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# GPC Data Interpretation in Mechanochemical Polymer Degradation\*

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Molecular weight distribution obtained by gel permeation chromatography (GPC) conceals a wealth of mechanistic information which can be disclosed only after adequate data treatment. This paper discusses how GPC chromatograms may be used for the elucidation of polymer degradation kinetics. The case of ultrasonic degradation of dilute polystyrene solutions was investigated in detail. The extent of bond scission was determined as a function of sonication time and initial polymer molecular weight. Different bond scission mechanisms were evaluated by comparing calculated molecular weight distributions with experimental data. Best agreement was obtained when multiple fragmentation was included in the degradation scheme, a result experimentally supported by spectroscopic chain ends titration. The results are rationalized by establishing a parallelism between transient elongational flow and ultrasonic degradation.

**Keywords:** Gel permeation chromatography; Molecular weight distribution; Kinetics modeling; Ultrasonic degradation; Mechanochemistry

## INTRODUCTION

With the advent of gel permeation chromatography (GPC), polymer scientists have a convenient and powerful technique of molecular weight distribution (MWD) characterization. However, GPC chromatograms are rarely used beyond fingerprinting and comparative

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purposes. For most of the time, mechanistic information from the chromatogram has been left unused because of the lack of an appropriate MWD prediction method. It is only during the last few years that comprehensive kinetics schemes have been developed which enable the MWD to be calculated for a wide range of polymerization<sup>[1]</sup> and degradation mechanisms.<sup>[2]</sup> Although it is well-recognized that a GPC tracing conceals a wealth of kinetics details, these can be disclosed only after adequate data treatment. In a few instances, computation can be fairly direct as in some free-radical polymerizations. Most degradation studies require, nevertheless, extensive calculations before correct scission mechanisms could be appraised.<sup>[2]</sup> In this article, we will focus on the application of chemical kinetics modeling combined with GPC analyses to the elucidation of chain scission processes. A case study taken from ultrasound-induced degradation will be presented to illustrate the possibilities and limitations of the technique.

## THEORETICAL BACKGROUND

### Differential MWD Representations

Correct representation of the MWD constitutes the first step in the transformation of raw GPC chromatogram into a set of useful data for kinetics modeling. A fundamental fact, frequently overlooked, is the nature of a distribution. By definition, the integral of a distribution function is normalized to unity. Unlike conventional graphs, the height of a point on a MW distribution does not have a simple physical meaning. Rather, it is the *area* under the distribution curve within a given interval of the horizontal scale that represents the fraction of material having the corresponding MW range. From this consideration, it is easy to understand why even qualitative features of a distribution could sometimes drastically depend on how the abscissa scale is defined. The MW at peak maximum ( $M_p$ ) and the "modality" of the distribution may change significantly with the type of representation. It can be readily shown, for instance, that the MWD of a blend of two different polymer fractions may appear as "bimodal" when plotted on a log  $M$  scale but becomes "monomodal" in a linear MW plot.<sup>[3]</sup> The converse is also true as will be evident in the following example.

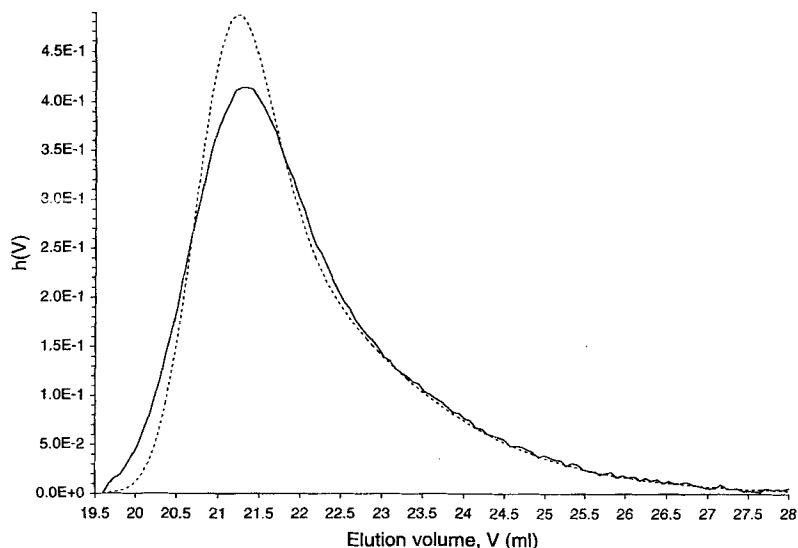


FIGURE 1 Simulated chromatogram of a  $1.04 \times 10^6$  polymer fraction degraded by random scission at  $s=1$  ( $s$  is the degradation index, defined as the number of broken bonds per initial macromolecule). Direct proportionality between the degradation rate  $K(M)$  and chain length was assumed. The initial polymer MW follows a Schulz–Zimm distribution with  $(M_w/M_n)_0=1.04$ . The dotted curve is calculated under ideal conditions (absence of noise and instrumental broadening). The solid curve is simulated under real experimental conditions; noise level (0.5% of peak maximum) and axial dispersion constant (0.25 mL) are actual values obtained on a set of three Ultrastragel columns ( $10^3 + 10^4 + 10^5 \text{ \AA}$ ) with eluent THF at 0.60 mL/min and UV detection.

Figure 1 presents a simulated GPC chromatogram of a narrow polymer fraction obeying Schulz–Zimm distribution with initial  $M_w/M_n = 1.04$  and degraded by random scission. To mimic real operating conditions, actual values for the calibration curve, axial dispersion and noise level were used in the simulation. Apart from comparative purpose, a chromatogram provides little hint about the molecular processes involved. The first step, evidently, is transformation of the chromatogram into a MWD by means of a calibration curve. At this stage, it is necessary to correct for the effect of instrumental broadening. Even with modern GPC columns, neglect of axial dispersion can lead to serious errors in subsequent comparison between experimental and calculated results (cf. Figures 4–7).

In the literature, MWD is frequently drawn on a semi-log scale with weight polymer fraction  $x(\log M)$  reported as a function of  $\log M$

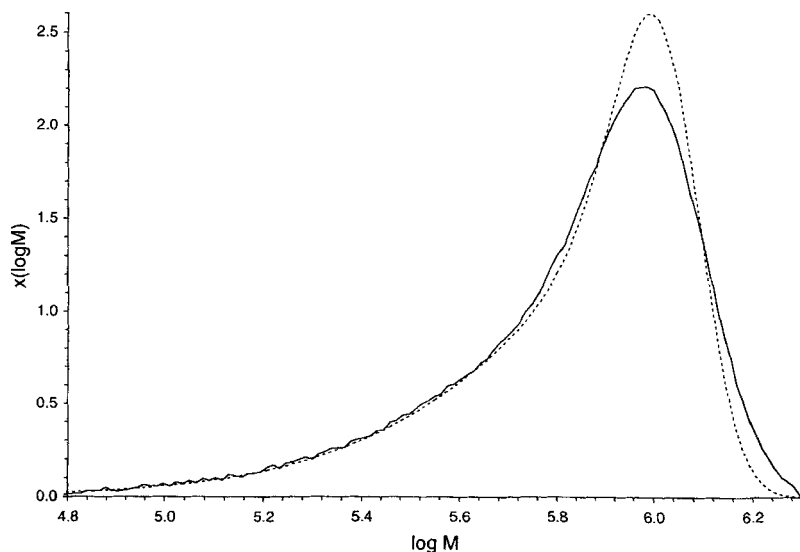


FIGURE 2 “Differential log” MWD representation of the data from Figure 1.

(Figure 2). Such a representation of MWD is convenient to cover the large MW range present in most commercial polymers. In addition, the “differential log” MWD (also known as the “GPC distribution”) is almost a mirror image of the chromatogram as a result of the quasi-proportionality between the elution volume,  $V_e$ , and  $\log M$  from the calibration curve. The nonlinear MW scale, however, tends to narrow artificially high MW fractions and broaden low MW components. Due to this distortion, the “differential log” MWD is not useful for kinetics modeling. From a terminology point of view, only linear plots of the weight fraction  $w(M)$  (Figure 3) or the molar fraction  $n(M)$  vs.  $M$  (Figure 4) could be called a MWD. Obviously, all of the different MWDs are interrelated through elementary algebraic relations<sup>[4]</sup> (Table I) and the interconversion between the different representations are readily achieved through the use of some commercial spreadsheet software like Excel<sup>TM</sup> or QuattroPro<sup>TM</sup>.

Amongst the different means of representing MWD, the  $n(M)$  plot is the most useful for understanding mechanisms. The reason is that rate equations involve *molar* concentrations given by the number of molecules (or moles) per unit volume. From this point of view, GPC

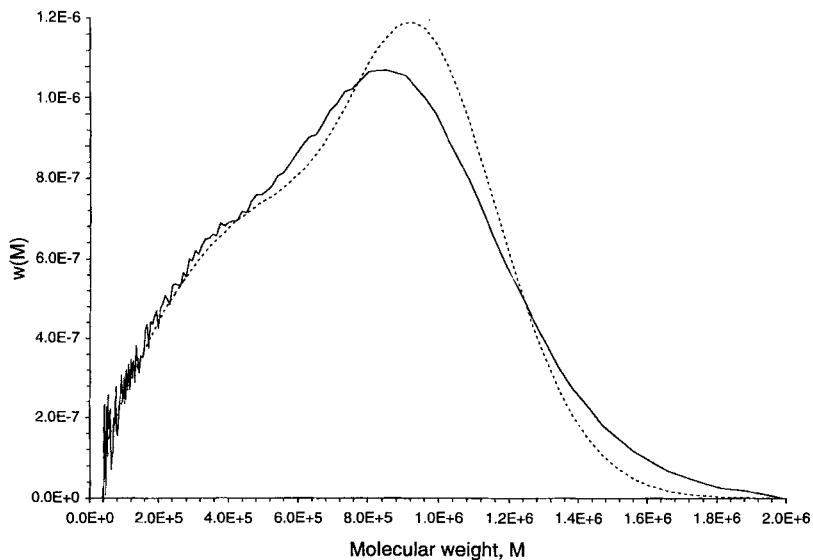


FIGURE 3 Weight fraction MWD representation of the data from Figure 1.

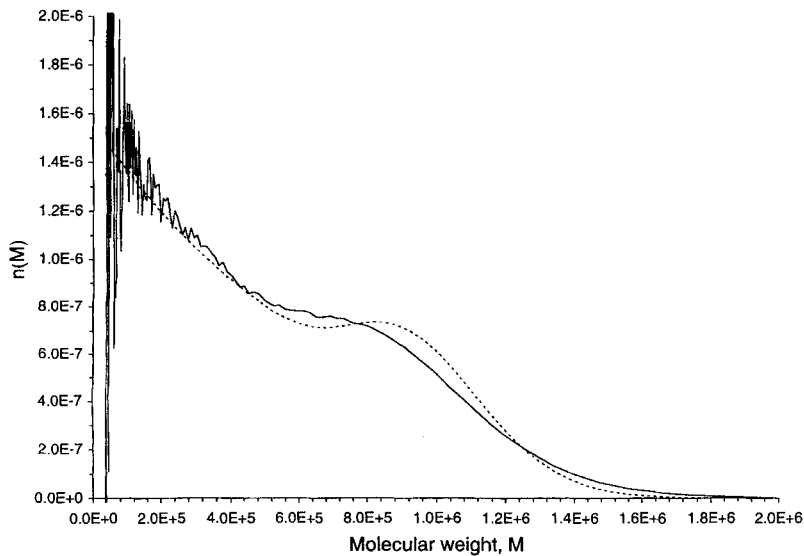


FIGURE 4 Molar fraction MWD representation of the data from Figure 1.

TABLE I Differential MWDs in GPC<sup>[4]</sup>


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(1) Chromatogram	$h(V)/\int h(V)dV = dF(V)/dV$ $h$ = concentration signal, $V$ = elution volume, $F(V)$ = weight fraction of eluant up to $V$
(2) Differential "log MWD" or "GPC distribution"	$x(\log M) = dW(M)/d(\log M) = (-1/(r(d \log M/dV))) \cdot h(V)/\int h(V)dV$ $W(M)$ = cumulative weight fraction up to $M$ . The quantity $d(\log M)/dV$ represents the local slope of the calibration curve
(3) Weight MWD	$w(M) = dW(M)/dM = (-\log e/(M(d \log M/dV))) \cdot h(V)/\int h(V)dV$
(4) Molar MWD	$n(M) = ((-A \cdot \log e)/(M^2(d \log M/dV))) \cdot h(V)/\int h(V)dV$
(5) Relation between the different MWDs	$h(V) \cong x(\log M) = \ln 10 \cdot w(M) \cdot M = A \cdot n(M) \cdot M^2$ where $A$ is a normalizing constant equal to $(\ln 10/M_n)$

---

suffers, from two notable drawbacks: (i) the MW of eluting fractions decreases roughly exponentially with the elution volume, resulting in the previously mentioned nonlinear  $\log M$  scale and (ii) most conventional detectors, like a differential refractive index, ultraviolet absorption, or evaporative light scattering, are sensitive to *mass* concentration with the recorded quantity,  $h(V)$ , given in grams of substance per unit volume. Although the "differential log" MWD could be directly obtained from the chromatogram, weight fraction and molar fraction necessitate division of experimental data by  $M$  and  $M^2$ , respectively. These calculation processes exacerbate the effect of noise and affect directly the  $n(M)$  distribution which becomes excessively dependent on signal and baseline fluctuations especially in the low MW region (Figures 3 and 4). Because of this reason, values for  $M_n$  determined by GPC are much less reliable than the corresponding  $M_w$  (a newly developed technique, MALDI-TOF does not seem to suffer from the mentioned weaknesses and should prove to be a valuable complement to GPC in some favorable situations<sup>[5]</sup>).

### Modeling Polymer Degradation

Modeling polymer degradation is generally an elaborate endeavor. The first source of difficulty stems from the variety of degradation mechanisms that may occur either consecutively and/or concurrently in the same degradative environment (thermal depolymerization of poly(vinyl chloride) constitutes a classical illustration of this complexity).

The second complication results from the large number of repetitive units which are chemically connected within a macromolecule. Although the reactivity of each bond may be identical when considered separately, details of the microstructure, like weak links, steric environment and branching, may influence the local rate of reaction, leading to a position-dependent reaction rate constant. The three most frequently encountered scission probability distribution functions are depicted in Figure 5, where  $k(j)$  is the individual scission rate constant for the

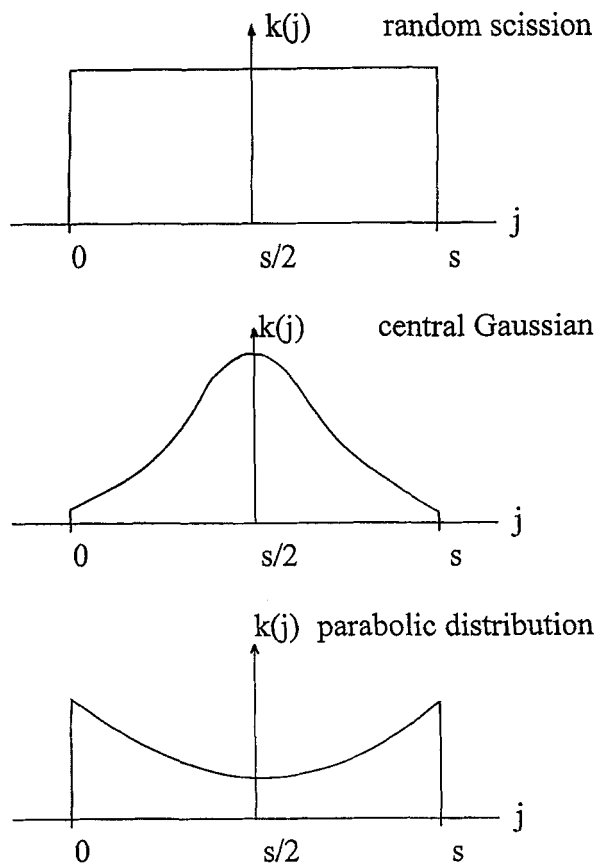


FIGURE 5 Some commonly encountered scission probability distribution functions: (a) random scission, (b) central scission with Gaussian distribution, and (c) parabolic distribution with  $k_{\text{chain ends}} = 5.5 k_{\text{center}}$  ( $k(j)$  is the individual scission rate constant for the  $j$ th bond and  $s$  the maximum number of bonds in the polymer chain).



$j$ th bond and  $s$  the maximum number of bonds in the polymer chain. Case (a) with equal probability for bond fracture corresponds to random scission. The truncated Gaussian distribution function (b) is typical for mechanochemical degradation, whereas the parabolic distribution function (c) which favors near chain end reaction is encountered in some hydrolytic degradation ( $k_{\text{chain ends}}$  and  $k_{\text{center}}$  are scission rate constants for bonds situated at the chain ends or at the polymer center, respectively).

In consideration of the complexities which have been enumerated, it is obvious that some data processing scheme must be formulated before pertinent mechanistic information could be extracted from the experimental chromatograms. Basically, solving the "inverse" problem, that is numerical determination of the parameters to describe experimental MWD, consists of three stages:

- (1) Selection of a coherent degradation scheme. Careful planning of the experiments is necessary to derive the maximum information from the system under investigation.
- (2) Mathematical description of the degradation scheme to derive a theoretical MWD. Three techniques are currently available for this purpose: (i) exact analytical solution, (ii) integration of chemical kinetics differential equations, and (iii) Monte Carlo simulation. This step constitutes the main computational efforts and a brief account of the merits and disadvantages of each technique will be examined below.
- (3) Comparison of the calculated MWD with experimental results. If a good fit between the predicted and the experimental data is obtained, the task is concluded and a physicochemical interpretation is given to explain the results from molecular considerations. Otherwise, an alternative degradation mechanism must be devised and the procedure repeated.

### Chain Scission Kinetics

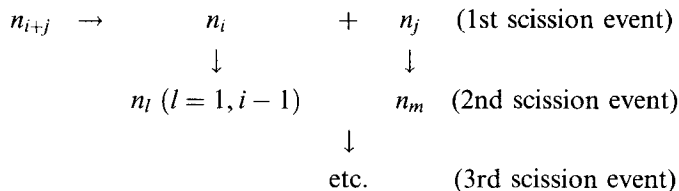
The task of obtaining kinetic parameters from a change in experimental MW and MWD is not trivial and has been tackled since the beginning of polymer chemistry. Basically, three techniques have been applied to resolve this problem.

(a) *Analytical solution* The first approach, pioneered by Kuhn<sup>[6]</sup> and Montroll and Simha,<sup>[7]</sup> used combinatorial statistics to derive changes in the dispersity index as a function of the degradation extent. For some limited initial distributions (Schulz–Zimm, log-normal, Weibull–Tung) and degradation mechanisms (random, exact central, simultaneous random scission and crosslinking), analytical solutions could be obtained for the whole MWD. Exact expressions, though admittedly elegant, are always mathematically complex and find little application since the evaluation and comparison with experimental changes in MWD are rather difficult. In the general case, it was necessary to use numerical calculations from some selected degradation models<sup>[8,9]</sup> to obtain either MW averages or some qualitative features of the MWD to extract kinetic and mechanistic information.<sup>[1,10]</sup>

(b) *Chemical kinetics equations* The second technique relies on the system of differential equations which describe the depolymerization rates of individual bonds during the degradation process. In principle, any chemical reaction including polymer degradation could be described by a set of differential kinetics equations. Integration of this set of equations should give the time evolution of the MWD for any arbitrary degradation scheme. Such a procedure, however, is impractical in view of the enormous number of coupled differential equations which is necessarily involved in a macromolecular system. It was shown that a general analytical expression could be obtained if the resulting system of differential equations is linear. In chemical terms, this means that the degradation rate must be of first-order with respect to the reactant concentrations and that recombination reactions could be neglected.<sup>[11]</sup> The first hypothesis should be verified but was found to be correct for many systems investigated.<sup>[12]</sup> The second assumption could be made valid with the addition of some efficient radical scavenger capable of preventing secondary reactions from the formed macroradicals. 2,2-Diphenyl-1-picrylhydrazyl (DPPH), Galvinoxyl<sup>®</sup>, or dissolved air and impurities can serve for that purpose. These two assumptions allow drastic simplification from the full degradation formalism, resulting in the degradation scheme presented below.

A polymer chain  $n_i$ , of degree of polymerization  $i$  has  $(i - 1)$  bonds linking monomeric units which may be split during the reaction. The reaction constant for cleavage of the  $j$ th bond is designated by  $k_{i,j}$ . At a given time, the fate of that polymer chain is described by the following

scheme (I):



The degradation kinetics equation for  $n_i$  is summarized in:

$$\begin{aligned}
 \frac{dn_i}{dt} &= - \sum_{j=1}^{i-1} k_{i,j} \cdot n_i + \sum_{j=1}^{r-i} (k_{i+j,j} + k_{i+j,i}) \cdot n_{i+j} \\
 &= -K_i \cdot n_i + \sum_{j=1}^{r-i} (k_{i+j,j} + k_{i+j,i}) \cdot n_{i+j}
 \end{aligned} \tag{1}$$

$K_i$  is the global scission rate constant for species with degree of polymerization  $i$  and  $r$  is the maximum degree of polymerization present in the sample. For most practical purposes, it is sufficient to consider a limited number of rate constants averaged over a "quasi-monomeric" unit containing a multiple of the true repetitive units. A value of  $r$  in the range of 100–200 is normally satisfactory for a faithful description of the polymer MWD.

The first term on the right-hand side of Equation (1) describes the decrease of concentration of  $n_i$  as a result of bond scission. However,  $n_i$  is generated if a polymer  $n_{i+j}$  is split at bond  $j$  or at bond  $(i-j)$ . This is taken into account by the second production term.

It is convenient to rewrite Equation (1) in a matrix notation:<sup>[13]</sup>

$$\frac{d\vec{n}}{dt} = \mathbf{A} \cdot \vec{n}(t) \tag{2}$$

where  $\mathbf{A}$  is an upper triangular matrix of rank  $r$  given by:

$$\left( \begin{array}{cccccc}
 0 & (k_{2,1} + k_{2,1}) & (k_{3,1} + k_{3,2}) & (k_{4,1} + k_{4,3}) & \dots & (k_{r,1} + k_{r,r-1}) \\
 0 & -k_{2,1} & (k_{3,2} + k_{3,1}) & (k_{4,1} + k_{4,3}) & \dots & (k_{r,2} + k_{r,r-2}) \\
 0 & 0 & (-\sum k_{3,j}) & (k_{4,1} + k_{4,3}) & \dots & (k_{r,3} + k_{r,r-3}) \\
 0 & 0 & 0 & (-\sum k_{4,j}) & \dots & (k_{r,4} + k_{r,r-4}) \\
 0 & 0 & 0 & 0 & \dots & \dots \\
 0 & 0 & 0 & 0 & 0 & (-\sum k_{r,j})
 \end{array} \right)$$

The presence of vanishing terms in the degradation matrix  $\mathbf{A}$  stems from the neglect of recombination reactions. An analytical solution to the system of Equation (3) is obtained from the relations:

$$\vec{n}(t) = \mathbf{C} \cdot z(t), \quad \text{with } z_i(t) = \alpha_i \exp(-K_i t) \quad (3)$$

The coefficients  $\alpha_i$  are obtained from the MWD of undegraded polymer:

$$\vec{n}_0 = \mathbf{C} \cdot \alpha \quad (4)$$

Starting from the bottom with the single term  $(-\sum k_{r,j})$ , a recurrent formula can be obtained for the successive values of  $C_{i,j}$ :

$$\sum_{i=1}^r \mathbf{A}_{r,j} \cdot \mathbf{C}_{k,j} = \mathbf{A}_{j,j} \cdot \mathbf{C}_{i,j} \quad i = r, r-1, \dots \quad (5)$$

(c) *Monte Carlo simulation* The integration technique exposed in the preceding paragraph is simple, accurate and necessitates little computer time. It is not applicable, however, to branched polymer chains and to degradation mechanisms accompanied by recombination, crosslinking or volatilization reactions. Monte Carlo techniques have been developed to overcome these limitations. Although the use of Monte Carlo method to solve chemical kinetics problems dated back from the mid-50s, its application to the polymer field is more recent.<sup>[14,15]</sup> To illustrate the technique, a simple example corresponding to random crosslinking is given below. First, the initial number MWD is entered into the computer memory as an array  $(n_i, N_i)$  with  $N_i$  = number of molecules having a degree of polymerization  $n_i$ . A number  $\psi$  is randomly generated from an equidistributed population in the range 0 to 1 (with as many significant digits as desired). The reacting macromolecule, of degree of polymerization  $n_x$ , is selected from the Equation (6) below and  $(n_x, N_x)$  deduced from the initial population:

$$\phi = \psi \cdot \sum_{i=0}^{i_{\max}} n_i N_i \leq \sum_{i=0}^x n_i N_i \quad (6)$$

Another polymer molecule of degree of polymerization  $n_y$  is selected in a similar manner. After summing up the degrees of polymerization, the newly created polymer with degree of polymerization  $n_{x+y}$  is reallocated and the procedure restarted as many times as necessary.

Monte Carlo method is a versatile tool capable of handling complex macromolecular reactions in a straightforward manner.<sup>[16–20]</sup> Realistic Monte Carlo simulations require, however, excessive amount of dynamic memory, generally well beyond the capacity of most laboratory computers. Due to computational limits, Monte Carlo results are subjected to large statistical errors. A new random sampling algorithm has recently been proposed to improve accuracy in Monte Carlo simulation results.<sup>[21]</sup>

## APPLICATION TO MECHANOCHEMICAL DEGRADATION

Unusual with small organic molecules, mechanochemical reactions are ubiquitous in polymer systems and can be induced either in the solid, melt or dilute state purely by the storage of elastic energy from chain deformation. In this section, we will focus on the application of GPC to the investigation of a particular class of mechanochemical degradation promoted by ultrasonication.<sup>[22–24]</sup> Bond scission by ultrasound irradiation provides an attractive system which is simple enough to be studied in detail, yet sufficiently general to display most of the features found in other types of degradation.

### Experimental

#### Chemicals

The polystyrene samples are narrow molecular weight standards from Polymer Laboratories (Shropshire, UK) with  $M_p$  (MW at peak maximum) in the range of  $50 \times 10^3$ – $8.5 \times 10^6$  g/mol. The dispersity index,  $M_w/M_n$ , is  $< 1.05$  for molecular weights below  $4 \times 10^6$  but increases to 1.20 for the highest molecular weight polymer. Chemicals are from Fluka AG (Switzerland). Decalin is a mixture of 58% trans, 41% *cis*-decahydronaphthalene + 1% tetrahydro naphthalene as determined by gas chromatography.

#### Degradation Experiments

Polymer solutions were prepared by dissolving 20 ppm of PS in decalin with 100 ppm of Galvinoxyl<sup>®</sup>. The excess of Galvinoxyl<sup>®</sup> (systematic

name: 2,6-di-*tert*-butyl-4-[(3,5-di-*tert*-butyl-4-oxo-2,5-cyclohexa-dien-1-ylidene)-methyl] phenoxy] served a dual purpose: to prevent radical recombination and to end-tag the degraded chains for subsequent spectrophotometric titration (section below). Irradiation was performed in a thermostated vessel with an ultrasonic horn at a power of 20 W and a frequency of 20 kHz (Branson Sonifier<sup>®</sup> model 250). After a predetermined period of ultrasonication, a small volume was withdrawn, the solvent evaporated and the polymer analyzed for MWD. Some typical results are shown in Figures 6 and 7 ( $R$  is the relative standard deviation defined in Equation (11) below).

Molecular weight distribution of the virgin and degraded polymers was determined by GPC on a Waters 150CV equipped with a triple detection scheme (differential refractometer, on-line viscometer and UV absorption). Axial dispersion in the GPC columns was calibrated with the recycling technique.<sup>[25]</sup> True molecular weight distribution was then recovered from the GPC tracing using a reshaping algorithm

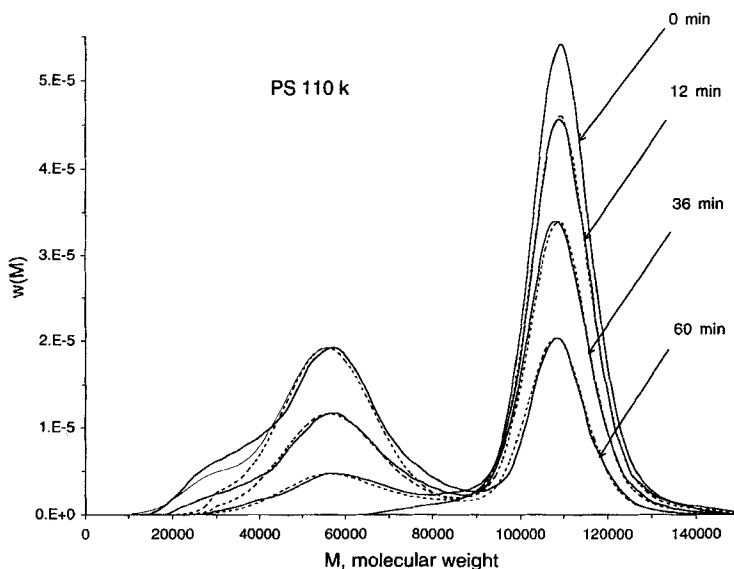


FIGURE 6 Experimental and simulated MWDs for a  $110 \times 10^3$  PS degraded by ultrasonication at the indicated irradiation time: (—) instrumental broadening corrected, experimental data, (----) calculated with the central Gaussian scission model with a relative standard deviation  $R=0.09$ , (—) calculated with the inclusion of 10% quaternary scission.

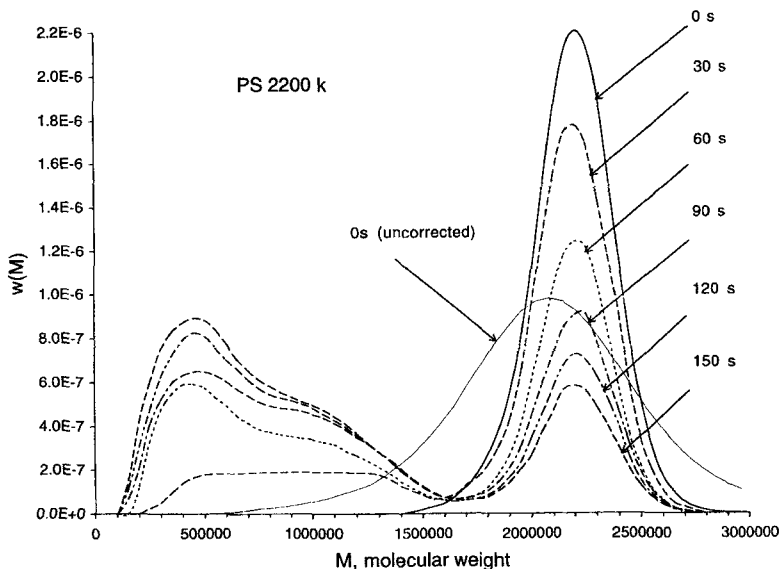


FIGURE 7 Change in experimental MWD with irradiation time for a  $2.2 \times 10^6$  polystyrene. All the data are corrected for axial dispersion; one example of an uncorrected curve is shown for the pristine sample.

described by Ishige *et al.* after smoothing the data to decrease the level of noise.<sup>[26]</sup>

## RESULTS AND DISCUSSION

In free-radical polymerization, the chemical kinetics is well understood and derivation of kinetics parameters from MWD is relatively straightforward.<sup>[1]</sup> This is not the case in ultrasonic degradation and experiments should be devised in such a way as to infer a correct degradation mechanism. Due to the increase of stress-transfer efficiency with chain length, mechanochemistry is strongly dependent on polymer MW and bond position along the chain. Apart from irradiation time, the fundamental parameter that was investigated was the initial polymer MW. In the present work, the influence of initial molecular chain length on degradation rate and degraded fragments distribution was determined over a 200-fold range in MW ( $50 \times 10^3$ – $8.5 \times 10^6$ ).

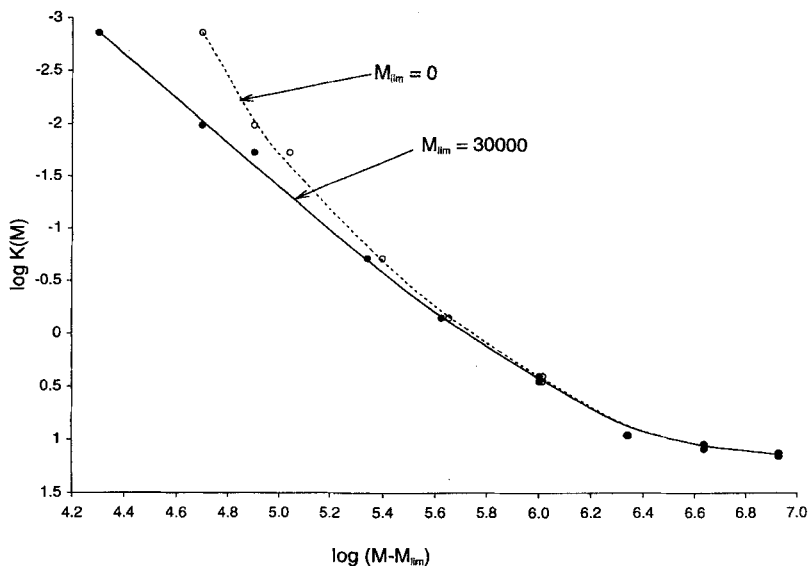


FIGURE 8 Double-logarithmic plot of the dependence of scission rate constant on initial polymer molecular weight  $M_0$  (-----) and on  $(M_0 - M_{lim})$  (—). The empirical value for  $M_{lim}$  is 30,000.

Two different behaviors were discerned from the plot depicted in Figure 8. Over the MW range  $50,000 \leq M \leq 2.2 \times 10^6$ , the rate for chain scission follows an empirical scaling law of the form:

$$K(M) \propto (M - M_{lim})^x \quad (7)$$

with  $x = 1.9$  and  $M_{lim} = 30,000$ ;  $M_{lim}$  is the limiting MW below which no chain scission would be observed regardless of the degradation time.

Above  $2.2 \times 10^6$ , the degradation rate becomes almost independent from  $M$  and the slope of the plot in Figure 8 leveled off to nearly 0. This sudden change in the slope, surprising at first thought, is in fact expected on physical grounds: the degradation rate cannot increase indefinitely with  $M$  but should reach some limiting level for a given sonication power.

Comparing Figures 6 and 7 reveals that the bond scission pattern depends on the initial polymer MW ( $M_0$ ). Chains are essentially



broken into halves at low  $M_0$ , into quarters at intermediate MW, and into multiple short fragments (down to  $M_0/32$ ) in the highest MW range. Any coherent degradation scheme should account for this observed trend.

### Mathematical Modeling

The analytical integration technique (method b) was applied to predict MWD. According to Equation (1), change of MWD with time is given by a system of  $r$  linear differential equations and  $r(r-1)$  unknown  $k_{i,j}$  terms. With the total number of variables largely surpassing the number of available equations, additional information is needed before this system could be resolved. Symmetry condition for linear chains reduces the unknown by a factor of  $\sim 2$ :

$$k_{i,j} = k_{i,i-j}. \quad (8)$$

Further simplification is possible from the experimental dependence of scission rate constant,  $K_i$ , on chain length (Equation (7)):

$$K_i = \sum_{j=1}^{i-1} k_{i,j} = \beta \cdot (i - i_{\text{lim}})^{1.9}. \quad (9)$$

In analogy to flow-induced degradation, one can assume as a starting point that the rate of bond breakage follows a truncated central Gaussian distribution for the different positions along the chain:<sup>[2]</sup>

$$k_{i,j} = \begin{cases} \beta/(\sigma_i\sqrt{2\pi}) \cdot \exp[-(j-i/2)^2/2\sigma_i^2] & \text{if } i > i_{\text{lim}} \text{ and } j \geq i_{\text{lim}}/2 \text{ or } j \leq i - i_{\text{lim}}/2 \\ 0 & \text{else} \end{cases} \quad (10)$$

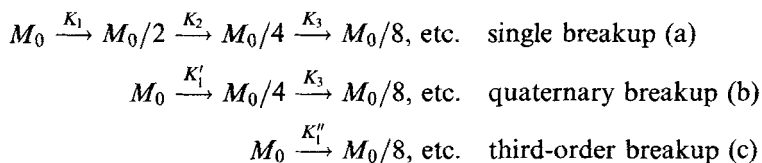
with  $i_{\text{lim}}$  = number of "quasi-monomeric" units equivalent to  $M_{\text{lim}}$ . Within a limited range of MW, the relative standard deviation  $R$  can be considered as constant and used as a fitting parameter:

$$\sigma_i = R \cdot i. \quad (11)$$

Equation (2) can be integrated after replacing the  $k_{i,j}$  by the corresponding numerical values given by Equations (10) and (11). Starting with the MWD of the virgin sample, MWDs of degraded polymer were calculated at different sonication times and compared with the experimental data. It is mandatory at this stage to consider exclusively true MWDs after appropriate axial dispersion correction. Failure to take instrumental broadening into account could deteriorate seriously the quality of the fit and lead to an erroneous assignment of the scaling exponent ( $x$ ) in Equation (8).

The system of differential equations (Equation (2)) is based on single-scission kinetics. Fair agreement between the simulated and experimental data was observed only for the lowest initial MWs. Deviations indicating an excess of short fragments were already observed for  $M_0 = 110 \times 10^3$  (Figure 6). In accord with the observations of Figures 6 and 7, multiple scission prevails over single scission with increasing  $M_0$ . The degradation Scheme I developed for single-scission kinetics must be modified to include the possibility for multiple scission. Techniques for computing MWD in the presence of multiple scission have been discussed in Ref. [27].

For ultrasonic degradation, multiple scission is modeled as a succession of single-scission events. The formation of fragments with  $\bar{M} \cong M_0/4$  can be formally described by the competitive reactions (a) and (b) below, while those with  $\bar{M} \cong M_0/8$  requires an additional step (c). The relative importance of each process depends on the initial  $M_0$ :



Any fragment, once formed, can be further degraded according to the described kinetics which will be referred as degradation Scheme II.

According to the proposed model, chains can only be broken in multiples of  $2^n$  fragments (2, 4, 8, etc.). No tertiary scission, for example, as found in solvent freezing degradation, was allowed in the calculations.<sup>[27]</sup> The rationale behind this procedure will be explained in the physicochemical interpretation. The influence of multiple

scission on the final MWD is shown in Figure 9. The best fit to the experimental data for the  $2.2 \times 10^6$  PS was obtained with the following repartition: 56% of the degradation by single scission, 27% by quaternary scission ( $M_0/4$ ) and 17% by third-order scission process ( $M_0/8$ ). For the highest MW range,  $4.34 \times 10^6$  and  $8.5 \times 10^6$ , chain halving was practically absent whereas simultaneous scission up to the fifth-order (fragments with  $M \cong M_0/32$ ) have to be included for a correct representation of the degradation results. Differences between degradation Schemes I and II are emphasized in Figures 9 and 10 where the weight fraction of different fragment populations are calculated and plotted for the  $2.2 \times 10^6$  PS sample. Without multiple scission, short fragments are created by consecutive reactions and can only be found for extended degradation times.

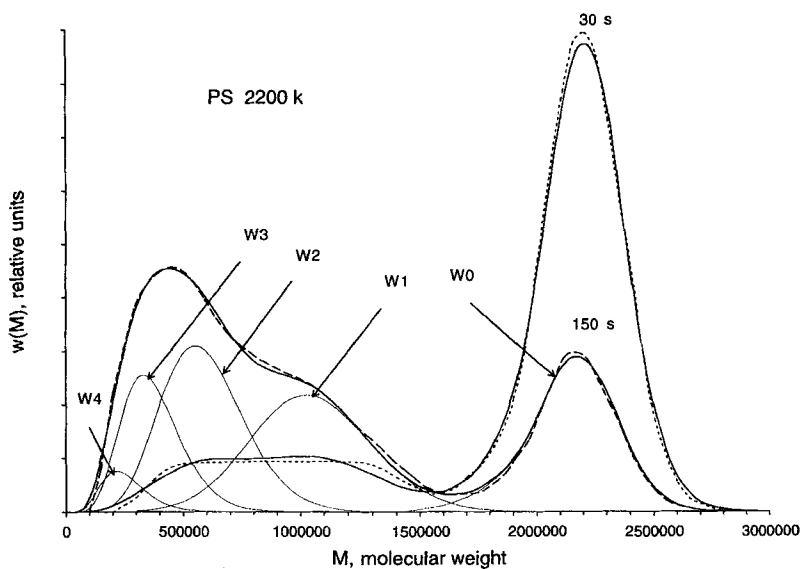


FIGURE 9 Experimental and simulated MWDs for a  $2.2 \times 10^6$  PS degraded by ultrasonication at irradiation time of 30 s and 150 s. The (----) indicate experimental data, the (—) are calculated with the multiple scission model (56% single scission, 27% quaternary scission and 17% third-order scission).  $W_0$  denotes the calculated weight fraction of all polymer chains which remain intact, while  $W_1, W_2, W_3, \dots$  refer to those fractions which have been broken once, twice, thrice, respectively, at the irradiation time of 150 s.

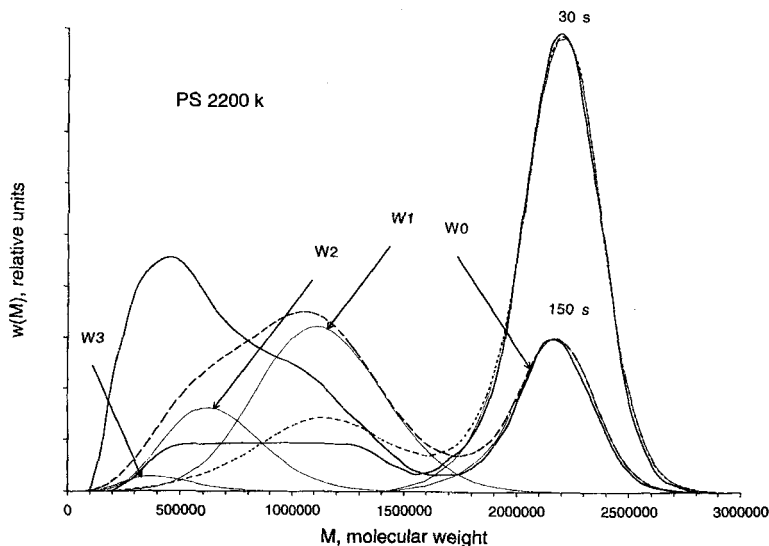
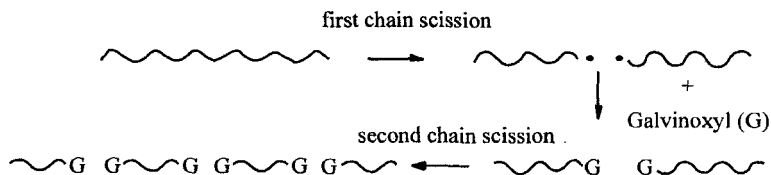


FIGURE 10 Experimental and calculated MWDs for an ultrasonically degraded  $2.2 \times 10^6$  PS using the central Gaussian scission model with a relative standard deviation  $R = 0.13$ . Conditions and notations are the same as in Figure 9.

### Quantification of Multiple Fragmentation

A unique chain-labeling technique combined with GPC analysis was utilized to differentiate between the different degradation populations. In the presence of excess Galvinoxyl<sup>®</sup>, it is expected that each free radical created by the degradation will be immediately scavenged. Because undegraded polymer does not contain Galvinoxyl<sup>®</sup>, the number of chromophore groups per fractured chain is given by  $\phi = (2N - 2)/N$  where  $N$  is the number of fragments formed from one initial macromolecule:



Chains which have been broken once bear a single chromophore moiety at one end, giving  $\phi = 1$ . For chains which have been fractured

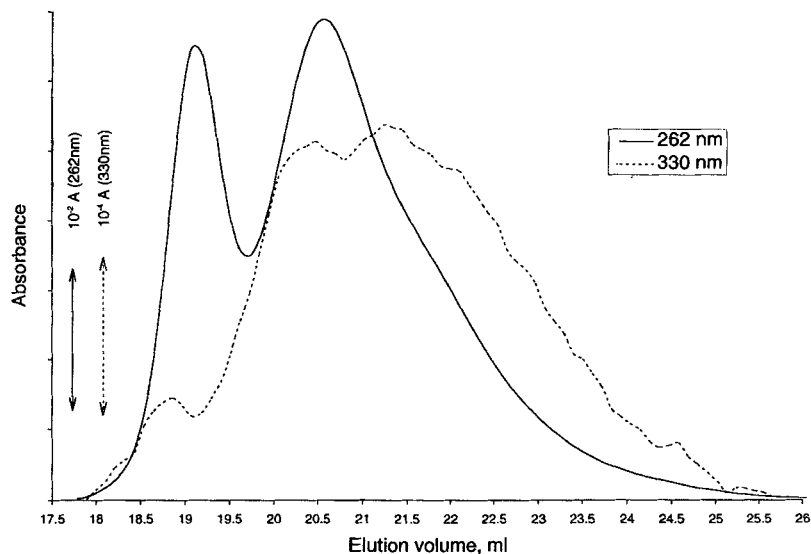


FIGURE 11 Chromatograms of a  $450 \times 10^3$  PS degraded by ultrasonication in presence of excess Galvinoxyl<sup>®</sup>, detected at two different wavelengths: 265 nm for PS and 330 nm for bound Galvinoxyl<sup>®</sup> (note the difference in the absorbance scale).

twice,  $\phi = 1.5$  and so forth. Difference in the UV absorption spectrum of styrene units ( $\lambda_{\max} = 262$  nm) and attached Galvinoxyl<sup>®</sup> ( $\lambda_{\max} = 330$  nm) allows easy determination of the parameter  $\phi$ . By using GPC coupled with a variable wavelength UV detector, the parameter  $\phi$  could be determined as a function of MW thus providing a mean for quantifying the different degradation populations  $W_0$ ,  $W_1$ ,  $W_2$ , etc. (Figure 11).

### Physicochemical Interpretation

In analogy with transient elongational flow degradation,<sup>[28]</sup> it is reasonable to assume that ultrasound-induced bond scission arises from the large shear gradient generated during the collapse of cavitation bubbles. Following the pioneering work of Lord Rayleigh in 1917, several mathematical treatments have been derived to describe bubble wall motion during the implosive collapse. An approximate equation describing the wall velocity ( $v_R$ ) is given by:<sup>[27]</sup>

$$v_R = dR/dt = (2P_h/3\rho)^{0.5} (R_m^3/R^3 - 1)^{0.5} \quad (12)$$

where  $\rho$  is the solvent density,  $P_h$  the external pressure,  $R_m$  the initial radius and  $R$  the instantaneous radius of the imploding cavity. According to Equation (12),  $v_R$  should reach infinity in the limit of  $R=0$ . More detailed theoretical and experimental investigations revealed, nevertheless, that  $R$  reaches a minimum radius of the order of  $0.5 \mu\text{m}$  during the final collapse.<sup>[29]</sup>

Neglecting solution compressibility, the strain-rate distribution can be readily computed as:

$$\dot{\epsilon}_{rr}(r) = (\partial v_R / \partial r)_t = -2v_R \cdot R^2 \cdot r^{-3}. \quad (13)$$

The strain-rate distribution, calculated from Equations (12) and (13) for different collapsing times, are reproduced in Figure 12. Degradation kinetics modeling requires knowledge of the strain-rate history of the flowing macromolecules.<sup>[31]</sup> This is obtained by adopting an Eulerian frame of references which moves with the surrounding fluid element. The results of this transformation are shown in Figure 13 and permit us to rationalize most of the experimental findings which include the empirical scaling law (Equation (7)), the existence of  $M_{lim}$  and the formation of low MW fragments.

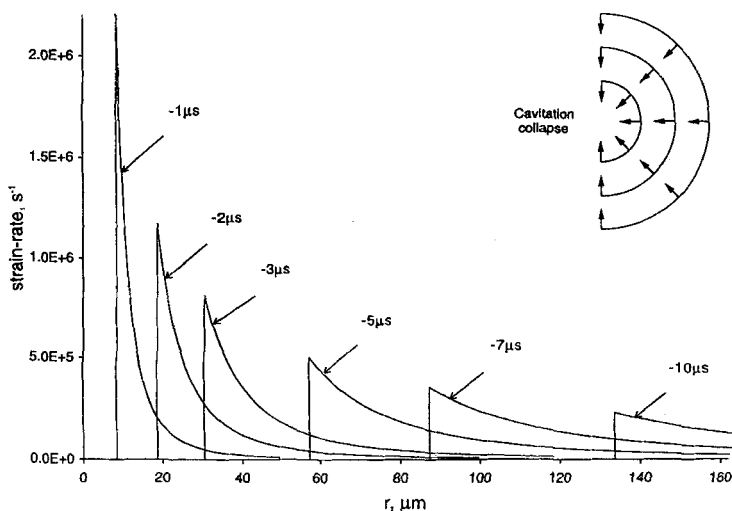


FIGURE 12 Strain rate distribution during a cavity collapse sketched for different implosion times. Full collapse occurs at  $t=0$ ;  $r$  is the distance from the cavity center.

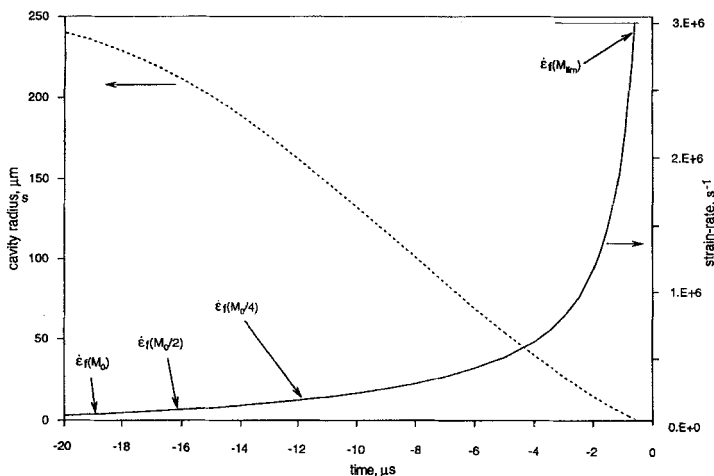


FIGURE 13 Temporal evolution of the bubble radius (left ordinates) and strain-rate maximum (right ordinates) during implosion collapse.

In transient elongational flow, it is well-established that chain fracture is observed only above a critical strain-rate  $\dot{\epsilon}_f$  which scales with polymer MW as:<sup>[32]</sup>

$$\dot{\epsilon}_f \propto M^{-1} \quad (14)$$

Multiple scission could be readily explained with the strain-rate curve of Figure 13. During the implosion, a polymer chain lying next to a cavity is exposed to a wide range of strain-rates with increasing magnitude. Low MW samples require high fluid strain-rate for fracture (Equation (14)), therefore the chance of being broken twice is negligible. In contrast, molecular fragments formed from long polymer chains in the early implosion stage can undergo several degradation events during the cavity lifetime until either  $M_{lim}$  or total bubble collapse is reached (Figure 13). By extrapolating the results obtained in transient elongational flow to ultrasonic degradation, it can be deduced from  $M_{lim}$  that the highest strain-rate attained during the implosion is of the order of  $3 \times 10^6 \text{ s}^{-1}$  (Figure 13).

## CONCLUSIONS

Polymer MWD is a record of all the kinetic events which occurred during a polymer lifetime. To exploit fully this invaluable source of

mechanistic information, a systematic approach should be strictly followed. The general methodology starts with an accurate MWD representation. Even with modern high performance columns, instrumental broadening correction remains an essential part in GPC data treatment to recover true MWD, particularly with narrow polymer fractions. Elaboration of a degradation scheme, derivation of the corresponding MWD and critical comparison with experimental data constitute some additional steps before a correct degradation model could be proposed. By applying the technique to ultrasound-induced degradation, it was determined that chain scission took place by multiple fragmentation. The experimental dependence of bond scission-rate constant on initial MW was rationalized by establishing a parallelism between ultrasonication and transient elongational flow degradation.

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