

Transition metal acetylide catalysts for polymerization of *p*-diethynylbenzene 4

Effect of transition metals on catalytic activity of complexes

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Received 30 May 2001; received in revised form 23 November 2001; accepted 30 November 2001

Abstract

The catalytic activity of a series of group VIII transition metal chlorides and acetylides containing different phosphine ligands: $ML_2(C\equiv CC_6H_5)_2$ and ML_2Cl_2 ($M = Co, Ni, Pd$ and Pt ; $L = PPh_3$ and PBu_3), towards polymerization of *p*-diethynylbenzene (*p*-DEB) is examined. The transition metals exert important effect on the catalytic activity of these complexes. The catalytic activity of these complexes falls in with the following order: $Co > Ni > Pd > Pt$. The catalytic properties of group VIII transition metal complexes are related to the electron configuration of metal elements. Cobalt and nickel chlorides and acetylides were found to be novel and efficient initiating systems for the polymerization of *p*-diethynylbenzene. The polymerization proceeds at room temperature to give soluble polymers with weight-average molecular weights as high as 2.2×10^4 in yields as high as 85%. The polymer obtained with these catalysts possesses a rich-*trans* extended π -conjugated polyene chain structure with the pendent groups of *p*- $C_6H_4C\equiv CH$. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Transition metal acetylide; Catalyst; Alkyne; Polymerization

1. Introduction

The research and development on organometallic catalysts for synthesis of polymers is an important and attractive field in polymer science and industry. The catalytic systems based on early transition metal complexes are extensively used for the polymerization of alkynes. For instance, the halides of molybdenum, tungsten, niobium and tantalum are most widely used to polymerize substituted acetylenes such as phenylacetylene [1,2]. This kind of catalysts are, however, extremely air- and moisture-sensitive and must be han-

dled in dry and inert atmosphere. In contrast to early transition metal system, late transition metal catalysts, e.g. the halides of nickel, palladium and platinum often dimerize, trimerize or oligomerize alkynes [3–5].

In recent years, late transition metal acetylides were found to be effective catalysts for alkynes polymerization. Russo and co-workers used nickel, palladium and platinum acetylides containing triphenylphosphine ligand as catalysts for polymerization of alkynes such as diethynylbiphenyl, ethynylfluorene, ethynyltrimethylsilane, phenylacetylene, *N,N*-dimethylamino-1-propyne, *N*-benzylpropargylamine and *iso*-propenylacetylene to give polymers with molecular weights of $500\text{--}10^4$ [6–9]. Kishimoto et al. reported stereospecific living polymerization of phenylacetylenes initiated by rhodium acetylides [10,11].

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To our knowledge, however, there have been no reports concerning systemic study on the effect of transition metals on catalytic activity of these complexes towards alkynes polymerization.

We have accomplished polymerization of propargyl alcohol, *p*-diethynylbenzene (*p*-DEB) and their derivatives with transition metal acetylides catalysts to give soluble polymers in high yields [12–15]. We found that nickel and palladium acetylides are capable of polymerizing both non-polar alkynes and polar substituted acetylenes [16]. We discussed the effect of ligands on catalytic activity of these acetylides towards the polymerization of alkynes and the polymerization mechanism [17–19]. In this work, we compare catalytic activity of Co, Ni, Pd and Pt chlorides and acetylides containing phosphine ligands towards polymerization of alkynes, and discuss influence of electronic structures of late transition metals on catalytic properties of their complexes.

2. Experiments

2.1. Materials

Only analytical grade quality chemicals were used. Diethyl amine was dried over CaH₂ and distilled under N₂ atmosphere prior to use. Diethyl ether was freshly distilled from sodium benzophenone ketyl under nitrogen prior to use. Other solvents were dried with activated alumina. The alkyne *p*-DEB [20] and the chlorides such as Co(PPh₃)₂Cl₂ [21], Co(PBu₃)₂Cl₂ [22], Ni(PPh₃)₂Cl₂ [23], Ni(PBu₃)₂Cl₂ [24], Pd(PPh₃)₂Cl₂ [25], Pd(PBu₃)₂Cl₂ [26], Pt(PPh₃)₂Cl₂ [25] and Pt(PBu₃)₂Cl₂ [27] were prepared by literature methods or modifying reported procedures. The Ni, Pd and Pt acetylides, i.e. Ni(PPh₃)₂(C≡CPh)₂ [28], Ni(PBu₃)₂(C≡CPh)₂ [29], Pd(PPh₃)₂(C≡CPh)₂ [30], Pd(PBu₃)₂(C≡CPh)₂ [31], Pt(PPh₃)₂(C≡CPh)₂ [32] and Pt(PBu₃)₂(C≡CPh)₂ [33] were prepared by literature methods or modifying reported procedures.

2.2. Measurements

Melting points were determined on a Yanaco MP-500 melting point apparatus. FT-IR spectra were taken on a Perkin-Elmer System 2000 FT-IR spectrometer with Nujol mulls or KBr pellets. ¹H

NMR spectrum (CDCl₃, tetramethylsilane as internal standard) was obtained with a Varian Unity 200 MHz NMR spectrometer at room temperature. ¹³C NMR spectrum was recorded in CDCl₃ solution at room temperature on a Varian Unity 200 MHz NMR spectrometer. Elemental analyses were carried out by a Carlo Erba Model 1106 elemental analyzer. 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. Catalyst synthesis

2.3.1. Co(PPh₃)₂(C≡CPh)₂

A solution of Co(PPh₃)₂Cl₂ (1 mmol, 654 mg) in absolute diethyl ether (20 ml) was added dropwise to a solution of KC≡CPh (2 mmol, 280 mg) in liquid ammonia (20 ml), which was stirred for 10 h. After addition of NH₄Cl (400 mg) and evaporation of NH₃, H₂O (20 ml) was added. A greenish-yellow solid formed at the interface. This solid can be recrystallized from methanol–acetone but with partial decomposition, and the isolated product (416 mg, 53%) contains traces of free phosphines: mp (decomposition), 165 °C. FT-IR (Nujol mull, cm⁻¹): 2089 (s, C≡C); 695 (s, C₆H₅); 538 (w, C–Co). Anal. Calcd. for CoC₅₂H₄₀P₂: C, 79.48; H, 5.13. Found: C, 78.54; H, 5.37%.

2.3.2. Co(PBu₃)₂(C≡CPh)₂

A solution of Co(PBu₃)₂Cl₂ (1 mmol, 534 mg) in absolute diethyl ether (20 ml) was added dropwise to a solution of KC≡CPh (2 mmol, 280 mg) in liquid ammonia (20 ml), which was stirred for 24 h. After addition of NH₄Cl (400 mg) and evaporation of NH₃, H₂O (20 ml) was added. A greenish-yellow solid formed at the interface. This solid can be recrystallized from *n*-hexane to yield greenish-yellow crystals (293 mg, 44%): mp, 81 °C. FT-IR (Nujol mull, cm⁻¹): 2098 (s, C≡C); 693 (s, C₆H₅); 568 (w, C–Co). Anal. Calcd. for CoC₄₀H₆₄P₂: C, 72.16; H, 9.69. Found: C, 71.66; H, 9.96%.

2.4. Polymerization

A typical polymerization procedure is as follows: 378 mg (3 mmol) of sublimed *p*-DEB and 24 mg (0.03 mmol) of Co(PPh₃)₂(C≡CPh)₂ were dissolved

Table 1

Comparison of catalytic activity of PPh₃-containing transition metal chlorides towards the *p*-DEB polymerization^a

Complex	Temperature (°C)	Time (h)	Yield (%)	$M_w \times 10^{-4}$	M_w/M_n
Co(PPh ₃) ₂ Cl ₂	25	3	0	–	–
Ni(PPh ₃) ₂ Cl ₂	25	6	81.2	1.5	1.8
Pd(PPh ₃) ₂ Cl ₂	50	24	86.0	2.6	3.2
Pt(PPh ₃) ₂ Cl ₂	60	24	0	–	–

^a Conditions: [cat]₀ = 0.01 mol l⁻¹; [M]₀ = 1.0 mol l⁻¹; HNEt₂/toluene = 1 (v/v).

in 1,4-dioxane (1.25 ml) and toluene (1.25 ml) mixed solvents. Under purified nitrogen atmosphere, the polymerization proceeded at 25 °C for 3 h. The resulting polymer was precipitated by the addition of methanol (100 ml), filtered from the solution, washed with CH₃OH, and dried in vacuum at room temperature for 24 h to give orange powder. Other polymerizations were carried out analogously.

3. Results and discussion

Late transition metals exhibit significant influence on catalytic activity of their chlorides containing phosphine ligands towards the *p*-DEB polymerization. Table 1 lists the results for the polymerization of *p*-DEB in HNEt₂/toluene mixed solvents initiated by group VIII transition metal chlorides containing PPh₃ ligands. Co(PPh₃)₂Cl₂ can not polymerize *p*-DEB because this complex is decomposed by HNEt₂ at room temperature. Ni(PPh₃)₂Cl₂ polymerizes *p*-DEB efficiently; the polymer yield reaches 81% when the polymerization is carried out at room temperature. The weight-average molecular weight and polydispersity index of the polymer are 1.5×10^4 and 1.8, respectively. The polymerization with Pd(PPh₃)₂Cl₂ catalyst does not occur at 25 °C, while the yield at

50 °C is as high as 86% and M_w of the polymer reaches 2.6×10^4 . Pt(PPh₃)₂Cl₂ is completely ineffective at 60 °C. Thus, the order of catalytic activity of these complexes is as follows: Ni(PPh₃)₂Cl₂ > Pd(PPh₃)₂Cl₂ > Pt(PPh₃)₂Cl₂.

Table 2 further compares the catalytic activity of these late transition metal chlorides containing PBu₃ ligands. In contrast to the cobalt chloride with triphenylphosphine ligand, the cobalt chloride with tributylphosphine ligand, i.e. Co(PBu₃)₂Cl₂ can efficiently initiate the *p*-DEB polymerization even at room temperature to give soluble polymers in 73% yield with a M_w of 1.2×10^4 . Butyl belongs to the electron-donating group, while phenyl is the electron-withdrawing group. Thus, PBu₃ shows greater basicity and σ -related donating ability than PPh₃, increasing the electron cloud density of nickel–phosphorus bond and then increasing the stability of the complex. Therefore, Co(PBu₃)₂Cl₂ is more stable than Co(PPh₃)₂Cl₂ in HNEt₂. Ni(PBu₃)₂Cl₂ can not initiate the *p*-DEB polymerization at 25 °C, while the yield and molecular weight of the polymer obtained at 50 °C are comparable (yield 51%, M_w 1.6×10^4). On the other hand, Pd(PBu₃)₂Cl₂ and Pt(PBu₃)₂Cl₂ exhibit no catalytic activity towards the alkyne polymerization under tested conditions. Thus, the catalytic activity

Table 2

Comparison of catalytic activity of PBu₃-containing transition metal chlorides towards the *p*-DEB polymerization^a

Complex	Temperature (°C)	Time (h)	Yield (%)	$M_w \times 10^{-4}$	M_w/M_n
Co(PBu ₃) ₂ Cl ₂	25	10	73.1	1.2	2.3
Ni(PBu ₃) ₂ Cl ₂	50	24	51.2	1.6	2.5
Pd(PBu ₃) ₂ Cl ₂	60	24	0	–	–
Pt(PBu ₃) ₂ Cl ₂	60	24	0	–	–

^a Conditions: [cat]₀ = 0.01 mol l⁻¹; [M]₀ = 1.0 mol l⁻¹; HNEt₂/toluene = 1 (v/v).

Table 3

Comparison of catalytic activity of PPh₃-containing transition metal acetylides towards the *p*-DEB polymerization^a

Complex	Solvent	Temperature (°C)	Time (h)	Yield (%)	$M_w \times 10^{-4}$	M_w/M_n
Co(PPh ₃) ₂ (C≡CC ₆ H ₅) ₂	dioxane/toluene	25	3	82.0	2.0	2.2
Ni(PPh ₃) ₂ (C≡CC ₆ H ₅) ₂	dioxane/toluene	25	3	71.5	1.7	2.3
Pd(PPh ₃) ₂ (C≡CC ₆ H ₅) ₂	pyridine	60	18	75.7	1.5	2.9
Pt(PPh ₃) ₂ (C≡CC ₆ H ₅) ₂	pyridine	60	24	0	–	–

^a Conditions: [cat]₀ = 0.01 mol l⁻¹; [M]₀ = 1.0 mol l⁻¹; dioxane/toluene=1 (v/v).

of PBu₃-containing transition metal chlorides follows the sequence: Co(PBu₃)₂Cl₂ > Ni(PBu₃)₂Cl₂ > Pd(PBu₃)₂Cl₂ and Pt(PBu₃)₂Cl₂.

To discuss the effect of late transition metals on catalytic properties of complexes, we further examine the *p*-DEB polymerization in the presence of Co, Ni, Pd and Pt acetylides containing phosphine ligands. Table 3 presents the results for the *p*-DEB polymerization initiated by these acetylides containing triphenylphosphine ligand. The polymerization initiated by cobalt and nickel acetylides with PPh₃ ligand can proceed in 1,4-dioxane/toluene at 25 °C to give high yields (>70%) and high molecular weights ($M_w \geq 1.7 \times 10^4$). Palladium and platinum acetylides with PPh₃ ligand can not polymerize *p*-DEB at 25 °C. Pd(PPh₃)₂(C≡CC₆H₅)₂ polymerizes *p*-DEB in pyridine at 60 °C to afford polymers in 76% yield with M_w of 1.5×10^4 , while Pt(PPh₃)₂(C≡CC₆H₅)₂ shows no catalytic activity under the same conditions. Clearly, the catalytic activity of PPh₃-containing transition metal acetylides decreases in the following order: Co(PPh₃)₂(C≡CC₆H₅)₂ and Ni(PPh₃)₂(C≡CC₆H₅)₂ > Pd(PPh₃)₂(C≡CC₆H₅)₂ > Pt(PPh₃)₂(C≡CC₆H₅)₂.

Table 4 further compares the catalytic activity of these late transition metal acetylides containing PBu₃ ligands. Co(PBu₃)₂(C≡CC₆H₅)₂ can efficiently initiate the *p*-DEB polymerization in DMSO even at room temperature to give soluble polymers in a high yield

up to 85% with a high M_w up to 2.2×10^4 . The *p*-DEB polymerization initiated by Ni(PBu₃)₂(C≡CC₆H₅)₂ in DMSO can not proceed at room temperature, but can efficiently at 60 °C and the yield and M_w of the polymers approach 90% and 2.6×10^4 , respectively. In contrast to Co and Ni acetylides with PBu₃ ligand, Pd(PBu₃)₂(C≡CC₆H₅)₂ and Pt(PBu₃)₂(C≡CC₆H₅)₂ show no activity towards the *p*-DEB polymerization in pyridine at 60 °C. Therefore, the catalytic activity of PBu₃-containing transition metal acetylides follows this order: Co(PBu₃)₂(C≡CC₆H₅)₂ > Ni(PBu₃)₂(C≡CC₆H₅)₂ > Pd(PBu₃)₂(C≡CC₆H₅)₂ and Pt(PBu₃)₂(C≡CC₆H₅)₂.

The polymerization of ethynylfluorenol, ethynyltrimethylsilane, phenylacetylene and *N*-benzylpropargylamine initiated by platinum acetylides containing PPh₃ ligand proceeded only at high temperature (>80 °C) for a long reaction time (100 h) to produce polymers with low molecular weights (<1500) in low yields (0–75%) [3,7,9,34], which also gives the evidence that platinum complexes exhibit very low catalytic activity. On the other hand, polymerization of phenylacetylene in the presence of rhodium acetylide containing PPh₃ ligand proceeded rapidly at room temperature, resulting in formation of stereospecific polyphenylacetylene with a high molecular weight ($M_n = 14,900$) and a narrow molecular weight distribution ($M_w/M_n = 1.15$) in a high yield (97%) [11],

Table 4

Comparison of catalytic activity of PBu₃-containing transition metal acetylides towards the *p*-DEB polymerization^a

Complex	Solvent	Temperature (°C)	Time (h)	Yield (%)	$M_w \times 10^{-4}$	M_w/M_n
Co(PBu ₃) ₂ (C≡CC ₆ H ₅) ₂	DMSO	25	9	84.7	2.2	2.4
Ni(PBu ₃) ₂ (C≡CC ₆ H ₅) ₂	DMSO	60	9	90.4	2.6	2.6
Pd(PBu ₃) ₂ (C≡CC ₆ H ₅) ₂	pyridine	60	48	0	–	–
Pt(PBu ₃) ₂ (C≡CC ₆ H ₅) ₂	pyridine	60	48	0	–	–

^a Conditions: [cat]₀ = 0.01 mol l⁻¹; [M]₀ = 1.0 mol l⁻¹.

indicating rhodium complex possesses higher activity than palladium and nickel complexes.

The catalytic activity of group VIII transition metal chlorides and acetylides towards polymerization of *p*-DEB is related to the electron configuration of the corresponding metal atoms. The catalytic activity of these complexes decreases with increasing the electron shell layers of the corresponding metal elements. For transition metals in the same period of the periodic table, the catalytic activity of the complexes decreases with increasing the electron numbers in the outer shell of the metal elements. Moreover, the activity of transition metal complexes may be related to the first ionization potential of the corresponding metal elements. The ionization potentials of Ni, Co, Pd and Pt are 7.63, 7.88, 8.33 and 9.00 eV, respectively. The catalytic activity of these transition metal complexes towards the *p*-DEB polymerization decreases in the following order: Co > Ni > Pd > Pt. Thus, except for Co, the greater ionization potential the metal element, the lower activity the corresponding complex.

Poly(*p*-diethynylbenzene) (PDEB) prepared is an orange powder. It is soluble in THF, CHCl₃ and toluene. The elemental analysis values of PDEB obtained with Co(PBu₃)₂(C≡CC₆H₅)₂ catalyst are consistent with the theoretical ones. Anal. Calcd. for (C₁₀H₆)_n: C, 95.24; H, 4.76. Found: C, 94.65; H, 4.91%.

The IR spectrum of PDEB obtained with Co(PBu₃)₂(C≡CC₆H₅)₂ catalyst is given in Fig. 1. The IR spectrum shows the characteristic absorption band at

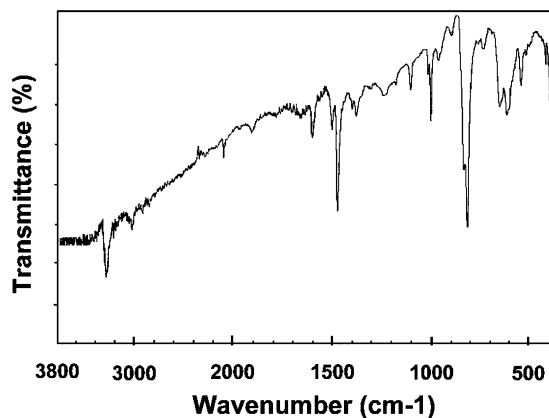


Fig. 1. IR spectrum of PDEB.

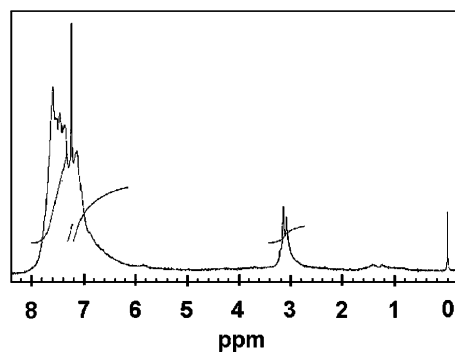


Fig. 2. ¹H NMR spectrum of PDEB.

1603 cm⁻¹ ($\nu_{C\equiv C}$), confirming formation of extended π -conjugated system, but still shows the presence of a $\nu_{C\equiv C}$ band at 2106 cm⁻¹ and a $\nu_{C\equiv C-H}$ band at 3293 cm⁻¹, indicating the presence of a great number of triple bonds in the polymer. Moreover, absorptions characteristic of *trans* structure (1250, 1018, 970, 910 cm⁻¹) [35,36] were observed for PDEB, while ones of *cis* structure (1380, 870, 740 cm⁻¹) [35,36] are very weak or absent. Thus, it is evident that PDEB has a rich-*trans* structure.

The rich-*trans* extended π -conjugated polyene chain structure with the pendent groups of *p*-C₆H₄C≡CH is further confirmed by ¹H NMR (Fig. 2) and ¹³C NMR spectra (Fig. 3). The strong and broad signal from 7.0 to 8.0 ppm can be assigned to aromatic protons. The peaks at 2.8–3.3 ppm are due to the protons of the pendent ethynyl groups. It is worth noticing that the signal at 5.82 ppm, assigned to *cis* polyenic protons [37], is absent, and that the signal

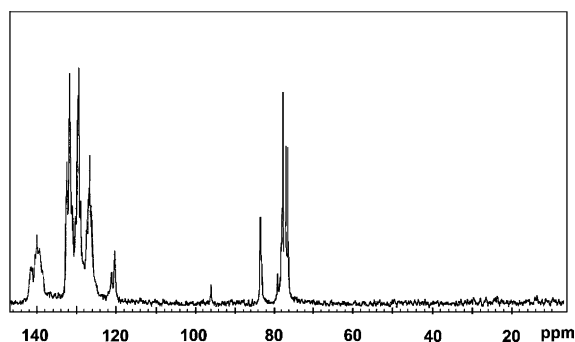


Fig. 3. ¹³C NMR spectrum of PDEB.

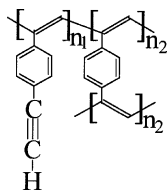


Fig. 4. The chemical structure of PDEB.

at 6.85 ppm, assigned to *trans* polyenic protons [37] is comparatively strong. The ratio of olefinic and aromatic protons to ethynylic protons is nearly equal to 8:1, so more than one triple bond per monomer is opened during the polymerization, because the theoretical ratio should be 5:1 if only one acetylenic group per monomer molecule participated in the polymerization. The peak at 127 ppm is attributed to CH group of *trans* vinylene units in analogy with poly(phenylacetylene) [38]. The carbon signals from the ethynyl groups are at 83 and 79 ppm.

Therefore, the IR, ^1H and ^{13}C NMR spectra support the expected structure of PDEB shown in Fig. 4.

Although the type of catalysts affects the yields and molecular weights of the polymers, the chemical structure of the polymers remains unchanged by varying the transition metals and phosphine ligands of the catalysts.

4. Conclusions

Group VIII transition metal chlorides and acetylides containing phosphine ligands are novel and efficient initiating systems for the *p*-DEB polymerization. The polymerization of *p*-DEB initiated by these complexes proceeds under mild conditions to give soluble polymers with high molecular weights in high yields. The transition metals exert important effect on the catalytic activity of the complexes, but hardly affect the structure of the polymers. The catalytic activity of these complexes falls in with the following order: $\text{Co} > \text{Ni} > \text{Pd} > \text{Pt}$. The catalytic properties of group VIII transition metal complexes are related to the electron configuration of metal elements. PDEB obtained with these catalysts possesses a rich-*trans* extended π -conjugated polyene chain structure with the pendent groups of $p\text{-C}_6\text{H}_4\text{C}\equiv\text{CH}$.

Acknowledgements

We gratefully acknowledge the financial support by National Natural Science Foundation of China.

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