

Transition metal acetylide catalysts for polymerization of alkynes

1. Effect of ligands on catalytic activity of nickel complexes

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Abstract

The catalytic activity of a series of nickel acetylides and chlorides containing different phosphine and alkynyl ligands: $\text{NiL}_2(\text{C}\equiv\text{CR})_2$; $\text{NiL}_2(\text{C}\equiv\text{CR})\text{Cl}$ and NiL_2Cl_2 ($\text{L}_2 = (\text{PPh}_3)_2$, $(\text{PBu}_3)_2$ and $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$; $\text{R} = p\text{-C}_6\text{H}_4\text{C}\equiv\text{CH}$, C_6H_5 , H , CH_2OH and $\text{CH}_2\text{OCOCH}_3$), towards *p*-diethynylbenzene polymerization is compared. The catalytic property of these acetylides is related to chlorine, phosphines and alkynyl ligands bonded to the metal atoms. The polarity, steric hindrance and electron-donating ability of ligands are main factors influencing the catalytic activity of these complexes. Nickel acetylides were found to be novel efficient initiating systems for the alkyne polymerization. The polymerization proceeds under mild conditions to give soluble π -conjugated polymers with weight average molecular weights as high as 4.8×10^4 in yields as high as 95%. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

Polyacetylenes possessing alternating olefinic bonds along the main chain are of intense interest because of their unique physical properties such as photoconductivity, optical nonlinear susceptibility, magnetic susceptibility, chirality and liquid crystallinity [1–5]. Poly(*p*-diethynylbenzene) (PDEB) is one member of the polyacetylenes family. Recently, we found that soluble PDEB shows conductivity, photoluminescence, electroluminescence, third-order nonlinear optical property and humidity sensitivity [6–10]. Research devoted to methods of synthesizing PDEB has been reported. However, the reported

procedures such as thermal, high pressure and shear, γ - and UV-irradiation, electroinitiated and catalytic polymerizations, almost led to insoluble and unstable products or resulted in partially soluble oligomers with low molecular weights in low yields [11–14].

The research and development on organometallic catalysts for synthesis of polymers is an important and attractive field in polymer science and industry. In recent years, transition metal acetylides were found to be effective catalysts for alkynes polymerization [15–20]. To our knowledge, however, there have been no reports on effect of transition metals and ligands on catalytic activity of transition metal acetylides towards alkynes polymerization. We have accomplished polymerization of propargyl alcohol, *p*-diethynylbenzene (*p*-DEB) and their derivatives with transition metal acetylide catalysts to give soluble polymers in high yields [21–25]. We found that

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the metal–carbon σ -bond plays an important role in the polymerization of alkynes initiated by these transition metal acetylides. However, the knowledge about properties of the metal–carbon σ -bond seems still insufficient. Only a few discussions on the infrared and electronic spectra of transition metal acetylides can be found [26–28].

In this work, we discussed the effect of ligands on the infrared and electronic spectra and catalytic activity of nickel acetylides towards the polymerization of alkynes.

2. Experiments

2.1. Materials

Only analytical grade quality chemicals were used. Diethylamine was dried over CaH_2 and distilled under N_2 atmosphere prior to use. Other solvents were dried with activated alumina. *p*-DEB [29], $\text{Ni}(\text{PPh}_3)_2\text{Cl}_2$ [30], $\text{Ni}(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)\text{Cl}_2$ [31], $\text{Ni}(\text{PPh}_3)_2(\text{C}\equiv\text{CC}_6\text{H}_4\text{C}\equiv\text{CH})_2$ [32], $\text{Ni}(\text{PBu}_3)_2(\text{C}\equiv\text{CC}_6\text{H}_4\text{C}\equiv\text{CH})_2$ [32], $\text{Ni}(\text{PPh}_3)_2(\text{C}\equiv\text{CPh})_2$ [32], $\text{Ni}(\text{PBu}_3)_2(\text{C}\equiv\text{CPh})_2$ [33], $\text{Ni}(\text{PBu}_3)_2(\text{C}\equiv\text{CH})_2$ [33], $\text{Ni}(\text{PBu}_3)_2(\text{C}\equiv\text{CCH}_2\text{OH})_2$ [33], $\text{Ni}(\text{PBu}_3)_2(\text{C}\equiv\text{CCH}_2\text{OCOCH}_3)_2$ [23] and $\text{Ni}(\text{PPh}_3)_2(\text{C}\equiv\text{CCH}_2\text{OCOCH}_3)_2$ [23] were prepared by literature methods or modifying reported procedures.

2.2. Measurements

Melting points were determined on a Yanaco MP-500 melting point apparatus. IR spectra were taken on a Nicolet 5-DX FT-IR with nujol mulls. UV–VIS spectra were recorded on a Beckman DU-50 spectrophotometer. 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. [1,2-Bis(diphenylphosphino)ethane]bis(*p*-ethynylphenyleneethynyl)nickel

A suspension of $\text{Ni}(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)\text{Cl}_2$ (1 mmol, 528 mg) in dry HNEt_2 (50 ml) was stirred

and degassed at room temperature for 30 min, and *p*-DEB (2.1 mmol, 265 mg) was added. The reaction mixture was then stirred for 72 h at room temperature. The solid was filtered off and the solvent was evaporated to give an orange oil. The oily residue was dissolved in 5 ml benzene and *n*-hexane (20 ml) was added. The orange crystals were filtered and recrystallized from benzene/*n*-hexane to yield orange crystals (163 mg, 23%): mp (decomposition), 170°C . UV–VIS λ_{max} (THF, nm): 355; 331; 308; 262. FT-IR (nujol mull, cm^{-1}): 3280 (m); 2090 (s); 1600 (m); 1305 (m); 1190 (s); 1175 (s); 1120(s); 1100 (m); 830 (s); 695 (s); 530 (m); 510 (m). Anal. Calcd. for $\text{NiC}_{46}\text{H}_{34}\text{P}_2$: C, 78.10; H, 4.84. Found: C, 77.55; H, 4.90%.

2.3.2. Bis(triphenylphosphine)(*p*-ethynylphenyleneethynyl)chloronickel

A suspension of $\text{Ni}(\text{PPh}_3)_2\text{Cl}_2$ (1 mmol, 654 mg) in dry HNEt_2 (50 ml) was stirred and degassed at room temperature for 30 min, and *p*-DEB (1.0 mmol, 126 mg) was added. The reaction mixture was then stirred for 5 h at room temperature. The solid is filtered off and the solvent was evaporated to give an orange oil. The oily residue was dissolved in 5 ml CHCl_3 and *n*-hexane (20 ml) was added. The orange crystals were filtered off and recrystallized from CHCl_3 /*n*-hexane to yield orange crystals (186 mg, 25%): mp (decomposition), 135°C . UV–VIS λ_{max} (THF, nm): 368; 304; 258. FT-IR (nujol mull, cm^{-1}): 3280 (w); 2089 (s); 1600 (m); 1435 (s); 1305 (w); 1100 (s); 1025 (w); 1000 (w); 840 (s); 740 (s); 695 (s); 628 (w); 550 (w); 522 (s); 510 (s); 497 (m); 460 (w); 420 (w); 390 (w). Anal. Calcd. for $\text{NiC}_{46}\text{H}_{35}\text{P}_2\text{Cl}$: C, 74.27; H, 4.74. Found: C, 74.54; H, 4.83%.

2.4. Polymerization

A typical polymerization procedure is as follows: 378 mg (3 mmol) of sublimed *p*-DEB and 25 mg (0.03 mmol) of [bis(triphenylphosphine)bis(*p*-ethynylphenyleneethynyl)]nickel complex were dissolved 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, filtered from the

solution, washed with CH₃OH, and dried under vacuum at room temperature for 24 h to give PDEB. Other polymerizations were carried out analogously.

3. Results and discussion

3.1. Effect of phosphine ligands on the metal–carbon stretching frequency and the lowest energy band of nickel acetylides

Table 1 lists the influence of phosphine ligands on the lowest energy band and the metal–carbon stretching frequency ($\nu(\text{M}-\text{C})$) of NiL₂(C≡CC₆H₄C≡CH)₂. The influence of phosphine ligands (L) such as PPh₃, PBu₃ and Ph₂PCH₂CH₂PPh₂ on $\nu(\text{M}-\text{C})$ is negligible. The intensity of absorption bands is of the order of four in log ϵ scale, attributed to intramolecular charge transfer transition [28,33]. The complexes almost show three intense absorption bands, and the lowest energy band is empirically assigned to the transition between the molecular orbitals involved in metal–carbon bonds [28,33]. We only discuss the lowest energy band because it is related to activity of the metal–carbon and the complexes. In contrast to infrared spectra, phosphine ligands exert an appreciable effect on the wavelength of the lowest energy band (λ_{max}). The lowest band shows a blue shift and λ_{max} follows the following order: L = PPh₃ > Ph₂PCH₂CH₂PPh₂ > PBu₃. The energy of the lowest band of the complexes increases with increasing the electron-donating ability of phosphines. The basicity and the σ -related donating ability of phosphines increase the density of electron cloud of the metal–carbon bond, and somewhat exert effect on metal–alkynyl charge transfer transitions and the lowest energy band.

Table 1

Effect of phosphine ligands on the metal–carbon stretching vibration and the lowest energy band of NiL₂(C≡CC₆H₄C≡CH)₂

L ₂	$\nu(\text{M}-\text{C})$ (cm ⁻¹)	λ_{max} (nm)
(PPh ₃) ₂	539	371
(PBu ₃) ₂	542	353
Ph ₂ PCH ₂ CH ₂ PPh ₂	540	355

Table 2

Comparison of catalytic activity of Ni(PPh₃)₂Cl₂, Ni(PPh₃)₂(C≡CC₆H₄C≡CH)Cl and Ni(PPh₃)₂(C≡CC₆H₄C≡CH)₂^a

Complex	Time (h)	Yield (%)	M_w × 10 ⁻⁴	M_w/M_n
Ni(PPh ₃) ₂ (C≡CC ₆ H ₄ C≡CH) ₂	3.5	81.2	1.7	2.3
Ni(PPh ₃) ₂ (C≡CC ₆ H ₄ C≡CH)Cl	5	71.2	2.1	1.7
Ni(PPh ₃) ₂ Cl ₂	48	0	–	–

^a Conditions: solvent, DMSO; catalyst concentration, [cat]₀ = 0.01 mol l⁻¹; monomer concentration, [M]₀ = 1.0 mol l⁻¹; 30°C.

3.2. Comparison of the catalytic activity of nickel chloride and acetylide

The results of *p*-DEB polymerization with nickel chloride and acetylide catalysts in DMSO are given in Table 2. Nickel dialkynyl complex shows a higher catalytic activity than nickel monoalkynyl complex, and nickel monoalkynyl complex much higher than nickel chloride: Ni(PPh₃)₂(C≡CC₆H₄C≡CH)₂ > Ni(PPh₃)₂(C≡CC₆H₄C≡CH)Cl ≫ Ni(PPh₃)₂Cl₂. In fact, the chloride shows no activity for *p*-DEB polymerization under tested conditions. It is evident that the chlorine ligand decreases the catalytic activity of the nickel complexes.

3.3. Effect of phosphine ligands on the catalytic activity of the acetylides

The phosphine ligands bonded to the metal atom play an important role on the catalytic properties of these complexes. Table 3 gives yields and molecular weights of PDEB obtained with nickel acetylides containing different phosphine ligands. The *p*-DEB polymerization can proceed at 30°C in the presence of Ni(PPh₃)₂(C≡CC₆H₄C≡CH)₂ to afford PDEB with

Table 3

Effect of phosphine ligands on catalytic activity of NiL₂(C≡CC₆H₄C≡CH)₂^a

L ₂	Temperature (°C)	Time (h)	Yield (%)	M_w × 10 ⁻⁴	M_w/M_n
(PPh ₃) ₂	30	3.5	81.2	1.7	2.3
(PBu ₃) ₂	60	9	95.2	2.2	3.1
Ph ₂ PCH ₂ CH ₂ PPh ₂	60	61	33.3	1.9	2.6

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

a high molecular weight in a high yield. The *p*-DEB polymerization with $\text{Ni}(\text{PBU}_3)_2(\text{C}\equiv\text{CC}_6\text{H}_4\text{C}\equiv\text{CH})_2$ and $\text{Ni}(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)(\text{C}\equiv\text{CC}_6\text{H}_4\text{C}\equiv\text{CH})_2$ catalysts can undergo only at 60°C. The *p*-DEB polymerization with $\text{Ni}(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)(\text{C}\equiv\text{CC}_6\text{H}_4\text{C}\equiv\text{CH})_2$ catalyst produced a polymer in a low yield (33%). Thus, the activity of nickel acetylides with different phosphines follows the sequence: $\text{Ni}(\text{PPh}_3)_2(\text{C}\equiv\text{CC}_6\text{H}_4\text{C}\equiv\text{CH})_2 > \text{Ni}(\text{PBU}_3)_2(\text{C}\equiv\text{CC}_6\text{H}_4\text{C}\equiv\text{CH})_2 > \text{Ni}(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)(\text{C}\equiv\text{CC}_6\text{H}_4\text{C}\equiv\text{CH})_2$. The nickel complex with tributylphosphine ligand exhibits a lower activity than that with triphenylphosphine ligand, probably owing to the greater basicity and the σ -related donating ability of PBU_3 which increases the density of electron cloud of nickel–carbon bond and decreases the reaction activity of this bond. The poor catalytic activity of $\text{Ni}(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)(\text{C}\equiv\text{CC}_6\text{H}_4\text{C}\equiv\text{CH})_2$ is related to the great steric hindrance of 1,2-bis(diphenylphosphino)ethane bridging ligand. The influence of phosphine ligands on catalytic activity of nickel complexes is similar to the effect of phosphine ligands on the lowest energy band of these complexes. The energy of the lowest energy band increases, and the catalytic activity of the complexes decreases with increasing the σ -related electron-donating ability of the phosphine ligands.

3.4. Effect of alkynyl ligands on the catalytic activity of the acetylides

The alkynyl ligands exhibit a great influence on the catalytic activity of nickel acetylides towards *p*-DEB polymerization. The effect of alkynyl ligands is different with varying phosphine ligands. Table 4 compares the catalytic activity of nickel acetylides containing non-polar and polar alkynyl ligands towards

Table 4
Effect of alkynyl ligands on catalytic activity of $\text{Ni}(\text{PPh}_3)_2(\text{C}\equiv\text{CR})_2^a$

R	Time (h)	Yield (%)	$M_w \times 10^{-4}$	M_w/M_n
<i>p</i> -C ₆ H ₄ C≡CH	3	74.3	1.4	2.4
C ₆ H ₅	3	71.5	1.7	2.3
CH ₂ OCOCH ₃	10	57.7	1.3	2.0

^a Conditions: $[\text{cat}]_0 = 0.01 \text{ mol l}^{-1}$; $[\text{M}]_0 = 1.0 \text{ mol l}^{-1}$; 1,4-dioxane/toluene = 1; 25°C.

Table 5
Effect of alkynyl ligands on catalytic activity of $\text{Ni}(\text{PBU}_3)_2(\text{C}\equiv\text{CR})_2^a$

R	Time (h)	Yield (%)	$M_w \times 10^{-4}$	M_w/M_n
<i>p</i> -C ₆ H ₄ C≡CH	48	27.8	2.5	3.0
C ₆ H ₅	48	47.1	3.3	3.4
H	33	76.7	4.8	3.6
CH ₂ OH	33	78.0	4.4	3.1
CH ₂ OCOCH ₃	33	51.6	2.8	2.6

^a Conditions: $[\text{cat}]_0 = 0.01 \text{ mol l}^{-1}$; $[\text{M}]_0 = 1.0 \text{ mol l}^{-1}$; 1,4-dioxane/toluene = 1; 60°C.

p-DEB polymerization in 1,4-dioxane/toluene mixed solvents at 25°C. Nickel acetylides with PPh_3 ligand are efficient initiators for *p*-DEB polymerization, and the polymerization can occur at room temperature to give satisfactory results. Nickel acetylides containing non-polar alkynyl ligands, i.e. *p*-C≡CC₆H₄C≡CH and C≡CC₆H₅, show a little higher activity than that with polar ligand, i.e. C≡CCH₂OCOCH₃, probably due to slight instability of the latter complex. We failed in our attempt to synthesize $\text{Ni}(\text{PPh}_3)_2(\text{C}\equiv\text{CH})_2$ and $\text{Ni}(\text{PPh}_3)_2(\text{C}\equiv\text{CCH}_2\text{OH})_2$ because of their instability.

Effect of polarity of alkynyl ligands on catalytic activity of nickel acetylides with PBU_3 ligand is different from that with PPh_3 ligand as shown in Table 5. The complexes containing polar alkynyl ligands show higher catalytic activity than the corresponding complexes containing non-polar ligands. The acetylides containing small-bulk alkynyl ligands show higher catalytic activity than the corresponding complexes containing large-bulk ligands. The nickel acetylides with PBU_3 ligand show much more stable and inert in solution than that with PPh_3 ligand owing to the great basicity and the electron-donating ability of PBU_3 . The extremely good stability and inertness of initiators are unfavorable to catalysis. The nickel acetylides containing polar alkynyl ligands possess medium stability and fair activity, but that with non-polar alkynyl ligands are too stable to be favorable catalysts for *p*-DEB polymerization. On the other hand, the steric hindrance of PBU_3 ligand is greater than that of PPh_3 ligand resulting from the long chain of *n*-butyl group. The steric repulsion of PBU_3 prevents the coordination of triple bonds of the monomer with metal atoms of the catalysts and the π -complex formation. The great-bulk alkynyl ligands are harmful to the π -complex

formation, which is a preliminary activation step necessary to catalytic polymerization. Therefore, the *p*-DEB polymerization in the presence of nickel acetylides with PBU₃ and great-bulk alkynyl ligands gives PDEB in lower yields.

4. Conclusions

Nickel acetylides are novel efficient initiating systems for *p*-DEB polymerization. Chlorine, phosphines and alkynyl ligands exhibit significant influence on the catalytic activity of transition metal acetylides. The polarity, steric hindrance and electron-donating ability of ligands are main factors influencing the catalytic activity of these complexes.

Acknowledgements

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References

- [1] J.C.W. Chien, Polyacetylene, Academic Press, New York, 1984.
- [2] E. Yashima, K. Maeda, Y. Okamoto, Nature 399 (1999) 449.
- [3] K. Akagi, G. Piao, S. Kaneko, K. Sakamaki, H. Shirakawa, M. Kyotani, Science 282 (1998) 1683.
- [4] E. Yashima, T. Matsushima, Y. Okamoto, J. Am. Chem. Soc. 117 (1995) 11596.
- [5] J.S. Moore, C.B. Gorman, R.H. Grubbs, J. Am. Chem. Soc. 113 (1991) 1704.
- [6] X.W. Zhan, M.J. Yang, Z.Q. Lei, Y. Li, Y.Q. Liu, G. Yu, D.B. Zhu, Adv. Mater. 12 (2000) 51.
- [7] G. Yu, Y.Q. Liu, X.W. Zhan, H.Y. Li, M.J. Yang, D.B. Zhu, Thin Solid Films 363 (2000) 126.
- [8] M.J. Yang, Y. Li, X.W. Zhan, M.F. Ling, J. Appl. Polym. Sci. 74 (1999) 2010.
- [9] X.W. Zhan, M.J. Yang, M.X. Wan, Synth. Met. 94 (1998) 249.
- [10] G. Casalbore-Miceli, N. Camaioni, M.J. Yang, M. Zheng, X.W. Zhan, A. D'Aprano, Solid State Ionics 100 (1997) 217.
- [11] M. Grovu-Ivanoiu, V. Bulacovschi, C.I. Simionescu, Makromol. Chem. 186 (1985) 2247.
- [12] O. Rhode, G. Wegner, Makromol. Chem. 179 (1978) 1999.
- [13] O. Rhode, G. Wegner, Makromol. Chem. 179 (1978) 2013.
- [14] H. Jabloner Jr., L.C. Cessna, Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.) 17 (1976) 169.
- [15] M.V. Russo, A. Furlani, P. Altamura, I. Fratoddi, G. Polzonetti, Polymer 38 (1997) 3677.
- [16] Y. Kishimoto, T. Miyatake, T. Ikariya, R. Noyori, Macromolecules 29 (1996) 5054.
- [17] M.V. Russo, A. Furlani, M. Cuccu, G. Polzonetti, Polymer 37 (1996) 1715.
- [18] Y. Kishimoto, P. Eckerle, T. Miyatake, T. Ikariya, R. Noyori, J. Am. Chem. Soc. 116 (1994) 12131.
- [19] A. Bolasco, F. Chimenti, A. Frezza, A. Furlani, G. Infante, E. Muraglia, G. Ortaggi, G. Polzonetti, M.V. Russo, G. Sleiter, Polymer 33 (1992) 3049.
- [20] M.V. Russo, G. Iucci, G. Polzonetti, A. Furlani, Polymer 33 (1992) 4401.
- [21] M.J. Yang, H.M. Sun, M.F. Ling, Acta Polym. Sinica (2000) 161.
- [22] M.J. Yang, M. Zheng, A. Furlani, M.V. Russo, J. Polym. Sci.: Part A, Polym. Chem. 32 (1994) 2709.
- [23] X.W. Zhan, M.J. Yang, H.M. Sun, Macromol. Rapid Commun., in press.
- [24] X.W. Zhan, M.J. Yang, Macromol. Rapid Commun. 21 (2000) 1263.
- [25] X.W. Zhan, M.J. Yang, H.M. Sun, Catal. Lett., in press.
- [26] H. Masai, K. Sonogashira, N. Hagihara, J. Organomet. Chem. 26 (1971) 271.
- [27] P.J. Kim, H. Masai, K. Sonogashira, N. Hagihara, Inorg. Nucl. Chem. Lett. 6 (1970) 181.
- [28] H. Masai, K. Sonogashira, N. Hagihara, Bull. Chem. Soc. Jpn. 44 (1971) 2226.
- [29] A.S. Hay, J. Org. Chem. 25 (1960) 637.
- [30] L.M. Venanzi, J. Chem. Soc. (1958) 719.
- [31] J. Chatt, F.A. Hart, D.T. Rosevear, J. Chem. Soc. (1961) 5504.
- [32] R. Nast, A. Beyer, J. Organomet. Chem. 204 (1981) 267.
- [33] P. Carusi, A. Furlani, Gazz. Chim. Ital. 110 (1980) 7.