Copolymerization of Carbon Monoxide and Norbornene with a Palladium Catalyst

Der-Jang LIAW* and Biing-Ferng LAY

Department of Chemical Engineering, National Taiwan Institute of Technology,
Taipei, Taiwan 106, Republic of China

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ABSTRACT: Carbon monoxide and norbornene (NBE) with $\text{Pd}(\text{CH}_3\text{COO})_2$ under various conditions were copolymerized at 90°C. Elemental analysis, infrared spectra and NMR spectra showed that the copolymers contained ketone and ring structures. Bidentate nitrogen and phosphorus ligands were more effective ligands to stabilize catalytic activity than monodentate arsenic or phosphorus ligands. Methanol and the protonic acid served as coinitiator and chain-transfer agents. X-Ray diffraction analysis shows the copolymer to be partially crystalline. Thermogravimetric analysis showed that the copolymer started to lose mass at 350°C and that maximum decomposition occurred at 447°C. The NBE/CO copolymer obtained from various ligands has a glass transition temperature (T_g) in the range 100–126°C. Hydrogenation of norbornene/CO copolymer with a reducing agent yielded a hydroxy-containing polymer.

KEY WORDS Copolymerization / Polyketone / Carbon Monoxide / Norbornene / Palladium Catalyst /

Many authors discuss the copolymerization of carbon monoxide and olefins.^{1–37} The first example of copolymerization of carbon monoxide and olefins involved free-radical-initiated copolymerization of CO and ethylene at high pressure and high temperature. A random copolymer of only small molar mass was obtained.^{1,2} Copolymerization of CO and olefins is of interest for the following reasons.³ First, CO is cheap. Secondly, polymers containing polyketones have the potential to become photodegradable^{4–6} or biodegradable polymers in a new class. 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 of new types.^{7,8}

According to several patents,^{9–12} the copolymerization of CO and ethylene with palladium catalysts yields polyketones of large molar mass; the catalytic systems all require reaction temperatures above 100°C. Sen *et al.* developed cationic Pd(II) compounds to catalyze copolymerization of CO with various olefins under mild conditions.^{13,14} They report that only cooligomer (molar mass = 350) is obtained from copolymerization of CO and norbornene for three days.¹³ Although the syntheses of copolymers of CO with norbornene or 5-norbornene-2,3-dicarboxylic anhydride are patented,^{15,16} only a few experimental results have been reported.

We reported previously the copolymerization of CO and 1,3-cyclopentadiene by palladium complexes.¹⁷ Phosphorus compounds were found more effective to stabilize ligands for catalytic activity than arsenic or nitric ligands.¹⁷ Here, we present results on the copolymerization of CO and norbornene under various conditions at 90°C. The structure of the copolymer was determined from IR, ¹H NMR and solid-state ¹³C NMR spectra. The effects of stabilizing ligand on catalytic activity, solvent, ligands and oxidant with regard to molar mass and yield, and other physical properties are discussed.

EXPERIMENTAL

Materials

Carbon monoxide (99.3% purity) was purchased (Air Products and Chemicals Inc.). Norbornene (Merck) was distilled twice from calcium hydride under dry nitrogen (purity > 99% by GC). Catalyst $\text{Pd}(\text{CH}_3\text{COO})_2$ and oxidants (nitrobenzene, 1,4-naphthoquinone, 1,4-benzoquinone) were purchased from Merck, Germany. Ligands 2,2-bipyridine and 1,10-phenanthroline (Merck), 5-nitro-1,10-phenanthroline (TCI), 1,3-bis(diphenylphosphino)propane, triphenylphosphine, triphenylarsine, and triphenylamine (Janssen), were used directly without purification. Solvents were purified according to standard methods.

Copolymerization of CO and Norbornene

The alternating copolymerization of CO and norbornene was conducted in a magnetically stirred stainless-steel reactor (volume 250 ml), according to the general procedure of ref 36. $\text{Pd}(\text{CH}_3\text{COO})_2$ (0.022 g; 0.1 mmol), 2,2-bipyridine (0.47 g; 3 mmol), nitrobenzene (2.05 ml; 20 mmol), and *p*-toluenesulfonic acid (0.36 g; 2 mmol), were dissolved in tetrahydrofuran (THF) (10 ml) and charged into the reactor. Norbornene (9.42 g; 0.1 mol) and CO (2.3 MPa) were added, and the system was heated to 90°C. After a given period (2 h), the reaction was quenched to room temperature and unreacted CO was vented. The product, a fine powder, was recovered by filtration, washed several times with methanol and dried in vacuum. The yield was about 3.02 g. The polymer did not melt below 225°C. *Anal.* Found: C, 77.86%; H, 8.12%; O, 13.11%; Calcd for a 1:1 copolymer ($\text{C}_7\text{H}_{10}\text{CO}$): C, 78.65%; H, 8.25%; O, 13.10%. The copolymer structure was proposed as follows:

* To whom all correspondence should be addressed.

Osmometric measurements showed that the NBE/CO copolymer obtained from THF has a number molar mass ($\bar{M}_n$) ca. 6100. Polymerization degree (n) was about 50.

The above procedure was used in other reactions where the temperature, time, pressure, solvent, the proportion of methanol, the concentration of acid and oxidant, and the added ligand were varied.

RESULTS AND DISCUSSION

Copolymerization of CO with Olefins

The results of copolymerization of CO and various olefins with catalyst palladium acetate in methanol are shown in Table I. As indicated, norbornene (NBE) is an effective olefin for copolymerization with carbon monoxide. The infrared spectrum of the product includes two features at 1725 and 1688 cm^{-1} for NBE/CO copolymer in CH_3OH that are attributed to carbonyl groups in ketones (repeating unit) and esters (end group), respectively. As described previously,¹⁷⁾ the formation of polyketoester $\text{RO}-(\text{CO}-\text{NBE})_n-\text{COOR}$ (in which $\text{R}=\text{CH}_3$), is considered to result from copolymerization in the polymer end with an alcohol as solvent.¹⁸⁾

The NBE/CO copolymer was insoluble in dimethylacetamide, dimethylsulfoxide, *N,N*-dimethylformamide, pyridine, xylene, benzene, toluene, acetonitrile, 1,2-dichloroethane, *m*-cresol, and acetone, but soluble in tetrahydrofuran, chloroform, sulfuric acid, and chlorobenzene.

Copolymerization with the Addition of Various Ligands

The influence of ligands on copolymerization of nor-

Table I. Copolymerization of CO and olefins with a palladium complex^a

Olefin monomers	Yield	Productivity	$\nu_{\text{C=O}}$ cm^{-1}
	g	g copolymer $\text{g}^{-1} \text{Pd h}^{-1}$	
Styrene	1.93	91	1747, 1703
Hexene	0.74	35	1728, 1691
Norbornene	11.34	533	1725, 1688
Phenylacetylene	0.044	2	1798, 1752

^a Experimental conditions: olefin (0.1 mol); methanol (10 ml); partial pressure of CO, $\text{P}(\text{CO})=3.3 \text{ MPa}$; $\text{Pd}(\text{CH}_3\text{COO})_2$ (0.1 mmol); 2,2'-bipyridine (3 mmol); *p*-toluenesulfonic acid (2 mmol); nitrobenzene (20 mmol); temperature, 90°C; reaction period, 2 h.

bornene with CO is shown in Table II. Bidentate ligands, 2,2-bipyridine, 1,10-phenanthroline, 5-nitro-1,10-phenanthroline, and 1,3-bis(diphenylphosphino)propane and monodentate ligands, triphenylphosphine, triphenylarsine, and triphenylamine were used. According to Table II, the activity of nitrogen and phosphorus bidentate ligands in copolymerization of NBE with CO clearly exceeded that of monodentate ligands. Drent *et al.*¹⁸ 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 show greater activity than arsenic or nitrogen compounds. Among phosphorus compounds, lower activity of catalyst was observed when less basic ligands such as $\text{P}(\text{OPh})_3$ were used instead of PPh_3 . It is possible that in the presence of less basic ligands, CO is bound too strongly to the $\text{Pd}(\text{II})$ center, thus poisoning the catalyst.^{14,17} The NBE/CO copolymer obtained from various ligands has a glass transition temperature (T_g) in the range 100–126°C. Two absorption features in the IR spectra in CH_3OH are attributed to ketone and ester carbonyl groups. As NBE/CO copolymers obtained from 1,4-benzoquinone as oxidant were insoluble in common organic solvents such as THF, chloroform, benzene, and chlorobenzene, we could not measure the molar mass by vapour-pressure osmometry.

Effect of Temperature on Copolymerization

The data of copolymerization yield and molar mass ($\bar{M}_n$) for various temperatures (T_p) are plotted in Figure 1. Both the yield and $\bar{M}_n$ increased initially and then decreased. This may be due to two competing effects.¹⁹ Increasing T_p increases R_p (tangent of the curve) but decreases the solubility of the monomer. However, maximum $\bar{M}_n$ is at $T_p=90^\circ\text{C}$, compared to the maximum yield at $T_p=110^\circ\text{C}$. This difference reflects the contribution of the activation energy to chain-transfer processes.¹⁹ When the temperature exceeded 130°C, the copolymers were insoluble in common organic solvents such as THF and chlorobenzene. This may have resulted from partial cross-linking of NBE/CO copolymer at high temperature.

Table II. Effect of ligand of copolymerization on norbornene and CO at 90°C^a

Ligands	Yield	Productivity	T_g^b °C	$\nu_{\text{C=O}}$ cm^{-1}
	g	g copolymer $\text{g}^{-1} \text{Pd h}^{-1}$		
2,2-Bipyridine	7.10	334	111	1727, 1692
1,10-Phenanthroline	7.89	371	113	1728, 1692
5-Nitro-1,10-phenanthroline	5.99	282	112	1727, 1692
1,3-Bis(diphenylphosphino)propane	1.24	58	126	1727, 1693
Triphenylphosphine, PPh_3	0.66	31	120	1725, 1687
Triphenylarsine, AsPh_3	0.60	28	100	1726, 1690
Triphenylamine, NPh_3	0.48	23	105	1729, 1694
Triphenylphosphate, $\text{P}(\text{OPh})_3$	0.15	7	—	—

^a Experimental conditions: norbornene (0.1 mol); methanol (10 ml); partial pressure of CO, $\text{P}(\text{CO})=3.0 \text{ MPa}$; $\text{Pd}(\text{CH}_3\text{COO})_2$ (0.1 mmol); ligands (3 mmol); *p*-toluenesulfonic acid (2 mmol); 1,4-benzoquinone (20 mmol); temperature, 90°C; reaction period, 2 h. ^b Measured by DSC; heating rate, 20°C min^{-1} .

Figure 1. Copolymerization yield and molar mass ($\bar{M}_n$) at various temperatures (T_p). Experimental conditions: norbornene (0.1 mol); methanol (10 ml); partial pressure of CO, $P(\text{CO}) = 2.7$ MPa; $\text{Pd}(\text{CH}_3\text{COO})_2$ (0.1 mmol); 2,2'-bipyridine (3 mmol); *p*-toluenesulfonic acid (2 mmol); nitrobenzene (40 mmol); reaction duration, 2 h. $\bar{M}_n$ was measured by osmometry for the copolymer in THF.

Table III. Copolymerization of norbornene and CO in various solvents^a

Solvents	Yield	Productivity	$\nu_{\text{C=O}}$ cm ⁻¹
	g	g copolymer g ⁻¹ Pd h ⁻¹	
CH ₃ OH	11.91	560	1727, 1691
CHCl ₃	1.40	66	1691
THF	0.73	34	1688
C ₆ H ₆	0.59	28	1689

^a Experimental conditions: norbornene (0.1 mol); solvent (10 ml); partial pressure of CO, $P(\text{CO}) = 3.3$ MPa; $\text{Pd}(\text{CH}_3\text{COO})_2$ (0.1 mmol); 2,2'-bipyridine (3 mmol); *p*-toluenesulfonic acid (2 mmol); 1,4-naphthoquinone (20 mmol); temperature, 90°C; reaction period, 2 h.

Copolymerization of Norbornene and CO in Various Solvents

Table III shows that the yield of copolymerization in a protonic solvent (such as CH₃OH) exceeds that of copolymerization in an aprotic solvent (such as CHCl₃, THF, and C₆H₆). A protonic solvent serves as both co-initiator and chain-transfer agent in its reaction with the palladium complex, which forms a palladium methoxy species¹⁸ (eq 1). The higher selectivity

to the esters is attributed to oxidation by an oxidant (1,4-naphthoquinone) of the proposed palladium species (eq 2).

Reactions in aprotic solvents in which the copolymerizations are initiated by dihydrogen, presumably involving formation of a palladium hydride species $[\text{L}_2\text{Pd-H}]$, give decreased yield.¹⁸ The IR spectra show only one carbonyl group.

Effects of Proportion of Methanol on Copolymerization

Table IV shows the effects of the proportion of methanol on copolymerization. The yield increased but molar mass decreased as methanol was added to the

Table IV. Effect of proportion of methanol on copolymerization^a

mol CH ₃ OH mol Pd	Yield	Productivity	$\nu_{\text{C=O}}$ cm ⁻¹	$\bar{M}_n^b$
	g	g copolymer g ⁻¹ Pd h ⁻¹		
0	3.02	142	1690	6100
246	7.01	329	1727, 1689	5500
491	7.22	339	1728, 1690	5300
737	9.12	429	1728, 1691	5000
983	9.41	442	1727, 1689	4800
1228	10.05	472	1727, 1689	4300

^a Experimental conditions: norbornene (0.1 mol); THF (10 ml); partial pressure of CO, $P(\text{CO}) = 2.3$ MPa; $\text{Pd}(\text{CH}_3\text{COO})_2$ (0.1 mmol); 2,2'-bipyridine (3 mmol); *p*-toluenesulfonic acid (2 mmol); nitrobenzene (20 mmol); temperature, 90°C; reaction period, 2 h. ^b $\bar{M}_n$ was measured by osmometry for the copolymer in THF.

reaction solution over the range of CH₃OH/Pd mol ratio 246–1228. Drent *et al.*¹⁸ reported that a palladium complex reacts with methanol to give a palladium methoxy species (eq 1), followed by nucleophilic attack by CO (eq 3) and subsequent displacement of the anionic ligand. Activation of $[\text{L}_2\text{PdX}_2]$ by methanol to form $[\text{Pd-O-CH}_3]$ that can initiate polymerization was also proposed by Chien *et al.*¹⁹ When the proportion of MeOH was increased in the copolymerization system,

the concentration of $[\text{L}_2\text{Pd}(\text{OMe})\text{X}]$ increased. Subsequently, the yield increased but the molar mass decreased.

Effects of Pressure of CO on Copolymerization with NBE

The effects of pressure of CO on copolymerization with norbornene at 90°C was investigated. The greater the pressure of CO, the greater were the yield and molar mass of the NBE/CO copolymer. The copolymerization of CO and norbornene was considerable (6.11 g) at pressures as small as 0.67 MPa with CH₃OH as solvent and with 1,4-naphthoquinone as oxidant. Two absorptions in the IR spectra in CH₃OH are attributed to the ketone and ester carbonyl groups. The procedure described above for the effects of pressure of CO on copolymerization was repeated using 1,4-benzoquinone instead of 1,4-naphthoquinone. The final NBE/CO copolymer had almost the same molar mass at the corresponding pressure of CO but the yield was smaller.

Effects of Duration of Polymerization on Yield and Molar Mass

The effects of duration of polymerization on yield and molar mass were investigated. The yield increased remarkably during the early stages of copolymerization and remained constant after 5 h. The latter might be explained by diminishing catalytic activity and concentration of CO, but the molar mass slightly increased with duration of polymerization.

Effects of Concentration of Acid on Copolymerization

The effects of concentration of acid such as *p*-toluenesulfonic acid on copolymer molar mass are shown in Figure 2. The molar mass decreased with increasing concentration of *p*-toluenesulfonic acid but yield in-

Figure 2. Effects of concentration of *p*-toluenesulfonic acid copolymer molar mass. Experimental conditions: norbornene (0.1 mol); THF (10 ml); Pd(CH₃COO)₂ (0.1 mmol); 2,2'-bipyridine (3 mmol); nitrobenzene (20 mmol); temperature, 90°C; partial pressure of CO, P(CO)=2.7 MPa; reaction duration, 2 h. $\bar{M}_n$ was measured by osmometry for the copolymer in THF.

creased. Drent *et al.*¹⁸ reported that a more electrophilic palladium center in acetone solution on addition of *p*-toluenesulfonic acid formed weakly coordinating anions. The replacement of acetate anions by *p*-toluenesulfonate anions is as follows (eq 4):

Such vacant coordination sites at which catalytic transformations occur are considered to be formed by nucleophilic substitution of the anions for monomer such as CO, or norbornene, or solvent molecules, *i.e.*, for complete nucleophilic substitution (eq 5):

The increased reactivity of catalytic systems formed from such anions partly stems from easier access of substrate molecules, solvent, norbornene and CO, to coordination sites on the metal center.¹⁸

Drent *et al.*¹⁸⁾ reported that *p*-toluenesulfonic acid is an essential co-catalyst in the catalytic system Ph₂P(CH₂)PPH₂·Pd(CH₃COO)₂/*p*-TsOH. The yield increased but the molar mass decreased when the active species of L₂Pd(O₃STol)₂ was increased. This was also observed by Chien *et al.* in the copolymerization of ethylene and carbon monoxide.¹⁹

Effects of Concentration of Oxidant on Copolymerization

The effects of the concentration of an oxidant such as 1,4-benzoquinone on copolymerization yield are shown in Table V. 1,4-Benzoquinone was added to promote the reaction.^{18,22,36} The yield increased with concentration of 1,4-benzoquinone, whereas the glass transition temperature decreased. This may be due to the increased palladium methoxy species obtained from reaction of oxidant (1,4-benzoquinone) and palladium hydride species [L₂Pd-H] in a protonic solvent (eq 6),

and may result in decreased molar mass. As mentioned

Table V. Effect of concentration of oxidant on copolymerization^a

1,4-Benzoquinone	Yield	Productivity	$\nu_{\text{C=O}}$	T_g^b
mmol	g	g copolymer g ⁻¹ Pd h ⁻¹	cm ⁻¹	°C
2.5	5.21	245	1723, 1694	141
5	5.41	254	1725, 1692	137
20	8.95	421	1728, 1692	103

^a Experimental conditions: norbornene (0.1 mol); CH₃OH (10 ml); Pd(CH₃COO)₂ (0.1 mmol); 2,2'-bipyridine (3 mmol); temperature: 90°C; partial pressure of CO, P(CO)=3.3 MPa; reaction period, 2 h.
^b Measured by DSC; heating rate, 20°C min⁻¹.

Figure 3. Solid-state ¹³C NMR spectrum of NBE/CO copolymer. Copolymerization conditions: norbornene (0.1 mol); methanol (10 ml); partial pressure of CO, P(CO)=2.7 MPa; Pd(CH₃COO)₂ (0.1 mmol); 2,2'-bipyridine (3 mmol); *p*-toluenesulfonic acid (2 mmol); nitrobenzene (40 mmol); reaction duration, 2 h.

above, the NBE/CO copolymers obtained from 1,4-benzoquinone were insoluble in common organic solvents, and thus the molar mass could not be measured.

Characterization of NBE/CO Copolymer by IR, ¹H NMR and Solid-State ¹³C NMR

The copolymer of norbornene and CO was almost insoluble in common organic solvents, and thus was characterized by IR, ¹H, and solid-state ¹³C NMR spectroscopy and supported by elemental analysis. A strong IR absorption about 1690 cm⁻¹ is ascribed to the carbonyl group. The ¹H NMR (CDCl₃) spectrum of the copolymer for soluble parts exhibited broad signals at 0.60–3.75 ppm indicating that the copolymer contained ring structures.²⁰⁾ According to Figure 3 (solid-state ¹³C NMR spectrum), the signal at 208.0 ppm is ascribed to the carbonyl carbon. The line at 174.8 ppm is due to the carbonyl group (CH₃-O-(C=O)-) at the end of the copolymer chain. The signals at 52.2, 40.7, and 29.7 ppm also support that NBE/CO copolymer contain ring structures. The signal of methyl group at the end of the copolymer chain overlaps with the ring structure of NBE/CO copolymer at 52.2 ppm. This further proves that CO is indeed copolymerized with norbornene.

X-Ray Diffractogram of Copolymer

Figure 4 shows the X-Ray diffractogram of the co-

Figure 4. X-Ray diffractogram of NBE/CO copolymer. Copolymerization conditions: norbornene (0.1 mol); methanol (10 ml); partial pressure of CO, $P(\text{CO})=2.7$ MPa; $\text{Pd}(\text{CH}_3\text{COO})_2$ (0.1 mmol); 2,2'-bipyridine (3 mmol); *p*-toluenesulfonic acid (2 mmol); nitrobenzene (40 mmol); reaction duration, 2 h.

Figure 5. TGA curve of NBE/CO copolymer in nitrogen (heating rate $20^\circ\text{C min}^{-1}$). Copolymerization conditions: norbornene (0.1 mol); methanol (10 ml); partial pressure of CO, $P(\text{CO})=2.7$ MPa; $\text{Pd}(\text{CH}_3\text{COO})_2$ (0.1 mmol); 2,2'-bipyridine (3 mmol); *p*-toluenesulfonic acid (2 mmol); nitrobenzene (40 mmol); reaction duration, 2 h.

polymer. The copolymer was confirmed to be partially crystalline. The shape of the X-Ray diffractogram diagram of this copolymer from a Pd catalyst was similar to that of a copolymer formed on γ irradiation.²¹

Thermogravimetric Analysis of NBE/CO Copolymer

A TGA curve of the copolymer of norbornene and CO appears in Figure 5 with a heating rate, $20^\circ\text{C min}^{-1}$ in nitrogen. Figure 5 shows that loss of mass starts at 350°C . The maximum decomposition occurs at 447°C according to the differential thermogravimetric analysis curve.

Hydrogenation

Hydrogenation of the polyketone with the reduction agent (lithium aluminum hydride, LiAlH_4) in THF yielded hydroxyl-containing polymer having units represented as in (eq 7) and Figure 6. The hydrogenated polymer was completely soluble in

chloroform, conc. H_2SO_4 , THF, dimethylformamide, pyridine, and chlorobenzene, partially soluble in di-

Figure 6. IR spectra of the hydrogenation of polyketone with a reducing agent (lithium aluminum hydride, LiAlH_4) in THF: (a) before; (b) after hydrogenation.

methylacetamide, dimethylsulfoxide, acetone, and insoluble in benzene, xylene, toluene, acetonitrile, 1,2-dichloroethane, and *m*-cresol. The absence of infrared absorption corresponding to the carbonyl group [1690 cm^{-1} , Figure 6(a)] and a specific absorption of ν_{OH} at 3396 cm^{-1} [Figure 6(b)] indicated the essentially complete conversion of ketone functional groups to alcohol groups without cleavage of the polyketone chain. According to the ^{13}C NMR spectrum, the appearance of the signal due to the methine group at 68 ppm and the disappearance of the signal due to the carbonyl group at 208 ppm after hydrogenation support the complete hydrogenation of the polyketone.

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