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Novel features of the rheological behaviour of metallocene catalysed atactic polypropylene

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Abstract

This study was designed to determine the linear viscoelastic properties of a family of metallocene-catalysed propylene homopolymers in the 'plateau' and terminal regions. A low value of the plateau modulus, around 4.8×10^5 Pa, was obtained. Our results differ from those reported for conventional amorphous polypropylene in several recent studies. As previously undertaken for metallocene-catalysed polyethylenes, the rheological behaviour observed was discussed in terms of a possible decrease in the entanglement density and/or an increase in chain flexibility with respect to other polymers of similar chemical composition. We subsequently applied an existing model, based on simplified molecular dynamics, that provided a correct description of the dynamic modulus from knowledge of the form of the molecular weight distribution and the materials' rheological constants G_N^0 and η_0. This method has been successfully applied to several types of polymer.

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1. Introduction

The successful testing of basic rheological principles in polymers largely depends upon how close a description we have of the molecular architecture of the system under study. Within the polyolefin group of polymers, polyethylene (PE) and polypropylene (PP) are good examples of the simplest molecular architectures. However, the rheological characterisation of these polymers has always been difficult, due to an inability to synthesise monodisperse samples. Model PP polymers have been produced in a select number of laboratories, either by fractionation of existing products [1–4] or by hydrogenation of anionically polymerised poly (1,3-dimethyl-1-butenylene) (HPDMB) [5]. Obviously, these model PP polymers have only been manufactured on a very small scale by a few research groups, and hence the experimental data information available is scarce. Furthermore, modern-day rheology now faces another threat linked to the technological demands of processing speeds, which require the control of flow instabilities generated at the high deformation rates employed in the processing industry. There is therefore a need for extrusion studies involving a relatively large amount of material.

This last decade has witnessed a huge step forward in polymerisation technology with the introduction of single-site catalysts as an alternative route for the polymerisation of α-olefins [6]. Indeed various types of organometallic-based catalyst have been, and continue to be, the subject of many research efforts. Metallocene-based catalysts deserve particular attention, since they have been successfully used on the industrial plant production scale to polymerise several commercial degrees of PE and PP [7,8]. These catalysts have a single active centre type and this leads to a high degree of molecular regularity, reflected by a relatively low dispersity number and lack of long chain branching (LCB) [9]. Thus, because of the limitations in preparing monodisperse samples of PE and PP by fractionation or hydrogenation, the use of single-site catalysts has been proposed as a good alternative to obtain model polymers. Further, compared to the Ziegler–Natta catalysts [10,11], various steps of the polymerisation reactions associated with this type of catalyst can be adequately computed by

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modern quantum mechanics. In many cases the results provide valuable preliminary information on which to base experimental work designed to develop new catalyst systems.

For linear PP, the expected correlations between Newtonian viscosity η_0 and weight average molecular weight M_w have been found to hold true. A power law exponent of 3.6–4.0 in the η_0–M_w relationships has been repeatedly reported [4,12–14], although the lower value of 3.4 was also published [39]. In general, these results have been considered to be in line with the behaviour predicted by the reptation theory for linear, long chain branchless, monodisperse polymers [15,16], and with the predicted behaviour for the loss modulus G'' in the terminal zone ($G'' \propto \omega$) according to the linear viscoelastic model [17]. However, it is not easy to experimentally determine some of the rheological variables needed to validate such theories, including the terminal relaxation time λ_0 and the plateau modulus G_N^0, particularly in the case of conventional isotactic PP, due to the relatively narrow experimental temperature window available, $160 < T < 200$ °C [18].

The linear viscoelastic model allows one to approach the value of the main relaxation time λ_0 by the longest relaxation time of the generalised Maxwell model [17]:

$$\lambda_0 = \lim_{\omega \to 0} \frac{G'}{\omega G''} = \eta_0 J_e^0 \tag{1}$$

where J_e^0 is the recoverable steady-state compliance defined in a constrained recoil experiment. In general, the scaling laws predicted by both the general viscoelastic model and the de Gennes–Doi–Edwards theory [15,16], $G' \propto \omega^2$ and $G'' \propto \omega$, hold for PP in the normal frequency range [4,5,12]. Newtonian viscosity and relaxation time are commonly estimated from viscosity experimental data by fitting to a given function and extrapolating to low frequencies. The literature provides several models that can be used to obtain these characteristic values of the terminal zone [17]. For dynamic viscosity data, the various models take the general form:

$$\eta(\omega) = \frac{\eta_0}{\left[1 + \left(\frac{\omega}{\omega_0}\right)^A\right]^B} \tag{2}$$

based on the variables η_0, ω_0, A and B, where ω_0 is the inverse of a relaxation time τ_0 related to the main relaxation time λ_0 and $AB \leq 1$. Linear correlations between τ_0 and η_0 have been found for polyolefins [19], according to theoretical considerations of the reptation model for polymer melts containing linear molecules.

In the case of G_N^0, values ranging from 4.2 to 8.6×10^5 for atactic and isotactic PP are reported in the literature [4,5,14,18,20–22]. The application of the theory of rubber elasticity yields a relationship between the characteristic value of the modulus and the critical length between entanglement points M_e and is most commonly described by the expression:

$$M_e = \frac{K\rho RT}{G_N^0} \tag{3}$$

where R is the universal gas constant, ρ the density, T the absolute temperature, and K is a constant with a value of 1 [23] or 4/5 [16] depending upon the various theories used. Moreover, the entanglement molecular weight is related to the critical molecular weight, and is determined by the onset of the effect of entanglements in the viscosity function $M_c = 2M_e$ [23]. Above this critical molecular weight, Newtonian viscosity follows the power law relation $\eta_0 \propto M_w\alpha$, where $\alpha = 3.4$. It has been suggested in the literature, that G_N^0 is independent of polydispersity [24,25]. However, this molecular feature may result in a largely extended terminal zone, shifting it to higher frequencies and thus provoking some uncertainty in the estimation of G_N^0. The latter is also insensitive to temperature for linear polymers and to chain length for long chains, and varies with polymer chemical nature. There seems to be a universal law between this viscoelastic property and molecular dimensions [26], and a very simple power law equation relating entanglement parameters (plateau modulus G_N^0 and entanglement molecular weight M_e) to melt density, ρ and chain dimensions has recently been proposed [27,28].

The present paper describes the rheological evaluation of a series of metallocene atactic PP. Due to the characteristics of the polymerisation process, relatively homogeneous molecular features can be obtained and almost ideal rheological behaviour is expected of these materials (note that the amount of syndotactic fraction is very small. See Table 1). Newtonian viscosity, relaxation time and the 'plateau' modulus were obtained for the materials in the temperature range 20–190 °C. By applying these rheological variables together with the molecular features defined by GPC, we were able to explain the viscoelastic response of the materials according to a relatively simple molecular model [29]. This model is based on a chain relaxation time convoluted with an average molecular weight, which can establish the effect of the environment in which the molecule reptates.

Table 1
Molecular characteristics of the polypropylenes, weight average molecular weight, M_w, polydispersity index, M_w/M_n and results of NMR analysis

Sample	M_w (g/mol)	M_w/M_n	mm	mr	rr	rrrr
mPP1	25,000	2.00	19.9	43.7	36.4	12.2
mPP2	26,800	2.00	16.4	48.8	34.8	13.4
mPP3	58,100	2.00	16.0	48.7	35.3	12.2
mPP4	78,300	1.95	16.3	48.6	35.0	9.1
mPP5	114,900	1.81	17.4	48.0	34.6	9.3
mPP6	183,500	2.00	15.9	48.5	35.6	13.9

2. Experimental

2.1. Characterising the materials

The PP materials were supplied by Repsol-YPF (Spain). The molecular variables of the materials, M_w and M_w/M_n, were determined by size exclusion chromatography (SEC) using a 150 CV Waters GPC coupled to a differential refractive index instrument and viscometer. Solution ^{13}C NMR spectra were run at 75.4 MHz on a Bruker 300 NMR spectrometer. Samples were run as 15% solution in $CDCl_3$ at 50 °C or in C_6D_6 at 90 °C. The scan number was higher than 3000 with a 6 s delay between pulses. The molecular and physical variables obtained are listed in Table 1. The structure of the samples is substantially atactic. Nevertheless, it is observed (Table 1) that the syndiotactic triads (rr) appear to be more numerous than the isotactic triads (mm). The methyl pentad analysis gives information on the tacticity of the polymeric chains finding about a 12% of rrrr pentads. All the samples are highly regioregular. In fact, from the ^{13}C NMR, signals relating to sequences $(CH_2)_n$ with $n \geq 2$ are no detectable.

2.2. Dynamic measurements

Small amplitude oscillatory measurements were conducted in a Polymer Laboratories MKII torsion system viscometer and in a Bohlin CVO torsion rheometer in the frequency range 10^{-3}–10^2 Hz. Deformation was set at around 0.1, corresponding to the linear viscoelastic region established by previous amplitude sweeps. Measurements were performed at temperatures ranging from 20 to 190 °C. The experiments were performed on test specimens of 25 mm diameter and 1 mm thickness moulded in a Schwabenthan Polystat 200T for 5 min at 30 °C at a nominal pressure of 50 bar. The thermal stability of the samples was tested by means of time sweeps of approximately 60 min at low frequencies (0.1–1 Hz) in the temperature range of the study.

3. Results and discussion

3.1. Time–temperature superposition principle

The data obtained at different temperatures were shifted at $T_0 = 75$ °C according to the method developed by Mavridis and Shroff [30], in which definition is made of the shift factors a_T and b_T, for the frequency and modulus respectively, obtained at different temperatures. The time–temperature superposition principle (TTSP) was found to be applicable over the temperature range examined, as expected for linear homopolymers. The shift factor a_T obeyed the Williams–Landel–Ferry (WLF) equation. Fitted values of $c_1 = 5$, $c_2 = 137$ have been obtained. However, it was found that a_T changed slightly more rapidly in mPPs of lower M_w. A master curve for the temperature dependence of a_T can be constructed, when a slight increase in the glass transition temperature T_g for the lowest M_w mPPs is suspected. The master curve obtained for a_T was highly consistent with results provided in the literature [4,22]. Fig. 1 shows the master curve of $T_0 + \Delta T$ ranging from 75 to 85 °C and assumes a 10 °C difference in the T_g values of the materials examined. Atactic PP, nevertheless, show highly variable T_g; with values ranging from -35 to 10 °C reported in the literature [1,4,5,31]. We are unaware of the reasons for this wide difference in T_g shown by our samples, but there are various contributing factors that could account for the behaviour observed, for example, (i) differences in tacticity; (ii) a certain degree of crystallinity; and (iii) errors in monomer position during polymerisation leading to head-to-head or tail-to-tail defects [31].

3.2. Newtonian viscosity

Fig. 2 provides complex viscosity master curves at 75 °C for the samples. The overlapping of the data collected at different temperatures was excellent for all the samples. As it is well known, values of zero shear viscosity η_0 can be obtained from the curves of complex viscosity at low frequencies, provided the linear viscoelastic model is applicable [17]:

$$\eta_0 = \lim_{\omega \to 0} \eta' = \lim_{\omega \to 0} |\eta^*| \tag{4}$$

Among the models available, the Cross-approach describes experimental results for linear metallocene polyolefins fairly well [19]. We consequently applied this fitting since it contains the lowest number of variables. Thus, Eq. (2) takes the general form:

$$|\eta^*(\omega)| = \frac{\eta_0}{1 + (\omega \tau_0)^A} \tag{5}$$

where η_0 is the Newtonian viscosity and τ_0 a relaxation time related to the longest relaxation time λ_0 as defined in Eq. (1).

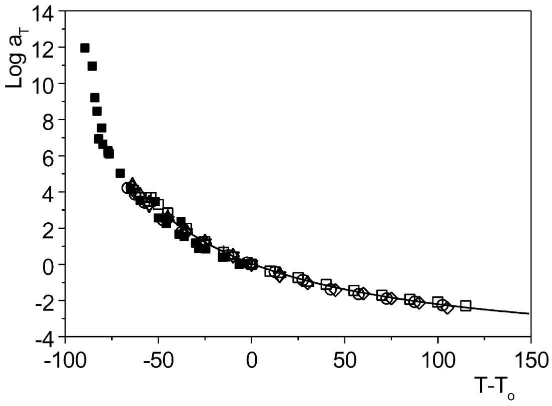

Fig. 1. Time-scale shift factor as a function of temperature. Open symbols represent the materials examined: (+) mPP1, (◆) mPP2, (▽) mPP3, (△) mPP4, (○) mPP5 and (□) mPP6. Closed symbols [4] and line [18] are results obtained from the literature.

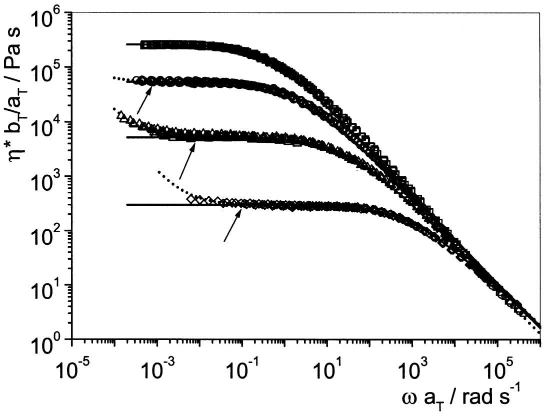

Fig. 2. Reduced dynamic viscosity against reduced frequency at $T_0 = 75$ °C for the polymers indicated.(◆) mPP1, (△) mPP2, (○) mPP4 and (□) mPP6. The solid lines represent the fitting of experimental data to Eq. (5). The dashed lines represent the fitting of experimental data to Eq. (6).

However, as we can see in Fig. 2, the Cross model does not fit the experimental results at very low frequencies for the materials showing the lowest M_w. These samples exhibit the behaviour of a yield stress fluid; η^* tending towards very high values. From these observations we could suspect the presence of high residual masses in the products or a certain degree of crystallinity. The former hypothesis would appear to be more plausible, since the enhanced viscosity was observed at temperatures at high as 190 °C, were PP are already in the melted state, precluding the possibility of any chain order in the melt. Deviations at low frequencies have also been observed in other materials, but the corresponding authors were not able to account for this behaviour [32]. A further possible explanation, would be a systematic error (concave upward curvature in the storage modulus, G') due to low instrument torque, as has been recently reported in PEs [33,34]. We opted for a Cross law with a yield stress (σ_0) to account for the increases at low frequency [35]:

$$|\eta^*(\omega)| = \frac{\sigma_0}{\omega} + \frac{\eta_0}{1 + (\omega\tau_0)^A} \tag{6}$$

Table 2
Rheological properties of the polypropylenes determined at 75 °C

Sample	η_0 (Pa s)	τ_0 (s)	$G_N^0 \times 10^6$ (Pa)
mPP1	300	0.00125	–
mPP2	375	0.00150	–
mPP3	5200	0.0403	0.57
mPP4	11,200	0.100	0.60
mPP5	54,000	0.478	0.54
mPP6	260,000	2.22	0.48

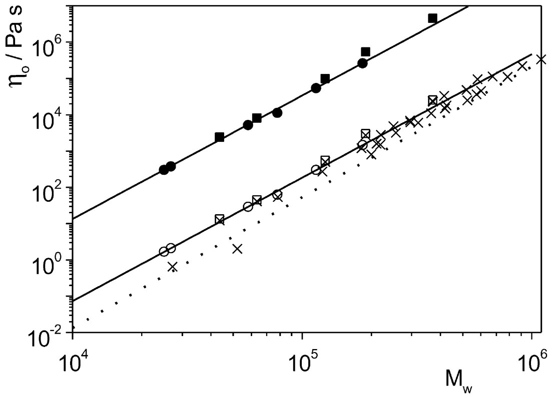

Fig. 3. Newtonian viscosity versus weight average molecular weight at $T = 75$ °C (black symbols) and 190 °C (white symbols) for a set of PPs: mPP examined herein (●, ○); solid line represents the fit to a power law function $\eta_0 \propto M_w^a$ (Eqs. (7) and (8)); the remaining symbols represent the behaviour described in the literature for model mPPs (■, □) [5] and conventional isotactic PPs (×) [35–38]. The dashed line represents the behaviour of conventional PPs reported in the literature.

The values of η_0, τ_0 and A are practically identical to those obtained by the cross-fit. The fitted values of η_0 and τ_0 at 75 °C are shown in Table 2. The values obtained for the apparent yield stress, σ_0, are of the order of 1 Pa in each case. The plots of η_0 versus M_w at 75 and 190 °C are shown in Fig. 3. Data for model atactic PPs [5] and conventional isotactic PPs [12–14,36–39] have been included in the plot, and appear to follow a power-law correlation with a critical exponent of 3.40:

$$\eta_0 = 3.40 \times 10^{-13} M_w^{3.40}\ \text{Pa s at 75 °C} \tag{7}$$

$$\eta_0 = 1.50 \times 10^{-15} M_w^{3.40}\ \text{Pa s at 190 °C} \tag{8}$$

where M_w is expressed in g/mol. In general, the results obtained are in good agreement with those reported by other authors. As in the case of PEs, the exact values of the exponent and pre-exponent have been a controversial issue for many years. Indeed, depending on tacticity, values for the pre-exponent constant in the η_0–M_w correlation at 190 °C from 5.32×10^{-17} to 2.84×10^{-16} have been cited [14], while values up to 4.0 have been reported for the power law exponent [12,21,22]. In general, the molecular weight intervals analysed have been somewhat limited. Along with the uncertainty associated with measuring the MWD and/or estimating η_0 and the different microstructure of the samples, this might be the cause of such disparity in these constants.

3.3. The plateau modulus

Fig. 4 shows the viscoelastic response of the sample of highest molecular weight in an oscillatory shear experiment run at a reference temperature of 190 °C. All the materials examined followed a similar trend, i.e. strong viscous behaviour at low frequencies ($G'' \gg G'$) and a well developed maximum value of G'' at high frequencies. G_N^0 is usually obtained via the following expression [23]:

$$G_N^0 = \frac{2}{\pi} \int_{-\infty}^{\infty} G''(\omega) \mathrm{d} \ln \omega \tag{9}$$

where the integral only extends across the terminal (low angular frequency, ω) peak of the loss modulus. Application of expression 9 requires that the terminal and transition

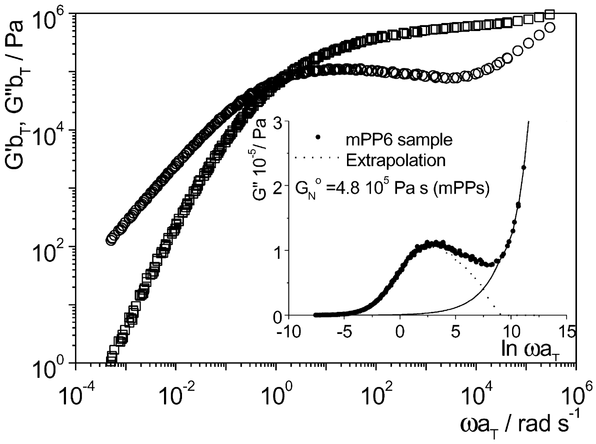

Fig. 4. Reduced viscoelastic response at the reference temperature of 75 °C for the highest molecular weight material mP6: G' (☐), G'' (○). The figure inset shows the extrapolation of the G'' curve to calculate G_N^0.

response be well resolved. A baseline, which takes into account the contribution of the glassy region, was subtracted from the experimental data, as can be seen in the inset to Fig. 4. The same method was applied to the other samples. The calculated values of G_N^0 are listed in Table 2. The uncertainties in the extrapolation procedure become greater as the molecular weight decreases, so the most precise value should correspond to the highest molecular weight sample: $G_N^0 = 4.8 \times 10^5$ Pa. This value is much lower than those quoted for conventional PPs [20–22], yet very similar to that recently obtained for a high M_w atactic PP metallocene [18]. The most widely accepted values for model PPs range from 4.20×10^5 to 5.20×10^5 Pa for atactic and isotactic PP. Syndiotactic PPs are associated with the much higher value of 1.35×10^6 Pa. This variation is thought to be due to a difference in chain structure; the latter being mainly comprised of trans chain conformations in the melt.

In a recent re-examination and extension of Graessley and Edwards studies [26], a very simple power law equation relating entanglement parameters (plateau modulus, G_N^0, and entanglement molecular weight, M_e), melt density ρ, and packing length p was proposed [27,28]:

$$G_N^0 \propto \frac{1}{M_e} \propto p^{-3} \tag{10}$$

Packing length can be linked to the 'thickness' of the chain, and can be defined as the volume occupied by a chain of molecular weight M, $M(\rho N_a)^{-1}$, divided by the mean-square end-to-end distance $\langle R^2 \rangle_0$:

$$p = \frac{M}{\langle R^2 \rangle_0 \rho N_a} \tag{11}$$

Taking into account the relations in Eqs. (10) and (11), a decrease in G_N^0 can be explained by a drop in the concentration of entanglement couplings or by reduced chain dimensions of the mPP, with respect to other PP. A lower entanglement density implies a higher value of the entanglement molecular weight M_e, which is in fact related to G_N^0 by means of Eq. (10). Using $K = 4/5$ in Eq. (3) for the homopolymers leads to a value of $M_e = 4850$ g/mol. As in the case of PE [19], values cited for the M_e of polypropylenes range also from 3500 to 5600 g/mol.

Compared to other PPs, we could suspect a discretely lower degree of entanglement density in our samples and mPPs in general, because of the use of a different catalyst system. This potential lower entanglement density is the consequence of the polymerisation method itself and has also been recently described for a family of mPEs [19]. Another possible source of the high G_N^0 values obtained in conventional crystalline PPs would be the presence of syndiotactic units.

3.4. Relaxation times

Linear polyolefins shows relaxation times proportional to $M_w^{3.40}$, with the exponent varying in a similar manner to η_0. This would imply a linear correlation between λ_0 and η_0; a conclusion easily attainable from the linear viscoelastic model assuming a single exponential relaxation modulus $G(t)$ in the terminal zone [17]. Fig. 5 shows the plot of τ_0 against η_0 at 190 °C. A clear linear correlation is obtained:

$$\tau_0 = 6.2 \times 10^{-6} \eta_0 \tag{12}$$

where the constant is expressed in Pa^{-1}. This figure also includes a plot of results obtained for mPE at the same temperature [19]. Higher values of the characteristic relaxation time for the same viscosity were shown by our mPP samples. A characteristic relaxation time $\tau_n = \eta_0 / G_N^0$ may be defined as the first moment of the relaxation time distribution, assuming that the relaxation spectra of the materials is gaussian. From this correlation, and considering the $G_N^0 \approx 10^6$ Pa recently obtained for mPE of polydispersity index $M_w/M_n = 2$ [19], it follows that, for the same value of η_0, the characteristic relaxation times of mPPs are double those corresponding to the mPE. This result coincides with that obtained in Fig. 5. In Fig. 6 we plotted reduced complex viscosity η^*/η_0 versus reduced angular frequency $\omega\eta_0$ for the mPP sample of highest M_w and

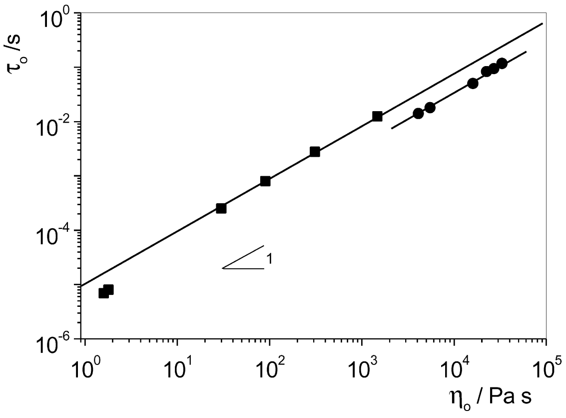

Fig. 5. Relaxation time against Newtonian viscosity at 190 °C for the materials analysed: (■) mPP and (●) mPE data from the literature [19].

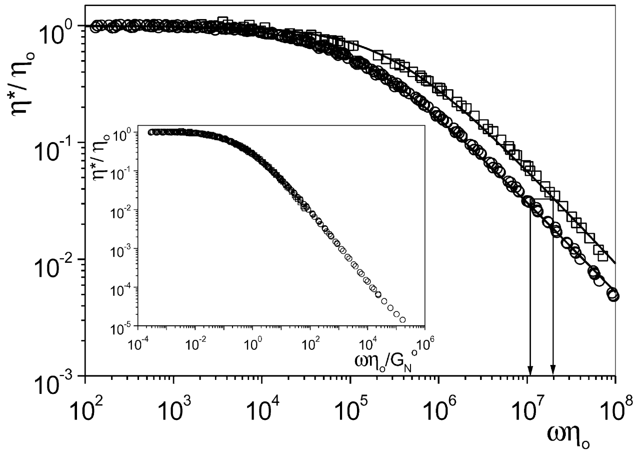

Fig. 6. Reduced complex viscosity η^*/η_0 versus reduced angular frequency $\omega\eta_0$, for the highest molecular weight mPP sample (○) and an mPE (□) described in the literature of similar M_w and M_w/M_n [19]. The figure inset shows the result of multiplying the reduced frequency of mPP6 by the factor $A = 2$.

compared this plot with that corresponding to a mPE sample of similar M_w [19]. It may be noted that the characteristic relaxation times of the mPP sample are lower than those of the mPE. In the inset to the figure, it can be seen that a master curve is obtained by multiplying the frequency by the characteristic relaxation time τ_n. All these results point to an identical viscoelastic fingerprint in the terminal region for the mPE and mPP samples, irrespective of microstructure and, as expected, only dependent on MWD.

3.5. Relaxation spectrum and molecular weight distribution

The relationship between rheological properties of polymer melts and MWD is a topic which is rapidly gaining interest. Current models are all based on the classical reptation theory of de Gennes [15], which was subsequently implemented by Doi-Edwards [16]. The monodisperse model assumes that the surrounding species of a polymer molecule constitute a time invariant matrix that can be considered as a fixed tube along which the polymer chain reptates. Several available models serve to test the ability of the viscoelastic properties of the transition zone, i.e. η_0 and G_N^0, to describe the viscoelastic behaviour of linear polymers. A good review of the state-of-the-art of this particular subject can be found elsewhere [40]. A relatively simple model has been recently developed by Llorens and co-workers [29]. This model provides a good description of linear polymers that have a MWD with polydispersity index around 2. The model is based on a chain relaxation time convoluted with an average molecular weight distribution that describes the effect of the environment where the molecule reptates. This assumption, together with the hypothesis that the MWD of the polymers may be approximated by a lognormal distribution, give rise to an equation that connects the rheological response with the MWD, without using the relaxation spectrum. GPC measurements have shown that the MWD of the materials analysed is invariably bell-shaped. In these conditions, and applying the rheological variables available, i.e. η_0 and G_N^0, the entire viscoelastic response is given by:

$$G'(\omega) + G''(\omega) = \frac{G_N^0}{c\pi^{1/2}} \int_0^{\infty} \exp\left[-\left(\frac{1}{c}\ln\frac{M}{M_0}\right)^2\right] \frac{A^2 + A}{1 + A^2} \frac{dM}{M} \tag{13}$$

$$A = \omega \frac{\eta_0}{G_N^0} \frac{\left[M_0 \exp\left(\frac{-c^2}{4}\right)\right]^{1.25} M^{2.15}}{\left[M_0 \exp\left(\frac{c^2}{4}\right)\right]^{3.4}} \tag{14}$$

$$M_0 = \frac{M_n}{\exp\left(\frac{-c^2}{4}\right)} = \frac{M_w}{\exp\left(\frac{c^2}{4}\right)} \tag{15}$$

We applied this simple model to our highest M_w sample using the molecular variables listed in Table 1 together with the values of G_N^0 and η_0 established at 190 °C. The solid lines in Fig. 7 represent the results of the model. Also provided are results obtained for a mPE of similar M_w at the same temperature [19]. A reasonable degree of accuracy between the experimental results and those obtained by application of the model can be observed in all cases. The use of the characteristic plateau modulus of conventional PP (8.6×10^5 Pa), recently tested by means of similar viscoelasticity–MWD conversion methods, yields a poor reproduction of the experimental values. The model used is only applicable from the rubbery to the terminal region, thus Eqs. (13)–(15) do not fit the glassy modes appearing at high frequencies in mPP samples.

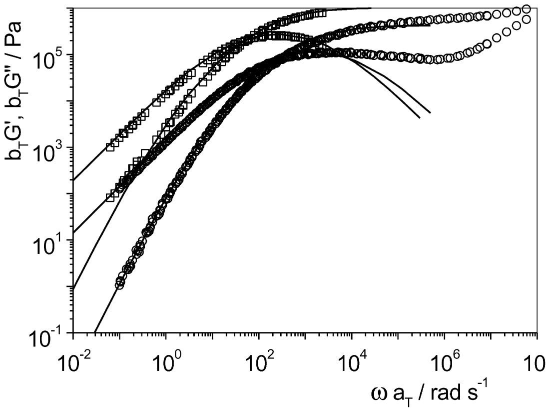

Fig. 7. Experimental viscoelastic response at 190 °C for mPP6 (○), and an mPE (□), described in the literature [19]. The solid line represents the curve obtained by fitting to Eqs. (13)–(15) the molecular properties provided in Table 1 (see Refs. [19,29] for details).

4. Conclusions

Zero shear viscosity was found to vary with the weight-average molecular weight to the exponent power of 3.40 for a set of different atactic polypropylenes in a broad molecular weight range. This result contradicts the most recently accepted value of 3.80. At the same time, the samples yield low values of the plateau modulus. The value obtained for the highest M_w sample was 4.8×10^5 Pa. This value is in the range obtained for high-M_w atactic mPEs and for the relaxation times observed for both types of polymer. The application of a simple model for polymers of bell-shaped MWD reproduces the viscoelastic response of the materials across the whole range of frequencies examined. This allowed us to confirm the values obtained for the rheological variables η_0 and G_N^0 and prompts the question of what could be causing the difference observed between metallocene and conventional polyolefins.

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