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Similarities between Gelation and Long Chain Branching Viscoelastic Behavior

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Introduction. Very low levels of long chain branching (LCB) are known to have large effects on the rheological behavior of polymers. These effects are essential to the utility of polymers that have LCB, such as low-density polyethylene. However, the fact that only a few long branches are required means that they are difficult to detect by most means. Here we show how the level of LCB can be correlated with a rheological measure of the gel-like behavior of a polymer, which may prove useful as a characterization technique.

Rheology of Polymers at the Gel Point. Long-range connectivity in a polymeric material can be achieved by either chemical or physical gelation. Chemical gelation occurs when permanent covalent bonds connect polymer chains into a three-dimensional network. In contrast, physical gelation occurs when temporary or reversible bonds, such as crystallites, hydrogen bonds, phase-separated domains, etc., connect the chains. A key difference between the two forms of gelation is that the molecular weight is finite for physical gels but diverges at the gel point for chemical gels.[1]

Critical gels exhibit simple relaxation behavior following a self-similar relaxation modulus, first described by Chambon and Winter[2−5]

$$G(t) = St^{-n} \qquad \text{for } \lambda_0 < t < \infty \tag{1}$$

In eq 1, S (Pa·s^n) is the gel stiffness and n the critical network relaxation exponent, and λ_0 corresponds to a relaxation time characteristic of a crossover to a different relaxation mechanism. The storage and loss moduli, G' and G'', of a critical gel also obey a scaling law with the same exponent, n:

$$G'(\omega),\ G''(\omega) \propto \omega^n \tag{2}$$

According to the theory of linear viscoelasticity, the complex modulus can be calculated from the relaxation modulus by

$$G^*(\omega) = i\omega\int_0^\infty G(t)\exp(-i\omega t)\,\mathrm{d}t \tag{3}$$

Therefore, the storage modulus, $G'(\omega)$, and the loss modulus, $G''(\omega)$, at the gel point are given by

$$G'(\omega) = S\Gamma(1-n)\omega^n\cos\left(\frac{n\pi}{2}\right) \tag{4}$$

and

$$G''(\omega) = S\Gamma(1-n)\omega^n\sin\left(\frac{n\pi}{2}\right) \tag{5}$$

where Γ is the gamma function. As a result, the loss angle is independent of frequency at the gel point.

$$\tan\delta_c = \tan\left(\frac{n\pi}{2}\right) \qquad \text{for } \omega < 1/\lambda_0 \tag{6}$$

Thus, the relationship between the frequency-independent value of the phase angle δ_c, in radians, and the network relaxation exponent n is given by $\delta_c = n\pi/2$, for $0 < n < 1$. A gel described by $n \rightarrow 1$ is predominantly viscous, whereas one described by $n \rightarrow 0$ behaves elastically.

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Table 1. Characteristics of Polymers Used in Study of Wood-Adams et al.[10] and Analysis of Rheological Data Using the Gelation Approach

polymer	comonomer type	ρ (g/cm^3)	M_w (g/mol; DRI)	M_w/M_n (DRI)	long chain branches per 10 000 carbons (NMR)	δ_c (rad)	n	S [Pa·s^n]
HDL1	butene		94 000	2.08		1.571	1	
HDB1	none	0.9592	78 000	1.98	0.26	1.117	0.711	2300
HDB2	none	0.9583	80 000	1.93	0.37	0.977	0.622	5000
HDB3	none	0.9575	82 000	1.99	0.42	0.925	0.589	6800
HDB4	none	0.9565	84 000	2.14	0.80	0.803	0.511	12700

The frequency independence of the loss tangent provides the most reliable and generally valid rheological method to determine gelation.[1] This approach has been used to study a variety of physical and chemical gels,[2,4,6–9] and a range of n values between 0 and 1 have been experimentally observed.

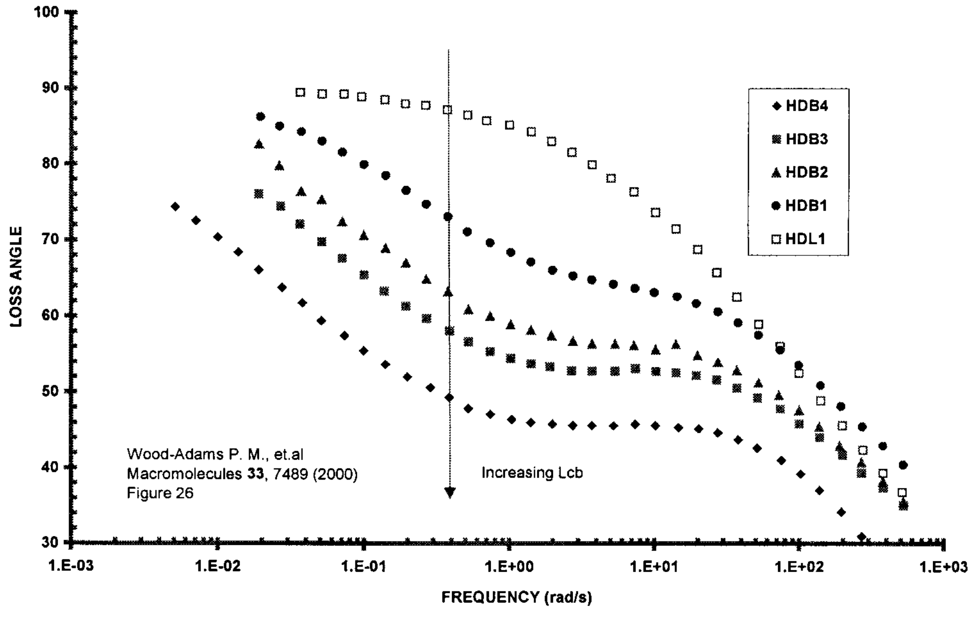
The magnitude of the dynamic viscosity for such gels can be calculated from eqs 4 and 5 giving

$$|\eta^*(\omega)| = S\Gamma(1 - n)\omega^{n-1} \qquad (7)$$

LCB Rheology. Recently, Wood-Adams and coworkers[10] studied the effect of molecular structure on the linear viscoelastic properties of polyethylene, specifically the effects of molecular weight and branching. One of their main objectives was to investigate the effect of LCB on the rheological behavior of metallocene-catalyzed polyethylenes. In their study, the extent of LCB was quantified using three techniques: rheology, ^{13}C NMR, and multidetector GPC measurements. The characteristics of these polymers as given by Wood-Adams et al. are shown in Table 1.

Given these measures of LCB, one can see a significant difference in the ways δ depends on ω for linear and branched polymers. This is shown in Figure 1 (Figure 26 of ref 10). An analysis of this plot shows that all the LCB polymers (HDB1, HDB2, HDB3, and HDB4) exhibit considerably different behavior from the linear polymer, HDL1, with this deviation increasing with increasing branching content. Perhaps the most interesting feature in the plot, but not mentioned in ref 10, is that all the LCB polymers exhibit a plateau in the loss angle, δ, as a function of frequency, whereas the linear polymer does not. Moreover, the frequency range of this plateau increases with the degree of branching. The existence of this plateau led us to believe that these LCB polyolefins show physical gel-like behavior and could be studied in terms of the Winter–Chambon analysis. Furthermore, the data of Wood-Adams et al. (Figure 2 here, Figure 24 in ref 10) show clearly that the LCB homopolymer HDB4 satisfies the congruency condition for a gel, stated in eq 2.

Using the approach of Winter and Chambon, we analyzed the data of Wood-Adams et al. to calculate the values of S and n for the linear and the LCB polymers. On the basis of previous studies by Winter et al., we would expect that increasing branching would result in increased values of S and decreased values of n (more elastic behavior). Indeed, the same conclusion can be arrived at from the findings of Wood-Adams et al., who stated that presence of LCB added a long time relaxation mode in the viscoelastic behavior that is not present in the linear polymer. It should also be emphasized here that these samples behave as physical gels only in a limited frequency (time) range of the experimental window employed here. In contrast to true critical gels, the relaxation behavior observed here is bounded by two characteristic relaxation times, λ_0 and λ_1 corresponding to crossover to different relaxation mechanisms. This can be hypothesized to be due to the fact that the branched molecules do not respond like linear molecules because of the constraints imposed by long chain branching. Even though at this point we do not have a complete physical understanding of this phenomenon, we do not believe that this is caused by the presence of a "physical structure" or aggregate in the material. Rather, we believe this to be caused by only a modification of the relaxation behavior caused by the presence of the long chain branching.



Wood-Adams P. M., et.al
Macromolecules **33**, 7489 (2000)
Figure 26

Figure 1. Effect of LCB on loss angle for high-density mPEs at 150 °C.

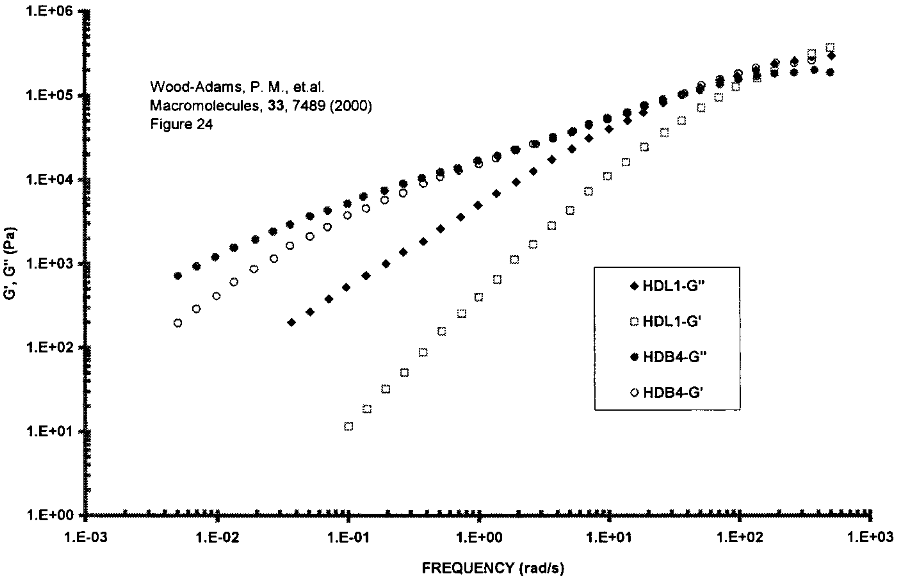


Figure 2. Comparison of dynamic moduli for HDB4 and HDL1.

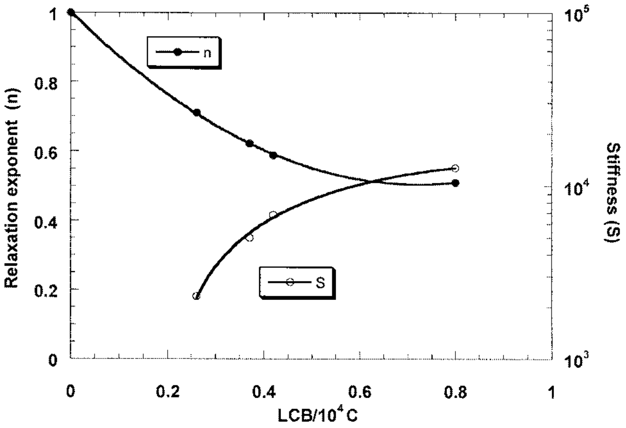


Figure 3. Effect of LCB on the network relaxation exponent *n* and gel stiffness *S*.

The results obtained by using the Winter–Chambon theory on these data are shown in Table 1. The values of the network relaxation exponent, *n*, were obtained using eq 6, and the values of the gel stiffness, *S*, were calculated by curve fitting the viscosity data using eq 7. Indeed, as expected, the relaxation exponent decreases with increasing branching, while the gel stiffness increases; these results are plotted in Figure 3. In essence, our analysis shows that some LCB structures exhibit gel-like behavior in their rheological response. Furthermore, such an analysis potentially carries the benefit of devising a quantitative measure of LCB content in polyolefin melts. Indeed, we have observed similar rheology in other LCB polymers as well, which will be the subject of a future paper.

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