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Controlling the melting kinetics of polymers; a route to a new melt state

Dissertation
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Summary

Polymers play an important role, both in nature and in the modern society. In contrast to polymers in nature, the so-called biopolymers, man-made polymers are thermally more robust and are in majority processed via the melt (plastics). Processing routes conventionally applied in the polymer industry are injection molding, extrusion, film blowing, and blow molding. All these processes start from a melt which flows into a (complex) shape. Synthetic polymer molecules in the molten state are highly entangled, to be compared with cooked spaghetti. There is no apparent order in the molten state and the conformation of the individual chain is a so-called random-coil, as evidenced by various neutron scattering experiments on deuterated polymer chains. Due to the presence of long chain polymer molecules, which are highly entangled, polymer melts exhibit a high

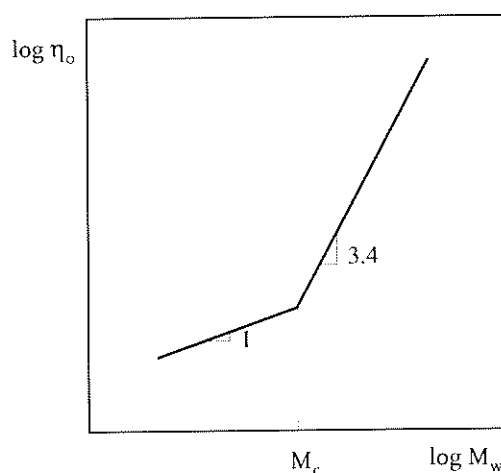


Figure 1: Universal relationship between zero shear viscosity (η_0) and molecular weight (M_w)

viscosity which increases strongly with increasing molecular weight. Experimental results on many polymeric systems show that the (zero-shear) viscosity of polymer melts, η_0 , scales with $M_w^{3.4}$, Figure 1 (M_w is the weight-average molar mass). scales with $M^{3.4}$ which implies that on doubling the molar mass, the melt-viscosity increases with more than a factor of 10!

This universal relationship, related to viscosity and motion of chains within the melt is well understood by a simple but elegant model put forward by P.G. de Gennes (Nobel prize for Physics, 1991), the so-called reptation model. In this model, the motion of a polymer chain in the molten state is hindered by its neighbors (entanglement), which generate a virtual "tube" confining the chain on a one dimensional pathway. The constraint chain dynamics gives rise to a characteristic time for a chain to diffuse its own length in the tube. Scaling as M^3 . The same scaling is predicted for the zero-shear viscosity. The experimentally observed discrepancy, see figure 1, $\eta_0 \sim M^{3.4}$, from the 3.0 dependence is attributed to "contour-length fluctuations" i.e. fluctuation-driven stretching and contractions of the chain along the tube. In the thesis, it is shown that the zero-shear melt-viscosity of carefully prepared samples of high molar mass polyethylene (PE), possessing a narrow molecular weight distribution, indeed follow the predictions of the reptation model, viz. η_0 scales with M^3 . The advantage of high molar mass polyethylenes is that chain-end effects do not play an important role or can be ignored. As a consequence of these results, high molecular weight polyethylenes have been used as a model substance throughout the thesis, notably ultra-high-molecular-weight PE (UHMW-PE).

The fundamental restriction related to the high melt viscosity make high molar mass polymers rather intractable via conventional processing routes. On the other hand, properties of polymers in the solid-state also increase with increasing molar mass, notably the strength and toughness. Consequently the processing of thermoplastic polymers, e.g. injection-moulding, extrusion, fiber spinning, is often a compromise between the ease of processing, viz. preference for lower molar mass (easy flow), and properties, with preference for high(er) molar masses.

An illustrative example showing the discrepancy between intrinsic properties related to high molecular weight and insufficient product performance due to difficulties in processing is found in UHMW-PE. UHMW-PE a linear polyethylene with molecular weight above 10^6 g/mol is currently processed via compression molding or ram extrusion into simple shapes such as rods, plates, or sheets, which are subsequently machined into the desired products. It has been found that all processed products of UHMW-PE possess residues of the original powder particles usually referred to as grain boundaries or fusion defects.

These flaws in the material are a consequence of the long reptation time needed for the molecular chain to cross from one powder particle to another. In high performance applications, for example knee and hip joint prosthesis, fusion defects within the UHMW-PE material on the submicron are considered to be one of the main reasons for intracellular and extracellular polyethylene wear debris found in prosthetic replacement. Furthermore, in knee prosthesis grain boundaries present between the particles of an as produced joint are weak points to sustain mechanical stresses, leading to delamination.

Figure 2 shows a light microscopy picture made on thin slices cut from a UHMW-PE hip cup, as received (Figure 2a) and retrieved from the body after 7 years (Figure 2b) In the Figure 2a grain boundaries related to the poor fusion of the original UHMW-PE powder particles can be observed. After retrieval of the hip cup from the body, these grain boundaries become more pronounced. Eventually the observed grain boundaries lead to failure of the knee prosthesis. Therefore in order to improve the performance of artificial prosthesis, the processability of the UHMW-PE melt should be improved.

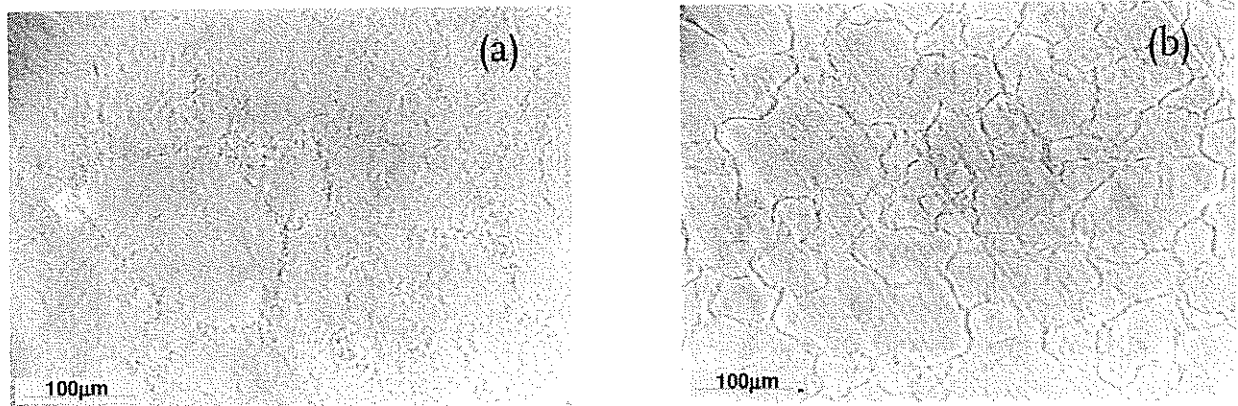


Figure 2: *Optical micrographs of thin sections cut from (a) the as-produced hip cup and (b) the hip cup retrieved from the human body after 7 years. The grain boundaries become more pronounced after usage. (reproduced from Kurelec et al.)*

To improve the processability of high molecular weight polymers, it is necessary to decrease the viscosity (or the number of entanglements per chain), without losing the favorable properties of these materials; therefore the molecular weight should not be (dramatically) changed.

In the solid state, entanglements can be removed effectively by dissolution of the polymer. In dilute solutions, below the so-called overlap concentration ϕ^* , entanglements can be removed

completely. In the case of crystallizable polymers, such as PE, the reduced entanglement density can be made permanent since the long chain molecules form folded-chain crystals, a well-studied phenomenon in polymer physics.

A more elegant and also technologically more advanced way to generate disentangled PE crystals is via direct polymerization in the reactor. At low polymerization temperatures and low catalyst activity/concentration, individual growing chains will form their own folded-chain crystals. In the limiting case where the growing chains are separated far enough from each other, monomolecular crystals can be formed.

If completely disentangled PE structures can be obtained via solution-crystallization and/or via direct controlled synthesis, the intriguing question is whether this disentangled state (and consequently lower melt-viscosity) will be preserved upon melting and what is the time scale to generate a fully entangled equilibrium polymer melt. **This question is the key issue of the thesis. What happens when we start from a non-equilibrium disentangled state and cross the melting temperature into the molten state? How does the equilibrium entangled melt state get restored?**

In the thesis, it is shown that starting from the disentangled solid state, in this case nascent UHMW-PE powder, for the first time a disentangled melt state is observed. The disentangled melt state takes time to “build-up” the plateau modulus in the melt, indicative of an entanglement formation process. (Figure 3). The entanglements formation scales as the reptation process (M_w^3). Therefore it is concluded that a time window exist where the melt has a lower melt viscosity. Parallel to rheology measurements, solid-state NMR is used to monitor the change in chain mobility. The time scale to reach the equilibrium melt as probed by the NMR and Rheology experiments is very different, suggesting that the mixing of the disentangled chains monitored by NMR are realized at an earlier stage than restrictions in segmental mobility imposed by effective entanglements.

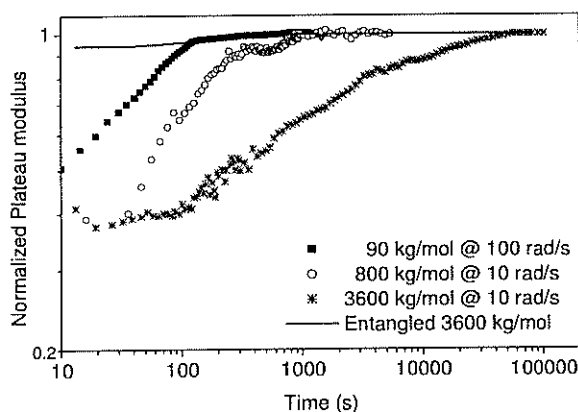


Figure 3: Modulus build-up in initially disentangled polymer melts as a function of time.

A peculiar phenomenon of nascent reactor powders is their high melting point, close to or equal to the so-called equilibrium melting point of PE. This phenomenon has puzzled researchers in the field for many years and various explanations have been given such as the growth of extended-chain crystals instead of folded-chain crystals or extensive reorganization during the melting process, but all these explanations were not supported by experimental data which show that nascent UHMW-PE reactor powders consist of “normal” folded-chain crystals without extensive reorganization (thickening) during the melting process. In the thesis it is shown that the unusual high melting temperature of nascent UHMW-PE is related to the tight-folding in the crystals. Melting is a cooperative process over several chain stems of the same crystal in contrast with e.g. melt-crystallized samples where a chain is incorporated in various folded-chain crystals and topologically, is in contact to different chains. (Figure 4)



Figure 4: *Depicting the melting process of the disentangled nascent crystals during fast heating. Upon fast heating the chains are likely to get mixed, leading to a gradual increase in the storage modulus with the formation of, ultimately resulting into a homogenous distribution of the entanglements in the melt.*

However when the heating rate is decreased, the melting process starts by detachment of single stems from the (lateral) surface of the crystals at a lower temperature, Figure 5. In this process, the molten chain ends can entangle, whereas the core of the molecule is still in the crystal, viz. in the tight folded-chain conformation. After complete melting by this mechanism, a heterogeneous melt-state is obtained since the central part of the individual chains is prevented from taking part in the entangling process.

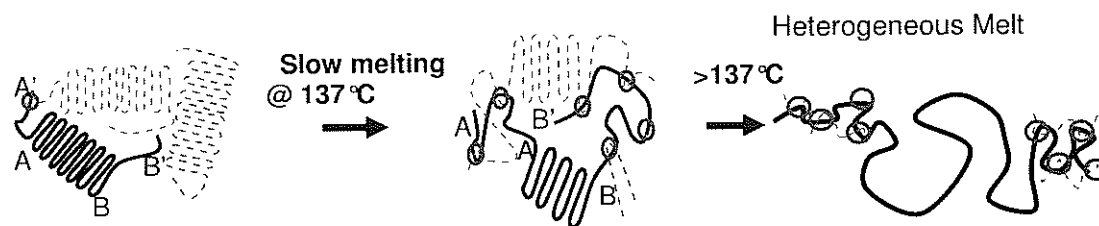


Figure 5: *Depicting the melting process of the disentangled nascent crystals during slow heating. Entanglements are encircled.*

By NMR experiments, it is observed that on decreasing the heating rate, the time required to mix the disentangled chain segments with the entangled chain segments increases. In rheometry it is observed that with the increasing time to mix the disentangled and entangled chain segments, the time for the formation of entanglements increases. Ultimately, it is feasible to melt the sample so slowly that mixing of the chains in part of the sample can be inhibited, maintaining the partially disentangled. Since the entanglements can not be achieved, the cooperative motion needed for the translational mobility is absent. As a consequence normal chain reptation is slowed down considerably and a long-living partially disentangled melt is obtained. (Figure 6)

This new melt state shows a decreased plateau modulus and viscosity, whereas the terminal stress relaxation rates remain the same. The observations are that stress relaxation is achieved without “normal” reptation of chains in the tube. This is explained by the partial reptation of the chains since only a fraction of the whole chain is required for the stress relaxation.

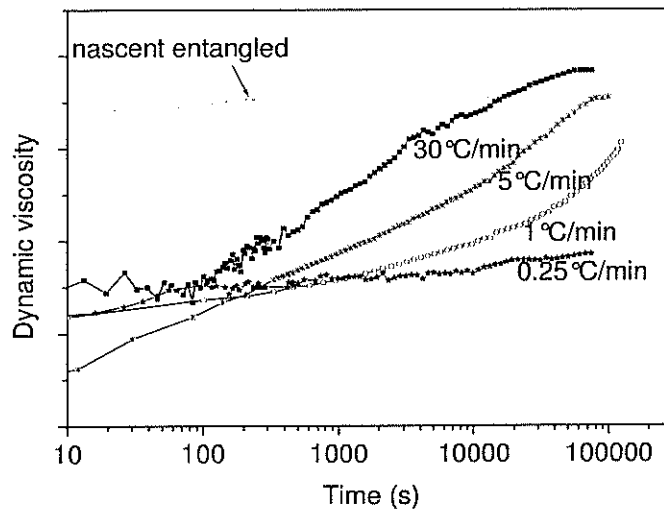


Figure 6: *Dynamic viscosity as function of time of the nascent disentangled and entangled samples melted at different heating rate.*

It is observed that the chain disentanglement has a profound effect on crystallization aspects. i.e. the disentangled chain segments crystallize faster than the entangled chains. This suggests that intra-molecular homogeneous nucleation occurs faster than the heterogeneous nucleation. Moreover, after crystallization from the heterogeneous melt, the solid-state drawability is still remarkably high, indicative of a certain state of disentanglement. Thus can be drawn into a fiber in the solid state because large disentangled blocks are present in the crystal.

The melting behavior of solution-crystallized UHMW-PE is similar to the nascent disentangled crystals. The differences in melting behavior, revealed during different heating rates, have consequences on the chain dynamics. Unlike the nascent disentangled samples, where modulus builds up with time, the solution-crystallized sample entangles immediately upon fast heating. The remarkable difference in the rate of entanglements formation can be attributed to the differences in the stacking of crystals, prior to melt. The solution-crystallized samples double their crystal size via intermixing of the regularly stacked crystals which upon melting facilitate the entanglement formation process contrary to the nascent disentangled samples where no regular stacking occurs.

An alternative route to achieve a reduction in the melt viscosity is explored in the thesis by the addition of the single-walled carbon nanotubes (SWNTs). When varying the content of SWNTs, the dynamic viscosity/storage modulus shows a minimum. The decrease in viscosity is attributed to the selective adsorption of the high molar mass fraction onto the nanotube surface. The increase in viscosity upon further increasing the nanotube content is attributed to the formation of an elastic nanotube-polymer network.

The concepts presented in the thesis, based on experimental validation, could have an important impact on novel processing techniques for UHMW-PE, e.g. sintering of UHMW-PE into products for demanding applications such as artificial hip-and knee joints, as is pictured in figure 7, but also solvent-free processing routes for UHMW-PE fibers and tapes.

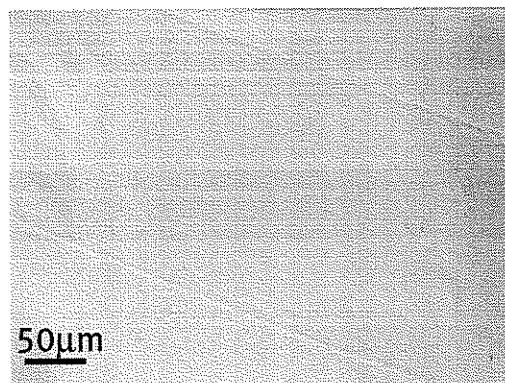


Figure 7: *Optical micrographs of UHMW-PE processed at 160 °C and 200 bar.*

It has to be noted that the studies performed are extended to low molecular weight polyethylenes and in principle can be extended to flexible semi-crystalline polymers where the adjacent re-entry is feasible.