590c Understanding the Structure Development in Hyperbranched Polymers: Comparison of Simulations and Experimental Results

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UNDERSTANDING THE STRUCTURE DEVELOPMENT IN HYPERBRANCHED POLYMERS: COMPARISON OF SIMULATIONS AND EXPERIMENTAL RESULTS

Hyperbranched polymers are used in many applications as blend additives and melt modifiers because of their properties such as the low viscosity and high solubility [1]. In addition, the presence of a large number of functional end groups offers the possibility for further modification for their use in various other applications. However, these materials have several drawbacks, including broad molecular weight distributions, irregular arm growth and poor mechanical properties due to the absence of entanglements.

Hyperbranched polymers can be obtained by the step-growth polymerization of trifunctional (B_3) and difunctional (A_2) monomers. The conventional procedure in step-growth polymerization is to mix all reactants together at the beginning of the reaction. When the monomers are highly reactive, polymerization reaction can be carried out by the dropwise addition of A_2 solution into B_3 solution or vice versa. This synthesis method offers advantages like control of structural regularity and prevention of premature gelation when compared with the conventional method [2].

Structure development in hyperbranched polymers prepared by oligomeric A_2+B_3 approach was investigated by experimental studies and kinetic Monte-Carlo simulations. In both simulations and experiments, hyperbranched polymers were produced by the slow addition of A_2 onto B_3. Experimental studies performed using a cycloalipthatic diisocyanate (A_2) and a triamine (B_3), showed strong influence of solution concentration on the gel point and the extent of cyclization in the polymers formed. In polymerizations conducted at a solution concentration of 25% by weight gelation took place at the stoichiometric ratio $[A_2]/[B_3]=0.886$. In very dilute solutions, such as 5% solids by weight, no gelation was observed although the stoichiometric amount of A_2 added well exceeded the theoretical amount for gelation. Both experimental studies by size exclusion chromatography (SEC) and kinetic Monte-Carlo simulations demonstrated a gradual increase in polymer molecular weights as more A_2 is added onto B_3. This was followed by a sharp increase in the polymer molecular weight as the gel point is approached. A very similar behavior was observed for the polydispersity values of the polymers formed. Kinetic Monte-Carlo simulations performed at different cyclization ratios showed very good agreement with experimental results.

Experimental and simulation results with different synthesis procedures will be presented. Evolution of molecular weight, molecular weight distribution (polydispersity), degree of branching and degree of cyclization with the addition of B_3 onto A_2 and A_2 onto B_3 will be compared. Also, the effect of the extent of cyclization on the molecular weight of the molecules will be discussed.

1. Voit B (2000), Journal of Polymer Science Part A: Polymer Chemistry, 38:2505

2. Hanselmann R, Hoelter D, Frey H (1998), Macromolecules, 31:3790