Melt Rheology of Dendritically Branched Polystyrenes

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Abstract:

Unique rheological properties of combined low melt viscosity and high melt elasticity are reported for a novel series of dendritically branched polystyrenes. Unlike previous studies, dendritically branched materials having different molecular weights but all possessing the same number of generations are studied; this allows the determination of true scaling relationships. Zero shear viscosities scale with the second power of molecular weight until corrected to a state of constant free volume, upon which they scale with the first power of molecular weight. Importantly, the steady state shear compliance for the materials increases with increasing molecular weight and is very large compared to other chain architectures. This finding holds potential technological importance as it may be possible to simultaneously decrease viscosity and increase elasticity by blending with these novel structures. Dynamic light scattering and small-angle neutron scattering studies demonstrate the self-similar nature of these highly branched polymers, thereby establishing that the chain architecture is well-defined. Evidence of entanglements is missing. Remarkably, this implies that it is possible to prepare unentangled polystyrenes having a molecular weight in excess of 1 000 000 (g/mol). Melt dynamics are complex; exhibited behavior encompasses aspects of both classical Rouse-Zimm response and the power-law behavior associated with fractal or gelling systems. Neither Rouse-Zimm nor power-law relaxation time distributions are capable of quantitatively describing the data. However, the corrected viscosity scaling and the viscosity shear thinning behavior are in rough agreement with a theory of polymeric fractals proposed by Muthukumar [*J. Chem. Phys.* **1985**, *83,* 3161].