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Unravelling Popular Myths in the Rheology of Entangled Polymer Melts RICHARD P. WOOL, Department of Chemical and Biomolecular Engineering, University of Delaware, Newark DE 19716 — Myth No 1: Constraint release and Chain End Fluctuation coupled with Reptation dominate stress relaxation of highly entangled chains. Fact: Experiments show that Percolation processes account for about 50% of the relaxation, coupled with deGennes Reptation dynamics. In fact, the random coils are not relaxed (via Neutrons) when the stress (Birefringence) goes to zero, a critical prediction of the percolation mechanism, which is not in violation of the stress-optical law.. Myth No 2: The Packing Length Entanglement Model for the critical entanglement molecular weight, $M_e = 354 \text{ p}^3$, provides a fundamental description of entanglements at the molecular level. Fact: Experiments show that the Packing Length model is fundamentally incorrect in all its predictions of rheological properties via $M_e \sim [M_o/C_\infty]^3$, especially at the nanoscale, as well as the bulk. This is due to an incidental relationship between the monomer molecular weight M_o and the characteristic ratio C_{∞} for vinyl type polymers. The correct entanglement model is given by $M_e \sim C \infty M_o$. Myth No 3: The Glass Transition T_g is dominated by Segmental Dynamics and Free Volume: Fact: Experiments show that T_g is dominated by the cluster dynamics of anharmonically interacting fractal aggregates which range from 1-100 nm in size (ave ~ 5 nm), as described by the TFT. In nanoconfined thin films, the segmental dynamics does not change much while huge decreases in T_g can be observed due to cluster size effects.

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