

Semianalytical Solution of Irreversible Anionic Polymerization with Unequal Reactivity in Batch Reactors

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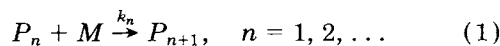
SYNOPSIS

Anionic polymerization with unequal reactivity in batch reactors is a nonlinear problem, and in order to determine the rate constants using the experimental molecular weight distribution (MWD) and conversion vs. time of polymerization, the simulation equations need to be solved repeatedly. In this work, we evolved an efficient algorithm in which the experimental MWD yields the reactivity ratio directly while conversion data give the values of all rate constants. For doing this, we proposed a series solution for the reacting species in terms of monomer conversion. A technique similar to the finite element method for boundary problems is used to divide the conversion into subdomains. The size of these steps is decided by a convergence criterion and results were determined at the end of the conversion domain through sequential computation. The scheme can be implemented on a personal computer and is considerably faster and more efficient. We used experimental data from the literature and demonstrated our technique of evaluating the rate constants.

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INTRODUCTION

Anionic polymerization is an important class of polymerization in which polymers having narrow molecular weight distribution (MWD) and well-defined molecular structure (star, branched, block copolymer, etc.) can be formed.¹⁻³ Normally, the initiation step is instantaneous and the chain growth can be represented as



Above, P_n is an oligomer having n repeat units and M represents a molecule of the monomer. The propagation has been shown to be affected by the initiator through the gegen ion effect, and in this regard, selection of a correct initiator is important for the formation of a polymer.⁴⁻⁶ In addition to this, experiments have shown that the overall propagation rate constant k_p depends not only upon the total number of growing species, λ_0 , because of the ion-pair for-

mation, but also upon the nature of the reaction mass because of the solvating effect.⁷⁻¹²

The termination in anionic polymerization can take place in following ways: (a) termination by counterions (b) chain transfer by monomer, and (c) chain deactivation by addition of impurities. In the "living" polymerization, however, these deactivations occur at a considerably slower rate and one normally ignores them in the mathematical analysis. Experimental investigations of various¹³⁻²² living systems have shown that different oligomers react with different rate constants. For example, the experimental data on the MWD of PMMA of Muller et al.⁵ required at least four rate constants to describe the polymerization mathematically.

The mathematical solution of irreversible anionic polymerization with unequal reactivity in a batch reactor is a nonlinear problem, and to obtain conversion as well as MWD of the polymer vs. time, the governing differential equations must be solved numerically.²³⁻²⁸ If it is desired to determine different rate constants, one must assume the set of rate constants and carry out the simulation repeatedly to check the theoretically determined MWD against the experimental data. Muller et al.¹⁵ proposed a global search optimization scheme which minimizes

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the least-square error for determining rate constants for anionic polymerization of methyl methacrylate. It is thus seen that there is a need for developing an efficient numerical method for this purpose and this is the focus of the present study.

In this article, we determined a semianalytical solution of irreversible anionic polymerization with unequal reactivity in batch reactors and show that this technique is computationally considerably more efficient compared to existing numerical techniques. Our results are ideally suited for determining rate constants for a given set of experimental data on MWD and conversion vs. time of polymerization. From the experimental MWD results, we can directly determine the unequal reactivity ratios (k_2/k_1 , k_3/k_1 , etc.) while the simulation gives k_1 in a simple one-dimensional search. We demonstrate our technique using the experimental data of Muller et al.¹⁵ and show that rate constants are obtained directly. Chang et al.¹⁸ reported the polydispersity index and average chain length for anionic polymerization of isoprene as a function of time. We used a two-parameter model and show that we can similarly determine the relevant rate constants using their experimental data.

MATHEMATICAL DEVELOPMENT

Suppose that we have a set of n nonlinear ordinary differential equations (ODEs):

$$\dot{x}_i = f_i(x_1, x_2, \dots, x_n); \quad i = 1, 2, \dots, n \quad (2)$$

where x_1 to x_n represent concentration variables which are normally bounded between 0 and 1. The commonly used numerical techniques divide the time domain, t , into small incremental values Δt and solve x_1 to x_n as an explicit function of time. In the numerical technique suggested in this work, we propose time t and x_2 to x_n explicitly in terms of x_1 as an infinite series. The choice of x_1 is based on the sensitivity of the problem, and for any given physical situation, it is self-evident. We now show through the problem of irreversible anionic polymerization with unequal reactivity that the technique proposed here is computationally extremely efficient and takes care of nonlinearity in a natural way.

Muller et al.¹⁵ experimentally investigated the anionic polymerization of methyl methacrylate at -46°C , and to mathematically explain the experimental data on the MWD, they assume P_1 - P_4 reacting with different rate constants as given in the kinetic model of Table I. In this kinetic model, the

initiation has been assumed to be instantaneous. The set of nonlinear ODEs governing the molecular weight distribution (MWD) of the species are also given in the same table. By dividing eqs. (TI.9)–(TI.10) with eq. (TI.6) of the table, we get

$$\frac{d[P_2]}{d[P_1]} = r_1 \frac{[P_2]}{[P_1]} - 1 \quad (\text{a})$$

$$\frac{d[P_3]}{d[P_1]} = -r_1 \frac{[P_2]}{[P_1]} + r_2 \frac{[P_3]}{[P_1]} \quad (\text{b})$$

$$\frac{d[P_4]}{d[P_1]} = -r_2 \frac{[P_3]}{[P_1]} + r_3 \frac{[P_4]}{[P_1]} \quad (\text{c})$$

$$\frac{d[P_5]}{d[P_1]} = -r_3 \frac{[P_4]}{[P_1]} + r_p \frac{[P_5]}{[P_1]} \quad (\text{d})$$

where

$$r_1 = k_2/k_1 \quad (\text{a})$$

$$r_2 = k_3/k_1 \quad (\text{b})$$

$$r_3 = k_4/k_1 \quad (\text{c})$$

$$r_p = k_p/k_1 \quad (\text{d})$$

Equations 3(a)–(d) can be easily integrated to give P_2 to P_5 in terms of P_1 subject to the following initial conditions:

$$\text{at } t = 0, \quad [P_i] = [P_i]_0 \quad \text{for } i = 1, 2, 3, 4, 5 \quad (\text{e}) \quad (4)$$

These expressions are given in Table II. We observe that eq. (TI.13) governing monomer concentration is highly nonlinear and the approach taken in the literature to solve it is to define a reduced time, τ , as

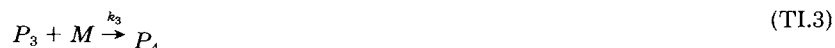
$$\tau = \int [M] dt \quad (5)$$

This eliminates the nonlinearity of eqs. (TI.6)–(TI.12) but still cannot be solved explicitly as $[P_i]$ for all i in Table II are known in terms of $[P_1]$ and not time t . As a result of this, to determine MWD as a function time, we must solve these equations numerically. Since these are numerically stiff equations, a large truncation error is introduced, and in this article, we determine the semianalytical solution as follows:

In this work, on the basis of sensitivity, we chose to make computations in the domain of monomer

Table I MWD Relations for Irreversible Anionic Polymerization with Unequal Reactivity

(1) Kinetic model:



(2) The MWD relations:

$$\frac{d[P_1]}{dt} = -k_1[P_1][M] \quad (\text{TI.6})$$

$$\frac{d[P_2]}{dt} = k_1[P_1][M] - k_2[P_2][M] \quad (\text{TI.7})$$

$$\frac{d[P_3]}{dt} = -k_2[P_2][M] - k_3[P_3][M] \quad (\text{TI.8})$$

$$\frac{d[P_4]}{dt} = -k_3[P_3][M] - k_4[P_4][M] \quad (\text{TI.9})$$

$$\frac{d[P_5]}{dt} = -k_4[P_4][M] - k_p[P_5][M] \quad (\text{TI.10})$$

$$\frac{d[P_n]}{dt} = k_p[M]([P_{n-1}] - [P_n]) \quad n = 6, 7, \dots \quad (\text{TI.11})$$

(3) Monomer balance:

$$\begin{aligned} \frac{d[M]}{dt} = & -k_p\lambda_0[M] - (k_1 - k_p)[M][P_1] - (k_2 - k_p)[M][P_2] \\ & - (k_3 - k_p)[M][P_3] - (k_4 - k_p)[M][P_4] - (k_5 - k_p)[M][P_5] \end{aligned} \quad (\text{TI.12})$$

where

$$\lambda_0 = \sum_{n=1}^{\infty} [P_n] \quad (\text{TI.13})$$

conversion, $x \{= 1 - [M]/[M]_0\}$. We divide it into smaller subdomains (not necessarily of equal size) as shown in Figure 1. In any given step (say the j th step), we define a variable u as

$$u = \frac{[M]_{j-1} - [M]}{[M]_{j-1}} \quad (6)$$

We write $[P_1]$ - $[P_5]$ and the time of polymerization in terms of infinite series as

$$\frac{[P_1] - [P_1]_{j-1}}{[M]_0} = \sum_{i=1}^{\infty} a_i u^i \triangleq S_1 \quad (\text{a})$$

$$\frac{[P_2] - [P_2]_{j-1}}{[M]_0} = \sum_{i=1}^{\infty} b_i u^i \triangleq S_2 \quad (\text{b})$$

$$\frac{[P_3] - [P_3]_{j-1}}{[M]_0} = \sum_{i=1}^{\infty} c_i u^i \triangleq S_3 \quad (\text{c}) \quad (7)$$

$$\frac{[P_4] - [P_4]_{j-1}}{[M]_0} = \sum_{i=1}^{\infty} d_i u^i \triangleq S_4 \quad (\text{d})$$

Table II Expressions for $[P_1]$ - $[P_5]$ Through Integration of Eq. (3) for ICs of Eq. (4)

$$y_2 = \frac{y_1}{(1 - r_1)} [y_1^{\gamma-1} - 1] + y_{20} y_1^{\gamma} \tag{TII.1}$$

$$y_3 = C_1 [P_1]_0^{\gamma-1} y_1^{\gamma} + r_1 \left[\frac{y_1}{(1 - r_1)(1 - r_2)} - \frac{C [P_1]_0^{\gamma-1} y_1^{\gamma}}{(r_1 - r_2)} \right] \tag{TII.2}$$

$$y_4 = C_2 [P_1]_0^{\gamma-1} y_1^{\gamma} - r_2 y_1 \left[\frac{C_1 [P_1]_0^{\gamma-1} y_1^{\gamma-1}}{(r_2 - r_3)} - \frac{r_2 C y_1^{\gamma-1} [P_1]_0^{\gamma-1}}{(r_1 - r_2)(r_1 - r_3)} + \frac{r_1}{(1 - r_1)(1 - r_2)(1 - r_3)} \right] \tag{TII.3}$$

$$y_5 = C_3 [P_1]_0^{\gamma-1} y_1^{\gamma} - r_3 \left[\frac{C_2 [P_1]_0^{\gamma-1} y_1^{\gamma}}{(r_3 - r_p)} - \frac{r_2 C_1 [P_1]_0^{\gamma-1} y_1^{\gamma}}{(r_2 - r_3)(r_2 - r_p)} - \frac{r_1 r_2 r_1}{(1 - r_1)(1 - r_2)(1 - r_3)(1 - r_p)} + \frac{r_1 r_2 C [P_1]_0^{\gamma-1} y_1^{\gamma}}{(r_1 - r_2)(r_1 - r_3)(r_1 - r_p)} \right] \tag{TII.4}$$

where

$$y_i = [P_i] / [P_1]_0 \quad i = 1, 2, 3, 4, 5$$

$$y_{i0} = [P_i]_0 / [P_1]_0$$

$$C = \frac{[P_2]_0 (1 - r_1) + [P_1]_0}{[P_1]_0^{\gamma} (1 - r_1)}$$

$$C_1 = \frac{\left\{ [P_3]_0 - r_1 \left[\frac{[P_1]_0}{(1 - r_1)(1 - r_2)} - \frac{C [P_1]_0^{\gamma}}{(r_1 - r_2)} \right] \right\}}{[P_1]_0^{\gamma}}$$

$$C_2 = \frac{\left\{ [P_4]_0 - r_2 \left[\frac{C_1 [P_1]_0^{\gamma}}{(r_2 - r_3)} - \frac{r_1 C [P_1]_0^{\gamma}}{(r_1 - r_2)(r_1 - r_3)} - \frac{r_1 [P_1]_0}{(1 - r_1)(1 - r_2)(1 - r_3)} \right] \right\}}{[P_1]_0^{\gamma}}$$

$$C_3 = \frac{\left\{ [P_5]_0 + r_3 \left[\frac{C_2 [P_1]_0^{\gamma}}{(r_3 - r_p)} - \frac{r_2 C_1 [P_1]_0^{\gamma}}{(r_2 - r_3)(r_2 - r_p)} - \frac{r_1 r_2 [P_1]_0}{(1 - r_1)(1 - r_2)(1 - r_3)(1 - r_p)} - \frac{r_1 r_2 C [P_1]_0^{\gamma}}{(r_1 - r_2)(r_1 - r_3)(r_1 - r_p)} \right] \right\}}{[P_1]_0^{\gamma}}$$

$$\frac{[P_4] - [P_5]_{j-1}}{[M]_0} = \sum_{i=1}^{\infty} e_i u^i \triangleq S_5 \tag{e}$$

$$t - t_{j-1} = \sum_{i=1}^{\infty} T_i u^i \triangleq S_6 \tag{f}$$

It is possible to derive this form of solution for $[P_2]$ - $[P_5]$ from Table II also. Once $[P_1]$ is known, we can substitute this in the results of this table, and on properly expanding terms, we can obtain the form of solutions in eq. (7).

The assumption of this form of solution in eq. (7) is valid as long as the series S_1 - S_6 are convergent. The motivation for assuming this form of solution is that the nonlinearity of differential equations in eqs. (TI.6)-(TI.12) of Table I are taken care of in a natural way. We would shortly show that the math-

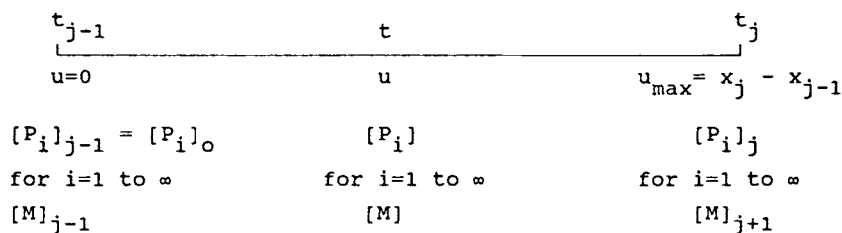
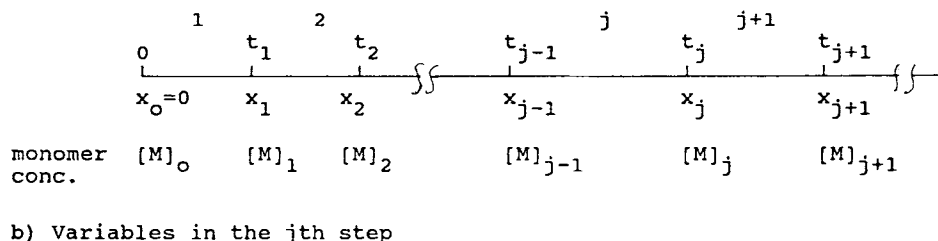
ematical manipulations like multiplication, division, raising to a given power, etc., do not destroy the series nature of the solution. In this way, it is possible to determine the coefficients a_i to e_i sequentially without trial and error as follows: As an example, we substitute eq. (6) in eq. (TI.12) of Table I and, in principle, obtain

$$\frac{du}{dt} = \sum_{i=0}^{\infty} A_i u^i \tag{8}$$

We now consider (say) eq. (TI.7) for P_2 and rewrite it as

$$\frac{d[P_2]}{dt} = \frac{d[P_2]}{du} \frac{du}{dt} = \left(\sum_{i=0}^{\infty} i b_i u^{i-1} \right) \left(\sum_{i=0}^{\infty} A_i u^i \right) \tag{9}$$

Division of Time Domain into Steps



We compare it with the right-hand side of eq. (TI.7), and by comparing coefficients of u^i , we can determine b_i sequentially. The specific algebraic details are given in Appendix A including the flow chart of the computational scheme (Fig. 2).

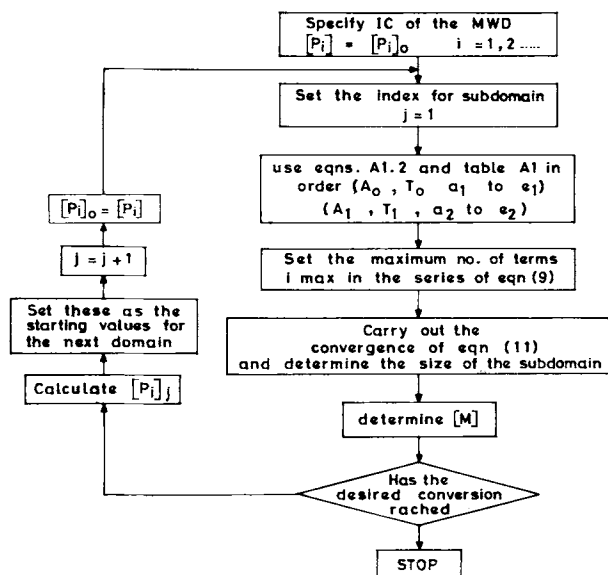


Figure 2 Flowsheet for implementing the semianalytical solution of this work for determining MWD at any time.

RESULTS AND DISCUSSION

In this work, we show that in irreversible anionic polymerization it is possible to relate the concentrations of the higher oligomers in terms of P_1 . To find the MWD vs. time, it is required to find P_1 and the monomer conversion in the time domain. We assume the form of solution as an infinite series involving u [defined in eq. (7)] and evaluate the coefficients of these series sequentially as shown in Appendix A.

In Table III, we examine the effect of total number of terms needed in the series of $[P_1]$ for obtaining the MWD. We can see that a series with five terms gives an error less than 1% and is sufficient to obtain the concentrations at any given conversion. Once $[P_1]$ is known, $[P_2]$ – $[P_5]$ can be determined by Table II. To determine the time of polymerization in the series form, it is desirable to have these also in the series form as proposed in eq. (7). The coefficients of these series can either be determined by substituting the results of Table II in the differential equation governing $[P_1]$ or substituting these series form of solution in their respective differential equation as was done for $[P_1]$ in Appendix A. Both these approaches are equivalent, and in this work, we adopted the latter. For these series to be con-

Table III Effect of No. Terms on Oligomer Concentrations at 80% Monomer Conversion

No. Terms	<i>t</i> (s)	[<i>P</i> ₁]	[<i>P</i> ₂]
1	1.8969	4.8040 × 10 ⁻⁹	1.5950 × 10 ⁻⁴
2	1.9188	1.1405 × 10 ⁻⁸	1.7247 × 10 ⁻⁴
3	1.9138	1.3988 × 10 ⁻⁸	1.7232 × 10 ⁻⁴
5	1.9143	1.3941 × 10 ⁻⁸	1.7382 × 10 ⁻⁴
15	1.9143	1.3941 × 10 ⁻⁸	1.7382 × 10 ⁻⁴
RK/Gear	1.8972	1.2948 × 10 ⁻⁸	1.7797 × 10 ⁻⁴

[<i>P</i> ₃]	[<i>P</i> ₄]	[<i>P</i> ₅]	[<i>P</i> ₆]
5.4373 × 10 ⁻⁴	9.1331 × 10 ⁻⁴	8.1471 × 10 ⁻⁴	2.3399 × 10 ⁻⁴
5.6808 × 10 ⁻⁴	9.3176 × 10 ⁻⁴	8.1000 × 10 ⁻⁴	2.3399 × 10 ⁻⁴
5.6907 × 10 ⁻⁴	9.4068 × 10 ⁻⁸	8.1297 × 10 ⁻⁴	2.3399 × 10 ⁻⁴
5.7300 × 10 ⁻⁴	9.3960 × 10 ⁻⁴	8.1673 × 10 ⁻⁴	2.3399 × 10 ⁻⁴
5.7300 × 10 ⁻⁴	9.3960 × 10 ⁻⁴	8.1673 × 10 ⁻⁴	2.3399 × 10 ⁻⁴
5.8299 × 10 ⁻⁴	9.5159 × 10 ⁻⁴	8.3551 × 10 ⁻⁴	2.3399 × 10 ⁻⁴

^a All concentrations are expressed in mol/L.

vergent, the Leibnitz convergence criterion must be satisfied, i.e.,

$$u_{1min} = \min_{i=1,10} \left| \frac{T_i}{T_{i+1}} \right| \tag{a}$$

$$u_{2min} = \min_{i=1,10} \left| \frac{a_i}{a_{i+1}} \right| \tag{b}$$

$$u_{3min} = \min_{i=1,10} \left| \frac{b_i}{b_{i+1}} \right| \tag{c}$$

$$u_{4min} = \min_{i=1,10} \left| \frac{c_i}{c_{i+1}} \right| \tag{d}$$

$$u_{5min} = \min_{i=1,10} \left| \frac{d_i}{d_{i+1}} \right| \tag{e}$$

$$u_{6min} = \min_{i=1,10} \left| \frac{e_i}{e_{i+1}} \right| \tag{f}$$

Thus, for the series solution to be valid, the step size *u*_{min} is given by

$$u_{min} = \min [u_{1min}, u_{2min}, u_{3min}, u_{4min}, u_{5min}, u_{6min}] \tag{11}$$

In Table IV, we give the values of *u* for different conversion levels. Further, we notice in Tables V and VI that the computation of the step size is invariably governed by *u*_{2min} (i.e., the series governing *P*₁), and as the conversion increases, the step size

falls drastically. To confirm this intuitive observation that the equation governing *P*₁ is the stiffest of all, we carried out strategies of computation listed in Table V. In the first strategy (abbreviated as st 1), we assume a series solution for all the oligomers and obtain *u*_{min} as envisaged in eq. (11). In the second strategy (st 2), we remove *u*_{2min} corresponding to *P*₁ series and determine *u*_{min}:

$$u_{min} = \min [u_{1min}, u_{3min}, u_{4min}, u_{5min}, u_{6min}] \tag{12}$$

However, at the end of the step, [*P*₁] is evaluated using the analytical result in eq. (TII.1) of Table II and not using the series solution given in eq. 7(a). The variations of this have been proposed in Table V and the number of steps needed to reach 95% conversion have been given in Table VI. The study of this table shows the drastic fall in the number of steps needed and the strategy of step size for evaluating the time series in the equation while [*P*₁]–[*P*₅] in a given step is governed by Table II. This has been found to be the best and we need only 30 iterations. We now compare our results with those obtained by the usual computation techniques (Table VII) commonly in use. The Runge–Kutta (RK) technique of computation requires a fixed step size, and a step size of 10⁻⁴ was found to give a stable solution. This requires the largest number of iterations, and for the conversion level of 80 and 95% conversion, 30,010 and 52,010 iterations are required. As opposed to this, the series solution technique requires only 30 iterations to reach 95% con-

Table IV The Trend of Changing Step Size for Different Levels of Conversion Using All the Six Series of Eq. (7)

Monomer Conversion	u_{1min}	u_{2min}	u_{3min}
1.7880×10^{-5}	0.1321	0.1117	0.1353
12.8400	2.2590×10^{-2}	4.4165×10^{-2}	4.4049×10^{-2}
21.2900	2.2510×10^{-2}	3.4630×10^{-2}	2.6840×10^{-2}
30.8000	0.1837	4.3980×10^{-2}	0.1039
35.8200	0.1998	3.1527×10^{-3}	0.1128
39.2040	0.1938	1.5620×10^{-3}	0.1189
40.5100	0.1854	5.2720×10^{-5}	0.1213
41.7200	0.1736	1.9830×10^{-5}	0.1236

u_{4min}	u_{5min}	u_{6min}
2.0350×10^{-3}	2.0360×10^{-7}	4.4800×10^{-7}
3.1543×10^{-2}	3.1544×10^{-2}	1.3995×10^{-2}
5.3770×10^{-3}	5.3770×10^{-3}	1.7330×10^{-2}
4.3600×10^{-2}	4.3100×10^{-2}	1.7550×10^{-2}
8.1010×10^{-2}	8.1010×10^{-2}	9.6210×10^{-2}
4.3051×10^{-2}	5.3120×10^{-2}	8.5060×10^{-2}
2.5140×10^{-2}	3.7630×10^{-2}	5.1630×10^{-2}
6.7186×10^{-3}	0.3415×10^{-2}	3.9290×10^{-2}

version. We also compared our solution using the Gear’s algorithm of computation where the step size is decided by the accuracy desired and changes from iteration to iteration. This is known to be the best numerical technique, and for irreversible anionic polymerization for a specified tolerance of 10^{-15} , the number of iterations needed are much fewer compared to that for the RK technique and is found to be 422 for 80% conversion as given in Table VI. Figure 3 shows a comparison between the Gear and

simulated results obtained and they are indistinguishable from each other.

It is necessary at this stage to highlight advantages of our approach for solving the set of ODEs from the regular finite element method for boundary value problems:

- (a) The independent variable is selected as an incremental conversion instead of reduced time.
- (b) The size of the step is not fixed a priori, but is directly determined using the convergence requirements. No adaptation of the sizes of steps is thus necessary.
- (c) On the j th step, u is zero at one end (as in the conventional technique) and is u_{min} (and not unity) at the other end.
- (d) The values of u and other variables are determined only at the other end of the step and at no intermediate location. However, if so desired, these values can easily be obtained using the series solution whose coefficients are already determined.
- (e) Since the series solution is valid up to u_{min} and beyond this new coefficients are determined which satisfy the ODEs, the slopes at the boundaries of adjacent steps are automatically matched.

Table V List of Strategies Adopted in Finding Out the No. Iterations

Strategy No.	Strategy
1	$u_{min} = \min_{i=1,6} u_{imin} $
2	$u_{min} = \min u_{1min}, u_{3min}, u_{4min}, u_{5min}, u_{6min} $
3	$u_{min} = \min u_{2min}, u_{3min}, u_{4min}, u_{5min} $
4	$u_{min} = \min u_{1min}, u_{3min}, u_{4min} $
5	$u_{min} = \min u_{1min}, u_{3min} $
6	$u_{min} = u_{1min} $
7	$u_{min} = \min_{i=1,4} u_{imin} $

Table VI No. Iterations Required for the % Conversion for Given Strategies of Table V

No. of table	50	60	70	80	90	95
St 1	9,144,550	—	—	—	—	—
St 2	12	15	16	30	32	33
St 3	39	4	16	27	28	30
St 4	39	41	43	60	69	71
St 5	12	41	43	60	69	71
St 6	13	14	16	27	29	30
St 7	525,510	—	—	—	—	—
Gear	305	336	362	422	509	932

- (f) The function evaluation is not needed (as done in the Gear or RK techniques). Only the computation of coefficients are necessary and is similar to the requirements of conventional finite element technique.
- (g) As in the case of conventional finite element methods for boundary value problems, algebraic manipulations are necessary before coefficients of the series could be determined. Once this is done, the method suggested in this work can be implemented on a personal computer.

We now show that our algorithm is ideally suited to determine rate constants from experimental data on MWD and time of anionic polymerization.

Experimental data on the anionic polymerization of methyl methacrylate at low temperatures of -46°C have been reported by Muller et al.¹⁵ At such a low temperature, the polymerization has been assumed to be irreversible with no side reactions. From the information of MWD, it is de-

sired to determine the chain length-dependent rate constants k_n given in eq. (1). Muller et al. used a global optimization scheme to determine the rate constants. In this method, the overall error ε defined as

$$\varepsilon = \sum_{i=1} (W_i^{\text{Exptl}} - W_i^{\text{Theo}})^2 \quad (13)$$

where W_i is equal to $[P_i]/\sum_{i=1}^{\infty} [P_i]$. W_i^{Exptl} and W_i^{Theo} are the experimental and theoretical W_i , respectively. We now show that the experimental measurements on the MWD of the polymer vs. time directly yield the information on rate constants. We evaluate $[P_1]/[P_1]_0$, $[P_2]/[P_2]_0$, etc., from the experimental MWD, and on substituting these results in Table II, we can easily find k_2/k_1 , k_3/k_1 , etc., directly. We then determine k_1 using our simulation program (see Appendix A for details) to give k_1 so that the computed and experimental time match. The rate constants so evaluated have been listed in Table VIII

Table VII No. Iterations Required for Various Conversion Levels for Strategy 6 of Table V

Conversion (%)	RK	Gear	Semianalytical Solution
20	3010	195	5
30	6010	257	9
40	10,010	287	10
50	13,010	305	12
60	17,010	336	14
70	23,010	362	16
80	30,010	422	26
90	43,010	509	29
95	54,010	593	30

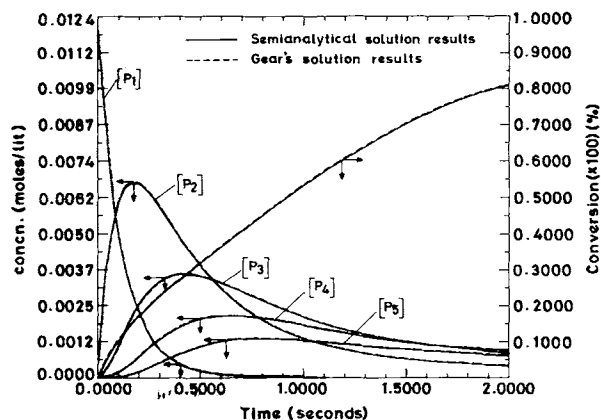
**Figure 3** Comparison of MWD using the semianalytical solution with that obtained by numerical computations.

Table VIII Rate Constants for Li⁺ and Na⁺ as Gegen Ions

Conversion (%)	Gegen Ion	Reported Values ¹⁵ [L/(mol-s)]	Simulated Values [L/(mol-s)]	Case
14	Li ⁺	$k_1 = 110.0000$ $k_2 = 32.0000$ $k_3 = 40.0000$ $k_4 = 50.0000$ $k_p = 70.0000$	$k_1 = 135.5850$ $k_2 = 45.9023$ $k_3 = 37.1226$ $k_4 = 54.2340$ $k_p = 67.7925$	A
23	Li ⁺	$k_1 = 110.0000$ $k_2 = 32.0000$ $k_3 = 40.0000$ $k_4 = 50.0000$ $k_p = 70.0000$	$k_1 = 170.1010$ $k_2 = 31.0676$ $k_3 = 33.2343$ $k_4 = 38.2599$ $k_p = 38.2579$	B
79	Na ⁺	$k_1 = 110.0000$ $k_2 = 310.0000$ $k_3 = 100.0000$	$k_1 = 216.6346$ $k_2 = 303.9380$ $k_3 = 108.3173$ $k_4 = 64.9904$ $k_p = 10.8317$	C

for different cases. These rate constants have been found to be substantially different from those reported by Muller et al. In Figure 4 we plot our simulated results for the three conversions listed in Table VIII and a good match with the experimental data of Muller et al. is seen.

Chang et al.¹⁸ carried out the anionic polymerization of isoprene and reported the polydispersity index (HI) of the polymer formed for time, $t = \infty$. We now show that our algorithm can be used for this case also. We assume that all the oligomers react with the same rate constant except P_1 which reacts differently as given in Table IX in which we have

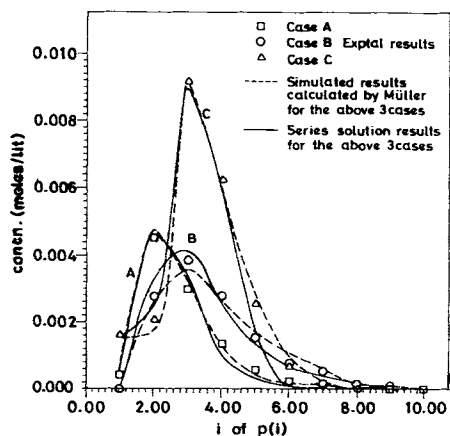


Figure 4 Comparison of the experimental MWD with those obtained by semianalytical technique.

summarized the MWD and moment relations. From eqs. (TIX.2), (TIX.4), and (TIX.5) of this table, we get

$$\frac{d\lambda_1}{dP_1} = \frac{r_p}{[P_1]} (\lambda_0 - [P_1]) - 1 \quad (\text{a})$$

$$\frac{d\lambda_2}{dP_1} = -3 - \frac{r_p}{[P_1]} (2\lambda_1 + \lambda_0 - 3[P_1]) \quad (\text{b}) \quad (14)$$

These can be integrated to get

$$y - y_0 = (1 - r_p)(1 - x_p) - r_p \frac{\lambda_0}{[P_1]_0} \ln x_p \quad (\text{a})$$

$$z - z_0 = 3(r_p - 1)(x_p - 1) - r_p \lambda_0^* \ln x_p - 2r_p \left[(1 - r_p) \ln x_p - (1 - r_p)(x_p - 1) - \frac{r_p \lambda_0^*}{2} (\ln x_p)^2 \right] \quad (\text{b}) \quad (15)$$

where

$$y = \lambda_1/[P_1]_0 \quad (\text{a})$$

$$y_0 = \lambda_{10}/[P_1]_0 \quad (\text{b})$$

$$z = \lambda_2/[P_1]_0 \quad (\text{c}) \quad (16)$$

$$z_0 = \lambda_{20}/[P_1]_0 \quad (\text{d})$$

$$x_p = [P_1]/[P_1]_0 \quad (\text{e})$$

Table IX Two-Parameter Model for Correlating Experimental Data of Chang et al. for Anionic Polymerization of Isoprene

(1) Kinetic model:



(2) MWD relations:

$$\frac{d[P_1]}{dt} = -k_1[P_1][M] \quad (\text{TIX.2})$$

$$\frac{d[P_n]}{dt} = k_p[M]([P_{n-1}] - [P_n]) \quad n = 2, 3, \dots \quad (\text{TIX.3})$$

(3) Relations for first three moments of MWD:

$$\lambda_0 = \text{constant} = [I]_0$$

$$\frac{d\lambda_1}{dt} = k_1[P_1][M] + k_p[M](\lambda_0 - [P_1]) \quad (\text{TIX.4})$$

$$\frac{d\lambda_2}{dt} = 3k_1[P_1][M] + k_p[M](2\lambda_1 + \lambda_0 - 3[P_1]) \quad (\text{TIX.5})$$

where

$$\lambda_i = \sum n_i[P_n] \quad i \geq 0 \quad (\text{TIX.6})$$

$$HI = \frac{\lambda_2\lambda_0}{\lambda_1^2}, \quad M_n = \frac{\lambda_1}{\lambda_0}, \quad M_w = \frac{\lambda_2}{\lambda_1} \quad (\text{TIX.7})$$

$$\lambda_0^* = \lambda_0/[P_1]_0 \quad (\text{f})$$

$$r_p = (k_p/k_1) \quad (\text{g})$$

$[P_1], \lambda_{00}, \lambda_{10},$ and λ_{20} are each 0.6317×10^{-3} mol/L. Hence,

$$y_0 = z_0 = \lambda_0^* = 1 \quad (17)$$

As an example, Chang et al. reported [run (a) in Table 3 of Ref. 18], the product had an HI of 1.26. The initiator concentration was taken to be 0.6317×10^{-3} mol/L. For instantaneous initiation, $[I]_0$,

and the values of y and z are, respectively, 3.1616 and 18.2723. On substituting these two into eq. (22a) and (22b), we find that $x_p = 0.508$ and $r_p =$

Table X Demonstration of Unequal Reactivity for the Anionic Polymerization of Isoprene for the Experimental Data of Ref. 18

PDI	\bar{M}_n	r_p (from λ_1)	x_p	r_p (from λ_2)
<u>Without modifier</u>				
1.26	215	6.426	0.448	6.425
1.44	339	14.361	0.457	14.361
<u>With TPPO modifier</u>				
1.35	235	7.9947	0.456	7.946
1.27	200	5.662	0.452	5.662
<u>With TMEDA modifier</u>				
1.15	255	7.968	0.430	7.970
1.05	160	2.713	0.422	2.713

TPPO: tripiperidinophosphine; TMEDA: tetramethylethylenediamine.

8.618 satisfy these equations. Table VIII gives r_p for various initiator concentrations and HI of the product polymer. This clearly demonstrates that P_1 reacts differently compared to the other species.

CONCLUSIONS

In this article, we analyzed the irreversible anionic polymerization of methyl methacrylate in which the lower oligomers have been assumed to react with different rates. The ODEs governing the concentration of these and the monomer conversion were solved using a series solution technique proposed in this work. To ensure the convergence of these series, the conversion domain is divided into smaller steps of size u , which is determined using the Leibnitz convergence criterion. The results obtained have been compared with those computed from the Runge Kutta and the Gear methods. In the series solution technique, the number of iterations required to achieve 95% conversion was only 30, while the above numerical technique require more than at least 10 times this number. A step size as small as 10^{-4} has been used in the Runge Kutta method to meet the demands in accuracy. We also compared the experimental measurements done by Muller et al. and Chang et al. with our simulated results. The results

have been found to be in excellent agreement with each other.

APPENDIX A: DETERMINATION OF COEFFICIENTS OF SERIES IN EQ. (7)

We substitute eqs. (6) and (7) in eq. (TI.13) of Table I to obtain

$$\frac{du}{dt} = \sum_{i=0}^{\infty} A^i u^i \quad (\text{A.1})$$

where

$$A_0 = k_p \lambda_0 + (k_1 - k_p)[P_1]_0 + (k_2 - k_p)[P_2]_0 + (k_3 - k_p)[P_3]_0 + (k_4 - k_p)[P_4]_0$$

$$A_1 = (k_1 - k_p)(a_1[M]_0 - [P_1]_0) + (k_2 - k_p)(b_1[M]_0 - [P_2]_0) + (k_3 - k_p)(c_1[M]_0 - [P_3]_0) + (k_4 - k_p)(d_1[M]_0 - [P_4]_0)$$

$$A_i = (k_1 - k_p)[M]_0(a_i - a_{i-1}) + (k_2 - k_p)[M]_0(b_i - b_{i-1})$$

Table A.I The Coefficients in the Series Given in eq. (7)

a_i	b_i	c_i
1. $\frac{-k_1[P_1]_{j-1}}{A_0}$	$\frac{(k_1[P_1]_{j-1} - k_2[P_2]_{j-1})}{A_0}$	$\frac{(k_2[P_2]_{j-1} - k_3[P_3]_{j-1})}{A_0}$
2. $\frac{1}{2A_0} [k_1[P_1]_{j-1} - [M]_0 k_1 a_1 - a_1 A_1]$	$\frac{1}{2A_0} [k_1[M]_0 a_1 - k_2[M]_0 b_1 - k_1[P_1]_{j-1} + k_2[P_2]_{j-1} - b_1 A_1]$	$\frac{1}{2A_0} [k_2[M]_0 b_1 - k_3[M]_0 c_1 - k_2[P_2]_{j-1} + k_3[P_3]_{j-1} - c_1 A_1]$
$i \geq 3$. $\frac{1}{iA_0} [k_1[M]_0(a_{i-2} - a_{i-1}) - \sum_{k=1}^{i-1} k a_k A_{i-k}]$	$\frac{1}{iA_0} [k_1[M]_0(a_{i-1} - a_{i-2}) + k_2[M]_0(b_{i-2} - b_{i-1}) - \sum_{k=1}^{i-1} k b_k A_{i-k}]$	$\frac{1}{iA_0} [k_2[M]_0(b_{i-1} - b_{i-2}) + k_3[M]_0(c_{i-2} - c_{i-1}) - \sum_{k=1}^{i-1} k c_k A_{i-k}]$
d_i	e_i	
1. $\frac{k_3[P_3]_{j-1} - k_4[P_4]_{j-1}}{A_0}$	$\frac{k_4[M]_0[P_4]_{j-1} - k_p[M]_0[P_5]_{j-1}}{A_0}$	
2. $\frac{1}{2A_0} [k_3[M]_0 c_1 - k_4[M]_0 d_1 - k_3[P_3]_{j-1} + k_4[P_4]_{j-1} - d_1 A_1]$	$\frac{1}{2A_0} [k_4([M]_0 d_1 - [P_4]_{j-1}) - k_p[M]_0(e_1 + \frac{[P_5]_{j-1}}{[M]_0}) - e_1 A_1]$	
$i \geq 3$. $\frac{1}{iA_0} [k_3[M]_0(c_{i-1} - c_{i-2}) + k_4[M]_0(d_{i-2} - d_{i-1}) - \sum_{k=1}^{i-1} k d_k A_{i-k}]$	$\frac{1}{iA_0} [k_4[M]_0(d_{i-1} - d_{i-2}) + k_p[M]_0(e_{i-1} - e_{i-2}) - \sum_{k=1}^{i-1} k e_k A_{i-k}]$	

$$\begin{aligned}
 &+ (k_3 - k_p)[M]_0(c_i - c_{i-1}) \\
 &+ (k_4 - k_p)[M]_0(d_i - d_{i-1}) \\
 &\text{for } i \geq 2 \quad (\text{A.2})
 \end{aligned}$$

To determine the time of polymerization, we integrate eq. (A.1) to get

$$t_j - t_{j-1} = \sum_{i=0}^{\infty} h_i u^{i+1} n_0(i+1) = \sum_{i=1}^{\infty} T_i u^i$$

where

$$\begin{aligned}
 h_0 &= \frac{1}{A_0} \\
 h_i &= -\frac{1}{A_0} \sum_{j=0}^{i-1} A_j h_{i-j} \quad \text{for } i \geq 2 \\
 T_i &= h_{i-1}/i \\
 \frac{d[P_i]}{dt} &= \frac{d[P_i]}{du} \frac{du}{dt} \quad (\text{A.3})
 \end{aligned}$$

The coefficients a_i to e_i are summarized in Table A.I. The flowsheet for sequential computation is given in Figure 2. First, for a given set of initial conditions, A_0 , h_0 , and a_1 to e_1 are computed and then A_1 , T_1 , a_2 to e_2 determined, and so on. Now, since we have obtained the time series, we can directly integrate eq. (TI.6) as follows:

$$\begin{aligned}
 &-\int_{[P_1]_0}^{[P_1]} \frac{d[P_1]}{[P_1]} \\
 &= k_1[M]_0 \int_0^u (1-u) \sum_{i=1}^{\infty} it_i u^{i-1} du \quad (\text{A.4})
 \end{aligned}$$

From eq. (A.4), we can derive

$$[P_1] = \frac{[P_1]_0}{\text{Exp} \left[k_1[M]_0 \left\{ \sum_{i=1}^{\infty} t_i u^i - \sum_{i=1}^{\infty} \frac{it_i u^{i+1}}{(i+1)} \right\} \right]} \quad (\text{A.5})$$

REFERENCES

1. M. Szwarc Carbanions, *Living Polymers and Electron Transfer Processes*, Interscience, New York, 1968.
2. A. Kumar and S. K. Gupta, *Fundamentals of Polymer*

Science and Engineering, Tata McGraw-Hill, New Delhi, 1978.

3. G. T. Chen, *J. Polym. Sci.*, **20**, 2915 (1982).
4. M. Szwarc, J. Smid, C. L. Lee, and D. N. Bhattacharya, *J. Phys. Chem.*, **69**, 612 (1965).
5. H. Sawada, *Thermodynamics of Polymerization*, Marcel Dekker, New York, 1976.
6. M. Szwarc, *Living Polymers and Mechanisms of Anionic Polymerization*, Advances in Polymer Science, Vol. 56, Springer-Verlag, Berlin, 1983.
7. A. D'Aparno and R. M. Fuoss, *J. Phys. Chem.*, **67**, 1704 (1963).
8. R. N. Young, R. P. Quirk, L. J. Fetters, J. Luston, and F. Vass, *Adv. Polym. Sci.*, **49**, 1 (1984).
9. V. V. Koshak, V. A. Kotelnikov, Y. A. Avakyan, V. V. Kurashov, T. M. Frunze, and S. P. Davtyan, *Chem. Abstr.*, **98**, 34998V (1983).
10. G. N. Arkhipovich, S. A. Dulrovskii, K. S. Kazanskii, N. V. Ptsina, and A. N. Shupek, *Eur. Polym. J.*, **18**, 569 (1982).
11. C. G. Screttas and G. A. Heropoulos, *J. Polym. Sci. A Polym. Chem.*, **30**, 1771 (1992).
12. Y. K. Han, J. M. Park, and S. K. Choi, *J. Polym. Sci.*, **20**, 1549 (1982).
13. A. H. E. Muller, C. Johann, and P. Kitz, *Polym. Prep. Am. Chem. Soc. Div. Polym. Chem.*, **27**, 153 (1986).
14. A. H. E. Muller and H. Jeuck, *Makromol Chem. Rapid Commun.*, **3**, 121 (1982).
15. C. B. Tsvetanov, A. H. E. Muller, and G. V. Schulz, *Macromolecules*, **18**, 863, (1985).
16. A. H. E. Muller, *Makromol. Chem.*, **182**, 2863 (1981).
17. C. C. Chang, J. W. Miller, and G. R. Schorr, *J. Appl. Polym. Sci.*, **39**, 2395 (1990).
18. C. C. Chang, A. F. Halasa, and J. W. Miller, Jr., *J. Appl. Polym. Sci.*, **47**, 1589 (1993).
19. I. Mita and H. Okuyama, *J. Polym. Sci. A1*, 3437 (1971).
20. A. H. E. Muller, L. Lochmann, and J. Trekoval, *Makromol. Chem.*, **187**, 1473 (1986).
21. L. Liang, S. Guo, and S. Ying, *Chem. Abstr.*, **110**, 8737f (1989).
22. R. Cunningham, *J. Polym. Sci. Polym. Chem. Ed.*, **19**, 1287 (1981).
23. D. J. Worsfold and S. Bywater, *J. Polym. Sci.*, **26**, 299 (1957).
24. A. V. Tobolsky, A. Rembaum, and A. Eisenberg, *J. Polym. Sci.*, **45**, 347 (1960).
25. A. V. Tobolsky, *J. Polym. Sci.*, **30**, 220 (1957).
26. A. Miyake and W. H. Stockmayer, *Makromol Chem.*, **88**, 90 (1965).
27. A. Vrancken, J. Smid, and M. Szwarc, *Trans. Faraday Soc.*, **58**, 2036 (1962).
28. D. A. Couso, L. M. Alassia, and G. R. Meira, *J. Appl. Polym. Sci.*, **30**, 3249 (1985).

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