Entangled Polymer Melts in Extensional Flow

Many commercial materials derived from synthetic polymers exhibit a complex response under different processing operations such as fiber formation, injection moulding, film blowing, film casting or coatings. They can be processed both in the solid or in the melted state. Often they may contain two or more different polymers in addition to additives, fillers or solvents in order to modify the properties of the final product. Usually, it is also desired to improve the processability. For example the supplement of a high molecular weight component improves the stability in elongational flows. On the other hand, addition of low-volatility solvents to polymers is also a common industrial practice that others a means for lowering the T_g of the polymers. Moreover industrial polymers present a wide distribution of chain lengths and/or branched architectures that strongly influence their response.

Understanding the behaviour of polymer melts and solutions in complex non-linear flows is crucial for the design of polymeric materials and polymer processes. Through rheological characterization, in shear and extensional flow, of model polymer systems, i.e. narrow molar mass distribution polymer melts and solutions or well defined polymer molecules architecture, researchers develop constitutive equations that can relate the stress induced into a material with its flow deformation history. Indeed experiments on samples with well-defined structure supply data that can be compared with models.

Current models have been shown to be quite successful in describing the dynamics of polymers although they are still continuously challenged by new experimental data on model polymer systems. At the same time, new methods for generating extensional flows [McKinley and Sridhar (2002), Sentmanat (2004), Bach et al. (2003b)] are being constantly refined to improve the quality of the data and to explore a wider range of rates and deformations. Moreover, recently rheometry methods have been supplemented by other techniques such as dielectric spectroscopy that can probe chain dynamics and neutron scattering which can monitor macromolecular chain orientation associated with induced flow fields. This work concerns linear and non-linear rheology of polystyrene melts and solutions coupled with neutron scattering experiments. The aim of this thesis is to investigate the extensional properties of well characterized polymer samples and provide new experimental data on extensional rheology that can validate constitutive models. Moreover we show how the extensional technique may be used in combination with small-angle neutron scattering (SANS) to perform single chain structural studies after uniaxial elongation both after steady extensional flow and at several times during true stress relaxation. Extensional experiments have been performed on a Filament Stretching Rheometer (FSR), placed at the Technical University of Denmark (DTU), equipped with an online controlled scheme that allows to operate in controlled strain rate or controlled stress mode. High temperatures measurements can be performed due to an oven that surrounds the sample environment. Also a new implemented version of the device, named VADER 1000, has been employed to prepare the neutron scattering samples. The reduced dimension, compared to the FSR, and the particular design of the oven meets the requirement of fast cooling of the sample, so that it can freeze the particular molecular orientation of the chains at different stages of the stretching or relaxing of the sample.