Pd(OAc)₂/(S)-P-PHOS 催化的丙烯与 CO 交替共聚合 成手性功能高分子

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摘要: 以丙烯和 CO 为原料, Pd(OAc)₂/(S)-P-PHOS 为手性催化剂, 在有机溶剂中, 经不对称交替共聚反应合成了手性功能高分子聚酮。当过量的还原剂 LiAlH₄ 和 NaBH₄ 分别还原聚酮时, 手性聚醇产率达 90%; 当 NaBH₄/羰基摩尔比分别为 0.5, 1 和 2, 紫外光谱 (200~400 nm) 检测证明, 手性聚酮中羰基的 29%, 71% 和 81% 分别被还原; 使用过量的还原剂 BH₃·THF 时, 手性聚酮中羰基只能部分被还原。手性聚醇的数均分子量比手性聚酮的低, 产物手性聚醇的摩尔旋光度随还原反应条件而变化。

关键词: 醋酸钯; 手性双膦配体; 丙烯; 一氧化碳; 手性聚酮; 还原剂; 手性聚醇

中图分类号: O643

文献标识码: A

Synthesis of Chiral Functionalized Polymers by Alternating Copolymerization of Propene and CO Using the Pd(OAc)₂/(S)-P-PHOS Catalyst

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Abstract: Pd(OAc)₂ (palladium acetate)/(S)-P-PHOS ((S)-2,2',6,6'-tetramethoxy-4,4'-bis(diphenyl)phosphino)-3,3'-bipyridine) catalysis systems were applied to the alternating copolymerization of propene and CO in organic solvents to synthesize chiral polyketones. The diastereoselective reduction of a chiral polyketone using excess LiAlH₄ (lithium aluminum hydride) and NaBH₄ (sodium borohydride) as reducing agents gave a new class of optically active polyalcohol and the product yield was more than 90%. In the presence of various amounts of NaBH₄ (NaBH₄/carbonyl molar ratio of 0.5, 1, and 2), quantitative measurements of the intensity of the carbonyl absorbance at 200–400 nm in the UV (ultraviolet) spectrum showed a reduction of 29%, 71%, and 81%, respectively, for the carbonyl groups. The use of excess BH₃·THF (borane tetrahydrofuran complex) as a reducing agent resulted in a partial reduction of the carbonyl groups of the chiral polyketone. The molecular weight of the product was lower than that of the chiral polyketone and the molar optical rotations of the product varied with the reductive conditions.

Key words: palladium acetate; chiral diphosphous ligand; propene; carbon monoxide; chiral polyketone; reducing agent; chiral polyalcohol

The alternating copolymerization of olefins and CO has attracted considerable attention from both academia and industry over the last few decades [1]. Initially, the reaction occurred in the presence of a radical initiator using ethylene as a starting material. Several polymers incorporating a variety of heteroatom functionalities have been synthesized and the product C₂H₄/CO ratio has been found to be more than 1 [2]. The obtained products exhibit engineering plastic properties. In the 1980s, a class of highly active palladium

catalysts for this reaction (Scheme 1) were reported [3,4]. A terpolymer derived from ethene, propene, and CO became commercially available under the trade name Carilon. The alternating copolymers (olefin/CO = 1) have the highest possible concentration of reactive carbonyl groups, which can be chemically modified to new functional groups such as hydroxyl, cyano, amino, etc. Polyketones are also excellent starting materials for other classes of polymers such as polyalcohols [2], polyamines [5], polyoximes [2,6–8], poly-

Received 30 June 2010. Accepted 17 September 2010.

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Foundation item: Supported by the National Natural Science Foundation of China (20343005, 20473107, 20673130, 20773147)

English edition available online at ScienceDirect (<http://www.sciencedirect.com/science/journal/18722067>).

Scheme 1. Ketone and spiroketal repeat units of a polyketone. A: poly(1-oxo-2-methyltrimethylene); B: poly[spiro-2,5-(3-methyltetrahydrofuran)].

acetals [9], polythiophene [10], etc.

Recently, a few examples of enantioselective copolymerization using either in situ or preformed Pd complexes modified by chiral phosphorus ligands [11] have been shown to give high regioregularity and an almost completely isotactic polyketone. Mixtures of stereoregular copolymers of opposite chirality have been shown to exhibit

Scheme 2. Chiral ligands used in asymmetric alternating copolymerization.

In this work, we used the Pd(OAc)_2 / (S) -P-PHOS catalyst (Scheme 2) for the alternating copolymerization of propene and CO to synthesize chiral polyketones. The chiral ligand (S) -P-PHOS was kindly supplied by the Hong Kong Polytechnic University. The novel chiral polyalcohol was synthesized by the reduction of these ketones using LiAlH_4 , NaBH_4 , and $\text{BH}_3\cdot\text{THF}$ as reducing agents. ^1H NMR (nuclear magnetic resonance), ^{13}C NMR, and IR (infrared spectroscopy) were consistent with the data expected for these compounds. The effect of various concentrations of NaBH_4 on the reduction of carbonyl groups has been investigated by UV. The molar optical rotations of the chiral polyalcohols varied with the reduction conditions.

1 Experimental

1.1 Copolymerization of propene and CO [15,16,17]

A mixture of Pd(OAc)_2 (10.3 mg, 0.046 mmol), (S) -P-PHOS (29.6 mg, 0.046 mmol), and $\text{BF}_3\cdot\text{Et}_2\text{O}$ (0.051 mmol) was stirred magnetically in $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{OH}$ (25:2, v/v) under nitrogen for 1.5 h at room temperature. The solution was transferred to a 100 ml stainless steel reactor under nitrogen and the reactor was then charged with 35 g of propene in a cold bath at 0 °C and under 4.0 MPa CO. The re-

curious melting behavior [12]. Jiang et al. [13] reported that $[\text{Pd}(\text{Me-DUPHOS})(\text{MeCN})_2](\text{BF}_4)_2$ [Me-DUPHOS = 1,2-bis(2,5-dimethylphosphorlano)benzene] (Scheme 2) is an effective catalyst for enantioselective alternating copolymerization, and the product was found to be an excellent starting material for the synthesis of chiral polyalcohols. For example, the complete reduction of the copolymer resulted in the formation of a novel, chiral polyalcohol using LiAlH_4 as a reducing agent. Recently, chiral polyketone has been synthesized using the catalyst $[\text{Pd}((R,S)\text{-BINAPHOS})(\text{Me})(\text{CH}_3\text{CN})][\text{BAR}_4]$ (Ar = 3,5-bis(trifluoromethyl)phenyl) (Scheme 2). Reduction of the product using tetrabutylammonium borohydride as a reducing agent gave the chiral polyalcohol in quantitative yield. The absolute configuration of the chiral centers was determined by comparison with four diastereomers of 3-methyl-2,5-hexanediol [14].

action mixture was stirred at 50 °C for 24 h. At the end of the reaction the reactor was cooled to room temperature and the unreacted gases were released. To remove the metal catalyst, the suspension was passed through a short silica gel column using CH_2Cl_2 as the eluant. The copolymer (3.36 g) with productivities as high as 28.6 g of polyketone (per gram of Pd per hour) was obtained after the complete removal of the solvent. $[\phi]_D^{20} = 0.35$ (c 0.5, THF, JASCOJ-20C); IR (cm^{-1}): 2964, 2931, 2873, 1738 (C=O), 1710 (C=O), 1093, 1030, and 802 (C–O–C, spiroketal group); ^1H NMR (Bruker IFS 120HR, 400 MHz, CDCl_3): δ 5.67–5.61 (1H, m), 3.50, 3.22–2.67 (–CH–), 2.63–1.70 (–CH₂–), 1.63–0.75 (–CH₃); ^{13}C NMR (Bruker AM125, 125 MHz, CDCl_3): δ 211 (C=O), 207 (C=O), 175 (CH₃O–), 115, 113, 51 (–CH₂–), 48–45 (–CH–), 16 (–CH₃).

1.2 Reduction of the polyketone using LiAlH_4 , NaBH_4 , and $\text{BH}_3\cdot\text{THF}$

When using LiAlH_4 as the reducing agent, to THF (30 ml) containing 0.321 g of polyketone was added 0.500 g of LiAlH_4 and the resulting mixture was stirred at 60 °C for 12 h. At the end of the reaction the solution was cooled to room temperature. The cold solution was left for 1 h and then enough distilled water was added to decompose the LiAlH_4

residue. Following the removal of the aqueous layer, the separated organic layer was dried over anhydrous MgSO₄. The organic layer was passed through a short silica gel column using THF as the eluant and the eluate was concentrated under reduced pressure to afford the polyalcohol as a white solid 0.296 g. Yield, 92.3%; $[\alpha]_D^{20} = +2.33$ (c 0.5, THF); IR (cm⁻¹): 3365 (–OH), 1183, 1089, and 862 (C–O–C, spiroketal group); ¹H NMR (CD₃Cl): δ 5.12 (1H, s), 3.90–3.25 (1H, br), 2.12–1.74 (2H, br), 1.40–1.12 (1H, m, br), 0.83 (3H, m); ¹³C NMR (CD₃Cl): δ 66, 62, 37, 35, 30, 28, 22, 18, 17, 15.

When using NaBH₄ as the reducing agent in procedure 1, to THF (30 ml) containing 0.321 g of polyketone was added 0.500 g of NaBH₄ and the resulting mixture was stirred using ultrasonication at 60 °C for 1 h and at 50 °C for 5 h. The reaction was quenched by the addition of an adequate amount of distilled water. Following the removal of the aqueous layer the separated organic layer was dried over anhydrous MgSO₄. The organic layer was passed through a short silica gel column using THF as the eluant and the eluate was concentrated under reduced pressure to afford the polyalcohol as a white solid (0.317 g). Yield, 98.7%; $[\alpha]_D^{20} = -0.75$ (c 0.5, THF); IR (cm⁻¹): 3377–3357 (–OH), 1193, 1080, and 812 (C–O–C, spiroketal group); ¹H NMR (CD₃Cl): δ 5.10 (1H, s), 3.96–3.64 (1H, br), 2.04–1.45 (2H, br), 1.40–1.20 (1H, br), 0.85 (3H, m); ¹³C NMR (CD₃Cl): δ 67 (C–OH), 62 (C–OH), 38, 32, 30, 28, 22, 18, 17, 14.

In procedure 2, to THF (30 ml) containing 0.200 g of polyketone was added various amounts of NaBH₄ (NaBH₄/carbonyl molar ratio of 2, 1, and 0.5) and the resulting mixtures were stirred at room temperature for 24 h. The reaction was quenched by the addition of an adequate amount of distilled water. Following the removal of the aqueous layer the separated organic layer was dried over anhydrous MgSO₄. The organic layer was passed through a short silica gel column using THF as the eluant and the eluate was concentrated under reduced pressure to afford the polyalcohol as a white solid (0.113, 0.117, and 0.160 g, respectively) with yield of 56.5%, 58.7%, and 80.0%, respectively. Quantitative UV analyses (HP 8453 UV-Vis spectrometer) at 200–400 nm in a 1-cm fused quartz cells were performed. Solutions of polyketones and polyalcohols in chloroform were irradiated. Chloroform was used as a control blank.

When using BH₃·THF as the reducing agent, to THF (15 ml) containing 0.321 g of polyketone was added 8 ml of BH₃·THF under a N₂ atmosphere and the resulting mixture was stirred at 0 °C for 1 h. The reaction was quenched by the addition of an adequate amount of distilled water. Following the removal of the aqueous layer the separated organic layer was dried over anhydrous MgSO₄. The organic layer was passed through a short silica gel column using

THF as the eluant and the eluate was concentrated under reduced pressure to afford the polyalcohol as a white solid (0.313 g). Yield, 97.3%; $[\alpha]_D^{20} = +2.57$ (c 0.5, THF); IR (cm⁻¹): 3482 (–OH), 1740 (C=O), 1103, 1030, and 832 (C–O–C, spiroketal group); ¹H NMR (CD₃Cl): δ 5.23 (1H, s), 3.95–3.61 (1H, br), 1.83–1.52 (2H, br), 1.10–1.06 (1H, br), 0.83 (3H, m); ¹³C NMR (CD₃Cl): δ 212 (C=O), 208 (C=O), 67, 62, 44, 32, 18, 17, 15, 13.

2 Results and discussion

2.1 ¹³C NMR of the chiral polyketone and polyalcohol

The weak resonances at $\delta = 211$ and 207 in the ¹³C NMR spectrum of the chiral polyketone indicated the presence of keto groups in the polymers. The resonance at 175 was attributed to the ester end group carbon (CH₃O–) and the resonances at 115 and 113 were attributed to the ketal carbons of the spiroketal repeating units in the polymer backbone (Scheme 1). The resonances at $\delta = 51$ –48 were attributed to the –CH₂– and –CH– of the spiroketal repeating units and the resonances at 45–16 were attributed to the –CH₂–, –CH–, and –CH₃ of the –CH(CH₃)CH₂C(O)– units in the copolymer.

The ¹³C NMR spectra of the polymer produced using excess NaBH₄ did not show any absorption at $\delta = 211$ or 207, which clearly indicated that the carbonyl groups of the polyketone were quantitatively reduced to alcohols. The ¹³C NMR absorptions of the polymer as a result of the –CH– (adjacent to –OH), –CH– (adjacent to –CH₃), –CH₂–, and –CH₃ groups were observed at $\delta = 67$, 62, and 38–14, respectively. The polymer obtained using NaBH₄ as a reductant showed broad ¹H NMR peaks. The resonance at 3.96–3.64 was due to the hydrogens on the carbons bearing the alcohol functionality and the resonance at 2.04–0.71 was attributed to the –CH(CH₃)CH₂C(OH)– units in the copolymer.

2.2 IR of the chiral polyalcohol

The IR spectrum of the polyketone showed absorbances at 2964, 2931, and 2873 cm⁻¹ because of the –CH–, –CH₂–, and –CH₃ groups, respectively. Moderate carbonyl absorbances at 1738 and 1710 cm⁻¹ and strong C–O–C bands at 1093, 1030, and 802 cm⁻¹ were also observed for the ketone and the spiroketal repeating units in the polymer backbones. The polymers obtained using excess LiAlH₄ and NaBH₄ showed a broad IR band at 3377–3357 cm⁻¹ because of the hydroxyl groups. The absence of IR absorptions at 1738 and 1710 cm⁻¹ indicated a complete carbonyl to alcohol reduction. The IR spectra of the new polymer obtained using excess BH₃·THF showed a band at 3482 cm⁻¹ and this was due

to hydroxyl groups. An additional IR absorption at 1740 cm^{-1} indicated the presence of unreduced carbonyl groups in the product. Therefore, the IR results of the product showed that the carbonyl groups of the chiral polyketone were partially reduced by the excess $\text{BH}_3\cdot\text{THF}$.

2.3 UV spectra of the chiral polyalcohol

It was possible to follow the extent of reduction quantitatively by monitoring the intensity of the carbonyl UV absorbance at 200–400 nm. Typical UV curves for the copolymers in chloroform are shown in Fig. 1. The maximum absorption found at 248 nm is similar to that for carbonyls in simple ketones. Some of the copolymers showed an absorption in the region of 350 nm. Under our experimental conditions and using various amounts of NaBH_4 (NaBH_4 /carbonyl molar ratio of 0.5, 1, and 2) at ambient temperature resulted in the reduction of 29%, 71%, and 81% of the carbonyl groups (Fig. 1).

2.4 Molar optical rotations of the chiral polyalcohol

Molecular weight measurements of the polymers were performed with water GPCV2000 liquid/gel permeation chromatography using ODS2 Hypersil columns and a VWDA detector. Catechol and polystyrene standards were used. The molecular weight and molar optical rotations of the chiral polyalcohol are shown in Table 1. We found that the molecular weight of the chiral polyalcohol was lower

Fig. 1. UV curves for a chiral polyketone and polyalcohol. (1) Chiral polyketone; (2)–(4) The product of reduction in NaBH_4 /carbonyl molar ratio of 0.5, 1, and 2, respectively.

than that of the chiral polyketone. These results are consistent with that of a similar chemically modified polymer reported by Refs. [18,19]. The polyalcohol obtained after NaBH_4 reduction had the same direction of optical rotation as the chiral polyketone [15–17] (Table 1, entries 2, 4, 5). However, LiAlH_4 and $\text{BH}_3\cdot\text{THF}$ reduction gave a product with an opposite direction of optical rotation for the polyalcohol and the degree of molar optical rotation for the chiral polyalcohol obtained after NaBH_4 reduction remained smaller than that after LiAlH_4 and $\text{BH}_3\cdot\text{THF}$ reduction (Table 1, entries 1–3).

Table 1 Effects of the reducing agents LiAlH_4 , NaBH_4 , and $\text{BH}_3\cdot\text{THF}$ on the reduction of chiral polyketones

Entry	Reducer	Reducer/carbonyl molar ratio	Time (h)	Temperature ($^{\circ}\text{C}$)	Yield (%)	$M_n/10^{-3} (M_w/M_n)$	$[\Phi]_D^{20}$
1	LiAlH_4	3	12	60	92.3	2.1 (1.2)	+2.33
2	NaBH_4	3	6	50	98.7	1.5 (1.1)	−0.75
3	$\text{BH}_3\cdot\text{THF}$	>10	1	0	97.3	2.0 (1.4)	+2.57
4	NaBH_4	2	24	20	56.5	1.3 (1.1)	−0.45
5	NaBH_4	0.5	24	20	80.0	1.8 (1.1)	−0.06

M_w is the weight average molecular weight, M_n is the number average molecular weight, and the ratio M_w/M_n is referred to as polydispersity. For polyketone, $M_w = 3.1 \times 10^3$, $M_n = 3.0 \times 10^3$, $M_w/M_n = 1.0$, $[\Phi]_D^{20} = -0.35$.

The stereochemistry of the reduction products of selected ketones by a variety of main group metal hydrides has been investigated under identical conditions. The stereochemistry of reduction by complex aluminohydrides has been shown to be dependent on the nature of the cation. A comparison between LiAlH_4 and LiBH_4 as reducing agents for ketones showed that LiBH_4 was less sensitive to steric interactions [20]. When various amounts of NaBH_4 were used different degrees of optical rotation were found for the polyalcohol (Table 1, entries 4 and 5). We propose that reducing agents approach from the least sterically hindered side of the chiral polyketone to give a new asymmetric α -carbon atom as

shown in Scheme 3. The enantioselectivity of an α -carbon atom depends on the absolute configuration of the γ -stereogenic center of the polyketone backbone while the direction of optical rotation of the products is mainly controlled by the absolute configuration of the α - and γ - stereogenic center.

Scheme 3. A chiral polyalcohol derived from a polyketone.

3 Conclusions

Chiral polyketones were synthesized by the alternating copolymerization of propene and CO using the Pd(OAc)₂/(S)-P-PHOS catalyst in H₂CCl₂/CH₃OH. The complete reduction of the carbonyl groups of polyketone using excess LiAlH₄ and NaBH₄ occurred in THF to afford a new class of chiral polyalcohol and the product yield was more than 90%. When various amounts of NaBH₄ (NaBH₄/carbonyl molar ratio of 0.5, 1, and 2) were applied, 29%, 71%, and 81% of the carbonyl groups were reduced. The use of excess BH₃·THF resulted in the partial reduction of the chiral polyketone. The molecular weight of the chiral polyalcohol was lower than that of the chiral polyketone. The molar optical rotations of the chiral polyalcohols varied with the reductive conditions and the results show that the enantioselectivity of the additional chiral center in the polyalcohol main chain was not extremely high.

Dedicated to Professor Albert S. C. CHAN on the occasion of his 60th birthday.

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