TRANSITION METAL CATALYZED CO/OLEFIN CO-POLYMERIZATION IN ROOM TEMPERATURE IONIC LIQUIDS

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ABSTRACT

The palladium-catalyzed co-polymerization of styrene and CO in ionic liquids has been investigated. Using the hydrophobic ionic liquid, 1-hexylpyridinium bis(trifluoromethanesulfonyl)imide, as solvent gave improved yields and increased molecular weights compared to the same reactions in methanol. The influence of the ionic liquid solvent, the nature and concentration of the palladium catalyst, and recycling of the liquid catalyst system are discussed.

INTRODUCTION

Ionic liquids (ILs) are currently under intense scrutiny with respect to their potential application as green replacements for volatile organic solvents (1). A great deal of work is based on the premise that, since ionic liquids, in general, exhibit little or no vapor pressure, they are necessarily more environmentally friendly than VOCs (2). Of greater significance to their utilization as a 'new class of solvents', is the combination of properties presented by ILs, and an appreciation of the differences between ILs and other conventional solvent systems. A range of techniques, including liquid-liquid partitioning (3), structure-activity relationship analysis (4, 5), spectroscopic probes (6, 7), and computational modeling (8) are beginning to provide a detailed description of IL characteristics and the interactions between ILs and solutes dissolved in them.

ILs have been successfully applied as solvents in a wide range of synthetic reactions, particularly those employing homogeneous metal catalysts (1). There is a phenomenal growth in the development of new ionic liquid systems, in our fundamental understanding of their behavior (9), and in their applications for a range of reactions, especially in green chemistry. In polymer chemistry, chloroaluminate ILs have been applied to cationic (10) and metal-catalyzed oligomerization and polymerization of alkenes (11). In addition, oligomerization reactions appear particularly suited to non-Lewis acidic ILs. Ethene oligomerization and polymerization reactions have been reported (12), as have a number of metal-mediated atom-transfer polymerizations of acrylates (13). Styrene and methyl-methacrylate polymerization, using conventional organic initiators, is both fast and yields higher molecular weight polymers in ILs than under conventional conditions (14).

In this paper, we describe results from palladium-catalyzed insertion co-polymerization reactions of styrene with carbon monoxide in ILs that form alternating...
The synthesis of alternating co-polymers from carbon monoxide (CO) and olefins using palladium catalysts has been an active area of research throughout the last two decades (16). Co-polymerization of α-olefins with CO is typically performed in conventional organic solvents, such as methanol using cationic palladium or nickel-containing catalysts. The resultant polyketone polymers have perfect alternation of monomer units (17), attributed to the formation of cationic Pd-alkyl-oxo chelates (18) (Figure 1) from the catalyst precursors, in which CO insertion is kinetically favored over olefin polymerization. The polymers have desirable thermal, mechanical, and barrier characteristics. For example, in comparison to polyethylene (mp 125 °C), polyethylketone is a semicrystalline polymer with a much higher melting point (mp 257 °C). The increased crystallinity, and higher melting point reflects group contribution from the CO units.

![Figure 1. Schematic representation of polymerization reaction (R = -C₆H₆).](image)

The characteristics of the co-polymers can be modified and optimized by changing the polymer compositions, for example forming CO/ethylene/propylene terpolymers. In particular, ethylene- and styrene-based polyketones are of specific interest due to their excellent mechanical properties including high thermal and wear resistance, high density, and excellent mechanical properties. Commercial examples include Carilon® and Kadel®, however, it should be noted that, despite impressive advances in catalyst discovery and polymer synthesis, Shell has recently discontinued their effort to commercialize this class of polyketones.

Insertion polymerizations of alkenes are typically catalyzed by cationic organometallic complexes with weakly coordinating anions (19). The polymerization of olefins with CO is performed in solution under moderate pressure of CO, using homogeneous cationic transition metal catalysts, for example [Pd(dppp)₂][PF₆]₂ (dppp = 1,3-bis(diphenylphosphino)propane). The nature of the catalyst counter ion (20) and choice of solvent have significant roles in controlling the efficacy of the reaction. Milani et al. first showed that [Pd(bipy)₂][PF₆]₂ (bipy = 2,2'-bipyridine) was a highly active catalyst precursor (Figure 2) for styrene co-polymerization with CO, in methanol or trifluoroethanol (21). High productivity of polyketone (ca. 17.4 kg CP/g Pd) was obtained in 48 h, with 32 ppm palladium contamination in the resultant polyketone. Several systems have been reported for the asymmetric co-polymerization of styrenes and CO; notably Brookhart and coworkers (19) reported a bisoxazoline ligated palladium complex that produces highly isotactic and optically active polymer from CO and p-tert-butyl styrene.
Figure 2. Cationic palladium-alkyl oxo chelate catalysts for CO/olefin co-polymerization.

Polar non-coordinating ILs are attractive solvents for these reactions, since they may stabilize the solvent separated ion pairs that are necessary for high catalytic activity. Ionic liquids offer a unique set of solvent properties. The polarities of common imidazolium and pyridinium based ionic liquids have been reported to be similar to those of acetonitrile and methanol (6), though the values depend on the probes used and the contributions to polarity measured. Ionic liquids containing weak donor anions, such as hexafluorophosphate ([PF₆]⁻) or bis(trifluoromethanesulfonyl)imide ([NTf₂]⁻), tend to act as non-coordinating solvents. The low volatility and adjustable solvent parameters of ILs also make them attractive solvents for recyclable catalytic systems.

Room temperature ionic liquids containing poorly coordinating anions have been found to be excellent solvents for the Pd(II)-catalyzed polymerization of CO and styrene under relatively mild conditions. Good conversion numbers and high quality polymers can be obtained (15, 22). Both the catalyst environment and the relative solubility of styrene and CO can be adjusted by choice, or modification, of the ionic liquid solvent, which allows for fine control of the reaction parameters. Methanol and dichloromethane are current solvents of choice for these reactions, although in a move towards environmentally friendly, green processing, the co-polymerization of CO and ethene in water, using modified water-soluble catalysts (23), and in supercritical CO₂ using perfluorinated catalysts (24), have been reported.

EXPERIMENTAL

General

Styrene, CO (C.P. grade), benzoquinone, p-toluenesulfonic acid, 2,2'-bipyridine, 1,10-phenanthroline, and palladium acetate were obtained from commercial sources and used without further purification. 1-Butyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide (solvent grade, 98%) was purchased from Covalent Associates (Woburn, MA). Trihexyltetradecylphosphonium chloride was a gift from Cytec, Inc. The catalyst precursors (bipy)Pd(OAc)₂ and (phen)Pd(OAc)₂ were prepared according to literature procedures (25). ¹H and ¹³C NMR analysis of the co-polymers were carried out in 1:1 D₂-hexafluoroisopropanol (HFIPA-D₂):CDCl₃. IR spectra were obtained as KBr disks. Gel permeation chromatography was carried out using a Jordi mixed bed (250 mm x 10 mm) column with chloroform as the mobile phase and UV detection at 254 nm. All GPC samples and standards were prepared by dissolving 3-5 mg of polymer in 150 µL of hexafluoroisopropanol followed by dilution with 5 mL of chloroform. Molecular weights are determined relative to narrow molecular weight polystyrene standards.
1-Hexylpyridinium bis(trifluoromethanesulfonyl)imide, ([C₆pyr][NTf₂])

[C₆pyr][NTf₂] was prepared using the literature procedure described for [C₄mim][NTf₂] (26). Pyridine (1 equivalent) and bromohexane (1.1 equivalent) were stirred together under nitrogen at 70 °C for 4 days. Upon completion of the reaction, the pyridinium salt was washed with ethyl acetate to remove any unreacted starting materials and volatile solvents were removed under vacuum at 60 °C. The resulting pyridinium bromide was combined with 1 equivalent of Li[NTf₂] in water. [C₆pyr][NTf₂] separated as a denser, water immiscible phase. The product was washed repeatedly with water and dried under vacuum overnight (0.1 torr, 70 °C). Karl-Fischer titration of a typical sample showed 0.28 % water content. Treatment with an aqueous AgNO₃ solution showed no residual bromide. *H NMR (CDCl₃, 360 MHz): δ 8.82 (2H, d, J 5.54 Hz); 8.48 (1H, t, J 7.70 Hz), 8.06 (2H, dd, J₁ 6.78, J₂ 7.40 Hz), 4.60 (2H, t, J 7.40 Hz), 2.00 (2H, m), 1.60-1.30 (6H, m), 0.87 (3H, t, J 7.10 Hz).

Trihexyltetradecylophosphonium bis(trifluoromethanesulfonyl)imide. ([C₆H₁₃)₃P][NTf₂].

This was prepared by anion exchange of the chloride with Li[NTf₂] in analogy to the preparation of [C₆pyr][NTf₂].

General procedure for CO/styrene co-polymerization.

Catalyst precursors (bipy)Pd(OAc)₂ (10.6 mg, 0.028 mmol) and 2,2'-bipyridine (75 mg, 0.475 mmol) were weighed into a small vial. Methanol (0.4 mL) was added to dissolve the solids followed by addition of the ionic liquid (4.0 mL). The mixture was stirred to give a homogeneous solution. p-Toluenesulfonic acid (96.0 mg, 0.50 mmol) and 1,4-benzoquinone (247.0 mg, 2.285 mmol) were added to the Parr pressure reactor followed by the pre-catalyst/IL solution. Styrene (10 mL) was used to quantitatively transfer the IL solution into the reactor. The reactor was sealed, purged with CO, adjusted to the desired CO pressure, and heated to the polymerization temperature while stirring with a magnetic stirring bar. Upon completion of the reaction, methanol (100 mL) was added to the reactor and the resulting suspension was filtered. The co-polymer was washed with methanol and dried overnight in vacuo (0.1 torr). *H NMR (360 MHz): δ 6.4-7.5 (5H, m), 3.92-4.02 (1H, m), 2.73-2.96 (2H, m). ¹³C NMR (90.6 MHz): δ 209.7, 135.6, 129.2, 128.2, 128.0, 53.9, 42.9. FTIR (KBr disk): 3028, 2908, 1708, 1600, 1494, 1453, 698 cm⁻¹.

Catalyst solution recycling experiments.

Styrene and CO were co-polymerized as described above. The polymer was filtered off and washed with methanol. The filtrate was concentrated under reduced pressure, and the remaining IL/catalyst solution was extracted with hexane to remove residual organic co-catalysts (i.e., benzoquinone, hydroquinone, bipyridine). The IL solution was dried under reduced pressure. An additional amount of 2,2'-bipyridine (75 mg, 0.475 mmol) was added to this solution, which was used as the pre-catalyst solution as described for the general procedure above.
RESULTS AND DISCUSSION

CO/styrene co-polymerization reactions (Figure 3) were investigated in IL solutions, using a cationic Pd-bipy catalyst system consisting of LPd(OAc)$_2$ (L = 2,2'-bipyridine and 1,10-phenanthroline), excess ligand, benzoquinone, and p-toluenesulfonic acid. Pyridinium based ILs were screened initially due to the known reaction of palladium salts with the more common imidazolium ILs to form Pd-carbene complexes (27). The weakly coordinating [NTf$_2$]$^-$ anion was chosen over [BF$_4$]$^- \text{ or [PF}_6\text{]}^- \text{ to minimize coordination of the IL anion to the cationic palladium catalyst (28).}

Co-polymerization of CO and styrene in [C$_6$pyr][NTf$_2$] (Figure 1) gave styrene homopolymer as the major product (Table I, 1). Addition of methanol (10 % v/v to IL) suppressed polystyrene formation and enabled formation of the co-polymer in high yields (2). Methanol reacts initially with the catalyst precursor, L$_n$Pd$_2^{2+}$, and CO to form the [LPdC(O)CH$_3$]$^+$ species, which initiates the co-polymerization (16).

![Figure 3. Co-polymer initiation and chain propagation steps on the palladium catalyst.](image)

Table I. Effect of IL Solvent on the Co-polymerization of Styrene and CO.
(All reactions were performed at T = 70 °C, CO = 40 bar.)

| Trial | IL                  | Volume MeOH | TON | $M_w$ | $M_n$ | PDI  |
|-------|---------------------|-------------|-----|-------|-------|------|
| 1     | [C$_6$pyr][NTf$_2$] | 2           | 0   | PS$^c$| 9,700 | 4,700 | 2.1  |
| 2     | [C$_6$pyr][NTf$_2$] | 2           | 0.2 | 1.1   | 6,000 | 3,100 | 1.9  |
| 3     | [C$_6$pyr][NTf$_2$] | 2           | 0.2 | 0.7   | 10,000| 6,200 | 1.6  |
| 4     | [C$_6$pyr][NTf$_2$] | 2           | 0.2 | 1.2   | 7,900 | 4,200 | 1.9  |
| 5     | [C$_6$pyr][NTf$_2$] | 4           | 0.2 | 1.7   | 34,000| 25,300| 1.3  |

$^a$Determined by GPC relative to polystyrene standards. $^b$M$_w$/M$_n$. $^c$Isolated polymer was largely polystyrene.
Co-polymerization activity was dependent on both \([\text{C}_6\text{pyr}]\)[\(\text{NTf}_2\)] and methanol volumes. Decreasing the volume of IL to 1 mL gave a slight increase in the yield of co-polymer, but higher yields were obtained upon increasing the volume to 4 mL (Table I, 5, 6). The molecular weight of the co-polymer approximately doubled as the volume was increased from 1 mL to 4 mL. Increasing the amount of methanol (to a maximum of 10 vol %) resulted in a much more significant increase in both polymerization activity and molecular weight (7, 8).

The effects of pressure and temperature were investigated using the \([\text{C}_6\text{pyr}]\)[\(\text{NTf}_2\)]/methanol solvent system (Table II). Decreasing the reaction temperature from 70 to 50 °C resulted in a decrease in the TON from 1.1 to 0.7 kg CP/g Pd (Table II, 9, 10), while polystyrene was formed at 90 °C (Figure 4). In reactions run at 70 °C, high yields of co-polymer were obtained at 20 and 40 bar. At higher pressures (Trials 12-14, and Figure 5), the yield of polymer and TON decreased. The highest molecular weight values were obtained for co-polymers prepared at 40 bar.

| Trial | IL (mL) | MeOH (mL) | T (°C) | P (bar) | TON (kg CP/g Pd) | \(M_w^{a}\) (Mw/Mn) | M\(_n^{a}\) (kg CP/g Pd) | PDI\(^b\) |
|-------|---------|-----------|--------|---------|------------------|-------------------|----------------------|--------|
| 9     | 2       | 0.2       | 50     | 40      | 0.7              | 20,800            | 8,000                | 2.6    |
| 10    | 2       | 0.2       | 70     | 40      | 1.1              | 9,700             | 4,700                | 2.1    |
| 11    | 2       | 0.2       | 90     | 40      | 1.2              | 3,700             | 1,500                | 2.4    |
| 12    | 4       | 0.4       | 70     | 20      | 2.5              | 12,200            | 7,200                | 1.7    |
| 13    | 4       | 0.4       | 70     | 40      | 2.7              | 34,000            | 25,300               | 1.3    |
| 14    | 4       | 0.4       | 70     | 60      | 1.8              | 8,400             | 5,000                | 1.7    |
| 15    | 4       | 0.4       | 70     | 40      | 2.9\(^c\)        | 23,000            | 14,100               | 1.6    |
| 16    | 4       | 0.4       | 70     | 20      | 2.3\(^d\)        | 11,000            | 6,700                | 1.6    |
| 17    | 4       | 0.4       | 70     | 20      | 0.006\(^e\)      | 46,800            | 23,300               | 2.0    |
| 18    | 4       | 0.4       | 70     | 20      | \(0^f\)          |                   |                      |        |

\(^a\)Determined by GPC relative to polystyrene standards. \(^b\)M\(_w^{a}/M_n^{a}\). 
\(^c\)(phen)Pd(OAc)_2 (0.026 mmol). \(^d\)0.1 %w/w [C\(_6\)pyr]Br. \(^e\)0.5 %w/w [C\(_6\)pyr]Br. \(^f\)1 %w/w [C\(_6\)pyr]Br.

The productivity was higher than is typically observed with this catalyst system in methanol under similar conditions (0.6-2.2 kg CP/g Pd) (16, 29). Co-polymers produced in \([\text{C}_6\text{pyr}]\)[\(\text{NTf}_2\)] also had higher molecular weights (M\(_n = 25,000\)) than are obtained in methanol. The co-polymers showed a narrow polydispersity range (1.3-2.5) suggesting a single-site catalyst. The isolated co-polymers were pale yellow indicating little precipitation of Pd metal during the co-polymerization reaction. Characterization of polymer samples by \(^1\)H and \(^{13}\)C NMR and IR was consistent with a syndiotactic, alternating co-polymer structure (16).
Figure 4. TON (□) increases and $M_n$ (○) of polymer decreases with increasing temperature (polyketone was formed at 50 and 70 °C; polystyrene was produced at 90 °C). Experimental conditions: Styrene 10 mL, CO 40 bar, (bipy)Pd(OAc)$_2$ 0.028 mmol, 2,2'-bipy 0.475 mmol, IL 2 mL, MeOH 0.2 mL, TsOH 0.5 mmol, 1,4-benzoquinone 2.285 mmol.

Figure 5. TON (□) and $M_n$ (○) optimized at 40 bar CO pressure. Experimental conditions: 70 °C, Styrene 10 mL, (bipy)Pd(OAc)$_2$ 0.028 mmol, 2,2'-bipy 0.475 mmol, IL 4 mL, MeOH 0.4 mL, TsOH 0.5 mmol, 1,4-benzoquinone 2.285 mmol.

Using 1,10-phenanthroline as ligand in place of 2,2'-bipyridine resulted in a small increase in productivity, but the co-polymer had a lower molecular weight (Table II, 15). Excess ligand (> 15 eq/Pd) and benzoquinone (75:1 benzoquinone:Pd) were necessary for co-polymer formation. In their absence only polystyrene was produced.
It is evident that the type of cation, alkyl chain length, and the anion govern both the yield and the catalytic activity. Polymerization in the N-alkylpyridinium IL was most successful, yielding polymers with high molecular weight and with conversion numbers comparable or significantly greater than reactions performed in methanol (29).

Reaction rates may be controlled by the relative solubility parameters for CO and styrene in the ILs. Ferve et al. have shown the effects of changing alkyl-chain lengths of ILs on the hydroformylation of hexene (30). Increased alkyl-chain substitution increases lipophilicity and solubility of both hexene and CO. The success of the co-polymerization of olefins and CO would largely depend upon the ease of CO diffusion from the gaseous phase into the liquid phase.

An increase in the reaction temperature (from 50 °C to 70 °C) resulted in an increase in activity and molecular weight. These results are in accordance with the previous reports on olefin co-polymerization. When the temperature was raised to 90 °C, polystyrene was obtained as the thermodynamic product from the reaction. Higher partial pressure of CO had an adverse effect on the productivity. The yield of polyketone increased when the partial pressure of CO was increased to a maximum at 40 bar under the operating conditions used. When the CO pressure was increased to 60 bar, a significant decrease in both TON and Mn of the resulting polymer was observed, consistent with results in conventional solvents, where polymerization was inhibited at high CO overpressures (31). Using the optimized conditions, the effects of IL type were investigated by screening the reactions using [C₆pyr][NTf₂], [C₄mim][NTf₂], and [R₄P][NTf₂]. Using the imidazolium-based IL (Table I, 3) resulted in lower polymer yields, while no co-polymer was formed in a phosphonium IL (Table I, 4). In the phosphonium IL, this may be due to halide contamination in the ionic liquid from non-optimal exchange of anions during the metathesis step.

In order to determine the tolerance of the catalytic system to the presence of halide contaminants, the effect of small amounts of bromide anions on co-polymerization activity was determined in [C₆pyr][NTf₂]. Addition of 0.1 wt % of [C₆pyr][Br] to [C₆pyr][NTf₂] resulted in no change in activity or molecular weight (Table II, 16), while increasing the amount of bromide to ≥0.5 wt % resulted in complete inhibition of the co-polymerization reaction. Halides coordinate strongly to the open coordination site inhibiting catalyst activity. Therefore, ensuring that IL solvents are halide free is critical to achieve high activity and molecular weight; direct alkylation to alkylsulfate (32), trifluoroacetate (26), or triflate (26) salts can be used to prepare intrinsically halide-free ILs.

An initial attempt was made to recycle the IL catalyst solution. An IL solution recovered from a co-polymerization reaction was washed with hexane to remove spent organic co-catalysts. Co-polymerization with the recovered catalyst solution gave a lower yield, although the TON was still 1.9 kg CP/g Pd (Figure 6). Recycling the IL catalyst solution a third time gave a significantly lower yield and the polymer obtained was orange rather than pale yellow. Decreased activity is most likely due to Pd precipitation during the polymerization reaction or work up. In addition, the need to extract and replenish organic co-catalysts results in some mechanical loss. Despite these difficulties, we have shown the potential for catalyst recycling using IL solvents.
Figure 6. Recycling of catalyst/[C₆pyr][NTf₂] solution. The reduction of catalyst efficiency (TON) is indicative of loss of catalytically active species.

CONCLUSIONS

We have studied several catalytic polymerizations using ILs as reaction solvents, in order to assess their viability as clean, environmentally benign solvents for polymerization chemistry, and to investigate the influence on the catalytic efficiency of the highly ionic, yet non-coordinating solvent environment available in the ionic liquid systems. Results are presented from batch co-polymerization reactions of styrene and CO in ionic liquids using cationic Pd(II)-containing catalysts and are compared to control experiments performed using methanol as solvent. The data indicate that using an IL solvent system can give significantly better conversions of styrene to polymer using conventional Pd(II) catalysts than when methanol is used as solvent, with increased catalyst stability and turnover number. The use of ILs as solvents also provides routes to minimize catalyst leaching and to facilitate catalyst recovery and reuse.

We have shown that [C₆pyr][NTf₂] is an effective solvent for the palladium-catalyzed co-polymerization of styrene and CO. Catalyst productivity in [C₆pyr][NTf₂] approaches that obtained in polar non-coordinating solvents such as 2,2,2-trifluoroethanol (16), while opening the possibility of catalyst recycling. In addition, higher molecular weights and improved catalyst stability are observed in [C₆pyr][NTf₂] compared with methanol. Methanol acts as a chain transfer agent and a reductant for Pd(II) catalysts to inactive Pd(0) clusters. By replacing the bulk of the methanol with [C₆pyr][NTf₂], chain transfer and catalyst decomposition appear to be inhibited. Increased activity could be due to improved catalyst stability, increased rate of propagation, or both.

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