Polymer Bulletin 35, 525–532 (1995)

Polymer Bulletin

Solutions of the general equations for the radiation dose dependence of the molecular weights of irradiated polymers with an initial Schulz-Zimm distribution

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Received: 20 April 1995/Revised version: 15 May 1995/Accepted: 19 May 1995

Summary

The general equations for the radiation dose dependence of irradiated polymer molecular weights have been solved exactly. For an initial most probable molecular weight distribution ($\sigma = 1$), the solutions are analytical and exact. For the general case ($\sigma \neq 1$) the solutions are numerical and exact. The present approach has resulted in the solutions for both $\sigma = 1$ and $\sigma \neq 1$ being incorporated into a group of FORTRAN computer programs which will solve experimental data for scission and crosslinking yields by both minimization and exact treatments. Simulated data treated using these FORTRAN programs are given. The FORTRAN programs are available from the authors.

Introduction

During the course of a study of the evaluation of scission and crosslinking yields of irradiated polymers by studying the weight–average and z–average molecular weights of polymers with an initial Schulz–Zimm molecular weight distribution(1), it was necessary to develop an approximate method(1) of solution of the general equations for the radiation dose dependence of molecular weights of polymers with an initial Schulz–Zimm distribution(2,3,4).

The present work expands and extends theoretical work reported in (1), particularly by developing exact numerical solutions of the general equations. These solutions allow G(S) and G(X), the scission and crosslinking yields to be evaluated exactly using either minimization calculations or the Brent method (see later).

The aim of this study is to find algebraic solutions to the general equations that are suitable for use in computer programs, so that the total work of solving for G(S) and G(X) for a set of experimental results may be automated. This aim has been achieved and the results are presented here.

The equations

The full set of general equations(3) for the dose dependence of each of the molecular weights, $\overline{M}_n$(number average), $\overline{M}_w$(weight average), and $\overline{M}_z$(z average) are given below:

$$\overline{M}_n(D) = \frac{\overline{M}_n(0)}{(1 + (\dot{\tau}/\dot{\chi} - 1)\,u\,\dot{\chi}D)} \qquad \ldots(1)$$

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$$\overline{M}_w(D) = \frac{2\ \overline{M}_n(0)\ \phi_1(u\dot{\tau}D, \sigma)}{(u\dot{\tau}D)^2\,[1 - (4\dot{\chi}/u\dot{\tau}^2D)\,\phi_1(u\dot{\tau}D, \sigma)]} \quad \ldots.(2)$$

$$\overline{M}_z(D) = \frac{3\ \overline{M}_n(0)\,[\phi_2(u\dot{\tau}D, \sigma)/\phi_1(u\dot{\tau}D, \sigma)]}{[1 - (4\dot{\chi}/u\dot{\tau}^2D)\,\phi_1(u\dot{\tau}D, \sigma)]^2} \quad \ldots.(3)$$

where

$$\phi_1(u\dot{\tau}D,\sigma) = u\dot{\tau}D - 1 + [1+(u\dot{\tau}D/\sigma)]^{-\sigma} \quad \ldots.(4a)$$

and

$$\phi_2(u\dot{\tau}D,\sigma) = 1 + [1+(u\dot{\tau}D/\sigma)]^{-(\sigma+1)} - (2/u\dot{\tau}D)\{1 - [1+(u\dot{\tau}D/\sigma)]^{-\sigma}\} \quad \ldots.(4b)$$

D denotes the radiation dose in gray, $\dot{\tau}$ and $\dot{\chi}$ are the respective probabilities per gray of scission and crosslinking of a single monomer unit, and

$\sigma = 1/[(\overline{M}_w(0)/\overline{M}_n(0)) - 1]$ and is a measure of the width of the initial molecular weight distribution.

Strategies for solution

(a) *Initial most probable distribution* ($\sigma = 1$)

For the case of the initial most probable distribution ($\sigma = 1$), the general equations become simplified and are given below:

$$\overline{M}_n(0)/\overline{M}_n(D) = 1 + (\dot{\tau}/\dot{\chi} - 1)u\dot{\chi}D \quad \ldots.(1a)$$

$$\overline{M}_w(0)/\overline{M}_w(D) = 1 + (\dot{\tau}/\dot{\chi} - 4)u\dot{\chi}D \quad \ldots.(5)$$

$$\overline{M}_z(0)/\overline{M}_z(D) = (1 + u\dot{\tau}D - 4u\dot{\chi}D)^2/(1 + u\dot{\tau}D) \quad \ldots.(6)$$

These equations are then amenable to solution as simultaneous equations in pairs by some of the more popular symbolic mathematics computer programs e.g. MATHEMATICA(5) and MACSYMA(6). The solutions are given below:

Considering $\overline{M}_n$ and $\overline{M}_w$

$$\dot{\tau} = \frac{4C - A - 3}{3uD} \quad \ldots.(7a)$$

$$\dot{\chi} = \frac{C - A}{3uD} \quad \ldots.(7b)$$

Considering $\overline{M}_w$ and $\overline{M}_z$

$$\dot{\tau} = \frac{A^2 - B}{BuD} \quad \ldots.(8a)$$

$$\dot{\chi} = \frac{A^2 - AB}{4BuD} \quad \ldots.(8b)$$

Considering $\overline{M}_n$ and $\overline{M}_z$

$$\dot{\tau} = \frac{-(48BC + B^2)^{1/2} + 24C + B - 18}{18uD} \quad \text{....(9a)}$$

$$\dot{\chi} = \frac{-(48BC + B^2)^{1/2} + 6C + B}{18uD} \quad \text{....(9b)}$$

Where

$$A = \frac{\overline{M}_w(0)}{\overline{M}_w(D)}, \quad B = \frac{\overline{M}_z(0)}{\overline{M}_z(D)}, \text{ and } C = \frac{\overline{M}_n(0)}{\overline{M}_n(D)} \quad \text{....(resp. 10a,10b,10c)}$$

There are two sets of solutions for $\overline{M}_n$ and $\overline{M}_z$. The negative roots of the function $(48BC + B^2)^{1/2}$ are accepted since they provide physically significant solutions and the positive ones do not. $\dot{\tau}$ and $\dot{\chi}$ are related to G(S) and G(X) by the following equations:

$$G(S) = 9.65\text{x}10^9\, u\dot{\tau}/\overline{M}_n(0)\ ;\ G(X) = 9.65\text{x}10^9\, u\dot{\chi}/\overline{M}_n(0) \quad \text{....(resp. 11a,11b)}$$

ANALYZE (S1ANMULT) is the computer program which utilizes the analytical solutions expressed in the present section. ANALYZE calculates the exact analytical solutions, $\dot{\tau}$ and $\dot{\chi}$, for the case of the initial most probable molecular weight distribution, for each of up to 10 different sets of dose/ molecular weight data, and gives averages of all the calculated values. Only two dose relationships of the three molecular weight averages $\overline{M}_n$, $\overline{M}_w$, and $\overline{M}_z$ are needed to find the two unknowns $\dot{\tau}$ and $\dot{\chi}$ and hence G(S) and G(X). ANALYZE allows any two dose relationships to be used, e.g. $\overline{M}_n$ and $\overline{M}_w$ vs dose, $\overline{M}_w$ and $\overline{M}_z$ vs dose, or $\overline{M}_n$ and $\overline{M}_z$ vs dose. For a single dose point (other than zero), the smaller program MONODOSE (S1ANAL) will calculate values of G(S) and G(X). Results for a single dose, however, may have limited experimental and physical significance, and it is better to have at least five points on a molecular weight/ dose relationship in order to get reliable estimates.

(*b*) *The general case* ($\sigma \neq 1$)
In this case, equations (1),(2) and (3) were taken in pairs and solved simultaneously:

Considering $\overline{M}_n$ and $\overline{M}_w$
From equation (2), by simple rearrangement,

$$(u\dot{\tau}D)^2\,\overline{M}_w(D) - 4u\dot{\chi}D\phi_1\overline{M}_w(D) - 2\phi_1\overline{M}_n(0) = 0 \quad \text{....(12)}$$

From equation (1) by rearrangement and multiplication of both sides by $\phi_1\,\overline{M}_w(D)$,

$$4\phi_1\overline{M}_w(D) + 4u\dot{\tau}D\phi_1\overline{M}_w(D) - 4\phi_1\overline{M}_w(D)\,\overline{M}_n(0)/\overline{M}_n(D) = 4u\dot{\chi}D\phi_1\overline{M}_w(D) \quad \text{....(13)}$$

Equation (13) may then be used to eliminate the term in $\dot{\chi}$ in equation (12) to give,

$$(u\dot{\tau}D)^2\overline{M}_w(D) - 2\phi_1\overline{M}_n(0) - 4\phi_1\overline{M}_w(D) - 4u\dot{\tau}D\phi_1\overline{M}_w(D) + 4\phi_1\overline{M}_w(D)\overline{M}_n(0)/\overline{M}_n(D) = 0 \quad \text{....(14)}$$

This equation is then suitable to use in the minimization and Brent methods discussed later in the present work.

Considering $\overline{M}_w$ and $\overline{M}_z$

Squaring both sides of equation (2) and dividing by equation (3) and rearranging eliminates $\dot{\chi}$ and gives,

$$3\phi_2 (u\dot{\tau}D)^4 [\overline{M}_n(0)/\overline{M}_z(D)] [\overline{M}_w(D)/\overline{M}_n(0)]^2 - 4\phi_1^3 = 0 \quad \text{....(15)}$$

Equation (15) is then suitable to use in the minimization and Brent methods discussed later in the present work.

Considering $\overline{M}_n$ and $\overline{M}_z$

Equation (3) may be written as

$$\overline{M}_z(D) = \frac{3\ \overline{M}_n(0)\ \phi_2/\phi_1}{X^2} \quad \text{....(16)}$$

where $X = 1 - 4\dot{\chi}\phi_1/u\dot{\tau}^2D$ ....(16a)

From rearrangement of equation (1),

$$\frac{4\dot{\chi}}{u\dot{\tau}^2D} = \frac{4}{(u\dot{\tau}D)^2} + \frac{4}{u\dot{\tau}D} - \frac{4\ \overline{M}_n(0)}{(u\dot{\tau}D)^2\ \overline{M}_n(D)} \quad \text{....(17)}$$

Substituting equation (17) into equation (16a) gives

$$X = 1 - \frac{4\phi_1}{(u\dot{\tau}D)^2} - \frac{4\phi_1}{u\dot{\tau}D} + \frac{4\phi_1\ \overline{M}_n(0)}{(u\dot{\tau}D)^2\ \overline{M}_n(D)} \quad \text{....(18)}$$

and equation (16) becomes

$$X^2\overline{M}_z(D) - 3(\phi_2/\phi_1)\overline{M}_n(0) = 0 \quad \text{....(16b)}$$

where X is defined by equation (18) and ϕ_1 and ϕ_2 are defined previously.

Thus, equation (16b) is suitable to use in the minimization and Brent methods discussed later.

Summary of the general case

Taking each of $\overline{M}_n$ and $\overline{M}_w$, $\overline{M}_w$ and $\overline{M}_z$, and $\overline{M}_n$ and $\overline{M}_z$, equations were derived so that $\dot{\chi}$ was eliminated and in each case the problem reduced to solution of an equation in one unknown, $\dot{\tau}$. In the general case, all attempts to find analytical solutions to equations(14), (15), and (16b) failed despite the use of the best symbolic computation programs available, e.g. MATHEMATICA(5) and MACSYMA(6). Thus, a method of minimization and the Brent method (explained later) were used

to find numerical solutions to these equations.

Minimization and the use of STEPT

(*a*) *Numerical solutions*

Numerical solutions could be obtained for equations (14), (15) and (16b) by using the minimization program STEPT(7). Essentially, this program calculates for initial values of the parameter $\dot{\tau}$, the value of the function to be minimized. It then takes a step in $\dot{\tau}$, recalculates the function at the new position and determines if the new position has a lower value than the old position. In this way, it searches for positions where the function is a minimum. Disadvantages are that it can sometimes detect a local minimum from which it cannot escape, and thus could miss a global minimum nearby. The philosophy for use of STEPT for each equation is the same. After input of an initial value for $\dot{\tau}$, STEPT defines values of $\dot{\tau}$ and then directs a subroutine to calculate the value of the square of the left hand side(LHS) of either equation (14), or (15) or (16b) depending on the problem. The LHS of the equations is squared so that negative values of the LHS will come out as positive, positive will remain positive and the position in $\dot{\tau}$ where the LHS = 0 will be a true global minimum. There are several solutions to each of the equations but the authors have found consistently that the most positive position of $\dot{\tau}$ where the LHS of the equations is zero is the solution with the most physical significance. Although STEPT provides an error matrix, the values are not reliable and the error range needs to be determined by calculating the range of G(S) and G(X) based on the range of the individual experimental data.

The computer programs MNWMONOD (for $\overline{M}_n$ and $\overline{M}_w$), MWZMONOD (for $\overline{M}_w$ and $\overline{M}_z$) and MNZMONOD (for $\overline{M}_n$ and $\overline{M}_z$) use the STEPT minimization to find numerically exact solutions for the three aspects of the general case ($\sigma \neq 1$). The programs all calculate $\dot{\tau}$ and $\dot{\chi}$ and G(S) and G(X) accurately for a single dose. If it is desired to analyze a complete molecular weight /dose relationship, then one must calculate G(S) and G(X) for each dose and average the values. The benefits of these programs are (i) the very accurate determination of the solutions, provided reasonable initial values are entered, and (ii) the ability to determine easily, variations of G(S) and G(X) with dose.

(*b*) *Nonlinear least squares analysis*

As well as the exact solutions mentioned previously, a nonlinear least squares fit to experimental data may be calculated using STEPT. In this case, the parameter to be minimized is the sum of the square of the deviations of each of $\overline{M}_n$, $\overline{M}_w$, and $\overline{M}_z$ from the theoretically predicted values calculated by the general equations (1), (2), and (3) using known values of $\overline{M}_n(0)$, σ, u, and D. The deviations are weighted by dividing each deviation by the standard error in that particular measurement. STEPT varies $\dot{\tau}$ and $\dot{\chi}$ independently and together and calculates the sum of the squares of the weighted deviations, then makes controlled steps in $\dot{\tau}$ and $\dot{\chi}$ to determine if a lower value for the sum of the squares exists. STEPT provides an error matrix which is not physically reliable. Errors need to be determined by judiciously choosing the combination of upper and lower limits of experimental data which adequately give the ranges of G(S) and G(X).

In the program TAUDCHID (MNWZMIN), any combination or all values of $\overline{M}_n$, $\overline{M}_w$, and $\overline{M}_z$ may be entered for the range of doses used. At least four dose points must be used for the minimization to proceed, but e.g. ten dose points gives a more reliable result. The program is not as sensitive to the (guessed) initial values of G(S) and G(X).

The Brent method

The Brent method referred to earlier is a method of numerical solution of an equation of the form

$$f(x) = 0 \qquad \ldots.(17)$$

The simple FORTRAN program (8) calculates the value of the function f(x) for two values x_1 and x_2 where $f(x_1)$ is negative and $f(x_2)$ is positive. The initial values of x_1 and x_2 are found by trial and error. By bisecting the interval between x_1 and x_2, and testing the values of f(x) at the midpoint, x_3, the program determines whether the solution to equation (17) (i.e. the position where the function f(x) crosses the x axis) lies between x_1 and x_3 or x_3 and x_2. The program then bisects the interval that it determines to be the one where $f(x) = 0$, and the testing process is repeated. By iterative repetition and testing, the program finds the position where $f(x) = 0$ to a preset tolerance. Thus a reliable numerical solution (independent of calculus) is found to analytically insoluble problems.

The programs which use this method are ZEROFMNW, ZEROFMWZ, and ZEROFMNZ. They solve equations (14), (15), and (16b) for pairs of values of $\overline{M}_n$ and $\overline{M}_w$, $\overline{M}_w$ and $\overline{M}_z$, and $\overline{M}_n$ and $\overline{M}_z$ respectively at a single dose point. For a complete molecular weight/dose relationship, one needs to calculate the values of G(S) and G(X) at one dose point at a time and then average the values. The programs are useful also if there is a variation of G(S) and G(X) with dose.

Simulation of molecular weights

Testing of the computer programs was performed using another program SIMULATE written to provide simulated $\overline{M}_n$, $\overline{M}_w$, and $\overline{M}_z$ vs dose for given values of u, σ, $\overline{M}_n(0)$ and D. SIMULATE uses the general equations (1), (2), and (3).

Testing of computer programs

Tables 1, 2, and 3 give data generated by SIMULATE. These data were used to test MNWMONOD MWZMONOD, and MNZMONOD, as well as ZEROFMNW, ZEROFMWZ AND ZEROFMNZ. Also, selected data from Tables 1, 2, and 3 were used to test TAUDCHID. All testing proved successful. There has been no instance where the program failed to provide the correct values for G(S) and G(X). However, care must be taken when using the STEPT–based minimization programs since it is possible to obtain values for G(S) and G(X) which come from a local minimum and not a global minimum. This inconvenience can be sidestepped by determining approximate values of G(S) and G(X) from the analytical solutions for $\sigma = 1$, and then using these as a guide for the initial values to be entered in the STEPT–based programs. More detail is in the manual available from the authors.

Table 1
Simulated molecular weights

$u=10^3$, $\sigma=1$, $\overline{M}_n(0)=10^5$, G(S)=0.2, G(X)=0.02

Dose/Gy	$\overline{M}_n$	$\overline{M}_w$	$\overline{M}_z$
10^4	98,169	197,544	298,742
$5x10^4$	91,469	188,293	293,461
$8X10^4$	87,016	181,904	289,315
$2x10^5$	72,831	160,167	272,150
$6x10^5$	47,189	114,541	220,754
10^6	34,901	89,146	183,129

Table 2
Simulated molecular weights

$u=10^3$, $\sigma=30$, $\overline{M}_n(0)=10^5$, G(S)=0.002, G(X)=0.02

Dose/Gy	$\overline{M}_n$	$\overline{M}_w$	$\overline{M}_z$
10^4	100,187	103,770	107,585
$5x10^4$	100,941	105,555	111,362
$8x10^4$	101,515	106,934	114,327
237,559	104,637	114,815	132,022
950,236	121,543	172,219	299,307
1,425,350	136,214	258,316	676,788

Table 3
Simulated molecular weights

$u=10^3$, $\sigma=0.2$, $\overline{M}_n(0)=10^5$, G(S) = 0.02, G(X)=0.02

Dose/Gy	$\overline{M}_n$	$\overline{M}_w$	$\overline{M}_z$
10^4	100,000	610,548	1,146,093
$5x10^4$	100,000	656,801	1,358,979
114,285	100,000	748,152	1,830,972
228,570	100,000	995,345	3,451,687
342,854	100,000	1,490,060	8,203,047
457,138	100,000	2,974,752	34,539,382

Availability of computer programs

The following FORTRAN computer programs based on the present work, and a manual explaining their use are available from the authors.

ANALYZE — Analytical solutions, $\sigma = 1$, multiple doses, gives G(S) and G(X).

MONODOSE — Analytical solutions, $\sigma = 1$, single dose, gives G(S) and G(X).

MNWMONOD, MWZMONOD and MNZMONOD — Minimization, numerically exact, $\sigma \neq 1$, single dose, gives G(S) and G(X).

ZEROFMNW, ZEROFMWZ, and ZEROFMNZ — Brent method, numerically exact, $\sigma \neq 1$, single dose, gives G(S) and G(X).

TAUDCHID — Nonlinear least squares, $\sigma \neq 1$, multiple doses Gives G(S) and G(X).

SIMULATE Exact $\overline{M}_n$, $\overline{M}_w$, $\overline{M}_z$ vs dose simulation.

A menu driven compendium of these programs is also available.

Conclusion

The authors have summarized here analytical and numerical solutions to the equations which describe the variation of polymer molecular weights with radiation dose. The authors have also documented the existence of FORTRAN computer programs which have become possible using the algebraic solutions provided here. These programs now automate the calculation of G(S) and G(X) from experimental data, thus removing tedious and time–consuming work from the determination of these quantities.

Acknowledgments

The authors would like to acknowledge and thank the following contributions to the present work:
Dr. Mark A. Barton, formerly of Physics Department, University of Queensland and presently of the Japanese National Astronomical Observatory, Tokyo, Japan for discussion and the first assessent of feasibility of solving equations using symbolic computation programs.
Dr. T. E. Peacock and Dr. R. G. Farmer for productive discussions regarding the FORTRAN programming.
Mr. I. H. M. Clarkson for discussion regarding the book Numerical Recipes and the Brent method(8)
Financial support from the Australian Research Council.

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