

Evolution of the Molecular Weight Distribution and Linear Viscoelastic Rheological Properties During the Reactive Extrusion of Polypropylene

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SYNOPSIS

Homogeneous and nonhomogeneous reactive extrusion of polypropylene is modeled using random chain scission statistics coupled with the double reptation mixing rule. In this manner, the evolution of both the molecular weight distribution and the linear viscoelastic material properties is quantitatively predicted for the reactive extrusion–pelletization process. Dispersion in the level of random chain scission has little impact on the MFI for a given average level of chain scission; however, dispersion does generate a marked increase in the recoverable compliance (melt elasticity) relative to the ideal homogeneous random chain scission case. Methods to quantitatively determine the degree of cracking dispersion in processing equipment are identified. Quality control issues such as blending materials of known linear viscoelastic properties to obtain a desired property set is considered in the context of known empirical relations consistent with the double reptation model. Simple mixing rules for the melt flow index and the steady-state recoverable compliance involving only single component MFI and J_e information are derived. © 1995 John Wiley & Sons, Inc.

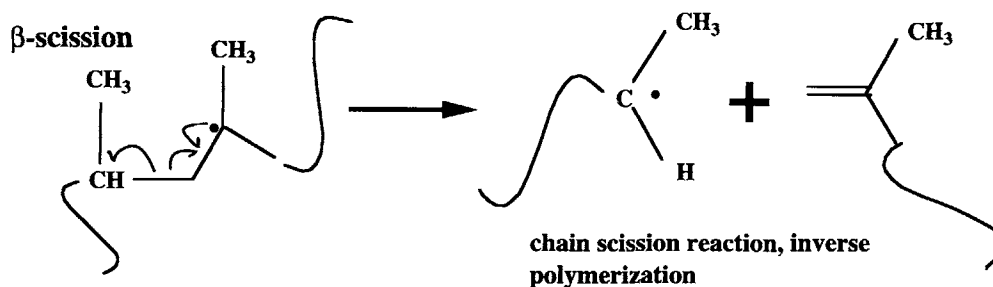
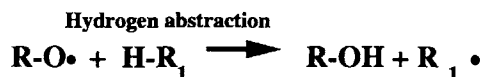
INTRODUCTION

Commercial polypropylenes are synthesized in a manner that typically generates polymer with a relatively broad distribution of molecular weights. The magnitude of the dispersion in molecular weight is often characterized by the ratio of the weight average to number average molecular weight, $Q \equiv M_w/M_n$. Values of Q depend on the specific polymerization route taken; however, they are typically around 10 for polypropylene,^{1,2} which is a truly broad distribution. Melts with broad molecular weight distributions are known to be highly elastic relative to narrow distribution melts. This situation severely restricts the throughput of common polymer processing operations, such as fiber spinning or injection molding, due to the onset of viscoelastic flow instabilities.^{3–5}

In order to attain a narrower molecular weight distribution of lower molecular weight “controlled rheology” material, what is typically done commercially is to start with a higher molecular weight re-

actor grade material and subsequently cleave, i.e., depolymerize or “crack,” the polymer by inducing random scissions along the chain backbone in a reactive extrusion process.^{6,7} In this manner, the polymerization reactor can be run at a constant, optimal set of operating conditions and a wide variety of lower average molecular weight, low viscosity, low elasticity polypropylene products can be postprocessed via a continuous reactive extrusion pelletization process. The resulting average molecular weight and molecular weight distribution of the polymer is controlled by setting the temperature and residence time in the extruder and metering the quantity of peroxide initiator injected into the system.

Chemically, chain scissions are made via a free radical chain reaction that induces breaks in the chain backbone.^{5,6,8,9} The generally accepted chemical mechanism for chain scission in polypropylene is shown in Figure 1. The free radicals can be generated thermally ($T > 300^\circ\text{C}$) in the presence of oxygen^{8,9} or at lower temperatures with initiators such as dialkyl peroxides.^{6,10} The key sequence is the free radical attack on tertiary hydrogens along the chain backbone and the subsequent β -scission

1) **Initiation**2) **Propagation**

And numerous other propagation steps

3) **Termination**

Figure 1 Free radical chain reaction mechanism thought to be responsible for the chain scission of polypropylene. β -Scission of tertiary radicals leads to cleavage of the polypropylene backbone. Not all possible propagation or termination reactions are explicitly considered.

decomposition of the free radical into two pieces, thereby cleaving the chain backbone. The reaction propagates by having the secondary free radical attack another tertiary hydrogen to generate an energetically more favorable tertiary free radical and, hence, continue the chain reaction. Thus, assuming all tertiary hydrogens along the chain backbone are chemically equivalent and equally accessible, the chain scission process is statistically random in the sense that breaks in the chain are equally likely to happen anywhere along the chain.

If the chemistry of the free radical cracking results in a statistically random chain scission, as suggested above, the process mimics Poisson statistics (random spacing of scissions along the chain backbone).¹¹⁻¹³ As such, it both lowers the molecular weight while driving the shape of the molecular weight distribution asymptotically toward the Flory-most probable distribution, $M_w/M_n = 2$. For initially broad distributions, this has the effect of narrowing the molecular weight distribution, although, clearly, if a monodisperse sample were to be cracked, the broader Flory distribution would ultimately result. The extent to which the final molecular weight distribution resembles the most probable distribution depends on the shape of the initial distribution and

the extent or "depth" of the cracking as characterized by the average number of chain scissions per original molecule.

The above discussion contains several severe physical idealizations that are not necessarily realized in practical reactive extrusion processes. For example, in order for the cracking to asymptotically drive the system to the most probable molecular weight distribution, the chain scission must be truly random in a statistical sense. This demands that every cleavable functional group (tertiary hydrogen in the case of polypropylene) throughout the system be equally likely to be cleaved.⁷ Any physical or chemical nonhomogenities within the extruder will corrupt this idealization, and realistic models of the process must account for such nonidealities.

Commercial polypropylenes are typically sold on the basis of their physical properties in both the solid semicrystalline and melt states. Physical properties, thus, constitute the relevant quality control criterion for polypropylene manufacture. The mechanical properties of the melt are of particular importance in situations where ease of processing is a key criteria. The physical properties themselves are intimately and inherently related to the underlying molecular weight distribution.

Equations that quantify such relationships are termed mixing rules. Thus, in order to understand the manner in which the physical properties evolve in a random chain scission reactive extrusion process, we shall first have to understand how the molecular weight distribution evolves under such conditions. With an accurate mixing rule in hand, the molecular weight distribution can be quantitatively converted into physical property information. The goal of this work is to translate the effects of both ideal and nonideal cracking into a quantitative description of the evolution of the molecular weight distribution in terms of the level of chain cracking and its dispersion. The evolution of the molecular weight distribution can be quantitatively transformed into the evolution of the mechanical properties of the resulting polymer melt utilizing a general mixing rule. An outline of the above ideas is presented in Figure 2(a).

With respect to physical property evolution, we specifically seek to quantitatively predict the effect of the reactive extrusion cracking process on the resulting steady-state recoverable compliance, which is known to correlate with the spinnability of the material,^{3,4} and the melt flow index (MFI). The steady-state creep compliance is the linear viscoelastic property most often used to assess the intrinsic elastic character of viscoelastic fluids. The melt flow index is empirically known to correlate with the weight average molecular weight,^{14,37} while the recoverable compliance is very sensitive to the breadth of the molecular weight distribution and physically reflects the inherent elasticity of the melt.^{15,37} Given that one of the principal objectives in performing a reactive cracking extrusion is to modify the mechanical properties, i.e. processability, of the melt, these are clearly the relevant parameters to monitor.¹

MODELING THE EVOLUTION OF THE MOLECULAR WEIGHT DISTRIBUTION AND THE RHEOLOGICAL PROPERTIES DURING REACTIVE EXTRUSION

Initially, we shall assume that ideal, statistically unbiased random cracking occurs throughout the melt. This is clearly a limiting, best case, scenario and will generate molecular weight distributions and their underlying rheological properties corresponding to an optimal processing situation. We shall subsequently relax the random chain scission requirement and model nonideal situations where random chain scission occurs nonhomogeneously.

The viability of any scheme to monitor the evolution of the mechanical properties of the melt is predicated on the existence of an accurate, general mixing rule characterizing the relationship of the linear viscoelastic material properties to the molecular weight distribution. In this regard, the rheology of linear flexible polymers has been the subject of intense theoretical and experimental work for at least 40 years. Considerable progress has been made as a result of these efforts, to the point where the linear rheology of monodisperse linear polymers is essentially a closed subject. The seminal contribution to this success was the tube and reptation concept originally proposed by de Gennes.¹⁶ Incorporation of polydispersity into the model proved considerably more difficult. The principal difficulty here lies in the fact that the tube is no longer a time invariant quantity on the time scale of stress relaxation, as it approximately is for the monodisperse case.

Recently, an accurate mixing rule for polydisperse systems based on the tube and reptation concept has been independently developed by Tsengoglou and des Cloizeaux.¹⁷⁻¹⁹ The basic idea in these "double reptation" models is that both the test chain and the surrounding polymer matrix simultaneously diffuse, enabling two independent, parallel relaxation mechanisms to operate; ordinary reptational diffusion and constraint release. The details of the double reptation model are described in the original references,¹⁷⁻¹⁹ for this work, we shall require only the general relation connecting the linear viscoelastic mechanical properties to the molecular weight distribution. The relation (1) summarizes the double reptation model generalized for a continuous distribution of weight based molecular weights, $W(M)$.

$$\sqrt{\frac{G_{\text{blend}}(t)}{G_N}} = \int_{M_e}^{\infty} W(M) \sqrt{F(M, t)} dM. \quad (1)$$

Here, $G(t)$ represents the linear relaxation modulus, G_N is the plateau modulus that scales the relaxation modulus to order unity in the plateau and terminal regimes. The function $F^{1/2}(M, t)$ represents the monodisperse relaxation function of a single chain in a matrix of fixed obstacles, which is often modeled as a single negative exponential, although other forms are possible. The lower limit of (1) is the entanglement molecular weight, M_e . Because the double reptation model is predicated on the notion that entanglements completely dominate the dynamics of concentrated systems, the model is not, in principle, capable of accounting for contributions to the rheology below M_e . However, it is well estab-

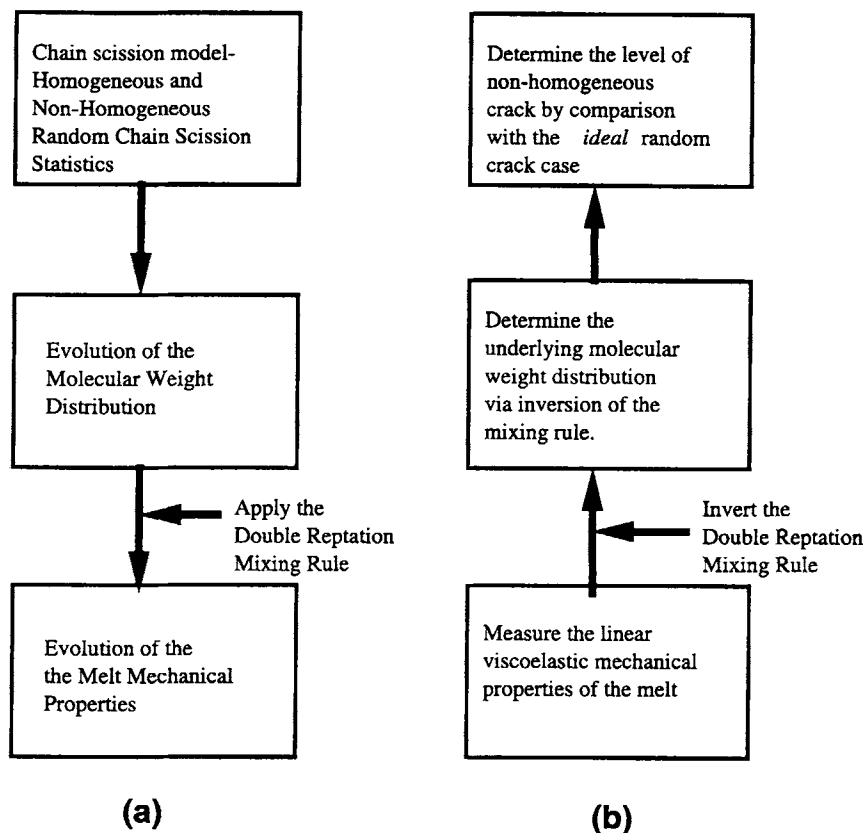


Figure 2 Flow sheet for the modeling of the reactive extrusion of polypropylene. (a) Predictive capability in the forward direction with processing parameters, such as the degree of random chain scission, all known. (b) Deduction of process parameters, such as the extent and dispersion of chain scission, from the mechanical properties of the emerging polymer melt.

lished that polymer with molecular weights below the entanglement level contribute to the rheological properties in a Rouse-like fashion. An additional term to account for this contribution can readily be incorporated into (1).

The physics describing how a given molecular weight distribution undergoing a random chain scission process evolves was first addressed by Montroll²⁰ in the 40s and subsequently developed by Saito,^{12,13} among others.^{11,21,22} The evolution of the weight-based molecular weight distribution in terms of the level of chain scission can be shown to be (see Appendix 1).

$$W(M, t) = e^{-Mt} \left[W(M, 0) + Mt \int_M^\infty \left[\frac{(2 + M't - Mt)}{M'} \right] W(M', 0) dM' \right]. \quad (2)$$

Here, $W(M, 0)$ is the initial, weight based, molecular weight distribution function and t is a di-

mensionless cracking parameter that reflects the number of chain scissions that have occurred per available chemical structural unit. When $t = 1$, all polymer has been reduced to its constituent monomer. As such, $t \ll 1$ in general.

$$t \equiv \frac{\mu t'}{M_t}. \quad (3)$$

Here, μ represents a steady rate of chain scission, M_t the total number of cleavable structural units, and t' is real time. It should be noted that although the time is scaled with a hypothetical steady rate of chain scission, the relation (2) applies regardless of the specific chemical kinetics of the degradation process. This point is a manifestation of the fact that it is actually the number of chain scissions per available functional group, $\mu t'/M_t$, that determines the evolution of the molecular weight distribution, i.e., there is no explicit time dependence in random chain scission statistics, the independent variable is the number of chain scissions. More generally, an

integral expression over a nonconstant rate of chain scission $\mu(t')$ will be required to determine t .¹³

$$t = \frac{1}{M_t} \int_0^{t'} \mu(t') dt'. \quad (4)$$

Thus, starting from a given molecular weight distribution $W(M, 0)$ we can integrate (2) and, coupled with the rheological mixing rule (1), monitor the evolution of the linear viscoelastic rheological properties as the molecular weight degrades in an ideal, random manner.

We can deduce the relevant parameters to characterize the chain scission process by considering the effect of scission on the number average molecular weight. Every chain scission results in the creation of an additional molecule. Because the number average molecular weight is simply the total mass divided by the total number of molecules, a quantitative assessment of the total number of scissions can be made if the number average molecular weight can be experimentally determined. The average number of chain scissions per original molecule can be directly calculated from changes in the number average molecular weight.²³

$$\gamma \equiv \bar{M}_n(0) \left[\frac{1}{\bar{M}_n(t)} - \frac{1}{\bar{M}_n(0)} \right] = \frac{N(t) - N(0)}{N(0)}. \quad (5)$$

Here, $N(t)$ is the total number of molecules in the ensemble at time t . Changes in the number average molecular weight necessarily impact the weight average molecular weight. Given the bias of the cracking procedure to longer molecules (see Appendix 1), chain scission will impact the weight based molecular weight more strongly than the number based molecular weight. As noted above, ideal random cracking drives the degraded molecular weight distribution asymptotically toward the most probable distribution. Practically, this distribution shape is achieved when the number of chain scissions per original molecule γ is greater than ~ 1 .

EVOLUTION OF THE MELT FLOW INDEX AND RECOVERABLE COMPLIANCE DURING THE REACTIVE EXTRUSION OF POLYPROPYLENE

We now proceed to combine the double reptation mixing rule (1) with the ideal random cracking molecular weight evolution eq. (2) to monitor the evolution of the linear viscoelastic material properties as outlined in Figure 2 (a). Such calculations reveal

the average number of chain scissions required to achieve a desired level of increase in the melt flow index and/or decrease in the steady-state recoverable compliance, two signature properties of controlled rheology polypropylene.

In order to quantitatively utilize the double reptation mixing rule, it is necessary to experimentally determine the plateau modulus and the monodisperse relaxation function for polypropylene. These are the only material parameters in the double reptation model. In this regard, we draw upon data reported by Wasserman.²⁴ Specifically, for the plateau modulus we shall use a value of 4.5×10^6 dynes/cm² and the corresponding expression for the single monodisperse relaxation time as a function of molecular weight,

$$F^{1/2}(M, t) = \exp \left\{ - \frac{t}{\lambda(M, T)} \right\}. \quad (6)$$

Here, $\lambda(M, T) = K_\lambda M^{3.6}$, where $K_\lambda = 2.0 \times 10^{-22}$ (s/a.m.u.) at 190°C. With these material parameters set, we can proceed to quantitatively monitor the evolution of the molecular weight distribution and mechanical properties of a polypropylene melt for several representative starting molecular weight distributions.

In order to make our data as accessible as possible, in addition to the predicted evolution of the zero shear viscosity with cracking we shall also present the evolution of the melt flow index (MFI) with depth of crack. It is well established that these two quantities are not independent, at least for linear polymers, being related to one another through the reciprocal relation (7), provided the stress level in the capillary is sufficiently low to ensure linear material response.

$$\text{MFI} = \frac{K_{\text{MFI}}}{\eta_0}. \quad (7)$$

Here, K_{MFI} is a constant that is determined empirically. In this work we select our $\text{MFI}-\eta_0$ parameters such that our numerical data match the polypropylene data presented in Bremner et al.¹⁴ ($K_{\text{MFI}} = 3.0 \times 10^5$ Poise for polypropylene at 190°C).

We examine the evolution of two distinct starting molecular weight distributions that illustrate properties of the ideal random chain scission process and how it interacts with the resulting rheological properties. The first distribution we examine is a bimodal distribution. Subsequently, we examine a Wesslau (log-normal) distribution, which is more typical of polypropylene polymerized via commercial catalysts.

Figure 3(a) illustrates the evolution of the MWD of an initially bimodal distribution as a function of the dimensionless cracking parameter, t , defined by eq. (4). The two modes are initially of equal mass fraction and are separated by about two orders of magnitude. The principal point illustrated here is that the mode corresponding to the high end of the molecular weight distribution is preferentially attacked during random chain scission. The basis for this bias lies in the proportionately greater number of available sites for attack on the larger molecules

(see Appendix 1). In this case, the large molecules are initially about 100 times more likely to be attacked than the smaller ones. As such, the higher moments of the molecular weight distribution are more severely impacted by the chain scission process, particularly during the early portions of the process. This point is illustrated in Figure 3(b), which shows the evolution of the number, weight and "z" average molecular weights during the chain scission process. The ordinate in these plots is the number of chain scissions per original molecule, γ ,

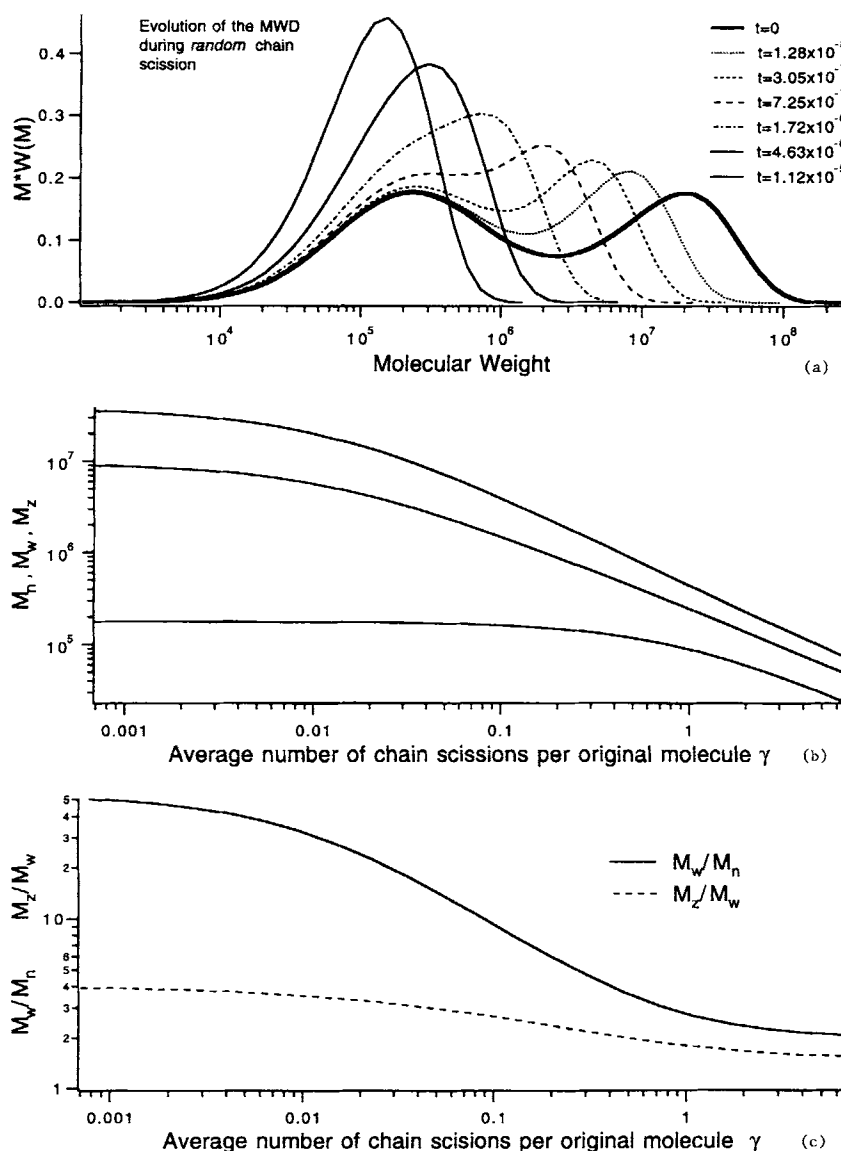


Figure 3 Evolution of a broad bi-modal molecular weight distribution during the course of ideal random chain scission. (a) Molecular weight distribution at various values of the dimensionless cracking parameter t . (b) Number, weight, and z average molecular weights as a function of the number of chain scissions per original molecule, γ . (c) Polydispersity indices; M_w/M_n and M_z/M_w as a function of the number of chain scissions per original molecule, γ .

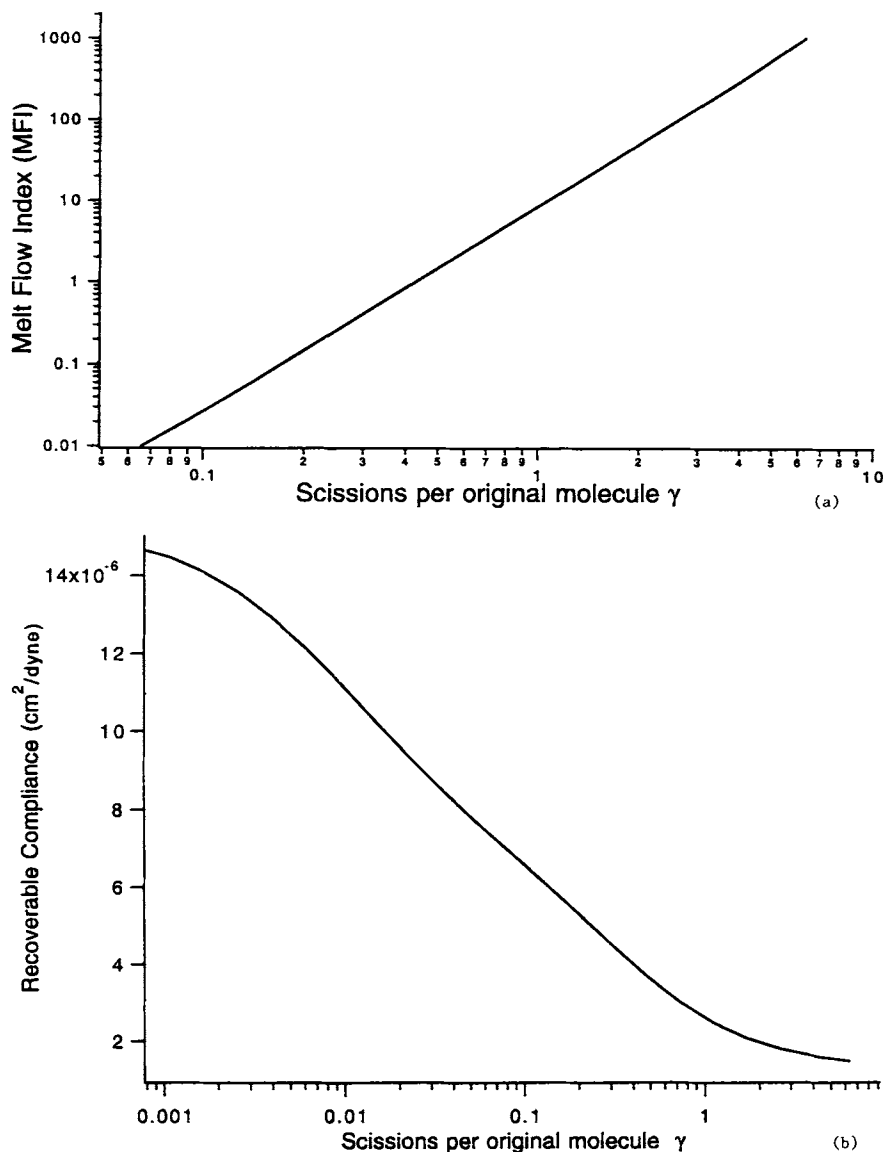


Figure 4 Evolution of the melt-flow index and steady-state recoverable compliance vs. chain scissions per original polypropylene molecule for the molecular weight distribution in Figure 3.

which is defined by eq. (5) and can, in principle, be experimentally measured. Note that when γ is of order unity, the molecular weight distribution is nearly at its asymptotic shape, i.e., the Flory most probable distribution.

Utilizing the double reptation mixing rule (1) with parameters appropriate for polypropylene melts, the information content in Figure 3(a) can be quantitatively transformed into linear viscoelasticity data. We present our results in terms of the melt flow index (MFI) and the steady-state recoverable compliance, which are typical quality control criteria for commercial polypropylenes. It is immediately obvious that the range of cracking depths

illustrated in this example are far greater than one would ever attempt in practice, i.e., typically one would crack from say, 0.5 MFI to 40 MFI, not the orders of magnitude shown in Figure 4(a). However, the calculations do serve to bring out general features of the cracking process in an obvious, if exaggerated manner.

The steady-state compliance is related to the breadth of the distribution and is an absolute minimum for a monodisperse material.¹⁵ As such, the compliance asymptotes when the molecular weight distribution approaches its asymptotic most probable shape, $M_w/M_n = 2.0$ and $M_z/M_w = 1.5$. The double reptation model predicts a corresponding

asymptotic value for the steady-state recoverable compliance of $\sim 1.5 \times 10^{-6}$ cm²/dyne, which is approximately consistent with the only available narrow distribution data for polypropylene,²⁵ $J_e = 4.8 \times 10^{-6}$ cm²/dyne for a broader molecular weight distribution, $M_w/M_n = 2.2$ and $M_z/M_w = 1.75$.

The second example we examine is more representative of a system likely to be encountered in actual commercial vis-cracking of polypropylene. The starting molecular weight distribution is a Wesslau (log-normal) distribution with an M_w/M_n of 20 and M_w of 5×10^6 . Figure 5 shows the molecular weight distribution both lower and narrow toward M_w/M_n of 2 as the depth of crack increases. Figure 6(b) illustrates the evolution of the two polydispersity indices, for which the initial value of both is 20 for a log normal distribution. Note that even when γ is 0.001, the value of M_z/M_w has already been reduced by a factor of 2. This phenomena is a manifestation of the proportionately higher likelihood that larger molecules will be attacked combined with the broad starting molecular weight distribution.

Figure 7 illustrates the evolution of the melt flow index (MFI) vs. depth of crack. An approximate power law relationship holds over the entire range of crack examined. The slope of the curve is ~ 2 . The power law relationship in Figure 7 results from the approximate power law fall off of the weight based molecular weight versus γ shown in Figure 6. The relationship between the two is apparent from eqs. (7) and (13).

Figure 8 shows the steady-state compliance vs. depth of crack. The compliance monotonically decreases about three orders of magnitude as a function of depth of crack asymptoting to its most probable MWD value. Here, again, the relationship is simpler and more compact for the case of a Wesslau distribution compared to the less commonly encountered bimodal distribution. This feature is a result of the less radical change in the shape of the molecular weight distribution as cracking evolves.

Although the change in shape of the molecular weight distribution is less radical for the Wesslau distribution, the change in the magnitude of the recoverable compliance is orders of magnitude larger than it is for the bimodal case even though the dispersion in the molecular weight distributions is larger in the latter case. However, even these radically different MWD shapes are consistent with the empirical relationship between the recoverable compliance and ratios of moments of the molecular weight distribution, specifically M_z/M_w . These empirical relationships and their relationship to the

double reptation model shall be discussed in detail in the next two sections.

EXAMINATION OF THE EFFECT OF NONHOMOGENEOUS CHAIN SCISSION ON THE EVOLUTION OF THE RHEOLOGICAL PROPERTIES

We now examine the effect of nonuniform chain scission on the evolution of the linear viscoelastic material properties. Such processing nonidealities can result from a variety of chemical or physical nonidealities in the extruder. For example, any nonhomogeneity in the spatial distribution (concentration gradient) of the cracking agent, typically an organic dialkyl peroxide, will obviously result in nonideal (nonhomogeneous) cracking. In this regard, it is relevant to note that despite the nominally high viscosity of polymer systems, the diffusivity of various low molecular weight organic peroxide free radical initiators is typically only slightly smaller than it is in common low molecular weight solvents.²⁶ This point can be physically understood by virtue of the fact that the ordinary Stokes–Einstein relation (8), where the solute diffusivity is inversely proportional to solvent viscosity, does not apply when the solvent is a concentrated polymeric system.

$$D = \frac{kT}{3\pi d_p \eta_0} \quad (8)$$

In entangled polymeric systems, the zero shear viscosity is proportional to the modulus times the longest terminal relaxation time.²⁷ The longest terminal relaxation time corresponds to orientational relaxation of the entire molecule. However, for molecular diffusion of low molecular weight molecules to occur, much smaller portions of the polymer chain are required to change their configuration in order to allow the solute to execute an elementary Brownian diffusion step. Smaller portions of the chain have commensurately smaller relaxation times as quantitatively described, for example, by the Rouse model.²⁷

Departures from ideal homogeneous random cracking can result from several different mechanisms, for example a nonhomogeneous temperature field can induce a concentration gradient of initiator in the extruder in the following manner. Because commercial extruders have large spatial dimensions and the thermal conductivity of polymer melts is quite low, significant temperature gradients can readily develop if adequate precautions are not taken. Given that the rate of peroxide free radical

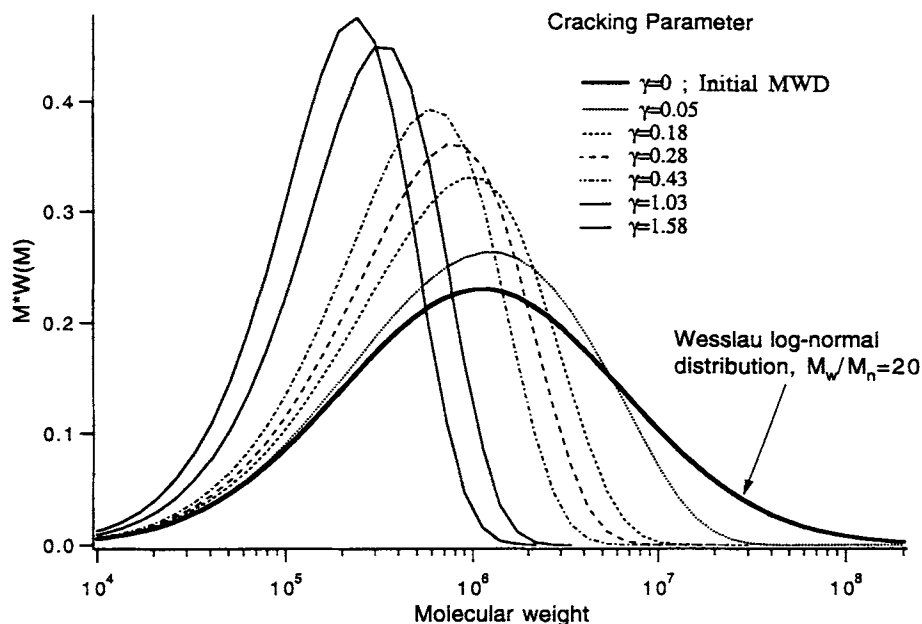


Figure 5 Evolution of a broad ($M_w/M_n = 20$) log-normal polypropylene molecular weight distribution during the course of ideal homogeneous random chain scission.

initiation is typically exponential in temperature, regions of high temperature will quickly consume the available peroxide and locally crack the polypropylene. This will generate large initiator concentration gradients. Given the relatively high diffusivity of the peroxide, peroxide from colder regions of the melt can diffuse or mix into the hotter regions that have depleted peroxide resulting in disproportionately high level of chain scission in the hotter region.

A dimensionless group characterizing this effect can be constructed. The rate of chemical reaction relative to the rate of mass transfer is characterized by a Thiele modulus, N_{Thiele} .

$$N_{\text{Thiele}} = \frac{\text{Rate of chemical reaction}}{\text{Rate of diffusion}} = \frac{k}{D/L^2} \quad (9)$$

In order to quantitatively assess the viability of the above mechanisms leading to nonhomogeneous chain scission, a simple one-dimensional model of the chain scission process was created (see Fig. 9). The polypropylene is imagined to be captured between two flat parallel plates with specified initial and boundary conditions. The peroxide-free radical initiator is mixed into the polypropylene with a prescribed concentration profile and is assumed to decompose homolytically with first-order reaction kinetics,

$$\frac{dC}{dt} = -k(T)C \quad (10)$$

Here, C is the peroxide concentration and $k(T)$ is the rate coefficient for the decomposition of peroxide initiator and is presumed to have the usual Arrhenius form;

$$k(T) = k_0 \exp\left\{-\frac{\Delta E}{RT}\right\} \quad (11)$$

Where ΔE is the activation energy for the reaction and R is the gas constant. The diffusivity of the peroxide is assumed to be orders of magnitude larger than that of the polypropylene and as such, the polypropylene is assumed to be immobile on the time scale of the reaction. Furthermore, the chain length of the scission process is assumed to be a constant, independent of temperature or position in the channel. Thus, the extent of the chain scission at a given position will be proportional to the amount of peroxide initiator that has decomposed at that position. Performing a mass balance on the initiator then allows one to monitor the cracking as a function of time and position in the presence of concentration gradients, temperature gradients, or both. In this manner, the sensitivity of the system to inhomogeneities can be quantitatively assessed, provided the relevant physical constants and reaction parameters are known. The mass balance governing

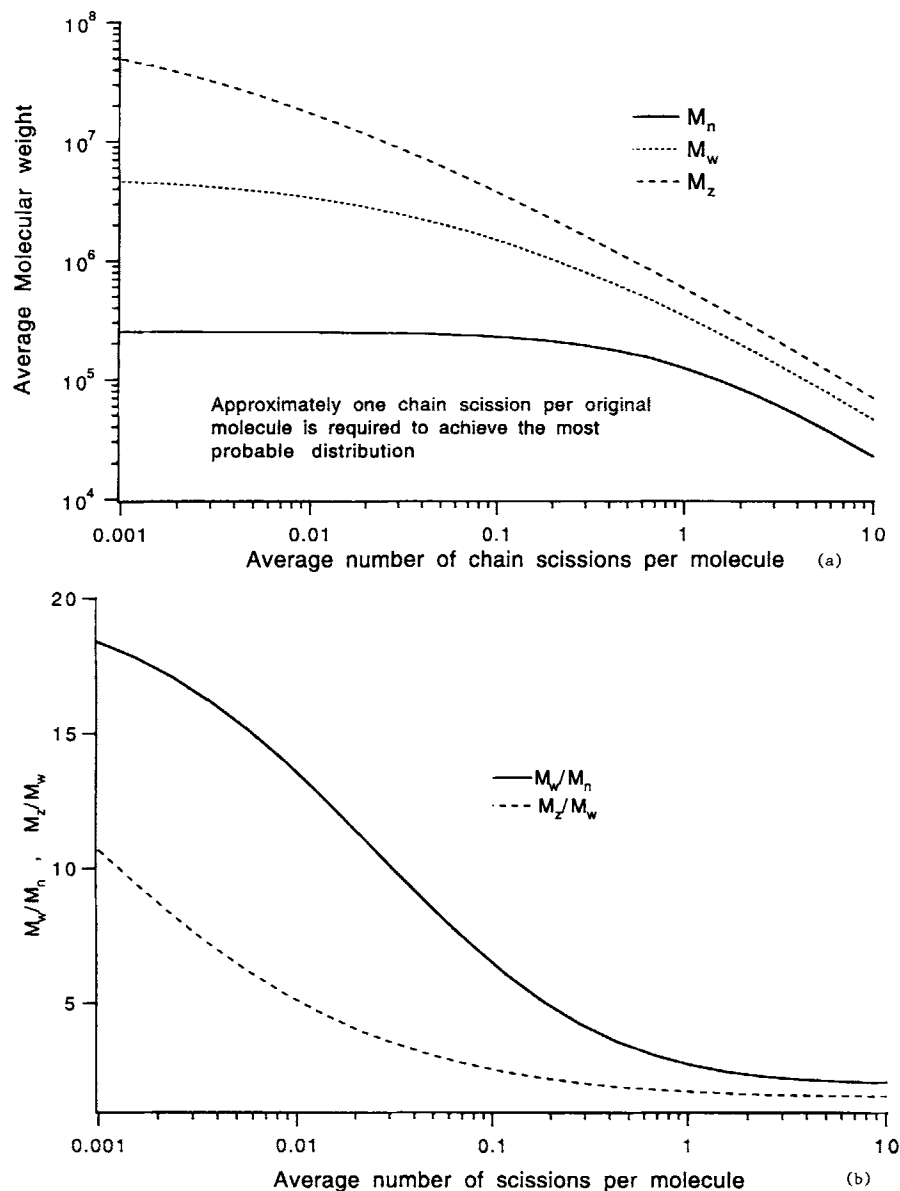


Figure 6 Evolution of moments of the molecular weight distributions shown in Figure 5. (a) Number, weight, and z average molecular weights. (b) Polydispersity indices; M_w/M_n and M_z/M_w .

the evolution of the initiator concentration adopts the usual form,

$$\frac{\partial C^*(x^*, t^*)}{\partial t^*} = \frac{\partial^2 C^*(x^*, t^*)}{\partial x^{*2}} - N_{\text{Thiele}} \exp\left\{-\frac{1}{T^*}\right\} C^*(x^*, t^*) \quad (12)$$

where the dimensionless variables are scaled to order unity and the Thiele modulus is defined as;

$$C^* \equiv \frac{C}{C_o} \quad x^* \equiv \frac{x}{L_o} \quad T^* \equiv \frac{TR}{\Delta E} \quad N_{\text{Thiele}} \equiv \frac{L_o^2}{D} k_o$$

Here, D is the diffusivity of the initiator in a matrix of polypropylene melt, L_o is the width of the channel and C_o is a characteristic initial concentration of initiator. For our calculations, we shall assume that D is a constant, independent of temperature. Although this is not strictly correct, relative to the changes in the chemical reaction rate constant, the diffusivity is relatively constant. Limiting cases of (12) can be readily identified. Specifically, if the

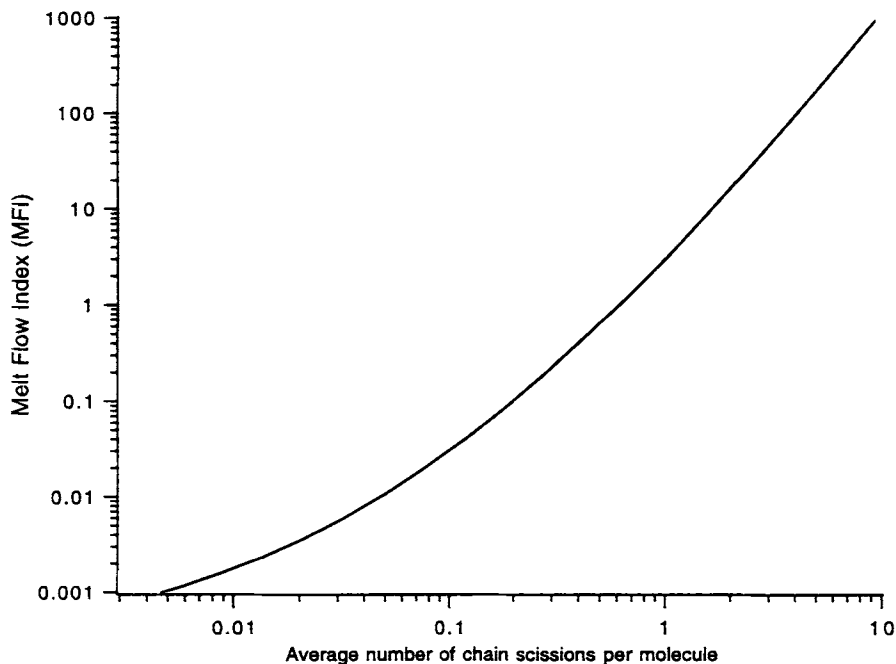


Figure 7 Evolution of the polypropylene melt-flow index for the molecular weight distributions in Figure 5.

Thiele modulus is small ($N_{\text{Thiele}} \ll 1$), molecular diffusion can effectively eliminate concentration inhomogeneities before the initiator can react and generate cracking inhomogeneities. However, if the Thiele modulus is large, molecular diffusion cannot suppress concentration gradients faster than reac-

tion takes place, and inhomogeneous cracking will result should initiator concentration gradients develop for whatever reason.

The system (12) is a linear partial differential equation that, in some instances, can be solved analytically and can always be solved numerically using

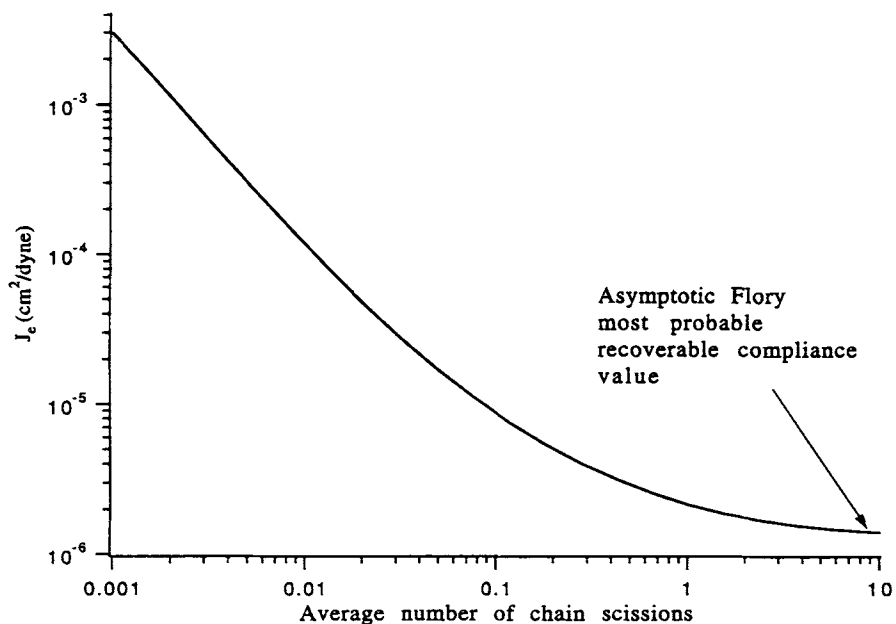


Figure 8 Evolution of the steady-state recoverable compliance vs. the number of chain scissions per original polypropylene molecule for the molecular weight distributions in Figure 5.

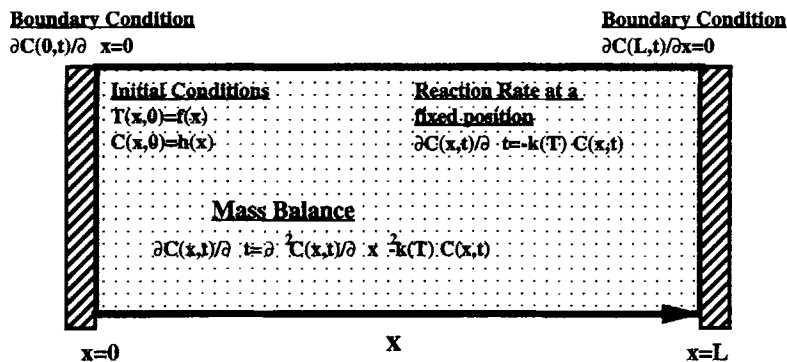


Figure 9 Sketch of the one-dimensional channel model used to quantitatively evaluate the viability of various physical mechanisms leading to nonhomogeneous chain scission.

the Crank–Nicholson method. Equation (12) was solved numerically with various boundary and initial conditions in order to quantitatively determine what specific values of temperature gradient, concentration gradient, and Thiele modulus will lead to levels of nonhomogeneous chain scission sufficient to significantly alter the quality control criteria from the ideal random cracking datum. Three specific model systems were examined;

1. constant Thiele modulus and initial peroxide concentration, vary the temperature gradient;
2. constant temperature gradient and initial peroxide concentration, vary the Thiele modulus;
3. constant initial concentration gradient and temperature, vary the Thiele modulus.

In the first example, we examine the potential of temperature gradients to induce nonhomogeneous crack. At a constant Thiele modulus of 0.1 and uniform initial dimensionless concentration profile of unity, the system is allowed to react and diffuse until all the initiator is exhausted. As noted above, the level of crack at any given point can be calculated by integrating the rate of initiation at any given point with respect to time,

$$\mu(x^*) = K_0 \int_0^{\infty} k(T^*(x^*))C^*(x^*, t^*) dt^*. \quad (13)$$

The constant of proportionality K_0 in (13) is factored out of our results by scaling μ with the average level of crack, μ/μ_0 . The dimensionless level of crack vs. dimensionless position in the channel is shown in Figure 10. In regions of higher temperature, the peroxide reacts more rapidly, inducing a concentration gradient that drives additional peroxide to diffuse

into the hot region and react. The result is that more peroxide reacts in the high temperature region, exactly how much more depends on the relative mobility of the peroxide (N_{Thiele}) and the magnitude of the temperature gradient. Figure 10 reveals that a dimensionless temperature gradient of ~ 1 is required to develop rheologically significant nonhomogeneities in the level of crack for these conditions.

In Figure 10(b), the normalized probability density distribution is deduced based on the ensemble of all polypropylene in the channel. The statistical description provides an alternative method of examining the level of nonhomogeneity and reinforces the conclusion that a minimum dimensionless temperature gradient of unity is required to develop significant levels of nonhomogeneity.

Figure 11 examines a different model system, that of a constant initial concentration profile of unity, temperature gradient of unity with varying values of the Thiele modulus. Figure 11 is, thus, the complement to Figure 10 above. In this situation, we clearly see that increasing the Thiele modulus always exacerbates the level of nonhomogeneity. Apparently, large changes in the Thiele modulus are required to induce significant modifications of the cracking profile, for example, the cracking nonhomogeneity expands only slightly when N_{Thiele} is decreased to 0.01. For these initial conditions, high values of the Thiele modulus lead to narrower distributions, because the faster all the initiator is consumed, the less time it has to diffuse to other portions of the channel and react.

The third and final example we consider is that of a constant initial concentration gradient of unity, no temperature gradient, and varying Thiele modulus. Figure 12 reveals that values of N_{Thiele} greater than 10 are required to induce significant nonhomogeneities in the level of crack. The shape of the

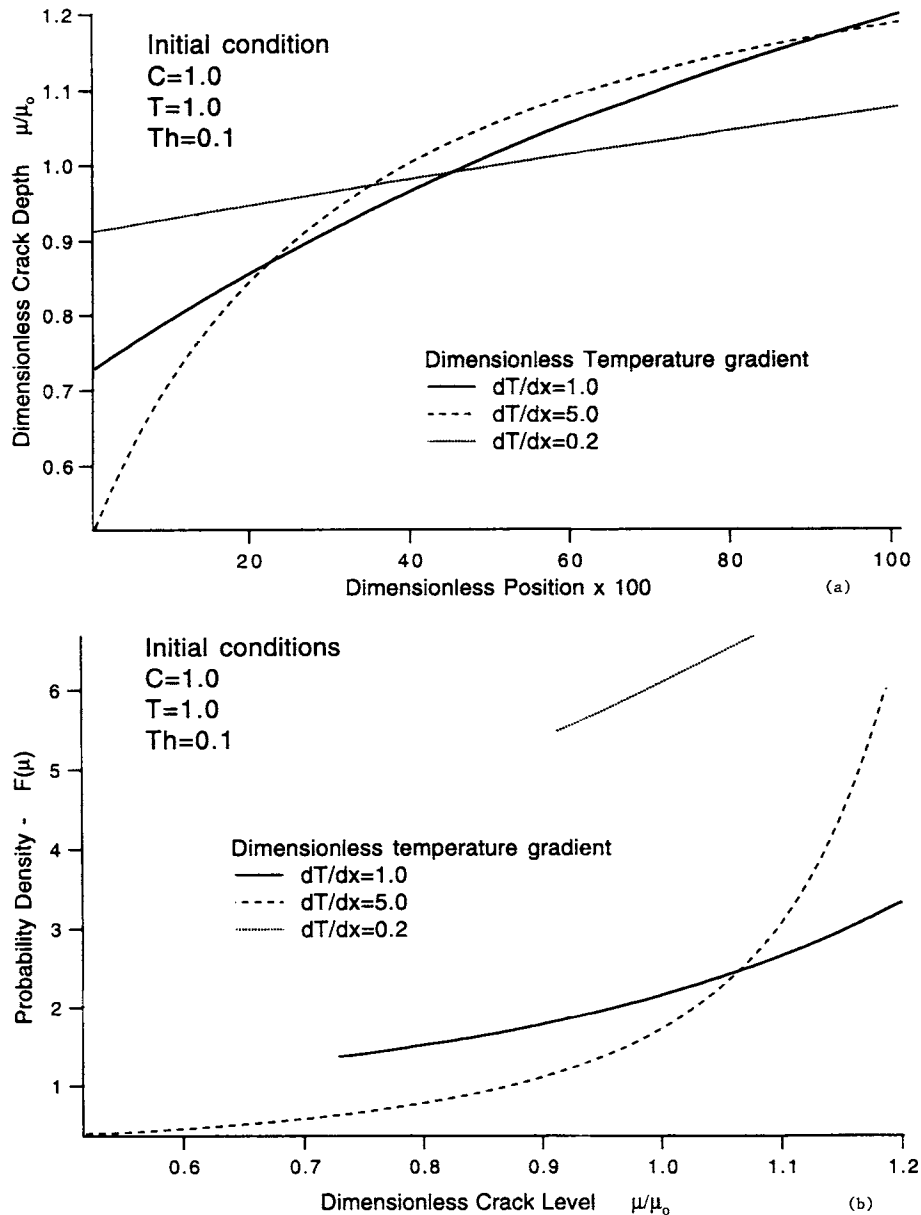


Figure 10 One-dimensional channel model of the polypropylene cracking process to assess the impact of temperature gradients. $N_{\text{Thiele}} = 0.1$, $T = 1.0$ and initial concentration $C = 1.0$ vary the dimensionless temperature gradient. (a) Dimensionless crack vs. dimensionless position in the channel. (b) Probability density of a given dimensionless crack level for all material in the one-dimensional channel.

cracking distribution function has a distinct “U” shape, which spreads dramatically with increasing Thiele modulus. However, the area under the large upswings is negligible compared to the large uniform central portions of the distribution. Thus, at high N_{Thiele} the uniform initial concentration gradient induces an effectively uniform distribution of crack levels, as anticipated.

The fundamental difficulty in properly evaluating the plausibility of the various mechanisms leading

to nonhomogeneous random chain scission is that no fundamental kinetic data is available for the peroxide initiated degradation reaction of polypropylene shown in Figure 1. Thus, fundamental parameters such as the Thiele modulus and activation energy are *unknown* precluding an objective diagnosis of the system.

Because elimination of temperature gradients in polymer melts usually involves increased mixing or agitation, the precise cause of the cracking

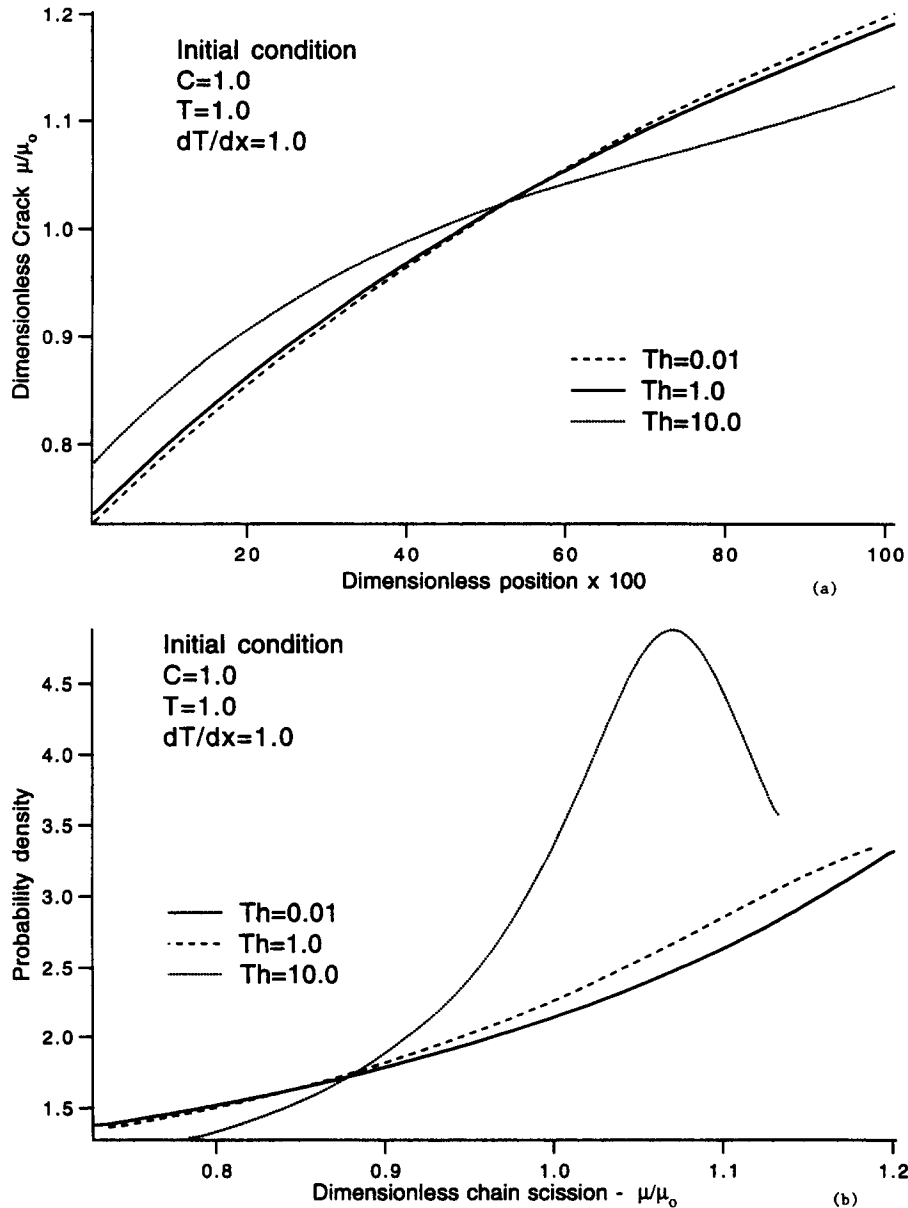


Figure 11 One-dimensional channel model of the polypropylene cracking process to assess the impact of the Thiele modulus at constant temperature gradient, $dT/dx = 1.0$, $T = 1.0$, and initial concentration $C = 1.0$ various N_{Thiele} . (a) Dimensionless crack vs. dimensionless position in the channel. (b) Probability density of a given dimensionless crack level for all material in the one-dimensional channel.

nonidealities can be misdiagnosed because mass transfer limitations and temperature gradients go hand in hand. However, examination of the order of magnitude of the dimensionless ratio of heat to mass diffusivities suggests that it is mass transfer that ultimately disrupts the ideal random cracking, although temperature gradients can interact and exacerbate this effect, as discussed above.

$$\begin{aligned}
 N &\equiv \frac{\alpha_{Heat}}{\alpha_{Mass}} \\
 &= \frac{\text{Thermal diffusivity} \sim 10^{-7} \text{ m}^2/\text{s}}{\text{Mass diffusivity} \sim 10^{-9} \text{ m}^2/\text{s}} \\
 &\approx 10^2 \text{ for poly propylene melts.} \quad (14)
 \end{aligned}$$

In any event, it is chemical and physical inhomogeneities that underlie all nonideal cracking mech-

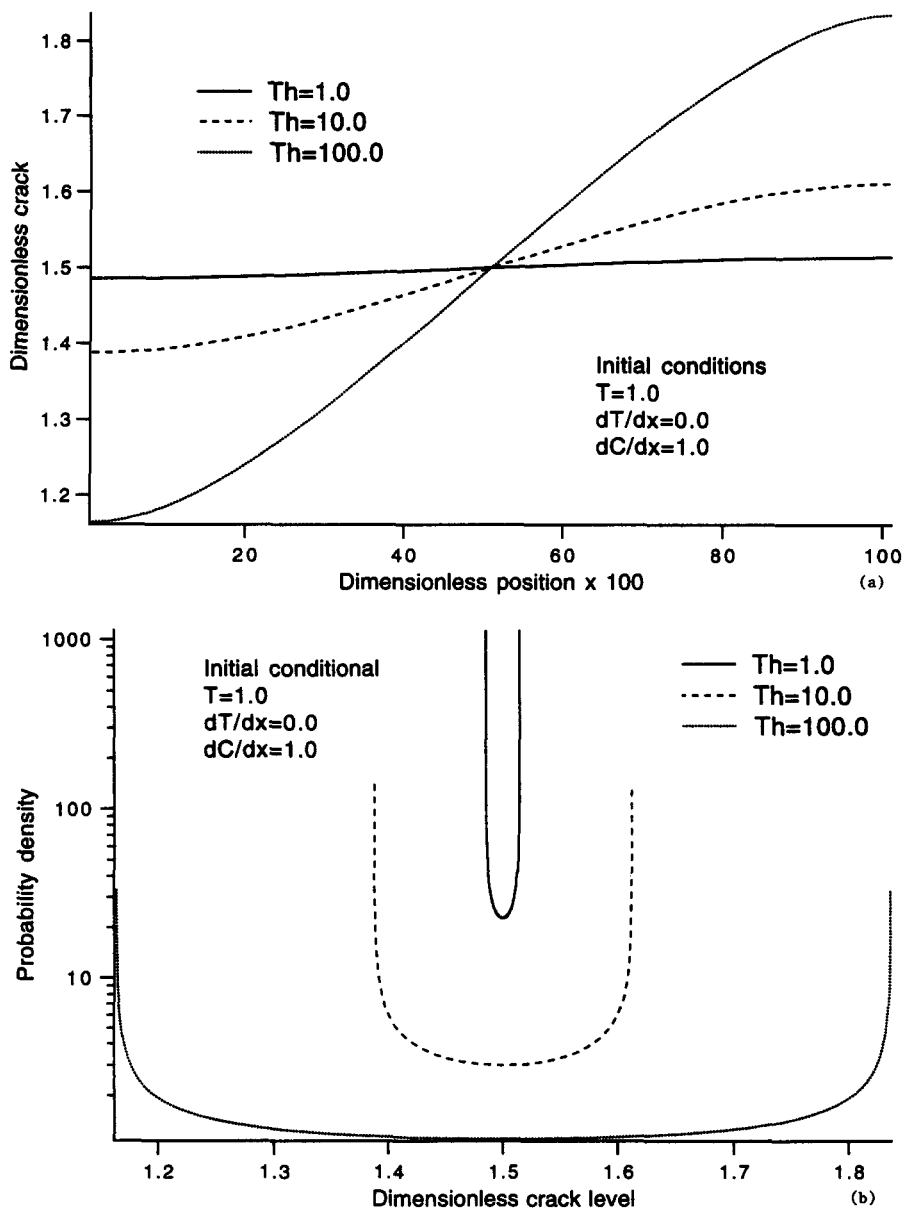


Figure 12 One-dimensional channel model of the polypropylene cracking process to assess the impact of the Thiele modulus at constant initial concentration gradient, $dC/dx = 1.0$, $dT/dx = 0.0$, $T = 1.0$, and various N_{Thiele} . (a) Dimensionless crack vs. dimensionless position in the channel. (b) Probability density of a given dimensionless crack level for all material in the one-dimensional channel.

anisms and proper and thorough mixing in the extruder is the remedy for all these deficiencies.

In order to quantitatively model the effect of nonuniform chain scission, we shall assume that a distribution of cracking depths exists within the process. Such a distribution could arise, for example, as a result of a distribution of residence times and/or time-temperature histories in the extruder, as discussed above.³⁸ Thus, we shall assume that the cracking is locally random in the sense that for a

given polymer chain associated with a specific material particle, all functional groups are equally likely to be cleaved. After exiting the process, we assume that the nonhomogeneous material is subsequently mixed uniformly and proceed to calculate the rheological properties of the resulting homogeneous blend. We define a normalized distribution function $H(\mu)$ as the weight fraction of polymer having random chain scission crack depths of level μ . The molecular weight distribution of the blend can be de-

duced from $H(\mu)$ by first calculating the molecular weight distribution for a given level of crack, $W(M, \mu)$ per eq. (2), and integrating over the distribution function $H(\mu)$.

$$\langle W(M) \rangle_{\text{Mixing cup}} = \int_0^\infty H(\mu) W(M, \mu) d\mu. \quad (15)$$

Utilizing the mixing rule (1), the material properties can be subsequently calculated from $\langle W(M) \rangle$ in the usual manner. We then quantitatively monitor the sensitivity of the rheological properties to the dispersion in the cracking depth distribution as measured by the standard deviation relative to the mean, σ/μ_o . Here, μ_o is the mean crack level and σ is the corresponding standard deviation. To illustrate the above ideas, we shall examine a Gaussian (normal) distribution of crack levels with known amounts of dispersion (variance) in the distribution. Of course, a specific normalized cracking distribution function developed from a detailed analysis of the mechanism responsible for the nonhomogeneous chain scission, such as a distribution of residence times, could be used. A Gaussian distribution is examined here merely as a simple, specific illustrative example.

$$H(\mu) = \frac{1}{\sigma\sqrt{2\pi}} \exp\left\{-\frac{[\mu - \mu_o]^2}{2\sigma^2}\right\}. \quad (16)$$

Because we are not assuming globally random chain scission, the molecular weight distribution will not asymptotically approach the Flory most probable distribution, but rather, a necessarily broader distribution, dependent on the level of dispersion in the cracking depth, σ .

If our rheological mixing rule relating the mechanical properties to the MWD is sufficiently accurate, we can subsequently deduce the level of non-random cracking present in the system in the following manner. The idealized random cracking rheological properties can be deduced for a given level of chain scission. From the measured rheological properties and techniques developed previously, the molecular weight distribution of the actual material can be calculated by inverting the mixing rule²⁸⁻³⁰ and compared to the ideal random crack distribution. In this manner, a detailed quantitative assessment of the departure from statistical randomness can be established by comparing the actual and ideal random scission molecular weight distributions and, more importantly, their consequent impact on the melt mechanical properties. These measurements can then be used as an analytical tool

to quantitatively and objectively evaluate design changes in the reactive extrusion process to improve the randomness of the cracking. These ideas are outlined in Figure 2(b). Alternatively, such a measurement tool can also be used to provide feedback in an online control scheme of such a reactive extrusion processes.³¹

Figure 13 illustrates the effect of dispersion in the level of crack on the quality control criteria for three widely separated levels of crack on a polypropylene system with an initial weight average molecular weight of 10^6 and an M_w/M_n of 10. The dispersion in the level of chain scission distribution is characterized with the standard deviation as a percentage of the mean level of crack, σ/μ_o . Clearly, the steady-state recoverable compliance is a strong function of the dispersion in the level of crack rising exponentially for standard deviations exceeding $\sim 15\%$ for all three average levels of crack examined. It is interesting to note that for standard deviations less than $\sim 10\%$, which corresponds to a broad distribution of crack levels, there is not a significant effect on the recoverable compliance or MFI. Physically, dispersion in the level of crack always leads to broader molecular weight distributions than would be obtained in the case of ideal random chain scission. Broader distributions lead to higher compliance levels as suggested by the empirical correlation below.

$$J_e^0 = K_1 \left(\frac{\bar{M}_z}{\bar{M}_w} \right)^b. \quad (17)$$

The exponent b is typically between 3.3 and 3.7 for most linear flexible polymers.^{15,24}

Although the recoverable compliance is a strong function of dispersion in the level of crack, the melt flow index shown in Figure 12(b) is decidedly less so. Here, only very small reductions in MFI are realized when large levels of dispersion in the level of crack is present. Reference to Figure 14 showing the evolution of the weight average molecular weight as a function of dispersion reveals the molecular reason for this effect. Equation (18) represents the well-established empirical relationship between the zero shear viscosity and weight average molecular weight^{2,24,37}

$$\eta_0 = K_v \bar{M}_w^a = \frac{K'}{\text{MFI}} \quad (18)$$

where the exponent a is typically between 3.3 and 3.6. For polypropylene, $K_v = 1.235 \times 10^{-14}$ and $a = 3.45$ at 180°C . Although the zero shear viscosity

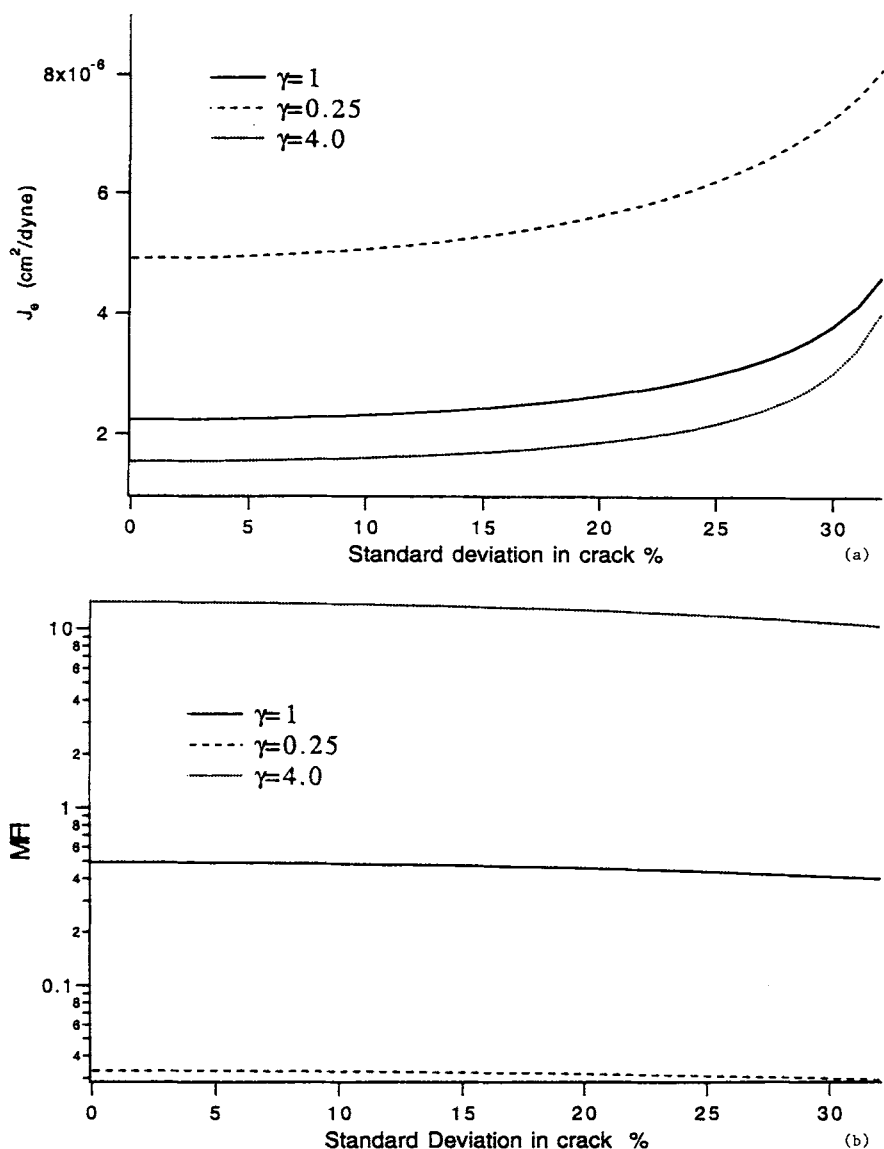


Figure 13 Evolution of the mechanical properties of a polypropylene melt with an initial weight average molecular weight of 10^6 and $M_w/M_n = 10$ undergoing nonhomogeneous random chain scission. A Gaussian distribution of crack levels with varying standard deviations is assumed. (a) Steady recoverable compliance at constant levels of average crack. (b) Melt-flow index at constant level of average crack.

is dependent on the breadth of the molecular weight distribution, this dependence is generally weak relative to the dependence on the weight average molecular weight.²⁴ From the eqs. (18) and (7), it is clear that the MFI scales as $\sim M_w^{-3.4}$. Reference to Figure 14 reveals that increases in the weight average molecular weight are very modest for all the levels of dispersion examined. Higher moments such as the “z” average molecular weight are more seriously impacted by dispersion in the crack level than are lower moments, as one would expect given the bias in the chain scission process toward larger molecules. These points are illustrated in Figure 14.

EMPIRICAL BLENDING RULES FOR PREDICTING QUALITY CONTROL CRITERIA FOR BLENDED COMMERCIAL LINEAR POLYMERS

Given the well-established quantitative predictive capability of the double reptation mixing rule,³¹ we proceed to develop simple, viable blending algorithms for polypropylene quality control parameters such as the melt flow index (MFI) and the steady-state recoverable compliance, J_e . We shall see that these two properties alone are sufficient to provide a reasonable estimate of the first moment of the

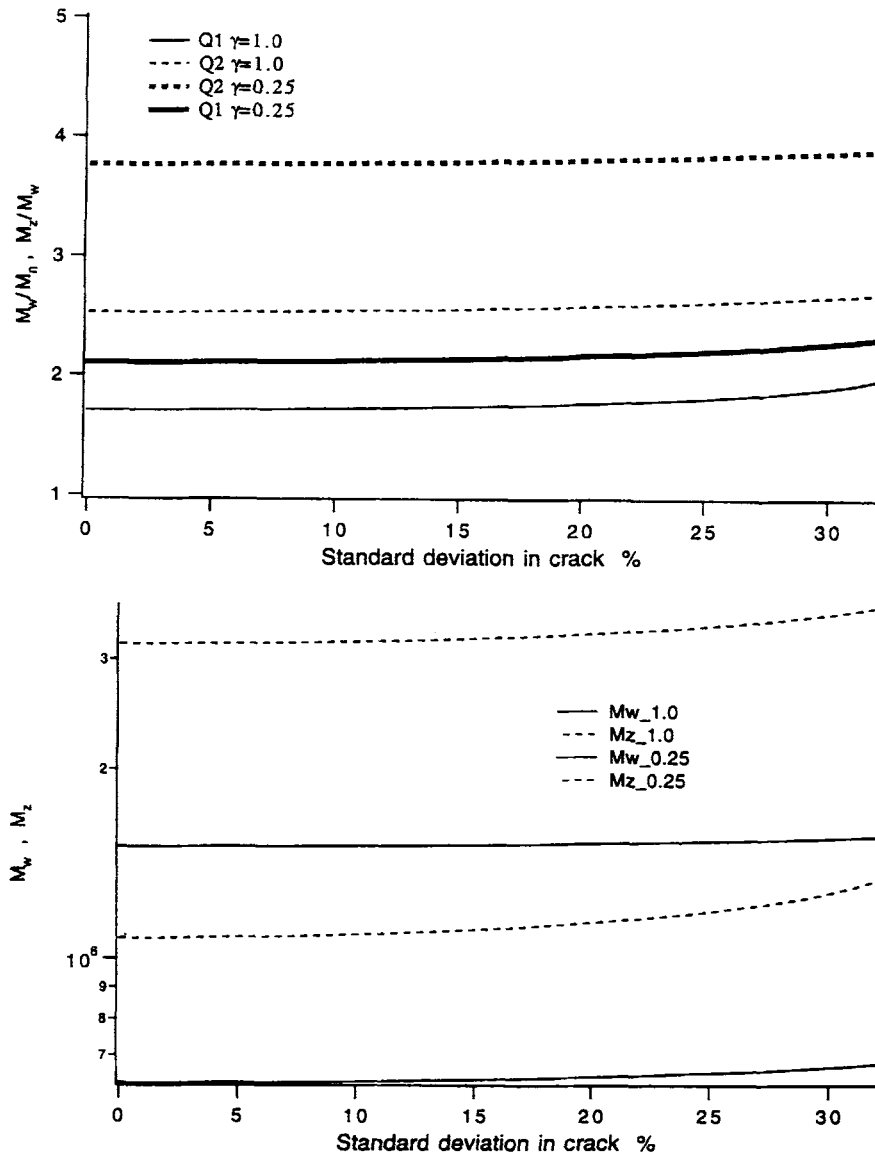


Figure 14 Evolution of the weight and “z” average molecular weights of a polypropylene melt undergoing nonhomogeneous random chain scission. A Gaussian distribution of crack levels with varying standard deviations is assumed, and as such, the number average molecular weight is constant, independent of the level of cracking dispersion.

molecular weight distribution as well as the dispersion or breadth of the distribution.

Blending rules are of considerable practical importance in that correct application of them allows off-spec material to be combined with other material in a deliberate manner that generates a mixture that is within established quality control criteria. This avoids waste and maximizes revenue. Additionally, in the advent of metallocene catalysts,¹ it will be possible to manufacture an array of narrow distribution polyolefins and subsequently blend them to achieve specific, desired final product property sets,

thereby eliminating the vis-cracking operation altogether.

The basis for our method pivots on the existence of well-known empirical relations connecting the linear viscoelastic material properties to moments of the molecular weight distribution. Specifically, we invoke the empirical relationship between the zero shear viscosity and weight average molecular weight (18) and the empirical relationship between the steady-state recoverable compliance and the dispersion in the molecular weight distribution (17). Dispersion here is measured by the ratio of

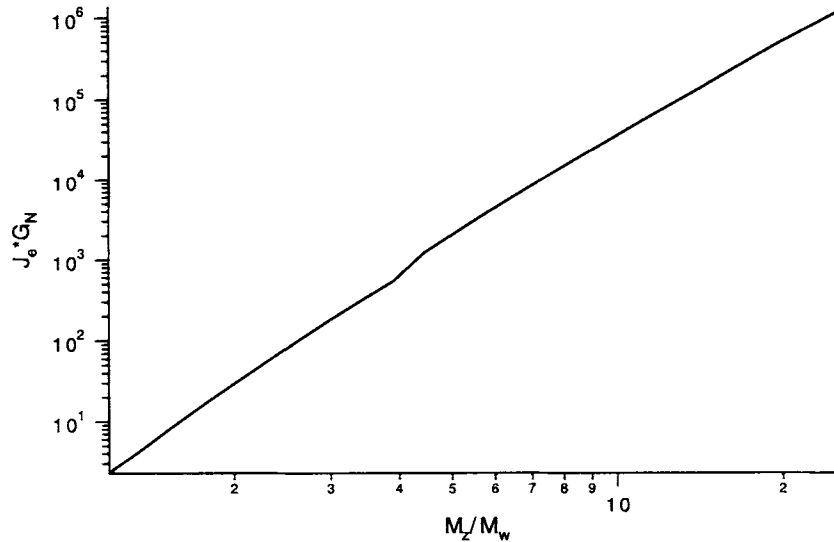


Figure 15 Dimensionless recoverable compliance vs. the ratio of the “z” average to the weight average molecular weights for a model Wesslau log-normal MWD. The power law dependence is manifest.

successive moments. The correlation (17) has been frequently observed for systems of linear flexible polymer.¹⁵

Both of the above empirical relations are predicted by the double reptation mixing rule. This point is illustrated in Figures 15, 16, and 17, for a model molecular weight distribution system. Specifically, a Wesslau log-normal molecular weight distribution was used to calculate the dimensionless recoverable compliance and viscosity as a function of average molecular weight and its dispersion. Figures 15 and 17 clearly indicate the consistency of the double reptation model with eqs. (17) and (18). Furthermore, Figure 16 demonstrates the insensi-

tivity of the recoverable compliance to the absolute value of the molecular weight for a given level of dispersion. Along similar lines, Figure 17 illustrates the weak dependence of the zero shear viscosity on dispersion in the molecular weight distribution, consistent with experiment.²⁴

With the relations (17) and (18) as our starting point, we can proceed to generate nonlinear blending rules involving only the known material properties and the established combining rules for moments of a statistical distribution such as the MWD. Specifically, for an N component blend of distinct polydisperse commercial homopolymers with component mass fractions Φ_i and physical properties $\eta_{o,i}$, MFI_i

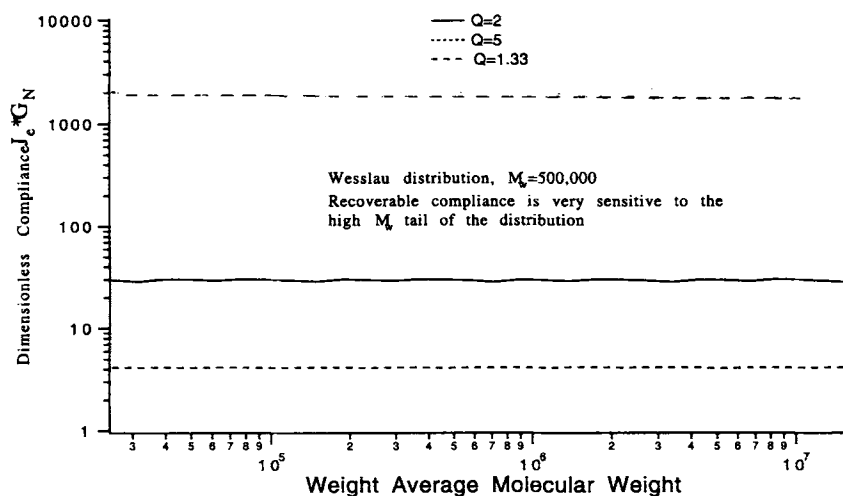


Figure 16 Dimensionless compliance vs. weight average molecular weight at fixed values of dispersion. $Q = M_w/M_n$.

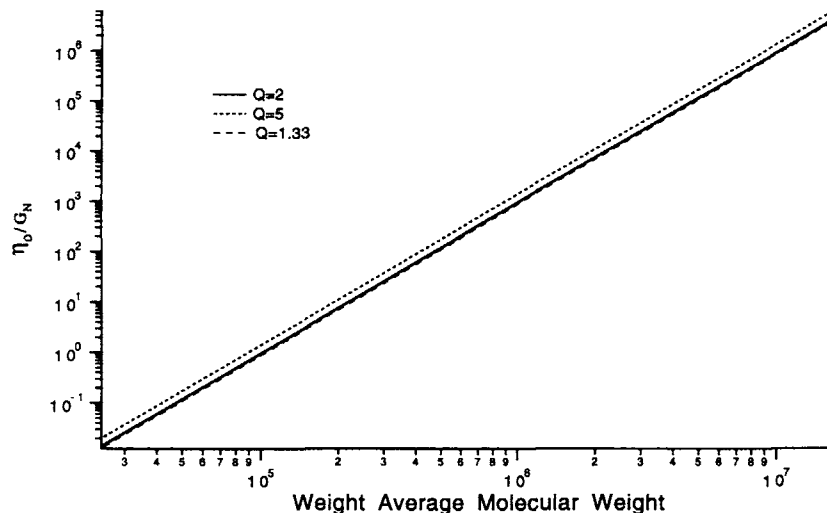


Figure 17 Dimensionless viscosity vs. weight average molecular weight. A clear power law relationship is apparent. $Q = M_w/M_n$. The relationship is insensitive to dispersion in the molecular weight distribution.

and $J_{e,i}$, the blend melt flow index and recoverable compliance can be predicted from the empirical relations (19) and (20).

$$\begin{aligned}
 J_e^0 |_{\text{Blend}} &= K_1 \left[\frac{\sum_{i=1}^N \Phi_i \left(\frac{\eta_{o,i}}{K_v} \right)^{2/a} \left(\frac{J_{e,i}^0}{K_1} \right)^{1/b}}{\left(\frac{\eta_{o,\text{Blend}}}{K_v} \right)^{2/a}} \right]^b \\
 &= K_1 \left[\frac{\sum_{i=1}^N \Phi_i \left(\frac{K'}{K_o \text{MFI}_i} \right)^{2/a} \left(\frac{J_{e,i}^0}{K_1} \right)^{1/b}}{\left(\frac{K'}{K_o \text{MFI}_{\text{Blend}}} \right)^{2/a}} \right]^b \quad (20)
 \end{aligned}$$

Essentially, the above method fixes one moment of the distribution with the melt flow index and subsequently characterizes the breadth of the distribution with the steady-state recoverable compliance. As demonstrated above, the nonlinear empirical correlations (17) and (18) utilized to deduce the above relations are consistent with the double reptation mixing rule. More accurate property blending rules can be developed starting from the original double reptation model (1) at the expense of algorithms of considerably greater complexity. Such methods have been exhaustively detailed by Wasserman and Graessley^{24,32} and tangentially by Mead.²⁸

CONCLUSIONS

Random chain scission theory,^{12,13} coupled with an appropriate rheological mixing rule,¹⁷⁻¹⁹ allows one

to monitor and/or predict the evolution of both the molecular weight distribution and the rheological properties for materials, such as polypropylene or polybutylene, undergoing a reactive extrusion chain scission process. Specifically, we are able to track the reduction of both the steady-state recoverable compliance and viscosity (and, hence, the melt flow index, MFI) during the course of statistically random and nonrandom chain scission. The basic forward prediction scheme is outlined in Figure 2(a).

With the ideal random chain scission result as a fundamental benchmark, one can quantitatively calculate the extent of the chain scission dispersion present as well as its impact on rheological quality control criteria. Quantifying the extent of the non-homogeneous dispersion in the chain scission process is essential in order to develop methods to correct it as well as determine the extent to which it can be tolerated in a process. In this regard, we have determined that relatively high levels of dispersion ($\sigma/\mu_o < 10\%$) in the level of crack can be tolerated before significant impact on quality control criteria occurs. Thereafter, the recoverable compliance rises dramatically while the MFI remains relatively insensitive to the level of dispersion in the crack.

The key to analytically determining the level of dispersion present in a given process lies in the ability to invert the double reptation mixing rule and quantitatively determine the molecular weight distribution underlying the linear viscoelastic rheological properties. This MWD can be compared to the ideal MWD resulting from homogeneous random chain scission for an equivalent level of crack. The methodology to invert the double reptation mixing

rule has been established by Mead.²⁸ An outline of the method to analyze the cracking products and subsequently determine processing parameters is shown in Figure 2(b).

In the event that nonhomogeneous chain scission is a critical issue for a given reactive extrusion process, deducing the specific physical and/or chemical mechanism responsible for the nonrandom chain scission is complicated by the lack of basic kinetic data for the free radical initiation and chain propagation process. This void precludes the evaluation of fundamental dimensionless parameters such as the Thiele modulus. One enigma concerns the fact that the stoichiometric efficiency of the peroxide initiator is quite low, typically of order unity. Given that the chain length of most free radical reactions is several orders of magnitude higher than this, the question of what becomes of the bulk of the peroxide is a relevant concern. One possibility is that once cleaved, the free radicals immediately recombine. A means to reduce this effect and boost efficiency would be more cost effective.

The principal difficulty in obtaining kinetic data is the high melting temperature of polypropylene ($\sim 180^\circ\text{C}$), which makes it difficult to fully mix and homogenize the melt before the initiator has begun to homolytically cleave. It is known that the decomposition rate of dialkyl peroxides that are typically used in the degradation of polypropylene, such as Lupersol 101, is strongly dependent on the local chemical environment.³⁶ In this regard, it would be useful to study the degradation of atactic, non-crystalline polypropylene.³³ With such an amorphous material, the initiator can be completely dissolved and premixed into the polypropylene prior to heating the system to start the reaction. The chemistry should not be seriously impacted by the absence of tacticity, and the kinetics could then be readily determined and extrapolated to the situation of interest.

Whether or not specific mechanisms underlying nonhomogeneous random chain scission can be identified, certain processing changes will always lead to improved homogeneity. Specifically, anything that improves the degree of mixing will necessarily remove nonhomogeneities leading to non-random chain scission. For example, it is well known that twin screw extruders are superior to single screw extruders at mixing and homogenizing polymers.³⁵ As such, twin screw extruders, with appropriate kneading blocks and mixing sections, are generally to be preferred over single-screw configurations in reactive extrusion processes.³⁹ In this regard, the scheme outlined in Figure 2(b) is useful in quantitatively and objectively evaluating a given reactive

extrusion process. Operating in the forward direction, Figure 2(a), this technology enables manufacturing personnel to control processing operations such that polymer with specific physical properties is consistently produced.

Dr. C. K. Harris of Konig/Shell Laboratorium Amsterdam has contributed to the analytical methods developed to address this problem. Dr. S. H. Wasserman of the Union Carbide Corporation has generously provided us with experimental material function data for polypropylene melts. Dr. J. Janzen of the Phillips Petroleum Co. has provided useful comments to preliminary versions of this article.

APPENDIX 1: DERIVATION OF THE EVOLUTION EQUATION FOR THE MOLECULAR WEIGHT DISTRIBUTION DURING STATISTICALLY RANDOM CHAIN SCISSION

In this appendix, we derive eq. (2), which describes the evolution of the molecular weight distribution for a statistically random chain scission process. The derivation is based on an elementary number balance of molecules of arbitrary mass M during the random chain scission process,^{12,13} and the free radical chain reaction mechanism presented in Figure 1, viz.

$$\begin{aligned} & \left(\frac{\text{Net Change in \# Molecules}}{\text{of molecular mass } M} \right) \\ & \quad \text{time} \\ & = \left(\frac{\text{\# of } M \text{ Molecules Created}}{\text{time}} \right) \\ & \quad - \left(\frac{\text{\# of } M \text{ Molecules Destroyed}}{\text{time}} \right) \quad (\text{A1.1}) \end{aligned}$$

$$\begin{aligned} \frac{\partial P(M, t)}{\partial t} = 2 \left(\frac{\mu}{M_t} \right) \int_M^\infty P(M', t) dM' \\ - \left(\frac{\mu M P(M, t)}{M_t} \right) \quad (\text{A1.2}) \end{aligned}$$

We define the following terms;

$P(M, t)$ = Probability that a randomly selected molecule has molecular weight M at time t . $P(M, t)$ is a number-based molecular weight distribution and is assumed to be effectively continuous.

μ = steady rate of random chain scission, (number of chain cuts/time)

M_t = Total length of all polymer (total mass)

Equation (A1.2) can be rewritten in terms of the weight-based molecular weight distribution $W(M, t)$ as;

$$\frac{\partial W(M, t)}{\partial t} = 2 \left(\frac{\mu}{M_t} \right) \int_M^\infty \frac{W(M', t)}{M'} dM' - \left(\frac{\mu M W(M, t)}{M_t} \right) \quad (\text{A1.3})$$

The first term on the right-hand side of (A1.2) represents the number of new molecules of molecular weight M created from the cleavage of larger molecules of weight M' . The chain scission process can only generate an M molecule via scission in two specific places in a molecule of greater molecular weight. This point is reflected in the fact that the rate is proportional to 2μ times the integral over all available larger molecules. The second term on the right-hand side of (A1.2) represents the rate of destruction of M molecules due to chain scission at arbitrary location along the backbone of an M molecule. As such, the destruction rate is proportional to μM , reflecting the total number of viable scission sites in an M molecule. Therefore, random chain scission is proportionately more likely to attack higher molecular weight polymers rather than lower molecular weight polymers. The bias toward cleaving high molecular weight polymer is physically what generates narrower molecular weight distribution polymer from initially broad MWD reactor grade material.

Reviewing the free radical mechanism in Figure 1, we have ignored any contributions to the number balance resulting from the termination step in the free radical chain scission process. The assumption here is that the propagation sequence dominates the chemistry and that the termination sequence contributes negligibly toward the overall number balance. The ratio of the number of propagation cycles per termination process is referred to as the chain length is typically several orders of magnitude.

Mathematically, the system (A1.2) constitutes a first-order linear ordinary differential equation in $P(M, t)$. The solution of such systems is well known and can be constructed from an integrating factor. Because the system (A1.2) is linear, there are alternatives other than using an integrating factor, such as Laplace transforms, which will obviously yield the same result. Solving (A1.2) generates (A1.4),

$$P(M, t) = \exp\left(-\frac{\mu M}{M_t} t\right) \left\{ P(M, 0) \right.$$

$$\left. + \frac{\mu}{M_t} t \int_M^\infty P(M', 0) dM' + \left(\frac{\mu}{M_t} t \right)^2 \times \int_M^\infty \int_{M'}^\infty P(M'', 0) dM'' dM' \right\}. \quad (\text{A1.4})$$

The evolution of the molecular weight distribution to the most probable (Poisson) distribution is apparent when $\mu t/M_t$ is large, i.e., when the last term in brackets is dominant. Equation (2) in the text is generated from (A1.4) after considerable manipulation and conversion to a weight-based molecular weight distribution, $W(M, t)$, rather than a number-based distribution $P(M, t)$. The relation between the two distributions is;

$$P(M) = \frac{W(M)}{M} \left[\int_0^\infty M^{-1} W(M) dM \right]^{-1}. \quad (\text{A1.5})$$

Any normalized probability distribution can be completely defined in terms of its complete set of integral moments.^{28,34} As such, the evolution equation of the molecular weight distribution (A1.2) can be equivalently rewritten in terms of a set of evolution equations for its moments. The relevant relations are obtained by multiplying (A1.2) by the appropriate power of M and integrating over all M . The general recursion relation connecting successive moments that results is:

$$\frac{\partial \langle M^{N-1} \rangle}{\partial t} = - \left(1 - \frac{2}{N} \right) \frac{\mu}{M_t} \langle M^N \rangle. \quad (\text{A1.6})$$

This result is important in that certain moments of the distribution are known to dominate rheological properties such as the MFI and recoverable compliance. With appropriate correlations, such as those illustrated in section IV, distinct evolution equations for the relevant quality control criteria can be directly determined, thereby eliminating the explicit integration of the double reptation model (1) to determine the quality control criteria. For example, from eq. (13) it is straightforward to show that the evolution of the zero shear viscosity is proportional to the third moment of $P(M, t)$,

$$\frac{\partial \eta_0}{\partial t} \propto - \langle M^3 \rangle \quad (\text{A1.7})$$

REFERENCES

1. J. N. Short, *Processes for Polypropylene Commercialization*, Industrial Research & Dev., Sept. 109 (1980).

2. J. L. White, *Principles of Polymer Engineering Rheology*, Wiley, New York, 1990.
3. H. Yamane and J. L. White, *Polym. Eng. Rev.*, **2**, 167 (1982).
4. W. Minoshima, J. L. White, and J. E. Spruiell, *Polym. Eng. Sci.*, **20**, 1166 (1980).
5. A. J. P. Franck, *J. Rheol.*, **29**, 833 (1985).
6. M. Dorn, *Adv. Polym. Technol.*, **5**, 87 (1985).
7. K. W. Scott, *J. Polym. Sci., Symp.*, **46**, 321 (1974).
8. J. C. Staton, J. P. Keller, R. C. Kowalski, and J. W. Harrison, U.S. Pat. 3,551,943 (1971).
9. R. C. Kowalski, U.S. Pat. 3,563,977 (1971).
10. H. G. Fritz and B. Stohrer, *Int. J. Polym. Proc.*, **1** (1986).
11. M. Inokuti, *J. Chem. Phys.*, **38**, 1174 (1963).
12. O. Saito, in *Radiation Chemistry of Macromolecules*, M. Dole, Ed., Academic Press, New York, 1972, p. 223.
13. O. Saito, *J. Phys. Soc. Jpn.*, **13**, 198 (1958).
14. T. Bremner, A. Rudin, and D. G. Cook, *J. Appl. Polym. Sci.*, **41**, 1617 (1990).
15. M. Kurata, *Macromolecules*, **17**, 895 (1984).
16. P. G. de Gennes, *J. Chem. Phys.*, **55**, 572 (1971).
17. J. des Cloizeaux, *Macromolecules*, **23**, 4678 (1990).
18. J. des Cloizeaux, *Europhys. Lett.*, **5**, 437 (1988).
19. C. Tsenoglou, *Macromolecules*, **24**, 1762 (1991); C. Tsenoglou, *ACS Polym. Preprints*, **28**, 185 (1987).
20. E. Montroll, *J. Am. Chem. Soc.*, **63**, 1215 (1941); E. Montroll and R. Simha, *J. Chem. Soc.*, **8**, 721 (1940).
21. A. M. Kotliar, *J. Poly. Sci., Part A*, **2**, 1057 (1964).
22. A. Charlseby, *Proc. R. Soc.*, **A222**, 60, 542 (1954).
23. T. L. Nemzek and J. E. Guillet, *Macromolecules*, **10**, 94 (1977).
24. S. H. Wasserman, Ph.D. Dissertation, Princeton University (1994).
25. G. R. Zeichner and P. D. Patel, *Proc. 2nd World Conf. Chem. Eng., Montreal*, **6**, 333 (1981).
26. P. V. Krishna Park and R. H. Boyd, *Macromolecules*, **26**, 679 (1993).
27. R. G. Larson, *Constitutive Equations for Polymer Melts and Solutions*, Butterworths, New York, 1988.
28. D. W. Mead, *J. Rheol.*, **38**, 1797 (1994).
29. W. H. Tuminello, *Polym. Eng. Sci.*, **26**, 1339 (1986).
30. W. H. Tuminello and N. Cudre-Mauroux, *Polym. Eng. Sci.*, **31**, 1496 (1991).
31. J. M. Starita and C. W. Macosko, *SPE Tech. Papers*, **29**, 522 (1983).
32. S. H. Wasserman and W. W. Graessley, *J. Rheol.*, **36**, 543 (1992).
33. D. S. Pearson, L. J. Fetters, L. B. Younghouse, and J. W. Mays, *Macromolecules*, **21**, 478 (1988).
34. H. B. Callen, *Thermodynamics*, Wiley & Sons, Inc., New York, 1960.
35. H. Potente, *J. Polym. Eng.*, **12**, 297 (1993).
36. G. A. Harpell and D. H. Walrod, *Rubber Chem. Technol.*, **46**, 1007 (1973).
37. M. Fujiyama and H. Awaya, *J. Appl. Polym. Sci.*, **16**, 275 (1972).
38. C. Tzoganakis, Y. Tang, J. Vlachopoulos, and A. E. Hamielic, *J. Appl. Polym. Sci.*, **37**, 681 (1989).
39. M. Lambla, *Macromol. Symp.*, **83**, 37 (1994).

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