

Supporting Information for
Copolymerization of Styrene and Carbon Monoxide in Room Temperature Ionic Liquids

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

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(trifluorosulfonylimide) ($C_4\text{mim}$ TFI, solvent grade) was purchased from Covalent Associates (Woburn, MA). Trihexyl tetradecyl phosphonium 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.¹ ¹H and ¹³C NMR analysis of the copolymers 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 μ l of hexafluoroisopropanol followed by dilution with 5 ml of chloroform. Molecular weights are determined relative to narrow molecular weight polystyrene standards.

1-Hexylpyridinium TFI ([C₆pyr][TFI]). [C₆pyr][TFI] was prepared in analogy to [C₄mim][TFI].² Pyridine (1 equivalent) and hexyl bromide (1.1 equivalent) were stirred together with moderate heating. Upon completion of the reaction, the pyridinium salt was washed with ethyl acetate to remove any unreacted starting materials followed by drying under vacuum. The resulting pyridinium bromide and LiN(O₂SCF₃)₂ were combined in water to give [C₆pyr][TFI] as a water immiscible oil. The product was washed repeatedly with water and dried under vacuum overnight (0.1 torr, 70 °C). Treatment with an aqueous AgNO₃ solution showed no residual bromide. Karl-Fischer titration of a typical sample showed 0.28 % water content. ¹H NMR (CDCl₃, 360 MHz): δ 8.82 (d, J = 5.54 Hz, 2H); 8.48 (t, J = 7.70 Hz, 1H), 8.06 (dd, J = 6.78, 7.40 Hz, 2H), 4.60 (t, j = 7.40 Hz, 2H), 2.00 (m, 2H), 1.60 - 1.30 (m, 6H), 0.87 (t, J = 7.10 Hz, 3H).

Trihexyl tetradecyl phosphonium TFI. This was prepared by anion exchange of the chloride with Li TFI in analogy to the preparation of [C₆pyr][TFI].

General procedure for CO/ styrene copolymerization. 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 (0.2470 g, 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 then adjusted to the desired CO

pressure and heated to the polymerization temperature while stirring with a magnetic stirring bar. Upon completion of the reaction, the methanol (100 mL) was added to the reactor and the resulting suspension was filtered. The copolymer was washed with methanol and dried overnight *in vacuo* (0.1 torr). ¹H NMR (360 MHz): δ 6.4 – 7.5 (m, 5H), 3.92 – 4.02 (m, 1H), 2.73-2.96 (m, 2H). 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 copolymerized 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 precatalyst solution as described for the general procedure above.

1. Milani, B.; Alessio, E.; Mestroni, B.; Sommazzi, A.; Garbassi, F.; Zangrando, E.; Bresciani-Pahor, N.; Randaccio, L. *J. Chem. Soc., Dalton Trans.* 1994, 1903-1911.
2. Bonhote, P.; Dias, A.-P.; Papageorgiou, N.; Kalyanasundaram, K.; Grätzel, M. *Inorg. Chem.* 1996, **35**, 1168-1178.