

Pd(II) Catalyzed Copolymerization of Styrene and CO in Quaternary Ammonium Ionic Liquids

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Received March 19, 2007; Revised August 17, 2007; Accepted October 27, 2008

Abstract: Poly(1-oxo-2-phenyltrimethylene) was synthesized by palladium-catalyzed copolymerization of styrene and carbon monoxide in quaternary ammonium ionic liquids. The $[\text{Pd}(\text{bipy})_2][\text{PF}_6]_2$ compound had relatively more catalytic activity than $[\text{Pd}(\text{bipy})_2][\text{BF}_4]_2$ in ionic liquids. The catalytic activity of palladium (II) composite catalyst was superior to the catalyst formed *in situ* from palladium acetate, 2,2-bipyridyl, and X^- ($\text{X}^- = \text{PF}_6^-, \text{BF}_4^-$) in ionic liquids. The effects of the volume of ionic liquids, reaction time and benzoquinone content on the copolymerization were also described.

Keywords: poly(1-oxo-2-phenyltrimethylene), ionic liquids, palladium catalyst, carbon monoxide, catalytic activity.

Introduction

It is known that aliphatic polyketones are prepared by perfectly alternating copolymerization of olefins and carbon monoxide (CO) in the presence of palladium-based catalysts,¹ especially for the materials supported by polyethylene and polystyrene. In the last ten years, efforts to improve the mechanical property,² high temperature resistance and ferro-electric properties³ by connection to the polyketones have received considerable attention. The chiral centers of the polymeric structure is important for basic chemical studies and has many technological applications such as chromatography, membrane separation, purification of optically-active substances and bio-photo-degradations. This area of research is too large to be surveyed here, but a review by Zuiderduin *et al.* or Durand *et al.* would show an outline of recent studies.^{4,5}

Ionic liquids (ILs), a "green" organic solvent, have strong polarity, low volatility and solvent parameter adjustability.⁶ ILs are useful in applications like alkylations,⁷ hydrogenations,⁸ hydroformylations,⁹ alkoxy-carbonylations,¹⁰ polymerizations of butyl acrylate¹¹ and olefins¹² and other homogeneous reactions. In 2002, Hardacre *et al.* reported the alternating co-polymerization of styrene and carbon monoxide catalyzed by Pd composite catalyst in imidazolium or pyridinium ILs.¹³ High molecular weight achiral polyketone was produced in better yields compared to the analogous reactions conducted in methanol as a solvent. Recently, Wang *et al.*¹⁴ reported the enantio-selective alter-

nating copolymerization of CO and propene in imidazolium or pyridinium ILs in the presence of Pd-chiral diphosphine complexes. The Pd-catalyzed co-polymerization of propene and CO gave almost complete regioregular polyketones, and the product polymer showed moderate stereoregularity.

Based on quaternary ammonium cations for the copolymerization of CO, styrene and recycling Pd catalysts from the ionic liquids, preparations of a novel catalytic system in ILs have been made. Several Pd^{2+} catalysts are tested in quaternary ammonium ionic liquids. Factors influencing the catalytic activity like the volume of ILs, reaction time and benzoquinone content are being thoroughly discussed.

Experimental

Materials. Carbon monoxide (>99.9%) was purchased from Beijing Analysis Instrument Company, China. Other reagents, including *N,N*-dimethylethanolamine, alkyl halide (C_2Br , C_4Br , C_6Br , C_8Br , C_{16}Br), styrene, 2,2-bipyridine, and 1,4-benzoquinone were of analytical grade or higher (Kewei Ltd., Tianjin, China), and used without further purification. The catalysts $[\text{Pd}(\text{bipy})_2][\text{PF}_6]_2$ and $[\text{Pd}(\text{bipy})_2][\text{BF}_4]_2$ were prepared and characterized according to the common process¹⁵ and stored under N_2 at 0 °C.

Measurements. FTIR spectra were collected on a BIO-RAD FTS3000 FTIR spectrometer as potassium bromide pellets. ¹H NMR analysis was acquired on a Varian Unity INOVA NMR spectrometer operating at 400 MHz in D_2O . Solid-state ¹³C NMR analyses were acquired on Varian Infinity plus 300WB NMR spectrometer operating at 75 MHz. The elemental analysis was carried out with a Perkin Elmer PE-

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2400 elemental analyzer. Molecular weights were obtained by Waters-600 gel permeation chromatography (GPC) and were expressed in terms of polystyrene equivalents.

Preparation of Ionic Liquids. The quaternary ammonium-based ionic liquids were prepared using a different method as described by Domanska, *et al.*¹⁶ To a mixture of 0.12 mol of freshly distilled *N,N*-dimethylethanolamine and 0.1 mol of alkyl halide, heat at 80 °C for 20 min in the microwave irradiation at 350 W. The mixture was then distilled under vacuum to remove unreacted *N,N*-dimethylethanolamine. All of the compounds were obtained with a yield of 95+%.

The tetrafluoroborate salts of ILs were synthesized by anion exchange reactions (at room temperature in water). To a slurry of 22.32 g (0.1 mol) of lead (II) oxide in 50 mL of water, 43.9 g (0.2 mol) of tetrafluoroboric acid (40% in water) was added and stirred vigorously. The mixture was then stirred for several hours. After the mixture became a colorless suspension, 0.1 mol quaternary ammonium salts in 200 mL of water was added and stirred for 1 h. The white precipitate formed (PbBr₂) was removed by filtration. The filtrate was distilled under vacuum to give quaternary ammonium tetrafluoroborate salt. The hexafluorophosphates salt of ILs was prepared using the similar approach to the tetrafluoroborate salt (Scheme I).

Copolymerization of CO and Styrene in Ionic Liquid.

To a solution of 2 mL of ionic liquid and 10 mL of styrene, add 0.025 mmol of palladium catalyst and 1.8 mmol of benzoquinone in a 100-mL of stainless steel reactor. Carbon monoxide was introduced to the system until inner pressure reached 2.0 MPa. The mixture was stirred for 4 h at 60 °C. The raw product was precipitated in ethanol and washed by Soxhlet extractor. The product was dried under vacuum and gave poly(1-oxo-2-phenyltrimethylene) as the form of white powder (See Figures 1 & 2). In addition, the upper liquid was condensed under vacuum at 50 °C and subsequently was copolymerized according to the procedure described above.

Results and Discussion

[Pd(bipy)₂][X]₂ (X=PF₆⁻, or BF₄⁻) as pre-synthesized com-

plexes, were introduced into ILs instead of Pd(CH₃COO)₂/bipy/X⁻ in copolymerization of CO with styrene, the catalytic system exhibited a higher activity and higher amounts of polyketone were observed (Figure 3). The reason was

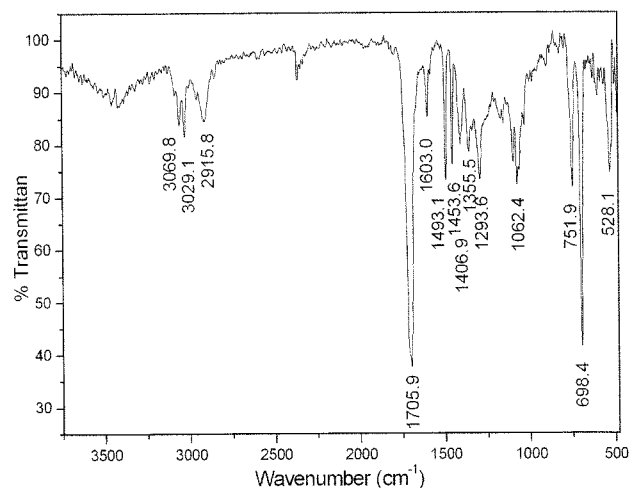


Figure 1. FTIR spectrum of poly(1-oxo-2-phenyltrimethylene).

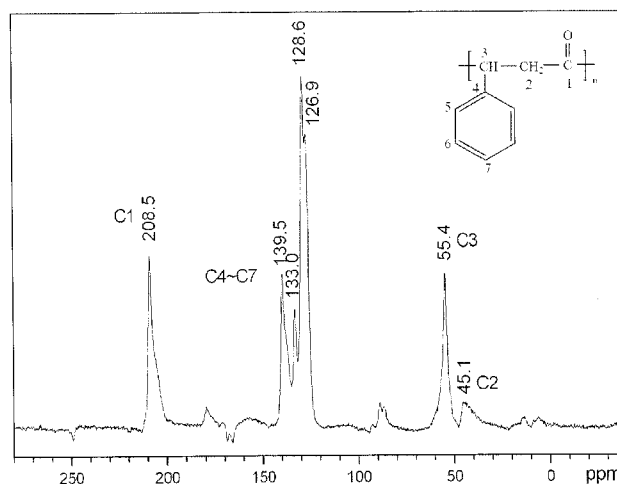
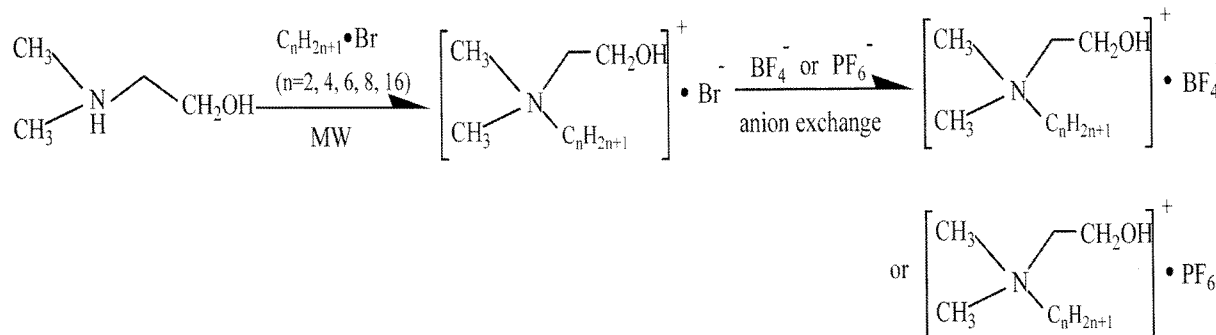


Figure 2. ¹³C solid-state NMR spectra of poly(1-oxo-2-phenyltrimethylene).

Scheme I



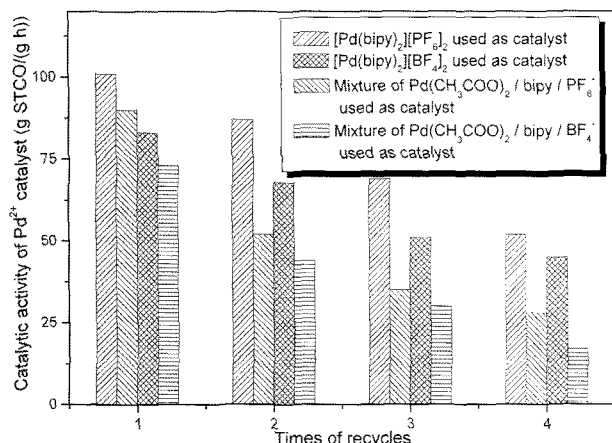


Figure 3. Comparison of catalytic activity between $[\text{Pd}(\text{bipy})_2][\text{X}]_2$ ($\text{X}=\text{PF}_6^-$, or BF_4^-) and $\text{Pd}(\text{CH}_3\text{COO})_2/\text{bipy}/\text{HX}$ catalytic system in ionic liquids (C_4NBF_4). (Reaction condition: 10 mL of styrene, 2 mL of ionic liquid, 1.8 mmol of benzoquinone, and 0.025 mmol of palladium catalyst. Reaction temperature is 60°C , P_{CO} is 2 MPa and reaction time is 4 h).

that when ILs were used as solvents, the system became viscous with the progress of reaction. In $\text{Pd}(\text{CH}_3\text{COO})_2/\text{bipy}/\text{X}^-$ ($\text{X}=\text{PF}_6^-, \text{BF}_4^-$) system, it was difficult for the bipy to coordinate with $\text{Pd}(\text{CH}_3\text{COO})_2$ and being converted to the bis-chelated palladium (II) catalytic intermediate rapidly and completely. Due to the higher yield return, the palladium (II) composite catalyst was to be used in the system.

The catalytic activity of the reused catalyst in ionic liquids is also shown in Figure 3. It is observed that the catalytic activity in the first run was higher than those of the second, third or fourth run. It can be deduced that part of Pd^{2+} was gradually lost possibly due to mechanical loss or they were embedded into the polyketone. Part of the Pd^{2+} still showed catalytic activity along with the recycle of the ILs. In Figure

3, $[\text{Pd}(\text{bipy})_2][\text{BF}_4]_2$ shows a relatively lower catalytic activity than that of $[\text{Pd}(\text{bipy})_2][\text{PF}_6]_2$ with similar conditions, and smaller amount of product is obtained both in the first run and in the following runs. It has been pointed out that the anion which balances the charge of the metal complex should be the conjugate base of a strong acid and the anion should be weakly coordinating so that the reacting monomers can easily be activated by coordination to the central metal ion.^{17,18} Obviously PF_6^- is a weaker σ -donor ligand than BF_4^- .

Based on the results obtained from the screening of ILs, styrene copolymerization with CO in ammonium ILs is compared with other solvents. The results are presented in Table I. When equal volumes of palladium (II) composite catalyst and methanol were used, polyketone with the lowest catalytic activity was obtained. However, by using *N,N*-dimethylethanolamine solely as a solvent in the same conditions, no polyketone was obtained. The molecular weight of the products is also influenced by the type of solvent. It is straightforward to note that the molecular weight is smaller with respect to the results observed by Hardacre *et al.*¹³ in pyridinium-based ILs. It is indicated that the pyridinium-based systems may be more coordinating than the ammonium-based systems in the copolymerization of styrene and CO.

A remarkable dependence of catalytic activity on the nature of cation is observed too. An increasing trend of catalytic activity was observed as the alkyl chain length increases in the range of C_2N^+ to C_6N^+ . However, using C_8NBF_4 as a solvent, lower yields and lower molecular weights were obtained. When the same volume of $\text{C}_{16}\text{NBF}_4$ was used, no polyketone was obtained. The type of anion similarly affects the *A* value. As seen in Table I, the *A* value is found to be decreasing in order as $\text{PF}_6^- > \text{BF}_4^-$ for the ILs with same alkyl chain lengths.

On the other hand, the anion type also shows significant

Table I. Comparison of Pd^{2+} Catalyst in Different Solvents on Copolymerization

Entry	Solvent	Catalytic Activity (<i>A</i>) ^a	M_w^b	M_n^b	PDI ^c
1	C_2NBF_4	96	7,000	2,800	2.5
2	C_2NPF_6	48	7,630	3,460	2.2
3	C_4NBF_4	101	8,500	4,650	1.8
4	C_4NPF_6	112	9,260	4,780	1.9
5	C_6NBF_4	105	7,920	4,550	1.7
6	C_8NBF_4	63	5,200	3,140	1.6
7	$\text{C}_{16}\text{NBF}_4$	-	-	-	-
8	Methanol	27	6,000	4,070	1.5
9	<i>N,N</i> -Dimethylethanolamine	0	-	-	-

^a(*A*) Catalytic activity defined as g polyketone/(g-Pd·h). ^bDetermined by GPC relative to PS. ^cPDI is polydispersity index (M_w/M_n). Reaction conditions: palladium catalyst $[\text{Pd}(\text{bipy})_2][\text{PF}_6]_2=0.025$ mmol, styrene=0 mL, solvent=2 mL, benzoquinone=1.8 mmol, reaction temperature= 60°C , $P_{\text{CO}}=2$ MPa, reaction time=4 h.

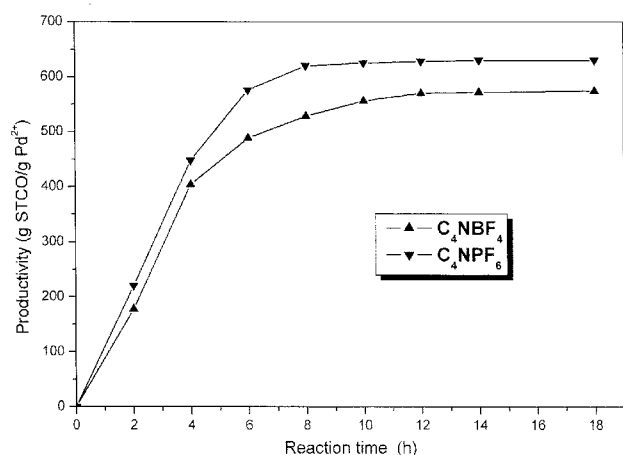


Figure 4. The effect of reaction time on productivity of polyketones in ionic liquids (reaction condition: 10 mL of styrene, 0.025 mmol of palladium catalyst and 1.8 mmol of benzoquinone. Reaction temperature is 60 °C, P_{CO} is 2 MPa).

effect on the recyclability, activity and the conversion (shown in Figure 4). We decided to work at 60 °C and the reaction time was prolonged from 2 to 18 h. The plot of productivity vs. the reaction time shows an asymptotic behavior in two different ILs and the active species are deactivated, after 8 h and 12 h, respectively. Moreover, Table II shows that the molecular weights of products increase when the reaction time is increased, although after 4 h, the catalytic activity of the composite catalyst drops sharply. These trends indicate that the stability of the catalyst is enhanced in C_4NPF_6 with respect to C_4NBF_4 .

From Figure 5, it is found that an increase in ILs volume of results in a remarkable increase in the activity and the reaction rate, although the study of reaction mechanism in ILs is still underway. With an initial increase in volume, the rate constant increases accordingly. Since the introduction of ILs enhances the solubility of the palladium (II) composite catalyst, it can increase the reaction rate. When the ratio of ionic liquids/ Pd^{2+} is 80, the catalytic activity reaches 112 g STCO/g·Pd·h. When the ratio of ionic liquids/ Pd^{2+} is higher than 80, any further incremental amount only results in a small increase of catalytic activity. Therefore, it is vital to

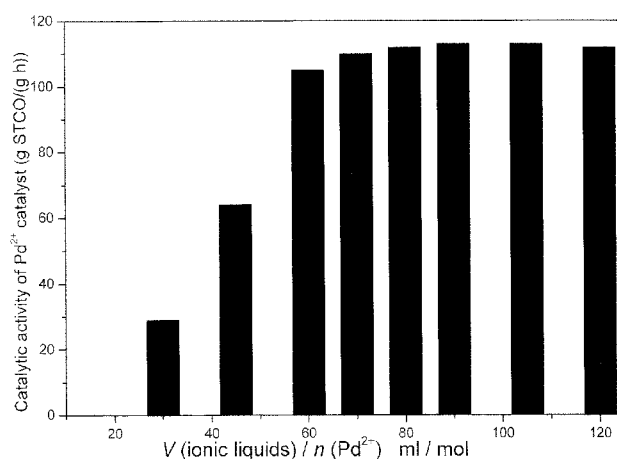


Figure 5. The effect of ratio of ionic liquids (mL) with Pd^{2+} (mol) on the catalytic activity of polyketones in ionic liquids (C_4NPF_6) (reaction condition: 10 mL of styrene, 0.025 mmol of palladium catalyst [$Pd(dipy)_2][PF_6]_2$ and 1.8 mmol of benzoquinone. Reaction temperature was 60 °C, P_{CO} was 2 MPa and reaction time was 4 h).

introduce a suitable amount of solvent that used to dissolve the Pd^{2+} composite catalyst while keeping the appropriate viscosity of the system during the reaction.

It is also observed that the yield of the polyketone is a function of the concentration of 1,4-benzoquinone (BQ). In this system, BQ can oxidize Pd (0) to Pd (II) again, and BQ itself is turned into H_2BQ (Scheme II). Therefore, the dosage of BQ is important to the copolymerization of styrene and CO catalyzed by Pd (II). As in Figure 6, increasing the ratio of benzoquinone/ Pd^{2+} (mol/mol) from 10 to 70, cause

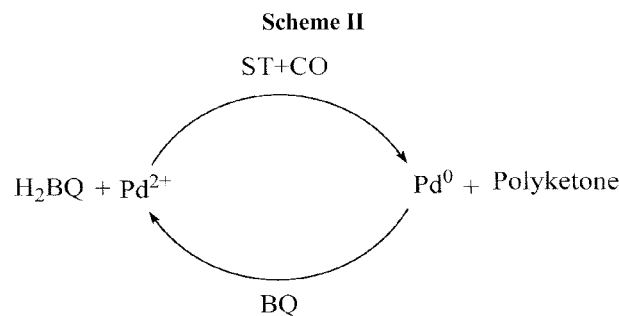


Table II. The Effect of Reaction Time on Yield of Polyketones in Ionic Liquids

Reaction Time (h)	Catalytic Activity (A) ^a		M_n ^b		PDI ^c	
	C_4NBF_4	C_4NPF_6	C_4NBF_4	C_4NPF_6	C_4NBF_4	C_4NPF_6
4	101	112	8,500	9,260	1.8	1.9
8	66	78	8,500	9,280	1.8	1.8
12	48	52	8,540	9,310	1.9	1.8
18	31	35	8,680	9,350	1.8	2.0

^a(A) Catalytic activity defined as g polyketone/(g·Pd·h). ^bDetermined by GPC relative to PS. ^cPDI is polydispersity index (M_w/M_n). Reaction conditions: palladium catalyst=0.025 mmol, styrene=10 mL, solvent=2 mL, benzoquinone=1.8 mmol, reaction temperature=60 °C, P_{CO} =2 MPa.

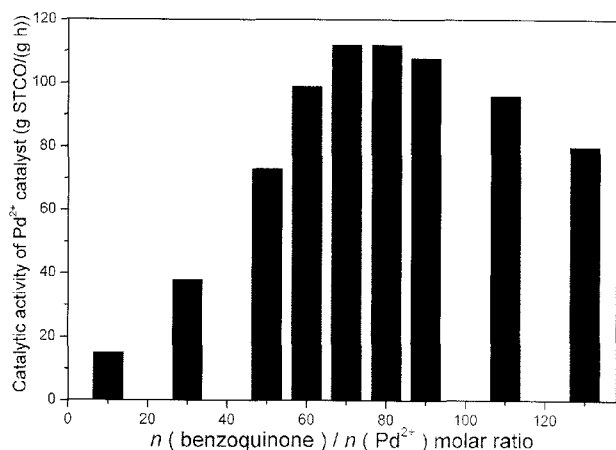


Figure 6. The effect of molar ratio of benzoquinone with Pd²⁺ on the catalytic activity of polyketones in ionic liquids (C₄NPF₆) (reaction condition: 10 mL of styrene, 2 mL of ionic liquid, 0.025 mmol of palladium catalyst [Pd(dipy)₂][PF₆]₂. Reaction temperature is 60 °C, P_{CO} is 2 MPa, and reaction time is 4 h).

the activity to increase from 15 to 112 g STCO /g·Pd·h. The optimum ratio of benzoquinone to Pd²⁺ ratio is at least 70. The reason is probably that when the concentration of benzoquinone is too high, benzoquinone cannot dissolve in styrene completely, causing the reaction system to transform into a heterogeneous state resulting in a decrease in catalytic activity.

Conclusions

Room temperature ILs as solvents for the synthesis of poly(1-oxo-2-phenyltrimethylene) showed lots of advantage over the conventional organic solvents which are commonly used in this system. It was found that different types of ILs affected the catalytic activity and recyclability of Pd²⁺ catalyst directly for this reaction. The different types of Pd²⁺ catalyst also exerted a great influence on the yield of polyketone. The results presented may be applied to find more suitable catalysts system in copolymerization of CO with styrene.

Acknowledgements. The authors are grateful for the financial support of this work by National Foundation of Natural Science of China (No. 20476080) and Tianjin Natural Science Foundation (No. 07JCYBJC00600). We are indebted to B. Wang, M.-H. Zhao, Y. Ti, H.-X. Zhang, and L.-N. Li of Tianjin University for very useful discussions.

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