stichting
mathematisch
centrum

MC

AFDELING TOEGEPASTE WISKUNDE TW 157/76 JULI
(DEPARTMENT OF APPLIED MATHEMATICS)

H.A. LAUWERIER

POLYCONDENSATION AND GELATION OF TRIFUNCTIONAL MONOMERS

PREPUBLICATION

2e boerhaavestraat 49 amsterdam

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

AMS(MOS) subject classification scheme (1970): 80A30, 34A05, 34E10

Polycondensation and gelation of trifunctional monomers[*)]

by

H.A. Lauwerier

ABSTRACT

The mathematical model of the polycondensation of trifunctional monomers is considered in great detail. The analysis follows the method of the generating function as proposed by Pis'men and Kuchanov. However, more explicit and more complete results are obtained which give a better understanding of the peculiarities of the mathematical model. There is no so-called gel-point at which a gel is formed almost instantaneously, but the gel-point rather starts a period of infinite duration during which the gel is built up from the free polymers. Explicit expressions are given both for the initial phase and for the phase of gel formation. Solutions for the different periods are connected in a continuous way. If the kinetic equations are perturbed by a small perturbation parameter there is a single solution for all values of time.

KEY WORDS & PHRASES: *Polycondensation, gelation, gel-point, generating function technique, explicit solutions, perturbation method.*

---

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

INTRODUCTION

In this paper the mathematical model of the polycondensation of monomers with three identical functional groups is studied in great detail. The analysis follows closely the method of the generating function as proposed by PIS'MEN & KUCHANOV in their paper (1971). However, the results obtained here seem to indicate that some conclusions as regards the mathematical model are erroneous or at least incomplete. In fact, the solution of the model breaks up into two distinct expressions. The first expression holds for the period up to the gel-point. The second expression relates to the behaviour of the free polymers in the period after the gel-point. The model shows that the ideas of FLORY about that period were correct. It turns out that after the gel-point the distribution function of the free polymers does not change in form and that all concentrations decrease at the same rate in favour to the gel component. This means that on the basis of the mathematical model there is a certain instant, the gel-point, at which gel formation starts and a subsequent period of infinite durating during which the gel is built up gradually until all free components are consumed. The analysis shows that the second solution, that relating to the post-gelation period, is closely connected to the first solution for the initial pre-gelation period. Both solutions can be combined to a single analytical solution by a simple perturbation procedure.

The outline of this paper is as follows. In the first section we discuss the set of kinetic equations (1.1). This model may be seen as the transport of mass from lower to higher polymers with an ever increasing speed, since the reaction rate is proportional to the number of free functional groups of each reacting molecule. This means a rapid broadening of the concentration distribution function $C_n(t)$, where n is the number of reacting groups. It is shown that at a certain instant t^*, the so-called gel-point, the second moment (1.5) becomes infinite. For $t < t^*$ the set of kinetic equations (1.1) is closed and can be shown to be consistent with the conservation law that the total reacting mass should be a constant. For this initial period simple explicit expressions for the zeroth moment $\mu_0(t)$ and the first moment $\mu_1(t)$ can be derived in an elementary way. However, this derivation depends essentially on the convergence of the second moment. This means that for $t > t^*$ a different procedure should be adopted.

In the second section the method of the generating function is used to obtain an explicit solution without using any previous knowledge about the first moment. The solution is of the same form in both the initial period $t < t^*$ as the period of gel formation $t > t^*$. However, the solution still contains $\mu_1(t)$ as a unknown function.

In the third section the first moment is determined by using the explicit form of the generating function obtained in the preceding section. It turns out that $\mu_1(t)$ is determined by a differential equation degenerating into two distinct factors. Thus different expressions are obtained for $\mu_1(t)$ in the different phases $t \lessgtr t^*$. We find $t^* = 1$ and

$$\mu_1(t) = \frac{1}{t+1} \qquad \text{for } t \leq 1,$$

$$\mu_1(t) = \frac{1}{3t-1} \qquad \text{for } t \geq 1.$$

The time behaviour of the concentration of the polymer with k reacting groups ($k \geq 2$) is explicitly given by (2.23) for $t \leq 1$ and by (3.14) for $t \geq 1$. For $t \geq 1$ the conservation law is violated. This means that a gel is formed, the amount of which is measured by the apparent mass defect

$$G = \frac{t-1}{3t-1} \qquad \text{for } t \geq 1.$$

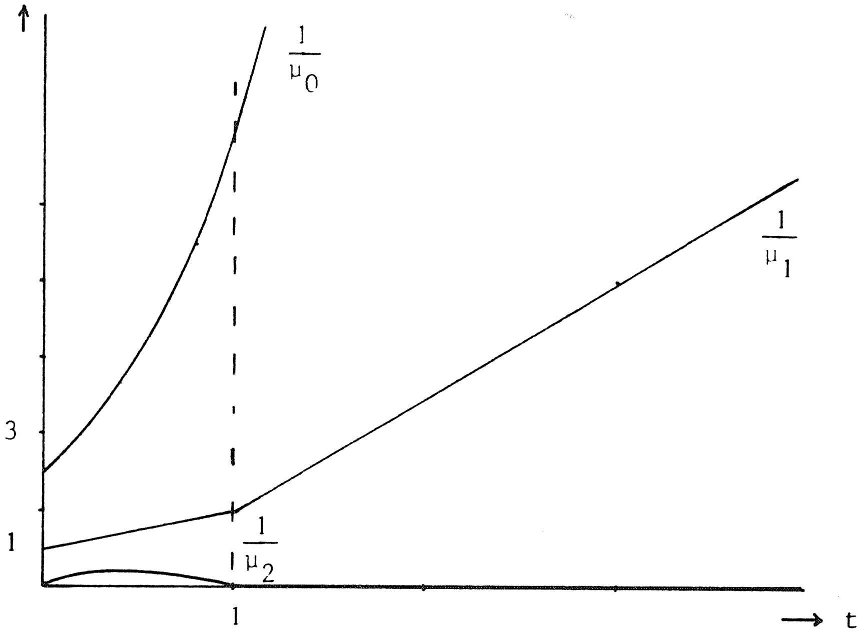


Figure 1.

In figure 1 the first three moments $\mu_0(t)$, $\mu_1(t)$ and $\mu_2(t)$ are sketched. We note that there is only a rather slight discontinuity in the derivative at the gel-point $t = 1$.

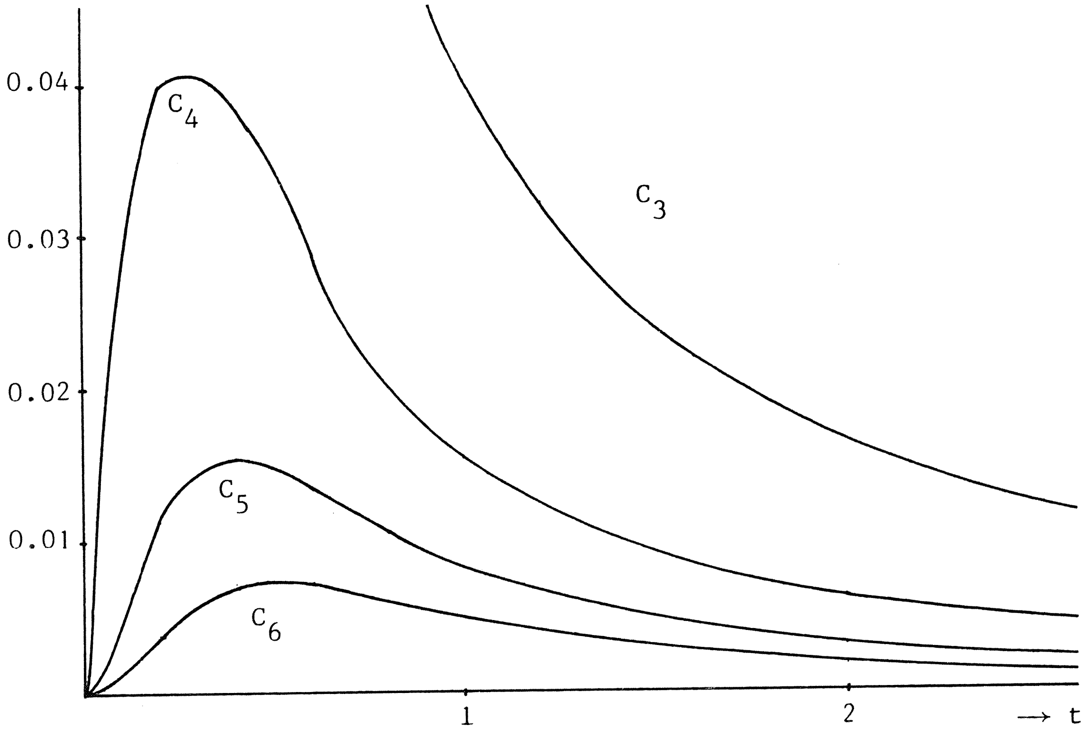


Figure 2.

In figure 2 the first four concentrations $C_3(t)$, $C_4(t)$, $C_5(t)$ and $C_6(t)$ are sketched.

The set of kinetic reaction equations (1.1) is in a sense a degenerate system which exhibits the development of a singularity in the course of time. In the fourth section it is shown that all singularities are removed if in the kinetic equations a small positive perturbation parameter ε is introduced. Thus we consider the system (4.1) which as a mathematical idealization is almost as good or bad as the unperturbed set (1.1). The solution of the perturbed system is of the same form as that of the unperturbed system, but it still contains the first moment $\mu_1(t)$ as a unknown function to be determined afterwards. The differential equation from which $\mu_1(t)$ can be derived does not degenerate here and there exists a single solution for all values of time. It is shown that for $\varepsilon \to 0$ the solution of the perturbed system approaches that of the original system.

t	$\frac{1}{\mu_0}$	$\frac{1}{\mu_0(\varepsilon)}$	$\frac{1}{\mu_1}$	$\frac{1}{\mu_1(\varepsilon)}$	$\frac{1}{\mu_2}$	$\frac{1}{\mu_2(\varepsilon)}$
0	3.00	3.00	1.00	1.00	0.33	0.33
0.2	4.00	4.01	1.20	1.20	0.34	0.35
0.4	5.25	5.26	1.40	1.41	0.32	0.33
0.6	6.86	6.86	1.60	1.62	0.27	0.28
0.8	9.00	8.96	1.80	1.83	0.16	0.19
1.0	12.00	11.80	2.00	2.07	0	0.05
1.5	21.00	20.66	3.50	3.48	0	0.02
2.0	30.00	29.58	5.00	4.98	0	0.02
2.5	39.00	38.49	6.50	6.48	0	0.03
3.0	48.00	47.40	8.00	7.98	0	0.04

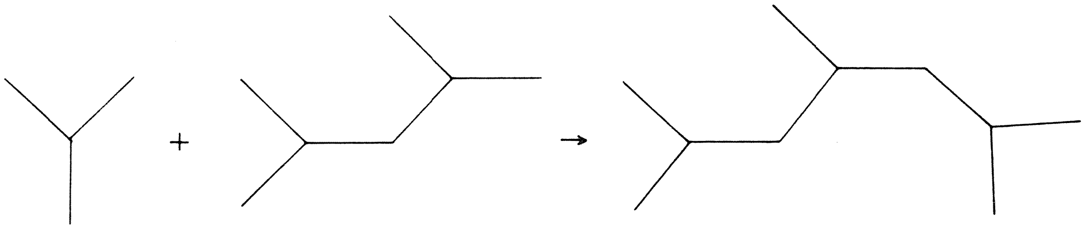
Table 1.

In Table 1 we have compared the numerical values of the first three moments of the perturbed system with $\varepsilon = 0.01$ to those of the original system. The perturbed system (4.1) does not imply a conservation law. If ε is very small, during the initial phase $t \ll 1$ material is lost in an almost imperceptible way, but in the phase of gel formation $t \gg 1$ the situation is as in the unperturbed case. The system (4.1) may be interpreted as describing reactions during which some part of the material is continuously removed either artificially or for the construction of a polymer with an infinity of functional groups, i.e., the gel.

The author wants to stress that the global properties of the model considered here are not restricted to the case of trifunctional monomers, but in fact are quite general. The general case and other applications will be considered in reports of the Amsterdam Mathematical Centre.

1. THE KINETIC EQUATIONS

We consider the polycondensation of trifunctional monomers as sketched in the following example.



Let the symbol C_n denote the concentration of a polymer molecule with n free functional units. Then the reaction scheme for irreversible polycondensation is of the form

$$C_k + C_\ell \rightarrow C_{k+\ell-2} \ .$$

The corresponding kinetic equations with respect to a suitable time scale are for $n \geq 3$

$$\frac{dC_n}{dt} = - \mu_1(t)nC_n + \frac{1}{2} \sum_{k+\ell=n+2} k\ell C_k C_\ell \ , \tag{1.1}$$

where $\mu_1(t)$ is the first moment

$$\mu_1(t) = \sum kC_k(t) \ . \tag{1.2}$$

The initial condition is

$$C_3 = 1/3, \quad C_n = 0 \quad n \geq 4, \quad \text{for } t = 0. \tag{1.3}$$

We shall also use the zeroth moment

$$(1.4) \qquad \mu_0(t) = \sum c_k(t),$$

which measures the total number of polymer chains and the second moment

$$(1.5) \qquad \mu_2(t) = \sum k^2 c_k(t),$$

which measures in a sense the average molecular weight.
The total number of building units of type C_3 is given by

$$(1.6) \qquad \sum (k-2)c_k = \mu_1 - 2\mu_0.$$

This should be a constant during the process of polycondensation. However, this conservation law does not follow automatically from the kinetic equations (1.1). Summation of the equations (1.1) with respect to n gives without difficulties

$$(1.7) \qquad \frac{d\mu_0}{dt} = -\tfrac{1}{2}\mu_1^2.$$

But, the next step raises some objections. If the n-th equation is multiplied by n then summation gives in view of $n = k+\ell-2$,

$$\frac{d\mu_1}{dt} = -\mu_1\mu_2 + \tfrac{1}{2}\sum_{k,\ell}(k+\ell-2)k\ell c_k c_\ell = -\mu_1\mu_2 + (\mu_1\mu_2 - \mu_1^2).$$

It is tempting to write

$$(1.8) \qquad \frac{d\mu_1}{dt} = -\mu_1^2 ,$$

but this is only true as far as $\mu_2(t) < \infty$, since otherwise the summation process would diverge.

With the initial condition (1.3) the last equation gives at once

$$(1.9) \qquad \mu_1(t) = \frac{1}{t+1} .$$

Then from (1.7) we obtain the solution

$$(1.10)\qquad \mu_0(t) = \frac{2-t}{6(t+1)}\ .$$

The conservation law $\mu_1 - 2\mu_0 = 1$ is true, but the result (1.10) cannot be true since then μ_0 becomes negative in course of time. This suggests that at some time the second moment indeed becomes infinite and that the result (1.9) does not hold any longer. Therefore, in the next section an independent derivation of $\mu_1(t)$ is given.

2. THE METHOD OF THE GENERATING FUNCTION

Following the method explained in the paper cited above, we introduce the generating function

$$(2.1)\qquad g(x,t) = \sum c_k(t)x^k.$$

If the n-th equation of (1.1) is multiplied by x^n then summation gives

$$(2.2)\qquad \frac{\partial g}{\partial t} = -\mu_1\, x\frac{\partial g}{\partial x} + \tfrac{1}{2}\left(\frac{\partial g}{\partial x}\right)^2\ .$$

It is to be expected that the summations do converge for $|x| < 1$ and that $g(x,t)$ is a regular analytic function of x for all values of t provided $|x| < 1$.

The moments of the polymer distribution can be written as

$$(2.3)\qquad \begin{cases} \mu_0(t) = g(1,t) & , \\ \mu_1(t) = g_x(1,t) & , \\ \mu_2(t) = g_{xx}(1,t) + g_x(1,t). \end{cases}$$

To the partial differential equation (2.2) we have to add the initial condition

(2.4) $$g(x,0) = \frac{1}{3}x^3 .$$

The equation (2.2) can be simplified by introducing the auxiliary function

(2.5) $$\sigma(t) = \exp - \int_0^t \mu_1(\tau)d\tau ,$$

and new independent variables u,v determined by

(2.6) $$u = \sigma(t)x, \qquad v = \int_0^t \sigma^2(\tau)d\tau.$$

Then (2.2) passes into

(2.7) $$\frac{\partial g}{\partial v} = \tfrac{1}{2}\left(\frac{\partial g}{\partial u}\right)^2 ,$$

with the initial condition

(2.8) $$g = \frac{1}{3}u^3 \qquad \text{for } v = 0.$$

Attention is drawn to the fact that no explicit use is made of the form of $\mu_1(t)$ and that the problem (2.7), (2.8) can be solved without any knowledge about $\mu_1(t)$. On the contrary, $\mu_1(t)$ can be determined from g(u,v) as

(2.9) $$\mu_1(t) = \sigma\left(\frac{\partial g}{\partial u}\right)_{u=\sigma} .$$

The right-hand side of (2.9) also contains μ_1 as an unknown function so that the actual determination of μ_1 requires still some extra work.

The solution of (2.7) and (2.8) is standard matter. The set of characteristic equations of (2.7) is given by

(2.10) $$\frac{du}{p} = \frac{dv}{-1} = \frac{dg}{q} = \frac{dp}{0} = \frac{dq}{0} ,$$

where $p = g_u$ and $q = g_v$. Integration gives

(2.11) $$p = A, \quad q = B, \quad u + Av = C, \quad g + Bv = D,$$

where A, B, C and D are constants of integration. The initial condition (2.8) requires

$$D = \frac{1}{3}C^3, \quad A = C^2, \quad B = \tfrac{1}{2}A^2. \tag{2.12}$$

Then for all values of v the solution of (2.7) and (2.8) is determined by

$$g(u,v) = \frac{1}{3}C^3 - \tfrac{1}{2}vC^4, \tag{2.13}$$

together with

$$u + vC^2 = C. \tag{2.14}$$

It is not difficult to eliminate the parameter C from (2.13) and (2.14). From (2.14) C can be solved as a two-valued function of u and v, but keeping in mind that for v → 0 C remains finite, we should take the single root

$$C = \frac{1 - \sqrt{1-4uv}}{2v}. \tag{2.15}$$

Then for g we obtain eventually

$$g(u,v) = \frac{-1 + 6uv - 6u^2v^2 + (1-4uv)^{3/2}}{12v^3} \tag{2.16}$$

or

$$g(u,v) = \frac{1}{3}u^3 \; {}_1F_1\left(\frac{3}{2}\,;4\,;4uv\right), \tag{2.17}$$

where

$${}_1F_1(a;b;z) = \sum_{k=0}^{\infty} \frac{(a)_k}{(b)_k} z^k, \tag{2.18}$$

with the notation

$$\begin{cases} (a)_k = a(a+1)\ \dots\ (a+k-1), & k \geq 1, \\ (a)_0 = 1. \end{cases} \tag{2.19}$$

During the initial phase of polycondensation the first moment is given by (1.9). Then from (2.5) and (2.6) we obtain

$$(2.20) \qquad \sigma(t) = \frac{1}{t+1}, \qquad v(t) = \frac{t}{t+1},$$

so that

$$(2.21) \qquad 4uv = \frac{4xt}{(t+1)^2}.$$

For $x = 1$ the function $4uv$ increases monotonously from 0 to 1 in the interval $0 \le t < 1$. At $t = 1$ the second derivative of $g(u,v)$ with respect to t becomes infinite so that also the second moment becomes infinite at that instant.

Thus the solution (2.16) with (2.20) and (2.21) does only hold for $0 \le t < 1$. A simple calculation shows that in addition to (1.9) and (1.10) the second moment is given by

$$(2.22) \qquad \mu_2(t) = \frac{3-t}{1-t^2}, \qquad 0 \le t < 1.$$

The individual concentrations follow from (2.16), (2.17) and (2.18) as

$$(2.23) \qquad C_k(t) = \frac{4(\frac{1}{2})_{k-2}}{k!} \frac{1}{(1+t)^3} \left\{\frac{4t}{(1+t)^2}\right\}^{k-3}, \qquad 0 \le t \le 1.$$

For a fixed value of k this function increases monotonously in $0 < t < \frac{k-3}{k}$ and decreases afterwards. This means that at the so-called gelation point $t = 1$ *all* concentrations are past their maximum. This could mean a violation of the conservation law of units, but the obvious interpretation is that after $t = 1$ the system ceases to behave as a closed system. After $t = 1$ matter leaves the system or, in other words, is transported to infinity. In a sense this means the formation of a molecule C_∞ with an infinity of bonds, i.e., a gel. The size of the gel is measured by the defect of the conservation law.

$$(2.24) \qquad G = \frac{1}{3} - \mu_1(t) + 2\mu_0(t), \qquad t \ge 1.$$

3. THE GELATION PHASE

The first moment $\mu_1(t)$ is determined by (2.9) and (2.16). It is, however, simpler to to start anew from (2.11) and (2.12) and keeping C as an independent parameter by way of time scale. Thus we start from the set

$$(3.1)\qquad \begin{cases} \mu_1 = \sigma C^2, \\ \sigma + vC^2 = C. \end{cases}$$

Differentiation of the second equation with respect to the time gives

$$(3.2)\qquad \dot{\sigma} + \dot{v}C^2 - (1-2vC)\dot{C} = 0.$$

But, since from (2.5) and (2.6)

$$(3.3)\qquad \dot{\sigma} = -\mu_1\sigma \quad \text{and} \quad \dot{v} = \sigma^2 ,$$

the latter equation reduces to

$$(3.4)\qquad (1-2vC)\dot{C} = 0.$$

Here we obtain the surprising result that the solution breaks up into two distinct parts. There is the general solution

$$(3.5)\qquad C = \text{constant},$$

and the singular solution

$$(3.6)\qquad 2vC = 1.$$

The first solution corresponds to the initial period of polycondensation during which $\mu_2 < \infty$. Then the solution is given by (1.9) as

$$(3.7)\qquad \sigma(t) = \mu_1(t) = \frac{1}{1+t}, \qquad v(t) = \frac{t}{1+t}.$$

The second solution corresponds to the subsequent phase of gel formation $t > 1$. Then we find from (3.1)

$$v = \frac{1}{2C}, \quad \sigma = \tfrac{1}{2}C, \quad \mu_1 = \tfrac{1}{2}C^3. \tag{3.8}$$

The correct time scale follows from (3.3) which gives

$$\dot{C} = -\tfrac{1}{2}C^4,$$

so that , with the initial condition

$$C(1) = 2\sigma(1) = 1,$$

we have

$$C(t) = \left(\frac{3}{2}t - \frac{1}{2}\right)^{-1/3} \tag{3.9}$$

Substitution into (3.8) gives for the first moment

$$\mu_1(t) = \frac{1}{3t-1}, \qquad t \geq 1. \tag{3.10}$$

By this and

$$u = \tfrac{1}{2}x\left(\frac{3}{2}t - \frac{1}{2}\right)^{-1/3}, \quad v = \frac{1}{2}\left(\frac{3}{2}t - \frac{1}{2}\right)^{1/3}, \tag{3.11}$$

the full solution (2.17) is given by

$$g(x,t) = \frac{1}{12(3t-1)}\ {}_1F_1\left(\frac{3}{2}\,;4\,;x\right), \qquad t \geq 1, \tag{3.12}$$

or

$$\frac{3}{4}\,g(x,t) = \frac{-1 + \frac{3}{2}x - \frac{3}{8}x^2 + (1-x)^{3/2}}{3t-1}, \qquad t \geq 1. \tag{3.13}$$

The rather surprising result is obtained that the distribution function does not change with time and that all concentrations are simultaneously decreasing with the time factor $(3t-1)^{-1}$. Explicitly for $k \geq 3$

(3.14) $$C_k(t) = \frac{(\tfrac{1}{2})_{k-2}}{k!}\frac{1}{3t-1}, \qquad t \geq 1.$$

The zeroth moment $\mu_0(t)$ follows from (3.13) as

(3.15) $$\mu_0(t) = \frac{1}{6(3t-1)}, \qquad t \geq 1.$$

Then, according to (2.24), the formation of the gel is given by

(3.16) $$G = \frac{t-1}{3t-1}, \qquad t \geq 1.$$

4. A MODEL WITH A SMALL PERTURBATION

If the system (1.1) of kinetic equations is replaced by

(4.1) $$\frac{dC_n}{dt} = -\mu_1(t)nC_n + \frac{1}{2(1+\varepsilon)}\sum_{k+\ell=n+2} k\ell C_k C_\ell,$$

where ε is a very small positive quantity, a model of polycondensation is obtained which differs only very little from the model studied so far. However, we shall soon see that this model does not have the singular behaviour exhibited by the previous model. It turns out that by the introduction of the very small perturbation parameter ε the two distinct solutions, one for the initial phase and one for the phase of gel formation, are glued together in a continuous manner. Of course for $\varepsilon \to 0$ the solution of the model (4.1) passes into the pair of solutions of the previous model.

Again we use the generating function (2.1). Then (4.1) is equivalent to

(4.2) $$\frac{\partial g}{\partial t} = -\mu_1 x\frac{\partial g}{\partial x} + \frac{1}{2(1+\varepsilon)}\left(\frac{\partial g}{\partial x}\right)^2 .$$

Next we introduce the auxiliary variables $\sigma(t)$ as defined by (2.5) and

(4.3) $$u = \sigma(t)x, \qquad v = \frac{1}{1+\varepsilon}\int_0^t \sigma^2(\tau)d\tau.$$

Then (4.2) passes into the partial differential equation (2.7) to which the initial condition (2.8) may be added. This means that the final results (2.16) and (2.17) do apply also here. The only problem is that $\mu_1(t)$ and $\sigma(t)$ are still to be determined. It is easily seen that the system (3.1) applies equally here and the same is true for (3.2). However, instead of (3.3) we have

$$(4.4) \qquad \dot{\sigma} = -\mu_1\sigma \quad \text{and} \quad \dot{v} = \frac{\sigma^2}{1+\varepsilon}\,.$$

Then substitution gives

$$(4.5) \qquad (1+\varepsilon)(1-2vC)\dot{C} + \varepsilon\sigma^2C^2 = 0.$$

If this equation is combined with the second equation of (4.4) we find a linear differential equation

$$(4.6) \qquad \varepsilon C^2\frac{dv}{dC} - 2vC + 1 = 0,$$

which can be solved in an elementary way. With the initial condition

$$\mu_1 = \sigma = 1, \quad v = 0, \quad C = 1 \qquad \text{for } t = 0,$$

we obtain

$$(4.7) \qquad v = \frac{C^{-1} - C^{2/\varepsilon}}{2+\varepsilon}\,.$$

Next from (3.1) we have

$$(4.8) \qquad \sigma = \frac{(1+\varepsilon)C + C^{2+2/\varepsilon}}{2+\varepsilon}\,, \qquad \mu_1 = C^2\sigma.$$

The time scale follows from (3.1) and (4.4) by integration of

$$(4.9) \qquad \dot{\sigma} = -\sigma^2C^2.$$

This gives

$$(4.10) \qquad t = \int_{\sigma}^{1} \frac{d\sigma}{\sigma^2 C^2} ,$$

which determines the dependance of C from t. Then by (4.7) and (4.8) also the time behaviour of σ, v, μ_1 is fixed.

For the zeroth moment μ_0 and the second moment μ_2 the following simple expressions can be derived

$$(4.11) \qquad \mu_0 = \frac{(1+2\varepsilon)C^3 + 3C^{4+2/\varepsilon}}{6(2+\varepsilon)} ,$$

$$(4.12) \qquad \mu_2 = \mu_1 + \frac{2(2+\varepsilon)\sigma^2 C}{\varepsilon+2C^{1+2/\varepsilon}} .$$

For $\varepsilon \to 0$ we may expect that

$$(4.13) \qquad \begin{cases} C(t,\varepsilon) \to 1 & \text{for } 0 \le t < 1, \\ C(t,\varepsilon) \to \left(\frac{3}{2}t - \frac{1}{2}\right)^{-1/3} & \text{for } t > 1. \end{cases}$$

For a very small value say $\varepsilon = 0.01$ numerical integration of (4.10) shows that $C(t,\varepsilon)$ is very close to these limits (see Table 2). In fact from (4.5) and (4.7) it follows that $C(t,\varepsilon)$ decreases monotonously. From (4.7), (4.8) and (4.9) it can be derived that in the beginning phase of polycondensation $t \ll 1$ $C(t,\varepsilon)$ can be approximated by

$$(4.14) \qquad C \approx \left(\frac{1-t}{1+t}\right)^{\frac{1}{2}\varepsilon} , \qquad 0 \le t \ll 1.$$

But later on in the gelation phase $t \gg 1$ we have the behaviour

$$(4.15) \qquad C \approx \left\{3\left(\frac{1+\varepsilon}{2+\varepsilon}\right)(t-c)\right\}^{-1/3} , \qquad t \gg 1,$$

where c is a constant.

t	C	C(ε)
0	1.00	1.00
0.2	1.00	1.00
0.4	1.00	1.00
0.6	1.00	0.99
0.8	1.00	0.99
1.0	1.00	0.98
1.5	0.83	0.83
2.0	0.74	0.74
2.5	0.68	0.67
3.0	0.63	0.63

Table 2.

It is of interest to see what remains of the conservation law (1.6). We find

$$(4.16) \qquad \mu_1 - 2\mu_0 = \frac{1}{3}C^3 .$$

This shows that the system (4.1) is always open and that at all times material is removed from the system which no longer will take part in the reaction scheme. In the initial phase $t < 1$ this happens in an almost imperceptible way. Later on the removal is as in the unperturbed case $\varepsilon = 0$. But here there is a gradual change in the rate of removal at the critical time $t = 1$.

The expression (4.12) shows that the second moment remains finite. More precisely we always have

$$(4.17) \qquad \mu_2 < 3 + \frac{4}{\varepsilon} .$$

The full solution (2.16), (2.17) does apply also here. The value of v is given by (4.7) and $uv = \sigma vx$ is determined by (4.7) and (4.8). In this perturbed model the argument $4\sigma v$ does not have the maximum 1 but instead

$$(4.18) \qquad 4\sigma v \to 1 - \frac{\varepsilon^2}{(2+\varepsilon)^2} .$$

This means that all moments of the concentration distribution function remain finite at all times.

REFERENCES

1. FLORY, P.J., *Principles of Polymer Chemistry*, Cornell University Press, New York, 1953.

2. PIS'MEN, L.M. & S.I. KUCHANOV, *Multifunctional Polycondensation and Gelation*, Polymer Science, U.S.S.R., 13 (4)(1971), 890-903.