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Rheokinetics

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CHAPTER 4

CONE AND PLATE RHEOMETER 1 VISCOSITY MEASUREMENTS

4.1. Introduction

Two different cone and plate rheometers have been used in the research described in this thesis. Since these rheometers operate in a different way and have different virtues and shortcomings, their results are complementary and are presented in two separate chapters.

In this chapter we shall discuss the results obtained with a shear controlled cone and plate rheometer (rheotron from Brabender, Duisburg, Germany).

The cone and the plate are stainless steel; the cone diameter and angle are 50 mm and 3°, respectively. The rheometer operates in the shear-controlled configuration, which makes it an ideal tool for performing experiments at constant shear rate. It measures the shear stress and then calculates the viscosity dividing the measured shear stress by the shear rate at which the experiment is performed. Moreover the “Brabender” rheometer has a wide range of operation and the experiments never had to be stopped because the torque sensor was overloaded.

The “Brabender” cone and plate rheometer allowed overfilling the gap between cone and plate without affecting the viscosity measurements. In this way it was possible to compensate the volume contraction that takes place during the polymerization and the evaporation of the monomer that could not be completely avoided since the system could be covered with a seal but could not be sealed off hermetically.

Compared with the other cone and plate rheometer used in this thesis (see chapter 5) the “Brabender” rheometer has some shortcomings. Temperature control is not very reliable and therefore many experiments had to be discarded and repeated. This chapter reports only the results obtained when the oscillations of the temperature could be kept under control and confined to $\pm 1^\circ\text{C}$. Moreover, the “Brabender” rheometer does not allow the measurement of the normal force. Finally, there is no automatic control of the distance between the cone and the plate, whose position has to be adjusted manually.

The increase of the viscosity during the bulk free radical polymerization of styrene and *n*-butylmethacrylate was measured in isothermal conditions and at constant shear rate. These two monomers were chosen as representative of a wide category of commodity polymers and resins. For all the experiments the same radical initiator (Trigonox 42S, Akzo Nobel) was used. No purification of the monomers and of the initiator was performed. Some experiments were repeated and stopped after different reaction times. Samples were taken and thermally quenched to stop the polymerization and subsequently analysed by nuclear magnetic resonance (NMR) and size exclusion chromatography (SEC) in order to determine the conversion and the average molar mass, respectively.

4.2. The double power law trend

Experiments have been performed at different temperatures and different shear rates. In all cases, the increase of viscosity during the polymerization has the same qualitative trend, whatever the monomer, the temperature or the shear rate. One typical result of the many obtained is shown in figure 4.1 in linear-linear and log-log coordinates.

Two different regions can easily be recognized. The increase of viscosity is faster at the end of the process than at the beginning. Experimental data are well fitted by two power laws:

$$\eta = at^b \quad (4.1)$$

a is a constant including the kinetic parameters of the initiation, propagation and termination reactions. The value of the exponent b is in all cases higher in the second part of the plot. The border between the two power law trends is chosen such that the highest possible values of the R^2 regression parameter are obtained.

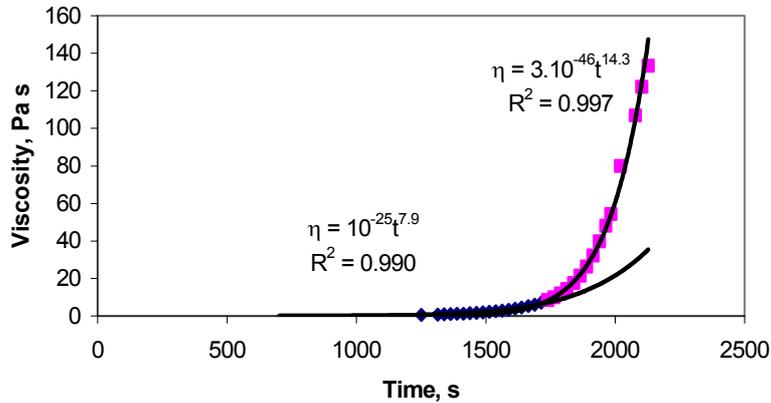


Figure 4.1.a. The increase of viscosity during the polymerization of *n*-butylmethacrylate. $T = 90\text{ }^{\circ}\text{C}$, $\dot{\gamma} = 30\text{ s}^{-1}$. R^2 is a regression parameter. Scale: linear-linear.

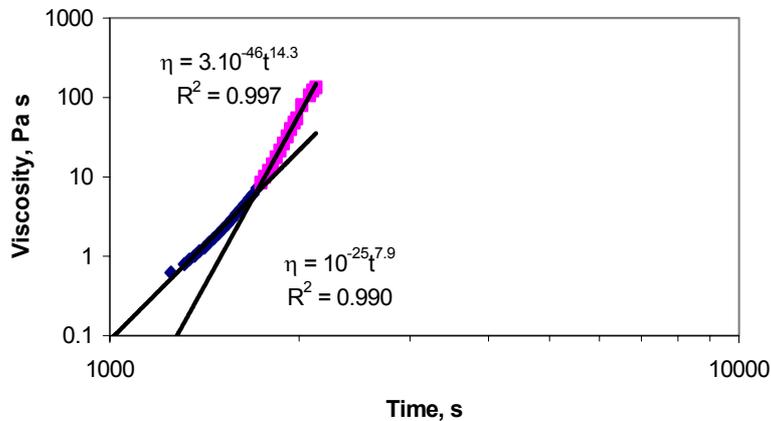


Figure 4.1.b. The increase of viscosity during the polymerization of *n*-butylmethacrylate. $T = 90\text{ }^{\circ}\text{C}$, $\dot{\gamma} = 30\text{ s}^{-1}$. Scale: log-log.

This result is in agreement with the literature: according to Yemelyanov *et al.* [1] and Malkin and Kulichikhin [2], the viscosity increase during bulk

free radical polymerization has a power law dependence on time and two, sometimes three regions can be distinguished.

- 1) $b \approx 1$ at the very beginning, where the degree of conversion is very low and there are no entanglements between macromolecules.
- 2) $5 < b < 7$ when the polymerization proceeds at a constant rate and no diffusion limitation (Trommsdorff effect) occurs.
- 3) $b \gg 7$ at high degrees of conversion, when the Trommsdorff effect takes place.

The two power law trends reported here refer to the last two regions and the two power law exponents are in agreement with the literature. The first region, where $b \approx 1$, regards too low values of the viscosity for the sensitivity of the “Brabender” rheometer.

The difference between the two exponents of the two power law trends resulting from the fitting of the experimental data can be considered as a measure of the autoacceleration of the polymerization, thus as a measure of the Trommsdorff effect.

4.3. The influence of the shear rate on the Trommsdorff effect

The influence of shear rate on the rate of increase of viscosity has been studied performing experiments at different shear rates but otherwise at the same experimental conditions (same temperature and same initiator concentration). The influence of the temperature and of the initiator concentration will be discussed in chapter 5. The viscosity data have been fitted according to the double power law trend and the two power law exponents have been plotted as a function of the shear rate (figures 4.2- 4.5).

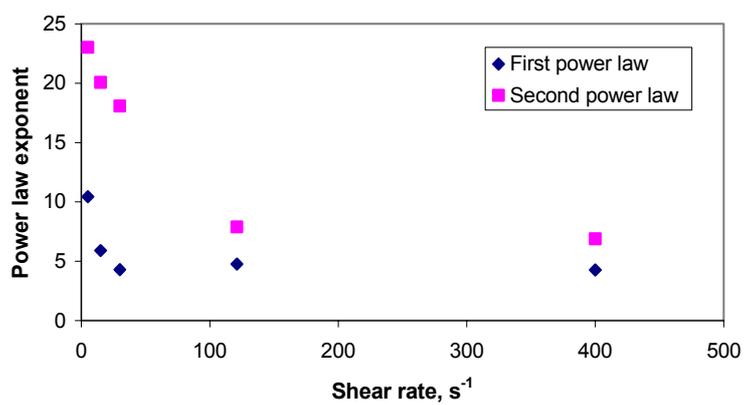


Figure 4.2. Power law exponents as a function of shear rate for the polymerization of styrene at 90 °C.

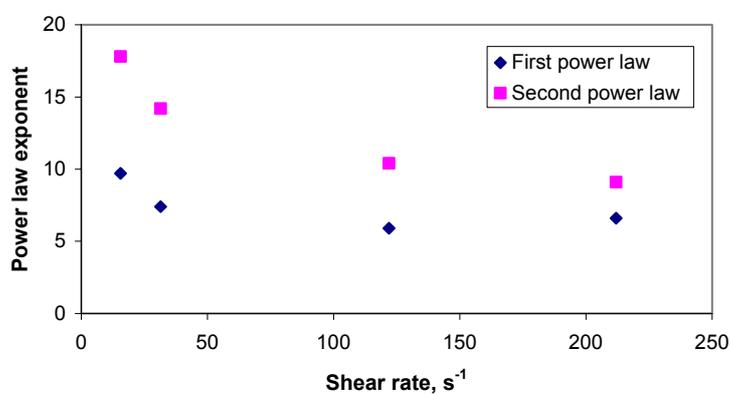


Figure 4.3. Power law exponents as a function of shear rate for the polymerization of *n*-butylmethacrylate at 110 °C.

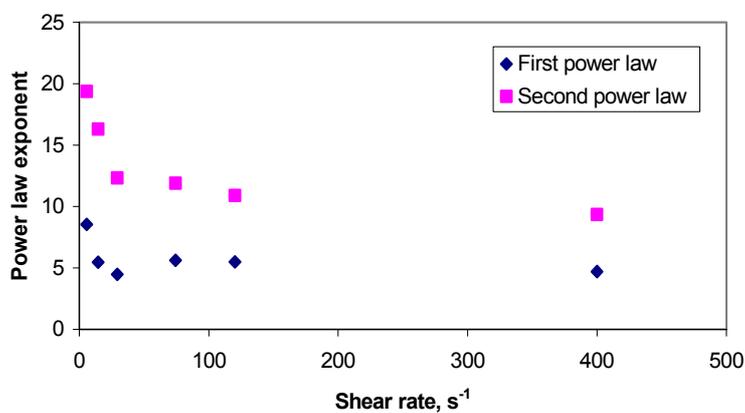


Figure 4.4. Power law exponents as a function of shear rate for the polymerization of styrene at 116 °C.

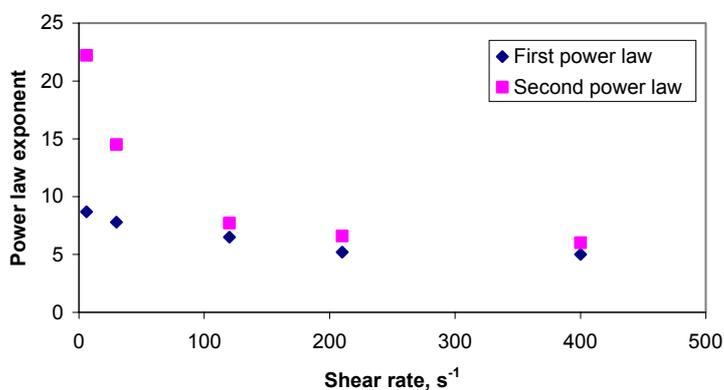


Figure 4.5. Power law exponents as a function of shear rate for the polymerization of n-butylmethacrylate at 90 °C.

The difference between the power law exponents is significant at low shear rates and tends to decrease as the shear rate increases. This leads to a remarkable conclusion: the Trommsdorff effect is reduced when the polymerization is performed at higher shear rates. Within the accuracy of

the measurements, no remarkable differences could be noticed between the two monomers considered.

In some cases, when the shear rate is higher than 200 s^{-1} , a single power law could fit the time-dependent increase of viscosity as well, suggesting that the Trommsdorff effect has been eliminated completely.

Since the Trommsdorff effect is a direct consequence of the decrease of the rate constant of the termination reaction, taking place at a certain degree of conversion, this rate constant k_t must be a function of the shear rate at which the polymerization is performed.

In other words, the rheokinetic experiments reported here indicate a way to solve the problem of autoacceleration in industrial polymerization processes. At the same time, they give important qualitative information about the dependence of the kinetic constant of the termination reaction on the shear rate.

The reduction of the Trommsdorff effect at high shear rate can be explained by arguing that shear induces elongation and orientation of the entangled macromolecules (figure 4.6), reducing the diffusion limitation that causes the autoacceleration.

Referring once again to the traffic jams in Italian cities (see chapter 2), we can imagine that shear acts like a policeman trying to put some order in a mass of “entangled” cars so that they can move more easily.

It must be noted that in the whole interval of shear rate considered, polymer systems normally show a shear-thinning behavior. However, shear-thinning can be ruled out as underlying reason for the reduction of the Trommsdorff effect at high shear rate. If that were the explanation, the power law exponents would decrease not only at shear rates lower than 100 s^{-1} , but also in the interval $100\text{-}400 \text{ s}^{-1}$, where they actually level off (see figures 4.2 - 4.5).

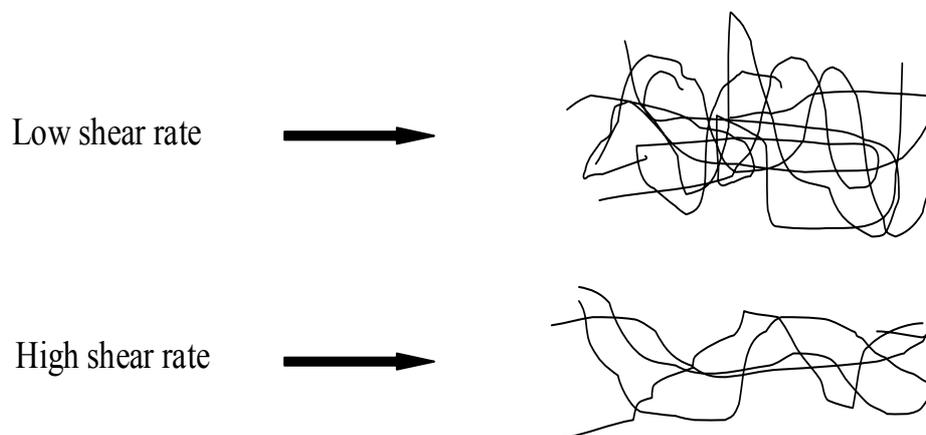


Figure 4.6. A schematic representation of the elongation and orientation of the macromolecules at high shear rate.

4.4. Onset of irregularities

Figure 4.1 refers only to the part of the polymerization process during which the increase of viscosity with time has a regular and reproducible trend. When the conversion tends towards completion a peculiar phenomenon occurs. In fact, the viscosity showed an irregular and irreproducible behavior, as shown in figure 4.7.

After reaching a certain value, the viscosity suddenly decreases and then shows a highly irregular trend. Similar trends were obtained in all the other experiments performed, both with styrene and with *n*-butylmethacrylate. This transition always occurred at very high conversions, around 90 %.

It would be easy to explain this irregular and erratic behavior by a limited reliability of the “Brabender” rheometer when a critical point is reached. If this were the explanation, a common value of the maximum shear stress, corresponding to the onset of the irregular and erratic trend, should be found for experiments performed at different shear rates. Such a common value could not be recognized. Moreover, no clear relationship could be found between the maximum shear stress and the shear rate from the experimental data.

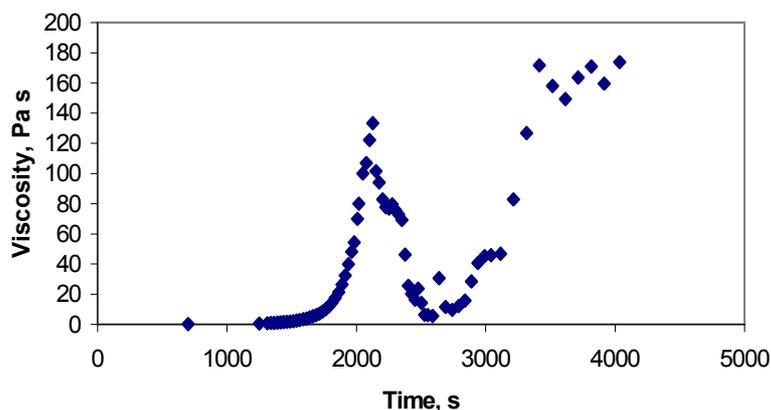


Figure 4.7. One example of the irregular trend of the viscosity during the polymerization of *n*-butylmethacrylate. $T = 90\text{ }^{\circ}\text{C}$, $\dot{\gamma} = 30\text{ s}^{-1}$.

Furthermore the values of the maximum shear stress were well within the reliability limits of the “Brabender” rheometer (25000 Pa, according to the producer).

In order to investigate the possibility of slip, experiments were also performed with a cone and a plate that were radially grooved. The same phenomenon occurred and no significant differences between the viscosity trends obtained with grooved and smooth cone and plate could be noticed. This result strengthens the contention that wall slip is not the underlying reason for the irregularities.

These considerations and experimental evidences induce to argue that some physical or chemical phenomena and not a failure of the rheometer cause the irregularities in the viscosity trend.

This contention is also strengthened by the following experimental evidence. There is an evident relationship between the maximum viscosity η_{max} just before the onset of the irregular trend and the shear rate. η_{max} decreases for increasing shear rates and the data are well fitted by a power

law trend, as shown in figures 4.8 and 4.9. The fact that the power law exponents are smaller than -1 indicates clearly that the phenomena under investigation are not simply due to a shear-thinning behavior.

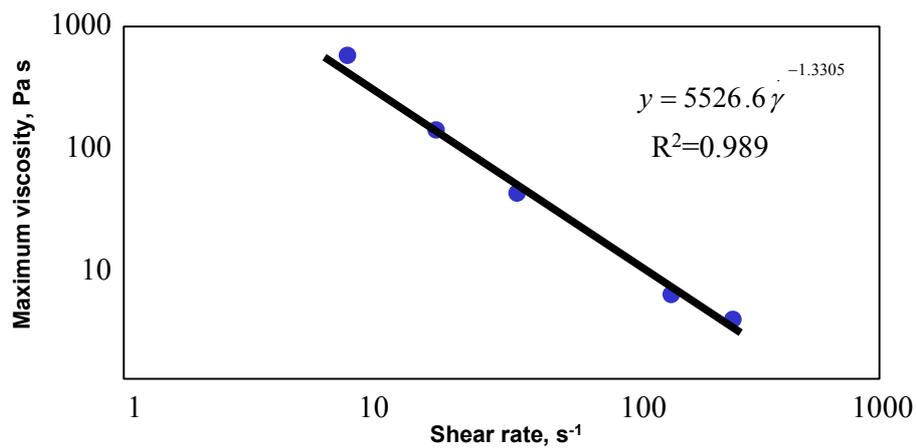


Figure 4.8. Maximum viscosity for the polymerization of styrene at 116°C.

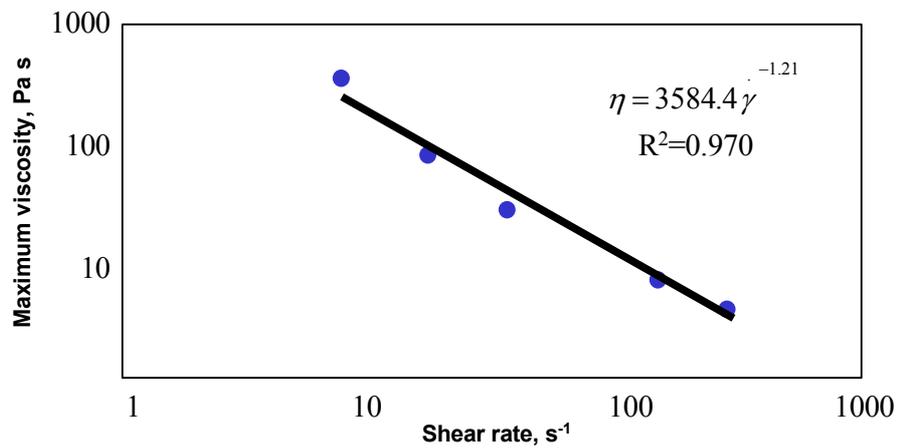


Figure 4.9. Maximum viscosity for the polymerization of n-butylmethacrylate at 104°C.

A possible explanation for the onset of the irregular behavior is that phase separation occurs and a *pseudo*-solid phase is formed. At a certain point of the process, the polymer is no longer soluble in the residual monomer and separates from the bulk phase, giving rise to instabilities of the viscosity trend. The instabilities can then be ascribed to the presence of *pseudo*-solid particles in the small gap between the cone and the plate, which causes the viscosity measurement to be irregular and irreproducible.

This hypothesis is confirmed by some literature evidence. Malkin and Kulichikhin [3] ascribe a sudden decrease in the viscosity during a polymerization process to phase separation, but they do not mention any irregular and irreproducible trend of the viscosity. Onuki [4] and Onuki *et al.* [5] review phase transitions of concentrated polymer mixtures in shear flow. They state that the oscillation and irreproducibilities of viscosity (they actually refer to shear stress at constant shear rate) versus time trends obtained by computer simulation are due to a phase separation. Finally Janssen and Janssen-van Rosmalen [6] studied the influence of the decrease of conformational entropy on phase transition phenomena, caused by the elongation and orientation of macromolecules in a shear flow field. They showed that there can be a positive driving force for phase separation when the polymeric system is sheared, even under experimental conditions in which the driving force would be negative in the absence of flow.

Indeed, this presumed phase separation seems to be strongly influenced, if not induced, by the shear rate. When the shear rate is high, a certain order in the spatial distribution of the macromolecules is produced, increasing their chemical potential. Therefore, the phase separation can occur at lower values of the viscosity.

Finally, the rheokinetic experiments performed with the “Brabender” rheometer give interesting indications about the possibility of shear-induced phase transition during bulk free radical polymerization. Unfortunately, it was not possible to verify the presence of phase separation analyzing the sample at the end of the experiments by a microscope technique. In fact, a

shear-induced phase separation would disappear when the sample is removed and prepared for microscope analysis.

The possibility of a shear-induced phase transition will be further discussed in chapter 7, that is dedicated to the influence of shear rate on the thermodynamics of bulk free radical polymerization.

4.5. Degree of conversion and average molar mass

As explained in chapter 3, removing a sample from the cone and plate rheometer and quenching the polymerization is a troublesome operation. However, some interesting indications were given by NMR and SEC about the trend of degree of conversion and average molar mass during the polymerization.

In order to establish the conversion at the onset of the Trommsdorff effect NMR analyses were performed. From the experiments as given in the previous sections the time of onset was determined. The experiments were then carefully repeated until the onset of the Trommsdorff effect. Then samples were taken and the reaction was quenched immediately. The degree of conversion could be detected with NMR by comparison of the ratio of double C=C bonds and single C-C bonds. A similar procedure was used to determine the conversion at the onset of the irregularities.

The NMR analyses make it possible to draw some interesting conclusions. They show that the onset of the Trommsdorff effect occurs at approximately 60% conversion. However, it should be remembered that, as already mentioned in chapter 2, the Trommsdorff effect does not set in at once, but gradually. Therefore, defining *the* conversion of onset is not only experimentally troublesome but also scientifically not correct.

Within the accuracy of the measurement technique no influence of the shear rate can be detected on the onset of the Trommsdorff effect. This is strengthened by the fact that also in the absence of shear rate the onset takes place at 60% conversion, as results from dynamic scanning calorimetry [7].

Moreover, NMR analyses show also that the irregularities of the viscosity trend always begin at conversion between 85-90%.

Finally, they show as well that the conversion is not complete even when the experiments are continued long after the onset of the irregularities. This is in agreement with the general theory of free radical polymerization. In fact, when the concentration of monomer is very low the rate of polymerization decreases (see equation (2.16)) because in this condition even the mobility of monomer molecules is strongly hindered. This problem will be further discussed in chapter 7.

The SEC analyses performed on samples taken after different reaction times show an increase of the average molar mass after the onset of the Trommsdorff effect. This can be explained with a longer average lifetime of the growing macromolecules due to the decrease of the rate of the termination reaction.

Finally, figure 4.10 shows the average molar mass at the end of the experiments as a function of the shear rate.

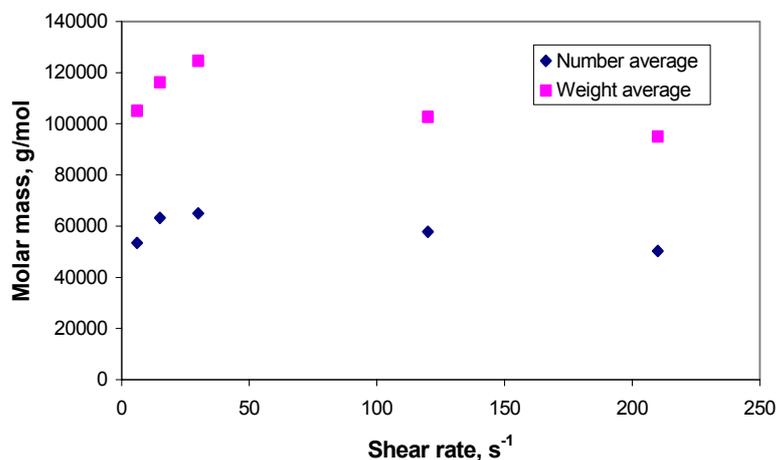


Figure 4.10. The average molar mass at the end of the polymerization of styrene at 116 °C.

There seems to be a trend that the molar mass passes a maximum. However, to our knowledge, there is no physical reason that would justify the presence of a maximum.

The data obtained induce to argue that the molar mass at the end of the polymerization is not influenced significantly by the value of the shear rate at which the polymerization is performed.

This would prove that increasing the shear rate, the Trommsdorff effect can be reduced without affecting the physical properties of the polymer produced. However the accuracy of the measurement is not enough to draw a firm conclusion.

4.6. Conclusions

The increase of viscosity during the polymerization of styrene or *n*-butylmethacrylate has been measured with a cone and plate rheometer at different temperature and different shear rate. The viscosity-versus-time trend can be fitted by a double power law curve and the difference between the two power law exponents can be considered a measure of the Trommsdorff effect.

The Trommsdorff effect can be significantly reduced if a free radical polymerization is performed at high shear rate. With knowledge of this, heat transfer problems and hot spots in polymerization reactors can be predicted more precisely and reduced. However it must be verified first whether this result is also valid for other configurations and not only for the cone and plate rheometers. This problem will be further discussed in chapter 6.

Size exclusion chromatography analyses show that the average molar mass of the polymer obtained at the end of the experiments is not influenced significantly by the shear rate. If confirmed on industrial scale, this result would imply that it is possible to reduce the Trommsdorff effect by increasing the shear rate at which the polymerization is performed without affecting the material properties of the end-product obtained.

At high degrees of conversion the viscosity has an irregular and erratic trend with time. Some experimental data and literature evidences induce to argue that this is not due to a failure of the cone and plate rheometer or to slip, and that phase separation might be the underlying reason for these irregularities. We shall discuss this problem further in the following chapters.

4.7. List of symbols

a, b	constant	-
t	time	s
R^2	regression parameter	-
T	Temperature	°C
η	viscosity	Pa s
η_{max}	maximum viscosity	Pa s
$\dot{\gamma}$	shear rate	s ⁻¹

4.8. Literature

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