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Transition metal acetylide catalysts for polymerization of polar alkynes

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A new series of single-component air-stable transition metal acetylide catalysts with the structures $ML_2(C\equiv CR)_2$ (M = Ni and Pd, L = PPh_3 and PBu_3, R = p-$C_6H_4C\equiv CH$, C_6H_5, H, CH_2OH, CH_2OCOCH_3, $CH_2OCOC_6H_5$ and $CH_2OCOC_6H_4OH$-*o*) for polymerization of polar alkynes were developed. Transition metals, phosphine and alkynyl ligands and solvents exhibited significant influence on the polymerization. Propargyl alcohol could be polymerized with these catalysts under mild conditions to give soluble rich-*trans* polymers with weight average molecular weights as high as 5.7×10^4 in yields as high as 79%.

Keywords: polymerization, propargyl alcohol, poly(propargyl alcohol), transition metal acetylide, catalyst

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, photoluminescence and electroluminescence [1–6]. Because of these unique properties, polyacetylenes seem promising as functional polymer materials. Poly(propargyl alcohol) (POHP) is one of polyacetylenes with a CH_2OH polar substituent. In recent years, we found that POHP could be employed as a sensitive element material in humidity sensors [7]. In the past 30 years, POHP was synthesized using plasma, high pressure, irradiation and catalytic polymerization methods, and effective catalysts for the polymerization of propargyl alcohol (OHP) were some transition metal complexes containing Pd, Ni, Mo, W and Zn [8–10]. However, the results of POHP synthesis were not very satisfying because the OHP polymerization proceeded at high temperature ($>100\,^{\circ}$C), and the resulting products were gel-like and insoluble in common organic solvents, or oligomers with low molecular weights.

The research and development on organometallic catalysts for synthesis of polymers is an important and attractive field in polymer science and industry. Organometallic complexes are generally sensitive to polar functional groups and not effective catalysts for polymerization of polar alkynes. In recent years, transition metal acetylides were found to be effective catalysts for alkynes polymerization [11–15]. We reported the OHP polymerization with a novel palladium catalyst $Pd(C\equiv CCH_2OH)_2(PPh_3)_2$ [16,17].

In this letter, we report our extended efforts in developing transition metal acetylide catalysts for polymerization of acetylenes with polar substituents. We systematically study catalytic behaviors of a series of transition metal acetylides in the polymerization of OHP and discuss the influence of transition metals, phosphine ligands and alkynyl ligands on the reaction activity of these complexes.

2. Experimental

Diethylamine was dried over CaH_2 and distilled under N_2 atmosphere prior to use. All other solvents were analytical grade and dried with activated alumina. OHP was distilled under nitrogen at reduced pressure. $Ni(PPh_3)_2(C\equiv CC_6H_4C\equiv CH)_2$ [18], $Ni(PBu_3)_2(C\equiv CC_6H_4C\equiv CH)_2$ [18], $Ni(PPh_3)_2(C\equiv CPh)_2$ [19], $Ni(PBu_3)_2(C\equiv CPh)_2$ [20], $Pd(PPh_3)_2(C\equiv CC_6H_4C\equiv CH)_2$ [21], $Pd(PPh_3)_2(C\equiv CH)_2$ [21], $Pd(PPh_3)_2(C\equiv CPh)_2$ [21], $Pd(PPh_3)_2(C\equiv CCH_2OH)_2$ [16], $Pd(PBu_3)_2(C\equiv CC_6H_4C\equiv CH)_2$ [22], $Pd(PPh_3)_2(C\equiv CCH_2OCOCH_3)_2$ [23], $Ni(PPh_3)_2(C\equiv CCH_2OCOCH_3)_2$ [24], $Ni(PBu_3)_2(C\equiv CCH_2OCOCH_3)_2$ [24], $Pd(PPh_3)_2(C\equiv CCH_2OCOC_6H_5)_2$ [24] and $Pd(PPh_3)_2(C\equiv CCH_2OCOC_6H_4OH$-*o*$)_2$ [24] were prepared according to the literature.

Bis(3-hydroxypropynyl)bis(tributylphosphine)palladium ($Pd(PBu_3)_2(C\equiv CCH_2OH)_2$) was prepared according to the following procedure. A solution of $Pd(PBu_3)_2Cl_2$ (1 mmol, 582 mg), CuI (0.02 mmol, 3.8 mg) and dry $HNEt_2$ (50 ml) was stirred and degassed at room temperature for 30 min, and OHP (3.4 mmol, 0.2 ml) 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 a yel-

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low oil. The oily residue was dissolved in 2 ml methanol and poured into ice water (20 ml). The yellow precipitate was filtered off and recrystallized from *n*-hexane to yield yellow crystals (270 mg, 43%): mp 78 °C. Anal. calcd. for $PdC_{30}H_{60}O_2P_2$: C 58.01 and H 9.74; found: C 57.89 and H 9.88%. UV-Vis λ_{max} (THF) 284 nm. FT-IR (Nujol mull) 3310 (s), 2120 (s), 1415 (s), 1342 (m), 1300 (m), 1200 (m), 1090 (s), 1018 (s), 945 (m), 900 (s), 785 (s), 690 (m), 660 (m), 570 (w), 447 (w), 388 (w) cm^{-1}.

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, $Pd(PPh_3)_2(C{\equiv}CCH_2OH)_2$ (0.04 mmol, 29.6 mg) and $CHCl_3$ (0.9 ml) were added, shaken to obtain a homogeneous solution, and then OHP (1.4 mmol, 0.8 ml) and CH_3OH (0.3 ml) were added. After the mixture stood at 60 °C for 24 h, methanol (2 ml) was added to dissolve the resulting polymer and then precipitated as a brown powder by the addition of acetone. POHP was filtered from the solution, washed with acetone, and dried *in vacuo* at room temperature for 24 h. For POHP: Anal. calcd. for $(C_3H_4O)_n$: C 64.30 and H 7.14%; found: C 63.75 and H 7.27%. ^1H NMR ($(CD_3)_2SO$) δ 6.90 (s, 1H), 3.35 (s, 2H) and 1.27 (s, 1H) ppm. ^{13}C NMR ($(CD_3)_2SO$) δ 140, 127 and 67 ppm. UV-Vis λ_{max} (CH_3OH) 325 nm. FT-IR (KBr) ν 3200–3500 (vs), 2920 (s), 1640 (m), 1420 (m), 1240 (m), 1020 (s), 920 (w) and 530–700 (m) cm^{-1}.

IR spectra were taken on a Nicolet 5-DX FT-IR with KBr pellets and Nujol mulls. UV spectra were recorded on a Beckman DU-50 spectrophotometer. ^1H-NMR spectral data are expressed in ppm relative to an internal standard of tetramethylsilane and were obtained in $(CD_3)_2SO$ on a Bruker dmx 300 NMR spectrometer. ^{13}C-NMR spectrum was observed in $(CD_3)_2SO$ solution (20% w/v) on a Bruker dmx 300 NMR spectrometer. The elemental analyses were obtained from a Carlo Erba model 1106 elemental analyzer. The weight average molecular weight (M_w) and polydispersity index of polymers were measured on a PL-GPC model 210 chromatograph at 35 °C, using DMF as eluent and standard polystyrene as reference. Melting points were determined on a Yanaco MP-500 melting point apparatus. Differential scanning calorimetry (DSC) measurement was performed on a Perkin–Elmer DSC 7 under N_2 at a heating rate of 20 °C. Thermal gravimetric analysis (TGA) measurement was performed on Perkin–Elmer series 7 thermal analysis system under N_2 at a heating rate of 20 °C.

3. Results and discussion

All the transition metal acetylides developed in this study are easy to prepare and soluble in common organic solvents. Moreover, they are air- and moisture-stable and can be handled with ease in open air. It is worth noticing that all the catalysts are single-component systems without any additives, obviating the trouble of preparing binary and ternary catalysts.

Influence of solvents on catalytic activity of palladium and nickel acetylides towards OHP polymerization is shown in table 1. The polymerization initiated by $Pd(PPh_3)_2(C{\equiv}CC_6H_4C{\equiv}CH)_2$ showed high reaction activity in chlorinated hydrocarbon, such as chloroform, chlorobenzene and 1,2-dichloroethane, probably due to good solubility and strong solvation of the palladium complex in these solvents. It was found that a chloroform–methanol mixed solvent system was favorable for the OHP polymerization catalyzed by palladium acetylide. The palladium catalyst was very soluble in $CHCl_3$ and the OHP polymer was soluble in MeOH, resulting in formation of a homogeneous polymerization system and soluble polymer. On the other hand, the palladium complex almost exhibited no catalytic activity in high-polarity solvents containing N, O and S atoms, such as DMSO, $HNEt_2$ and pyridine, maybe owing to slight decomposition of the catalyst in polar solvents.

The polymerization of OHP catalyzed by $Ni(PPh_3)_2(C{\equiv}CC_6H_4C{\equiv}CH)_2$ showed high reaction activity in some solvents containing oxygen atoms, such as THF, 1,4-dioxane and DMSO, and the reaction was in some cases instantaneous and assumed explosive characteristics even at 15 °C. The oxygen-containing solvents and OHP could coordinate with the nickel complex and activate it. Although the polymerization system exhibited high reaction activity, the yield of the linear polymer was low because the cyclotrimerization reaction of alkynol took place easily in the presence of nickel complexes [19,25]. On the other

Table 1
Effect of solvents on catalytic activity of palladium and nickel acetylides.[a]

Solvent	Yield (%)	
	$Pd(PPh_3)_2(C{\equiv}CC_6H_4C{\equiv}CH)_2$	$Ni(PPh_3)_2(C{\equiv}CC_6H_4C{\equiv}CH)_2$
$CHCl_3/MeOH = 3:1$	57.4	0
Chlorobenzene	51.3	6.9
CH_2ClCH_2Cl	46.3	0
THF	18.1	17.7
1,4-dioxane/toluene = 1	16.9	8.3
Pyridine	12.7	4.1
$HNEt_2$	3.4	0
DMSO	2.5	11.9

[a] Conditions: catalyst concentration [cat] = 0.02 mol/l, monomer concentration [OHP] = 7.0 mol/l, temperature 60 °C, time 24 h.

Table 2
Comparison of catalytic activity of palladium acetylides.[a]

Complex	Polymer		
	Yield (%)	$M_w \times 10^{-4}$	M_w/M_n
$Pd(PPh_3)_2(C{\equiv}CPh)_2$	57.4	2.8	1.6
$Pd(PPh_3)_2(C{\equiv}CH)_2$	53.8	2.5	2.2
$Pd(PPh_3)_2(C{\equiv}CC_6H_4C{\equiv}CH)_2$	66.4	3.3	1.8
$Pd(PPh_3)_2(C{\equiv}CCH_2OH)_2$	58.2	1.7	1.4
$Pd(PPh_3)_2(C{\equiv}CCH_2OCOCH_3)_2$	67.2	2.2	1.9
$Pd(PPh_3)_2(C{\equiv}CCH_2OCOC_6H_5)_2$	71.0	1.9	2.0
$Pd(PPh_3)_2(C{\equiv}CCH_2OCOC_6H_4OH\text{-}o)_2$	79.1	2.6	2.2
$Pd(PBu_3)_2(C{\equiv}CC_6H_4C{\equiv}CH)_2$	21.2	5.7	2.5
$Pd(PBu_3)_2(C{\equiv}CCH_2OH)_2$	45.9	4.4	2.3

[a] Conditions: [cat] = 0.02 mol/l, [OHP] = 7.0 mol/l, $CHCl_3$/MeOH = 3 : 1, 60 °C, 24 h.

Table 3
Comparison of catalytic activity of nickel acetylides.[a]

Complex	Polymer		
	Yield (%)	$M_w \times 10^{-3}$	M_w/M_n
$Ni(PPh_3)_2(C{\equiv}CC_6H_4C{\equiv}CH)_2$	13.5	5.4	1.6
$Ni(PPh_3)_2(C{\equiv}CPh)_2$	11.3	6.9	1.8
$Ni(PPh_3)_2(C{\equiv}CCH_2OCOCH_3)_2$	11.8	4.6	1.4
$Ni(PBu_3)_2(C{\equiv}CC_6H_4C{\equiv}CH)_2$	4.6	7.3	1.7
$Ni(PBu_3)_2(C{\equiv}CPh)_2$	3.5	8.8	2.4
$Ni(PBu_3)_2(C{\equiv}CCH_2OCOCH_3)_2$	5.7	8.3	2.1

[a] Conditions: [cat] = 0.02 mol/l, [OHP] = 7.0 mol/l, THF, 60 °C, 48 h.

hand, the OHP polymerization catalyzed by the nickel complex took hardly place in 1,2-dichloroethane, chloroform–methanol and diethylamine due to decomposition of the complex.

The results of OHP polymerization in the presence of nine palladium acetylides are given in table 2. Palladium acetylides containing different alkynyl and phosphine ligands were found to be effective catalysts for OHP polymerization. The OHP polymerization proceeded under mild conditions to give soluble polymers in yields as high as 79%. The obtained POHP possessed weight average molecular weights of $1.7–5.7 \times 10^4$ with polydispersity index of 1.4–2.5. This is one of the best results for synthesis of POHP.

The phosphine ligands bonded to the palladium atom played an important role on the catalytic properties of these complexes. The complexes of palladium with tributylphosphine ligand exhibited a lower activity than those with triphenylphosphine ligand, which is similar to the experimental results reported by Furlani et al. [9].

The alkynyl ligands bonded to the palladium atom also exerted an influence on the catalytic activity of these complexes, which was maybe related to the polarity of the ligands. The complexes containing polar alkynyl ligands showed higher catalytic activity than the corresponding complexes containing non-polar ones. The complexes containing alkynyl ester ligands showed higher catalytic activity than the corresponding complex containing alkynyl alcohol ligand. The catalytic activity of the complexes containing alkynyl ester ligands increased with increasing acidity of the corresponding acids. The acidity of the organic acids followed the sequence: salicylic acid ($K_a = 105 \times 10^{-5}$) > benzoic acid ($K_a = 6.3 \times 10^{-5}$) > acetic acid ($K_a = 1.75 \times 10^{-5}$) [26]. The electron-withdrawing effect of the R group in alkynyl ligands $C{\equiv}CCH_2OR$ decreased in the following order: $o\text{-}OHC_6H_4CO > C_6H_5CO > CH_3CO > H$; the density of the electron cloud of the palladium–carbon bond in palladium complexes containing $C{\equiv}CCH_2OR$ ligands increased and the reaction activity of the Pd–C bond decreased according to the above sequence.

The results of OHP polymerization in the presence of six nickel acetylides are reported in table 3. Nickel acetylides containing both polar alkynyl ligand $C{\equiv}CCH_2OCOCH_3$ and non-polar ones $p\text{-}C{\equiv}CC_6H_4C{\equiv}CH$ and $C{\equiv}CPh$ exhibited much lower catalytic activity than palladium complexes, and were not favorable catalysts for OHP polymerization, probably due to instability of nickel acetylides in alcohol [18] and cyclotrimerization of OHP. The weight average molecular weights of POHP prepared in the presence of nickel acetylides were $4.6–8.8 \times 10^3$, lower than those obtained in the presence of palladium acetylides. Just like palladium acetylides, the complexes of nickel with triphenylphosphine showed a little higher catalytic activity than the corresponding complexes of tributylphosphine.

POHP so prepared by palladium and nickel acetylides was a brown powder. It was soluble in methanol, *N,N*-dimethylformamide (DMF) and dimethylsulfoxide (DMSO). It gave an elemental analysis corresponding to the theoretical one. The infrared spectrum of POHP showed the characteristic peaks at 1640 (conjugated C=C bonds), 1020 and 3200–3500 cm^{-1} (CH_2OH). The peaks characteristic of *trans* structure (1240, 1020 and 920 cm^{-1}) [1,27] were observed for POHP, while those of *cis* structure (1380, 870 and 740 cm^{-1}) [1,27] are absent. Therefore, it is evident that POHP has a rich-*trans* structure. The rich-*trans* extended π-conjugated polyene chain structure with a pendent CH_2OH group is further confirmed by ^{1}H-NMR and ^{13}C-NMR spectra. In the ^{1}H-NMR spectrum, the signal at 5.82 ppm, assigned to *cis* polyenic protons [28], is absent, but the signal at 6.90 ppm, assigned to *trans* polyenic protons [28], is comparatively strong. In the ^{13}C-NMR spectrum, the peak at 127 ppm is attributed to the CH group of *trans*-vinylene units in analogy with poly(phenylacetylene) [29]. The structure of the polymers obtained with different nickel and palladium acetylide catalysts is almost the same.

The thermal properties of POHP were determined by TGA and DSC. POHP possessed good thermal stability with an onset decomposition temperature (T_d) of 293 °C. In DSC an endothermic peak at 93 °C was observed due to the loss of adsorptive water. Just like POHP prepared with the $Pd(PPh_3)_2(C{\equiv}CCH_2OH)_2$ catalyst [7], POHP prepared with other nickel and palladium acetylide catalysts also showed resistance-type humidity sensitivity. It is worthwhile to notice that the humidity-sensitive device fabricated with POHP was stable and efficient at high relative humidity (>80%). All the preliminary results indicated that POHP is a promising new material for a good performance humidity sensor.

4. Conclusions

We have explored a new series of transition metal acetylide catalysts for polymerization of alkynes with polar groups. All the catalysts are single-component, easy to prepare, stable in air, soluble in common organic solvents and convenient to initiate the polymerization. Transition metals, phosphine and alkynyl ligands and solvents exhibited significant influence on the polymerization. Palladium acetylides with PPh_3 ligand were efficient catalysts for OHP polymerization in $CHCl_3$–MeOH mixed solvent. POHP so prepared possessed rich-*trans* structure, good solubility, thermal stability and humidity sensitivity with high molecular weights.

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