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Rheology and reptation of linear polymers. Ultrahigh molecular weight chain dynamics in the melt

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Synopsis

The melt rheology of ultrahigh molecular weight polymeric materials characterized by a narrow molecular weight distribution has been analyzed. Ultrahigh molecular weight polyethylene obtained from a metallocene catalyst shows a well-developed “plateau” modulus in a range of angular frequency of more than 3 decades. The characteristic value of the plateau modulus (~ 2 MPa) is in close agreement with those reported for a model high molecular weight monodisperse polyethylene. From this value one can determine a characteristic molecular weight between entanglements of 1200 g mol^{-1} . The molecular weight dependency of different, experimentally based relaxation times obtained from the linear viscoelastic response exhibits an exponent power law close to 3.0 for these materials. This seems to contradict the 3.4 dependence observed in the usual molecular weight range, which is based on the chain contour length fluctuation approach, but is in agreement with the latest reptation-based models. These models predict a crossover from the 3.4 to a 3.0 exponent for very long chains as used here at a constant critical value of the molecular weight M_r close to $100M_c$ ($200M_c$ when using the well accepted relationship $M_c = 2M_e$). This predicted crossover is independent of the polymer’s chemical composition. However, combining results from our experiments with results from literature shows that the experimental values of M_r extend from $15M_c$ for polystyrene, $25M_c$ for polyisobutylene, $100M_c$ for polybutadiene to $220M_c$ for polyethylene. These results are not predicted by molecular models and demand for new theoretical considerations of chain dynamics, in which the chemical structure is, most probably, a key factor that should be taken into account. It should be noticed that the influence of the molecular weight distribution on the differences observed is not understood. Unfortunately, it is very difficult to obtain monodisperse samples of ultrahigh molecular weight polyethylene and, therefore, the use of the samples studied here the best choice possible, up to now to test and revisit basic and novel aspects of the rheology of polyolefin’s. © 2004 The Society of Rheology.

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I. INTRODUCTION

Polymer melt chain dynamics and rheological properties have found a common physical framework in the reptation model [de Gennes (1979), Doi and Edwards (1986)]. This model is based on the assumption that large-scale transverse chain motions are hindered by topological constraints caused by the neighboring chains. Chain dynamics is then restricted to a snake-like motion (reptation) along an imaginary tube formed by these neighboring molecules. The constrained chain dynamics give rise to a characteristic time,

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τ_d , for a chain to diffuse one tube length. One appealing feature of the theory is that it requires a very few parameters: the Kuhn step length, b , the tube diameter, a (equivalently, the molecular weight between topological constraints, M_e , or the plateau modulus, G_N^0) and the monomeric friction coefficient, $\zeta_0(T)$. Once these parameters and the polymer's molecular weight distribution are known, quantitative predictions for the linear rheology, as determined by the stress relaxation modulus $G(t)$ or the complex modulus $G^*(\omega)$, are possible at any given temperature T . Another important feature is that within the tube concept, other relaxation mechanisms can be incorporated. For example, in the case of linear polymers, besides bare reptation, a more exact approach for quantitative predictions includes chain contour length fluctuations (CLF) [Doi and Edwards (1986), Milner and McLeish (1997, 1998), McLeish and Milner (1999)], and cooperative effects of constraint release, i.e., double reptation (DR) [des Cloiseaux (1988, 1990a, 1990b), Tsenoglou (1991)] and dynamic tube dilation [Marrucci (1985), Pattamaprom *et al.* (2000), Pattamaprom and Larson (2001)].

Until the development of metallocene catalyst systems, the available ethylene-based polymers lacked the desirable molecular homogeneity for systematic studies of the effect of molecular architecture on chain dynamics. Nevertheless, a number of studies have been performed on monodisperse hydrogenated polybutadiene, which has been considered for a long time as model polyethylene (PE) [Arnett and Thomas (1980), Carella *et al.* (1984), Pearson *et al.* (1994), Fetters *et al.* (1994, 1999a), Lohse *et al.* (2002)]. This synthesis method is, however, limited to the range of molecular weight's below 10^6 . Ziegler–Natta catalysts can polymerize longer molecular species, but create a large heterogeneity in the molecular weight distribution. Novel metallocene catalysts allow to synthesize PE samples with a molecular weight well above the 10^6 limit, having a linear molecular structure and a narrow molecular weight distribution with polydispersity indexes close to 2.

The objective of this work is to apply reptation concepts to measured linear viscoelastic properties in the melt of a series of well-defined linear polymers, including metallocene synthesized polypropylene (PP) and ultrahigh molecular weight PE (UHMWPE).

II. THEORETICAL BACKGROUND

We use a straightforward expression for the terminal relaxation time of a reptating chain of molar mass M that accounts for the effects of CLF in terms of the Rouse time τ_e for an entanglement segment of molecular weight M_e : [Milner (1996), Milner and McLeish (1997, 1998)]:

$$\tau_d = 3\tau_e \left(\frac{M}{M_e}\right)^3 \left[1 - \kappa \left(\frac{M_e}{M}\right)^{0.5} \right]^2, \quad (1)$$

where the first term $3\tau_e(M/M_e)^3$ is the reptation time that arises from the topological theory for linear monodisperse polymer melts [Doi and Edwards (1986)]. The second term represents the contribution of the CLF to the relaxation time, in which κ is a constant of the order unity. Ketzmerick and Ottinger (1989) first already obtained similar results by means of equilibrium Brownian dynamics simulations. The expression for τ_d accounts for a decrease in the relaxation time as the molecular weight decreases, deviating from the predicted asymptotic reptation power law with exponent 3.0 that holds for very long chains and is given by the first term.

The Rouse relaxation time, τ_e , can be expressed as a function of the earlier mentioned parameters the Kuhn step length b , the tube diameter a , and the monomeric friction coefficient ζ_0 [Doi and Edwards (1986), Milner (1996), McLeish and Milner (1997, 1998), Watanabe (1999)]:

$$\tau_e = \frac{\zeta_0 a^4}{3\pi^2 K_B T b^2}. \quad (2)$$

By using the relationships between the characteristic lengths a and b with equilibrium random coil features, $a^2 = M_e \langle R^2 \rangle / M$ and $b^2 = m_0 \langle R^2 \rangle / M$, we obtain the following expression for τ_e :

$$\tau_e = \frac{\zeta_0 \frac{\langle R^2 \rangle}{M} M_e^2}{3\pi^2 K_B T m_0}, \quad (3)$$

where $\langle R^2 \rangle / M$ is the monodisperse chain end-to-end distance molecular weight ratio for an ideal equilibrium random coil, M_e is the average molecular weight between topological constraints, m_0 is the molecular weight of the monomeric unit, K_B is the Boltzmann constant, and T is the absolute temperature.

Next using τ_d , which includes the CLF effect, the tube survival probability $P_i(t)$ of a chain i at time t , can be calculated with the expression for reptation [Doi and Edwards (1986)]:

$$P_i(t) = \frac{8}{\pi^2} \sum_{p=\text{odd}} \frac{1}{p^2} \left[\exp\left(-\frac{p^2 t}{\tau_d}\right) \right]. \quad (4)$$

The effect of polydispersity can be taken into account by considering the experimental curve obtained by size exclusion chromatography (SEC), approximated with a Gaussian function and split up into parts of molecular weight M_i and weight fraction w_i . The cooperative constraint release events can be included in the model by means of the DR concept [des Cloiseaux (1988, 1990a, 1990b), Tsenoglou (1991)]. The expression for the relaxation modulus $G(t)$ then reads

$$G(t) = G_N^0 \left[\sum_i w_i F_i(t)^{1/\beta} \right]^\beta = G_N^0 \left[\sum_i w_i P_i(t) \right]^\beta, \quad (5)$$

where G_N^0 is the ‘‘plateau’’ modulus, $F_i(t)$ the reduced relaxation function of the i th monodisperse molecular species, and β the DR exponent, which originally has the value of 2. The DR approach has been successfully tested for different polydisperse polymers [Léonardi *et al.* (2000, 2002)].

Applying the rubber elasticity theory, a relationship is found between the characteristic value of G_N^0 and the critical molecular weight between entanglement points M_e . This relationship is most commonly given by [Doi and Edwards (1986), Ferry (1980)]:

$$M_e = \frac{K\rho RT}{G_N^0}, \quad (6)$$

TABLE I. Molecular and rheological features of the materials studied obtained by size exclusion chromatography.

Material	M_w g mol ⁻¹	M_w/M_n	η_0 /kPa s	τ_0 /s	τ_x /s	τ_m /s
PE180	180 000	2.2	27	0.11	0.04	0.18
PE800	800 000	1.8	3400	6.4	3.3	12
PE3600	3 600 000	2.9	450 000 ^a	635	500	1900
PE4500	4 500 000	10.0	n.e.	n.e.	n.e.	n.e.

^aFrom stress relaxation results: n.e. means not estimated.

where R is the universal gas constant, ρ is the density, T is the absolute temperature, and K is a constant with a value of $4/5$ [Doi and Edwards (1986)] or 1 [Ferry (1980)], depending upon convention. Equations (1)–(3) have been defined for $K = 4/5$ [Larson *et al.* (2003)].

At this point we have to stress that our main objective is not to test the model described earlier for the materials studied but, instead, to define a simple way (universal and valid for all polymer chemistries and accounting for the effects of polydispersity) to have a linear viscoelastic fingerprint of the polymer melts considered.

III. MATERIALS AND EXPERIMENT

We studied three metallocene PE samples of varying molecular weight and relatively narrow molecular weight distribution (NWMD) (see Table I). For comparison purposes we included other linear polymers in our study: a commercial polydisperse Ziegler–Natta UHMWPE with a broad molecular weight distribution, a series of PP samples with varying molecular weight and polydispersity index and one polystyrene (PS) sample (see Table II). All the molecular properties of the materials were obtained from SEC.

Oscillatory shear and transient stress relaxation measurements in the linear viscoelastic were carried out on a Rheometrics ARES and a Rheometrics RMS800 strain-controlled torsion spectrometers for a broad range of temperatures (from melting point to 250 °C), angular frequencies ω (from 0.01 to 100 rad s⁻¹), and strain γ . In each measurement, the applied strain was maintained at a constant nominal value within the linear viscoelastic range, determined by the aid of previous strain sweeps (typically between 0.01 and 0.1). Torsion compliance of the apparatus can be an important issue when the sample stiffness is high relative to that of the instrument, as is the case for the UHMWPE samples. The torsion compliance of the rheometer force rebalance transducer used is equal to 1.3×10^{-6} Nm rad⁻¹. If the sample stiffness approaches the spring constant of the instrument ($1/\text{compliance}$) the transducer becomes unstable [Macosko (1994)]. There-

TABLE II. Molecular features of the polypropylenes and polystyrene studied.

Materials	M_w	M_w/M_n	Tacticity/%
PP80	86 100	2.5	n.e. ^a
PP130	132 000	2.2	n.e.
PP180	180 000	2.0	n.e.
PP250	250 000	3.4	95.0
PP350	350 000	5.6	96.2
PP500	500 000	6.0	96.0
PS100	100 000	2.0	...

^an.e. means not estimated.

fore, small sample sizes should be used. We used specimens with dimensions of 8 and 12 mm diameter, for which values of the moduli up to 10^8 could be measured without transducer instabilities. The measurements were performed using a parallel plate geometry, maintaining a distance between the plates of about 1 mm. All measurements were carried out under nitrogen atmosphere and with well-stabilized samples to avoid thermo-oxidative degradation.

The characteristic viscoelastic functions, storage modulus G' , loss modulus G'' , complex viscosity η^* , and relaxation modulus $G(t)$, have been obtained for different temperatures. The time-temperature superposition was applied with as a reference temperature 190 °C [Ferry (1980)]. From the complex viscosity data the characteristic zero-shear viscosity η_0 , and an average relaxation time τ_0 , were extracted by fitting a Cross model [Bird *et al.* (1987)]:

$$|\eta^*| = \frac{\eta_0}{1 + (\omega\tau)^a}. \quad (7)$$

Other characteristic experimental relaxation times as τ_x , defined as the reciprocal frequency at the cross-point between G' and G'' , and τ_m , the reciprocal frequency at the maximum of the out-of-phase component of the complex viscosity $\eta'' = G''/\omega$, are also listed in Table I.

In Eq. (5), the measured shear relaxation modulus $G(t)$ is required. While for the high molecular weight samples $G(t)$ was obtained from stress relaxation measurements, for the lower molecular weight samples $G(t)$ was calculated using the spectrum obtained from oscillatory shear experiments. For the calculations we used the linear viscoelasticity theory to obtain a discrete relaxation spectrum $\{g_i, \tau_i\}$, which satisfies [Ferry (1980)]:

$$G'(\omega) = \sum_{i=1}^N g_i \frac{\omega^2 \tau_i^2}{1 + \omega^2 \tau_i^2}, \quad (8)$$

$$G''(\omega) = \sum_{i=1}^N g_i \frac{\omega \tau_i}{1 + \omega^2 \tau_i^2}, \quad (9)$$

and then the relaxation modulus and Newtonian viscosity can be obtained as

$$G(t) = \sum_{i=1}^N g_i \exp\left(-\frac{t}{\tau_i}\right), \quad (10)$$

$$\eta_0 = \sum_{i=1}^N g_i \tau_i. \quad (11)$$

IV. RESULTS AND DISCUSSION

A. Analysis of the results

Within the temperature range tested the time-temperature superposition principle was found to be applicable for all materials, as expected for linear homopolymers. The temperature dependence of the viscoelastic properties was shown to obey an Arrhenius-type of equation in the temperature range studied [Aguilar *et al.* (2001, 2003)]. The materials showed no signs of thermorheological complexity.

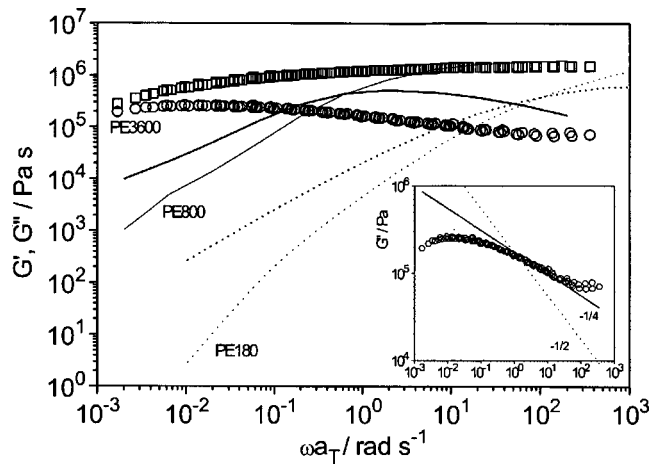


FIG. 1. Linear viscoelastic response in oscillatory shear of PE samples in Table I at a reference temperature of 190 °C (thin lines and \square for G' , and thick lines and \circ for G''). The inset of the figure shows the angular frequency dependence of G'' function for PE3600. The lines are power law relationships with $-1/4$ and $-1/2$ slopes.

Storage G' and loss G'' moduli of the NMWD metallocene PE samples, at a reference temperature of 190 °C, are given in Fig. 1. The overlapping of the data, obtained at different temperatures, was excellent. We observe in this figure the typical response in oscillatory shear of polymers with a linear structure and a relatively narrow molecular weight distribution; a sharp transition from the plateau region at high frequencies to the terminal region ($G' \propto \omega^2, G'' \propto \omega$) at low frequencies. Obviously this is not the case for the highest molecular weight, metallocene sample, PE3600, which shows a characteristic nearly plateau behavior for the whole experimental frequency range. It is also clearly observed that for this sample that the loss modulus G'' in the high-frequency zone shows a characteristic power law with an exponent close to $-1/4$, as is predicted by the Milner and McLeish's reptation-CLF theory (1998) for a sufficient entanglement concentration (see the inset of Fig. 1). Unfortunately the expected Rouse dependence (with exponent $-1/2$) between the maximum value of G'' and the $-1/4$ power law region it is not observable, probably due to polydispersity (constraint release phenomena) [Likhtman and McLeish (2002)].

For the PE3600, and for the commercial ZN-UHMWPE sample (PE4500), the experimental angular frequency range has been expanded using the stress relaxation data of $G(t)$ from which we calculate the Fourier transform $G^*(\omega)$. The combined shear oscillatory and stress relaxation data are given in Fig. 2. The differences we observe in the viscoelastic fingerprint of both materials are due to the different molecular weights and molecular weight distributions. The commercial sample, with the highest molecular weight and the broad molecular weight distribution, shows a wide viscoelastic response, extended to lower frequencies [$G'(\omega)$] and higher times [$G(t)$], reflecting a broad relaxation time spectrum. Both polymers show the same plateau region at high frequencies, as a consequence of the extreme large number of entanglements per molecule $N_e = M_w/M_e$. The experimental value of G_N^0 is 2 MPa. Using Eq. (6) with $K = 4/5$ a molecular weight between entanglements M_e of 1200 g mol $^{-1}$ at 190 °C ($\rho = 0.760$ g cm $^{-3}$) is obtained. This value is very close to those obtained for model PEs in other works [Carella *et al.* (1984), Fetters *et al.* (1994, 1999a), Lohse *et al.* (2002)].

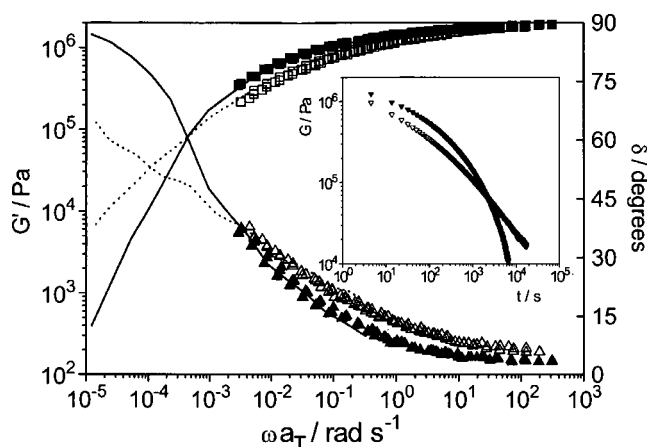


FIG. 2. Extended linear viscoelastic response (combination of oscillatory shear and stress relaxation) of UHMWPE samples at 190 °C. (■) G' and (▲) δ for PE3600 sample, and (□) G' and (△) δ for commercial PE4500 sample. The solid and dotted lines represent the calculated values of the corresponding viscoelastic functions from stress relaxation results at the same temperature: see in the inset of the figure: (▼) PE3600 and (▽) commercial PE4500.

It is also possible to study the characteristic parameters of the terminal region, at low frequencies, by applying Eq. (7). This gives the two characteristic parameters, η_0 and τ_0 , (see Table I). The results of the fitting procedure to $|\eta^*|$ values are also plotted in Fig. 3 for the metallocene samples only. Since the metallocene PE with the highest molecular weight does not show a noticeable leveling off of $|\eta^*|$ at low frequencies, we included the calculated $|\eta^*|$ values from the stress relaxation experiments in the fitting procedure [using Eq. (11) gives rise to similar results]. The effect of molecular weight is clearly observed in the low-frequency region, resulting in strong differences in the limiting η_0 values, and also in τ_0 (see Table I). The difference disappears at high frequencies, where the plateau region is approached.

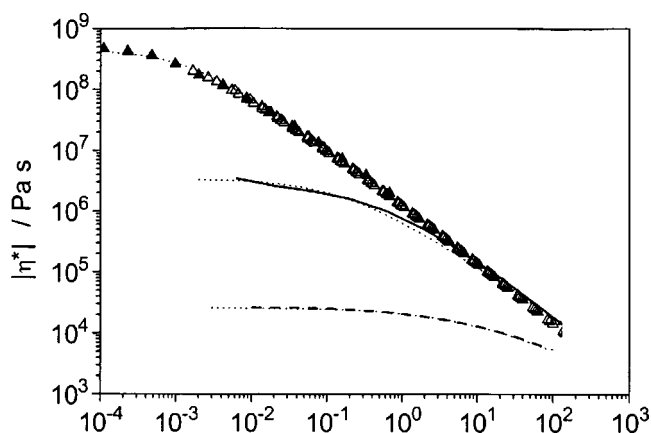


FIG. 3. Angular frequency dependence of the modulus of the complex viscosity of PE samples: (dashed line) PE180, (solid line) PE800, and (△) PE3600. The calculated data from stress relaxation (▲) are included for PE3600 sample. Dotted lines represent the data fit using Eq. (7)

TABLE III. Constants and results of the application of the model.

Material	^a $\langle R^2 \rangle / M \text{ \AA}^2$	^a $\rho / \text{g cm}^3$	G_N^0 / MPa	^b $M_e / \text{g mol}^{-1}$	^c $\zeta_0 / \text{kg s}$	^d $\zeta_0 / \text{kg s}$
PE	1.21	0.760	2.0	1200	1.3×10^{-12}	2.9×10^{-12}
PP	0.680	0.765	^a 0.45	5200	2.3×10^{-12}	8.2×10^{-12}
PS	0.434	0.969	^a 0.20	14900	0.7×10^{-9}	2.5×10^{-9}

^aFrom Fetters *et al.* (1994, 1999a).

^bCalculated from $M_e = 4\rho RT/5G_N^0$ at 190 °C.

^cBest fitting results to Eqs. (1)–(5).

^dLiterature results [Luettmer-Strahmann (2000); Pattamaprom and Larson (2001)]. Literature ζ_0 values of PP and PS are shifted to 190 °C from the reported temperatures using Williams–Landel–Ferry parameters [Eckstein *et al.* (1998); Schausberger *et al.* (1985)]

B. Modeling and discussion

To apply Eqs. (1)–(5) [with $\kappa = 1$; in fact we have seen that Eq. (1) is not very sensitive to the choice of κ] to the linear viscoelastic response we need to know the molecular weight distribution $\{w_i, M_i\}$, the weight average molecular weight between entanglements M_e , the monomeric friction coefficient ζ_0 , and the mean square end-to-end distance molecular weight ratio $\langle R^2 \rangle / M$, or, alternatively, the characteristic time for the relaxation of the chain segments between entanglements τ_e . All these parameters are available in the literature for a number of materials (see Table III) [Ferry (1980), Fetters *et al.* (1994, 1999), Pattamaprom *et al.* (2000), Pattamaprom and Larson (2001)]. However, to obtain reliable values for ζ_0 is not easy. The values available in the literature are determined from results in the transition zone and might not be very accurate for calculating a slow relaxation process [Larson *et al.* (2003)]. Therefore, we used the model described by Eqs. (1)–(5) in determining the friction coefficient ζ_0 (or τ_e) from the best fit to our experimental data.

For some of the NMWD samples the results of this procedure, in terms of the normalized relaxation modulus $G(t)/G_N^0$, are presented in Fig. 4. The data listed in Tables I,

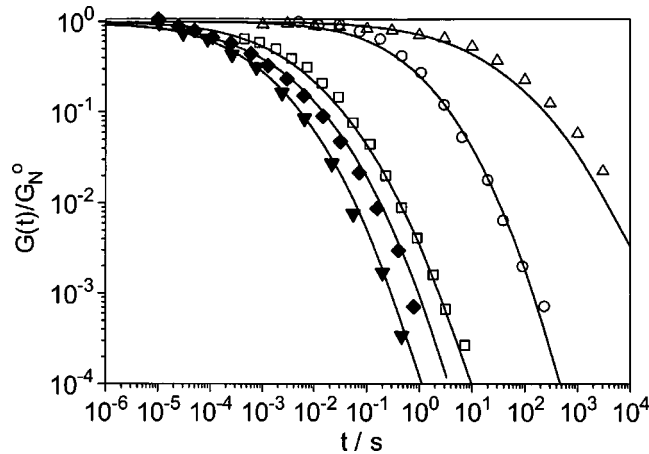


FIG. 4. Application of the reptation approach given by Eqs. (1)–(5) to the normalized viscoelastic relaxation of various polymers of different chemistry and polydispersity index around 2 at 190 °C. (□) PE180, (○) PE800, and (△) PE3600; (◆) PP180; and (▼) PS100. The solid lines represent the modeled response with fitted ζ_0 values.

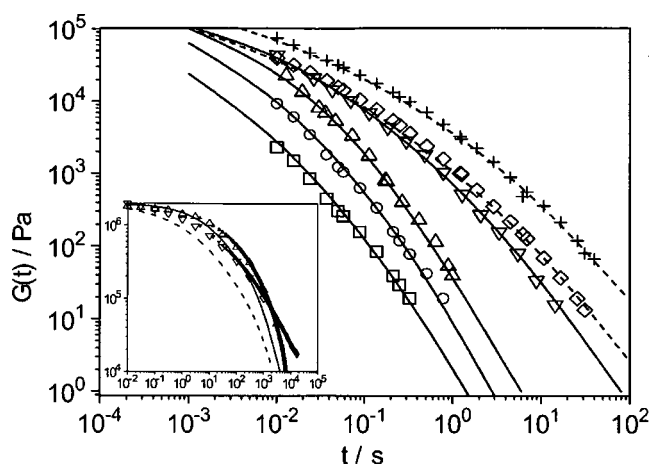


FIG. 5. Application of the reptation approach given by Eqs. (1)–(5) to the viscoelastic relaxation modulus at 190 °C of various isotactic PP samples: (\square) PP80, (\circ) PP130, (\triangle) PP180, (∇) PP250, (\diamond) PP350, (+) PP500. UHMWPE samples: (\triangle) PE3600 and (∇) commercial PE4500, are included in the inset of the figure: open symbols are converted results from oscillatory shear and closed symbols are results from stress relaxation. The values of ζ_0 in Eqs. (1)–(5) has been set at 2.3×10^{-12} kg s for PP and 1.3×10^{-12} kg s for PE as obtained from the fitting procedure, see also Fig. 4. The solid lines represent the calculated values for the samples with narrow molecular weight distribution ($\beta = 2$). Dashed lines represent the calculated values for the samples with a broad molecular weight distribution ($\beta = 2.4$).

II, and III were used for the fit. The ζ_0 values obtained in this way are, together with those gathered from the literature, listed in Table III. The values are of the same order of magnitude but our results are lower than the literature data which were obtained by applying similar models [Pattamaprom *et al.* (2000), Pattamaprom and Larson (2001)]. It can be demonstrated that this discrepancy is due to a different definition of M_e . Recently, it has been shown that these papers contained some errors concerning the prefactor $K = 4/5$ in Eq. (6) [Larson *et al.* (2003)].

Notice that the model does not seem to match the results for PE3600, the metallocene UHMWPE with the broadest MWD, as good as for the others. It underpredicts the experimental data in this specific case. A variation in τ_e (and thus in ζ_0) has been found for certain polymers when the molecular weight range studied is very broad. However, in principle τ_e must be held constant for varying molecular weight or molecular weight distribution in well-entangled polymer melts.

To further explore the possibilities of the model and to strengthen the results obtained for ζ_0 , at least in the usual range of M_w , we applied Eqs. (1)–(5) to a series of PP samples with M_w ranging from 8×10^4 to 5×10^5 and polydispersity indices from 2.0 to 6.0, and to a commercial ZN-UHMWPE sample ($M_w = 4.5 \times 10^6$ g mol $^{-1}$ and $M_w/M_n = 10$). We used the values of ζ_0 obtained from our fitting procedure (see Table III). Figure 5 shows an excellent agreement between the calculated and experimental results for the PP samples with different molecular weight and polydispersity indexes lower than 3.4, but poor agreement for the UHMWPE samples. For the PPs with a broader molecular weight distribution it was necessary to allow the DR exponent β in Eq. (5) to vary. Using a value of $\beta = 2.4$ instead of $\beta = 2$ the calculated values nicely fit the experimental results for these polydisperse PP samples. Also in other works a slightly more rapid relaxation modeled with values of $\beta = 2.25$ – 3.84 was required for better fitting experimental results when applying reptation models [Groves *et al.* (1996), Maier

et al. (1998), Thimm *et al.* (1999), van Ruymbeke *et al.* (2002)]. Maier *et al.* (1998) suggested that a large exponent might be due to transition modes in the relaxation spectrum, especially in samples whose molecular weight is closer to the critical value for the onset of the entanglements effect. Other authors justified this higher value of β by the presence of entanglements involving more than two chains [van Ruymbeke *et al.* (2002)]. Also the early tube enlargement models, as proposed for linear polydisperse polymers by Marrucci (1985) and for star-branched polymers by Ball and McLeish (1989), assume a slightly faster relaxation. More recently the “dual constraint release” model [Pattamaprom *et al.* (2000), Pattamaprom and Larson (2001)] has been developed. Besides DR, this model also accounts for another mechanism; the dynamic dilution or tube dilation, i.e., the reduced effectiveness, or loosening, of the entanglement network due to the widening of the tube. More general views tried to incorporate constraint release Rouse mechanisms, which are especially important in the case of diluted chain systems with very high relaxation times in a matrix of shorter chains [Milner (1996)]. In contrast, Thimm *et al.* (2000) considered a decomposed relaxation spectrum in a model evoking both Rouse processes and an entanglement regime, to explain values of β higher than 2. Applying a procedure that separates Rouse processes, these authors reported β values consistent with the DR theory ($\beta = 2$).

The applied model seems to be able to describe the viscoelastic response of materials with a different chemistry in a broad range of molecular weights and limited molecular weight distributions without any adjustable parameter. Only for the broad distributions a slightly faster relaxation has to be taken into account. To explain this, a more complete picture of the model has to be developed, but this is not the aim of this work.

The question that arises now is why the model does not describe the experimental results of the commercial, polydisperse UHMWPE samples; see the inset in Fig. 5, where we included the total experimental relaxation spectrum resulting from the combination of stress relaxation and oscillatory shear measurements. Even when applying the enhanced constraint release (exponent $\beta > 2$) which is active in these high molecular weight materials [Watanabe (1999)], the results are unsatisfactory. The key arguments of reptation models are deduced from experimental observations on many different materials: (i) above a critical molecular weight, M_c , the viscosity (or the relaxation time) increases approximately with $M_w^{3,4}$; (ii) at high molecular weights the rheological response of the polymers exhibits an elastic modulus G_N^0 nearly independent of frequency that defines the entangled state by means of a critical molecular weight between entanglements M_e ; and (iii) $M_c = 2M_e$ for all amorphous melts independently of their chemistry. If all these statements are true, the viscoelastic fingerprint of linear polymers should be universal for a constant number of entanglements per chain N_e , and for a given relaxation time (molecular weight) distribution [McLeish and Milner (1999)]. For monodisperse linear polymers Raju and co-workers (1981) demonstrated this fact experimentally years ago. However, it is worthwhile to explore these statements for our narrow molecular weight, but still polydisperse, samples. From the relaxation time values for the metallocene PE samples listed in Table I, it can be seen that their ratio is approximately constant ($\tau_m \sim 1.5\tau_0 \sim 4\tau_x$), similar as for other single-site metallocene PE and PP samples in the conventional molecular weight range [Vega *et al.* (2003)]. This is direct evidence for the similarity of the relaxation time distribution. Then, the shape of the relaxation modulus in the terminal zone is the same, and one can use the values of the relaxation times for testing their molecular weight dependence. We have selected τ_0 , as one can easily find values of this parameter in the literature for metallocene samples with a polydispersity index of 2 (for which the same relationship between the different relaxation times holds).

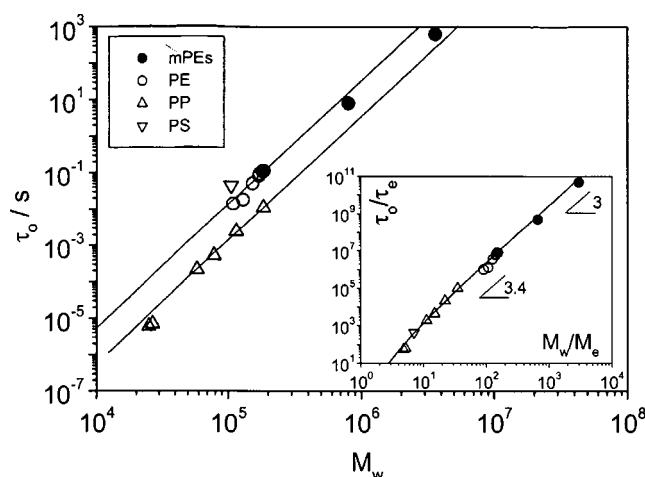


FIG. 6. Molecular weight dependence of the relaxation time obtained from the Cross model fit, Eq. (7) for (●) PE samples in Table I. Values from the literature have been included for (●) PE, (Δ) PP [Aguilar *et al.* (2001, 2003)] and for (∇) PS sample studied here at 190 °C. The inset of the figure shows the normalized relaxation time vs the number of entanglements (the line has been drawn to guide the eye).

Figure 6 shows the molecular weight dependence of this viscoelastic property for the mPEs and the PS sample studied here; all with a polydispersity index around 2. Literature results obtained for PE [Aguilar *et al.* (2001)] and PP [Aguilar *et al.* (2003)] are included.

The results for the very high molecular weight PE samples deviate from the 3.4-power law correlation for very high molecular weights. This result is in agreement with the behavior predicted by the reptation and CLF theory for very long molecular species [Milner and McLeish (1997, 1998), Watanabe (1999)]. The effect of temperature in the relaxation times is mainly present through the ratio ζ_0/T in τ_e given by Eq. (3). The universal relaxation behavior for species of similar molecular weight distributions is demonstrated at least in the 3.4-exponent zone; by dividing τ_0 by the corresponding value of τ_e , calculated from the results in Table III (see the inset of Fig. 6). The reduced τ_0 only depends on the number of entanglements $N_e = M_w/M_e$, at least within the CLF region. The crossover point between the two different regimes seems to occur around $M_w/M_e = 100$ – 200 [Milner and McLeish (1998), Watanabe (1999)]. The solid line in the figure has been drawn only to guide the eye (it is not a result of applying the model tested in this work).

Next we consider the linear correlation between the relaxation time and the Newtonian viscosity, envisaged in a linear viscoelastic model with a single exponential relaxation for the relaxation modulus $G(t)$ in the terminal zone [Bird *et al.* (1987)]. From this, it is easily demonstrated that the correlation between relaxation time and molecular weight also holds for the Newtonian viscosity. The results, in terms of reduced viscosity and reduced molecular weight, are depicted in Fig. 7. This figure also includes the results obtained for a model monodisperse PE or hydrogenated polybutadiene, (HPB) [Pearson *et al.* (1994)], 1,4-polybutadiene (1,4-PBd) [Colby *et al.* (1987)], polyisobutylene (PIB) [Fetters *et al.* (1991)] and PS [Montfort *et al.* (1984)]. In this case we have used the M_c values from the work of Fetter and co-workers (1999b) as scaling parameters to get the reduced molecular weight. The reduced viscosity is obtained by dividing η_0 with the value of the viscosity at the critical molecular weight M_c , as obtained from the experimental $\eta_0 - M_w^{3.4}$ relationships of each material [Pearson *et al.* (1994), Colby *et al.*

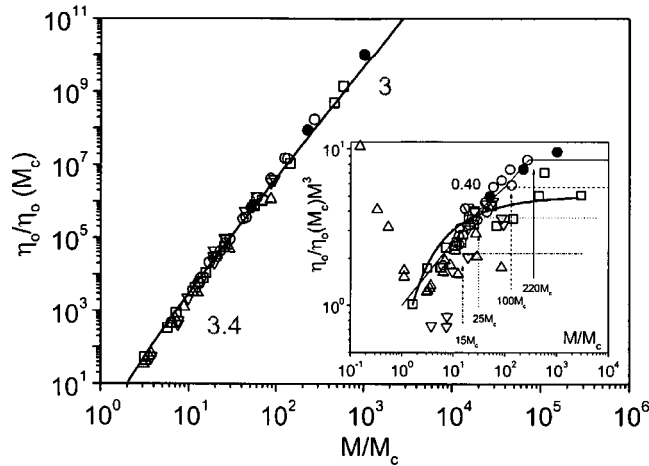


FIG. 7. Reduced plot of Newtonian viscosity vs molecular weight for different materials; (●) PE in Table I, and (○) HPB, (□) 1,4-PBd, (▽) PIB, (△) PS from the literature. The inset of the figure shows the reduced η_0/M^3 values of the same materials. The thick solid lines represent the predicted behavior by Eqs. (1)–(5) using the parameters in Table II. The thin lines in the inset figure represent the behavior expected for the reptation regime from scaling concepts Fetters *et al.* (1999b).

(1987), Fetters *et al.* (1991), Montfort *et al.* (1984), Majeste *et al.* (1998)]. The results in this figure apparently verify the universality of the linear viscoelastic response at least in the 3.4-power law region. Moreover, the crossover from this power law region to the classical reptation region with exponent of 3.0 is observed for the molecular weights higher than $M_w/M_c \sim 50$ –100.

To make the results more clear we show the reduced η_0 values of the samples divided by M^3 in the insert of Fig. 7. Most of the dependence on the molecular weight is removed in this way, and we can observe the departure from the nominal 3.4 dependence at high molecular weights more easily. The solid line in the figure gives the dependence with 0.4-power law; it represents the contribution of the additional CLF mechanisms to reptation in the usual molecular weight range. However, it is observed that the value of the *reduced* molecular weight at the onset of the pure reptational regime M_r/M_c , seems to be different for each molecular species. To our knowledge experimental values of M_r are only available for two materials, 1,4-PBd ($M_r \sim 100M_c \sim 600\,000$) [Colby *et al.* (1987), Fetters *et al.* (1999b)] and PIB ($M_r \sim 25M_c \sim 450\,000$) (Fetters *et al.* (1991, 1999b)]. For PS is difficult to ascertain a value of M_r , but a rough estimation leads to $M_r \sim 15M_c \sim 480\,000$ using experimental values of η_0 obtained by Montfort and co-workers (1984). The value obtained for PE is close to $M_r \sim 220M_c \sim 800\,000$. Both values are very close to the recently proposed values for PS and PE by Fetters and co-workers (1999b) using scaling concepts.

The reduced η_0 and η_0/M^3 theoretical values have also been obtained using Eqs. (1)–(5). The results are also plotted in Fig. 7. Apparently, the model captures the reduced η_0 function rather well, but as seen from a detailed analysis, fails to predict the experimental M_r/M_c values. It only describes in average the observed tendencies; it is a universal model that only depends on the number of entanglements, M_w/M_e .

At this point, we have to notice that, in the case of PS from Montfort and co-workers (1984) and for the metallocene PE samples studied here, polydispersity should have an effect in this very high molecular weight zone, causing the behavior observed. In fact, the

results obtained by Schausberger *et al.* (1985) for monodisperse PS samples exhibit no crossover, even though the molecular weight range extends up to $2.5 \times 10^6 \text{ g mol}^{-1}$. But then, the difference found between PS and PE samples would indicate that the effect of polydispersity is not the same for both polymers (higher M_r/M_c values in PE and lower M_r/M_c values in PS). The clear trend in M_r/M_c values found in this work for the four different polymers suggests the possibility of an effect of molecular chemistry (if we accept no effect of polydispersity) on the crossover between the contour length fluctuations and the pure reptation regimes. Obviously it is desirable to test this possibility with monodisperse samples, but, at least in the case of PE, this turns out to be problematic. To obtain monodisperse samples requires hydrogenation of HPB or fractionation of polydisperse samples. With the first method it is not possible to get completely linear PE species [Lohse and co-workers (2002)], and it could also have limitations in the molecular weight range achievable. With respect to the second one, we think that it is still a challenge to separate the very high molecular species required for this study.

Fetters and co-workers (1999b) studied the scaling relationship between M_r , M_c , and M_e for several materials and they concluded that statement (iii) ($M_c = 2M_e$) is not universal. This means that M_e alone cannot define the entanglement state of polymeric systems. The results obtained here show basically that the range of M_w for which the CLF mechanism holds, depends on polymer chemistry. The results in Figs. 4, 5, and 7 point towards the observation that this range of molecular weight is especially broad for PE, likely due to the high chain flexibility and a higher chain end mobility when compared to other stiffer polymer chains like PS. This would also explain the different values of τ_e found in the literature when models are applied to a specific material in the broad molecular weight range [Pattamaprom *et al.* (2000)]. In the same way, the recent theoretical framework for linear monodisperse polymers of Likhtman and McLeish (2002) applied to experimental values, shows that it is not possible to explain the behavior of different materials without important considerations with respect to the definition of the entangled state. This implies independent M_e and G_N^0 values, but in this way the relationship between M_e and G_N^0 given in Eq. (6) is lost.

The materials studied differ in the so-called packing length p that varies from 1.79 Å in PE to 3.99 Å in PS [Fetters *et al.* (1994, 1999a, 1999b)]. The different values in p are thought to cause different nonuniversal M_r/M_c and M_c/M_e relationships. Figure 8 shows the relation between the M_r/M_c ratio and p for the materials studied here. It is clear from this figure that as p increases the range of molecular weight within which CLF affects reptation becomes narrower. This fact, as Fetters and co-workers (1999b) pointed out, has great implications on models based on reptation. The model does actually not capture this specific feature.

As a final remark we want to emphasize the strong effects of chain end dynamics on the viscoelastic relaxation of polymer melts. Recent numerical results by Carlon *et al.* (2002) have shown a decreasing exponent in the correlation $\tau_d \sim (M/M_e)^z$ when chain “end-reptons” dynamics is hindered. The numerical results suggest, in case of this hindered dynamics, also increasing values for the characteristic molecular weight between entanglements given by M_e . The authors propose that modified chain end dynamics can be attained for example by attaching branches or molecules with a large size to the chain ends, or by modifying the chain ends so that they are stiffer than the rest of the chain. All these molecular architectures are expected to affect the tube renewal process by the CLF mechanism. In this context recent experimental work at our university on metallocene UHMWPE is of special interest. For a highly disentangled UHMWPE, which can be obtained by controlled synthesis, i.e., using single-site catalyst, the resulting melt state

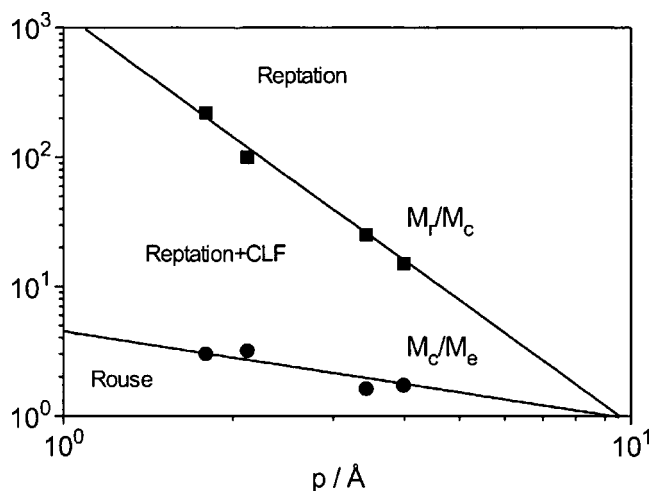


FIG. 8. Characteristic reduced molecular weight values for (●) the entangled CLF reptation and (■) the pure reptation regimes as a function of the packing length p of various polymers. Data of p are from Fetters *et al.* (1999b).

strongly depends on the kinetics involved in the melting process. By controlling the thermal history, pronounced differences in the rheological properties can be generated; it is stated that heterogeneous melt states are formed with inhomogeneous distribution of topological constraints—leading to a distribution of more entangled and less entangled (disentangled) domains. It is suggested that in this “new melt” the chain end dynamics is hindered due to the entanglement domains, which gives lower values of the relaxation exponent z and higher values of M_e , similarly to the numerical results obtained on polymeric systems with hindered chain ends by Carlon *et al.* (2002).

V. CONCLUSIONS

Metallocene ultrahigh molecular weight polyethylene shows a well-developed plateau modulus that approaches to 2 MPa. This value gives a molecular weight between entanglements of 1200 g mol^{-1} , using the reptation concept of Doi and Edwards (1986). The reptation model, using this characteristic value of M_e together with the main features of a random coil at equilibrium, seems to be able to predict the viscoelastic response of the polymers, but only in the contour length fluctuation regime. The theoretical number of entanglements required for the crossover to pure reptation behavior is approximately $M_r/M_c = 100$. However, the model gives a kind of average for all materials studied here that have experimental characteristic ratios of M_r/M_c between 15 and 220. Viscosity results show that the molecular weight for the onset of pure reptation for PE takes a value of around $M_r = 800\,000$, much higher than in 1,4-PBd, PIB, and PS. This is in agreement with recent calculated values from scaling and packing length concepts. New theoretical developments are therefore necessary. These should most likely be related to the chemical composition.

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