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Rheological characterization of molten ethylene–α-olefin copolymers synthesized with Et[Ind]$_2$ZrCl$_2$/MAO catalyst

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Abstract

The linear viscoelastic behavior of copolymers of ethylene with 1-hexene, 1-octene, 1-decene and 1-octadecene prepared with Et[Ind]$_2$ ZrCl$_2$/MAO is analyzed. The copolymers with α-olefin concentration greater than approximately 14 mol% have the simple rheological behavior with temperature that may be associated to linear polyethylenes with short chain branches. On the other hand, the polymers having comonomer concentration lower than approximately 14 mol% are thermo-rheologically complex materials. The rheological behavior of these copolymers may not be explained solely by the presence of long chain branching. A dendritic-like molecular structure with branches-on-branches has to be considered to explain the complexity observed in the case of the ethylene copolymers with low comonomer concentration and ethylene homopolymer. The complex chain structure would be the result of the incorporation of branched macromonomers in the polymers produced by single-site catalysts. The level of branching and complexity of molecular structure increases as the comonomer concentration decreases. No dependence with the length of the α-olefin was found in any of the analyzed parameters. © 2001 Elsevier Science Ltd. All rights reserved.

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1. Introduction

The synthesis of polyolefins by metallocene catalysts represents a revolution in the polymer industry. These single-site type catalysts offer the chance of producing polymers with controlled molecular structure and narrow molecular weight distributions. Furthermore, the specificity with which the metallocene catalysts may be built enables the production of polymers with highly defined structures and tailored properties [1]. In the particular case of polyethylenes obtained by metallocene catalysts (PEm), the polymers show larger zero-shear-rate viscosities and relaxation times, and also larger flow activation energies [2–5] than those obtained by conventional Ziegler–Natta catalysts, which have multiple reaction sites. The larger zero-shear-rate viscosities and narrower molecular weight distributions lead to polymers with improved mechanical and optical properties but with reduced melt processability [1].

Previous theoretical and rheological studies of ethylene homo and copolymers produced using different metallocene catalysts have lead their authors to suggest the presence of long chain branches (LCB) in these polymers [2,3,5–13]. Classical techniques like nuclear magnetic resonance (NMR) or gel permeation chromatography (GPC) do not provide all the information needed in order to have a complete and detailed characterization of the molecular structure of these new polymers. Malmberg and coworkers [8] and Kolodka and coworkers [11] were able to observe by ^{13}C NMR the presence of branches longer than six carbon atoms in ethylene homopolymers synthesized with Et[Ind]$_2$ ZrCl$_2$/MAO and Cp$_2$ZrCl$_2$/MMAO catalysts, respectively. Wood-Adams and coworkers [13] used ^{13}C NMR as well as a triple-detector GPC and a rheology technique to characterize LCB in polyethylenes synthesized with a constraint geometry catalyst [1]. But most of the authors have based their suggestion of presence of LCB in ethylene homo and copolymers on the results of the rheological characterization of the polymers.

The linear viscoelastic behavior of polymer melts is very sensitive to both the high molecular weight tail of the

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molecular weight distribution and to the complex structure of the macromolecules. The rheological studies of PEm and ethylene copolymers have shown that the behavior of the linear viscoelastic parameters of many of these polymers do not agree with that of conventional high density polyethylene (HDPE) and linear low density polyethylene (LLDPE) of equivalent molecular weights [3,5,8–10,12,13]. Furthermore, the observed behavior rather corresponds to materials of much larger molecular weight or formed by branched complex molecules. The supposition that most PEm and ethylene–α-olefins copolymers have LCB is further supported by the large values of the flow activation energy measured by some researchers [5,8,10] and by the failure in applying the time–temperature superposition principle [12]. The time–temperature principle fails when applied to LCB polyethylenes [14]. Walter and coworkers [12] are the only authors who analyzed in detail the applicability of the time–temperature superposition principle in metallocene polymers. They clearly prove the failure of this method when applied to ethylene–1-eicosene copolymers obtained using $Me_2Si(Me_4Cp)(N^tBu)TiCl_2$/MAO. This result leaves a doubt about how and with which range of validity were the flow activation energies determined by the other authors. Furthermore, analyzing the effect of comonomer concentration in the rheological behavior of ethylene–1-eicosene copolymers, Walter and coworkers found that copolymers with 27 and 30 mol% of 1-eicosene are thermo-rheologically simple, while the ethylene homopolymer and the copolymers with less than 6 mol% are thermo-rheologically complex materials which do not obey the time–temperature superposition principle.

The LCB in the PEm molecules may only appear if the catalysts produce vinyl-terminated chains that are then in situ incorporated into the growing polyethylene chains. According to the previously mentioned works, the extent of long chain branching in the polyethylene molecules depends mainly on the catalyst system and the conditions used in the polymerization. Polymerization condition such as polymer and monomer concentrations, type of catalyst, and temperature are also important variables to be considered. Seppälä and coworkers [5,8] suggest the presence of complex branches-on-branches structures in polyethylene produced with $Et[Ind]_2ZrCl_2$/MAO that would explain the high complex viscosities of the polymers at low frequencies. They found that the polyethylene molecules are increasingly branched as the ethene concentration in the reactor decreases and the polymerization time increases. Zhu and Li [15] made an equivalent proposition but from a theoretical point of view. They propose that the long-chain branched polymers assume either dendritic or comb-like structure. The complex molecular structure, in which the long branches are further branched, has to be the result of the incorporation of branched macromonomers during the copolymerization.

In the present work, we study the rheological behavior of molten copolymers of ethylene and α-olefins (1-hexene, 1-octene, 1-decene, and 1-octadecene) prepared using the catalyst $Et[Ind]_2ZrCl_2$/MAO [16], and we analyze the measured and calculated rheological parameters as a function of the molecular structure of the polymers.

2. Experimental section

2.1. Polymerization

All polymers were synthesized under inert atmosphere of argon using a 1 l glass reactor for 30 min at 60°C [16]. A pressure of 1.6 bar of ethylene was used in all the polymerizations except in the synthesis of the ethylene–1-octadecene copolymer. In this case, a pressure of 0.6 bar was used. Ethylene was a polymer grade material deoxygenated and dried by passage through columns of BASF R3-11 catalyst and 4 Å molecular sieves. The comonomers, 1-hexene, 1-octene, 1-decene and 1-octadecene, were purified by distillation over metallic sodium. The catalyst, $Et[Ind]_2ZrCl_2$, was prepared following a procedure described in the literature [17] while the cocatalyst, methylaluminoxane (MAO) from Witco, was used as received ($[Al]/[Zr] = 1750$, 1.9×10^{-6} mol Zr). Polymerization reactions were terminated by addition of a 2 vol% HCl/CH_3OH solution. The synthesized polymers were precipitated from the reaction medium using cold methanol and then washed with methanol and dried under vacuum at room temperature [16].

2.2. Structure and molecular characterization

The amount of comonomer incorporated in the copolymers was measured by ^{13}C NMR at 80°C using a VARIAN XL-300 spectrometer operating at 75 MHz [16]. The tested samples were dissolved in *o*-diclorobenzene with a 20 vol% of d_6-benzene as internal lock and chromium(III) triacetylacetonate as paramagnetic substance to reduce the relaxation times. Spectra were taken with a flip angle of 70°, an acquisition time of 1.5 s and a delay of 5.0 s. Under these conditions the spectra can be regarded as quantitative. Table 1 shows the obtained results. The nomenclature used to identify the copolymers is of the type ‘L#’ where L and # are letters and numbers that identify, respectively, the comonomer used (H = 1-hexene, O = 1-octene, D = 1-decene, OD = 1-octadecene) and the amount of comonomer measured by ^{13}C NMR, respectively. Table 1 also includes the characteristics of a polyethylene homopolymer synthesized with the same metallocene catalyst (PE) and a commercial ethylene–1-octene copolymer (O-Co) produced with a metallocene catalyst, the Affinity 1140 from Dow Chemical Co., which is also used in the rheological study. The ^{13}C NMR results of the synthesized copolymers indicate that the comonomer units are found isolated between ethylene units in the case of the polymers with low comonomer concentrations, while sequences where two comonomer units can be found together or separated by one ethylene unit are observed in the polymers with more than

Table 1
Characteristics of the studied materials: type and content of the comonomer used, molecular weights, melting temperature and degree of crystallinity

Polymer	Comonomer	Content (mol%)	M_n ($\times 10^{-3}$)	M_w ($\times 10^{-3}$)	M_w/M_n	T_m (°C)	X_c (%)
PE	–	0	95	241	2.54	136	74
H3	1-hexene	2.5	63.2	110	1.75	100	25
H15	1-hexene	14.8	36.3	56.8	1.56	50	11
O2	1-octene	2.3	55.3	105	1.90	110	36
O10	1-octene	10.0	48.0	82.8	1.73	68	16
O-Co	1-octene	6.6	48.8	93.8	1.92	94	20
D2	1-decene	1.6	52.9	107	2.01	104	28
D16	1-decene	16.1	41.0	69.4	1.69	35	8
OD6	1-octadecene	5.5	61.0	128	2.10	88	22

8 mol% comonomer content [18,19]. Low concentrations of LCB cannot be detected by the above-mentioned NMR system nor computed from the amount of comonomer present in the copolymer. Furthermore, the NMR is a technique that does not distinguish the length of the branches when they have more than six carbons. It should be remember that, from the rheological point of view, branches are considered long when they are longer than approximately two molecular weight between entanglements (approximately 180 carbons in the case of polyethylene).

The thermal characterization of the polymers was carried out in a differential scanning calorimeter (DSC, Perkin Elmer Pyris 1). All the samples were subjected to the same thermal history: heated to 160°C, kept at this temperature for 5 min to erase the thermal history, and then cooled down to −30°C at the fasted cooling rate allowed by the calorimeter (~300°C/min). Finally, the samples were heated from −30 to 160°C at 10°C/min. The melting temperature and the heat of fusion were calculated from the thermograms obtained during the second heating. The values of heat of fusion were used to estimate the degree of crystallinity of each material using 288.7 J/g as the value of the enthalpy of fusion of a completely crystalline polyethylene [20]. Table 1 lists the melting temperature (T_m) and the degree of crystallinity (X_c) of all the polymers.

The number- and weight-average molecular weight (M_n and M_w) of all the copolymers were measured by GPC (Waters 150C) coupled with multi-angle laser light scattering (MALLS, Wyatt Dawn DSP). The measurements were obtained using 1,2,4-trichloro benzene (TCB) at 135°C with a flow rate of 1 cm^3/min. The GPC–MALLS was previously calibrated with well-characterized polyethylene standards (NIST). Table 1 includes the obtained molecular weights and the polydispersity index M_w/M_n.

The rheological characterization of the melted polymers was carried out in nitrogen atmosphere using a Rheometrics RDA-II rheometer with a 25 mm parallel plate geometry. The viscoelastic properties of the polymers (the elastic modulus G' and the viscous modulus G'') were measured in small-amplitude oscillatory shear flow as a function of frequency and temperature. The dynamic viscosity $\eta'(\omega)$ ($= G''/\omega$) and the phase angle δ ($= \tan^{-1} G''/G'$) are parameters that are also used in the paper. The phase angle corresponds to the phase shift of the shear stress with respect to the sinusoidal deformation. This is a bounded parameter that ranges from 0 to 90°. The frequencies used ranged from 0.04 (or 0.1) up to 500 s^{-1}. Different ranges of temperature were used in different polymers according to their melting point (H3: 107–200°C, O2: 120–200°C, D2: 110–200°C, O-Co: 110–210°C, OD6: 110–200°C, O10: 96–145°C, H15: 91–154°C, D16: 70–100°C). Small strains were used in all the dynamic tests, which were selected from previously made strain sweeps, to ensure the linear relation between stress and deformation. The polymers used in the rheological experiments were stabilized with 0.05 wt% of Irganox 1010 antioxidant which was added to the copolymers dissolved in boiling xylene. The polymers were then precipitated using cold methanol and dried under vacuum at room temperature. When all the solvent was eliminated, the materials were pressed at 190°C into 1 mm thick plates. All the results shown in this paper were carefully verified. All the runs were repeated, at least two times, using different polymeric samples. No degradation was observed in any of the materials. Several of the series of frequency sweeps at different temperatures were repeated two times with the same sample. In all the cases, it was found excellent agreement between the results.

3. Results and discussion

3.1. Molecular and morphological results

Fig. 1 displays the molecular and morphological parameters listed in Table 1 as a function of the comonomer concentration of the polymers. All of them decrease practically linearly as the amount of comonomer in the polymers increases, and no dependence can be detected with the type of comonomer used. The molecular weight of the ethylene–1-octadecene copolymer is relatively larger when compared with the rest of the copolymers. This is a consequence of the lower ethylene pressure used during the synthesis of this copolymer. The decrease in the melting temperature and degree of crystallinity with the increase of the comonomer concentration has been observed in previous works [21]. These effects are a consequence of the rejection of the

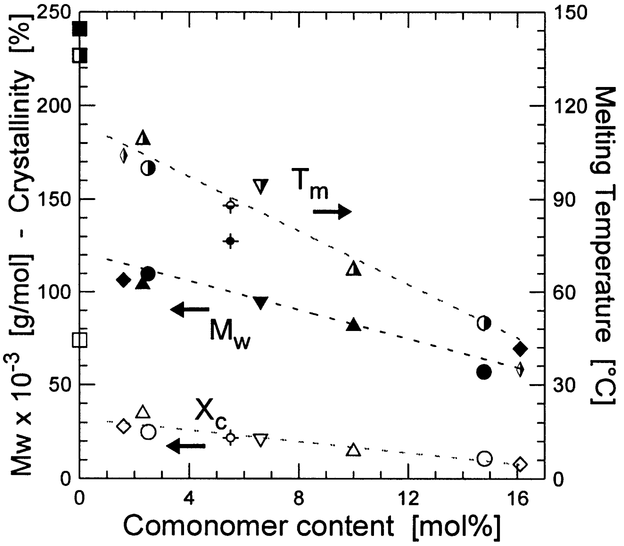

Fig. 1. Weight-average molecular weight (full symbols), crystallinity (open symbols) and melting temperature (half-full symbols) of the analyzed ethylene–α-olefins copolymers. Symbols: (□) PEm; (○) H3, H15; (△) O2, O10; (◇) D2, D16; (⊕) OD6; (▽) O-Co.

side groups of the copolymers from the crystal cores. An increase in the concentration of short chain branches (SCB) reduces the length and the concentration of sequences of units capable of crystallize. In this way, the size and amount of crystals are reduced [19,22,23]. The measured melting temperature and crystallinity level of the copolymers are similar to those reported for random ethylene copolymers in the present range of comonomer concentration.

The decrease in the molecular weights of the synthesized polymers with the increase in the comonomer concentration has also been previously reported in the literature [16,24]. The presence of α-olefins during the polymerization of ethylene augments both the activity and the chain transfer reaction rate. Consequently, the resulting polymers show smaller molecular weights [25]. No quantification is reported in this paper of the LCB present in the polymers [13] since, according to our results, the ethylene homopolymers and the copolymers of ethylene with relatively low concentrations of α-olefins prepared using Et[Ind]$_2$ ZrCl$_2$/MAO catalyst have a complex branch-on-branches structure.

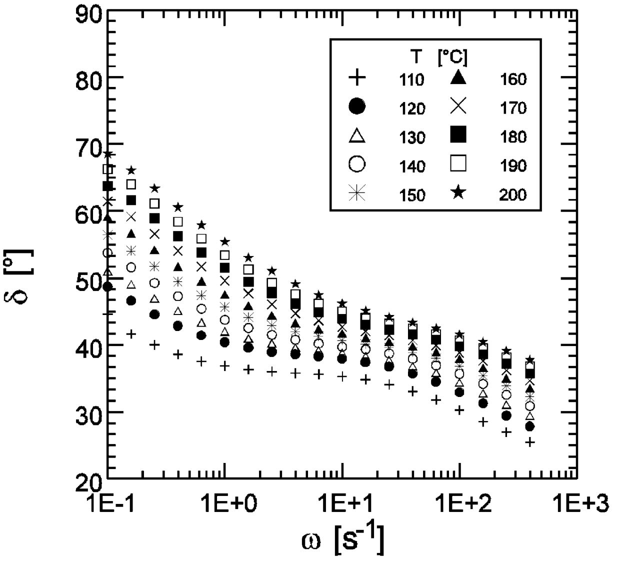

Fig. 2. Frequency dependence of the phase angle of the D2 copolymer (1.6 mol% of 1-decene content) at different temperatures.

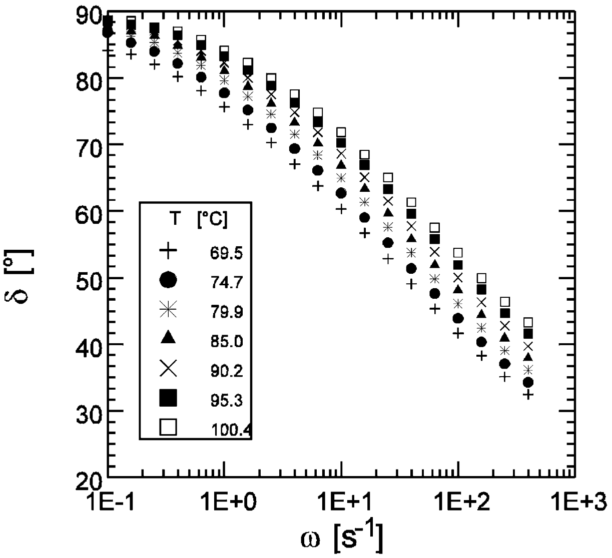

Fig. 3. Frequency dependence of the phase angle of the D16 copolymer (16.1 mol% of 1-decene content) at different temperatures.

3.2. Rheological results and temperature dependence

Figs. 2 and 3 display the phase angle of polymers D2 and D16 measured as a function of frequency at different temperatures. D2 and D16 have been selected as representative of the rheological behavior observed in all the studied materials with temperature because they are the polymers with the lower and higher comonomer concentrations, respectively. Fig. 2 clearly shows that D2 has a *thermo-rheologically complex* behavior. The time–temperature superposition principle cannot be used in this material to generate master curves. On the other hand, D16 is a *thermo-rheologically simple* polymer in the range of frequencies covered in this study. The master curve of the phase angle of D16 at the reference temperature of 120°C is shown in Fig. 4. H15 was also found to be a thermo-rheologically simple polymer. Comparing the behavior of all the polymers with temperature, it may be concluded that they are thermo-rheologically simple materials when the concentration of comonomer is greater than approximately 14 mol% and that they show increasing thermo-rheological complexity as the amount of comonomer decreases. Thermo-rheological simplicity implies that all the relaxation processes that determine the observed

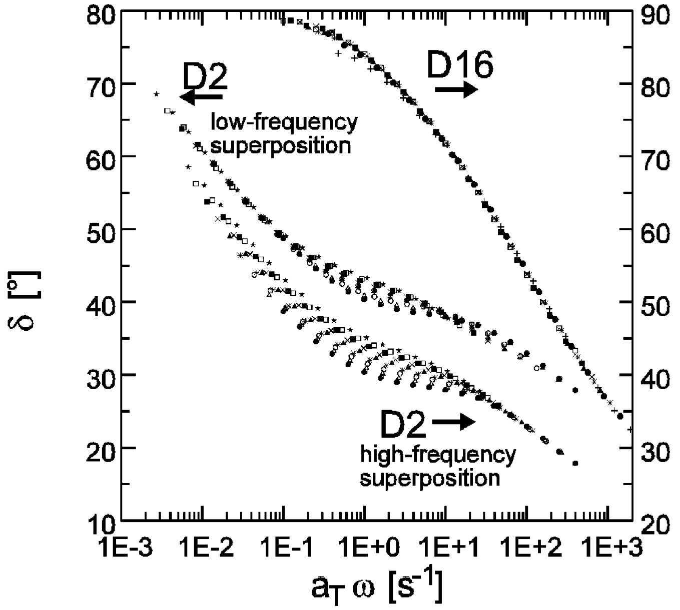

Fig. 4. Master curve of the phase angle of D16 and pseudo-master curves of the phase angle of D2 obtained applying the time–temperature superposition principle in the range of small and large frequencies, respectively. Reference temperature: 120°C.

rheological behavior of the polymers with large concentrations of comonomer have the same dependency with temperature (the same flow activation energy). The thermo-rheological complexity observed as the amount of comonomer concentration in the polymers decreases means that the molecular structure has to change in such a way that the different relaxation processes that affect the rheological behavior in the analyzed range of frequencies have different dependency with temperature (different flow activation energies). This is the typical behavior of structurally complex molecules like polyethylene with long branches [14]. Equivalent results were obtained by Walter and coworkers [12]. They found that ethylene–1-eicosene copolymers with large comonomer concentration were simple materials and that the time–temperature superposition principle was applicable. On the other hand, the copolymers with small or no concentration of 1-eicosene behaved like complex materials. The time–temperature superposition principle was not applicable to these polymers, and no flow activation energy was calculated by the authors in these cases.

Notwithstanding the thermo-rheological complexity of the polymers, the curves of δ, like the ones shown in Fig. 2, may be superposed in such a way that they agree in the region of small or large frequencies. As an example, Fig. 4 shows the results of superposing the phase angle data of D2. The temperature shift factors, a_T, used to shift the δ curves of D2 and D16 are shown in Fig. 5. The full lines shown in this figure correspond to the fitting of the shift factors to the Arrhenius-type of equation:

$$\ln a_T = \frac{\Delta H}{R}\left[\frac{1}{T} - \frac{1}{T_0}\right] \tag{1}$$

where ΔH, R and T_0 are the flow activation energy, the universal gas constant and the reference temperature, respectively. A reference temperature of 120°C is used in this paper. The temperature shift factors of all the polymers are shown in Figs. 5 and 6. The uncertainty in the determination of the a_T values was always very small (less than 10%). All the temperature shift factors are well fitted by the Arrhenius model.

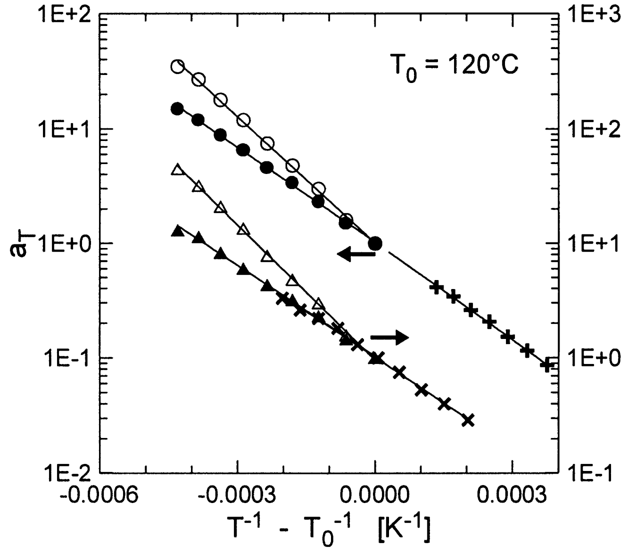

Fig. 5. Temperature dependence of the shift factors a_T used to generate the master curves of the phase angle of D2, D16, H3 and H15. Maximum uncertainty in the data: ±10%. Full lines: fits from the Arrhenius equation (Eq. (1)). Symbols: (+) D16; (○) D2, low frequencies; (●) D2, high frequencies; (×) H15; (△) H3, low frequencies; (▲) H3, high frequencies.

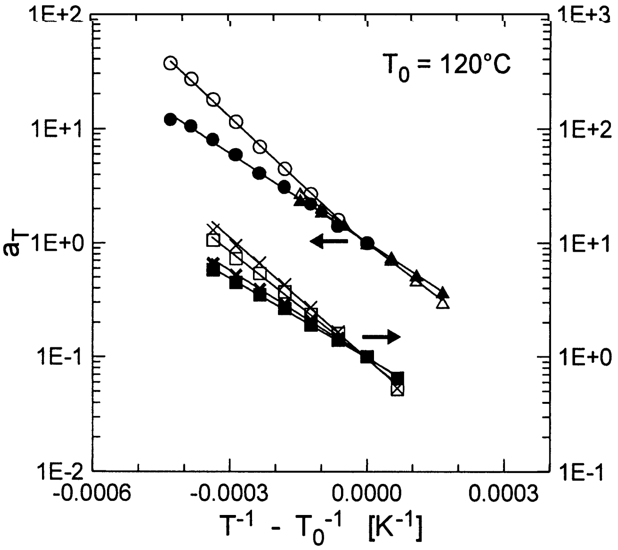

Fig. 6. Temperature dependence of the shift factors a_T used to generate the master curves of the phase angle of O2, O10, O-Co and OD6. Maximum uncertainty in the data: ±10%. Full lines: fits from the Arrhenius equation (Eq. (1)). Symbols: (○) O2, low frequencies; (●) O2, high frequencies; (△) O10, low frequencies; (▲) O10, high frequencies; (□) O-Co, low frequencies; (■) O-Co, high frequencies; (×) OD6, low frequencies; (×) OD6, high frequencies.

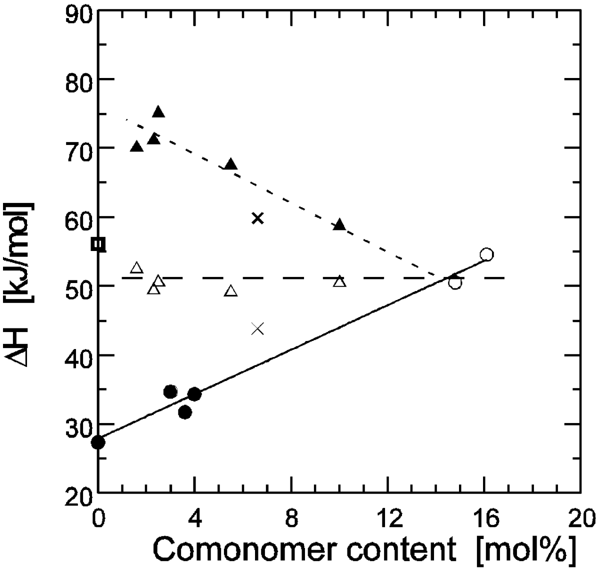

Fig. 7. Flow activation energies of conventional and metallocene-based ethylene homo and copolymers as a function of comonomer concentration. Maximum uncertainty in the data: ±1.3 kJ/mol. Symbols: (●) HDPE, LLDPE and HPB; (□) LDPE; (○) H15 and D16; (▲) ΔH_1 of H3, O2, D2, OD6 and O10; (△) ΔH_2 of H3, O2, D2, OD6 and O10; (×) ΔH_1 of O-Co; (×) ΔH_2 of O-Co.

The flow activation energies of all the polymers are displayed in Fig. 7. The maximum uncertainty in the determined values is ±1.3 kJ/mol. D16 and H15 have a unique value of ΔH, while the rest of the polymers have two. The large (ΔH_1) and the small (ΔH_2) flow activation energies of each of these polymers (full and empty triangles in Fig. 7 respectively) are calculated from the fitting of Eq. (1) to the shift factors used to superpose the dynamic data at small and large frequencies, respectively. The larger flow activation energy, ΔH_1, describes the temperature dependency of the slower relaxation processes in the terminal region, i.e. the ones that dominate the response of the polymer at small frequencies and that may be associated to the large-scale dynamics of the molecules. ΔH_2 describes the temperature dependency of relaxation processes that are several order of magnitude faster than the previous ones. These relaxation processes also affect the terminal flow region but in the zone approaching the transition region. The relaxation times that dominate the response of the polymer in this range of frequencies can be associated to molecular movements of smaller scale than the previous ones but larger than the distance between entanglements that affect mainly the plateau region.

All the measured flow activation energies are larger than the values observed in the case of linear polyethylene and polyethylenes with SCB obtained with conventional catalysts (see Fig. 7). The conventional HDPE has a ΔH of approximately 27.3 kJ/mol in the temperature range of 140–200°C [26–29]. A conventional LLDPE ($M_w = 119\,000$ g/mol, $M_w/M_n = 2.9$) with ca. 3 mol% of 1-octene and an hydrogenated polybutadiene [30] (HPB, $M_w = 78\,000$ g/mol, $M_w/M_n = 1.06$) have flow activation energies of 34.7 and 34.3 kJ/mol, respectively. This last polymer is a model copolymer of ethylene with ca. 4 mol% of 1-butene obtained by hydrogenation of a polybutadiene obtained by anionic polymerization in a nonpolar medium [30–32]. Using ^{1}H NMR y ^{13}C NMR, Carella and coworkers [33] were able to conclude that the vinyl and ethyl groups in the polybutadiene with low vinyl content are essentially random. The full line shown in Fig. 7 ($\Delta H = 1.61 \times$ [comonomer conc.] $+ 27.9$) was obtain from the fitting of the ΔH of HDPE, LLDPE, HPB, H15 and D16. The results suggest that the flow activation energy of thermo-rheologically simple copolymers of ethylene and α-olefins increases when the amount of SCB in the polymer molecules increases. Carella [34] studied the rheological behavior of hydrogenated polybutadienes with different concentration of ethyl branches showing that the temperature dependence of the zero-shear-rate viscosity increases as the number of ethyl branches in the polymers increases. Wasserman and Graessley [28] report a flow activation energy of 55.3 kJ/mol for a conventional LDPE from the National Institute of Standards.

The rheological behavior of the metallocene-based copolymers with less than approximately 14 mol% comonomer suggests that they have a complex molecular structure. The value of the flow activation energy of these copolymers are much larger than the ΔH of linear polymers with equivalent concentration of SCB. This result means that even in the intermediate scale of molecular distances, the relaxation

Table 2
Flow activation energies of a conventional high density polyethylene and an hydrogenated polybutadiene modified by irradiation and by reaction with an organic peroxide

Polymer	Modified polymer	Description	ΔH (kJ/mol)	ΔH_1 (kJ/mol)	ΔH_2[a] (kJ/mol)
HDPE[b]			28.7		
	HDPE-p1	Modified with 250 ppm peroxide		58.0	–
	HDPE-p2	Modified with 500 ppm peroxide		77.5	–
	HDPE-p3	Modified with 1000 ppm peroxide		91.5	–
	HDPE-i1	Modified with 5 kGy irradiation		42.4	31.3
HPB[c]			33.3		
	HPB-p1	Modified with 1000 ppm peroxide		61.5	31.7
	HPB-p2	Modified with 2000 ppm peroxide		~113	30.3

[a] ΔH_2 is not reported when there were no sufficient data to determine its value.
[b] $M_w = 53\,000$ g/mol; $M_w/M_n = 2.6$; material: Equistar-alathon H6017.
[c] $M_w = 116\,000$ g/mol; $M_w/M_n = 1.01$; ca. 4 mol% 1-butene.

processes do not correspond to the structure of a simple copolymer with SCB although one would expect that both the metallocene-based and the conventional polyolefins would have equivalent molecular structure in this molecular scale. It is interesting to notice that all the values of ΔH_2 are very similar. The average value of ΔH_2 of H3, O2, D2, O10 and OD6 is 50.7 ± 1.3 kJ/mol (long dashed line) which is not far from the flow activation energy of the LDPE. This result suggests that the structure of the metallocene-based copolymers with comonomer concentration smaller than 14 mol% have intermediate-scale molecular structure which is comparable to that of the long chain branched polyethylene and not to that of conventional polyethylene copolymers with low SCB concentration. ΔH_1 is much larger and seems to increase when the concentration of the comonomer decreases (short dashed line). The commercial polymer displays the same qualitative behavior although both, ΔH_1 and ΔH_2, fall a little lower with respect to the dashed lines.

Malmberg and coworkers [8] reported values of 27, 33 and 55 kJ/mol for the flow activation energy of conventional HDPE, LLDPE and LDPE and values of 40–60 kJ/mol for ethylene–1-hexene copolymers catalyzed with $Et[Ind]_2ZrCl_2/MAO$ and $Et[IndH_4]_2ZrCl_2/MAO$, although no information is given of how these values were obtained. Vega and coworkers [9,10] inform that the flow activation energy of copolymers of ethene and 1-hexene increases exponentially with the degree of butyl branches. However, the flow activation energies of several copolymers studied by these authors are much larger than expected. These polymers were suspected to have not only the butyl short branches but also LCB.

It is interesting to compare the value of the flow activation energies reported in Fig. 7 with those of lineal conventional polyethylenes modified by chemical reaction with an organic peroxide or by irradiation. Both kinds of modification methods produce macroradicals that participate, mainly, in chain-linking reactions. The polyethylenes and hydrogenated polybutadienes modified with these methods are thermo-rheologically complex polymers with $\delta(\omega)$ curves of similar shape to those shown in Fig. 3. Table 2 displays the flow activation energies of a HDPE (Alathon H6017) and an HPB modified with different mechanisms and doses [29]. It may be noticed that ΔH_2, when measurable, has practically the same value than the flow activation energy of the original polymer. This means that the LCB and complex molecular structure generated in the polymers does not change the intermediate scale molecular structure which it is equivalent to that of the original polymer. On the other hand, ΔH_1 shows the effect of the generated complex structures. Low doses of irradiation or low concentrations of peroxide introduce LCB giving place to polyethylenes with flow activation energies similar to that of the commercial LDPE. As the peroxide concentration or irradiation dose increases, and the chain-linking reactions produce more complex molecules, ΔH_1 increases.

Comparing the values of flow activation energies reported in Table 2 with those of the ethylene–α-olefins copolymers with low comonomer concentration of Fig. 7 it may be concluded that (a) the intermediate-scale molecular structure of the metallocene-based copolymers does not correspond to that of simple copolymers with equivalent concentration of SCB but rather to that of copolymers with large concentrations of LCB; and (b) the large-scale molecular structure corresponds to polyethylenes with high levels of chain-linking which generates branches-on-branches structures.

Vega and coworkers [10] report another anomalous behavior. They comment that, in some cases, the PEms show a very large elastic modulus that is higher than the viscous modulus in the whole range of frequencies studied. This is a rheological behavior that may be expected in crosslinked materials. Nevertheless, the referred polymers could be dissolved in 1,2,4-trichlorobenzene at 160°C. We have seen the same behavior in several ethylene homopolymers obtained with $Et[Ind]_2ZrCl_2/MAO$ catalysts in three different laboratories (PLAPIQUI, Argentina; UFRGDS, Brasil; Universidad de Chile). Furthermore, although the materials

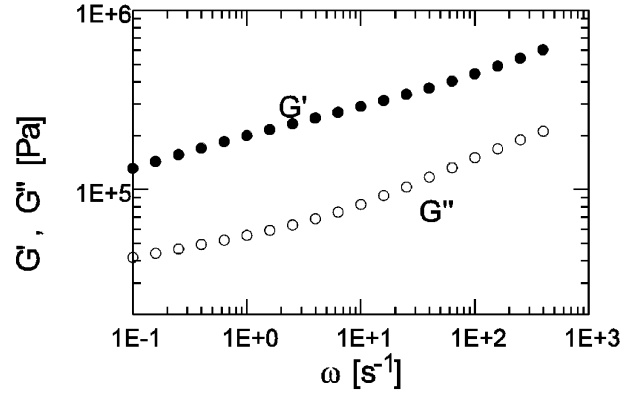

Fig. 8. Frequency dependence of the dynamic moduli of PEm at 141°C.

proved to be soluble in boiling xylene at 130°C, when disks of these polymers were placed in the rheometer with an applied normal force of 1 kg, no relaxation of the force was observed even when the sample was left for more than two hours at 200°C in N_2 atmosphere. The material was soluble even after this test. Fig. 8 shows the dynamic moduli of PE measured at 141°C. The elastic modulus of PE is much larger than the viscous one at all frequencies showing a behavior characteristic of a crosslinked or partially crosslinked polymer. The comparison of this behavior with the observed increased molecular complexity of the studied copolymers as the comonomer concentration decreases suggests that the ethylene homopolymer molecules may have a very complex branches-on-branches structure. This type of structure may explain the very long relaxation times observed, comparable to those of a practically crosslinked material.

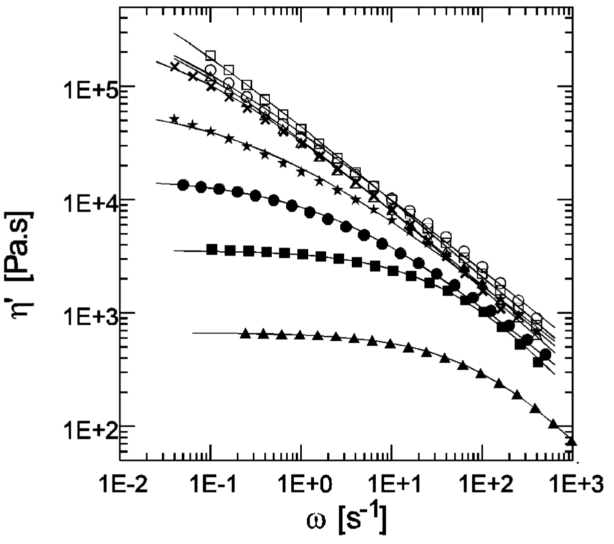

Fig. 9. Frequency dependence of the dynamic viscosity of all the studied copolymers at 120°C. Full lines: predictions of the Carreau–Yasuda model (Eq. (2)) with the corresponding coefficients listed in Table 3. Symbols: (△) D2; (▲) D16; (□) H3; (■) H15; (○) O2; (★) O-Co; (●) O10; (×) OD6.

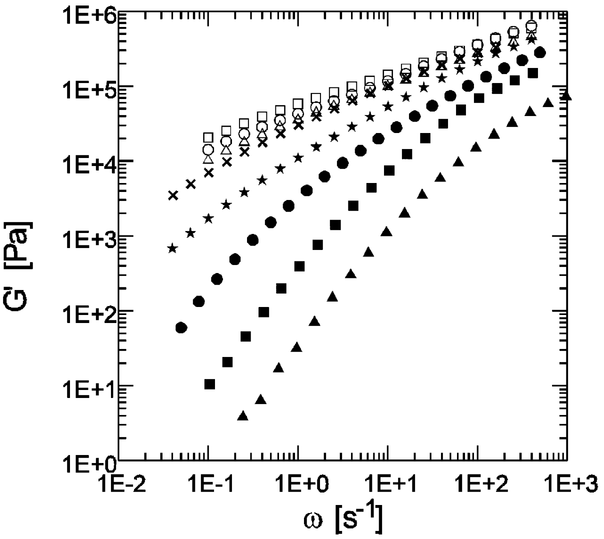

Fig. 10. Frequency dependence of the elastic modulus of all the studied copolymers at 120°C. Symbols: (△) D2; (▲) D16; (□) H3; (■) H15; (○) O2; (★) O-Co; (●) O10; (×) OD6.

3.3. Rheological results and molecular weight dependence

Figs. 9 and 10 show the η' and G' results at 120°C of all the polymers studied. The relative position of the curves is not only affected by the molecular structure but also by the molecular weight of the polymers. The value of the zero-shear-rate viscosity may be calculated from these data using an equation of the Carreau–Yasuda type [35]:

$$\eta' = \eta_0[1 + (\Gamma\omega)^a]^{(n-1)/a} \tag{2}$$

where η_0 is the zero-shear-rate viscosity, Γ is a time constant, n is the 'power-law exponent', and a is a dimensionless parameter that describe the transition between the zero-shear-rate and the power-law regions. The empirical model of Carreau–Yasuda is used to calculate η_0 because the inflection point presented by the dynamic data is not very noticeable in the dynamic viscosity curves (see Fig. 9) and this model is known to give close fittings of viscosity data for several kinds of polymer melts. Table 3 lists the values of the coefficients calculated by nonlinear minimization

Table 3
Coefficients of the Carreau–Yasuda model obtained by fitting the dynamic experimental data shown in Fig. 9, and calculated terminal relaxation times

Polymer	η_0 (Pa. s)	Γ (s)	n	a	λ_0 (s)
H3	2.66×10^6	3.63×10^2	0.321	0.454	1.91×10^3
H15	3.58×10^3	1.71×10^{-2}	0.052	0.663	3.25×10^{-1}
O2	6.38×10^5	6.22×10^1	0.362	0.483	3.44×10^5
O10	1.55×10^4	3.66×10^{-1}	0.316	0.532	1.64
O-Co	7.00×10^4	3.28	0.373	0.495	3.02×10^1
D2	7.20×10^5	6.76×10^1	0.321	0.454	4.15×10^2
D16	6.68×10^2	8.49×10^{-3}	0.097	0.695	9.66×10^{-2}
OD6	3.78×10^5	1.75×10^1	0.279	0.456	1.20×10^2

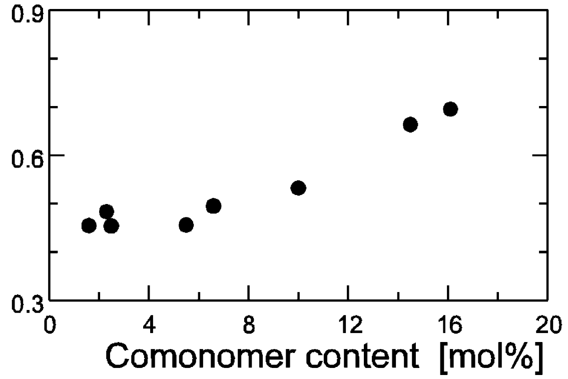

Fig. 11. Parameter *a* of the Carreau–Yasuda model obtained from fitting the data of Fig. 9 to Eq. (2) as a function of the comonomer concentration of the copolymers.

procedures fitting the measured dynamic data at 120°C of each material to Eq. (2). No restrictions were set upon the values of the parameters. The values of η_0 are practically the same when are calculated from the complex viscosity data. The full lines in Fig. 9 are the predictions of Eq. (2) using the coefficients of Table 3. The zero-shear-rate viscosity of H3, O2 and D2 are surely underpredicted because of the lack of data in the terminal region, although not as much as using other models. The parameter *a* is an inverse measure of the breath of the transition from Newtonian to power law behavior. It is interesting to notice that the value of *a* decreases as the comonomer concentration decreases (see Fig. 11). Since the polydispersity index of all these samples are small and very similar, the above-mentioned behavior is just another consequence of the presence of the long branches that affect the terminal relaxation of these polymers [13].

Another parameter that may be calculated is the terminal relaxation time (λ_0) as

$$\lambda_0 = \lim_{\omega \to 0} \frac{\eta''}{\omega\, \eta'} \tag{3}$$

Fig. 12 shows the predicted zero-shear-rate viscosities and terminal relaxation times plotted as a function of the weight-average molecular weight of the polymers. Lines of slope 3.6 have been added to the figures to compare the results with the theoretical $M_w^{3.6}$ dependency expected for η_0 in the case of materials with linear molecules and for λ_0 in the case of narrow molecular weight distribution materials with linear molecules [26]. The position of the lines corresponds to the location of $\eta_0(M_w)$ and $\lambda_0(M_w)$ of conventional HDPE at the reference temperature of 120°C. When the value of the parameter η_0 of different polymers are compared, it is necessary to consider not only the molecular weight of the materials but also the molecular structure and the temperature at which the parameters have been measured relative to the glass transition temperature of the polymers [34]. In the present case, the comparison may be done using the values of η_0 calculated at 120°C since all the copolymers have very similar glass transition temperature [19,36]. Consequently, the data plotted in Fig. 12 show the effect of both the molecular weight and the chain branching of the molecules.

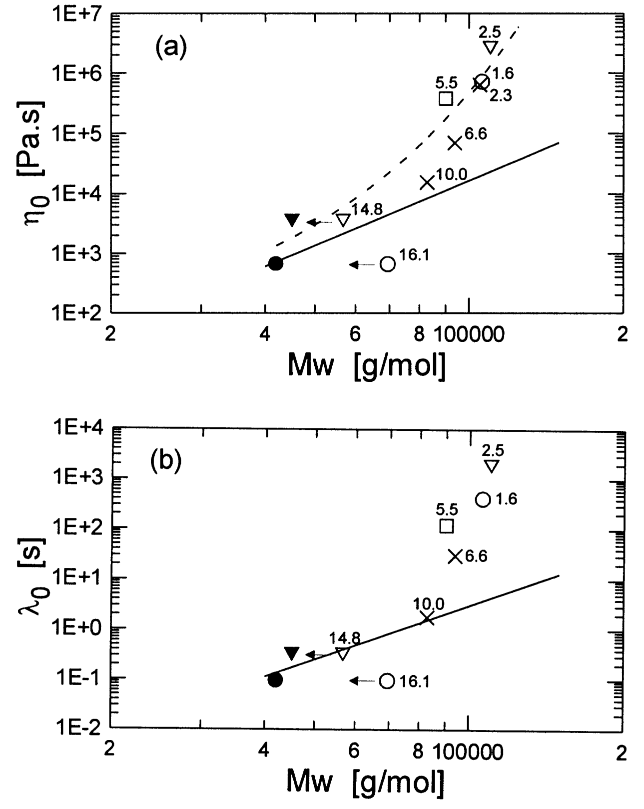

Fig. 12. Weight-average molecular weight dependency of the zero-shear-rate viscosity (a) and relaxation time (b) of all the copolymers at 120°C. Symbols: (○) D2 and D16; (×) O2, O10 and O-Co; (▽) H3 and H15; (□) OD6; (●) location of the D16 results at the molecular weight of the backbone; (▼) location of the H15 results at the molecular weight of the backbone. The numbers next to the symbols indicate the corresponding comonomer content in mol%. Full lines: $\eta_0 \sim M_w^{3.6}$ and $\lambda_0 \sim M_w^{3.6}$. Dashed line: exponential fitting (e^{M_w}) of η_0 considering the shifted data.

The presence of branches produces a decrease in the radius of gyration (R_g) of the molecules compared to that of linear chains of the same molecular weight. The decrease in R_g results in fewer entanglements and a lower zero-shear-rate viscosity. When the branch length is sufficiently long, it begins to participate in the entanglements, and the entanglement network has then a much longer lifetime and larger viscosity. The copolymers H15 and D16 have large concentrations of SCB but no LCB which means that the η_0 of these polymers are smaller than the expected values for equivalent linear materials of the same molecular weights. To show the effect of the SCB, η_0 and λ_0 of these polymers have also been plotted in Fig. 12 (open symbols) at the molecular weight of the backbones. Since only the backbone of molecules with SCB participate in entanglements, this is a valid way to present the $\eta_0(M_w)$ results although the data should also be corrected considering the steric hindrances that the SCB may produce on the possible conformations of the molecules [34].

According to the rheological results discussed previously, the copolymers with less than 14 mol% of comonomer concentration have not only SCB but also LCB that decrease and increase, respectively, as the comonomer concentration decreases. Consequently, even though the data of Fig. 12 must be corrected to take into account the effect of the SCB, they are a clear evidence of the presence of LCB in the copolymers with low comonomer concentration. A line corresponding to a exponential fitting of the η_0 data has been added to Fig. 12(a) to visualize the mentioned effect. The above conclusion is obtained even considering that the values of η_0 and λ_0 of H2, O2 and D3 are probably underpredicted by the Carreau–Yasuda model (see Fig. 9). Equivalent results were obtained by Kokko and coworkers [5] using the same catalyst system. The values of η_0 calculated by these authors from the expected $M_w^{3.6}$ dependency were consistently lower than the obtained zero-shear-rate viscosities of all the PEm. On the other hand, Vega and coworkers [3,9,10] found a dependence of the form $\eta_0 \sim M_w^a$, with $a = 3.6$–3.9, for a series of ethylene/1-hexene copolymers synthesized with their own catalyst.

4. Conclusions

The analysis of the rheological behavior of a series of ethylene–α-olefins copolymers synthesized with Et[Ind]$_2$ ZrCl$_2$/MAO catalyst has been used to examine the molecular structure of these polymers. No dependence with the length of the α-olefin has been found in any of the studied rheological or morphological parameters. The introduction of SCB into the polyethylene backbone with increasing comonomer concentration decreases the melting temperature and the crystallinity of polyethylene. The values of these parameters indicate that the SCB are homogeneously distributed in all the copolymers. The molten copolymers with α-olefin concentration greater than approximately 14 mol% were found to have the simple rheological behavior that may be associated to polyethylenes with equivalent levels of SCB. On the other hand, all the observations presented in this paper confirm the existence of a complex structure in the copolymers with comonomer concentration smaller than 14 mol%. This complexity increases as the comonomer concentration decreases. Although the time–temperature superposition principle fails in the case of materials with complex molecular structure, it still may be applied in smaller frequency regions to study the temperature dependence of the relaxation processes that dominate the flow response in those regions. The flow activation energy results obtained in this way indicate that the copolymers have a complex molecular structure even in the intermediate-scale of molecular distances and that the presence of long branches is not the only complexity of the metallocene-obtained molecules. Dendritic-like molecular structures with branch-on-branch arrangements must be generated during the polymerization process.

According to the obtained results, the polymerization has to proceed in such a way that a high concentration of LCB are formed by reinsertion of vinyl terminated polymer chains. The reinsertion of the macromonomers requires not only the presence but also the adequate mobility of the vinyl chain ends. The incorporation of many branches in a chain would give place to complex branches-on-branches structures. Further work has to be done to better understand the steps and reactions that take place during the synthesis of polyethylene and ethylene copolymers with metallocene catalysts and the influence of the polymerization conditions on the molecular structure of these materials.

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