Public Release: Ring Opening Polymerization of Cyclic Siloxanes by PFLAs

Sometime ago[1] our research group began studies on the preparation of highly crosslinked polysiloxanes similar to those detailed in the literature.[2-4] In particular, our interest has focused on the polymerization of cyclic siloxanes bearing Si-H functionalities with the ultimate goal of producing castable resins that give rise to elastomers with low T_g and very high decomposition temperatures. As an offshoot of work conducted on the aqueous polymerization of isobutene (IB) using Group 13 perfluoroarylated Lewis acids (PFLAs)[5] we began preliminary investigations into the ring opening polymerization (ROP) of pentamethylcyclopentasiloxane (D_5^H) under similar reaction conditions. These introductory experiments have shown that $Al(C_6F_5)_3$ is not active for the polymerization of D_5^H in aqueous media despite being highly active for the polymerization of IB under similar reaction conditions.[1] These studies also showed that polymerization of bulk D_5^H using $Al(C_6F_5)_3$ leads to the rapid generation of a highly crosslinked polymer with concomitant gas evolution. These polymers are completely insoluble in hydrocarbon solvents (e.g. toluene, tetrahydrofuran, and acetone) and are produced in high yields at ambient reaction temperatures in very short reaction times (ca. 1 min). Moreover, both the resultant polymer and the polymerization behavior of these systems differ greatly in comparison to analogous reaction using $AlBr_3$ (i.e. standard cationic ROP). It is believed that polymerization occurs via a mechanism proposed by Polish researchers[6] on polymerization of D_4^H with $B(C_6F_5)_3$. Interestingly, polymerization of dilute toluene solutions of D_5^H with $Al(C_6F_5)_3$ did not lead to the generation of polymer, at least within a short period of time (ca. 15 min). Future studies on these polymerizations (in both bulk monomer and in aqueous media) with $Al(C_6F_5)_3$ as well as other PFLAs are ongoing.

References:

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