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Cyclocopolymerization of α,ω-Dienes with Carbon Monoxide Catalyzed by (*R*,*S*)-BINAPHOS–Pd(II)

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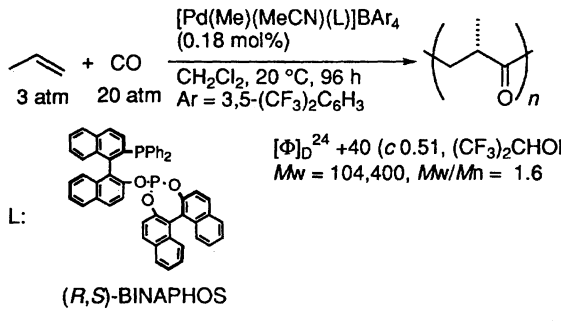
Cyclocopolymerization of 1,4-pentadiene with carbon monoxide gave polyketone **3** in the presence of a Pd(II) catalyst bearing an unsymmetrical bidentate ligand, (*R*,*S*)-BINAPHOS {=(*R*)-2-(diphenylphosphino)-1,1′-binaphthalen-2′yl (*S*)-1,1′-binaphthalene-2,2′-diyl phsophite}. In the repeating unit of **3**, exclusive formation of a cyclopentanone framework rather than cyclohexanone has been revealed by ^{13}C NMR and IR spectroscopies. A single-unit analog **2** was prepared to identify the structure of **3**. In the cyclopentanone unit of **3**, the two substituents are *cis* and *trans* to each other in almost 1 : 1 ratio. The polymer **3** showed different behavior in thermal analysis from that of propene–CO alternating copolymer. 1,5-Hexadiene also afforded the corresponding cyclocopolymer **5**. The molar optical rotation of polymer **3** was much lower than that of **5**.

Ethene–CO alternating copolymer is of great importance as a new engineering plastic in industry.[1] The inexpensiveness and the easy availability of the monomers are the advantages of this polymer. Easy transformation into other functionalized polymers is another important feature.[2] When α-olefins are used in place of ethene, regio- and enatioface selections are required to obtain stereoregular copolymers. Extremely high regioselectivity for propene[3] and styrene,[4] that is head-to-tail selectivity, has been established recently. The latest interest in this copolymerization is focused on the tacticity control. Asymmetric synthesis of the isotactic copolymer from α-olefins with carbon monoxide is one of the hottest topics in this area.[5,6] The resulting polyketone has chirotopic centers in the main chain. This polymer is therefore chiral regardless of its higher order conformation such as its helicity. We recently reported a highly enantioselective alternating copolymerization of propene with CO catalyzed by a palladium complex of an unsymmetrical bidentate phosphine–phosphite ligand, (*R*,*S*)-BINAPHOS (Eq. 1).[7] The corresponding polyketone was obtained in almost perfect head-to-tail regioselectivity and isotacticity. The molecular weight and the molar optical rotation showed the highest values ever reported.[8]



(1)

In contrast to the intensive studies on the copolymerization of ethene and α-olefins, little has been reported on the use of diene as a substrate. With norbornadiene, it was reported that both of the two olefinic bonds in one molecule were involved in the copolymerization to give cross-linked polymers.[9] When dicyclopentadiene was used as a substrate, only the more strained olefinic bond was incorporated in the main chain.[10] 1,3-Cyclopentadiene was also used as a substrate. For this diene, 1,2- and 1,4-additions of acylpalladium were reported to compete.[11] In a patent, Drent reported the copolymerization of α,ω-dienes (from 1,4-pentadiene to 1,7-octadiene) with carbon monoxide.[12,13] However, the structure of the copolymer was not disclosed in detail. Especially, the regioselectivity at the stage of olefin insertion, that is 1,2- or 2,1-insertion, remained to be controlled until very recently.[14]

In the course of our studies on olefin–CO copolymerization, we became interested in the use of α,ω-dienes as the olefin moiety. If the copolymer is synthesized with strict stuctural regularities, new properties of this copolymer might be explored. For this purpose, we used the (*R*,*S*)-BINAPHOS–Pd(II) system which performed the extremely high regio- and enantioselectivities with propene. In this paper, we describe the regioselective synthesis of the polyketones having cyclopentanone or cyclohexanone framework in the repeating units from 1,4-pentadiene or 1,5-hexadiene, respectively.

Results and Discussion

Cyclocopolymerization of 1,4-Pentadiene with Carbon Monoxide. 1,4-Pentadiene was treated with CO in the presence of [Pd(Me)(CH_3CN){(*R*,*S*)-BINAPHOS}]·[B{3,5-$(CF_3)_2C_6H_3$}$_4$] (**1**) under various conditions. The results are summarized in Table 1. Under the conditions of Run 1, polymer of M_w=2410 (determined by GPC, polystyrene

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Table 1. Copolymerization of 1,4-Pentadiene with CO Catalyzed by (*R*,*S*)-BINAPHOS–Pd(II)[a)]

Run	Diene M	CO atm	C_6F_5OH M	Cat. M	Temp °C	Time h	Productivity g/g of [Pd]	M_w[b)]	M_w/M_n[b)]
1	0.48	20	—	0.0011	20	3	24.7	2410	1.23
2	0.48	20	—	0.0011	20	6	28.9	2280	1.21
3	0.48	20	—	0.0011	20	12	25.2	2270	1.25
4	0.48	20	—	0.0011	20	24	19.0	2270	1.21
5	0.48	20	—	0.0011	0	24	41.9	1750	1.28
6	0.048	20	—	0.0011	20	24	7.2	1930	1.31
7	0.48	20	0.19	0.0011	20	24	88.4	2110	1.35
8	0.48	20	0.19	0.0011	0	24	69.4	1740	1.35
9	0.48	10	0.19	0.0011	20	24	22.1	1630	1.25
10	0.48	35	0.19	0.0011	20	24	38.7	1690	1.30
11	0.48	20	0.19	0.011	20	24	25.7	1420	1.32

a) 1,4-Hexadiene in CH_2Cl_2 (5 mL) was treated with CO in a 50-mL autoclave in the presence of [Pd(Me)(CH_3CN){(*R*,*S*)-BINAPHOS}]·[BAr_4] (**1**). b) Determined by GPC analysis using polystyrene as a standard.

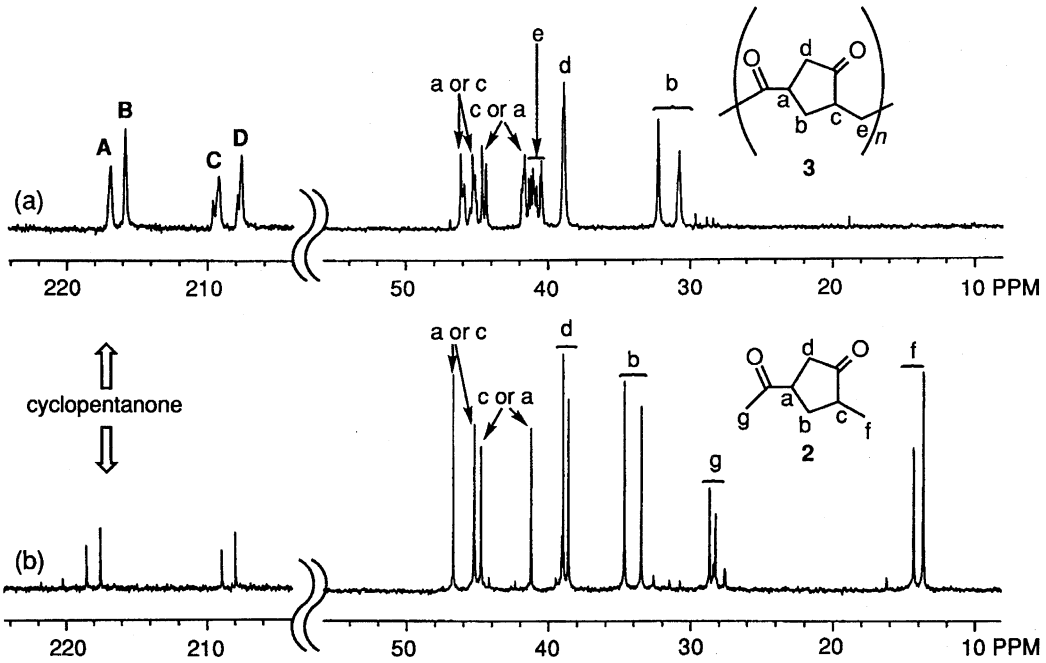


Fig. 1. (a) ^{13}C NMR spectrum for the *poly*(1,4-pentadiene-*alt*-CO) (**3**). Carbonyl carbons A and B were assigned as cyclopentanone and C and D were attributed to acyclic ketones. Carbons a—e were determined by DEPT. (b) ^{13}C NMR spectrum for a *cis*/*trans* mixture of 4-acetyl-2-methyl-cyclopentanone (**2**). All carbons were assigned in the same manner as for (a).

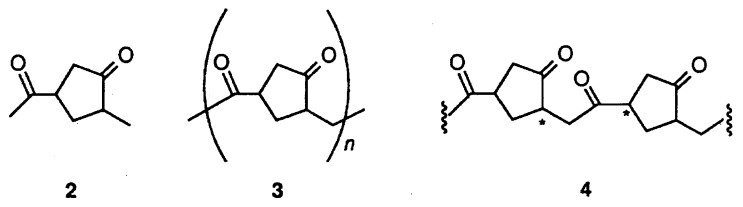
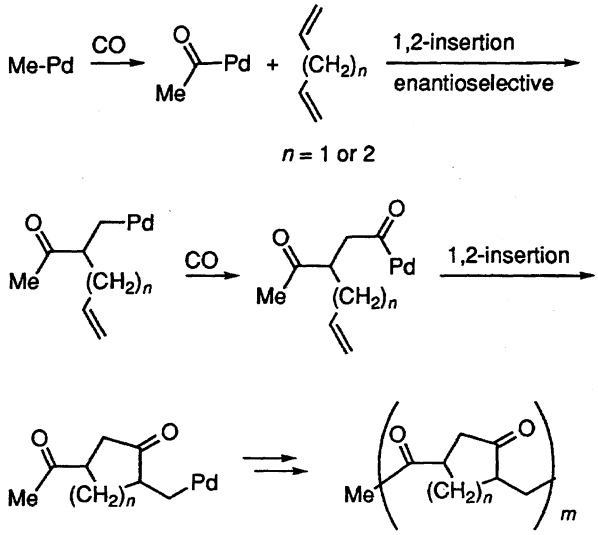
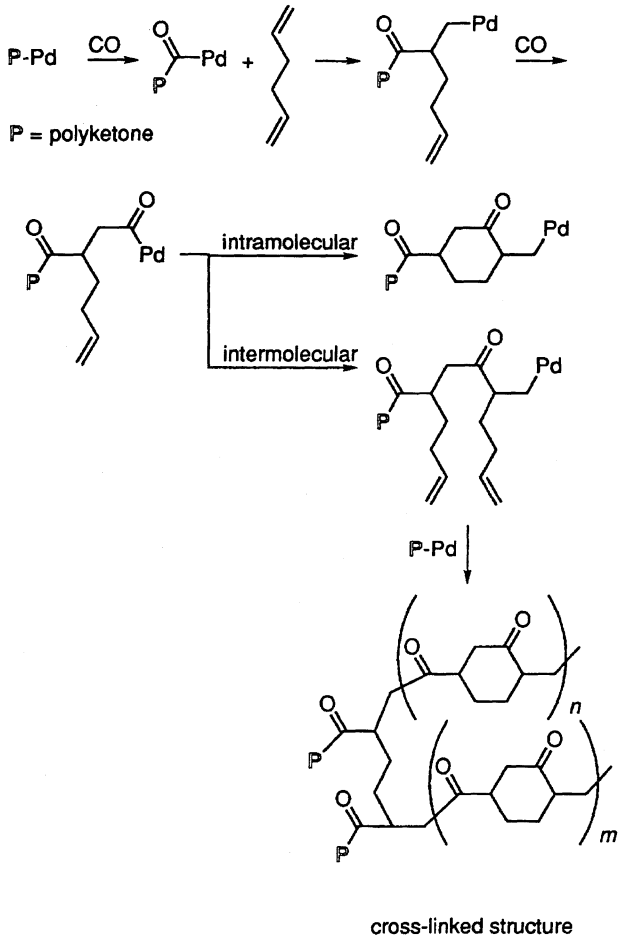


Chart 1.

standard) was obtained in a poor productivity. The prolonged reaction time improved neither of the productivity nor the molecular weight (Runs 2—4). Thus it is suggested that some chain-termination takes place when the polymer grows up to the molecular weight of ca. 2400. At this point, the catalyst should have been deactivated and no further polymerization took place. At lower temperature, 0 °C, the polymer was obtained in higher productivity but the molecular weight was lower (Run 5). It seems that the catalyst-deactivation was retarded at the lower temperature. At the lower concentration of the diene, both the molecular weight and the productivity were low (Run 6). In case that the resulting polyketone is



Scheme 1.



Scheme 2.

insoluble in the solvent, addition of perfluorophenol is known to improve the solubility of the polymer and to give higher molecular weights. Although no precipitation was observed in the present condition, the addition of perfluorophenol was examined. The addition resulted in the higher productivity along with unchanged molecular weight (Runs 7 and 8). In fact, it is reported that methanol accelerates chain-transfer reactions.[1a,14] And therefore, the protic nature of perfluorophenol may have caused a similar effect. CO pressure of 20 atm was the best condition for the catalytic activity (Runs 9 and 10). A higher concentration of the catalyst resulted in the lower productivity and M_w (Run 11).

Table 2. Copolymerization of 1,5-Hexadiene with CO Catalyzed by (*R*,*S*)-BINAPHOS–Pd(II)[a]

Run	Diene M	Olefinic H/ other H (%)[b]	Productivity g/g of [Pd]	M_w	M_w/M_n
1	2.11	8.2	52.3	15600	2.20
2	0.42	2.8	134.6	8380	2.02
3	0.06	0.7	164.7	6160	1.28
4	0.02	<0.1	21.2	2010	1.28

a) 1,5-Hexadiene in CH_2Cl_2 (10 mL) was treated with CO (20 atm) in the presence of [Pd(Me)(CH_3CN){(*R*,*S*)-BINAPHOS}]·[BAr_4] (**1**) (0.0011 M), at 20 °C for 24 h. b) Determined by the integration in ^1H NMR spectrum.

The reason why the catalyst gets deactivated at the stage of $M_w \approx 2000$—2500 is unclear. One possibility was the formation of stable π-allyl palladium complexes, which might be inert for the copolymerization. Such π-allyl palladium species would be formed via isomerization of the 1,4-pentadiene into 1,3-pentadiene by Pd–H addition–elimination process followed by addition of the Pd–H to 1,3-pentadiene. However, no 1,3-pentadiene was detected in the reaction mixture after the reaction was completed, which contradicts the above possibility.

Structure Determination of the Copolymer by ^{13}C NMR and IR. The structure of the polymer has been manifested as follows. The $^{13}C\{^1H\}$ NMR of the polyketone obtained in Run 7 of Table 1 is shown in Fig. 1(a). Polymers from the other conditions in Table 1 gave similar charts. As an analog of the repeating unit, a mixture of *trans*- and *cis*-4-acetyl-2-methylcyclopentanone (**2**) has been prepared (Chart 1); its ^{13}C $\{^1H\}$ NMR is shown in Fig. 1(b). Good agreement of Figs. 1(a) and 1(b) in the carbonyl region indicates the polymer structure of **3**. In Fig. 1(a), four peaks due to the carbonyl carbons are exhibited at δ=217.4 (A), 216.3 (B), 209.7 (C), and 208.1 (D). Two of them (peaks A and B) are in the region for cyclopentanone C=O and the other two (peaks C and D) are attributed to acyclic ketones. The ratio of the four peaks is A : B : C : D=22 : 28 : 22 : 28. Such results suggest that there are two diastereomeric structures for the single unit in the present copolymer and that peaks B and D are due to the major structure and A and C are due to the minor one. The major : minor ratio is 56 : 44. The two

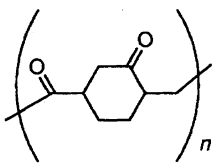


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Chart 2.

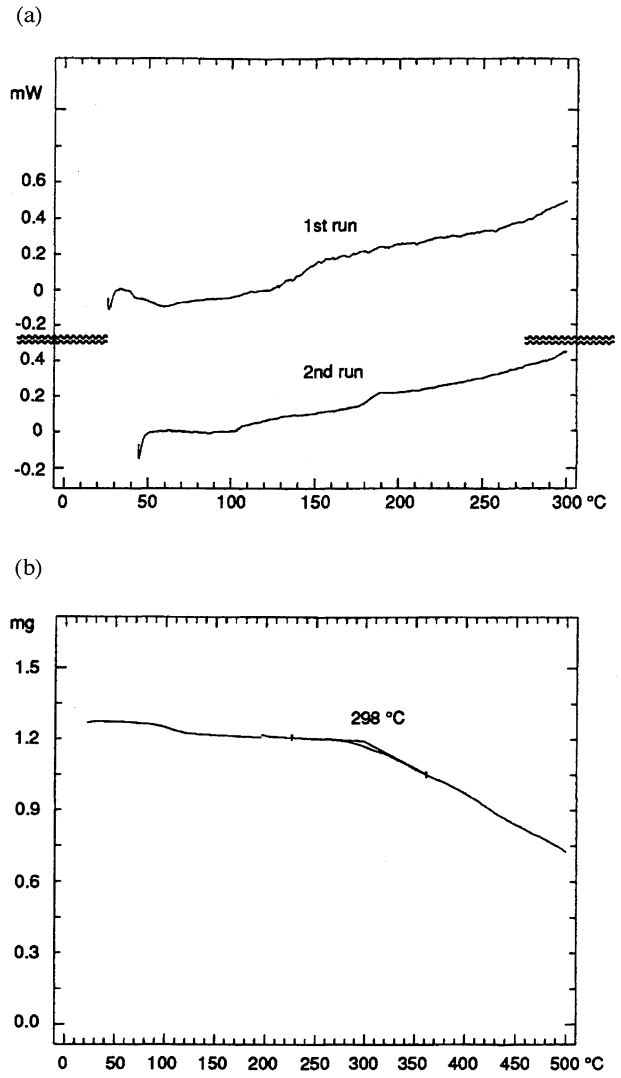

Fig. 2. (a) Differential scanning calorimetry analysis (10 °C min^{-1}, under N_2) or the polymer obtained in Table 1, Run 7. No clear T_m nor T_g points were observed either at the first run or at the second run. (b) Thermogravimetric analysis (10 °C min^{-1}, under N_2) of the same polymer. The molecular loss started at around 280 °C but half of the weight standed even at 500 °C.

diasteromeric structures are also observed in **3**. Accordingly, it has been proven that those two diastereomeric structures arise from the relative configuration of the two substituents, that is, *cis* and *trans* on the cyclopentanone ring. Carbon-13 NMR by DEPT method allowed us to assign other aliphatic carbons. The results are also drawn in Figs. 1(a) and (b). The IR spectrum also supports the structure of **3**. Absorption due to carbonyl stretching was observed at 1741 and 1715 cm^{-1} for the polymer **3**. The former is attributed to the C=O in cyclopentanone and the latter to acyclic C=O. These data are in good agreement with 1742 and 1713 cm^{-1} for the single-unit analog **2**.

Cyclohexanone exhibits the C=O peak at almost the same region as acyclic ketones. If the intramolecular olefin insertion in Scheme 1 proceeded in 2,1-insertion, cyclohexanone would be formed. However, the possibility of the cyclohexanone formation in the polymer should be excluded as follows. If cyclohexanone were formed, the ratio of (cyclopentanone–C=O)/(other C=O) would be smaller than one. The ratio of the four peaks, (A+B)/(C+D)=1, indicates that the formation of cyclohexanone is negligible. This exclusive formation of the five-membered ring via the 1,2-insertion of 1,4-pentadiene is in sharp contrast to the uncontrolled 1,2- and 2,1-insertions reported by Drent.[12]

In Fig. 1(a), slight splits are observed in the two peaks C and D (the acyclic ketones). The slight split can be attributed to the relative configuration of the neighboring two asymmetric carbons marked with asterisks in formula **4** (Chart 1). Based on the high enantioselectivity observed in our previous study on propene–CO copolymerization, we may expect that the first olefin insertion into an acylpalladium occurs in enatioselective fashion (Scheme 1). At the insertion of the second olefinic bond to the catalyst, two factors, catalyst control and the chain-end control, may compete to give the 56 : 44 mixture (vide infra).

Thermal Analysis of the Copolymer. Differential scanning calorimetry analysis (10 °C min^{-1}, under N_2) of the cyclocopolymer obtained in Table 1, Run 7, showed no clear T_m nor T_g points. This is in sharp contrast to the fact that unambiguous T_m (164 °C) and T_g (8 °C) values were observed for the copolymer of propene and CO in our previous study.[8] By thermogravimetric analysis (10 °C min^{-1}, under N_2), we found that the molecular loss of the cyclocopolymer started at around 280 °C but half of the weight remained even at 500 °C, while clear weight loss started at 300 °C and less than 10% of the polymer was left at 380 °C in the case of propene–CO copolymer.[8]

Cyclocopolymerization of 1,5-Hexadiene with Carbon Monoxide. 1,5-Hexadiene also afforded the cyclocopolymer by using the present catalyst system. The results are described in Table 2. When the reaction was carried out under a similar concentration of diene as for 1,4-pentadiene (0.42 M, Run 2, 1 M=1 mol dm^{-3}), the presence of vinylic protons which arise from the non-cyclized structure was shown in ^{1}H NMR spectrum of the obtained polymer. The molecular weight was larger than that obtained from 1,4-pentadiene. At higher concentration of the diene, higher M_w and higher content of vinylic proton were observed (Run 1). These results indicate that an intermolecular olefin insertion competes with the intramolecular insertion, as shown in Scheme 2. The difference between 1,4-pentadiene and 1,5-hexadiene should arise from the entropical disadvantage of the six-membered-ring formation. The higher molecular weight seems to have resulted from a cross-linked structure as shown in the scheme. Accordingly, lower concentrations were employed so that the intramolecular cyclization would prevail over the intermolecular cross-linking (Runs 3 and 4). Fewer vinylic protons were observed in those cases and the M_w dropped to the level obtained by 1,4-pentadiene. Thus the reaction proceeded via intramolecular cyclization. The even lower concentration in Run 4 seems to have prevented

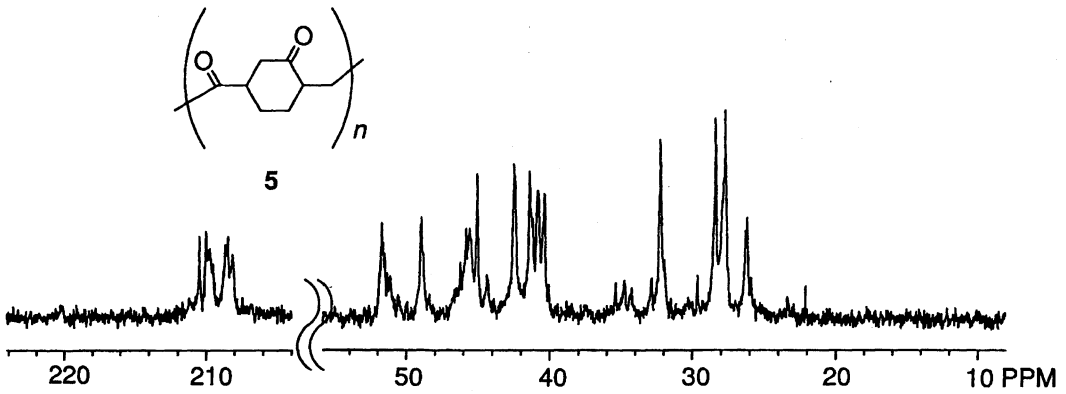

Fig. 3. ^{13}C NMR spectrum for the *poly*(1,5-hexadiene-*alt*-CO) (**5**). Carbonyl carbons do not show clear four peaks.

the polymerization itself. The productivity shows its highest value in Run 3, but the reason is not known.

In relation to the studies on 1,4-pentadiene, a structure drawn in formula **5** is considered for the product (Chart 2). Its ^{13}C NMR appears in Fig. 3. The same cyclocopolymer has been reported very recently by Borkowsky and Waymouth.[14] Comparison of our chart with their work reveals the following two facts. (1) Our polymer consists of only 6-membered ring; this is in contrast to what Drent first observed, a mixture of 5- and 6-membered rings.[12] (2) The present polymer is almost 50 : 50 diastereomeric mixture of *cis* and *trans* structure in cyclohexanone unit. Thus with 1,5-hexadiene, in the same way as with 1,4-pentadiene, the regioselectivity has been controlled almost completely to 1,2-insertion. About enantiofacial selection, however, the second olefin-insertion proceeded with poor *cis*/*trans*-control.

Optical Rotation of the Cyclocopolymers. The copolymer derived from 1,4-pentadiene, **2**, showed almost no optical rotation. The $[\Phi]_D$ value of 0.37 was obtained at 20 °C (*c* 0.50, CH_2Cl_2). On the other hand, the polymer from 1, 5-hexadiene, **5**, had a molar optical rotation of $[\Phi]_D^{20}=13.8$ (*c* 0.50, CH_2Cl_2). The absolute configurations of the chirotopic carbons are unknown. Nevertheless, if our assumption that the enantiofacial selection of the first olefinic bond of the dienes proceeds via the catalyst control is correct, the *Si*-face might have been selected by palladium, as was so for propene in our previous study.[8] The degree of enantiofacial discrimination seems quite low for the second olefinic bond insertion. This may be explained by the competing two factors; these are, (1) the catalyst selection for the *Si*-face of the olefin, and (2) the chain-end selection for the *trans*-substituted cycloalkanone.

Conclusion

The present study has demontrated the efficient use of our catalyst system (*R*,*S*)-BINAPHOS–Pd(II) for cyclocopolymerization of α,ω-dienes with carbon monoxide. Cyclocopolymerization of 1,4-pentadiene with carbon monoxide catalyzed by this catalyst gave the cyclopentanone polymer **3** in high regioregularity, which was accomplished by the extremely high olefin-regioselectivity of the catalyst. The relative configuration of the two substituents on the five-membered ring could not be controlled in this study. 1,5-Hexadiene also afforded the cyclohexanone polymer **5** in high regioregularity and low *cis*/*trans* selectivity. Higher stereocontrol would be performed by further improvement of the ligand.

Experimental

General. Nuclear magnetic resonance spectra were taken with a JEOL EX-270 (^1H 270 MHz, ^{13}C 68 MHz) spectrometer using tetramethylsilane (^1H) and $CDCl_3$ (^{13}C) as internal standards and the coupling constants were given in Hertz. IR spectra were measured on a JASCO IR-810 spectrometer. GPC analyses were performed by HPLC system equipped with PU610 pump form GL Science, Showdex KF 804L column, and Showdex RI SE-61 detector using polystyrene as standards. All manipulations of oxygen- and moisture-sensitive materials were conducted under purified argon atmosphere (BASF-Catalyst R3-11) by use of Schlenk techniques.

Chemicals. Unless otherwise noted, reagents were purchased and used as delivered. CH_2Cl_2 and CH_3CN were dried over P_2O_5 and distilled under an argon atmosphere. Benzene was distilled over CaH_2 under argon.

A Representative Procedure for Copolymerization of 1,4-Pentadiene with CO Catalyzed by [Pd(Me)(CH_3CN){(*R*,*S*)-BINAPHOS}]·[B(3,5-(CF_3)$_2$$C_6H_3$)$_4$]. A solution of (*R*,*S*)-BINAPHOS (17.4 mg, 0.022 mmol) in benzene (1.0 mL) was added to a solution of Pd(Me)(Cl)(COD) (6.0 mg, 0.022 mmol) in benzene (1.0 mL). The solution was stirred at 20 °C for 1 h and concentrated in vacuo. The product was dissolved in CH_2Cl_2 (2.0 mL) and then to the solution was added a solution of NaB(3,5-(CF_3)$_2$$C_6H_3$)$_4$ (20.0 mg, 0.022 mmol) in CH_3CN (2.0 mL). After the solution was stirred at 20 °C for 1 h, the solvents were removed to give the catalyst. The resulting solid was dissolved with CH_2Cl_2 (5 mL) and the solution was degassed by three cycles of freeze-thaw. After the solution was treated with CO (1 atm) in 0.5 h, the solution was charged with 1, 4-pentadiene (0.25 mL, 2.4 mmol). The mixture was transferred to a 50-mL autoclave and treated with CO (20 atm) at 20 °C for 24 h. To this was added MeOH (100 mL) to give poly(1,4-pentadiene-*alt*-CO) as a white precipitate in 3.7% yield (11.0 mg). $M_w=2180$, $M_n=1700$ were determined by GPC (polystyrene-standard). T_m and T_g were not observed by DSC analysis. $[\Phi]_D^{20}=0.37$ (*c* 0.50, CH_2Cl_2). ^1H NMR ($CDCl_3$) δ=1.60 (m, 1H), 1.90 (m, 1H), 2.30—3.40 (m, 6H). ^{13}C NMR spectrum ($CDCl_3$) is shown in Fig. 1(a). The chemical shifts are δ=216.92, 215.88, 209.27, 207.69, 46.18, 45.95, 45.37, 45.19, 44.69, 44.40, 41.67, 41.40, 41.26, 41.11, 40.86, 40.52, 38.90, 32.27, 30.78. IR 1741 and 1715 cm^{-1} (for two carbonyls). Other experiments were carried out under the conditions described in Table 1.

Preparation of 4-Acetyl-2-methylcyclopentanone (2). 4-Methyl-3-oxocyclopentanecarboxylic acid[15] (1.80 g, 12.7 mmol) in THF (100 mL) was treated with isobutyl chloroformate (1.90 mL, 14.5 mmol) in the presence of triethylamine (1.80 mL, 12.7 mmol). The mixture was stirred at 20 °C for 0.5 h, and to this crude unsynmetrical anhydride was added *O,N*-dimethylhydroxylamine (0.940 g, 15.6 mmol) at −10 °C in 0.5 h. After stirring for 46 h, workup with aqueous HCl (1 M) followed by distillation at 80—100 °C (0.5 Torr, 1 Torr=133.322 Pa) gave 1.88 g of the corresponding amide (80% yield). Without further purification, 0.86 g (4.6 mmol) of this amide was treated with methyl orthoformate (70.0 mg, 6.60 mmol) in MeOH (10 mL) in the presence of *p*-toluenesulfonic acid (0.47 mmol). After 10 h, the reaction mixture was washed with aq $NaHCO_3$ (1 M) and the organic layer was concentrated to give the corresponding acetal. The crude acetal was dissolved in ether (10 mL) and 0.65 mL of methyllithium (1.50 M in ether) was added at 0 °C in ether (5.0 mL). The mixture was warmed up to 20 °C in 1 h, and workup with aqueous HCl (1 M) followed by distillation gave 4-acetyl-2-methylcyclopentanone (**2**) as a 53 : 47 diastereomeric mixture in 16% yield. Bp 40—55 °C (bath temp, 0.1 Torr). ^{1}H NMR ($CDCl_3$) δ=1.09 (d, J=6.9 Hz, $CHC\underline{H}_3$ for the minor diastereomer), 1.12 (d, J=6.6 Hz, $CHC\underline{H}_3$ for the major), 1.40—2.60 (m), 2 25. (s, $C(=O)C\underline{H}_3$ for the major), 2.26 (s, $C(=O)C\underline{H}_3$ for the minor), 2.90—3.15 (m). ^{13}C NMR ($CDCl_3$) for major, δ=217.47, 207.91, 46.72, 44.76, 38.96, 34.63, 28.66, 13.64; for minor, δ=218.49, 208.89, 45.25, 41.22, 38.58, 33.44, 28.23, 14.32. IR 1713 (C=O), 1742 cm^{-1} (C=O). High resolution mass spec. Found: M^+, *m/z* 141.0921. Calcd for $C_8H_{12}O_2$: M^+, 141.0915.

A Representative Procedure for Copolymerization of 1,5-Hexadiene with CO Catalyzed by [Pd(Me)(CH_3CN){(*R,S*)-BINAPHOS}] · [B(3,5-$(CF_3)_2C_6H_3)_4$]. 1,5-Hexadiene was copolymerized with CO in the same procedure for 1,4-pentadiene. M_w and M_n shown in Table 2 were determined by GPC (polystyrene-standard). $[\Phi]_D^{20}$=13.8 (*c* 0.50, CH_2Cl_2). ^{1}H NMR ($CDCl_3$) δ=1.00—3.40. ^{13}C NMR spectrum ($CDCl_3$) is shown in Fig. 2. The chemical shifts are δ=210.51, 209.76, 208.52, 208.16, 51.74, 49.04, 45.84, 45.09, 44.40, 42.55, 41.46, 40.88, 40.43, 34.77, 32.24, 31.97, 28.41, 27.74, 26.20. IR 1710 cm^{-1} (C=O). Other experiments were carried out under the conditions described in Table 2.

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