In extensional flow of entangled polymer liquids, fracture may happen when the stretch rate is fast enough (Fig.1). High-speed imaging shows that the local shear rates near the crack tip can be 3 orders of magnitude higher than the stretch rate imposed during uniaxial extension [1, 2]. For entangled polymer systems, such high shear rates correspond to the frequencies close to the third crossover point (in the glassy region) in linear viscoelastic (LVE) measurements [1]. This observation suggests that fracture happens in a much shorter length scale than entanglement strands, and thus the number of entanglements per chain (Z) may be an unimportant parameter in fracture.

In this work we investigate two groups of entangled polymer liquids. In Group I we compare polystyrene (PS) solutions at the same concentration. The samples have the same number of Kuhn segments per entanglement strand ($N_e$), but have different values of Z. We also investigate the effect of solvents in this group. In Group II we compare PS solutions at different concentrations (i.e. different $N_e$) but with the same Z.

We first perform LVE measurements up to the frequency at the third crossover point. It has been experimentally confirmed that the distance between the first and second crossover points is related to Z for both melts and solutions [3]. We here experimentally show that the distance between the second and third crossover points is related to $N_e$ for both melts and solutions. We then stretch the samples in uniaxial extensional flow. We show that the critical strain at fracture decreases with increasing stretch rate, and reaches a constant value at faster stretch rates. The value of the constant critical strain seems to be related to the maximum stretch ratio of the polymer chain (determined by $N_e$), but not influenced by Z. The results are also compared with the critical strain of chemically crosslinked polymer networks.

References