# RHEOLOGICAL PROPERTIES AND MODEL LINEAR AND BRANCHED HOMOPOLYMER TOPOLOGIES

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For a better understanding of the extent of branching and its influence on the rheological properties, well-defined linear and branched (comb) model polymers of Poly(p-methylstyrene) (PpMS) and Polystyrene (PS) with a low degree of branching were synthesized. The branching degree as well as the molecular weight of the branches was systematically varied, ranging from slightly entangled (15 kg/mol) to fully entangled (42 kg/mol) branches with a branching degree from 0.1 to 1 mol% (2-15 branches per backbone).

The melt rheological properties of the linear and comb polymers were obtained for both oscillatory shear and uniaxial extensional flow. Using the so-called van Gurp-Palmen plot [1], clear differences between both synthesized topologies are clearly seen (Fig. 1a). The appearance of a second minimum for lower values of the complex modulus in shear is a clear indication of a second relaxation process due to the entangled side chains of the comb [2-5]. The presence of the entangled side chains is also responsible for the observed strain hardening (i.e. positive deviation from the linear viscoelastic behavior) obtained in extensional viscosity experiments [6], as compared to the linear polymers (Fig. 1b). These results validate the presence of a low degree of entangled branches in the current comb polymers synthesized [7].

Correlations between the non-linear behavior and polymer topologies are further investigated by medium- (MAOS) or large amplitude oscillatory shear (LAOS) in combination with Fourier-Transform rheology (FT-Rheology). The relative intensities and phases of higher harmonics (in particular $I_{3/1}$ and $\Phi_3$, for the third harmonic) as well as the non-linear coefficient Q [8] are used to quantify the inherent mechanical non-linearity, e.g. between linear polymers and polymers with different topology.

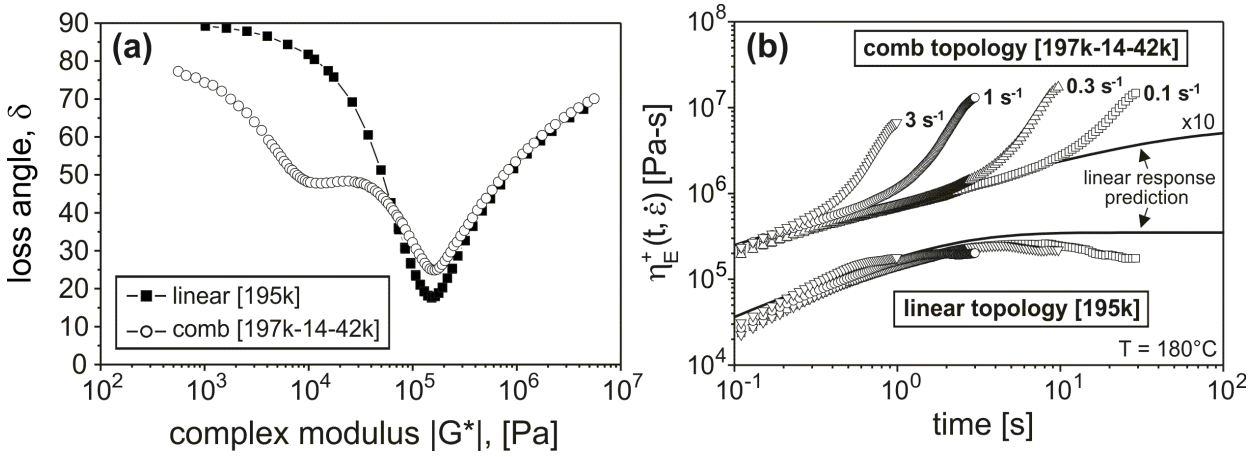


Figure 1: comparison between linear PpMS ($M_w \approx 195$ kg/mol) and PpMS comb ($M_{w,\ backbone} \approx 197$ kg/mol, number of branches = 14; $M_{w,\ side\ chains} \approx 42$ kg/mol) at 180 °C: (a) van Gurp Palmen plot, (b) extensional flow measurements (strain rates of 0.1- 3 $s^{-1}$).

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