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CHAPTER 5

CONE AND PLATE RHEOMETER 2 VISCOSITY AND NORMAL FORCE MEASUREMENTS

5.1. Introduction

In this chapter the results obtained with a "TA Instruments" rheometer will be discussed.

This cone and plate rheometer allows simultaneous measurement of the viscosity and of the normal force. Therefore it has been used to obtain further insight into the evolution of rheological and viscoelastic properties during polymerization.

The "TA Instruments" rheometer is provided with a Peltier Plate for heating and temperature control. The latter is particularly precise and no deviations of the temperature from the set-point value could be noticed, within the sensitivity of the instrument (0.1 °C). Moreover, this rheometer is provided with a "solvent trap cover" that prevents evaporation of the monomer.

Therefore, the "TA Instruments" rheometer allows a better control of the experimental conditions than the "Brabender" rheometer. On the other hand, the "TA Instruments" rheometer has a worse performance at high stress (therefore at the very end of the polymerization). The experiments discussed in this chapter were all stopped when either the torque or the normal force sensor were overloaded, which often occurred before the onset of the irregularities.

5.2. Comparison of the two cone and plate rheometers. Stress controlled and shear controlled

The most important qualitative difference between the two cone and plate rheometers used in this thesis is that only the "TA Instruments" rheometer permits to measure both the viscosity and the normal force simultaneously. However the range of operation of this rheometer is smaller. All the experiments had to be stopped when the torque and/or the normal force sensor were overloaded.

Another important difference concerns the way in which the two rheometers carry out a measurement.

The "Brabender" rheometer is a shear-controlled rheometer. It operates controlling the shear rate and measuring the shear stress. Therefore, it is particularly convenient for performing measurements at constant shear rate. In fact, it is able to give a value of the viscosity every five seconds during the rheokinetic experiments.

On the other hand, the "TA Instruments" rheometer operates in the stress-controlled configuration. The stress is controlled during the measurement and the rotational velocity is measured. The shear rate is kept constant by means of the software incorporated in the rheometer. Only a value of the viscosity every 90 seconds could be provided by the rheometer when performing the rheokinetic experiments at constant shear rate. A lower sampling time resulted in oscillations of the shear rate during the experiments, especially in the later stages of the polymerization where the increase of the viscosity is faster and the rheometer works almost at its maximal capacity.

In conclusion, the "Brabender" rheometer is, in principle, better designed to perform experiments at constant shear rate. However, the "TA Instruments" rheometer has a better temperature control and prevents the evaporation of the monomer. Moreover, it is equipped with an electronic control of the distance between the cone and the plate, whereas this distance has to be adjusted manually with the "Brabender" rheometer.

5.3. *n*-Butylmethacylate experiments

5.3.1. Experiments at different shear rate

The experiments with the "TA Instruments" rheometer had to be performed with a higher initiator concentration than the ones discussed in chapter 4. This is due to the fact that different batches of monomer and initiator had to be used. Probably, the *n*-butylmethacrylate used for these experiments contained more inhibitor than the one used for the experiments with the "Brabender" rheometer. Hence the need for a higher initiator concentration.

Experiments were also performed with the same value of initial initiator concentration $[I]_0$ as in chapter 4 (0.33% v/v) but this resulted in very long initial lag times of the increase of viscosity.

Because of the use of different batches, a direct quantitative comparison between the results obtained with the two rheometers appeared not to be possible.

However, the results obtained with the "TA Instruments" rheometer are in good agreement with the ones discussed in chapter 4. In fact, the increase of viscosity could be well fitted with a double power law trend, confirming the presence of the Trommsdorff effect. Moreover, in the latest stages of the polymerization irregularities in the viscosity trend were often noticed. This can be seen as further confirmation that the irregularities were not due to instrument failure.

The results of experiments performed at different shear rate but otherwise the same experimental conditions are reported in figures 5.1 and 5.2, in terms of the power law exponents obtained from the fitting of the increase of the viscosity until the onset of the irregularities.
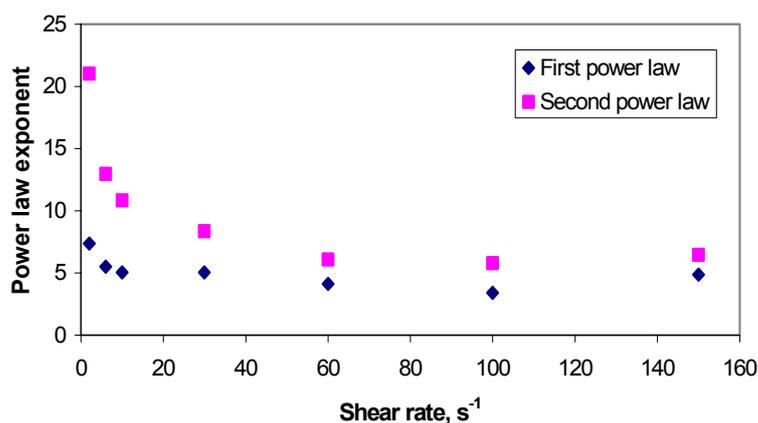

Figure 5.1. Power law exponents for the polymerization of n-butylmethacrylate. T = 100 °C, $[I]_0$ = 1 % v/v.

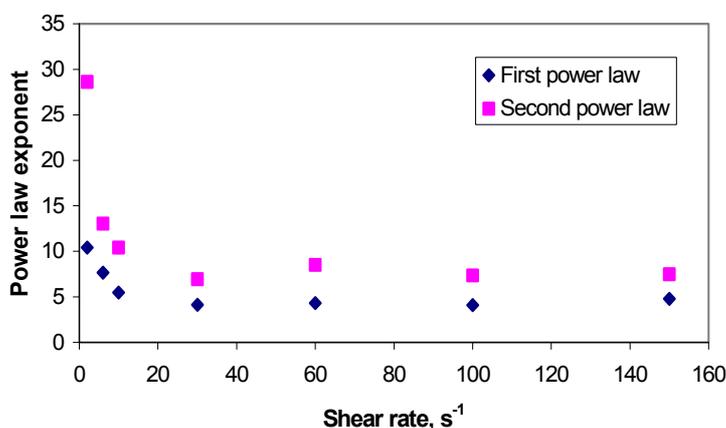*Figure 5.2. Power law exponents for the polymerization of n-butylmethacrylate. $T = 110\,°C$, $[I]_0 = 0.5\%$ v/v.*

These results confirm the qualitative trend noticed with the "Brabender" rheometer and discussed in chapter 4. The extent of the Trommsdorff effect is reduced when the polymerization is performed at a higher shear rate. From these experiments it results that a shear rate of about 100 s^{-1} is required to reduce significantly, if not eliminate, the Trommsdorff effect.

5.3.2. Experiments at different initiator concentration

Some experiments were performed at different values of the initial initiator concentration $[I]_0$ in order to test the influence of this parameter on the Trommsdorff effect. The results are reported in figure 5.3 in terms of viscosity-versus-time curves and in figure 5.4 in terms of power law exponents.

The data shown in figure 5.3 show the influence of the initiator concentration on the time required to perform the polymerization. The higher is $[I]_0$, the shorter are the initial lag time, and the time necessary to reach a certain value of the viscosity.

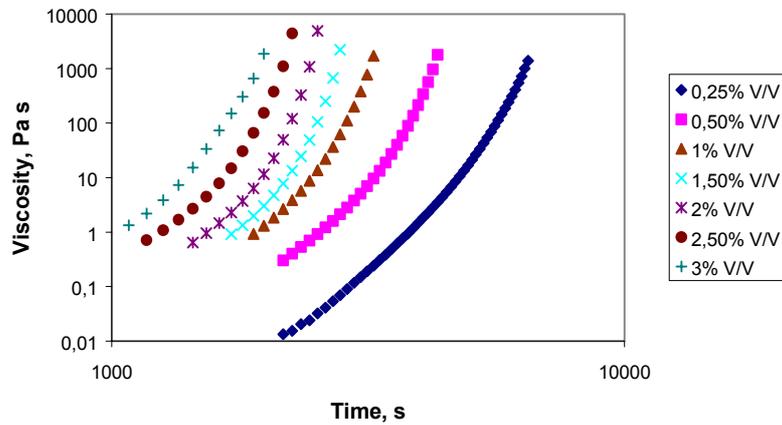*Figure 5.3. The viscosity increase during the polymerization of n-butylmethacrylate. T = 110 °C, $\dot{\gamma} = 2\ s^{-1}$.*

Figure 5.4. points out the influence of the initiator concentration on the Trommsdorff effect.

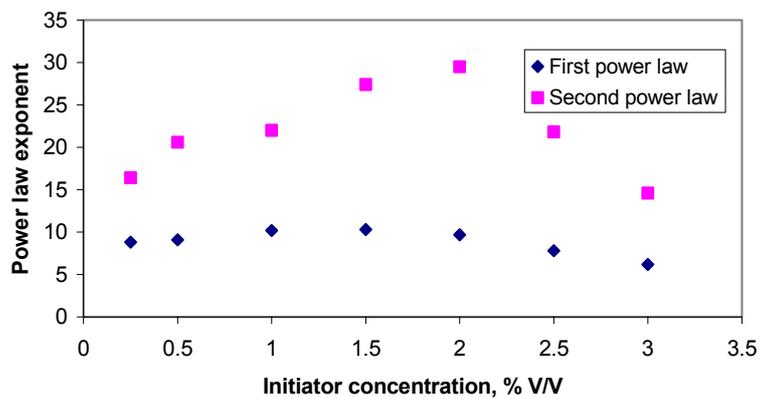*Figure 5.4. Power law exponents for the polymerization of n-butylmethacrylate. T = 110 °C. $\dot{\gamma} = 2\ s^{-1}$.*

Initially the Trommsdorff effect increases with $[I]_0$ and then it decreases after reaching a maximum. A complete explanation for the initial increase in the severity of the Trommsdorff effect with initiator concentration is not available, but it is intuitively reasonable that the diffusion limitation of the termination reaction – which gives rise to the effect – is less severe when the initiator concentration is low, and therefore the chemical reaction kinetics in the system are slower. The presence of a maximum in figure 5.4 can be explained with the influence of the initiator concentration on the average molar mass of the polymer obtained. As we have seen in chapter 2 (equation 2.19), a high initial initiator concentration results in a lower average molar mass of the polymer obtained, which reduces the entanglements and the diffusion limitations that are the originating cause of the Trommsdorff effect [1-3].

We could argue that this situation would correspond to traffic jams formed by only small city cars. In this situation the mobility of cars would be higher than in a traffic jam formed by big cars, limousines and trucks.

Therefore the Trommsdorff effect can be reduced by an appropriate choice of the initial initiator concentration. At low values of $[I]_0$, a price has to be paid in terms of longer reaction times required (see figure 5.3). Virtually, a zero value of the initial initiator concentration results in no polymerization, and therefore, in no Trommsdorff effect. At high values of $[I]_0$, the price to pay to reduce the Trommsdorff effect is a lower average molar mass of the polymer, which usually results in worse mechanical properties of the end product.

5.3.3. Experiments at different temperature

The effect of the temperature at which the polymerization is carried out on the extent of the Trommsdorff effect was studied performing different experiments at varying temperature but otherwise the same experimental conditions. The results are shown in figures 5.5 and 5.6.
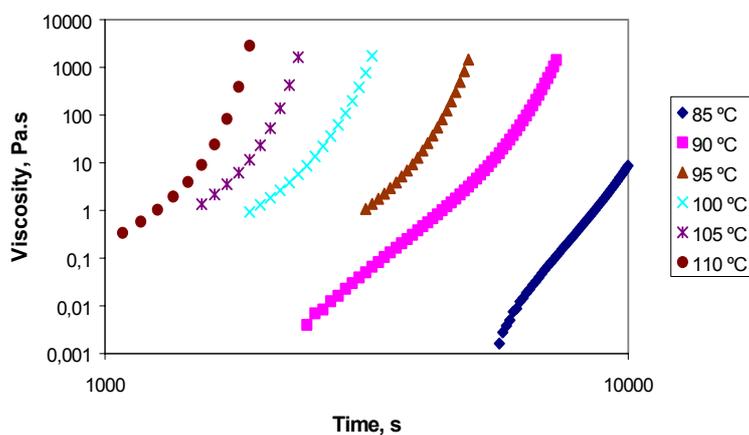
Figure 5.5. The viscosity increase during the polymerization of n-butylmethacrylate. $[I]_0 = 1\%$ v/v. $\dot{\gamma} = 2\ s^{-1}$.
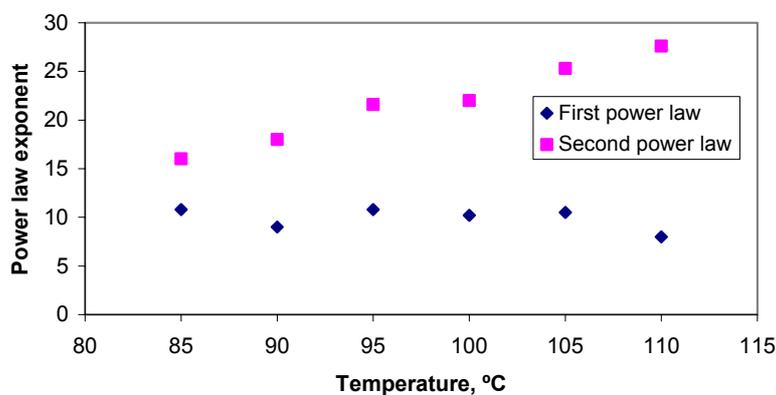
Figure 5.6. Power law exponents for the polymerization of n-butylmethacrylate. $[I]_0 = 1\%$ v/v. $\dot{\gamma} = 2\ s^{-1}$.

Figure 5.6 shows clearly that the Trommsdorff effect is larger when the polymerization is performed at a higher temperature. A low temperature results in a slow polymerization and a long initial lag time (figure 5.5) during which the entanglements and the diffusion limitations set in slowly.

At higher temperatures, the polymerization is faster and, presumably, the sudden appearance of the entanglements causes a stronger Trommsdorff effect.

In general, the role that the temperature plays on the extent of the Trommsdorff effect is controversial. On one side, a higher temperature results in lower values of the viscosity, and therefore, in smaller diffusion limitations, which should lead to a less pronounced autoacceleration. On the other side, a higher temperature results in a faster polymerization, which should imply a larger Trommsdroff effect. Moreover, the temperature influences in a different way the propagation and the termination reaction.

Therefore, it is still dangerous to generalise the trend shown in figure 5.6. This trend should be considered to be valid only for *n*-butylmethacrylate, and not for any bulk free radical polymerization.

5.4. Styrene experiments

The experiments with styrene were characterized, especially at relatively low temperatures, by particularly pronounced irregularities in the increase of viscosity.

At T ≤ 120 °C, the power law exponents could be determined trustfully only for shear rates smaller than 10 s^{-1}. They were in agreement with the values obtained with the "Brabender" rheometer and with *n*-butylmethacrylate. However, at higher shear rates, the increase of viscosity was affected by irregularities. These irregularities occurred at relatively low conversion. In fact, they occurred in the region where the onset of the Trommsdorff effect is due to happen and they resulted in unreliable values of the power law exponents.

At higher temperatures (130 °C) these irregularities were less pronounced and the data reported in figure 5.7 could be obtained.
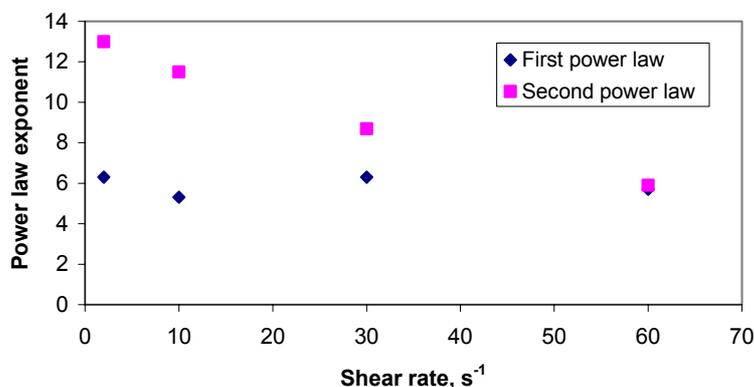
Figure 5.7. Power law exponents for the polymerization of styrene. T = 130 °C, [I]$_0$ = 0.5% v/v.

They show that also for polystyrene the Trommsdorff effect can be reduced by performing the polymerization at high shear rate.

The irregularities can be due to the fact that the polymerizations are performed at temperatures close to the glass transition temperature for polystyrene (T$_g$ = 100 °C). The formation of a *pseudo*-solid phase alters the torque measurement and interferes with the software keeping the shear rate constant. This interpretation is strengthened by the observation that the irregularities are more pronounced at higher shear rate. In this case, probably, the more pronounced orientation and elongation of the macromolecules result in a more consistent formation of the *pseudo*-solid phase, which interferes with the torque measurement.

The glass transition temperature for polybutylmethacrylate is much lower (T$_g$ = 40 °C). Therefore, the formation of a *pseudo*-solid phase occurs only very late in the polymerization, which results in the presence of irregularities only at relatively high shear rate and at the latest stage of the polymerization. Therefore these irregularities do not hinder the determination of the power law exponents in the case of the polymerization of *n*-butylmethacrylate.

5.5. Comparison of the viscosity measurements performed with the two cone and plate rheometers

Notwithstanding the problems and irregularities discussed in the previous paragraph, both cone and plate rheometers used in this thesis yielded the following qualitative results.

1) If the initial time lag is neglected, the increase of viscosity during a bulk free radical polymerization can be fitted by a double power law trend.

2) The Trommsdorff effect is reduced, or even eliminated, when the polymerization is carried out at a higher shear rate.

The experiments performed with the "Brabender" rheometer were characterized, for both the monomers investigated in the same way, by the onset of irregularities at high degree of conversion. A regular trend could be noticed between the value of the viscosity at the onset of the irregularities and the shear rate at which the experiments were performed (figures 4.8 and 4.9).

Some irregularities were noticed also in the experiments performed with the "TA Instruments" rheometer.

In the case of styrene, especially at lower temperatures and higher values of the shear rate, the irregularities hindered the determination of reliable values of the power law exponents.

A possible explanation of this difference of behavior between the two rheometers can be the fact that the "TA Instruments" rheometer is stress-controlled, whereas the "Brabender" rheometer is shear-controlled. In the former case the formation of a *pseudo*-solid phase can have negative influence on maintening a constant value of the shear rate during the experiments.

In the case of *n*-butylmethacrylate the irregularities were noticed only at shear rates higher than 30 s^{-1}. At lower shear rates the experiments had to be stopped before the onset of the irregular and irreproducible trend, because the torque and normal force sensor were overloaded.

These irregularities occurred after the onset of the Trommsdorff effect and at very high conversion. In fact, they did not hinder the fitting of the viscosity data and the determination of the power law exponents. Moreover they set in at a lower viscosity when the shear rate at which the polymerization is carried out increases.

Therefore they are shear-induced, in agreement with the experimental results obtained with the "Brabender" rheometer (see figures 4.8 and 4.9).

5.6. Normal stress

A typical characteristic of visco-elastic polymeric systems is the presence of normal stress in shear flow [5]. When a non-elastic fluid is sheared between the cone and plate of a rheometer, only a tangential stress is recorded from which the value of the viscosity of the fluid can be derived. On the contrary shearing of visco-elastic fluids results in the presence of a normal stress and therefore the cone and the plate are pushed apart or pulled together.

The presence of normal stresses in shear flow can be described on a macroscopic scale with the phenomenon of the rod climbing. When a rod is turned in a beaker containing a Newtonian liquid, the fluid will tend to move away from the rod because of inertial forces. On the contrary, visco-elastic fluids will climb the rod, as a consequence of the normal stress (see figure 5.8).

The normal stress is also responsible for extrudate swell. The latter can be considered to be a normal stress indication and can be used to compare different materials. Therefore the rheokinetic study of the increase of normal stress during polymerization can be important for reactive extrusion processes.

The following of this chapter is dedicated to the discussion of the increase of normal stress during bulk free radical polymerization measured with the "TA Instruments" rheometer.
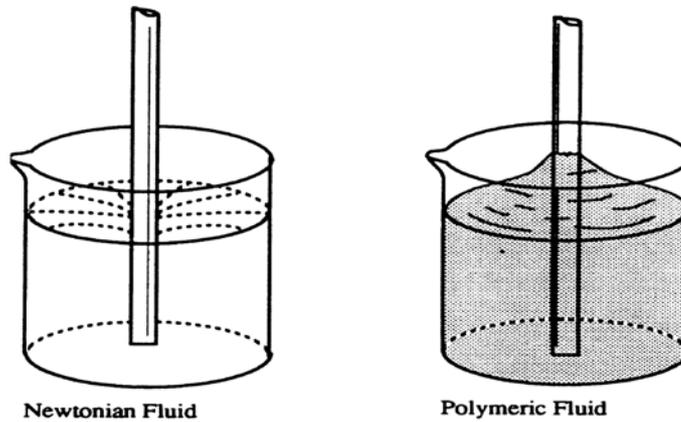
Newtonian Fluid   Polymeric Fluid

Figure 5.8. The rod climbing of polymeric fluids due to the presence of normal stress.

5.7. The normal stress and the Trommsdorff effect

The increase of the normal force during polymerization is reported in figures 5.9 and 5.10 for two particular experimental conditions. Also the increase of the viscosity is reported to compare the two experimental trends.
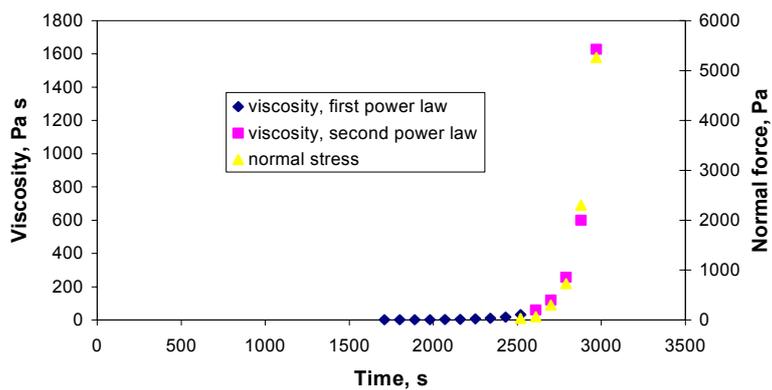

Figure 5.9. Viscosity and normal stress for the polymerization of n-butylmethacrylate. $\dot{\gamma} = 2\ s^{-1}$, $T = 100\ °C$, $[I]_0 = 1\%$.

Similar trends refer to the part of the experiment not affected by irregularities and were obtained in all the experiments performed with *n*-butylmethacrylate.
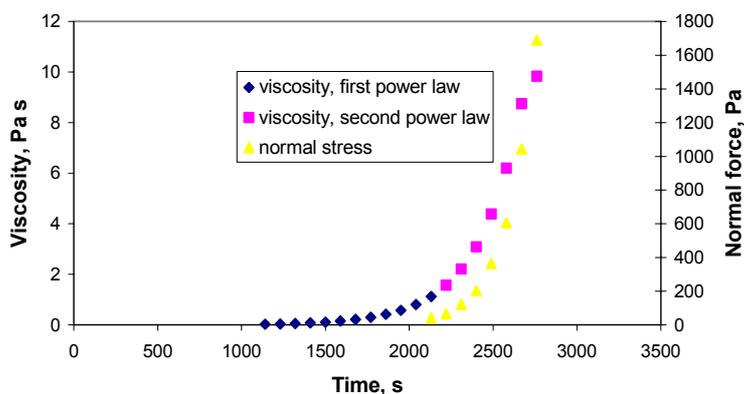

Figure 5.10. Viscosity and normal stress for the polymerization of n-butylmethacrylate. $\dot{\gamma} = 60\ s^{-1}$, *T = 100 °C, [I]$_0$ = 1%.*

The normal force is negligible in the first part of the polymerization. Then it starts to increase parallel to the viscosity when the Trommsdorff effect sets in. This experimental observation leads to the following conclusion. During bulk free radical polymerization the normal force begins to be significant when the conversion and the entanglements between the random coils are high enough to give rise to the diffusion limitations that are the cause of the Trommsdorff effect.

The increase of the normal force can be fitted by a power law. Then the power law exponent can be used to compare experiments performed at different shear rates. This results in figures 5.11 and 5.12.
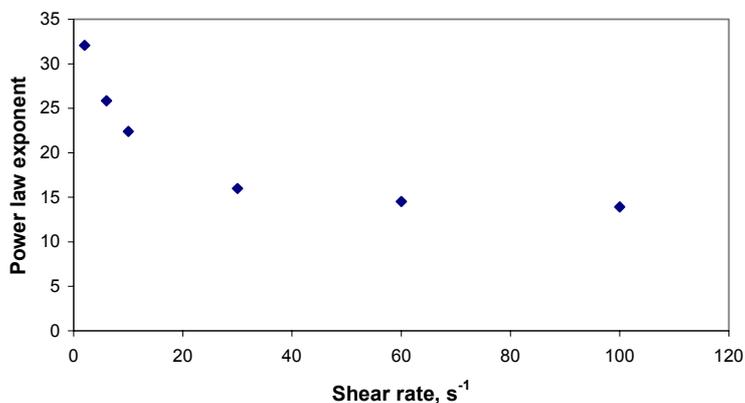
Figure 5.11. The power law exponent for the increase of the normal force during the polymerization of n-butylmethacrylate at different shear rate. T = 100 °C, [I]$_0$ = 1%.
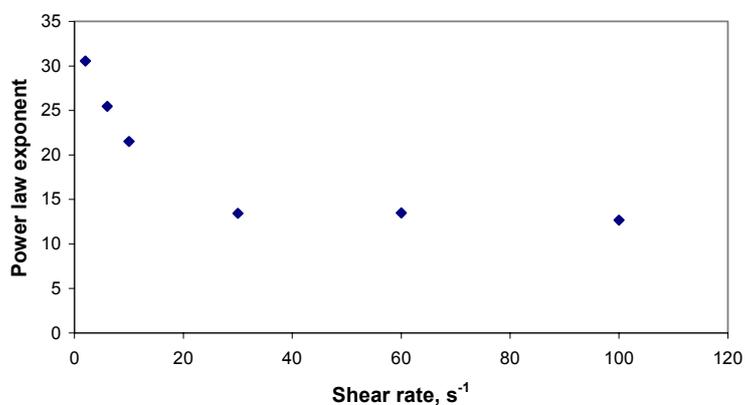

Figure 5.12. The power law exponent for the increase of the normal force during the polymerization of n-butylmethacrylate at different shear rate. T = 110 °C, [I]$_0$ = 0.5%.

The power law exponent decreases when the shear rate at which the polymerization is performed increases. Therefore there is a similarity between the difference of the power law exponents resulting from the fitting of the viscosity and the power law exponent resulting from the fitting of the

normal force. The reduction of the Trommsdorff effect at high shear rate goes along with a slower increase of the normal force.

This experimental evidence proves that also normal force measurements can be useful for a rheokinetic analysis of polymerization processes. In particular, the rate of increase of the normal force during a bulk free radical polymerization can be used as a measure of the Trommsdorff effect.

The experiments performed at different initiator concentrations and at different temperatures strengthen this contention. Also in these cases there is a similarity between the power law exponent of the normal force and the power law exponents of the viscosity. In fact the power law exponent resulting from fitting of the normal force data increases with the increase of the initiator concentration, reaches a maximum and then decreases, as reported in figure 5.13. This trend is qualitatively similar to the one reported in figure 5.4 for the viscosity. On the other end, the power law exponent regarding the normal force increases when the polymerization is performed at a higher temperature (see figure 5.14), which is in good agreement with figure 5.6.
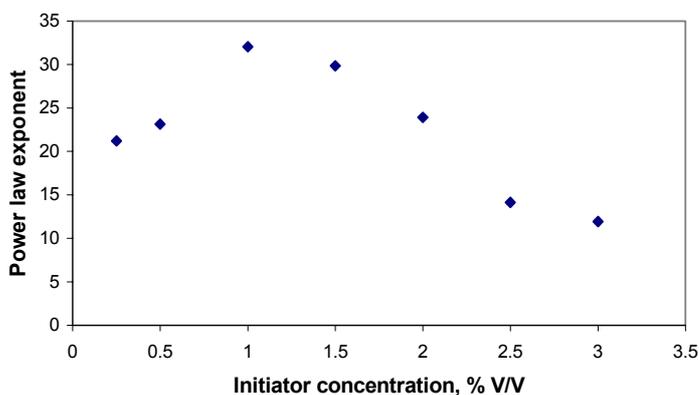

Figure 5.13. The power law exponent for the increase of the normal force during the polymerization of n-butylmethacrylate at different initiator concentration. T = 110 °C, $\dot{\gamma}$ = 2 s⁻¹.
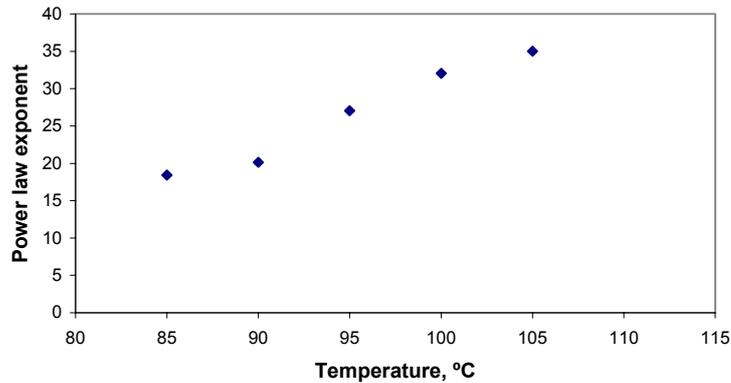
Figure 5.14. The power law exponent for the increase of the normal force during the polymerization of n-butylmethacrylate at different temperature. $[I]_0 = 0.5\%$, $\dot{\gamma} = 2\ s^{-1}$.

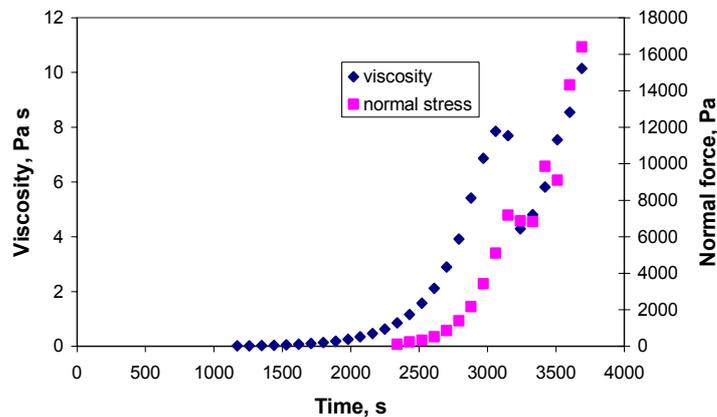Finally, also the normal force assumed an irregular behavior when the viscosity did, as shown in figure 5.15.

Figure 5.15. The parallel irregularities of the normal force and of the viscosity during the polymerization of n-butylmethacrylate. $[I]_0 = 0.5\%$, $\dot{\gamma} = 100\ s^{-1}$, $T = 100\,°C$.

This experimental evidence strengthens the contention that a phase transition is the underlying reason for the irregularities. By all appearances, the formation of a *pseudo*-solid phase between the cone and plate interferes with the measurement of the still increasing viscosity and normal force.

5.8. Conclusions

The experiments performed with the "TA Instruments" rheometer confirmed qualitatively the results obtained with the "Brabender" rheometer, especially for the polymerization of *n*-butylmethacrylate. In particular, the same influence of the shear rate on the Trommsdorff effect was noticed.

Moreover, these experiments showed that a higher temperature results in a larger Trommsdorff effect. The same is also true for the initial initiator concentration but only until a certain value, after which the Trommsdorff effect decreases because high values of initiator concentration results in low average molar mass.

The normal force is negligible initially and it begins to increase exactly when the Trommsdorff effects sets in. Moreover the increase of the normal force can be fitted by a power law. The power law exponent resulting from the fitting of the normal force decreases when the shear rate increases. It increases when the temperature increases. It increases, reaches a maximum and then decreases when the initiator concentration increases. This behavior corresponds qualitatively to the viscosity measurements.

Therefore also the measurement of the normal force during bulk free radical polymerization is a useful rheokinetic tool that yields valuable qualitative information on the Trommsdorff effect and on the possibility to reduce it.

Finally, also the experiments performed with the "TA Instruments" resulted in irregularities of the viscosity trend. They were accompanied by parallel irregularities also in the normal force. This strengthens the contention that a shear-induced phase separation yielding a *pseudo*-solid phase is the underlying reason for the irregularities.

5.9. List of symbols

$[I]_0$	initial initiator concentration	$m^3\,m^{-3}$
T	temperature	°C
T_g	glass transition temperature	°C
$\dot{\gamma}$	shear rate	s^{-1}

5.10. Literature

[1] E. Abuin, E.A. Lissi, *Methyl methacrylate polymerization at high conversion. II. Factors determining the onset of the gel effect*, J. Macromolec. Sci. Chem., 1977, Vol. A11, 287-294.

[2] J.N. Cardenas, K.F. O'Driscoll, *High-conversion polymerization. I. Theory and application to methyl methacrylate*, J. Polym. Sci., Polym. Chem. Ed., 1976, Vol. 14, 883-887.

[3] J.N. Cardenas, K.F. O'Driscoll, *High-conversion polymerization. II. Influence of chain transfer on the gel effect*, J. Polym. Sci., Polym. Chem. Ed., 1977, Vol. 15, 1883-1888.

[4] J.N. Cardenas, K.F. O'Driscoll, *High-conversion polymerization. III. Kinetic behavior of ethyl methacrylate*, J. Polym. Sci., Polym. Chem. Ed., 1977, Vol. 15, 2097-2108.

[5] C.W. Macosko, *Rheology. Principles, measurements and applications*. VCH Publishers Inc., 1994