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

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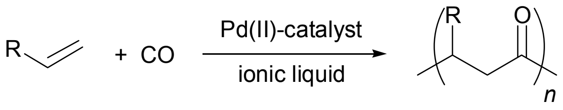
CO/olefin co-polymerization[1] offers routes to important new high density, industrial engineering polymers, including Carilon® and Kadel®, which have high thermal and wear resistance, and excellent mechanical properties. The polymerization of olefins with CO is performed in solution under moderate pressure of CO, using homogeneous cationic transition metal catalysts, for example $[Pd(dppp)_2][PF_6]_2$ [dppp = 1,3-bis(diphenyl-phosphino)propane]. The nature of the catalyst counter ion[2], and choice of solvent have significant roles in controlling the efficacy of the reaction.

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. 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[3], and in super critical $CO_2$, using perfluorinated catalysts[4] has been reported.

We have studied these catalytic polymerizations using ionic liquids 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 ionic liquids as solvents also provides routes to minimize catalyst leaching and to facilitate catalyst recovery and reuse with no loss of activity.



Schematic representation of polymerization reaction, in these studies R = $-C_6H_6$.

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