Available online at www.sciencedirect.com

SCIENCE DIRECT®

Tetrahedron: *Asymmetry* 17 (2006) 7–11

Tetrahedron: *Asymmetry*

Pd-catalyzed asymmetric alternating co-polymerization of propene with carbon monoxide using ionic liquids

Hai-Jun Wang,[a] Lai-Lai Wang,[a,*] Wing-Sze Lam,[b] Wing-Yiu Yu[c] and Albert S. C. Chan[b,*]

[a] *State Key Laboratory for Oxo Synthesis and Selective Oxidation, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, Lanzhou 730000, China*

[b] *Open Laboratory of Chirotechnology of the Institute of Molecular Technology for Drug Discovery and Synthesis and Department of Applied Biology and Chemical Technology, The Hong Kong Polytechnic University, Hong Kong, China*

[c] *Open Laboratory of Chemical Biology of the Institute of Molecular Technology and Department of Chemistry, The University of Hong Kong, Pokfulam Road, Hong Kong, China*

Received 17 October 2005; accepted 25 November 2005
Available online 9 January 2006

Abstract—A protocol for Pd-catalyzed stereoselective co-polymerization of propene and carbon monoxide using chiral ligands, such as (2*S*,3*S*)-DIOP and (*R*)-P-Phos in [C_4mim][PF_6]/[C_6mim][PF_6] as an ionic liquid medium was developed. With (2*S*,3*S*)-DIOP as chiral ligand and [C_4mim][PF_6] as medium, the Pd-catalyzed co-polymerization of propene and CO gave almost completely regioregular polyketones, and the product polymer showed moderate stereoregularity (61% of ℓ-diads). The highest molar optical rotation = +15.9 and polydispersity = 1.2 were attained when (*R*)-P-Phos was used as the ligand and [C_6mim]PF_6 as the solvent. The co-polymer exhibited regioregularity of H–H/H–T/T–T (%) = 17:66:17.

---

1. Introduction

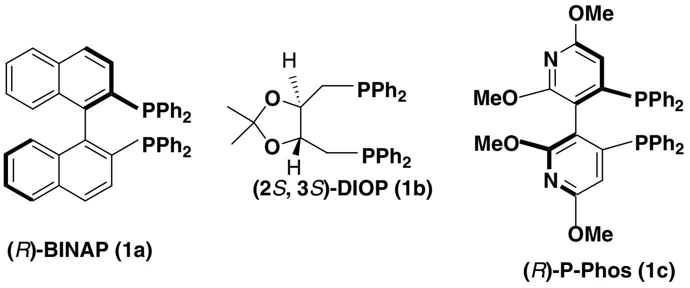
Polyketones belong to a class of thermoplastics that exhibit unique chemical and physical properties such as bio- and photodegradability, strong rigidity, impact strength and tracking resistance.[1] Asymmetric co-polymerization of alkenes and carbon monoxide catalyzed by cationic Pd complexes bearing chiral bidendate ligands has received considerable interest, since the chiral polyketones may be valuable materials such as piezo-, pyro- and ferroelectric materials, non-linear optical material and chromatographic supports.[2–7] For asymmetric propene/CO co-polymerization, control of the regio- and stereoselectivity of the alkene insertion is essential for obtaining stereoregular co-polymers. Several examples involving the use of chiral diphosphines, such as DIOP and BINAP have been documented in the literature.[8] However, the catalytic systems that exhibit high activity and produce high molecular weight chiral co-polymers are rare. Recently, Consiglio et al. reported that Pd complexes modified with chiral ferrocenyl diphosphines are effective catalysts for asymmetric alternating co-polymerization of propene with carbon monoxide.[9] We consider that new catalytic systems, which can offer high productivity, high molecular weight and narrow polydispersities of chiral co-polymers are highly desirable.

Room temperature ionic liquids (ILs)[10] have been extensively investigated as green replacements for organic solvents in homogeneous catalytic reactions such as alkylation,[11] hydrogenation,[12] hydroformylation,[13] alkoxycarbonylation[14] and polymerization of butyl acrylate[15] or olefins.[16] As reaction media, ILs have low volatility and adjustable solvent parameters. Moreover, ILs as polar and non-coordinating solvent may stabilize transition metal catalysts. Recently, Hardacre and Shaughnessy independently reported the alternating co-polymerization of styene and carbon monoxide catalyzed by complexes Pd–bipyridine in ILs,[17] and high molecular weight achiral polyketone was produced in better yields compared to the analogous reactions conducted in methanol as a solvent. Our aims were to develop environmentally friendly catalytic systems for asymmetric alkene/CO co-polymerization, and the use of ILs for related endeavours remains unexplored.

---

[*] Corresponding authors. Tel.: +852 2766 6693; fax: +852 2364 9932 (A.S.C.C.); e-mail: bcachan@polyu.edu.hk

0957-4166/$ - see front matter © 2005 Elsevier Ltd. All rights reserved.
doi:10.1016/j.tetasy.2005.11.030



(*R*)-BINAP (1a)

(2*S*, 3*S*)-DIOP (1b)

(*R*)-P-Phos (1c)

Figure 1. Chiral diphosphine ligands.

Herein, we report our initial studies on the enantioselective alternating co-polymerization of propene with carbon monoxide in ILs catalyzed by Pd complexes bearing chiral diphosphines such as (*R*)-P-Phos, (*R*)-BINAP and (2*S*,3*S*)-DIOP (Fig. 1).

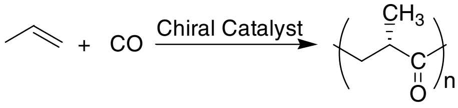
2. Results and discussion

The Pd^{II} catalysts were prepared in situ by reacting $Pd(OAc)_2$ with chiral diphosphines and $BF_3{\cdot}Et_2O$ in CH_2Cl_2/CH_3OH (25:2 mL).[9] With (*R*)-BINAP as a ligand and CH_2Cl_2/CH_3OH (25:2 mL) as solvent, co-polymerization of propene and CO produced low molecular weight ($M_n = 1.1 \times 10^3$) polyketones within 5 h, with polydispersity of the product polymer determined to be 2.9 (Table 1, entry 1).[18] Comparable results ($M_n = 0.97 \times 10^3$; $M_w/M_n = 4.4$) were obtained with (2*S*,3*S*)-DIOP as ligand under similar reaction conditions (entry 2). Lower productivity (24 g poly./g Pd h) and lower molecular weight ($M_n = 0.58 \times 10^3$) of the co-polymer were obtained when (*R*)-P-Phos was employed as a ligand (entry 3). The co-polymer is soluble in polar organic solvents, including CH_2Cl_2, $CHCl_3$, CH_3CN and THF, with no product precipitation observed upon adding CH_3OH into the reaction mixture. The product chiral polyketones obtained in this work exhibit comparable molar optical rotation, IR, ^1H, and ^{13}C NMR spectral features to the reported examples.[8]

Figure 2 shows the ^{13}C NMR spectra of the chiral co-polymer synthesized using $[Pd(DIOP)(OAc)_2]$ as catalyst with CH_2Cl_2/CH_3OH (25:2 mL) as a solvent. The absorption peaks at 212.3 and 207.8 ppm were assigned to the C=O groups flanked by the head-to-tail and tail-to-tail propene units, respectively. The peaks at 44.7, 40.4, and 16.5 ppm were attributed to the $–CH_2CH(CH_3)–$ backbone of the co-polymer. Notably, the ^{13}C NMR resonance signals due to the C=O groups flanked by head-to-head propene units were absent. Based on the intensities of the ^{13}C NMR carbonyl resonances of the product, the regioregularity (H–H/H–T/T–T in %) of the product was evaluated to be 0:95:5. The product polyketones showed low molar optical rotation of $[\Phi]_D^{20} = +1.2–2.4$ (entries 1–3).[8]

Having found a condition for Pd-catalyzed co-polymerization of propene and CO in CH_3OH/CH_2Cl_2, we turned to examine the analogous transformations in ionic liquid media. In this work, several imidazolium

Table 1. Asymmetric alternating co-polymerization of propene with CO catalyzed by $[(P\text{-}P)Pd(OAc)_2]$[a]



Entry	L.	Solvent[b]	Prod.[c]	M_n[d] ($\times 10^{-3}$) (M_w/M_n)	Regioregularity (%)[e]			$[\Phi]_D^{20}$[f]
					h–h	h–t	t–t	
1	**1a**	CH_2Cl_2/CH_3OH	48	1.1 (2.9)	13	77	10	+2.40
2	**1b**	CH_2Cl_2/CH_3OH	41	0.97 (4.4)	0	95	5	+1.20
3	**1c**	CH_2Cl_2/CH_3OH	24	0.58 (4.0)	9.0	75	16	+1.40
4	**1b**	$[C_4mim]PF_6$	85	4.7 (1.7)	0	100	0	+0.84
5	**1b**	$[C_6mim]PF_6$	50	5.2 (1.7)	0	100	0	+0.62
6	**1c**	$[C_6mim]PF_6$	40	5.1 (1.2)	17	66	17	+15.9
7	**1b**	$[C_8mim]PF_6$	17	9.1 (1.6)	0	100	0	+1.00
8	**1b**	$[C_4mim]BF_4$	47	4.5 (1.4)	0	100	0	+2.39

[a] Reaction conditions as described in Refs. 18 and 21.

[b] Abbreviations: $[C_4mim]$ is 1-*n*-butyl-3-methylimidazolium, $[C_6mim]$ is 1-*n*-hexyl-3-methyl-imidazolium, and $[C_8mim]$ is 1-*n*-octyl-3-methyl-imidazolium.

[c] Productivity (g poly./g Pd h) were calculated for the reactions at 50 °C for 5 h using 4.0 MPa of CO and 35 g of propene.

[d] M_n is the number average molecular weight, and the ratio M_w/M_n is referred to as polydispersity, and catechol and polystyrene standards were used to calibrate a HP 1100 gel permeation chromatograph with Ultrastyragel columns and a differential refractometer.

[e] Percentages of head-to-head (h–h), head-to-tail (h–t), and tail-to-tail (t–t) arrangements in the polymer backbone were obtained from the intensities of the ^{13}C NMR carbonyl resonances of the product.

[f] $[\Phi]_D^{20}$, molar optical rotation.

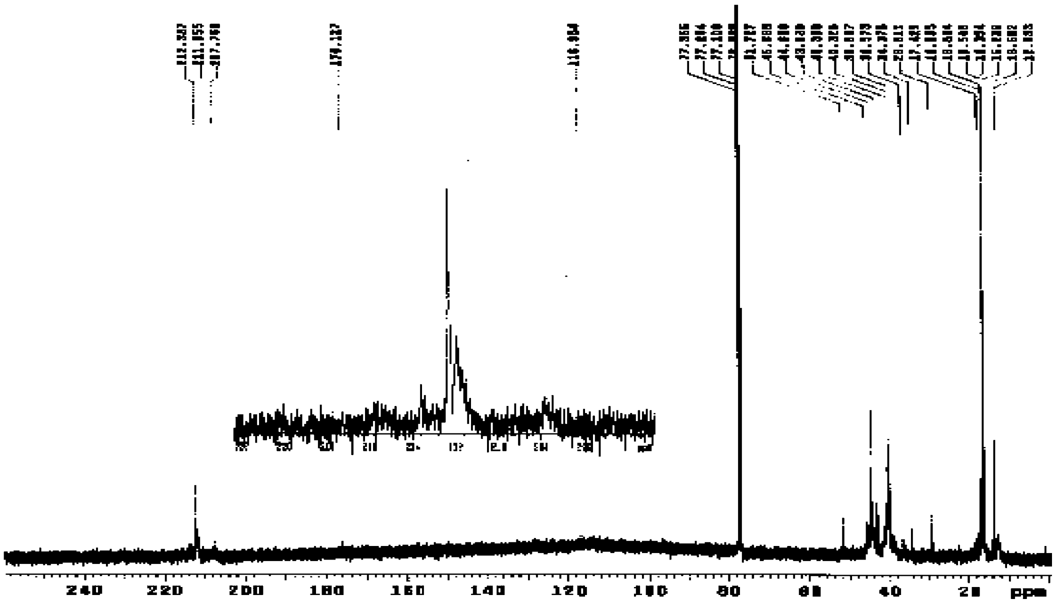


Figure 2. ^{13}C NMR spectrum (125 MHz, $CDCl_3$) of the co-polymer synthesized using catalyst [(2*S*,3*S*)-(DIOP)Pd(OAc)$_2$] in CH_3OH/CH_2Cl_2 (v/v, 25:2 mL).

salts namely [C_4mim]PF_6, [C_6mim]PF_6, [C_8mim]PF_6 and [C_4mim]BF_4 were examined as ionic liquid medium for the co-polymerization reaction. These imidazolium salts were prepared according to a reported procedure.[19] In the presence of a catalytic quantity of [Pd(DIOP)-(OAc)$_2$], and [C_4mim]PF_6 as a solvent (4 mL) containing CH_3OH (0.4 mL), effective co-polymerization of propene with CO was achieved. Compared to the reactions performed in the CH_3OH/CH_2Cl_2 medium, the use of ionic liquid as solvent resulted in higher productivity (85 g poly./g Pd h) and formation of higher molecular weight polyketone product ($M_n = 4.7 \times 10^3$) with narrow polydispersity ($M_w/M_n = 1.7$, Table 1, entry 4). However, the optical rotation value of the polyketone product remained small ($[\Phi]_D^{20} = +0.84$, compare result with entry 2). Without CH_3OH as additive, no co-polymer was formed using ILs alone as solvent. This finding is consistent with the results obtained by Shaughnessy et al.[17] ILs/CH_3OH (4:0.4 mL) was chosen as reaction media.[17,20,21]

The co-polymer obtained using ionic liquid as solvent exhibit poor solubility in polar organic solvents such as CH_3OH, CH_3CN, and THF, probably due to the rather high molecular weight and to high regioregularity.[22] The ^{13}C NMR spectra of the co-polymer (Fig. 3)

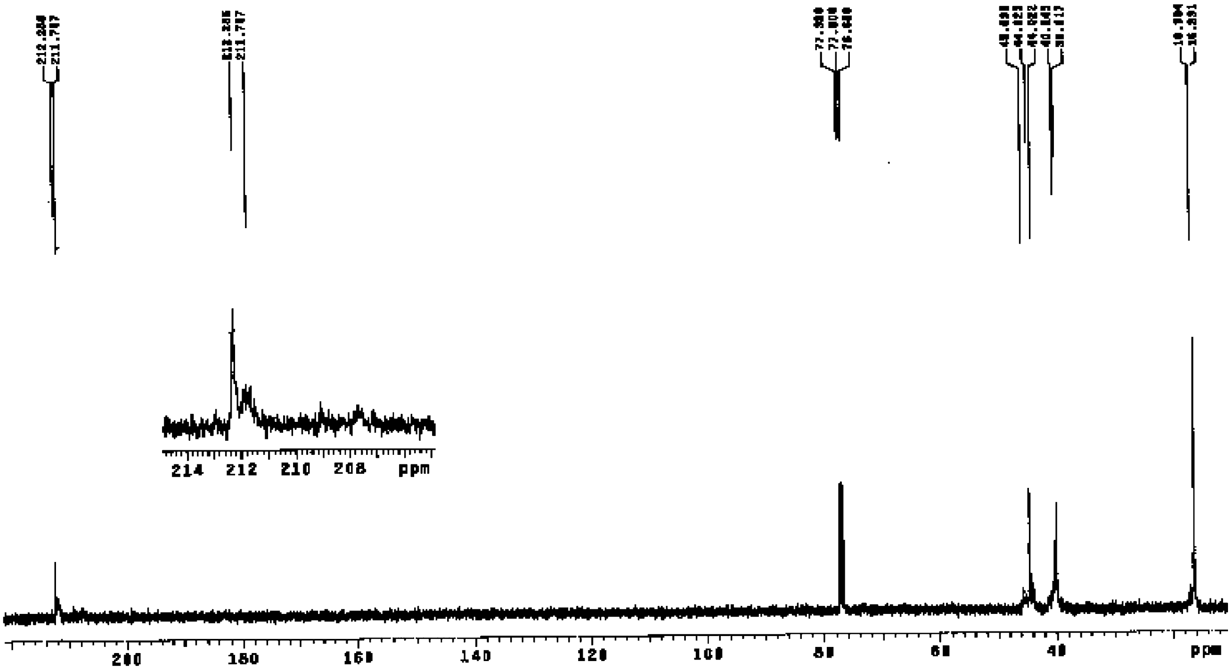


Figure 3. ^{13}C NMR spectrum (125 MHz, $CDCl_3$) of the co-polymer synthesized using catalyst [(2*S*,3*S*)-(DIOP)Pd(OAc)$_2$] in IL [C_4mim]PF_6.

synthesized using [C$_4$mim]PF$_6$ as a solvent and (2*S*,3*S*)-DIOP as ligand showed absorption peaks at 212.3, 44.0, 40.2, 16.9 ppm. The 212.3 ppm resonance was assigned to the C=O groups flanked by the head-to-tail propene units. The resonances at 44.4, 40.2, and 16.9 ppm corresponded to the –CH$_2$CH(CH$_3$)– backbone of the co-polymer. Notably, the resonance signals due to the C=O group flanked by head-to-head and tail-to-tail propene units were not found. Therefore, the regioregularity (H–H/H–T/T–T in %) of polyketone being 0:100:0 was achieved. Based on the relative intensity of the largest signal of the carbonyl groups of the head-to-tail enchainment, which was assigned to $\ell\ell\ell\ell$-tetrad,[22] the stereoregularity (in % ℓ-diads) of the product was determined to be 61%. The IR spectra of the co-polymers, synthesized in organic solvent and in ILs, showed that both spiroketal and pure ketone structures were present. The results were consistent with that reported by Sen et al.[23]

As noted earlier, co-polymer with polydispersity (M_w/M_n) = 1.7 was obtained using [C$_4$mim]PF$_6$ as solvent for the alternating co-polymerization of propene and CO. Similar results ($M_n = 5.2 \times 10^3$, $M_w/M_n = 1.7$, H–H/H–T/T–T in % = 0:100:0, $[\Phi]_D^{20} = +0.62$) were obtained with [C$_6$mim]PF$_6$ as solvent and (2*S*,3*S*)-DIOP as ligand (Table 1, entry 5). When (*R*)-P-Phos was used as ligand and [C$_6$mim]PF$_6$ as solvent, the Pd-catalyzed co-polymerization of propene and CO afforded a polyketone product with $M_n = 5.1 \times 10^3$ and polydispersity (M_w/M_n) = 1.2 (entry 6). Moreover, the regioregularity (H–H/H–T/T–T in % = 17:66:17) and a molar optical rotation ($[\Phi]_D^{20}$) value up to +15.9 were attained. The reasons underlying the narrower polydispersity and high molar optical rotation using ligand (*R*)-P-Phos for the asymmetric alternating propene/CO co-polymerization in ILs remain unclear. The best result with respect to polydispersity and molar optical rotation was achieved using [C$_6$mim]PF$_6$ as solvent and (*R*)-P-Phos as ligand (Table 1, entry 6).

The results in Table 1 illustrate the effect of the alkyl chain length of the imidozolium salts on regioregularities, molar optical rotation, molecular weight, and productivities for the Pd-catalyzed alternating propene/CO co-polymerization. With PF_6^- as counterion, the Pd(DIOP)-catalyzed co-polymerization of propene and CO gave almost completely regioregular co-polymer (H–H/H–T/T–T in % = 0:100:0) for the imidazolium salts of increasing alkyl chain length (for $n = 4$–8). While the product co-polymer showed comparable molar optical rotation, the molecular weight of the co-polymer increased with increasing the alkyl chain length of the imidazolim salts. However, the productivity of chiral catalysts showed an opposite trend (Table 1, entries 4, 5 and 7). This observation is probably due to more effective CO transfer in less viscous ILs ([C$_4$mim]PF$_6$ < [C$_6$mim]PF$_6$ < [C$_8$mim]PF$_6$).

Effect on the counteranion associated with the imidazolium salts was also noted.[24] For example, with [C$_4$mim]PF$_6$ as solvent, the Pd(DIOP)-catalyzed alternating co-polymerization of propene with CO produced almost completely regioregular co-polymer with higher molecular weight ($M_n = 4.7 \times 10^3$) and higher productivity (85 g poly./g Pd h) compared to the results ($M_n = 4.5 \times 10^3$, productivity = 47 g poly./g Pd h, H–H/H–T/T–T in % = 0:100:0, $[\Phi]_D^{20} = +2.39$) using [C$_4$mim][BF$_4$] as a solvent (Table 1, entries 4 and 8)]. This finding is compatible with a report by Hardacre and co-workers[17a] that the yields of the alternating co-polymerization of styene with carbon monoxide in ILs decreased in the order $[NTf_2]^- > [PF_6]^- > [BF_4]^-$ for both pyridinium and imidazolim based ILs. Similar anion effects are also known for the carbonylation of aryl halides[25] and the hydrogenation of dienes.[26]

3. Conclusion

A protocol for Pd-catalyzed stereoselective co-polymerization of propene and carbon monoxide using chiral ligands (2*S*,3*S*)-DIOP and (*R*)-P-Phos in ILs medium such as [C$_4$mim][PF$_6$]/[C$_6$mim][PF$_6$] was developed. The product co-polymer exhibited almost complete regioregularity and moderate stereoregularity. The reaction features high productivity, production of high molecular weight polyketones with narrow polydispersity. Further works on recycling chiral catalysts in the ionic liquid are in progress.

Acknowledgements

We are grateful for the financial support of this work by the National of Nature Foundation of China (No. 20343005 and 20473107) and the Foundation of Chinese Academy of Sciences (No. KGXCX2-SW-211) and the Areas of Excellence Scheme (AoE P10/01) administered by the University Grants Committee (HKSAR, China).

References

1. Sen, A.; Lai, T. W. *Organometallics* **1984**, *3*, 866.
2. (a) Barsacchi, M.; Batistini, A.; Consiglio, G.; Sutter, U. W. *Macromolecule* **1992**, *25*, 3604; (b) Batistini, A.; Consiglio, G.; Sutter, U. W. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 303; (c) Batistini, A.; Consiglio, G. *Organometallics* **1992**, *11*, 1766; (d) Batistini, A.; Consiglio, G.; Sutter, U. W. *Polym. Mater. Sci. Eng.* **1992**, *67*, 104; (e) Bronco, S.; Consiglio, G.; Hutter, R.; Batistini, A.; Suster, U. W. *Macromolecule* **1994**, *27*, 4436; (f) Bronco, S.; Consiglio, G.; Di Benedetto, S.; Fehr, M.; Spindler, F.; Togni, A. *Helv. Chim. Acta* **1995**, *78*, 883; (g) Barsacchi, M.; Consiglio, G.; Medici, L.; Petrucci, G.; Suter, U. W. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 989; (h) Sesto, B.; Consiglio, G. *J. Am. Chem. Soc.* **2001**, *123*, 4097–4098.
3. (a) Sen, A.; Lai, T. W. *J. Am. Chem. Soc.* **1982**, *104*, 3520; (b) Sen, A. *Adv. Polym. Sci.* **1986**, *73*, 125; (c) Sen, A. *Acc. Chem. Res.* **1993**, *26*, 303–310.
4. Bianchini, C.; Meli, A. *Coord. Chem. Rev.* **2002**, *225*, 35–66.
5. Xu, F. Y.; Zhao, A. X.; Chien, C. W. *Makromol. Chem.* **1993**, *194*, 2579–2603.
6. (a) Drent, E.; van Broekhoven, J. A. M.; Doyle, M. J. *J. Organomet. Chem.* **1991**, *417*, 235–251; (b) Drent, E.; Budzelaar, P. H. M. *Chem. Rev.* **1996**, *96*, 663–681.

7. (a) Nozaki, K.; Sato, N.; Takaya, H. *J. Am. Chem. Soc.* **1995**, *117*, 9911; (b) Nozaki, K.; Sato, N.; Tonomura, Y.; Koga, N. *J. Am. Chem. Soc.* **1997**, *119*, 12779; (c) Nozaki, K.; Komaki, H.; Kawashima, Y.; Hiyama, T.; Matsubara, T. *J. Am. Chem. Soc.* **2001**, *123*, 534; (d) Naoki, K.; Yasutomi, M.; Nakamoto, K.; Hijama, T. *Polyhedron* **1998**, *17*, 1159; (e) Nozaki, K.; Hiyama, T. *J. Organomet. Chem.* **1999**, *576*, 248–253.
8. Jiang, Z.; Scott, E. A.; Sen, A. *Macromolecule* **1994**, *27*, 2694.
9. Gambs, C.; Chaloupka, S.; Consiglio, G.; Togni, A. *Angew. Chem., Int. Ed.* **2000**, *39*, 2486.
10. (a) Welton, T. *Chem. Rev.* **1999**, *99*, 2071–2084; (b) Dupont, J.; De Souza, R. F.; Suarez, P. A. Z. *Chem. Rev.* **2002**, *102*, 3667–3692; (c) Welton, T. *Coord. Chem. Rev.* **2004**, *248*, 2459; (d) Dongbin, Z.; Min, W.; Yuan, K. *Catalysis Today* **2002**, *74*, 157–189; (e) Gordon, C. M. *Appl. Catal.* **2001**, *222*, 101–117; (f) Przemysalaw, K. *Prog. Polym. Sci.* **2004**, *29*, 3–12.
11. Christopher, J. M.; Paul, J. S.; Thomas, Welton *Chem. Commun.* **2000**, 1249.
12. Xhauvin, Y.; Mussmann, L.; Olivier, H. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2698.
13. Murielle, F. S.; Paul, B. W.; David, J. C.-H. *Chem. Commun.* **2001**, 781.
14. Zim, D.; Souza, R. F.; Duont, J.; Monteiro, A. L. *Tetrahedron lett.* **1998**, *39*, 7071.
15. Carmichael, A. C.; Haddketon, D. M.; Bon, S. A. F.; Seddon, K. R. *Chem. Commun.* **2000**, *55*, 1237–1242.
16. (a) Wasserscheid, P.; Goordon, C. M.; Hilgers, C.; Muldoon, M. J.; Dunkin, R. *Chem. Commun.* **2001**, 1186; (b) Hlatky, G. G., World Pat. WO 0181436, 2001.
17. (a) Hardacre, C.; Holbrey, J. D.; Katdare, S. P.; Seddon, K. R. *Green Chem.* **2002**, *4*, 143–146; (b) Klingshirn, M. A.; Broker, G. A.; Hokbrey, J. D.; Shaughnessy, K. H.; Rogers, R. D. *Chem. Commun.* **2002**, 1394–1395.
18. A typical procedure for the co-polymerization of propene and CO in organic solvents: a mixture of Pd(OAc)$_2$ (10.3 mg, 0.046 mmol), DIOP (23.0 mg, 0.046 mmol) and BF$_3$·Et$_2$O (2 equiv) was stirred magnetically in CH$_2$Cl$_2$/CH$_3$OH (25:2 mL) under dry nitrogen for 1.5 h at room temperature. The solution was transferred to a stainless steel reactor under nitrogen, and the reactor was then charged with 35 g of propene under a cold bath and 4.0 MPa of CO. The reaction mixture was stirred at 50 °C for 5h. At the end of the reaction, the reactor was cooled to room temperature, the unreacted gases were released. To remove the metal catalyst, the suspension was passed through a short stem of silica gel column using CH$_2$Cl$_2$ as eluant. The co-polymer was obtained after complete removal of the solvent. Yield, 1.01 g; $[\Phi]_{\mathrm{D}}^{20}+1.20$ (*c* 0.5, CH$_2$Cl$_2$); ^{13}C NMR (125 MHz, CDCl$_3$) δ: 212.3 (C=O), 207.8 (C=O), 44.7 (–CH$_2$–), 40.4 (–CH–); 16.5 (–CH$_3$); ^{1}H NMR (400 MHz, CDCl$_3$) δ: 0.98 (–CH$_3$), 2.14–2.47 (–CH$_2$–), 2.92–3.13 (–CH–). IR (KBr, cm^{-1}): 1708 (C=O), 844 and 1042–1081 (C–O–C, spiroketal group).
19. A typical procedure for the synthesis of ionic liquid: an equal amount of 1–chlorobutane and 1–methylmidazole was added to a round-bottomed flask and refluxed for 72 h at 70 °C until the formation of a golden viscous liquid. The viscous liquid was cooled and washed three times with ethyl acetate. After the residual solvent was removed, the product [C$_4$mim]Cl was mixed with an equal amount of potassium hexafluorophosphate solution, followed by stirring the mixture at room temperature for 2 days. Two phases were formed, where [C$_4$mim][PF$_6$] was the bottom phase and HCl was the upper phase. The upper phase was decanted, and the bottom phase was washed successively with dichloromethane and distilled water until the washing become neutral. The ionic liquid was dried with anhydrous magnesium sulfate and the solvent was removed under vacuum. ^{13}C NMR (125 MHz, CDCl$_3$) δ: 134.8, 128.3, 53.4, 35.9, 26.8, 19.1; ^{1}H NMR (400 MHz, CDCl$_3$) δ: 0.76 (t), 1.18 (s), 1.74 (q), 3.80 (s), 4.08 (t), 7.27 (s), 7.39 (s), 8.39 (s).
20. Peng, J. J.; Deng, Y. Q. *Tetrahedron Lett.* **2001**, *42*, 403.
21. A typical procedure for the co-polymerization of propene and CO in ILs: a mixture of Pd(OAc)$_2$ (10.3 mg, 0.046 mmol), DIOP (23.0 mg, 0.046 mmol) and BF$_3$·Et$_2$O (2 equiv) was stirred magnetically in CH$_2$Cl$_2$/CH$_3$OH (25:2 mL) under nitrogen for 1.5 h at room temperature. After concentrating the solution under vacuum, [C$_4$mim]PF$_6$ (4 mL) and CH$_3$OH (0.4 mL) were added under a flow of nitrogen. When the catalyst dissolved completely, the resultant solution was transferred to a stainless steel reactor under nitrogen, then the reactor was charged with 35 g of propene under a cold bath and 4.0 MPa of CO. The reaction mixture was stirred at 50 °C for 5 h. At the end of the reaction, the reactor was cooled to room temperature, the unreacted gases were released. The product co-polymer was precipitated by the addition of methanol into the reaction mixture, and separated by filtration. The polymer product (2.25 g) was washed with methanol and dried under reduced pressure. $[\Phi]_{\mathrm{D}}^{20}+0.84$ (*c* 0.5, CH$_2$Cl$_2$); ^{13}C NMR (125 MHz, CDCl$_3$) δ: 212.3 (C=O), 44.0. (–CH$_2$–), 40.2 (–CH–); 16.9 (–CH$_3$). ^{1}H NMR (400 MHz, CDCl$_3$) δ: 1.06 (–CH$_3$), 2.30–2.86 (–CH$_2$–), 3.06–3.49 (–CH–). IR (KBr, cm^{-1}): 1706 (C=O), 844 and 1023–1168 (C–O–C, spiroketal group).
22. Bronco, S.; Consiglio, G. *Macromol. Chem. Phys.* **1996**, *197*, 355–365.
23. Jiang, Z.; Dahlen, G. M.; Houseknecht, K.; Sen, A. *Macromolecules* **1992**, *25*, 2999.
24. Huddleston, J. G.; Visser, A. E.; Reichert, W. M.; Willauer, H. D.; Broker, G. A.; Rogers, R. D. *Green Chem.* **2001**, *3*, 156.
25. Mizushima, E.; Hayashi, T.; Tanaka, M. *Green Chem.* **2001**, *3*, 76.
26. Dupont, J.; Suarez, P. A. Z.; Umpierre, A. P.; de Souza, R. F. *J. Braz. Chem. Soc.* **2000**, *11*, 293.