

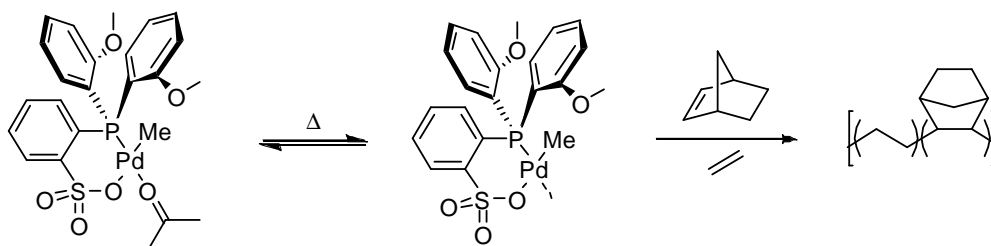
Copolymerization of Ethylene with Norbornene by Neutral Aryl Phosphine Sulfonate Palladium Catalyst

Andrea RAVASIO, Laura BOGGIONI, Incoronata TRITTO
Istituto per lo Studio delle Macromolecole, Consiglio Nazionale delle Ricerche,
Via E. Bassini 15, I-20133 Milano, Italy i.tritto@ismac.cnr.it

The strong need of copolymerizing olefins with polar functional monomers led to development of neutral nickel and palladium catalysts with monoanionic chelating mixed ligands (N⁺O, P⁺O, etc). Drent first reported that the *in situ* generated neutral Pd(II) catalyst, bearing a phosphonium-sulfonate ligand, effectively copolymerizes ethylene with acrylates to linear copolymers.^{1a} Well-defined neutral alkyl phosphine sulfonate Pd(II) species have recently been described and used in copolymerization of ethylene with a variety of functionalized monomers such as acrylates and vinyl sulfone.^{1b,c}

In recent years, there has been also enhanced interest around cyclic olefin copolymers (COCs), owed to their unique properties. Among the family of COCs the most versatile and interesting ones are the copolymers of ethylene with norbornene. Glass-like clarity as well as high thermal stability made such materials attractive as high-tech engineering materials.² Only one example of ethylene-norbornene copolymerization with a neutral alkyl phosphine sulfonate Pd(II) species was reported so far.³

Herein, we report on copolymerization reaction of ethylene and norbornene with a well defined $[(\kappa^2\text{-P}^+\text{O})\text{PdMe}(\text{dmsO})]$.⁴



The $[(\kappa^2\text{-P}^+\text{O})\text{PdMe}(\text{dmsO})]$ system at 90 °C afforded an amorphous E–N alternating copolymer. Molar masses increase with N concentration in the feed. Activities and molar masses increase with ethylene pressure. It is particularly noteworthy that this catalyst system showed alternating copolymers at relatively low [N]/[E], indicating a strong affinity of norbornene for the Pd active site. This unique nature thus led to rapid and exclusive formation of the alternating E–N copolymers. This is also revealed from the reactivity ratios.

References:

1. (a) Drent, E.; van Dijk, R.; van Ginkel, R.; van Oort, B.; Pugh, R. I. *Chem. Commun.* **2002**, 744. (b) Guironnet, D.; Roesle, P.; Runzi, T.; Gottker-Schnetmann, I.; Mecking S. *J. Amer. Chem. Soc.* **2009**, *131*, 422. (c) Bouilhac, C.; Rünzi, Mecking, S. *Macromolecules* **2010**, *43*, 3589.
2. Tritto, I.; Boggioni, L.; Ferro, D. R. *Coord. Chem. Rev.* **2006**, *250*, 212.
3. Skupov, K. M.; Marella, P. R.; Sismard, M.; Yap, G. P. A.; Allen, N.; Conner, D.; Goodall, B. L.; Claverie, J. P. *Macromol. Rapid. Comm.* **2007**, *28*, 2033.
4. We thank Stefan Mecking and Boris Neuwald for kindly supplying the catalyst.