The thesis focuses on the determination of the physical origin of chain stretch in complex branched polymers. The uniaxial extensional rheology of linear polymers is rate dependent and the onset rate of experimental strain hardening (the macroscopic consequence of chain stretch) is equivalent to the theoretical prediction of the inverse Rouse time. The molecular dynamic picture becomes more complicated when introducing two or more branch points. We study well-defined comb polymers (Roovers, 1979) with long molar mass of backbone $M_b$ and rather short arms. When systematically doubling the number of entanglements of the arms while keeping the $M_b$ constant, the onset of chain stretch occurs at earlier rates. This can be rationalized by accounting for the effect of dynamic tube dilation and extra drag from the arms which results in an effectively slower stretch relaxation time. We modify the original differential pom-pom model by introducing drag strain coupling and by specifying the coupling of stretch between adjacent backbone segments. The model is validated successfully by comparison with a wide variety of combs (with different molecular features) and a wide range of extensional rates. At high rates, the maximum stretch condition is reached and branch point withdrawal occurs, when arms are first oriented and then withdrawn into the stretched backbone tube segments, first from the free ends and then gradually progressing towards the centre.

Moreover, our study focuses on the effects of the environment on the reptation and fluctuations of model H and comb polymers. By systematically varying the length of the linear chains, we study the acceleration factor related to the arm and backbone relaxation times. The acceleration factor has a strong dependence on the length of the linear chains. We model the SAOS data using the Time Marching Algorithm by estimating a priori whether the linear polymer would be taken as a theta solvent or whether the reptation occurs in a skinny tube. The criterion for this estimation is based on the relaxation time scale separation between the linear matrix and the H or comb.