Copolymerization of carbon monoxide with phenylacetylene by palladium complex

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Abstract

Carbon monoxide was copolymerized with phenylacetylene (PA) using initiation by a palladium complex [Pd (CH$_3$CN)$_4$] (BF$_4$)$_2$ under various conditions. Good yields were obtained at 90°C in methanol. Elementary analysis, infrared and NMR spectroscopy showed that the copolymers contained ketone and olefinic structures. 2,2'-bipyridine was a more effective stabilizing ligand than monodentate phosphorus, arsenic or nitrogen ligands. The copolymer yield, molar mass and *trans* configuration of the vinylene increased with increasing temperature. Methanol and the protonic acid served as coinitiator and chain-transfer agents. The copolymers have increasingly higher *trans* vinylene structure with the increase of pressure of carbon monoxide. X-ray diffraction analysis shows the copolymer to be partially crystalline. Thermogravimetric analysis showed that the copolymer started to lose mass at 213°C and that maximum decomposition occurred at 390°C. The PA/CO copolymer obtained under the influence of various ligands has a glass transition temperature (T_g) in the range 75–130°C. Hydrogenation of PA/CO copolymer with a reducing agent yielded a hydroxy-containing polymer.

Keywords: Carbon monoxide; Phenylacetylene; Palladium catalyst; Copolymerization; Polyketone

1. Introduction

Copolymerization of CO and olefins is of interest for the following reasons [1]. First, CO is cheap. Secondly, polymers containing polyketones are potentially photodegradable [2–4] or biodegradable. Thirdly, because the carbonyl group can be easily modified chemically, such polyketones are expected to be excellent starting materials for a synthesis of functional polymers [5,6]. Fourthly, if CO copolymerized with substituted acetylene a conjugated double bond ex-

isted in a polymer chain and is a convenient site for chemical modification such as doping [7].

Phenylacetylene (PA) has been reported to polymerize in the presence of [Pd (CH$_3$CN)$_4$] (BF$_4$)$_2$ to yield high molar mass ($\overline{Mn}$ = 9000) by Sen et al. [8]. On the other hand, Chien et al. [7] studied an acetylene/CO copolymer which had its backbone conjugation interrupted every 6–10 vinylenes in order to elucidate the relationship between conjugation length and electrical conductivity.

We reported previously the alternating copolymerization of CO with 1,3-cyclopentadiene [9] or norbornene [10] initiated by palladium complexes. If the palladium complex is active for the polymerization of both CO and

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substituted acetylenes, a possibility arises that alternating copolymerization will occur between them, to produce a novel type of copolymer.

In this study, we present results on copolymerization of CO and phenylacetylene in the presence of $[Pd(CH_3CN)_4](BF_4)_2$ under various conditions. The structure of the copolymer was determined from IR, ^1H NMR and ^{13}C NMR spectroscopy. The effects of stabilizing ligands solvent, temperature and pressure of CO on catalytic activity, molar mass, yield and physical properties are discussed.

2. Experimental

2.1. Materials

Carbon monoxide (99.3% purity) was purchased (Air Products and Chemicals Inc.). Phenylacetylene was purchased from Merck chemical company and purified by fractional distillation from calcium hydride and distilled immediately before use, bp 63°C/52 mm Hg. Gas chromatography showed that the purity of phenylacetylene was higher than 99.9%. Oxidant (1,4-naphthoquinone) and acid (p-toluenesulfonic acid) were purchased from Merk, Germany. Ligands 2,2'-bipyridine (Merck), triphenylphosphine, triphenylarsine and triphenylamine (Janssen), were used directly without purification. Solvents were purified according to standard methods.

2.2. Preparation of [Pd (CH3CN)4] (BF4)2

Catalyst $[Pd (CH_3CN)_4] (BF_4)_2$ was prepared according to the published method [9,11]. That is, 0.5 g (4.7 mmol) of Pd sponge and 1.1 g (9.4 mmol) of $NOBF_4$ were stirred in 25 ml of dried and deoxygenated CH_3CN under vacuum. The mixture was stirred for 12 h to gradually remove NO in the course of the reaction. The mixture was filtered and concentrated to 5 ml by distillation to yield a yellow filtrate from which a pale yellow compound was obtained by the addition of anhydrous ether.

2.3. Copolymerization of CO and phenylacetylene

Alternating copolymerization of CO and phenylacetylene was conducted in a magnetically stirred stainless-steel reactor (volume 250 ml), according to the general procedure [12]. [Pd $(CH_3CN)_4$] $(BF_4)_2$ (0.033 g, 0.075 mmol), 2,2'-bipyridine (0.47 g, 3 mmol), 1,4-naphthoquinone (3.16 g, 20 mmol), and p-toluenesulfonic acid (0.36 g, 2 mmol), were dissolved in chloroform (10 ml) and charged into the reactor under nitrogen. Phenylacetylene (5.11 g, 0.05 mol) and CO (3.3 MPa) were added, and the system was heated to the desired temperature (90°C). After a given duration, the reaction was quenched to room temperature and unreacted CO was vented. The product, a deep brown fine powder, was recovered by filtration, washed several times with methanol and dried in vacuum. The yield was about 0.42 g. The polymer did not melt below 163°C. Found: C, 83.89%; H, 4.58%; O, 11.53%; Calculated for a 1:1 copolymer: (C_8H_6CO): C, 83.06%; H, 4.65%; O, 12.29%. The results are consistent with the alternating copolymer structure proposed.
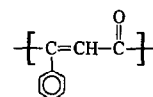
The above procedure was used in other reactions where the temperature, pressure, solvent, and the added ligand were varied.

3. Results and discussion

3.1. Copolymerization with the addition of various ligands

The influence of the ligands on the copolymerization of phenylacetylene (PA) with CO is shown in Table 1. Bidentate ligands (e.g., 2,2'-

Table 1
Effect of ligand of copolymerization on phenylacetylene and CO at 90°C [a]

Ligands	Yield (g)	Productivity g copolymer $(g^{-1} Pd h^{-1})$	$\nu_{C=0}$ (cm^{-1})	A_{870}/A_{910}	T_g (°C) [b]
2,2-bipyridine	0.79	49	1797, 1755	0.196	130
Triphenylphosphine	0.72	45	1797, 1755	0.517	114
Triphenylarsine	0.58	36	1801, 1763	0.096	75
Triphenylamine	0.53	33	1797, 1755	0.479	85

[a] Experimental conditions: phenylacetylene (0.05 mol); methanol (10 ml); partial pressure of CO, P(CO) = 3.3 MPa; $Pd(CH_3CN)_4(BF_4)_2$(0.075 mmol); ligand (3 mmol); p-toluenesulfonic acid (2 mmol); 1,4-naphthoquinone (20 mmol); temperature: 90°C; reaction period: 2 h
[b] DSC measurements were conducted with a heating rate of 20°C min^{-1} in nitrogen.

bipyridine) and three kinds of monodentate ligands-triphenylphosphine, triphenylarsine and triphenylamine were used. According to Table 1, the activity of nitrogen bidentate ligands in copolymerization of PA with CO clearly exceeded that of monodentate ligands. Drent et al. [13] reported that the two phosphine groups of a bidentate ligand are likely to bind exclusively in a cis configuration to a single palladium center. This effect maximizes the concentration of species for which propagation is possible.

Phosphines showed greater activity than arsenic or nitrogen compounds. In general, lower catalyst activity was observed when less basic ligands were used. It is possible that in the presence of less basic ligands, CO is bound too strongly to the Pd (II) center, thus poisoning the catalyst. [9,11] Two absorption features in the IR spectrum (1755 and 1797 cm^{-1}) in CH$_3$OH are attributed to ketone and ester carbonyl groups, respectively. The cis and trans contents

in the copolymers can be calculated from the absorbances at 870 and 910 cm^{-1}, respectively. It is observed that in this work the copolymers have high trans structure regardless of kind of ligands used which may be due to isomerization to the thermodynamically preferred isomer at 90°C. The high trans content in the structure of PA/CO copolymer is similar to that of acetylene/CO copolymers [7].

3.2. Effect of temperature on copolymerization

The copolymerization yield, molar mass $(\overline{Mn})$ and ratio of cis–trans configuration are given in Table 2. From Table 2, the yield, molar mass $(\overline{Mn})$ and trans configuration of the copolymer increased with increasing temperature. This result indicates that as the temperature is raised, the copolymerization rate increased. The copolymers have high trans structure which may be due to isomerization when the copoly-

Table 2
Effect of temperature on copolymerization [a]

Temperature (°C)	Yield (g)	Productivity g copolymer $(g^{-1} Pd h^{-1})$	$\nu_{C=0}$ (cm^{-1})	A_{870}/A_{910}	V.P.O. [a] $(\overline{Mn})$
40	0.02	1	1798, 1755	0.884	insoluble [b]
60	0.13	8	1796, 1757	0.884	insoluble [b]
80	0.33	21	1798, 1757	0.835	insoluble [b]
90	0.79	49	1797, 1755	0.196	1000 [c]
110	1.58	99	1800, 1749	0.139	1100 [c]
130	2.88	180	1800, 1750	0.095	1300 [c]

[a] Experimental conditions: phenylacetylene (0.05 mol); methanol (10 ml); partial pressure of CO, P(CO) = 3.3 MPa; $Pd(CH_3CN)_4(BF_4)_2$(0.075 mmol); 2,2'-bipyridine (3 mmol); p-toluenesulfonic acid (2 mmol); 1,4-naphathoquinone (20 mmol); reaction period: 2 h.
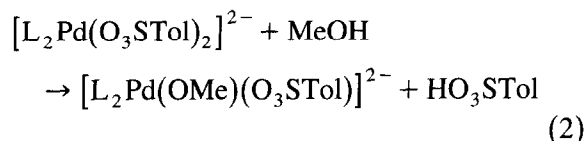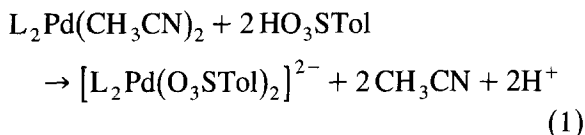[b] The copolymer was insoluble in THF, DMSO or chlorobenzene.
[c] $\overline{Mn}$ was measured by osmometry for the copolymer in THF.

mers were heated [7]. Copolymers of CO with PA having a relative high *cis* content are insoluble, which may be due to higher crystallinity [7].

3.3. Copolymerization of phenylacetylene and CO in various solvents

Table 3 shows that the yield of copolymerization in a protic solvent (such as CH_3OH) exceeds that of copolymerization in an aprotic solvents (such as $CHCl_3$, THF and C_6H_6). A protonic solvent serves both co-initiator and chain-transfer agent in its reaction with the palladium complex, which forms a palladium methoxy species [13–15] (Eqs. (1) and (2)).

$$L_2Pd(CH_3CN)_2 + 2HO_3STol$$

$$\rightarrow \left[L_2Pd(O_3STol)_2\right]^{2-} + 2CH_3CN + 2H^+ \quad (1)$$

$$\left[L_2Pd(O_3STol)_2\right]^{2-} + MeOH$$

$$\rightarrow \left[L_2Pd(OMe)(O_3STol)\right]^{2-} + HO_3STol \quad (2)$$

Furthermore, the higher selectivity to ester formation, as evidenced by the IR data, is attributed to oxidation by the oxidant (1,4-naphthoquinone) of the proposed palladium species (Eq. (3)).
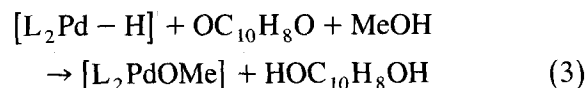
$$[L_2Pd - H] + OC_{10}H_8O + MeOH$$

$$\rightarrow [L_2PdOMe] + HOC_{10}H_8OH \quad (3)$$

Table 4
Effect of pressure of CO on copolymerization with phenylacetylene [a]

$P(CO)$ (MPa)	Yield (g)	Productivity g copolymer $(g^{-1}Pd\,h^{-1})$	$\nu_{C=O}$ (cm^{-1})	A_{870}/A_{910}
0.67	2.84	178	1800, 1757	0.384
2.0	2.59	162	1800, 1757	0.282
3.3	0.79	49	1797, 1755	0.196
5.3	0.75	47	1800, 1759	0.163
6.0	0.36	23	1797, 1757	0

[a] Experimental conditions: phenylacetylene (0.05 mol); methanol 10 ml); $Pd(CH_3CN)_4$ $(BF_4)_2$ (0.075 mmol); 2,2'-bipyridine (3 mmol); p-toluenesulfonic acid (2 mmol); 1,4-naphthoquinone (20 mmol); temperature: 90°C; reaction period: 2 h.

For reactions in aprotic solvents in which the copolymerizations are initiated by dihydrogen, presumably involving formation of a palladium hydride species $[L_2Pd-H]$, a decreased yield is obtained [13] and the IR spectra show only one carbonyl group.

3.4. Effects of pressure of CO on copolymerization with phenylacetylene

The effects of pressure of CO on copolymerization with phenylacetylene at 90°C are given in Table 4, the results indicate that the greater the pressure of CO, the lower the yield and *cis* vinylene configuration. Chien et al. reported that CO is acting merely as a retarder in acetylene polymerization [7]. That is, copolymers have higher *trans* structure as the pressure of carbon monoxide increased. This apparent dis-

Table 3
Copolymerization of phenylacetylene and CO in various solvents [a]

Solvents	Yield (g)	Productivity g copolymer $(g^{-1}Pd\,h^{-1})$	$\nu_{C=O}$ (cm^{-1})	A_{870}/A_{910}	V.P.O [a] $(\overline{Mn})$
CH_3OH	0.79	49	1797, 1755	0.196	1000 [b]
$CHCl_3$	0.42	26	1757	0.613	insoluble [b]
THF	0.32	20	1760	0.635	insoluble [b]
C_6H_6	0.11	7	1763	0.200	insoluble [b]

[a] Experimental conditions:phenylacetylene (0.05 mol); solvent (10 ml); partial pressure of CO, P(CO) = 3.3 MPa; $Pd(CH_3CN)_4$ $(BF_4)_2$ (0.075 mmol); 2,2'-bipyridine (3 mmol); p-toluenesulfonic acid (2 mmol); 1,4-naphthoquinone (20 mmol); temperature: 90°C; reaction period: 2 h.
[b] The copolymer was insoluble in THF, DMSO or chlorobenzene.

crepancy may be due to isomerization when the copolymers were brought to the higher temperature of 90°C.

The PA/CO copolymer was insoluble in common solvents (e.g., THF, C_6H_5Cl and acetone). It showed two peaks in the IR spectrum at 1755 and 1797 cm^{-1} in CH_3OH which are attributed to ketone and ester carbonyl groups, respectively.

3.5. Characterization of PA / CO copolymer by IR, ^1H NMR and ^{13}C NMR

The copolymer of phenylacetylene and CO was almost insoluble in common organic solvents, and thus was characterized by IR, ^1H and ^{13}C NMR spectroscopy for soluble parts and by elemental analysis. The IR spectrum of the PA/CO copolymer, obtained from the Pd $(CH_3CN)_4$ $(BF_4)_2/CH_3OH$ catalyzed reaction, shows a peak at 1614 cm^{-1} due to the stretching vibration of a trisubstituted double bond; there are two peaks (1755 and 1797 cm^{-1} for PA/CO copolymer in CH_3OH which are attributable to the ketone carbonyls (repeating unit) and ester carbonyls (end group), respectively (vide supra). The formation of polyketoester at the chain end has been suggested as the result of the copolymerization when alcohol is used as solvent [9]. The strong absorption at 3046 cm^{-1} is the typical C–H stretching vibration of an olefinic proton and those at 755 and 694 cm^{-1} are due to C–H out-of-plane bending vibrations of monosubstituted benzene compounds which is confirmed by the characteristic pattern of the overtone absorptions at 1800–2000 cm^{-1}.

The ^1H NMR $(CDCl_3)$ spectrum of the PA/CO copolymer for the soluble part of the copolymer is shown in Fig. 1. The broad resonance at 6.3 ppm is characteristic of olefinic and aromatic protons, and suggest a polymer of low stereoregularity [16,17,19]. The absence of a well-defined resonance at 5.82 ppm is usually taken as evidence for a *trans*-rich polymer
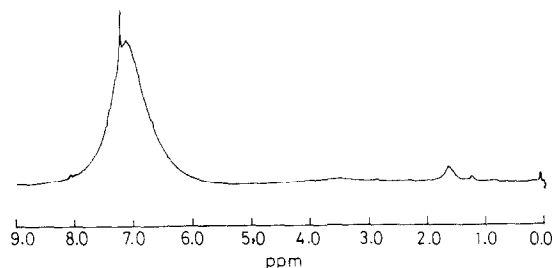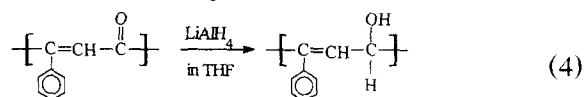

Fig. 1. ^1H NMR spectrum of PA/CO copolymer for soluble parts in $CDCl_3$. Experimental conditions: phenylacetylene (0.05 mol); methanol (10 ml); partial pressure of CO, $P(CO) = 3.3$ MPa; $Pd(CH_3CN)_4$ $(BF_4)_2$ (0.075 mmol); 2,2'-bipyridine (3 mmol); p-toluenesulfonic acid (2 mmol); 1,4-naphthoquinone (20 mmol); temperature: 90°C; reaction period: 2 h.

[18,19]. The signal in the ^{13}C NMR spectrum $(CDCl_3)$ at 207.8 ppm is ascribed the carbonyl carbon. The line at 185.8 ppm is due to the ester group $[CH_3-O-(C=O)-]$ at the end of the copolymer chain. The C=C double bond and resonance of the phenyl ring fall in the range of 108–150 ppm. This further proves that CO is indeed copolymerized with phenylacetylene.

3.6. Reduction of PA / CO copolymer

Reduction of the polyketone (soluble parts) with lithium aluminum hydride in THF yielded hydroxyl-containing polymer having units represented as in Eq. (4).

$$\left\{C=CH-\overset{\overset{O}{\|}}{C}\right\} \xrightarrow[\text{in THF}]{LiAlH_4} \left\{C=CH-\overset{OH}{\underset{H}{C}}\right\} \qquad (4)$$

The reduced polymer was completely soluble in chloroform, THF, dimethylforamide, pyridine, chlorobenzene, dimethylacetamide, dimethylsulfoxide, acetone, benzene, xylene, toluene, acetonitrile and 1,2-dichloroethane. The absence of infrared absorption corresponding to the carbonyl group (1756 cm^{-1}) and a specific absorption of ν_{OH} at 3394 cm^{-1} indicated the essentially complete conversion of ketone functional groups to alcohol groups without cleavage of the polymer chain [10,21].
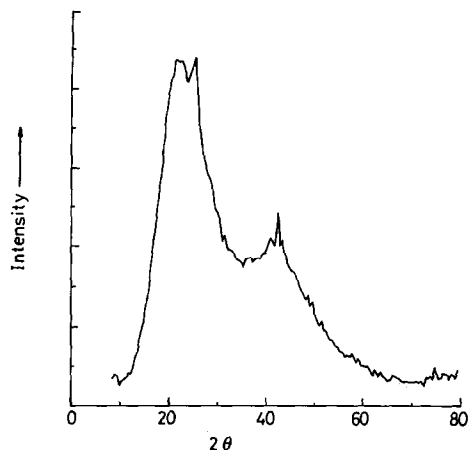
Fig. 2. X-ray diffractogram of PA/CO copolymer. Experimental conditions: phenylacetylene (0.05 mol); methanol (10 ml); partial pressure of CO, $P(CO) = 3.3$ MPa; Pd(CH$_3$CN)$_4$ (BF$_4$)$_2$ (0.075 mmol); 2,2′-bipyridine (3 mmol); p-toluenesulfonic acid (2 mmol); 1,4-naphthoquinone (20 mmol); temperature: 90°C; reaction period: 2 h.

Fig. 4. DSC traces (at a heating rate of 20°C min^{-1} in nitrogen) of PA/CO copolymer. Experimental conditions: phenylacetylene (0.05 mol); methanol (10 ml); partial pressure of CO, $P(CO) = 3.3$ MPa; Pd(CH$_3$CN)$_4$ (BF$_4$)$_2$ (0.075 mmol); 2,2′-bipyridine (3 mmol); p-toluenesulfonic acid (2 mmol); 1,4-naphthoquinone (20 mmol); temperature: 90°C; reaction period: 2 h.

3.7. X-ray diffractogram of copolymer

Fig. 2 shows the X-ray diffractogram of the copolymer. The copolymer was confirmed to be partially crystalline. The shape of the X-ray diffractogram diagram of this copolymer from a Pd catalyst is similar to that of a copolymer formed on γ irradiation [20].
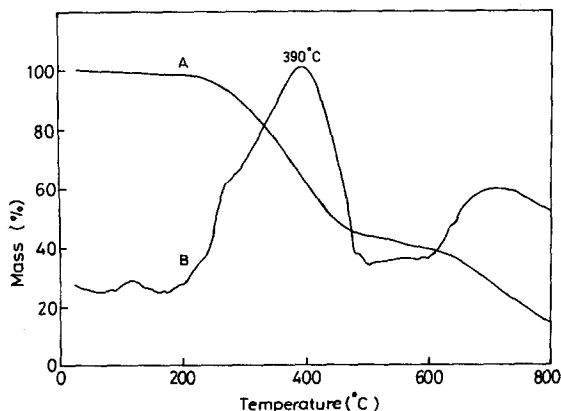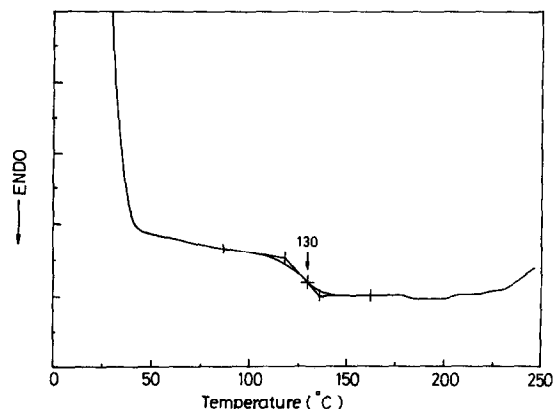
3.8. Thermal properties of PA / CO copolymer

A TGA curve of the copolymer of phenylacetylene and CO appears in Fig. 3 recorded with a heating rate 10°C min^{-1} in nitrogen. Fig. 3 shows that loss of mass starts at 213°C. The maximum decomposition occurs at 390°C according to the differential thermogravimetric analysis curve. DSC measurement was conducted with a heating rate of 20°C min^{-1}. In all cases the samples were quenched from elevated temperature to room temperature to produce an easier detectable glass transition step. Fig. 4 shows the typical DSC traces of PA/CO copolymer obtained from 2,2′-bipyridine ligand and T_g was measured to be 130°C. The PA/CO copolymers obtained from initiation in the presence various ligands had glass transition temperatures (T_g) in the range 75–130°C as shown in Table 1.

Fig. 3. TGA curve of PA/CO copolymer in nitrogen (heating rate 10°C min^{-1}). (A) TGA; (B) DTG Experimental conditions:phenylacetylene (0.05 mol); methanol (10 ml); partial pressure of CO, $P(CO) = 3.3$ MPa; Pd(CH$_3$CN)$_4$ (BF$_4$)$_2$ (0.075 mmol); 2,2′-bipyridine (3 mmol); p-toluenesulfonic acid (2 mmol); 1,4-naphthoquinone (20 mmol); temperature: 90°C; reaction period: 2 h.

Acknowledgements

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