

POLYMERIZATION OF A NEW SUBSTITUTED ACETYLENE BEARING A FURAN RING WITH PALLADIUM ACETYLIDE CATALYSTS*

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Abstract A substituted polyacetylene bearing a furan ring, poly(2-propynyl 2-furoate) (PPF), was synthesized for the first time with palladium acetylide complex catalysts in CHCl_3 at 60°C to give a soluble and stable polymer with a yield of *ca.* 75%. Some features for polymerization of 2-propynyl 2-furoate are described and discussed. The resulting polymer was characterized by IR, GPC and ^1H -NMR analysis.

Keywords Substituted polyacetylene, 2-propynyl 2-furoate, Furan ring, Palladium acetylide catalyst

INTRODUCTION

For many years, conjugated polymers have been the subject of research due to their unique physical properties such as conductivity, photoconductivity, third-order nonlinear optical property, magnetic susceptibility, liquid crystallinity, sensitivity to chemical vapors, photoluminescence and electroluminescence^[1–6]. Great advances have been made in improving preparative methods to obtain soluble polymers and tailoring their properties^[7]. Following the extensive studies on polyacetylene and its derivatives, polyaniline and polymers containing heterocyclic moieties, such as polypyrroles, polythiophenes, have also been investigated. The later report on the synthesis of poly(*p*-phenylene vinylene) stimulated the research for similar but more stable structures by replacing the phenyl ring with heterocycles, and led to the creation of a new type of conjugated polymers poly(heteroarylene vinylene)s^[8–10].

Despite the numerous reports on various types of conjugated polymers, little attention was paid to those bearing furan rings, which is probably due to the difficulty of obtaining polymers with well-defined structures and their poor stability^[9]. Recently, a few papers have reported the preparation of conjugated polymers with furan ring in the backbone both by chemical and electrochemical methods^[9–16]. However, with regard to polyacetylenes bearing a furan ring, still very little is known. Only Hagakawa *et al.* reported the preparation of poly(2,5-difluoro-methyl-3-ethynylfuran) using $\text{WCl}_6/\text{Ph}_4\text{Sn}$ as catalyst and investigated their possible use as selective permeation membrane^[17]. Gandini *et al.* also investigated the polymerization of alkynes bearing a furan ring with Mo-based catalysts, but the polymerization encountered with some difficulties from the reactivity of furan ring, and had to envisage an indirect way to obtain the polymers by using an aromatic polymer as precursor^[18].

In recent years, we have successfully developed a series of new transition metal acetylide catalysts for homo- and copolymerization of both polar and non-polar alkynes^[19–26]. Differing from traditional Ziegler catalysts, metathesis catalysts and rare earth catalysts, they exhibit the advantage of being single-component, easy to prepare, environmentally stable and having high catalytic efficiency. An insertion-coordination mechanism has also been proposed for polymerization of acetylenes initiated by these catalysts^[27].

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This paper reports the polymerization of a new substituted acetylene bearing furan ring, 2-propynyl 2-furoate (PF) by using palladium acetylide as catalyst. The palladium acetylide complexes exhibit very effective catalytic activity for the polymerization of PF, and a soluble and stable polymer, poly(2-propynyl 2-furoate) (PPF) was obtained (Fig. 1).

EXPERIMENTAL

Materials

Only analytically pure grade chemicals were used, and all the solvents were dried with activated alumina. Propargyl alcohol (OHP) was distilled under reduced pressure before use. $\text{Pd}(\text{PPh}_3)_2(\text{C}\equiv\text{CCH}_2\text{OH})_2$ (PPO)^[20], $\text{Pd}(\text{PPh}_3)_2(\text{C}\equiv\text{CC}_6\text{H}_5)_2$ (PPA)^[28] and 2-furoyl chloride^[29] was prepared by following the literature methods.

Synthesis of 2-Propynyl 2-Furoate

2-Propynyl 2-furoate was prepared by a modified literature method^[18]. A typical procedure is described as follows: To a suspension containing 18.5 g (0.142 mol) 2-furoyl chloride and 114 mL (1.42 mol) pyridine, OHP 8.77 mL (0.149 mol) was slowly added dropwise with magnetic stirring and cooling in ice-water bath. After addition, the mixture was stirred at room temperature for 2 days, then poured into large volume of water, and extracted with several portions of dichloromethane. The organic phase was further washed with deionized water several times, dried with Na_2SO_4 overnight, filtered and rotary evaporated to remove the solvent. The resulting ester was purified by vacuum distillation to give a colorless liquid with a yield of 71%.

Preparation of $\text{Pd}(\text{PPh}_3)_2(\text{C}\equiv\text{CC}(\text{CH}_3)_2\text{OH})_2$ (PPB)

To a suspension of $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ (263 mg, 0.336 mmol) and CuI (5 mg) in diethylamine (HNEt_2) (15 mL), $\text{HC}\equiv\text{CC}(\text{CH}_3)_2\text{OH}$ (0.287 mL, 2.77 mmol) was slowly added dropwise with magnetic stirring. The mixture was stirred at room temperature for about 30 min, then diluted with 10 mL HNEt_2 , filtered, washed with HNEt_2 and ethanol, and dried under vacuum for 18 h to give a white powder with a yield of ca. 60%.

The m.p. of PPB is 159–160°C, FT-IR (KBr, cm^{-1}): 3588 (s), 2110 (m), 1600 (m), 1435 (s), 1321 (m), 1099 (s), 1028 (w), 1000 (w), 891 (m), 746 (s), 694 (s), 559 (w), 522 (s), 497 (m), 459 (w) and 432 (w).

Elemental anal. Calcd. for $\text{PdO}_2\text{P}_2\text{C}_{46}\text{H}_{44}$: C 69.30%, H 5.52%. Found: C 70.03%, H 5.76%.

Polymerization

A typical polymerization procedure is as follows: in a well-dried ampoule, PPB (16 mg, 0.02 mmol) and PF (600 mg, 4 mmol) were dissolved in CHCl_3 (1.46 mL) to form a homogeneous solution. Under argon (Ar) atmosphere, the polymerization proceeded at 60°C for 24 h. The resulting polymer PPF was precipitated by the addition of petroleum ether (30–60°C fraction), filtered, washed with petroleum ether, and dried under vacuum for about 18 h to give a brown powder with a yield of ca. 75%.

Measurements

IR spectra of PF and PPF were recorded on a Bruker Vector model 22 spectrometer by using KBr pellets, or films obtained by casting the liquid monomer or by evaporating CHCl_3 solutions of the polymer on NaCl plates. ^1H -NMR spectra were measured on a Bruker Avance DMX 500 MHz spectrometer (solvent: CDCl_3) and Bruker AC 200 MHz spectrometer (solvent: $(\text{CD}_3)_2\text{CO}$). The number-average (M_n) and weight-average molecular weight (M_w) of polymers were measured on a Waters 208 gel permeation chromatograph (GPC) at 30°C using THF as eluent and standard polystyrene as reference.



Fig. 1 Chemical structure of (a) PF and (b) PPF

RESULTS AND DISCUSSION

The monomer PF used in the present study bears a furan ring as the pendant group. In a previous report on the polymerization of its analogues, 3-butynyl 2-furoate with MoCl_5 catalytic system, the resulting product exhibits poor stability and solubility. Since side-reactions can not be avoided, its structure can not be determined readily^[18]. In this study, three palladium acetylide catalysts, PPB, PPO and PPA, were employed, and it was found that PF polymerizes readily with all these palladium catalysts under mild conditions, as summarized in Table 1. The suitable polymerization conditions are: $[\text{cat}] = 0.01 \text{ mol/L}$, $[\text{PF}] = 2 \text{ mol/L}$, CHCl_3 solvent, $T = 60^\circ\text{C}$, $t = 24 \text{ h}$.

From Table 1, it can be seen that the solvent system has a great effect on the polymerization. Though the polymerizations in all the solvent systems are homogeneous, the yields of polymers vary greatly. The highest yield obtained in CHCl_3 reaches 71%, while the lowest in pyridine is only 44%. It seems that higher yields are obtained from chlorinated solvents and solvents containing O atom, while solvent containing N atom, *i.e.* pyridine, is not so favorable for the polymerization.

Table 1. Polymerization of PF with palladium acetylide catalysts^a

Catalyst	Catalyst: Monomer ratio	Solvent	Reaction time (h)	Yield (%)
$\text{Pd}(\text{PPh}_3)_2(\text{C}\equiv\text{CC}(\text{CH}_3)_2\text{OH})_2$	1:200	CHCl_3	16	71
$\text{Pd}(\text{PPh}_3)_2(\text{C}\equiv\text{CC}(\text{CH}_3)_2\text{OH})_2$	1:200	$\text{CHCl}_3/\text{MeOH}=3/1^b$	16	66
$\text{Pd}(\text{PPh}_3)_2(\text{C}\equiv\text{CC}(\text{CH}_3)_2\text{OH})_2$	1:200	$\text{CHCl}_3/\text{CCl}_4=1/1^b$	16	64
$\text{Pd}(\text{PPh}_3)_2(\text{C}\equiv\text{CC}(\text{CH}_3)_2\text{OH})_2$	1:200	THF	16	64
$\text{Pd}(\text{PPh}_3)_2(\text{C}\equiv\text{CC}(\text{CH}_3)_2\text{OH})_2$	1:200	1,4-Dioxane	16	65
$\text{Pd}(\text{PPh}_3)_2(\text{C}\equiv\text{CC}(\text{CH}_3)_2\text{OH})_2$	1:200	Pyridine	16	44
$\text{Pd}(\text{PPh}_3)_2(\text{C}\equiv\text{CC}(\text{CH}_3)_2\text{OH})_2$	1:200	CHCl_3	24	70
$\text{Pd}(\text{PPh}_3)_2(\text{C}\equiv\text{CC}_6\text{H}_5)_2$	1:200	CHCl_3	24	70
$\text{Pd}(\text{PPh}_3)_2(\text{C}\equiv\text{CC}(\text{CH}_3)_2\text{OH})_2$	1:200	CHCl_3	24	75
$\text{Pd}(\text{PPh}_3)_2(\text{C}\equiv\text{CC}(\text{CH}_3)_2\text{OH})_2$	1:400	CHCl_3	45	68
$\text{Pd}(\text{PPh}_3)_2(\text{C}\equiv\text{CC}(\text{CH}_3)_2\text{OH})_2$	1:600	CHCl_3	45	59
$\text{Pd}(\text{PPh}_3)_2(\text{C}\equiv\text{CC}(\text{CH}_3)_2\text{OH})_2$	1:800	CHCl_3	45	40

^a Reaction temperature: 60°C , $[\text{cat}] = 0.01 \text{ mol/L}$; ^b Volume ratio

Table 1 also shows that all these palladium acetylide complexes PPB, PPO and PPA can effectively catalyze the polymerization of PF under mild conditions and their catalytic activities are quite similar in spite of the difference in polarity and steric hindrance of the acetylide ligands bonded to palladium atom. Therefore it can be seen that palladium acetylide complex catalysts have the advantage of being able to effectively catalyze the polymerization of terminal alkynes bearing aromatic^[21], aliphatic^[20, 23] and furanic substituents.

The effect of concentration of catalysts on polymerization has also been investigated by varying the catalyst/monomer ratios from 1/200 to 1/800. It was found that PPB shows a high catalytic activity for the polymerization of alkyne with furan ring, and the yield reaches 75% with a catalyst/monomer ratio of 1/200. Even with a lower ratio of 1/600, the yield reaches *ca.* 60% after reaction of 45 h. This further proves that palladium acetylide catalysts are effective catalysts for the polymerization of alkyne containing furan ring.

The polymer so obtained is a light brown powder having a M_w of *ca.* 3000 and MWD of *ca.* 1.4 as determined by GPC. It is highly soluble in common organic solvents, such as CHCl_3 , acetone, CH_2Cl_2 , THF, DMSO, pyridine, 1,4-dioxane, partially soluble in toluene and methanol, and insoluble in ethanol. After storing in the atmosphere for about six months, the solubility and the IR spectrum of the polymer do not change appreciably (Fig. 2b), suggesting that PPF exhibits good stability in air.

The IR spectra of the monomer (PF) and freshly prepared polymer (PPF) are shown in Figs. 2(a) and (b), respectively. In the spectrum of monomer (Fig. 2a), sharp absorption bands at 3300 and 2120 cm^{-1} are attributed to the $\equiv\text{CH}$ group, and 3140 and 1020 cm^{-1} can be assigned to the absorption bands of the furan ring. In addition,

the absorption at 1720 cm^{-1} , and the two bands at 2920 and 2880 cm^{-1} are due to $\text{C}=\text{O}$ group and CH_2 group, respectively. All these suggest that the monomer prepared has a structure as shown in Fig. 1. The spectrum of the polymer also shows the characteristic absorption bands of furan ring ($3140, 1020\text{ cm}^{-1}$), $\text{C}=\text{O}$ group (1722 cm^{-1}) and CH_2 group ($2945, 2882\text{ cm}^{-1}$), indicating that the pendant group remains unchanged, except that the sharp absorption bands at 2120 and 3300 cm^{-1} disappear, which suggests that the chain growth proceeds through the opening of the triple bonds. Furthermore, a weak absorption at $3600\text{--}3300\text{ cm}^{-1}$ also appears in the polymer spectrum, which can be attributed to the characteristic absorption of OH group. This OH group may result from the moisture absorbed by the polymer since PPF is sensitive to moisture and can be used as humidity sensitive material^[30]. The polymers prepared under different conditions all exhibit similar IR spectra.

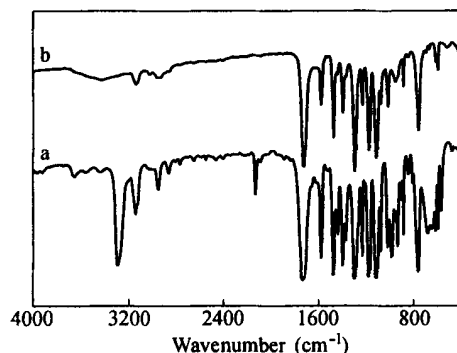


Fig. 2 IR spectra of (a) PF and (b) PPF
The preparation conditions for PPF: $[\text{M}] = 2\text{ mol/L}$;
 $[\text{PPB}] = 0.02\text{ mol/L}$; CHCl_3 solvent; 60°C ; 40 h

Figures 3(a) and (b) present the ^1H -NMR spectra of the monomer (PF) and polymer (PPF), respectively. Well-resolved proton signals are detected in the spectrum of the monomer. The signals at $\delta = 6.5, 7.2$ and 7.6 are attributed to the protons in furan rings, and the signals at $\delta = 4.9$ and 2.6 can be assigned to the CH_2 protons and the $\equiv\text{C}-\text{H}$ proton, respectively. The ^1H -NMR spectrum further confirms the chemical structure of the monomer, and shows it to be of high purity. The spectrum of the polymer, however, shows the broadening of the proton signals and lack of resolution, which may be due to the random configuration of the polymer. The resonance of the olefinic proton can not be seen, probably because it was masked under the broad features observed^[31]. The signals at $\delta = 6.6, 7.2, 7.8$ are due to protons in the furan ring, and the very broad signal between $\delta = 4\text{--}6$ can be attributed to CH_2 protons in the pendant group. The signal at $\delta = 2.85$ may result from water absorbed by the polymer, or water contaminated solvent, and signal of the solvent should appear at $\delta = 2.05$ ^[32]. The signal of $\equiv\text{C}-\text{H}$ proton in the monomer at $\delta = 2.6$ is absent. The above analysis confirms that highly soluble PPF having π -conjugated $\text{C}=\text{C}$ backbone was obtained.

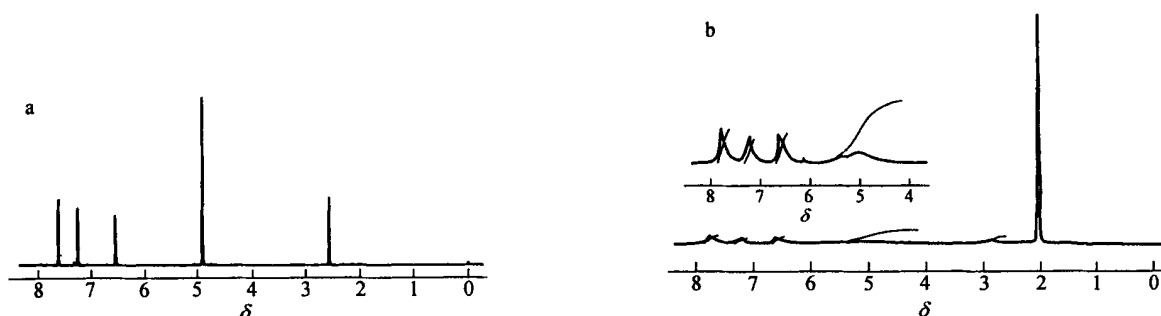


Fig. 3 ^1H -NMR spectra of (a) PF (in CDCl_3) and (b) PPF (in $(\text{CD}_3)_2\text{CO}$)
The preparation conditions for PPF: $[\text{M}] = 2\text{ mol/L}$; $[\text{PPB}] = 0.005\text{ mol/L}$;
 CHCl_3 solvent; 60°C ; 45 h

Just like the doped polyacetylenes bearing aliphatic or aromatic substituent^[33, 34], PPF can also be used as a humidity sensitive material with high sensitivity and no hysteresis^[30]. The furan ring in the side chain seems to be related to its high reversibility to humidity. However, more work to understand the sensing mechanism and correlate the specific structure of the polyacetylene bearing furan moiety to its sensing behavior, especially the high reversibility, is needed.

CONCLUSIONS

Palladium acetylide complexes, PPB, PPO and PPA, are effective catalysts for the polymerization of substituted acetylene bearing furan PF. The polymer so obtained possesses alternating olefinic bonds along the main chain and furan ring as the pendant group, and shows high solubility in common organic solvents, such as CHCl_3 , THF and acetone.

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