

# Polymerization of styrene by Novel Ni(II)- and Pd(II)-based complexes

SUN, Hong-Mei\*<sup>a</sup> (孙宏枚)      YANG, Mu-Jie<sup>b</sup> (杨慕杰)

<sup>a</sup> Department of Chemistry and Chemical Engineering, Suzhou University, Jiangsu 215006, China

<sup>b</sup> Department of Polymer Science and Engineering, Zhejiang University, Zhejiang 310027, China

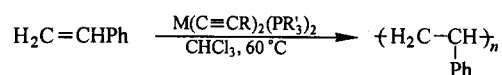
The catalytic activities of nine neutral nickel and palladium  $\sigma$ -acetylide complexes [ $M \equiv (C \equiv CR)_2(PR'_3)_2$ ,  $M = Ni, Pd$ ;  $R = Ph, CH_2OH, CH_2OOCCH_3, CH_2OOCPh, CH_2OOCPhOH-o$ ;  $R' = Ph, Bu$ ] are compared. Among them,  $Ni(C \equiv CPh)_2(PBu_3)_2$  shows the highest catalytic activity and gives the polystyrene with high molecular weight ( $M_w = 188800$ ) and a syndio-rich microstructure. The catalytic behavior of transition metal acetylides is related to metal, phosphine, and alkynyl ligands bonded to the metal atoms.

**Keywords** Styrene, later transition metal acetylide complex, catalyst, polymerization, syndio-rich

## Introduction

Homogeneous organometallic catalytic systems based on early transition metal  $d^0$  complexes are extensively used for the coordination polymerization of nonpolar olefins such as ethylene, propylene, and styrene.<sup>1</sup> These well-defined initiators also can serve as mechanistic models for traditional Ziegler-Natta catalysts. In contrast to early metal systems, late metal catalysts often dimerize or oligomerize olefins due to the competing  $\beta$ -hydride elimination reaction.<sup>2</sup> In 1995, Brookhart *et al.*<sup>3</sup> first reported that Pd(II)- and Ni(II)-based catalysts were able to polymerize ethylene to afford high molecular mass polymers. Since then, there has been intense interest in the use of soluble late transition metal based catalysts for  $\alpha$ -olefin oligomerizations and polymerizations,<sup>4</sup>  $\alpha$ -olefin copolymerizations,<sup>5</sup>  $\alpha$ -olefin/functionalized vinyl monomer copolymerizations,<sup>6</sup> and ethylene/CO copolymerizations.<sup>7</sup> These homogeneous, well-defined

palladium, nickel, iron, and cobalt-based catalysts have emerged as a new versatile class of initiators for insertion-type polymerization of linear and cyclic olefins,<sup>8</sup> and most of the Pd(II)- and Ni(II) initiators are cationic methyl complexes incorporating bulky  $\alpha$ -diimine ligands which effectively retarding the rate of chain transfer.<sup>6b</sup> However, there is few report referred to the polymerization of styrene with single-component catalytic system of late transition metal. We report here the first example of neutral Ni(II)- and Pd(II)-based complexes catalysts [ $M(C \equiv CR)_2(PR'_3)_2$ ,  $M = Ni, Pd$ ;  $R = Ph, CH_2OH, CH_2OOCCH_3, CH_2OOCPh, CH_2OOCPhOH-o$ ;  $R' = Ph, Bu$ ] for the polymerization of styrene, and discussed the influence of metals, phosphine ligands, and alkynyl groups on their catalytic activities.



$M = Ni, Pd$ ;  $R = Ph, CH_2OH, CH_2OOCCH_3, CH_2OOCPh, CH_2OOCPhOH-o$ ;  $R' = Ph, Bu$

## Experimental

### Materials

Diethylamine was dried over  $CaH_2$  and distilled under  $N_2$  atmosphere prior to use. All the other solvents were analytical grade and dried with activated alumina. Styrene (St) was dried over  $CaH_2$  and distilled under  $N_2$

\* E-mail: Wangsung@public1.sz.js.cn

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atmosphere at reduced pressure. Transition metal chloride such as  $\text{Pd}(\text{PPh}_3)_2\text{Cl}$ ,<sup>9a</sup>  $\text{Pd}(\text{PBu}_3)_2\text{Cl}_2$ ,<sup>9b</sup>  $\text{Ni}(\text{PPh}_3)_2\text{Cl}$ <sup>9c</sup> and  $\text{Ni}(\text{PBu}_3)_2\text{Cl}_2$ <sup>9d</sup> were prepared according to the literature. Nine transition metal acetylides  $\text{Pd}(\text{PPh}_3)_2(\text{C}\equiv\text{CPh})_2$  (PPP),<sup>10b</sup>  $\text{Pd}(\text{PPh}_3)_2(\text{C}\equiv\text{CCH}_2\text{OH})_2$  (PPO),<sup>11a</sup>  $\text{Pd}(\text{PPh}_3)_2(\text{C}\equiv\text{CCH}_2\text{OOCCH}_3)_2$  (PPA),<sup>11b</sup>  $\text{Pd}(\text{PPh}_3)_2(\text{C}\equiv\text{CCH}_2\text{OOCPh})_2$  (PPB),<sup>11b</sup>  $\text{Pd}(\text{PPh}_3)_2(\text{C}\equiv\text{CCH}_2\text{OOCPhOH-}o)_2$  (PPS),<sup>11b</sup>  $\text{Ni}(\text{PPh}_3)_2(\text{C}\equiv\text{CPh})_2$  (NPP),<sup>11c</sup>  $\text{Ni}(\text{PBu}_3)_2(\text{C}\equiv\text{CCH}_2\text{OH})_2$  (NBO),<sup>10a</sup> and  $\text{Ni}(\text{PBu}_3)_2(\text{C}\equiv\text{CPh})_2$  (NBP),<sup>10a</sup> were prepared according to the literature.

*Trans-Bis (2-phenylethynyl) bis (tributylphosphine) palladium* [ $\text{Pd}(\text{C}\equiv\text{CPh})_2(\text{PBu}_3)_2$ ] (PBP)

$\text{Pd}(\text{PBu}_3)_2\text{Cl}_2$  (0.5 mmol, 0.291 g),  $\text{CuI}$  (0.005 mmol, 0.00095 g), dry  $\text{NH}(\text{C}_2\text{H}_5)_2$  (45 mL), and  $\text{HC}\equiv\text{CPh}$  (2.0 mmol, 0.22 mL) were introduced into a reaction vessel under nitrogen atmosphere. The reaction solution turned from a yellow color to a colorless one after the mixture was stirred at room temperature for 5 h. The solid was filtered off and the solvent was evaporated to give a colorless oil. The oil residue was dissolved in benzene (5 mL) and treated with ethanol (5 mL) in turn. The suspension was kept at low temperature (0°C) overnight. The grey crystals were filtered off to yield grey crystals (45%): mp 83°C.  $\nu_{\text{max}}$ : 2097 (s,  $\text{C}\equiv\text{C}$ ), 693 and 720 (s,  $\text{C}_6\text{H}_5$ ), and 583 (w, C-Pd)  $\text{cm}^{-1}$ . Anal.  $\text{PdC}_{40}\text{H}_{64}\text{P}_2$ . Calcd: C, 67.32; H, 8.99. Found: C, 67.21; H, 9.39.

### Polymerization

*Typical polymerization procedure* Into a 30 mL well-dried ampoule, 10.6 mg (0.016 mmol) of NBP was dissolved in  $\text{CHCl}_3$  (0.20 mL), then 0.80 mL (6.83 mmol) of styrene was injected. Under purified nitrogen atmosphere, the polymerization was held at 60°C for a definite reaction time. Then,  $\text{HCl}$ /ethanol (10%, 0.5 mL) was added to decompose the catalyst, and  $\text{CHCl}_3$  (6 mL) was added to dissolve the polymer, which was precipitated as white wadding with the addition of large excess of ethanol. Polystyrene (PS) was washed with ethanol and dried *in vacuo* at room temperature for 24 h.

### Measurements

Melting points were determined on a Yanaco MP-500 melting point apparatus. Elemental analyses were obtained on a Carloerba Model 1106 elemental analyzer. IR spectra were taken on a Nicolet 5-DX FTIR as Nujol mulls or KBr pellets.  $^{13}\text{C}$  NMR spectral data were expressed relative to internal standard and were obtained in  $\text{CDCl}_3$  on a Varian Unity 200 NMR spectrometer. The molecular weights of PS ( $M_n$  and  $M_w$ ) and the polydispersity index were measured on a Waters 208 gel permeation chromatograph with three  $\mu$ -styragel linear columns ( $10^4$  nm,  $10^3$  nm, and  $10^2$  nm) versus polystyrene standard, in THF at 25°C.

### Results and discussion

The effects of structural variations of transition metal acetylides on their catalytic activities for styrene polymerization in  $\text{CHCl}_3$  at 60°C are summarized in Tables 1 and 2. The phosphine ligands play an important role on the catalytic behavior of these complexes. It is observed that the complex with tributylphosphine ligand showed no decomposition during polymerization, and showed a much higher catalytic activity (as a higher conversion of polymerization is obtained) than the one with triphenylphosphine ligand does. Moreover, the polymerization by tributylphosphine derivative gives polystyrene with much higher molecular weight. For example, the number-average molecular weight ( $M_n$ ) of PS obtained with  $\text{Pd}(\text{PBu}_3)_2(\text{C}\equiv\text{CPh})_2$  reaches 123100 while it is only 17700 for PS with  $\text{Pd}(\text{PPh}_3)_2(\text{C}\equiv\text{CPh})_2$  under the same conditions, meanwhile a slight higher monomer conversion (20%) and a narrower molecular weight distribution (MWD) (1.96) of PS were obtained with the former catalyst. The difference of catalytic activity between the two catalysts may be mainly caused by the different stability of these complexes in the polymerization reaction. As shown in Table 1, the complex with triphenylphosphine ligand is unstable during the course of St polymerization. It will lose  $\text{PPh}_3$  ligand and even the precipitation of black Pd appeared. The instability of the triphenylphosphine complex might be due to the weaker  $\sigma$ -donor ability of  $\text{PPh}_3$  together with the greater rigid steric hindrance.

The alkynyl ligands also have an influence on the

catalytic activity. Take the triphenylphosphine palladium acetylides as an example, the conversion of polymerization by the catalyst with non-polar alkynyl ligand [such as  $\text{Pd}(\text{PPh}_3)_2(\text{C}\equiv\text{CPh})_2$ , (Table 1, experiment 1)] is higher than that with polar alkynyl ligand [such as  $\text{Pd}(\text{PPh}_3)_2(\text{C}\equiv\text{CCH}_2\text{OH})_2$ , (Table 2, experiment 2)]. Besides, the polystyrene (PS) with higher molecular weight ( $M_n = 17700$ ) and more narrow molecular weight distribution (MWD) (2.12) were obtained with the former catalyst. Furthermore, for the palladium acetylides with ester group, the catalytic activities of these complexes decrease with increasing acidity of the corresponding acids (Table 1, experiment 3—5). As we have known, the acidity follows the sequence: salicylic acid ( $K_a = 105 \times 10^{-5}$ ) > benzoic acid ( $K_a = 6.3 \times 10^{-5}$ ) >

acetic acid ( $K_a = 1.75 \times 10^{-5}$ ).<sup>12</sup> Besides, it is found that dichloro derivative, for example,  $\text{Pd}(\text{PBu}_3)_2\text{Cl}_2$ , does not catalyze the polymerization of styrene at all. These results disclose that the existence of metal-carbon (M—C) bond with definite stability in the acetylide complex is necessary for the St polymerization reaction.

Transition metals also exhibit great influence on the catalytic activity. As shown in Tables 1 and 2, the conversion of polymerization with the nickel diphenylethynyl complex [such as  $\text{Ni}(\text{PBu}_3)_2(\text{C}\equiv\text{CPh})_2$ ] is higher than that with the palladium complex [such as  $\text{Pd}(\text{PBu}_3)_2(\text{C}\equiv\text{CPh})_2$ ]. However, the molecular weight of PS obtained with nickel catalyst is much lower than that with palladium catalyst.

**Table 1** Comparison of catalytic activities of palladium and nickel acetylides for St polymerization

No.	Catalyst	Catalyst in polymerization system	Yield (%)	Polymer colour
1	$\text{Pd}(\text{PPh}_3)_2(\text{C}\equiv\text{CPh})_2$	decomposition <sup>a</sup>	18	light-yellow
2	$\text{Pd}(\text{PPh}_3)_2(\text{C}\equiv\text{CCH}_2\text{OH})_2$	decomposition <sup>a</sup>	12	grey-white
3	$\text{Pd}(\text{PPh}_3)_2(\text{C}\equiv\text{CCH}_2\text{OOCCH}_3)_2$	decomposition <sup>a</sup>	18	light-yellow
4	$\text{Pd}(\text{PPh}_3)_2(\text{C}\equiv\text{CCH}_2\text{OOCPh})_2$	decomposition <sup>b</sup>	12	light-yellow
5	$\text{Pd}(\text{PPh}_3)_2(\text{C}\equiv\text{CCH}_2\text{OOCPhOH-}o)_2$	decomposition <sup>b</sup>	7	light-yellow
6	$\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$	no decomposition	0	—
7	$\text{Pd}(\text{PBu}_3)_2(\text{C}\equiv\text{CPh})_2$	no decomposition	20	white
8	$\text{Pd}(\text{PBu}_3)_2\text{Cl}_2$	no decomposition	0	—
9	$\text{Ni}(\text{PBu}_3)_2(\text{C}\equiv\text{CPh})_2$	no decomposition	30	white
10	$\text{Ni}(\text{PBu}_3)_2(\text{C}\equiv\text{CCH}_2\text{OH})_2$	no decomposition	14	white
11	$\text{Ni}(\text{PPh}_3)_2(\text{C}\equiv\text{CPh})_2$	decomposition <sup>c</sup>	16	white

Conditions: [St] = 6.84 mol/L, [Cat] = 0.016 mol/L,  $\text{CHCl}_3$ , 24 h, 60°C,  $\text{N}_2$ .

<sup>a</sup> crystal grains, <sup>b</sup> crystal grains and black powder, <sup>c</sup> muddy and opaque body.

**Table 2** Molecular weight and its distribution of PS obtained with different catalysts

Catalyst	$M_n \times 10^4$	$M_w \times 10^4$	MWD
$\text{Pd}(\text{PPh}_3)_2(\text{C}\equiv\text{CPh})_2$	1.77	3.77	2.12
$\text{Pd}(\text{PPh}_3)_2(\text{C}\equiv\text{CCH}_2\text{OH})_2$	1.08	3.12	2.88
$\text{Pd}(\text{PBu}_3)_2(\text{C}\equiv\text{CPh})_2$	12.31	24.17	1.96
$\text{Ni}(\text{PPh}_3)_2(\text{C}\equiv\text{CPh})_2$	1.02	8.65	8.52
$\text{Ni}(\text{PBu}_3)_2(\text{C}\equiv\text{CPh})_2$	9.73	18.88	1.94

Conditions are the same as Table 1.

$M_n$ : number-average molecular weight;  $M_w$ : Weight-average molecular weight.

The polystyrene (PS) obtained with  $\text{Ni}(\text{PBu}_3)_2(\text{C}\equiv\text{CPh})_2$  in  $\text{CHCl}_3$  at 60°C has a high molecular weight ( $M_w = 188800$ ) and a syndio-rich microstruc-

ture, which is confirmed by the <sup>13</sup>C NMR spectrum of PS. The aromatic C-1 spectrum of a syndiotactic-rich polystyrene is shown in Fig. 1. Three distinct peaks were appeared at  $\delta$  145.22—145.28 (rr), 145.62 (mr), and 145.86—146.91 (mm),<sup>13</sup> and the relative amount of the rr triad is much higher than those of other triads in the PS obtained.

In conclusion, nickel and palladium acetylides complexes are novel single-component catalysts for styrene polymerization. The catalytic behavior of late transition metal acetylides complexes is mainly related to the rigid steric hindrance, polarity, and electron-donating ability of ligands in the complexes as well as the metal. Among the nine nickel and palladium complexes,

$\text{Ni}(\text{PBu}_3)_2(\text{C}\equiv\text{CPh})_2$  showed the highest catalytic activity in  $\text{CHCl}_3$  at  $60^\circ\text{C}$  and gives the polystyrene with a high molecular weight ( $M_w = 188800$ ) and a syndio-rich microstructure. The study focus on improving the catalytic activity of late transition metal complexes as a single-component catalyst, together with the polymerization mechanism are in progress.

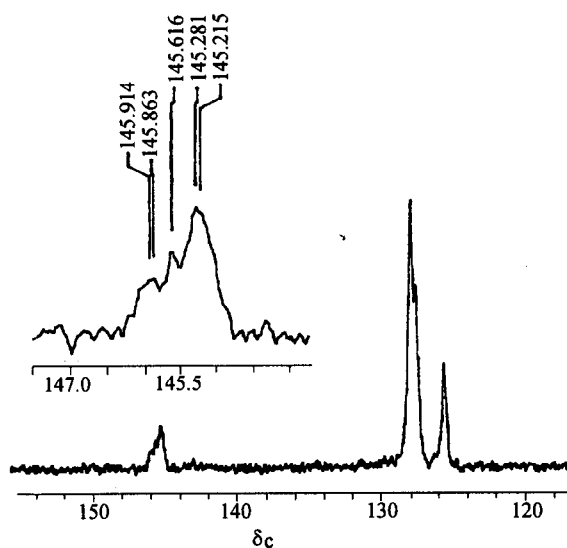


Fig. 1  $^{13}\text{C}$  NMR spectrum of polystyrene ( $\text{CDCl}_3$ , 50 MHz).

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