

The Grubbs' first and second generation catalysts were occluded into cross-linked slabs of polydimethylsiloxane with volumes from 1 mm<sup>3</sup> to 1 cm<sup>3</sup> by swelling the polymer with catalyst and methylene chloride. Methylene chloride was evaporated under vacuum to yield occluded catalysts where their solvent was polydimethylsiloxane. These occluded catalysts were reacted with alkenes dissolved in H<sub>2</sub>O or H<sub>2</sub>O/MeOH mixtures that diffused into the polydimethylsiloxane to react by ring-closing metathesis and cross metathesis. Control experiments revealed that the catalysts remained occluded and metathesis did not occur in the solvent. Occlusion of these catalysts allowed commercially available Grubbs' catalysts to be used with H<sub>2</sub>O as the solvent while isolating the H<sub>2</sub>O sensitive ruthenium methylidene from exposure to H<sub>2</sub>O. Functional group selective experiments were carried out where the polydimethylsiloxane was an "active" membrane to exclude salts. Polydimethylsiloxane is a hydrophobic polymer, so the deprotonated salt of diallylmalonic acid did not diffuse into it while a diallylether diffused into it and reacted by metathesis. Thus, by controlling the polarity of reagents their reactivity can be controlled owing to the properties of polydimethylsiloxane rather than those of the Grubbs' catalysts. Occlusion of catalysts in polydimethylsiloxane has been shown to add new selectivities to mature catalysts.