Effect of high molar mass species on linear viscoelastic properties of polyethylene melts

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ABSTRACT

The molecular features and the linear viscoelastic melt properties of a series of polydisperse high density polyethylene are investigated. The main molecular characteristic of the materials studied is the presence of high molar mass species, which give rise to unusual values of the M_z/M_w ratio. This molecular particularity strongly affects to the linear viscoelastic melt properties as the Newtonian viscosity and the steady-state shear recoverable compliance. Both the third and the fourth moments of the molecular weight distribution affect to the values of these properties, which follow the trend expected by the reptation model. The evidences clearly prove the effect not only of the polydispersity index, but more interestingly of the shape of the molecular weight distribution on the dynamics of the systems. The behavior shown by the experimental samples studied in this work is interesting as the linear viscoelastic properties have become widely used, not only to test the molecular weight distribution dependence of the viscoelastic fingerprint and the processability, but also to assess the possible presence of long chain branching.

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1. Introduction

The effect of the molecular weight distribution (MWD) on the viscoelastic response of linear polyethylene (PE) melts has been widely reported in the literature since the 1960s, but the results are certainly contradictory. Bueche [1] and Graessley [2] considered the existence of an averaged molecular weight of the distribution, M_t, located between the second and the third moments, M_w and M_z, respectively, that best represents the average to explain the dependence of the Newtonian viscosity, η_0, in linear polymers with polydispersity index higher than $M_w/M_n = 2$. Later, Saeda and co-workers [3] found the experimental support to these ideas in polydisperse samples. Locati and Gargani [4] empirically expressed M_t in terms of the polydispersity index using Saeda's experimental data. In the same direction, Malkin and co-workers [5] proposed an empirical modification of the average molecular weight for the dependence of the rheological properties, later validated for polydisperse polypropylene (PP) [6,7] and PE [7]. The equation of Malkin and co-workers [5], obtained for polydisperse polybutadiene (PB), nicely agrees with recent theoretical predictions [8,9], based in the determination of the linear viscoelastic response from the MWD trace using the double reptation approach. The approximate correlation found by Nobile and Cocchini takes the form [8]:

$$\eta_0 = 0.51 K M_w^\alpha \left(\frac{M_z}{M_w}\right)^\beta \tag{1}$$

with K the corresponding pre-exponential constant for monodisperse species at a given temperature, $\alpha = 3.4$ and $\beta = 0.8$. This expression resembles the correlation found by den Doelder, but in this case with $\beta = 0.7$ [9]. Other authors did not observe these MWD effects on η_0 for polydisperse PE samples with $M_z/M_w = 2.2 \pm 0.7$ [10]. A more recent work has revealed that the width of the MWD

strongly affects to both η_0 and steady-state shear recoverable compliance, J_e^0, in linear PE samples with values of M_z/M_w between 4.0 and 11.2 [11,12]. It is widely accepted that J_e^0 does not relate to M_w, but it is very sensitive to the measure of the MWD. Many relations (empirical and theoretical) have been proposed to correlate J_e^0 with MWD. The one suggested by Mieras and van Rijn [13] (Eq. (2)) with power law exponent of $\gamma = 3.7$, was successfully tested by Mills [14] in polydimethylsiloxane (PDMS), polystyrene (PS) and PE.

$$J_e^0 \propto \left(\frac{M_z}{M_w}\right)^{\gamma} \tag{2}$$

The blending laws of Bogue et al. [15] and Kurata et al. [16] established values for γ of 2.0 and 3.7, respectively. More recently, Nobile and Cocchini [8] have obtained a similar correlation based in the double reptation approach, but with an exponent of $\gamma = 5.5$. Other correlations were proposed by Ferry et al. [17] based in the Rouse model, and Agarwal [18] from empirical observations, in which higher moments of the MWD are involved:

$$J_e^0 \propto \left(\frac{M_{z+1}M_z}{M_w^2}\right) \tag{3}$$

$$J_e^0 \propto \left(\frac{M_{z+1}M_z}{M_w M_n}\right) \tag{4}$$

By the other hand, Ressia et al. [19] proposed an expression based on the blending laws of Montfort et al. [20] and Zang et al. [21] for mixtures of monodisperse systems, which included not integer moments of the MWD ($Q_a = \Sigma w_i M_i^a$, with "a" values between 3.4 and 4.4):

$$J_e^0 \propto \left(\frac{Q_a}{Q_1^a}\right) \tag{5}$$

Finally, den Doelder has recently established a relationship based also on the double reptation model [9]:

$$J_e^0 \propto \left(\frac{M_z}{M_w}\right)^2 \left(\frac{M_{z+1}}{M_z}\right)^4 \tag{6}$$

From all these expressions strong effects of the highest moments of the MWD on the melt elastic character of polymeric materials are expected, as a slight increase in the moment ratios can cause values of J_e^0 several orders of magnitude higher than the characteristic value of monodisperse species.

In previous works we have reported that tridentate bis(imino)pyridyl iron complexes, when combined with a co-catalyst, such as methylaluminoxane (MAO) and aluminum alkyls (AlEt$_3$ and AliBu$_3$), form very active catalytic systems that yields linear PE with very broad MWD [22–24]. We have investigated the performance of this type of catalyst from the simulation [25–27] and experimental points of view [28]. We have also reported the effect of the MWD on η_0 for these materials in a recent contribution [29], on the basis of the applicability of Eq. (1). We must point out here that the reported values of M_z/M_w in the experimental PE samples studied in this work are extremely high, between 20 and 30 (2–3 times higher than

those reported until now in linear polydisperse PE), so the effect of the very high-M_w tail has to be especially noticeable. For this reason, we extend the study of the physical properties of these materials and report: (i) basic physical properties of the materials; (ii) the effect of the presence of high-M_w tails on the melt linear viscoelastic properties, and more specifically on J_e^0, and (iii) the modeling of the linear viscoelastic response within the reptation framework by using the experimental MWD together with simulated values of the entanglement features.

2. Experimental methods

The materials were kindly supplied by Centro Tecnológico Repsol-YPF (Spain). The samples labeled from PE1 to PE4 listed in Table 1 were obtained from a bis(imino)pyridyl iron catalysts [28]. The polymerizations were carried out in a Buchi reactor (except the PE1 sample in Table 1, obtained in autoclave reactor in equivalent conditions and a slightly higher concentration of catalyst). Isobutene solvent (1 dm^3) and the required amount of MAO co-catalyst were introduced into the reactor under inert nitrogen atmosphere. The total pressure was adjusted to 40 bars. Reactions were carried out at a temperature of 90 °C and kept constant throughout the polymerization. In the Buchi series hydrogen was introduced continuously in the polymerization reactor to control the molecular weight of the final products. The total concentration of hydrogen is adjusted to remain constant during polymerization and increased from 0 to 1 mol% in the subsequent polymerizations (from PE2 to PE4). Polymerizations were carried out along 1 h. Two samples obtained from a metallocene single-site catalyst (mPE) have been included in this study, for comparison purposes [30].

The samples were analyzed by ^{13}C nuclear magnetic resonance (^{13}C NMR) on a Bruker DRX500 spectrometer. The spectra were recorded at 100 °C on a Bruker DRX 500 spectrometer operating at 125 MHz. The samples were dissolved in hot 1,2,4-trichlorobenzene (TCB) and d6-benzene. ^{13}C NMR results corroborate the linear structure of all the materials studied in this work in agreement with previous results [28].

The MWD of the samples was determined by means of high-temperature size exclusion chromatography (SEC) analyzer Waters 150C, equipped with refractive index (RI) and viscometer (V) detectors. All measurements were conducted at a flow rate of 1 mL min^{-1} and at temperature

Table 1
Molecular features of the samples studied.

Samples	M_w (kg mol^{-1})	M_w/M_n	M_z (kg mol^{-1})	M_{z+1} (kg mol^{-1})
	sd = ±5%			
mPE1[a]	65.0	3.6	195.0	585.0
mPE2[a]	152.0	2.3	350.0	805.0
PE1	35.0	6.1	1000	4730
PE2	49.4	7.8	1340	5770
PE3	71.7	9.7	1400	5300
PE4	92.5	13.3	1730	5200

[a] Single-site metallocene samples [30].