Topological constraints and the role of polymerization conditions

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In all cases, by using the heterogeneous catalytic systems, the polymerization reactions show no reactor fouling and the morphology of the synthesized polymers as observed by SEM, show good replication of the silica morphology. The $M_w$ and $D$ of the synthesized polymers are estimated from rheological measurements and show that MAO-S5/FI, MAO-S1/FI and MAO-S2/FI are capable to promote the synthesis of UHMWPE having $11.9 \times 10^6$, $7.4 \times 10^6$ and $5.1 \times 10^6$ g/mol with a broad $D$ of 8.3, 9.4 and 10.2 respectively. Due to the low yield of PE-MAO-S3/FI and PE-MAO-S4/FI, the polymers show high silica content heavily affecting the rheological characterization; therefore, $M_w$, $D$ and entangled state have not been estimated. Characterized by rheological measurements, the synthesized polymers show a weakly entangled state based on the low starting values of $G'$ and their build-up as a function of time in the melt, corroborated with the presence of two melting peaks with variable areas as a function of time in the melt as observed by DSC. To further strengthen the low entangled state, the nascent reactor powders have been compressed below the melting temperature (125 °C) for hand-drawn tests (~130 °C) and all the samples can be drawn, showing the ability of the synthesized polymer to be processed in the solid-state, especially for PE-MAO-S5/FI. Due to the apparent lowest entangled state with a petal-like morphology, high yield and high molar mass, PE-MAO-S5/FI has been used to test the solid-state processability and mechanical properties. As studied, PE-MAO-S5/FI can be stretched to high draw ratio up to 220 time and capable to achieve mechanical properties up to 2.48 GPa in tensile strength and 129 GPa in tensile modulus.

In Chapter 6, the effect of silicas on the chain dynamics of the polymer synthesized using the heterogeneous catalyst systems is address. In order to visualize the terminal regime (or close to), the silicas used in Chapter 5 (mesoporous silica S1, spherical silica S4, nano-size silica S5) are pre-activated with MAO and complex 11 (FI27 catalyst, bis[N-(3-tert-butylsalicylidene)-aniline] titanium(IV) dichloride) has been used to produce polymers having lower $M_w$. The polymers synthesized by heterogeneous catalytic systems show a lower $M_w$ around 0.6 million g/mol compared with the polymer synthesized by homogeneous catalytic system, having $M_w$ of 1.0 million g/mol characterized by HT-GPC. According to the reported work, where supported FI catalysts (among them complex 2) over silica/MAO lead to increased chain transfer to the bounded TMA, the reason for the unusual lower molecular weights could be due to the enhanced chain transferring to anchored trimethylaluminum (TMA) from the heterogeneous catalytic systems. Upon melting, all the polymers show lower initial values of $G'$ and they increase as function of time in the melt in oscillatory time sweep experiments, suggesting a low entangled state of the polymers produced. These results are corroborated with a higher melting temperature of the synthesized polymers from DSC isothermal crystallization experiments. Unusually, there is no crossover point observed from the oscillatory frequency sweep in PE-MAO-Silicas/FI27 melts, in contrast to the observed two crossover points in PE-MAO/FI27 melt in the same frequency region, which suggests the presence of silicas (i.e. particle size and the amount of residual silica) probably have a significant influence on the chain relaxation process. Meanwhile, an uptrend of $G'$ with decreased frequency in the low frequency region has been observed in PE-MAO-S1/FI27 and PE-MAO-S4/FI27 melts, which is ascribed to chain degradation occurring in the sample during the rheological characterization. Overall, the influence of silicas from heterogeneous catalytic systems on the polymer chain dynamics cannot be neglected.

### 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
Conclusions and Impact

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 °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.