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Molecular structure of high melt strength polypropylene and its application to polymer design

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Abstract

We report a numerical technique to investigate the branching process of linear Ziegler–Natta polypropylenes. Using an iterative procedure, linear chains are created based on the molecular weight distribution (MWD) of linear Ziegler–Natta polypropylenes as determined by GPC. By varying one parameter, MWDs of polymers with various levels of branching are simulated, and the simulated MWDs agree very well with experimental GPC data of branched polymers. From the simulation, the average branching parameters as well as the branching distributions of the polymers can be obtained. The branching information is related to the moments of the MWD, and a criterion of the onset of gelation is proposed. The melt flow rate (MFR) is correlated with the weight-average molecular weight. These relationships make it possible to design a polymer having a prescribed MFR.

Keywords: High melt strength polypropylene; Monte Carlo simulation; Branching structure

1. Introduction

Linear polypropylene has very attractive solid-state properties such as high modulus and tensile strength, rigidity and excellent heat resistance. However, its linear structure leads to poor processability in processes involving melt stretching, such as extrusion coating, foam extrusion and film blowing. Branches are introduced into linear polypropylene to produce 'high melt strength polypropylene' having enhanced processability.

Two techniques have been developed to make branched polypropylene: post-reactor treatment, and in situ polymerization. Post-reactor treatment, which includes curing in the presence of crosslinker (such as peroxide and co-agent), electron beam irradiation and macro monomer grafting, is the more popular way to introduce branches into polypropylenes.

It is desirable to know the level of branching and relate it to the flow and end-use properties of the polymer. This is especially important for industrial polymer design to determine how many branched molecules to create to make a polymer having a prescribed processability.

Weng et al. [1] reported the determination of the branching density, λ, (number of branch points per 1000 carbons) using ^{13}C NMR for in situ synthesized metallocene long-chain branched polypropylenes. However, ^{13}C NMR is not applicable to polypropylenes crosslinked in a post-reactor process, because the NMR peaks corresponding to the crosslinked structure are often very small or even missing in the spectrum due to the shielding effect of surrounding carbons at the branch point, and, if there are peaks, their assignment is complicated by the different structures at the branching point for branched metallocene polypropylene and polypropylenes crosslinked in a post-reactor process. Tsenoglou and Gotsis [2] proposed a rheological method to estimate the average number of branches per chain, β, in slightly crosslinked polypropylenes. The method is based on the following assumptions: (1) the polymer can be considered as a 'blend' of a number fraction $(1-\beta)$ of linear chains and a number fraction β of

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nonlinear chains; (2) the nonlinear chains are three-armed stars, with the average molecular weight of an arm being half that of the linear precursor; (3) the weight-average molecular weight of a linear component is the same in the precursor and in the branched system.

In the polypropylene industry, branching can be introduced into linear polypropylene by a post-reactor process. Currently, there are limited analytical techniques to measure directly the branching level in these materials, and the branched system and branching structure cannot be simplified as in the work of Tsenoglou and Gotsis [2]. Therefore, methods other than direct measurement are needed to determine the structure of branched polypropylenes. An attractive approach is the numerical simulation of the branching reaction.

Tobita [3] used a random sampling technique to investigate non-linear structure in polymers. This technique randomly samples polymer chains from a 'sea' of chains. There are two approaches to random sampling: number-based sampling, and weight-based sampling. In number-based sampling one randomly selects a chain end from the sea of chains. As in Flory's random branching [4], all the chains have the same probability of being selected, regardless of size. In weight-based sampling, all monomer units have the same probability of being selected, and the longer the chain, the higher the probability of being selected. The combination of random sampling and a Monte Carlo (MC) method provides a powerful technique to simulate the branching process and predict the structure of a polymer.

Tobita [5] used the random sampling technique to obtain analytical solutions for the molecular weight distribution (MWD) for various types of nonlinear polymerization where initial chains follow the most probable distribution. In the case of random crosslinking, he obtained an analytical solution for the weight-average chain length ($\bar{P}_w$), which is the weight-average molecular weight divided by the molecular weight of the monomer, for a gel-free system. One example of the structure of a crosslinked molecule is shown in Fig. 1.

The weight-average chain length $\bar{P}_w$ is given by the following expression:

$$\bar{P}_w = \frac{\bar{P}_{wp}(1+\rho)}{1-(\bar{P}_{wp}-1)\rho} \tag{1}$$

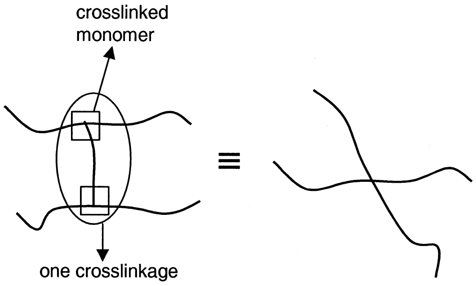

Fig. 1. Sketch of structure of a crosslinked molecule.

where $\bar{P}_{wp}$ is the weight-average chain length of the linear precursor, and ρ is the crosslinking density, defined as:

$$\rho = \frac{\text{no. of cross linked monomers}}{\text{total no. of monomers}} \tag{2}$$

A crosslinked monomer is a monomer unit with a branch point, so one crosslinkage contains two crosslinked monomers, as shown in Fig. 1.

Macosko and Miller [6] derived a generalized formula for calculating M_w and M_n of nonlinear polymers by using the recursive nature of the branching process and a probability law. They arrived at a formula for the weight-average chain length $\bar{P}_w$ that is identical to Eq. (1). The number-average chain length $\bar{P}_n$, i.e. the number-average molecular weight divided by the molecular weight of the monomer, is given by:

$$\bar{P}_n = \frac{\bar{P}_{np}}{1-\rho\bar{P}_{np}} \tag{3}$$

where, $\bar{P}_{np}$ is the number-average chain length of the linear precursor.

Because of the chemical nature of the branching used to make the polypropylenes in this study, the weight-based sampling technique is used and combined with a MC method to simulate the branching process of polypropylenes to obtain detailed structural information.

2. Materials and GPC measurements

A group of samples that includes one linear and several branched samples will in the following be called a 'set'. Two sets of samples were investigated, based on linear precursors 35L and 12L, which have melt flow rates (MFR) of 35 and 12 dg/min respectively. MFRs were determined using ASTM Standard Test Method D-1238 at 230 °C with a 2.16 kg weight. Based on each precursor, three branched polypropylenes were produced, having various branching levels. For example, 35B1, 35B2 and 35B3 are the three branched samples based on linear precursor 35L with increasing levels of branching.

The MWDs were determined by high-temperature gel permeation chromatography (GPC) incorporating a refractive index detector, a viscometer, and a light scattering detector. Gel permeation chromatographic columns separate molecules according to their hydrodynamic volume in solution. After leaving the GPC columns, the molecules pass through the light scattering detector, which is able to measure the absolute molecular weight without the need for calibration standards. This separation process is well suited to the determination of the MWD of linear polymers. However in the case of branched polymers, for a given hydrodynamic volume, branched molecules have higher molecular weights than linear ones but are eluted at the same time. Yet it has been shown that a light scattering detector provides a MWD closer to the true one than conventional GPC. Although it would be possible to 'imitate' the GPC separation by size in the MC simulation, at the price of additional parameters and hypotheses, we chose to simply compare the simulated MWD with the most correct experimental distribution, as measured using a light scattering detector. The molecular characteristics of the samples are listed in Table 1.

3. Numerical procedures of the Monte Carlo simulation

3.1. Creation of linear precursor chains

The MC algorithm is a technique based on the use of random numbers and probability statistics to model stochastic processes. It is widely used in polymer science to predict molecular structure and is especially useful in the numerical solving of reaction kinetics equations when a direct solution is not possible. The first step in our MC algorithm is to generate a set of linear chains that have the MWD indicated by GPC data.

From the GPC measurements, we have the MWD in terms of weight fraction $w(\log M)$ as a function of molecular weight M. First we calculate the corresponding number fraction, $n(\log M)d\log M$, using Eq. (4).

$$n(\log M)d\log M = \frac{[w(\log M)d\log M]M_n}{M} \tag{4}$$

The cumulative number distribution is then obtained by summing the number fractions from $M_{\min}$ to $M_{\max}$, where $M_{\min}$ and $M_{\max}$ are the low and high limiting molecular weights, respectively, of the distribution. By definition, the cumulative number distribution ranges from 0 to 1. Next we generate a random number in this range and determine the corresponding molecular weight from the cumulative number fraction using an iterative procedure [7]. A chain of this molecular weight is then stored in memory. To determine the number of chains required to generate a statistically consistent population, we ran the simulation using various numbers of chains. The results are shown in Fig. 2 where we see that the results for 10^5 chains are too sparse to provide the needed statistics. The results for 10^6 and 10^7 chains are very similar, but the simulation for 10^7 chains took much longer time. Taking into account the smoothness of the MWD and the computational time required, we consider that 10^6 is a sufficiently large population for the simulation. By creating chains in accordance with the cumulative number fraction curve, a set of linear chains having the same MWD as the GPC MWD of the linear precursor is produced.

Table 1
Properties and molecular characteristics of PP samples

Sample	M_n (kg/mol)	M_w (kg/mol)	M_z (kg/mol)	PDI (M_w/M_n)	MFR (dg/min) (230 °C)
35L	49.4	179	428	3.62	35.0
35B1	53.5	195	489	3.65	24.4
35B2	52.5	246	776	4.68	13.3
35B3	55.4	307	1136	5.53	3.9
12L	41.3	248	744	6.00	12.0
12B1	38	328	1229	8.63	4.7
12B2	40.1	391	1578	9.75	1.1
12B3	47.9	488	2051	10.19	0.8

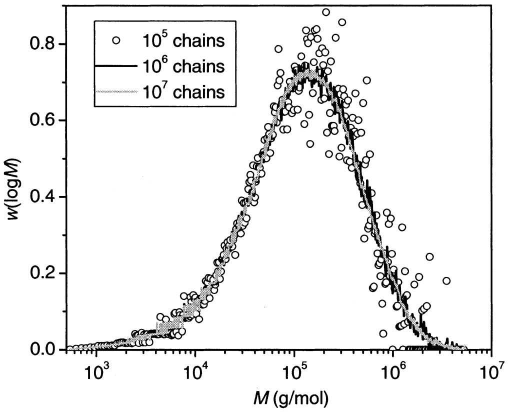

Fig. 2. Comparison of simulated molecular weight distributions of 12L using several total chain numbers.

The simulated MWDs of the linear precursors 35L and 12L are shown in Figs. 3 and 4 and compared with the GPC results. Very good agreement is obtained, which ensures that the number of chains created statistically represents the real sample.

3.2. Creation of branched chains

The real branching process of polypropylene is very complex. To simulate and capture the main features of the process we need to make some simplifying assumptions. First we assume that the system is perfectly mixed and that molecular diffusion effects are negligible. Second, we suppose that the branching process is random, so that every monomer in the system has an equal probability of

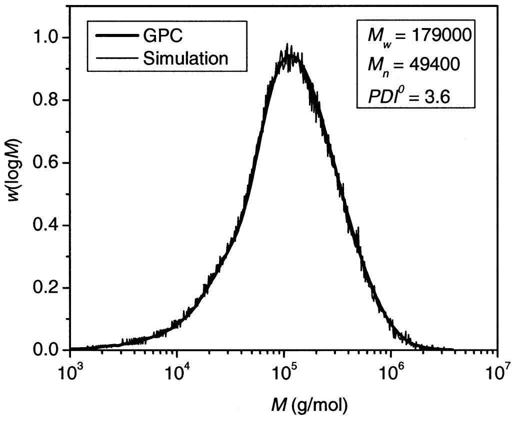

Fig. 3. Molecular weight distribution of 35L from Monte Carlo simulation (thin line) and from GPC measurements (thick line).

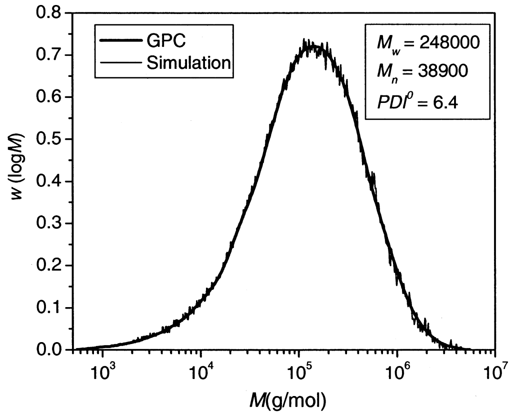

Fig. 4. Molecular weight distribution of 12L from Monte Carlo simulation (thin line) and from GPC measurements (thick line).

becoming a branch point. Finally, we consider only branch points that are formed and survive until the end of the branching process. In reality some branch points undergo incomplete reaction, or scission, or branched molecules have chain cleavage at the branch point. Here we only consider the net result of the branching process, using a simulation parameter α that is the number of branch points per precursor chain at the end of the process.

Based on these assumptions, a weight-based random sampling technique is employed to simulate the branching process. The structure of the algorithms used in the MC simulation is shown in Fig. 5.

To create a branch point, we randomly select any monomer in the system, and identify the chain containing the monomer. We repeat the process with a second monomer and replace the two chains by a single chain with one more branch point. We allow the possibility of the two monomers selected belonging to the same chain, thus leading to a cycle. However, for the levels of branching considered here, the simulation results show that the occurrence of such cycles is extremely rare (less than six cycles per 10^6 molecules) and is of no statistical significance. The number of cycles would become significant in the simulation if the level of branching were increased into the vicinity of the gel point that will be further described in Section 4.2. The occurrence of cyclic molecules during the experimental process might have a different probability than in the simulation, depending on the technique and the conditions used for the branching. The good agreement between our random model and the experimental data seem to indicate that the phenomenon is marginal.

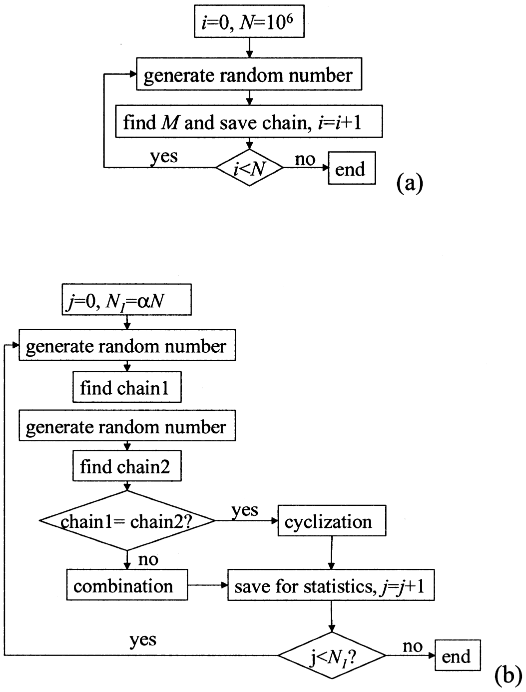

Fig. 5. Algorithm of the Monte Carlo simulation (a) creation of linear chains; (b) creation of branched chains.

3.3. Comparison of simulation results with experimental GPC data

Starting with the same simulated linear chains, by varying a single parameter, α, we obtain MWDs for polypropylenes having various levels of branching. For each branched sample, we choose the value of α that gives the best agreement between the shape and moments of the simulated MWD and those of the GPC data. The precision of α has the order of 3% for the values considered here. At low α values, the shape of the simulated MWD is not sensitive to the α value, we choose the right α value by comparing the moments of the MWDs. The minimum α value can be determined by the comparison is 0.004. Typical simulated MWDs of branched polypropylenes 35B3 and 12B2 are shown in Figs. 6 and 7 and compared with the corresponding GPC data. The simulated MWD matches the GPC results very well for all the samples based on precursor 35L and 12L. The values of α are reported in Table 2. The good match of experimental and simulated data indicates that the assumption of random branching and

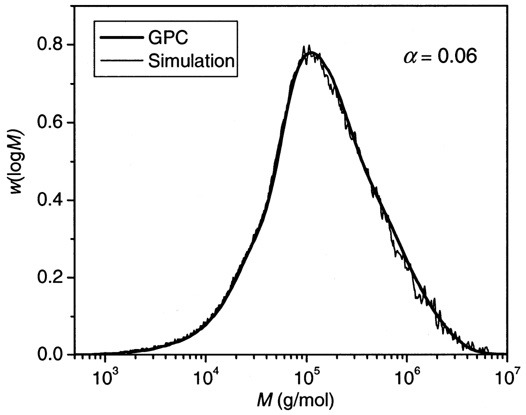

Fig. 6. Molecular weight distribution of 35B3 from Monte Carlo simulation (thin line) and from GPC measurements (thick line).

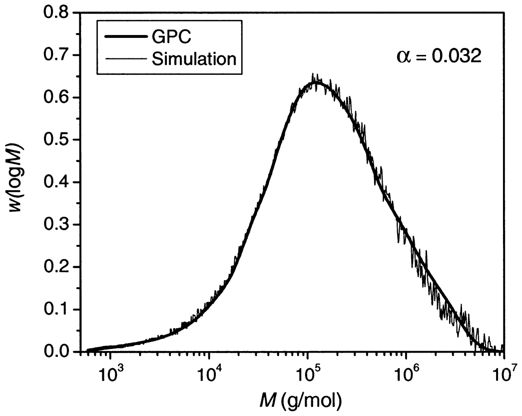

Fig. 7. Molecular weight distribution of 12B2 from Monte Carlo simulation (thin line) and from GPC measurements (thick line).

the use of weight-based sampling are suitable for modeling the polypropylene branching process.

4. Results and discussion

It has been shown that the weight-based random sampling technique together with the MC method can successfully simulate the MWDs of branched polypropylenes. In addition to the branching parameter α, the simulation provides a wealth of information about the structure of the branched polymer, such as the branching distribution, which cannot be obtained directly from GPC data and yet is necessary to understand how the processability is affected by long-chain branching.

4.1. Branching information

From the value of α we can calculate β, the average number of branch points per molecule. The number of chains present after branching is reduced by the factor $(1 - \alpha)$, and the two parameters are related as shown by Eq. (5a).

$$\beta = \frac{\alpha}{1-\alpha} \tag{5a}$$

The number-average molecular weight of the system, M_n, is also obtained from that of the linear precursor, M_n^0, by

$$M_n = \frac{M_n^0}{1-\alpha} \tag{5b}$$

Another parameter used to describe the branching level is λ, the number of branch points per 10^3 carbons, which can be expressed in terms of α as shown by Eq. (6):

$$\lambda = \frac{14000\beta}{M_n} = \frac{14000\alpha}{M_n^0} \tag{6}$$

The values of β and λ were calculated using Eqs. (5a) and (6) for all the branched samples and are listed in Table 2.

From Table 2 we can see that for a set of branched samples, as the branching level goes up, the average branching parameters β and λ, measured by fitting the MWDs, increase.

From the simulation we can calculate not only the average branching parameters β, and λ, but also the number (and weight) branch point distributions that describe the number (and weight) fractions of molecules having various branch points k_b. The number and weight branch point distributions of the 35 MFR series are shown in Fig. 8. The graph shows that sample 35B1 consists mainly of linear chains and about 1% of three-arm stars, while molecules with more than two branch points (highly branched chains) represent fewer than 0.1% of the molecules and account for less than 1% of the mass of the sample. For 35B2 and 35B3, the number and weight fractions of highly branched chains increase. The same tendency is found in the 12 MFR series.

While the average branching parameters β and λ are useful for classifying branching structure and for predicting processability and solid-state properties, it is more important to know the distribution of branching levels to better understand the relationships between structure and properties. The branching distribution $\beta(M)$ is obtained by computing the average number of branch points per chain in each bin of the molecular weight histogram. A typical example for 35B3 is shown in Fig. 9, where we see that $\beta(M)$ increases with molecular weight. At low molecular weight ($M < 10^5$ g/mol), the value of $\beta(M)$ is very low (<0.01), which indicates that small chains are mainly linear and that branch points are found mostly in the large molecules ($M > 10^6$ g/mol). This type of branching distribution improves processability without sacrificing solid-state properties. If branch points are concentrated in small

Table 2
The values of β and λ calculated from parameter α for all the branched samples

Sample	α (branches/precursor chain)	β (branches/molecule)	λ (branches/1000 carbons)
35B1	0.009	0.0091	0.0025
35B2	0.035	0.0363	0.0098
35B3	0.06	0.0638	0.0168
12B1	0.022	0.0225	0.0075
12B2	0.032	0.0331	0.011
12B3	0.043	0.0449	0.015

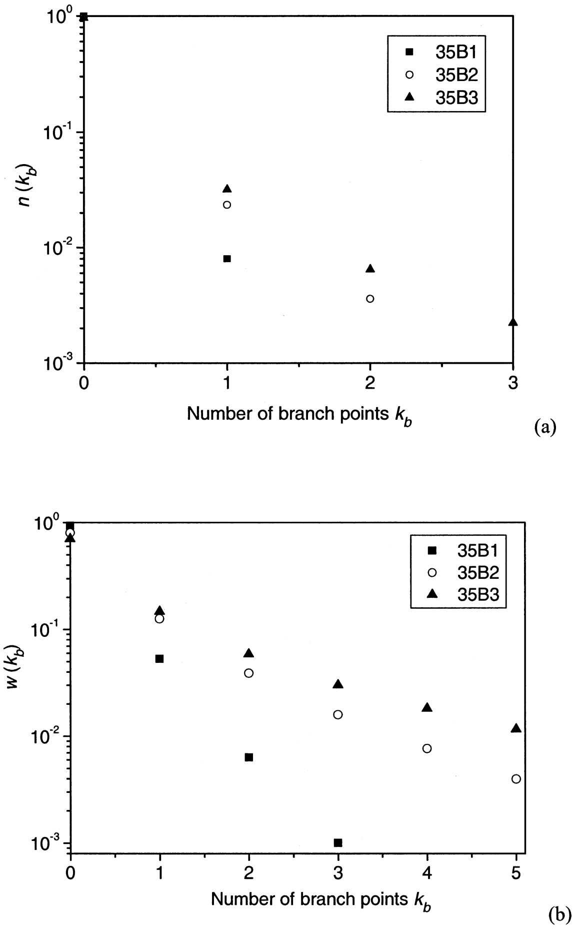

Fig. 8. Number (a) and weight (b) branch point distributions of 35MFR series.

chains, strain hardening does not occur due to the short branch segment, and the solid properties are degraded because of the significantly smaller chain size [8].

A typical branching density distribution $\lambda(M)$ for 35B3 is shown in Fig. 10, where we see that λ increases with molecular weight and then levels off, which indicates that the lengths of segments between two successive branch points decrease toward a constant value at the high molecular weight end.

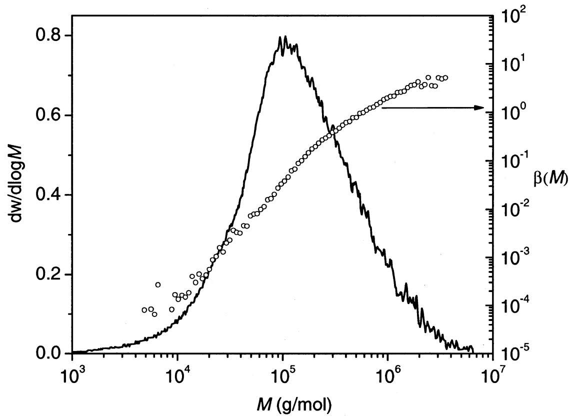

Fig. 9. Branching $\beta(M)$ and molecular weight distributions of 35B3.

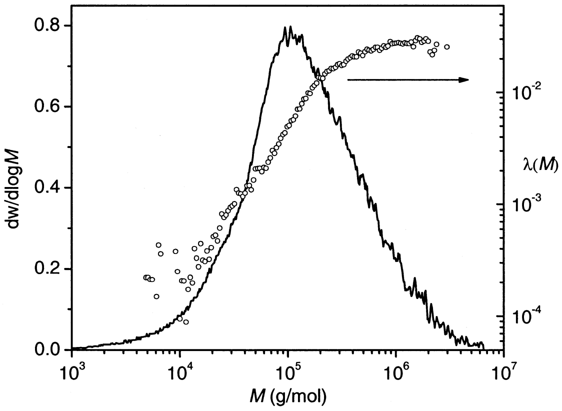

Fig. 10. Branching $\lambda(M)$ and molecular weight distributions of 35B3.

4.2. Relationship between molecular weights and branching parameters

The relationship between β and the reduced number-average molecular weight, M_n/M_n^0, is shown in Fig. 11, where M_n^0 is the number-average molecular weight of the linear precursor. The linear behavior is a simple consequence of Eq. (5b), which can be written in terms of β as follows:

$$\beta + 1 = \frac{M_n}{M_n^0} \tag{7}$$

The weight-based random branching process is very similar to the iterative branching process considered by Macosko and Miller [6]. In the limit of low levels of branching $\alpha < 0.1$, Eq. (7) is the same as Eq. (3).

Using Eq. (7) the branching parameter β can be calculated from the number-average molecular weights, M_n and M_n^0, which can be determined using GPC.

While it is convenient to use Eq. (7) to calculate the branching parameter β from the number-average molecular

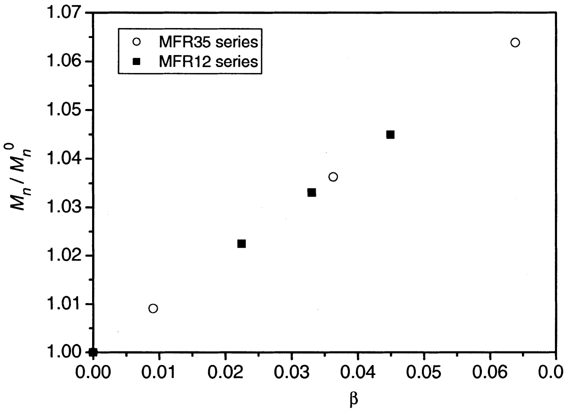

Fig. 11. Relationship between branching parameter β and reduced number-average molecular weight M_n/M_n^0 for branched polypropylenes and their linear precursors.

weights, it is preferable to use the weight-average molecular weights for this purpose, because for branched polymers, triple-detector GPC gives more accurate results for M_w than for M_n. It is found that the reduced weight-average molecular weight, M_w^0/M_w, is related to $\alpha(\mathrm{PDI})^0$ as shown in Fig. 12, where M_w^0 and $(\mathrm{PDI})^0$ are the weight-average molecular weight and the polydispersity index of the linear precursor, respectively.

The relationship is described by Eq. (8).

$$\frac{M_w^0}{M_w} = 1 - 2\alpha(\mathrm{PDI})^0 = 1 - \frac{2\beta}{1+\beta}(\mathrm{PDI})^0 \qquad (8)$$

We notice that Eq. (8) is similar to the one found by Tobita [3] for randomly crosslinked polymer chains, noting that the fraction of crosslinked monomers ρ is related to the simulation parameter α as follows:

$$\rho = \frac{2\alpha M_0}{M_n^0} \qquad (9)$$

where M_0 equals 42 for propylene. With the approximation $\bar{P}_{wp} \gg 1$ and $\rho \ll 1$, Eq. (1) takes the form of Eq. (8). Provided that the moments of the experimental MWD are known with a good precision, one can make use of Eq. (8) to obtain the branching parameters α and β.

Eq. (8) implies that as $[1 - 2\alpha(\mathrm{PDI})^0]$ approaches zero, M_w goes to infinity, which indicates that the system has reached its gel point. In industrial applications, it is important to keep the branching level below the gel point, and the criterion for this is:

$$\alpha < \frac{1}{2(\mathrm{PDI})^0} \qquad (10)$$

4.3. Branching efficiency

As mentioned before, there are several ways of achieving an incomplete branching reaction. The number of branch points per precursor chain α can be obtained for each branched sample by simulation. On the other hand, the nominal number of branch points per precursor chain α_{nom} can be determined from knowledge of the branching process (radiation energy, number of crosslinker or peroxide molecules mixed with the linear polymer, etc). For example, if the crosslinker concentration is x ppm, and its molecular weight is M_p, then the nominal number of branch points per precursor chain α_{nom} can be calculated as follows:

$$\alpha_{nom} = \frac{xM_n^0}{10^6 M_p} \qquad (11)$$

A comparison of α with α_{nom} for all our branched samples is shown in Fig. 13.

Fig. 13 shows that the slopes of the linear fits for the 12 MFR and 35 MFR series data are very similar. The value of α divided by α_{nom} defines the branching efficiency E_{bran}. Therefore, E_{bran} values for these two sets of samples are the same and equals to 40%.

The branching efficiency can be related to characteristics such as chemical composition and purity, and to the temperature of the reaction. Knowing the branching efficiency E_{bran} and the value of α at the gel point, the maximum α_{nom} for a gel-free branched system can be calculated. For example, for the 35 MFR series, the α value at the gel point is:

$$\alpha_{gel} = \frac{1}{2\mathrm{PDI}^0} = \frac{1}{2\times 3.6} = 0.138 \qquad (12)$$

The maximum α_{nom} equals α_{gel} divided by E_{bran}, and has a value of 0.345. Therefore, for branched polymers based on linear precursor 35L, the nominal number of branches per precursor chain α_{nom} should be less than 0.345 in order to ensure a gel-free system.

4.4. Relating an engineering property to structural information

The MFR, a parameter widely used in industry to

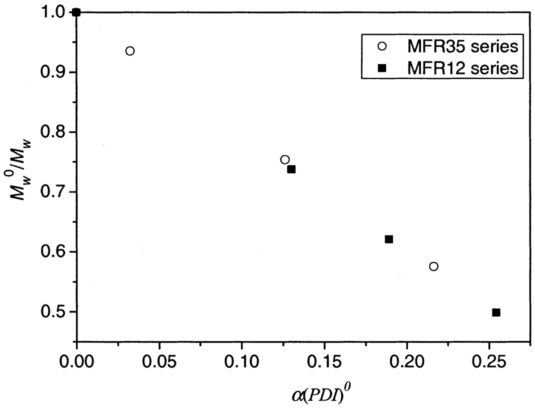

Fig. 12. Relationship between $\alpha(\mathrm{PDI})^0$ and the reduced weight-average molecular weight M_w/M_w^0 for branched polypropylenes and their linear precursors.

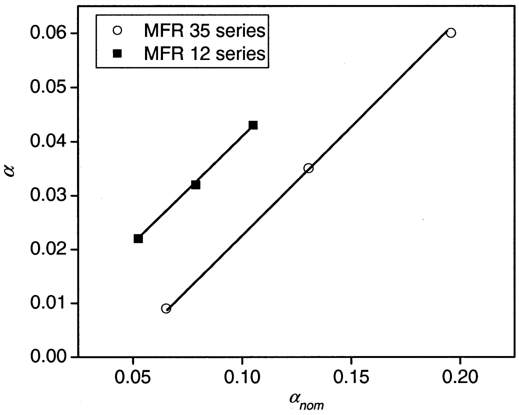

Fig. 13. Comparison of α (branch points per precursor chain) and α_{nom} (nominal branch points per precursor chain) for all branched polypropylenes.

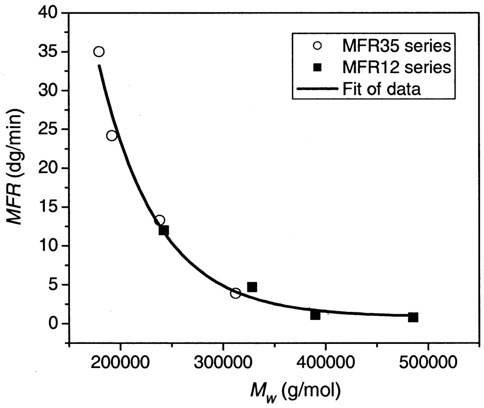

Fig. 14. Melt flow rate (2.16 kg weight at 230 °C) vs. weight-average molecular weight of the linear and branched polypropylenes.

characterize polymers, is related to the molecular weight of the branched system, M_w, as shown in Fig. 14.

Fig. 14 shows that MFR decreases exponentially with increasing weight-average molecular weight. The relationship for the polypropylenes studied here can be expressed as:

$$\mathrm{MFR} = 297.4\exp(-1.32\times 10^{-5}M_w) \tag{13}$$

In industrial polymer design, one often wishes to make a branched polymer having prescribed MFR. The relationships obtained from our simulation provide a convenient way to design such polymers. First using Eq. (13) we calculate the weight-average molecular weight of the branched polymer, M_w, from the desired final MFR. Then given the value of M_w^0 for a particular linear precursor, using Eq. (8) we can calculate the value of α needed to achieve the final MFR. Finally the nominal value α_{nom} is determined by dividing α by the branching efficiency E_{bran}, or directly from a plot similar to Fig. 13. It is then possible, starting from various MWDs, to achieve the same MFR by introducing various levels of branching, which means various branching structures. Materials with a good balance of melt strength and processability can then be designed to meet process requirements.

5. Conclusions

A MC technique was used to simulate the branching process of polypropylene, making it possible to obtain a simulated MWD of a branched material that is in good agreement with that from GPC measurement.

Branching parameters β and λ can be calculated from the simulation parameter α for a given branched sample. The distributions of $\beta(M)$ or $\lambda(M)$ show that small chains are nearly linear and that most of the branch points are located on the large molecules. This type of branching distribution improves the processability of a polymer without sacrificing its solid-state properties.

The branching parameter β is linearly related to the ratio of the number-average molecular weights of the branched system and the corresponding linear precursor. The branching parameter α is related to the ratio of the weight-average molecular weight of the branched system to that of its linear precursor and to the polydispersity index of the linear precursor.

The branching efficiency is calculable. Knowing the branching efficiency and the value of α at the gel point, the maximum nominal number of branch points per chain α_{nom} that will not cause gelation can be estimated. The MFR decreases exponentially with increasing weight-average molecular weight.

The relationships between the branching parameter and the MFR, on the one hand, and the molecular weight, on the other, can be used in the design of polymers for demanding industrial processes.

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References

[1] Weng W, Hu W, Dekmezian AH, Ruff CJ. Macromolecules 2002;35:3838–43.
[2] Tsenoglou CJ, Gotsis AD. Macromolecules 2001;34:4685–7.
[3] Tobita H. Macromolecules 1993;26:836–41.
[4] Flory PJ. Chem Rev 1946;39:137–45.
[5] Tobita H. Macromol Theory Simul 1996;5:1167–94.
[6] Macosko CW, Miller DR. Macromolecules 1976;9:199–206.
[7] Costeux S, Anantawaraskul S, Wood-Adams PM, Soares JBP. Macromol Theory Simul 2002;11:326–41.
[8] Bersted BH, Encyclopedia of fluid mechanics, vol. 7. Houston: Gulf Publishing Company; 1988. Chapter 22.