# University of Groningen

## Rheokinetics

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# CHAPTER 6

# THE HELICAL BARREL RHEOMETER

## 6.1. Introduction

In chapter 4 and 5 we have discussed the results of a rheokinetic study of bulk free radical polymerization performed with two cone and plate rheometers. Particular attention has been given to the investigation of the influence of the shear rate on the kinetics of the polymerization. The rheokinetic experiments showed that the Trommsdorff effect can be significantly reduced, if not eliminated, when the polymerization is performed at a high shear rate.

In this chapter we shall present the results of a similar rheokinetic investigation performed with a helical barrel rheometer. This rheometer is geometrically similar to a single screw extruder. Therefore the results obtained with the helical barrel rheometer represent a first step in the translation of the results from cone and plate rheometers to industrial reactors and are particularly interesting in view of possible further applications of reactive extrusion to produce polymers profitably.

## 6.2. The helical barrel rheometer

The helical barrel rheometer is essentially a small single-screw extruder that is used as a batch reactor (closed die) to measure the increase of the viscosity during the polymerization by means of two pressure transducers.

The viscous flow in the helical channel of a conventional single-screw extruder is usually characterized by a volumetric drag flow $Q_d$ and a pressure flow $Q_p$.

$$Q_d = f_d \frac{\pi DWhN \cos\theta}{2} \tag{6.1}$$

$$Q_p = f_p \frac{Wh^3 \Delta P \sin\theta}{12\eta L} \tag{6.2}$$

where $N$ is the screw rotational speed, $D$ is the screw diameter, $W$ is the width of the channel, $\theta$ is the screw helix angle (i.e. the angle of the flights with the axis of the screw), $h$ is the channel depth, $\Delta P$ is the pressure difference measured over the length $L$ and $\eta$ is the viscosity. $f_d$ and $f_p$ are corrections factor for drag flow and pressure flow, respectively, that account for the finite width of the channel and for its curvature.

The volumetric drag flow is directed towards the die of the extruder, the pressure flow in the opposite direction.

At closed discharge, the drag flow and the pressure flow must be equal and opposite, since the overall flow must be equal to zero.

$$Q_d = Q_p \tag{6.3}$$

Substituting equations (6.1) and (6.2) into equation (6.3), we obtain

$$\eta = \frac{\Delta P h^2}{6 N \pi^2 D^2} \frac{f_p}{f_d} \tag{6.4}$$

if we set L, the distance over which $\Delta P$ is measured, equal to $\pi D \tan(\theta)$, which is the channel length over one screw pitch. The dimension of the helical barrel rheometer was chosen such that the ratio $f_p/f_d$ of the two correction factors is equal approximately to 1.

Therefore measuring the pressure difference with two pressure sensors, it is possible to determine the increase of viscosity during the polymerization.

As the term helical barrel rheometer suggests, the thread is mounted on the barrel and not on the rotating element. If the thread were mounted on the rotating element, as in ordinary extruders, it would pass along the pressure sensors, and this would result in oscillations and inaccuracy of the measurement of the pressure drop, and therefore of the viscosity [1].

The helical barrel rheometer used in this study was constructed in the workshops of the University of Groningen and is shown in figures 6.1 and

6.2. During the experiments the metering section of the helical barrel rheometer was positioned in a steel housing (not shown in the figures) that was electrically heated. The heaters were connected to a temperature controller (Plasticorder PL 2000-6, Brabender, Duisburg, Germany). The temperature was stable during the experiments and only small deviations from the set point ($\pm$ 1 °C) were noticed.

The measurements were stopped when the pressure inside the helical barrel rheometer reached 30 bar, in order not to damage the pressure sensors and the rheometer itself. Occasionally samples were thermally quenched at the end of the experiments and tested by nuclear magnetic resonance. This revealed that conversion was approximately 90% at the end of the experiments.
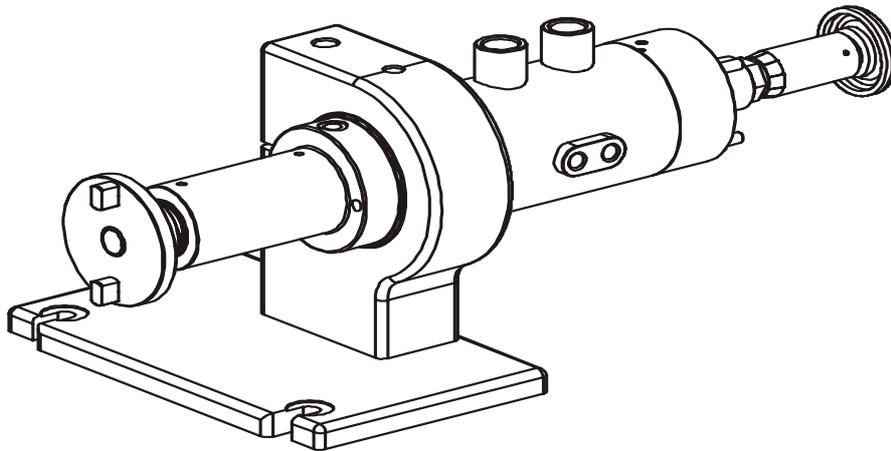


*Figure 6.1. The helical barrel rheometer. It is here reported a picture of the helical barrel rheometer as it looks from the outside.*

To the best of our knowledge, only Todd *et al*. [1] successfully performed viscosity measurements of polymer melts with a helical barrel rheometer, but this device has not been used so far for rheokinetic investigations. These authors also affirm that the helical barrel rheometer can be a useful tool for on-line measurements of the viscosity during industrial processes. This can

be done by connecting the two ends of the helical barrel rheometer to the industrial device.
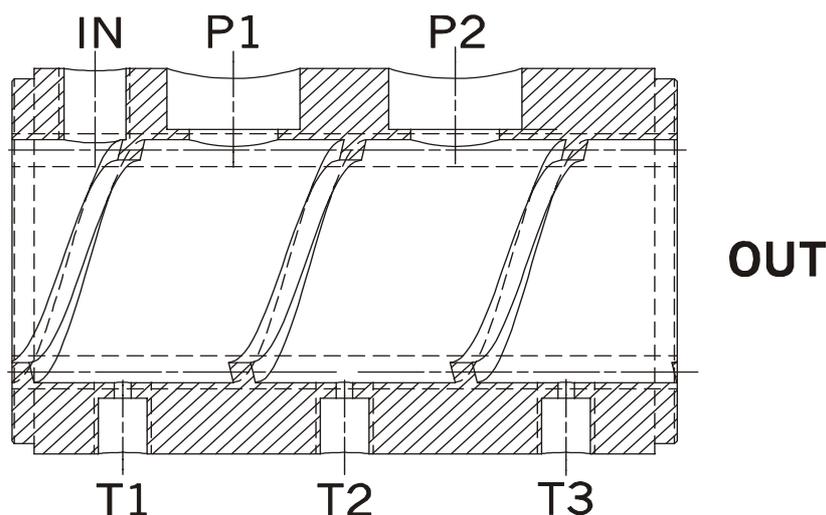


*Figure 6.2. The Helical barrel rheometer. A section view of the measuring part of the helical barrel rheometer is reported here. The monomer-initiator solution is fed through "IN" until it fills up the gap completely. The helical barrel rheometer is heated electrically and the heating system is connected to a control system. P1 and P2 are the positions of the pressure sensors. T1, T2 and T3 are the positions of three thermocouples used to check that the temperature of the sample is uniform across the whole rheometer. After the experiment the polymer is removed through "OUT".*

The major qualitative difference between the cone and plate rheometer and the helical barrel rheometer regards the shear flow profile to which the polymerizing liquid is subjected. In the case of the cone and plate rheometer the shear rate is the same everywhere in the sample, whereas the helical barrel rheometer is characterized by a very complicated profile of the shear rate.

Because of the uniform shear rate, the cone and plate rheometer is ideal for investigating the influence of shear rate on the rheological properties of

polymeric systems. However, the shear flow profile that it generates is very far from those occurring in industrial applications.

In contrast, the helical barrel rheometer induces a very complicated shear flow profile, more similar to those occurring in industrial applications, especially in reactive extrusion.

Another advantage of the helical barrel rheometer is that it can handle fluids that contain solid particles or fibers. In fact, the viscosity is derived by a measurement of the pressure drop across one flight of the rheometer and the reliability of the pressure sensors is not influenced by the presence of a solid phase, as long as the solid phase does not deteriorate the surface of the pressure sensors.

## 6.3. The average shear rate

The determination of the shear flow profile and of the average shear rate in the helical barrel rheometer is a complex mathematical problem that will not be dealt with in this thesis in detail. However, in first approximation, we can assume that the channel between the helical barrel and the screw is equivalent to the gap between two parallel infinite plates. One plate is fixed and the other plate moves horizontally with velocity equal to $\pi DN$ and a pressure drop contrary to the direction of the movement of the plate is applied (see figure 6.3).

It can be demonstrated that the velocity profile for Newtonian fluid is parabolic and that the average shear rate $\dot{\gamma}_{av}$ is given by:

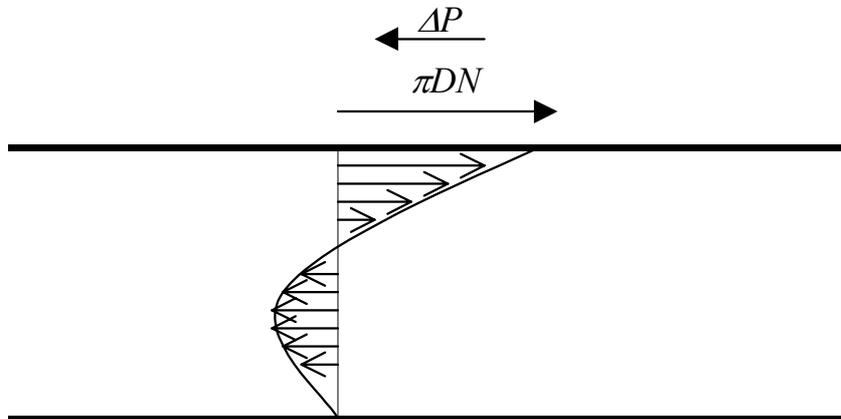$$\dot{\gamma}_{av} = \frac{5}{3}\frac{\pi ND}{h} \tag{6.5}$$

*Figure 6.3. The approximated velocity profile in the helical barrel rheometer.*

The average shear rate is therefore proportional to velocity of the horizontal plate, or, in other words, to the rotational speed of the screw.

Todd *et al*. [1] showed that also for non-Newtonian fluids a similar relationship is valid for the helical barrel rheometer. The coefficient on the right hand side of equation (6.5) is different. In particular, this coefficient is a function of the power law index of the non-Newtonian fluid.

In conclusion, it can be stated that the helical barrel rheometer, in analogy with the cone and plate rheometer, allows to perform experiments at different *average* shear rate by varying the velocity of the rotating element.

## 6.4. Scale-up

We can argue that the helical barrel rheometer permits to scale-up experiments performed with a cone and plate rheometer. In fact, the volume of the polymerizing sample in the helical barrel rheometer (about 30 ml) is an order of magnitude larger than in a cone and plate rheometer (about 1 ml) but still very small compared to industrial reactors or extruders. However, the qualitative difference between the two geometrical configurations is significant.

Our major interest was to check if a high shear rate can reduce the extent of the Trommsdorff effect also when performing the polymerization in a reactor more similar to the ones used in industrial applications. Therefore, the dimensions of the helical barrel rheometer where chosen to allow measurements of high viscosities, corresponding to high conversions. The helical barrel rheometer used in this experimental study is not reliable at the beginning of the polymerization, where, anyway, the Trommsdorff effect is not expected to occur.

## 6.5. Results

The reliability of our self-constructed helical barrel rheometer was tested performing viscosity measurements with water solutions of glucose syrup and comparing the results with those obtained with the Brabender rheometer. These solutions are Newtonian and therefore allow comparing viscosity measurements performed in different devices and in different flow regimes. The results are reported in table 6.1 and show a good agreement between the cone and plate rheometer and the helical barrel rheometer.

| Helical Barrel Rheometer (Pa s) | Cone and Plate Rheometer (Pa s) |
|:---:|:---:|
| 0.21 | 0.19 |
| 0.39 | 0.41 |

*Table 6.1. Viscosity data obtained with a cone and plate rheometer and with the helical barrel rheometer at room temperature for two water solutions of glucose syrup.*

The increase of viscosity during bulk free radical polymerization was measured in different experimental conditions. One typical example of the results obtained is shown in figure 6.4.
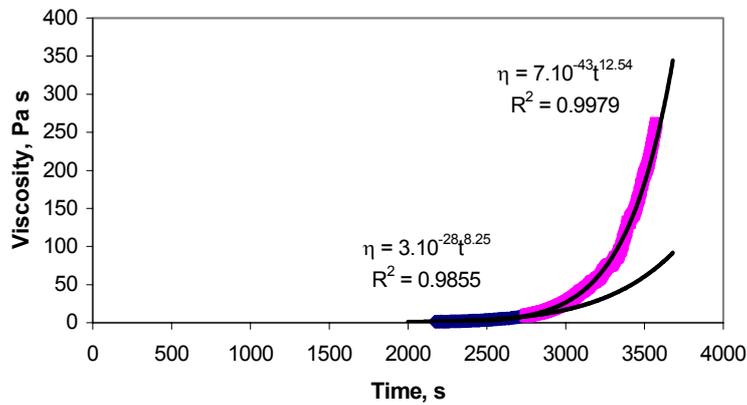
*Figure 6.4. The double power law trend of the increase of viscosity during the polymerization of n-butylmethacrylate. T = 100 °C, N = 10 min$^{-1}$, [I]$_0$ = 1% v/v.*

The data are in good agreement with the ones obtained with the cone and plate rheometers and can be fitted with a double power law, whatever the temperature, the initiator concentration or the monomer used. As we have seen in chapter 4 and 5, the difference between the two power law exponents can be considered as a measure of the Trommsdorff effect.

Experiments were performed at different rotational velocities (i.e. different average shear rate), but otherwise the same experimental conditions, in order to verify the influence of shear rate on the Trommsdorff effect.

The data regarding *n*-butylmethacrylate are shown in figure 6.5 and 6.6. They show clearly that in the helical barrel rheometer the Trommsdorff effect can be reduced performing the bulk free radical polymerization at a higher rotational speed of the rotating element or, in other words, at a higher average shear rate.
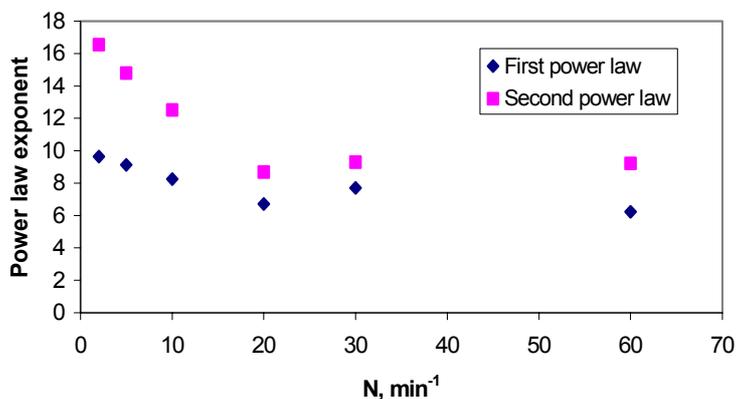
*Figure 6.5. The power law exponents for the polymerization of n-butylmethacrylate at different rotational speed of the screw. T = 100 °C, [I]$_0$ = 1% v/v.*



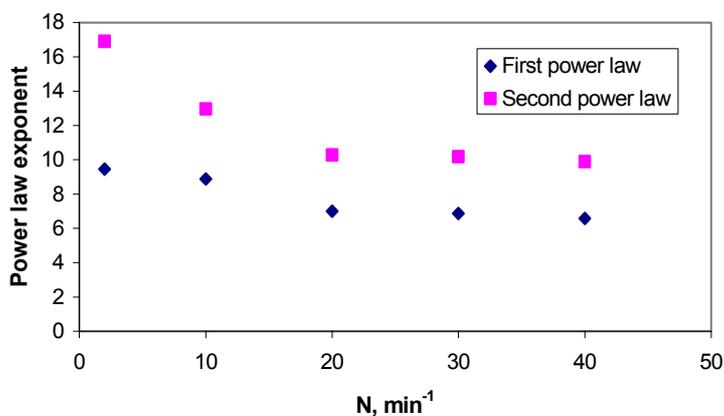*Figure 6.6. The power law exponents for the polymerization of n-butylmethacrylate at different rotational speed of the screw. T = 110 °C, [I]$_0$ = 0.33% v/v.*

In the case of the experiments performed with styrene, a remarkable extension of the initial lag time of the polymerization was noticed, which affected the values of the power law exponents. They are in the range 20-40.

These values are not in agreement with the results obtained with the cone and plate rheometer, where no conspicuous difference could be observed between styrene and *n*-butylmethacrylate. These exponents are also not in agreement with other rheokinetic studies published by other authors [2-4].

The experiments with styrene were troubled by the formation of bubbles inside the helical barrel rheometer. This can be ascribed to the fact that the boiling temperature of styrene (145 °C) is too close to the operating temperature (110-120 °C).

However, these bubbles could be removed slowly during the experiments. Nevertheless during the initial phase of the experiments the helical barrel rheometer was partially empty and the monomer-initiator solution had to be added gradually as long as bubbles were removed.

Since a large amount of monomer-initiator concentration had to be fed during the experiments, we can argue that the real initiation lag time must be shorter than the one resulting from the experiments. If initiation lag times similar to the ones obtained with *n*-butylmethacrylate are assumed, the data reported in figure 6.7 are obtained.
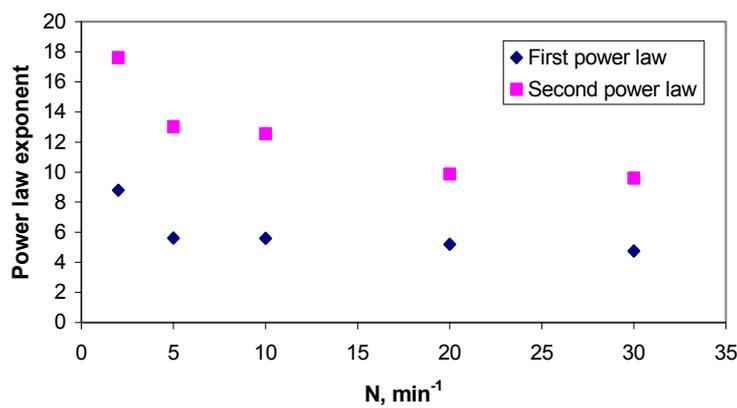


*Figure 6.7 The power law exponents for the polymerization of styrene at different rotational speed of the screw. T = 110 °C, [I]$_0$ = 2.5% v/v.*

Although this procedure is not rigorous, the choice of the modified values of the lag times being to some extent arbitrary, the data reported in figure 6.7 indicates that also for the bulk free radical polymerization of styrene the Trommsdorff effect can be reduced performing the polymerization at high rotational speed of the rotating element.

However, the evaporation of the monomer and the formation of bubbles inside the gap between the barrel and the rotating element are experimental evidence interesting in itself. In fact, they can explain the very high residence time required in reactive extrusion to obtain a desired conversion.

## 6.6. Absence of irregularities

The experiments performed with the helical barrel rheometer resulted in no irregularities of the increase of the viscosity, which is not in agreement with the results obtained with cone and plate. It must be noted, however, that the viscosity is derived from the pressure measurements in the helical barrel rheometer and from torque measurements in the cone and plate rheometer. The occurrence of a phase transition, leading to the formation of a *pseudo-*solid phase, interferes only with the torque measurement and not with the pressure measurement. In fact, as previously explained, the presence of a solid phase in the liquid would not alter the pressure drop measurement. On the other hand, the presence of a solid phase in the cone and plate rheometer would result in particles of the same order of magnitude of the gap between cone and plate, altering therefore the torque measurement.

Another interesting result consisted of some visual observations at the end of the experiments performed with the helical barrel rheometer. It was noticed that the material subjected to shear for the entire measurement was opaque, whereas the material that had been stagnant in the die, and therefore had not been subjected to shear during the experiment, was transparent.

This once more strengthens the contention, discussed already in the previous chapters, that shear can induce a phase modification, presumably a partial crystallization.

## 6.7. Conclusions

The helical barrel rheometer can be a useful tool for rheokinetic investigation. Although its volume is relatively small, its geometrical similarity with large-scale reactors, particularly extruders, makes it possible to perform a preliminary scale up of results obtained with a classical cone and plate rheometer.

The results presented in this chapter show that the Trommsdorff effect in bulk free radical polymerization of *n*-butylmethacrylate can be reduced performing the polymerization at a high rotational speed of the screw or, in other words, at a high average shear rate. Experiments performed with styrene were troubled by the evaporation of the monomer in their initial stage, but some considerations indicate that the same conclusion is valid also for styrene.

The experiments performed with the helical barrel rheometer resulted in the absence of irregularities of the viscosity trend. This is due to the fact that the occurrence of a partial solidification does not alter the viscosity measurement performed with the helical barrel rheometer. However, visual observation of the polymer obtained at the end of the experiments induces to argue that also in the helical barrel rheometer shear induced a partial solidification.

These results are in agreement with the ones discussed in the previous chapters and obtained with two different cone and plate rheometers and are encouraging in view of better-designed bulk free radical polymerization processes on industrial scale.

## 6.8. List of symbols

| | | |
|---|---|---|
| *h* | channel depth | m |
| *D* | screw diameter | m |
| *L* | length | m |
| *N* | screw rotational speed | s$^{-1}$ |

| $Q_d$ | drag flow | $m^3 s^{-1}$ |
|---|---|---|
| $Q_p$ | pressure flow | $m^3 s^{-1}$ |
| $W$ | width of the channel | m |
| $\Delta P$ | pressure difference | Pa |
| $\theta$ | screw helix angle | - |
| $\eta$ | viscosity | Pa |
| $\dot{\gamma}_{av}$ | average shear rate | $s^{-1}$ |

## 6.9. Literature

[1] D.B. Todd, C.G. Gogos, M. Esseghir, D.-W. Yu, S. Widagdo, *Monitoring Process Viscosities with a new on-line Rheometer*, Plastics Engineering, 1997, Vol. 53, 107-108.

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[4] A.Ya. Malkin, S.G. Kulichikhin, *Rheokinetics*. Hüthig & Wepf, Heidelberg, 1996.