Rheokinetics

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CHAPTER 1

GENERAL INTRODUCTION

1.1. Introduction

When studying the kinetics of ordinary chemical reactions in the liquid phase the viscosity is not an important parameter. Both the reactants and the products are chemical compounds of low molar mass of the same order of magnitude. Therefore, the viscosity does not depend significantly on the degree of conversion, or on the experimental conditions, such as the temperature and the pressure of the system. Thus, the viscosity remains essentially constant during the reaction and has no influence on its kinetics.

In contrast to this, polymerization processes lead to the formation of macromolecules, whose average molar mass is larger than that of the reactants by many orders of magnitude. Moreover, these macromolecules can entangle with each other leading to the formation of aggregates of macromolecules.

A desired effect of the formation of high molar mass molecules are the excellent mechanic properties of polymeric materials that are nowadays so popular in virtually any field of application.

A less desired effect is the dramatic increase of viscosity that occurs during a polymerization process, often in very short time intervals. In other words, polymerization processes are characterized by a significant and fast change of the fluidodynamic behaviour of the reacting medium. Moreover, polymeric systems are often non-Newtonian and, in that case, their rheological properties depend strongly on the flow field.

Therefore the design of polymerization reactors is not an easy task. Heat and mass transfer are difficult at high viscosity, the heat and mass transfer coefficients are a function of the degree of conversion and the increase of viscosity is a function of the velocity of the rotating elements of the reactor.

A very common approach to these problems is trying to bypass them. In fact, polymers are often produced in the presence of a solvent. In this way the increase of viscosity can be limited and the heat and mass transfer are enhanced. Moreover, the reacting medium can be considered as Newtonian.

This procedure is not ideal because it implies much larger reactors and an extra separation step to separate the polymer from the solvent. Furthermore the solvents are usually organic chemicals that are neither cheap nor environmentally friendly and their use is subjected to increasing legal limitations.

1.2. Rheokinetics

Generally speaking, a complete quantitative understanding of the change of rheological properties during polymerization is still missing. Therefore industrial processes are often designed on a trial-and-error base and are, consequently, far from being performed in optimal conditions [1].

The rheological study of polymeric systems changing with time is a relatively new field of research called rheokinetics. Its major objectives are modelling the increase of viscosity during polymerization and understanding how this increase is influenced by different parameters, such as temperature, shear rate and concentration of initiators, catalysts, and molar mass regulators [2].

A rheokinetic analysis can also provide important and useful information concerning the kinetics of the polymerization itself. In fact, the kinetics of polymerization is mostly studied with spectrometric or calorimetric techniques that do not permit to investigate the influence of shear rate on the kinetics.

In other words rheokinetics can be used to derive kinetic information or data from the measurement of the viscosity increase during polymerization.

The viscosity η of a polymeric system is a function of the average molar mass of the polymer M and of its concentration C (figure 1.1).

This function can be determined performing a rheological study of different polymer-monomer solutions.

Both the average molar mass and the concentration of the polymer depend on the degree of conversion β. A kinetic model allows defining how the degree of conversion depends on the time. Therefore it is possible to

determine how the average molar mass and the concentration of the polymer depend on the reaction time.

Finally, combining a rheological study of non-reacting polymeric systems (yielding the function $\eta(M,C)$) and a kinetic model of the polymerization (yielding the functions $M(t)$ and $C(t)$), it is possible to model quantitatively the viscosity increase during the polymerization. In this way, the so-called direct rheokinetic problem can be solved.

The validity of this prediction must then be verified performing rheokinetic experiments, i.e. measuring the increase of the viscosity during the polymerization.

An alternative approach is to use the rheokinetic results to determine some kinetic parameters of the polymerization reaction. In this way the so-called inverse rheokinetic problem can be solved.

The rheokinetic scheme suggested by Malkin and Kulichikhin [3] reported in figure 1.1 does not consider the influence of the shear rate on the viscosity. Therefore, it must be considered valid only for the early stages of bulk polymerization, or for solution polymerization. In fact, in those cases the polymerizing system can be considered Newtonian and the influence of shear rate can be neglected.
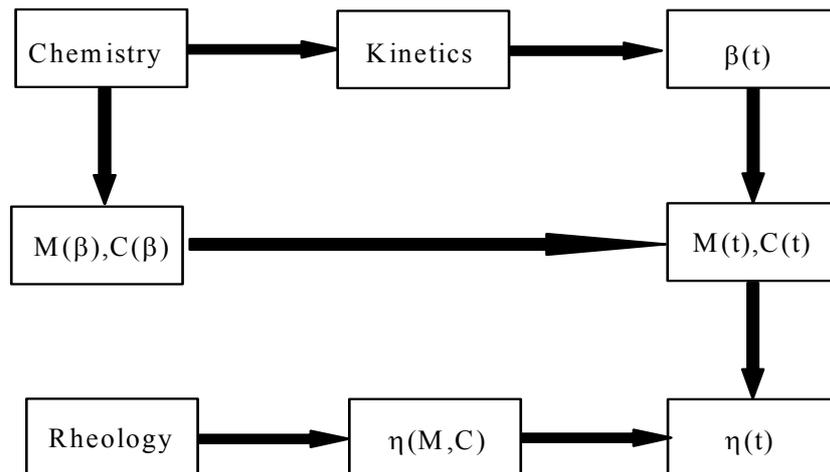

Figure 1.1. The rheokinetic scheme [3].

Finally, it must be noted that, generally speaking, the viscosity is measured at a certain shear rate, while the conversion and the molar mass distribution are measured in quiescent conditions. Therefore viscosity data can be safely compared and combined with conversion and molar mass distribution data only when the polymerizing fluid is assumed to be Newtonian. When this assumption is not valid, the rheokinetic analysis becomes more complicated and more interesting and challenging as well.

1.3. Scope of the thesis

In this thesis the rheokinetics of bulk free radical polymerization is investigated at intermediate and high degrees of conversion. Particular attention is dedicated to the influence of the shear rate on the kinetics of the polymerization and on an undesired autoacceleration phenomenon (Trommsdorff effect).

The experimental work has been performed with two cone and plate rheometers having different characteristics and with a helical barrel rheometer that permits a preliminary scale-up of the results obtained with the cone and plate rheometers.

Finally, the influence of the shear rate on the thermodynamics of the polymerization has also been investigated.

Chapter 2 is dedicated to an introduction to free radical polymerization and to the Trommsdorff effect that often occurs at intermediate or high conversion. In chapter 3 the scientific literature concerning rheokinetics is reviewed, some experimental problems are discussed as well as the still open problems. In chapter 4 and 5 the results obtained with the cone and plate rheometers are discussed, whereas chapter 6 is dedicated to results obtained with the helical barrel rheometer. Finally, chapter 7 is dedicated to the influence of shear rate on the thermodynamics of free radical polymerization.

1.4. List of symbols

C	concentration	mol m^{-3}
M	average molar mass of the polymer	Kg mol^{-1}
β	degree of conversion	-
η	viscosity	Pa s
t	time	s

1.5. Literature

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[3] A.Ya. Malkin, S.G. Kulichikhin, *Rheokinetics*. 1996, Ed. Hüthigh &Wepf, Heidelberg.