# Chloro-nickel and chloro-cobalt complexes containing phosphine ligands: efficient initiators for polymerization of alkynes

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Received 31 October 2001; accepted 23 January 2002

We have developed a new series of single-component air- and moisture-stable catalysts for alkyne polymerization based on chloro-nickel and chloro-cobalt complexes containing phosphine ligands. The polymerization of *p*-diethynylbenzene initiated by these complexes proceeds smoothly in the presence of amines at room temperature to afford soluble $\pi$-conjugated polymers in yields as high as 81% with weight-average molecular weight up to 17 600.

**KEY WORDS:** transition metal chloride; catalyst; alkyne; polymerization.

## 1. Introduction

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]. These kinds of catalysts are, however, extremely air- and moisture-sensitive and must be handled in dry and inert atmosphere. Moreover, these catalysts are almost binary- or ternary-component systems and preparation procedures are troublesome. In contrast to early transition metal system, efficient late transition metal catalysts for polymerization of alkynes have remained rare. For example, $[Rh(diene)Cl]_2$ effectively polymerizes substituted phenylacetylene [3,4]. However, the halides of nickel, palladium and platinum often dimerize, trimerize or oligomerize alkynes [5–7].

In recent years, late transition metal acetylides were found to be effective catalysts for alkyne polymerization. Russo *et al.* used nickel, palladium and platinum acetylides containing triphenylphosphine ligand as catalysts for polymerization of alkynes to give polymers with molecular weights of $500–10^4$ [8,9]. Kishimoto and his coworkers reported stereospecific living polymerization of phenylacetylenes initiated by rhodium acetylides [10]. We found that nickel and palladium acetylides are capable of polymerizing both non-polar alkynes and polar substituted acetylenes [11–14].

In general, the transition metal acetylides are prepared from their chlorides and terminal alkynes in amines [15]. If the transition metal acetylides can be made *in situ* in amines from the simple chlorides and monosubstituted acetylenes and then initiate the polymerization of the acetylenic monomers, the polymer synthesis is convenient and obviates the trouble of preparing the acetylide catalysts. Such a consideration prompted us to exploit the simple transition metal chlorides as the initiators for the alkyne polymerization. We now report that late transition metal nickel and cobalt chlorides containing phosphine ligands are efficient initiators for polymerization of alkynes. All these catalysts are single-component, commercially available or easy to prepare, stable in air, soluble in common organic solvents and convenient to initiate the polymerization.

## 2. Experimental

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*-Diethynylbenzene [*p*-DEB, $HC{\equiv}CC_6H_4C{\equiv}CH$] [16] and the chlorides such as $Co(PBu_3)_2Cl_2$ [17], $Ni(PPh_3)_2Cl_2$ [18] and $(\pi\text{-}C_5H_5)(PPh_3)NiCl$ [19] were prepared by literature methods or by modifying reported procedures.

A typical polymerization procedure is as follows: 567 mg (4.5 mmol) of sublimed *p*-DEB and 39 mg (0.06 mmol) of $Ni(PPh_3)_2Cl_2$ were dissolved in $HNEt_2$ (1.25 ml) and toluene (1.25 ml) mixed solvents. Under nitrogen atmosphere, the polymerization proceeded at 25 °C for 6 h. The resulting polymer was precipitated by the addition of methanol, filtered from the solution, washed with $CH_3OH$, and dried under vacuum at room temperature for 24 h to give yellow powder (460 mg, 81.2%). Other polymerizations were carried out analogously. $^1H$ NMR ($CDCl_3$): $\delta$ 6.8–8.0 (m,

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1011-372X/02/0500-0059/0 © 2002 Plenum Publishing Corporation

$C_6H_4$ and H$-$C$\equiv$), 2.8–3.3 (m, H$-$C$\equiv$). $^{13}$C NMR ($CDCl_3$): $\delta$ 140 and 129 (H$-$C$=$C), 139 and 120 (quaternary C of $C_6H_4$), 132 and 127 (CH of $C_6H_4$), 83 and 79 (H$-$C$\equiv$C). FT-IR (KBr): $\nu$ 3293 (s, $\equiv$C$-$H), 2106 (m, C$\equiv$C), 1603 cm$^{-1}$ (m, C$=$C). Raman: 2106 (m, C$\equiv$C), 1598 and 1562 cm$^{-1}$ (s, C$=$C). Anal. calcd. for $(C_{10}H_6)_n$: C, 95.24; H, 4.76. Found: C, 94.42; H, 4.91%.

Separation and characterization of nickel acetylide: 567 mg (4.5 mmol) of sublimed *p*-DEB and 78 mg (0.12 mmol) of $Ni(PPh_3)_2Cl_2$ were dissolved in $HNEt_2$ (2.5 ml) and toluene (2.5 ml) mixed solvents. Under nitrogen atmosphere, the reaction mixture was then stirred for 2 h, and an orange solution resulted. The solid is filtered off and $HNEt_2$ was evaporated to give an orange oil. *n*-Hexane (10 ml) was added. The orange crystals were filtered off and recrystallized from benzene/*n*-hexane to yield orange crystals: mp (decomposition) 160 °C. Anal. calcd. for $NiC_{56}H_{40}P_2$: C, 80.69; H, 4.84. Found: C, 80.64; H, 4.82%. UV–vis $\lambda_{max}$ (THF): 371, 302, 261 nm. FT-IR (Nujol mull): $\nu$ 3280 (s, $\equiv$C$-$H), 2097 (s, C$\equiv$C), 539 cm$^{-1}$ (m, Ni$-$C). These characterization data are almost consistent with those in the literature [15].

FT-IR spectra were taken on a Perkin-Elmer System 2000 FT-IR spectrometer with KBr pellets or Nujol mulls. The FT Raman spectrum was acquired on a Bio-rad FTS6000 spectrometer fitted with a quartz beam splitter and equipped with a Raman III accessory with a liquid nitrogen-cooled germanium detector. The defocused 1064 nm line of an air-cooled Nd:YAG near IR laser (coherent) was used to excite the spectrum. The sample was excited in 180 arrangement with a laser power of 130 mW. UV–vis spectra were recorded on a Beckman DU-50 spectrophotometer. $^1$H and $^{13}$C NMR spectral data are expressed in ppm relative to internal standard of tetramethylsilane and were obtained in $CDCl_3$ 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.

## 3. Results and discussion

Table 1 summarizes the results for the polymerization of *p*-DEB initiated by chloro-nickel and chloro-cobalt complexes containing phosphine ligands. The solvent plays an important role in the *p*-DEB polymerization. $Ni(PPh_3)_2Cl_2$ cannot polymerize *p*-DEB in toluene at room temperature, but initiates the polymerization efficiently in $HNEt_2$. Although the polymer yield is high (75%), the product is hardly soluble. It was found that $HNEt_2$-toluene mixed solvent is favorable for the polymerization since the catalyst, monomer and polymer are soluble in this mixed solvent, resulting in formation of a homogeneous polymerization system and a soluble polymer. The *p*-DEB polymerization initiated by $Ni(PPh_3)_2Cl_2$ in $HNEt_2$–toluene proceeds smoothly at room temperature after an induction period of ~2 h. The polymer yield is as high as 81%; the weight-average molecular weight ($M_w$) and polydispersity index ($M_w/M_n$) of the polymer are 15 300 and 1.8, respectively. The real initiator of the polymerization is a tetracoordinate Ni acetylide, *i.e.*, $Ni(C\equiv CC_6H_4C\equiv CH)_2(PPh_3)_2$. The acetylide is generated *in situ* in $HNEt_2$ from $Ni(PPh_3)_2Cl_2$ and *p*-DEB during the induction period at room temperature. The formation of the acetylide is confirmed by the color changing from dark green (chloride) to orange (acetylide) and by isolating it from the polymerization system and characterization by melting point, elemental analysis, FT-IR and UV–vis spectra. In fact, *p*-DEB can be polymerized in the presence of $Ni(C\equiv CC_6H_4C\equiv CH)_2(PPh_3)_2$ under the same conditions to give polymers in a yield of 81% [20].

In recent years, transition metal and rare earth metallocene complexes were found to be efficient catalysts for polymerization of olefins to give polymers with high molecular weights, low polydispersity and high stereoregularity in high yields [21]. These metallocene complexes are, however, air- and moisture-sensitive and must be handled in dry and inert atmosphere. Moreover, these catalysts are binary or ternary systems. We have successfully employed nickelocene acetylides as initiators for polymerization of alkynes [12]. We now attempt to use simple, single-component and stable nickelocene

Table 1
Polymerization of *p*-DEB initiated by chloro-nickel and chloro-cobalt complexes containing phosphine ligands. Catalyst concentration: 0.02 M; monomer concentration: 1.5 M; $HNEt_2$/toluene = 1 (volume). In the absence of $HNEt_2$ or pyridine, no polymer was formed in the presence of these catalysts under the same conditions

| Complex | Solvent | $T$ (°C) | $t$ (h) | Yield (%) | $M_w \times 10^{-4}$ | $M_w/M_n$ |
|---|---|---|---|---|---|---|
| $Ni(PPh_3)_2Cl_2$ | $HNEt_2$ | 25 | 6 | 74.7 | – | – |
| $Ni(PPh_3)_2Cl_2$ | $HNEt_2$/toluene | 25 | 6 | 81.2 | 1.53 | 1.8 |
| $(\pi\text{-}C_5H_5)(PPh_3)NiCl$ | pyridine | 30 | 24 | 75.8 | 1.76 | 2.7 |
| $Co(PBu_3)_2Cl_2$ | $HNEt_2$/toluene | 25 | 10 | 81.0 | 1.67 | 2.2 |

chloride as a catalyst for polymerization of substituted acetylenes. Table 1 presents the results for the *p*-DEB polymerization initiated by ($\pi$-$C_5H_5$)($PPh_3$)NiCl. Just like $Ni(PPh_3)_2Cl_2$, its cousin containing cyclopentadienyl ligand also cannot polymerize *p*-DEB in toluene at 30 °C, while it initiates the polymerization efficiently in pyridine. The yield and $M_w$ of the polymer are 76% and 17 600, respectively.

We further examine the catalytic properties of chlorocobalt complex containing $PBu_3$ ligands. In contrast to the polymerization in toluene, the cobalt chloride with tributylphosphine ligand, *i.e.* $Co(PBu_3)_2Cl_2$, can efficiently initiate the *p*-DEB polymerization in the presence of $HNEt_2$ even at room temperature to give soluble polymers in 81% yield with a $M_w$ of 16 700.

The IR data of poly(*p*-diethynylbenzene) obtained with $Ni(PPh_3)_2Cl_2$ catalyst show the characteristic band at $1603\,cm^{-1}$ ($\nu_{C=C}$) confirming the formation of an extended $\pi$-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 carbon–carbon triple bonds in the polymer. The Raman band of the skeletal $\nu_{C=C}$ mode of $\pi$-conjugated sequences was found at $1598\,cm^{-1}$ with a shoulder at $1562\,cm^{-1}$ [22]. The band at $2106\,cm^{-1}$ is attributed to a $\nu_{C\equiv C}$ mode.

The extended $\pi$-conjugated polyene chain structure with the pendent groups of $p$-$C_6H_4C\equiv CH$ is further proved by $^1H$ and $^{13}C$ NMR spectral data. The strong and broad signal from 6.8 to 8.0 ppm can be assigned to aromatic and olefinic protons. The peaks at 2.8–3.3 ppm are due to the protons of the pendent ethynyl groups. The peak at 129 ppm is attributed to the CH group of vinylene units in the main chain of the polymer in analogy with polyphenylacetylene [23], and the signal at 140 ppm is attributed to the quaternary main chain carbon. The carbon signals from the benzene ring are at 139 and 120 ppm (quaternary C of $C_6H_4$) and 132 and 127 ppm (CH of $C_6H_4$) [22]. The carbon signals from the ethynyl groups are at 83 and 79 ppm.

Although the type of catalyst affects the yields and molecular weights of the polymers, the chemical structure of the polymers remains unchanged by varying the structure of the catalysts.

## 4. Conclusions

We have explored chloro-nickel and chloro-cobalt complexes containing phosphine ligands as catalysts for polymerization of alkyne such as *p*-DEB. All the catalysts are single-component, commercially available or easy to prepare, stable in air, soluble in common organic solvents and convenient for initiating the polymerization. The polymerization of *p*-DEB initiated by these complexes proceeds smoothly in the presence of amines at room temperature to afford soluble $\pi$-conjugated polymers with high molecular weights in high yields. Solvents exhibit significant influence on the polymerization. The real initiator of the polymerization is a Ni or Co acetylide generated *in situ* in $HNEt_2$ from the chloride and *p*-DEB.

## Acknowledgments

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

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