Polymers under Multiple Constraints

Polymer- & Soft-Matter-Seminar

Tuesday, 18th February 2014

at: 5.15 pm

VSP1 1.26, Von-Seckendorff-Platz 1, 06120 Halle

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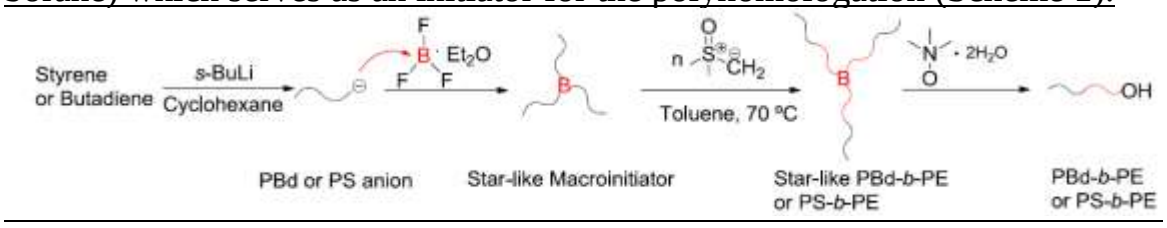
" WELL-DEFINED POLYETHYLENES AND POLY-ETHYLENE-BASED BLOCK COPOLYMERS BY ANIONIC POLYMERIZATION AND POLYHOMOLOGATION"

Access to model (high degree of structural, molecular weight and compositional homogeneity) polyethylenes (PEs) and PE-based block copolymers is necessary in order to elucidate the structure-properties relationships, which are very important for polymer performance. The synthesis of such polymers requires a truly living process. These approaches usually require high vacuum techniques, which are demanding, time consuming and leads to a small quantities of products. Nevertheless, this is a small price to pay given the tremendous potential of model macromolecules for selecting the appropriate structures needed for specific applications. Our group is using the following two methodologies to synthesize PEs and PE-based block copolymers:

a) Anionic polymerization and Hydrogenation Hydrogenation of 1,4-polybutadiene with various architectures (star, comb, dendritic, etc.) synthesized by anionic polymerization high vacuum techniques and appropriate post polymerization chemistry [1]. A few examples will be given, showing the importance of access to a variety of well-defined structures for a deeper understanding of polyethylene performance.

b). Combination of Anionic polymerization and Polyhomologation

Recently, Shea developed a novel polymerization methodology leading to perfectly linear PEs [2]. The general reaction scheme involves the formation of an organoboron zwitterionic complex between a methylide (monomer) and a trialkylborane Lewis acid (initiator) which breaks down by the intramolecular 1,2-migration. As a consequence, the methylene group of methylide is randomly inserted one by one into the three branches of the trialkylborane leading to a 3-arm PE star. The resulting star is subsequently oxidized/ hydrolysed to give perfectly OH-end-capped linear PEs. By combining anionic polymerization and polyhomologation, through a "bridge" molecule (BF3OEt2), a novel one-pot methodology was developed for the synthesis of PE-based block copolymers [3]. The anionically synthesized macroanion reacts with the "bridge" molecule to afford a 3-arm star (trimacromolecular borane) which serves as an initiator for the polyhomologation (Scheme 1).



Scheme 1. Synthesis of PE-based diblock copolymers by combining anionic polymerization and polyhomologation

References

[1] N. Hadjichristidis et al., Macromolecules 2000, 33, 2424-2436.

[2] J. Luo, K. J. Shea. Acc. Chem. Res. 2010, 43, 1420-1433.

[3] N. M. Neisius, B. Plietker, Angew. Chem. Int. Ed. 2009, 48, 1-5.

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