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Asymmetric terpolymerization of styrene or its derivative and aliphatic 1-alkenes with CO catalyzed by Pd–(*R*,*S*)-BINAPHOS

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Dedicated in honor of Professor Pierre Braunstein

Abstract

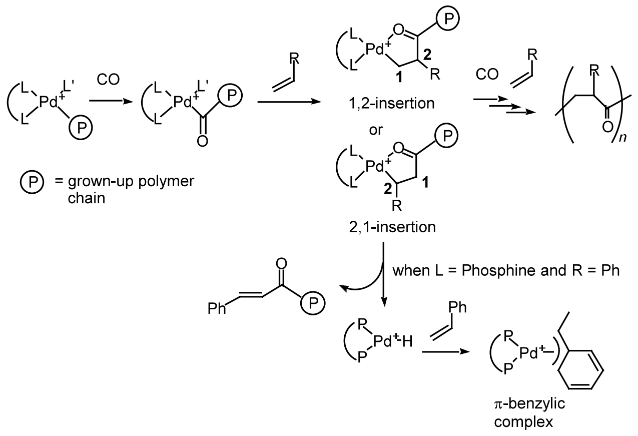
Asymmetric terpolymerization of aliphatic 1-alkenes, vinylarenes and carbon monoxide has been studied using Pd–(*R*,*S*)-BINAPHOS complex as a catalyst. The glass transition temperature is changeable and dependent on the content of each olefin unit. The terpolymers synthesized by Pd-(*R*,*S*)-BINAPHOS system consist of higher 1-alkene content, the fact being in sharp contrast to the results with Pd–nitrogen ligand systems. The incorporation degree of [4-*tert*-butylstyrene–CO] unit in the terpolymer was much lower than that of [1-alkenes–CO] although the insertion of 4-tert-butylstyrene into acetyl–Pd was faster than 1-alkenes.

Keywords: Carbonylation; Olefin; Asymmetric alternating copolymerization; Terpolymerization; Pd catalyst

1. Introduction

Palladium catalyzed alternating copolymerization of olefins with CO attracted much attention because of its potential applications. Precise stereocontrol is a topic of interest in the polyketone synthesis when substituted ethenes are employed as an olefin [1–4]. The chain-propagation of the copolymerization consists of two major steps, the insertion of CO into a Pd–alkyl bond and the subsequent insertion of an olefin into a Pd–acyl bond (Scheme 1) [1b]. In most cases, an aliphatic 1-alkene inserts in a 1,2-fashion while vinylarenes in a 2,1-fashion.

The copolymerizations of aliphatic 1-alkenes with CO are usually carried out using Pd-catalysts with phosphine-based ligands and Pd-catalysts with nitrogen ligands show lower activity [1a,3,5]. On the other hand, nitrogen-based ligands are used for vinylarenes [3b,4,6,7] and phosphine-based ligands are less effective for the copolymerization of styrene with CO, because the 2,1-insertion of styrene is often followed by a rapid β-hydride elimination in the latter case [1b,8]. In addition, it was reported to be slow for CO to insert into a stable π-benzylic complex generated by the styrene insertion to Pd–H [9]. Previously, we reported that [Pd(CH_3)(CH_3CN){(*R*,*S*)-BINAPHOS}]·[B{3,5-$(CF_3)_2C_6H_3$}$_4$] (**1**), although it is a phosphorous ligand,



Scheme 1.

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catalyzes the asymmetric copolymerization of not only propene with CO, but also 4-*tert*-butylstyrene with CO (Scheme 2) [10]. In order to explain this unique feature of (*R*,*S*)-BINAPHOS, we proposed that the styrene–CO copolymerization catalyzed by Pd–(*R*,*S*)-BINAPHOS proceeds via an exclusive 1,2-insertion [11].

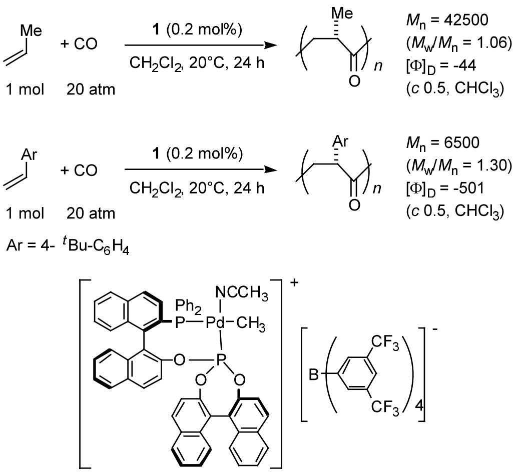
Studies have been devoted not only to copolymerization but also to terpolymerization of more than two kinds of olefins with CO. Especially, intensive efforts have been made for the terpolymerization of ethene and 1-alkenes with CO in order to control physical properties of the polyketones [5b,12,13]. On the other hand, there are few reports of terpolymerization of 1-alkenes, vinylarenes and CO [14–16]. We recently communicated that the asymmetric terpolymerization of propene, 4-*tert*-butylstyrene and CO was efficiently catalyzed by Pd–(*R*,*S*)-BINAPHOS complex [15]. Later, Muellers and his coworkers reported the asymmetric terpolymerization of 1-alkenes, such as 1-hexene and 1-decene, para-substituted styrene and CO using bisoxazoline ligand [16].

Here we describe our further studies on the asymmetric terpolymerization of propene or 1-hexene with vinylarenes and CO, and DSC analysis of the terpolymers. The glass transition temperature could be controlled by changing the content of each unit. We also discuss the relation between the reactivity of each olefin and the incorporation ratio of olefins in the terpolymers.

2. Experimental

2.1. General remarks

All experiments were carried out using standard Schlenk techniques under an atmosphere of argon purified by passing through a hot column packed with BASF catalyst R3-11. All NMR spectra were recorded on Varian Mercury 200 (^{1}H NMR 200 MHz and ^{13}C NMR 50 MHz), JEOL EX-270 (^{1}H NMR 270 MHz and ^{13}C NMR 68 MHz) and JEOL ECP-500 (^{1}H NMR 500 MHz and ^{13}C NMR 126 MHz) using tetramethylsilane as an internal standard (^{1}H). Gel permeation chromatography (GPC) was performed by Shodex KF-804L using THF as an eluate. A calibration curve was obtained with polystyrene standard. DSC measurements were carried out on a Seiko Instruments Inc. DSC 6200 at a cooling rate of 10 °C min^{-1}. TLC analysis was carried out by means of Merck Kieselgel 60 F254. Elemental analyses were performed at the Microanalytical Center, Kyoto University.



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Scheme 2.

Most of the reagents were purchased from Wako Pure Chemical Industries Ltd., Tokyo Kasei Kogyo Co., Ltd. and Aldrich Chemical Co., Inc. and used without further purification unless otherwise noted. Solvents were purified by distillation under argon after drying over suitable drying reagents. Styrene and 4-*tert*-butylstyrene was stabilized by *tert*-butylcatechol and used as received. Carbon monoxide (99.9%) was obtained from Teisan Co. (*S*)-(−)-binaphthol came from Sumikin Chemical Co. Ltd.

2.2. Terpolymerization of propene, 4-*tert*-butylstyrene, and CO (Table 1, run 4)

After treating a solution of [Pd(CH_3)(CH_3CN){(*R*,*S*)-BINAPHOS}]·[B(3,5-$(CF_3)_2C_6H_3)_4$] (**1**, 22.4 mg, 0.0125 mmol) in CH_2Cl_2 (5.0 ml) with CO (1 atm), 4-*tert*-butylstyrene (1.14 ml, 6.24 mmol) was added to the clear yellow solution. The mixture was transferred into a 50 ml-autoclave and then stirred by magnetic stirrer under partial pressures of propene (1 atm, 2.08 mmol) and of CO (20 atm) for 24 h at 20 °C. The resulting mixture was poured into CH_3OH (100 ml) to precipitate poly{(propene; 4-*tert*-butylstyrene)-*alt*-CO} (112.1 mg, 31% and 6% yields from propene and 4-*tert*-butylstyrene, respectively): ^{1}H NMR ($CDCl_3$) δ 1.01 (bs, CH_3), 1.28 (s, $C(CH_3)_3$), 2.30–3.18 (m, $-CHH-CHCH_3-C(=O)-$, $-CHH-CHAr-C(=O)-$), 3.10–3.58 (m, $-CHH-CHAr-C(=O)-$), 3.90–4.15 (m, $-CH_2-CHAr-C(=O)-$), 6.85–7.15 (aromatic), 7.20–7.38 (aromatic). ^{13}C NMR ($CDCl_3$) δ 16.4 (CH_3), 31.2 ($C(CH_3)_3$), 34.4 ($C(CH_3)_3$), 40.0 ($-CH_2-CHMe-C(=O)-$), 44.7 ($-CH_2-CHMe-C(=O)-$), 45.0 ($-CH_2-CHAr-C(=O)-$), 51.9 ($-CH_2-CHAr-C(=O)-$), 125.8 (aromatic, CH), 127.7 (aromatic, CH), 134.3 (aromatic, quarternary), 150.1 (aromatic, quarternary), 207.0–208.2 ($-CH_2-CHAr-C(=O)-$), 211.2–212.6 ($-CH_2-CHMe-C(=O)-$). For ^{13}C NMR, the peak assignment of either CH or CH_2 was carried out by DEPT measurement. IR: 1708 cm^{-1} (C=O). M_n=8100; M_w/M_n=1.5. $[\Phi]_D^{26}=-220$ (*c* 0.50, $CHCl_3$). TLC Analysis ($CHCl_3$ as an eluate):

The R_f value for the terpolymer was 0.00 while for poly(4-*tert*-butylstyrene-*alt*-CO) was 0.85. The absence of any spots at 0.85 suggested the coexistence of unit A (–$CH_2CHMeC(=O)$–) and unit B (–$CH_2CHArC(=O)$–). Elemental *Anal*. Found: C, 76.72; H, 8.61. Calc. for $(CH_2CHMeC(=O))_{1.85}$ $(CH_2CHArC(=O))_{1.00}$: C, 77.89; H, 8.28%.

2.3. Terpolymerization of 1-hexene, 4-*tert*-butylstyrene and CO

After treating a solution of $[Pd(CH_3)(CH_3CN)\{(R,S)\text{-BINAPHOS}\}]\cdot[B(3,5\text{-}(CF_3)_2C_6H_3)_4]$ (**1**, 17.9 mg, 0.010 mmol) in CH_2Cl_2 (5.0 ml) with CO (1 atm), 4-*tert*-butylstyrene (0.92 ml, 5.0 mmol) and 1-hexene (0.62 ml, 5.0 mmol) were added to the clear yellow solution. The mixture was transferred into a 50 ml-autoclave and then stirred by magnetic stirrer under CO (20 atm) for 24 h at 20 °C. The resulting mixture was poured into CH_3OH (100 ml) to precipitate poly{(1-hexene; 4-*tert*-butylstyrene)-*alt*-CO} (220.5 mg, 31 and 5% yields from 1-hexene and 4-*tert*-butylstyrene, respectively): ^1H NMR ($CDCl_3$) δ 0.82 (bs, CH_3), 1.05–1.73 (m, $(CH_3)_3$, –$(CH_2)_3$–), 2.38–3.15 (m, –CHH–$CHCH_3$–C(=O)–, –CHH–CHAr–C(=O)–), 3.20–3.52 (m, –CHH–CHAr–C(=O)–), 3.85–4.15 (m, –CH_2–CHAr–C(=O)–), 6.85–7.15 (aromatic), 7.15–7.38 (aromatic). ^{13}C NMR ($CDCl_3$) δ 13.9, 22.7, 29.0, 31.0, 31.3, 34.4, 44.6, 45.3, 51.8, 125.7, 127.7, 143.5, 150.0, 207.6–208.4 (–CH_2–CHAr–C(=O)–), 211.7–212.8 (–CH_2–CHMe–C(=O)–). IR: 1708 cm^{-1} (C=O). $M_n = 14\,000$; $M_w/M_n = 1.5$. $[\Phi]_D^{26} = -123$ (c 0.53, $CHCl_3$)

2.4. Kinetic studies for the olefin insertion

For (1) Propene insertion to acetyl–Pd **2** and (2) 4-*tert*-butylstyrene insertion to **2**, the experimental procedures were reported in Ref. [15]. (3) 1-Hexene insertion to **2**: Cationic methylpalladium **1** (18.7 mg, 0.011 mmol) in dry and degassed $CDCl_3$ (1.0 ml) was treated with CO (1 atm) for 30 min at 25 °C to produce acylpalladium **2**. An aliquot (0.6 ml) was transferred into an NMR tube under argon and cooled down to 0 °C. To this, large excess (30 equiv. to Pd) of freeze-thawed 1-hexene was added at 0 °C to start the reaction. The decay of a singlet at δ 2.30 due to the methyl protons of **2** was monitored by ^1H NMR in relation to the unchanging aromatic protons to determine the first-order rate constant for the reaction. The product structure has characterized as alkyl-complex formed by the primary insertion of 1-hexene into **2**. Spectra were recorded every 12 min in the first 1 h and after that every hour for 3 h at 0 °C. The rate constant ($k_{obs} = 0.35 \times 10^{-3}$, $\Delta G^{\ddagger} = 19.5$ kcal mol^{-1}) was thus determined.

3. Results and discussions

3.1. Terpolymerization of propene and 4-*tert*-butylstyrene with CO

The terpolymerization of propene and 4-*tert*-butylstyrene with CO was carried out with Pd-(R,S)-BINAPHOS catalyst (Scheme 3). As we previously communicated, the obtained terpolymers contained unit [propene-*alt*-CO] (unit A) and unit [4-*tert*-butylstyrene-*alt*-CO] (unit B) randomly in the point of the order of each unit but the olefins orientation were head-to-tail and the enantioface of olefins were selected as precise as in the [propene-*alt*-CO] or [4-*tert*-butylstyrene-*alt*-CO] copolymerizations [15]. The incorporation degree of [4-*tert*-butylstyrene–CO] unit in the terpolymer was much lower than that of [1-alkenes–CO]. However, at least, the incorporation ratio of each unit, namely, a/b was changeable by varying the initial monomer ratio (Table 1). The glass transition temperatures (T_g) of the terpolymers measured by DSC are also described in Table 1. The T_g values are changeable from 28 to 98 °C by varying the ratio of each unit. The higher content of [propene-*alt*-CO] unit decreased T_g. Such a T_g dependency on the units' ratio has recently been mentioned by Muellers et al. for their terpolymerization of 1-alkenes, styrene derivatives, and CO [16]. In the case of Muellers' system bearing the bisoxazoline ligand; (1) T_g in the terpolymer of 1-alkene and vinylarenes with CO, such as 1-hexene/4-*tert*-butyl styrene/CO, 1-decene/4-*tert*-butyl styrene/CO, and 1-decene/4-methylstyrene/CO, varied from 1 to 145 °C; and (2) the styrene content in the terpolymers was higher than 1-alkenes, for example, styrene derivative content was 54–65% even the initial olefin ratio of 1-alkenes/styrene derivative was over 80/20. Thus, our phosphorus-based ligand (R,S)-BINAPHOS, which gives the highly propene enchained terpolymer, exhibits the complementary nature to the nitrogen-based bisoxazoline.

3.2. Terpolymerization of 1-hexene, 4-*tert*-butylstyrene and CO

In place of propene, 1-hexene was also applicable as an aliphatic 1-alkene monomer. The reaction of 1-hexene and 4-*tert*-butylstyrene with CO afforded a terpolymer with unit [4-*tert*-butylstyrene-*alt*-CO], namely unit B, and unit [1-hexene-*alt*-CO], namely

Scheme 3.

Table 1
Asymmetric terpolymerization of propene, 4-^{t}butylstyrene and CO catalyzed by **1** [a]

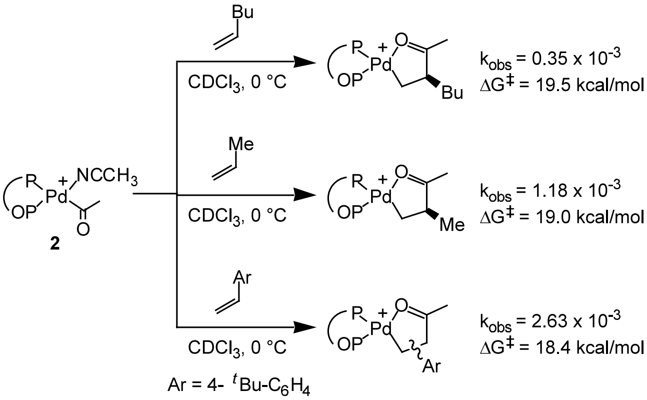
Run	Propene:4-^{t}Bu-styrene	Product (mg)	a/b	M_n	M_w/M_n	T_g (°C) [b]	$[\Phi]_D$ [c]
1	2:1	228	23.7	30 200	1.3	28	−81
2	1:1	172	11.0	28 000	1.2	36	−115
3	2:3	90	3.38	14 800	1.3	55	−198
4	1:3	112	1.85	8100	1.5	77	−220
5	1:6	103	0.87	8500	1.4	98	−283

[a] a/b ratio, M_n, M_w/M_n and $[\Phi]_D$ have been reported in our communication.

[b] Determined by DSC (10 °C min^{-1}).

[c] c 0.49–0.57 (CHCl$_3$, 25.6–26.8 °C).

unit C (Scheme 4). The c/b ratio of incorporated units C/units B was 6.22. The ratio is a little lower than the a/b of 11.0 which was detected for propene/CO (Table 1, run 2). This corresponds to the slightly lower activity of 1-hexene compared with propene. The order of these units B and C is random. Using the $[\Phi]_D$ values of poly(1-hexene-*alt*-CO) (−46) and poly(4-*tert*-butylstyrene-*alt*-CO) (−503) [10e], $[\Phi]_D$ can be estimated by calculation as $[\Phi]_{Dcalcd} = \{(-46)c + (-503)b\}/(c+b)$. Based on the measured molar optical rotation $[\Phi]_D$ compared with $[\Phi]_{Dcalcd}$, the enantioselectivity of each olefin insertion was as high as the copolymerization of 1-hexene-CO and 4-*tert*-butylstyrene-CO. The c/b ratio determined by ^{1}H NMR was 6.22. Thus, again aliphatic 1-alkene is preferably incorporated to 4-*tert*-butylstyrene.

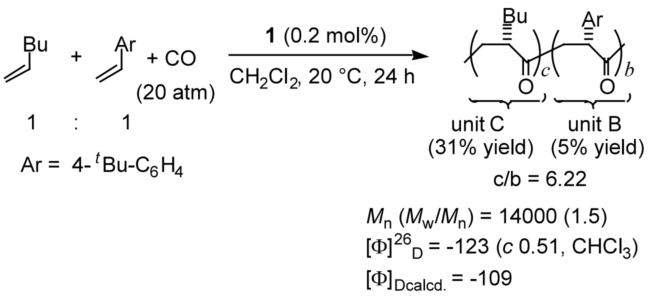


Scheme 5.

3.3. Kinetic studies on the olefin insertion into acyl–Pd bond

In order to compare the reactivity of each olefin in terpolymerization, the reaction rate of olefin insertion into the acetyl–Pd was measured for propene, 4-*tert*-butylstyrene and 1-hexene (Scheme 5) [10b,15]. The rate constant k_{obs} and the activation energy $\Delta G^{††}$ for each olefin are also described. Although the rates of propene and 1-hexene into acetyl–Pd complex **2** are smaller than that of 4-*tert*-butylstyrene, the content of propene and 1-hexene in terpolymer was higher than 4-*tert*-butylstyrene.

Consiglio also mentioned a similar contradiction in the terpolymerization of ethene and styrene with CO using Pd catalysts having phosphine–oxazoline-based ligands [17]. That is, although styrene showed higher productivity than ethene in their copolymerizations with CO, ethene preferentially enchained during the terpolymerization. They explained that the low productivity for ethene/CO copolymerization is attributable to the slower CO insertion to the alkylpalladium species compared with styrene/CO, and that the ethene insertion to acylpalladium itself is faster than styrene insertion [18].



Scheme 4.

In contrast to their system, however, the content of styrene unit was lower than that of 1-alkene in our case, in spite of the rapid styrene insertion into the acetyl–Pd **2**. Thus, another hypothesis should be suggested. Shown in Fig. 1 are the relation between the reaction time and the conversion for (i) propene in propene/CO copolymerization, (ii) 4-*tert*-butylstyrene in 4-*tert*-butylstyrene/CO copolymerization, (iii) propene in propene/4-*tert*-butylstyrene/CO terpolymerization, and (iv) 4-*tert*-butylstyrene in propene/4-*tert*-butylstyrene/CO terpolymerization. The copolymerization of propene/CO is much faster than that of 4-*tert*-butylstyrene/CO and the conversion of each olefin in the terpolymerization after 24 h was similar to the corresponding copolymerization.

Our current hypothesis is as follows. The styrene insertion into a Pd–acyl bond in the chain propagation may become slower than the initiation step due to the

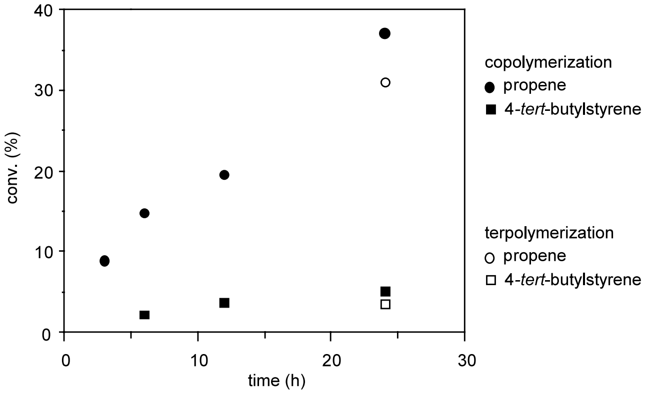


Fig. 1. Conversion of olefins plotted against the reaction time in the co- and terpolymerization. (i) Propene in propene/CO copolymerization (●); (ii) 4-*tert*-butylstyrene in 4-*tert*-butylstyrene/CO copolymerization (■); (iii) propene in propene/4-*tert*-butylstyrene/CO terpolymerization (○); and (iv) 4-*tert*-butylstyrene in propene/4-*tert*-butylstyrene/CO terpolymerization (□).

effect of the grown-up polymer chain. In fact, the regioselectivity of an olefin differs between the initial and the propagation step due to the steric changes of the active site [11,19–21]. In other words, an active site in the propagation should be regulated by the steric interaction not only between the incoming monomer and the ligand, but also between the monomer and the grown-up polymer chain.

4. Conclusions

We studied the asymmetric terpolymerization of 1-alkenes, vinylarene and CO catalyzed by Pd–(*R*,*S*)-BINAPHOS complex. In sharp contrast to Pd–nitrogen ligand systems, the terpolymers synthesized by Pd–(*R*,*S*)-BINAPHOS consists of higher 1-alkene content. The incorporation ratio of 4-*tert*-butylstyrene unit in the terpolymer was much lower than that of 1-alkenes, in conflict with the faster insertion of styrene into acetyl–Pd than of 1-alkenes. Although we do not have any evidence currently, the contradiction may be attributable to the difference of the insertion rate between the initiation step and the propagation, especially in the case of vinylarene. In other words, the copolymerization of styrene and CO is likely to proceed by the site-control formed by the steric interaction with both of the ligand and the grown-up polymer chain. The glass transition temperature is changeable and dependent on the content of each unit.

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