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### Rheokinetics

Cioffi, Mario

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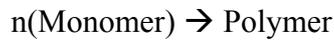
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## **CHAPTER 7**

# **THERMODYNAMICS OF BULK FREE RADICAL POLYMERIZATION**

## 7.1. Introduction

In first approximation, bulk free radical polymerizations are generally considered to be non-equilibrium reactions under normal experimental or industrial conditions. This would result in complete conversion of the monomer into the polymer.



However, complete conversion of the monomer into the polymer within limited reaction times is not achieved in many applications. In bulk free radical polymerizations only conversion in the range 95-98% can usually be obtained. This creates the need of a purification step of the polymer obtained from the unreacted residual monomer in many industrial applications, because monomers are often volatile and dangerous chemicals. The incomplete conversion of the monomer is generally ascribed to kinetic limitations. As we have seen in chapter 2, the rate of polymerization can be expressed as follows:

$$R_p = k_p [M] \left( \frac{fk_d [I]}{k_t} \right)^{1/2} \quad (2.15)$$

When, at the end of the polymerization, the concentration of the monomer is very low, the rate of polymerization decreases, so that very long reaction times would be needed to convert the residual monomer.

In this chapter we shall discuss the possibility that also thermodynamic limitations prevent the conversion of the monomer from being complete, particularly when the polymerization is performed under shear.

## 7.2. The ceiling temperature

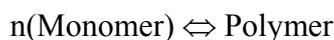
The ceiling temperature  $T_c$  is defined as the temperature at which the free energy of the bulk free radical polymerization is equal to zero.

$$\Delta G_p = \Delta H_p - T\Delta S_p \quad (7.1)$$

$$T_c = \frac{\Delta H_p}{\Delta S_p} \quad (7.2)$$

$\Delta G_p$ ,  $\Delta H_p$  and  $\Delta S_p$  are the free energy, the enthalpy and the entropy of the polymerization, respectively.

At temperatures close enough to the ceiling temperature the polymerization must be considered as an equilibrium reaction



Therefore the conversion of the monomer is thermodynamically hindered at temperatures close enough to the ceiling temperature.

Some typical values of  $T_c$ ,  $\Delta H_p$  and  $\Delta S_p$  taken from the literature [1, 2] are reported in table 7.1.

Monomer	$T_c$ (°C), measured	$\Delta H_p$ (kJ mol <sup>-1</sup> of polymerized monomer)	$\Delta S_p$ (J K <sup>-1</sup> mol <sup>-1</sup> )	$T_c$ (°C), calculated
Styrene	310	-73	-116	356
MMA	220	-56	-117	205

Table 7.1. Thermodynamic data for the polymerization of styrene and methyl methacrylate (MMA).

It must be noted that the values of the ceiling temperature, of the enthalpy and of the entropy of polymerization for a certain monomer are not obtained simultaneously, but by different experiments performed in different conditions. Moreover, the value of the entropy of polymerization depends to a certain extent on the degree of crystallinity of the polymer obtained [2]. On the other hand, the value of the ceiling temperature is usually obtained by extrapolation of experimental data [2].

As a consequence of this, the data of the ceiling temperature obtained experimentally (see second column of table 7.1) do not agree with the values of the ceiling temperature (reported in the fifth column) that are obtained dividing the enthalpy of polymerization  $\Delta H_p$  by the entropy of polymerization  $\Delta S_p$ .

However, the values of  $T_c$  reported in table 7.1, no matter how they are obtained, are significantly higher than the temperatures at which classical free radical polymerizations are usually carried out (about 100 °C). Therefore, thermodynamic limitations are normally ruled out, and the incomplete conversion of the monomer is attributed to kinetic constraints. However, in reactive extrusion the polymerizations are generally performed at higher temperatures (about 200 °C), and in this case thermodynamic limitations to the conversion cannot be ruled out.

Some experimental evidence contrasts the generally accepted idea that thermodynamics constraints are not important in free radical polymerization. For example, Bywater [3] studied the photocatalyzed polymerization of methyl methacrylate in solution at 100-150 °C and concluded that the reactions did not proceed to completion and that at each temperature the concentration of the residual monomer corresponded to the concentration of monomer in equilibrium with the polymer. The same lack of complete conversion has been found in reactive extrusion [4-7]. Even post-initiation by further addition of initiator towards the end of the extruder did not lead to conversions over 98 %.

It is important to note that the values of the enthalpy and of the entropy of polymerizations as they are available in the scientific literature have been

obtained in the absence of shear flow, whereas the polymerizations are often carried out under considerable shear. The problem that then arises is to establish if shear flow can influence the thermodynamic equilibrium and the ceiling temperature.

While the reaction enthalpy of the polymerization  $\Delta H_p$  is certainly not affected by shear, the question is not as straightforward for the entropy of polymerization.

### 7.3. The flow-induced change of entropy

In the case of ordinary reactions in the liquid phase involving small molecules, the shear flow cannot change the molecular structure and therefore cannot influence the thermodynamic equilibrium.

In contrast, during polymerization reactions flow can stretch and align the polymer chains. We can imagine that a confusion of entangled random coils at rest becomes a more or less ordered system of aligned stretched molecules under flow, as shown schematically in figure 4.6.

Therefore, the shear flow induces an increased order in the system and gives a negative contribution  $\Delta S_{Flow}$  to the change of entropy associated with the polymerization.

$$\Delta S_{Flow} < 0 \quad (7.3)$$

$$\Delta G_{Flow} = \Delta H_p - T(\Delta S_p + \Delta S_{Flow}) \quad (7.4)$$

$\Delta G_{Flow}$  is the change of free energy when the polymerization is performed in the presence of shear flow.

An estimation of the order of magnitude of the flow-induced change of entropy  $\Delta S_{Flow}$  is required to understand to which extent the shear flow can influence the ceiling temperature and the thermodynamics of bulk free radical polymerization.

#### 7.4. The dumbbell model and the Maxwell-Oldroyd model

The dumbbell model and the Maxwell-Oldroyd theory can be used to derive an approximate expression for the entropy of flow.

The dumbbell model has been described in details in many books [8, 9] and scientific publications. According to this model, the polymer molecule is represented by two beads joined by an elastic Hookean spring. The solution of the polymer in a solvent, that can also be the monomer from which the polymer is formed, is represented schematically by a solution of these polymer-dumbbells in the solvent.

The polymer solution can then be described in terms of

- the viscosity of the Newtonian solvent in which the dumbbells are suspended
- the number of dumbbells per unit volume
- the mass of the dumbbell, that schematically represents the average molar mass of the polymer
- the friction coefficient of a bead as it moves through the solvent.

Marrucci [10] published a fundamental paper concerning the dumbbell model. He showed that in the case of dilute solutions under flow, the flow-induced change of free energy per unit volume of the solution can be expressed by the following very simple relationship.

$$\Delta G_{Flow} = \frac{1}{2} tr \boldsymbol{\tau} \quad (7.5)$$

where  $tr \boldsymbol{\tau}$  is the trace of the stress tensor  $\boldsymbol{\tau}$  associated with the flow.

$$tr \boldsymbol{\tau} = \tau_{xx} + \tau_{yy} + \tau_{zz} \quad (7.6)$$

The following equation can be derived [11] from equation (7.5) for the specific flow-induced change of entropy

$$\Delta S_{Flow} = \frac{tr \boldsymbol{\tau}}{2CT} \quad (7.7)$$

where  $C$  is the concentration of the polymer and  $T$  is the absolute temperature.

The trace of the stress tensor can be expressed with the help of the Maxwell-Oldroyd model [12] that is also valid in the case of dilute solutions. The Maxwell-Oldroyd model consists of the following constitutive relationship between the stress tensor and the shear tensor:

$$\boldsymbol{\tau} + \lambda \overset{\nabla}{\boldsymbol{\tau}} = -CRT\lambda \dot{\boldsymbol{\gamma}} \quad (7.8)$$

where  $\boldsymbol{\tau}$  is the stress tensor,  $\lambda$  is the relaxation time,  $\dot{\boldsymbol{\gamma}}$  is the shear rate tensor,  $\overset{\nabla}{\boldsymbol{\tau}}$  is the Maxwell-Oldroyd derivative of the stress tensor and  $R$  is the ideal gas constant.

In a Cartesian system of co-ordinates, the general term of the Maxwell-Oldroyd derivative of the stress tensor is given by the following equation:

$$\frac{\delta}{\delta t} \tau_{ij} = \frac{\partial \tau_{ij}}{\partial t} + u_k \frac{\partial \tau_{ij}}{\partial x_k} - \tau_{kj} \frac{\partial u_i}{\partial x_k} - \tau_{ik} \frac{\partial u_j}{\partial x_k} \quad (7.9)$$

where  $u_i$ ,  $u_j$  and  $u_k$  are the components of the velocity vector.

In the case of simple unidimensional shear flow, as in a cone and plate rheometer, it can be demonstrated [8] that the following relationship holds:

$$\begin{pmatrix} \tau_{xx} & \tau_{xy} & 0 \\ \tau_{xy} & \tau_{yy} & 0 \\ 0 & 0 & \tau_{zz} \end{pmatrix} + \lambda \begin{pmatrix} -2\tau_{xy} & -\tau_{yy} & 0 \\ -\tau_{yy} & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} \dot{\gamma} = -CRT\lambda \dot{\gamma} \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} \quad (7.10)$$

where  $\tau_{ij}$  are the components of the stress tensor,  $\lambda$  is the relaxation time and  $\dot{\gamma}$  is the shear rate. From equation (7.10) we can derive

$$\tau_{xx} - 2\lambda \dot{\gamma} \tau_{xy} = 0 \quad (7.11)$$

$$\tau_{xy} = -CRT\lambda \dot{\gamma} \quad (7.12)$$

$$\tau_{yy} = \tau_{zz} = 0 \quad (7.13)$$

Substituting equation (7.12) in (7.11), we obtain

$$\tau_{xx} = -2\lambda^2 \dot{\gamma}^2 CRT \quad (7.14)$$

Since  $\tau_{yy}$  and  $\tau_{zz}$  are equal to zero,

$$tr \boldsymbol{\tau} = -2\lambda^2 \dot{\gamma}^2 CRT \quad (7.15)$$

and substituting this latter equation in (7.7), we obtain the following expression for the flow-induced change of entropy.

$$\Delta S_{Flow} = -R\lambda^2 \dot{\gamma}^2 \quad (7.16)$$

The Maxwell-Oldroyd model also yields the following relationship for the relaxation time, in the case of unidimensional shear flow:

$$\lambda = \frac{\tau_{xx}}{2\eta\dot{\gamma}^2} \quad (7.17)$$

where  $\eta$  is the viscosity.

### 7.5. The rheokinetic determination of the flow-induced change of entropy

The rheokinetic experiments performed with the “TA instrument” rheometer (chapter 5) can be used to calculate the order of magnitude of the flow-induced change of entropy. In fact, those experiments were performed at a constant shear rate and allowed determining the viscosity and the normal force. From the data obtained, the relaxation time  $\lambda$  and the flow-induced change of entropy  $\Delta S_{Flow}$  can be determined by equations (7.17) and (7.16), respectively.

For example, the experiment performed with *n*-butylmethacrylate at  $30 \text{ s}^{-1}$  and  $110 \text{ }^\circ\text{C}$  resulted in a viscosity of  $57.12 \text{ Pa}\cdot\text{s}$  and in a normal stress of  $24640 \text{ Pa}$  at the end of the experiment. This results in a relaxation time of the order of magnitude of  $0.1$  seconds (see equation 7.17). According to equation (7.16), this corresponds to

$$\Delta S_{Flow} = -R\lambda^2 \dot{\gamma}^2 = -75 \text{ J mol}^{-1} \text{ K}^{-1}$$

This value is of the same order of magnitude as the entropy of polymerization for styrene and methyl methacrylate. This would result in a significant decrease of the ceiling temperature in the presence of shear flow. In the case of styrene, for example, this value of  $\Delta S_{Flow}$ , combined with the data of  $\Delta H_p$  and  $\Delta S_p$  reported in table 7.1 would give a ceiling temperature for styrene of  $110 \text{ }^\circ\text{C}$  when the polymerization is performed at a shear rate of  $30 \text{ s}^{-1}$ .

This value of the ceiling temperature is certainly too low. Therefore our model overestimates the value of the flow-induced change of entropy. However, the approximate calculation of  $\Delta S_{Flow}$  based on the model outlined in the previous paragraph shows that shear flow can have a significant influence on the thermodynamics of free radical polymerization. In addition to this, it can also be noted that even a smaller value of  $\Delta S_{Flow}$  would have a remarkable influence on the ceiling temperature.

In other words, the possibility that thermodynamic restraints prevent the conversion of the monomer from being complete when the polymerization is performed under shear should not be ruled out.

It must be noted that this result has been obtained on the base of the dumbbell and Maxwell-Oldroyd models, that are both based on the assumption of dilute solution, whereas our rheokinetic experiments concern the later stage of the polymerization, and therefore concentrated solutions of polymer into its own monomer. Moreover these models assume the relaxation time of the polymer system to be unique, because all the polymer molecules are schematically represented with the same dumbbell.

Generally speaking, polymeric systems are characterized by a distribution of molar mass and therefore must be described in terms of a spectrum of relaxation times. In the following paragraph, the order of magnitude of  $\Delta S_{Flow}$  will be estimated on the base of some of these spectra.

## 7.6. Relaxation time spectra

Real polymeric systems can be described by a single relaxation time only in first approximation. In the previous paragraph we have assumed, following the dumbbell model, that all the polymer molecules could be represented by the same dumbbell, which resulted in a unique relaxation time. Real polymeric systems are characterized by a distribution of molar mass and therefore should be represented by a distribution of dumbbells, whose beads have different mass. This results in a spectrum of relaxation times.

A polymeric system can be described by a set of relaxation times and weighting constants or by a relaxation time spectrum  $H(\lambda)$  (e.g. Macosko [9]). While the choice of the set of relaxation times and weighting constants may be not unique, the relaxation time spectra provide a univocal description of the viscoelastic properties of a polymeric systems. These properties can be expressed as functions of the relaxation time spectra  $H(\lambda)$ . From  $H(\lambda)$  a weight-average relaxation time  $\lambda_{av}$  can be calculated using the following relationship:

$$\lambda_{av} = \frac{\sum_i H_i \lambda_i}{\sum_i H_i} \quad (7.18)$$

where  $H_i$  and  $\lambda_i$  are the ordinata and the abscissa of different points of the relaxation spectrum.

The spectra obtained by Weese and Fridrich [12] and by Jackson *et al.* [13] have been used to calculate the average relaxation time. In some cases, a value of the order of magnitude of 0.1 seconds has been obtained. As showed previously, a similar value will result in a flow-induced change of entropy of the same order of the entropy of polymerization when the polymerization is carried out at  $30 \text{ s}^{-1}$ .

## 7.7. Measurement of equilibrium conversion

The Brabender rheometer has been used to investigate the influence of the shear rate on the final conversion at the end of the polymerization. As mentioned in chapter 5, the torque and/or the normal force sensor of the “TA Instruments” rheometer are overloaded at very high conversion.

The polymerization of *n*-butylmethacrylate was performed at constant shear rate as described in chapter 4. The experiments were continued after the end of the regular increase of the viscosity that can be fitted with the double

power law trend in order to attain the equilibrium conversion. The shearing was stopped approximately 15 minutes after the end of the regular trend of the viscosity, which is approximately the same time required to obtain the double power law trend. Then a sample was taken, thermally quenched and stored for conversion analysis by nuclear magnetic resonance (NMR).

The conversion values obtained in this way can be considered to be the final conversion value for any practical purpose. The final conversion values corresponding to polymerizations performed at different shear rate are reported in figure 7.1.

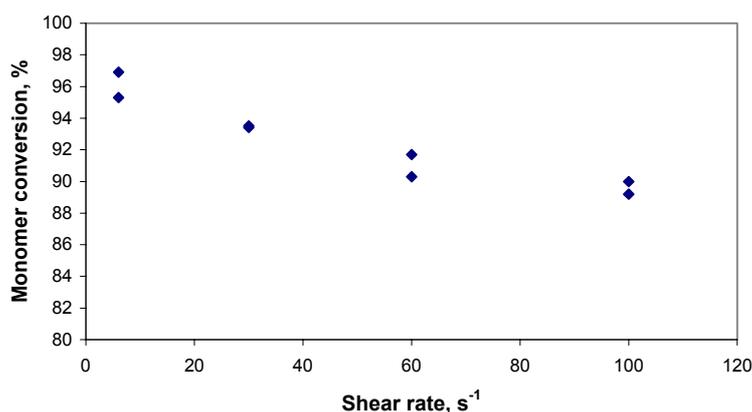


Figure 7.1. The influence of the shear rate on the final conversion of *n*-butylmethacrylate at 105 °C.

The final conversion decreases when the shear rate at which the polymerization is carried out increases.

This experimental evidence strengthens the contention that thermodynamic constraints can play a relevant part in bulk free radical polymerization and that the flow-induced change of entropy cannot be neglected.

However, a final conclusion cannot be drawn. In fact, the rheokinetic experiments do not allow to conclude that the values of the final conversion reported correspond also to a situation of thermodynamic equilibrium. It is not possible to deduce from the viscosity trends, which are highly irregular

and erratic at high conversion, if the conversion is at equilibrium when the experiments are stopped and the samples are taken. Anyway, since the conversion at the end of the regular trend is approximately 85-90%, as reported in chapter 4, we can argue that the values reported in figure 7.1 are, in the worst case, not very far from thermodynamic equilibrium.

### 7.8. The shear-induced solidification

In the case of ordinary chemical compounds of low molar mass the temperature of solidification can be defined as follows (e.g. Atkins [14])

$$T_s = \frac{\Delta H_s}{\Delta S_s} \quad (7.19)$$

where,  $T_s$  is the solidification temperature and  $\Delta H_s$  and  $\Delta S_s$  are the enthalpy and the entropy changes associated with the solidification process. The solidification occurs at a constant temperature and  $T_s$ ,  $\Delta H_s$  and  $\Delta S_s$  are defined and determined unambiguously for ordinary compounds. These values are reported in many books and data companions. Shear cannot alter the structure of the molecules and therefore has no influence on these three thermodynamic parameters.

The situation is not as straightforward in the case of polymers of high molar mass. Because of the dimensions of the macromolecules and of the presence of entanglements among them, the symmetry requirements necessary for solidification to take place are only partially met. In general, this results in a solidification process that involves only a part of the polymer sample and occurs not at constant temperature but across a wide range of temperatures. The solidification temperature is usually defined as the one at which the solidification begins [1]. The enthalpy and the entropy of solidification cannot be defined unambiguously. In the scientific literature there are only a few data available for the former and no data for the latter. Moreover, the

possibility that shear would influence the process of solidification cannot be ruled out.

The rheokinetic experiments discussed in chapter 4 and chapter 5 resulted in a irregular and erratic trend of the viscosity at very high conversions. This has been ascribed to a shear-induced formation of a solid phase that interferes with cone and plate measurements.

This interpretation is strengthened by the thermodynamic analysis reported previously that led to the qualitative determination of the shear-induced change of entropy. In fact, equation (7.19) is still valid for polymeric systems in principle, although it is practically of no use for any quantitative purpose because of the intrinsic impossibility to obtain reliable thermodynamic data. When the solidification occurs in the presence of shear, equation (7.19) must be modified to account for the shear-induced change of entropy.

$$T_{s,flow} = \frac{\Delta H_s}{\Delta S_{s,flow}} \quad (7.20)$$

where  $T_{s,flow}$  and  $\Delta S_{s,flow}$  are the solidification temperature and the solidification entropy in the presence of shear flow.

The presence of shear results in a higher absolute value of the solidification entropy and therefore in a lower value of the solidification temperature. As a consequence of this, polymeric systems have a higher tendency to form a solid phase when they are subjected to shear. This is in qualitative agreement with the contention that the shear-induced irregularities of the rheokinetic experiments can be ascribed to a shear-induced partial solidification.

## **7.9. Conclusions**

It is generally accepted that thermodynamics constraints are not important when free radical polymerizations are carried out in ordinary experimental or industrial conditions. The fact that a complete conversion of the monomer is rarely, if never, obtained is attributed to kinetic constraints by the scientific community, and, particularly, to the fact that the rate of polymerization is particularly low at very high conversion of the monomer. However, this belief is based on thermodynamic data obtained in absence of shear, which results in values of the ceiling temperature significantly higher than ordinary temperatures for free radical polymerization.

Nevertheless, shear can align and orientate the random coils and therewith induce a higher order in the polymeric system and cause an extra contribution to the entropy change associated with the polymerization.

The order of magnitude of this flow-induced change of entropy has been estimated with the help of rheokinetic experiments during which the viscosity and the normal force were determined simultaneously at a fixed shear rate. Some correlations between the viscosity, the relaxation time, the shear rate and the normal force derived from the theory of Maxwell-Oldroyd and from the dumbbell model have been used as well. These correlations are, strictly speaking, valid only for dilute polymer solutions, and they have been used because of the absence of more sophisticated rheological models. It appears that the flow-induced change of entropy at ordinary conditions of temperature and shear rate can be of the same order of magnitude as the values for entropy of polymerization, obtained from the literature.

The same conclusion can be obtained when the relaxation time is not obtained from the rheokinetic experiments performed in this thesis but from relaxation spectra derived by other authors.

This result indicates that thermodynamic constraints may well be the underlying reason for the incomplete conversion of the monomer and show, once again, the utility of a rheokinetic approach to the study of free radical polymerization.

This contention is confirmed by conversion data obtained at the end of rheokinetic experiments performed at different shear rate that resulted in lower final conversion values at higher shear rate.

Finally it can also be noted that the thermodynamic data on the entropy of polymerization available in the scientific literature do not consider the influence of the average molar mass of the polymer. In other words, it is assumed that the entropy of polymerization is the same whatever the average molar mass of the polymer produced. Intuitively, we can argue that the higher the average molar mass of the polymer obtained, the more order is induced to the system by the polymerization. Therefore also the absolute value of the entropy of polymerization should be, at least in principle, higher when the polymer obtained has a higher average molar mass.

The contention that the entropy of the polymerization might depend on the average molar mass is strengthened by some literature evidence. In fact, some authors [13] noticed that monodisperse linear polymers having different average molar mass are characterized by different relaxation time spectra. This would result in a different average relaxation time, and therefore in a different flow-induced change of entropy, according to equation (7.16)

To the best of our knowledge, the problem of the dependence of the entropy of polymerization on the shear rate at which the polymerization is performed and on the average molar mass of the polymer obtained has not been approached by the scientific community yet. This problem should be the subject of thorough scientific study.

### 7.10. List of symbols

$f$	efficiency of the initiation	-
$k_d$	rate constant for the initiator dissociation	$s^{-1}$
$k_p$	rate constant for the propagation step	$m^3 mol^{-1} s^{-1}$
$k_t$	rate constant for the termination step	$m^3 mol^{-1} s^{-1}$
$tr \tau$	trace of the stress tensor $\tau$	Pa

$C$	concentration	$\text{mol m}^{-3}$
$H(\lambda)$	relaxation time spectrum	Pa
$H_i$	ordinata of the relaxation spectrum	Pa
$K$	equilibrium constant	-
$I$	initiator	
$M$	monomer	
$R$	ideal gas constant	$\text{J mol}^{-1} \text{ } ^\circ\text{K}^{-1}$
$R_p$	rate of polymerization	$\text{mol m}^{-3} \text{ s}^{-1}$
$T$	temperature	$^\circ\text{C}$
$T_c$	ceiling temperature	$^\circ\text{C}$
$\Delta G_{Flow}$	change of free energy in the presence of flow	$\text{J mol}^{-1}$
$\Delta G_p$	free energy of the polymerization	$\text{J mol}^{-1}$
$\Delta H_p$	enthalpy of the polymerization	$\text{J mol}^{-1}$
$\Delta S_{Flow}$	flow-induced change of entropy	$\text{J mol}^{-1} \text{ } ^\circ\text{K}^{-1}$
$\Delta S_p$	entropy of the polymerization	$\text{J mol}^{-1} \text{ } ^\circ\text{K}^{-1}$
$\eta$	viscosity	Pa s
$\lambda$	relaxation time	s
$\lambda_i$	abscissa of the relaxation spectrum	s
$\lambda_{av}$	weight-average relaxation time	s
$\dot{\gamma}$	shear rate	$\text{s}^{-1}$
$\dot{\boldsymbol{\gamma}}$	shear rate tensor	$\text{s}^{-1}$
$\boldsymbol{\tau}$	stress tensor	Pa
$\tau_{ij}$	elements of the stress tensor	Pa

## 7.11. Literature

- [1] G. Odian, *Principles of polymerization*. Ed. John Wiley & Sons, Third Edition, 1991.
- [2] J. Brandrup, E.H. Immergut, E.A. Grulke, *Polymer handbook*. Ed. John Wiley & Sons, Fourth Edition, 1999.

- [3] S. Bywater, *Photosensitized polymerization of methyl methacrylate in dilute solution above 100 °C*, Trans. Faraday Soc., 1955, Vol. 51 1267-1273.
- [4] H.A. Jongbloed, R.K.S. Mulder, L.P.B.M. Janssen, *The co-polymerization of methacrylates in a counter-rotating twin-screw extruder*, Polym. Eng. Sci., 1995, Vol. 35, 587-597.
- [5] H.A. Jongbloed, J.A. Kiewiet, J.H. Van Dijk, L.P.B.M. Janssen, *The self-wiping co-rotating twin-screw extruder as polymerization reactor for methacrylates*, Polym. Eng. Sci., 1995, Vol. 35, 1569-1579.
- [6] A.J. Van Der Goot, R. Hettema, L.P.B.M. Janssen, *The working domain in reactive extrusion, Part I: the effect of the polymer melt viscosity*, Polym. Eng. Sci., 1997, Vol. 37, 511-518.
- [7] A.J. Van Der Goot, S.A. Klaassens, L.P.B.M. Janssen, *The working domain in reactive extrusion. Part II: the effect of the polymerization rate*, Polym. Eng. Sci., 1997, Vol. 37, 519-528.
- [8] R.B. Bird, O. Hassager, R.C. Armstrong, C.F. Curtis, *Dynamics of polymeric liquids, Volume 2, kinetic theory*. Ed. John Wiley & Sons, 1977
- [9] C.W. Macosko, *Rheology. Principles, measurements, and applications*. Ed. VCH Publishers, 1994
- [10] G. Marrucci, *The free energy constitutive equation for polymer solutions from the dumbbell model*, Trans. Soc. Rheol., 1972, Vol. 16, 321-330.
- [11] L.P.B.M. Janssen, R. Janssen van Rosmalen, *An analysis of flow induced formation of long fibers*, Rheol. Acta, 1978, Vol. 17, 578-588.
- [12] J. Weese, C. Friedrich, *Relaxation time spectra in rheology: calculation and examples*, Rheology, 1994, Vol. 4, 69-76.
- [13] J.K. Jackson, M.E. De Rosa, H.H. Winter, *Molecular weight dependence of relaxation time spectra for the entanglement and flow behavior of monodisperse linear flexible polymers*, Macromolecules, 1994, Vol. 27, 2426-2431.
- [14] P.W. Atkins, *Physical Chemistry*. Oxford University Press, Fourth Edition, 1990