Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

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Heinz P. Plaumann[a]
[a] Polysar Limited, Sarnia, Ontario, Canada

To cite this Article Plaumann, Heinz P.(1987) 'Simulation of Molecular Weight Distribution After Polymer Breakdown. I. A Least-Squares Parameter Estimation Method on Monte Carlo Models', Journal of Macromolecular Science, Part A, 24: 10, 1167 — 1174
To link to this Article: DOI: 10.1080/00222338708076936
URL: http://dx.doi.org/10.1080/00222338708076936

J. MACROMOL. SCI.—CHEM., A24(10), pp. 1167-1174 (1987)

SIMULATION OF MOLECULAR WEIGHT DISTRIBUTION AFTER POLYMER BREAKDOWN. I. A LEAST-SQUARES PARAMETER ESTIMATION METHOD ON MONTE CARLO MODELS

HEINZ P. PLAUMANN

Polysar Limited
Sarnia, Ontario, Canada N7T 7M6

ABSTRACT

The degradation index (*DI*) has been used in previous work for Monte Carlo simulation of breakdown of polymers with narrow initial molecular weight distribution. However, the definition of *DI* is inadequate for polymers of broader molecular weight distribution. A least-squares method for estimating *DI* for such systems is described.

INTRODUCTION

Monte Carlo simulations have been widely used in polymer science [1], particularly in areas in which closed-form solutions are not readily available. These include the simulation of molecular weight distribution during polymerization and polymer degradation and the simulation of monomer sequence distribution during copolymerization. Such simulations have also been used to elucidate the site selectivity of the degradation process in polymer breakdown [3]. These simulations have been based on various assumptions about the probability of polymer chains breaking randomly or in some regular fashion with regard to the molecular weight of a particular molecule and the site of chain scission along the molecular chain. Glynn et al. [2] calculated an "extent of breakdown" or degradation index (*DI*) from the molecular

weight distribution (MWD). The *DI* represents the number of chain scissions per polymer molecule in the original MWD. Various assumptions were applied to the simulations, and the resulting MWDs, based on the observed *DI* values, were compared with the observed MWDs. This produced the conclusion that the probability of scission of a polystyrene molecule by exposure to ultrasonic energy is greatest at the center of the polymer chain.

An attempt was made to apply the experience of Glynn et al. to the degradation of *cis*-polyisoprene by both ultrasound and ozone, but the definition of the *DI* parameter was found to be unsatisfactory for polymers of such broad MWD. *DI* is defined algebraically as $DI = (\bar{M}_{n,0}/\bar{M}_n) - 1$, where $\bar{M}_{n,0}$ is the number-average molecular weight of the polymer before degradation and $\bar{M}_n$ is that after degradation. Similar limitations to the definition have been noted [5].

It became necessary to approach the problem sequentially. First, assumptions had to be made about a) the probabilities that a molecule of a given molecular weight would undergo scission, and b) the location of the fracture on the chain. In essence, this defines the Monte Carlo model. Second, some procedure for estimating *DI* was required, one which incorporated the elements of the model. One could then adjust model assumptions until the fit to the observed MWDs was satisfactory. The development of the *DI* parameter estimation procedure is described here. The general approach is applicable to systems of more than one parameter.

MATHEMATICAL BACKGROUND

In fitting mathematical models to data, a commonly used approach is minimization of the sum of the squares of the differences between the data points and the estimated data points arising from the fitted model. Expressing this in the form of an objective function:

$$\min \phi = \sum_{i=1}^{n} (y_i - \hat{y}_i)^2,$$

where $\hat{y}_i$ is the estimated value of y_i, which is the observed value. In most instances $\hat{y}_i$ can be expressed as an explicit function of the model parameters and independent variables. Minimization of ϕ usually provides the best estimate of these parameters, given the data and the model. In the case of Monte Carlo simulation, however, $\hat{y}_i$ arises as the result of probabilistic experimenta-

tion and cannot be expressed explicitly as a function of the parameters and independent variables. Rather, it is expressed implicitly. There exists some set of parameter values which, when employed in a Monte Carlo experiment, produces a sum of squares value that is less than that obtained for other parameter values. Of course, because of the probabilistic nature of the Monte Carlo experiments, there will be some variations in the sum of squares even when replicate experiments are run with the same parameter values. However, there will be some region that will contain the true value of the parameter, and in this region the sum of squares will be low relative to the rest of the parameter space. In this case we can say that the parameter set approximately minimizes the objective function. In the particular case under study, the value of *DI* is being estimated as the sole parameter that defines the model. Given the original MWD and the model assumptions, a value of *DI* will define a new MWD after the Monte Carlo trial. We define *DI** as that *DI* value which minimizes the sum of squares.

What is required at this point is the development of a process that will lead us to the region containing *DI**. In a related problem, Duever et al. [4] used formal likelihood functions to define the probability distribution of reactivity ratios by using Monte Carlo simulations. However, the procedure employed here leads directly to an estimate of *DI**.

PARAMETER ESTIMATION PROCEDURE

The procedure shown in the flow sheet (Fig. 1) was used to obtain estimates of *DI**. An appropriate model was selected which embodied two probabilities: first, the probability that a molecule of a particular molecular weight will undergo scission, and second, the location of the scission along that polymer chain. It is also assumed that the lowest molecular weight material accumulates and does not undergo further breakdown. Thus, any particular molecule may undergo several scissions until its fragments reach this limiting molecular weight. Simulations were performed for each of three initial *DI* values. Because of the natural variations that arise in Monte Carlo trials, each simulation was run 10 times and the average of the runs was used as the trial result for that *DI* value. The simulated MWDs were compared with the observed MWD by calculating the sum of squares. A parabola was fitted to the three (*DI, SSQ*) pairs using Cramer's rule. The *DI* at minimum of the parabola, designated DI_0, was used in the next iteration to replace the *DI* value giving the highest *SSQ*. This produces a new parabola through the current three *DI* values and, hence, a new DI_0. The iterations are continued until the convergence criterion is met;

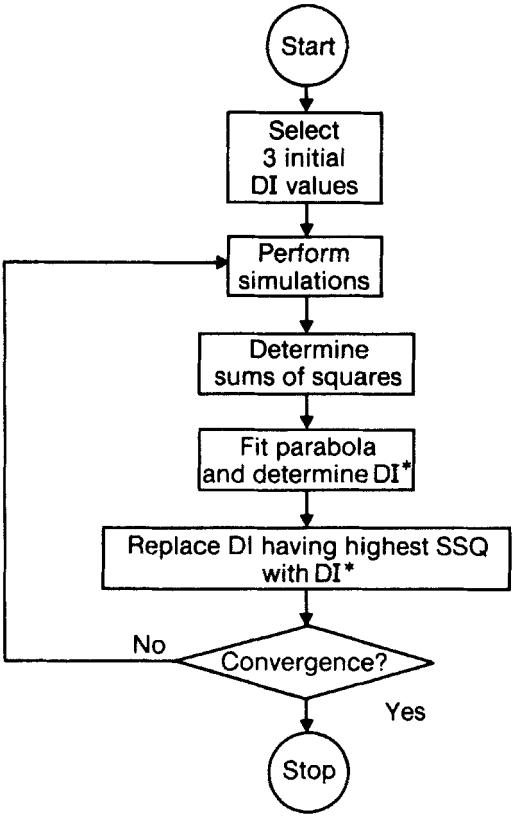

FIG. 1. Flow sheet for *DI* estimation procedure.

i.e., all three current *DI* values are very close together as quantified by the sum of the absolute differences between them and their mean.

AN ILLUSTRATIVE EXAMPLE

A simple example to test the parameter estimation procedure was devised by considering 100 molecules of a monodisperse polymer having a degree of polymerization of 20. Two assumptions were made: i) the probability that any molecule is selected for scission is proportional to the number of molecules of that

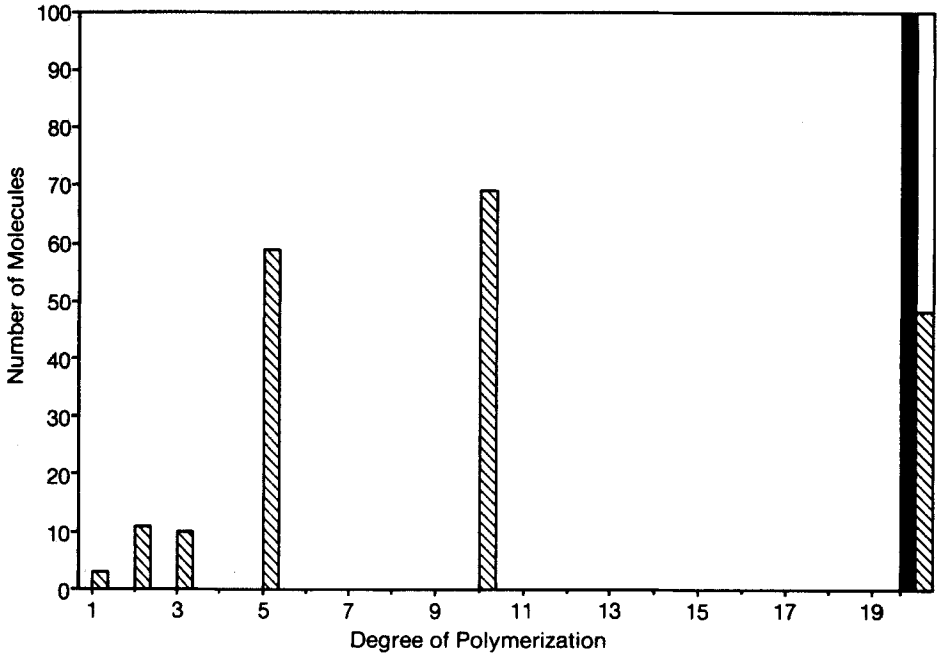

FIG. 2. Test example MWD: Solid bar, before breakdown; hatched bars, after breakdown with $DI = 100$.

molecular weight; ii) the molecule undergoes scission at its center (the so-called center-break model [3]). The first scission will produce two molecules of $DP = 10$. The second may either produce two more of $DP = 10$ or two of $DP = 5$ if the participating molecule is one of $DP = 10$. When such a break would produce fragments of nonintegral DP, the values were rounded. The process continues then, producing molecules of $DP = 10, 5, 3, 2$, or 1, where 1 is the limiting value.

More than 200 Monte Carlo trials were run on the monodisperse polymer, the average of which was used as the "observed" MWD (Fig. 2). In these simulations, DI was unity ($DI^* = 1.00$), so that for each of the molecules present initially, one chain scission occurred.

In order to illustrate the principle behind the parameter estimation procedure, simulations were performed over a range of DI values, and the sum of squares was calculated. Although the relationship between DI and SSQ was not perfectly parabolic in nature (Fig. 3), it does show appropriate curvature

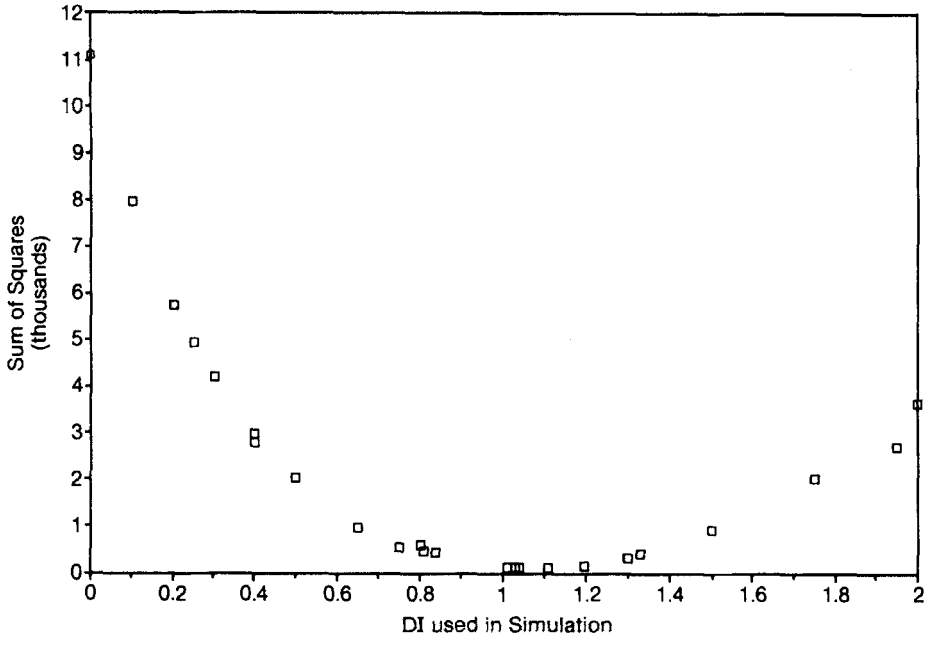

FIG. 3. Effect of trial *DI* values on sum of squares.

and smoothness over the range tested. The scatter in *SSQ* values due to the probabilistic nature of the Monte Carlo process does not appear to be a serious concern.

The parameter estimation procedure was tested for a variety of starting values for *DI*. It was found that, in general, convergence was achieved in three or four iterations if the range of the original three *DI* values either included *DI** or was reasonably close to it. In one case, in which the convergence criterion was too stringent, the three current *DI* values were nearly equal and the parabola fitted through them had a minimum value at $DI < 0$. Those runs which converged successfully produced estimates of *DI** from about 0.90 to 1.10. This is viewed as being a reasonably good estimate of *DI**. The course of one run is ullustrated in Fig. 4.

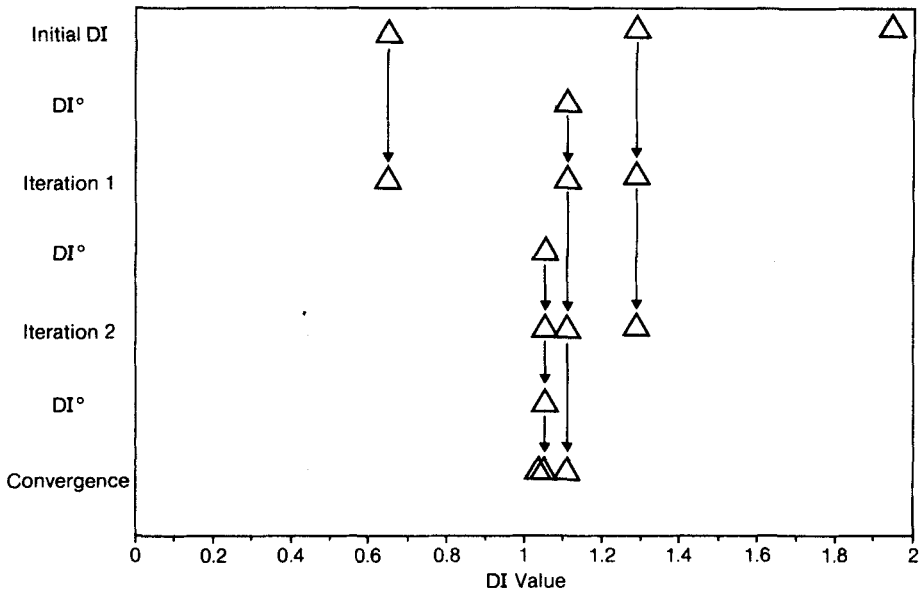

FIG. 4. Schematic representation of the course of the iterations for 0.65, 1.30, and 1.95 as the initial *DI* values. The "true" *DI* is 1.00.

CONCLUSIONS

A simple parameter estimation procedure has been developed and demonstrated for application to Monte Carlo simulation of polymer degradation [3]. However, the basic principles and method should prove useful in parameter estimation in any system where closed-form solutions are either arduous to achieve or not available. However, a serious prerequisite for using the method is that one must have some knowledge about the nature of the breakfown. Such information is not available by merely estimating the extent of breakdown.

ACKNOWLEDGMENT

The author would like to thank Polysar Limited for permission to publish this work.

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Received November 14, 1986
Revision received January 17, 1987