POLYMERS IN FAST FLOW: LINKING RHEOLOGY WITH STRUCTURE

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Polymer processing operations involve fast flows and large deformation rates. As a result, the polymer flow properties during processing cannot be determined from measurement of their linear viscoelastic functions, which merely describe relaxation from small deviations from equilibrium. In strong flows, the polymer molecular configurations deviate strongly from their equilibrium configurations. This deviation is particularly apparent in extensional flows encountered in many processing operations such as fiber spinning and film blowing. As a step towards a platform for the rational design of new molecules and polymer processing operations, we here report rheological and structural measurements of specific model polymers in controlled extensional flow. We illustrate the techniques with two special architectures: A star polymer synthesized at the Technical University of Denmark and a ring polymer synthesized at Pohang University of Science and Technology in Korea. Both polymers have a polystyrene backbone. Due to the atactic nature of the backbone, crystallization is avoided and the samples can be quenched rapidly below the glass transition temperature for studies of molecular configurations ex-situ. The rheological technique employed is that of Filament Stretching Rheology which allows for measurement of steady extensional viscosity.

The star molecule is compared with a linear molecule of the same span length. While the star molecule relaxes slower than the linear molecule in linear viscoelastic characterization, the steady extensional viscosity at large rates of the star and the linear molecules are identical. This can be understood from the fast flow configuration that we determine from small angle neutron scattering. For ring molecules, an even more dramatic effect is observed. While the zero shear-rate viscosity of a ring molecule is more than an order of magnitude smaller than that of a linear molecule of the same contour length, their extensional viscosity in strong extensional flow are identical.