New Use of Size Exclusion Chromatography in Kinetics of Mechanical Degradation of Polymers in Solution

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SYNOPSIS

A new method to investigate the mechanical degradation of polymers in solution is described that uses size exclusion chromatograms of the initial polymer and of the degraded sample. The incipient parts of these chromatograms are analyzed to obtain kinetic data about degradation at the level of infinitesimal fractions. The procedure is based on the fact that mechanical degradation of the polymers is a first-order reaction and macromolecules are cleaved mostly in their central region. The rate constant and the variation in the rate constant with molecular weight are determined in a single experiment, avoiding additional fractionation steps. Moreover, the slope of the size exclusion chromatographic calibration curve is derived, opening new ways to determine polydispersities or even to make rapid calibration for unknown polymers. To verify the method, the rate constant and the molecular weight dependence of the rate constant were determined for the sonic degradation of polystyrene in toluene. The rate constant is found to vary with the square of the molecular weight, and its value is in good agreement with results reported using much more laborious methods. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

Mechanical degradation of polymers in solution[1,2] continues to be investigated due to its practical and theoretical interest. Studies concerning the kinetics and mechanism of these processes have received considerable attention, but they have been performed mostly on bulk samples, the time dependence of degradation being expressed in terms of average molecular weight (MW) or average degree of polymerization (p). In a few cases, the variation in the rate constant with MW has been reported using different fractionation techniques.[3-5] It is recognized that mechanical degradation processes follow first-order kinetics and that there exists a limiting degree of polymerization below which main-chain scission does not occur. However, even in the case of the same mechanical treatment, different kinetic expressions have been suggested.[6]

The most commonly encountered investigation methods are the measurements of intrinsic viscosities[7-9] and the ensuing of molecular weight distribution (MWD) and average MWs by size exclusion chromatography (SEC).[10-13] In some works, radical scavengers have been used for the detection of the free macroradicals caused by bond ruptures in the polymer main chains.[9,14] Studies concerning radical polymerization of unsaturated monomers initiated upon subjecting polymers to mechanical degradation in the presence of monomers have also been reported.[15,16]

SEC is known to be a very useful polymer characterization tool for determining MWD and different mean MWs. This technique is not, however, a primary method for determining MW and the calibration curve depends on molecular structure.

If during degradation the change in MW is not accompanied by a change in molecular structure, a straightforward analysis of the chromatograms of the initial and degraded samples can provide information about the rate of the process. In this article, a method is described for evaluating the rate constant of mechanical degradation at the level of infinitesimal fractions, using only the two mentioned chromatograms. The approach uses the incipient portion of the chromatograms, corresponding to the

high MW range. In this domain, the chromato-graphic heights can be used to express the degra-dation rate of infinitesimal MW fractions. Usually, this cannot be achieved, since, on the chromatogram of the degraded sample, the degradation products interfere with the unaltered fractions. It is possible, however, to interpret the initial part of such chromatograms, taking into account that

- Macromolecules are cleaved mostly in their central region during the mechanical degradation of polymers in solution[13,14,17];
- The concentrations of the fractions decrease rapidly toward extreme MW values, so that the concentrations of the high MW degradation products will be low.

DEVELOPMENT

The mechanical degradation of an infinitesimal polymer fraction obeys first-order kinetics if the change in the number of molecules occurs only through self-degradation. Therefore, the degradation rate for a given species of polymer, i, may be written as[3,5]

$$\ln(N_0/N_t)_i = k_i \cdot t \qquad (1)$$

where N_0 is the initial number of molecules; N_t, the number of molecules after a degradation time t, and k_i, the rate constant for this species.

We can consider a polymer sample chromatographed by SEC to be the sum of the fractions actually eluted at different retention volumes V_i. The chromatographic height at a certain elution volume is proportional to the weight concentration of the corresponding fraction so that the ratio of the number of the molecules $(N_0/N_t)_i$ in eq. (1) can be substituted with the ratio of the respective chromatographic heights $(h_0/h_t)_i$, resulting in

$$\ln(h_0/h_t)_i = k_i \cdot t \qquad (2)$$

where h_0 is the height of the chromatogram of the initial sample at V_i, and h_t, the height of the chromatogram of the degraded sample at the same retention volume.

This equation is valid as long as degradation products do not interfere with the measurements of chromatographic heights. As already mentioned, this is true only for the incipient portion of the chromatogram of the degraded sample.

The molecular weight dependence of the rate constant may be expressed as follows:

$$k_i = k \cdot (M_i)^n \qquad (3)$$

where k is a constant independent of the molecular weight, and n is a constant.

This formulation of (3) is consistent with mechanisms and kinetic expressions reported for sonic,[14] ultrasonic,[3-5] and high-speed stirring[2] degradation of polymers. Limiting molecular weight is not included, since we are concerned only with the very narrow (infinitesimal) fractions that undergo degradation and not with the whole polymer sample.

The calibration relationship, assumed to be linear, between MW and SEC retention volumes may be written as

$$\log(M_i) = A - B \cdot V_i \qquad (4)$$

where A and B are the intercept and the slope of the calibration curve, respectively.

Substituting eqs. (3) and (4) in eq. (2) and converting the resulted relation to the double (decimal) logarithmic form, we find

$$\log \log[(h_0/h_t)_i]$$
$$= \log(0.434 \cdot k \cdot t) + n \cdot A - n \cdot B \cdot V_i \qquad (5)$$

This equation is the basis of the method. Its application requires routine processing of the chromatograms, involving measurements of the chromatographic heights at constant volume increment, subtraction of the corresponding base-line values, and normalization of the resulted heights. Then, by plotting loglog$[(h_0/h_t)_i]$ vs. V_i, a linear dependence is obtained for the incipient portion of the chromatograms, followed by deviation from the linearity, due to the interference of degradation products.

The slope of the plot is $n \cdot B$ and the intercept is $\log(0.434 \cdot k \cdot t) + n \cdot A$. Least-squares regression can be used to calculate these parameters. Then, if the calibration relationship is known, the values of n and k may be derived.

Difficulties that may arise during the application of this method are related to the instrumental spreading of the chromatograms and chromatographic system stability. Corrections made by conventional methods[18-21] may distort the results. On the other hand, for broad MWD polymer samples, the spreading correction becomes less important. No attempt was made to correct the chromatograms for instrumental dispersion. Under these conditions, eq.

(5) may be applied only if the MWDs of the initial and final samples are close with respect to each other. This is achieved by slight or moderate degradation of broad MWD polymer samples. Thus, the corresponding SEC curves are similarly affected by the instrumental broadening, and, hence, on both the chromatograms, for a particular elution volume, V_i, one finds the same MW, M_i. Also, in this way, the change of the viscosity due to degradation will be minimum and its effect[14] on the rate of the process may be neglected.

Without spreading corrections, the value of the slope of the real calibration line may be slightly different from that determined by the peak position method. This depends on the polidispersities of the samples. If the spreading function is symmetrical and constant within the MW range of the chromatograms (assumptions often used to make corrections for the instrumental spreading[19-21]), the corresponding value of B is similar to that which resulted using the "effective calibration line" method.[18]

Flow-rate stability is very important for the accuracy of determinations and may be quite a critical factor, especially in the case of the narrow samples.

EXPERIMENTAL

To check the method, different MWD polystyrene samples were subjected to sonic degradation: two narrow standards from Pierce Chemical Co. (Rockford, IL), with reported MW values of 233,000 (**I**) and 600,000 (**II**), and a broad MWD industrial polystyrene (**III**).

Degradation was carried out in a Raytheon DF 101 sonic oscillator operating at 10 kc; 40 mL of 0.3% w/v polymer solutions in toluene was used, thermostated during degradation at 30°C. After different irradiation times, 1.5 mL was withdrawn and chromatographed.

SEC was performed using a Gilson HPLC system equipped with a differential refractive index detector and controlled by the GME-712 HPLC System Controller Software, the flow rate being automatically compensated for by compressibility of the solvent. The separation was performed on a kit of two Zorbax PSM-S bimodal columns. Sample concentration was 0.3% w/v. The mobile phase was tetrahydrofuran at a flow rate of 1 mL/min. The recording of the chromatograms was started by a position sensing switch, mounted on the Rheodyne 7125 injection valve, and the reproducibility of the chromatograms was tested by successive injection

of the same narrow polystyrene standard. No significant differences were observed between the peak positions of the chromatograms.

Chromatograms were taken over to a spreadsheet software, as h_i-V_i pairs, and were processed therein. Regression calculations on the $\log\log(h_0/h_t)$ vs. V_i plot were performed by excluding some values at the beginning of chromatograms, affected by noises or whether complete degradation of the fraction had occurred. The other values were considered until a deviation from linearity could be observed.

SEC calibration was made using polystyrene standards from DuPont Instruments. The calibration curve for the column set is linear within the range of 10^2–10^6 MW units (corresponding to polystyrene). Its parameters were A = 11.404 and B = 0.869, with a linear correlation coefficient, r = −0.999.

RESULTS AND DISCUSSION

The degradation of the three polymer samples illustrated by some SEC chromatograms is presented in Figures 1–3. A distinct second peak, corresponding to degradation products, appears as a result of sonic degradation of polymer **I**. The maximum of this peak is detected about the half MW value of the original polymer, as expected. In the case of polymer **II**, the peak of the degradation products is less distinct since macromolecules undergo repeated degradation due to higher initial MW. Also, as Figures 1 and 2 show, the two polymer samples have different initial polydispersities. Polymer **III** has a
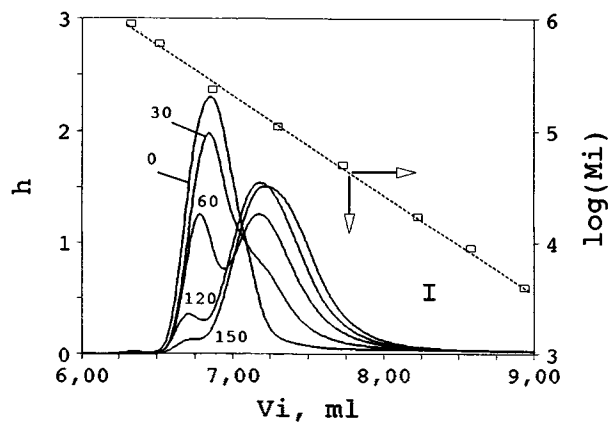

Figure 1 SEC chromatograms illustrating sonic degradation of polymer **I** as a function of irradiation time, in minutes, as specified on each curve. The dotted line represents the polystyrene peak position calibration curve.
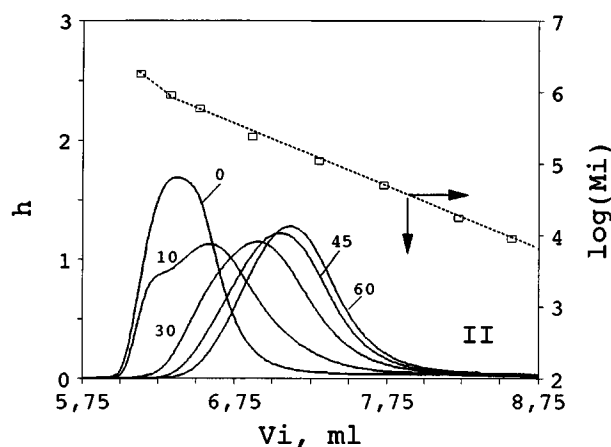
Figure 2 SEC chromatograms illustrating sonic degradation of polymer **II**.

Figure 4 Plot of $\log\log(h_0/h_t)_i$ vs. V_i corresponding to SEC chromatograms of samples that resulted from sonication of polymer **II** for 45 and 60 min, respectively.

large MWD that becomes narrower with the increase of sonic irradiation time.

Samples with broad MWD were obtained in the case of polymer **III**, by moderate degradation, and in the case of polymer **II**, after a degradation time longer than 30 min. The above-described approach was applied to samples that resulted from successive degradation. In each determination, the sample degraded a shorter time was considered as the starting sample. In these cases, the values that resulted for the slope of the linear portion of the $\log\log(h_0/h_t)_i$ vs. V_i plot were very close to $2 \cdot B$. Typical results are presented in Figures 4 and 5. It follows from this that $n = 2$. This value agrees with the results reported by Thomas,[14] who determined the MW dependence of the initial rates of sonic degradation for many polymer fractions. As expected, greater values
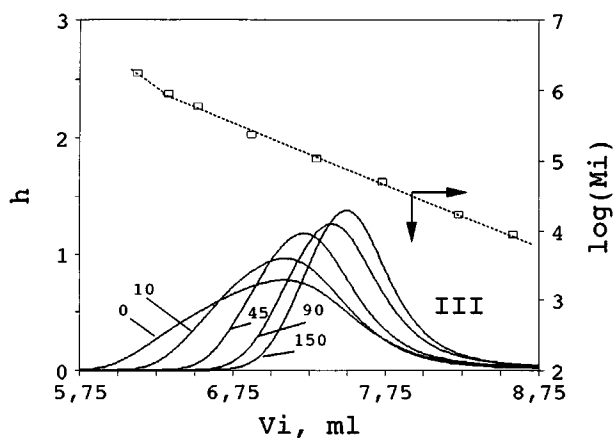
than $2 \cdot B$ were observed in the range of MW outside the linear domain of calibration.

An attempt was made to apply the method in the case of narrow MWD polymers using two chromatograms of relatively similar MWD samples (Fig. 6). The value of the slope was much lower than $2 \cdot B$. This result emphasizes the great importance of the instrumental spreading in the case of narrow MWD samples.

By long-time degradation of polymer **III**, narrower polystyrene samples were obtained. By applying eq. (5) to chromatograms of such samples, it was observed that the value of the slope diminishes with the reduction of the polydispersity. A slight decrease of the extent of the linear range was also noticed.

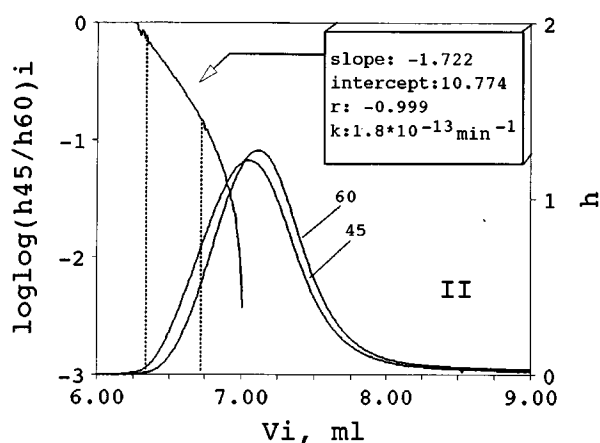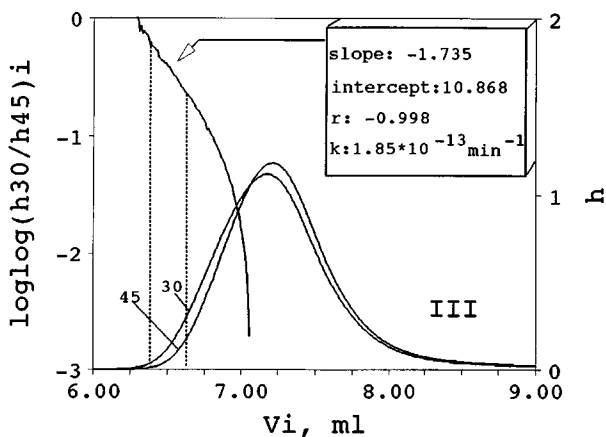**Figure 3** SEC chromatograms illustrating sonic degradation of polymer **III**.

Figure 5 Plot of $\log\log(h_0/h_t)_i$ vs. V_i corresponding to SEC chromatograms of samples resulted from sonication of polymer **III** for 30 and 45 min, respectively.
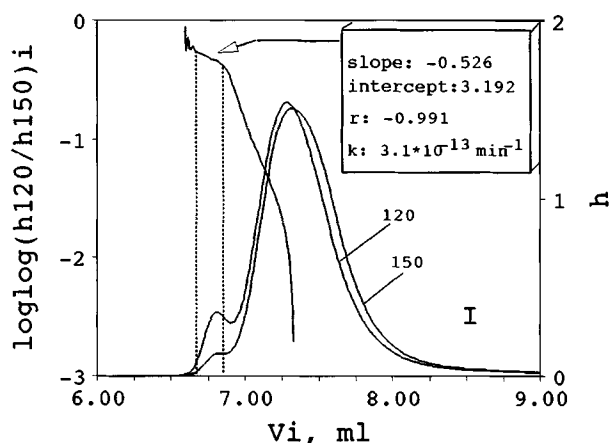
Figure 6 Plot of loglog$(h_0/h_t)_i$ vs. V_i corresponding to SEC chromatograms of samples that resulted from sonication of polymer **I** for 120 and 150 min, respectively.

Knowing the n value, as obtained for broad MWD polystyrene samples, it is possible to determine the slope of the calibration line for any polymer type. The value thus determined is considered similar to the slope obtained by the "effective linear calibration" method. As an immediate application of this approach, one can obtain the polydispersities of unknown polymer samples (see Appendix I), using the slope derived as it was described. The method requires neither calibration nor dispersion correction.

To determine accurately the rate constant, the value of the intercept of the SEC calibration line must be adjusted, taking into account the slope derived by this method for each sample pair. It was shown[19] that the effective calibration line rotates counterclockwise relative to the peak position calibration line about an anchor point located near the average retention volume of a polydisperse sample. Therefore, assuming symmetrical and constant spreading, these two calibration lines intersect each other at the average retention volume. From these considerations, the effective calibration line can be derived:

$$\log(M_i) = A' - B' \cdot V_i$$

where B' is derived from the slope of the plot of eq. (5) and A' is obtained from the intersection of this line with the peak position calibration line (the method uses two chromatograms with close average retention volumes). It is obvious that for each pair of chromatograms there is a different "effective" calibration line.

The rate constant, k (MW independent), was calculated for different samples from the intercepts of the plots of eq. (5) using instead of A (narrow standards calibration) the corrected values, A' (effective calibration). The k values obtained for the broad samples resulted by the degradation of polymers **II** and **III** are in the range 1.7–$1.8 \cdot 10^{-13} \, \text{min}^{-1}$. Figure 6 shows that the rate constant obtained for the narrow MWD samples is higher, to a certain extent, than those derived for the broad samples. The same applies for the pair of the samples that resulted from polymer **III** by degradation for, respectively, 120 and 150 min. These could be explained by the influence of viscosity on the rate constant, but in this case, the accuracy of the determination of A' is lower (due to the greater difference between B and B').

To estimate the accuracy of the method, the value of the rate constant (independent of degree of polymerization, k_i/p_i^2) was determined from data reported by Thomas[14] and converted to k (k_i/M_i^2), resulting in $k = 4.6 \cdot 10^{-13} \, \text{min}^{-1}$. This is in good agreement with the values mentioned above, despite the differences between the methods.

The rate constant, k, is influenced only by degradation conditions and polymer structure and not by the MWD of the samples. Therefore, its value characterizes the stability of the polymer structure to mechanical degradation. Stability to mechanical degradation of different polymers may be compared rapidly by their rate constants provided that the samples are degraded in the same conditions.

In Figures 4–6, the dotted lines frame the linear portion of the plot of loglog$(h_0/h_t)_i$ vs. V_i. For polymers **II** and **III**, the extent of this domain is about 0.4–0.5 mL (including also the noisy beginning part). Excellent linear correlation is found in these cases (see the values of the correlation coefficient, r) and, generally, for broad samples. The linear part of the plot in Figure 6 is much shorter owing to the lower polydispersity and, especially, to the change in instrumental spreading at the limit between the narrow (undegraded original polymer) and broader (degradation products) fractions of the two samples.

As was shown, the MWD profiles of the samples must be close in respect to each other in order to minimize the effect of instrumental spreading on the accuracy of the determinations. However, the use of two very close chromatograms may result in a decrease of the correlation coefficient of the plot of eq. (5). This can be explained by the influence of base-line noises on the h_0/h_t ratio since the difference between h_0 and h_t values become comparable with the level of the noises. Therefore, more samples with close MWD must be obtained by progressive degradation of a broad MWD starting polymer.

Then, the analysis of more chromatograms in pairs indicates the optimum to be considered.

As regards other polymers than polystyrene, SEC calibration is not a critical problem of this approach. A rapid method for the determination of Mark–Houwink constants was reported by Price et al.[22] This method uses samples with different average MW that resulted from a single sample by sonication and requires the determination of the intrinsic viscosities and the universal calibration.[23]

On the other hand, new ways to calibrate the chromatographic system arise, using the slope of the calibration line derived in this approach in combination with (a) an average molecular weight of the unknown polymer or (b) an intrinsic viscosity and the universal calibration:

(a) Using, e.g., the number-average molecular weight (obtained by osmometry) of a broad sample and the corresponding slope of the MW calibration, derived by our approach for this sample, the intercept of the calibration line can be determined (see Appendix II). In this way, there is no need of previous calibration of the chromatographic system with polystyrene standards.

(b) Using the universal calibration, the slope of the MW calibration derived by our method and the intrinsic viscosity of an unknown polymer sample, the intercept of the MW calibration can be calculated (see Appendix III).

Certainly, the accuracy of these calibration techniques needs to be tested, this being beyond the scope of this article.

CONCLUSIONS

The degradation rate of infinitesimal polymer fractions can be expressed in terms of the heights of the SEC chromatograms of the original and degraded samples. This is true for the incipient part of the chromatograms, corresponding to the high MW range.

This approach allows the rate constant (MW independent) and the variation in the rate constant with MW to be determined. Next, the slope of an "effective" calibration line may be derived for any polymer sample. This can be used to determine polydispersity, without SEC calibration.

By this method, the rate constant of the sonic degradation of polystyrene was found to vary with

the square of the MW. The values of the rate constant of this process are in good agreement with data obtained by other investigations.

APPENDIX I

The polydispersity, d, is usually expressed as a ratio of the weight-average molecular weight, M_w, to the number-average molecular weight, M_n:

$$d = M_w/M_n \qquad (AI.1)$$

$$M_w = \sum_i h_i M_i \Big/ \sum_i h_i \qquad (AI.2)$$

$$M_n = \sum_i h_i \Big/ \sum_i h_i/M_i \qquad (AI.3)$$

Substituting eq. (AI.2) and (AI.3) in eq. (AI.1) and then substituting M_i from the calibration line [eq. (4) in the text], we write the polydispersity as

$$d = \left[\sum_i h_i \cdot \exp(-B \cdot V_i)\right]\left[\sum_i h_i \Big/ \exp(-B \cdot V_i)\right]\Big/$$

$$\left(\sum_i h_i\right) \qquad (AI.4)$$

Taking into account that the slope of the calibration, B, is an "effective" slope, it corrects for band-broadening.

APPENDIX II

Substituting eq. (4) from the text into eq. (AI.3), we obtain

$$A = \log\left[M_n \Big/ \left(\sum_i h_i \Big/ \sum_i h_i/10^{-B \cdot V_i}\right)\right] \qquad (AII.1)$$

APPENDIX III

We consider the following calibration relationships:

(a) The universal calibration:

$$\log M_i \cdot [\eta]_i = U1 - U2 \cdot V_i, \qquad (AIII.1)$$

where $[\eta]_i$ is the intrinsic viscosity of the infinitesimal fraction i, and $U1$ and $U2$, the intercept and the slope of the universal calibration line, respectively.

(b) The MW calibration line of the unknown polymer [eq. (4) in the text].

(c) The [η] calibration line of the unknown polymer:

$$\log[\eta]_i = C - D \cdot V_i \qquad \text{(AIII.2)}$$

where C and D are the intercept and the slope of the [η] calibration line, respectively.

The intrinsic viscosity of a polydisperse sample may be expressed as

$$[\eta] = \sum_i h_i \cdot [\eta]_i \qquad \text{(AIII.3)}$$

or substituting eq. (AIII.2) into eq. (AIII.3), we obtain

$$[\eta] = 10^C \cdot \sum_i h_i \cdot 10^{-D \cdot V_i} \qquad \text{(AIII.4)}$$

The slope of the MW calibration of the unknown polymer, B, is obtained by the method in discussion for a broad MWD sample. Subtracting B from the slope of the universal calibration, $U1$, we obtain the slope of the [η] calibration, D. Using D and the intrinsic viscosity of the sample, the parameter C is derived:

$$C = \log\left([\eta] \middle/ \sum_i h_i \cdot 10^{-D \cdot V_i}\right) \qquad \text{(AIII.5)}$$

It is expected that the accuracy of the determination is affected by the instrumental band broadening effect of the SEC elution curve used to compute the value of C. A correction method may be taken into account.

Further, the intercept of the MW calibration, A, is calculated subtracting the intercept of [η] calibration, C, from the intercept of the universal calibration, $U1$.

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