

Transition metal acetylide catalysts for polymerization of alkynes

2. Effect of ligands on catalytic activity of palladium complexes

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Abstract

Single-component and environmentally stable palladium acetylides with the structures of $\text{PdL}_2(\text{C}\equiv\text{CR})_2$ ($\text{L} = \text{PPh}_3$, PBu_3 ; $\text{R} = p\text{-C}_6\text{H}_4\text{C}\equiv\text{CH}$, C_6H_5 , H , CH_2OH , $\text{CH}_2\text{OCOCH}_3$, $\text{CH}_2\text{OCOC}_6\text{H}_5$, $\text{CH}_2\text{OCOC}_6\text{H}_4\text{OH-}o$) are novel efficient initiating systems for *p*-diethynylbenzene polymerization. The polymerization proceeds under mild conditions to give soluble π -conjugated polymers with molecular weights as high as 1.8×10^4 in yields as high as 84%. The catalytic property of these acetylides is related to phosphine and alkynyl ligands bonded to the metal atoms. Palladium complexes containing PPh_3 ligand are much more active than that containing PBu_3 ligand. The complexes containing polar alkynyl ligands show higher catalytic activity than the corresponding complexes containing non-polar ligands. For the complexes containing non-polar alkynyl ligands, the greater the conjugation degree of the alkynyl ligand, the higher the catalytic activity of the corresponding complex. For the complexes containing polar alkynyl ligands, the complexes containing ester ligands show higher catalytic activity than the corresponding complex containing alcohol ligand, and the catalytic activity of the complexes containing ester ligands increases with increasing acidity of the corresponding acids. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

Scientific interest in substituted polyacetylenes has been rapidly growing for many years and recently focused on the unique physical properties such as ferromagnetism, electroluminescence, third-order non-linear optical property, humidity sensitivity and so on [1–6]. The polymerization of substituted acetylenes has been attempted by using heat, light, plasma, high pressure, irradiation and catalytic polymerization methods [7,8]. Various types of cata-

lysts for polymerization of substituted acetylenes have been developed, for example, Ziegler catalysts, metathesis catalysts, rare earth catalysts, Rh complex catalysts and Pt or Ni complex catalysts [9–14]. Among these catalysts, Ziegler catalysts and metathesis catalysts, e.g. the halides of molybdenum and tungsten are most widely used. These two 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. Recently we have developed a new series of single-component and environmentally stable catalysts based on nickel acetylides for polymerization of non-polar and polar alkynes [15–18]. Moreover, we found that

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single-component stable palladium acetylides are effective initiators for polymerization of polar alkynes, e.g. propargyl alcohol and its esters [19–23]. In the present work, we compare the catalytic activity of a series of palladium acetylides towards polymerization of non-polar alkynes, e.g. *p*-diethynylbenzene (*p*-DEB), and discuss the influence of phosphine and alkynyl ligands on the catalytic activity of these complexes.

2. Experimental section

2.1. Materials

p-DEB [24], Pd(PPh₃)₂(C≡CC₆H₄C≡CH)₂ [25], Pd(PPh₃)₂(C≡CPh)₂ [25], Pd(PPh₃)₂(C≡CH)₂ [25], Pd(PBu₃)₂(C≡CC₆H₄C≡CH)₂ [26], Pd(PPh₃)₂(C≡CCH₂OH)₂ [22], Pd(PPh₃)₂(C≡CCH₂OCOCH₃)₂ [20], Pd(PPh₃)₂(C≡CCH₂OCOC₆H₅)₂ [19], Pd(PPh₃)₂(C≡CCH₂OCOC₆H₄OH-*o*)₂ [19] and Pd(PBu₃)₂(C≡CCH₂OH)₂ [23] were prepared by literature methods or modifying reported procedures.

2.2. Measurements

IR spectra were taken on a Nicolet 5-DX FT-IR with Nujol mulls. UV–VIS spectra in THF were recorded on a Beckman DU-50 spectrophotometer. 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. Polymerization

A typical polymerization procedure is as follows: 378 mg (3 mmol) of sublimed *p*-DEB and 26.4 mg (0.03 mmol) of Pd(PPh₃)₂(C≡CC₆H₄C≡CH)₂ were dissolved in pyridine (2.5 ml). Under purified nitrogen atmosphere, the polymerization proceeded at 60°C for 18 h. The resulting polymer was precipitated by the addition of methanol, filtered from the solution, washed with CH₃OH, and dried in vacuum at room temperature for 24 h to give polymers. Other polymerizations were carried out analogously.

3. Results and discussion

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

The IR spectra of palladium acetylides, Pd(PPh₃)₂(C≡CR)₂, were recorded from 4000 to 180 cm⁻¹, where R is *p*-ethynylphenyl, phenyl or hydrogen. The metal–carbon stretching frequencies ($\nu(\text{M}-\text{C})$) are sensitive to the change of R as shown in Table 1. For Pd(PPh₃)₂(C≡CR)₂, $\nu(\text{M}-\text{C})$ decreases in the following order of R: H > C₆H₅ > *p*-C₆H₄C≡CH. The acidity of the free alkynes follows the sequence: *p*-HC≡CC₆H₄C≡CH > HC≡CC₆H₅ > HC≡CH; the basicity of the corresponding anions falls in with the order: ⁻C≡CH > ⁻C≡CC₆H₅ > *p*-⁻C≡CC₆H₄C≡CH. The interaction of these weak bases with the weak acid Pd²⁺ decreases according to the following order: Pd–C≡CH > Pd–C≡CC₆H₅ > Pd–C≡CC₆H₄C≡CH, and the force constant (*k*) and frequency of the metal–carbon stretching vibration decreases according to the above sequence.

Electronic absorption spectra (UV) of Pd(PPh₃)₂(C≡CR)₂ were recorded from 400 to 220 nm. The lowest energy band is sensitive to the conjugation degree of alkynyl ligands as shown in Table 1. For Pd(PPh₃)₂(C≡CR)₂, the wavelength of the lowest energy band (λ_{max}) becomes shorter in the following order of R: *p*-C₆H₄C≡CH > C₆H₅ > H. The band at the lowest energy is presumably due to the transition from the bonding π -orbital of alkynyl groups to the unoccupied p_z orbital of the metal and from the occupied d_{z²} orbital of the metal to the anti-bonding π -orbital (π^*) of C≡CR ligands. The substituents (R) having greater bathochromic effect afford lower π^* levels of C≡CR ligands [27], and the energy between the π^* orbitals and d orbitals of the central metal may become lower. Thus, the d π –p π interaction can be

Table 1
Effect of alkynyl ligands on the metal–carbon stretching vibration and lowest energy band of Pd(PPh₃)₂(C≡CR)_n

R	$\nu(\text{M}-\text{C})$ (cm ⁻¹)	λ_{max} (nm)
<i>p</i> -C ₆ H ₄ C≡CH	547	364
C ₆ H ₅	573	307
H	590	273

Table 2
Effect of alkynyl and phosphine ligands on catalytic activity of PdL₂(C≡CR)₂^a

L	R	Time (h)	Yield (%)	$M_w \times 10^{-4}$	M_w/M_n
PPh ₃	<i>p</i> -C ₆ H ₄ C≡CH	18	79.9	1.8	3.8
PPh ₃	C ₆ H ₅	18	75.7	1.5	2.9
PPh ₃	H	18	55.5	1.3	3.0
PPh ₃	CH ₂ OCOC ₆ H ₄ OH- <i>o</i>	15	84.1	1.4	3.0
PPh ₃	CH ₂ OCOC ₆ H ₅	17	79.1	1.3	2.8
PPh ₃	CH ₂ OCOCH ₃	18	70.9	1.1	2.6
PPh ₃	CH ₂ OH	18	58.2	1.5	3.3
PBu ₃	CH ₂ OH	48	0	–	–
PBu ₃	<i>p</i> -C ₆ H ₄ C≡CH	48	0	–	–

^a Conditions: catalyst concentration: [cat]₀=0.01 mol/l, monomer concentration: [*p*-DEB]₀=1.0 mol/l, pyridine, 60°C.

facilitated [28]. Hence, the energy of the lowest energy band of transition metal acetylides decreases with increasing conjugation degree of alkynyl ligands.

3.2. Effect of ligands on the catalytic activity of palladium complexes

The results of *p*-DEB polymerization in the presence of nine palladium acetylides are given in Table 2. 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. Palladium acetylides containing PPh₃ ligand were found to be effective catalysts for *p*-DEB polymerization. The *p*-DEB polymerization proceeded under mild conditions to give soluble polymers with weight average molecular weights as high as 1.8×10^4 in good yields (as high as 84%).

The alkynyl ligands bonded to the palladium atom exert an influence on the catalytic activity of these complexes, which is maybe related to polarity of ligands. The complexes containing polar alkynyl ligands show higher catalytic activity than the corresponding complexes containing non-polar ligands. For the complexes with non-polar alkynyl ligands, the greater the conjugation degree of the alkynyl ligand, the higher the catalytic activity of the corresponding complex. The metal–carbon stretching frequency in IR spectra and the lowest energy band in UV spectra are related to

the interaction between the central metal and alkynyl ligands and to the activity of the metal–carbon bond or the complexes. The effect of ligands on catalytic activity of these complexes towards alkynes polymerization is consistent with the effect of ligands on the metal–carbon stretching frequency and the lowest energy band of the complexes. The factors decreasing the metal–carbon stretching frequency and the energy of the lowest energy band result in enhancing the catalytic activity of the complexes.

For the complexes with polar alkynyl ligands, the complexes containing ester ligands show higher catalytic activity than the corresponding complex containing alcohol ligand, and the catalytic activity of the complexes containing ester ligands increases with increasing acidity of the corresponding acids. The acidity of acids follows the sequence: salicylic acid ($K_a = 105 \times 10^{-5}$) > benzoic acid ($K_a = 6.3 \times 10^{-5}$) > acetic acid ($K_a = 1.75 \times 10^{-5}$) [29]. The electron-withdrawing effect of R' group in alkynyl ligands C≡CCH₂OR' decreases in the following order of R': *o*-OHC₆H₄CO > C₆H₅CO > CH₃CO > H; the density of electron cloud of palladium–carbon bond in palladium complexes containing C≡CCH₂OR' ligands increases and the reaction activity of Pd–C bond decreases in the turn as above.

Palladium complexes containing triphenylphosphine (PPh₃) ligand are much more active than that containing tributylphosphine (PBu₃) ligand. In fact, the complexes with PBu₃ ligand show no catalytic activity towards *p*-DEB polymerization under tested conditions. This is probably due to the greater basicity and the related σ -donating ability of PBu₃,

which increases the density of electron cloud of palladium–carbon bond and decreases the reaction activity of this bond.

4. Conclusions

Palladium acetylides are novel efficient initiating systems for *p*-DEB polymerization. All the catalysts are single-component and environmentally stable. Phosphine and alkynyl ligands exhibit significant influence on the catalytic activity of these acetylides. The polarity and electron-donating ability of ligands are main factors influencing the catalytic activity of the complexes.

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