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Small-Amplitude Oscillatory Shear Flow Measurements as a Tool To Detect Very Low Amounts of Long Chain Branching in Polyethylenes

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ABSTRACT: Dynamic viscoelastic results of 23 noncommercial metallocene-catalyzed polyethylenes and poly(ethylene/1-hexene) copolymers, in the range 130−190 °C, are presented. The effects of well-determined structural parameters such as molecular weight, polydispersity, and degree of short chain branching (SCB), are analyzed. The molecular weight varies between 60 000 and 325 000, the polydispersity between 1.8 and 7.3, and SCB between 0 and 48.5 branches/1000 C atoms. It is observed that a group of 11 polymers displays rheological specific features which can be summarized as follows: (a) higher dynamic viscosities at low frequencies than other polyethylenes and ethylene/1-hexene copolymers of similar molecular weight, polydispersity and SCB degree; (b) higher relaxation times than narrow molecular weight distribution polyethylenes of similar dynamic viscosities at low frequencies but similar relaxation times to those of broad molecular weight distribution; (c) higher values of elastic modulus, in comparison with polyethylenes of similar molecular weight, polydispersity, and SCB but of the same order of magnitude as those of broader molecular weight distribution; (d) higher activation energy of flow than linear polyethylenes of the same molecular weight, polydispersity, and SCB level. An analysis of the literature results leads us to suspect that the polymers which show a “dissident” behavior possess a certain very low degree of long chain branching (LCB). The analysis of the samples by SEC coupled with intrinsic viscosimetry reveals that some of these 11 polymers are long chain branched. However, this technique does not appear to be enough sensitive to detect very small amounts of LCB, and an alternative single rheological method, based on the effect of temperature on dynamic viscosity, is proposed to evaluate the possible presence of LCB.

Introduction

Since the early 1950s, the effects on physical properties of short chain branching (SCB) and long chain branching (LCB) that occur during the free radical polymerization of ethylene have been known.[1] Roedel established in 1953 that C_4 should be the most probable length for SCB, followed by C_5 and C_3, while LCB moieties were comparable in length with the polymer main chain. The former type of branching mainly affects properties in the crystalline state, whereas the latter has a great influence on rheological properties. SCB is determined without any particular difficulty by IR and NMR analysis, but determination of LCB is somewhat ambiguous because it requires assumptions on the relationship between the molecular weight distribution and the branching frequency.[2] IR and NMR analysis have not been very successful to measure the degree of LCB because the number of chain ends associated to long branches is small. A quantitative analysis of long chain branched polyethylenes by ^{13}C Fourier Transform NMR[3] reveals that, with respect to branch type and concentration, there is no unique low-density polyethylene molecule since the concentration, type, and distribution of subgroups vary widely. Very recent ^{13}C and 2-D NMR analysis of novel polyethylene made with new late metal catalysts demonstrates that a large percentage of the branches are “branches on branches”, which can be explained by a catalyst “walking” mechanism.[4]

The influence of LCB on the viscoelastic properties of polyethylenes has been extensively studied in the past decades and the following general conclusions can be extracted for the rheological effect of moderate and high degrees of LCB. (a) Long chain branched polyethylenes show lower Newtonian viscosities and higher values of $\dot{\gamma}_0$ for the onset of shear thinning behavior than linear polyethylenes of the same molecular weight.[5−16] (b) LCB causes a decrease in the severity of pseudoplastic behavior: linear polyethylenes show a bigger change in the viscosity with shear rate than highly branched polyethylenes.[13,17−19] (c) The activation energy of flow increases with LCB[20−30] depending on the length, concentration and distribution of the branches.[31] (d) Long chain branching produces an enhancement in melt elasticity, expressed by an increase in first normal stress difference, steady-state compliance, and extrudate swell.[6,7,14,15,18,19,32−34] However, points a and b are not obeyed by polyethylenes with low degrees of LCB: an enhancement in Newtonian viscosity values and an increased pseudoplastic behavior for slightly branched than for linear polyethylenes of the same molecular weight have been observed by several authors.[9,19,26,30,35−41] Wild et al.[36] explained this result, pointing out the predominating effect of entanglements at low degrees of LCB and the molecular size reduction effect at medium and high degrees of LCB. A model developed by Bersted[30] predicts a maximum of Newtonian viscosity with branching level at approximately 0.25 branches/1000 CH_2, in thermomechanical modified polyethylenes. On the other hand, it has been reported[14,19,40,42] that

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small amounts of long chain branching impart a more pseudoplastic (shear thinning) behavior to the polyethylenes as compared to linear analogues.

Similar conclusions were drawn by Graessley et al.[43−45] on model branched star and comb materials: they observed lower Newtonian viscosities in comparison with linear polymers at the same molecular weight but enhancement in these values when comparisons were made at constant radius of gyration or molecular size. On the other hand, the studies of Long et al.,[46] Kraus and Gruver,[47,48] and Ghijsels and Mieras[49] on random, star, and comb polymers showed that the melt viscosity of branched polyvinyl acetates and polybutadienes was usually higher than that of linear polymers of the same average molecular weight at sufficient high branch lengths, M_b, above the characteristic molecular weight between entanglements, M_e. It is interesting to contrast the ideas reported by Graessley et al.[43,45] with the data of Bersted.[26,30] The difference between their samples is expected to be in the distribution of LCB. Owing to the method of preparation, the former are uniformly branched, even at the low levels discussed for the random branched samples studied by Bersted. Whereas Graessley suggest that the viscosity enhancement of the model branched species depends on branch length, the analysis of Bersted predicts enhancement either from (a) an increased concentration of branched species in a linear species "matrix" if branches are formed on linear molecules or (b) from increased molecular size if branches are formed on branched species.

Polyethylenes obtained via single-site metallocene catalysts have been the subject of several papers which mention the effect of long chain branching on rheological properties.[50−64] Besides oscillatory and continuous shear flow experiments results, elongational flow results have been presented.[62] Our incipient works on the rheology of metallocene-catalyzed polyethylenes led us to suspect the presence of LCB, but neither polymerization process nor NMR analysis results supported this assumption. Therefore we interpreted the differences found with respect to conventional polyethylenes as a consequence of the total absence of short chain branching in these new polyethylenes.[61] During the last months we have carried out more research to elucidate the presence of small amounts of LCB in the polyethylenes obtained by Repsol using single-site catalysts. The nowadays accepted fact that traditional methods (SEC combined with intrinsic viscosity and ^{13}C NMR) are hardly applicable to measure LCB concentrations below about 0.1 branch per 1000 C atoms, has led us to analyze rheological special features of very slightly long chain branched polyethylenes. The recent comments of Carella[65] on our first results suggest that this rheological data indicate the presence of long chain branching. We have now enough data to be in a position to assert that the interpretation of Carella is correct. In this paper we present rheological results of 6 conventional polyethylenes and 23 noncommercial metallocene-catalyzed polyethylenes, from which 11 are suspected to possess small amounts of LCB. The analysis of our data in comparison with the literature results allows us to establish a set of criteria, based on dynamic viscoelastic measurements, to determine the presence of LCB in polyethylenes.

Experimental Section

Table 1. Structural Parameters of Commercial HDPE Grades and a Commercial LLDPE

material	M_w	M_w/M_n	mol % of comonomer and type	short chain branching[c]
PE-6006-L[a]	171 500	7.7	0.15/1-hexene	1.40
PE-5502-A[a]	192 500	10.1	0.09/1-hexene	1.08
TUB-125[b]	273 000	15.7	0.59/1-butene	3.12
NCPE-2494[b]	314 000	16.7	0.66/1-butene	3.75
GM-5010-T2E[b]	318 000	21.8	0.54/1-butene	3.62
F2	125 000	3.1	2.51/1-octene	11.7

[a] Commercial polydisperse monomodal HDPE's (Repsol, Spain). [b] Commercial polydisperse bimodal HDPE's (from Solvay, Neste, and Hoechst, respectively). [c] Branches due to comonomer given as the number of CH_3/1000 C atoms.

Table 2. Structural Parameters of Metallocene-Catalyzed HDPE's and LLDPE's (Repsol)

material	M_w	M_w/M_n	mol % of comonomer and type	short chain branching[a]
cPEH1	63 000	2.5	1.20/1-hexene	5.85
P148	70 300	1.8	7.70/1-hexene	25.5
cPEH2	87 800	2.7	2.16/1-hexene	10.3
SA-2163	156 000	2.3	1.74/1-hexene	8.38
P150	157 500	2.4	12.2/1-hexene	48.5
cPEH4	160 300	3.0	1.78/1-hexene	8.59
SA-2161	181 900	2.3	0.89/1-hexene	4.38
SA-2160	190 000	2.3	0.47/1-hexene	2.34
PCWSB13	200 000	2.9	1.66/1-hexene	8.50
SA-2164	307 800	2.0	0.86/1-hexene	4.19
BP102	319 500	7.3	0.94/1-hexene	4.62
SA-2157	326 800	2.1		

[a] Branches due to comonomer given as the number of CH_3/1000 C atoms.

Table 3. Structural Parameters of Metallocene-Catalyzed HDPE's and LLDPE's Containing Long Chain Branches or Suspected To Contain LCB

material	M_w	M_w/M_n	mol % of comonomer and type	CH_3 (Hex+)[b]
PE02	69 000	3.5	...	0.00

material	M_w	M_w/M_n	mol % of comonomer and type	short chain branching[a]
P120	92 120	2.4	1.28/1-hexene	6.24
P169	97 000	2.1	4.00/1-hexene	18.5
P109	124 000	2.7	0.72/1-hexene	3.56
BP58	125 500	2.4	0.75/1-hexene	3.91
P162	130 900	2.7	1.52/1-hexene	7.82
GSMC2R	134 700	2.0	1.23/1-hexene	6.35
XV	135 400	3.9	0.75/1-octene	3.66

material	M_w	M_w/M_n	mol % of comonomer and type	CH_3 (Hex+)[b]
BP313	158 200	2.9	...	4.90
PE03	190 000	2.9	...	0.00
BP318R	278 700	2.5	...	1.72

[a] Branches due to comonomer given as the number of CH_3/1000 C atoms. [b] Measured by ^{13}C NMR.

Materials and Characterization. The molecular parameters of the materials are shown in Table 1 to 3. Commercial HDPE grades, as well as one LLDPE grade, are included in Table 1; Table 2 corresponds to linear metallocene-catalyzed polyethylenes and Table 3 to metallocene-catalyzed polyethylenes with a very low degree of LCB. These new polyethylenes were prepared via single-site metallocene catalyst system following the method of Kaminsky et al.[66] using Cp_2ZrCl_2 as a catalyst. The reactivity ratios for the ethylene/1-hexene copolymers were $R_1 = 56$ and $R_2 = 0.008$. The latter low value indicates that the insertion of comonomer in the polymer chain is difficult, which is consistent with the absence or very low presence of LCB. The polymers were carefully prepared in a 1.3 L glass autoclave reactor operated in batch mode at 70 °C, 4 bar ethylene pressure, and 600 mL of *n*-heptane. Polymerizations were stopped by rapid depressuration followed by addition of methanol. Finally, the materials were stirred in a mixture of methanol/HCl overnight, filtered, and washed with plenty of methanol, to eliminate the remaining catalyst residues in the form of soluble metal−alkoxides formed by hydrolysis. Polymer samples were obtained free of catalyst impurities.

The use of metallocene-based catalyst systems allows us to ensure that the processes of polymerization were well controlled in terms of the absence of high molecular weight tails and the obtention of materials with characteristic narrow molecular weight distributions, unlike those commercial processes that employ Ziegler−Natta catalyst systems, characterized for the broad distribution of active sites, that produce polymers of high molecular weight and broad molecular weight distribution.

All samples were characterized. Size exclusion chromatography (SEC) measurements were carried out in a Waters 150C equipment coupled with differential refractive index (DRI) and a 150R model viscosimeter detector with Unical software from Viscoteck. The systems have been developed to meet high-sensivity polymer analyses and are able to give, among other results, absolute molecular weight and long chain branching contents as well as low and high molecular weight polymer fractions (below 10^4 and above 10^6). To avoid polymer degradation during SEC operation, measurements were performed with adequately stabilized samples (e.g. 0.04 wt % of Irganox 1010) and optimal experimental conditions (i.e., sample concentrations, injection volumes, and flow rates). High molecular weight components, which if not detected can conduct to a misleading interpretation of the rheological data, have been evaluated for samples of molecular weights higher than 1.3×10^5. We have not found differences between the samples of Table 2 and Table 3: the weight fractions above molecular weight 10^6 are on the order of 0.1%.

The method described by Drott and Mendelson[67] was used to determine the LCB degree. However, this method is not accurate in the case of very small amounts of LCB, because samples which show very different melt viscoelastic properties do not display changes in the molecular weight distribution and intrinsic viscosity evaluated by the aforementioned method. The level of short chain branches (SCB) was measured by ^{13}C NMR.

Rheological Measurements. Small-amplitude oscillatory shear flow functions, dynamic viscosity, $\eta'(\omega)$, storage modulus, $G'(\omega)$, and loss modulus, $G''(\omega)$, were obtained with the CarriMed CSL-100 Viscometer with parallel plates geometry in the frequency range 0.01−10 Hz (0.063 to 63 rad/s). The amplitude was 0.0006 rad, which belongs to the linear viscoelastic region, located by the aid of a previous torque sweep. The temperature range of measurements was 130−190 °C. The experiments were performed with test specimens (20 mm of diameter and 2 mm of thickness) molded in a CS-183 Mini-Max Molder at 160 °C over 5 min.

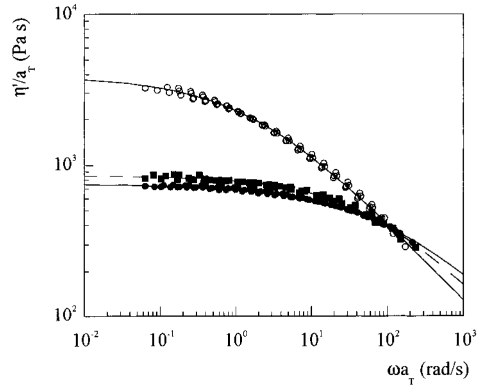

Figure 1. Master curves at T_R = 190 °C of the dynamic viscosity as a function of frequency for the samples of molecular weight around 60 000: (●) cPEH1, (■) P148, and (○) PE02 (Tables 2 and 3). The shift factor, a_T, is defined in eq 1. The data are fitted to eq 2.

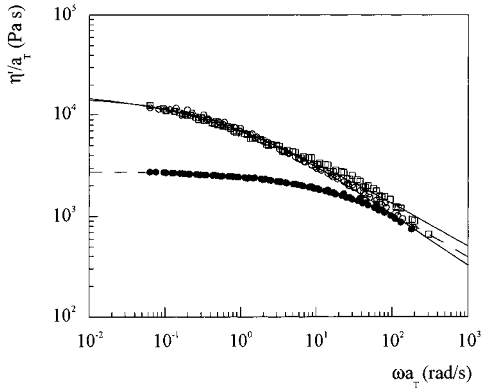

Figure 2. Master curves at T_R = 190 °C of the dynamic viscosity as a function of frequency for the samples of molecular weight around 90 000: (●) cPEH2, (○) P120, and (□) P169 (Tables 2 and 3). The shift factor, a_T, is defined in eq 1. The data are fitted to eq 2.

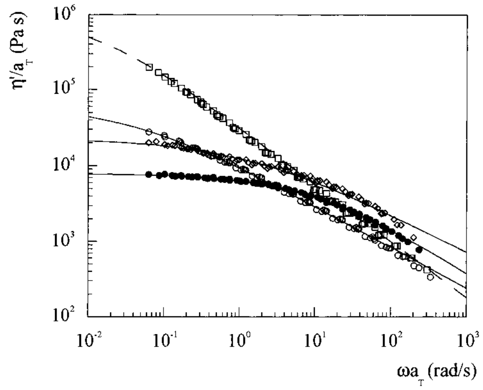

Figure 3. Master curves at T_R = 190 °C of the dynamic viscosity as a function of frequency for the samples of molecular weight around 130 000: (●) F2, (○) BP58, (□) P109, and (◇) P162 (Tables 1 and 3). The shift factor, a_T, is defined in eq 1. The data are fitted to eq 2.

Results and Discussion

In Figures 1−6 we present the dynamic viscosity function $\eta'(\omega)$ of several of the polyethylenes listed in Tables 2 and 3, gathered in groups of similar molecular weight around, respectively, M_w = 70 000, M_w = 100 000, M_w = 130 000, M_w = 160 000, M_w = 190 000, and M_w = 200 000−300 000. It is worth pointing out the differences found in these figures for polymers of practically the same M_w, M_w/M_n, and SCB. Actually in each group there is a polyethylene, but not necessarily the most or the less short branched, which shows a more frequency sensitive behavior and considerably larger viscosity at low frequencies. In this set of figures data for $\eta'(\omega)$, obtained at temperatures ranging from 130 to 190 °C, are superposed to the latter temperature using a shift factor a_T which is correlated to temperature through the Arrhenius-like equation

$$a_T = \exp\left[\frac{E_a}{R}\left(\frac{1}{T} - \frac{1}{463}\right)\right] \qquad (1)$$

The corresponding activation energies of flow are listed in Table 4, with the rest of the rheological parameters

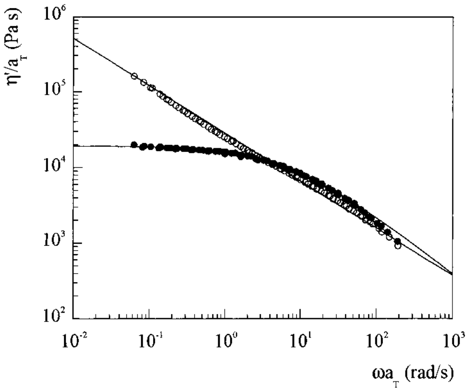

Figure 4. Master curves at T_R = 190 °C of the dynamic viscosity as a function of frequency for the samples of molecular weight around 160 000: (●) cPEH4 and (○) BP313 (Tables 2 and 3). The shift factor, a_T, is defined in eq 1. The data are fitted to eq 2.

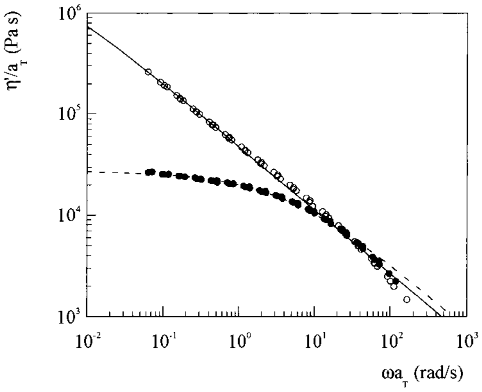

Figure 5. Master curves at T_R = 190 °C of the dynamic viscosity as a function of frequency for the samples of molecular weight around 190 000: (●) SA2160 and (○) PE03 (Tables 2 and 3). The shift factor, a_T, is defined in eq 1. The data are fitted to eq 2.

which are discussed in this work. The experimental results of Figures 1–6 have been fitted to the Briedis and Faitel'son equation[68,69] which is equivalent to the Cross model[70] (which actually is a particular case of the Carreau–Yasuda equation[71]), but using the $\eta'(\omega)$ function instead of the steady-state viscosity function $\eta(\dot{\gamma})$:

$$\eta' = \frac{\eta_0}{[1 + (\omega\tau_0)^{\alpha}]} \qquad (2)$$

where η_0 is the Newtonian viscosity, $\eta_0 = \lim_{\omega\to 0} \eta'$, which is a consequence of the general linear viscoelastic model,[71] τ_0 is a relaxation time which inversely accounts for the onset of nonlinear pseudoplastic region and "α" is a pseudoplasticity or shear thinning index.

For some of the samples a continuous shear thinning region is observed in all the frequency range considered, without practically any symptom of leveling off at low frequencies. In these cases the value of the parameter η_0 can hardly be associated to the linear (Newtonian) viscosity of the general linear viscoelastic model. To correlate experimental data with chain architecture, besides the parameters of eq 2 we also use the values of the dynamic viscosity η' and relaxation time λ (see below) taken at a frequency of 0.01 Hz. These parameters are included in Table 4.

Data of storage modulus, $G'(\omega)$, and loss modulus, $G''(\omega)$, superposed at 190 °C are shown in Figure 7 for a series of samples. Some of the samples have a higher elasticity than the expected with regard to their molecular weight and molecular weight distribution: this point will be discussed below. The general linear viscoelastic model allows to define a relaxation time, which is approximately equal to the longest relaxation time of the generalized Maxwell model[71]

$$\lambda_0 = \lim_{\omega\to 0} \frac{G'}{\omega G''} = \eta_0 J_e^{\circ} \qquad (3)$$

where J_e° is the steady-state compliance defined in constrained recoil experiments. Since in the case of polyethylenes the scaling laws of the general linear viscoelastic model, $G' \propto \omega^2$ and $G'' \propto \omega$, are not fulfilled, we have to define a characteristic relaxation time of the terminal zone. From data of storage and loss moduli vs frequency (Figure 7) and using the relation between G' and G'' expressed in eq 3, we obtain the characteristic relaxation time, λ, at ω = 0.01 Hz. The value of λ for each sample is included in Table 4. The following experimental relation is found for entangled polymers:[14]

$$\eta_0 \dot{\gamma}_0 J_e^{\circ} = \text{constant} \qquad (4)$$

This (where $\dot{\gamma}_0$, the inverse of τ_0, defines the onset of pseudoplastic behavior), combined with eq 3, leads to a linear relation between λ_0 and τ_0.

The correlation of the Newtonian viscosity and the weight average molecular weight is shown in Figure 8, which make evident that many of the data (but not all of them) are well fitted to the equation proposed by Raju et al.:[37]

$$\eta_0 = 3.4 \times 10^{-15} M_w^{3.6} \qquad (5)$$

This equation is independent of polydispersity and, we have observed that it holds well for conventional Ziegler–Natta polyethylenes of polydispersities, M_w/M_n, ranging from 3 to 35,[72,73] as well as metallocene-catalyzed polyethylenes. However, bimodal commercial polyethylenes cause this equation to fail, because of a plastification effect of low molecular weight tails. As can be seen in Figure 8, several polymers (those of Table 3 which are not different from the others in molecular weight, polydispersity, and short chain branching concerns; see Tables 1 and 2) deviate upward from this equation. Since some of the values of η_0 used in this figure do not correspond to a noticeable leveling off of the $\eta'(\omega)$ function but to a straight fitting of eq 2, in Figure 9 we show experimental, not extrapolated, dynamic viscosity data taken at a frequency of 0.01 Hz as a function of molecular weight. The same trend is observed: higher viscosities for the polyethylenes suspected of having a small amount of LCB (Table 3) with regard to linear polyethylenes of the same molecular weight. The results found in Figures 8 and 9 resemble those found for branched poly(vinyl acetates),[46] star-shaped polybutadienes,[45,47,48,73] branched polyisoprenes,[14] and branched polystyrenes.[38,43,44,75] As we have mentioned in the Introduction, for conventional slightly long chain branched polyethylenes it has been noted that the viscosity at low shear rates (in the linear region) may be several times greater than the viscosity of linear polyethylenes of the same value of M_w.

In a paper focused to asses the development and future of the use of metallocene catalysts in the polym-

Table 4. Rheological Parameters of the Samples Considered in This Work (See Text)

material	η_0 (Pa s)	τ_0 (s)	α	η'(0.01 Hz) Pa s	λ (0.01 Hz) s	E_a (kcal/mol)
			Materials from Table 1			
PE-6006-L	49 025	47.1	0.48	18 478	8.28	6.5
PE-5502-A	177 420	183	0.51	40 921	11.2	7.0
TUB-125	78 113	4.99	0.63	52 586	5.22	5.2
NCPE-2494	141 390	20.7	0.65	65 717	8.66	5.3
GM-5010-T2E	291 420	34.6	0.68	109 900	13.6	5.4
F2	7 830	0.103	0.60	7 700	1.19	7.5
			Materials from Table 2			
cPEH1	749	0.00798	0.52	729	0.237	7.3
P148	850	0.0127	0.57	820	0.313	8.5
cPEH2	2 755	0.0253	0.55	2 724	0.750	7.5
SA2163	20 792	0.195	0.63	19 163	1.66	7.0
P150	20 322	0.243	0.67	18 302	2.64	10.7
cPEH4	21 000	0.142	0.66	20 000	1.38	7.2
SA2161	27 444	0.216	0.66	26 595	2.09	6.2
SA2161	34 694	0.302	0.70	35 173	2.56	6.0
PCWSB13	48 000	0.414	0.64	45 185	2.84	7.0
SA2164	311 470	2.29	0.75	266 400	7.61	6.0
BP102	261 080	24.9	0.65	112 280	11.17	6.9
SA2157	342 420	2.72	0.75	293 970	7.61	5.3
			Materials from Table 3			
PE02	3 894	0.527	0.54	3 122	1.61	8.1
P120	15 420	1.36	0.53	11 757	2.14	8.6
P169	17 396	2.65	0.44	12 384	2.02	9.7
P109[a]	996 634	97.1	0.75	196 880	18.3	8.1
BP58	65 730	26.2	0.55	27 742	7.14	10.0
P162	22 614	0.68	0.53	20 118	2.90	7.8
GSMC2R	31 363	7.98	0.53	17 651	2.86	7.2
XV	17 822	1.71	0.52	12 653	5.53	8.6
BP313[a]	6.81×10^7	2.44×10^5	0.63	160 430	26.8	7.5
PE03[a]	6.01×10^6	2.46×10^3	0.62	262 140	20.5	8.9
BP318R[a]	1.72×10^9	2.47×10^6	0.70	406 970	36.3	7.5

[a] Leveling off on viscosity not observed at low frequencies.

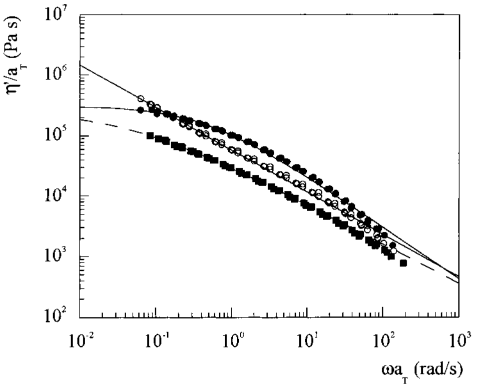

Figure 6. Master curves at $T_R = 190$ °C of the dynamic viscosity as a function of frequency for the samples of molecular weight around 200 000−300 000: (●) SA2157, (■) BP102, and (○) BP318R (Tables 2 and 3). The shift factor, a_T, is defined in eq 1. The data are fitted to eq 2.

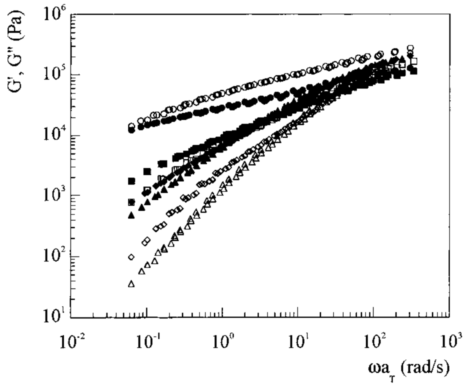

Figure 7. Master curves at $T_R = 190$ °C of the storage (open symbols) and loss (close symbols) moduli as a function of frequency for some of the samples of $M_w = 130000$. (▲, △) F2, (◆, ◇) P169, (■, □) BP58, and (●, ○) P109.

erization of polyolefines, Garbassi et al.[55] emphasize the effect of low levels of long chain branching on the viscosity curves, pointing out the high values of the viscosities extrapolated to zero shear rate. An effort to correlate viscosity results of metallocene-catalyzed polyethylenes with LCB degree has been undertaken recently by Dow's researchers.[51−54,57−60] Their published findings, although limited to molecular weights in the range 70 000−130 000, constitute a base to understand our experimental results. Practically all the mentioned works refer to the high value of the viscosity at low shear rates, found for slightly long chain branched systems, but the paper by Lai and Knight[53] explicitly refers to the deviation of this group of polymers from η_0−M_w correlation found for systems with no LCB at all. On the other hand a correlation between η_0 and τ_0 (eq 2, but using $\dot{\gamma}$ instead of ω) has been used[54,57−60] to define a named Dow Rheological Index, which reflects the deviation from a η_0−τ_0 linear equation and would allow one to evaluate the degree of LCB. However this method requires good fittings in the experimental results to the Cross equation and the observation of a leveling off in the viscosity function at low shear rates (to obtain a reliable η_0), which may not be the case when dealing with polyethylenes of higher molecular weights (M_w > 130 000) than those divulged by Dow's researches. In Figures 10 and 11 we show, respectively, the η_0−τ_0 plots and η'−λ plots of our data listed in Table 4. We observe that both polydisperse conventional polyethylenes and metallocene-catalyzed polyethylenes suspected of containing LCB (Table 3) deviate from the

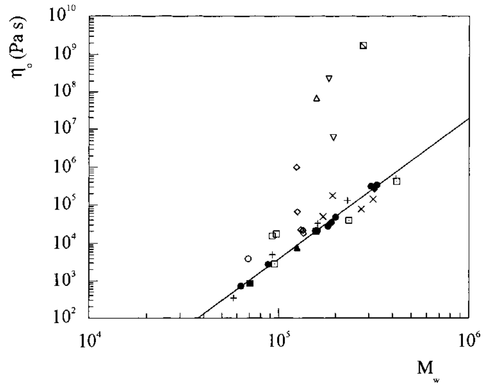

Figure 8. Extrapolated Newtonian viscosity, η_0 (eq 2), vs molecular weight, M_w, for all the samples studied at 190 °C: (▲, ×) commercial polyethylenes (Table 1), (⊡, +) literature data,[72,73] (●) metallocene-catalyzed linear homo- and copolymers of low SCB content (Table 2), (■) metallocene-catalyzed linear copolymers of high SCB content (Table 2), and (◆) metallocene-catalyzed linear polydisperse copolymer (Table 2). Metallocene-catalyzed long chain branched or suspect long chain branched homo- and copolymers (Table 3): (○) M_w = 70 000, (□) M_w = 100 000, (◇) M_w = 130 000; (△) M_w = 160 000; (▽) M_w = 190 000, and (⧄) M_w = 200 000–300 000. The line corresponds to eq 5.

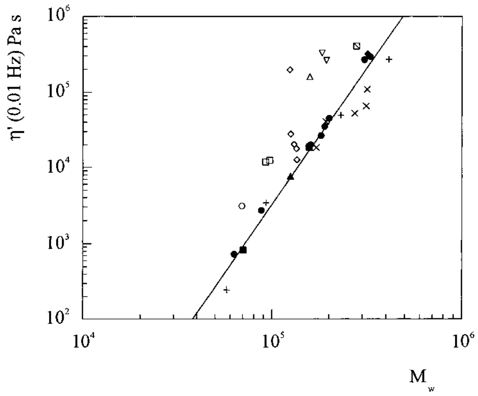

Figure 9. Weight average molecular weight dependence of dynamic viscosity at ω = 0.01 Hz and T = 190 °C. Symbols are the same than in Figure 8. The line corresponds to the equation $\eta'(0.01\ \text{Hz}) = 3.29 \times 10^{-15} M_w^{3.6}$.

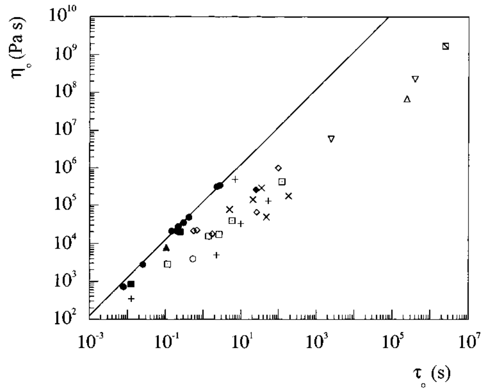

Figure 10. Extrapolated Newtonian viscosity, η_0, vs relaxation time, τ_0, calculated from the Briedis and Faitel'son expression (eq 2) at 190 °C for all the material studied. Symbols are the same than in Figures 8 and 9. The line corresponds to the equation $\eta_0 = 1.25 \times 10^5 \tau_0$.

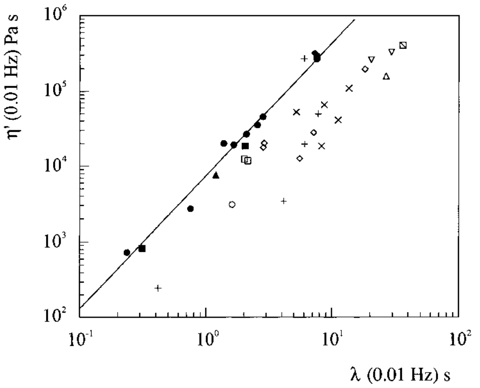

Figure 11. Dynamic viscosity, $\eta'(\omega)$, vs relaxation time, $\lambda(\omega)$, for all the samples studied. Both have been taken at ω = 0.01 Hz and T = 190 °C. Symbols are the same as those in Figures 8–10. The line corresponds to the equation $\eta'(0.01\ \text{Hz}) = 7568\lambda^{1.76}$.

lines which fit linear polyethylenes of narrow molecular weight distribution, showing higher relaxation times. The Dow Rheological Index is not able, therefore, to separate molecular weight distribution and LCB effects, as has been pointed out by Schroff and Mavridis.[76] We have instead to say that, unlike the viscosity–relaxation time plots, viscosity–M_w plots (Figures 8 and 9) would allow one to distinguish between long chain branched and non long chain branched polyethylenes whatever the polydispersity is.

We can consider other alternatives to explain the peculiar behavior of a group of polyethylenes, like chains bonded to catalysts residue or small (or even larger) amounts of very high molecular weight components. However we dare to say that in our case the presence of LCB is the most sound hypothesis, because as can be seen in the Experimental Section our laboratory samples are free of catalyst impurities and a careful SEC analysis reveals that the weight fractions above a molecular weight of 10^6 are 0.1% (such a small amount cannot explain the high viscosity differences found in Figures 8 and 9). The limitation of the SEC technique is a factor to bear in mind: very high molecular weight components can hardly be detected, but the extremely high control of metallocene catalyst systems over polymer structure leads us to say that the presence of the above-mentioned species is very improbable.

Rheologists involved in polymer processing know well that increasing polydispersity leads to lower values of the critical value for the onset of shear thinning behavior, $\dot{\gamma}_0$. Equation 4 reflects this general rule, since the steady-state compliance, $J_e°$, increases with M_w/M_n following a power law with an exponent which ranges from 3.7 to 9.[77] Accounting for the aforementioned relation between $\dot{\gamma}_0$, τ_0 and λ_0, we can assert that the long relaxation times found in Figures 10 and 11 for some of the polyethylenes studied reflect an interesting feature: the possibility of attaining the pseudoplastic behavior at low frequencies without broadening the molecular weight distribution. The severity of the nonlinear behavior of the viscosity is given by the parameter "α" of the Cross and Briedis–Faitel'son (eq 2) models. The bigger this parameter is, the more pseudoplastic the polymer is, an important point when dealing with high shear rates as those involved in polymer processing. In Figure 12 the effect of chain parameters on "α" of conventional and metallocene-catalyzed polyethylenes is shown. An increase of polydispersity in conventional polyethylenes produces an increase of "α", giving rise to more pseudoplastic materials. However, in the case of the polyethylenes catalyzed via metallocene, the same rheological effect

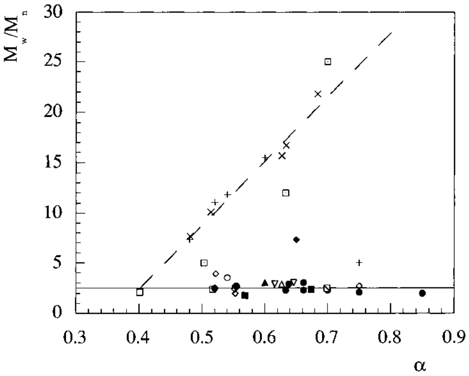

Figure 12. Polydispersity vs the "α" parameter of the Briedis and Faitel'son equation for all the samples studied at 190 °C. The symbols are the same than in Figures 8–11. Lines are drawn to guide the eye.

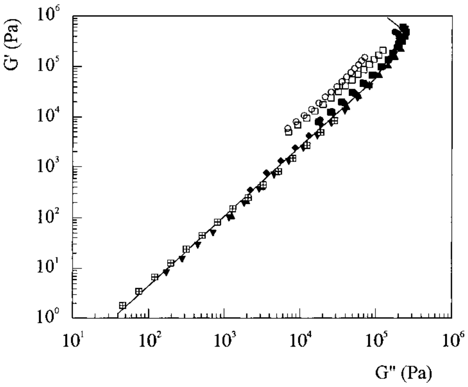

Figure 13. Storage modulus vs loss modulus at 190 °C for some of the samples studied. Key: low polydispersity, (⊞) cPEH1, (▼) cPEH2, (▲) F2, (◆) cPEH4, (■) SA2160, and (●) SA2157; high polydispersity, (○) GM-5010-T2E and (□) BP 102. The line is the fit to linear homo- and copolymers (eq 7; see text).

can be produced increasing molecular weight or the potential LCB degree, keeping the polydispersity index below $M_w/M_n = 3$.

In complex polymer systems log G' vs log G'' plots have been probed to be a useful tool to investigate, for instance, order–disorder transitions in block copolymers,[78] heterogeneity of thermotropic copolyesters,[79] the effect of polydispersity in polyethylenes,[80] and miscibility of polymer blends.[81] The application of the general viscoelastic model leads to the following equation:[81]

$$G' = J_e°(G'')^2 \tag{6}$$

Doi–Edwards theory leads us also to a quadratic dependence of G' on G''.[81] In our case the experimentally lowest accessible frequencies are outside the terminal zone, where both aforementioned models hold, and the slopes of log G'–log G'' plots are lower than 2, typically between 1 and 1.45 as can be seen in Figures 13 and 14. We also observe that at the highest frequencies (higher values of both moduli) a direction change can be guessed. This behavior has been explained by a theoretical interpretation, involving an entanglement plateau, given by Han and Kim.[77] The main features of Figures 13 and 14 are, respectively, the effect of polydispersity and the possible presence of LCB, as one could expect from eq 6 and from the dependence of $J_e°$ on molecular chain architecture. Both chain parameters give rise to a deviation from the correlation found for

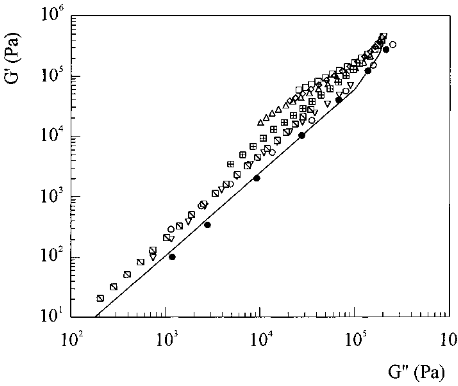

Figure 14. Storage modulus vs loss modulus at 190 °C for some of the samples studied. Key: (▧) PE02, (▽) P169 (○) BP58, (⊞) BP313, (△) PE03, and (□) BP318R, where the line is the fit to linear homo- and copolymers of Figure 13 (eq 7); (●) literature data[76] (narrow MWD HDPE).

narrow molecular weight distribution ($M_w/M_n = 3$), completely lineal (total absence of LCB), polyethylenes of different degrees of SCB:

$$G' = 0.00541(G'')^{1.42} \tag{7}$$

Actually we have been compelled to show our experimental data in separated figures, because of the similar and competing effect of polydispersity and LCB on elasticity, as has been pointed out by Hatziriakos and Kazatchkov[82] in a recent paper about metallocene polyethylenes. In double logarithmic plots of storage vs loss modulus the data of polydisperse samples and presumably long chain branched samples deviate from those of narrow molecular weight and short chain branched samples, which can be adjusted to a single line.

The effect of several molecular parameters (molecular weight, volume of side groups, parameter σ for the thermodynamic flexibility, and number of carbon atoms in pendant group) on the polyolefines activation energy of flow has been analyzed in the past few decades.[38,83–85] Long chain branching in general increases the sensivity of rheological properties of polymers to temperature, depending on the length, concentration, and distribution of branches.[31] In the case of polyethylenes, Bersted,[30] as well as Hughes,[28] analyzed the effect of very low degree of long chain branching (promoted in the polymer from peroxide decomposition and thermal or mechanical degradation) on the activation energy of flow, E_a, showing that the LCB content of HDPE resins can be determined from activation energies. A recent patent[86] presents the equation proposed by Hughes (12 years before!) as a tool to determine the number of long chain branches per 1000 C atoms in polyethylenes polymerized in the presence of a metallocene complex. However, Wasserman and Graessley[41] remark that they do not observe the elevation in E_a that would be expected on commercial high density polyethylenes suspected of containing long branches but do not leave out this possibility since these materials show a enhancement on low frequency viscosity values and no explanations for these anomalously large values other than LCB have been put forward. They suppose that only a small fraction of the chains are branched, and E_a values are dominated by the contribution of the linear chain majority. This result agrees with those obtained by Kraus and Gruver[47] in polybutadiene with long branches.

Table 5. Long Chain Branching Degree

material	LCB/1000 CH_2 by SEC	LCB/1000 CH_2 Bersted[a]	index defined in eq 9
PE02		n.a.[b]	0.421
P120		n.a.	0.277
P169		n.a	0.169
P109	0.007	0.0610	0.283
BP58	0.120	1.10	0.570
P162	0?	0.0150	0.120
GSMC2R	0?	0.00930	0.0665
XV	0.0100	0.0800	0.359
BP313	0.940	n.a.	0.149
PE03		n.a.	0.561
BP318R	0?	n.a.	0.249

[a] Bersted Model, see text. [b] n.a. means not applied.

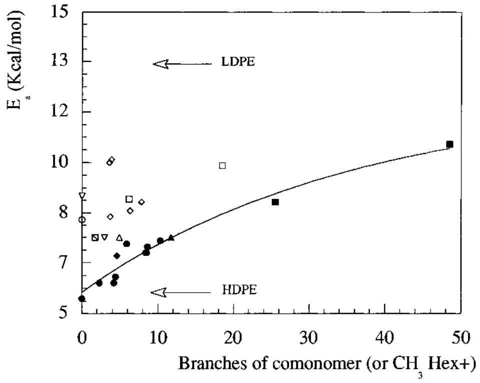

Figure 15. Activation energy of flow, E_a, vs SCB content for all the materials studied. Symbols are the same as those in Figures 8−12. The line corresponds to eq 8.

These authors found that E_a values for these materials were not higher than that for linear polyethylene. The length, concentration, and distribution of branches may be insuficient in this case to produce the feature found for long branched polyethylene.[87]

In our case values of E_a for the materials that show a "dissident" behavior in viscosity and elasticity are higher than those correspond to the assumed linear polymers. Using the activation energies of these polyethylenes, listed in Table 4, as well as SEC chromatograms, the model proposed by Bersted[30] (assuming trifunctional branching) is applied, giving rise to the LCB degrees shown in Table 5. The method proposed by Hughes[28] ignores the effect of SCB on the activation energy of flow, since it takes commercial polyethylenes as a reference. In our case this hypothesis cannot be accepted, accounting for the values of E_a shown in Figure 15, and therefore, this method to determine LCB degree must be rejected. In Figure 15 the variation of the activation energy of flow with SCB level is displayed. Assumed non long chain branched, linear polyethylenes, (except bimodal commercial polyethylenes that show a very low E_a, due probably to low molecular weight tails) fit reasonably well the following equation which, however, is not suitable for polyethylenes in Table 3 suspected of containing some LCB:

$$(E_a)_l = 5.7 + 6.4\left[1 - \exp\left(-\frac{\mathrm{SCB/1000CH_2}}{35.4}\right)\right] \quad (8)$$

Notwithstanding that more rheological tests of well-characterized polyethylenes will be necessary to confirm our results, we consider that an evaluation of the long chain branching degree can be performed analyzing the deviation of E_a with respect to eq 8 for the same SCB level. We define what we call a "LCB index associated to activation energy of flow" as

$$I_{\mathrm{LCB}} = \frac{(E_a)_{\mathrm{LCB}} - (E_a)_l}{(E_a)_l} \quad (9)$$

where $(E_a)_{\mathrm{LCB}}$ is the activation energy of flow of a LCB polyethylene with a known degree of SCB and $(E_a)_l$ is the activation energy of flow of a linear polyethylene of the same SCB degree, obtained from eq 8. As can be seen in Table 5 the values of I_{LCB} for the polyethylenes of this work follow the trend marked by SEC measurements and the Bersted model,[30] opening the possibility of appraising the presence of LCB in polyethylenes by a simple rheological method.

Conclusions

Metallocene-catalyzed narrow molecular weight distribution polyethylenes and poly(ethylene/1-hexene) copolymers listed in Table 3, which, compared to those of Table 2, constitute a "rheologically peculiar" group, are defined by the following features: (a) higher dynamic viscosities at low frequencies than other polyethylenes and ethylene/1-hexene copolymers of similar molecular weight, polydispersity, and SCB degree; (b) higher relaxation times than narrow molecular weight distribution polyethylenes of similar dynamic viscosities at low frequencies, but similar relaxation times to polyethylenes of broad molecular weight distribution; (c) higher values of the elastic modulus, in comparison with polyethylenes of similar molecular weight, polydispersity, and SCB, but on the same order of magnitude as those of broader molecular weight distribution; (d) higher activation energies of flow than linear polyethylenes of the same molecular weight, polydispersity ans SCB degree.

The best explanation we have found for the anomalous behavior in viscosity and elasticity functions is the presence of very low amounts of LCB.We remark that although LCB lays out a specific, different, effect on features "a" and "d", polydispersity masks rheological effects on features "b" and "c". The analysis of the effect of temperature on η', which allows one to determine accurately the activation energies of flow, can be considered as a simple and practical tool to evaluate the possible LCB level of metallocene-catalyzed polyethylenes and ethylene/1-hexene copolymers, provided that eq 8 is fulfilled for the effect of short chain branching.

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