

Transition metal acetylide catalysts for polymerization of alkynes

3. Polymerization mechanism

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Abstract

A coordination insertion mechanism is proposed for the polymerization of alkynes initiated by transition metal acetylides on the basis of some experimental results. A transition metal acetylide coordinates with an alkyne resulting in the formation of a penta-coordinated complex, which is a preliminary activation and rate-determining step. The polymeric chain begins by insertion of the π -coordinated monomer molecule into the metal–carbon σ -bond. For large-bulk monomers such as *p*-diethynylbenzene and its derivatives, the insertion is almost *trans*-type to give rich *trans* polymers. On the other hand, for small-bulk monomers such as phenylacetylene, *cis* insertion easily occurs to yield cyclotrimers. The propagation of the polymer chain can be interrupted when the π -bonded monomer transfers its acidic hydrogen to the growing chain. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

Polyacetylenes possess alternating double bonds along the main chain. This structure often endows them with the following characteristics: conductivity, photoconductivity, optical nonlinear susceptibility, magnetic susceptibility, chirality, liquid crystallinity, solvatochromism, self-organization, humidity sensitivity, photoluminescence and electroluminescence [1–5]. The polymerization of substituted acetylenes was initiated by various catalysts: Ziegler catalysts [6], rare earth catalysts [7], molybdenum- and tungsten-based catalysts [8]. However, Ziegler and

rare earth catalysts are inactive towards polymerization of polar alkynes such as propiolic acid and propargyl alcohol (OHP). Although MoCl_5 could polymerize not only non-polar alkynes such as *t*-butylacetylene, but also polar alkynes like propiolic acid, the molecular weights of the polar polymers were low (<2000) [9]. In recent years, transition metal acetylides were found to be effective catalysts for alkynes polymerization. Russo et al. used nickel, palladium and platinum acetylides containing triphenylphosphine ligand as catalysts for polymerization of alkynes such as diethynylbiphenyl, ethynylfluorene, ethynyltrimethylsilane, phenylacetylene (PA), *N,N*-dimethylamino-1-propyne, *N*-benzylpropargylamine and isopropenylacetylene to give polymers with molecular weights of 500–10⁴ [10–15]. Kishimoto and coworkers reported stereospecific living polymerization of phenylacetylenes using $\text{Rh}(\text{C}\equiv\text{CC}_6\text{H}_5)(\text{nbd})$

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[PPh₃]₂ [16,17]. We have synthesized a series of nickel and palladium acetylides, and employed these complexes to initiate polymerization of not only polar alkynes such as OHP and its esters but also non-polar alkynes like *p*-diethynylbenzene (*p*-DEB) and its derivatives [18–25]. In the present work, we proposed a coordination insertion polymerization mechanism for polymerization of alkynes initiated by transition metal acetylides on the basis of some experimental results.

2. Experiments

2.1. Materials

Only analytical grade quality chemicals were used. OHP was distilled under nitrogen at reduced pressure. Phenylacetylene (Aldrich) and diphenylacetylene (Aldrich) were used as purchased. *p*-DEB [26], HC≡CC₆H₄C≡CC₆H₅ [22] and Ni(PPh₃)₂(C≡CC₆H₄C≡CH)₂ [27] were prepared by literature methods.

2.2. Measurements

Electron spin resonance (ESR) measurements were carried out on a JES-FEIXG ESR spectrometer. The weight-average molecular weight (M_w) and polydispersity index (M_w/M_n) of polymers were measured on a PL-GPC Model 210 chromatograph at 35°C using THF as eluent and standard polystyrene as reference.

2.3. Polymerization

All procedures for polymerization were carried out under purified nitrogen atmosphere. A typical polymerization procedure is as follows: into a 30 ml well dried ampoule, Ni(PPh₃)₂(C≡CC₆H₄C≡CH)₂ (0.04 mmol, 33.3 mg), 1,4-dioxane (0.6 ml) and toluene (0.6 ml) were added, shaken to obtain a homogeneous solution, and then OHP (1.4 mmol, 0.8 ml) was added. After the mixture stood at 60°C for 48 h, methanol (2 ml) was added to dissolve the resulting polymer and then precipitated as a brown powder by the addition of acetone. The polymer was filtered from the solution, washed with acetone, and dried under vacuum at room temperature for 24 h.

Table 1
Effect of electron donors on *p*-DEB polymerization initiated by Ni(PPh₃)₂(C≡CC₆H₄C≡CH)₂^a

Electron donors ^b	Yield (%)	$M_w \times 10^{-4}$	M_w/M_n
–	67.7	1.1	1.6
EtOH	77.0	2.7	8.6
NEt ₃	88.4	2.4	8.2
H ₂ O	54.8	1.4	5.9
Hydroquinone	60.0	1.0	1.6

^a Catalyst concentration: [cat]₀ = 0.01 mol/l; monomer concentration: [M]₀ = 1.0 mol/l; 1,4-dioxane/toluene = 1 (volume ratio); 25°C; 5 h.

^b Electron donor/catalyst = 5 (mole ratio).

3. Results and discussion

Table 1 shows effect of some electron donors on *p*-DEB polymerization initiated by Ni(PPh₃)₂(C≡CC₆H₄C≡CH)₂. It was observed that *p*-DEB polymerization could not be suppressed by hydroquinone. Moreover, the free radical signal did not exist at the initial stage of the polymerization confirmed by ESR measurement. The above results demonstrate that the polymerization did not proceed by a radical mechanism [28].

The addition of NEt₃, EtOH and H₂O exhibits no inhibitory effect on the polymerization. On the other hand, the overall activation energy is high [29], and not in the range expected of ionic-type polymerization. So the polymerization shows no cationic or anionic polymerization characteristics [30,31].

The catalytic activity of transition metal acetylides is improved by the addition of electron donors such as EtOH and NEt₃. The polymers obtained possess a rich *trans* conjugated polyene structure [29], indicating the polymerization shows stereospecific characteristics. One can presume that the polymerization follows a coordination mechanism [32,33].

The phosphine ligands bonded to the metal atom play an important role on the catalytic properties of these complexes. The poor catalytic activity of Ni(PBu₃)₂(C≡CC₆H₄C≡CH)₂ and Ni(Ph₂PCH₂CH₂PPh₂)(C≡CC₆H₄C≡CH)₂ is related to the great steric hindrance of 1,2-bis(diphenylphosphino)ethane bridging ligand and of PBu₃ ligand due to the long chain of *n*-butyl group [24]. The nickel acetylides Ni(PBu₃)₂(C≡CR)₂ containing small-bulk alkynyl ligands show higher catalytic

Table 2

Polymerization of alkynes with different steric hindrance by $\text{Ni}(\text{PPh}_3)_2(\text{C}\equiv\text{CC}_6\text{H}_4\text{C}\equiv\text{CH})_2$ catalyst^a

Monomer	Temperature (°C)	Time (h)	Yield (%)	$M_w \times 10^{-4}$	M_w/M_n
PhC≡CPh	60	24	0	–	–
HC≡CC ₆ H ₄ C≡CH	25	3	74.3	1.4	2.4
HC≡CC ₆ H ₄ C≡CC ₆ H ₅	60	24	63.4	0.9	2.1

^a 1,4-Dioxane/toluene = 1 (volume ratio); $[\text{M}]_0 = 1.0 \text{ mol/l}$; $[\text{cat}]_0 = 0.01 \text{ mol/l}$.

activity than those containing large-bulk alkynyl ligands [24]. Table 2 shows the results of polymerization of different alkynes in the presence of $\text{Ni}(\text{PPh}_3)_2(\text{C}\equiv\text{CC}_6\text{H}_4\text{C}\equiv\text{CH})_2$. The polymerization activity of *p*-DEB derivative is lower than that of *p*-DEB due to its greater steric repulsion. Transition metal acetylides could not initiate the polymerization of disubstituted acetylenes such as diphenylacetylene because of the great steric hindrance of internal alkynes. The above results show the steric hindrance of the monomers and the ligands of the initiators is unfavorable to the polymerization. It is inferred that the coordination of triple bonds in the monomers with the metal atoms in the catalysts and the π -complex formation is a preliminary activation step necessary to the catalytic polymerization. The steric repulsion prevents the coordination and the π -complex formation.

Nickel acetylide exhibits much higher catalytic activity than nickel chloride [22,24]. On the other hand, *p*-DEB polymerization with $\text{Ni}(\text{PPh}_3)_2(\text{C}\equiv\text{CC}_6\text{H}_4\text{C}\equiv\text{CH})_2$ catalyst could not proceed in carbon dioxide atmosphere [29], which may be owing to that carbon dioxide could insert into nickel–carbon bond and coordinate with nickel to form a stable complex [34], so that *p*-DEB cannot insert into nickel–carbon bond to propagate. So it is presumed that nickel–carbon bond is a key factor to catalysis. The alkynyl ligands bonded to the palladium atom exert an influence on the catalytic activity of these complexes, which is related to

electronic properties of ligands [24,25]. The catalytic activity of these complexes is dependent on activity of metal–carbon bonds. Considering the important role of metal–carbon bond in transition metal acetylides, one can infer that initiation and propagation reactions are carried out through inserting of the monomers into metal–carbon σ -bonds with the preliminary activation at the expense of π -complex formation.

The molecular weights and polydispersity index (M_w/M_n) of the polymer decreases with increasing the monomer concentration, indicating chain transfer to the monomer probably occurred during the polymerization of *p*-DEB initiated by $\text{Ni}(\text{PPh}_3)_2(\text{C}\equiv\text{CC}_6\text{H}_4\text{C}\equiv\text{CH})_2$ [35].

The results of polymerization of different alkynes in the presence of $\text{Ni}(\text{PPh}_3)_2(\text{C}\equiv\text{CC}_6\text{H}_4\text{C}\equiv\text{CH})_2$ are listed in Table 3. PA and OHP show high reaction activity in 1,4-dioxane/toluene at 60°C, and the reactions are in some cases instantaneous and explosive. Although the polymerization systems exhibit high reaction activity, the yields and molecular weights of the linear polymers are low, and the cyclotrimers were obtained, which is similar to the literatures [36,37]. On the other hand, polymerization of *p*-DEB produces a linear polymer in a high yield.

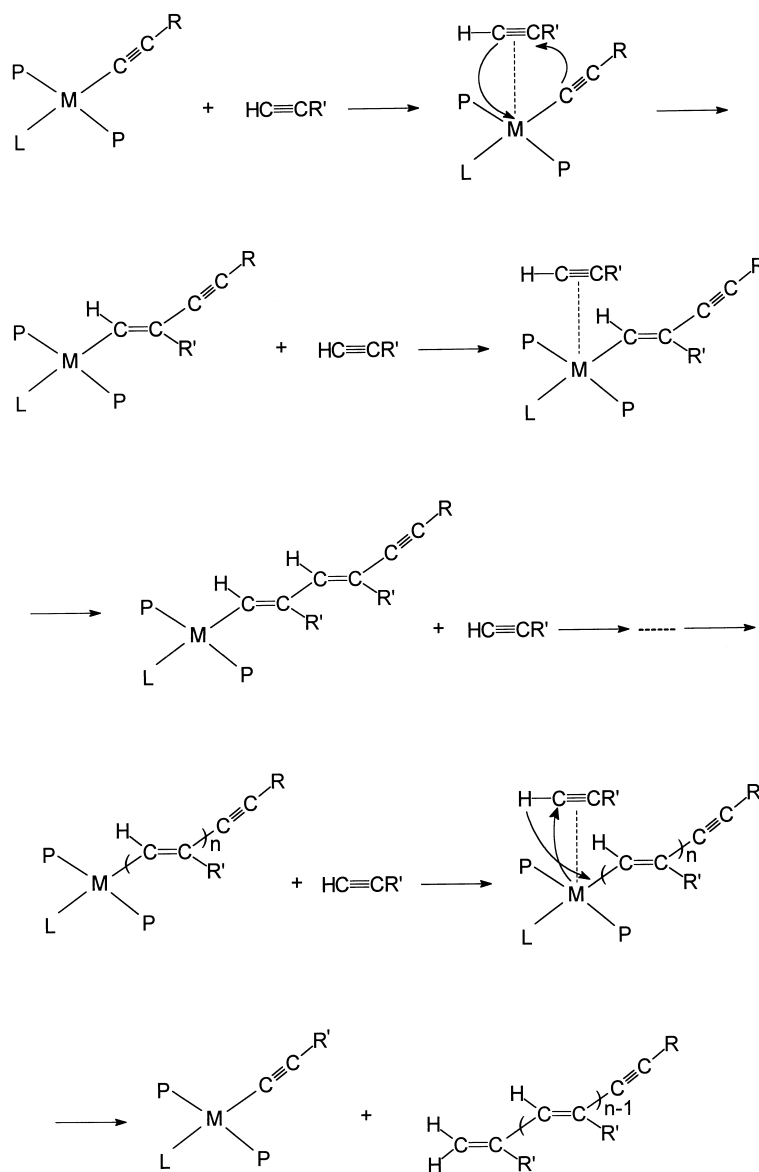
According to the results and discussion above, the following polymerization mechanism (Scheme 1) can be depicted for the polymerization of alkynes initiated by transition metal acetylides. A transition

Table 3

Comparison of polymerization of *p*-DEB, PA and OHP initiated by $\text{Ni}(\text{PPh}_3)_2(\text{C}\equiv\text{CC}_6\text{H}_4\text{C}\equiv\text{CH})_2$ ^a

Monomer	$[\text{cat}]_0$ (mol/l)	$[\text{M}]_0$ (mol/l)	Temperature (°C)	Time (h)	Yield (%)	$M_w \times 10^{-3}$	M_w/M_n
<i>p</i> -DEB	0.01	1.0	25	3	74.3	14.0	2.4
PA	0.02	3.0	60	64	14.8	4.3	1.4
OHP	0.02	7.0	60	48	8.3	5.4	1.6

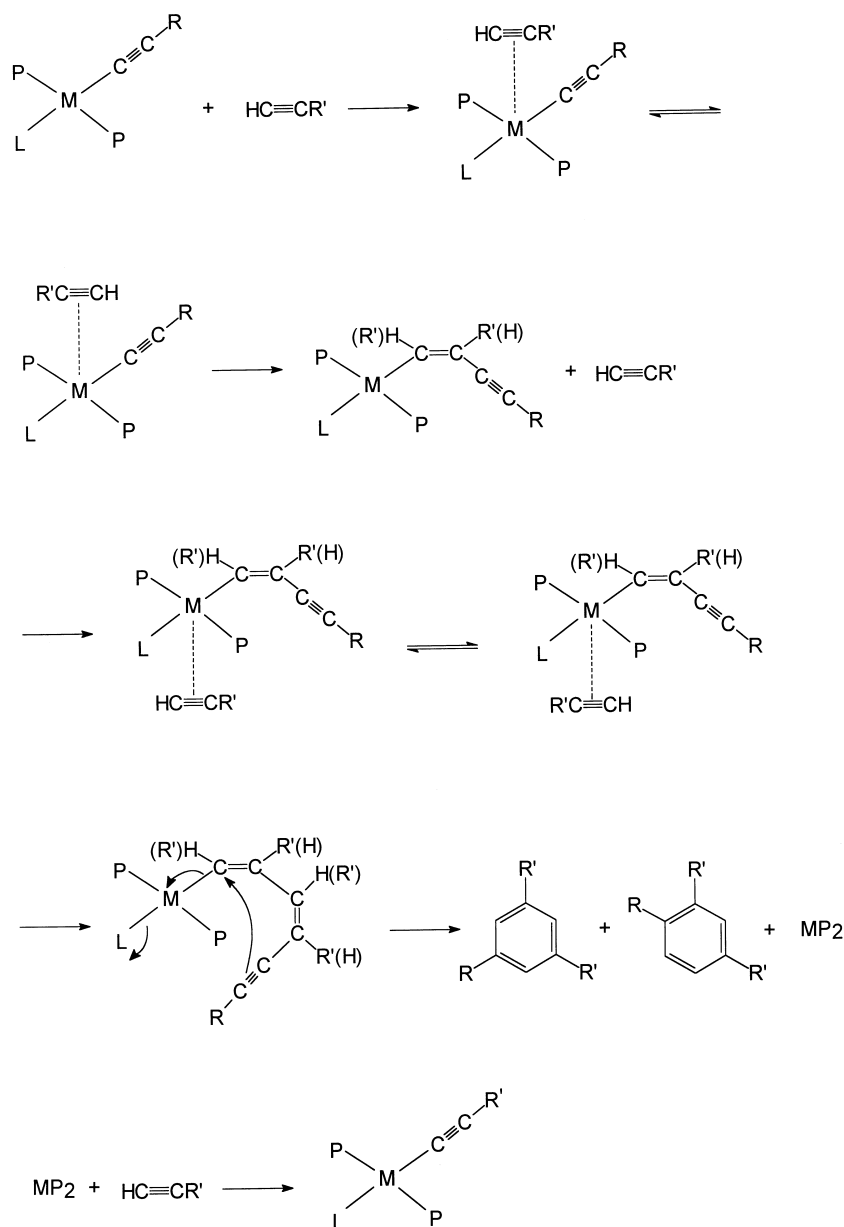
^a In 1,4-dioxane/toluene = 1 (volume ratio).



Scheme 1. Polymerization mechanism of alkynes by transition metal acetylide catalysts. P: PPh_3 , PBu_3 , $Ph_2PCH_2CH_2PPh_2$; L: $C\equiv CR$, Cl; M: Ni, Pd.

metal acetylide coordinates with an alkyne resulting in formation of a penta-coordinated complex. The complex involves π -complex formation between the triple bond and the p_z orbital of the metal atom, the z -axis goes through the center of the triple bond, and the alkyne molecule lies roughly parallel to the plane of the complex [38]. The slow rate-determining step

in the reaction sequence is probably the formation of the penta-coordinated complex [39]. The polymeric chain begins by insertion of the π -coordinated monomer molecule into the metal-carbon σ -bond. For large-bulk monomers such as *p*-DEB and its derivatives, the insertion almost is *trans*-type to give rich *trans* polymers since the steric repulsion from the R'



Scheme 2. Cyclotrimerization mechanism of alkynes by transition metal acetylide catalysts.

group is unfavorable to *cis* insertion. The growth of the chain is interrupted when the π -bonded monomer transfers its acidic hydrogen to the propagating chain, regenerating the starting complex. For small-bulk monomers such as PA, *cis* insertion could occur to yield cyclotrimers as shown in Scheme 2.

4. Conclusions

The polymerization of alkynes initiated by transition metal acetylides follows a coordination insertion mechanism. Polymers can be formed by the insertion of monomers into metal–carbon σ -bonds with the

preliminary activation at the expense of π -complex formation, which may be rate-determining step. Steric hindrance exerts a significant influence on *cis* or *trans* insertion, resulting in cyclotrimerization or linear polymerization, respectively. The propagation of the polymer chain can be interrupted when the π -bonded monomer transfers its acidic hydrogen to the growing chain.

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