517a Ethylene-Norbornene Copolymerizations Via Silica-Immobilized Ti Cgc-Inspired Polymerization Catalysts

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The copolymerization of ethylene and norbornene has seen a great deal of recent interest. Typically, ethylene-norbornene copolymers have high glass transition temperatures, high thermal stability, and high clarity, which makes the products of these copolymerizations viable for microelectronic applications, pharmaceutical packaging, and optical media. There have been many reports in the literature of the use of Group IV metallocenes, or the related constrained geometry catalysts (CGC), for this polymerization. However, all of the reports concerning CGCs have used homogeneous catalysts. In olefin (i.e. ethylene and propylene) polymerizations, the use of supported metallocenes and CGCs allow for synthesis of polymers with higher densities and higher degrees of crystallinity. By using a silica supported catalyst for the copolymerization of norbornene with ethylene, the polymer products could be tailored to better suit industrial needs.

We have developed a synthetic protocol to support a constrained geometry-inspired complex on silica such that the sites are more well-defined and isolated than materials synthesized via traditional methods. We have previously shown that the “patterned” precatalyst is substantially more active than traditionally immobilized CGC-type catalysts in ethylene polymerization. Here we show that this is also the case for ethylene-norbornene polymerizations, with catalysts prepared via traditional methods displaying little or no measurable activity. Furthermore, the “patterned” catalysts even displays increased activity compared to a homogeneous system. CGC-inspired catalysts synthesized via the “patterning” protocol also showed an ability to copolymerize functionalized norbornenes, for example quinoline-functionalized norbornene, with ethylene. This is in contrast to the catalysts prepared via traditional methods. Reported here is the first use of a silica-tethered catalyst for the copolymerization of norbornenes with ethylene.