SFB TRR 102

Polymers under Multiple Constraints

Polymer- & Soft-Matter-Webinar

Tuesday, 19th January 2021

at: **5.15pm**

Online via Zoom!

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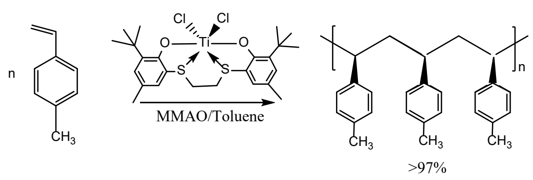
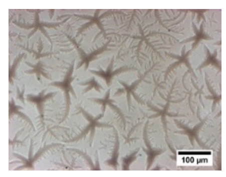
"From Isotactic Polystyrene (iPS) or Poly(*p*-methyl styrene) (i*p*PMS) to Semicrystalline iPS / POSS Hybrid Materials"

Nanostructured organic-inorganic hybrid materials are attractive families of structural and functional polymers with designed architectures and tailor-made property profiles. Hybrid molecules combine the good properties of ceramics, like mechanical reinforcement, flame retardancy and thermal stability, with easy processability of organic polymers. Functionalized nanosiliactes and silicate nanomolecules have attracted considerable attention in materials sciences because of their very high versatility with respect to molecular design of hybrid nanoparticles and unprecedented property combinations. Semicrystalline isotactic polystyrene (iPS) and syndiotactic polystyrene (sPS) are specialty engineering plastics which exhibit improved stiffness and higher dimensional stability as compared to atactic PS. Contrary to sPS, iPS does not crystallize during polymerization and stays soluble. However during melt-compounding or by annealing iPS crystallizes.

In the present work, the synthesis of iPS is realized by homogeneous catalytic styrene polymerization on a MAO-activated titanium bisphenolate catalyst, in the presence of a non-conjugated diene acting as chain transfer agent (CTA) leading to vinyl-terminated iPS (vinyl-iPS). The same catalytic system was tested for the coordination polymerization of *p*-methyl styrene (*p*MS).[1] (reaction scheme and optical micrograph of a i*p*PMS film below)





Crystalline nanostructured inorganic-organic hybrid materials containing isotactic iPS were prepared by means of hydrosilylation coupling of vinyl-iPS with octakis (dimethylsilyloxy) silsesquioxane (Q_8M_8H). *Via* fractionation, it is possible to isolate well-defined linear hybrids containing one iPS chain and seven ethyl groups per silica core (iPS-$Q_8M_8E_7$) as well as star-shaped hybrids containing up to eight iPS side chains(iPS$_{6-8}$-Q_8M_8).[2] These new iPS/polyhedral oligomeric silsesquioxane hybrid materials crystallize when the number average molar mass of iPS side chain exceeds 5500 g.mol. Contrary to classical semi-cristalline polymers, measurements by means of broadband dielectric spectroscopy reveal a reduction of the mean relaxation time by up to 1 decade.[3]

1. Wu, T. Valencia, L.; Pfohl, T.; Heck, B.; Reiter, G.; Lutz, P. J.; Mülhaupt, R. Fully Isotactic Poly(p-methylstyrene): Precise Synthesis via Catalytic Polymerization and Crystallization Studies. *Macromolecules* **2019,** 52, 4839-4846
2. Vielhauer, M.; Reiter, G.; Lutz, P. J.; Mülhaupt, R. Linear and Star-shaped POSS Hybrid Materials Containing Crystalline Isotactic Polystyrene Chains. *J. Polym Sci., Part A: Polym. Chem.* **2013,** 51, 947-953.
3. Tress, M.; Vielhauer, M.; Lutz, P. J.; Mülhaupt, R.; Kremer, F. Crystallization-Induced Confinement Enhances Glassy Dynamics in Star-Shaped Polyhedral Oligomeric Polysilesquioxane–Isotactic Polystyrene (POSS–iPS) Hybrid Material. *Macromolecules* **2018,** 51, 504-511.

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