8280 *Macromolecules* **1996,** *29,* 8280−8281

Comments on the Paper "Comparison of the Rheological Properties of Metallocene-Catalyzed and Conventional High-Density Polyethylenes"[1]

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Received June 24, 1996
Revised Manuscript Received August 20, 1996

It was claimed in a recent paper[1] that some metallocene-catalyzed high-density ethylene homopolymers (HDPE) show a markedly different rheological behavior than conventional HDPE. The main structural differences reported for both series of HDPEs are the presence of a few short-chain branches in conventional HDPEs and narrower molecular weight distributions for the metallocene-catalyzed HDPEs.

In that article:[1]

(a) Reported zero shear rate viscosities for metallocene-catalyzed HDPEs are higher than values previously published by other authors for conventional HDPEs of the same molecular weights and molecular weight distributions.[2−7]

(b) Viscosity is said to depend on molecular weight with an exponent of 4.2 for metallocene-catalyzed HDPE and 3.6 for conventional HDPE.

(c) Flow activation energies (E_a) higher than previously observed for conventional HDPE with similar molecular weights and molecular weight distributions[2,6,7] are reported.

(d) The values of the spectra of relaxation times of metallocene-catalyzed polyethylenes are reported to be higher, at long relaxation times, than those corresponding to conventional polyethylene of practically the same molecular weight.

(e) Some of the observed differences in rheological properties are assumed to be originated in the "total absence of branching". As shown by ^{13}C-NMR data (Table 1, fifth column[1]), the metallocene-catalyzed HDPEs do not have any appreciable amount of short-chain branching, and the "conventional HDPE" show up to 3.7 CH_3/1000 C.[1] It is stated[1] that "above the critical molecular weight (M_c) the large scale structure and the chain configurations are different in both types of polymers, thereby giving rise to a more entangled system".

Since the relationship between the molecular structure of this type of polymer and its melt rheological properties has been thoroughly studied—from theoretical approaches and carefully obtained experimental data[2−7]—and reported in the literature, it is important that these claims be seriously examined.

Two important points must be emphasized now:

(1) There is no theoretical development or experimental evidence in the literature which may suggest that—for linear polyethylenes—the difference between zero short branching ("total absence of branching", as reported for the metallocene-catalyzed HDPEs)[1] and a maximum of 3.7 CH_3/1000 C (as reported for conventional HDPEs)[1] may cause such differences in rheological properties between both types of HDPE, as reported in ref 1.

(2) All the above mentioned aspects, (a) to (d), suggest that the metallocene-catalyzed HDPE are not really linear polymers from the rheological properties point of view; the reported rheological properties strongly indicate the presence of long-chain branching, which may not be detected by ^{13}C-NMR. Even when the microstructure is an almost pure polymethylene chain, as observed by ^{13}C-NMR, the concentration of tertiary carbon atoms necessary for a few long chain branches in some molecules (it is not necessary that every molecule be branched) is well below the detection limits of the instrument (a rough estimation may place the concentration of tertiary carbon atoms—enough to cause these differences in rheological properties—on the order of 10^{-5}−10^{-4} fraction of carbon atoms).

In what follows, the reported data[1] will be reexamined and compared with already published results, to support the suggestion that these polymers have a polymethylene microstructure and contain some long branches.

The zero shear rate viscosity (η_0) has been defined as a function of the loss modulus ($G''(\omega)$) at sufficiently low frequencies:[8]

$$\eta_0 = \lim_{\omega \to 0} \frac{G''(\omega)}{\omega} \tag{1}$$

Here η_0 is understood as a limiting, constant value and must not be taken as the value obtained at the lowest frequency attainable with the equipment available in the laboratory.

In the above mentioned paper,[1] in Figure 2 the correlation $\eta_0 = 3.4 \times 10^{-15}(\bar{M}_w)^{3.6}$ is erroneously compared with the complex viscosity function (η^*), calculated as

$$\eta^* = ((G'/\omega)^2 + (G''/\omega)^2)^{1/2} \tag{2}$$

and measured at an arbitrary value of $\omega = 0.01$ s^{-1}. A straight line is fitted:

$$\eta^*(0.01) = 2.3 \times 10^{-17}(\bar{M}_w)^{4.2} \tag{3}$$

which intercepts $\eta_0 = 3.4 \times 10^{-15}(\bar{M}_w)^{3.6}$ at about M_c, and erroneous conclusions are drawn when comparing the data for the metallocene-catalyzed polyethylenes with the data for the "slightly branched HDPEs".[1] As at low frequencies η^* should be close to η_0, due to the lack of better information I will use η^* data to stress the above mentioned suggestions for branching.

(a, b) The fact that η_0 for entangled, linear, flexible polymers depends on molecular weight with an exponent of 3.4−3.6 has been well established, from theory[9−11] and from experimental data.[2−9,12−15] In the case of conventional HDPE (linear ethylene homopolymer with less than 3−4 CH_3/1000 C), the relationship $\eta_0 = 3.4 \times 10^{-15}(\bar{M}_w)^{3.6}$ [6,7] has been widely accepted for linear polymers with narrow molecular weight distributions; the same relationship holds (within experimental error limits) for linear ethylene polymers containing some short-chain branching (up to 20 CH_3/1000 C).[7]

For the molecular weight range used in ref 1, even the values obtained for η^* are quite higher than those obtained from $\eta_0 = 3.4 \times 10^{-15}(\bar{M}_w)^{3.6}$, and the slope of η^* vs $\bar{M}_w$ data is higher (4.2). In fact, the data fitted by eq 3 closely resemble η_0 vs $\bar{M}_w$ data obtained for *star-branched* ethylene polymers with up to 20 CH_3/1000 C,[7] which are higher than data for the *linear* ethylene polymers with up to 20 CH_3/1000 C and the same molecular weight, and show a slope higher than 3.6. This fact, together with the experimental evidence for the nil effect of low levels of short-chain branching on

S0024-9297(96)00909-6 CCC: $12.00

viscosity of ethylene linear polymers,[7] suggests that the high values observed for η^* in metallocene-catalyzed HDPEs used in ref 1 are rather originated by the presence of long-chain branching.

It has been shown in the literature that the shape and location (in the (ω) scale) of the $G'(\omega)$ and $G''(\omega)$ curves in the terminal zone of the relaxation spectrum, for entangled, linear, flexible polymers with narrow molecular weight distributions, depend on the monomeric friction factor, the contour length concentration, the radius of gyration, and the ($T - T_g$) temperature difference;[8,16−18] none of these variables changes in an appreciable amount when going from 3−4 CH_3/1000 C to zero short branching.[19−24] $G''(\omega)$ determines η_0, as shown in eq 1; therefore, η_0 should not change (within the limits of experimental error) in a detectable amount when going from 3−4 CH_3/1000 C to zero short branching. This has been confirmed experimentally.[6,7]

Some results for η_0 are also reported in Table 2;[1] as expected, those are slightly higher than the corresponding values of $\eta^*(0.01)$, and also higher than predicted from the correlation $\eta_0 = 3.4 \times 10^{-15}(\bar{M}_w)^{3.6}$.[6] Similar results have been found by other authors for some types of linear polyethylene fractions. Raju and co-workers[6] correlated melt viscosities for HDPE fractions with intrinsic viscosities and found—for two samples—η_0 values much higher than expected, on the basis of their intrinsic viscosities, and "shapes of the $G'(\omega)$ and $G''(\omega)$ curves markedly different from those of the other samples"; the higher than expected values of η_0 were suspected to be originated in the presence of long branches.

(c) Other data for the metallocene-catalyzed HDPEs[1] point toward the presence of long branches in these polymers: flow activation energies (E_a) higher than previously observed for HDPEs[2,6,7] are reported.[1]

A theoretical basis has been provided[25] for the previously observed thermorheological complexity of polymers with long branching,[7] on the basis of additional relaxation mechanisms associated with long branches and the chain dimensions temperature coefficient ($K = \partial \ln\langle R^2\rangle/\partial T$). It is proposed (and experimentally confirmed[26]) that long branches in polymers with a negative K (like HDPEs) should produce an increase in the values of E_a, when calculated from η_0; the differences of E_a with the linear polymers depend on the number of branches per molecule, on branch length, and on the value of K.[7,26] Based on this background, it may be suggested that the higher than expected viscosities and E_a values indicate the presence of long branches in the metallocene-catalyzed HDPEs. The authors[1] cite E_a values for ethylene−octene copolymers with long-chain branching which coincide with theirs, adding further evidence for long-chain branching presence in the metallocene-catalyzed HDPEs.

(d) In Figure 7,[1] relaxation spectra for some of the HDPEs are shown. When comparing conventional HDPE with metallocene-catalyzed HDPE of similar molecular weights, one can see that "the values obtained for the metallocene-catalyzed material are significantly higher at longer relaxation times". This is assigned[1] to the "concentration of relaxation mechanisms caused by entanglement couplings between high molecular chains in the rubbery or plateau region". This statement contradicts the M_e previous calculation[1] which seems to agree well with M_e values published for linear ethylene polymers with about 20 CH_3/1000 C.[6,7,24] Higher concentrations of entanglement couplings should result in higher values for G_{N° and lower M_e values.[18,25] It is more likely that these high values obtained for the metallocene-catalyzed HDPEs at longer relaxation times are originated in additional relaxation mechanisms originated by the presence of long branches.[7,8,11,18,26]

In this context, it may also be pointed out that the G_{N° calculation based in Figure 5[1] looks extremely uncertain, because of doubtful, long extrapolations; it has been shown[17−24] that slightly higher G_{N° values should be expected for HDPE, on the order of $(2.2-2.5) \times 10^6$ Pa. Also, the accepted relation for linear polymers with narrow molecular weight distributions,[18] $G_{N^\circ} = 3.56\ G_{\max}$ is not held for the metallocene-catalyzed HDPEs, $G''_{\max}$ being lower than expected. This may be caused either by broad molecular weight distributions or by the presence of long-chain branching.[7,8] Careful examination of low-frequency rheological data may be useful to elucidate these matters.

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MA960909V