Topological constraints and the role of polymerization conditions

7.2 Impact

It is well accepted that increasing the molar mass, the mechanical and physical properties of a polymer increase. Ultra High Molecular Weight Polyethylene, having molar mass exceeding a million g/mol, is one of such a prime example where a commodity polymer changes into an engineering material meeting the societal requirements in health care (prostheses), security (body vehicle armor, cut resistant gloves, light weight cables), energy transportation (battery separators), automotive (light weight composite). Considering the sustainable monomer, ethylene that can be obtained from fossil fuel as well as bio-based

resources the polymer made from ethylene holds considerably lifetime while meeting the societal requirements. The polymer also holds potential in resolving the challenges of composite recycling by replacing the hybrid composites by one component composites, especially in the sector where temperature requirement is limited to 70 ^{o}C. However, in spite of the mentioned advantages the usage of the polymer remains restricted due to its fundamental challenge in melt processing, and the usage of more than 90 wt.% of toxic solvent (decalin or fluoro carbons) required in solution (or gel) processing.

In this thesis, we have addressed the fundamental challenge of processing of this intractable polymer. Here we have shown a route to reduce the entangled state by controlled synthesis to an extent that the polymer can be processed, below its melting point without using any solvent, to make uniaxial drawn films. The method differentiates from the earlier reported studies that made use of commercially not feasible route of homogeneous synthesis. The earlier reported route could not be up-scaled due to reactor fouling. Here we demonstrated that the use of nano-silica particles as a support can help in obtaining disentangled state to the extent that the material can be processed in solid state without reactor fouling.

In the process of the development of our study, it is also realized that while the non-equilibrium polymer melt monitored by rheological studies reached its equilibrium state, the topological constraints established during the process are found to be strongly dependent on the chosen catalytic system and the polymerization conditions. This fundamental difference is found to have major everlasting implications in mechanical response of the semi-crystalline material. It invokes the concept of concatenated and uncocatenated rings having equivalence to the overlapping of double stranded DNA molecules. Unlike the bio-polymers and the small rings, in our case, the long molecules are found to show differences in the mechanical performance, a subject that is beyond the scope of this thesis and has been taken over in the follow-up thesis of my colleague Mr Roel Bröker.

The realization of the difference in the topological constraints is further strengthened by the development of a weaker network, at low frequency and low modulus that tends to strengthen with time. This fundamental aspect, to our knowledge, is addressed for the first time in a linear polymer. It is clear that by using the models developed so far, the double crossover point cannot be explained. In this thesis, we are lying the fundamentals to develop a more precise theoretical model that takes into consideration the different topological constraints in the equilibrated high molecular weight polymer melts.

In this respect, we consider the work reported here opening a new paradigm in polymer science having impact on technological development.