A Journal of the Gesellschaft Deutscher Chemiker
Angewandte Chemie
International Edition
www.angewandte.org

Accepted Article

Title: Revisiting the Polymerization of Diphenylacetylenes with Tungsten(VI) Chloride and Tetraphenyltin: An Alternative Mechanism by a Metathesis Catalytic System

Authors: Mami Miyairi, Tsuyoshi Taniguchi, Tatsuya Nishimura, and Katsuhiro Maeda

To be cited as: *Angew. Chem. Int. Ed.* 10.1002/anie.202005964

Link to VoR: https://doi.org/10.1002/anie.202005964

WILEY-VCH

Revisiting the Polymerization of Diphenylacetylenes with Tungsten(VI) Chloride and Tetraphenyltin: An Alternative Mechanism by a Metathesis Catalytic System

Mami Miyairi,[a] Tsuyoshi Taniguchi,*[a] Tatsuya Nishimura,[a] and Katsuhiro Maeda*[a],[b]

[a] M. Miyairi, Dr. T. Taniguchi, Prof. Dr. Tatsuya Nishimura, Prof. Dr. Katsuhiro Maeda
Graduate School of Natural Science and Technology
Kanazawa University
Kakuma-machi, Kanazawa 920-1192 (Japan)
E-mail: tsuyoshi@p.kanazawa-u.ac.jp
E-mail: maeda@se.kanazawa-u.ac.jp
[b] Prof. Dr. Katsuhiro Maeda
Nano Life Science Institute (WPI-NanoLSI)
Kanazawa University
Kakuma-machi, Kanazawa 920-1192 (Japan)

Supporting information for this article is given via a link at the end of the document.

Abstract: An alternative reaction mechanism of the polymerization of diphenylacetylelnes using a catalytic system composed of tungsten(VI) chloride and tetraphenyltin has been proposed through the optimization of reaction conditions and investigation of the effect of the electronic nature of diphenylacetylene monomers on the polymerizability. The detailed structures of the polymers have been suggested by mass spectrometric analysis of the obtained polymers and oligomers, which suggested that a phenyl group of tetraphenyltin has been introduced to an initiating end of the polymer chain. Mass spectrometric analysis also provided information about the termination processes of the polymerization. The experimental results strongly suggested that the polymerization of diphenylacetylenes using tungsten(VI) chloride and tetraphenyltin proceeds through a migratory insertion mechanism rather than the long-accepted metathesis mechanism.

Introduction

A catalytic system composed of tungsten(VI) hexachloride (WCl_6) and alkylating reagent, such as alkyl aluminum, alkyl lithium, alkyl magnesium or alkyl tin reagent, is one of the pioneering catalytic systems for olefin metathesis reactions.[1] Tungsten carbenoid complexes have been identified as active species inducing metathesis reactions, and they can be formed by α-hydrogen atom elimination of alkylated tungsten(VI) species generated from the catalytic system.[1d] In current organic synthesis, such an “ill-defined” catalytic system has been replaced by more useful “well-defined” metal carbenoid complexes such as Schrock and Grubbs catalysts as metathesis catalysts.[2] However, an ill-defined catalytic system with tungsten(VI) chloride is still used for the polymerization of disubstituted acetylenes such as diphenylacetylenes because well-defined carbenoid complexes are often inefficient catalysts in such a polymerization due to a steric factor.[3]

Poly(diphenylacetylene)s are potential π-conjugated polymers as functional materials in practical use because they have excellent thermal stability, mechanical properties and photochemical resistance and they exhibit good photoluminescent properties even in a solid state, high gas permeability, and liquid crystallinity.[4] Moreover, poly(diphenylacetylene)s carrying optically active pendants have been reported to form a preferred-handed helical conformation and show a good circularly polarized luminescence (CPL) property and chiral recognition ability as a chiral stationary phase for HPLC or an enantioselective menbrane owing to the helical chirality.[5]

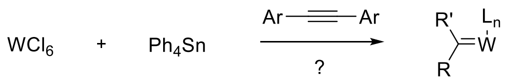
A catalytic system composed of WCl_6-Ph_4Sn is often used for the polymerization of diphenylacetylene.[3] As an analog, the $TaCl_5$-$^{n}Bu_4Sn$ system works as a catalyst to induce polymerization of diphenylacetylenes.[3] However, the $TaCl_5$-$^{n}Bu_4Sn$ system is often inefficient in polymerization of diphenylacetylenes having electron-withdrawing polar functional groups such as esters.[5d,g,6,7] Even in such a case, the WCl_6-Ph_4Sn system induces the polymerization but often suffers from low molecular weights and low yields of obtained polymers.

A sensible metathesis mechanism has been proposed in the polymerization of diphenylacetylenes using the WCl_6-Ph_4Sn system (Figure 1b) because this system and its related systems are pioneering catalysts of olefin metathesis reactions as aforementioned.[1] However, it is unclear how metal carbenoids that induce the polymerization of diphenylacetylenes are formed from the WCl_6-Ph_4Sn system (Figure 1a). If $^{n}Bu_4Sn$ is used instead of Ph_4Sn as a co-catalyst, tungsten carbenoid $^{n}PrCH{=}WCl_4$ might be formed by α-proton elimination of $^{n}BuWCl_5$ formed by transmetallation between WCl_6 and $^{n}Bu_4Sn$ as aforementioned.[1d,2a] However, this is not the case in the WCl_6-Ph_4Sn system because there is no α-proton in $PhWCl_5$ formed by transmetallation between WCl_6 and Ph_4Sn. Tungsten vinylidene complexes might be formed by 1,2-migration of a carbon substituent of a tungsten–alkyne complex formed in the presence of an acetylene monomer. The formation of vinylidene complexes is likely in the tungsten-catalyzed polymerization of terminal alkynes such as phenylacetylene because 1,2-hydrogen atom migration of tungsten–alkyne complexes could easily occur.[8,9] On the other hand, there are only limited examples of metal vinylidene complexes from diphenylacetylenes.[10] Otherwise, Ph_4Sn might work as a reducing reagent to generate an active

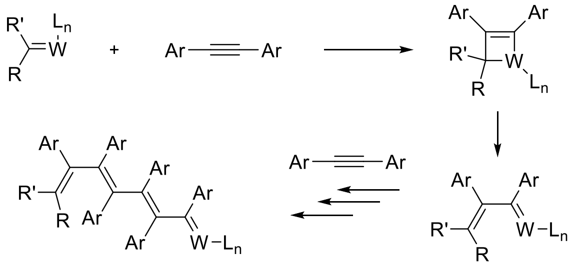
10.1002/anie.202005964

metathesis catalyst which might be a tungsten(IV) species formed by double transmetallation between WCl_6 and Ph_4Sn followed by reductive elimination.[1c,f,h,8b] In any case, there is very poor evidence of the formation of tungsten carbenoid species or any species that induce a metathesis reaction in the polymerization of diphenylacetylenes with WCl_6-Ph_4Sn.

(a) Unclear formation of tungsten carbenoid species



(b) Metathesis polymerization of diphenylacetylenes



(c) Structure of a poly(diphenylacetylene) synthesized with WCl_6-Ph_4Sn

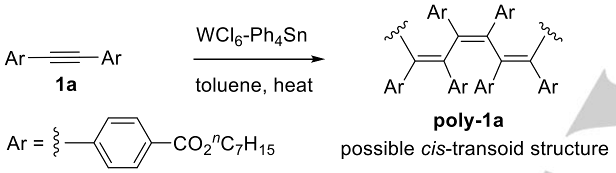


Figure 1. Unclear formation of an active metathesis catalyst from WCl_6-Ph_4Sn (a), a proposed metathesis mechanism of the polymerization of diphenylacetylenes (b) and the polymerization of **1a** with WCl_6-Ph_4Sn and the possible *cis*-transoid structure of **poly-1a** (c).

Very recently, we have reported the synthesis of one-handed helical poly(diphenylacetylene)s bearing carboxy groups based on macromolecular helicity induction through noncovalent interaction with chiral amines and its subsequent memory of the helicity, as well as their detailed helical structures including the main-chain configuration (*cis* or *trans*) and conformation (*cisoid* or *transoid*) and also the absolute helical handedness (right- or left-handed helix) and its helix-sense excess.[11] In that study, a symmetrically substituted poly(diphenylacetylene) bearing carboxy groups was synthesized by polymerization of the diphenylacetylene monomer **1a** having ester groups at the *para*-positions using WCl_6-Ph_4Sn followed by hydrolysis of the ester groups in the obtained poly-**1a** (Figure 1c).[5g,11] Various spectroscopic analyses of the obtained polymers combined with theoretical calculations suggested that the obtained poly(diphenylacetylene)s have a highly *cis*-stereoregular (*cis*-transoidal) structure. However, it is difficult to clearly rationalize such a high *cis*-stereoregularity from the viewpoint of the polymerizatin reaction of diphenylacetylenes through a methathesis mechanism.

Therefore, we decided to reinvestigate the polymerization of diphenylacetylenes using tungsten(VI) chloride and Ph_4Sn to elucidate the polymerization mechanism through the optimization of polymerization conditions. In this paper, we describe the improvement of tungsten-catalyzed polymerization of diphenylacetylenes and structural elucidation of the obtained poly(diphenylacetylene)s, and we propose an alternative to the metathesis polymerization mechanism based on experimental results.

Results and Discussion

Investigation of Reaction Conditions and Monomers in the Polymerization

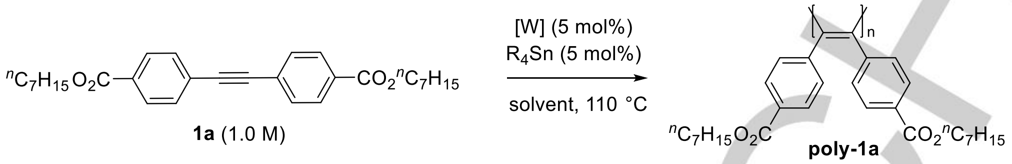
First, we reinvestigated the polymerization of diphenylacetylene **1a** using 5 mol% of WCl_6-Ph_4Sn (1:1). The polymerization was conducted by heating a mixture of monomer **1a** and catalysts in toluene at 110 °C. The corresponding polymer **poly-1a** with a low molecular weight was obtained in a low yield (entry 1, Table 1), whereas we previously obtained **poly-1a** with a higher molecular weight (M_n = 1.3–1.5 × 10^4) in a good yield (~80%) under similar conditions.[5g,11] These results indicate that the reproducibility of the polymerization of diphenylacetylenes with WCl_6-Ph_4Sn is low or moderate.[13] Replacement of the solvent with chlorobenzene did not affect the results (entry 2). Polar solvents such as 1,4-dioxane could not be used for the polymerization due to deactivation of the catalyst. However, we found that the replacement of WCl_6 with tungsten(VI) oxychloride ($WOCl_4$) significantly improved the results in terms of yield and molecular weight of **poly-1a** (entries 3 and 4) and the reproducibility of the polymerization using $WOCl_4$ instead of WCl_6 was very good.[13] The replacement of Ph_4Sn with more electron-rich 4-methylphenyl and 4-methoxyphenyl derivatives gave good results (entries 5 and 6), whereas the polymerization hardly proceeded when an electron-deficient 4-trifluoromethylphenyl derivative was used instead of Ph_4Sn (entry 7). Clearly, these results suggest that the electronic nature of the co-catalyst affects the polymerization. $^nBu_4Sn$ did not work as a good co-catalyst (entry 8), and this result is similar to that of previous reports for the polymerization of diphenylacetylenes.[6] The use of twice the amount of Ph_4Sn [$WOCl_4$-Ph_4Sn (1:2)] significantly inhibited the polymerization, indicating that the present polymerization is sensitive to the amount of a co-catalyst (entry 9). In previous works, a mixture of WCl_6 and Ph_4Sn was often aged in a solvent prior to the polymerization,[5,6,8b] but this "aging" procedure did not work in the polymerization of **1a** using WCl_6 and $WOCl_4$ (entries 10 and 11). Polymerization at a lower temperature (80 °C) resulted in lower yield and lower molecular weight of the polymer (entry 12).

Next, we applied the $WOCl_4$-Ph_4Sn system to other representative diphenylacetylene monomers (Table 2). First, we tested the polymerization of asymmetrically substituted diphenylacetylenes analogues **1b** and **1c** having a bromo atom and a trifluoromethyl group instead of an ester group, respectively. Both polymerizations were readily completed under the standard conditions (the same conditions as those shown in entry 3 in Table 1) and gave the corresponding polymers **poly-1b** and **poly-1c** in good yields (entries 2 and 3). On the other hand, the polymerization of asymmetrically substituted diphenylacetylene analogue **1d** omitting an ester group from **1a** was not completed even after 24 h under the standard conditions, and **poly-1d** having a low molecular weight was obtained in a low yield (entry 4). However, we found that the use of twice the amount of Ph_4Sn (10 mol%) improved the result unlike the polymerization of **1a** (entry 5). The polymerization of diphenylacetylene **1e** having a *p*-

10.1002/anie.202005964

alkoxy group was sluggish under the conditions using 5 and 10 mol% of Ph_4Sn (entries 6 and 7), but the use of an increased amount of Ph_4Sn (20 mol%) afforded the corresponding polymer **poly-1e** in a good yield (entry 8). Similarly, **1f** having a *p*-alkoxy group readily polymerized under the condition using 20 mol% of Ph_4Sn, and **poly-1f** was obtained in a good yield (entry 9). These results suggest that the polymerization is greatly affected by the electronic nature of diphenylacetylene monomers and the amount of Ph_4Sn used.

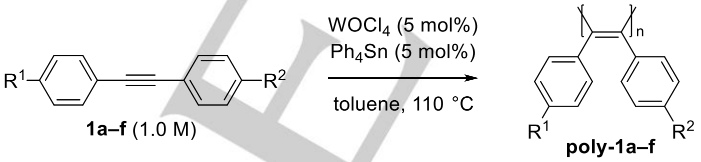
Table 1. Polymerization Results of Diphenylacetylene **1a**.[a]



Entry	[W]	R in R_4Sn	solvent	**poly-1a**		
				Yield [%][b]	M_n[c]	M_w/M_n[c]
1	WCl_6	Ph	toluene	11	8,000	1.35
2	WCl_6	Ph	PhCl	17	7,700	1.37
3	$WOCl_4$	Ph	toluene	91	21,900	1.71
4	$WOCl_4$	Ph	PhCl	89	19,500	1.60
5	$WOCl_4$	4-Me-Ph	toluene	86	21,200	1.67
6	$WOCl_4$	4-MeO-Ph	toluene	89	27,600	1.48
7	$WOCl_4$	4-CF_3-Ph	toluene	<5	6,100	1.14
8	$WOCl_4$	^{n}Bu	toluene	<5	9,400	1.36
9[d]	$WOCl_4$	Ph	toluene	16	7,400	1.33
10[e]	WCl_6	Ph	toluene	18	7,100	1.40
11[e]	$WOCl_4$	Ph	toluene	<5	6,300	1.17
12[f]	$WOCl_4$	Ph	toluene	48	15,800	1.95

[a] Conditions: **1a** (2 mmol), [W] (0.1 mmol), R_4Sn (0.1 mmol) in solvent (2 mL) for 5–24 h at 110 °C in a sealed tube. [b] Yield obtained from MeOH–THF (3:1)-insoluble fraction. [c] Determined by SEC based on polystyrene standards (THF, 40 °C). [d] 10 mol% of Ph_4Sn was used. [e] A mixture of a tungsten catalyst and Ph_4Sn in toluene was stirred for 10 min at room temperature before addition of monomer **1a**. [f] At 80 °C.

Table 2. Polymerization Results of Various Diphenylacetylenes **1a–f**.[a]



Entry	R^1	R^2	**1**	**poly-1a–f**		
				Yield [%][b]	M_n[c]	M_w/M_n[c]
1[d]	$CO_2{}^nC_7H_{15}$	$CO_2{}^nC_7H_{15}$	**1a**	91	21,900	1.71
2	$CO_2{}^nC_7H_{15}$	Br	**1b**	70	29,300	4.26
3	$CO_2{}^nC_7H_{15}$	CF_3	**1c**	74	26,800	1.78
4	$CO_2{}^nC_7H_{15}$	H	**1d**	26	4,700	1.33
5[e]	$CO_2{}^nC_7H_{15}$	H	**1d**	56	14,000	1.59
6	OMe	$^nC_5H_{11}$	**1e**	13	7,900	1.68
7[e]	OMe	$^nC_5H_{11}$	**1e**	38	8,500	2.55
8[f]	OMe	$^nC_5H_{11}$	**1e**	63	10,800	2.20
9[f]	$O^nC_8H_{17}$	H	**1f**	72	12,000	2.53

[a] **1a–f** (2 mmol), $WOCl_4$ (0.1 mmol), Ph_4Sn (0.1 mmol) in toluene (2 mL) for 6–24 h at 110 °C in a sealed tube. [b] Yield obtained from MeOH-THF (3:1)-insoluble fraction. [c] Determined by SEC based on polystyrene standards (THF, 40 °C). [d] The same data shown in Entry 3 in Table 1. [e] 10 mol% of Ph_4Sn was used. [f] 20 mol% of Ph_4Sn was used.

Characterization of Poly(diphenylacetylene)s

To get information on the structures of the obtained poly(diphenylacetylene)s, we performed MALDI-TOF-MS analysis (DIT+NaCl) of **poly-1** having a low molecular weight (M_n = 2,880, M_w/M_n = 1.14) obtained by polymerization with the $WOCl_4$-Ph_4Sn system. A series of peaks having a 462 u difference corresponding to a monomer unit was observed up to *m/z* 4,000 in the HRMS spectrum (Figure 2a). Representatively, the molecular ion at *m/z* 3334.9544 corresponds to $C_{216}H_{270}O_{28}Na^+$ $[M + Na]^+$ (calcd, 3334.9596) and would be composed of 7-mer of **1a** ($C_{210}H_{266}O_{28}$) and an additional C_6H_4 unit. This suggests that a terminal structure of the polymer has a phenyl group (C_6H_5), but a hydrogen atom (H) is somehow lost from the polymer structure. The loss of a hydrogen atom suggests an oxidation process is somewhere involved in the reaction, but two hydrogen atoms are lost in a typical oxidation

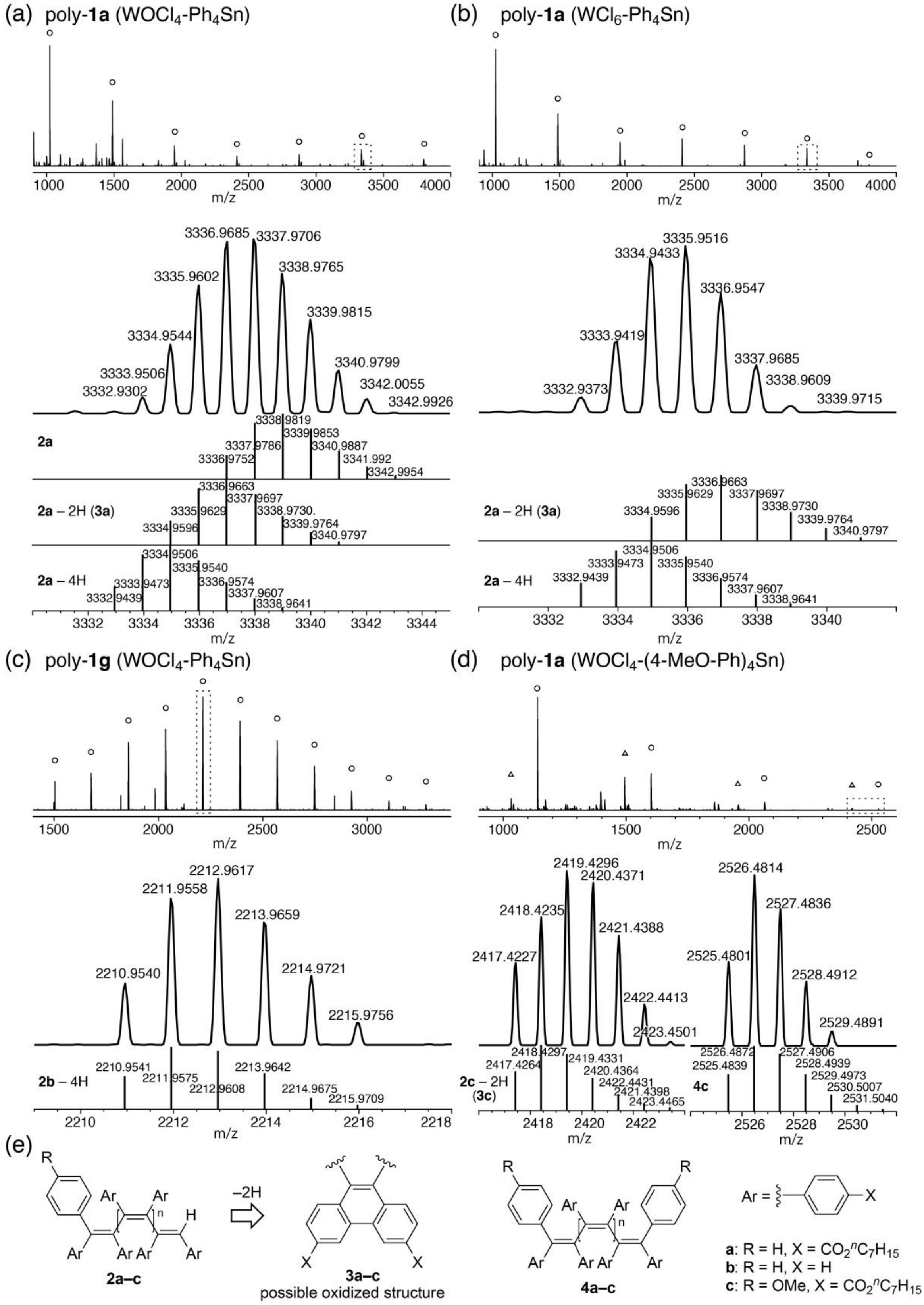


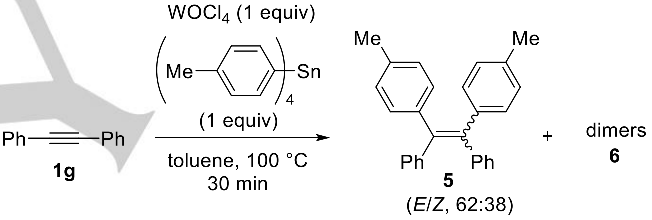
Figure 2. MALDI-TOF-MS spectra of **poly-1a** (a, b, d) and **poly-1g** (c) and their proposed structures **2**–**4** (e). (a) **poly-1a** ($WOCl_4$-Ph_4Sn) corresponding to **2a**, **2a** – 2H and **2a** – 4H (b) **poly-1a** (WCl_6-Ph_4Sn) corresponding to **2a** – 2H and **2a** – 4H, (c) **poly-1g** ($WOCl_4$-Ph_4Sn) corresponding to **2b** – 4H, (d) **poly-1a** ($WOCl_4$-(4-MeO-Ph)$_4$Sn) corresponding to **2c** – 2H (△) and **4c** (◯).

process. This suggests that the primary structure of the polymer is **2a** having a hydrogen atom at another terminal end, but an oxidative coupling between two aromatic rings of the polymer would compete to give the structure including a phenanthrene ring **3a**. We also performed MALDI-TOF-MS analysis (DCTB + NaCl) of **poly-1a** (M_n = 2,500, M_w/M_n = 1.19) synthesized with the WCl_6-Ph_4Sn system and observed a similar series of peaks based on the polymer. However, each molecular ion indicated that four hydrogen atoms were lost from the structure **2a**. Representatively, the molecular ion at *m/z* 3332.9373 corresponds to $C_{216}H_{268}O_{28}Na^+$ [M + Na]$^+$ (calcd, 3332.9439) and would be composed of 7-mer of **1a** ($C_{210}H_{266}O_{28}$), a phenyl group (C_6H_5) and a terminal hydrogen atom (H), but there are four hydrogen atoms missing (4H) (Figure 2b). This clearly indicates that further oxidative coupling occurred at another site when the WCl_6-Ph_4Sn system was used probably because WCl_6 is a stronger oxidant than $WOCl_4$. With this information in hand, we scrutinized the HRMS spectrum of the case of the $WOCl_4$-Ph_4Sn system again, and the isotope distribution of each molecular ion was slightly different from that of the calculation as shown in Figure 2a, indicating a mixture of **2a** and their oxidized structures (**2a** – 2H (**3a**) and **2a** – 4H).

For comparison, simple poly(diphenylacetylene) (**poly-1g**) (M_n = 1,900, M_w/M_n = 1.16) was prepared from diphenylacetylene (PhC≡CPh, **1g**) with the $WOCl_4$-Ph_4Sn system,[14] and MALDI-TOF-MS analysis (DIT) was performed. A series of peaks having a 178 u difference corresponding to a monomer unit was clearly observed up to *m/z* 3,500 in the HRMS spectrum, and the representative molecular ion at *m/z* 2210.9540 corresponds to $C_{174}H_{122}^+$ [M]$^+$ (calcd, 2210.9541) (Figure 2c). This would be composed of 12-mer of **1g** ($C_{204}H_{120}$), a phenyl group (C_6H_5) and a terminal hydrogen atom (H), and there are four hydrogen atoms missing (4H), indicating the over-oxidized structure **2b** – 4H similar to that of **poly-1a** synthesized with WCl_6-Ph_4Sn. Probably, oxidative coupling was promoted even with the $WOCl_4$-Ph_4Sn system because phenyl groups of **poly-1g** are more electron-rich than those of **poly-1a** having an ester group.

We presumed that the origin of the phenyl group would be Ph_4Sn used as a co-catalyst. Therefore, we focused on mass spectrometric analysis of **poly-1a** synthesized using (4-MeO-Ph)$_4$Sn instead of Ph_4Sn to check if a 4-methoxyphenyl group was similarly introduced to the polymer. In MALDI-TOF-MS analysis (DCTB) of **poly-1a** (M_n = 2,100, M_w/M_n = 1.11), a series of peaks having a 462 u difference that was identified as structure **2c** – 2H (**3c**) was detected (Figure 2d). Representatively, the molecular ion at *m/z* 2417.4227 corresponds to $C_{157}H_{196}O_{21}^+$ [M]$^+$ (calcd, 2417.4264) and would be composed of 5-mer of **1a** ($C_{150}H_{190}O_{20}$) and an additional C_7H_6O unit corresponding a 4-methoxyphenyl group (C_7H_7O) minus a hydrogen atom (H) (in other words, C_7H_7O + H – 2H). In this spectrum, another series of peaks was detected and a representative peak at *m/z* 2525.4801 corresponds to $C_{164}H_{204}O_{22}^+$ [M]$^+$ (calcd, 2525.4839) composed of 5-mer of **1a** ($C_{150}H_{190}O_{20}$) and an additional $C_{14}H_{14}O_2$ unit (Figure 2d). This additional unit corresponds to two 4-methoxyphenyl groups (C_7H_7O × 2), suggesting that the structure **4c** has 4-methoxyphenyl groups at both polymer ends. Interestingly, a molecular ion indicating the loss of a hydrogen atom from **4c** was not detected. These results indicate that the polymerization of diphenylacetylenes using the $WOCl_4$-Ph_4Sn system is initiated by the addition of a phenyl group to a triple bond from Ph_4Sn and has at least two possible termination processes to form a cyclic structure or a structure capped by a phenyl group. As another supportive fact, small signals tentatively assigned as methyl and methoxy groups were observed in ^{1}H NMR spectra of **poly-1a** synthesized with (4-Me-Ph)$_4$Sn (Entry 5 in Table 1) and (4-MeO-Ph)$_4$Sn (Entry 6 in Table 1), respectively (see the Supporting Information).

To confirm that a phenyl group is introduced to the polymer initiating end from Ph_4Sn, we tested the reaction of diphenylacetylene (**1g**) with stoichiometric amounts of $WOCl_4$ and (4-Me-Ph)$_4$Sn (Scheme 1). The starting diphenylacetylene was fully consumed by heating the mixture in toluene at 100 °C for 30 min, and 1,2-diphenyl-1,2-di-*p*-tolylethene (**5**) as a mixture of geometrical isomers was isolated along with mixtures of dimers **6**, though the reaction was somewhat complex due to production of oligomers. Both isomers of compound **5** are known compounds, and the spectral data accorded with those of a previous report.[15] Production of **5** clearly indicates that one of the phenyl groups in Ph_4Sn is introduced to an initiating end of the poly(diphenylacetylene)s synthesized with tungsten(VI) chloride and Ph_4Sn. Dimers **6** could not be isolated as pure forms, but mass spectrometric analysis of the mixture of dimers **6** indicated the production of structures similar to **2b**, **3b** and **4b** (see Figures S3 and S4). These products suggest the involvment of a migratory insertion in the reaction.



Scheme 1. The stoichiometric reaction of diphenylacetylene (**1g**) and $WOCl_4$-(4-Me-Ph)$_4$Sn.

Discussion of the Polymerization Mechanism

The experimental results are inconsistent with the metathesis polymerization mechanism shown in Figure 1b, and we therefore propose a new polymerization mechanism involving a migratory insertion reaction as shown in Figure 3. First, the starting tungsten(VI) chloride WCl_6 or $WOCl_4$ is converted to phenylated tungsten(VI) species **7** or **8**, respectively, by a transmetallation process with Ph_4Sn (Figure 3a).[1f,8b] The degree of phenylation would depend on the amount of Ph_4Sn used.

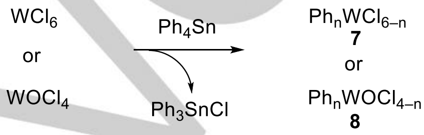
Since the experimental results indicated that a phenyl group was introduced to the initiating end of the polymer chain, the polymerization of diphenylacetylenes would be initiated by a 1,2-insertion reaction of phenylated tungsten(VI) species **7** or **8** to a triple bond of a monomer to form alkenyltungsten(VI) species **9** (Figure 3b).[16] Subsequently, the chain would propagate from **9** by repetition of the 1,2-insertion reaction to the monomer. Masuda and coworkers reported that the metathesis polymerization of diphenylacetylenes using a well-defined ruthenium carbene complex (Grubbs-Hoveyda catalyst) gave a polymer having a backbone structure different from that of the polymer synthesized using the WCl_6-Ph_4Sn system.[17] This might be rationalized by a difference of the polymerization mechanism. Since organometallic 1,2-insertion to multiple bonds typically occurs in a *syn*-selective manner,[18] the backbone of the resultant polymer would have a *cis*-rich structure from a mechanistic viewpoint, and this is consistent with our recent report.[11] The moderate *E*-selectivity in production of compound **5** from **1g** might be the result of isomerization of the primary product by $WOCl_4$ as a Lewis acid or HCl formed in situ under the heating conditions. However, this result of geometrical selectivity in compound **5** could not be simply applied to the structure of the polymer because the rigid internal polyene backbone of the polymer might have a higher registance to geometrical isomerization by acids. Structures **2a**–**c** and **3a**–**c** suggested by mass spectrometric analysis of the polymer indicate two possible termination processes in the polymerization (Figure 3c and 3d). The phenanthrene structure **3a**–**c** could be formed by intramolecular oxidative coupling between two aromatic rings by the tungsten(VI) species **12** at the propagating chain end (R' = polymer) and/or external ones (R' = Cl or Ph) because tungsten(VI) chloride derivatives could oxidize aromatic compounds via single electron transfer due to a high oxidation potential.[19,20] In addition, hydrogen chloride (HCl) generated by this redox process would protonate an active tungsten(VI) species **10** to give polymer **2** having a hydrogen atom at the terminal end. The second termination process would be caused by reductive elimination of the tungsten(VI) species **13** having a phenyl group(s) at the propagating chain end to form the end-capped polymer **4** and reduced tungsten(IV) species (Figure 3d). The tungsten(VI) species **13** could be formed when the polymerization was induced from tungsten(VI) species having multiple phenyl groups or when a chloride on tungsten(VI) species **12** at the propagating chain end is replaced with a phenyl group by transmetallation with unreacted Ph_4Sn. Compound **5** in Scheme 1 would be produced from **9** by this mechanism.

Since a molecule oxidized from the end-capped polymer **4** was not detected in the mass spectrometric analysis, the primary redox reaction shown in Figure 3c might occur via intramolecular electron transfer processes of **10** at the propagating chain end, and oxidative aromatic coupling and protonation would follow. On the other hand, further oxidation would be an intermolecular process when it occurs (e.g., WCl_6-Ph_4Sn system or polymerization of PhC≡CPh).

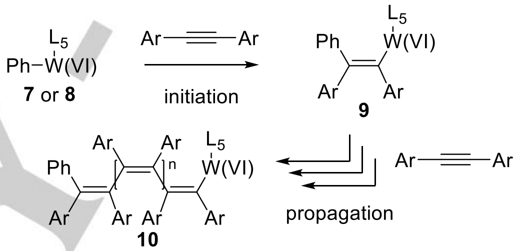
Given the proposed mechanism, we suggest the reason why the use of $WOCl_4$ improved the results of polymerization of diphenylacetylene and the reproducibility. Probably, termination by the redox process becomes a serious problem due to the high oxidation potential of WCl_6 (Figure 3c), and the use of $WOCl_4$ could suppress the termination because the oxidation potential of $WOCl_4$ is lower than that of WCl_6.[21] This is consistent with the results of mass spectrometric analysis of **poly-1a** synthesized with $WOCl_4$-Ph_4Sn and WCl_6-Ph_4Sn because over-oxidation of polymer side chains was suggested in the latter catalytic system (Figure 2a and 2c).

The termination process by the redox reaction could also explain why the polymerization is sensitive to the amount of Ph_4Sn used as the co-catalyst depending on monomers (Tables 1 and 2). Strongly electron-deficient monomers such as **1a**–**c** were readily polymerized under the conditions using the smallest amount of Ph_4Sn (5 mol%) (entries 1–3 in Table 2), and the use of a larger amount of Ph_4Sn resulted in low monomer conversion (entries 3 and 9 in Table 1). On the other hand, this tendency reverses in the polymerization of electron-richer monomers such as **1d**–**f** (entries 4-9 in Table 2). The rate of the redox reaction would depend on the electron density of aromatic rings of **11** and tungsten(VI) species **12**. In the case of electron-rich monomers, undoubtedly, the termination process by the intramolecular oxidative aromatic coupling reaction would become a serious problem because electron-rich aromatic rings have a lower oxidation potential. Indeed, promotion of oxidative aromatic coupling was suggested in the mass spectrometric analysis of simple poly(diphenylacetylene) (Figure 2c). Therefore, multi-phenylated tungsten(VI) species, which could be formed in the presence of an increased amount of Ph_4Sn, could suppress the termination process by oxidative aromatic coupling reactions because such a chloride-less species would be a milder oxidant than mono-phenylated tungsten(VI) species. In this case, however, it should be noted that another termination process by an end-capping reaction might be a problem due to the use of excess amounts of Ph_4Sn (Figure 3d).

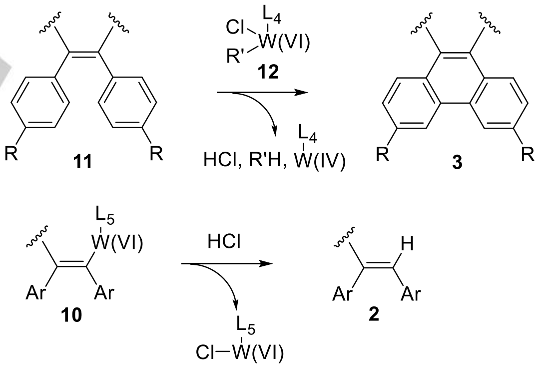
(a) Formation of phenylated tungsten(VI) species



(b) Insertion polymerization



(c) Termination by redox reactions and protonation



(d) Termination by an end-capping reaction

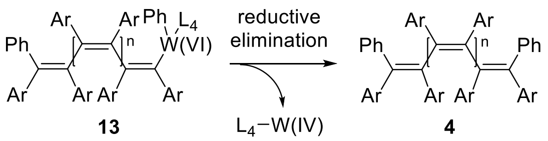


Figure 3. The proposed mechanism of the polymerization of diphenylacetylenes with tungsten(VI) chloride (WCl_6 or $WOCl_4$) and tetraphenyltin (Ph_4Sn).

Conclusion

We have revisited the polymerization of diphenylacetylene with tungsten(VI) chloride and Ph_4Sn through optimization of the conditions using diphenylacetylene monomer **1a** having two ester groups at the *para*-positions. As a result, we found that the replacement of WCl_6 with $WOCl_4$ improved the results of the polymerization of **1a**, and it also worked in the polymerization of other diphenylacetylene monomers. Mass spectrometric analysis of the polymer structure combined with the results of a stoichiometric reaction of diphenylacetylene (**4**) with $WOCl_4$-Ph_4Sn suggested an initiating process by insertion of a phenyl group from Ph_4Sn and two termination processes in the polymerization. Interestingly, these processes indicated a migratory insertion polymerization mechanism rather than a metathesis polymerization mechanism that has been believed for a long time. It should be noted that the present study does not rule out the possibility of a metathesis mechanism in the polymerization of other types of monomers, such as norbornenes and mono-substituted acetylenes, using WCl_6-Ph_4Sn.[1,8] Similarly, the mechanism of the polymerization of diphenylacetylenes with the $TaCl_5$-$^{n}Bu_4Sn$ system is still an interesting issue, though a previous report suggests a similarity between WCl_6-Ph_4Sn and $TaCl_5$-$^{n}Bu_4Sn$ systems.[17]

Our study serves as a starting point to develop substantially improved catalytic systems for polymerization of various diphenylacetylenes, which are essential for research and development of novel functional materials based on poly(diphenylacetylene)s.[22] More generally, we anticipate that an discovery of the alternative pathway by “ill-defined” metathesis catalysts will promote the development of novel “well-defined” tungsten catalysts in organometallic and synthetic chemistry.

Acknowledgements

This work was partially supported by JSPS KAKENHI (Grant-in-Aid for Specially Promoted Research, No. 18H05209 (K.M) and Grant-in-Aid for Scientific Research (C), No. 18K04723 (T.N) and 19K06972 (T.T)) and the World Premier International Research Center Initiative (WPI), MEXT, Japan.

Keywords: Diphenylacetylenes • Insertion • Polymerization • Polymers • Tungsten

[1] Selected early reports of tungsten-catalyzed olefin metathesis reactions: a) G. Natta, G. Dall’Asta, G. Mazzanti, *Angew. Chem., Int. Ed. Engl.* **1964**, *3*, 723-729; *Angew. Chem.* **1964**, *76*, 765-772; b) N. Calderon, H. Y. Chen, K. W. Scott, *Tetrahedron Lett.* **1967**, 3327-3329; c) J.-L. Wang, H. R. Menapace, *J. Org. Chem.* **1968**, *33*, 3794-3796; d) J.-L. Hérisson, Y. Chauvin, *Makromol. Chem.* **1971**, *141*, 161-176; e) N. Calderon, *Acc. Chem. Res.* **1972**, *5*, 127-132; f) K. Ichikawa, T. Takagi, K. Fukuzumi, *Transition Met. Chem.* **1976**, *1*, 54-58; g) W. J. Feast, B. Wilson, *J. Mol. Catal.* **1980**, *8*, 277-296; h) D. Villemin, *Tetrahedron Lett.* **1980**, *21*, 1715-1718; i) B. Matyska, H. Balcar, M. Smutek, *React. Kinet. Catal. Lett.* **1982**, *20*, 193-196.

[2] Selected reviews: a) R. R. Schrock, A. H. Hoveyda, *Angew. Chem., Int. Ed.* **2003**, *42*, 4592-4633; *Angew. Chem.* **2003**, *115*, 4740-4782; b) O. M. Ogba, N. C. Warner, D. J. O’Leary, R. H. Grubbs, *Chem. Soc. Rev.* **2018**, *47*, 4510-4544.

[3] a) J. W. Y. Lam, B. Z. Tang, *Acc. Chem. Res.* **2005**, *38*, 745-754; b) J. Liu, J. W. Y. Lam, B. Z. Tang, *Chem. Rev.* **2009**, *109*, 5799-5867; c) M. Shiotsuki, F. Sanda, T. Masuda, *Polym. Chem.* **2011**, *2*, 1044-1058.

[4] Reviews: a) T. Masuda, *J. Polym. Sci. Part A: Polym. Chem*. **2007**, *45*, 165-180; b) Y.-J. Jin, G. Kwak, *Polym. Rev.* **2017**, *57*, 176-200; c) X. Wang, J. Z. Sun, B. Z. Tang, *Prog. Polym. Sci.* **2018**, *79*, 98-120.

[5] a) T. Aoki, Y. Kobayashi, T. Kaneko, E. Oikawa, Y. Yamamura, Y. Fujita, M. Teraguchi, R. Nomura, T. Masuda, *Macromolecules* **1999**, *32*, 79-85; b) M. Teraguchi, J. Suzuki, T. Kaneko, T. Aoki, T. Masuda, *Macromolecules* **2003**, *36*, 9694-9697; c) T. Fukushima, K. Tsuchihara, *Macromolecules* **2009**, *42*, 5453-5460; d) C. K. M. Jim, J. W. Y. Lam, C. W. T. Leung, A. Qin, F. Mahtab, B. Z. Tang, *Macromolecules* **2011**, *44*, 2427-2437; e) D. Lee, Y.-J. Jin, N. Suzuki, M. Fujiki, T. Sakaguchi, S. K. Kim, W.-E. Lee, G. Kwak, *Macromolecules* **2012**, *45*, 5379-5386; f) B. A. S. Jose, S. Matsushita, K. Akagi, *J. Am. Chem. Soc.* **2012**, *134*, 19795-19807; g) X. A. Zhang, A. Qin, L. Tong, H. Zhao, Q. Zhao, J. Z. Sun, B. Z. Tang, *ACS Macro Lett.* **2012**, *1*, 75-79; h) H. Kim, K.-U. Seo, Y.-J. Jin, C.-M. Lee, M. Teraguchi, T. Kaneko, T. Aoki, G. Kwak, *ACS Macro Lett.* **2016**, *5*, 622-625; i) K. Maeda, M. Maruta, K. Shimomura, T. Ikai, S. Kanoh, *Chem. Lett.* **2016**, *45*, 1063-1065; j) K. Maeda, M. Maruta, Y. Sakai, Y. Ikai, S. Kanoh, *Molecules* **2016**, *21*, 1487.

[6] a) C. C. W. Law, J. W. Y. Lam, A. Qin, Y. Dong, H. S. Kwok, B. Z. Tang, *Polymer* **2006**, *47*, 6642-6651; b) W. Z. Yuan, A. Qin, J. W. Y. Lam, J. Z. Sun, Y. Dong, M. Häussler, J. Liu, H. P. Xu, Q. Zheng, B. Z. Tang, *Macromolecules* **2007**, *40*, 3159-3166.

[7] T. Sakaguchi, S. Azuma, T. Hashimoto, *Synth. Met.* **2016**, *212*, 174-179.

[8] Selected examples of the polymerization of terminal alkynes by tungsten catalysis: a) T. Masuda, N. Sasaki, T. Higashimura, *Macromolecules* **1975**, *8*, 717-721; b) T. Masuda, K.-Q. Thieu, N. Sasaki, T. Higashimura, *Macromolecules* **1976**, *9*, 661-664; c) K. Hasegawa, *Eur. Polym. J.* **1977**, *13*, 315-323; d) C. I. Simionescu, V. Percec, S. Dumitrescu, *J. Polym. Sci. Part A: Polym. Chem.* **1977**, *15*, 2497-2509; e) C. I. Simionescu, V. Percec, *Prog. Polym. Sci.* **1982**, *8*, 133-214; f) J. F. Kunzler, V. Percec, *Polym. Bull.* **1987**, *18*, 303-309; g) J. Kunzler, V. Percec, *J. Polym. Sci. Part A: Polym. Chem.* **1990**, *28*, 1043-1057; h) J. Kunzler, V. Percec, *J. Polym. Sci. Part A: Polym. Chem.* **1990**, *28*, 1221-1236; i) J. Sedlacek, J. Vohlidal, J. Kares, M. Pacovska, B. Maca, *Collect. Czech. Chem. Commun.* **1994**, *59*, 2454-2471; j) J. Sedláček, M. Pacovská, J. Vohlídal, Z. Grubišić-Gallot, M. Žigon, *Macromol. Chem. Phys.* **1995**, *196*, 1705-1712; k) S. Hayano, T. Masuda, *Macromolecules* **1999**, *32*, 7344-7348. l) C. H. Roland, H. Li, K. A. Abboud, K. B. Wagener, A. S. Veige, *Nat. Chem.* **2016**, *8*, 791-796.

[9] S. J. Landon, P. M. Shulman, G. L. Geoffroy, *J. Am. Chem. Soc.* **1985**, *107*, 6739-6740.

[10] J. M. Lynam, *Chem. Eur. J.* **2010**, *16*, 8238-8247.

[11] K. Maeda, M. Nozaki, K. Hashimoto, K. Shimomura, D. Hirose, T. Nishimura, G. Watanabe, E. Yashima, *J. Am. Chem. Soc.* **2020**, *142*, 7668-7682.

[12] A similar problem has been reported by another research group.5g

[13] The obtained poly-**1a** showed almost the same ^{1}H and ^{13}C NMR spectra as those of the previously reported polymer obtained by WCl_6-Ph_4Sn, indicating both polymers have the same main chain structure (Figures S1 and S2).

[14] T. Masuda, H. Kawai, T. Ohtori, T. Higashimura, *Polym. J.* **1979**, *11*, 813-818.

[15] N.-W. Tseng, J. Liu, J. C. Y. Ng, J. W. Y. Lam, H. H. Y. Sung, I. D. Williams, B. Z. Tang, *Chem. Sci.* **2012**, *3*, 493-497.

[16] There are limited examples of migratory insertion of tungsten complexes to alkynes: a) M. H. Chisholm, J. A. Heppert, J. C. Huffman, *J. Am. Chem. Soc.* **1984**, *106*, 1151-1153; b) E. R. Burkhardt, J. J. Doney, R. G. Bergman, C. H. Heathcock, *J. Am. Chem. Soc.* **1987**, *109*, 2022-2039; c) L. Carlton, W. A. Wan Abu Bakar, J. L. Davidson, *J. Organomet. Chem.* **1990**, *394*, 177-193.

[17] T. Katsumata, M. Shiotsuki, S. Kuroki, I. Ando, T. Masuda, *Polym. J.* **2005**, *37*, 608-616.

[18] J. F. Hartwig, Organotransition Metal Chemistry: From Bonding to Catalysis; University Science Books: Sausalito, CA, 2010.

[19] a) M. Grzybowski, K. Skonieczny, H. Butenschön, D. T. Gryko, *Angew. Chem., Int. Ed.* **2013**, *52*, 9900-9930; *Angew. Chem.* **2013**, *125*, 10084-10115; b) N. Zhang, S. R. Samanta, B. M. Rosen, V. Percec, *Chem. Rev.* **2014**, *114*, 5848-5958.

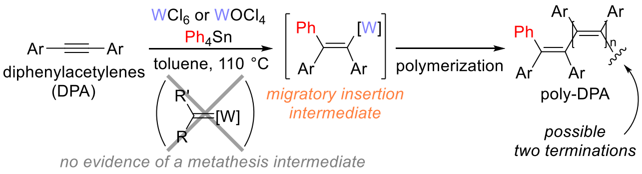
[20] L. Eberson, L. Jönsson, O. Sänneskog, *Acta Chem. Scand. B* **1985**, *39*, 113-121.

[21] I.-W. Sun, A. G. Edwards, G. Mamantov, *J. Electro. Soc.* **1993**, *140*, 2733-2739.

[22] A recent example of successful living polymerization based on well-defined metal catalysts for the synthesis of helical polymers: J.-H. Chu,

X.-H. Xu, S.-M. Kang, N. Liu, Z.-Q. Wu, *J. Am. Chem. Soc.* **2018**, *140*, 17773-17781.

Entry for the Table of Contents



A migratory insertion mechanism has been proposed for the polymerization of diphenylacetylenes by a classic metathesis catalytic system composed of tungsten(VI) chloride (WCl_6 or $WOCl_4$) and Ph_4Sn. Experimental results suggest that the polymerization is initiated by addition of a phenyl group coming from Ph_4Sn to diphenylacetylene monomers and has two possible termination processes.