NUMERICAL SOLUTION OF STIFF ORDINARY DIFFERENTIAL EQUATIONS FOR POLYMERISATION KINETICS

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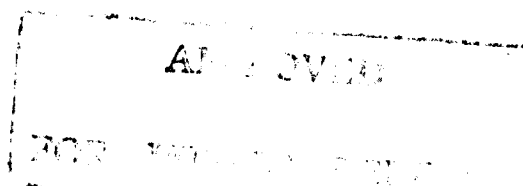
D.A. JONES AND V. NANUT

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Abstract

This report describes the derivation of a set of ordinary differential equations to model radical chain polymerisation. These equations have the mathematical property of stiffness and are difficult to solve numerically. We show how these equations can be solved efficiently using either the Gear or Kaps-Rentrop method. We also show how the kinetic scheme can be expanded to allow for the presence of contaminant scavenger molecules, and we apply these schemes to model experimental results for the polymeri sion of N-vinyl-2-pyrrolidone obtained from dilatometry measurements.

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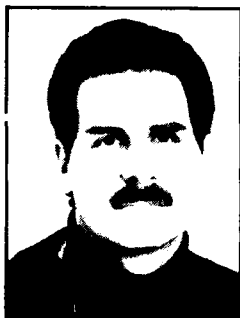
David Jones

David graduated from Monash University in 1972 with a BSc(Hons). He obtained his PhD from Monash in 1976. His thesis was titled "Anisotropic diffusion in the Townsend-Huxley experiment". After working at Strathclyde University, London University and the University of Sydney he joined MRL in 1983.

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Contents

Numerical Solution of Stiff Ordinary Differential Equations for Polymerisation Kinetics

1. Introduction

Materials Research Laboratory is currently engaged on a program of research and development on a number of cast-cured polymer bonded explosives (PBXs) as part of the the development of an Australian Insensitive Munitions capability. These fillings are formulated by dispersing solid explosive filler in a liquid pre-polymer, adding curing agent, mixing, then casting into the munition and curing *in situ*. Among the PBX formulations being studied is one which consists of RDX in an acrylic binder which is formed in situ by the copolymerisation of 2-ethylhexyl-acrylate (EHA), dioctylmaleate (DOM), and N-vinyl-2-pyrrolidone (NVP).

As part of a study of the curing of the binder in this PBX formulation an investigation of the mathematical modeling of the polymerisation reactions has also started. The aim is to use the modeling as an aid to understanding the curing process and to have some predictive capability for cure rate as a function of various parameters such as temperature, inhibitors, initiators and monomer ratios. We have begun by considering the polymerisation of NVP in isolation from other binder monomers and RDX. The polymerisation is initiated using 2,2´-azobis (2-methylpropionitrile) (AIBN) and the rate of the reaction is followed by dilatometry.

The mathematical model of this process is described by a set of coupled ordinary differential equations (ODEs) which have the mathematical property of stiffness, which means that the dependent variables can change on two or more very different scales of the independent variable. This seriously complicates the numerical solution of the coupled equations when simple explicit numerical schemes are employed because the stability analysis shows that very small time steps must be

used even in regions where the solution is only slowly varying. For the NVP system this implies up to one million iterations of the solution procedure to follow the system for just one second.

Fortunately practical algorithms for the numerical solution of stiff ODEs have been devised and implemented in various software packages. A typical example is the method due to Gear [1], which is implemented in the NAG routine D02EBF and is available at MRL [2]. The solution of these equations is so error prone, however, that it is both comforting and advisable to have a completely independent check on their accuracy. To provide such a practical and independent method of checking the solutions of our kinetic schemes we have implemented an efficient and relatively simple algorithm for the numerical solution of stiff sets of ODEs. It is based on the Kaps-Rentrop method [3] as described by Press and Teukolsky [4] and uses an implicit Runge-Kutta method. The algorithm requires no more than a few hundred lines of FORTRAN coding and could easily be converted to BASIC and run on a PC if so desired.

The purpose of this report is firstly to derive the equations which model the radical chain polymerisation process, and then to describe several numerical techniques for the efficient solution of those equations. In the next section we describe the standard kinetic scheme for radical chain polymerisation of monomers such as NVP and then briefly discuss some approximate solutions of these equations. In Section 3 we then describe several numerical methods for their solution. We have obtained solutions using an explicit 4th order Runge-Kutta routine, the NAG routine D02EBF based on the Gear method, and solutions using the Kaps-Rentrop method. Using the Kaps-Rentrop method we found excellent agreement with previous results, but with far less computational effort. To follow the model out to 8 000 seconds for example requires only 100 solution steps, whereas to check the results using the explicit Runge-Kutta code would have required approximately one billion steps. In Section 4 we extend the kinetic scheme described in Section 2 to include the presence of radical scavenger molecules and illustrate the process of cure inhibition/retardation. We also compare the numerical solutions with experimental data on the polymerisation of NVP contaminated with an as yet unidentified impurity.

2. Kinetic Scheme for NVP Polymerisation and Approximate Solutions

The polymerisation of NVP occurs by the radical chain mechanism. This scheme is described in detail in standard texts [5, 6], and is briefly summarised here. Radical polymerisation is a chain reaction which requires the steps of initiation, propagation, and termination. The initiation step involves two reactions; first an initiator I dissociates to form a pair of radicals $R^\bullet$, and then in the second step a radical combines with a monomer molecule M to produce a chain initiating species $M_1^\bullet$. These reactions are written as

$$I \longrightarrow 2R^\bullet \tag{1}$$

$$R^\bullet + M \longrightarrow M_1^\bullet \tag{2}$$

and occur with rate constants k_d and k_i respectively[1]. In the propagation step the chain radical formed in the initiation step $(M_1^\bullet)$ grows by the addition of very large numbers of monomer molecules according to the general scheme

$$M_1^\bullet + M \longrightarrow M_2^\bullet \xrightarrow[\text{steps}]{\text{n successive}} M_{n+2}^\bullet \tag{3}$$
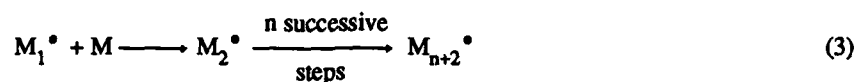
The rate constant for propagation is denoted by k_p and its numerical value is independent of the size of the growing radical after the first few additions. The final step is the termination of polymer growth and this can occur in one of two ways, either combination or disproportionation. Both processes involve a bimolecular reaction of the radical sites at the ends of growing polymer molecules. A combination reaction results in a single molecule, i.e. two ends have been joined by a chemical bond producing a larger chain. Disproportionation involves one radical centre gaining a proton resulting in one chain with a saturated chain termination and the other with a double bond termination. Termination can also occur by a combination of coupling and disproportionation. The termination step is generally represented by

$$M_n^\bullet + M_m^\bullet \longrightarrow M_{n+m} \tag{4}$$

where the particular mode of termination is not specified, and the rate constant k_t is the sum of the rate constants for each individual termination process.

Equations (1) through (4) can be described by the following set of coupled rate equations for the concentrations of initiator [I], radicals [$R^\bullet$], monomers [M], and growing polymer molecules [$M^\bullet$].

$$\frac{d[I]}{dt} = -k_d [I] \tag{5}$$

1 The scheme depicted in equation (1) is true only for a symmetrical initiator I. A more typical scheme is as follows

$$I \longrightarrow R1^\bullet + R2^\bullet ,$$

with only one of the decomposition products being the reactive species.

$$\frac{d[R^\bullet]}{dt} = 2k_d\,[I] - k_i\,[R^\bullet][M] \qquad (6)$$

$$\frac{d[M]}{dt} = -k_i\,[R^\bullet][M] - k_p\,[M^\bullet][M] \qquad (7)$$

$$\frac{d[M^\bullet]}{dt} = k_i\,[R^\bullet][M] - 2k_t\,[M^\bullet]^2 \qquad (8)$$

Equation (5) indicates a simple exponential decay for the initiator concentration [I], and so the set of equations (5) through (8) can be replaced by the more convenient set

$$\frac{dR^\bullet}{dt} = 2fk_d\,I_0 \exp(-k_d t) - k_i\,R^\bullet M \qquad (9)$$

$$\frac{dM}{dt} = -k_i\,R^\bullet M - k_p\,MM^\bullet \qquad (10)$$

$$\frac{dM^\bullet}{dt} = k_i\,R^\bullet M - 2k_t\,(M^\bullet)^2 \qquad (11)$$

where we have introduced the initiator efficiency f, which is defined as the fraction of the radicals produced in the decomposition reaction which initiate polymer chains. The value of f is usually less than one and we have used a value of 0.47, which was determined by Braun and Quella [7] for the initiation system being used. We have also dropped the bracket notation and simply let $R^\bullet$, M and $M^\bullet$ denote the concentrations of radical, monomer, and growing polymer molecules respectively.

The rate constants k_d, k_i, k_p and k_t will determine the degree of stiffness of the set of equations (9) through (11). The rate of decomposition of the initiator k_d (equation 1) can to a large degree be selected by choosing the appropriate chemical system, and the rate of the overall polymerisation process can also be adjusted substantially by adjusting the concentration of the initiator and conditions to suit the purpose of the polymer production process. For example, in a compilation of decomposition rate constants edited by Brundip and Immergut[8], k_d varies over a range from 10^{-10} s^{-1} to 10^{-1} s^{-1} for various initiators under various conditions. In the case of the PBX the situation is complicated by the use of two peroxide initiators as well as cobalt (II) bisacetylacetonoate (CoAA). The CoAA allows the PBX to cure at room temperature because it facilitates the peroxide dissociation, i.e. k_d is increased by the presence of CoAA. We have not yet measured k_d for the peroxides used in the PBX in the presence of CoAA, and for this study of the NVP polymerisation a simpler initiation system using AIBN was chosen so that comparisons could be made with literature data. Braun and Quella[7] have

measured k_d and found a value of 1.62×10^{-5} s^{-1} at 60°C for AIBN. Our experiments have not yet yielded a value for k_d.

The rate constants for the propagation step k_p (equation 3) and the termination step k_t (equation 4) have been extensively studied for large numbers of monomers. Some of the data relevant to monomers in the PBX binder have been found in the literature, but the relevant data is very limited. However it is known that for most systems the values of k_p and k_t lie in the range 10^2 to 10^4 l mole^{-1} s^{-1} and 10^6 to 10^8 l mole^{-1} s^{-1} respectively [6].

The rate constant k_i for the initiation step (equation 2) is not known and rate constants for reactions of this type have not been found in the literature. However the rates of reactions involving the so called "primary radicals" and the monomer should be of similar magnitude to the propagation rate constant k_p (equation 3). This lack of knowledge regarding the value of k_i is not critical as we will shortly demonstrate that it has little effect on the overall rate of polymerisation.

With the above considerations in mind we have chosen to use the following set of values for the four rate constants for our preliminary investigation of the system:

$$k_d = 1.6 \times 10^{-5} \text{ s}^{-1}$$

$$k_i = 1.0 \times 10^3 \text{ l mole}^{-1} \text{ s}^{-1}$$

$$k_p = 1.0 \times 10^3 \text{ l mole}^{-1} \text{ s}^{-1}$$

$$k_t = 1.0 \times 10^7 \text{ l mole}^{-1} \text{ s}^{-1}$$

The range of values for the rate constants noted above means that the set of equations (9) through (11) will have the mathematical property of stiffness. Technical definitions of stiffness can be given in terms of the eigenvalues of the Jacobian matrix formed from the equations [1], but here it simply suffices to note that any set of equations in which the dependent variables can change on two or more very different scales of the independent variable are called stiff. Stiff sets of equations are notoriously difficult to solve numerically using explicit schemes because the stability of the scheme is governed by the size of the time step needed to resolve details of changes occurring on the fastest time scale. This means that very small time steps are required to follow changes over very much longer periods of time, even though the solutions may not be varying rapidly on this time scale. Before describing a practical method for overcoming this problem in the next section, we first briefly describe an approximate solution of the equations (9) through (11) to get a feel for their behaviour.

The analysis of radical chain polymerisation in most textbooks begins by assuming the steady state condition, i.e. the assumption is made that the rate of initiation is equal to the rate of termination, so that the concentration of free radicals becomes essentially constant very early in the reaction. We use this assumption ourselves in a moment, but first note that the decrease in monomer concentration

during a typical polymerisation of the type involved in our PBX binder studies is very slow, decreasing by approximately 10% over a time of several hours. This means that we can replace the variable M in equation (9) by its initial value M_0 at t equals zero. Also, the value of k_d is such that the exponential in equation (9) may be replaced by unity for times shorter than one hour. Equation (9) then becomes

$$\frac{dR^\bullet}{dt} = 2fk_d I_0 - k_i M_0 R^\bullet \tag{12}$$

with solution

$$R^\bullet(t) = \frac{2fk_d I_0}{k_i M_0} \{1 - \exp(-k_i M_0 t)\} \tag{13}$$

indicating a rise to a steady state value of $2fk_d I_0 / k_i M_0$ in a time of order $(k_i M_0)^{-1}$. Appropriate experimental values for M_0 and I_0 are 9.08 moles l^{-1} and 1.52×10^{-3} moles l^{-1} respectively and these lead to a steady state value of $R^\bullet_{eq} = 2.5 \times 10^{-12}$ moles l^{-1} in a time of about 10^{-4} s.

We now set $dM^\bullet/dt$ equal to zero in equation (11) and assume that the radical concentration has reached its equilibrium value $R^\bullet_{eq}$. We then obtain the following expression for the equilibrium value of $M^\bullet$

$$M^\bullet_{eq} = \left[\frac{k_i}{2k_t} R_{eq} M_0 \right]^{1/2} \tag{14}$$

Using the values for the constants given above this leads to a value of $M^\bullet_{eq} = 3.4 \times 10^{-8}$ mole l^{-1}. We could solve equation (11) exactly to obtain an estimate of the time taken for $M^\bullet$ to reach this equilibrium value by substituting the solution for $R^\bullet$ given by equation (13) into equation (11). The resulting equation is a Riccati equation, which is not easy to solve, but solutions can be expressed in terms of the solutions of two auxiliary equations [9]. We have not pursued this approach however as we know from prior experience that this time scale is on the order of seconds or less.

We now consider the decrease in monomer concentration on the slower time scale. Assuming that both $R^\bullet$ and $M^\bullet$ do not vary greatly from their equilibrium values as M begins to decrease, we can treat equation (10) as a simple equation in the single variable M. The solution is then

$$M(t) = M_0 \exp(-kt) \tag{15}$$

where

$$k = k_i R^\bullet_{eq} + k_p M^\bullet_{eq} \tag{16}$$

With the values for k_i, k_p, $R^\bullet_{eq}$ and $M^\bullet_{eq}$ used above k can be approximated very closely by $k_p M^\bullet_{eq}$ and the exponential can be expanded to first order to give

$$M(t) = M_0 \{1 - k_p [(k_d/k_t) f I_0]^{1/2} t\}, \tag{17}$$

indicating that a plot of monomer concentration versus time for the early stage of monomer consumption should lie on a straight line and have a negative gradient of $M_0 k_p \{(k_d/k_t) f I_0\}^{1/2}$. That this is indeed the case can be seen in Figure 1, which shows a relationship between monomer concentration and time, derived from experimental data obtained with a dilatometer during an NVP polymerisation reaction. The monomer concentration versus time data was obtained from the volume change versus time data by using a conversion factor which incorporates the densities of NVP and the polymer at the temperature of the reaction. This conversion factor is only known at 20°C at present and this value was used even though the data was obtained at 60°C. The data cannot therefore yet be used to obtain accurate values of kinetic parameters, but it can be used to provide a comparison for the model output and approximate values of parameters.
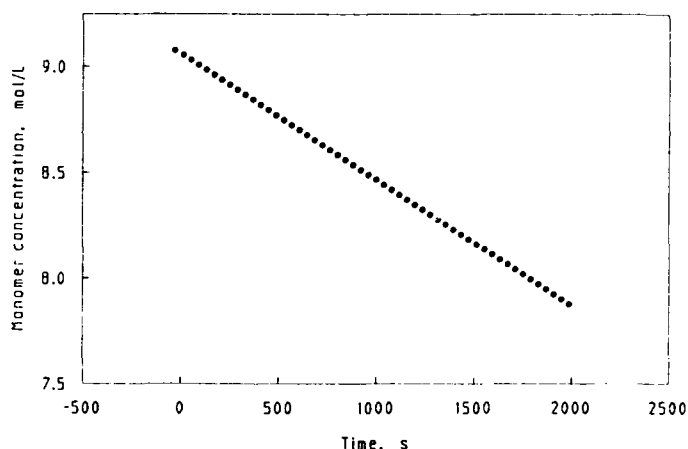

Figure 1: Experimental data for monomer concentration versus time for NVP.

Given that k_d, f, I_0 and M_0 are known, a value for the ratio k_p^2/k_t can be obtained from the straight line fit to the experimental data in Figure 1. In practise, a more accurate method of doing this is to obtain the gradient dM/dt for several values of the initial initiator concentration I_0. From equation (17) we easily have

$$- dM/dt = [M_0(fk_d)^{1/2} (k_p/k_t)^{1/2}] I_0^{1/2} \tag{18}$$

and so a plot of gradient versus $I_0^{1/2}$ again leads to a value of k_p^2/k_t. Measurements of k_p^2/k_t as a function of temperature lead to useful information about the thermochemistry of polymerisation, but it is important to note that values for k_p and k_t separately can only be obtained by non steady-state methods [5]. We are currently reviewing the need to use a non-steady-state method such as the rotating sector method [6] to obtain the additional experimental data required to separate k_p and k_t.

Equation (17) also indicates that, with the range of values for the rate constants we are using, the initial rate of polymerisation is effectively independent of the rate constant k_i and justifies our assertion that knowledge of an exact value for k_i is not required for the polymerisation experiments we are planning.

3. Numerical Solution of Kinetic Equations

The initial rapid rise of $R^\bullet$ to its equilibrium value $R^\bullet_{eq}$ on a time scale of the order of milliseconds is easily demonstrated using a simple 4th order Runge-Kutta integration routine. Figures 2 and 3 show solutions of equations (9) through (11) obtained using the program RKUTTA. (The source code for the programs referred to in this report are available from the authors). The rate constants k_d, k_i, k_p, k_t and the initial constants M_0 and I_0 were set to the values used in the previous section. Figure 2 was calculated using a time step Δt of 1 μs and shows that $R^\bullet$ reaches an equilibrium value of 2.5×10^{-12} mole l^{-1} in a time of approximately 0.5 ms, which is in good agreement with the approximate calculation in the previous section. On this time scale M remains constant while $M^\bullet$ increases linearly with time, as can be seen in Figure 3, which shows both $R^\bullet$ and $M^\bullet$ between $t = 0$ and 5.0 ms calculated using a time step of 5.0 μs.

To use the program RKUTTA to follow the time variation of either $M^\bullet$ or M would be completely impractical. A time step of the order of 10 μs would be needed to establish the equilibrium value of $R^\bullet$ accurately, and then many millions of steps would be needed to track either $M^\bullet$ or M. The sensible procedure to follow for the solution of stiff sets of equations such as (9) through (11) is to use one of the software packages specifically designed for the solution of these equations. These are usually based on implicit schemes with variable step length and automatic local error control. A particularly well known procedure for the solution of stiff sets of equations is the Gear method [1], which is available at MRL as subroutine D02EBF of the NAG group of software packages. We have used the Gear method to follow the full time dependence of the variables in equations (9) through (11).
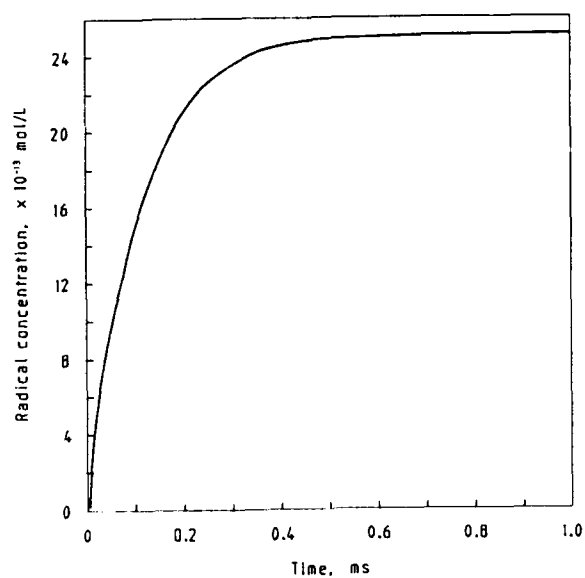
Figure 2: Radical concentration versus time calculated from program RKUTTA with $\Delta t = 1$ μs.

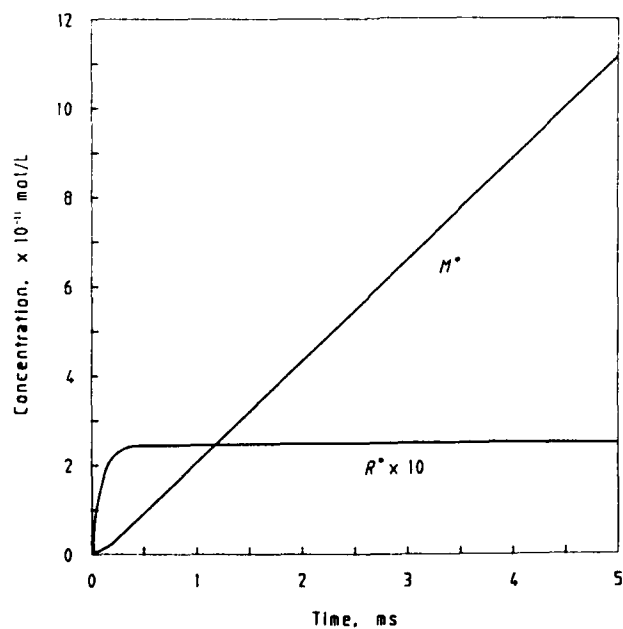*Figure 3: Concentrations of radicals and growing polymer molecules calculated from program RKUTTA with $\Delta t = 5.0$ μs.*

Figure 4 shows the time dependence of $M^\bullet$ on a time scale of seconds. We see that $M^\bullet$ approaches a steady state value of 3.4×10^{-8} moles l^{-1}, which is again in good agreement with the approximate solution in the previous section. Figure 5 shows $R^\bullet$, $M^\bullet$ and M over a longer time scale. We see that both $R^\bullet$ and $M^\bullet$ vary little from their equilibrium values, justifying the assumption made in the previous section, and that over this time scale M decreases linearly with time, again in agreement with the analysis in the previous section. To display the exponential time dependence of M requires following the solution over a much longer time scale. We have done this and show the solutions in Figure 6. The exponential decay of M is now clearly evident.
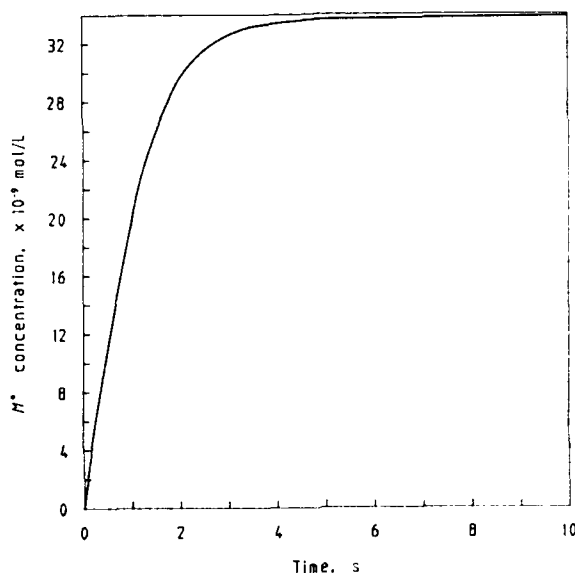

Figure 4: Concentration of growing polymer molecules versus time calculated using the Gear method.

We have used the subroutine D02EBF to check some of the assumptions and conclusions of the previous section. In particular, our analysis predicts that over a time scale of just a few hours M should decrease linearly with time, and that the gradient of this time should be independent of k_i, and depend on k_p and k_t only in the ratio k_p^2/k_t. We have checked these results by varying k_i over the range 1×10^2 to 1×10^4 and found that it has had no effect on the time dependence of M over the time scale of interest. We have also varied the values of k_p and k_t, and again found that the time dependence of M is unaltered if the value of the ratio k_p^2/k_t remains constant.

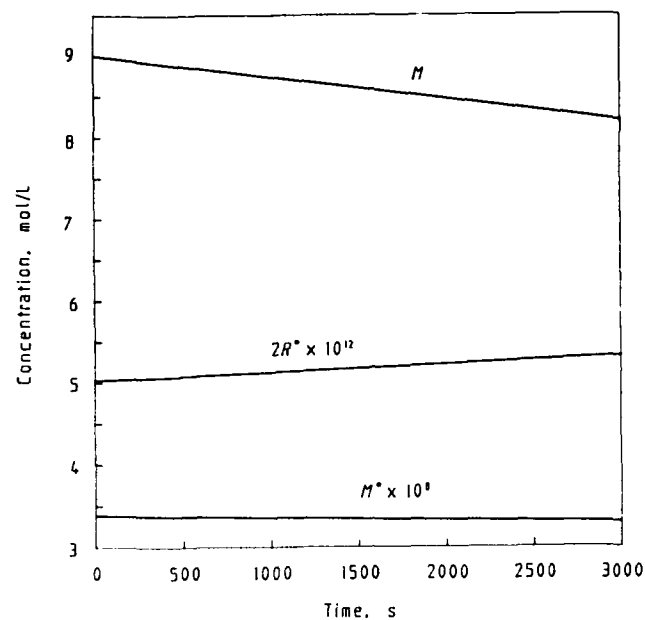*Figure 5:* *Concentration of radicals, monomer, and growing polymer chains versus time calculated using the Gear method.*
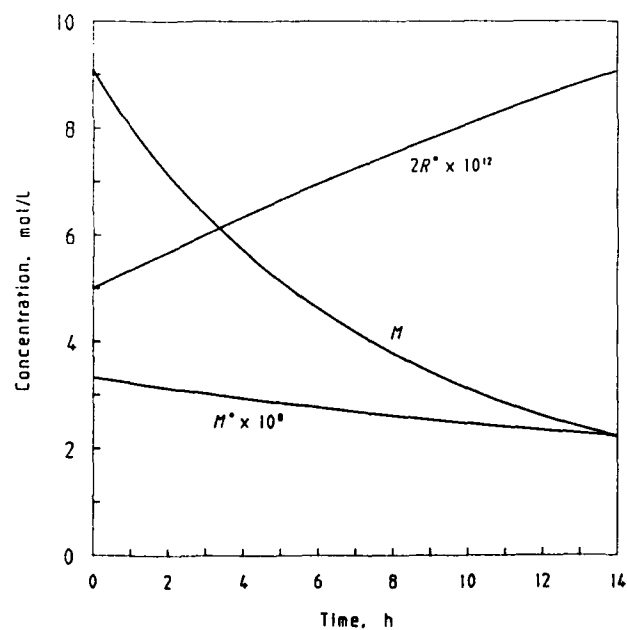

Figure 6: *Concentration of radicals, monomer, and growing polymer chains versus time calculated using the Gear method.*

The Gear method, as implemented in D02EBF, is both simple and efficient to use, and capable of providing solutions to any desired degree of accuracy by setting an appropriate value of the parameter TOL in the calling sequence. It is however a "black box", and on the few occasions when the method has failed it has not been easy to trace the underlying cause of this failure. To overcome this problem, and also to provide a completely independent means of checking the accuracy of the solutions produced by D02EBF, we have recently implemented a new method for the solution of stiff sets of equations. The method is due to Kaps and Rentrop [3], and the implementation described here was devised by Press and Teukolsky [4].

A set of non-linear ODEs can be written in the form

$$y' = f(y) \tag{19}$$

where y is the vector $(y_1, y_2, \ldots y_N)$ of N dependent variables, and the prime denotes differentiation with respect to time. The Kaps-Rentrop method seeks a solution of the form

$$y(t_0 + h) = y_0 + \sum_{i=1}^{s} C_i k_i \tag{20}$$

where the corrections k_i are found by solving s linear equations of the form

$$(1 - \gamma h f') \cdot k_i = h f (y_0 + \sum_{j=1}^{i-1} \alpha_{ij} k_j)$$

$$+ h f' \cdot \sum_{j=1}^{i-1} \gamma_{ij} k_j, \, i = 1, \ldots, s. \tag{21}$$

Here the coefficients γ, C_i, α_{ij} and γ_{ij} are fixed constants independent of the problem. Automatic step size adjustment is provided using the Runge-Kutta-Fehlberg method [4]; two estimates having the form of equation (20) are computed, one of higher order than the other; the difference between the two then leads to an estimate of the local truncation error, which can then be used for step size control. Control of the local step size error can be maintained by a suitable choice of the parameter EPS in the calling program.

Tables 1 through 3 illustrate the degree of accuracy obtainable using both the Gear and Kaps-Rentrop methods. It should be noted that the Gear method is implemented in double precision, while the Kaps-Rentrop method uses only single precision. The KAPS program is marginally faster than the GEAR program, but both take no more than a few seconds of CPU time.

Table 1:   Gear Method : TOL = 10^{-4}

t(s)	$R^{\bullet} \times 10^{12}$	M	$M^{\bullet} \times 10^8$
500	2.5364	8.9412	3.3680
1000	2.5587	8.7939	3.3540
2000	2.6032	8.5048	3.3789
3000	2.6484	8.2274	3.3007
4000	2.6935	7.9612	3.2744

Table 2:   Gear Method : TOL = 10^{-10}

t(s)	$R^{\bullet} \times 10^{12}$	M	$M^{\bullet} \times 10^8$
500	2.5401	8.9284	3.3674
1000	2.5625	8.7796	3.3540
2000	2.6075	8.4911	3.3272
3000	2.6526	8.2143	3.3007
4000	2.6978	7.9487	3.2744

Table 3:   Kaps-Rentrop Method : EPS = 10^{-6}

t(s)	$R^{\bullet} \times 10^{12}$	M	$M^{\bullet} \times 10^8$
500	2.5432	8.9284	3.3689
1000	2.5676	8.7796	3.3568
2000	2.6113	8.4911	3.3291
3000	2.6578	8.2143	3.3035
4000	2.7021	7.9457	3.2766

4. Extended Kinetic Scheme and Numerical Solution

The analysis presented in Section 2 for radical chain polymerisation using typical values for the rate constants k_d, k_i, k_p, k_t and the initial constants I_o and M_o clearly shows that the monomer concentration will decay linearly with time for times less than one or two hours. Slight variations in some of the values of these constants will not change this general picture, the slope of the line may change, but the decrease will still be linear with time. Figure 7 shows some experimental points for NVP monomer concentration versus time which were obtained dilatometrically in the same manner as described in Section 2. The only significant difference in the experimental procedure was that a different batch of NVP was used. The pronounced downward concavity of these points indicates that some mechanism other than simple radical chain polymerisation must be operating.

To explain these results we have assumed the existence of a contaminant scavenger molecule which removes both radicals and activated monomer. We can include the presence of such a contaminant by slightly expanding the kinetic scheme outlined in section 2. We define a scavenger concentration $[S^\bullet]$ which acts on both $[R^\bullet]$ and $[M^\bullet]$ as follows

$$R^\bullet + S^\bullet \longrightarrow RS \tag{22}$$

$$M^\bullet + S^\bullet \longrightarrow MS \tag{23}$$

Formation of the molecular species RS and MS removes both $R^\bullet$ and $M^\bullet$ from active participation in the radical chain growth process. We assume rate constants k_1 and k_2 for equations (22) and (23) respectively. Equations (22) and (23) can now be included in an expanded kinetic scheme which has the following form

$$\frac{d[I]}{dt} = -k_d [I] \tag{24}$$

$$\frac{d[R^\bullet]}{dt} = 2k_d [I] - k_i [R^\bullet][M] - k_1 [R^\bullet][S^\bullet] \tag{25}$$

$$\frac{d[M]}{dt} = -k_i [R^\bullet][M] - k_p [M^\bullet][M] \tag{26}$$

$$\frac{d[M^\bullet]}{dt} = k_i [R^\bullet][M] - 2k_t [M^\bullet]^2 - k_2 [M^\bullet][S^\bullet] \tag{27}$$

$$\frac{d[S^\bullet]}{dt} = -k_1 [R^\bullet][S^\bullet] - k_2 [M^\bullet][S^\bullet] \tag{28}$$

We again simplify this set of equations by incorporating the exponential solution of equation (24) and dropping the bracket notation. The equations then become

$$\frac{dR^\bullet}{dt} = 2fk_d I_0 \exp(-k_d t) - k_i R^\bullet M - k_1 R^\bullet S^\bullet \qquad (29)$$

$$\frac{dM}{dt} = -k_i R^\bullet M - k_p M^\bullet M \qquad (30)$$

$$\frac{dM^\bullet}{dt} = k_i R^\bullet M - 2k_t (M^\bullet)^2 - k_2 M^\bullet S^\bullet \qquad (31)$$

$$\frac{dS^\bullet}{dt} = -k_1 R^\bullet S^\bullet - k_2 (M^\bullet S^\bullet) \qquad (32)$$

We have solved the set of equations (29) through (32) using both the NAG routine D02EBF and the Kaps-Rentrop method and found the results to be identical within the error tolerances of both schemes. We have no knowledge of the values of k_1 and k_2 so we have simply set $k_1 = k_2 = k$, and used k as a parameter to be varied until agreement can be found with the experimental results. The curve shown in Figure 7 was calculated using $k = 5.0 \times 10^5$, with the other constants having their previous values. The good agreement with experiment indicates that our assumption of the presence of a contaminant scavenger molecule appears to be correct.

5. Conclusion and Discussion

This report has described our analysis of the kinetics of the polymerisation of NVP. We have discussed the kinetic scheme appropriate to radical chain polymerisation and derived appropriate equations to model this system. We have shown how to obtain approximate solutions to these equations, and also discussed appropriate numerical algorithms for the efficient solution of these equations. Our analysis has shown that by following the polymerisation rate using dilatometry methods we can obtain a value for the ratio k_p^2/k_t, but that further experimental information is required to obtain values for k_p and k_t separately. We are currently evaluating the feasibility of several experimental techniques to provide this information.

We have applied the mathematical model to some preliminary experiments on NVP polymerisation and found good agreement between the model and the experimental results. We plan to expand the experimental part of this program considerably, the objective being to determine the kinetic parameters necessary to model a terpolymerisation involving the three monomers NVP, EHA and DOM. In addition we wish to study the effects of inhibitors (radical scavanger molecules).
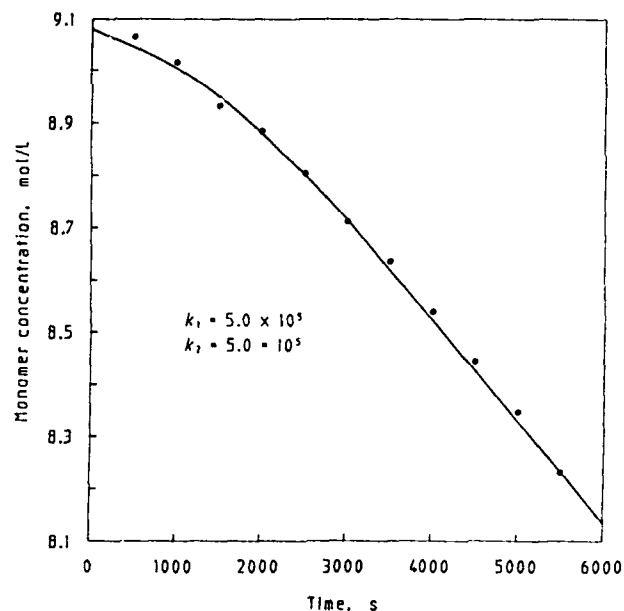
Figure 7: Comparison of experimental values of monomer concentration versus time with theoretical prediction from extended polymerization scheme.

We anticipate that the model we have derived for NVP polymerisation will be applicable, with slight modifications, to the additional chemical systems we plan to investigate, and expect that both the Gear and Kaps-Rentrop algorithms will provide efficient and accurate solution procedures for the analysis of future experimental results.

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ABSTRACT

This report describes the derivation of a set of ordinary differential equations to model radical chain polymerisation. These equations have the mathematical property of stiffness and are difficult to solve numerically. We show how these equations can be solved efficiently using either the Gear or Kaps-Rentrop method. We also show how the kinetic scheme can be expanded to allow for the presence of contaminant scavenger molecules, and we apply these schemes to model experimental results for the polymerisation of N-vinyl-2-pyrrolidone obtained from dilatometry measurements.