

## University of Groningen

### Rheokinetics

Cioffi, Mario

**IMPORTANT NOTE: You are advised to consult the publisher's version (publisher's PDF) if you wish to cite from it. Please check the document version below.**

*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.

#### Copyright

Other than for strictly personal use, it is not permitted to download or to forward/distribute the text or part of it without the consent of the author(s) and/or copyright holder(s), unless the work is under an open content license (like Creative Commons).

The publication may also be distributed here under the terms of Article 25fa of the Dutch Copyright Act, indicated by the "Taverne" license. More information can be found on the University of Groningen website: <https://www.rug.nl/library/open-access/self-archiving-pure/taverne-amendment>.

#### Take-down policy

If you believe that this document breaches copyright please contact us providing details, and we will remove access to the work immediately and investigate your claim.

*Downloaded from the University of Groningen/UMCG research database (Pure): <http://www.rug.nl/research/portal>. For technical reasons the number of authors shown on this cover page is limited to 10 maximum.*

## **CHAPTER 2**

# **BULK FREE RADICAL POLYMERIZATION**

## 2.1. Introduction

Free radical polymerization is one of the most common processes used to produce vinylic polymers. It is a chain reaction consisting of a sequence of three steps, initiation, propagation and termination.

The polymerization is initiated by the formation of radicalic monomer molecules. These molecules add successively many monomer molecules, so that growing chains are formed. The growth of polymeric chains is usually terminated when two growing chains collide, yielding one or two stable macromolecules. Another possibility is that the growth stops when the radicalic center is transferred to a monomer molecule (chain transfer).

An initial lag time is required to produce the active centers. Afterwards, high molar mass polymer is formed very quickly: the active center, once produced, adds many monomer units in a chain reaction and grows rapidly to a large size. At any moment during the polymerization the reacting mixture contains only monomer, polymer and growing chains, and, as long as the process goes on, the polymer concentration increases whereas the monomer concentration decreases.

At low conversion the average molar mass is constant with the reaction time. At high conversion the average molar mass increases and the molar mass distribution broadens, especially when autoacceleration phenomena occur [1].

In the following paragraphs the chain mechanism of the bulk free radical polymerization will be described in detail, a kinetic model will be presented and an expression for the rate of polymerization will be derived.

## 2.2. The kinetic model

Free radical polymerization consists of a sequence of three steps: initiation, propagation and termination.

The initiation step involves two reactions. The first reaction is the production of free radicals by one of a number of different methods. The

most common, and the one used in this thesis, is the thermal homolytic dissociation of an initiator (usually a peroxide)  $P$  into a couple of radicals  $R\cdot$ .



$k_d$  is the rate constant for the initiator dissociation.

The second reaction of the initiation step consists of the addition of a monomer molecule  $M$  to the radical  $R\cdot$  to produce the chain initiating species  $M_1\cdot$ .



$k_i$  is the rate constant for the production of the radicalic monomer molecule  $M_1\cdot$ .

The propagation step consists of the growth of  $M_1\cdot$  by means of successive addition of many monomer molecules. Each addition produces a new radical group equal to the previous except that it is larger by one monomer unit.



etc., etc.,

In general terms



$k_p$  is the rate constant for the propagation step. It is here assumed that  $k_p$  is equal for each single addition reaction. Generally speaking this assumption is true with the only exceptions of the first two or three monomer additions

[2]. Since hundreds or thousands of monomer molecules are added in the propagation step, this assumption is generally accepted in the derivation of the kinetic model and of the expression of the rate of polymerization.

Growth finishes when two growing molecules collide with each other. This termination step can produce one (coupling) or two (disproportionation) stable macromolecules:



where  $k_{tc}$  and  $k_{td}$  are the rate constants for termination by coupling and disproportionation, respectively.

In general terms, it is also possible to describe the termination step without specifying the mode of termination



where

$$k_t = k_{tc} + k_{td} \quad (2.9)$$

Also  $k_t$  is generally assumed to be independent of the size of the growing macromolecules.

### 2.3. The rate of polymerization

The rate of polymerization is given by the rate at which the monomer disappears, or, in other words, by the time derivative of the monomer concentration. Since the latter decreases as a consequence of the initiation and of the propagation reaction, the rate of polymerization  $R_p$  is given by

$$R_p = -\frac{d[M]}{dt} = R_i + R_{prop} \quad (2.10)$$

where  $R_i$  and  $R_{prop}$  are the rates of initiation and propagation, respectively. The minus sign is included to have an intrinsically positive rate of polymerization.

Since most monomer molecules are involved in the propagation step, it is possible to neglect  $R_i$  in equation (2.10). Since the rate constant for all the reactions of the propagation steps is the same, it is possible to express the rate of polymerization by

$$-\frac{d[M]}{dt} = k_p[M\cdot][M] \quad (2.11)$$

where  $[M\cdot]$  is the total concentration of all the radical species  $M_n\cdot$ .

$[M\cdot]$  is very difficult to measure. It must therefore be eliminated from equation (2.11) in order to derive a useful relationship for the rate of polymerization.

This can be done by assuming that  $[M\cdot]$  is constant during the polymerization. This *steady-state* assumption has been confirmed experimentally in many polymerizations and is often used to describe kinetic models for chemical reactions not involving the formation of high polymers.

Assuming that  $[M\cdot]$  is constant during the polymerization means that the rate of initiation and termination must be equal. In fact, free radicals are created by the initiation step and neutralized by the termination step.

$$R_i = 2k_t[M\cdot]^2 \quad (2.12)$$

Substituting  $[M\cdot]$  in equation (2.11) yields

$$R_p = k_p[M] \left( \frac{R_i}{2k_t} \right)^{1/2} \quad (2.13)$$

The expression of the rate of initiation  $R_i$  depends on the type of initiation used. For initiation by thermal homolysis of an initiator, the initiation takes place in two steps, as mentioned before (equations (2.1) and (2.2)). In most cases, the second step is much faster than the first. Therefore the homolysis of the initiator is the rate-determining step for the initiation, given by

$$R_i = 2fk_d[I] \quad (2.14)$$

where  $[I]$  is the initiator concentration and  $f$  is the *initiator efficiency*. The latter is defined as the fraction of the radicals produced in the homolysis reaction that initiate polymer chains. Because of secondary reactions,  $f$  is usually less than but very close to 1.

Substituting equation (2.14) into (2.13) yields the following expression of the rate of polymerization

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

The rate constant of the propagation reaction  $k_p$  is for most monomers in the range of  $10^2$ - $10^4$  liters/mole·s, whereas  $k_t$  is in the range of  $10^6$ - $10^8$  liters/mole·s, and therefore larger than  $k_p$  by a few orders of magnitude. This fact does not prevent the polymerization from taking place because the concentration of radical species is much lower than the concentration of monomer. Moreover the rate of polymerization depends only on the half-power of  $k_t$ . It is also interesting to note that doubling the rate of initiation does not double the polymerization rate, but increases it only by a factor  $\sqrt{2}$ .

## 2.4. Molar mass

The *kinetic chain length*  $\nu$  of a free radical polymerization is defined as the average number of monomer molecules polymerized per radical that initiates a polymer chain. It is, of course, a measure of the average molar mass of the polymer produced.

The kinetic chain length is given by the ratio of the polymerization rate to the initiation or termination rate, the last two being equal if the *steady state* assumption of the total concentration  $[M\cdot]$  of all the radical species  $M_n\cdot$  is made.

$$\nu = \frac{R_p}{R_i} = \frac{R_p}{R_t} \quad (2.16)$$

Combination of previous equations (2.11) and (2.12) with (2.16) yields

$$\nu = \frac{k_p[M]}{2k_t[M\cdot]} \quad (2.17)$$

or

$$\nu = \frac{k_p^2[M]^2}{2k_tR_p} \quad (2.18)$$

Further substitution of (2.15) into (2.18) yields

$$\nu = \frac{k_p[M]}{2(fk_dk_t[I])^{1/2}} \quad (2.19)$$

Equation (2.19) shows a very significant peculiarity of free radical polymerization. The kinetic chain length, and therewith the average molar mass, decreases when the initiator concentration is increased. Therefore any

attempt to increase the rate of polymerization by increasing the initiator concentration results in the production of polymer with a lower average molar mass.

## 2.5. Chain transfer

In many polymerization systems chain transfer occurs. The chain transfer consists of a premature termination of a growing polymer by transfer of the active center to a monomer molecule. This molecule is the starting point for the growth of a new chain. Therefore, chain transfer results in a decrease of the average molar mass.

Chain transfer can occur spontaneously or be induced by adding some chain transfer agents. In the former case, the rate of reinitiation is comparable to that of the growth of the original propagating chain. Thus, spontaneous chain transfer has no influence on the rate of polymerization and equation (2.15) remains valid.

In contrast, the addition of chain transfer agents allows to control the average molar mass of the polymer obtained. Depending on the agent used, it can also result in a decrease of the rate of polymerization.

In this thesis no chain transfer agent has been used.

## 2.6. The Trommsdorff effect

Considering the equation (2.15) one might conclude that the rate of polymerization decreases as long as the polymerization proceeds as a consequence of the decrease of  $[M]$ . However, exactly the contrary is very often observed. At a certain point the rate of polymerization increases with the conversion, or with the reaction time. This is shown qualitatively in figure 2.1, giving the expected and the actual trends of the increase of the conversion with the reaction time.

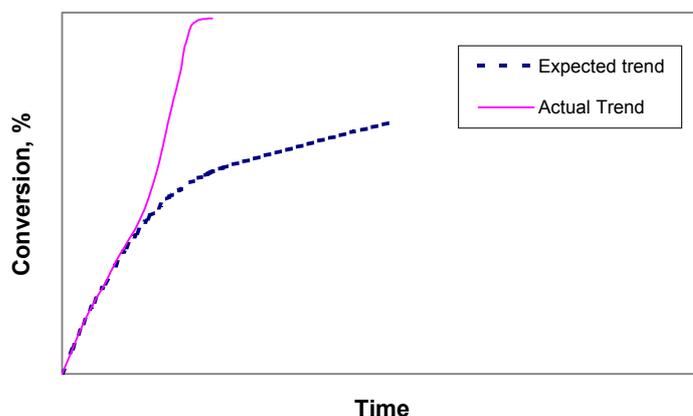


Figure 2.1. The Trommsdorff effect causes the conversion versus time profile to deviate from the expected trend.

This phenomenon is commonly known in the scientific literature as *Trommsdorff effect* or *gel effect*. The latter term is mostly used in the literature, but it is quite inappropriate because this phenomenon has got nothing to do with the formation of a gel. Therefore, we shall use the term *Trommsdorff effect* in this thesis.

This autoacceleration has been observed for many monomers including styrene and many acrylates [3-13] since the late 40s and is considered to constitute a normal behavior for free radical polymerization. According to O' Driscoll and Huang [14], the polymerization rate for a styrene homopolymerization can be as high as 15 times the theoretical rate as expressed by equation (2.15).

The Trommsdorff effect must not be confused with the "Arrhenius" autoacceleration that takes place in non-isothermal condition because of the increase of temperature due to heat released during the polymerization. The Trommsdorff effect is the autoacceleration that occurs also when the polymerization is performed in isothermal conditions.

The Trommsdorff effect is due to a decrease of the translational diffusion of the growing macromolecules. It usually takes place at intermediate or high

conversion, when the viscosity of the reacting fluid is high and the random coils entangle with each other. This limited mobility causes the rate of the termination reaction to decrease, since the termination reaction occurs when two growing macromolecules collide. On the other hand, the mobility of small monomer molecules is not affected by the increasing viscosity of the reacting fluid. Therefore the limited mobility of macromolecules affects the rate of propagation to a much smaller extent.

This molecular picture leading to the Trommsdorff effect is somehow equivalent to what can be easily observed in the streets of big Italian cities. When the concentration of cars increases over a certain limit, their mobility is reduced significantly, but the mobility of scooters and bikes is hardly affected because they can still use the empty spaces left by the “entangled” cars.

In first approximation, we can conclude that the decreased mobility of growing macromolecules results in a decrease of  $k_t$  at constant  $k_p$ , which results in an increase of the rate of polymerization according to equation (2.15).

Equation (2.19) predicts that the Trommsdorff effect causes an increase in the average molar mass. Also the polydispersity of the molar mass distribution curve usually increases.

It must be noted that the Trommsdorff effect is not an “Off-On” phenomenon, but it sets in gradually over a certain interval of conversion, or reaction time, during which the mobility of growing macromolecules becomes gradually more and more limited.

The Trommsdorff effect is highly undesirable in industrial applications. In fact, it occurs when the viscosity is already high and therefore when heat and mass transfer are hindered. Therefore the Trommsdorff effect results in hot spots and erratic behavior, which worsens the quality of the end product, and even can lead to reactor explosion [15, 16].

The scientific literature concerning the Trommsdorff effect has been recently reviewed [3]. Most of the studies performed so far have been aimed

at the investigation of the causes that determine the Trommsdorff effect on a molecular level, rather than to limiting or avoiding the Trommsdorff effect. A very easy way to avoid the Trommsdorff effect is to reduce as much as possible the formation of entanglements that reduce the mobility of macromolecules by performing the polymerization in the presence of large amounts of solvent. The data presented in the figure 2.2, for example, refer to the free radical polymerization of methyl methacrylate in benzene solution [17].

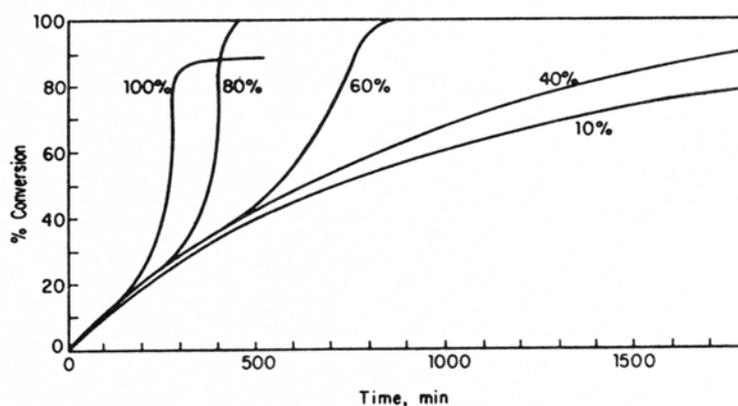


Figure 2.2. Autoacceleration in the free radical polymerization of methyl methacrylate in benzene. The different curves refer to different initial concentrations of the monomer in the solvent [17].

It can be clearly seen that the autoacceleration is reduced when the initial concentration of monomer in the solution is lower.

However, as already mentioned in chapter 1 the addition of a solvent has many negative consequences and is not the most desirable solution to the problem.

Chen *et al.* [18] have been able to reduce the Trommsdorff effect using mixtures of initiators, tailored to balance the decrease of  $k_t$  with a corresponding decrease of  $k_d$ . Other authors [19] have performed bulk free radical polymerization of styrene in the presence of nitroxide-stable free

radicals. In this way the conventional termination reaction (equation (2.8)) could be strongly suppressed and therefore the Trommsdorff effect did not take place.

These studies show that in some specific cases the Trommsdorff effect can be reduced or eliminated. However, in general, it remains an unsolved problem.

## 2.7. List of symbols

|            |  |  |
|------------|--|--|
| $I$        | initiator  |  |
| $M$        | monomer  |  |
| $M_i\cdot$ | radicalic chain of length $i$                        |  |
| $P$        | initiator (peroxide)                                 |  |
| $R\cdot$   | radical  |  |
| $R_p$      | rate of polymerization                               | $\text{mol m}^{-3} \text{t}^{-1}$          |
| $R_i$      | rate of initiation                                   | $\text{mol m}^{-3} \text{t}^{-1}$          |
| $R_{prop}$ | rate of propagation                                  | $\text{mol m}^{-3} \text{t}^{-1}$          |
| $f$        | efficiency of the initiation                         | -  |
| $k_d$      | rate constant for the initiator dissociation         | $\text{s}^{-1}$                            |
| $k_i$      | rate constant for the production of $M_i\cdot$       | $\text{m}^3 \text{mol}^{-1} \text{s}^{-1}$ |
| $k_p$      | rate constant for the propagation step               | $\text{m}^3 \text{mol}^{-1} \text{s}^{-1}$ |
| $k_{tc}$   | rate constant for the termination by coupling        | $\text{m}^3 \text{mol}^{-1} \text{s}^{-1}$ |
| $k_{tp}$   | rate constant for the termination disproportionation | $\text{m}^3 \text{mol}^{-1} \text{s}^{-1}$ |
| $k_t$      | rate constant for the termination step               | $\text{m}^3 \text{mol}^{-1} \text{s}^{-1}$ |
| $\nu$      | kinetic chain length                                 | -  |

## 2.8. Literature

- [1] G. Odian, *Principles of polymerization*. Ed. John Wiley & Sons, Third Edition, 1991.
- [2] J.A. Kerr, *Rate process in the gas phase*, Chap. 1 in "Free Radicals", Vol. I, J.K. Kochi, Ed. Wiley, New York, 1973.

- [3] G.A. O'Neil, J.M. Torkelson, *Recent advances in the understanding of the gel effect in free-radical polymerization*, Trends in Polym. Sci., 1997, Vol. 5, 349-355.
- [4] E. Abuin, E.A. Lissi, *Methyl methacrylate polymerization at high conversion. II. Factors determining the onset of the gel effect*, J. Macromolec. Sci. Chem., 1977, Vol. A11, 287-294.
- [5] S.T. Balke, A.E. Hamielec, *Bulk polymerization of methyl methacrylate*, J. Appli. Polym. Sci., 1973, Vol. 17, 905-949.
- [6] J.N. Cardenas, K.F. O'Driscoll, *High-conversion polymerization. I. Theory and application to methyl methacrylate*, J. Polym. Sci., Polym. Chem. Ed., 1976, Vol. 14, 883-887.
- [7] J.N. Cardenas, K.F. O'Driscoll, *High-conversion polymerization. II. Influence of chain transfer on the gel effect*, J. Polym. Sci., Polym. Chem. Ed., 1977, Vol. 15, 1883-1888.
- [8] J.N. Cardenas, K.F. O'Driscoll, *High-conversion polymerization. III. Kinetic behavior of ethyl methacrylate*, J. Polym. Sci., Polym. Chem. Ed., 1977, Vol. 15, 2097-2108.
- [9] P.A. Small, *Long-chain branching in polymers*, Adv. Polym. Sci., 1975, Vol. 18, 1-64.
- [10] D.T. Turner, *Autoacceleration of free-radical polymerization. 1. The critical concentration*, Macromolecules, 1977, Vol. 10, 221- 226.
- [11] K. Yamamoto, M. Sugimoto, *Rate constant for long-chain branch formation in free-radical polymerization of ethylene*, J. Macromol. Sci. Chem., 1979, Vol. A13, 1067-1080.
- [12] H.A. Jongbloed, R.K.S. Mulder, L.P.B.M. Janssen, *The copolymerization of methacrylates in a counter-rotating twin-screw extruder*, Polym. Eng. Sci., 1995, Vol. 35, 587-597.
- [13] H.A. Jongbloed, J.A. Kiewit, J.H. Van Dijk, L.P.B.M. Janssen, *The self-wiping co-rotating twin-screw extruder as a polymerization reactor for methacrylates*, Polym. Eng. Sci., 1995, Vol. 35, 1569-1579.

- [14] K.F. O'Driscoll, J. Huang, *The rate of copolymerization of styrene and methyl methacrylate II. The gel effect in copolymerization*, Eur. Polym. J., 1990, Vol. 26, 643-647.
- [15] I.R. Epstein, J.A. Pojman, *Nonlinear dynamics related to polymeric systems*, Chaos, 1999, Vol.9, 255-259.
- [16] L.P.B.M. Janssen, *On the stability of reacting extrusion*, Polym. Eng. Sci., 1998, Vol.38, 2010-2019.
- [17] G.V. Schulz, G. Haborth, *The mechanism of the explosive polymerization of methyl methacrylate*, Makromol. Chem., 1948, Vol. 1, 106-139.
- [18] C.Y. Chen, C.S. Chen, J.F. Kuo, *The multiple-component initiator technique for constant-rate free-radical homopolymerization*, Polymer, 1987, Vol. 28, 1396-1402
- [19] M.D. Saban, M.K. Georrges, R.P.N. Veregin, G.K. Hamer, P.M. Kazmaier, *Nitroxide-mediated free radical polymerization of styrene. Absence of the gel effect*, Macromolecules, 1995, Vol. 28, 7032-7034.