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Rheokinetics

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CHAPTER 8

CONCLUSIONS

8.1. Rheokinetics

The kinetics of polymerization processes is generally studied with calorimetric or spectrometric techniques. The conversion and the rate of polymerization are determined measuring the heat released during the reaction or the concentration of particular functional groups.

A common aspect of all traditional techniques is that the polymerizing sample does not flow during the kinetic measurement. Therefore these techniques do not allow investigating the influence of flow conditions on the kinetics of the polymerization.

Rheokinetics is an alternative approach to the study of the kinetics of polymerization. Rheokinetics is based on the measurement of the rheological properties, particularly of the viscosity, *during* the polymerization. The measurement of the rheological properties *must* be performed in the presence of some kind of flow. Therefore, simply varying the flow conditions in which the experiments are performed it is possible to study how the increase of the viscosity is influenced by the flow conditions at which the polymerization is carried out.

Thus, a rheokinetic analysis can yield valuable information to the designer of polymerization reactors: how the increase of the viscosity is influenced by the experimental conditions, in particular by the shear rate. Moreover, the rheokinetic approach can give additional information on the kinetics of the polymerization itself.

However, measuring the viscosity of a polymerizing sample is not an easy task. In fact, polymerization processes are usually fast and imply an increase of the viscosity of up to six or seven order of magnitudes. Part of chapter 3 of this thesis has been dedicated to a detailed discussion of the most common measurement techniques, of their virtues and of their deficiencies. We can here summarize that the cylinder-cylinder rheometer and the cone and plate rheometer are the most used viscometers. The former is particularly used when the viscosity is relatively low, the latter when the viscosity is relatively high. Neither of them can usually cover the whole

polymerization with a single experiment. Both of them have a particular geometry and thus induce a particular flow field that is very far from the ones encountered in polymerization reactors on industrial scale.

Therefore another challenge consists of the scale-up of rheokinetic results obtained at laboratory scale.

8.2. The Trommsdorff effect

In this thesis a rheokinetic analysis of bulk free radical polymerization has been performed. The reaction mechanism of bulk free radical polymerizations is outlined in chapter 2 and consists of an initiation, a propagation and a termination step. Also an expression for the rate of the polymerization is derived.

Bulk free radical polymerizations are usually characterized by a peculiar autoacceleration phenomenon called Trommsdorff effect. This autoacceleration takes place at intermediate or high degree of conversion and is caused by diffusion limitations that hinder only the termination step. As showed in chapter 2, this results in an increase of the rate of polymerization.

Because of the Trommsdorff effect, a noticeable amount of heat is suddenly produced when the viscosity is relatively high and mass and heat transfers are hindered. This results in hot spots in the polymerizing fluid. Therefore, the Trommsdorff effect is particularly undesirable in industrial applications, leading to difficulties in controlling operating conditions, highly polydisperse final products or even runaway and explosion of the reactor.

The problem of the Trommsdorff effect is usually avoided by performing the free radical polymerization in solution, thus adding a solvent to the reactor. In this way the increase of the viscosity can be limited and the diffusion constraints, that are the cause of the Trommsdorff effect, can be eliminated. However, the use of considerable amounts of solvent implies much larger reactors and an extra separation step. Moreover the solvents are

usually hazardous chemicals and their use is subjected to increasing limitation.

In this thesis particular attention has been dedicated to the latest stages of the polymerization, where the Trommsdorff effect is expected to occur, and to the influence of the shear rate on the viscosity increase and on the kinetics.

Two different cone and plate rheometers have been used. The results obtained with the two rheometers are in good agreement with each other. They show that the increase of the viscosity can be well fitted by a double power law trend, after an initial lag time during which the viscosity is too low to be measured reliably. In all the experiments performed the power law exponent corresponding to the second part is higher than the one corresponding to the first part. This means that the Trommsdorff effect, as expected, takes place. The difference between the two power law exponents can be considered has a measure of the Trommsdorff effect.

The influence of the shear rate on the Trommsdorff effect has been studied performing different rheokinetic experiments at different shear rate but otherwise the same experimental conditions (temperature and initiator concentration). The difference of the power law exponents decreases significantly when the shear rate at which the polymerization is carried out increases.

In other words, the Trommsdorff effect can be reduced performing the polymerization at a high shear rate. A shear rate of about 100 s^{-1} is enough to eliminate practically the Trommsdorff effect.

This remarkable experimental result can be explained by observing that shear orientates and elongates the random coils, inducing more order into the polymerizing system. In this way, the diffusion limitations to the movement of the chains are reduced, and therewith the Trommsdorff effect.

The influence of the initiator concentration and of the temperature on the Trommsdorff effect has also been studied with a rheokinetic approach.

The Trommsdorff effect increases initially with the increase of initiator concentration. In fact, very low initiator concentration results in very slow

polymerization. When the initiator concentration exceeds a certain value the Trommsdorff effect decreases because a high initiator concentration results in a lower average molar mass of the polymer obtained. This implies smaller chains and, therefore, reduced diffusion limitations. This result has been obtained for the polymerization of *n*-butylmethacrylate but, in agreement with the literature concerning the Trommsdorff effect, can be considered of general validity.

On the other hand, an increase of the temperature results in a higher Trommsdorff effect for the polymerization of *n*-butylmethacrylate. This experimental evidence cannot be easily generalized for all the monomers. In fact, the temperature can influence in different ways the propagation and the termination steps depending on the energies of activation.

Also the increase of the normal force during the polymerization of *n*-butylmethacrylate has been measured. The normal force begins to increase significantly when the Trommsdorff effect sets in. In other words, when the conversion is high enough to originate the entanglements and the diffusion limitations that are the cause of the Trommsdorff effect, also normal stress in shear flow appears. Moreover, the increase of the normal force can be fitted by a power law and the power law exponent decreases when the shear rate increases. Also the experiments at different initiator concentration and at different temperature show an agreement between the trends of the viscosity and of the normal force.

Therefore, the rheokinetic measurements of the normal force validate the viscosity measurements and show once again that rheokinetics can be a very useful tool for the study of the kinetics of polymerization processes.

With both cone and plate rheometers used in this thesis, irregularities were noticed in the viscosity trend at the very end of the polymerization. After the double power law trend the viscosity assumes an irregular and irreproducible trend. This is also the case for the normal force. These irregularities are ascribed to a shear-induced phase transition, leading to the formation of a *pseudo*-solid phase. The presence of this phase interferes with the cone and plate measurements.

The most striking property of cone and plate rheometers is that they induce an equal shear rate on the whole sample while measuring its rheological properties. Thus they are particularly suitable for the study of the influence of the shear rate on any phenomenon of interest. However, a similar flow field is very far from the ones occurring in industrial applications. In fact, large-scale polymerization reactors are characterized by very complex flow fields. Hence the need to scale-up the rheokinetic results obtained with the cone and plate rheometers.

Therefore a helical barrel rheometer has been used in this thesis. The helical barrel rheometer is geometrically similar to a single-screw extruder. It allows measurement of the viscosity during the polymerization when used as a batch reactor. Its volume is approximately 15 times larger than the volume of the cone and plate rheometer. Moreover, it is characterized by a very complex flow field, similar to the ones encountered in reactive extrusion. However, an average shear rate can be defined that is proportional to the velocity of the rotating element of this rheometer.

The rheokinetic investigation performed with the helical barrel rheometer confirmed the results obtained with the cone and plate rheometers. Particularly, the Trommsdorff effect is reduced when the polymerization is performed at a higher *average* shear rate. No irregularities were noticed in the viscosity trend. However, visual observation of the polymer obtained at the end of the experiments induce to argue that also in the helical barrel rheometer a phase transition does occur, with the formation of a *pseudo-solid* phase.

8.3. Thermodynamics

Chapter 7 of this thesis has been dedicated to study the thermodynamics of free radical polymerization. It is generally believed that no thermodynamic limitations hinder the polymerization, at least at ordinary temperatures in laboratory and industrial applications. The fact that a 100 % conversion is not reached within limited reaction times is generally ascribed to the

presence of kinetic constraints when only a few percent of the monomer is still to react.

However, the available thermodynamic data have been obtained in the absence of the shear rate. In fact, shear induces a change of entropy that must be taken into account when considering the possibility of thermodynamic constraints to the conversion.

The order of magnitude of this shear-induced change of entropy has been estimated with the help of the Maxwell-Oldroyd model and of the dumbbell model. It resulted that under ordinary shear rate values, the shear-induced change of entropy can be of the same order of magnitude of the entropy of polymerization. This would result in thermodynamic constraints in ordinary conditions of temperature and shear rate.

This conclusion is confirmed by some preliminary results concerning the conversion at the end of the polymerization. This conversion is a decreasing function of the shear rate at which the polymerization is carried out.

All in all, this thesis confirms the utility of a rheokinetic approach in the study of the kinetics of bulk free radical polymerization and gives some qualitative information that could not have been obtained with classical methods. At the same time, it paves the way for a possible solution of the problem of the Trommsdorff effect in industrial application, and therefore, for better designed, better controlled, more environmentally friendly and more profitable polymerization processes at industrial scale.

Further rheokinetic research should concern other polymerization processes. Particularly, the influence of the shear rate on the kinetics of the polymerization and on the average molar mass of the product and on its final properties is still to be investigated.

Also the role that shear plays in the thermodynamics of polymerization should be the subject of further scientific investigation.