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Rheological Characterization of Long Chain Branching in a Melt of Evolving Molecular Architecture

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A simple rheological method is presented for estimating the degree of long chain branching, x (fraction of branched chains or, equivalently, the average number of branches per chain), of a polymer melt undergoing the early stages of a cross-link inducing reactive modification. The model is tested on a series of polypropylenes of increasing x, all produced from the same linear precursor in the presence of varied peroxide concentrations. The branching indices predicted from analyzing the zero shear viscosity of the samples are in good agreement with those evaluated by size exclusion chromatography combined with intrinsic viscosity measurements.

Varying the molecular architecture is one of the most effective methods of tailoring processing characteristics and end-product properties of polymers. It has long been a useful empirical knowledge, for example, that while linear polymers are often unsuitable for extensional flow processing due to their low "melt strength", the situation improves significantly in the presence of even limited long chain branching (LCB).[1] This is especially true for polypropylene (PP), which due to its many desirable properties (high melting point, low cost, high tensile modulus, low density) is the fastest growing commodity resin; its production by Ziegler−Natta or metallocene catalysts results in highly linear chains of relatively narrow molecular weight distribution and, therefore, of poor melt strength. To improve melt strength, branching is introduced to linear PP through radical reactions, initiated by irradiation[2] or chemical means, such as peroxides.[3,4] Some of these modification processes take place in the course of reactive extrusion.[4]

Monitoring the degree of branching is essential in optimizing such a modification or, conversely, in preventing accidental cross-linking, which in other cases is an undesirable consequence of process-induced degradation. This is a nontrivial task considering the difficulties in characterizing molecular sizes and shapes of polyolefins by conventional GPC methods. Since even a modest reorganization of the molecular architecture can alter the viscoelastic behavior significantly,[5] monitoring the rheology, instead, seems to be an appealing and inexpensive alternative to the standard characterization techniques.[6−8] Branching progression, for example, translates into a dramatic increase in elasticity[5] as manifested by changes in the zero shear recoverable compliance, J_e^o. This, however, is difficult to monitor given the inability of experimentally reaching the necessary $G'(\omega)/\omega^2$ low-frequency plateau in dynamic mechanical measurements, and the extreme sensitivity of J_e^o to molecular weight polydispersity (ω is the frequency of the oscillations and $G'(\omega)$ is the storage modulus).[9] Monitoring and interpreting the relatively modest, yet readily measurable, increase of the zero shear rate viscosity which accompanies branching is a more appealing alternative, on which our method is based.

Theory. Correlating rheological behavior with microstructural evolution in a melt undergoing LCB reactive modification necessitates a number of simplifying assumptions concerning the extent, nature, and mechanism of the induced changes, as well as the molecular size and architecture of the end product. Irrespective of whether this modification occurs accidentally due to degradation or is caused deliberately to improve processability, the following points are known:

(1) Linear polymer chains of initial (weight-average) molecular mass M_L break through scission and some of their fragments cross-link with neighbors to form new molecules.

(2) Of those newly created units, the ones resulted from fragments connected close to a chain-end maintain (more or less) the linear architecture of their precursors while the rest assume branched configurations.

If the modification is of *limited extent* and does not progress much above the insertion of a single branching point per molecule on average, the following is also expected:

(3) Most of the reacted linear fragments end up as parts of larger branched polymers. A fraction of the initially linear chains, of average molecular mass M_L, after breaking (on the average) in the middle, cross-link with mostly unbroken chains. If cross-linking occurs not too far from a chain middle-point, this results in structures resembling three-arm stars of average arm-molecular mass $M_a \approx M_L/2$ and, therefore, of total molecular mass $M_B = 3M_a \approx 3M_L/2$. If such an addition occurs close to a free end, or if it pertains to a small fragment, it merely affects the linear chain population.

(4) Linear to linear chain transformations do not cause any major shift in the weight-average molecular weight of the linear chain component; while there are always several unreacted linear fragments smaller than the original size, some of the reacted ones have joined initial chains on or close to a free end, to form an even longer linear molecule. Therefore, the weight-average molecular mass of the linear component remains roughly the same, equal to M_L.

(5) The melt under modification can therefore be considered a "blend" of a $(1 - x)$ fraction of linear M_L chains mixed with an ever increasing x fraction of $1.5M_L$ three-arm stars. Here, the subscript a signifies an arm, L and B signify a linear or a branched molecule (or melt), and BL signifies a modified sample.

Naturally, as the reaction progresses, most of the above assumptions fail. Eventually, the originally linear chains will fragment in pieces smaller that $M_L/2$, on the average, cross-linking will become more extensive, and a number of multifunctional and multigenerational long chain branched structures will be created in treelike architectures characterized by this shorter strand size.

Estimates of the impact of the evolving microstructure on the melt fluidity may be made based on fundamental precepts of molecular rheology of the entangled state.[10]

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Table 1. Number and Weight Average Molecular Mass, Degree of Branching, and Zero Shear Viscosity Data of a Series of Branch-Modified Samples Produced from the Same Linear Polypropylene Precursor ($x = 0$) Using, in Set 1, Varied Amounts of the Same EHP Peroxydicarbonate Initiator and, in Set 2, 2 mmol of Different Peroxydicarbonates Species per 100 g of Polypropylene

sample code (set 1)	mmol of EHP/ 100 g of PP	M_n	M_w	M_w/M_n	x	η_0 (Pa·s)
A0	0	74 000	410 000	5.54	0.00	28 300
A1	0.5	69 000	400 000	5.74	0.03	41 700
A2	1.0	62 000	410 000	6.56	0.15	51 500
A3	2.0	68 000	460 000	6.81	0.23	85 100
A4	3.0	71 000	485 000	6.81	0.36	120 500

sample code (set 2)	PODIC: 2 mmol/ 100 g of PP	M_n	M_w	M_w/M_n	x	η_0 (Pa·s)
A5	diethyl (EP)	71 000	425 000	5.98	0.15	38 000
A6	dicetyl (CP)	74 000	465 000	6.29	0.34	70 000
A7	diethylhexyl (EHP-1)	72 000	455 000	6.34	0.33	120 000
A8	diisopropyl (IPP)	69 000	460 000	6.66	0.28	75 000

The molecular weight dependence of the viscosity of the linear (L) component is subject to the following well-established power law:

$$\eta_L = \eta_C\left(\frac{M_L}{M_C}\right)^{3.5} \tag{1}$$

Here, M_C is the molecular weight at the onset of entanglements, a material constant that depends on molecular rigidity and equals twice the molecular weight between two successive entanglements: $M_C \approx 2M_e$. For PP, M_e is roughly equal to 5600. η_C is the melt viscosity at the entanglement crossover, where $M_L = M_C$.

Following Graessley's review analyzing the up to then experimental evidence on the viscoelastic behavior in the presence of branching,[5] and de Gennes' introduction of path fluctuations as the mechanism of the conformational renewal of long tethered chains,[11] explanations of increasing exactitude started appearing on why the zero-shear viscosity, η_B, and relaxation time of a melt of entangled starlike molecules (B stands for branched), vary (in essence) exponentially with the molecular weight of each of the protruding arms:[12−15]

$$\frac{\eta_B}{\eta_C} = \sqrt{\frac{M_a}{M_e}}\exp\left\{\alpha\left(\frac{M_a}{M_e} - 1\right)\right\} \tag{2}$$

Since $M_C \approx 2M_e$ and, in our case, $M_a \approx M_L/2 \approx M_B/3$, this is equivalent to

$$\frac{\eta_B}{\eta_C} = \sqrt{\frac{M_L}{M_C}}\exp\left\{\alpha\left(\frac{M_L}{M_C} - 1\right)\right\} \tag{3}$$

According to the molecular theory, the coefficient α is independent of the branching point functionality, and equal to 15/8; comparison with experiment indicates a smaller value instead, $\alpha \approx 0.43$[16]−0.60.[15] This is most likely due to unaccounted constraint release interference since the 15/8 value was derived for tethered chain relaxation in an environment of unmovable obstacles, while in a melt that environment is quite fluid.

It has already been assumed that the melt of evolving microstructure is a blend of mostly linear chains with an ever-increasing portion of *three*-arm stars. Phenomenology,[16] corroborated by the "dynamic dilution theory" results,[17] indicate that, as a rule, the viscosity of a BL blend, η_{BL}, is subject to logarithmic additivity; i.e., $\eta_{BL} \approx (\eta_B)^x(\eta_L)^{1-x}$. For the melt under modification, one therefore obtains

$$\eta_{BL} \approx \eta_C \exp\left\{\alpha x\left[\frac{M_L}{M_C} - 1\right]\right\}\cdot\left(\frac{M_L}{M_C}\right)^{3.5-3x} \tag{4}$$

Equation 4 expresses the thought that the rheology of a melt of mixed architecture resembles that of a linear polymer or a branched polymer melt in proportion to the relative participation of the linear or branched component. By comparing eqs 1 and 4, an expression for estimating the degree of branching may then be derived; it utilizes the measured viscosity ratio between the melt-strengthened (BL) and the initial (L) state and, since $\eta_{BL}/\eta_L \approx (\eta_B/\eta_L)^x$

$$x \approx \frac{\ln\left\{\dfrac{\eta_{BL}}{\eta_L}\right\}}{\alpha\left[\left(\dfrac{M_L}{M_C}\right) - 1\right] - 3\ln\left\{\dfrac{M_L}{M_C}\right\}} \tag{5}$$

If weight-average molecular mass data for the initial linear polymer are not available, this may be approximately calculated, provided that the viscosity is known for another linear size, L′, at the same temperature, since by eq 1

$$M_L = M_{L'}\left(\frac{\eta_L}{\eta_{L'}}\right)^{1/3.5} = M_C\left(\frac{\eta_L}{\eta_C}\right)^{1/3.5} \tag{6}$$

Equation 5 may then be restated as follows:

$$x \approx \frac{\ln\left\{\dfrac{\eta_{BL}}{\eta_L}\right\}}{\alpha\left[\left(\dfrac{\eta_L}{\eta_C}\right)^{1/3.5} - 1\right] - \dfrac{6}{7}\ln\left\{\dfrac{\eta_L}{\eta_C}\right\}} \tag{7}$$

Experimental Verification. In a recent study for the development of new high melt strength polypropylene resins, limited long chain branching was introduced on an initially linear polypropylene.[18] Bulky peroxydicarbonates (PODIC) were used for radical initiation in reactive extrusion. The degree of branching x in the modified melt (branched fraction of initial PP chains or, equivalently, average number of branches per chain) was controlled by increasing the added amount of Ethylhexyl PODIC (sample set 1) or by varying the PODIC species used: PODICs with larger side groups resulted in more polypropylene branching (set 2). The molecular weight data of the initial and modified polymers, their zero shear viscosity, and the number of branches per molecule of these samples are listed in Table 1. The molecular weight variation with modification in conjunction with the corresponding change of the intrinsic viscosity indicated that the dominant outcome was long chain branching in a pattern consistent with the one assumed in our model development.

The weight-average molecular weight and the degree of branching was determined using a high-temperature size exclusion chromatograph (SEC) by Viscotek, with the ability for on-line, fixed angle light scattering, refractive index, and intrinsic viscosity measurements on the effluent. According to this procedure, viscometric data is used to correct the scattering data to zero angle,

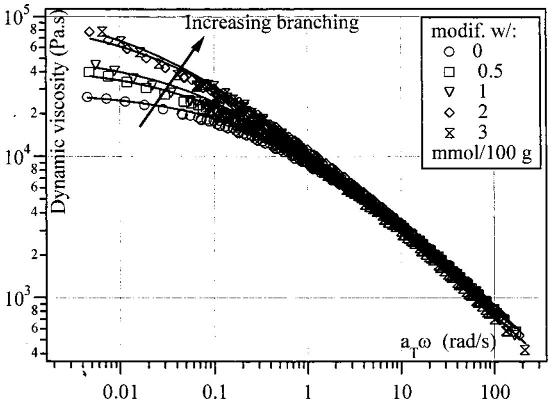

Figure 1. Dynamic complex viscosity of the linear PP precursor and its branched derivatives, produced by using increasing amounts of ethyl–hexyl peroxydicarbonate initiator (set 1).

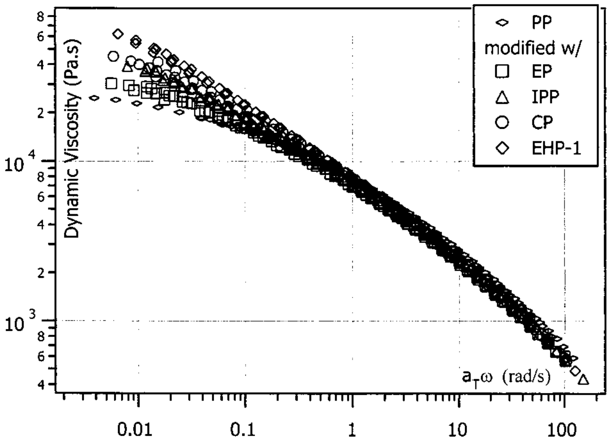

Figure 2. Dynamic complex viscosity (referenced at 190 °C) of the same linear PP precursor, branch-modified at various degrees by adding the same amount of different peroxydicarbonate species (set 2).

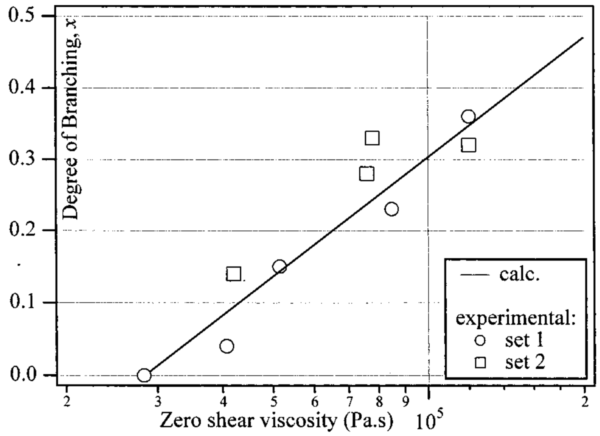

Figure 3. Degree of branching as a function of zero shear viscosity of the modified PP. Circles and squares represent experimental results of sample sets 1 and 2, while the line represents the predictions of eq 5 for $\alpha = 0.42$.

as discussed by Haney.[19] The number of branches per molecule was then calculated by applying the Zimm–Stockmayer model[20] to explain the divergence of the Mark–Houwink curve from that of the linear polymer precursor. Despite the limited degree of branching in these samples, there is a remarkable increase in elasticity (J_e^0) and melt strength, as well as strain hardening in extensional flow.[18]

The dynamic shear viscosity of the samples was measured as a function of the frequency at temperatures between 170 and 230 °C, and since frequency–temperature superposition worked well in our case of low x, all data were shifted to 190 °C (Figures 1 and 2). The viscosity increases with the degree of branching at low ω, yet this increase disappears at high rates of shear. The zero shear viscosity was determined by extrapolating to zero frequency.

The predictive effectiveness of the proposed model is demonstrated in Figure 3 where for all tested samples, branching indices x calculated via eq 5 are compared with measured ones by SEC and dilute solution viscometry, and are plotted vs the corresponding zero shear viscosity, η_0. Considering that for the given linear polypropylene precursor, M_L is 410 kg/mol and M_C = 11.2 kg/mol, the extracted value for parameter α is equal to 0.42. Not surprisingly and consistent with all prior observations, this value is smaller than the theoretical, $\alpha = 15/8$. We therefore conclude by stating that measurable changes of the shear rheology upon introduction of long chain branches on a linear polymer can be used as a characterization tool for the molecular structure that results from this modification.

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