

Transition metal acetylide catalysts for polymerization of alkynes

5. Homogeneous copolymerization of polar with non-polar alkynes

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Abstract

A series of palladium acetylide complexes with the structures of $\text{Pd}(\text{PPh}_3)_2(\text{C}\equiv\text{CR})_2$ ($\text{R} = \text{C}(\text{CH}_3)_2\text{OH}$, $\text{CH}_2\text{OCOCH}_3$, CH_2OH , $p\text{-C}_6\text{H}_4\text{C}\equiv\text{CH}$, C_6H_5) were developed for homogeneous copolymerization of polar with non-polar alkynes. The catalytic activity of the five palladium acetylide complexes towards copolymerization of propargyl alcohol (OHP) with p -diethynylbenzene (p -DEB) is compared and discussed. The complexes containing polar alkynyl ligands show higher activity than corresponding complexes containing non-polar ligands. Solvent systems exhibit significant influence on realizing homogeneous polymerization and obtaining soluble copolymer. The copolymerization of OHP with p -DEB initiated with these catalysts could proceed under mild conditions to give soluble π -conjugated copolymer in yields as high as 66%. Features for copolymerization of OHP with p -DEB using $\text{Pd}(\text{PPh}_3)_2(\text{C}\equiv\text{CCH}_2\text{OH})_2$ in $\text{CHCl}_3/\text{MeOH}$ mixed solvents have been described. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Transition metal acetylide catalyst; Copolymerization; p -Diethynylbenzene; Propargyl alcohol

1. Introduction

Polyacetylenes possess π -conjugated structure, which often makes them exhibit the following characteristics: conductivity, photoconductivity, optical non-linear 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, and have attracted great attention in the past years.

In recent years, transition metal acetylides were found to be effective catalysts for alkynes polymerization. Russo et al. used nickel, palladium and plati-

num acetylides containing triphenylphosphine ligand as catalysts for polymerization of alkynes such as diethynylbiphenyl, ethynylfluorene, ethynyltrimethylsilane, phenylacetylene, N,N -dimethylamino-1-propyne, N -benzylpropargylamine and isopropenylacetylene to give polymers with molecular weights of 500– 10^4 [7–12]. Kishimoto et al. [13,14] reported stereospecific living polymerization of phenylacetylenes using $\text{Rh}(\text{C}\equiv\text{CC}_6\text{H}_5)(\text{nbid})(\text{PPh}_3)_2$. We have synthesized a series of nickel and palladium acetylide complex catalysts for polymerization of not only polar alkynes such as propargyl alcohol (OHP) and its esters but also non-polar alkynes like p -diethynylbenzene (p -DEB) and its derivatives. These transition metal acetylide complex catalysts with the structures $\text{ML}_2(\text{C}\equiv\text{R})_2$ ($\text{M} = \text{Ni}$ and Pd , $\text{L} = \text{PPh}_3$ and PBU_3 , $\text{R} = p\text{-C}_6\text{H}_4\text{C}\equiv\text{CH}$, C_6H_5 , H , CH_2OH , $\text{CH}_2\text{OCOCH}_3$, $\text{CH}_2\text{COC}_6\text{H}_5$ and $\text{CH}_2\text{OCOC}_6\text{H}_4\text{OH}$) are easy to

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prepare, stable in air, soluble in organic solvents and show good catalytic activity towards polymerization of alkynes [15–22]. The polymers so obtained, in general, can be soluble in organic solvents and exhibit humidity sensitivity (poly(propargyl alcohol), POHP) and conductivity, photoluminescence, and third-order non-linear optical properties (poly(*p*-diethynylbenzene), PDEB) [16,23–28].

As mentioned above, over the past years there have been many reports on the homogeneous polymerization of alkynes, but none on the copolymerization of polar with non-polar alkynes by transition metal acetylide complex catalysts, because it is not easy to copolymerize polar with non-polar monomers by organometallic complex catalysts. In this paper, we report new investigations on copolymerization of polar with non-polar alkynes with transition metal acetylide complex catalysts, which in turn is a development based upon our previous work. The study revealed that palladium acetylide complexes containing triphenylphosphine ligands are effective catalysts for the homogeneous copolymerization of polar OHP with non-polar *p*-DEB alkynes. The influence of alkynyl ligands on the catalytic activity of palladium acetylides towards copolymerization of OHP with *p*-DEB has been discussed. Features for copolymerization of OHP with *p*-DEB have been described.

2. Experimental

2.1. Materials

All solvents are of analytical grade and dried with activated alumina. OHP was distilled under nitrogen at reduced pressure. *p*-DEB [29], Pd(PPh₃)₂(C≡CC₆H₄C≡CH)₂ [30], Pd(PPh₃)₂(C≡CCH₂OH)₂ [17], Pd(PPh₃)₂(C≡CC(CH₃)₂OH)₂ [31], Pd(PPh₃)₂(C≡CC₆H₅)₂ [30], Pd(PPh₃)₂(C≡CCH₂OCOCH₃)₂ [15] were prepared by methods specified in the literature or modifying reported procedure.

2.2. Measurements

IR spectra were taken on a Nicolet Magna-IR 560 FT-IR with KBr pellets. ¹H-NMR spectra data were expressed in ppm relative to an internal standard of tetramethylsilane and were obtained in (CD₃)₂SO on

a Bruker Avance dmx 500 NMR spectrometer. The weight-average molecular weight (*M_w*) and molecular weight distribution (MWD) of polymers were measured on a Waters GPC Model 208 chromatography at 30 °C, using THF as eluant and standard polystyrene as reference. The composition of copolymers was determined by IR analysis using standard curve obtained from the characteristic bands at ~837 cm⁻¹ for *p*-DEB unit and at ~1027 cm⁻¹ for OHP unit, respectively, and confirmed by ¹H-NMR analysis [32].

2.3. Polymerization

A typical polymerization procedure is as follows: Into a well-dried ampoule, sublimed *p*-DEB (126 mg, 1 mmol), Pd(PPh₃)₂(C≡CCH₂OH)₂ (22.2 mg, 0.03 mmol) and chloroform (1.5 ml) were added, shaken to obtain a homogeneous solution, and then OHP (56 mg, 1 mmol) and absolute methanol (0.5 ml) were added. After the polymerization proceeded at 60 °C for 16 h, the resulting solution was diluted with THF and precipitated in petroleum ether (30–60 °C fraction). The copolymer (DEB-co-OHP) was filtered, washed with petroleum ether, and dried under vacuum for 16 h.

3. Results and discussion

Homogeneous polymerization system is especially suitable for comparing catalytic activity of different catalysts, and solvent system is important for realizing homogeneous copolymerization of polar with non-polar alkynes. Table 1 lists the results of copolymerization of OHP with *p*-DEB in different solvent systems by Pd-catalyst Pd(PPh₃)₂(C≡CCH₂OH)₂ (PPO). The copolymerization initiated by the palladium acetylide complex catalyst is heterogeneous in chlorinated hydrocarbon, such as chloroform and chlorobenzene, and insoluble solid products are obtained in low yields. In high polarity solvent containing S atom such as DMSO, the copolymerization system is homogeneous, but polymers cannot be precipitated from the solution, probably due to their low molecular weight. In high polarity solvent containing N atom such as pyridine, copolymer is obtained in high yields (>80%) from homogeneous polymerization system, but the resulting polymer exhibits poor solubility

Table 1
Effect of solvent on copolymerization of *p*-DEB with OHP by Pd(PPh₃)₂(C≡CCH₂OH)₂ catalyst^a

Solvent	Polymerization system	Solubility of polymer in THF	Yield (%)
CHCl ₃	Heterogeneous	All	31.7
DMSO	Homogeneous	–	–
Pyridine	Heterogeneous	Partly	81.0
Chlorobenzene	Heterogeneous	All ^b	18.1
CHCl ₃ /MeOH (3/1)	Homogeneous	All	50.3
CHCl ₃ /MeOH (3/1) ^c	Homogeneous	All	40.3
CHCl ₃ /MeOH (3/1) ^d	Homogeneous	Insoluble	58.2

^a Conditions: [cat.] = 0.01 mol/l; [*p*-DEB] = [OHP] = 1.0 mol/l; 60 °C; 24 h.

^b Product precipitated from solution.

^c Homopolymerization of *p*-DEB. Conditions: [cat.] = 0.01 mol/l; [M] = 1.0 mol/l; 60 °C; 24 h.

^d Homopolymerization of OHP. Conditions: [cat.] = 0.02 mol/l; [M] = 7.0 mol/l; 60 °C; 24 h (Ref. [20]).

in THF. It was found that a chloroform–methanol mixed solvent is a favorable solvent system for the copolymerization of *p*-DEB with OHP by palladium catalysts, resulting in the formation of a homogeneous polymerization system and obtaining *p*-DEB-co-OHP copolymer soluble in THF under an optimum volume ratio of CHCl₃/MeOH = 3/1. This is because CHCl₃ is a good solvent for both Pd catalyst and PDEB, and MeOH can solve POHP [17], thus CHCl₃/MeOH mixed solvents have a synergetic effect for solving the copolymer under the optimum volume ratio of the two solvents.

Catalysts are the key for the success of polymerization. In our previous study, it was found that nickel acetylide complexes can effectively catalyze polymerization of non-polar *p*-DEB, while their catalytic activity towards polymerization of polar OHP are low [20,21]. On the other hand, palladium acetylide complexes are effective catalysts for polymerization of both *p*-DEB and OHP [20,22]. Therefore, palladium acetylide complexes were employed for copolymerization of OHP with *p*-DEB in the present study.

It was found that both phosphines and alkynyl ligands bonded to metal atoms played an important role in the catalytic properties of palladium complexes towards the polymerization of alkynes. Due to the smaller basicity and σ -related donating properties of triphenylphosphine, palladium complexes with triphenylphosphine ligands exhibit higher catalytic activity in comparison to those with tributylphosphine ligands towards the polymerization of both *p*-DEB and OHP. As a result, only palladium catalysts with triphenylphosphine ligands Pd(PPh₃)₂(C≡CCR)₂ are used in the copolymerization of OHP with *p*-DEB. The results of copolymerization of OHP with *p*-DEB by Pd(PPh₃)₂(C≡CCR)₂ in CHCl₃–MeOH mixed solvent at 60 °C are given in Table 2. It is seen that palladium acetylides with PPh₃ ligands are effective catalysts for the copolymerization of OHP with *p*-DEB, and the polymerization can occur under mild conditions to give soluble copolymers with molecular weight (M_w) of ~3000 and yields as high as 66%. However, the catalytic activity of palladium acetylide complexes towards copolymerization of

Table 2
Comparison of catalytic activity of palladium acetylides^a

Complex	Polymer		
	Yield (%)	$M_w \times 10^{-3}$	M_w/M_n
Pd(PPh ₃) ₂ (C≡CC ₆ H ₄ C≡CH) ₂	47.6	3.0	1.9
Pd(PPh ₃) ₂ (C≡CCH ₂ OCOCH ₃) ₂	66.2	3.1	1.9
Pd(PPh ₃) ₂ (C≡CC ₆ H ₅) ₂	48.6	2.6	1.6
Pd(PPh ₃) ₂ (C≡CCH ₂ OH) ₂	60.5	2.6	1.7
Pd(PPh ₃) ₂ (C≡CC(CH ₃) ₂ OH) ₂	65.0	2.5	1.7

^a Conditions: [cat.] = 1.5×10^{-2} mol/l; [*p*-DEB] = [OHP] = 0.5 mol/l; CHCl₃/MeOH = 3:1 (volume ratio); 60 °C; 16 h.

OHP with *p*-DEB is different with varying alkynyl ligands. Palladium acetylide complex containing polar alkynyl ligands ($\text{Pd}(\text{PPh}_3)_2(\text{C}\equiv\text{CCH}_2\text{OCOCH}_3)_2$, $\text{Pd}(\text{PPh}_3)_2(\text{C}\equiv\text{CCH}_2\text{OH})_2$, $\text{Pd}(\text{PPh}_3)_2(\text{C}\equiv\text{CC}(\text{CH}_3)_2\text{OH})_2$) show higher catalytic activity than the corresponding complexes containing non-polar ones ($\text{Pd}(\text{PPh}_3)_2(\text{C}\equiv\text{CC}_6\text{H}_4\text{C}\equiv\text{CH})_2$, $\text{Pd}(\text{PPh}_3)_2(\text{C}\equiv\text{CC}_6\text{H}_5)_2$). It indicated that polarity of alkynyl ligands bonded to the palladium atom greatly influenced the catalytic activity of these complexes towards the homogeneous copolymerization of OHP with *p*-DEB, which is consistent with the case of influence of polarity of alkynyl ligands on catalytic activity of these complexes towards the homopolymerization of OHP [20] or *p*-DEB [22]. It is due to that the polymerization of alkynes initiated by transition metal acetylides which follows a coordination insertion mechanism [31]. Polymer can be formed by the insertion of monomers into metal–carbon σ -bonds with the preliminary activation at the expense of π -complex formation. For the case of polar alkynyl ligands bonded to the palladium atom, its larger electron-withdrawing ability results in decreasing the density of electron cloud of the palladium–carbon bond in palladium complex containing polar alkynyl ligands, that is, increasing the reaction reactivity of Pd–C bond in comparison with the case of non-polar ones, which facilitates the insertion of monomer into Pd–C bond for chain propagation. Thus, palladium acetylide complexes containing polar alkynyl ligands exhibit higher catalytic activity than that containing non-polar ones. Besides, in accordance with the polymerization mechanism of alkynes initiated by transition metal acetylides, the growth of the chain is interrupted when π -bonded monomers transfer their acidic hydrogens to the propagating chain, regenerating the starting complex [31]. Due to the different polarity between *p*-DEB and OHP, the transfer of acetic hydrogen is greatly promoted and the chain propagation is terminated more easily. As a result, the copolymer DEB-co-OHP so obtained has lower molecular weight (Table 3) in comparison with polymers PDEB and POHP obtained using transition acetylide complexes.

The copolymerization of *p*-DEB with OHP can proceed by palladium acetylide complex catalysts in CHCl_3 –MeOH mixed solvents. The optimum copolymerization conditions are as follows: $[\text{Pd}] = 1.5 \times 10^{-2} \text{ mol/l}$; $[\text{M}] = 1.0 \text{ mol/l}$; $\text{CHCl}_3/\text{MeOH} = 3/1$

Table 3

Composition of copolymers in different feeding ratio^a

f_1 , <i>p</i> -DEB in feed (mol%)	F_1 , <i>p</i> -DEB in copolymer (mol%)
16.7	13.3
25.0	23.1
33.3	31.1
50.0	44.9
66.7	65.3
75.0	71.0
83.3	82.1

^a Conditions: cat.: $\text{Pd}(\text{PPh}_3)_2(\text{C}\equiv\text{CCH}_2\text{OH})_2$, the other conditions are the same as Table 2.

(volume ratio); and 60 °C for 16 h. The copolymer DEB-co-OHP so obtained is a brown powder with a molecular weight (M_w) of ~ 3000 , and MWD of < 2 . It is soluble in THF and DMSO. The composition of copolymers with different feeding ratio was determined by IR analysis using the integration of characteristic absorption peak of DEB and OHP units, and confirmed with ¹H-NMR analysis as depicted in Ref. [32], and the results are reported in Table 3. By using Mayo–Lewis equation and non-linear least-square procedure, the reactivity ratio of the two monomers was calculated to be $r_1 = 0.89$ (*p*-DEB) and $r_2 = 1.18$ (OHP). The above results indicated that the copolymerization of OHP with *p*-DEB by palladium acetylide complex catalyst in CHCl_3 –MeOH mixed solvents is an ideal one, having the tendency of constant proportion copolymerization [32].

4. Conclusions

Palladium acetylides with PPh_3 ligands are novel efficient catalysts for copolymerization of polar (OHP) with non-polar (*p*-DEB) alkynes. Homogeneous copolymerization of OHP with *p*-DEB can be realized in CHCl_3 –MeOH mixed solvents, giving soluble copolymers. There is significant influence of polarity of alkynyl ligands on catalytic activity of palladium acetylides with PPh_3 ligands. The copolymerization of OHP with *p*-DEB with $\text{Pd}(\text{PPh}_3)_2(\text{C}\equiv\text{CCH}_2\text{OH})_2$ catalyst in CHCl_3 –MeOH mixed solvents is an ideal one, having the tendency of constant proportion copolymerization.

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