Regio- and stereoselective alternating copolymerization of carbon monoxide with functionalized olefins

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Abstract

Enantioselective alternating copolymerization of carbon monoxide with ω-undecylenic acid (Ua), ethyl acrylate (Ea), and butyl acrylate (Ba) were carried out for the first time using palladium catalyst modified by 1,4:3,6-dianhydro-2,5-dideoxy-2,5-bis(diphenylphosphino)-L-iditol (DDPPI). Optical rotation, elemental analysis, spectra of ^{1}H-NMR, ^{13}C-NMR, and IR showed that our copolymers were optically active, isotactic, alternating poly(1,4-ketone) or poly(spiroketal) structure. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Palladium catalyst; Chiral ligand; Enantioselective alternating copolymerization; Isotactic copolymer; Optical activity

1. Introduction

The palladium(II)-catalyzed alternating copolymerization of olefins with carbon monoxide has been receiving increasing attention over the last few decades [1–4]. Few copolymers have been formed using electron-poor olefins [5–7], but these types of monomers have been shown to insert into palladium–acyl bonds [8,9] which is a key step in CO/olefin copolymerizations. Indeed, the copolymerization stopped or became very slow when some alkenes with the functional group closer to the C=C bond were employed. A possible reason may be that the functional group blocks a coordination site on the metal through coordination.

Copolymerization of CO with styrene, dicyclopentadiene, dimethyl dicyclopentadiene have been successfully carried out using PdCl₂-CuCl₂-chiral diphosphine catalyst [10]. Here, we report enantioselective copolymerization of CO with functional alkenes bearing COOH or COOR group using [(DDPPI)Pd(CH₃CN)₂](BF₄)₂ catalyst (DDPPI [10,11]: 1,4:3,6-dianhydro-2,5-dideoxy-2,5-bis(diphenylphosphino)-L-iditol). In view of the limited information available in the scientific literature about the copolymerization of CO with functionalized olefins, we wish to present the results of copolymerization of CO with ω-undecylenic acid (Ua), ethyl acrylate (Ea), and butyl acrylate (Ba) catalyzed by chiral palladium catalyst (Scheme 1).
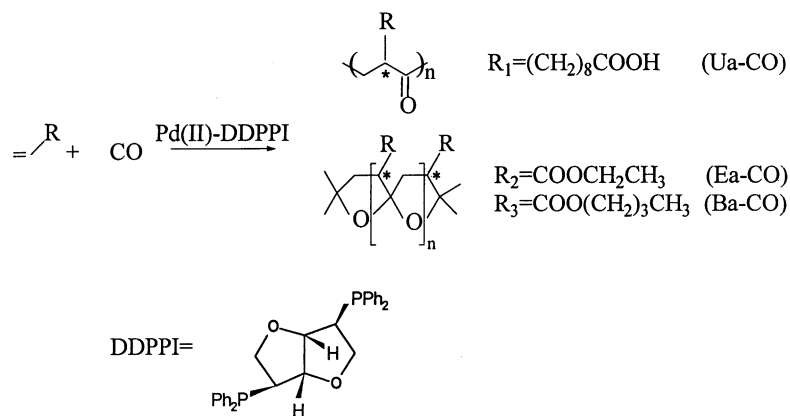
2. Results and discussion

2.1. The characterization of the catalyst [(DDPPI)Pd(CH₃CN)₂](BF₄)₂

The molecular structure of DDPPI was determined by X-ray diffraction analysis [11]. The crystal data are:

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Scheme 1.

$F(0\,0\,0) = 1016$, orthorhombic space group $P2_1 2_1 2_1$, $a = 9.460(8)$ Å, $b = 14.822(5)$ Å, $c = 18.424(6)$ Å, $v = 2.583(2)$ Å^3, $z = 4$. DDPPI has four chiral carbon centers, two of them connected to phosphorus atoms are in S-form. The distance between P_1 and P_2 is 6.24 Å. These features lead to a non-chelating or weak chelating character and are responsible for highly chiral induction of the copolymerizaton reactions.

The catalyst [(DDPPI)Pd(CH$_3$CN)$_2$](BF$_4$)$_2$ was prepared by codissolving a 1:1 molar ratio of [Pd(CH$_3$CN)$_2$](BF$_4$)$_2$ and DDPPI in dry CH$_3$CN. It could be isolated from CH$_3$CN solution in high yield, and its elemental analysis was consistent with the structure shown.

We have characterized the catalyst precursor [Pd(CH$_3$CN)$_2$](BF$_4$)$_2$ using ^{1}H-NMR. The signals at ~2.60 ppm clearly indicate that CH$_3$CN is coordinated to the palladium center.

We have also characterized the catalyst using ^{31}P-NMR. The ^{31}P-NMR spectrum shows a weak resonance at +31.0 ppm, which indicates that the P atoms coordinate to the palladium center (the P atoms of free DDPPI shows one signal at −14.3 ppm).

According to the weak or non-chelating structure of DDPPI, the P atoms should coordinate to palladium center with one strong coordination and one weak coordination. The copolymerization of CO and olefins always requires *cis*-fashion of vacant sites, so we would rather suggest that the P atoms coordinate to palladium center with one strong coordination and one weak coordination, and the strong coordination
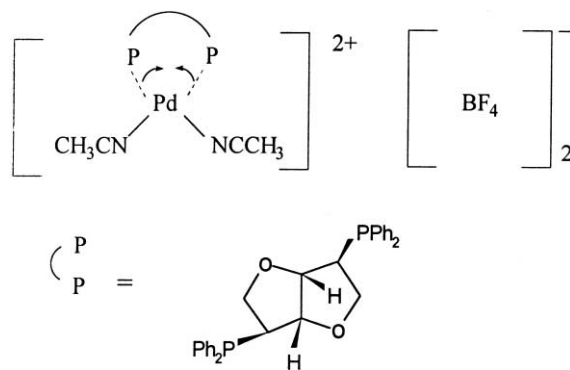
Scheme 2.

and weak coordination can be exchanged during catalysis (Scheme 2).

2.2. The reactivity of the functional olefins

We have studied the copolymerization of CO with the alkenes bearing COOH and COOR functionalities; the results are shown in Table 1. Alkenoic acids that were successfully copolymerized with CO were ω-undecylenic acid and 3-butenoic acid (Bua), but the rate of copolymerization of acrylic acid (Aa) with CO was very slow. Table 1 shows that the reactivity of olefins bearing COOH group decreases, as C=C bond is closer to the COOH group. One possible reason may be that the functional group blocks a coordination site on the metal through coordination [5–7]. Another rea-

Table 1
Copolymerization of functional olefins with carbon monoxide[a]

		Ua–CO	Bua–Co[b]	Aa–CO	Ma–CO	Ea–CO	Ba–CO
Productivity ($g\,g^{-1}\,Pd\,h^{-1}$)		40.6	0.9	Trace	Trace	30.1	35.5
$[\Phi]_{589}^{20}$ [c] ($5\,mg\,ml^{-1}$)		$+43^0$				$+29^0$	$+33^0$
M_n[d]		1.1×10^4				1.6×10^5	1.0×10^5
M_w[d]		2.0×104				2.3×10^5	4.0×10^5
M_w/M_n[d]		1.84				1.42	3.99
Elemental analysis	Calculated	C: 69.0[e]				C: 56.3	C: 61.5
		H: 9.7[e]				H: 6.3	H: 7.7
	Found	C: 68.6				C: 56.7	C: 62.1
		H: 9.5				H: 6.1	H: 7.9
IR (cm^{-1})	C=O	1703[f]					
	C–O–C					851	848
	COOR	1729				1732	1733

[a] Reaction conditions: olefins 10 g; [(DDPPI)Pd(CH$_3$CN)$_2$](BF$_4$)$_2$ 0.05 mmol; 2,6-dimethylbenzoquinone 0.08 mmol; solvent [3:1 (v/v) methylethylketone/CH$_3$OH] 6 ml; CO 9 MPa; temperature 45°C; time: 20 h (Ua–CO), 72 h (Bua–CO), 42 h (Ea–CO), 42 h (Ba–CO).

[b] The purification is difficult because of its poor solubility, so it remains poorly characterized.

[c] CH$_3$COOCH$_2$CH$_3$ was used as the solvent, 5 mg/ml.

[d] Molecular weight and its distribution were measured by GPC relative to polystyrene standard.

[e] The unit of calculation is –CH[(CH$_2$)$_8$COOCH$_3$]CH$_2$CO–; the copolymerization of ω-undecylenic acid with CO invariably led to polymer in which the acid functionality was converted to the corresponding methyl ester due to the use of methanol in the solvent mixture.

[f] The samples were reprecipitated from (CF$_3$)$_2$CHOH by addition of methanol.

son may be electron effect, the ability of coordination of the C=C bond is weaker as the COOH group is closer to the C=C bond because of the attractive electron effect of the COOH.

Similarly, the rate of copolymerization of methyl acrylate (Ma) with CO was very slow. The rate of copolymerization of ethyl acrylate and butyl acrylate with CO is faster than that of methyl acrylate. A possible factor is that the bulky groups CH$_2$CH$_3$ and CH$_2$CH$_2$CH$_2$CH$_3$ block the coordination of the functional group COOR to metal coordinating center, thus the coordination of C=C bond is more easy than that of methyl acrylate.

2.3. The regio- and stereoselectivity of the copolymerization of functional olefins with carbon monoxide

The nature of chiral phosphine ligands plays an important role in enantioselective copolymerization reactions of olefins with carbon monoxide. The results in Table 1 show that DDPPI is a highly effective chiral ligand for the enantioselective copolymerization of carbon monoxide with ω-undecylenic acid, ethyl acrylate, and butyl acrylate. The molecular structure of

DDPPI shows that this diphosphine is a bicycle compound with high rigidity, and it contains four chiral carbon atoms whose configurations are all of *S*-form. Highly optical activity and good yields were obtained under our reaction conditions.

The ω-undecylenic acid–CO, ethyl acrylate–CO, and butyl acrylate–CO copolymers synthesized appear to be isotactic, since optically active materials were obtained when enantiomerically pure DDPPI was used. Note that syndiotactic olefin–CO copolymers should only exhibited vanishingly small optical activity.

Sen and Jiang [12] reported that the spiroketal structure (the resonance at ~113 ppm of ^{13}C-NMR and the absorption at 840 cm^{-1} of IR indicate the presence of spiroketal structure) was formed after the copolymerization, but Consiglio and Batistin [13] suggested the spiroketal structure was formed during the copolymerization. Both of them found the spiroketal structure of CO/α-olefin copolymers, and also found that the spiroketal structure can convert to the 1,4-ketone structure in certain conditions, for example treatment with acidic solvent (CF$_3$)$_2$CHOH. The pure poly(1,4-ketone) of ω-undecylenic acid–CO copolymer can be obtained by treating the copolymer

containing spiroketal units with acidic solvents such as 1,1,1,3,3,3-hexafluro-2-propanol. But, the spiroketal isomers of Ea–CO and Ba–CO copolymers are considerably more stable than that of CO/α-olefin copolymers: even prolonged stirring in $(CF_3)_2CHOH$ do not lead to conversion to the polyketone isomer. Possibly, the COOR group close to the main chain can increase the stability of the spiroketal isomer in $(CF_3)_2CHOH$.

The pure polyketones (ω-undecylenic acid–CO) and the dominant polyspiroketals (ethyl acrylate–CO and butyl acrylate–CO) showed a single carbonyl absorption at 211.2 ppm and ketal absorption at 112–114 ppm in the ^{13}C-NMR spectra due to an exclusive head-to-tail structure [12]. Dominant resonances for the CH_2 (38–42 ppm) and CH (44–50 ppm) groups in the polymer backbones confirm the presence of highly stereoregularity in the polymers (Fig. 1). It is very clear from the resonances of carbonyl or spiroketal region, the backbone CH, the backbone CH_2 groups that the degrees of regioregularity and stereoregularity in the optically active, isotactic ω-undecylenic acid–CO, ethyl acrylate–CO, and butyl acrylate–CO copolymers are greater than 98% [12].

The high tacticity of the polymers was also supported by their ^{1}H-NMR spectra (Fig. 2). The solution of the ω-undecylenic acid–CO copolymer in $CDCl_3/(CF_3)_2CHOH$ showed that the
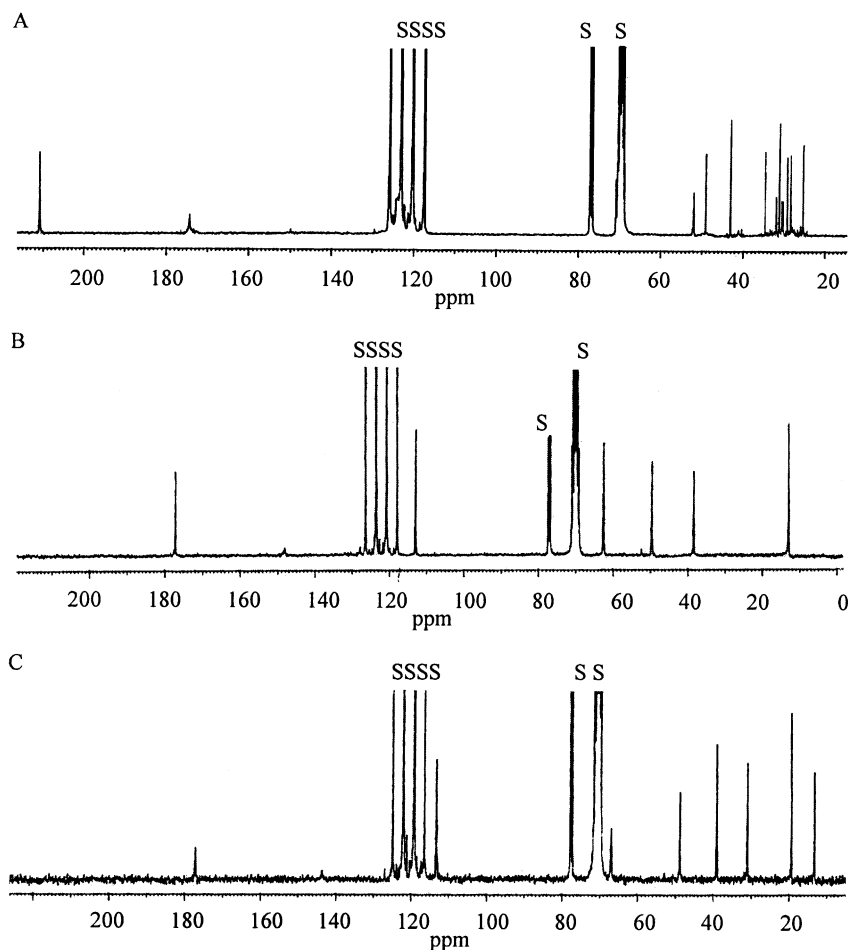

Fig. 1. ^{13}C-NMR spectra (1:1 (v/v) $CDCl_3/(CF_3)_2CHOH$): (A) spectrum of alternating isotactic Ua–CO copolymer; (B) spectrum of alternating isotactic Ea–CO copolymer; (C) spectrum of alternating isotactic Ba–CO copolymer (S = solvent).
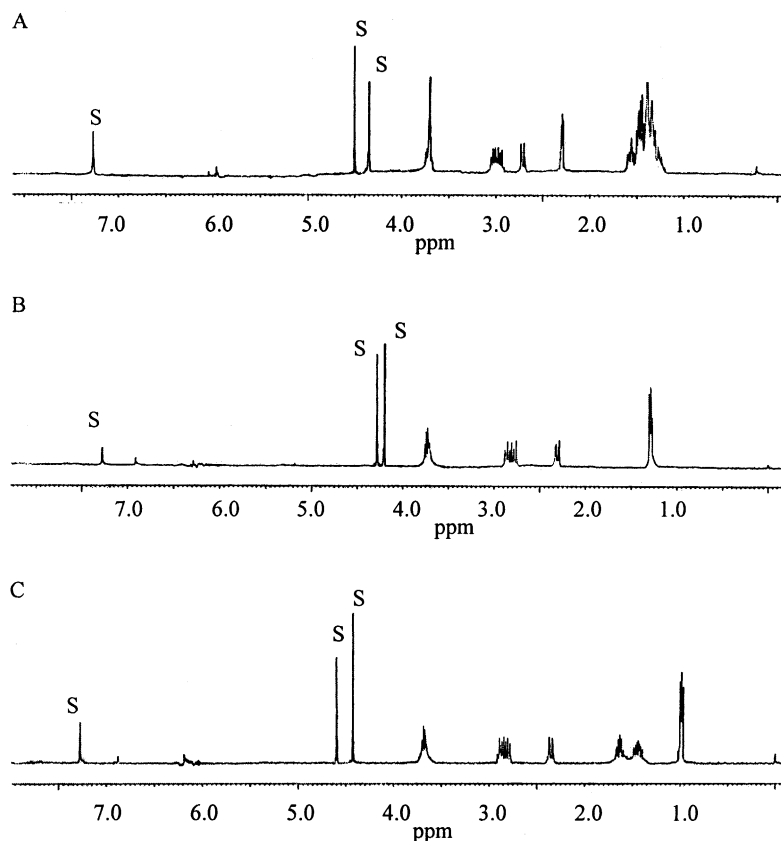
Fig. 2. ^{1}H-NMR spectra (1:1 (v/v) CDCl$_3$/(CF$_3$)$_2$CHOH): (A) spectrum of alternating isotactic Ua–CO copolymer; (B) spectrum of alternating isotactic Ea–CO copolymer; (C) spectrum of alternating isotactic Ba–CO copolymer (S = solvent).

^{1}H-NMR (Fig. 2A) resonance at 3.76 (3H, s, COOC$\underline{H}_3$) ppm was clearly due to three hydrogen atoms of COOCH$_3$ group in the repeating unit, –CH((CH$_2$)$_8$COOCH$_3$)CH$_2$CO–. The coupling constants indicated that the H atom absorbing at 2.70 (1H, d, $J = 15.3$ Hz, backbone CH$\underline{H}$) ppm was not coupled with the side chain CH$_2$ group therefore was one of the backbone CH$_2$ hydrogens, and that the CH hydrogen resonated at the 2.82–3.01 (2H, m, backbone C$\underline{H}$H and C$\underline{H}$) ppm, overlapping with the absorption of the second H atom of the backbone CH$_2$ group in which the two H atoms are diastereotopic and therefore nonequivalent. Resonances at 2.26 (2H, t, $J = 6.9$ Hz, side chain C$\underline{H}_2$COOCH$_3$), 1.56 (2H, m, side chain C$\underline{H}_2$CH$_2$COOCH$_3$), and 1.31 (12H, m, side chain (C$\underline{H}_2$)$_6$CH$_2$CH$_2$COOCH$_3$) were due to the hydrogen atoms of side chain CH$_2$

groups. The ^{13}C-NMR (CDCl$_3$/(CF$_3$)$_2$CHOH) spectrum (Fig. 1A) exhibited resonances at 211.2, 174.5, 52.2, 49.7, 42.9, 34.6, 31.4, 31.0, 30.7, 30.1, 29.7, 28.6, and 25.3 ppm due to the backbone C=O, side chain $\underline{C}$OOCH$_3$, side chain COO$\underline{C}$H$_3$, backbone CH, backbone CH$_2$, and side chain (CH$_2$)$_8$ groups of the –CH((CH$_2$)$_8$COOCH$_3$)CH$_2$CO– units in the copolymer, respectively. These NMR parameters are in accord with those reported by Sen et al. [6].

The solution of ethyl acrylate–CO copolymer in a 1:1 (v/v) CDCl$_3$/(CF$_3$)$_2$CHOH mixture showed ^{1}H-NMR absorbances (Fig. 2B) at 3.70 (2H, q, $J = 6.3$ Hz, side chain COOC$\underline{H}_2$CH$_3$), 2.82 (2H, m, backbone CH$\underline{H}$ and C$\underline{H}$), 2.31 (1H, d, $J = 15.9$ Hz, backbone CH$\underline{H}$), 1.28 (3H, t, $J = 6.7$ Hz, side chain COOCH$_2$C$\underline{H}_3$) ppm due to the hydrogens of side chain CH$_2$ group, the two overlapping protons from

both the backbone CH_2 and CH groups, the other diastereotopic proton of the backbone CH_2 group, and the hydrogens of side chain CH_3 groups in the spiroketal repeating unit of the polymer (Scheme 1), respectively. The ^{13}C-NMR ($CDCl_3/(CF_3)_2CHOH$) spectrum of ethyl acrylate–CO copolymer (Fig. 1B) exhibited absorptions at 176.8, 112.7, 62.0, 49.7, 38.7, and 12.9 ppm due to, respectively, side chain $\underline{C}OOCH_2CH_3$, the backbone spiroketal C–O–C, the side chain CH_2, backbone CH, backbone CH_2, and side chain CH_3 groups in the spiroketal repeating unit of the polymer (Scheme 1).

Similarly, the solution of butyl acrylate–CO copolymer in a 1:1 (v/v) $CDCl_3/(CF_3)_2CHOH$ mixture showed ^{1}H-NMR absorbances (Fig. 2C) at 3.71 (2H, t, $J = 5.4$ Hz, side chain $COOC\underline{H}_2CH_2CH_2CH_3$), 2.83 (2H, m, backbone C$\underline{H}$H and C$\underline{H}$), 2.34 (1H, d, $J = 16.7$ Hz, backbone CH$\underline{H}$), 1.67 (2H, m, side chain $COOCH_2C\underline{H}_2CH_2CH_3$), 1.41 (2H, m, side chain $COOCH_2CH_2C\underline{H}_2CH_3$), 0.99 (3H, t, $J = 5.6$ Hz, side chain $COOCH_2CH_2CH_2C\underline{H}_3$) ppm due to the hydrogens of side chain CH_2 group adjacent to the oxygen atom, the two overlapping protons from both the backbone CH_2 and CH groups, the other diastereotopic proton of the backbone CH_2, and the protons of side chain $CH_2CH_2CH_3$ group in the spiroketal repeating unit of the polymer (Scheme 1), respectively. The ^{13}C-NMR ($CDCl_3/(CF_3)_2CHOH$) spectrum of ethyl acrylate–CO copolymer (Fig. 1C) exhibited absorptions at 177.2, 113.3, 66.5, 48.9, 39.1, 30.6, 19.3, and 13.2 ppm due to, respectively, side chain $\underline{C}OOCH_2CH_2CH_2CH_3$, the backbone spiroketal

C–O–C, the side chain CH_2 adjacent to the oxygen atom, backbone CH, backbone CH_2, and side chain $CH_2CH_2CH_3$ groups in the spiroketal repeating unit of the polymer (Scheme 1).

Acknowledgements

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