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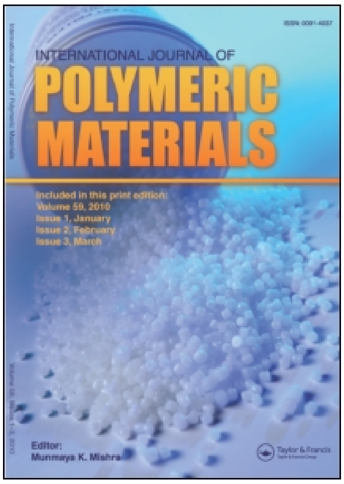

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A SEGREGATION APPROACH TO MOLECULAR WEIGHT CONTROL IN CONTROLLED DEGRADATION OF POLYMERS

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In a reactive extrusion process a new approach – degrading only a portion of the input followed by a mixing process with unreacted portion – has been proposed as a method to control the molecular weight and molecular weight distribution (MWD). The number average molecular weight, M_n, and the weight average molecular weight, M_w, are studied through the Schulz–Zimm molecular weight distribution. The results indicate that M_n and M_w can be regulated separately during degradation. M_w and the polydispersity index (PDI) of a segregated degradation process are higher than the corresponding results of a uniform system. In the later stage of a segregated degradation the PDI can be higher than that of the original polymers. Starting from a narrow unimodal MWD it is possible to produce a bimodal MWD.

Keywords: controlled degradation, polypropylene, molecular weight distribution, polydispersity index

INTRODUCTION

Many degradation processes can be considered as a random degradation process. A degradation process is considered to be random if the probability of a chain breakage is the same regardless of chain length and the distance of the breakage from the ends of the polymer molecule. It has considerable interest from theoretical and practical viewpoints. In practical applications the degradation of polypropylene is the most prominent one [1–9]. When propylene is polymerized using heterogeneous Ziegler–Natta catalysts the polypropylene produced has M_w in the range of 3×10^5 to 5×10^5 and PDI between 5 and 20 [1]. The level of elasticity of high molecular weight polypropylene is very high and could cause some elastic strain being frozen into products in high speed processing.

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In polypropylene the molecular weight and MWD can be modified easily and economically in a simple post reactor process by employing controlled degradation in an extruder. This process removes the high molecular weight tails and leads to the production of specialty polypropylene having narrowing tailor made MWD's. Controlled degradation is accomplished by a suitable peroxide initiator, which decomposes and generates free radicals in molten polypropylene. When a diversity of small batches of polypropylene is needed for the market place, controlled degradation using mass produced raw materials appears to be an economically feasible route.

Due to the random nature of the degradation process the PDI gradually moves toward two when molecular weights decrease. As a result, the breadth of the MWD and the molecular weights can not be controlled independently. This presents a process limitation since many times M_w and PDI have opposing effects on processing properties. In polypropylene, at a given draw ratio, tenacity decreases with decreasing M_w and increases with decreasing PDI. Also, elongation at a given draw ratio increases with decreasing M_w and decreases with decreasing PDI [9]. Therefore, it is crucial to be able to independently control these two parameters in a reactive extrusion process.

A new application of MWD control appears to be possible in the new polypropylene prepared from metallocene catalysts. Metallocene catalysts have uniform activity and the polymers produced could have near monodisperse molecular weight. In this case controlled degradation can be used to broaden MWD. Another application in studying MWD during degradation is the monitoring of degradable polymers [10, 11]. When a degradable polymer undergoes degradation the molecular weight decreases continuously. The knowledge of the MWD of degradable polymers is important because the low molecular weight fraction can be dissolved by solvents or metabolized by microbes and lead the way to total disintegration. A knowledge of the amount of the low molecular weight end of a degraded polymer is useful in monitoring the extent of degradation.

It has been proposed by Davison [8] that a cyclical concentration variation of initiators in the reactive extrusion of a monodisperse polypropylene can produce a bimodal product in addition to a reduction of molecular weights. Experimental verification of this concept was made by Dickson *et al.* [9] by segregating polymers into degrading and nondegrading portions. In this study the Schulz–Zimm molecular weight distribution is used to derive some mathematical relations which relate molecular weights with the extent of degradation and the proportion of segregation.

MATHEMATICAL MODEL

If a linear polymer with an unimodal MWD undergoes random main-chain scission the number average molecular weight, M_n, decreases with an increasing degree of degradation. Its relation with the initial number average molecular weight, $M_{n,0}$, is [10]:

$$\frac{M_n}{M_{n,0}} = \frac{1}{1+\alpha} \tag{1}$$

where α denotes the average number of scissions per initial molecule. It also represents the extent of degradation. In the case of peroxide initiated degradation the parameter α can be estimated based on the number of molecules of initiators and polymers in the system. This is possible because the mechanism proposed by Tzoganakis *et al.* [2, 5] includes initiation, scission and termination. For each successful attack of initiator fragments on the polymer molecule a break in the polymer chain and a new molecule are created.

The weight average molecular weight, M_w, depends on the initial MWD in addition to α. If the initial MWD is known the M_w of a random degradation is derived from the following equation [10]:

$$\frac{M_w}{M_{w,0}} = \frac{2}{\alpha\sigma_o}\left\{1 - \frac{1}{\alpha}\left[1 - \int_0^\infty \frac{\omega(y)}{y/X_{1,0}} e^{-\tau y} dy\right]\right\} \tag{2}$$

where

σ_o = molecular polydispersity index at the beginning.
$\omega(y)$ = weight fraction of y-mer initially present.
τ = number of scissions per monomer unit.

Equations (1) and (2) hold for the case $X_{1,0} \gg 1 \gg \tau$. With the assumption of an analytical MWD expression Eq. (2) can be integrated. The Schulz–Zimm MWD is used in this study. It has the following expression:

$$\omega(y) = v^{(b+1)} y^b \frac{e^{-vy}}{\Gamma(b+1)} \tag{3}$$

The parameters v and b are related to M_w and M_n by the following relationships:

$$M_n = \frac{b}{v}, \quad M_w = \frac{b+1}{v} \text{ and } b = \frac{1}{\sigma - 1}$$

The weight average molecular weight, M_w, in a stage of the degradation process is related to the initial value $M_{w,0}$ by the relation:

$$\frac{M_w}{M_{w,0}} = \frac{2}{\alpha\sigma_o}\left\{1 + \frac{1}{\alpha}\left[\left(1 + \frac{a}{b_o}\right)^{-b_o} - 1\right]\right\} \tag{4}$$

where b_o and σ_o are initial parameters before degradation takes place. From Eqs. (1) and (4) DPI is related to α by:

$$\sigma = \frac{2(1+\alpha)}{\alpha}\left\{1 + \frac{1}{\alpha}\left[\left(1 + \frac{a}{b_o}\right)^{-b_o} - 1\right]\right\} \tag{5}$$

From values of b_o and σ_o the molecular weight averages, M_n and M_w, and the polydispersity index, σ, at different stages of degradation can be calculated. Some results with different b_o and σ_o were shown by Schnabel [10]. Equation (5) gives $\sigma = 2$ when $\alpha \rightarrow \infty$. Therefore, in a highly degraded polymer system, the MWD becomes a Schulz–Zimm distribution with $\sigma = 2$, which is also called the most probable distribution. For a system with an initial value of σ greater than two, the value gradually decreases to two as degradation takes place. For a system with an initial value of σ less than two, the index gradually increases to two as the degradation process progresses.

The simultaneous dependence of Eqs. (1) and (4) on α is a very restrictive one as far as molecular weight control is concerned. When a value of M_n is selected, M_w is also fixed by Eq. (4), which is about twice M_n. In practical applications a broad MWD has the advantage of low crystallinity and a better non-Newtonian flow behavior [12]. It is useful to have a method to control M_n and M_w separately to some degree in the preparation of polymers. Several studies reported that a nonuniform system could produce a broad molecular weight distribution. Ryu *et al.* [7] prepared a multilayer film with different initiator concentrations and studied its melt flow index. Segregation also occurs in a Brabender mixer when the temperature is high and decomposition of initiators takes place in a short period of time. The results indicated that the melt flow index of a nonuniform system is the lowest, and any nonuniformity of initiator distribution decreases the melt flow index. Davison [8] also proposed a cyclical concentration variation of initiators to produce bimodal materials with improved rheology for fiber spinning.

NUMERICAL METHOD

In this study a periodical on–off scheme for adding initiators is proposed as a method for controlling the molecular weight. It is assumed that, after addition of an initiator, the molecular degradation process is completed, and the mixing of degraded and unreacted polymers can occur in the later stage of the extruder or by a second extrusion mixing process. At the end a product containing both unreacted portion and degraded portion is produced. The weight fraction of polymer that has been degraded is w and the weight fraction of unreacted portion is $1-w$. Compared to the system with uniform degradation of α, the w fraction will receive α/w degree of degradation. The number and weight average molecular weights of the degraded portion are:

$$\frac{M_n}{M_{n,0}} = \frac{1}{1 + \alpha/w} \tag{6}$$

$$\frac{M_w}{M_{w,0}} = \frac{2w}{\alpha\sigma_o}\left\{1 + \frac{w}{\alpha}\left[\left(1 + \frac{a}{wb_o}\right)^{-b_o} - 1\right]\right\} \tag{7}$$

When combined with $1 - w$ weight fraction of unreacted polymer, the following expressions for the overall mixture are obtained:

$$\frac{M_n}{M_{n,0}} = \frac{1}{1 + \alpha} \tag{8}$$

$$\frac{M_w}{M_{w,0}} = \frac{2w^2}{\alpha\sigma_o}\left\{1 + \frac{w}{\alpha}\left[\left(1 + \frac{a}{wb_o}\right)^{-b_o} - 1\right]\right\} + 1 - w \tag{9}$$

and the polydispersity index is:

$$\sigma = \frac{2(1 + \alpha)w^2}{\alpha}\left\{1 + \frac{w}{\alpha}\left[\left(1 + \frac{a}{wb_o}\right)^{-b_o} - 1\right]\right\} + \sigma_o(1 - w)(1 + \alpha) \tag{10}$$

In the limit $w = 1$, Eq. (10) becomes Eq. (5) and the system represents uniform degradation. In the limit $w = 0$

$$\sigma = \sigma_o(1 + \alpha) \tag{11}$$

and

$$M_w = M_{w,0} \tag{12}$$

The physical picture of this situation is that a pulse of initiator degrades a small portion of polymer into very small fragments and the fragments are mixed with the remaining original polymer. Because M_w is dominated by the high molecular weight fraction, M_w of the mixture is essentially unaffected by the partial degradation process. However, M_n decreases based on the amount of initiators added into the system, which increases the number of molecules proportionally, independently of the manner that the initiator is added into the system, the result is an increase of the DPI. Similar conclusions were also shown by Dickson *et al.* [9].

In the case $0 < w < 1$ but $\alpha \to \infty$, Eq. (8) gives:

$$M_n = 0 \tag{13}$$

and Eq. (9) gives:

$$M_w = M_{w,o}(1 - w) \tag{14}$$

The physical situation is a complete breakdown of the w fraction into monomer and the $1-w$ fraction remains unreacted. Since M_n is dominated by the low molecular weight species, M_n is reduced to zero. M_w is weighted more by the high molecular species and is reduced only in proportional to its weight fraction.

RESULTS AND DISCUSSION

To illustrate the use of Eq. (9) two initial MWD's are considered: One with $M_w = 30000$ and $M_n = 10000$, another with $M_w = 15000$ and $M_n = 10000$. Since molecular weight is proportional to the degree of polymerization, these figures can also be considered as the degree of polymerization. The former gives $\sigma_o = 3$ and the later gives $\sigma_o = 1.5$. The results of various w are plotted in Figures 1 and 2, respectively. In Figure 1, both M_n and M_w reduce to zero when degradation continues in uniform composition, *i.e.*, $w = 1$. The slope of the curve reaches two at the low molecular weight region. This agrees with Eq. (5) when $\alpha \rightarrow \infty$. In case $w < 1$, M_w reaches a finite value in accordance with Eq. (14). In a segregated model M_w decreases slower than M_n because slopes of all curves decrease when M_n decreases. It is interesting to point out that in cases of $w = 0.25$ and $w = 0.5$ the DPI increases during the degradation almost from the beginning. It is also true in the later stage of the curve with $w = 0.75$. Only in $w = 1$ the DPI decreases continuously from three to two.

In Figure 2 the starting polydispersity index is 1.5. For $w = 1$ the slope increases from 1.5 to 2 when M_n decreases. The curve with $w = 0.75$ also has an increasing slope as degradation occurs. However, for curves with $w = 0.25$ and $w = 0.5$ it can be seen clearly that the slope decreases as degradation continues. In all cases with $w < 1$ finite values of M_w are seen when $\alpha \rightarrow \infty$. This is similar to Figure 1. It is interesting to point out that for cases with $w < 1$ it is possible to have $\sigma > 2$ after sufficient degradation. Only the curve with $w = 1$ reaches 2 at the limit. It is clear that the segregation method offers an ability to broaden the molecular weight beyond the most probable distribution.

It has been proposed that a cyclical concentration variation of initiators in the input of a monodisperse polypropylene can produce a bimodal product in addition to a reduction of molecular weight [8, 9]. The molecular weight averages and molecular weight distribution can be integrated by adding the contribution from each fraction. A simple model for cyclical input would be an on–off input of the initiators. Figure 3

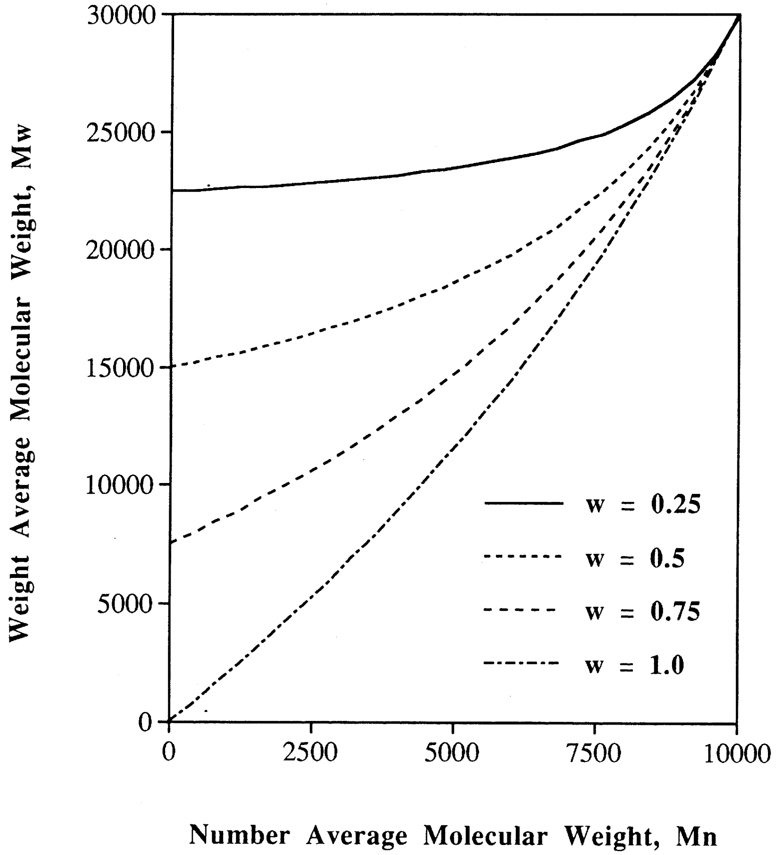

FIGURE 1 Weight average molecular weight *versus* number average molecular weight during segregated degradation for a Schulz–Zimm distribution with initial $M_w = 30{,}000$ and $M_n = 10{,}000$.

shows the result of a polymer with initial $M_n = 10000$ and $M_w = 15000$. The sample is divided into two equal parts, with one of them subject to a uniform degradation, then mixed to produce a mixture. The parameter α in Figure 3 is the overall degree of degradation as defined in Eq. (6). At $\alpha = 2$ half of the polymer is degraded to a MWD with $M_n = 2000$ and the overall M_n is 3333. The MWD appears to be a unimodal distribution with its maximum located near M_n. In this case two peaks were fused together. At $\alpha = 4.5$ half of the polymer is degraded to a MWD with $M_n = 1000$ and the overall M_n is 1111. It can be seen that two peaks were clearly separated with their maximum at M_n near 1000 and 10000, respectively.

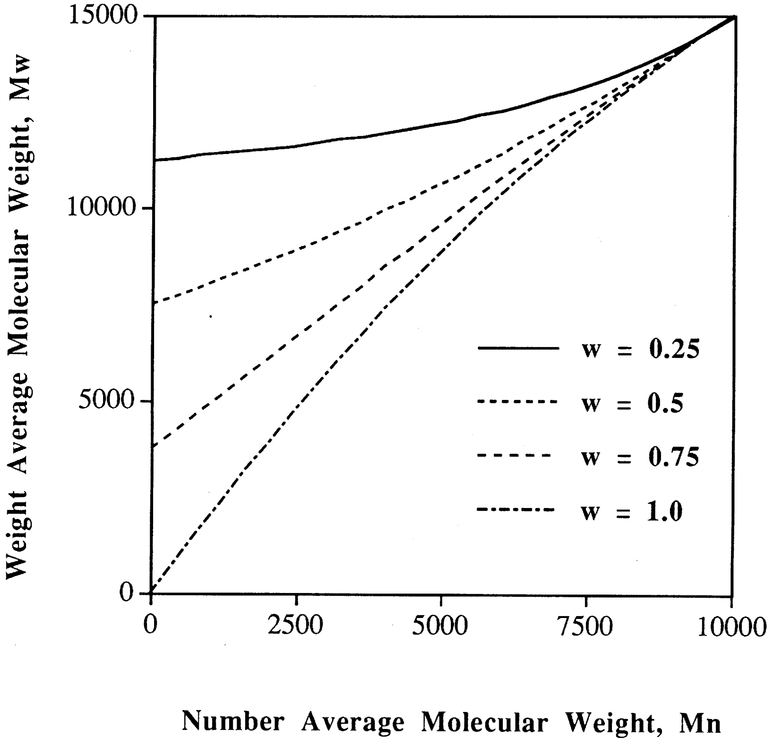

FIGURE 2 Weight average molecular weight *versus* number average molecular weight during segregated degradation for a Schulz–Zimm distribution with initial $M_w = 15{,}000$ and $M_n = 10{,}000$.

Although not shown here a similar result can be observed for a system with initial σ greater than two.

A decrease of molecular weight generally helps to improve the processability of a polymer. Melt fracture is a phenomenon that may severely limit processing speed of polymers. Melt fracture usually happens when the wall stress of a polymer exceeds a certain critical shear stress [13, 14]. Using controlled rheology polypropylenes Biak and Tzoganakis [15] obtained the following two relations:

$$\sigma_c(\text{MPa}) = -1.73306 \times 10^{-7}\, M_w + 0.16503 \tag{15}$$

$$\sigma_c(\text{MPa}) = -0.00611 \times \text{PDI} + 0.17202 \tag{16}$$

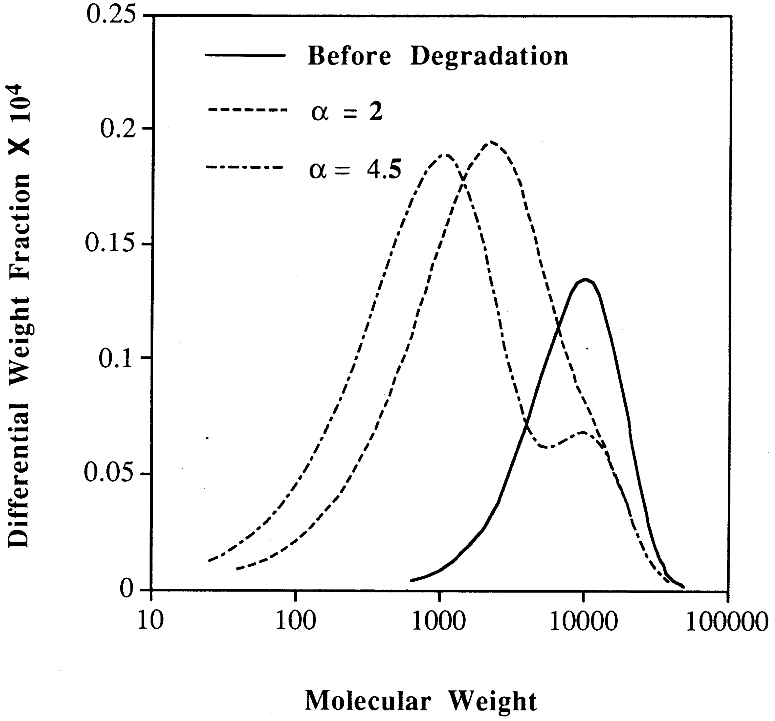

FIGURE 3 Differential weight fraction distribution of a Schulz–Zimm distribution with $M_w = 15{,}000$ and $M_n = 10{,}000$ subject to segregated degradation with $w = 0.5$.

Equation (15) indicates that the critical shear stress decreases when M_w increases, which agrees with results on other polymers [16]. Equation (16) indicates that the critical shear stress decreases when DPI increases, but this dependence is very small. Since the effect of decreasing M_w outweighs the effect of increasing PDI it can be concluded that after segregated degradation the critical stress will decrease and will not reduce the processing rate because of the melt fracture.

CONCLUSIONS

The model of segregating polymers can be used to produce a polymer with wider molecular weight distribution. The Schulz–Zimm molecular weight distribution is used for calculation. The results show segregation increases the polydispersity index. Also a bimodal molecular weight distribution can be produced from a unimodal molecular weight distribution.

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