensitivity between the Pd and Mo catalysts towards polar groups was clearly evidenced by the polymerization of polar monomer **4** bearing a *para*-carbamate substituent. Pd catalyst **6** polymerized monomer **4** to give a polymer (M_w = 6000) in 21% yield (entry 7). In contrast, Mo catalyst **7** gave no polymer from monomer **4**, and the monomer was quantitatively recovered from the reaction mixture after evaporating the solvent (entry 8), indicating the higher oxophilicity of Mo than that of Pd.

Next, we examined the polymerization of the *ortho*-isopropyl substituted monomer **5**. Pd catalyst **6** polymerized monomer **5** to give poly(**5**) in a good yield (77%, entry 9), while Mo catalyst **7** gave poly(**5**) in a lower yield (10%, entry 10). It has been reported that Mo catalysts perform poorly the polymerization of steric hindered monomers[3f] and most probably the *ortho*-isopropyl substituent in **5** is sterically hampering the activity of the Mo catalyst **7**. The Pd catalyst **6** can perform better in the polymerization of the steric hindered monomer **5** probably because it has plenty of room around its coordination sphere due to its T-shape structure coordinated only by three ligands which is in contrast to the usual crowded four-coordinated structure of other common Pd catalysts.[7]

We compared the difference of the properties between the polymers synthesized by the polymerization using the Pd and Mo catalysts. The Pd-based polymers were partly (16–49%) insoluble in common organic solvents (THF, $CHCl_3$, CH_2Cl_2, benzene, toluene, MeOH) as listed in Table 1. It is likely that the THF-insoluble fractions are high molecular weight polymers featuring high cis-contents formed by the polymerization via the coordination-insertion mechanism in a manner similar to Rh-catalyzed polymerization of monosubstituted acetylenes,[7] as well as reports suggesting low solubility of substituted cis-cisoidal polyacetylenes.[3d,9] In fact, both the THF-soluble and insoluble parts exhibited similar IR spectra. Morokuma and coworkers have reported the formation of cis-stereoregulated substituted polyacetylenes by the coordination-insertion mechanism.[10] On the other hand, the Mo-based polymers were completely soluble in THF, presumably due to the low stereoregularity of the main chain originated during the polymerization via the metathesis mechanism.[3a,3b,3d,8d]

The difference of structures between the polymers synthesized by Mo and Pd catalysts was also suggested by ^{1}H NMR spectroscopy, in particular at the region of the aromatic protons. For instance poly(**2**)-Pd displayed a signal around 6.64 ppm and a shoulder around 6.85 ppm, while poly(**2**)-Mo displayed two broad signals of almost the same intensity around 6.88 and 6.68 ppm (Figure 1). On the other hand, the chemical shift of the signal assignable to isopropyl group remained practically unaffected regardless of the catalyst employed. The shape of the aromatic proton signal was also dependent on the catalyst employed in the cases of poly(**3**) and poly(**5**), especially in the latter (Figures 2 and 3).

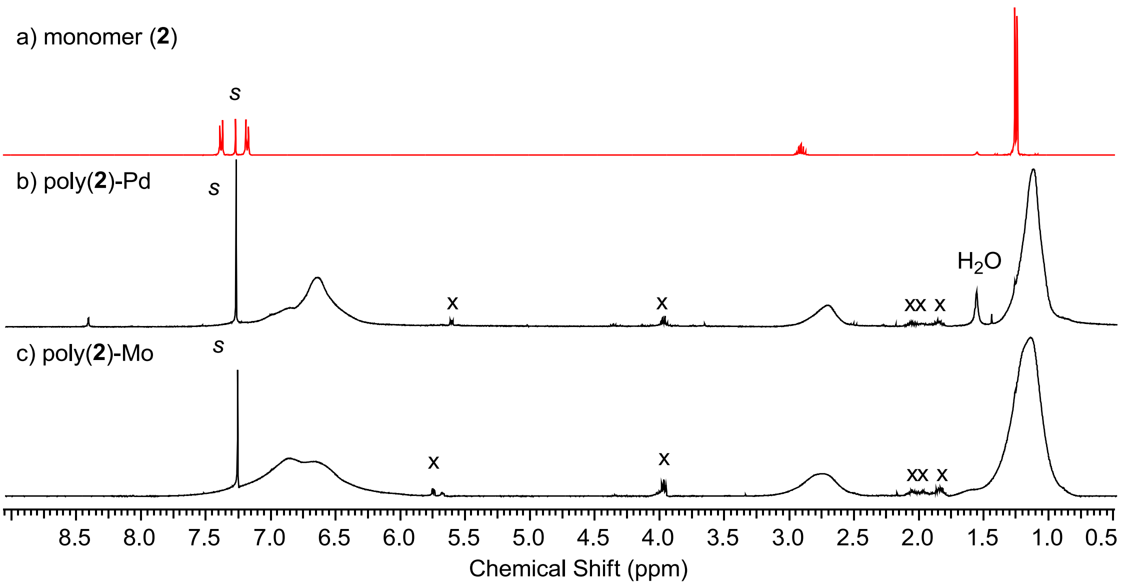


Figure 1. ^{1}H NMR spectra of: a) monomer **2**; b) poly(**2**) synthesized by the polymerization using *t*Bu$_3$PPdMeCl (**6**)/AgOTf (Table 1, entry 3) and, c) poly(**2**) synthesized using MoCl$_5$/SnBu$_4$ (Table 1, entry 4). All spectra were measured in CDCl$_3$ at room temperature (*s*: solvent, x: impurity).

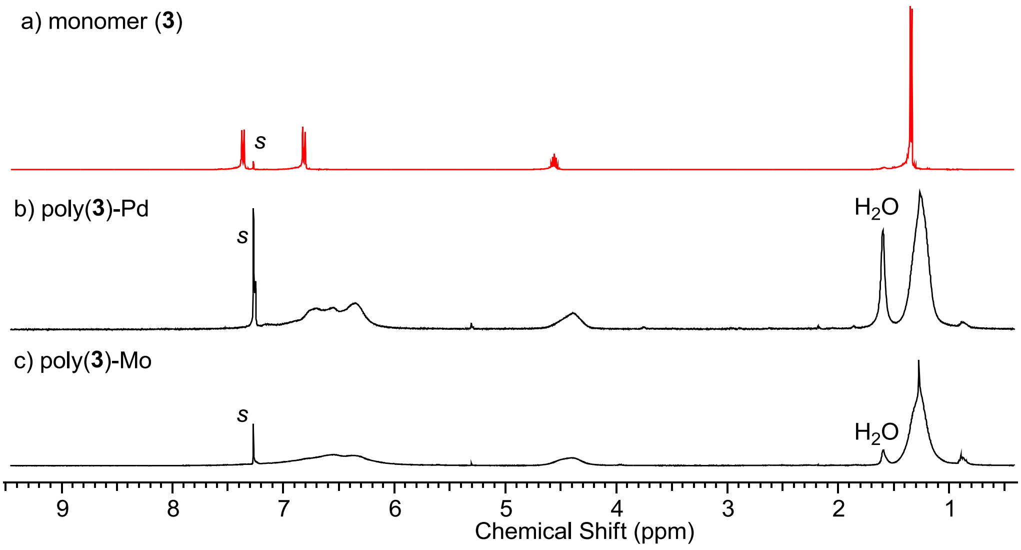


Figure 2. ^{1}H NMR spectra of: a) monomer **3**; b) poly(**3**) synthesized by the polymerization using *t*Bu$_3$PPdMeCl (**6**)/AgOTf (Table 1, entry 5) and, c) poly(**3**) synthesized using MoCl$_5$/SnBu$_4$ (Table 1, entry 6) measured in CDCl$_3$ at room temperature (*s*: solvent).

In the ^{13}C NMR spectra of poly(**2**) and poly(**3**), no C≡C carbon signals of the monomers but broad C=C carbon signals corresponding to the main chain were observed around 137–139 ppm. Unfortunately, no clear information was obtained regarding the stereoregularity of the polymers (Figures 4 and 5) due to the broadness of the main chain carbon signals in the ^{13}C NMR spectra of the polymers. No significant difference was observed in the signals of the aryl and isopropyl groups. Poor solubility of poly(**5**)-Pd prevented the ^{13}C NMR spectroscopic measurement.

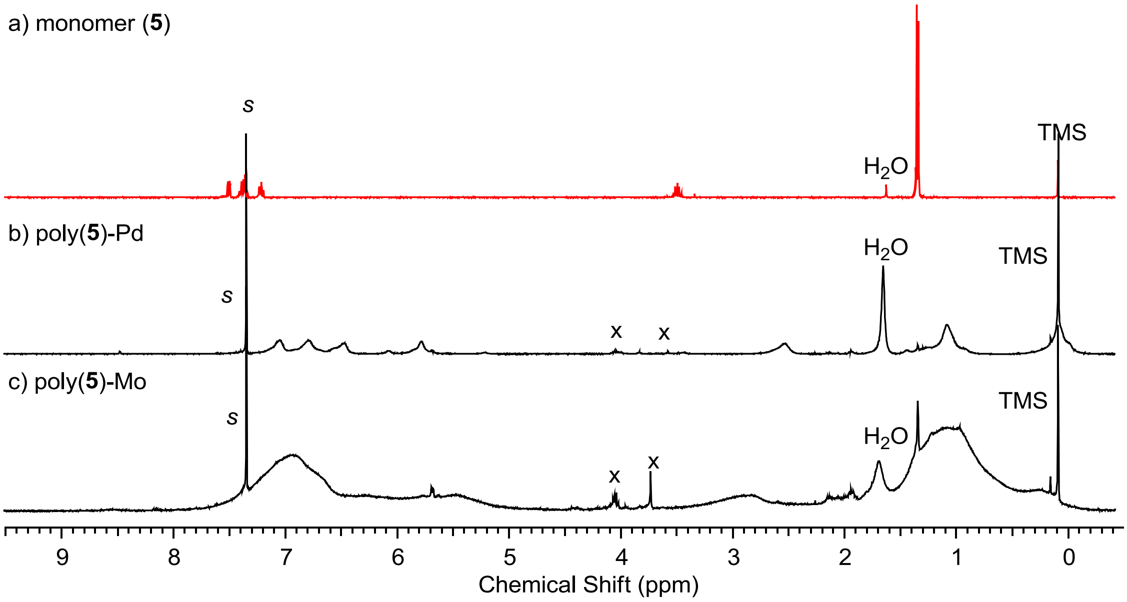


Figure 3. ^{1}H NMR spectra of: a) monomer **5**; b) poly(**5**) synthesized by the polymerization using *t*Bu$_3$PPdMeCl (**6**)/AgOTf (Table 1, entry 9) and, c) poly(**5**) synthesized by MoCl$_5$/SnBu$_4$ (Table 1, entry 10) measured in CDCl$_3$ at room temperature (*s*: solvent, x: impurity).

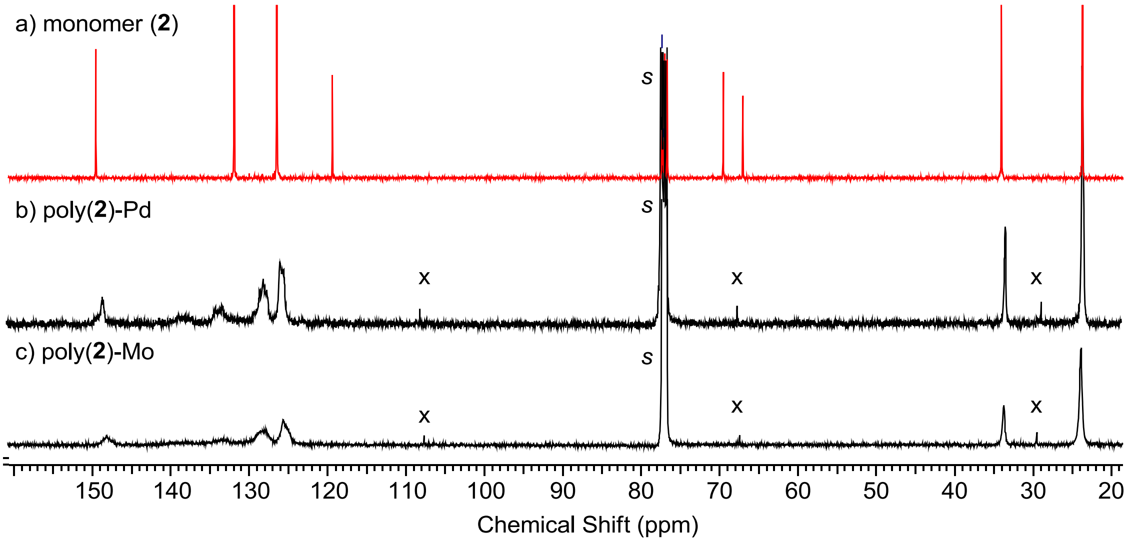


Figure 4. ^{13}C NMR spectra of: a) monomer **2**; b) poly(**2**) synthesized by the polymerization using *t*Bu$_3$PPdMeCl (**6**)/AgOTf (Table 1, entry 3) and, c) poly(**2**) synthesized using MoCl$_5$/SnBu$_4$ (Table 1, entry 4) measured in CDCl$_3$ at room temperature (*s*: solvent, *x*: impurity).

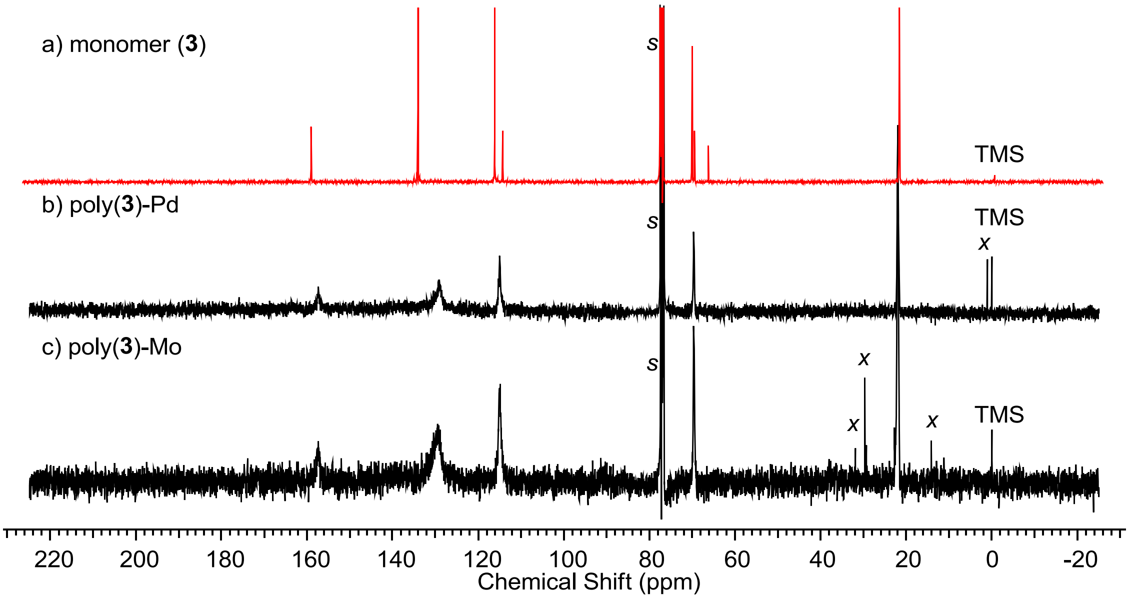


Figure 5. ^{13}C NMR spectra of: a) monomer **3**; b) poly(**3**) synthesized by the polymerization using *t*Bu$_3$PPdMeCl (**6**)/AgOTf (Table 1, entry 5) and, c) poly(**3**) synthesized by MoCl$_5$/SnBu$_4$ (Table 1, entry 6) measured in CDCl$_3$ at room temperature (*s*: solvent, *x*: impurity).

The IR spectra of the polymers also confirmed the complete consumption of the C≡C triple bond of the acetylene monomers; no signal characteristic for the carbon triple bond stretching band around 2221 cm^{-1} (Figures 6–8) was observed in the polymers IR. Intense C–Cl stretching absorption bands were observed around 750–835 suggesting no significant loss of Cl atom from the polymers.

Next, we analyzed the optical properties of the polymers to examine the difference arising from the catalysts used in the polymerization. The UV-vis spectroscopic analysis revealed the shorter absorption length of Pd-based poly(**2**), poly(**3**) and poly(**5**) than those of the corresponding Mo-based polymers (Figure 9). In particular, the $\lambda_{\max}$ of poly(**5**)-Pd (337 nm) was observed at a

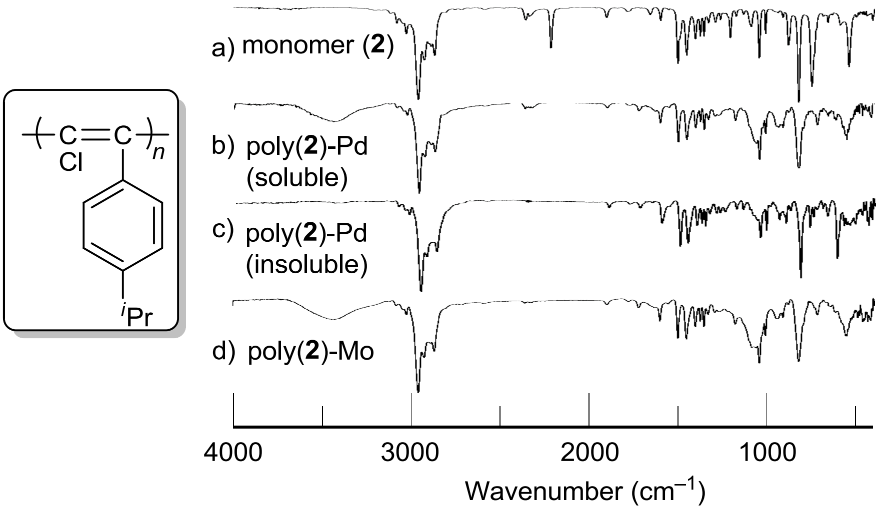


Figure 6. IR spectra of: a) monomer **2**; b) poly(**2**) synthesized by the polymerization using *t*Bu$_3$PPdMeCl (**6**)/AgOTf (Table 1, entry 3), c) insoluble fraction of poly(**2**) synthesized using *t*Bu$_3$PPdMeCl (**6**)/AgOTf (Table 1, entry 3) and, d) poly(**2**) synthesized using MoCl$_5$/SnBu$_4$ (Table 1, entry 4) measured by the KBr pellet method.

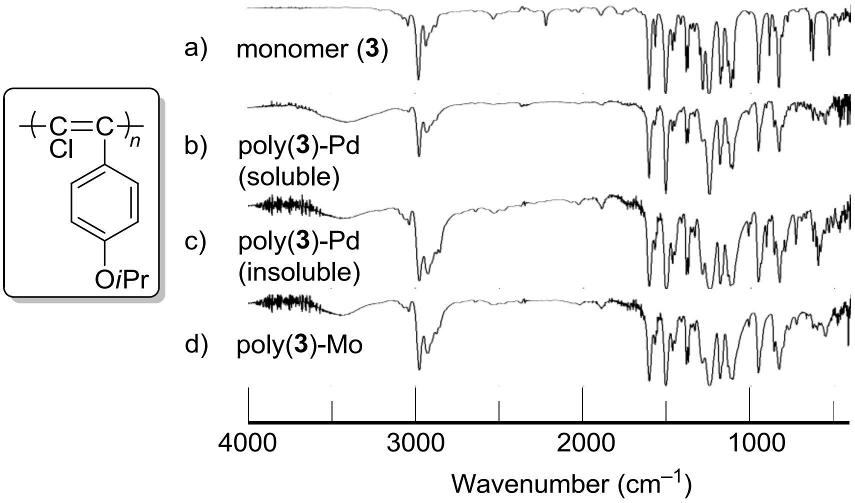


Figure 7. IR spectra of: a) monomer **3**; b) poly(**3**) synthesized by the polymerization using *t*Bu$_3$PPdMeCl (**6**)/AgOTf (Table 1, entry 5), c) insoluble fraction of poly(**3**) synthesized using *t*Bu$_3$PPdMeCl (**6**)/AgOTf (Table 1, entry 5) and, d) poly(**3**) synthesized using MoCl$_5$/SnBu$_4$ (Table 1, entry 6) measured by the KBr pellet method.

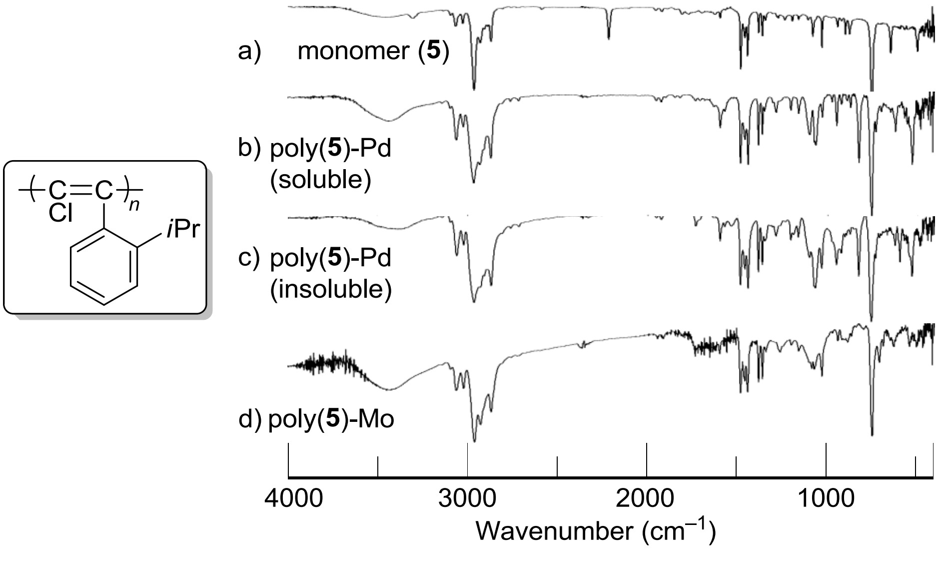


Figure 8. IR spectra of: a) monomer **5**; b) poly(**5**) synthesized by the polymerization using *t*Bu$_3$PPdMeCl (**6**)/AgOTf (Table 1, entry 9), c) insoluble fraction of poly(**5**) synthesized using *t*Bu$_3$PPdMeCl (**6**)/AgOTf (Table 1, entry 9) and, d) poly(**5**) synthesized using MoCl$_5$/SnBu$_4$ (Table 1, entry 10) measured by the KBr pellet method.

considerable shorter wavelength position than that of poly(**5**)-Mo (382 nm). The color difference between the two polymers could be clearly noticed by naked eye, dark yellow (Pd-based polymer) and orange (Mo-based polymer).

The lower absorption wavelength of the Pd-based polymers than that of the Mo-based counterparts is attributable to a shorter conjugation length which presumably originates from higher cis-contents of the Pd-based polymers.[7]

Figure 9 [bottom of (a), (b) and (c)] shows the emission spectra of poly(**2**), poly(**3**) and poly(**5**). As summarized in Table 2, *para*-substituted poly(**2**) and poly(**3**) emitted fluorescence with very small quantum yields (Φ_{emi} = 0.7–1.1%) regardless of the catalyst employed in the polymerization. Interestingly, *ortho*-substituted poly(**5**)-Pd emitted fluorescence with a moderate quantum yield (Φ_{emi} = 14.0%), while poly(**5**)-Mo did with a small value (Φ_{emi} = 0.7%). The *ortho*-substituents and high *cis*-content are effective to enhance the fluorescence emission. No relevant tendency was observed between the molecular weights and fluorescence (Table 2, entry 5 and 6).

Figure 9 [bottom of (a), (b) and (c)] shows the emission spectra of poly(**2**), poly(**3**) and poly(**5**). As summarized in Table 2, *para*-substituted poly(**2**) and poly(**3**) emitted fluorescence with very small quantum yields (Φ_{emi} = 0.7–1.1%) regardless of the catalyst employed in the polymerization. Interestingly, *ortho*-substituted poly(**5**)-Pd emitted fluorescence with a moderate quantum yield (Φ_{emi} = 14.0%), while poly(**5**)-Mo did with a small value (Φ_{emi} = 0.7%). The *ortho*-substituents and high *cis*-content are effective to enhance the

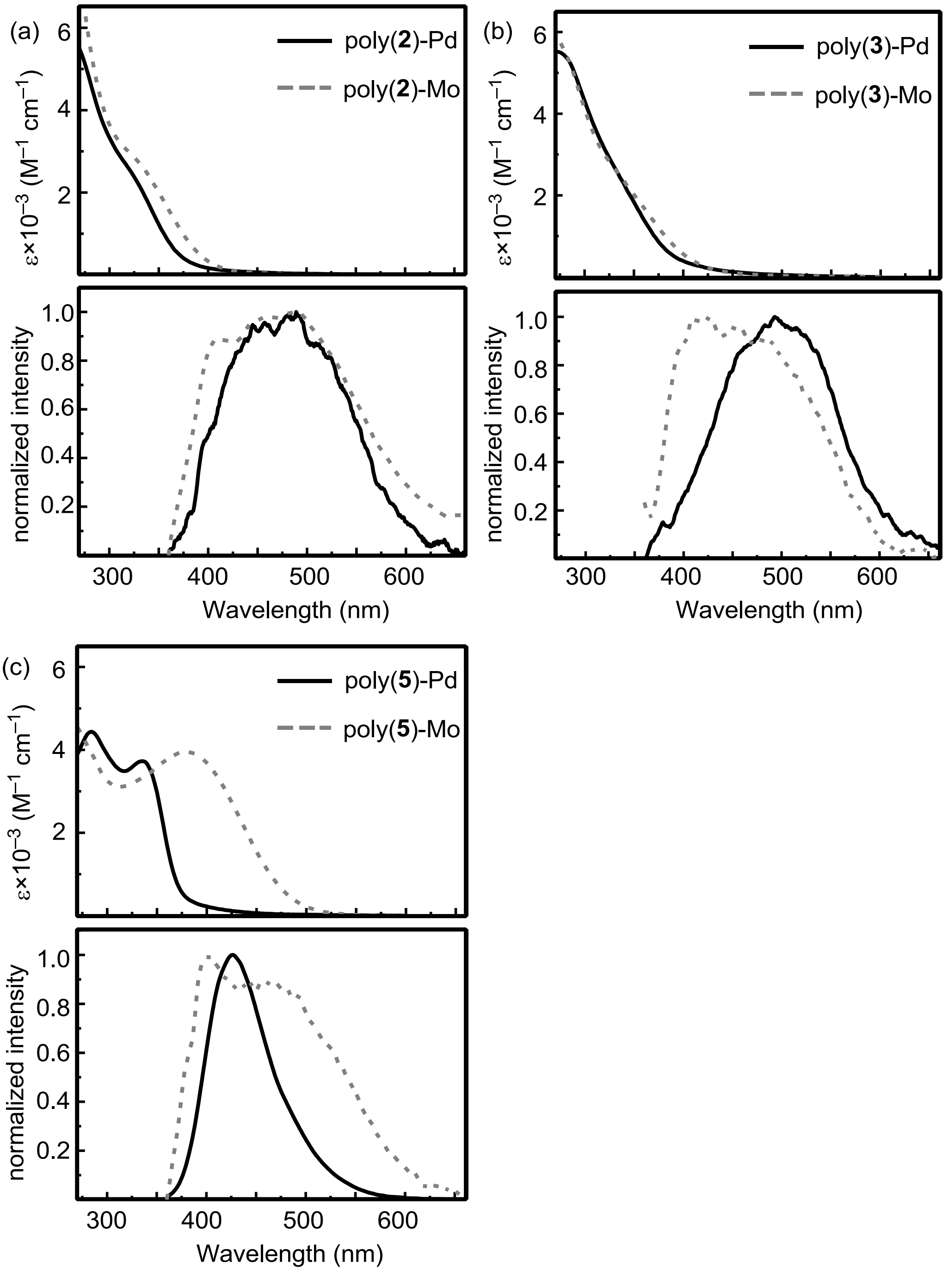


Figure 9. UV-vis absorption (top of a, b and c) and emission (bottom of a, b and c) spectra of poly(**2**) (a), poly(**3**) (b) and poly(**5**) (c) synthesized by the polymerization using tBu$_3$PPdMeCl (**6**)/AgOTf (solid line) and $MoCl_5$/$SnBu_4$ (dotted line) measured in THF at room temperature (c = 0.02 mM). Excitation wavelength: 320 nm.

fluorescence emission. No relevant tendency was observed between the molecular weights and fluorescence.

Table 2. Fluorescence quantum yields of poly(**2**), poly(**3**) and poly(**5**) synthesized by the polymerization using [(*t*Bu$_3$P)PdMeCl] (**6**)/AgOTf and MoCl$_5$ (**7**)/SnBu$_4$ [a]

entry	monomer	catalyst	Φ_{emi},[b] %
1	**2**	Pd	1.1
2	**2**	Mo	1.1
3	**3**	Pd	0.7
4	**3**	Mo	1.9
5	**5**	Pd	14.0
6[c]	**5**	Pd	11.5
7	**5**	Mo	0.7

[a] Samples synthesized in Table 1. [b] Calculated from the emission spectra of the polymers excited at 320 nm measured in THF using anthracene as a standard in EtOH (Φ_{emi} = 0.27). The values were corrected using the refractive indeces of THF and EtOH. [c] Fraction separated from poly(**5**)-Pd Et$_2$O-soluble part (Table 1) employing preparative HPLC.

Conclusion

In summary, the author have presented the polymerization of 1-chloro-2-arylacetylenes **1**–**5** with various substituents using Pd and Mo catalysts as well as the comparative study of the properties of the formed polymers. Pd catalyst **6** outperformed Mo catalyst **7** for the polymerization of the polar group substituted monomers **3**–**5**. The ^{1}H NMR spectra suggested the difference of stereostructures between the Pd- and Mo-based polymers. The

UV-vis spectra indicated a higher cis-content of the Pd-based polymers than that of the Mo-based polymers. The Pd-based cis-rich polymer derived from an ortho-substituted monomer emitted fluorescence with a higher intensity than that of the Mo-based polymer counterpart. As far as we know, this is the first study on the relationship between the main chain stereoregularity and absorption-emission properties of disubstituted acetylene polymers.

Experimental Sections

Materials. The reagents were used as received from commercial suppliers (Aldrich and Wako) without further purification. Tri-*tert*-butylphosphine was received from Nippon Chemical Industrial and used without further purification. $ClC{\equiv}CC_6H_5$,[11], $HC{\equiv}CC_6H_4$-*o*-*i*Pr,[12] $HC{\equiv}CNHC(O)O$*t*Bu[13] and *t*$Bu_3PPdMeCl$[14] were synthesized according to the procedures in the literature. The solvents used for the air and moisture sensitive procedures were purified employing standard procedures.

Synthesis and instrumentation. All air and moisture sensitive manipulations were performed under argon using standard Schlenk techniques. ^1H and ^{13}C NMR spectra were recorded at 400 MHz and 100 MHz, respectively, in a JEOL ECA-400. Chemical shifts were referenced to TMS (δ = 0.00 ppm) or $CHCl_3$ (δ = 7.26 ppm) as an internal standard. IR spectra were measured on a JASCO FT/IR-4100 spectrophotometer using the KBr method. Elemental analysis was performed at the Microanalytical Center of Kyoto University. High-resolution mass spectra were obtained with a JEOL JMS-MS700 (EI), Thermo Fisher SCIENTIFIC EXACTIVE (ESI, APCI) spectrometer or a triple quadrupole mass spectrometer TSQ (ThermoFisher) in a positive ion mode. The weight-average molecular weights (M_w) and the polydispersity indices (PDI) of the polymers were determined on a JASCO system equipped with Shodex columns KF805×3 (molecular weight limit $\approx 4 \times 10^6$, eluted with THF) at 40 °C by using polystyrene standards for calibration purposes. UV-vis absorption spectra were recorded on a V-550 spectrometer (JASCO) and fluorescence spectra were recorded on a FP-750 spectrometer (JASCO).

Synthesis of Monomers

Synthesis of 1-chloro-2-(4-isopropyl)phenylacetylene (2). 1-bromo-4-isopropylbenzene (10 g, 50.2 mmol), $(CH_3CN)_2PdCl_2$ (390 mg, 1.5 mmol), tBu$_3$P (609 mg, 3.0 mmol), CuI (191 mg, 1.0 mmol) and HNiPr$_2$ (8.4 mL, 60.2 mmol) were placed under Ar in a round-flask provided with a three-way stopcock. After adding dioxane (50 mL), the solution was cooled to 0 °C. Then, trimethylsilylacetylene was added to the misture dropwise and the resulting mixture was stirred overnight. The solution was diluted with Et_2O (70 mL) and extracted with saturated NH_4Cl aq. (2 × 50 mL), saturated $NaHCO_3$ aq. (2 × 50 mL) and saturated aqueous NaCl (2 × 50 mL). The organic phase was dried with anhydrous $MgSO_4$, filtrated and concentrated on a rotatory evaporator.

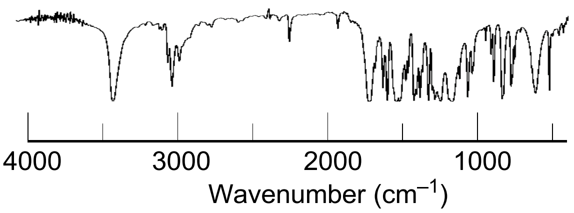
The crude product was purified by silica gel flash chromatography (hexane as eluent) to obtain [(4-isopropylphenyl)ethynyl]trimethylsilane as a yellow liquid in 92% yield (9.98 g, 46.1 mmol). The ^{1}H and ^{13}C NMR spectra were in agreement with those reported in the literature.[15]

Next, CCl_4 (120 mL) was fed to a mixture of [(4-isopropylphenyl)ethynyl]trimethylsilane (4.98 g, 23.0 mmol) and K_2CO_3 (3.18, 23.0mmol) under N_2. To the resulting mixture, a solution of tetra-*n*-butylammonium fluoride in THF (1.0 mol/L, 46 mL, 46.0 mmol) was added and allowed to stir overnight. The reaction mixture was diluted with Et_2O (60 mL) and washed with 1 M HCl solution (2 × 50 mL), saturated $NaHCO_3$ aq. (2 × 50 mL) and saturated aqueous NaCl (2 × 50 mL). The organic phase was dried over anhydrous $MgSO_4$, filtrated and concentrated on rotaroty evaporator. The residual mass was purified by preparative HPLC eluted with $CHCl_3$ to obtain a light yellow oil in 99% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.39 (d, J = 8.0 Hz, 2H), 7.19 (d, J = 8.0 Hz, 2H), 2.91 (m, J = 8.0 Hz, 1H), 1.26 (d, J = 8.0 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 149.6, 132.0, 126.5, 119.4, 69.5, 67.1, 34.05, 23.7.

Synthesis of 1-chloro-2-(4-isopropoxy)phenylacetylene (3). This compound was synthesized according to a similar procedure to **2** employing 1-iodo-4-isopropoxybenzene instead of 1-bromo-4-isopropylbenzene. Product **3** was obtained as a red oil in 74% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36 (d, J = 8.7 Hz, 2H), 6.81 (d, J = 8.7 Hz, 2H), 4.56 (m, J = 6.0 Hz, 1H), 1.34 (d, J

= 6.0 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.2, 133.4, 115.7, 113.8, 69.9, 69.4, 66.2, 21.9. HR-MS (ESI): *m/z* calcd for $C_{11}H_{11}ClO$: 194.0489 [*M*]; found 194.0489.

Synthesis of 1-chloro-2-(*N*-Boc-amino)phenylacetylene (4). This compound was synthesized by a modified procedure reported in the literature.[8a] The details are as follows. $HC{\equiv}CC_6H_4$-*p*-NHC(O)O*t*Bu (2.0 g, 9.2 mmol), potassium carbonate (2.4 g, 11.0 mmol) and CCl_4 (9 mL) were fed into a flask equipped with a three-way stopcock after flushing with nitrogen gas. Then, a solution of tetra-*n*-butylammonium fluoride in THF (1.0 mol/L, 500 μL, 0.5 mmol) was added to the mixture. After stirring the resulting mixture at 45 °C overnight, MeOH (5 mL) and $CHCl_3$ (40 mL) were added to the mixture. The resulting solution was washed with 1 M hydrochloric acid (2 × 50 mL) and then with water (50 mL). The organic phase was dried with anhydrous magnesium sulfate and the solvent was evaporated. The crude product was purified by preparative HPLC to yield the desired product (0.5 g, 2.0 mmol) as a light yellow crystalline solid. Yield = 21%. ^{1}H NMR ($CDCl_3$, 25 °C, TMS): δ 7.29–7.37 (m, 4H; Ar), 6.52 (s, 1H; N*H*), 1.51 (s, 9H; CH_3). ^{13}C NMR ($CDCl_3$, 25 °C, TMS): δ 152.3, 138.7, 132.8, 118.0, 116.3, 81.0, 69.2, 67.0, 28.3; HR-MS (ESI): *m/z* calcd for $C_{13}H_{14}ClNO_2 + NH_4$: 269.1051 [*M*]; found 269.1057; elemental analysis calcd (%) for $C_{13}H_{14}ClNO_2$: C, 62.03; H, 5.61; N, 5.56; Cl, 14.08; found: C, 61.75; H, 5.55; N, 5.50; Cl, 14.12. The IR spectra of **4** is shown below:



Synthesis of 1-chloro-2-(2-isopropyl)phenylacetylene (5). This compound was synthesized in a similar manner to a procedure in the literature.[8a] The details are as follows. HC≡CC$_6$H$_4$-*o*-*i*Pr (1.4 g, 9.7 mmol), potassium carbonate (1.6 g, 11.6 mmol) and CCl$_4$ (9.7 mL) were fed into a flask equipped with a three-way stopcock under nitrogen gas. Then, a solution of tetra-*n*-butylammonium fluoride in THF (1.0 mol/L, 550 μL, 0.5 mmol) was added to the mixture. After stirring the resulting mixture at 45 °C overnight, MeOH (1 mL) and CHCl$_3$ (40 mL) were added to the mixture. The resulting solution was washed with 1 M hydrochloric acid (2 × 40 mL) and then with water (40 mL). The organic phase was dried with anhydrous magnesium sulfate and the solvent was evaporated. The crude product was purified by preparative HPLC to yield the desired product as a colorless oil in 15% yield. ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.40–7.42 (m, 1H), 7.25–7.32 (m, 2H), 7.10–7.14 (m, 1H), 3.40 (m, J = 6.8 Hz, 1H), 1.27 (d, J = 6.8 Hz, 6H). ^{13}C NMR (100 MHz, CDCl$_3$): δ 151.1, 132.8, 128.8, 125.5, 125.0, 120.8, 70.9, 68.3, 31.6, 23.2. HR-MS (ESI): *m/z* calcd for C$_{11}$H$_{11}$Cl: 178.0549 [*M*]; found 178.0541; elemental analysis calcd (%) for C$_{11}$H$_{11}$Cl: C, 73.95; H, 6.21; Cl, 19.84; found: C, 74.06; H, 6.36; C, 20.03.

Polymerization reactions

Polymerization by Pd catalyst (6/AgOTf). Monomers **1**–**5** were polymerized employing standard Schlenk techniques following the same procedure. Typical procedure: Monomer **2** (200.0 mg, 1.12 mmol) was fed into a Schlenk tube, and toluene (280 μL) was added to the monomer. In another Schlenk tube, a catalyst solution was prepared by stirring 1.0 equivalent of (tBu$_3$P)PdMeCl (16.0 mg, 0.04 mmol) with 1.2 equivalents of AgOTf (14.0 mg, 0.05 mmol) in toluene (560 μL) at 50 °C. After 30 min the catalyst solution was filtrated and a portion of the catalyst solution (280 μL) was added to the monomer solution. After stirring at 80 °C for 24 h, CH_3COOH (100 μL) was added and the reaction mixture was poured into MeOH (200 mL) to precipitate a solid, which was separated by filtration. The MeOH-insoluble solid was washed with THF until no color was observed in the THF washings. The solid obtained after evaporating the THF washings was dissolved in a small amount of $CHCl_3$ (0.5 mL), reprecipitated with Et_2O/MeOH 1:3 (80 mL), and vacuum dried to obtain a yellow solid.

Polymerization by Mo catalyst 7 ($MoCl_5$/$SnBu_4$). Polymerization of monomers **2**–**5** followed a similar procedure employing standard Schlenk techniques. Typical procedure: Monomer **2** (200 mg, 1.12 mmol) and toluene (560 μL) were placed under Ar. In a separate Schlenk tube, a solution of Mo catalyst was prepared by stirring $MoCl_5$ (12 mg, 0.04 mmol) and $SnBu_4$ (14 μL, 0.04 mmol) in toluene (1.12 mL). A portion of the Mo catalyst solution (560 μL) was added to the monomer solution. After 24 h at 30 °C the reaction mixture was poured in MeOH. The solid product was obtained after filtration and vacuum drying.

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Part III

Development of Rh Catalytic System for the Synthesis of Substituted Polyacetylenes with Well-Defined Structures

Chapter 5

Characterization of the Polymerization Catalyst [(2,5-norbornadiene)Rh{C(Ph)=CPh$_2$}(PPh$_3$)] and Identification of the End Structures of Poly(phenylacetylenes) Obtained by Polymerization Using This Catalyst

Abstract

The structures of [(2,5-norbornadiene)Rh{C(Ph)=CPh$_2$}(PPh$_3$)] (**1**) and its reaction product with CH_3CO_2H were elucidated by ^{1}H, ^{13}C, and ^{31}P NMR spectroscopy, mass spectrometry, and single crystal X-ray analysis. The presence of two conformational isomers of **1** was verified by NMR spectroscopy, which was well-supported by DFT calculations. Phenylacetylene was polymerized using **1** as a catalyst with $[M]_0/[Rh] = 10$ and quenched with CH_3CO_2H and CH_3CO_2D. The incorporation of H and D at the polymer ends was confirmed by MALDI-TOF mass spectrometry, and ^{1}H and ^{1}H–^{13}C HSQC NMR spectroscopy. The polymerization degree was calculated to be 11 by ^{1}H NMR spectroscopy, which agreed well with the theoretical value.

Introduction

Substituted polyacetylenes have attracted considerable attention owing to their optoelectronic properties stemming from the π-conjugated backbone. The introduction of functional groups at the side chains provides polyacetylenes with useful structural features such as a helical conformation and liquid crystallinity, and they have been applied in molecular recognition, stimuli-responsive materials, catalytic studies and gas permeability.[1] Substituted polyacetylenes are commonly synthesized by polymerization of the corresponding acetylene monomers using transition metal catalysts. Polymerization of substituted acetylenes based on early transition metal catalysts, including Nb, Ta, Mo, and W, occurs via a metathesis mechanism, while late transition metal catalysts, such as those composed of Rh, Pd, and Ir, display a coordination-insertion mechanism. Rh-based catalysts are especially useful for the synthesis of cis-stereoregular substituted polyacetylenes because they are highly tolerant toward polar groups. Since the first report on the $[(nbd)RhCl]_2/Et_3N$-catalyzed polymerization of phenylacetylene (PA) derivatives by Tabata and coworkers,[2] various efforts have been aimed at developing well-defined Rh catalysts to improve control over polymerization and catalytic activity. Some Rh catalysts enable the living polymerization of PA derivatives, leading to the synthesis of end-functionalized polymers and block copolymers. Noyori and coworkers have reported the living polymerization of PA derivatives by two- and three-component Rh catalyst systems such as $[(nbd)Rh(C{\equiv}CPh)(PPh_3)_2]$/DMAP [nbd = 2,5-norbornadiene, DMAP = 4-(dimethylamino)pyridine] and [(nbd)Rh(μ-OMe)]$_2$/PPh$_3$/DMAP.[3] Farnetti and coworkers proposed another Rh-based living polymerization catalyst system based on [(nbd)Rh(μ-OMe)]$_2$/1,4-bis(diphenylphosphino)butane.[4] Misumi and Masuda accomplished the living polymerization of PA derivatives using [(nbd)RhCl]$_2$/PPh$_3$/[LiC(Ph)=CPh$_2$],[5] which showed quantitative initiation efficiency. Here, [(nbd)RhCl(PPh$_3$)] was formed by the reaction of [(nbd)RhCl]$_2$ and PPh$_3$, followed by its transformation into the active species [(nbd)Rh{C(Ph)=CPh$_2$}(PPh$_3$)]. The reaction is initiated by the insertion of a triple bond of the monomer between the Rh center and a vinylic carbon atom, and successive monomer insertions give the polymer. An analogous complex, [(nbd)Rh{C(Ph)=CPh$_2$}{P(4-F-C$_6$H$_4$)$_3$}] was isolated and proved to mediate the living polymerization of PA.[6] This complex also catalyzes the pseudo-living polymerization of *N*-propargylamides.[7] Poly(*N*-propargylamide)s adopt a helical conformation stabilized by intramolecular hydrogen bonding as well as steric repulsion between the side chains.[8] Interestingly, the helical structure can transform into a random conformation, accompanied by a color change and a decrease in stiffness upon a rise in temperature and/or the addition of a polar solvent, and it is expected that sophisticated stimuli-responsive materials can be developed based on substituted polyacetylenes of controlled stereoregularity and molecular weight. We have recently demonstrated that Rh catalysts containing a strongly π-acidic diene, tetrafluorobenzobarrelene (tfb), show an extremely high catalytic activity compared to their nbd counterparts. Examples of these tfb-liganded Rh catalysts include $[(tfb)Rh\{C(Ph){=}CPh_2\}(PPh_3)]/PPh_3$,[9] $[(tfb)Rh^+(\eta^6\text{-}Ph)B^-Ph_3]$[10] and $[(tfb)Rh^+(PPh_3)_2](B^-Ph_4)]$.[11]

The mechanistic aspects of polymerization, especially that of initiation and propagation together with cis-stereoselectivity have been studied extensively using various experimental techniques such as NMR spectroscopy combined with isotope labeling[12] and DFT calculations.[13] In contrast, the termination mechanism of Rh-catalyzed acetylene polymerization has so far only been elucidated to a minor extent, presumably due to the difficulties arising from the spectroscopic analysis of polymer termini. Matrix assisted laser desorption/ionization-time of flight (MALDI-TOF) mass spectrometric analysis of polymers can identify the structure of the polymer termini, allowing a detailed investigation of the polymerization mechanism and the effect of the termini on the polymer properties.[14–20] To the best of our knowledge, there is no report regarding the mass spectrometric analysis of the terminal structures of substituted polyacetylenes obtained by Rh-catalyzed polymerization. Regarding the utility of the properties of substituted polyacetylenes, the elucidation of the terminal structures may give rise to the development of end-functionalized substituted polyacetylenes, leading to an even broader utilization of Rh-based polymers. In the present study, we analyze the terminal structure of poly(PA), obtained by living polymerization with a well-defined Rh catalyst, using mass spectrometry together with NMR spectroscopy and DFT calculations, and provide a discussion of the termination mechanism.

Results and Discussion

Analysis of the product of Rh Catalyst 1 and CH_3CO_2H. Rh catalysts are mostly used for the polymerization of monosubstituted acetylene monomers because of their high functional group tolerance and the cis-stereoregularity of the resulting polymers, which are useful for application in functional materials.[1k] It remains, however, unclear what the result is of their isolation by means of pouring the polymerization mixture into poor solvents such as methanol. It has been reported that acetic acid (CH_3CO_2H) quenches the Rh-catalyzed polymerization of monosubstituted acetylenes.[3] In the course of this study, we first analyzed by ^{31}P, ^{13}C, ^{1}H NMR spectroscopy and GC-MS a mixture of **1** and CH_3CO_2H, which served as a model for the reaction between the growing polymer chain and CH_3CO_2H.

The synthesis of complex **1** and its analogous complex was reported previously in literature[21] although no spectroscopic data for **1** was given.[22] We therefore characterized the structure of **1** by ^{1}H, ^{13}C and ^{31}P NMR spectroscopy along with single crystal X-ray analysis of **1**. In the ^{31}P NMR spectrum of **1** (measured in CD_2Cl_2) two sets of doublets were observed in a ratio of 1.00:2.72 at 26.7 and 26.2 ppm having coupling constants of J_{Rh-P} = 183 and 185 Hz (Figure 1). In order to obtain information on the presence of conformational

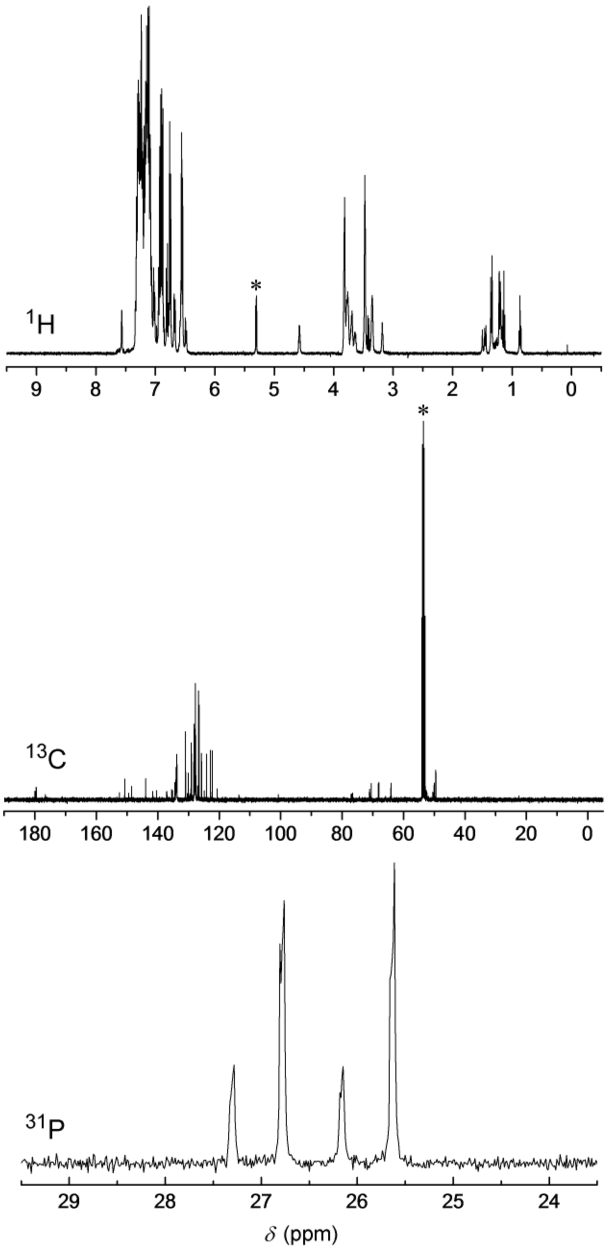


Figure 1. ^{1}H (400 MHz), ^{13}C (100 MHz) and ^{31}P (162 MHz) NMR spectra of **1** measured in CD_2Cl_2 ([**1**] = 2.55×10^{-2} M) at room temperature. * indicates the solvent.

isomers, we measured the variable-temperature (VT) ^{31}P NMR spectra of **1** in toluene-d_8. Two sets of doublets were observed in a ratio of 1:2.15 at 26.9 and 26.3 ppm having coupling constants $J_{\mathrm{Rh-P}}$ = 183 and 187 Hz at room temperature.

The ratio of the two signal sets depended on solvents. The coalescence temperature was 89 °C in toluene-d_8. Thus, the two signal sets are assigned to two conformational isomers that exist within the time scale of the NMR experiment. The rotational barrier between the two isomers was estimated to be 73.2 kJ/mol.[23] The ^{1}H and ^{13}C NMR spectra support the presence of the conformational isomers indicated by the ^{31}P NMR spectroscopic measurement.

The solid-state structure of **1** was determined by single crystal X-ray analysis (Figure 2). The Rh atom exists in a distorted square-planar coordination geometry, i.e., the α-carbon of –C(Ph)=CPh$_2$ is located in a plane formed by the Rh atom and the centers of the two norbornadiene double bonds, while the phosphorus atom of PPh$_3$ lies 31.5° aside the plane, presumably because of steric repulsion between the bulky PPh$_3$ and –C(Ph)=CPh$_2$ groups.

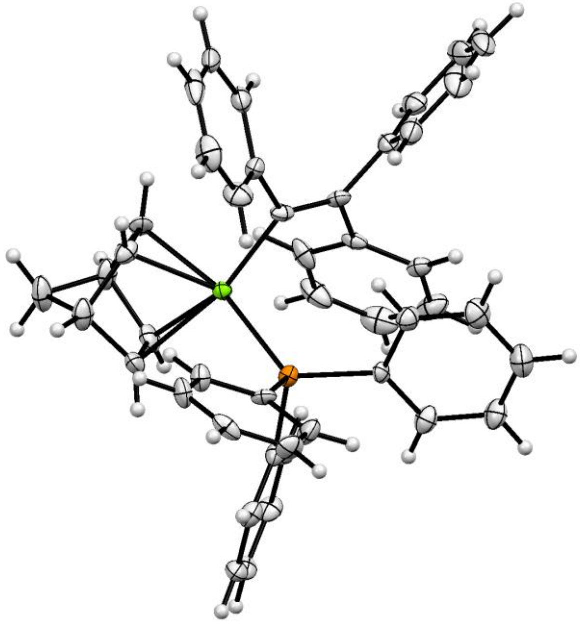


Figure 2. ORTEP drawing of molecular structure of **1** (50% probability ellipsoids).

DFT calculations[24] were performed to obtain more detailed information on the conformation of complex **1**. Figure 3 shows the energy map of the conformers of **1** optimized by the B3LYP/LANL2DZ method.[25,26] The dihedral angle ϕ of the P–Rh–C=C atoms was varied by 15° increments.[27] The presence of two rotational isomers was indeed well supported by the existence of two conformers with ϕ = 90° and 270° and very close energy minima (energy difference: 0.009 kJ/mol).[28] The rotational barrier between them was calculated to be 75.5 kJ/mol, which well agreed with that (73.2 kJ/mol) estimated by the VT NMR measurement mentioned above. X-ray crystallographic analysis (Figure 2) revealed that the ϕ of the conformer is 80.5° in the solid state, which agrees with that of the most stable conformer predicted by DFT calculations. The crystallographic geometries coincide with the calculated geometries, which supports the accuracy of the DFT method in predicting the conformation.

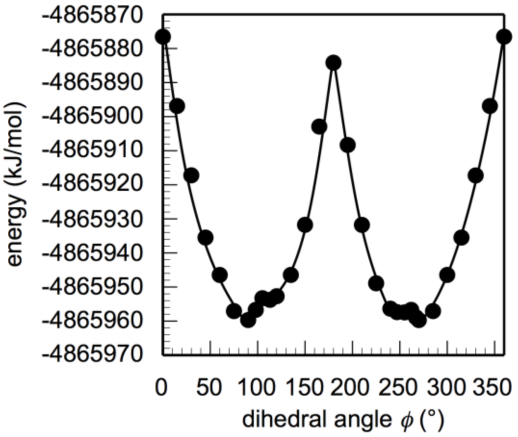


Figure 3. Relationship between the dihedral angle (ϕ) values of P–Rh–C=C and energies of **1** calculated by the B3LYP/LANL2DZ method.

Figures 4 shows the ^{1}H, ^{13}C and ^{31}P NMR spectra of a mixture of catalyst **1** and 100 equiv of CH_3CO_2H in CD_2Cl_2. One doublet was observed at 28.8 ppm with $J_{Rh–P}$ = 174 Hz, whereas no singlet was observed at –5.6 ppm assignable to PPh_3, indicating that no PPh_3 was liberated from Rh.[29] The formation of triphenylethylene (*m*/*z* = 256) was, however, confirmed by GC-mass spectrometry and ^{1}H and ^{13}C NMR spectroscopy by comparison with an authentic sample (Figure 5). From these results, it is tentatively concluded that the –C(Ph)=CPh_2 group of **1** was replaced with –OAc by the addition of CH_3CO_2H, while PPh_3 remained coordinated to Rh to form complex **2** or **3** (Scheme 1). Unfortunately, no concrete evidence for the formation of **2**/**3** was obtained from the ^{1}H and ^{13}C NMR spectra.

Although [(nbd)Rh(OCOR)(PPh_3)] (R = CH_3, CF_3)[30,31] has been synthesized previously by reaction of $[(nbd)Rh(OCOR)]_2$ and PPh_3, the detailed stereo-configuration has not yet been elucidated. In the present study, DFT (B3LYP/LANL2DZ) calculations were carried out to gain insight into the species formed by the addition of CH_3CO_2H to **1**. Figure 6 shows three starting geometries **S2**, **S3A** and **S3B**. Here, **S2** is a square planar conformer tetracoordinated by nbd, $OCOCH_3$ and PPh_3, **S3A** is a square pyramid conformer pentacoordinated by nbd, chelating acetate and PPh_3, where PPh_3 is oriented nearly perpendicular to the square planar surface, while **S3B** is a second square pyramid conformer, in which one oxygen atom of $OCOCH_3$ is oriented nearly perpendicular to the square planar surface. After full geometry optimization, **S2**

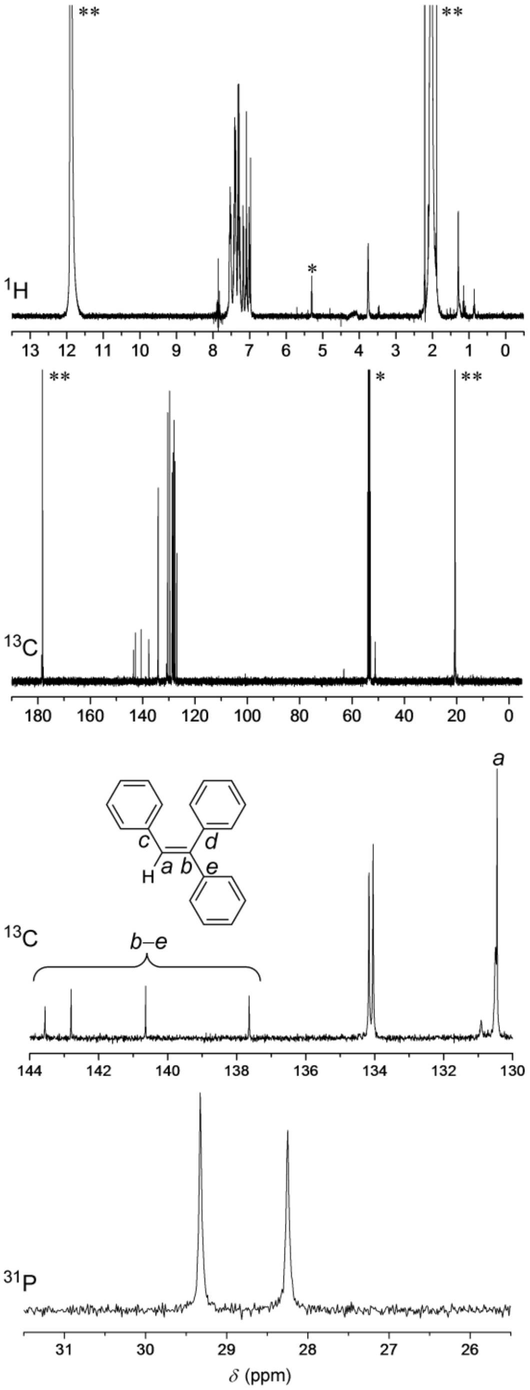


Figure 4. ^{1}H (400 MHz), ^{13}C (100 MHz) and ^{31}P (162 MHz), NMR spectra of a mixture of **1** and 100 equiv of CH_3CO_2H measured in CD_2Cl_2 ($[\mathbf{1}]_0 = 2.55 \times 10^{-2}$ M). *: Solvent. **: CH_3CO_2H. No change was observed between spectra of the samples recorded immediately after mixing of the reagents, or spectra that were acquired one day later.

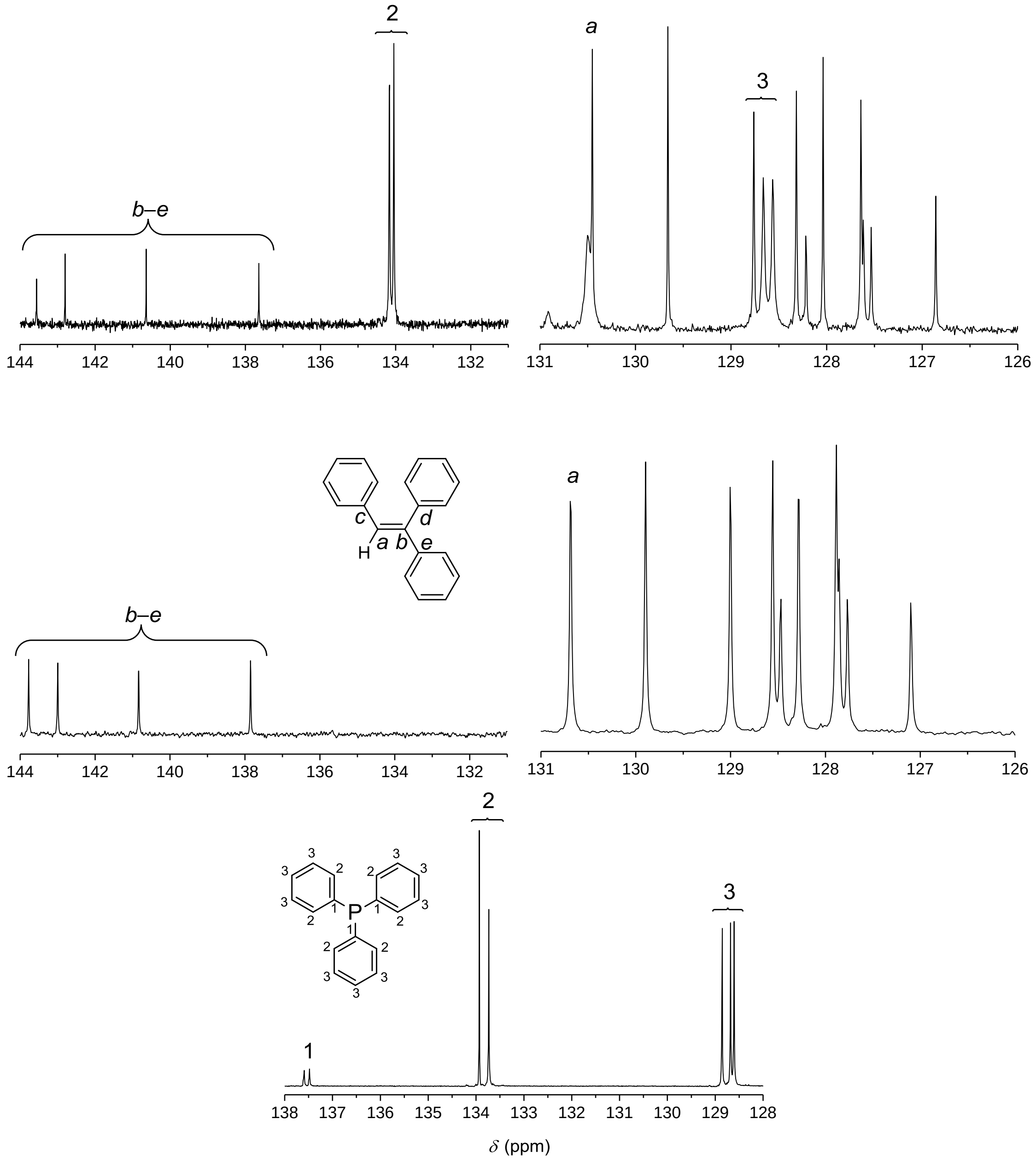
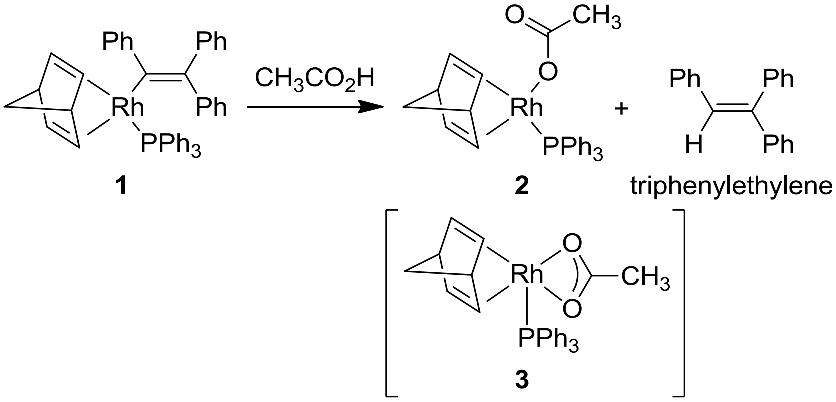


Figure 5. ^{13}C (100 MHz) NMR spectra of a mixture of **1** and 100 equiv of CH_3CO_2H ([**1**]$_0$ = 2.55 × 10^{-2} M) (upper), triphenylethylene (middle), and PPh_3 (bottom) measured in CD_2Cl_2.

gave a square planar conformer **S2$_{opt}$** (E = –3441548.5 kJ/mol), whereas both **S3A** and **S3B** yielded the square planar conformers **S3A$_{opt}$** (E = –3441548.5 kJ/mol) and **S3B$_{opt}$** (E = –3441535.7 kJ/mol). The unfavorable conformation of

Scheme 1. Reaction of **1** with CH_3CO_2H



S2 can be understood from the relatively small chelate angle of O–Rh–O (64°) compared to that of ene–Rh–ene (73°) and O–Rh–P (89°). Interestingly, conformations **S2**$_{\mathbf{opt}}$ and **S3A**$_{\mathbf{opt}}$ were completely identical, even though their starting geometries (**S2** and **S3A**) differed significantly. Considering that **S3A**$_{\mathbf{opt}}$ and **S3B**$_{\mathbf{opt}}$ are superimposable via rotation of the Rh–O and Rh–P bonds, and **S2**$_{\mathbf{opt}}$ (=**S3A**$_{\mathbf{opt}}$) is 12.8 kJ/mol more stable than **S3B**$_{\mathbf{opt}}$, **S3B**$_{\mathbf{opt}}$ is regarded as one conformation of local minimum conformers, whose population is much smaller than that of **S2**$_{\mathbf{opt}}$ (=**S3A**$_{\mathbf{opt}}$). Consequently, it seems likely to assume that Rh complex **2** is formed by reaction of **1** with CH_3CO_2H as illustrated in Scheme 1, accompanied by the formation of triphenylethylene.[32]

Polymer Synthesis. Poly(PA) was synthesized by the polymerization of PA using **1** as an initiator in the presence of PPh_3 as a cocatalyst, which stabilizes the active species leading to living polymerization (Scheme 2).[5] To obtain a low molecular weight polymer the monomer/initiator ratio was 10:1, which makes the analysis of the chain end relatively straightforward. Directly

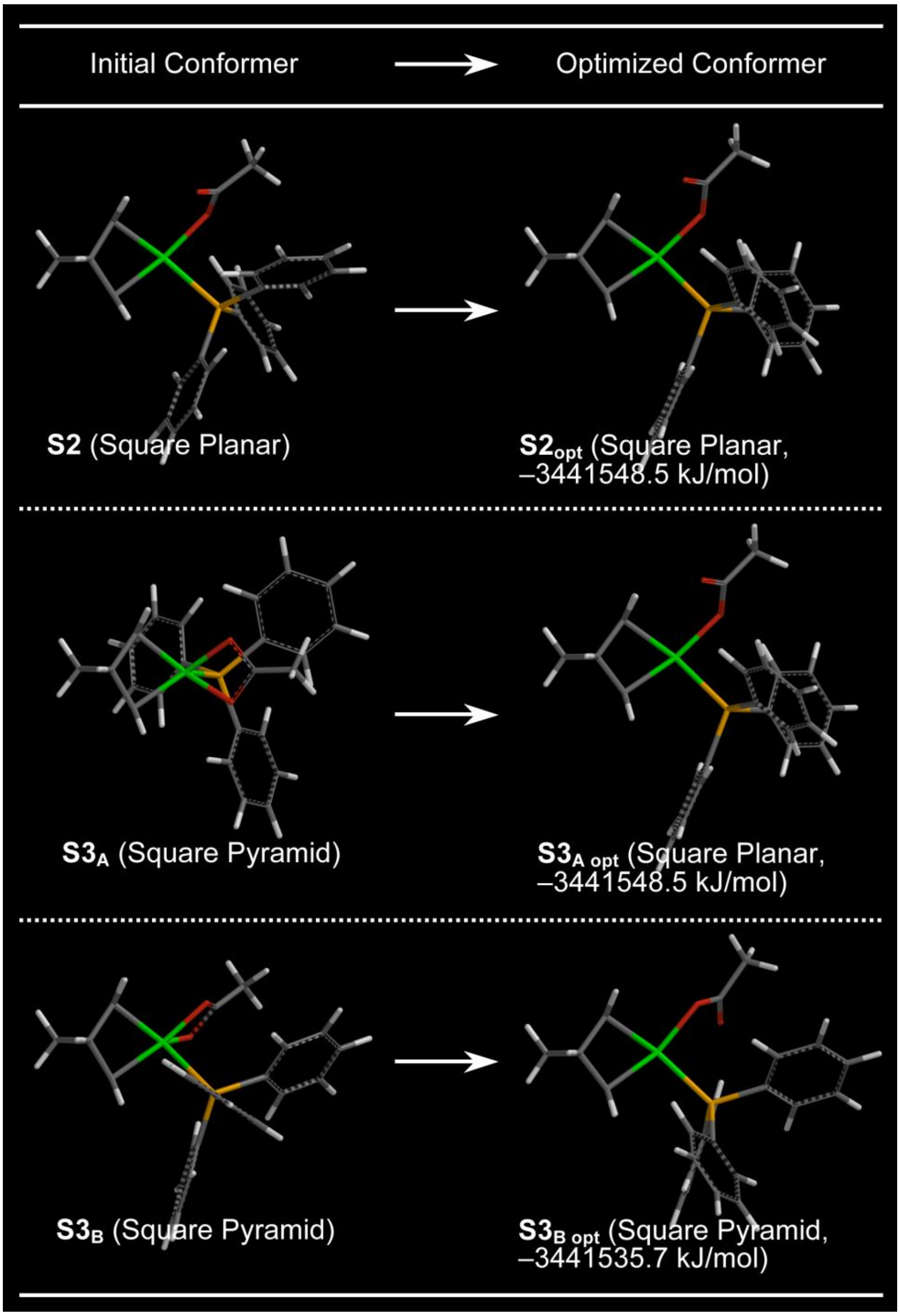


Figure 6. Possible conformers of [(nbd)Rh(OCOCH$_3$)(PPh$_3$)] before (**S2**, **S3$_A$**, **S3$_B$**) and after (**S2$_{opt}$**, **S3$_{A\ opt}$**, **S3$_{B\ opt}$**) full geometry optimization by the DFT method (B3LYP/LANL2DZ). Rh: green, P: orange, O: red, C: gray, H: white.

after the beginning of the polymerization the color of the polymerization mixture changed from pale yellow to orange, gradually becoming deep orange, which indicated the presence of the conjugated acetylene backbone. After 1 h, the polymerization mixture was divided into two parts and 100 equivalents of CH_3CO_2H and CH_3CO_2D (vs. Rh) were added to each reaction mixture separately, followed by stirring for 10 min to quench the polymerization. The polymers were isolated by precipitation in methanol, followed by preparative HPLC separation to remove lower molecular weight oligomers and initiator residues. The collection of only a fraction around the peak top accounted for the relatively low polymer yield (53%) in both cases. The yields, molecular weights and polydispersity index of the polymers obtained by quenching with either CH_3CO_2H or CH_3CO_2D were almost identical (Table 1), indicating the absence of an effect of the acidity difference between the quenchers on the isolation of the polymers.[33]

Scheme 2. Polymerization of PA using **1** as a catalyst.

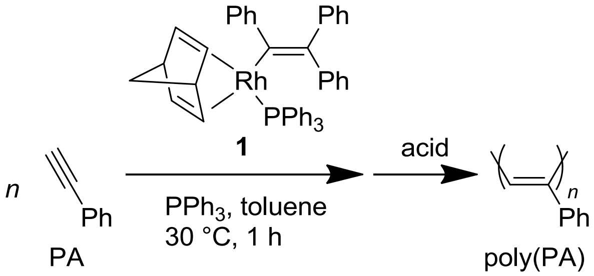


Table 1. Polymerization of PA[a]

acid[b]	polymer		
	Yield,[c] %	M_n[d]	M_w/M_n[d]
CH_3CO_2H	53	1,700	1.10
CH_3CO_2D	53	1,900	1.10

[a] Conditions: $[M]_0 = 0.50$ M in toluene, $[M]_0/[Rh] = 10$, $[PPh_3]/[Rh] = 10$, 30 °C, 1 h. [b] [acid]/[Rh] = 100. [c] Isolated by precipitation in MeOH, followed by preparative HPLC separation, where only the fraction corresponding to the peak top was collected. [d] Estimated by SEC (polystyrene standards, THF).

The structures of the polymers were examined by MALDI-TOF mass spectrometry (Figure 7). The peaks feature an interval of 102 amu, which is consistent with the calculated *m/z* (102.05) of a monomer unit. Since no other peaks are observed outside of this series, it can be concluded that the polymers consist of a homogenous combination of repeating units, initiator groups and end groups. The isotope pattern of the two samples agreed well with those calculated for polymers bearing H and D termini, respectively (Chart 1, Figure 8). In both cases, $–C(Ph)=CPh_2$ is considered as the initiating end group. Furthermore, the *m/z* difference between the polymers is 1.011, which is consistent with the calculated value of 1.006.

Scheme 3 illustrates the polymerization pathways of monomer coordination–insertion and termination with CH_3CO_2H. First, the triple bond of a PA monomer coordinates to the Rh center, accompanied by the simultaneous

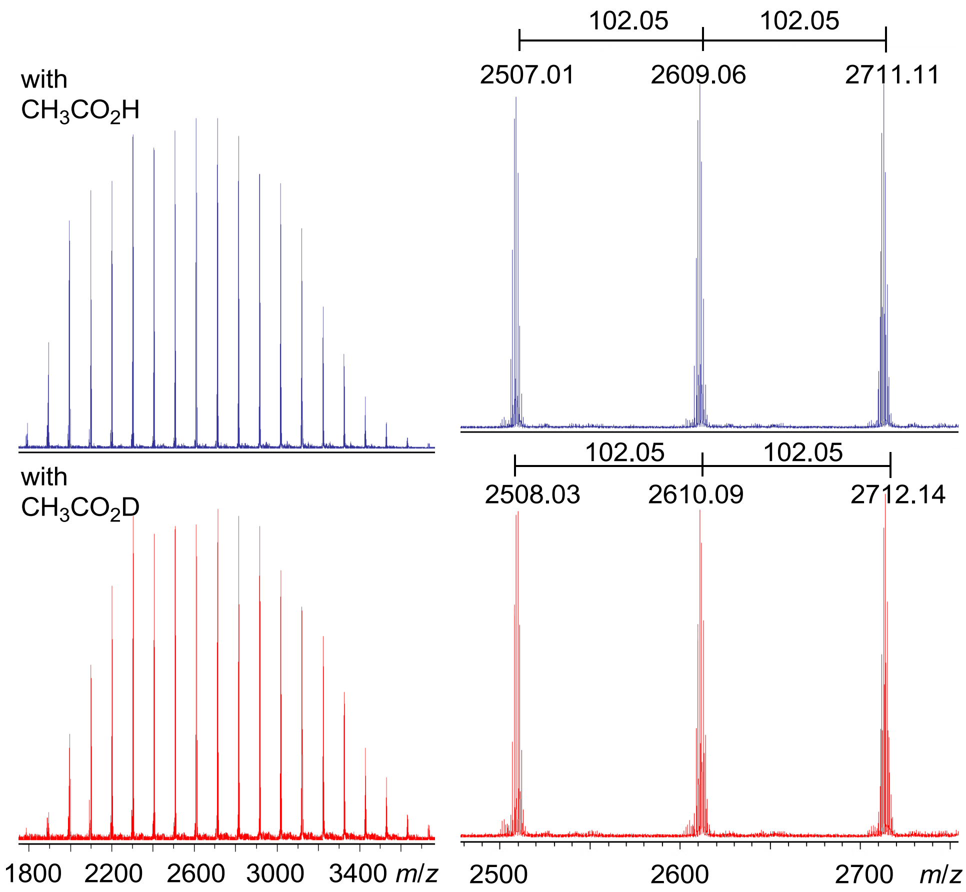
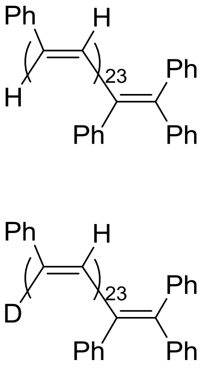


Figure 7. Left: MALDI-TOF mass spectra of poly(PA)s quenched with CH_3CO_2H and CH_3CO_2D. Right: Expanded spectra between 2480 and 2750 *m*/*z*.



m/*z* = 2713.114
calcd for $C_{204}H_{154}Ag^+$

m/*z* = 2714.120
calcd for $C_{204}H_{153}DAg^+$

Chart 1. PA 23-mers obtained by the polymerizations quenched with CH_3CO_2H and CH_3CO_2D.

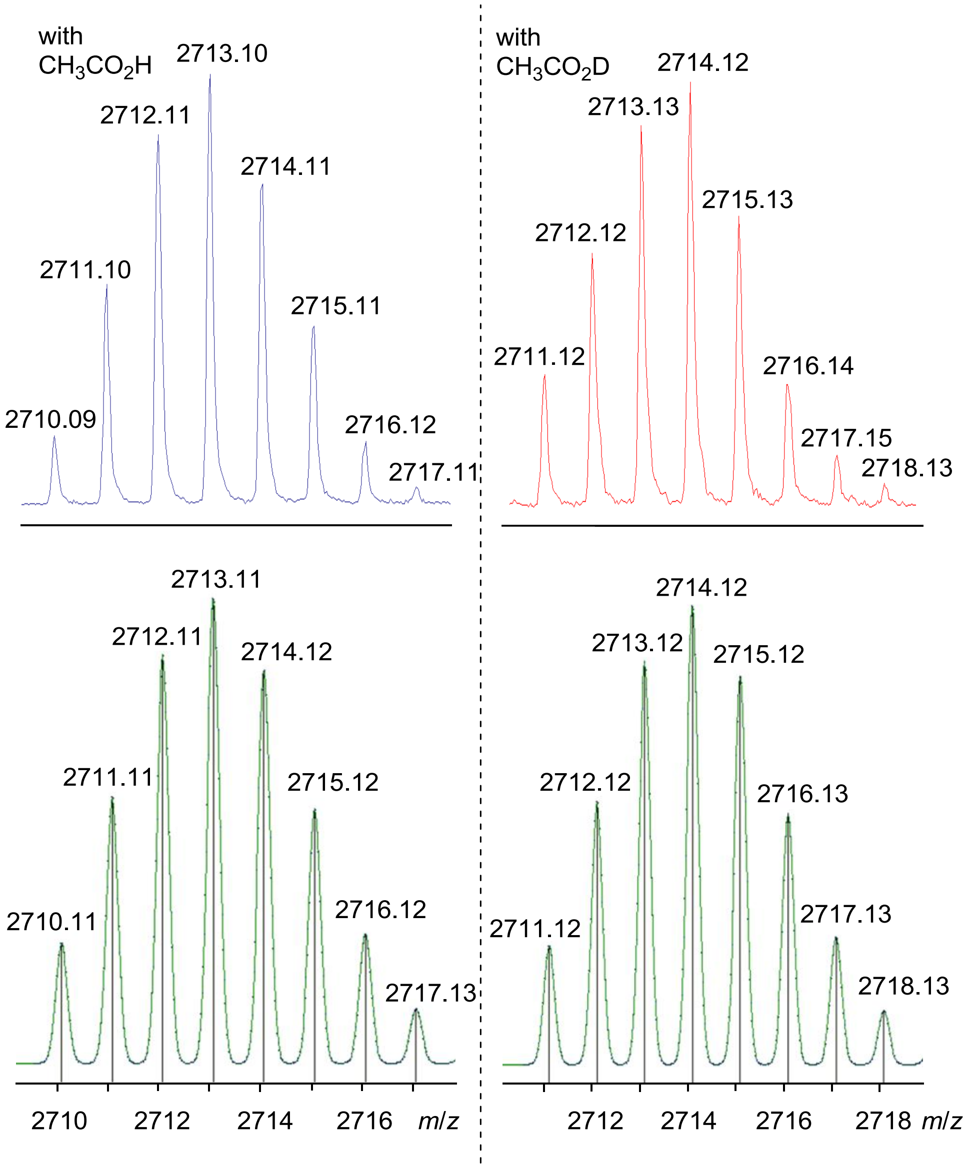
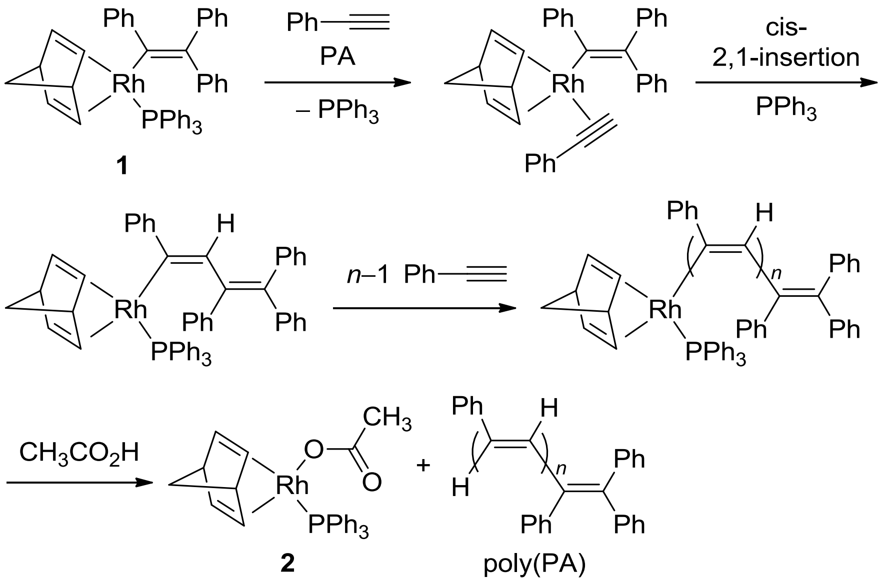


Figure 8. Isotope patterns of the observed (top) and calculated (bottom) MALDI-TOF mass spectra for poly(PA) quenched with CH_3CO_2H and CH_3CO_2D.

dissociation of PPh_3 from Rh. Next, the PA inserts between the Rh and vinylic carbon atom. During this step, 2,1-insertion is more likely than 1,2-insertion because the π-orbital of the benzene ring of PA significantly interacts with the *d*-orbital of Rh during 2,1-insertion to stabilize the transition state, while no such interaction is observed during 1,2-insertion.[34] The insertion is expected to take place in a cis-manner, as commonly observed in Rh catalyzed acetylene polymerizations. It is likely that the propagating end is quenched in a fashion similar to the reaction illustrated in Scheme 1 and, as a result, poly(PA) with –H and –C(Ph)=CPh$_2$ ends forms together with **2**.

Scheme 3. Polymerization pathway of PA using **1** as an initiator.



NMR Spectroscopic Analysis of the Polymers. Figure 9 shows the ^{1}H NMR spectra in CD$_2$Cl$_2$ of the polymers obtained by quenching with CH$_3$CO$_2$H and CH$_3$CO$_2$D.[35] A clear difference is the presence of a doublet signal centered at 6.10 ppm for the CH$_3$CO$_2$H-quenched polymer (Figure 9, top), which can be assigned to the terminal H$_a$ proton and is absent in the CH$_3$CO$_2$D-quenched polymer (Figure 9, bottom). The coupling constant of J = 16.7 Hz indicates a trans geometry of H$_a$ and H$_b$,[36] supporting a cis-stereoregular polymerization. For the CH$_3$CO$_2$H-quenched polymer the H$_b$ proton is observed as a doublet signal coupled to H*a*, both of which partly overlap with other signals. On the other hand for the CH_3CO_2D-quenched polymer, the H*b* proton is observed as a singlet due to the absence of H*a*, where H*b* partly overlaps with other signals as well. The polymerization degree was calculated to be 11 based on the integrals between H*a* and H*c*.[37] This value agrees well with the theoretical value (i.e., 10).[38] The ^1H–^{13}C HSQC spectra of the two poly(PA)

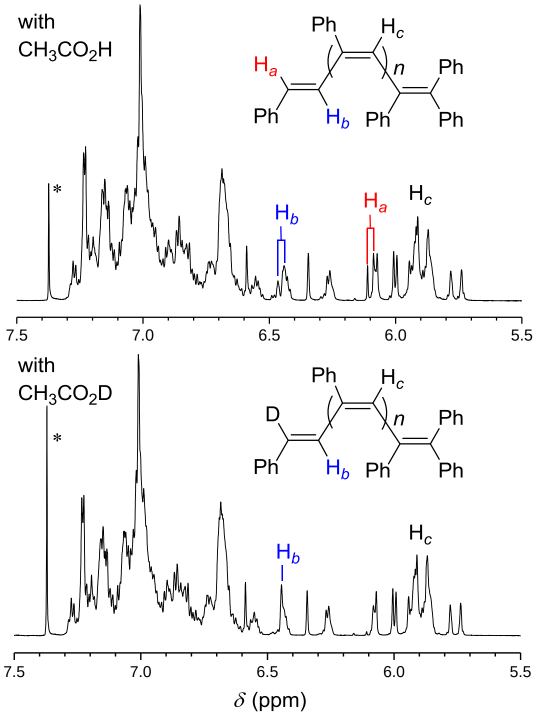


Figure 9. ^1H NMR spectra (700 MHz) in CD_2Cl_2 of poly(PA) quenched with CH_3CO_2H and CH_3CO_2D. *: $CHCl_3$ contamination from the preparative HPLC purification. The chemical shifts are calibrated to the CH_2Cl_2 signal (5.33 ppm, not shown).[32]

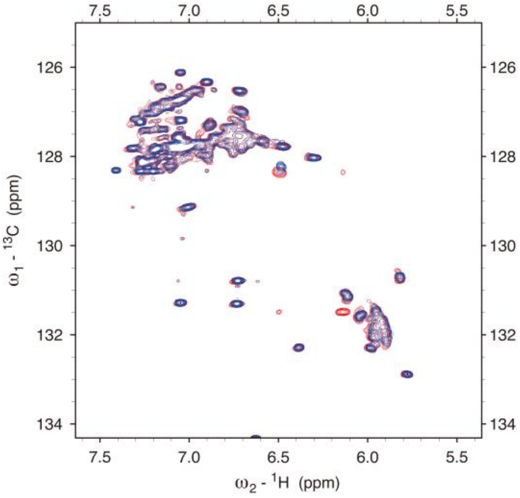


Figure 10. ^{1}H–^{13}C HSQC NMR spectra (700 MHz) in CD_2Cl_2 of poly(PA) obtained by the polymerization quenched with CH_3CO_2H (red) and CH_3CO_2D (blue).

samples furthermore clearly indicate the presence and absence of an H_a signal in the polymers quenched with CH_3CO_2H and CH_3CO_2D, respectively (Figure 10).

Conclusion

In this chapter, we elucidated the structure of [(nbd)Rh{C(Ph)=CPh$_2$}(PPh$_3$)] (**1**) by ^{1}H, ^{13}C and ^{31}P NMR spectroscopy, and single crystal X-ray analysis. ^{31}P NMR spectroscopic analysis and DFT calculations revealed the presence of two stable conformational isomers with a dihedral angle ϕ at the P–Rh–C=C atoms of 90° and 270°, one of which was confirmed by single crystal X-ray analysis (ϕ = 80.5°). The reaction of **1** with CH_3CO_2H was carried out as a model reaction for studying the CH_3CO_2H-quenching of PA polymerization catalyzed by **1**. The formation of triphenylethylene was observed together with the formation of Rh complex **2**, which was coordinated by nbd, CH_3CO_2– and PPh_3, indicating the replacement of the end-group Rh moiety with a proton by its quenching with CH_3CO_2H. In addition, poly(PA)s with H and D end groups were obtained by the polymerization of PA using **1** as a catalyst and subsequent quenching with CH_3CO_2H and CH_3CO_2D, respectively. Their structures were reliably confirmed by MALDI-TOF mass spectrometry, ^1H and ^1H–^{13}C HSQC NMR spectroscopy. The cis-insertion of PA between the Rh center and C(Ph)=CPh_2 was confirmed by determination of the ^1H NMR coupling constant of the two vinylene protons at the polymer ends. To our knowledge, the present study is the first successful end-group analysis of polyacetylenes based on MALDI-TOF mass spectrometry.

Experimental

Instrumentation. X-ray crystal structure data was collected on a Rigaku RAXIS RAPID imaging plate area detector with graphite monochromated Mo Kα radiation (λ = 0.71075 Å). Crystals of suitable size were mounted on a nylon loop and then transferred to a goniostat for characterization and data collection. The structure was solved by direct methods and expanded using Fourier techniques. All calculations were performed using the crystallographic software package of Rigaku Corporation and Rigaku/MSC CrystalStructure version 3.7. ^{1}H (400 or 700 MHz), ^{13}C (100 MHz), ^{1}H–^{13}C heteronuclear single quantum coherence (HSQC) and ^{31}P NMR (162 MHz) spectra were recorded on a JEOL EX-400, AL-400 or BRUKER DRX-700 spectrometer. Polymers were isolated by preparative high performance liquid chromatography (HPLC) on JAIGEL-1H and JAIGEL-2H. Number and weight-average molecular weights (M_n and M_w) were determined by size exclusion chromatography (SEC) on a JASCO PU-980/RI-930 chromatograph, using a KF-805 (Shodex) × 3 column with a molecular weight limit of 4×10^6 calibrated with polystyrene standards, and using THF as the eluent (column temperature 40 °C, flow rate 1 mL/min). MALDI-TOF mass spectra were recorded on a Bruker Daltonics ultraflex III TOF/TOF equipped with a 355 nm YAG laser in reflectron mode and using an acceleration voltage of 25 kV. Samples for MALDI-TOF mass spectrometry were prepared from a CH_2Cl_2 solution by mixing the sample (10 mg/mL) in a volume ratio of 1:100:1 with the matrix *trans*-2-[3-(4-*tert*-butylphenyl)-2-methyl-2-propenylidene]malononitrile (20 mg/mL), and $AgOCOCF_3$ (2 mg/mL), respectively. All mass differences were calculated by comparing mass values of two base peaks (the peak of most populated isotopomers). GC-mass spectra were recorded on an Agilent Technologies GC/MS HP-6890 or a JEOL JMS-700. The injector temperature and GC/MS interface temperature were set at 230 and 260 °C, respectively, and helium was used as a carrier gas (1 mL/min). Chromatographic separation was achieved using a GL sciences GC capillary column (30-meter-long InertCap

5MS/Sil, 0.25 mm i.d., 0.25 μm film thickness). The column temperature was maintained at 70 °C for 2 min, raised to 320 °C at 20 °C/min, and then kept at 320 °C for 30 min. The operation was carried out at a mass resolution of 1,000 (for low resolution measurements) and 5,000 (for high resolution measurements), while the electron ionization energy was 70 eV with an ion-source temperature of 260 °C.

Materials. Unless otherwise stated, reagents and solvents were purchased and used without purification. The polymerization catalyst [(nbd)Rh{C(Ph)=CPh$_2$}(PPh$_3$)] (**1**) was synthesized by reaction of [(nbd)RhCl]$_2$, [MgBr{C(Ph)=CPh$_2$}] with PPh$_3$ following a literature method.[5,6,21,39] PA (Aldrich) was distilled over CaH$_2$ under reduced pressure before use. Toluene used for the polymerization was distilled over CaH$_2$ immediately before use.

Polymerization. A typical procedure was as follows: a solution of **1** (71 mg, 0.10 mmol) and PPh$_3$ (262 mg, 1.0 mmol) in toluene (1.89 mL) was fed under argon into a glass tube equipped with a three-way stopcock. PA (0.11 mL, 1.0 mmol) was added to the solution, and the resulting mixture was stirred at 30 °C for 1 h. CH$_3$CO$_2$H (0.57 mL, 10 mmol) was added, and the resulting mixture was stirred at room temperature for 10 min to quench the reaction. The solution was poured into methanol (50 mL) to precipitate the polymer. The yellow precipitate was filtered and dried under vacuum at room temperature for several hours. The polymer was purified by preparative HPLC (for details see instrumentation section). The polymer sample was finally freeze-dried from a benzene solution to remove the solvent.

Computation. All calculations were performed with the GAUSSIAN 09 program[40] running on the supercomputer system of the Academic Center for Computing and Media Studies, Kyoto University. The density functional theory (DFT)[24] method with Becke's three-parameter hybrid functional,[41] and the LYP correlation functional (B3LYP)[25] were utilized in conjunction with the LANL2DZ basis set to fully optimize geometries.[26]

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(27) In some instances the increments were 30° because of the unsuccessful structure optimization of some conformers.

(28) The ^{31}P NMR chemical shift of the conformer with $\phi = 270°$ is predicted by the GIAO method to be 0.0014 ppm higher than that of the conformer with $\phi = 90°$.

(29) The ^{31}P NMR chemical shift of **2** (both square planar and square pyramid) was calculated to be 2.1 ppm lower than that of **1** ($\phi = 90°$) by the GIAO method. This value well agrees with the observed ones (2.1–2.6 ppm, shown in Figures 1 and 4).

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List of Publications

Chapter 1

"Synthesis of End-Functionalized Poly(phenylacetylene)s with Well-Characterized Palladium Catalysts"

Shiotsuki, M.; Nakagawa, A.; Rodriguez Castanon, J.; Onishi, N.; Kobayashi, T.; Sanda, F.; Masuda, T.

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

Chapter 2

"Synthesis of End-Functionalized Polyacetylenes Bearing Polar Groups Employing Well-Defined Pd Catalysts"

Rodriguez Castanon, J.; Kuwata, K.; Shiotuki, M.; Sanda, F.

Chem. Eur. J. **2012**, *18*, 14085–14093.

Chapter 3

"A New Approach to the Polymerization of Disubstituted Acetylenes by Bulky Monophosphine-Ligated Palladium Catalysts"

Rodriguez Castanon, J.; Sano, N.; Shiotuki, M.; Sanda, F.

ACS Macro Lett. **2013**, *on press*, DOI: 10.1021/mz400562m.

Chapter 4

"Synthesis of Poly(1-chloro-2-arylacetylene)s with High *cis*-Content and Examination of Their Properties"

Rodriguez Castanon, J.; Shiotsuki, M.; Sanda, F.

Under preparation

Chapter 5

"Characterization of the Polymerization Catalyst [(2,5-norbornadiene)Rh{C(Ph)=CPh_2}(PPh_3)] and Identification of the End Structures of Poly(phenylacetylenes) Obtained by Polymerization Using This Catalyst"

Kumazawa, S.; Rodriguez Castanon, J.; Onishi, N.; Kuwata, K.; Shiotsuki, M.; Sanda, F.
Organometallics, **2012**, *31*, 6834–6842.

Other Publications Not Included in This Thesis

"Control of the Helical Sense by Changing the Ratio of a Chiral Amine to an Achiral Rhodium Complex in Helix-Sense-Selective Polymerization of a Phenylacetylene Having Two Hydroxyl Groups"
Zhang, G.; Aoki, T.; Teraguchi, M.; Kaneko, T.; Rodriguez Castanon, J.; Shiotsuki, M.; Sanda, F.
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