The need for dynamic materials which can self-assemble in a well-defined fashion is irrefutable. Exploiting modern polymer and supramolecular chemistry the concept of self-assembly has evolved significantly. On the other hand, characterization techniques such as rheology and X-ray scattering have been an inalienable part of supramolecular polymers. Although the analysis of supramolecular polymer dynamics based on linear rheology has improved a lot recently, there are a large number of insecurities behind the conclusions, which originate from the complexity of these novel systems. The comparison of different models and approaches on the linear rheology of these complex materials is therefore, inevitable (Chapter one). Above all, it is important to focus on the parameters affecting the rheology of supramolecular polymers, namely, (1) association number per hydrogen-bonding entity (sticker) in supramolecular polymers, (2) phase separation of stickers, (3) strength of association, and (4) the position of sticker in the polymer (end-group(s), side groups, or in the main chain). Probably the most important parameter can be considered to be association number which dictates the macroscopic properties of the material such as viscosity and moduli. The association number (which is the number of associations per sticker) can be tuned by using different ratios of metal:ligand or different chemistry of hydrogen-bonding moiety. Therefore, the material can show liquid (viscous) to solid (elastic) behavior on demand. Phase separation can also affect the mechanical properties. In designing an ideal association, which is the complementary bonding of stickers, one has to eliminate the probability of phase separation. This is in order to simplify the dynamics and have a system only comprised of predictable kinetics. Moreover, sticker position matters as it can be used to mimic sophisticated covalent structures like networks, comb, brush, branched, hyperbranched etc. A network can be considered as the most studied system whereby a sticker is attached on a linear polymeric chain and depending on the time-scale and the strength of association, solid to liquid properties can be obtained. In Chapter 2, a weak sticker was used to study the effect of sticker strength on the dynamics of these materials. It was concluded that even a fully
functionalized polymer could not show any network formation, whereas surprisingly, a stable cluster was formed. This proves that weakly associated networks do not dissociate rapidly and can relax as a cluster at extended time before the dissociation of stickers can lead to the relaxation of linear analogous (slow kinetics similar to strong physical or even chemical bonds.) On the other hand, the absence of a gel even in fully sticker-functionalized polymers shows that the weakness of these polymers can be described as their weakness in complete association (thermodynamically not favored).

In chapter 3, a new sticker was developed (ODIN) which could show enhanced stacking and aggregation properties in comparison to other known moieties. A variety of conformers (tautomers) was attributed to ODIN which in essence justified its mediocre association constant $K_a$. ODIN then was used as the end-group of well-defined, newly synthesized poly(tetrahydrofuran)s to investigate its application in polymer brushes. In particular polymer brushes were chosen due to their unique rheological behavior (hierarchical relaxation) as well as their interesting morphologies. Linear rheology showed that a hierarchical relaxation, which is usually observed in bottlebrush polymers, occurs in these materials, too. The polymer chain segments close to the supramolecular backbone are highly immobilized due to strong association in the center of polymer brush and cannot relax via reptation mechanism, which is mainly responsible for linear entangled polymer relaxations. Therefore, disentanglement can take much longer through contour length fluctuations and arm retraction processes similar to covalent bottlebrush polymers and combs. The relaxed ends of polymers then act as solvent to let the remaining segments of the polymeric brush undergo Rouse-like motions (constraint release Rouse). At longer times, additional plateau appears, which can be attributed to the relaxation of the entire supramolecular bottlebrush polymer via hopping or reptative motions. With an increase of temperature, viscoelastic solid behavior turns into viscoelastic liquid due to reversible depolymerization of the supramolecular backbone of the bottlebrush polymer. The elastic modulus ($G'$ in the order of kPa) was much less than the values found for the entanglement plateau modulus of linear poly(tetrahydrofuran) (in order of MPa). This low modulus value, which exists up to very low frequencies (high temperatures), makes them a good candidate for supersoft elastomers.

In order to have a better idea of supramolecular comb polymers, a systematic study was carried out in chapter 4 whereby three sets of polymers were synthesized
and mixed based on a specific interaction between the main chain and the side chain polymers. The first two sets based on the combination of 2,4-diamino-1,3,5-triazine (DAT) : thymine (THY) and 2-ureido-4[1H]-pyrimidinone (UPy) : (1-(6-Isocyanatohexyl)-3-(7-oxo-7,8-dihydro-1,8-naphthyridin-2-yl)-urea) (ODIN) were a blend and the third one using ODIN:ODIN interactions was used without a main chain. The polymer set using ODIN:ODIN interaction showed long-range ordering due to strong ODIN aggregation, whereas UPy:ODIN based polymer combs showed comb-like clusters without any ordering. The phase separation in THY:DAT system was more pronounced and was further improved after addition of more equivalents of side chains.

Last but not the least, a systematic approach was taken in order to unravel the rheology and dynamics of supramolecular polymer brushes. Therefore, in chapter 5, the origin of unique rheological response in these polymers was studied. Different polymer chemistries, topologies and molecular weights, were used and in all cases ODIN was the chosen sticker. At low molecular weights of mono-functionalized polymers, the formed brushes show colloidal behavior, and therefore they do not flow even at highest experimentally studied temperatures (or at longest time scales). These polymers, that are not a transient network (they are not necessarily crosslinked) show an elastic plateau close to what has been seen in hyperstars and covalent bottlebrush polymers ($G_N$ close to 10 kPa). Despite similarities between covalent and transient bottlebrush polymers the elastic response in the later does not originate from the brush entanglements with large $M_e$ (entanglement molecular weight), it rather stems from the impenetrable rigid backbone and caging effect similar to hyperstars. With increasing the molecular weight, a transition from colloidal to polymeric materials is observed whereby doubled-sized polymers as well as star-like aggregates are formed. With introducing crosslinking to the bottlebrush polymers, they show enhanced elasticity until they sacrifice their colloidal properties by network formation in tetra-functionalized polymers.

In conclusion, this thesis contributes largely to the concept of supramolecular polymer chemistry and can be used as a reference for design and analysis of complex dynamic architectures. A deeper understanding of polymer dynamics and self-assembly, relies on the artistry of the theoreticians. Nevertheless, the path towards
novel smart materials is open and promising. In the near future these polymers can be applied in 3-D printing technology as well as sustainable coatings and adhesives.