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Polystyrene with Dendritic Branching by Convergent Living Anionic Polymerization

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Abstract:

The synthesis of two types of polystyrene with dendritic branching was achieved through the development of a novel method that combines living anionic polymerization with a convergent process in a one-pot reaction. The method is based on the slow addition of a reactant such as 4-(chlorodimethylsilyl)styrene (CDMSS), which contains a polymerizable vinyl group and a moiety capable of undergoing quantitative S_N2 reaction, to a solution of living polystyryl anions. The sequence of reactions results in star-shaped polymers with the initial chains forming the arms and the residue from the CDMSS forming a hyperbranched core. Different amounts of styrene monomer were added along with the CDMSS in order to increase the molecular weight between branch points. The molecular weights and polydispersities of the dendritic polystyrenes were characterized by GPC coupled with MALLS. The molecular weights of dendritic polystyrenes without added comonomer corresponded to dendritic growth of the core of 3.1-3.4 average generations with polydispersities less than 1.5. The observed narrow molecular weight distributions were interpreted using a kinetic model that relates increased steric hindrance around the reactive site to the reaction rate constants of different size dendritic polymers formed during the reaction. Adding a comonomer along with the coupling agent allowed for the synthesis of high molecular weight dendritic polystyrene (up to M_n > 600 000 g/mol) and generational growth approaching an average of six generations. Intrinsic viscosities of all dendritic polystyrenes produced were found to be much lower than that of linear polystyrene. Thermal analysis of the dendritic polystyrenes showed that T_g versus molecular weight corresponded well to that of linear polystyrene normalized to the number of end groups, being slightly higher due to the effect of branching.