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# Polar, non-coordinating ionic liquids as solvents for the alternating copolymerization of styrene and CO catalyzed by cationic palladium catalysts†

**Marc A. Klingshirn, Grant A. Broker, John D. Holbrey, Kevin H. Shaughnessy* and Robin D. Rogers***

*The Department of Chemistry and Center for Green Manufacturing, The University of Alabama, Box 870336, Tuscaloosa, AL 35487-0336, USA. E-mail: kshaughn@bama.ua.edu; rdrogers@bama.ua.edu*

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**The palladium-catalyzed copolymerization of styrene and CO in an ionic liquid solvent, 1-hexylpyridinium bis(trifluoromethanesulfonyl)imide, gave improved yields and increased molecular weights compared to polymerizations run in methanol.**

Ionic liquids (ILs) have received significant interest recently due to their potential application as green replacements for volatile organic solvents.[1] Based on this promise, ILs have been successfully applied as solvents in a wide range of synthetic reactions, particularly those employing homogeneous metal catalysts.[2,3] The common imidazolium and pyridinium based ionic liquids have polarities similar to those of acetonitrile and methanol,[4] yet due to their weak donor anions, such as hexafluorophosphate or bis(trifluoromethanesulfonyl)imide ($NTf_2$), they act as non-coordinating solvents. The low volatility and adjustable solvent parameters of ILs also make them attractive solvents for recyclable catalytic systems.

Insertion polymerizations of alkenes are typically catalyzed by cationic metal complexes with weakly coordinating anions.[5–7] Polar, non-coordinating ILs are attractive solvents for these reactions, since they may stabilize the solvent separated ion pairs that are necessary for high activity. Chloroaluminate ILs have been applied to cationic[8–10] and metal-catalyzed[11,12] oligomerization and polymerization of alkenes. Chloroaluminate ILs are air- and moisture-sensitive, thus they have been supplanted by second generation ILs incorporating stable anions (*i.e.*, $[BF_4]^-$ or $[PF_6]^-$). To date the only examples of alkene polymerization in air-stable ILs are a report of ethylene oligomerization[13] and a brief patent claiming ethylene polymerization, both in $[C_4mim][PF_6]$ (Fig. 1).[14] Herein we report our initial studies on the suitability of ILs as solvents for the palladium-catalyzed, alternating copolymerization of styrene and CO (eqn. (1)).[5,15]

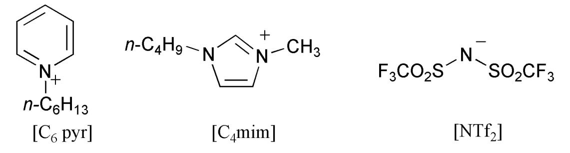
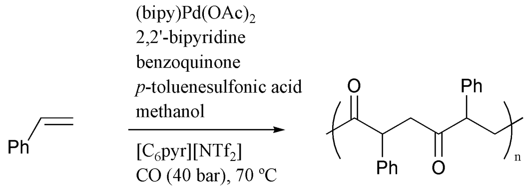


**Fig. 1**



(1)

The productivity of a standard catalyst system consisting of $LPd(OAc)_2$ (L = 2,2′-bipyridine and 1,10-phenanthroline), excess ligand, benzoquinone and *p*-toluenesulfonic acid was tested in IL solvents.[16] Pyridinium based ILs were screened initially due to the known formation of Pd–carbene complexes from imidazolium ILs.[17] The weakly coordinating $NTf_2$ anion was chosen over $[BF_4]^-$ or $[PF_6]^-$ to minimize coordination of the IL anion to the cationic palladium catalyst.[18] Copolymerization of CO and styrene in $[C_6pyr][NTf_2]$ (Fig. 1) gave styrene homopolymer as the major product (Table 1, run 1). Addition of methanol (10% v/v to IL) gave high yields of copolymer, while suppressing polystyrene formation (run 2). Methanol reacts with $L_nPd^{2+}$ and CO to form $[LPdC(O)OCH_3]^+$, which initiates the copolymerization.[5] Lower yields were obtained in an imidazolium based IL ($[C_4mim][NTf_2]$),[19] while no copolymer was formed in a phosphonium ionic liquid (run 4).

Copolymerization activity was dependent on both $[C_6pyr][NTf_2]$ and methanol volumes. Decreasing the volume of IL to 1 mL gave a slight increase in productivity, but higher yields were obtained upon increasing the volume to 4 mL (runs 5 and 6). The molecular weight of the copolymer approximately doubled as the volume was increased from 1 to 4 mL. Increasing the amount of methanol resulted in a more significant increase in productivity and molecular weight (runs 7 and 8).

The reaction parameters were further optimized using the $[C_6pyr][NTf_2]$/methanol solvent system (Table 2). 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)$^{-1}$ (Table 2, runs 1–2), while polystyrene was formed at 90 °C. In reactions run at 70

**Table 1** Solvent effects on the copolymerization of styrene and CO[a]

| Run | IL/mL | MeOH/mL | TON/kg CP (g Pd)$^{-1}$ | $M_w$[b] | $M_n$[b] | PDI[c] |
|---|---|---|---|---|---|---|
| 1 | $[C_6pyr][NTf_2]$ (2) | 0 | PS[d] | | | |
| 2 | $[C_6pyr][NTf_2]$ (2) | 0.2 | 1.1 | 9700 | 4700 | 2.1 |
| 3 | $[C_4mim][NTf_2]$ (2) | 0.2 | 0.7 | | | |
| 4 | $[C_{14}H_{29}P(C_6H_{13})_3][NTf_2]$ (2) | 0.2 | 0 | | | |
| 5 | $[C_6pyr][NTf_2]$ (1) | 0.2 | 1.2 | 6000 | 3100 | 1.9 |
| 6 | $[C_6pyr][NTf_2]$ (4) | 0.2 | 1.7 | 10000 | 6200 | 1.6 |
| 7 | $[C_6pyr][NTf_2]$ (4) | 0.1 | 1.4 | 7900 | 4200 | 1.9 |
| 8 | $[C_6pyr][NTf_2]$ (4) | 0.4 | 2.7 | 34000 | 25300 | 1.3 |

[a] $T$ = 70 °C, CO = 40 bar. See Electronic Supplementary Information (ESI†) for procedure. [b] Determined by GPC relative to polystyrene standards. [c] $M_w/M_n$ [d] Isolated polymer was largely polystyrene.

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† Electronic supplementary information (ESI) available: experimental details. See http://www.rsc.org/suppdata/cc/b2/b203367d/

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**Table 2** Optimization of the copolymerization of styrene and CO in [C$_6$pyr][NTf$_2$][a]

| Run | [C$_6$pyr][NTf$_2$]/mL | MeOH/mL | $T$/°C | $P_{CO}$/bar | TON/kg CP (g Pd)$^{-1}$ | $M_w$[b] | $M_n$[b] | PDI[c] |
|---|---|---|---|---|---|---|---|---|
| 1 | 2 | 0.2 | 50 | 40 | 0.7 | 20800 | 8000 | 2.6 |
| 2 | 2 | 0.2 | 70 | 40 | 1.1 | 9700 | 4700 | 2.1 |
| 3 | 2 | 0.2 | 90 | 40 | 1.2 | 3700 | 1500 | 2.4 |
| 4 | 4 | 0.4 | 70 | 20 | 2.5 | 12200 | 7200 | 1.7 |
| 5 | 4 | 0.4 | 70 | 40 | 2.7 | 34000 | 25300 | 1.3 |
| 6 | 4 | 0.4 | 70 | 60 | 1.8 | 8400 | 5000 | 1.7 |
| 7 | 4 | 0.4 | 70 | 40 | 2.9[d] | 23000 | 14100 | 1.6 |
| 8 | 4 | 0.4 | 70 | 40 | 2.3[e] | 11000 | 6700 | 1.6 |
| 9 | 4 | 0.4 | 70 | 40 | 0.006[f] | 46800 | 23300 | 2.0 |
| 10 | 4 | 0.4 | 70 | 40 | 0[g] | | | |

[a] See Electronic Supplementary Information (ESI†) for procedure. [b] Determined by GPC relative to polystyrene standards. [c] $M_w/M_n$ [d] (phen)Pd(OAc)$_2$ (0.026 mmol). [e] 0.1% (w/w) [C$_6$pyr][Br]. [f] 0.5% (w/w) [C$_6$pyr][Br]. [g] 1% (w/w) [C$_6$pyr][Br]

°C, high yields of copolymer were obtained at 20 and 40 bar, but the yield decreased at higher pressures (runs 4–6). The highest molecular weight values were obtained for copolymers prepared at 40 bar. Excess ligand ( > 15 eq./Pd) and benzoquinone (75 : 1 benzoquinone : Pd) were necessary for copolymer formation. In their absence only polystyrene was produced, while under these conditions thermal polymerization of polystyrene was surpressed. Using 1,10-phenanthroline as ligand in place of 2,2′-bipyridine resulted in a small increase in productivity, but the copolymer had a lower molecular weight (run 7).

Under the optimal conditions of 4 mL of [C$_6$pyr][NTf$_2$], 0.4 mL methanol, 40 bar CO and 70 °C, an average of 2.7 ± 0.2 kg CP (g Pd)$^{-1}$ was obtained over several runs. 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)$^{-1}$).[16,20] Copolymers produced in [C$_6$pyr][NTf$_2$] also had higher molecular weights ($M_n$ = 25000) than are obtained in methanol.[20,21] The polydisperities of the copolymers were narrow (1.3–2.5) suggesting a single-site catalyst. The isolated copolymers were pale yellow rather than the grey polymer produced in MeOH. Characterization of polymer samples by $^1$H and $^{13}$C NMR and IR was consistent with a syndiotactic alternating copolymer structure.[5]

Since IL purity is difficult to determine, the effects of small amounts of residual bromide on copolymerisation activity was studied. Addition of 0.1% (w/w) of [C$_6$pyr][Br] to [C$_6$pyr][NTf$_2$] resulted in no change in activity or molecular weight (Table 2, run 8), while increasing the amount of bromide to = 0.5% resulted in complete inhibition of the copolymerization 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.

An initial attempt was made to recycle the IL catalyst solution. An IL solution recovered from a copolymerization reaction was washed with hexane to remove spent organic cocatalysts. Copolymerization with the recovered catalyst solution gave a lower yield, although the TON was still 1.9 kg CP (g Pd)$^{-1}$ (Table 3, cycle 2). 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, extraction of the IL catalyst solution results in some mechanical loss. Despite these difficulties, we have shown the potential for catalyst recycling using IL solvents.

**Table 3** Recycling of the catalyst [C$_6$pyr][NTf$_2$] solution[a]

| Cycle | TON/kg CP (g Pd)$^{-1}$ | $M_w$[b] | $M_n$[b] | PDI[c] |
|---|---|---|---|---|
| 1 | 2.9 | 26300 | 12700 | 2.1 |
| 2 | 1.9 | 51900 | 32700 | 1.6 |
| 3 | 0.8 | 19200 | 11400 | 1.7 |

[a] See Electronic Supplementary Information (ESI†) for procedure. [b] Determined by GPC relative to polystyrene standards. [c] $M_w/M_n$

In conclusion, we have shown that [C$_6$pyr][NTf$_2$] is an effective solvent for the palladium-catalyzed copolymerization of styrene and CO. Catalyst productivity in [C$_6$pyr][NTf$_2$] approaches that obtained in polar, non-coordinating solvents such as 2,2,2-trifluoroethanol,[21] while opening the possibility of catalyst recycling. In addition higher molecular weights and improved catalyst stability are observed in [C$_6$pyr][NTf$_2$] compared with methanol. Methanol acts as a chain transfer agent and a reductant for Pd(II) catalysts to inactive Pd(0) clusters. By replacing methanol with [C$_6$pyr][NTf$_2$], 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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