Elucidation of Polymer Chain Growth in Syndiospecific Polymerization of Styrene in a Silica Nanotube Membrane with Metallocene Catalysts

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Research Background and Significance

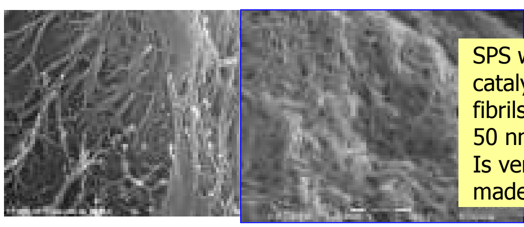
Understanding the mechanism of polymer chain growth in heterogeneous transition metal catalyzed olefinic polymerization is an important research problem in developing advanced commercial polymerization technology. The study of heterogeneous polymerization mechanism is difficult because reactions occur inside the pores of porous catalyst supports such as silica.

In this study, anodized nano-porous alumina membranes are used to anchor catalytic compounds onto the surface of pore walls for polymerization and to make a direct visual observation of polymer chain growth at a single catalytic site. This is a new technique that has never been attempted before. Syndiotactic polystyrene, a highly heat resistant semicrystalline polymer, is polymerized with $Cp^*Ti(OMe)_3$/MAO catalyst supported onto the silica layers formed inside the nanoporous membrane walls. This work demonstrates that advanced nanotechnology can be applied to developing a new understanding of heterogeneous catalytic polymerization of olefins and vinyl monomers.

Polymerization in a confined geometry

When monomers are polymerized in a confined geometry, polymerization rate and polymer chain growth can be restricted, resulting in unexpected reaction behavior and polymer properties. Nanoporous membranes can also be used to make polymer wires and rods through *in situ* catalytic polymerization.

Polymerization of sPS: Extraordinary polymer morphology



SPS with supported metallocene catalysts exhibit unusual morphology: fibrils and noodles of diameter less than 50 nm are formed. The observed morphology Is very different from that of polyolefins made with same types of catalysts.

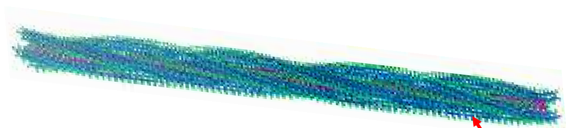
Metallocene catalyst supported onto nano-porous membranes

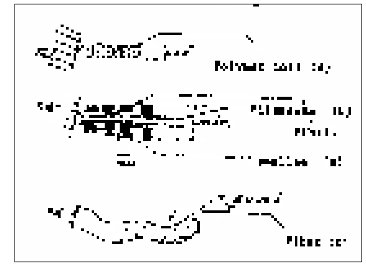
Nano membrane (anodisc from Whatman, avg. pore size: 200nm)

→ Coat pore walls with silica → Calcine at 350°C
→ Deposit Methylaluminoxane (MAO, cocatalyst) onto nano membrane pores
→ Impregnate the membrane in metallocene catalyst ($Cp^*Ti(OMe)_3$) solution
→ Support catalyst
→ Polymerization in gas or slurry phase → Dissolve alumina pore walls
→ Observe polymer chains grown inside silica tubes

Growth of polymer fibrils

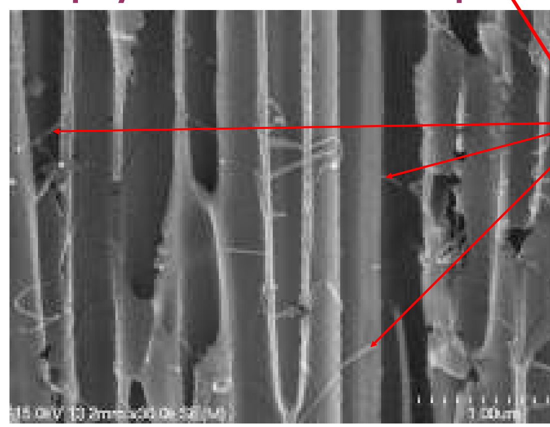
sPS polymer chain with TTGG conformation formed in presence of liquid diluent



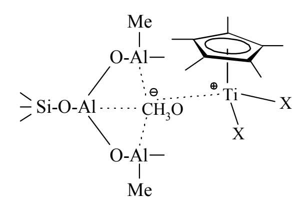


Proposed but unconfirmed mechanism of Polyethylene chain growth at a catalyst surface

sPS polymerization inside nanoporous membrane



"Single" polymer fibril from a Catalytic (Ti) site inside pore walls



where X= CH_3 or $Cp^*Ti(OMe)_3$

$Cp^*Ti(OMe)_3$/MAO catalyst

Proposed polymer chain growth mechanism