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Rheokinetics

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Document Version

Publisher's PDF, also known as Version of record

Publication date:

2002

[Link to publication in University of Groningen/UMCG research database](#)

Citation for published version (APA):

Cioffi, M. (2002). *Rheokinetics*. s.n.

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CHAPTER 3

EXPERIMENTAL METHODS LITERATURE REVIEW

3.1. Introduction

For many industrially important materials the rheology determines the ease and manner of processing. Especially for polymeric materials the rheology will be a major factor of concern. Therefore a relevant part of the scientific literature on polymers is concerned with the rheology of polymeric systems and with the non-Newtonian behavior of solutions of polymers in their monomers or in other solvents. Many papers and books have been published regarding the relationship between the viscosity or other rheological properties (the elastic modulus, the loss modulus, the normal stress differences) and the average molar mass, the polydispersity and the concentration of the polymer in different flow situations.

Surprisingly, a similar attention has not been dedicated to the study of rheology *during* polymerization processes. All the same, major viscosity changes occur during the polymerization due to the formation of large, high molar mass molecules and their subsequent entanglement. As shown in the previous chapter, this increase in viscosity can have an effect on the kinetics of polymerization and on the final product properties. Therefore understanding the changing rheological properties and their effects during polymerization processes is a very important research area, especially in view of the significant industrial applications. In fact, at present polymerizations are often performed at far-from-optimal conditions, because of a lack of understanding of the relationship between rheology and kinetics [1, 2].

A complete understanding of the kinetics of rheological changes during polymerization is still missing. This coupling between the increasing viscosity of the reacting solution and the kinetics of the polymerization process is a relatively new field of research and has been called rheokinetics. In this chapter the most recent results that appeared in the scientific literature are reviewed and the experimental methods for rheokinetic investigation are discussed.

3.2. An overview of experimental methods used

A rheokinetic study of polymerization requires reliable measurements of the viscosity. Since the viscosity may increase by as much as 6-7 orders of magnitudes in a relatively short time, it is very difficult, if not impossible, to cover the whole polymerization with a single experiment.

The Ubbelohde viscometer and the Couette rheometer have been mostly used to investigate the early stages of the polymerization. The former measures the viscosity in a close-to-zero-shear situation, the latter in shear flow.

The later stages of the polymerization, characterized by a high viscosity, are better studied with a cone and plate rheometer. This geometry induces a uniform shear rate in the whole sample. The cone and plate rheometer is therefore an ideal tool to investigate the influence of shear rate on the viscosity increase and on the kinetics of a polymerization.

When using the Couette or the cone and plate rheometer the rotational velocity of the rotating element is an important parameter. A higher value of the rotational speed results in a higher value of the torque, from which the viscosity is derived.

Some authors [3-5] have successfully performed experiments with the Couette geometry. They decreased the rotational speed, and therewith the shear rate, during the polymerization in order to have viscosity measurements over a wider range of values.

However, this procedure is, generally speaking, rather tricky and valid only in the initial stage of the polymerization, where the sample can be considered to be Newtonian and viscosity data obtained at different shear rate can be easily compared. Moreover the high rotational velocity required at very low viscosity might induce secondary flows in the gap between the two cylinders, affecting the reliability of the measurement.

Although the measurement of the viscosity is the main feature of a rheokinetic study, a parallel analysis of the increase of the conversion during the polymerization is useful to confirm and/or refine the rheokinetic

results. A further insight would be gained as well by a simultaneous measurement of the evolution of the average molar mass and polydispersity of the polymerizing sample.

Unfortunately, experimental equipment capable of measuring the viscosity, the conversion and the molar mass (or even only two of these three parameters) at the same time is not available on the market. Modified versions of the Ubbelohde rheometer [6, 7] can measure the viscosity and, at the same time, the conversion with a dilatometric technique, but they work in the absence of shear and can be used only in the early stage of the polymerization.

In general, the viscosity, the conversion and the molar mass must necessarily be measured in different pieces of equipment, and thus under different flow and, probably, different thermal conditions. Therefore the results obtained in parallel with different experimental pieces of equipment must be compared carefully.

The conversion is usually measured in quiescent conditions by a calorimetric or spectrometric technique, whereas the viscosity is measured in shear flow. Therefore the data can be coupled properly only in the initial stages of the polymerization, where Newtonian behavior can be assumed. In later stages this is possible only under the assumption that the shear rate has no influence on the kinetics of the polymerization. This assumption will be thoroughly discussed and verified in the following of this thesis.

The only possible alternative experimental approach is to perform the polymerization in the rheometer several times in the same experimental conditions, stop the polymerization after different reaction times by thermal quenching and/or adding an inhibitor and store the samples for conversion analysis.

However, the conversion versus time curves obtained in this way can be affected by the inherent poor reproducibility of initial lag times of polymerization processes. Furthermore the poor reproducibility of the manual operations required to remove and quench the sample may cause further errors because polymerizations are, in general, very fast processes.

Finally, removing a highly viscous sample from the cone and plate rheometer may be troublesome and induce damages to the surfaces of the cone and of the plate that must remain smooth and free of grooves.

Therefore this procedure is complex, uncertain and time demanding.

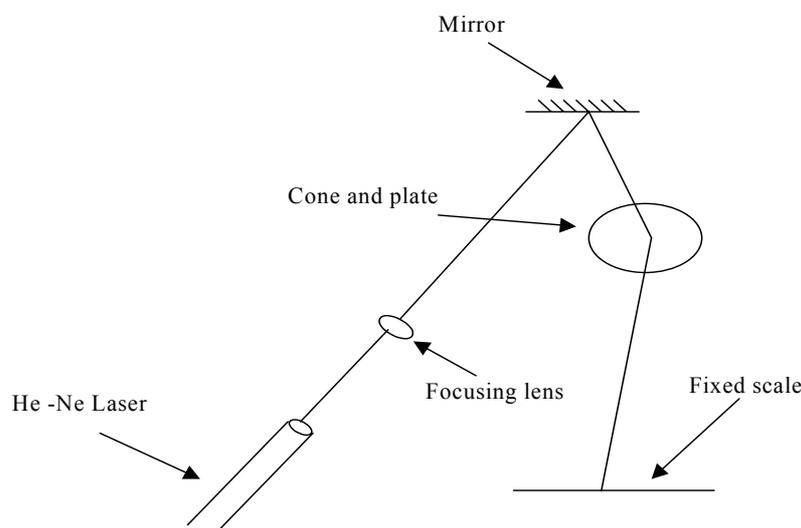
In order to overcome these problems, some authors have tried to develop self-made rheometers that allow simultaneous measurement of viscosity and conversion.

Malkin [8], for example, studied the rheokinetics of the anionic polymerization of dodecalactam with a reactor vessel provided with a thermocouple and a transducer of an ultrasonic viscometer under near adiabatic conditions. The temperature increase due to the heat released during the polymerization was used as a measure of the degree of conversion.

Kale and O'Driscoll [9] studied the rheokinetics of the free radical polymerization of *n*-laurylmethacrylate with a modified rheometer. This rheometer was of the cone and plate type and also allowed determination of the conversion by measuring the change in diffraction of a laser beam shining through the polymerizing sample (figure 3.1).

Biesenberger *et al.* [10] tried to modify a Couette rheometer and provide it with a calorimetric cell for differential scanning calorimetry (DSC). This would allow measuring the viscosity and the conversion increase during polymerization simultaneously. Unfortunately the many technological problems encountered could not be overcome completely, as these authors themselves admitted. Moreover the very complicated structure of this rheocalorimeter caused cleaning problems when performing experiments with real polymeric systems and not with model fluids for testing purposes.

Rosendale and Biesenberger [11] had more success a few years later. They modified a Couette rheometer with a very narrow gap to facilitate temperature control of the polymerizing sample (figure 3.2).



*Figure 3.1. A schematic representation of the modified cone and plate rheometer used by Kale and O'Driscoll [9] to measure the viscosity and the conversion simultaneously during the polymerization of *n*-laurylmethacrylate. A laser beam shines through the sample and the change in the refractive index is monitored on a fixed scale, which gives a measurement of the conversion.*

A temperature sink was provided by a cooling liquid circulating around the annulus at approximately 20°C below the reaction temperature. The rate of reaction was determined measuring the power output of the heaters that maintained the reaction temperature. As long as the polymerization produced heat, the heaters decreased their power output.

Other authors preferred to perform rheokinetic studies with completely different techniques. Meissner and Poltersdorf [12], for example, used not only a “classical” Couette rheometer but also laboratory processing machines as a midget kneader or a laboratory extruder.

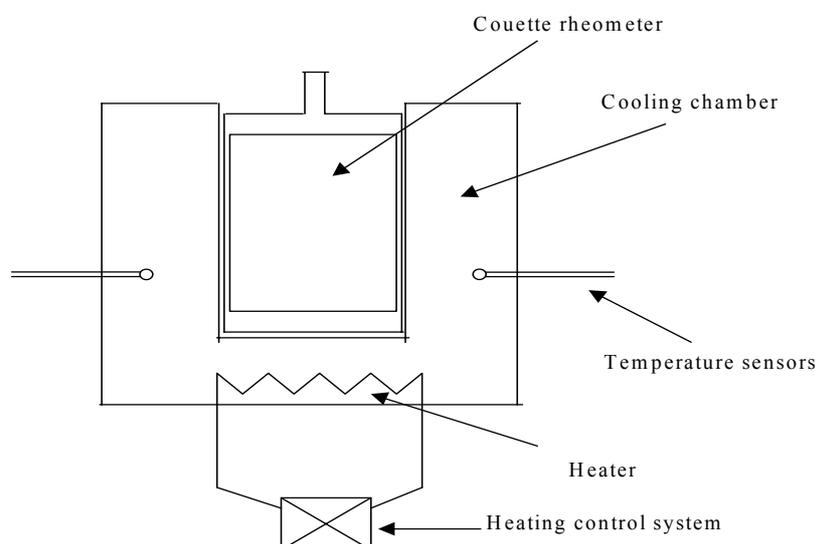


Figure 3.2. The rheocalorimeter used by Rosendale and Biesenberg [11]. It combines Couette rheometry with dynamic scanning calorimetry.

Finally, Malkin *et al.* [13] followed an alternative and original approach to rheokinetics. They exploited the so-called ‘Toms’ effect to study the very early stages of a polymerization process. The Toms effect consists of the increase in pumpability of a fluid caused by the addition to the fluid of small amounts of a polymer, which reduces the turbulence, and therewith the friction in pipelines [15, 16].

These authors performed the polymerization of 1-hexene with a Ziegler-Natta catalyst and took samples of the polymerizing mass at fixed times. The samples were then diluted with heptane and transferred to a handmade capillary “turbulent” rheometer. The diluted samples were forced to flow in the capillary rheometer and the friction factor λ was determined according to

$$\lambda = \frac{D}{4L} \frac{\Delta P}{\frac{1}{2} \rho v^2} \quad (3.1)$$

where D is the diameter, L is the length of the capillary, ΔP is the applied pressure across the capillary, ρ is the density and v is the average velocity. The latter was determined by measuring the amount of liquid collected at the end of the capillary in a certain time. The Toms effect is expressed by the value of the drag reduction, DR , defined according to:

$$DR = \frac{\lambda_0 - \lambda(t)}{\lambda_0} 100\% \quad (3.2)$$

where λ_0 is related to the time zero of the polymerization and $\lambda(t)$ is the value of the friction factor of the diluted sample after a certain reaction time t .

The drag reduction, and thus the Toms effect, increases as the polymerization goes on. Concentration versus time profiles could be calculated beginning from the very early stages of the polymerization with the help of a calibration curve of the drag reduction that was defined dissolving known amount of a polymer in the solvent.

3.3. Rheokinetics of polymerization

3.3.1. Low conversion. Newtonian behavior

In this paragraph we shall discuss data referring to low degrees of conversion and/or to polymerization performed in solution. For this reason, the authors of the papers reviewed in this paragraph could assume, sometimes implicitly, that the polymerizing fluid was Newtonian.

The term “rheokinetics” appeared for the first time in the scientific literature in 1980. Biesenberg and Gogos [16] recognized the importance of modeling the viscosity increase during the polymerization process as a function of

- experimental conditions (shear rate, temperature),
- average molar mass
- conversion

in order to make reactive polymer processing more profitable. They also acknowledged the almost complete lack of useful literature data.

Malkin [8] wrote one of the classic papers on rheokinetics. In this paper, he defined rheokinetics as the rheology of systems changing with time because of ongoing polymerization.

The underlying idea of this paper (and of much of the literature regarding rheokinetics) is that the rheological behavior of a reacting polymer system at a certain time and of a non reacting system having the same concentration of polymer and the same average molar mass are the same.

The viscosity η was considered to be a power law function of the average degree of polymerization N and of the concentration of the polymer ϕ .

$$\eta = KN^a\phi^b \quad (3.3)$$

where a , b and K are constant.

This relationship was the starting point for deriving a rheokinetic model, i.e. a relationship for the viscosity increase during polymerization as a function of time or conversion β . In fact, with the help of models for the chemical kinetics, N and ϕ can be expressed as a function of β and β as a function of time t .

The derivation of the *rheokinetic* model is different for different kind of polymerizations and will be explained in the following of this chapter. For the time being it will suffice to say that the rheokinetic models derived in [8] consisted of power law relationships. Experimental data confirmed this trend, and the power law exponents of the rheokinetic experiments were in agreement with the ones obtained performing a rheological study of non reacting polymer solutions in their own monomer. They also validated the

assumption that the rheological behavior of a reacting system is equivalent to the one of non-reacting polymer solutions.

Moreover, performing the rheokinetic experiments - i.e. measuring the viscosity increase with time - at different temperatures it was possible to obtain Arrhenius plots and to derive the apparent activation energy of the polymerization process.

In the subsequent years a few papers were published following Malkin's footsteps.

Malkin *et al.* [7] studied in details the rheokinetics of free radical polymerization, but only in the early stages before the Trommsdorff effect occurs. For free radical polymerization the concentration of polymer ϕ is equal to the degree of conversion of the monomer:

$$\phi = \beta = \frac{[M]_0 - [M]}{[M]_0} \quad (3.4)$$

where $[M]_0$ and $[M]$ are the initial and the current concentration of the monomer.

Moreover the following two relationships hold if chain transfer reactions are excluded from the analysis [7]:

$$N = \frac{[M]_0 \beta}{[I]_0 (1 - e^{-k_d t})} \quad (3.5)$$

$$\beta = 1 - \exp\left(-\left(\frac{k_p k_d^{1/2} f^{1/2}}{k_t^{1/2}}\right) [I]_0^{1/2} t\right) \quad (3.6)$$

where $[I]_0$ is the initial concentration of the initiator, f is the initiator efficiency, t is the time and k_d , k_p and k_t are the rate constants of the initiation propagation and termination reaction.

Substituting (3.4) and (3.5) in (3.3) gives a rheokinetic model for the dependence of the viscosity on the degree of conversion.

$$\eta = K\beta^b \left(\frac{[M]_0\beta}{[I]_0(1 - e^{-k_d t})} \right) \quad (3.7)$$

Further substitution of (3.6) in (3.7) yields the relationship between viscosity and time.

$$\eta = K[M_0]^a [I_0]^{-a} \left[1 - \exp \left(- \frac{2f^{1/2}k_p}{k_d^{1/2}k_t^{1/2}} [I_0]^{1/2} (1 - e^{-k_d t}) \right) \right]^{(a+b)} \quad (3.8)$$

Equations (3.7) and (3.8) make it possible, according to Malkin *et al.* [7], to give a complete description of the change of the viscosity during free radical polymerization if the kinetic constants are known.

However, this is only partially true because Malkin and co-authors do not take into account the influence of the shear rate on the viscosity. Moreover they do not consider that the kinetic constants may change during the polymerization because of autoacceleration of the rate of polymerization (Trommsdorff or gel effect).

Therefore, Malkin and co-authors had to confine their analysis to low degrees of conversion, where the Trommsdorff effect is not likely to occur and the reacting system can be considered Newtonian. In this way, the kinetic constants could be assumed to be invariable, and equations (3.5) and (3.6) could be simplified expanding them into power series until the linear terms.

Substituting (3.4) and the linearized forms of (3.5) and (3.6) into (3.3) the following simple relationships were obtained:

$$\eta = A_1 [I]_0^{-(1/2)a} \beta^b \quad (3.9)$$

$$\eta = A_2 [I]_0^{(1/2)(b-a)} t^b \quad (3.10)$$

A_1 and A_2 are proportionality factors containing the kinetic constants of the initiation, propagation and termination reaction. The viscosity is proportional to $[I]_0^{-a/2}$ when the degree of conversion and all the other experimental conditions are kept constant and to $[I]_0^{(b-a)/2}$ when the reaction time and all the other experimental conditions are kept constant.

Malkin and co-authors [7] investigated the bulk polymerization of a few methacrylates and of styrene with an Ubbelohde rheometer. Comparing experiments performed at different initiator concentration, but otherwise the same experimental conditions, it was possible to calculate the power law exponents a and b . They agreed once again with the ones obtained from viscometry of non reactive polymer solutions.

Some experiments were also performed for the solution free radical polymerization of methyl methacrylate, using cyclohexane as a precipitant and toluene as a solvent. A very peculiar behavior was obtained. The viscosity increased initially, then decreased and finally increased again after reaching a local minimum (figure 3.3).

This was attributed to precipitation of the polymer, which begins exactly when the viscosity starts to decrease, and could be observed to cause turbidity of the system. Rheokinetic experiments can thus give useful information about changes of the system physical state.

Bulai *et al.* [17] used viscosity measurements for a better understanding of the kinetics of a polycondensation process, where the relationship between the overall rate of the process and the rate of elementary reactions is not straightforward as in free radical polymerization. NMR (nuclear magnetic resonance) spectroscopy was used to follow the rate of formation or consumption of seven chemical species (among which the two monomers), while viscosity changes were studied with a Couette rheometer to investigate the 'macrokinetic' of the whole process.

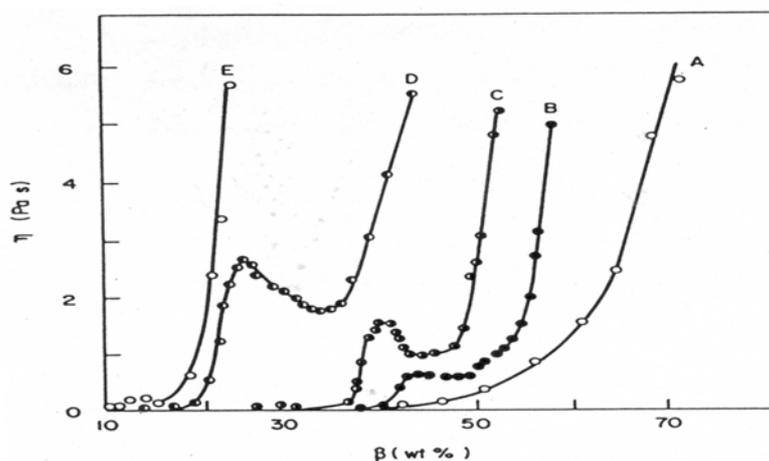


Figure 3.3. Viscosity vs. degree of conversion during the polymerization of methyl methacrylate in the presence of cyclohexane and toluene [7]. A local minimum in the curves is due to the precipitation of the polymer. Different curves refer to different initial mixture compositions. Mixture composition, methyl methacrylate : cyclohexane : toluene (wt%) respectively: curve A, 50:15:35; B, 50:30:20, C, D, 50:32.5:17.5; E, 50:37.5:12.5.

The authors defined the degree of conversion as follows:

$$\beta = \frac{x_0 - x}{x_0} \quad (3.11)$$

where x_0 and x are the initial and current concentration of a reactive group. Then, for polycondensation processes the number-averaged degree of polymerization can be expressed as:

$$N = (1 - \beta)^{-1} \quad (3.12)$$

They considered polycondensation processes of bifunctional compounds that are not complicated by diffusion limitation. The kinetics of such a reaction was described by an equation of second order

$$\frac{dx}{dt} = -kx^2 \quad (3.13)$$

where k is a kinetic constant.

Integrating equation (3.13) with the assumption that $x_0kt \gg 1$ and substituting in (3.12), the following expression for N was obtained:

$$N = x_0kt \quad (3.14)$$

In the case of polycondensation Bulai *et al.* found that the following relationship holds between the viscosity and the degree of polycondensation:

$$\eta = KN^a \quad (3.15)$$

They substituted (3.14) in (3.15) and obtained the following rheokinetic equation:

$$\eta = K(x_0kt)^a \quad (3.16)$$

Therefore also for polycondensation the rheokinetic model consists of a power law relationship. According to the theory of rheology of non-reacting polymer solutions, the exponent a is equal to 1 until a critical molar mass is reached. Afterwards it is equal to 3.4.

In order to test the validity of the rheokinetic model with these values of a , Bulai *et al.* polymerized polyarylsulphoxide by mixing equimolar

solutions of dichlorodiphenylsulphone and the sodium salt of diphenilolpropane in both a Couette and a cone and plate rheometer.

Viscosity measurements confirmed the value of 3.4 after a short initial reaction time. The change with time of the number average degree of polycondensation was in agreement with the assumed second-order kinetics. Experiments performed at different temperature made it possible to determine the value of the apparent activation energy. The value was found in agreement with literature data. When the dichlorodiphenylsulphone content was decreased, the viscosity increase brought about a deceleration of the process because the reaction passed into the diffusion-controlled stage. This was confirmed by a reduction of the reaction rate constants derived by NMR spectrometry.

Another rheokinetic study was performed also by Kulichikhin *et al.* [3], and Polushkina *et al.* [4].

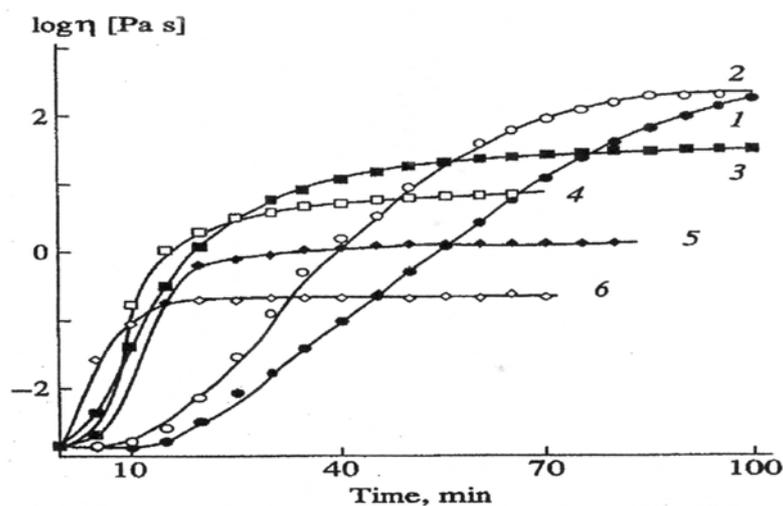


Figure 3.4. The increase of viscosity during the acrylamide polymerization in water solutions [5]. Different curves refer to different initiator concentration: 0.1 wt% for curve 1, 0.2 for curve 2, 0.5 for curve 3, 0.7 for curve 4, 1.0 for curve 5 and 5.0 for curve 6. A lower initiator concentration results in longer reaction times, but higher plateau values of the viscosity.

They studied in detail the influence of initiator and monomer concentration on the increase of viscosity during the free radical polymerization of acrylamide in aqueous solution. Increasing the initiator concentration, the time required to complete the reaction decreased, as well as the final value of the viscosity (figure 3.4). As showed in chapter 2, a higher initiator concentration results in a lower molar mass of the polymer. These results are therefore in agreement with the general theory of free radical polymerization [18] outlined in chapter 2.

Polushkina *et al.* [5] made a further step in the rheokinetic analysis by defining and, for one particular case, solving the ‘direct’ and the ‘indirect’ rheokinetic problem.

As already explained in chapter 1, the direct rheokinetic problem consists in predicting the viscosity increase during the polymerization with the help of a kinetic model. The indirect rheokinetic problem consists in determining the kinetic parameters on the basis of rheokinetic measurements of the viscosity change during the polymerization.

The direct problem was solved in the initial stage of a free radical polymerization characterized by a second order initiation reaction. The indirect rheokinetic problem was solved deriving the $\beta(t)$ relationship from the experimental dependence $\eta(t)$. The derived $\beta(t)$ relationship was linear and from its slope it was possible to determine that $k_p/k_t^{1/2} = 3.4$. This value falls within the interval 3.0-4.7 reported in the literature for the polymerization studied by Polushkina *et al.* [5].

3.3.2. Intermediate and high conversions. Non-Newtonian behavior

A few papers have also been published concentrating on the latest stages of polymerization, where the hypothesis of Newtonian behavior is no longer valid.

Kale and O’Driscoll [9] studied the rheokinetics of the free radical polymerization of *n*-laurylmethacrylate with a modified cone and plate rheometer in oscillatory mode. The viscosity and conversion data showed

the absence of the Trommsdorff effect, in agreement with the literature concerning their reaction. The viscosity increased with the conversion according to a power law trend, in agreement with [8]. The storage modulus G' and the loss modulus G'' both increased with the reaction time. Initially $G'' > G'$ but at a certain critical conversion an inversion occurred, denoting the presence of entangled polymer coils.

Yemelyanov *et al.* [6] studied the rheokinetics of free radical polymerization of many vinyl monomers using two different rheometers, one for low and one for high conversions. They confirmed that there is a power law relationship between viscosity and conversion. The power law exponent, though, is not constant throughout the polymerization. It is equal to 1, 4 to 6 and 10 to 25 at low, intermediate and high conversions, respectively (figure 3.5).

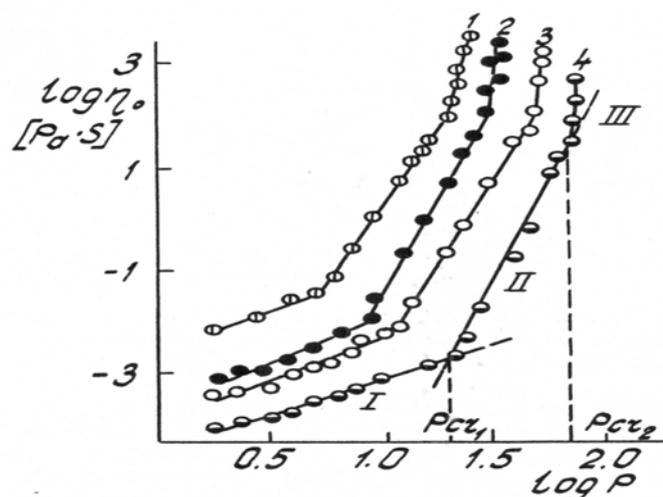


Figure 3.5. The increase of viscosity during the polymerization of vinyl pyrrolidone (curve 1) and octyl methacrylate (curves 2-4) [6]. Three different power law regions can be distinguished.

The exact values depend on the vinyl monomer and on the experimental conditions. These three regions correspond, respectively, to Newtonian

fluid, non-Newtonian fluid and high elastic rubbery state. The transition from the second to the third region coincides with the onset of autoacceleration of the polymerization. According to the authors, a fourth region is also present at the very end of the polymerization where the systems are in the glassy state, but no viscosity data are presented to prove it, probably because steady shear measurement of glassy materials resulted in irregular and irreproducible viscosity trends.

Rosendale and Biesenberger [11] followed the approach of Malkin [7] with some modification to outline a rheokinetic model for free radical polymerization similar to equations (3.9) and (3.10) that implements the possibility of autoacceleration and therefore can also be applied at later stages of the polymerization. Moreover, they dropped the assumption made in [7] that the degree of polymerization remains constant throughout free radical polymerization. They also used a rheocalorimeter to measure simultaneously the increase of conversion and viscosity (in oscillatory mode) during two different free radical polymerizations. The experimental results agreed with the rheokinetic model. Particularly, a peak in the heat released during the polymerization was obtained simultaneously with an exponential growth of the viscosity, denoting the onset of autoacceleration. Also the polycondensation of a linear polyurethane was studied but in this case the rheocalorimeter failed to give useful results. In fact, polycondensation reactions usually have huge viscosity effects but negligible thermal effects and therefore measurement of conversion with a calorimetric method was troublesome in this case.

The above-mentioned three research teams, Kale and O'Driscoll [9], Yemelyanov *et al.* [6] and Rosendale and Biesenberger [11] performed their experiments at a fixed shear rate and did not investigate the influence of the shear rate on rheokinetics. The shear rate was only applied to be able to measure the viscosity and was not a relevant parameter of their research.

3.3.3. Alternative approaches to rheokinetics

The rheokinetic models discussed so far are based on rheological and kinetic relationships among viscosity, molar mass, conversion, and kinetic constants. A complete alternative approach was attempted by Meissner and Poltersdorf [12].

They acknowledged the validity of Malkin's approach based on the chemistry of the polymerization but preferred to follow a different route that they considered more valid for possible application of rheokinetics to reactive processing of polymers involving complex reactions. Meissner and Poltersdorf assumed that the viscosity changes are due to competing destruction and structurization processes. They both consist of complex reactions of unknown order. Structurization processes lead to the formation of the polymer molecules, while the destruction processes cause their decomposition and can be of chemical, thermal or mechanical origin.

A rheokinetic model of the viscosity change during polymerization was derived which consists in a very complicated differential equation containing 11 parameters. These parameters are mainly the kinetic constants and the exponents describing the reaction orders of the structurization and destruction processes.

A Couette rheometer and laboratory processing machines (midget kneader, laboratory extruder) were used to study the effect of thermomechanical loads on the rheological properties at small and high mechanical loads, respectively. The model parameters were determined by fitting experimental results to the model. Although this approach is quite interesting and directly oriented towards practical applications, its major limitation is that the number of parameters is too high to give clear-cut indications about the validity of the model and the reliability of the values of the parameters. Moreover, the physical meaning of some of the parameters is not clear.

Some authors used rheokinetic arguments to model the behavior of tubular reactors aiming at the use of continuous reactors for the production of polymers. Malkin *et al.* [19] pointed out that the velocity profile inside a

tubular reactor differs considerably from the Poiseuille profile as a consequence of the rheokinetic effect, i.e. the ongoing polymerization in the tube and the consequent increase of viscosity. They developed a mathematical model to determine the average molar mass and the polydispersity inside a tubular reactor at different degrees of conversion for the isothermal polymerization of dodecalactam, whose enthalpy of polymerization is practically equal to zero. Solving the equations they found out that even for this isothermal polymerization the deviation of the real velocity profile from the Poiseuille profile has a great influence on the average molar mass and on the molar mass distribution.

Baillagou and Song made a step further and used successfully a rheokinetic approach to model the prepolymerization of methyl methacrylate in tubular reactors below [20] and above [21] the glass-transition temperature. They combined mass and heat balances for the tubular reactor with constitutive equations for the viscosity and performed experiments that confirmed the validity of their model. Higher temperatures avoided sedimentation of glassy polymer in the tubes but resulted in a lower molar mass of the product.

An alternative and original approach to rheokinetics was also followed by Malkin *et al.* [13], who exploited the Toms effect to study the very early stages of a polymerization process, as explained previously. The polymer formation was noticeable even 30 second after the start of the polymerization when the polymer concentration in the reactive mass was only 15 ppm. At this early stage other widely used techniques to follow polymerization kinetics (dilatometric, calorimetric, spectral, chromatographic) or rheokinetics are not sensitive enough. The advantage of being able to follow the very early stages of the polymerization lies in the fact that they reflect to the inherent activity of the catalyst. This method therefore makes it possible to compare different catalysts.

The method is valid for polymerizations that proceed at a constant average molar mass. In this case the variation of the drag reduction is only due to the change in concentration of polymer. If the molar mass and the concentration

of polymer both change, the drag coefficient increases also as a consequence of the increase of average molar mass and it is difficult to separate the two contributions to the drag reduction. Therefore, in this case it is not possible to define a reliable relationship between the conversion and the drag coefficient.

In principle, the Toms effect can be used also to follow the later stages of polymerization, simply diluting the samples, but it should be remembered that very high dilution ratios induce experimental errors.

3.4. Conclusions

A good knowledge of the increase of the viscosity during a polymerization process is fundamental for the optimal design of polymerization reactors and of processes where the polymer is produced directly in the desired shape (reactive extrusion, reactive injection molding). Solvents are often used to minimize the viscosity increase, and all the technological difficulties that it brings about, but they are neither cheap, nor environmentally friendly. Moreover, they cause an increase in the energy required and they imply an extra separation step at some point of the production process.

Therefore a rheokinetic study of polymerizations is necessary to design improved and more profitable polymerization processes.

Surprisingly, the scientific literature concerning rheokinetics is not abundant, probably because the rheological studies of reacting fluids is not straightforward with the rheometers currently available on the market, that are designed mainly for non-reacting materials.

So far most authors have concentrated on the early stages of the polymerization and on solution polymerization. In fact, in both cases the reacting fluid can be assumed as Newtonian, which simplifies greatly the experiments themselves, the interpretation of experimental data and the modeling of the viscosity increase. A result common to all the papers examined was the power law trend of the increase in viscosity, after an initial lag time. The possibility of predicting the increase of the viscosity

and of determining kinetic parameters from rheokinetic experiments are significant results.

At high degrees of conversion non-Newtonian behavior sets in, which complicates the rheokinetics greatly and, at the same time, makes the rheokinetic results much more valuable with a view to possible industrial application. The possibility of autoacceleration and the search for conditions to reduce it are a complicating factor and, at the same time, an important challenge.

Notwithstanding the remarkable results described so far, many intriguing problems still have to be solved.

For example, the influence of the shear rate on the rheokinetics and the possibility of scale-up of laboratory rheokinetic results are problems still to be faced. They are the subject of the following chapters of this thesis.

3.5. List of symbols

K, A_1, A_2	proportionality factors	
I	initiator	
M	monomer	
D	diameter	m
DR	drag reduction	-
G'	storage modulus	Pa
G''	loss modulus	Pa
L	length of the capillary,	m
N	average degree of polymerization	-
a, b	constant	-
f	efficiency of the initiation	-
k	kinetic constant	$\text{m}^3 \text{s mol}^{-1}$
k_d	rate constant for the initiator dissociation	s^{-1}
k_p	rate constant for the propagation step	$\text{m}^3 \text{mol}^{-1} \text{s}^{-1}$
k_t	rate constant for the termination step	$\text{m}^3 \text{mol}^{-1} \text{s}^{-1}$
t	time	s

v	average velocity	m s^{-1}
x	concentration	mol m^{-3}
β	conversion	-
ΔP	applied pressure across the capillary	Pa
ϕ	concentration	-
λ	friction factor	-
ρ	density	kg m^{-3}
η	viscosity	Pa s

3.6. Literature

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