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AFDELING TOEGEPASTE WISKUNDE TW 160/76 JULI
(DEPARTMENT OF APPLIED MATHEMATICS)

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# POLYCONDENSATION AND GELATION: THE GENERAL CASE
PREPUBLICATION

2e boerhaavestraat 49 amsterdam

*Printed at the Mathematical Centre, 49, 2e Boerhaavestraat, Amsterdam.*

*The Mathematical Centre, founded the 11-th of February 1946, is a non-profit institution aiming at the promotion of pure mathematics and its applications. It is sponsored by the Netherlands Government through the Netherlands Organization for the Advancement of Pure Research (Z.W.O), by the Municipality of Amsterdam, by the University of Amsterdam, by the Free University at Amsterdam, and by industries.*

AMS(MOS) subject classification scheme (1970): 80A30, 34A05.

# Polycondensation and gelation: the general case[*)]

by

H.A. Lauwerier

## ABSTRACT

The mathematical model of multifunctional polycondensation is considered by means of the method of the generating function as proposed by Pis'men and Kuchanov. This paper is a sequel to an earlier paper in which we studied the special case of polycondensation of trifunctional monomers. Here the general case is considered. The results are similar as in the special case. The model does not only describe the process of polycondensation up to the possible gelpoint but does give quantitative information for the subsequent period during which the gel is built up. A technique has been developed for determining the main statistical characteristics of the mixture before and after the gelpoint. This method has been worked out for the special case of a mixture which originally contains molecules of type $C_3(3,0)$ and $C_1(0,2)$ only.

KEY WORDS & PHRASES: *polycondensation, gelation, gelpoint, generating function technique, explicit solutions.*

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*) This paper is not for review; it is meant for publication elsewhere.

## 1. INTRODUCTION

In a previous paper we studied the mathematical model of the polycondensation of trifunctional monomers by using the method of the generating function as described by PIS'MEN and KUCHANOV [2] in their paper. In our analysis it was made clear that the mathematical model describes the process of polymerisation both before and after the gelpoint. In particular the model appears to give quantitative information on the formation of the gel. In the case of trifuctional monomers an explicit solution could be obtained for the period up to the gelpoint and for the subsequent infinite period with a continuous transition at the gelpoint. In particular we obtained simple expressions for the first few moments in both periods.

In this paper we consider the general case of polycondensation of polymers with an arbitrary number of functional groups of a first type and of a second type. The reaction scheme is the same as that considered by Pis'men and Kuchanov. Our notation corresponds very closely to that used in their paper (often quoted as PK followed by the formula number).

It turns out that the ideas developed in our previous paper can also be used in the general case. In fact, all essential points of the general model are already present in the much simpler model considered before.

We have the impression that so far the potentialities of the mathematical model have not been fully appreciated. Pis'men and Kuchanov rejected the model for the period after the gelpoint and missed accordingly the second part of the full solution. On the contrary also in the general case the model neatly describes the possible formation of a gel. Gel formation as described by this model is no instantaneous process but evolves rapidly or slowly as the case may be.

The mathematical analysis in this paper is a generalization of that in our previous paper. The general line is as follows. Using the technique of the generating function the infinite number of kinetic equations is transformed into a single partial differential equation. This equation still contains the first moments $\mu_1(t)$ and $\mu_2(t)$ measuring the total number of free functional groups of either kind. For $t < t_g$ where $t_g$ is the possible gelpoint these moments are simple functions of time that can be determined in advance but for $t > t_g$ their determination requires complete solution of the problem. However, by using well-chosen independent variables it is possible to solve the partial differential equation without making explicit use of the first moments. This solution holds for all values of time, irrespective of possible gelation. Assuming a known generating function the first moments can be determined in a simple manner. But in reality for $t > t_g$ the generating function which solves the partial differential equation contains $\mu_1(t)$ and $\mu_2(t)$ still as unknown functions. Thus there exists an implicit way of determining these moments. Eventually we arrive at solutions of $\mu_1(t)$ and $\mu_2(t)$ which are different in form before and after the gelpoint but with a continuous transition at $t = t_g$. In a similar way, we may derive an expression for the zeroth moment $\mu(t)$, which measures the total number of free molecules reacting with each other and an expression for the total number M of elementary units. Up to the gelpoint M is constant as it should be, but for $t > t_g$ M is decreasing with time. This means that the total mass initially present in the mixture is now divided between the reacting molecules and the gel which in a sense may be seen as a molecule with an infinity of functional groups.

The contents of this paper may be summarized as follows. The most important formulae and results are summed up in the second section. The reader who wants to work out some specific case will find here all relevant material. In the third section we consider the infinite set of kinetic equations in the form considered by Pis'men and Kuchanov. It is shown that from these equations the zeroth moment $\mu(t)$ and the first moments $\mu_1(t),\mu_2(t)$ can be determined only under the condition of finite second moments. In the fourth section a general solution is obtained by means of the technique of the generating function. Expressions for the first few moments and the total mass are given. In the fifth section the solution for the period $t < t_g$ is worked out. Explicit formulae for the gelpoint are given. Our results fully agree with those obtained by Pis'men and Kuchanov. In the sixth section an essentially new addition to the theory, the case $t > t_g$, is discussed at length. A method has been developed by means of which all interesting functions such as the first few moments can be determined in terms of suitable auxiliary variables. Eventually this leads to a single ordinary differential equation which can be solved analytically in specific cases of course. In the seventh and last section the theory is applied to the important case of a mixture containing initially molecules of type $C_3(3,0)$ and $C_1(0,2)$ only. For this case considered earlier by FLORY [1] a complete and explicit analytical solution is obtained. The symmetric case is worked out numerically.

## 2. SUMMARY OF THE RESULTS

In order to facilitate further applications of the theory we summarize the most important formulae. The concentration of molecules of type $C_k(a_1,a_2)$ at time t is denoted by $C_k(a_1,a_2,t)$. They are all combined in the generating function

$$(2.1) \qquad g = \sum C_k(a_1,a_2,t) s^k x_1^{a_1} x_2^{a_2}.$$

The initially given mixture is described by

$$(2.2) \qquad g(s,x_1,x_2,0) = h(s,x_1,x_2).$$

The zeroth moment $\mu$, the first moments $\mu_i$ and the total amount of elementary units M are defined by (3.3), (3.4) and (3.6). Their initial values follow at once from the given polynomial h. For $t \leq t_g$ they are explicitly given by (3.14), (3.11) or in the symmetric case $\mu_1 = \mu_2$ by (3.13), (3.15) i.e.

$$(2.3) \qquad \mu_1(t) = \mu_2(t) = \frac{1}{t+\theta}, \qquad t \leq t_g,$$

$$(2.4) \qquad \mu(t) = \mu(0) - \frac{t}{\theta(t+\theta)}, \qquad t \leq t_g.$$

The gelpoint $t_g$ can be calculated from (5.11) in the general case or from (5.13) in the symmetric case. However, in some cases a gelpoint is absent what betrays itself in an imaginary value.

For the period $t > t_g$ we need auxiliary parameters $C_1, C_2$ and an auxiliary time variable v. Using the notations

$$h_1 = \frac{\partial}{\partial x_1} h(1,C_1,C_2), \qquad h_2 = \frac{\partial}{\partial x_2} h(1,C_1,C_2),$$

$$h_{11} = \frac{\partial^2}{\partial x_1^2} h\ (1,C_1,C_2), \qquad \text{etcetera,}$$

we have (cf. 6.11)

$$(2.5) \qquad \begin{cases} \mu = h - vh_1h_2\ , \\ \mu_1 = C_1h_1 - vh_1h_2\ , \\ \mu_2 = C_2h_2 - vh_1h_2\ , \end{cases}$$

and

$$(2.6) \qquad M = \frac{\partial}{\partial s} h\ (1,C_1,C_2).$$

The functions $C_1(v)$, $C_2(v)$ follow from (6.8) and (6.9) or

$$(2.7) \qquad \begin{cases} v(h_{12} + \sqrt{h_{11}h_{22}}) = 1\ , \\ \sqrt{h_{11}}\ dC_1 = \sqrt{h_{22}}\ dC_2\ , \end{cases}$$

where $C_1 = C_2 = 1$ at the gelpoint $v = v_g$ determined by

$$(2.8) \qquad v_g\{h_{12}(1,1,1) + \sqrt{h_{11}(1,1,1)h_{22}(1,1,1)}\} = 1.$$

The relation between v and the real time t is given by the integral (6.10) or (6.12) viz.

$$(2.9) \qquad t - t_g = \int_{v_g}^{v} (C_1-vh_2)^{-1}(C_2-vh_1)^{-1}dv.$$

The full distribution function or generating function is determined by (4.14). However, the parameters $C_1,C_2$ have a more general meaning since they also depend on s, $x_1$ and $x_2$. Therefore we modify the expression as follows

$$(2.10) \qquad \begin{cases} g = h(s,\lambda_1,\lambda_2) - vh_1(s,\lambda_1,\lambda_2)h_2(s,\lambda_1,\lambda_2), \\ x_1\sigma_2 = \lambda_1 - vh_2(s,\lambda_1,\lambda_2), \\ x_2\sigma_1 = \lambda_2 - vh_1(s,\lambda_1,\lambda_2), \end{cases}$$

where $\sigma_1(t)$, $\sigma_2(t)$ and $v(t)$ are determined by (4.7), (4.8) as

$$(2.11)\quad \begin{cases} \sigma_i(t) = \exp - \int_0^t \mu_i(\tau)\, d\tau, \\ \\ v(t) = \int_0^t \sigma_1\sigma_2 d\tau. \end{cases}$$

For $t < t_g$ $\sigma_i(t)$ and $v(t)$ are simple functions as given by (5.1) and (5.2). However, for $t > t_g$ $\sigma_1$ and $\sigma_2$ can only be expressed as a function of $v$ in the following way. In addition to (2.5) we have

$$(2.12)\quad \begin{cases} \sigma_1 = C_2 - vh_1, \\ \\ \sigma_2 = C_1 - vh_2. \end{cases}$$

The following example, worked out in more detail in section 7, shows the manner in which these formulae can be applied. Starting from the symmetric mixture with monomers of type $C_3(3,0)$ and $C_1(0,2)$ we have

$$(2.13)\quad h = \frac{2}{9} s^3 x_1^3 + \frac{1}{3} s x_2^2 .$$

Using

$$\mu(0) = \frac{5}{9} \qquad \text{and} \qquad \mu_1(0) = \mu_2(0) = \frac{2}{3}$$

we obtain from (2.3) and (2.4) for the first period

$$(2.14)\quad \begin{cases} \mu_1(t) = \mu_2(t) = \dfrac{2}{2t + 3}, \\ \\ \mu(t) = \dfrac{15 - 2t}{9(2t+3)} . \end{cases}$$

The gelpoint is

$$t_g = \frac{3}{2} (1+\sqrt{2}) = 3.62.$$

From (2.7) we obtain for $t > t_g$

$$(2.15)\qquad C_1 = \frac{9}{8} v^{-2}, \qquad C_2 = \frac{9}{8} v^{-3} + 1 - \frac{2}{3}\sqrt{2}\,.$$

Then using (2.5) we obtain for $\mu_1$ and $\mu_2$

$$(2.16)\qquad \begin{cases} \mu_1 = \frac{2}{3} C_1^3 - \frac{4}{9} vC_1^2C_2, \\ \mu_2 = \frac{2}{3} C_2^2 - \frac{4}{9} vC_1^2C_2. \end{cases}$$

The relation between v and t has been determined by (7.22). It appears that the equality of $\mu_1$ and $\mu_2$ stops at the gelpoint. For $t \to \infty$ $\mu_1$ tends to zero whereas $\mu_2$ has a non-vanishing limit. In the limit situation the gel has consumed all trifunctional monomers but a small amount of molecules of type $C_1(0,2)$ is still present.

Of course we should realize that the mathematical model considered here is an idealization of the chemical situation. It may be expected that with the formation of more and more complex polymers the model departs gradually from the chemical reality. However, the merits of the mathematical model can only be assessed by comparing the mathematical results with chemical experiments.

## 3. THE KINETIC EQUATIONS

Let the symbol $C_n(a_1,a_2)$ denote a polymer molecule with n units, $a_1$ functional groups of a first type I and $a_2$ functional groups of a second type II. The reaction scheme is assumed to be of the form (cf. PK 1)

$$(3.1)\qquad C_k(b_1,b_2) + C_\ell(c_1,c_2) \to C_{k+\ell}(b_1+c_1-1,b_2+c_2-1).$$

With a dimensionless time scale the kinetic equations are (cf. PK 3)

$$(3.2)\qquad \begin{aligned} \frac{d}{dt} C_n(a_1,a_2,t) &= -C_n(a_1,a_2,t) \sum (a_1b_2 + a_2b_1)C_k(b_1,b_2,t) + \\ &+ \frac{1}{2} \sum (b_1c_2+b_2c_1)C_k(b_1,b_2,t)C_\ell(c_1,c_2,t)\ , \end{aligned}$$

where $C_n(a_1,a_2,t)$ is the concentration of molecules $C_n(a_1,a_2)$ at time t, and where the summations are taken with $b_1 + c_1 = a_1 + 1$, $b_2 + c_2 = a_2 + 1$, $k + \ell = n$. For a fixed value of t and $n,a_1,a_2$ running through the set of the natural numbers the concentrations $C_n(a_1,a_2,t)$ determine the concentration distribution function. Its first few moments are of considerable importance both in theory and practice.

The zeroth moment

$$(3.3) \qquad \mu(t) = \sum C_k(a_1,a_2,t)$$

measures the total number of polymer chains. The first moment of either kind

$$(3.4) \qquad \mu_i(t) = \sum a_i C_k(a_1,a_2,t), \qquad i = 1,2,$$

measures the total number of free functional groups of type I or II. The three second moments $\mu_{11}, \mu_{12} = \mu_{21}, \mu_{22}$ are defined as

$$(3.5) \qquad \mu_{ij}(t) = \sum a_i a_j C_k(a_1,a_2,t), \qquad i,j = 1,2.$$

They measure in a sense the broadness of the concentration distribution function.

The total number of monomer units involved in the reactions is measured by

$$(3.6) \qquad M = \sum kC_k(a_1,a_2,t).$$

It is to be expected that M does not change in time. However, we shall soon see that this so-called conservation law is not unconditionally implied by the equations (3.2).

If the equations (3.2) are summed with respect to $n,a_1,a_2$ we obtain without difficulty the single ordinary differential equation

$$(3.7) \qquad \frac{d\mu}{dt} = -\mu_1\mu_2.$$

If the equation (3.2) is multiplied by $a_1$ then summation gives

$$\frac{d\mu_1}{dt} = -(\mu_{11}\mu_2 + \mu_{12}\mu_1) + (\mu_{11}\mu_2 + \mu_{12}\mu_1) - \mu_1\mu_2.$$

However, the summations can only be justified under the condition of the convergence of the second moments (3.5). Thus, only if $\mu_{ij}(t) < \infty$ the equation obtained above is true and can be replaced by

$$\frac{d\mu_1}{dt} = -\mu_1\mu_2, \tag{3.8}$$

and similarly

$$\frac{d\mu_2}{dt} = -\mu_1\mu_2. \tag{3.9}$$

The conservation law, M = constant, can be derived in an analogous way. In particular we obtain the result

$$\frac{dM}{dt} = 0 \tag{3.10}$$

provided

$$\sum ka_1C_k < \infty \qquad \text{and} \qquad \sum ka_2C_k < \infty.$$

Generally speaking there is a moment $t = t_g$, the gelpoint, where some or all second moments become infinite and where the relations (3.8), (3.9) and (3.10) are no longer true. The relation (3.7) remains true, however, also for $t \geq t_g$.

During the initial period up to the gelpoint the moments $\mu$, $\mu_1$ and $\mu_2$ can be determined from the equations (3.7), (3.8) and (3.9). A simple integration shows that

$$\mu_1(t) = \frac{\lambda \exp - \lambda(t+\theta)}{\sinh \lambda(t+\theta)}, \qquad \mu_2(t) = \frac{\lambda \exp \lambda(t+\theta)}{\sinh \lambda(t+\theta)}, \tag{3.11}$$

where $\lambda$ and $\theta$ are constants of integration.

Of course to (3.2) a given initial distribution should be added. From this we may obtain $\mu(0)$, $\mu_1(0)$, $\mu_2(0)$ as given constants. Then (3.11) gives

$$2\lambda = \mu_2(0) - \mu_1(0), \qquad 2\lambda\theta = \ln \mu_2(0) - \ln \mu_1(0). \tag{3.12}$$

For a stoichiometric mixture we have a symmetrical situation with $\lambda = 0$. Then (3.11) can be replaced by

$$(3.13) \qquad \mu_1(t) = \mu_2(t) = \frac{1}{t + \theta} .$$

From (3.7) we obtain

$$(3.14) \qquad \mu(t) = \mu(0) - \frac{\lambda \sinh \lambda t}{\sinh \lambda\theta \sinh \lambda(t+\theta)} ,$$

and in the symmetrical case

$$(3.15) \qquad \mu(t) = \mu(0) - \frac{t}{\theta(t+\theta)} .$$

Assuming the validity of (3.11) and (3.14) for all values of t we would find for $t \to \infty$

$$\mu(\infty) = \mu(0) - \frac{\lambda e^{-|\lambda|\theta}}{\sinh \lambda\theta} ,$$

or

$$(3.16) \qquad \mu(\infty) = \mu(0) - \mathrm{Min}\{\mu_1(0), \mu_2(0)\}.$$

According to (3.3) and (3.4) this would lead to a negative value of $\mu(\infty)$ in many situations. If there are molecules of mixed type only, i.e., of type $C_n(a_1,a_2)$ with $a_1 \geq 1$, $a_2 \geq 1$, (3.16) would give $\mu(\infty) \leq 0$ with the equality sign for $a_1 = a_2 = 1$ only. The obvious conclusion is that a negative value of the right-hand side of (3.16) implies the existence of a gelpoint and the restricted validity of (3.11) and (3.14).

## 4. THE METHOD OF THE GENERATING FUNCTION

According to the method followed by Pis'men and Kuchanov in their paper we introduce the generating function (cf. PK 1)

$$(4.1) \qquad g(s,x_1,x_2,t) = \sum C_k(a_1,a_2,t) s^k x_1^{a_1} x_2^{a_2} .$$

Since from (3.3)

$$\mu(t) = g(1,1,1,t), \tag{4.2}$$

the convergence of the right-hand side of (4.1) is guaranteed in the cube $|x_1| \leq 1$, $|x_2| \leq 1$, $|s| \leq 1$. The next moments (3.4) can be derived from (4.1) as

$$\mu_i(t) = \frac{\partial}{\partial x_i} g(1,1,1,t) . \tag{4.3}$$

The total amount of monomer units (3.6) is given as

$$M(t) = \frac{\partial}{\partial s} g(1,1,1,t). \tag{4.4}$$

The second moments (3.5) follow in a similar way from (4.1) but we may expect infinity for $t \geq t_g$. By multiplying each of the equations (3.2) by $s^n x_1^{a_1} x_2^{a_2}$ and summing them with respect to n, $a_1, a_2$ we arrive at the partial differential equation (cf. PK 13)

$$\frac{\partial g}{\partial t} = -\mu_2 x_1 \frac{\partial g}{\partial x_1} - \mu_1 x_2 \frac{\partial g}{\partial x_2} + \frac{\partial g}{\partial x_1} \frac{\partial g}{\partial x_2} . \tag{4.5}$$

To this we may add an initial condition

$$g(s,x_1,x_2,0) = h(s,x_1,x_2), \tag{4.6}$$

where h is a given polynomial.

It should be realized that the equation (4.5) holds for all values of t but that the first moments are known in advance only for the period up to the gelpoint. Therefore we shall solve (4.5) by a method which does not use the explicit form of $\mu_i(t)$ such as (3.11). We introduce the auxiliary functions

$$\sigma_i(t) = \exp - \int_0^t \mu_i(\tau) d\tau , \qquad i = 1,2, \tag{4.7}$$

and new independent variables u,v determined by

$$(4.8)\qquad u_1 = x_1\sigma_2(t), \qquad u_2 = x_2\sigma_1(t), \qquad v = \int_0^t \sigma_1\sigma_2 d\tau.$$

If now g is considered as a function of $s,u_1,u_2$ and v the equation (4.5) takes the following simple form

$$(4.9)\qquad \frac{\partial g}{\partial v} = \frac{\partial g}{\partial u_1}\frac{\partial g}{\partial u_2},$$

with the initial condition

$$(4.10)\qquad g = h(s,u_1,u_2) \qquad \text{for } v = 0.$$

The equation (4.9) can be solved by the standard method of Charpit-Lagrange. The characteristics of (4.10) are determined by

$$(4.11)\qquad \frac{du_1}{p_2} = \frac{du_2}{p_1} = \frac{dv}{-1} = \frac{dg}{q} = \frac{dp_1}{0} = \frac{dp_2}{0} = \frac{dq}{0},$$

where

$$p_i = \frac{\partial g}{\partial u_i}, \qquad q = \frac{\partial g}{\partial v}.$$

Integration gives

$$(4.12)\qquad \begin{cases} p_1 = A_1, & q = B, & u_1 + A_2 v = C_1, \\ p_2 = A_2, & g + Bv = D, & u_2 + A_1 v = C_2, \end{cases}$$

where $A_i$, B, $C_i$ and D are constants of integration.

Fitting of the initial condition (4.10) requires

$$(4.13)\qquad \begin{cases} D = h(s,C_1,C_2), \\ A_i = h_i(s,C_1,C_2), \end{cases}$$

where

$$h_i = \frac{\partial h}{\partial u_i}, \qquad i = 1,2.$$

The final solution is determined by (4.12) and (4.13). Using $C_1$ and $C_2$ as independent parameters we obtain the following result (cf. PK 21,22)

$$
(4.14)\quad \begin{cases} g(s,u_1,u_2,v) = h(s,C_1,C_2) - vh_1(s,C_1,C_2)h_2(s,C_1,C_2), \\ \qquad u_1 = C_1 - vh_2(s,C_1,C_2), \\ \qquad u_2 = C_2 - vh_1(s,C_1,C_2). \end{cases}
$$

Elimination of $C_1$ and $C_2$ can be carried out explicitly in a few special cases only. The determination of the first few moments is much simpler. The zeroth moment (4.2) is determined by (4.14) for $s = x_1 = x_2 = 1$. This means that $u_1 = \sigma_2(t)$ and $u_2 = \sigma_1(t)$. Thus we have

$$
(4.15)\qquad \mu(t) = h(1,C_1,C_2) - vh_1(1,C_1,C_2)h_2(1,C_1,C_2)
$$

with

$$
(4.16)\quad \begin{cases} \sigma_2 = C_1 - vh_2(1,C_1,C_2), \\ \sigma_1 = C_2 - vh_1(1,C_1,C_2). \end{cases}
$$

For the first moments we have from (4.3), (4.12) and (4.13)

$$
\mu_1 = \frac{\partial}{\partial x_1} g(1,1,1,t) = \sigma_2 \frac{\partial}{\partial u_1} g(1,\sigma_2,\sigma_1,t) = \sigma_2 A_1 = \sigma_2 h_1
$$

so that

$$
(4.17)\quad \begin{cases} \mu_1 = \sigma_2 h_1(1,C_1,C_2), \\ \mu_2 = \sigma_1 h_2(1,C_1,C_2), \end{cases}
$$

where $C_1, C_2$ satisfy the equations (4.16).

If we are in the initial phase of the process of polymerisation the form of $\mu_1(t)$ and $\mu_2(t)$ is known in advance. So (4.17) only may confirm the expressions (3.11). But in the subsequent phase of gelation no such knowledge is available. Then the equations (4.16) and (4.17) can be used to determine $\mu_1$ and $\mu_2$ for $t > t_g$.

The total amount of monomer units follows from (4.4) and (4.14). By the second and third relations of (4.14) $C_1$ and $C_2$ are determined as functions depending also on s. Thus we proceed as follows. Starting from

$$g = h(s,C_1,C_2) - v^{-1}(C_1-u_1)(C_2-u_2),$$

we differentiate with respect to s. This gives

$$\frac{\partial g}{\partial s} = \frac{\partial h}{\partial s} + h_1 \frac{\partial C_1}{\partial s} + h_2 \frac{\partial C_2}{\partial s} - v^{-1}(C_2-u_2)\frac{\partial C_1}{\partial s} - v^{-1}(C_1-u_1)\frac{\partial C_2}{\partial s} .$$

The right-hand side simplifies to $\frac{\partial h}{\partial s}$ so that eventually

$$M = \frac{\partial}{\partial s} h(1,C_1,C_2) . \tag{4.18}$$

## 5. THE INITIAL PERIOD UP TO THE GELPOINT

During the initial phase of the polymerisation process the second moments (3.5) are finite and the first moments are given by (3.11). Then for the auxiliary functions (4.7) we obtain the explicit expressions

$$\sigma_1(t) = \frac{\sinh \lambda\theta . e^{\lambda t}}{\sinh \lambda(t+\theta)} , \qquad \sigma_2(t) = \frac{\sinh \lambda\theta . e^{-\lambda t}}{\sinh \lambda(t+\theta)} , \qquad t \le t_g. \tag{5.1}$$

For v(t) we obtain without difficulty the following expression

$$v(t) = \frac{\sinh \lambda\theta . \sinh \lambda t}{\lambda \sinh \lambda(t+\theta)} , \qquad t \le t_g. \tag{5.2}$$

The known expressions of $\mu_i(t)$, $\sigma_i(t)$ and v(t) should be compatible with the system (4.16) and (4.17). It follows at once that

$$\begin{cases} C_1 = \sigma_2 + v\mu_2/\sigma_1, \\ C_2 = \sigma_1 + v\mu_1/\sigma_2. \end{cases} \tag{5.3}$$

A simple calculation gives the rather surprising result that

(5.4) $C_1 = C_2 = 1.$

However, this result can be obtained in a much simpler way. If the first equation (4.16) is differentiated with respect to t we find

$$\dot{C}_1 = \dot{\sigma}_2 + h_2\dot{v} + v(h_{21}\dot{C}_1 + h_{22}\dot{C}_2),$$

but in view of (4.17) we have

$$\dot{\sigma}_2 + h_2\dot{v} = -\mu_2\sigma_2 + \sigma_1\sigma_2h_2 = 0.$$

With a similar argument for the second equation we obtain

$$(5.5) \qquad \begin{cases} (1-vh_{12})\dot{C}_1 = vh_{22}\dot{C}_2, \\ (1-vh_{12})\dot{C}_2 = vh_{11}\dot{C}_1. \end{cases}$$

This set has the almost trivial solution with constant values of $C_1$ and $C_2$. For $t = 0$ we have $\sigma_1 = \sigma_2 = 1$ and $v = 0$ so that (4.16) gives $C_1 = C_2 = 1$.

But, this is not the only solution of (5.5). There may exist a second solution where $C_1$ and $C_2$ are changing in time and where

$$(5.6) \qquad \{1 - vh_{12}(1,C_1,C_2)\}^2 = v^2h_{11}(1,C_1,C_2)h_{22}(1,C_1,C_2).$$

We shall soon see that this second solution holds for the period after the gelpoint.

So far nothing new has been found. The first moments are already known in advance. Also the zeroth moment $\mu(t)$ can be determined without making use of the solution (4.14). However, checking of the conservation law and the calculation of the second moments necessitate the use of the full solution (4.14). Let us try to calculate the moment $\mu_{11}(t)$. This requires knowledge of $\frac{\partial^2}{\partial u_1^2} g(1,\sigma_2,\sigma_1,t)$ but, since $\frac{\partial g}{\partial u_1} = h_1$, it is sufficient to determine $\frac{\partial}{\partial u_1} h_1(s,C_1,C_2)$ for $s = 1$, $u_1 = \sigma_2$, $u_2 = \sigma_1$. From (4.14) we obtain by differentiation with respect to $u_1$

$$(5.7)\quad \begin{cases} (1-vh_{12})\dfrac{\partial C_1}{\partial u_1} - vh_{22}\dfrac{\partial C_2}{\partial u_2} = 1, \\ \\ vh_{11}\dfrac{\partial C_1}{\partial u_1} - (1-vh_{12})\dfrac{\partial C_2}{\partial u_2} = 0. \end{cases}$$

This set has to be considered for $s = 1$, $u_1 = \sigma_2$, $u_2 = \sigma_1$. But this means that also $C_1 = C_2 = 1$. The corresponding values of $\frac{\partial C_1}{\partial u_1}$ and $\frac{\partial C_2}{\partial u_2}$ which are needed for the calculation of the second moments can be solved from (5.7). However, the solution breaks down when the determinant of the system vanishes at some time. This happens when

$$\{1 - vh_{12}(1,1,1)\}^2 = v^2h_{11}(1,1,1)h_{22}(1,1,1),$$

or when

$$(5.8)\qquad v = \{h_{12}(1,1,1) + \sqrt{h_{11}(1,1,1)h_{22}(1,1,1)}\}^{-1}.$$

The function $v(t)$ increases monotonously from $v(0) = 0$ to a finite value. In fact, assuming the validity of (5.2) for all $t$ we would have

$$v(\infty) = \frac{1 - \exp - 2|\lambda|\theta}{2|\lambda|} \leq 1.$$

Thus there may be a value $t = t_g$ for which $v$ equals the right-hand side of (5.8). If this happens there is an instant at which the second moments become infinite, i.e. the gelpoint is determined by (5.8) (cf. PK 45).

From (5.2) and (5.8) a formula can be derived which expresses $t_g$ in terms of the h-derivatives. We obtain in the first place from (5.2)

$$(5.9)\qquad \operatorname{cth} \lambda t + \operatorname{cth} \lambda\theta = \frac{1}{\lambda v}.$$

Using the relations (3.12) or

$$(5.10)\quad \begin{cases} \mu_1(0) + \mu_2(0) = \lambda \operatorname{cth} \lambda\theta, \\ \\ -\mu_1(0) + \mu_2(0) = \lambda \qquad , \end{cases}$$

we arrive at the following expression for the gelpoint (cf. PK 46)

$$(5.11)\qquad t_g = \frac{1}{\mu_2(0) - \mu_1(0)} \ln \frac{h_{12}(1,1,1) + \sqrt{h_{11}(1,1,1)h_{22}(1,1,1)} - \mu_1(0)}{h_{12}(1,1,1) + \sqrt{h_{11}(1,1,1)h_{22}(1,1,1)} - \mu_2(0)} .$$

In the symmetric case there are a number of simplifications. From (3.13) and (5.1), (5.2) we have for $\lambda \to 0$

$$(5.12)\qquad \begin{cases} \mu_1(t) = \mu_2(t) = \dfrac{1}{t+\theta} , \qquad \sigma_1(t) = \sigma_2(t) = \dfrac{\theta}{t+\theta} , \\ v(t) = \dfrac{\theta t}{t+\theta} . \end{cases}$$

Next (5.8) may be written as (cf. PK 47)

$$(5.13)\qquad t_g = \frac{\theta}{\theta\{h_{12}(1,1,1) + \sqrt{h_{11}(1,1,1)h_{12}(1,1,1)}\} - 1} .$$

## 6. THE SUBSEQUENT PERIOD AFTER THE GELPOINT

The solution (4.14) is also valid for $t \geq t_g$. The only problem is that the form of $\mu_i(t)$, $\sigma_i(t)$ and $v(t)$ is not known beforehand. We repeat that $u_1$, $u_2$ and $v$ are given by

$$(6.1)\qquad u_1 = x_1\sigma_2(t), \qquad u_2 = x_2\sigma_1(t), \qquad v = \int_0^t \sigma_1\sigma_2 d\tau .$$

In section 4 we have shown that the first moments are implicitly determined by (4.16) and (4.17). We shall start from these relations using the auxiliary variables $w_i$ determined by

$$(6.2)\qquad w_1 = \frac{\mu_1}{\sigma_2} , \qquad w_2 = \frac{\mu_2}{\sigma_1} .$$

Further we shall take $v$ as an independent time variable. Then (4.16), (4.17) can be replaced by (cf. 5.3)

$$(6.3)\qquad \begin{cases} C_1 = \sigma_2 + vw_2, \\ C_2 = \sigma_1 + vw_1, \end{cases}$$

and

$$w_1 = h_1(1,C_1,C_2), \qquad w_2 = h_2(1,C_1,C_2). \tag{6.4}$$

From the definition of $\sigma_i$ and v we obtain by differentiation

$$\dot{\sigma}_1 = -\sigma_1\sigma_2 w_1, \qquad \dot{\sigma}_2 = -\sigma_1\sigma_2 w_2, \qquad \dot{v} = \sigma_1\sigma_2 . \tag{6.5}$$

By taking appropriate combinations we have

$$w_1 = -\frac{d\sigma_1}{dv}, \qquad w_2 = -\frac{d\sigma_2}{dv} . \tag{6.6}$$

These relations can be used to eliminate $\sigma_1$, $\sigma_2$, $w_1$, $w_2$ in (6.3) and (6.4). Differentiation of the first relation of (6.3) with respect to v gives

$$\frac{dC_1}{dv} = \frac{d\sigma_2}{dv} + w_2 + v\frac{dw_2}{dv} = v\frac{d}{dv}h_2(1,C_1,C_2) .$$

Thus we arrive at the following pair of equations (cf. 5.5)

$$\left\{\begin{aligned} &(1 - vh_{12}(1,C_1,C_2))\frac{dC_1}{dv} = vh_{22}(1,C_1,C_2)\frac{dC_2}{dv} , \\ &(1 - vh_{12}(1,C_1,C_2))\frac{dC_2}{dv} = vh_{11}(1,C_1,C_2)\frac{dC_1}{dv} . \end{aligned}\right. \tag{6.7}$$

Also this system holds for all values of t. For $t < t_g$ we had the trivial solution $C_1 = C_2 = 1$ but for $t > t_g$ we have a second solution where $C_1$ and $C_2$ may vary with v. From the vanishing of the determinant of the system we obtain in view of (5.6) and (5.8)

$$\frac{1}{v} = h_{12}(1,C_1,C_2) + \sqrt{h_{11}(1,C_1,C_2)h_{22}(1,C_1,C_2)} , \tag{6.8}$$

which in contrast to (5.8) should be considered as a time dependent relation between $C_1(v)$ and $C_2(v)$. We know already that for $t = t_g$, and accordingly $v = v_g$, $C_1 = C_2 = 1$. From (6.7) we may derive a second independent equation

$$\sqrt{h_{11}(1,C_1,C_2)}\frac{dC_1}{dv} = \sqrt{h_{22}(1,C_1,C_2)}\frac{dC_2}{dv}$$

or

$$(6.9) \qquad \frac{dC_1}{dC_2} = \left(\frac{h_{22}(1,C_1,C_2)}{h_{11}(1,C_1,C_2)}\right)^{\frac{1}{2}}$$

The equations (6.8), (6.9) enable us to determine $C_1$ and $C_2$ as functions of v. Of course the integration can be carried out explicitly in a few simple cases only. As soon as $C_1(v)$ and $C_2(v)$ are known the auxiliary variables $w_1(v)$ and $w_2(v)$ can be determined using (6.4). Next $\sigma_1(v)$ and $\sigma_2(v)$ follow from (6.3). At this stage it is possible to recover the real time by determining v as a function of t from (6.5) as

$$(6.10) \qquad t - t_g = \int_{v_g}^{v} \frac{dw}{\sigma_1(w)\sigma_2(w)} \, .$$

In practical applications one might be interested only in the time behaviour of $\mu$, $\mu_1$, $\mu_2$ and M. In that case it is not necessary to use explicit expressions of $\sigma_1$, $\sigma_2$, $w_1$ and $w_2$. By (6.8) and (6.9) $C_1$ and $C_2$ are determined as functions of v. Next from (4.15), (4.16), (4.17) and (4.18) we have

$$(6.11) \qquad \begin{cases} \mu = h(1,C_1,C_2) - vh_1(1,C_1,C_2)h_2(1,C_1,C_2) \, , \\ \mu_1 = C_1h_1(1,C_1,C_2) - vh_1(1,C_1,C_2)h_2(1,C_1,C_2) \, , \\ \mu_2 = C_2h_2(1,C_1,C_2) - vh_1(1,C_1,C_2)h_2(1,C_1,C_2) \, , \\ M = \frac{\partial}{\partial s} h(1,C_1,C_2) \, . \end{cases}$$

Finally from (4.16) and (6.10)

$$(6.12) \qquad t - t_g = \int_{v_g}^{v} (C_1 - vh_2)^{-1}(C_2 - vh_1)^{-1} dv.$$

## 7. A SPECIAL CASE

We consider the polymerisation of a mixture consisting initially in monomers of type $C_3(3,0)$ and $C_1(0,2)$. Thus for t = 0 the generating function is given as

$$h(s,x_1,x_2) = \frac{2}{9} as^3x_1^3 + \frac{1}{3} bsx_2^2. \tag{7.1}$$

The stoichiometric case corresponds with a = b. For future use we note that

$$h_1(1,x_1,x_2) = \frac{2}{3} ax_1^2, \qquad h_2(1,x_1,x_2) = \frac{2}{3} bx_2, \tag{7.2}$$

and

$$h_{11}(1,x_1,x_2) = \frac{4}{3} ax_1, \quad h_{12}(1,x_1,x_2) = 0, \quad h_{22}(1,x_1,x_2) = \frac{2}{3} b. \tag{7.3}$$

According to (3.12) we have

$$\lambda = \frac{1}{3} (b-a), \qquad 2\lambda\theta = \ln \frac{b}{a}, \tag{7.4}$$

so that

$$\mu_1(t) = \frac{2a\lambda e^{\lambda t}}{be^{\lambda t} - ae^{-\lambda t}}, \qquad \mu_2(t) = \frac{2b\lambda e^{-\lambda t}}{be^{\lambda t} - ae^{-\lambda t}}. \tag{7.5}$$

Next from (5.1) and (5.2)

$$\sigma_1(t) = \frac{(b-a)e^{\lambda t}}{be^{\lambda t} - ae^{-\lambda t}}, \qquad \sigma_2(t) = \frac{(b-a)e^{-\lambda t}}{be^{\lambda t} - ae^{-\lambda t}}, \tag{7.6}$$

and

$$v(t) = \frac{3 \sinh \lambda t}{be^{\lambda t} - ae^{-\lambda t}}. \tag{7.7}$$

The possible gelpoint is given by (5.11) as

$$t_g = \frac{3/2}{b - a} \ln \frac{\sqrt{a}(\sqrt{2b} - \sqrt{a})}{\sqrt{b}(\sqrt{2a} - \sqrt{b})}. \tag{7.8}$$

There is only a real value under the conditions

$$\frac{1}{2} b < a < 2b. \tag{7.9}$$

Thus only when there are enough monomers of either kind gelation is possible. It may be of interest to construct a table which shows the values of $t_g$ for various combinations of a and b. In the following table we have given the values of $(a+b)t_g$ for a number of values of b/a.

| $(a+b)t_g$ | b/a |
|---|---|
| $\infty$ | 0.5 |
| 9.88 | 0.6 |
| 8.24 | 0.7 |
| 7.59 | 0.8 |
| 7.32 | 0.9 |
| 7.24 | 1.0 |
| 7.30 | 1.1 |
| 7.47 | 1.2 |
| 8.11 | 1.4 |
| 9.29 | 1.6 |
| 11.66 | 1.8 |
| $\infty$ | 2.0 |

Table 1

It appears that a minimum is reached for a symmetric mixture.

If we consider the special case a = b = 1 we have from (5.12) and (5.13)

$$(7.10)\quad \begin{cases} \mu_1(t) = \mu_2(t) = \dfrac{2}{2t+3}, & \sigma_1(t) = \sigma_2(t) = \dfrac{3}{2t+3}, \\ v(t) = \dfrac{3t}{2t+3}, & \end{cases}$$

and

$$(7.11)\quad t_g = \frac{3}{2}(1+\sqrt{2}) = 3.62.$$

From (3.15) we obtain for the total number of molecules

$$(7.12)\quad \mu(t) = \frac{5}{9} - \frac{4t}{3(2t+3)}\ .$$

Next we analyse the situation in the second period but we shall consider here the symmetric case a = b = 1 only. From (6.8) and (6.9) we obtain

$$\frac{1}{v} = \frac{2}{3}\sqrt{2C_1}\ , \tag{7.13a}$$

and

$$\frac{dC_1}{dC_2} = (2C_1)^{-\frac{1}{2}}\ . \tag{7.13b}$$

This gives at once

$$C_1 = \frac{9}{8}v^{-2}\ , \tag{7.14a}$$

and

$$C_2 = \frac{9}{8}v^{-3} + C\ , \tag{7.14b}$$

where C is a constant of integration. But we know that at the gelpoint $v_g = \frac{3}{2\sqrt{2}} = 1.061$ we should have $C_2 = 1$. This gives

$$C = 1 - \frac{2}{3}\sqrt{2} = 0.057. \tag{7.15}$$

Next from (6.4) we obtain

$$\left\{\begin{aligned} w_1 &= \frac{27}{32}v^{-4}\ , \\ w_2 &= \frac{3}{4}v^{-3} + \frac{2}{3}C\ . \end{aligned}\right. \tag{7.16}$$

From (6.2) there follows

$$\left\{\begin{aligned} \sigma_1 &= \frac{5}{32}v^{-3} + C\ , \\ \sigma_2 &= \frac{3}{8}v^{-2} - \frac{2}{3}Cv\ . \end{aligned}\right. \tag{7.17}$$

Combining (7.16) and (7.17) we find for the first moments the expressions

$$\left\{\begin{aligned} \mu_1 &= \frac{81}{256}v^{-6} - \frac{9}{16}Cv^{-3}\ , \\ \mu_2 &= \frac{27}{128}v^{-6} + \frac{15}{16}Cv^{-3} + \frac{2}{3}C^2\ . \end{aligned}\right. \tag{7.18}$$

The zeroth moment can be obtained from (4.16), (7.1), (7.2) as

(7.19) $$\mu = \frac{2}{9} C_1^3 + \frac{1}{3} C_2^2 - \frac{4}{9} vC_1^2C_2 .$$

The total amount of free monomers participating in the reactions is determined by (4.18) and (7.1) as

(7.20) $$M = \frac{2}{3} C_1^2 + \frac{1}{3} C_2 .$$

We note that the relations (7.17), (7.18), (7.19) and (7.20) are valid at all times. For $t \leq t_g$ we have simply $C_1 = C_2 = 1$ which incidentally gives $M = 1$, but for $t \geq t_g$ $C_1$ and $C_2$ are dependent on t in a way yet to be determined.

The real time scale follows from (6.10) as

(7.21) $$t - t_g = \int_{v_g}^{v} \frac{dv}{(\frac{9}{32} v^{-3} + C)(\frac{3}{8} v^{-2} - \frac{2}{3} Cv)} .$$

This is an elementary integral. A simple calculation shows that

(7.22) $$t = \frac{1}{6C^2} \ln (9 + 32Cv^3)^{-1}(9 - 16Cv^3)^{-2} + \text{constant}.$$

In table 2 we have combined v, $\mu_i$, $\mu$, M in their dependence on t for a number of values either for $t \leq t_g$ as for $t \geq t_g$.

For $t \to \infty$ we observe the following behaviour

$$v(\infty) = (\frac{16}{9} C)^{-\frac{1}{3}} = 2.143,$$

$$\mu_1(\infty) = 0,$$

$$\mu_2(\infty) = 3C^2 = 0.010,$$

$$\mu(\infty) = C^2 = 0.0033,$$

$$M(\infty) = 6C^2 = 0.020.$$

| $t$ | $v$ | $\mu_1$ | $\mu_2$ | $\mu$ | $M$ |
|---|---|---|---|---|---|
| 0 | 0 | 0.67 | 0.67 | 0.56 | 1 |
| 0.5 | 0.38 | 0.50 | 0.50 | 0.39 | 1 |
| 1 | 0.60 | 0.40 | 0.40 | 0.29 | 1 |
| 1.5 | 0.75 | 0.33 | 0.33 | 0.22 | 1 |
| 2 | 0.86 | 0.29 | 0.29 | 0.18 | 1 |
| 2.5 | 0.94 | 0.25 | 0.25 | 0.14 | 1 |
| 3 | 1.00 | 0.22 | 0.22 | 0.11 | 1 |
| $t_g$ | 1.06 | 0.20 | 0.20 | 0.08 | 1 |
| 4 | 1.09 | 0.16 | 0.17 | 0.07 | 0.85 |
| 4.5 | 1.13 | 0.13 | 0.14 | 0.06 | 0.71 |
| 5 | 1.16 | 0.11 | 0.13 | 0.05 | 0.61 |
| 5.5 | 1.18 | 0.10 | 0.11 | 0.05 | 0.53 |
| 6 | 1.21 | 0.08 | 0.10 | 0.04 | 0.47 |
| 6.5 | 1.23 | 0.07 | 0.10 | 0.04 | 0.42 |
| 7 | 1.25 | 0.07 | 0.09 | 0.03 | 0.38 |
| 7.5 | 1.27 | 0.06 | 0.09 | 0.03 | 0.35 |
| 8 | 1.29 | 0.06 | 0.08 | 0.03 | 0.33 |
| $\infty$ | 2.14 | 0 | 0.01 | 0.00 | 0.02 |

Table 2

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