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A. Ya. Malkin and S. G. Kulichikhin

# **Rheokinetics**

## **Rheological Transformations in Synthesis and Reactions of Oligomers and Polymers**

With 202 Figures and 8 Tables

Hüthig & Wepf Verlag Zug · Heidelberg · Oxford, CT/USA

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## Preface

The idea that rheology is a theoretical base for polymer processing is encountered in many original papers and text-books. However, the field of application of rheology in polymer technology is much wider. The authors of this book suspect that no real technological process in polymer synthesis can be quantitatively described or modelled without a proper description of rheological effects. The rheologic properties of a reactive medium need closer consideration because they reflect the chemical transformation and influence the course of the process.

The logical basis of this book is summarized as follows:

- in the course of polymer synthesis and transformations of oligomers and polymers great changes in the molecular structure take place.
- these changes lead to tremendous evolution of rheological properties of the sample; i. e. viscosity changes by millions (!) of times. This situation is special for polymer technology because with low-molecular weight products changes in rheological properties of reactants are negligible;
- variation of rheological properties can be easily monitored by simple instrumental methods. Therefore it is a convenient method for controlling a technological process;
- a reactive system must be sensible to changes of the rheological state because the velocity of molecular movements (and therefore the rate of reaction) depends on viscosity of the medium;
- all real technological processes are connected with a flow of reactants. It is important to have a method to influence the hydrodynamic situation in a reactor and to realize the role of deformation in the kinetics of a chemical reaction.

At last, dealing with real technological processes, we must consider the time scale of the process, as it is a problem of productivity, economical factors and finally its competitiveness.

So three key words determine the approach of this book

technology – rheology – kinetics

The latter two gave the book its title but in fact its value comes from being a foundation of real polymer technology.

Everybody knows that technology is something highly sophisticated, which was up to now considered as an industrial analogue of the art of cookery. It would be incorrect to disclaim the partial truth of this conception, but it is only half the truth. The more we know about the fundamentals of a technological process the more obedient and controlled it becomes, and the latter means: more safety, more profitability, more reproducibility.

Rheokinetics is one of the keystones to successful of polymer technology. It unites knowledge adopted from various branches of science. It is rather easy to teach students at Universities incorporating it into courses on chemistry, on rheology, on hydrodynamics or

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similar topics. It is very difficult to combine information and rules coming from different sides but it appears to be necessary when we face real life and technology exists in real life but not in text-books.

The main goal of the authors was to find general rheological roots inside numerous technological processes of polymer syntheses and transformations and to suggest a generalized description of the kinetics of chemical transformations and how to monitor them with rheological methods. This is a rather new approach in polymer technology due to limited data available by publications in periodicals. Certainly the authors are well aware of the fact that this book cannot completely cover the problem. On the contrary we are sure that there are a lot of flaws in the book and the only thing which can excuse us is the fact that we deal with a very lively and rapidly developing field. Therefore any attempt to conceal our knowledge under a book cover opens new unexplored fields. (Once Goethe said that the solution of any problem leads to the appearance of a new one. This is completely true for science as a whole and for rheokinetics in particular).

We express our sincere thanks to our colleagues who read the (Russian-language) version of this book and made useful comments.

Mr. B.M. DuKhan is to be thanked for translating the book in English.

A. Ya. Malkin  
S. G. Kulichikhin

Moscow, Russia,  
February 1995

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## List of Symbols and Abbreviations

$a$	constant, exponent, factor of heat conductivity
A	activator
[A]	concentration of active centres
$A$	certain degree of polymerization, Arrhenius constant
AN	acrylonitrile
$b$	constant, exponent
BM	butylmethacrylate
BPO	benzoylperoxide
$c$	constant of autocatalysis, concentration, heat capacity
C	constant
$D$	constant, diffusion coefficient
DBP	dibutylphthalate
DCDA	dicyandiamide
DMSO	dimethylsulfoxide
DPMDI	diphenylmethanediisocyanate
$E$	activation energy
$\bar{E}$	dimensionless activation energy
$E_{\text{ch}}$	activation energy of a chemical process
$E_{\text{eff}}$	"effective" activation energy
$E_{\beta}$	"effective" activation energy to achieve some preset degree of conversion
$E_{\eta}$	"effective" activation energy to achieve a certain level of viscosity
EM	ethylmethacrylate
$f$	efficiency of initiation, functionality
$g$	free fall acceleration
$G'$	rubbery modulus
$G''$	loss modulus
$G^*$	complex dynamic (at a constant frequency) rubbery modulus
$G_0$	elasticity modulus
$G_{\infty}$	equilibrium rubbery modulus
GPC	gel permeation chromatography
$h$	height
$H$	hardness, enthalpy
HDMI	1,6-hexamethylenediisocyanate
[I]	concentration of the initiator
$k$	reaction rate
$k_D$	diffusion controlled reaction rate
$k_i, k_p, k_t$	rate constant of the initiation reaction, of chain propagation, of chain termination
K	Kelvin
$K$	constant
$l$	length
$m$	empirical constant, exponent
$M$	molecular mass, torque
$\bar{M}$	average molecular mass

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$M(t)$	time-dependent change of torque
M	monomer
[M]	concentration of monomer
$\bar{M}_c$	critical value of molecular mass
$\bar{M}_c$	average distance between the points of the network
$\bar{M}_w$	mass-average molecular weight
MDI	4,4'-methylenedi(phenylisocyanat)
MFR	melaminoformaldehyde resin
MM	molecular mass
MMA	methylmethacrylate
MW	molecular weight
MWD	molecular weight distribution
$n$	empirical constant, material constant
$N$	quantity of active loci, ionogenic catalyst concentration
$\bar{N}$	number-average degree of polymerization
$N_{cr}$	critical chain length
OI	oligo imide
PA	polyamide
PA-12	poly-( $\epsilon$ -lauro lactam)
PA-6	poly-( $\epsilon$ -caprolactam)
PA-610	poly-(hexamethylene sebacinamide)
PAS	polyarylsulfon
PB	polybutadiene
PBMA	polybutylmethacrylate
PBTP	polybutoxytitanphosphoroxane
PEMA	polyethylmethacrylate
PETP	polyethyleneterephthalate
PFR	phenolfomaldehyde resin
PM	polymethacrylate
PMMA	polymethylmethacrylate
PS	polystyrene
PSF	polysulfone
PU	polyurethane
PVA	polyvinylalkohol
PVC	polyvinylchloride
$q$	heat
$\tilde{q}$	dimensionless heat effect
$Q$	total heat of a reaction
$Q_m$	integral registered heat effect of a reaction at a given temperature
$r$	radius, equimolar factor
R	gas constant
$R$	radius
S	constant, product surface, entropy
$t$	time

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$\tilde{t}$	dimensionless time
$t^*$	time of gel formation, time to reach some critical value, induction period
$t_n^*$	time before reaching the gel-point in the non-isothermal regime of curing, dimensionless induction period in a non-isothermal process
$\tilde{t}_n^*$	dimensionless curing time in the non-isothermal regime
$t_{ac}$	characteristic time of acceleration
$t_c$	time to reach a critical molecular mass
$t_{ch}$	characteristic time
$t_h$	characteristic time determining the rate of heat propagation
$t_{opt}$	optimal curing time
$t_p$	time of microphase separation
$t_\alpha$	characteristic time for heat transfer with the environment
$T$	absolute temperature
$\tilde{T}$	dimensionless temperature
$T_{cure}$	temperature of curing
$T_f$	temperature of fluidity loss
$T_g$	temperature of relaxation transition, glass transition
$T_{ph}$	temperature of phase transition
$\tan \delta$	angle of mechanical (or dielectric) losses
TBT	polytetrahydroxytitan
TDI	2,4-toluene diisocyanate
TES	tetraethoxysilane
$U$	activation energy of a chemical reaction
$V$	volume
$\alpha$	complex variable, factor of heat transfer
$\alpha^*$	branching factor
$\beta$	degree of conversion
$\beta$	reaction rate
$\beta_c, \beta_k, \beta_r$	“calorimetric”, “kinetic”, “rheological” degree of conversion
$\beta_{cr}^*, \beta_{cr}^{**}$	critical values of the degree of conversion
$\gamma$	shear strain, rate of temperature increase
$\dot{\gamma}$	shear rate
$\delta$	loss angle, solubility parameter
$\Delta$	difference
$\varepsilon$	dimensionless shear rate, dimensionless rate of temperature increase
$\varepsilon_i$	Euler function
$\eta$	viscosity
$\eta_0$	maximum value of Newtonian viscosity, initial value of viscosity
$\eta^*$	viscosity of the reactive mass
$\eta_m$	viscosity of the monomer, microviscosity
$\eta_{sp}$	specific viscosity
$\kappa$	dimensionless energy of activation

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$\lambda$	wavelength
$\mu$	material constant
$\Delta\mu$	chemical potential
$\xi$	constant of self-deceleration
	coefficient of normal stresses, measure of solution elasticity at shear flow
	dimensionless parameter reflecting the contribution of self-deceleration
$\phi$	concentration of active loci, concentration of polymer, gel concentration
$\phi_{cr}$	critical concentration of polymer in solution
$\phi_{max}$	maximum content of filler in a system
$\psi$	coefficient of the time dependency of the degree of conversion
$\rho$	density, share of reactive groups
$\tau$	time of relaxation, shear stress
$\tilde{\tau}$	dimensionless time
$\tilde{\tau}^*$	dimensionless non-isothermal time of curing
$\tau_S$	shear stress in the region of viscous flow
$\tau_y$	fluidity limit
$\theta$	constant characterizing the rate of viscosity change, dimensionless temperature
	characteristic time of solution relaxation
$\omega$	frequency

#### Indices

0	initial value, value at time $t = 0$
ac	characteristic value referring to acceleration
c	calorimetric
c, cr	critical value
ch	chemical, characteristic
D	diffusion controlled parameter
eff	effective
f	refers to fluidity loss
g	refers to glass transition
i	initiation
m	monomer
max	maximum value
or	orientation
p	propagation
r	parameter determined by rheological methods
sp	specific
t	at time $t$ ; termination
w	refers to molecular weight
$\alpha$	refers to heat transfer
$\beta$	refers to a certain degree of conversion
$\eta$	refers to a certain viscosity
$\infty$	final value

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## Chapter 1

### Introduction

Numerous operations in the technology of polymer synthesis and processing are connected with the flow of material – caused either by the rotation of the mixer in the reactor, the screw in the extruder or by melt flow filling the form. Evaluations of such operations inevitably require the determination of the properties of a flowing liquid. Experts in lacquers, pigments and polymer solutions came across this problem more than 50 years ago. The determination of the fundamental principle – dependence of material properties on the regime of deformation – gave rise to a new scientific field – rheology investigating anomalous media. This “anomaly” is, of course, only an arbitrary term denoting the fact that the properties of all “rheologically complex liquids” of this kind differ somewhat from those of common low molecular liquids with constant viscosity.

Later the rheology of polymers took the shape of an independent dynamic field with its own approaches, techniques and applications. Most of the results achieved in investigating rheological properties on polymers are presented in [1] which is far from exhausting a long list of innovative articles and treatises devoted to this subject. However, if we try to place the rheology of polymers among fundamental sciences, it can to a certain extent be attributed to the branch of physical chemistry the basic subject of which is the determination of the relationship between the substance composition and its properties, these properties being assumed as constant and inherent in the substance.

At the same time, a somewhat different approach initially existed in the rheology of polymers involving consideration of the time (or kinetic) factor. This factor was introduced in classical rheology in two different ways.

The most obvious are the changes in material behaviour with time caused by relaxation phenomena leading to a number of viscoelastic effects. Investigations abound in this field. However, the variations in material behaviour depending on the time (frequency) scale of observation, are only seeming. Indeed, though a material (at a given temperature) can behave either as a liquid, a rubber or a glass, it is still the same material, possessing a stable structure and properties, the change of the observed behaviour being caused by a spectrum of relaxation times and different correlation between the time scales of the experiment and relaxation.

The time factor plays quite a different role when the structure of the material is being changed. In this case, the observed changes in its behaviour are caused by other reasons and are manifested in a different way. One of the first subjects of rheological studies where structural transformation occurred were thixotropic media, i. e. the materials with properties that change in the course of deformation and relaxation. It is noteworthy, however, that though such media are known to be quite numerous and very important from both theoretical and experimental viewpoints, the level of their investigation remained, to a great extent, merely descriptive. Only a few attempts were made to develop consequent quantitative ideas of their behaviour. One of the main achievements in the thixotropic theory remains the revealing of the kinetic nature of

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processes, leading to changes of the observed behaviour of the substance, even without going into details of the mechanism of these processes. Therefore time is included into the system of equations describing the behaviour of thixotropic media in an essentially different way than the behaviour of viscoelastic bodies.

The aforementioned examples, however, do not exhaust the most important cases, where the time factor plays a marked role in the rheology of polymers. There is a vast field of considerable theoretical and practical significance, the basic subject of which is the kinetic factor. This field can be defined as “synthesis and transformation of polymers”. Changes in the viscosity of reactive media in the processes associated with the chemistry of low-molecular products do not play any significant role, since the viscosities of initial and final products do not differ appreciably. Quite a different behaviour is observed in polymer synthesis, when the viscosity of a reactive medium changes by several thousand times during the reaction. We deal here not with thixotropic transformations, but with irreversible changes in the material structure (composition). The processes under consideration inevitably reveal their kinetic nature, however, which is similar to thixotropic transformations.

In fact, the term “polymer production and transformation” denotes different processes, the main of which being:

- 1) formation of linear polymers from monomers;
- 2) curing, i. e. transition from relatively low viscous solutions of oligomers to three-dimensional net-structured non-fluid materials. The processes of polymer analogous transformations are also covered by this term.

In all mentioned cases a marked change in the whole complex of rheological properties occurs, obviously caused by changes in molecular composition and substance structure. Indeed, the viscosity changes by many decimal orders during polymerization (and polycondensation), rubbery deformation emerges with all consequences inherent in it: large elastic deformations, normal shear stress, and some mechanical relaxation phenomena are initiated within the time scale available in the course of the experiment.

Similarly, viscosity increases unlimited during solidification, i. e. the material loses its fluidity and the rubbery modulus changes by many decimal orders.

The aim of this book is to consider – consecutively and quantitatively – these changes.

The problem of correlating the composition and the properties of reactive systems in the polymer synthesis is closely connected with two fundamental questions:

- a) kinetics of occurring reactions;
- b) inherent rheological properties of reactive masses.

No matter whether the polymer formation occurs in a solvent or in a block, the reactive medium presents in itself a solution of the forming polymer in its own monomer (oligomer) or in a multi-component solution where this monomer is present. Therefore the first problem to be solved is whether it is possible to identify the reactive mass with the stable polymer solution or, more precisely, where is the limit for this identification. As it will be shown later, the answer to

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this question depends to a large extent upon the phase of the reactive mass, i. e. whether or not the polymer being formed is soluble in its monomer or in the solvent applied. This idea makes it reasonable to include the diagrams of reactive mass phases into our consideration.

Further consideration depends upon the point, whether we deal with linear polymers or with branched macromolecules or, consequently, with a three-dimensional network. The problem of estimating the rheological properties of a reactive mass for linear polymer synthesis appears to be relatively simple, since the relations describing the dependence of solution viscosity of linear polymers upon the solution concentration and molecular mass of the dissolved polymer are well-known. Some peculiar effects of the solvent nature on the rheological properties of the solution have been also established. In case of branched polymer synthesis and particularly for transition from polyfunctional reactive oligomers to network polymers, such general regulations are unknown which necessitates the establishing of more or less universal relationships describing changes in rheological properties of a reactive mass. As it will be shown further in corresponding chapters, such relationships can be found through phenomenological rheological equations.

Let us examine in more details the principles determining rheokinetics of the synthesis of linear polymers, since they are of general value for further consideration. From the above statements it follows that the relationships of change in rheological properties of a reactive mass during polymer synthesis are determined by the following general factors:

- 1) the reaction path which establishes interdependence between the degree of conversion  $\beta$  on the one hand, and the length of initiated chains and their content in a reactive mass on the other hand;
- 2) the kinetics of the process and, consequently, the time dependence of the degree of conversion  $\beta$ ;
- 3) rheological properties of the reactive mass being a dispersion of a certain type and composition.

As an example, let us examine the three simplest patterns of polymer formation simulating the main actual processes [2]. As any model they represent the major features of the phenomenon determining the final result without going into details.

Thus, let the process follow scheme I: Some quantity  $N$  of active loci is introduced to the monomer whose concentration in the reactive mass equals  $\varphi$ . These form the basis for the unrestrained growth of molecular chains until the monomer is entirely converted. Then it becomes quite evident that at a degree of conversion  $\beta$ , the content of the polymer will be  $\varphi\beta$ , and the average molecular mass of the obtained chains is  $\varphi\beta M_0/N$ , where  $M_0$  is the molecular mass of the monomer. Thus, in this case, at a degree of conversion  $\beta$ , the reactive medium represents a solution of  $\varphi\beta$  concentration with the molecular mass of the polymer  $\varphi\beta M_0/N$ .

Let the polymerization follow scheme II in such a way that the chain growth occurs up to a certain degree of polymerization  $A$ , beyond which the growth of another chain is initiated, etc. Then, the reactive medium at a degree of conversion  $\beta$  represents a polymer solution with the molecular mass  $AM_0$  and its concentration is proportional to the degree of conversion  $\beta$ .

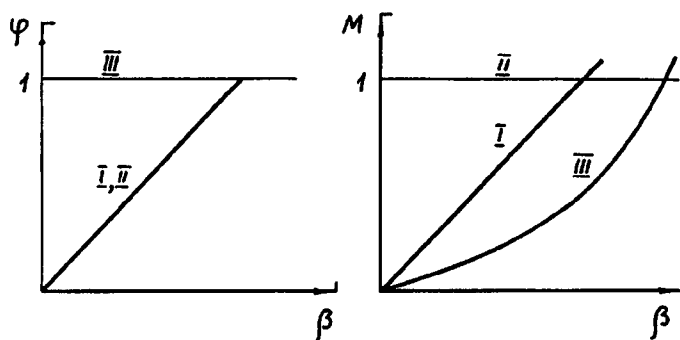
Finally, according to scheme III, all the molecules of the monomer are simultaneously involved in the process of polymer formation and the mean numerical degree of polymerization  $(1 - \beta)^{-1}$ , at polymer concentration = 1, corresponds to the degree of conversion  $\beta$ .

Thus, for the three simplest models we can present the dependencies of concentration  $\varphi$  and molecular mass  $\bar{M}$  of the polymer in a reactive mass upon the degree of conversion in the following way:

Type of process:	I	II	III
$\varphi$	$\beta$	$\beta$	1
$\bar{M}$	$\beta$	1	$(1 - \beta)^{-1}$

Hence, an essential difference is evident between the assumed patterns of dependencies  $\varphi$  and  $\bar{M}$  and, consequently, of rheological properties of a reactive mass on the degree of conversion  $\beta$  for different hypothetical schemes of polymer formation.

Thus, the models given above reveal, in the first approximation, the change of the reactive mass composition depending on the chemical nature of the process with the increase of the degree of conversion  $\beta$ . It is shown in Fig. 1.1, where the differences in anticipations following from the mechanisms denoted as I, II, III are clearly seen.



**Figure 1.1:** Pattern of polymer concentration and molecular mass change for three different reaction paths of polymerization.

The three simplest hypothetical models of polymer formation mentioned above can be compared to the three main mechanisms of polymerization which are considered in the chemistry of polymers.

Thus, the chain growth of active centres the quantity of which remains constant (scheme I) is a model of ionic polymerization, where  $N$  is the ionogenic catalyst concentration. The formation in the course of polymerization of macromolecules with constant (on the average) chain length (scheme II) is inherent in free radical polymerization. And finally, the involvement of all molecules present in the reactive region in the process of polymer formation (scheme III) is typical of addition polymerization (polycondensation).

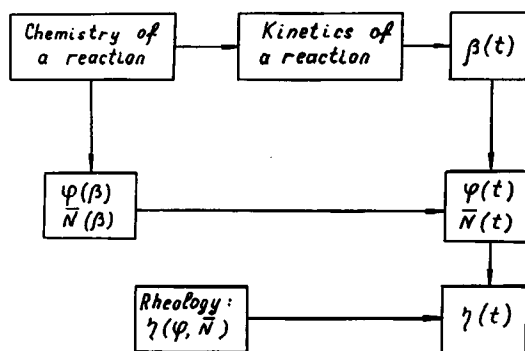
Actually, all these reactions are much more complicated and have a lot of by-effects making the situation more intricate. However, the aforementioned model schemes adequately simulate, in the first approximation, the essential features of the described types of reactions.

They may be applied, therefore (and it will be shown further in subsequent sections of the book), to qualitative rheological analysis of the process of polymer formation taking various reaction paths.

All the above considers the degree of conversion  $\beta$  as the main criterion. The determination of  $\beta$ , however, constitutes a special problem *per se*, being solved in the analysis of chemical kinetics of polymerization. This problem can be solved with the aid of different physical and chemical methods and the value itself can be determined in different ways, for instance, through concentration changes of reactive groups or of a monomer. It is convenient to reduce the concentration values to limit values reached at the end of the process, formally at  $t \rightarrow \infty$ . Thus, for instance, if the monomer concentration in the reactive system at the start of the reaction  $[M]_0$ , and all the monomer chains are found to be involved into the polymer chain when the polymerization is over, i. e. the final monomer concentration at  $t \rightarrow \infty$  is zero, the value of  $\beta$  which alters with time may be defined as  $\{[M]_0 - [M](t)\} / [M]_0$  where  $[M](t)$  is a current value of monomer concentration in the reactive system which depends upon the time  $t$ . Then it is evident that if  $t = 0$ ,  $\beta = 0$  and at  $t \rightarrow \infty$ ,  $[M] = 0$  and  $\beta = 1$ , i. e.  $\beta$  will alter from 0 to 1. Such a reduction of  $\beta$  will be applied further in all cases.

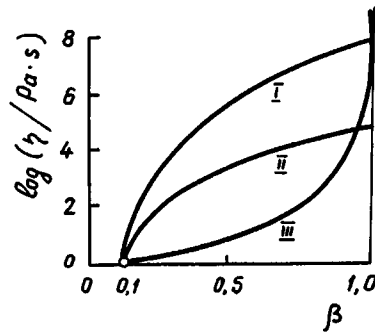
Thus, the rheological analysis of the processes of linear polymer production comprises three points:

- α) solving the problem of chemical kinetics to obtain the relation  $\beta(t)$ ;
- β) establishing the reaction nature which permits to relate the composition of a reactive mass to  $\beta$ ;
- γ) independent description of properties of a polymer solvent which permits to interpret the rheological parameters of a material in terms of  $\beta$  and to present them eventually as the time function. The latter presents the solution of a direct rheokinetic problem. This formalism is clearly demonstrated by the scheme in Fig. 1.2.



**Figure 1.2:** Pattern of the solution of a direct problem; calculation of the relationship  $\eta(t)$ .

The scheme can be converted, i. e. we can estimate the kinetic constant of the reaction and its origin according to the dependence of viscosity on time  $\eta(t)$ .



**Figure 1.3:** Pattern of the viscosity dependence upon the degree of conversion anticipated by various rheokinetic models.

Indeed, even a qualitative consideration of the relation  $\eta(t)$  for the three model patterns discussed (Fig. 1.3.) shows essential differences between them [3]. For more convenience of comparison the chosen starting point is the same in this figure. Its coordinates are  $\eta = 1 \text{ Pa}\cdot\text{s}$  at  $\beta = 0.1$ . The constants for dependencies  $K_i$  are chosen respectively for the given schemes of polymer formation. Increase in viscosity in these schemes is expressed by the following formulae:

$$\text{I: } \eta_1 = K_1 \beta^{a+b}$$

$$\text{II: } \eta_2 = K_2 \beta^b$$

$$\text{III: } \eta_3 = K_3 (1 - \beta)^{-a}$$

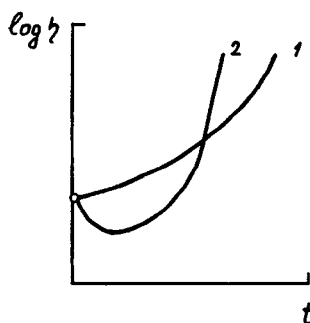
and values  $a$  and  $b$  are assumed to be  $a = 3.5$ ,  $b = 5.0$ .

If the reaction path is known, the measured dependencies can be quite obviously transformed into kinetic curves for the constants of kinetic equations to be determined. It is natural, however, that such an analysis should be applied to values of  $\beta$  and not to viscosity itself, since formally we can write a “kinetic equation” for viscosity but it is devoid of any physical sense. The possibility for analysis of chemical kinetics of a polymer formation reaction through rheological measurements constitutes a solution of the inverse kinetic problem.

Further considerations of rheokinetic analysis in the processes of polymer formation and conversion make it necessary to consider also non-isothermal phenomena, inevitably concurring these processes [4]. Non-isothermal effects occur either due to some inner reasons, since many chemical reactions run with significant endothermic effects, or due to heat transfer from an external source when the reaction is initiated (“ignited”) in an inert cold system from the reactive mass which is preheated by the walls of the reactor. In any case, it is either practically unfeasible to maintain constant temperature due to large volumes of reactors and low heat

conductivity of a reactive mass, or totally unreasonable due to processing problems necessitating the optimisation of a process. Therefore non-isothermal phenomena appear to be an inevitable constituent of rheokinetic problems.

The rise of temperature leads to two consequences. First, the rates of all chemical reactions increase and therefore the changes in rheological properties accelerate, particularly, a sharp rise in viscosity is observed. Second, due to increase of temperature the viscosity of a reactive mass decreases. Relative influence of these phenomena upon a general character of changes in rheological behaviour of the medium is different at the start and at the end of the process. Qualitatively it is illustrated in Fig. 1.4, where the plots of viscosity change of a polymerising mass at  $T_0 = \text{const.}$  and at linearly increasing temperature starting from  $T_0$  are compared. It is noteworthy that the scale of the effects at the start and at the end of the reaction differs appreciably. If we arbitrarily assume the activation energy of viscous flow at the start of the reaction to be 40 kJ/mole, at temperature rise by 10 to 20 K a 2- or 3-fold drop of viscosity is to be expected. For relatively low viscous initial medium this effect appears to be rather pronounced. However, at  $10^3$  to  $10^5$ -fold increase in viscosity in the course of polymerization, its 2- to 3-fold decrease as a result of the reactive mass heating is an effect of the second order. At the same time, considerable acceleration of polymerization (several times over) caused by the heating appears to be an essential factor of the accelerated increase in viscosity as shown in Fig. 1.4.:



**Figure 1.4:** *Pattern of viscosity changes during polymerization at  $T_0 = \text{const.}$  (1) and at temperature rise during the reaction (2).*

Some precise methods of determining non-isothermal phenomena in polymer synthesis and oligomer curing for specific typical situations will be considered further in the corresponding sections of the book as applied to the solution of direct problems. It should also be noted that the analysis of non-isothermal effects may be regarded as basic for the solution of inverse problems as well. This is a more intricate problem. Its analysis, however, may appear to be very fruitful, since it permits to estimate the kinetic constants of reactions in the context of relatively poor experimental information. Some examples of this approach will be given in subsequent chapters.

The analysis of change in rheological properties of a reactive mass in non-isothermal processes of polymer formation and conversion constitutes a direct rheological problem. At the same time the possibility of solving an inverse problem is of great interest, which means to determine the kinetic parameters of a process using the results of measuring the rheological

properties of the reactive mass. The analysis of this far more complex problem is, nonetheless, also attached to rheokinetic problems both in an isothermal and in the more general, non-isothermal case. Some versions of solving inverse problems will be considered further.

In the course of polymer formation and transformation the whole complex of rheological parameters of the reactive mass changes and, generally speaking, the analysis of different properties of the process permits to clarify various points of the process. Therefore the more representative the initial rheological information is, the more fruitful can be the conclusions. Meanwhile, it is not exactly the case. Primarily, it should be born in mind that it is very difficult technically to measure the whole complex of rheological parameters in the course of the process, especially if it runs relatively fast. Furthermore, the lack of sufficiently reliable theoretical bases deprives the initial experimental data of their informative value, these data remaining just a list of facts not allowing unambiguous quantitative interpretation. It is preferable, therefore, to restrict ourselves to the employment of relatively simple methods of viscometric measurements and dynamic analysis [5], which constitute the two major groups of methods used nowadays in rheokinetics. The sphere of their application is quite arbitrary and is determined primarily by the properties of the material under study.

If the subject of investigation is a relatively low-viscous liquid, namely, a reactive mass in the process of polymerization, the major role is to be ascribed to the viscometric method, i. e. the monitoring of the viscosity change of the medium in the course of the chemical process.

This monitoring can be carried out through different viscometric techniques available or with the aid of specially designed instruments – capillary or rotational viscometers or vibration instruments – but the parameter to be measured is, in any case, the viscosity of the medium.

The viscometric technique can be unrestrictedly used in the analysis of initial stages of oligomer curing of a very wide range of states – from the initial state of relatively low viscous liquids almost up to the gel point. What is common for all the above mentioned cases is the fact that the range of viscosity changes appears to be very broad and comprises lot less than three to four decimal orders. All that influences the choice of techniques for viscosity measurements.

If the objects of investigation are liquids of high viscosity or cross-linked systems, for instance, gels, cured oligomers or cross-linked elastomers, the major experimental techniques are dynamic measurements. This technique can be applied to the materials in different physical states and, from this viewpoint it is more universal than the viscometric one. Though capable of measuring the range of parameters (rubbery modulus and loss modulus) not wider than four to five decimal orders, this technique possesses two advantages of paramount significance – it is applicable both before and after the transition to the loss of fluidity (i. e. it can be used before the material has reached the gel point as well as at greater degrees of conversion). This technique does not influence the process itself, being “non-destructive”.

The latter is of particular importance, since there is always a danger that the viscometric measurements due to more or less intensive deformations of the medium under study can influence the rate and the degree of a chemical reaction. Dynamic techniques are also indispensable in cases when profound degrees of conversion in rheokinetics of network polymers or conversion in a solid phase are under investigation. If we take into account that the dynamic

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techniques are also very good in practical applications of rheokinetic investigations, the important role of these techniques becomes quite evident. A certain restriction in their use is associated with the necessity of being aware of viscous properties of the material as they are, which is of paramount significance for technical calculations of output pressure patterns of tubular reactors and pipe-lines, for evaluations of mixers, for determining the mechanism of flow of the resins being cured or the properties of oligomer-based compositions during injection moulding, etc.

The rheological measurements are inevitably connected with mechanical action on the mass. These inputs can be either instantaneous or continuous in monitoring the state of a substance. In general, three cases should be differentiated:

- α) mechanical deformation influences the nature and the rate of a chemical reaction in no way;
- β) it changes the hydrodynamic pattern promoting the agitation, intensifying the heat exchange;
- γ) it plays its own kinetic role influencing the phase state of the system and/or the rates of reactions.

The viscometric measurements should be considered the most "active" ones at large deformations occur in this case. The dependence of the results obtained on shear rate is the criterion of this active role in deformations during viscometric measurements. Therefore when speaking about viscosity change in the course of chemical reactions, the rate of the deformation at which the results have been obtained should be taken into account. It is also important, whether the results depend upon the shear rate. However, even if the influence of shear upon the viscosity change is distinctly pronounced in the experiment, two possibilities should be distinguished.

First, intensive deformation may cause significant heat release and, therefore, the influence of shear rate can be attributed to the non-isothermal pattern of a reactive medium (and the result of measurements here will certainly depend upon the shear rate).

Second, the deformation itself can play a "kinetic" role.

Thus, even if the results of viscometric measurements depend upon the shear rate, the cause of the effects observed should be thoroughly analysed, first of all estimating the role of the dissipative factor, of mixing, of shear rate influence upon the phase state of the system, etc.

The measurements of changes in the rheological properties at harmonic oscillations are less sensitive to the regime of deformation. Two particularly significant situations again can be distinguished in this case:

- α) the deformation at which the measurements are taken can turn "large", not in the rheological sense when it can cause non-linear phenomena, but in the sense of influencing the structure of a material. The latter is especially typical of highly loaded compositions and heterogeneous compositions of any other type;
- β) The results of measurements can be sensitive to the frequency of deformation.

The dependence of relaxation (viscoelastic) properties upon the frequency is in general inherent in polymeric materials, therefore, it can appear in rheokinetic measurements as well. Of particular consideration is the question why the shape of rheokinetic curves depends (if ever

observed in an experiment) on the frequency, i. e. whether it is the consequence of the polymeric origin of the substance, or these are entirely different and, generally speaking, non-equivalent processes observed at different frequencies.

To conclude this chapter, let us establish the scope of the domain which the present book is to cover though it seems clear from the title, the subject needs to specify its place. The main aim of the book is – on the basis of identical approaches – to try to classify and to consider a rather large amount of experimental information obtained by the authors and reported in periodic literature before mid 1989. The choice of data is determined by the task of considering the measurements of rheological properties of reactive masses in the following cases:

- α) synthesis of linear polymers;
- β) chemical transformations caused by presence of reactive groups in a chain;
- γ) curing of oligomers leading to network polymer formation;
- δ) gel formation from solutions.

The general treatment of these processes is associated with the fact that the rheological transformations are regarded as the consequence of a reaction with its chemical kinetics inherent in it. This very fact justifies the use of the term “rheokinetics”. Unfortunately, such an approach is not applicable in all cases, since the kinetics of chemical reactions is not always known. It is also rather difficult and sometimes quite impossible to determine the relationship between the composition of a reactive mass and its rheological properties. It is inevitable, therefore, in such cases to restrict ourselves to an exclusively empirical pattern of a process, though it is desirable to present it in a generalised form based on general ideas of relaxation of a material and valid for a wide range of objects.

All the above mentioned specifies an intermediate position of our subject between places the subject of the present book as an intermediate between the rheology of polymers proper and the kinetics of chemical reactions of polymerization constituting its basis. On the other hand, the development of the theoretical considerations and experimental facts presented in the book suggests their use in hydrodynamics of the media possessing variable rheological properties. This is a relatively new domain of investigation *per se*, falling outside the scope of classical hydrodynamics of viscous liquids which is the basis for synthesis and processing of polymers. This subject is of particular importance for tubular reactor design and for evaluations of instruments with agitators, for estimating the quality of polymer products, for analysis of injection moulding processes, etc.

The latter trend of the rheology of oligomer and polymer transformation is of paramount significance, especially if we take into consideration the new opportunities in new technologies such as, for instance, moulding, injection moulding and resin blend extrusion, various RIM-processes, etc. Some important engineering applications following from the rheokinetic analysis of polymer synthesis and transformation are evident already at this stage of investigation. This trend is worth considering, specially and systematically, therefore, the analysis of hydrodynamic problems associated with the flow of liquids having variable rheological properties and their processing application is also beyond the scope of this book.

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Thus, the subject of the present books is, on the one hand, intermediate between the rheology of polymers and kinetics of polymerization, and on the other hand, it is close to hydrodynamics of liquids with variable viscosity. It should be noted that while on the former subjects many studies have been reported, the latter remains “terra incognita” which has been explored by only a few researchers and which is still awaiting those who would create here an appropriate environment.

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## Chapter 2

# Rheokinetics of Linear Polymer Formation

### 2.1 General

Changes in the rheological behaviour of reactive systems are determined by two major factors: first, by the kinetic path of the chemical reactions occurring in the course of polymer formation, second, by rheological characteristics proper of the mass being polymerized. These are the decisive factors in the rheokinetic analysis of any process. The problem is to define the way of distinguishing their effects, since the initial experimental material presents a combination of rheological properties and kinetic characteristics of a process.

Thus, the changes in viscosity of a reactive system  $\eta(t)$  are determined firstly by the change pattern of the degree of conversion  $\beta(t)$  and secondly by the dependence of the viscosity on concentration and the molecular weight (MW) of the resulting polymer  $\eta(\bar{M}, \varphi)$ . It is only possible to distinguish participation of these factors in the function  $\eta(t)$  if independent kinetic experiments or rheological measurements with model solutions simulating a reactive system are conducted. For this reason, there are two possible patterns of experimental research in rheokinetic analysis of chemical processes reported in literature.

Some authors stress the necessity of conducting rheokinetic experiments with the kinetic experiments analysing functionality, heat release patterns and molecular weight change to determine the kinetic pattern of the reaction. Even if this approach may appear justified, the rheokinetic method is thereby somewhat restricted, since only a direct problem is under consideration. However, if viscous properties of model solutions  $\eta(\bar{M}, \varphi)$  are determined independently and their influence on the experimental kinetic curves of viscosity change  $\eta(t)$  is taken into account, the solution of an inverse problem becomes possible, i. e., we can estimate the kinetic properties of the process using the initial experimental data for viscosity change of the reactive system.

This approach enables us to solve both the direct and the inverse kinetic problems. Investigation of rheological properties acquires thereby rheokinetic features. The starting point for obtaining the rheokinetic relationships for polymerizing systems is the assumption that the rheological behaviour of growing and inert macromolecules is equivalent. This assumption enables us to apply the main patterns obtained for polymer solutions to reactive systems. In this treatise we have considered some rheokinetic features of linear polymer formation in the course of ionic and radical polymerization and polycondensation.

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## 2.2 Ionic Polymerization

### 2.2.1 A Direct Rheokinetic Problem

Anionic polymerization of caprolactams is a typical example of the process of polymer synthesis running the ionic polymerization path. The reaction path and the kinetics of this reaction change considerably due to initial monomers and activators being used, which presents fruitful opportunities for analyses of major rheokinetic patterns in these processes.

In the simplest case of ionic polymerization, the following kinetic pattern is realized: the chain propagation occurs at active centres the concentration  $[A]$  of which is assumed to be invariable in the course of the reaction, no chain termination occurring thereby\*. The end (limiting) value of the number-average degree of polymerization  $\bar{N}$  for this model pattern equals  $[M_0] / [A]$ . If at a certain moment of time  $t$  the current concentration of a monomer is  $[M]$ , i. e., the degree of conversion

$$\beta = \frac{[M_0] - [M]}{[M_0]} \quad (2.2.1)$$

the current value of the number-average degree of polymerization in this case will be

$$\bar{N} = \frac{[M_0] - [M]}{[A]} = \beta \bar{N}_\infty \quad (2.2.2)$$

The mass share of the polymer being formed represents the ratio of the concentration of monomer chains included into a polymer chain to their total (initial) concentration, i. e.:

$$\varphi = \frac{[M_0] - [M]}{[M_0]} = \beta \quad (2.2.3)$$

This simple model pattern corresponds to the case of anionic polymerization, or, at least its first stages when one can neglect the exchange reactions of overamidisation and ignore the possibility of reaction transition from a homogeneous to a heterogeneous nature, even if it is conducted at a temperature below the melting point of the polymer being formed.

In the most general case, the viscosity  $\eta$  of the solution – actually the reactive mass – is determined by the two factors:

- 1) the polymer chain length,
- 2) its concentration, i. e.  $\eta = f(\bar{N}, \varphi)$ .

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\* The case when the change in the concentration of active centres occurs in the course of the reaction is considered elsewhere.