Quantitative Size Exclusion Chromatography of Polypropylene I: Method Development

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Synopsis

Polypropylene was analyzed by size exclusion chromatography (SEC) at 145°C using a single-differential refractometer detector. The objective was to provide data for characterization of polypropylene degradation during a reactive extrusion process. Two antioxidants [tetrakis (methylene (3,5-di-*tert*-butyl-4-hydroxyhydrocinnamate)) methane (I) and octadecyl 3,5-di-*tert*-butyl-4-hydroxyhydro cinnamate (II)] were tested for their ability to prevent thermal degradation of the polypropylene during sample preparation. The use of 0.20 wt% of (I) was effective during the 36–48 h required to completely dissolve the samples in trichlorobenzene for SEC analysis. "Reshaping" of the chromatograms by resolution correction demonstrated that, while the molecular weight averages were changed by 8% because of axial dispersion, most of the individual heights of the distributions were changed by less then 2%. Tail heights of the distributions were more affected but were also shown to be highly imprecise. Selecting individual heights of the distributions rather than molecular weight averages therefore minimized axial dispersion error and also circumvented errors in molecular weight averages originating from dilution of distribution tails below detector sensitivity limits. Various forms of distributions were examined and the equations linking the chain length distribution predicted by polymerization kinetic models to the SEC chromatogram are presented. The analytical method developed provided precise data for kinetic modeling. However, absolute accuracy requires further assessment.

INTRODUCTION

The flow properties of commodity polypropylene are improved by intentionally degrading the polymer in an extruder.[1-3] Other papers described the effect of processing variables[2,3] and showed the development of a kinetic model[4,5] for this reactive extrusion process. All of this work strongly depended upon measurement of polypropylene molecular weight distributions by size exclusion chromatography (SEC) at high temperature (145°C).

Room temperature SEC with organic solvents is now widely considered a reliable analytic method for many polymers. However, it is continually evolving as new packings, detectors, and computer software are introduced. Many options are available. High temperature SEC is subject to the same developments. However, in contrast to the room temperature analysis, high temperature SEC must contend with serious problems of sample and column packing degradation. Even data reproducibility remains a subject of research.[6,7] Furthermore, the problem of analyzing polymers with a high molecular weight tail is a particularly difficult one. Recent work[8] proposed that the most

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commonly used SEC system, SEC with a single differential refractometer, was inadequate for this task.

This article shows the development of the method used to analyze polypropylene for the reactive extrusion study. A high temperature SEC equipped with only a differential refractometer detector was utilized. A following paper[9] shows our efforts to further test and improve the analysis method along with the consequences to the results of the reactive extrusion study.

THEORY

Sample Preparation

Polyolefins can be very difficult to completely dissolve and at the same time very sensitive to thermal degradation. Recently, Utracki and Dumoulin[6] found that dissolving polyethylene required heating in an oven at 165°C for 1.5 h followed by 2.5 h in the SEC injection chamber at 135°C. Less time resulted in insufficient dissolution. Two antioxidants were added to the mobile phase of the chromatograph and this mobile phase was used to dissolve the samples. Absence of the antioxidants resulted in degradation. Samples dissolved using times greater than 68 h showed molecular weight averages which increased with dissolution time.

Grinshpun et al.[10] attributed dissolution difficulties in polyethylene to the presence of stable aggregates. Using low-angle laser light scattering (LALLS), they derived two criteria for detecting when dissolution was complete: the absence of spikes in the chromatogram obtained from the LALLS and a value of the second virial coefficient which agreed with theoretically predicted values. Sample preparation involved addition of an antioxidant to the trichlorobenzene solution and heating in an oven at 145°C for two hours followed by heating at 160°C for one hour.

Earlier publications on polypropylene analysis by high temperature SEC[11-13] do mention the addition of antioxidants to the mobile phase to prevent degradation but make no comment on dissolution difficulties. Grinshpun and Rudin[14] considered that stable aggregates were a problem for polypropylene as they were for polyethylene, but determined that their method for sample preparation of the latter could not be directly applied to the former. Polypropylene solutions so treated plugged the SEC system or resulted in discolored solutions. Instead, they found that a "window" of dissolution times at 30–50 h at 145°C for stabilized solutions permitted aggregate-free solutions to be obtained without degradation. This window was defined by examining molecular weight averages along with the second virial coefficient. The same LALLS-based criteria for aggregate-free solutions were used as with polyethylene.

Shear and thermal degradation are the other major concerns for polypropylene analysis by high temperature SEC. From a review by Barth and Carlin[15] and recent work by McIntyre et al.,[16] it appears likely that shear degradation for molecular weights below several million is negligible under normal operating conditions. However, there are so many variables that shear degradation is always a possibility for high molecular weights. Without molecular weight detectors (such as LALLS), probably the most reasonable

way of checking for such degradation is to inspect the polystyrene calibration curve for unexpected deviations and to compare molecular weight averages of standards with known values.

Thermal degradation of the polymer as it passes through the SEC is also possible. Many workers attempt to prevent it by adding antioxidants to the mobile phase.[6,11-13] However, some add them only to the sample solution.[14]

Detection

This study employed only a single-differential refractometer as detector. Grinshpun et al.[8] recently pointed out that, alone, such a detector is inadequate for SEC analysis of polyethylene. The reason for their conclusion was that, for some samples, the molecular weight averages can be highly dependent upon a long distribution "tail." This tail is diluted to such an extent in the SEC that it becomes invisible to the detector and inaccurate molecular weight averages result. Increasing injected sample concentration is ineffective because it causes resolution problems. Grinshpun and co-workers were concerned mainly with the high molecular weight end and the weight-average molecular weight ($\overline{M}_w$) or higher averages. However, an analogous situation could exist for the low molecular weight end and number-average molecular weight ($\overline{M}_n$). Also, of course, the problem could exist with polypropylene or other polymers as well as polyethylene.

One way of attempting to avoid this problem is to utilize heights of the chromatogram (i.e., ordinates of the molecular weight distribution) directly instead of molecular weight averages. One assumption in this approach is that the concentration of molecules which the detector is unable to see is too small to significantly affect the concentration of the detected molecules. Considering that all but a very tiny fraction of the polymer can be detected, this assumption is likely valid. Another assumption is that a useful characterization of the reactive extrusion process can be obtained despite our limited view of the polymer. Whether this assumption is true or not depends upon the influence of undetected molecules on the degradation kinetics. Also, more pragmatically, it depends on whether or not the conclusions obtained regarding required process conditions to produce a given product will be accurate. Considering that the very high molecular weights will be most subject to degradation and that their concentrations are very low, it is likely that the second assumption will be valid and a useful characterization of the process will result.

To utilize the ordinates of the molecular weight distribution rather than the averages, the SEC chromatogram is first normalized by dividing each height ($W(t)$) by the total area under the chromatogram:

$$W_N(t) = \frac{W(t)}{\int_0^\infty W(t)\,dt} \tag{1}$$

Because normalized chromatograms ($W_N(t)$ versus t) are all of the unit area,

they are often used to inspect sample to sample variations. However, they are insufficient for the kinetic model development application.

The abscissa of the molecular weight distribution that best suits SEC is the logarithm of molecular weight (log M). The ordinate of the normalized distribution [symbolized by W_N (log M)] is calculated from:

$$W_N(\log \mathrm{M}) = -W_N(t)\frac{dt}{d(\log \mathrm{M})} \tag{2}$$

where $W_N(\log \mathrm{M})\ d\ \log \mathrm{M}$ is the weight fraction of polymer with log (molecular weight) between log M and log M + d log M. Note that it is incorrect to simply change the abscissa of the normalized chromatogram to log M. The new ordinate value given by Eq. (2) must be calculated and the curve plotted as $W_N(\log \mathrm{M})$ versus log M. Otherwise, the curves can be quite misleading.

Typically, kinetic models can readily be made to provide predictions of $[P_r]$ versus r, where r is chain length (i.e., molecular weight divided by the monomer molecular weight) and $[P_r]\ dr$ is the concentration of polymer (i.e., mol/L of polymer) of chain length r between chain lengths r and $r + dr$.

The relationship between this "chain length" distribution and the molecular weight distribution just described is given by:

$$[P_r] = \frac{\rho_P}{2.303\ m_o r^2} W_N(\log \mathrm{M}) \tag{3}$$

where ρ_P is the density of the polymer and m_o is the monomer molecular weight.

Equations (1) to (3) link the output of the kinetic model to the SEC chromatogram through the molecular weight distribution.

Calibration

Universal calibration employing hydrodynamic volume is now well established and has been shown to be valid for polypropylene.[13] Although it is customary to simply plot the product of intrinsic viscosity $[\eta]$ and molecular weight M as "hydrodynamic volume", more rigorously, hydrodynamic volume, V_∞, is given by[17]:

$$V_\infty = \frac{4\pi[\eta]M}{9.3 \times 10^{24}} \tag{4}$$

Equation (4) assumes that the polymer is present at infinite dilution. It is now well known that this assumption is questionable for narrow standards because they are not significantly diluted in their passage through the SEC. However, correcting for this effect remains an active area of research. Rudin and Wagner[17] have developed a concentration correction model which provides a corrected value of hydrodynamic volume for narrow standards. "Broad" molecular weight distribution samples are assumed to be at infinite dilution. There are many other methods.[18] Also, the distinction between narrow and

broad molecular weight distribution samples requires some attention. In this paper, no concentration correction was attempted. A following paper will apply the Rudin model and see the effect on the kinetic model results.

Resolution Correction

There were three fundamental approaches available in this work for overcoming the "imperfect resolution" of SEC: experimentally improving resolution via better column packings and SEC operating conditions; selection of properties of the chromatogram which are least affected by axial dispersion; and resolution correction.

With regards to the first mentioned approach, only one set of columns and SEC operating conditions were employed. Others were examined later.[9] Use of chromatogram heights rather than molecular weight averages is in agreement with the second approach: selection of properties of the chromatogram least affected by axial dispersion.[19-20] For "broad" chromatograms, heights are much less affected by axial dispersion than are molecular weight averages. This result is attributed to the loss in concentration of one molecular weight at a particular retention time being compensated for by the gain in concentration from the molecular weights of its neighbors.

The third primary option is "resolution correction": computational enhancement of resolution. Whether the chromatogram is "reshaped" or a correction factor is applied directly to the averages, the main difficulty here is determination of the shape of the chromatogram of a truly monodisperse standard. This shape may be a function of concentration.

In this paper, resolution correction is done only to provide an estimate of the error involved in using chromatogram heights without resolution correction. For this purpose, Method II of Ishige et al.[21,22] was used to reshape the raw chromatogram assuming a Gaussian spreading function and variance values compatible with the differences between SEC molecular weight averages for narrow standards and their known values.

EXPERIMENTAL

A Waters model 150C high temperature size exclusion chromatograph was used with 1,2,4-trichlorobenzene (TCB) at 145°C as the mobile phase at 1 mL/min, and 3 Polymer Laboratories Ltd. (Amherst, MA) columns (PL-Gel 10-μm particle size, 30 × .75 cm; 1×10^6, 1×10^4, 500 Å pore size). Data were collected by an Apple IIe microcomputer (with an ADALAB card, Mandel Scientific, Rockwood, ON) and transferred to a PC-compatible microcomputer equipped with a plotter (Hewlett Packard Colorpro) for final processing. For calibration and resolution assessment, TSK "monodisperse" polystyrene standards (Toyo Soda Manufacturing Co., Ltd., Tokyo, Japan) were used. Polystyrene sample preparation involved room temperature dissolution for less than 24 h in TCB at various concentrations, but most often at 0.10 wt% (200 μL). 0.20 wt% antioxidant [tetrakis(methylene (3,5-di-*tert*-butyl-4-hydroxyhydrocinnamate)] methane (Irganox 1010, Ciba-Geigy, Mississauga, Ontario) was added to most samples.

Polypropylene samples included the feed to the extruder (Himont, PD 888, Mississauga, Ontario) and the extrudate degraded using various concentra-

tions of free radical initiator injected into the extruder.[2,3] Initially, antioxidant was added to the mobile phase of the SEC. However, this was considered a probable cause of persistent baseline drift encountered during start-up of the SEC and was discontinued. Thereafter, antioxidant was added only to the sample solution.

To determine the type of antioxidant and the concentration to be used in sample preparation, polypropylene samples of 0.20 wt% were prepared with antioxidant concentrations of 0.05, 0.10, and 0.20 wt%. Dissolution of samples were carried out at 145°C with total oven times of 16, 24, 32, 40, and 48 h. Two phenolic antioxidants, Irganox 1010 and octadecyl 3,5-di-*tert*-butyl-4-hydroxyhydro cinnamate (Irganox 1076, Ciba-Geigy, Mississauga, Ontario) were investigated.

From monitoring impurity and stabilizer peak positions as internal standards, it was determined that no flow rate correction was necessary.

COMPUTATIONAL

The universal calibration curve was calculated using the following Mark Houwink constants: 1.21×10^{-2} cm^3/g and 0.707 for the "K" and "a", respectively of polystyrene; 1.37×10^{-2} cm^3/g and 0.750 for polypropylene.[11,23] This curve was fit to a cubic polynomial by linear regression. The polynomial was then used with the Mark Houwink constants for polypropylene to generate the required calibration curve.

This approach was taken in order to allow concentration correction as a convenient option later.[9] The alternative approach involving first fitting the polystyrene molecular weight calibration curve gave identical results when no concentration correction was involved. The normalized chromatogram [Eq. (1)] and the molecular weight distribution [$W_N(\log M)$ versus log M, Eq. (2)] were calculated for each polypropylene sample. Molecular weight averages were also calculated. No resolution correction method was employed. However, as mentioned above, it was the distribution ordinates themselves (W_N (log M) or [P_r]) which were matched by the engineering model of the process and not the molecular weight averages.[4,5]

RESULTS AND DISCUSSION

Figure 1 shows the molecular weight averages of narrow polystyrene standards plotted against the values known for these standards. Agreement in both $\overline{M}_n$ and $\overline{M}_w$ is quite good up to a molecular weight of 3×10^6. Figure 2 shows the molecular weight calibration curves for polystyrene and for polypropylene (from the universal calibration curve).

Figures 3 and 4 show chromatograms obtained for PD 888 at various sample preparation times with 0.05, 0.10, and 0.20 wt% Irganox 1010 and 1076, respectively. In each case, the chromatograms clearly show when degradation increased with dissolution time. Concentration was a much more critical variable when Irganox 1076 was used instead of Irganox 1010. Samples dissolved for less than 24 h caused an immediate distinct pressure pulse when injected into the SEC. This was attributed to the presence of undissolved aggregates. As a consequence of these results, all subsequent analyses of polypropylene were done using a sample solution containing 0.2 wt% of

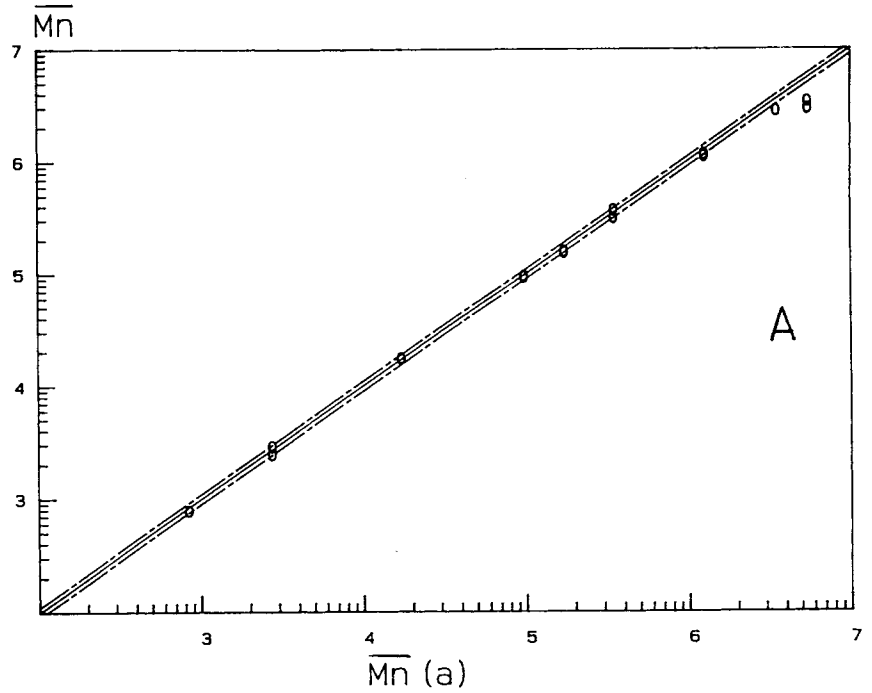

Fig. 1A. SEC Number-average molecular weight values ($\overline{M}_n$) versus corresponding absolute values for standards [$M_n(a)$]: System I. (Dashed lines bracketing diagonal indicate $\pm 10\%$ limits.)

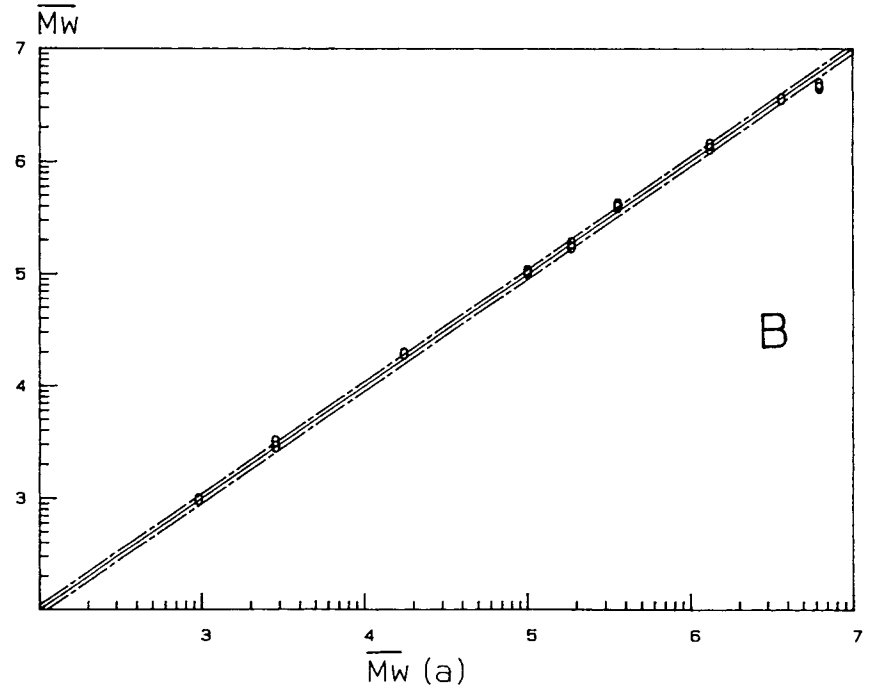

Fig. 1B. SEC Weight-average molecular weight values ($\overline{M}_w$) versus corresponding absolute values for standards [$M_w(a)$]: System I. (Dashed lines bracketing diagonal indicate $\pm 10\%$ limits.)

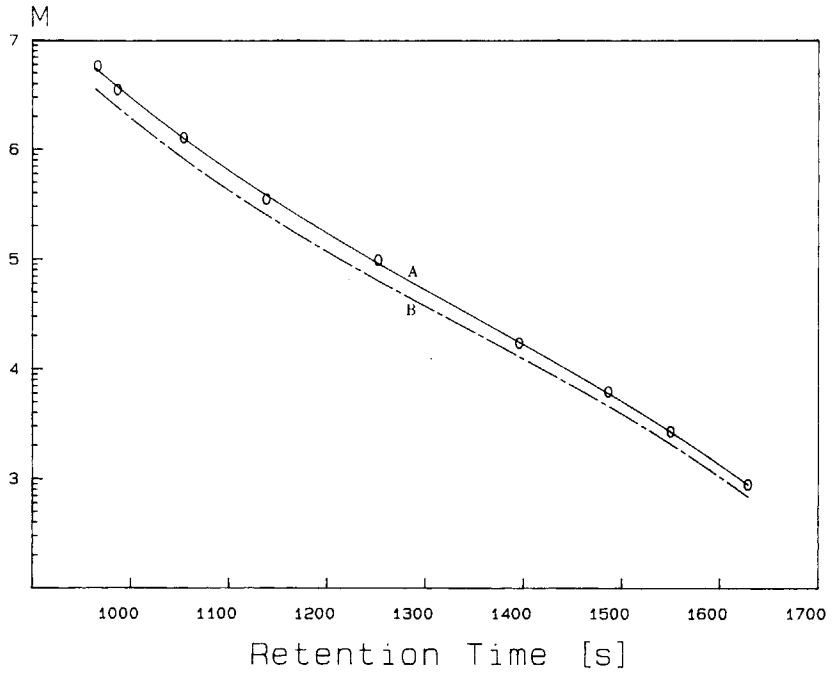

Fig. 2. Molecular weight calibration curves: polystyrene (A); polypropylene (B).

Irganox 1010 and a dissolution time of 36 to 48 h at 145°C including at least 3 h in the SEC injection chamber just previous to injection.

Figure 5 shows the results of a reproducibility study of the extrusion process, sampling procedure, and SEC analysis together (not the SEC analysis alone). Standard deviations of the ordinates of the molecular weight distribution divided by the ordinate and plotted versus log M are shown. The standard deviations were determined by calculating the sum of squares of the deviations from the mean for the ordinate values at each molecular weight and dividing this value by one less than the number of values (i.e., 5). Reproducibility is better than 5% except at the extreme tails of the distributions. Analogous values for $\overline{M}_n$ and $\overline{M}_w$ were 1.5% and 3.0%, respectively. It was important to the modeling work to realize that the variances in Figure 5 were not proportional to the magnitude of the ordinate. This was shown in Figure 3 in Ref. 5 where these standard deviations were plotted versus $[P_r]$.

Figure 6 shows the variation of molecular weight distribution obtained as a result of resolution correction for different degrees of axial dispersion. Method II of Ishige et al.[21,22] was applied assuming a Gaussian-shape function for the chromatogram of a truly monodisperse sample with standard deviations of 1.2 mL and 2.1 mL corresponding, respectively, to 8% and 25% errors in both $\overline{M}_n$ and $\overline{M}_w$. As expected, the corrected distributions are slightly narrower than the uncorrected curve. Also, shown are the seven height points used in fitting the kinetic model to the data. Considering that error in molecular weight averages was less than 8%, axial dispersion apparently introduced an error of less than 2% into six of the seven height values

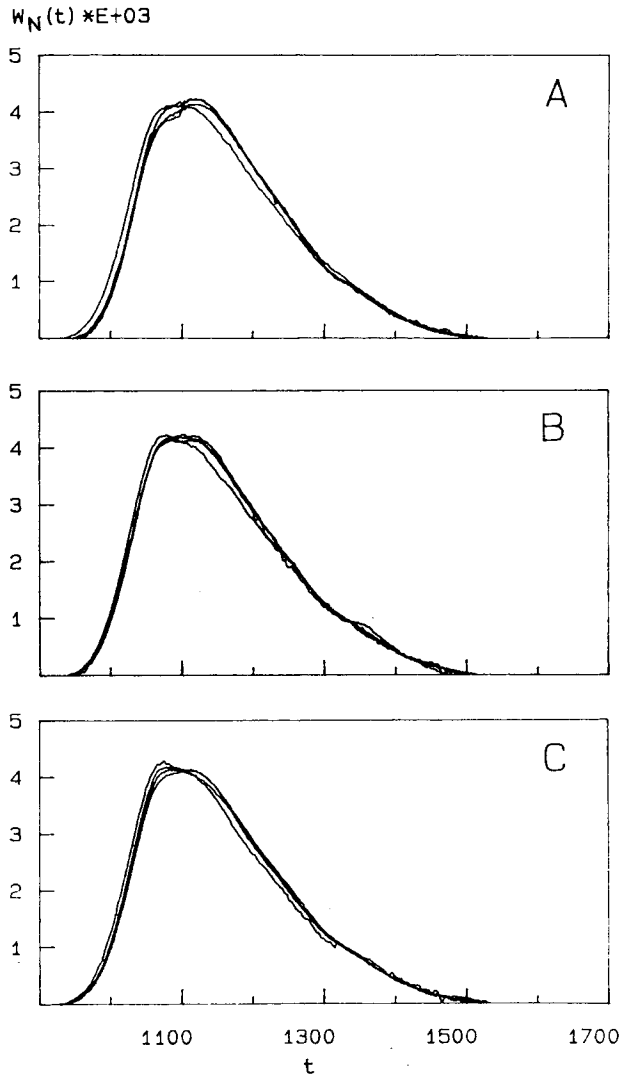

Fig. 3. Normalized SEC chromatograms showing the effect of concentration of Irganox 1010 and dissolution time: A. 0.05 wt%; B. 0.10 wt%; C. 0.20 wt%. Dissolution times are 24, 32, 40, and 48 h, respectively, for each chromatogram with the longest time showing the most degradation.

used. The seventh height, corresponding to a molecular weight of 2.24×10^6, was changed by 15%. However, this height, being at the tail of the distribution, was also of very low precision, and therefore was not weighted heavily in the fitting process.

Figures 7 to 10 show the changes in molecular weight during reactive extrusion as shown in four different ways using the same SEC data: a normalized chromatogram ($W_N(t)$ versus t); a chain length distribution ($[P_r]$ versus r); an incorrectly calculated molecular weight distribution ($W_N(t)$ versus log M); and a correctly calculated molecular weight distribution (W_N (log M) versus log M).

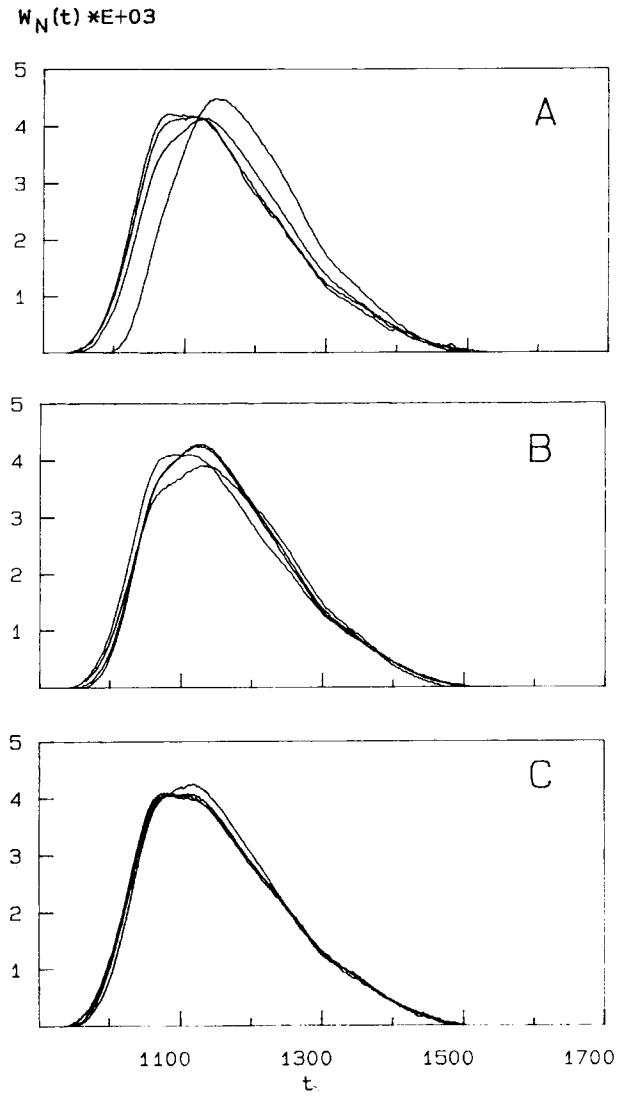

Fig. 4. Normalized SEC chromatograms showing the effect of concentration of Irganox 1076 and dissolution time: A. 0.05 wt%; B. 0.10 wt%; C. 0.20 wt%. Dissolution times are 24, 32, 40, and 48 h, respectively, for each chromatogram with the longest time showing the most degradation.

There are several points to note:

1. The correctly calculated molecular weight distribution (Fig. 10) closely resembles the normalized chromatogram.
2. The incorrectly calculated molecular weight distribution (Fig. 9) causes the high molecular weight tail of the distribution to appear more pronounced than it really is.
3. The chain length distribution (Fig. 8) causes the higher molecular weights to appear negligible in concentration although they appear significant in the molecular weight distribution.

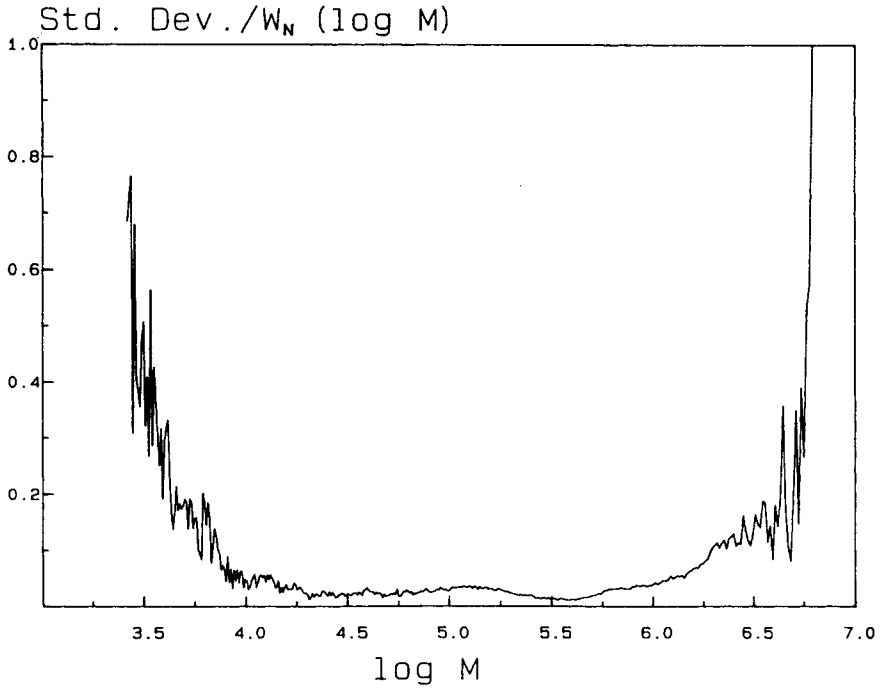

Fig. 5. Ratio of the error standard deviation to the distribution height versus the logarithm of molecular weight.

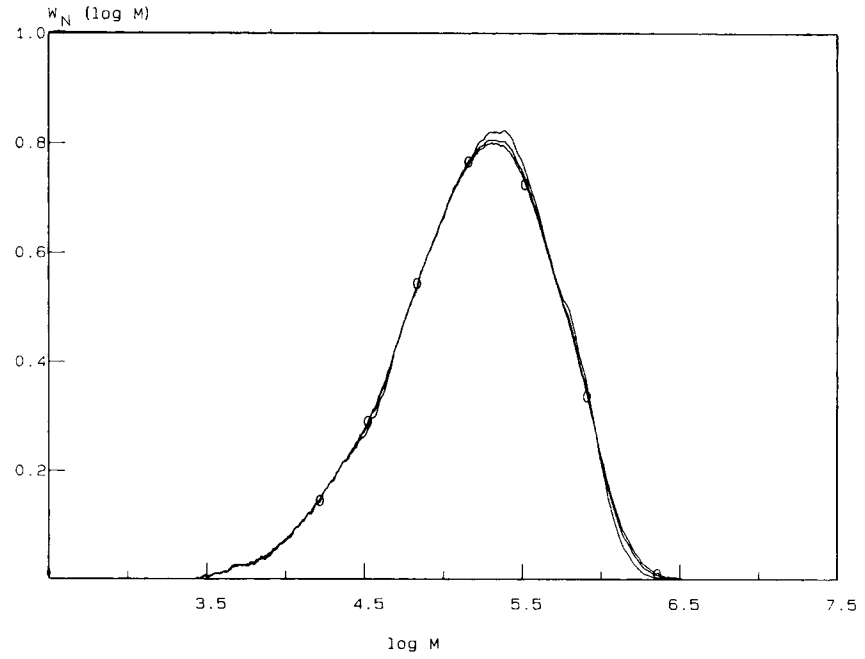

Fig. 6. Effect of resolution correction on the measured molecular weight distribution: (A) correction corresponding to a 8% correction in $\bar{M}_w$, (B) correction corresponding to a 25% change in $\bar{M}_w$.

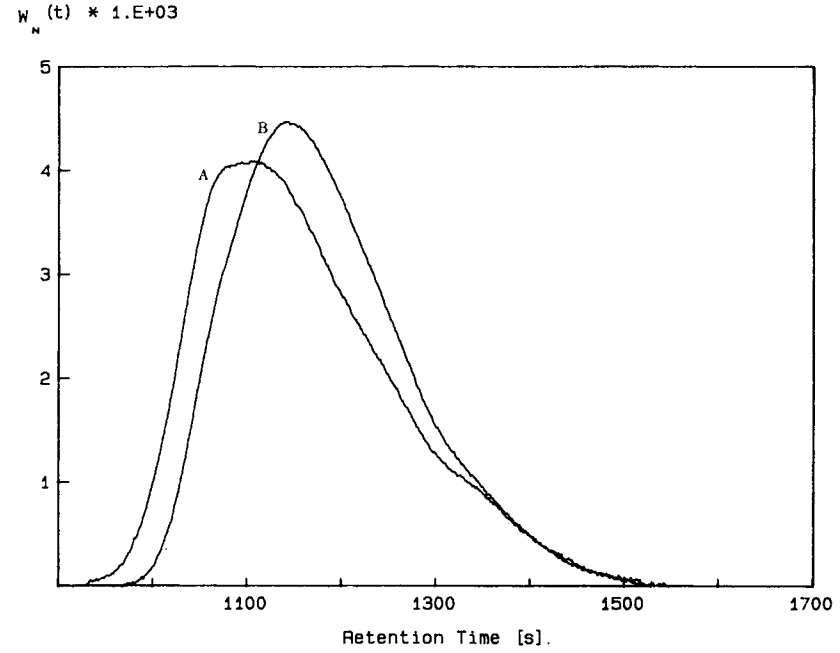

Fig. 7. Molecular weight changes during reactive extrusion of polypropylene: normalized SEC chromatograms of extrudate at 0.00 wt% initiator (A) and at 0.04 wt% initiator (B).

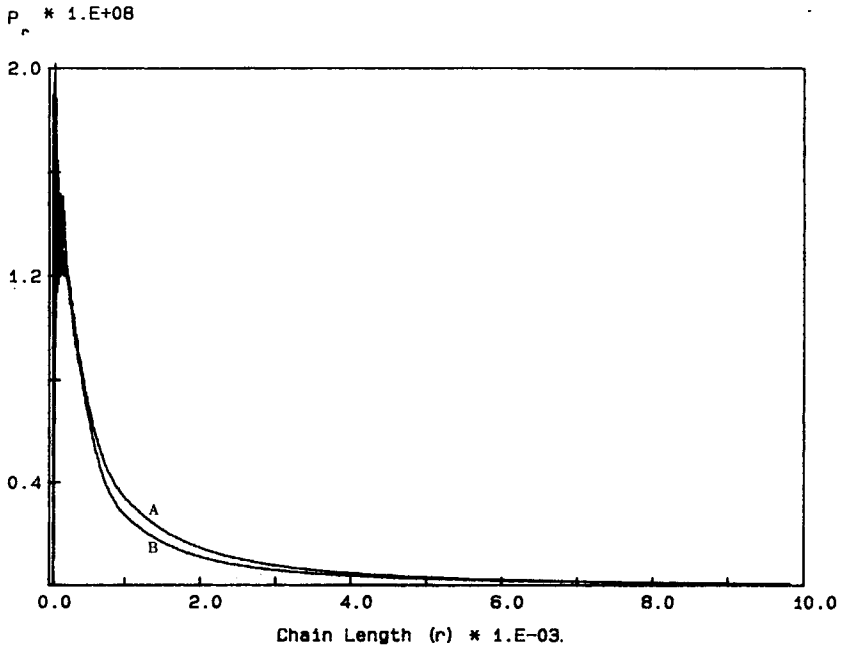

Fig. 8. Molecular weight changes during reactive extrusion of polypropylene: chain length distribution of extrudate at 0.00 wt% initiator (A) and at 0.04 wt% initiator (B).

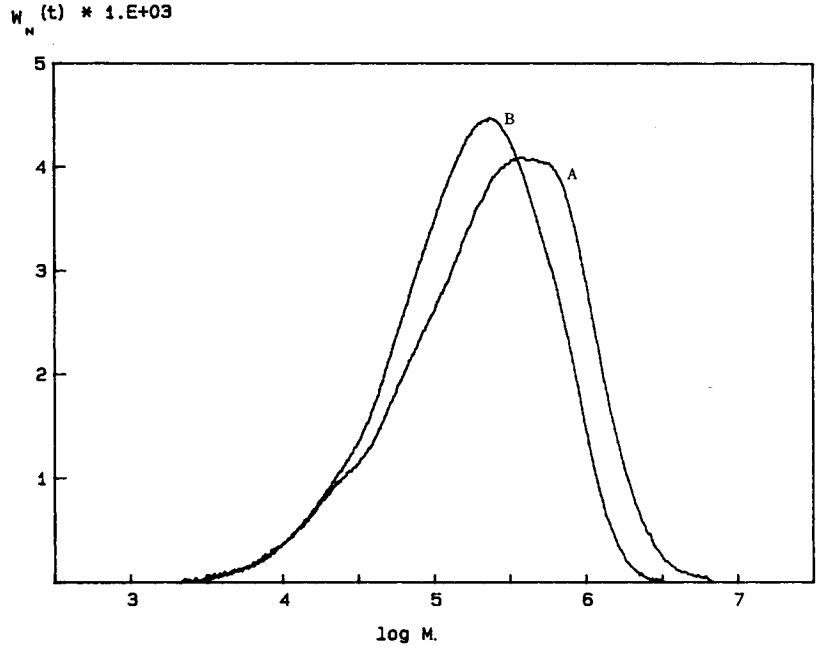

Fig. 9. Molecular weight changes during reactive extrusion of polypropylene: normalized SEC chromatogram heights versus the logarithm of molecular weight at 0.00 wt% initiator (A) and at 0.04 wt% initiator (B).

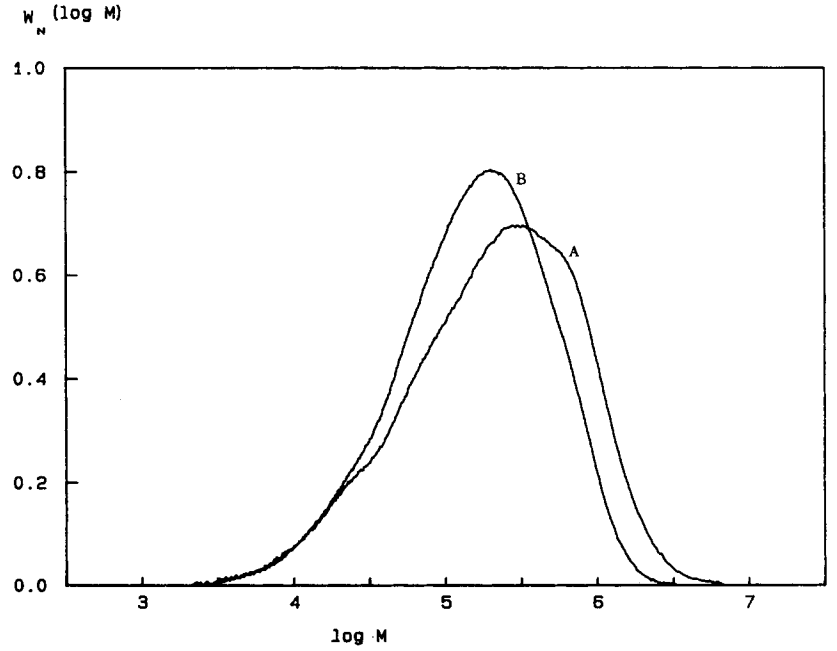

Fig. 10. Molecular weight changes during reactive extrusion of polypropylene: molecular weight distribution of extrudate at 0.00 wt% initiator (A) and at 0.04 wt% initiator (B).

CONCLUSIONS

Extended sample dissolution times (36–48 h at 145°C), universal calibration, and use of molecular weight distribution ordinates (rather than molecular weight averages) enabled kinetic modeling of polypropylene degradation during reactive extrusion using a SEC equipped with only a refractometer detector.

Equations relating the SEC chromatogram to the chain length distribution obtained in kinetic models were detailed and the characteristics of the distributions obtained were discussed.

Irganox 1010 was found to be superior to Irganox 1076 as an antioxidant for high temperature SEC analysis of polypropylene.

Resolution correction was applied to provide an estimate of the error involved in using uncorrected chromatogram heights rather than uncorrected molecular weight averages. An 8% error in molecular weight averages due to axial dispersion corresponded to less than a 2% error for most individual height values.

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NOMENCLATURE

M	Molecular weight.
$\overline{M}_n$	SEC number-average molecular weight uncorrected for axial dispersion.
$\overline{M}_n(a)$	Number-average molecular weight known for standard.
$\overline{M}_w$	SEC weight-average molecular weight uncorrected for axial dispersion.
$\overline{M}_w(a)$	Weight-average molecular weight known for standard.
m_o	Monomer molecular weight.
N_o	Avogadro's number.
P_r	Concentration of polymer of chain length r.
r	Polymer chain length (M/m_o).
t	Retention time.
V_∞	Hydrodynamic volume at infinite dilution.
$W(t)$	Chromatogram height assuming perfect resolution.
$W_N(t)$	Normalized chromatogram height (Eq. (1)) assuming perfect resolution.
$W_N(\log M)$	Ordinate of molecular weight distribution with log M abscissa (Eq. (2)).
$[\eta]$	Intrinsic viscosity.
ρ_P	Polymer density.

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