Reactive Extrusion of Polypropylene I: Controlled Degradation

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Synopsis

Polypropylene was degraded by injection of a free-radical initiator during extrusion. Molecular weight distribution, molecular weight averages, and melt flow index were measured to see the effect of initiator concentration (0.00 to 0.04 wt%), temperature (200 and 220°C), and screw rpm (31 and 44). Initiator concentration was the most significant variable. In all cases, increased initiator concentration degraded the high molecular weight tail of the polypropylene and narrowed the molecular weight distribution. Melt flow index varied linearly with initiator concentration beyond 0.01 wt% initiator. Reaction temperature had no effect on the measured properties of the extrudate. This was attributed to the minimum residence time in the extruder being sufficient for all degradation reactions to be completed. It also implied that the same reactions occurred at both temperatures. Increased screw rpm slightly increased molecular weight. No interaction among initiator concentration, temperature, and screw rpm was observed.

INTRODUCTION

Polypropylene can be intentionally degraded with a free-radical initiator during extrusion. This reactive extrusion process causes the removal of the high molecular weight tail and the narrowing of the molecular weight distribution. The "specialty polymer" product ("controlled rheology polypropylene") is known to exhibit less swell, draw resonance, and melt fracture than the parent "commodity polymer".[1-5] Mechanical properties such as stiffness, brittleness, and tensile strength are unchanged.[6]

This is the first paper in a series describing an investigation of this process. Our main objective is to show the effect of processing variables on the molecular weight distribution of the product. Following papers will present a kinetic model of the degradation,[7] and size exclusion chromatography (SEC) method development.[8,9] Preliminary results have already been presented and published.[10-12]

BACKGROUND INFORMATION

Effect of Processing Variables

Several methods have been used for degrading polypropylene. Batch thermal degradation has been carried out at temperatures between 250 and 450°C for 1 to 24 h. This process required a high energy input over a long processing

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time, and resulted in a relatively low degree of degradation.[1,6,13-15] The presence of oxygen reduced the required processing temperature below 240°C and the processing time below 1 h. However, the products then showed significant concentrations of low molecular weight and oxygen containing materials.[6,16,17]

In current practice, peroxide initiators are generally used. Also, using an extruder as a reactor, continuous degradation processes have been developed.[1,2] However, there is very little published information on the effect of processing variables.

Initiator selection is one variable which can significantly affect results. Important considerations in the selection are low residual initiator concentrations in the product (i.e., a sufficiently high reactivity), ease of accurate metering, low product toxicity, and negligible losses due to vaporization or sublimation.

2,5-Dimethyl-2,5-bis(t-butylperoxy) hexane (DHBP), a dialkyl peroxide, was selected for this work. This material is commonly used for polypropylene degradation.[18,19] It exhibits first-order decomposition kinetics with a half life of only 5.9 s at 200°C, the lowest temperature to be used here. Residence time in the extruder was known to exceed 2 min.[10,20] Also, DHBP is a liquid and therefore not subject to powder handling and blending problems.[20,21] Its boiling point of 249°C is significantly higher than the maximum temperature of 220°C to be used in the study. The typical decomposition byproducts are methane, ethane, ethylene, acetone, and t-butyl alcohol. DHBP is considered an accepted food additive.[22]

Both single-screw and twin-screw extruders have been used for polypropylene degradation.[1,2,10] A single-screw extruder was used here. Residence time distribution is an important characteristic of any extruder used for reactions. Determination of residence time distribution involves injecting a pulse of tracer material at the extruder entrance and measuring the distribution of its concentration at the exit.

Both patent[6] and vendor literature[18] indicate that temperatures from 230 to 266°C and initiator concentrations of 0.01 to 0.08% have been used for polypropylene degradation. Very recently, Fritz[1] described continuous degradation of polypropylene in an extruder controlled via direct monitoring of the viscosity of the product. A maximum temperature of 245°C and a peroxide concentration range of 0.01 to 0.10% were cited.

Response Variables

The main response variable examined in this study was molecular weight distribution. It was measured by size exclusion chromatography (SEC) at 145°C. Details of the development method have been published.[8,9,12] Molecular weight averages were also calculated. However, particularly in the kinetic modeling work,[7,10,11] emphasis was placed upon the use of the distributions themselves because of their superior accuracy and higher information content.

Melt flow index[23] (MFI) is easily measured and is commonly used to characterize polymer flow. However, it is only a single numerical value and is affected by many variables: polymer property distributions (e.g., molecular weight), the shear history of the polymer, die end effects, elasticity, thermal

degradation, etc. It can be ambiguous with respect to indicated flow properties and very difficult to relate to molecular properties.

Despite these potential problems, other investigators in this area of reactive extrusion have successfully shown correlations of melt flow index with polymer properties. Tzoganakis et al.[2] correlated melt flow index of degraded polypropylene with its $\overline{M_w}$ and $\overline{M_z}$. Fritz[1] showed that his melt flow index data from polypropylene subjected to degradation in an extruder were approximately inversely proportional to the complex shear viscosity. He also correlated MFI with feed initiator concentration. The correlation was a straight line which he termed the "static curve":

$$\text{MFI} = 466[I]_o + B \tag{19}$$

where $[I]_o$ = the feed initiator concentration, B = a constant dependent on operating condition. Fritz found that changing operating temperature or extruder type simply shifted this straight line to higher or lower MFI.

EXPERIMENTAL

A Deltaplast D40-150-24 single-screw extruder with a 1.5″ barrel diameter and a L/D ratio of 24/1 was used as a reactor. A more detailed description is available.[20] Argon could be introduced at the feed port if inert atmosphere was required in the system. The peroxide initiator was introduced at the feed port using a Sage-355 syringe pump. The pump was calibrated off-line over the range 0 to 0.2 g/min. It was found to provide a 2σ precision of $\pm 1.46 \times 10^{-4}$ g/min at its lower setting (0 to 0.02 g/min) and $\pm 3.27 \times 10^{-4}$ at its higher setting (0 to 0.2 g/min). Product was sampled at 15 s intervals.

All the work reported here employed PD 888 polypropylene from Himont. PD 888 contains a proprietary long-term stabilizer and gives a melt flow index of 0.7 g/10 min. Attempts to use an unstabilized polypropylene, Flake 6701 polypropylene, a pure polypropylene powder without stabilizer, resulted in data which had extremely poor reproducibility. The DHBP initiator used was Lupersol 101 (Lucidol), a liquid containing 90 wt% (by weight) of 2,5-dimethyl-2,5-bis(t-butylperoxy) hexane.

All extruder runs were done with argon blanketing and with water quenching of the extrudate. These measures were intended to reduce thermo-oxidative degradation. Run conditions used to examine their effect are shown in Table I. Three main experimental variables were systematically examined: concentration of peroxide initiator, operating temperature and screw rpm. Operating conditions are summarized in Table II.

Extruder residence time distributions were determined by injecting 0.08 g of manganese dioxide as a pulse into the feed port of the extruder.[24] Samples were collected at 15 s intervals for a 10 min period. Approximately 0.3 g of the samples were weighed and then irradiated for 60 s at 5 kW power in a Slowpoke reactor. Irradiated samples were then counted for 90 s. Counts were converted into concentration of manganese dioxide in polypropylene using a potassium permanganate standard solution calibration curve.

SEC molecular weight distribution and molecular weight average data were obtained by using a Waters Model 150 C with trichlorobenzene at 145°C and

TABLE I
Reactive Extrusion Experiments: Argon Blanketing and Water Quenching

Run	Condition	$[I]_o$ (wt %) 10^2	T (°C)	$\overline{M}_n$ 10^{-4}	$\overline{M}_w$ 10^{-5}
S1	A, W	0.00	220	7.89	4.06
N1	AO, W	0.00	220	7.69	3.72
S3	A, W	2.00	220	7.33	2.98
N3	AO, W	2.00	220	7.70	3.00
S4	A, W	4.00	220	6.98	2.66
N4	AO, W	4.00	220	7.03	2.53
S10	A, W	1.00	200	7.66	3.78
N10	A, WO	1.00	200	7.89	3.79
S11	A, W	2.00	200	6.99	2.74
N11	A, WO	2.00	200	7.38	2.98
S12	A, W	4.00	200	7.25	2.67
N12	A, WO	4.00	200	7.43	2.96

Abbreviations: A is with Argon; AO is with no Argon; W is with water quench; WO is with no water quench.

1 mL/min as the mobile phase. Duplicate analyses of all samples were run. Details of the method are provided elsewhere.[8,9,12,20]

MFI were determined using an extrusion plastometer (Custom Scientific Instruments Inc.) standardized according to ASTM D1238-79.[23] Procedure A and condition L of ASTM D1238-79 were employed to measure MFI of polypropylene samples with flow rates below 50 g/10 min. The temperature was set at 230°C and the total load, including the piston, was 2160 g. Measurements were repeated at least three times and averaged. Error standard deviation was estimated to be 7.3%.

TABLE II
Reactive Extrusion Experiments: Feed Initiator Concentration, Temperature, and Screw rpm

Run	$[I]_o$ (wt %) 10^2	T (°C)	Screw rpm	$\overline{M}_n$ 10^{-4}	$\overline{M}_w$ 10^{-5}	MFI (g/10 min)
PD 888	(feed)			8.19	4.00	0.68
S1	0.00	220	44	7.89	4.06	0.85
S2	1.00	220	44	8.15	3.87	1.24
S3	2.00	220	44	7.33	2.98	2.75
S4	4.00	220	44	6.98	2.66	5.38
S5	0.00	220	31	8.02	3.83	0.76
S6	1.00	220	31	7.77	3.43	1.25
S7	2.00	220	31	7.86	3.22	2.59
S8	4.00	220	31	6.58	2.30	5.47
S9	0.00	200	44	8.10	4.11	0.76
S10	1.00	200	44	7.66	3.78	1.17
S11	2.00	200	44	7.38	2.98	2.52
S12	4.00	200	44	7.25	2.67	4.41
S13	0.00	200	31	8.18	3.85	0.79
S14	1.00	200	31	7.79	3.20	1.06
S15	2.00	200	31	6.82	2.72	2.05
S16	4.00	200	31	6.50	2.28	4.53

RESULTS AND DISCUSSION

Reproducibility and Accuracy

High temperature SEC can be subject to irreproducibility caused by shear and thermal degradation of the polymer both during sample preparation and while travelling through the columns.[25] The extrusion experiments were also subject to error due to fluctuation of temperatures, feed flow rates and sampling. Figure 1 shows the molecular weight distributions of the six runs listed in Tables I and II (Runs PD 888, S1, N1, S5, S9, S13) at zero feed initiator concentration. These runs were conducted over a three month period. Error analysis[8, 12, 20] shows that the coefficient of variance (standard deviation divided by the mean) is better than 5% for the ordinate of the molecular weight distribution between molecular weights of 1.0×10^4 and 1.0×10^6 molecular weight. In quantitative work here the heights of the distribution were specifically chosen over this range. High standard deviation to height ratio at molecular weights lower than 1.0×10^4 and higher than 1.0×10^6 were caused by very small heights. The coefficient of variation for $\overline{M_n}$ and $\overline{M_w}$ was found to be 1.5 and 3.0%. This reproducibility includes both processing and SEC analysis error.

There was concern that these highly precise results might be optimistic for the process however, since no initiator was present and it was known that the degradation was highly sensitive to initiator concentration fluctuation. However, isolated checks indicated that this reproducibility was maintained during initiator runs. Also, much care was taken to obtain highly precise flow rates in off-line calibration of the initiator pump. Furthermore, systematic
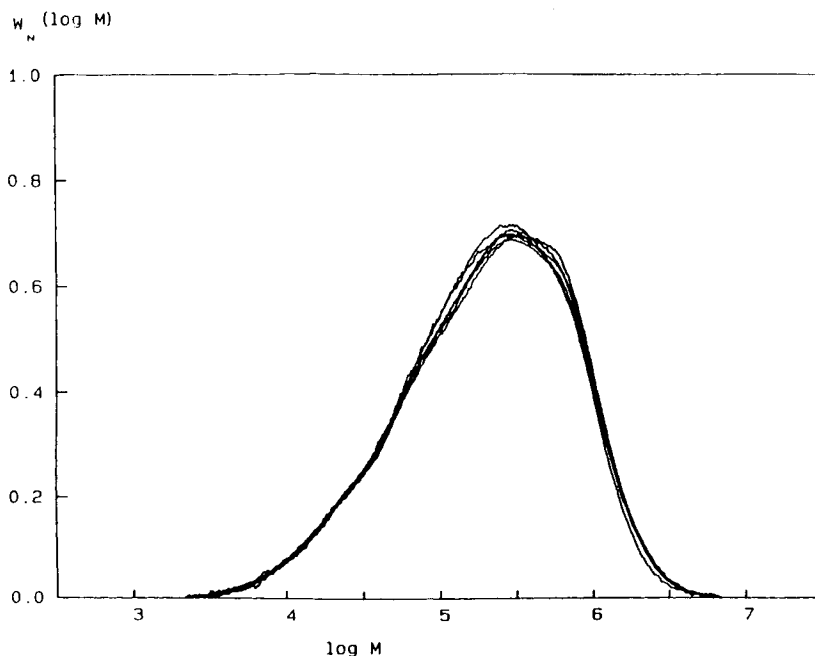

Fig. 1.   Molecular weight distributions of polypropylene extrudate from six different extruder runs, all with zero feed initiator concentration. Random experimental error and absence of thermal degradation are evident.

variation of processing conditions generally provided a corresponding systematic variation in response which appeared in agreement with the determined precision.

Figure 1 also demonstrates the lack of any thermal or thermo-oxidative degradation under these conditions. This was in accord with the work of Fritz[1] who perceived no such degradation below 245°C.

Although our SEC development method[8,9,12] managed to provide acceptable reproducibility, absolute accuracy remained an open question. There were many options available in the analysis. Selection of different options can provide markedly different results. There is, even now, serious question as to whether absolute accuracy in molecular weight averages can be obtained at all by SEC for any polymer with a high molecular weight tail.[8,9,25] For this reason among others,[8,9,26,27] the molecular weight distribution heights provide more absolute accuracy than averages. In the next paper in this series we show the effect of a specific method of SEC "concentration correction" on the molecular weight distribution and examine consequences with regards to the degradation kinetic model.

Argon Blanketing and Water Quenching

Table I shows the effect on the molecular weight averages of argon gas blanketing and product water quenching. The former had no effect. The latter slightly lowered the molecular weight. A higher molecular weight would have been more in keeping with degradation prevention. However, since the result
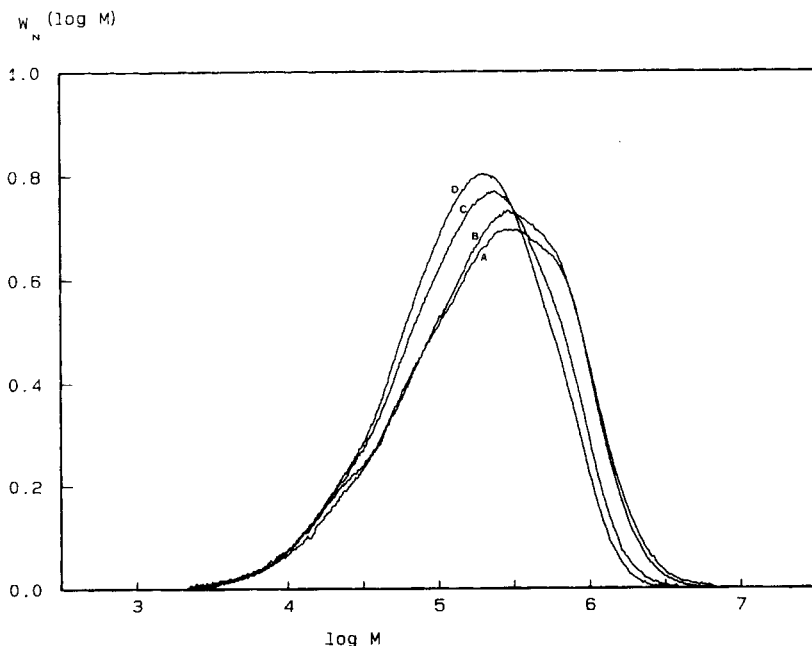

Fig. 2. Effect of feed initiator concentration on polypropylene extrudate molecular weight distribution (reaction temperature 220°C and screw rpm 44). Curves A, B, C, and D correspond to 0.00, 0.01, 0.02, and 0.04 wt% initiator, respectively.
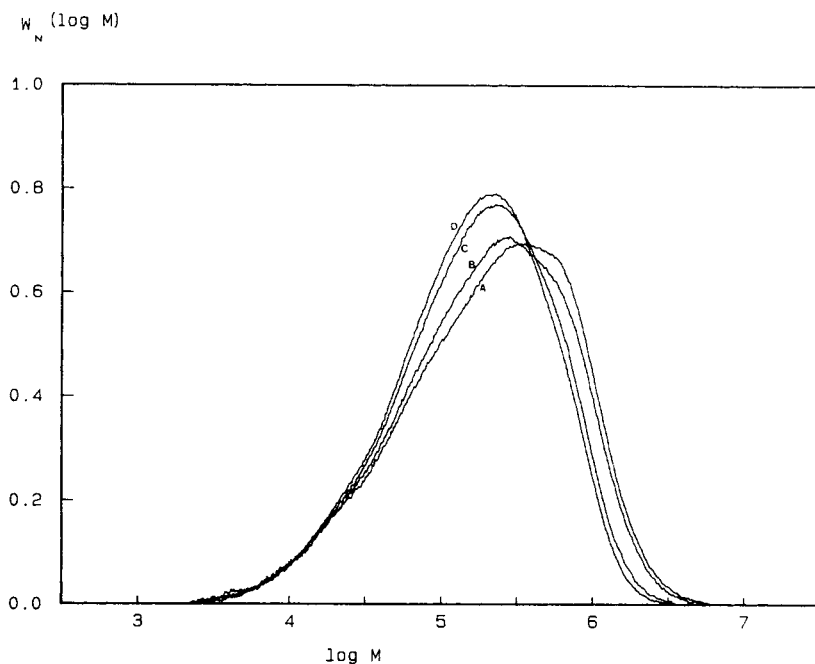
Fig. 3.   Effect of feed initiator concentration on polypropylene extrudate molecular weight distribution (reaction temperature 220°C and screw rpm 31). Curves A, B, C, and D correspond to 0.00, 0.01, 0.02, and 0.04 wt% initiator, respectively.

was a small one, and since slow cooling of the extrudate was an obvious source of error, it was assumed that the water quench provided a more accurate result. Both argon blanketing and water quenching were used for all remaining experiments.

The Effect of Initiator Concentration

Figures 2 to 5 show the effect of feed initiator concentration on the molecular weight distributions of PD 888 polypropylene exiting the extruder. In all cases, as initiator concentration is increased, the high molecular weight tail degrades, the low molecular weight tail remains unchanged, the distribution narrows.

Table II and Figures 6 and 7 show the corresponding changes in molecular weight averages. $\overline{M_w}$ decreases while $\overline{M_n}$ remains almost constant. $\overline{M_w}/\overline{M_n}$ decreases from approximately 5 to 4 in every case as feed initiator concentration increases from 0.00 to 0.04 wt%. These results were all in reasonable agreement with previous work. It is strongly evident here that initiator concentration is by far the most influential processing variable.

Table II also shows the MFI of PD 888 polypropylene and its extrusion products at various operating conditions. Figure 8 shows MFI plotted against initiator concentration. No significant effect of screw rpm and a possible minor lowering of MFI by decreased reaction temperature were evident. This latter observation could be attributed to different shear history caused by increased viscosity at the lower reaction temperature.
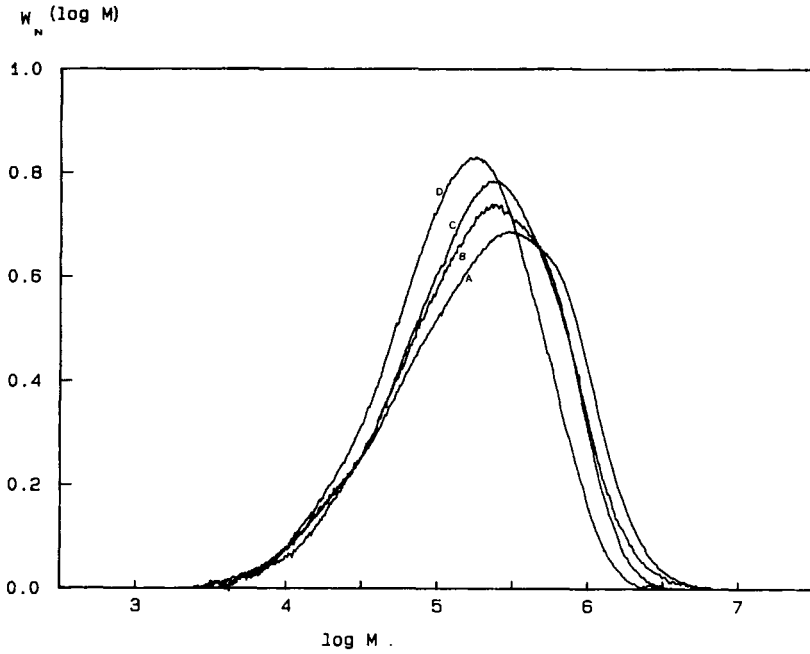
Fig. 4. Effect of feed initiator concentration of polypropylene extrudate molecular weight distribution (reaction temperature 200°C and screw rpm 44). Curves A, B, C, and D correspond to 0.00, 0.01, 0.02, and 0.04 wt% initiator, respectively.
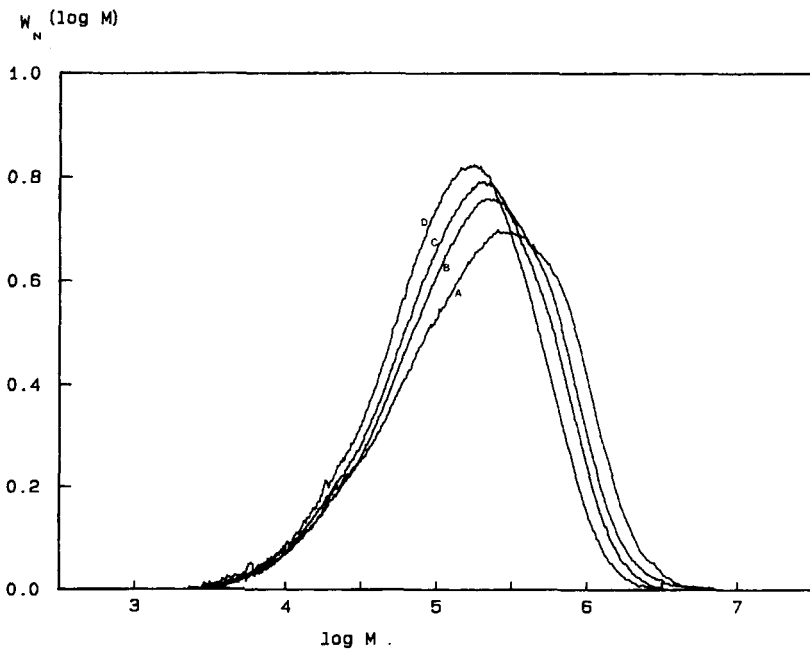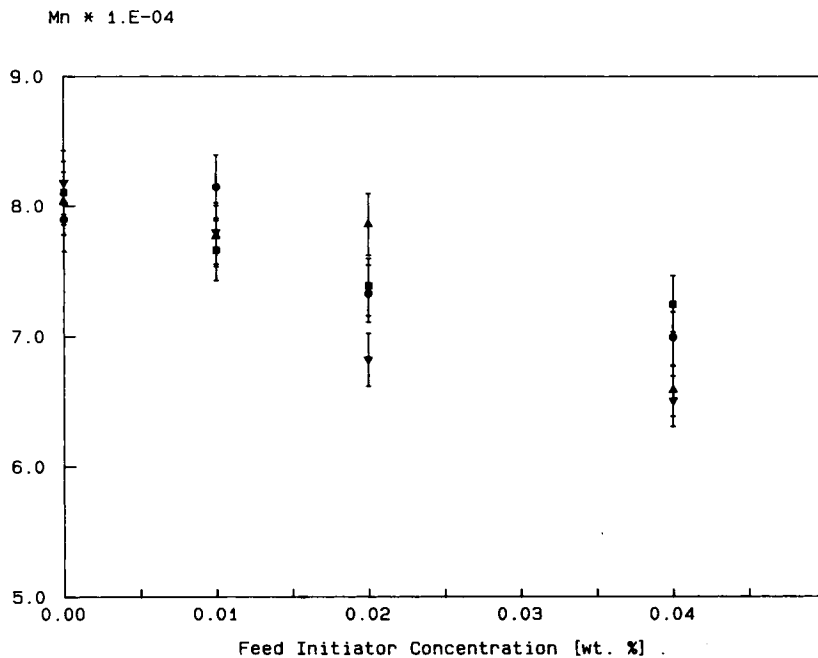

Fig. 5. Effect of feed initiator concentration on polypropylene extrudate molecular weight distribution (reaction temperature 200°C and screw rpm 31). Curves A, B, C, and D correspond to 0.00, 0.01, 0.02, and 0.04 wt% initiator, respectively.

Mn * 1.E-04

Fig. 6. $\overline{M_n}$ variation with feed initiator concentration for polypropylene reactive extrusion. (●) 220°C, 44 rpm; (▲) 220°C, 31 rpm; (■) 200°C, 44 rpm; (▼) 200°C, 31 rpm.
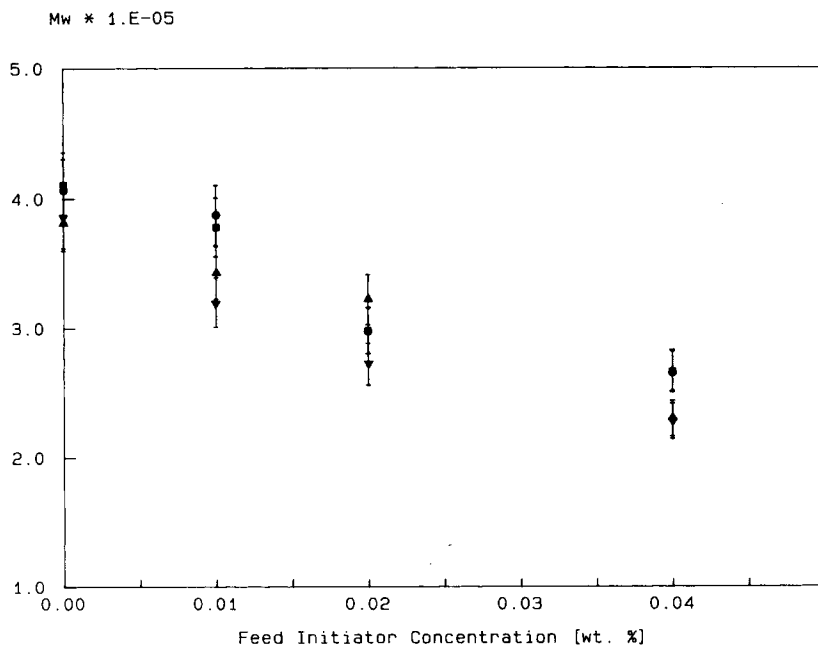
Mw * 1.E-05

Fig. 7. $\overline{M_w}$ variation with feed initiator concentration for polypropylene reactive extrusion. (●) 220°C, 44 rpm; (▲) 220°C, 31 rpm; (■) 200°C, 44 rpm; (▼) 200°C, 31 rpm.
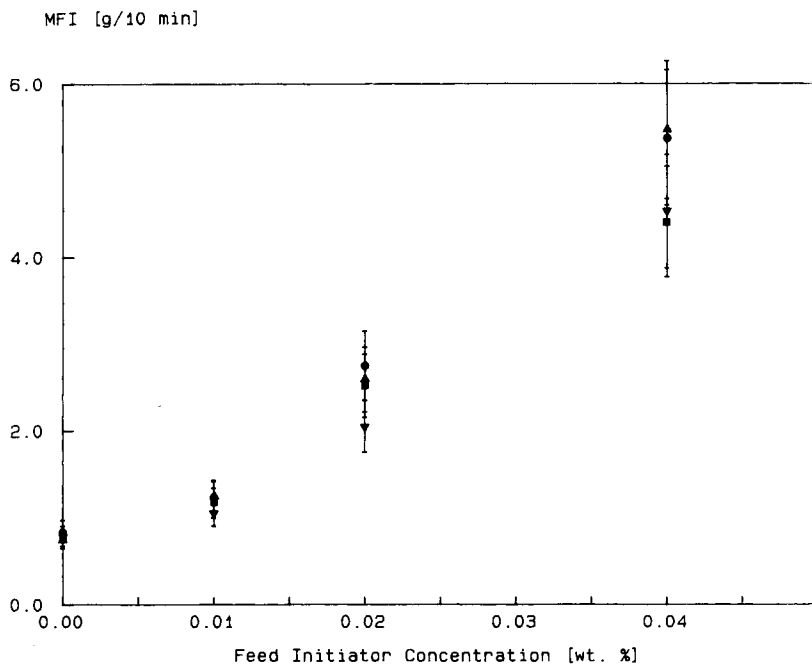
MFI [g/10 min]

Fig. 8.   Melt flow index (MFI) variation with feed initiator concentration for polypropylene
reactive extrusion. (●) 220°C, 44 rpm; (▲) 220°C, 31 rpm; (■) 200°C, 44 rpm; (▼) 200°C, 31 rpm.

Figure 8 also shows that the plot of MFI versus feed initiator concentration could be considered a straight line beyond 0.01 wt% initiator in agreement with the work of Fritz.[1] However, the slope of this line is 126 with an estimated error standard deviation of 16. This is considerably lower than the slope of 466 determined by Fritz.[1] This discrepancy is not surprising considering the number of variables affecting MFI.

The Effect of Temperature

Both the molecular weight distributions (Figs. 2–5) and the molecular weight averages (Table II) show no effect of temperature. This result appears surprising since the initiator decomposition rate constant increases from 7.08 min^{-1} to 39.42 min^{-1} over the 200–220°C temperature range examined. An explanation can be obtained by examining the extruder residence time distributions. Figure 9 shows typical residence time distribution curves. The distributions for different operating conditions all showed the same shape: a time delay followed by a sudden exit of tracer which exponentially decreased. This "plug flow-continuous stirred tank" type of behavior has been observed previously for extruders.[28] As shown in Table III, the time delay ranged from 2.8 min to 3.8 min for the various conditions. If the degradation reactions were complete before 2.8 min and if the same reactions occur at different temperatures then no effect would be observed. The extruder "plug flow time" was too long for the increased rate to be seen. A kinetic model compatible with this explanation has been published[11] and will be examined in more detail in a subsequent paper.[7]
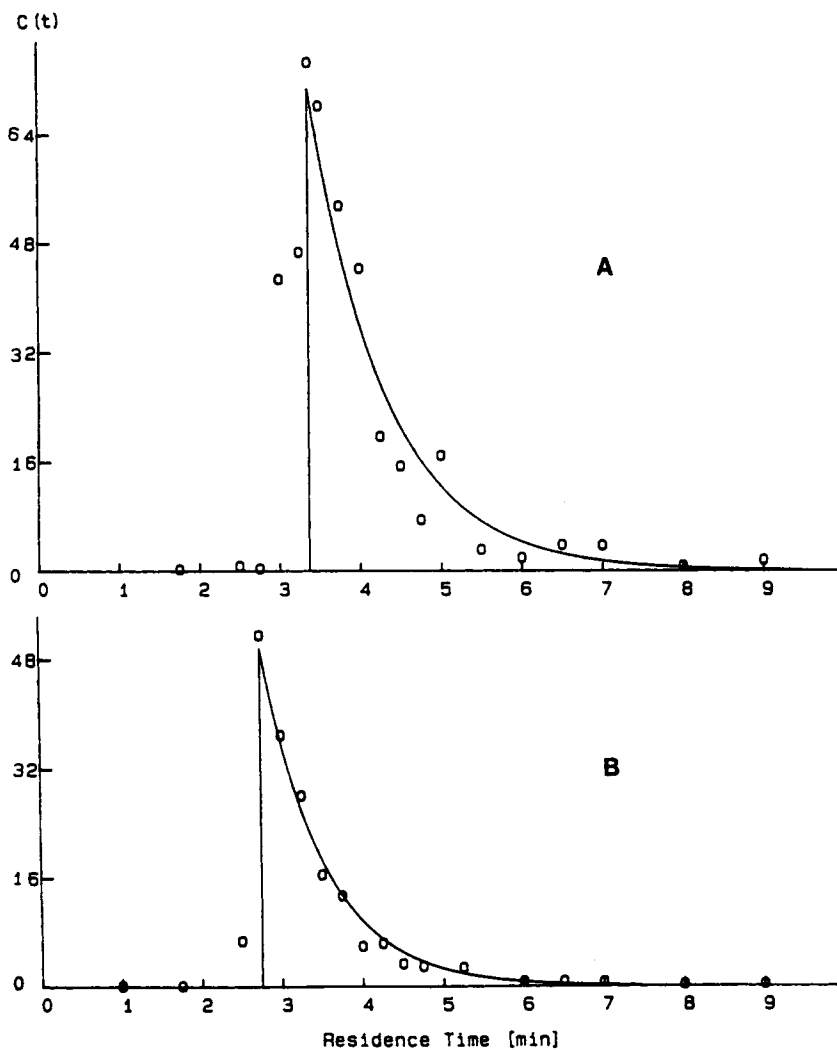
Fig. 9. Residence time distributions (plotted as concentration of tracer (C(t)) versus residence time) showing the effect of increasing temperature (44 rpm, 0.00 wt% peroxide). (A) 200°C; (B) 220°C.

TABLE III
Simple Time Delay Component of the Residence Time Distributions

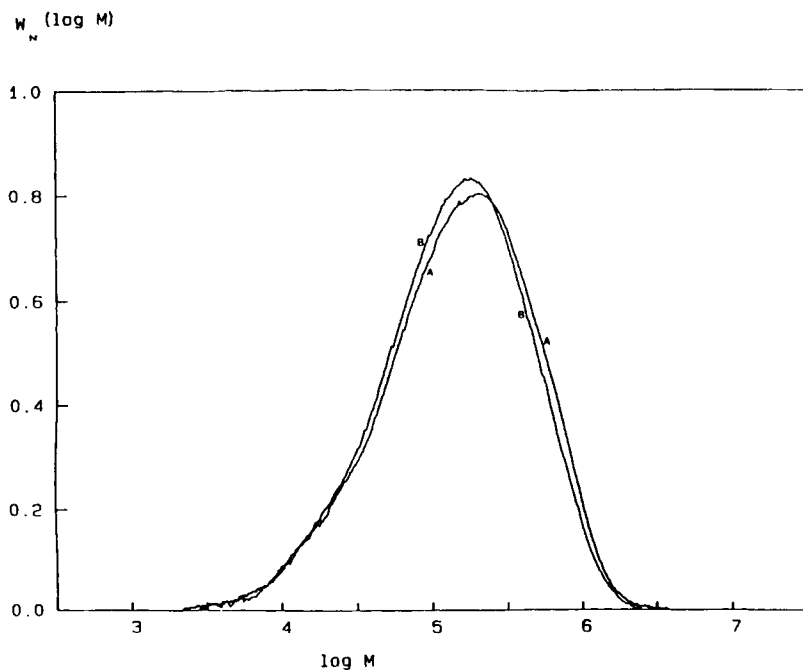| Run	$[I]_o$ (wt %) 10^2	T (°C)	Screw rpm	Time delay (δ) (min)
S1	0.00	220	44	2.8
S2	1.00	220	44	2.8
S4	4.00	220	44	2.8
S5	0.00	220	31	3.8
S8	4.00	220	31	3.6
S9	0.00	200	44	3.3
S13	0.00	200	31	4.1

W_M (log M)

Fig. 10.   Example of the effect of screw rpm on the molecular weight distribution (220°C).
(A) 44 rpm; (B) 31 rpm.

The Effect of Extruder Screw RPM

Figure 10 shows a typical variation in molecular weight attributable to the extruder screw rpm change from 31 to 44 rpm. Table II and Figures 6 and 7 show the change in molecular weight averages. Comparison of the molecular weight distribution variation with the reproducibility of such data (Fig. 1) indicates that screw speed likely has a slight but significant effect. Inspection of the averages also lead to this conclusion.

Examination of residence time changes caused by different screw speeds do not reveal a cause for the higher molecular weights (i.e., less degradation) obtained at the higher screw speeds. From Table III it can be seen that increasing screw speed decreased the "plug flow time" in the extruder from 3.8 min to 2.8 min. However, increasing temperature decreased it from 3.3 min to 2.8 min and caused no change in molecular weight distribution. Possible reasons for the effect of the screw speed effect include: mixing effects other than residence time and initiator feed error. The former refers to the likelihood that the higher screw speed enabled more rapid mixing of the initiator throughout the polymer and therefore more efficient use of the amount injected. However, this should have decreased rather than increased molecular weights as rpm was increased. The latter refers to the possibility that the pump delivered a slightly different quantity of initiator under the new conditions.

Interaction Effects

Treating the data as a factorial design[29] led to the same conclusions as mentioned above. In addition, no interaction effects among initiator concentration, temperature and screw rpm were evident.

CONCLUSIONS

Good reproducibility for molecular weight distributions and molecular weight averages were obtained (less than 5% coefficient of variation). However, absolute accuracy was unlikely because of current uncertainties in high temperature SEC interpretation.

Initiator concentration was the most significant processing variable examined. Levels of DHBP from 0.01 to 0.04 wt% caused removal of the high molecular weight tail with a consequential narrowing of the molecular weight distribution. At levels of 0.04 wt% a decrease in $\overline{M_w}$ of about 34% was typical.

Changing temperature from 200 to 220°C caused no change in the molecular weight distribution of the extrudate. This was attributed to the "simple time delay" component of the residence time of the extruder exceeding the time necessary for all degradation reactions to be completed combined with the same reactions occurring at each temperature.

Increasing extruder screw rpm from 31 to 44 slightly increased molecular weight. Neither residence time or increased mixing provided a justification for the effect. Initiator injection rate sensitivity to rpm was considered a possibility.

No interaction among initiator concentration, rpm, and temperature was observed.

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