

Stress relaxation in the nonequilibrium state of a polymer melt.

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Stress relaxation in the nonequilibrium state of a polymer melt

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Synopsis

The influence of entanglement density on the constraint renewal time is studied experimentally in transitory nonequilibrium polymer melts. The entanglement density, as quantified by the rubber elasticity, increases as the linear polymer melt transforms into the equilibrium state. The relaxation modulus obtained from linear step-strain deformations, performed at different points during the equilibration, shows an increase in constraint renewal time as the entanglement density increases. The normalized relaxation modulus curves collapse onto a single curve by rescaling the time axis with a factor $\overline{G}'(t)^{0.9}$ (where $\overline{G}'(t)$ is the normalized instantaneous modulus). These findings suggest that, though the relaxation time increases with the increasing number of entanglements, the mechanism responsible for stress relaxation, after application of step-strain, is similar to that in a fully entangled melt. © 2014 The Society of Rheology.
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I. INTRODUCTION

Temporary polymer melt states with lower entanglement density compared to equilibrium are commonly found in spin-cast polymer films [Barbero and Steiner (2009); Raegen *et al.* (2010)], polymers freeze-dried from solution [Liu and Morawetz (1988)], and semicrystalline polymers with reduced entanglement density in their amorphous

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regions [Rastogi *et al.* (2005)]. These transitory nonequilibrium states are identified by their lower resistance to mechanical deformation compared to the equilibrium state. Their resistance increases during the equilibration process until the melt reaches the fully entangled state. The time required for the melt to reach equilibrium exceeds by at least one order of magnitude the equilibrium constraint renewal time. This observation raises the question: How is the chain constraint renewal process influenced by nonequilibrium entanglement distributions? Usually, changes in the nonequilibrium melt state are followed by measuring the evolution in time of either rubber elasticity, G' , or viscosity, η . However, neither of these quantities alone are able to explore the constraint renewal process. Rubber elasticity on one hand is measured at frequencies in the so called plateau region and thus contains little information about reptation [Doi and Edwards (1986); de Gennes (1971)]. On the other hand, zero shear viscosity is, at equilibrium, given by $\eta_0 = 0.822G_N\tau_d$, where G_N is the equilibrium plateau modulus and τ_d is the longest relaxation time [Dealy and Larson (2006)]. Thus it might be expected that, also in nonequilibrium conditions, η_0 contains combined information on both elasticity and relaxation dynamics.

To recall, with the help of controlled synthesis, it is feasible to synthesize linear polyethylenes having more than 10^5 methylene units. On crystallization from dilute solution, these units tend to fold back and forth within platelet-like crystals having a thickness of approximately 12 nm [Keller (1957); Fisher (1957); Flory and Yoon (1978)]. The nature of folding, either adjacent or nonadjacent re-entry, and the sharing of methylene segments with the neighboring crystals both influence the formation of entanglements in the amorphous region of the semicrystalline polymer [Sadler and Keller (1977)]. The resulting polymers have a heterogeneous distribution of entanglements located in the amorphous regions between crystals and on melting the semicrystalline material, a nonequilibrium melt state is obtained, which has a higher average molar mass between entanglements and tends to reach the equilibrium state with time. The time required for the transition from the nonequilibrium to the equilibrium melt depends on the entangled state in the amorphous region and the chain length [Lippits *et al.* (2006); Pandey *et al.* (2011)]. It is now feasible to tailor the entanglement conditions and molar mass directly by crystallization during synthesis, instead of crystallization from dilute solution. On melting of these “disentangled” crystals, the resulting nonequilibrium melt state can be observed for several hours [Rastogi *et al.* (2005)]. This provides the opportunity in terms of experimental time to apply conventional linear rheological techniques to study the average chain dynamics in nonequilibrium conditions. The equilibration process of a nonequilibrium ultra-high molecular weight polyethylene (UHMWPE) melt is characterized by the monotonic increase of its rubber elasticity in time (modulus build-up). The modulus build-up is associated with entanglement formation as chains reconfigure to increase the melt entropy. The elastic modulus, measured at a frequency in the plateau region, increases until it reaches its value at equilibrium G_N , mathematically described as [Doi and Edwards (1986)]

$$G_N = \frac{4}{5} \frac{\rho k_B T}{M_e}. \quad (1)$$

Here, ρ is the melt density, T is the absolute temperature, k_B is the Boltzmann constant, and M_e is the molar mass between entanglements. The time required to complete the modulus build-up depends on the weight-average molecular weight M_w following the relationship $M_w^{2.6}$ [Pandey *et al.* (2011)]. Thus, UHMWPE melts having M_w greater than

2.3×10^6 g/mol take a long time to equilibrate, providing the opportunity to study the influence of physical chain interaction via entanglements in the constraint renewal process compared to the equilibrium melt state.

In this paper, we address these long lasting nonequilibrium melt states by means of linear step-strain rheology. After applying a sudden deformation, the continuous decrease in stress is related to the escape of chains from their initial constraint, thus renewing their surroundings. Hence, such experiments provide information on changes in the chain constraint renewal process as the melt traverses from the nonequilibrium to the thermodynamic equilibrium state. The nonequilibrium polymer melt state is obtained on melting of semicrystalline UHMWPE having the reduced number of entanglements in the amorphous phase.

II. EXPERIMENTAL

A. Materials

All polymers used in these studies are synthesized in our laboratory using a Bis-Phenoxyimine titanium (IV) catalyst activated by Methylaluminoxane. Reaction conditions are controlled in order to synthesize UHMWPE crystals with a lower number of entanglements. Reaction time is varied to tailor differences in molar mass and entangled state of the crystals. A more detailed description of the polymer synthesis and molar mass determination by means of linear rheology can be found elsewhere [[Romano *et al.* \(2013\)](#); [Talebi *et al.* \(2010\)](#)].

B. Rheological characterization

In order to perform the rheological characterization, polymers are sintered by compression molding into disks with a thickness of approximately 0.8 mm. Sintering is carried out at a constant temperature of 125 °C for 20 min using an average force of 20 tons.

All rheological measurements are performed in a TA Instruments, strain controlled rheometer (ARES LS2) using a 12 mm parallel plates geometry. During measurements, polymers are kept in the nitrogen atmosphere provided by a convection oven. The polymer is taken to the melt state by increasing the temperature at a constant rate of 10 °C/min from 130 to 160 °C, about 20 °C above the equilibrium melting temperature of polyethylene. All further characterizations are performed at a constant temperature of 160 °C. Oscillatory time experiments were carried out at a frequency of 10 rad/s, which is within the frequency plateau region even out of equilibrium as shown below. Both these tests and oscillatory frequency sweeps are performed in the linear viscoelastic regime, using 0.5% strain.

III. RESULTS AND DISCUSSION

The linear elastic modulus G' at fixed frequency (10 rad/s) is measured as a function of time, starting 90 s after the experimental temperature is reached. Figure 1(a) shows the modulus build-up of two different UHMWPE samples after melting. In agreement with previous work [[Rastogi *et al.* \(2005\)](#); [Lippits *et al.* \(2006\)](#); [Pandey *et al.* \(2011\)](#)], the difference between the initial values of G' is related to the entanglement density of the nascent polymer. The lower modulus refers to the lower entanglement density. Additionally, the modulus build-up time suggests significant differences in molar mass of the two

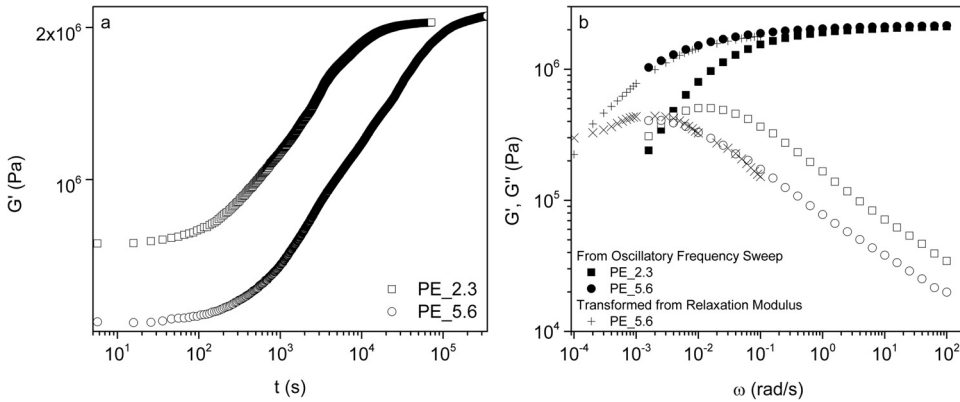


FIG. 1. (a) Build-up of elastic modulus G' of UHMWPE polymers PE_2.3 and PE_5.6 with respective molecular weights of 2.3×10^6 and 5.6×10^6 g/mol. (b) Oscillatory frequency sweeps performed in the equilibrium melt state of PE_2.3 and PE_5.6. Filled symbols refer to elastic modulus G' while the unfilled symbols denote loss modulus G'' . To extend the frequency regime, crossed symbols are values obtained on transformation of the relaxation modulus (obtained with a step-strain test at equilibrium) to the frequency domain.

samples. To recall, the modulus build-up rescales with the weight-average molar mass as $M_w^{2.6}$. In order to estimate the molar mass distribution of the polymers, dynamic oscillatory frequency sweep and step-strain tests are performed in the linear regime, after the polymer has reached its equilibrium state. The relaxation modulus $G(t)$ obtained from step-strain experiments is Fourier transformed to obtain the elastic G' and viscous G'' moduli. More details on the transformation of $G(t)$ are given in further discussion. The viscoelastic functions (G' and G''), obtained by combining these tests, correspond to linear polymers with relaxation times τ_d around 300 and 5000 s, Fig. 1(b). The times are calculated as the reciprocal of the G'/G'' cross over frequency. A longer relaxation time refers to higher weight-average molar mass, M_w . To estimate the molar mass distribution from the relaxation moduli, we used the inversion method developed by Mead (1994), as implemented in the TA ORCHESTRATOR software. We assumed a unimodal Schulz distribution in combination with the double reptation mixing rule and the following parameters for the calculation: $G_N = 2.0 \times 10^6$ Pa; relaxation time exponent = 3.4, and $M_e = 1900$ g/mol. These parameters have been used successfully in earlier work for the same purpose in UHMWPEs having a similar range of molar masses [Talebi *et al.* (2010)]. The exact value of M_e for polyethylene at equilibrium has been disputed in literature, with values ranging from 800 to 2400 g/mol [Fetters *et al.* (1994); Litvinov *et al.* (2013)]. Here, we use 1900 g/mol as an average value for estimations of molar mass (distribution) and Rouse times. Using Mead's method, molar masses of the polymers are estimated to be 2.3×10^6 and 5.6×10^6 g/mol with polydispersities M_w/M_n of 2.0 and 3.0, respectively. Hereafter, the two polymers will be referred as PE_2.3 and PE_5.6. Table I summarizes the material properties and fitting parameters that are used in the discussion of this work.

As mentioned above, Eq. (1) establishes a proportionality between the plateau modulus and the entanglement density in the melt, which is strictly valid only under equilibrium conditions, where the polymer chains are modeled as Gaussian walks. We will assume that this proportionality still holds in the nonequilibrium melt state as proposed by Teng *et al.* (2012). This assumption is needed to follow the kinetics of entanglement formation. If the increase rate of G' is supposed to be proportional to the difference ($G_N - G(t)$), the elastic modulus will increase following

TABLE I. Material properties and fitting parameters of the polymers investigated in this work.

Polymer	M_w^a ($\times 10^6$ g/mol)	M_w/M_n^a	τ_R^a (s)	τ_{max}^b (s)	$G'_1{}^c$	$G'_2{}^c$	$\tau_{m1}{}^c$ (s)	$\tau_{m2}{}^c$ (s)
PE_2.3	2.3	2.0	0.08	400	0.55	0.1	5300	36 000
PE_5.6	5.6	3.0	0.8	5100	0.49	0.3	6000	56 500

^aDetermined by linear rheology.

^bFrom fit of equilibrium stress relaxation [Eq. (3)].

^cFrom fit of the build-up curves [Eq. (2)].

$$G'(t) = G_N - \sum_{i=1}^N G'_i \exp(-t/\tau_{mi}), \quad (2)$$

where G'_i is the increment in elasticity corresponding to the relaxation mode with characteristic time τ_{mi} . Two modes are necessary to fit the curves in Fig. 1(a), corresponding to the two build-up regimes previously defined for similar UHMWPE materials [Pandey *et al.* (2011)]. The fitting values are $\tau_{m1} = 5300$ s, $\tau_{m2} = 36\,000$ s, $G'_1 = 0.55 * G_N$, and $G'_2 = 0.1 * G_N$ for PE_2.3 and $\tau_{m1} = 6000$ s, $\tau_{m2} = 56\,500$ s, $G'_1 = 0.49 * G_N$, and $G'_2 = 0.3 * G_N$ for PE_5.6. The first regime (τ_{m1}) at short times is related to the fast segmental dynamics of the chains during the initial entropic mixing process. A second regime (τ_{m2}) at longer times relates to chain diffusion. [Supplementary Material](#) shows build-up curves and corresponding fitting parameters from Eq. (2) for polymers having a wider range of M_w . The large total equilibration time of these systems is also a characteristic of other transitory nonequilibrium melt states [Barbero and Steiner (2009); Raegen *et al.* (2010)].

The linear rheology of entangled polymer melts is successfully described by modeling the interaction among chains as a mean field approximation represented by a tube formed by entanglements among each chain and its neighbors [Doi and Edwards (1986); de Gennes (1971)]. Fast Rouse motion occurs within chain segments corresponding to the average distance between consecutive entanglements (or tube diameter) with characteristic time $\tau_e = \tau_R/Z^2$. Here, τ_R is the Rouse time of the full chain and $Z = M_w/M_e$ represents the average number of entanglements per chain. At longer times, the movement of chains in the perpendicular direction to the tube is hindered by entanglements. After a small deformation, one fifth of the total stress stored in the tube relaxes within time τ_R by longitudinal Rouse dynamics involving the whole chain [Likhtman and McLeish (2002)]. Afterward, the remaining stress relaxes by reptation-like movement of the chain along the one-dimensional tube axis. This slower relaxation process has a characteristic time $\tau_d = 3Z \cdot \tau_R$. In this picture, topological constraints are responsible for the plateau region, where the melt response is predominantly elastic, Fig. 1(b). G' shows a well-defined plateau over a broad frequency range, of which the absolute value is related to M_e , thus to the entanglement density, Eq. (1). These concepts are valid for melts at thermodynamic equilibrium, where the average number of entanglements is constant, thus the viscoelastic response of the melt is time independent. During the equilibration process of a nonequilibrium UHMWPE melt, the modulus build-up shows that viscoelasticity of the melt changes continuously in time, and during this process chain dynamics at different scales might be influenced by the creation of new entanglements. In order to study possible changes in chain dynamics during the equilibration process, frequency sweep linear oscillatory tests in a range around the Rouse frequency of the melt are performed. The Rouse frequency corresponds to the reciprocal value of the Rouse relaxation time τ_R . For

polyethylene melts with M_w of 2.3×10^6 and 5.6×10^6 g/mol, assuming $M_e = 1900$ g/mol, τ_R values of 0.08 and 0.8 s, respectively, are estimated. Other estimations are shown in [Supplementary Material](#), where molar mass determination is performed assuming pure reptation process ($\tau_d \sim M_w^3$) with lower values of M_e and equilibration time $\tau_e = 1.2 \times 10^{-8}$ s. The value of τ_e was extrapolated from an estimation done at 190°C [[Pattamapron and Larson \(2001\)](#)] by using the Arrhenius model and assuming a flow activation energy of 26 kJ/mol [[Ngai and Plazek \(1985\)](#)]. Pure reptation might be assumed due to the large molar mass of the polyethylene melts studied here [[Milner and McLiesh \(1998\)](#)]. Values of the Rouse time shown there differ by a factor of at most 2.4. This uncertainty in τ_R is acceptable considering the purpose of estimating a Rouse time for our melts is only to establish a range of frequencies where the associated dynamics might have an important contribution to the linear viscoelastic response. Data collection for each frequency sweep took 60 s. Considering a total modulus build-up time larger than 10^4 s, changes in the properties of the melt can be considered negligible during each frequency sweep. Experiments were performed at intervals during equilibration, while in between these experiments a time sweep was carried out to follow the modulus build-up. A well-defined plateau for G' is found during the modulus build-up, with absolute values larger than the viscous modulus G'' by at least one order of magnitude. This difference in the viscoelastic response is observed in the damping factor $\tan(\delta)$, which is defined as the ratio G''/G' , Fig. 2. As evident from the decrease in $\tan(\delta)$, it is clear that during the equilibration process G' increases at a higher rate than G'' . Therefore, with entanglement formation, the plateau region shows a slight decrease in energy dissipation in favor of energy storage, indicating a clear influence of the entanglement formation on chain dynamics. In the case of an entangled melt at equilibrium, this region contains both longitudinal Rouse motion (at chain length scales) and reptation dynamics. The changes in $\tan(\delta)$ are especially evident at frequencies larger than the Rouse frequency, suggesting that this observation is more likely related to a decrease in the contribution to dissipation by longitudinal Rouse motion. In a nonequilibrium melt having a heterogeneous distribution of entanglement lengths, longitudinal Rouse motion might be aided by the increased disparity in M_e . When the melt reaches equilibrium, the distribution of entanglements is expected to become more homogeneous and chain dynamics no longer change in time.

In Fig. 2, the presence of a plateau suggests the existence of constraints even in the nonequilibrium polymer melt. Thus, similar to the melt at equilibrium, the relaxation

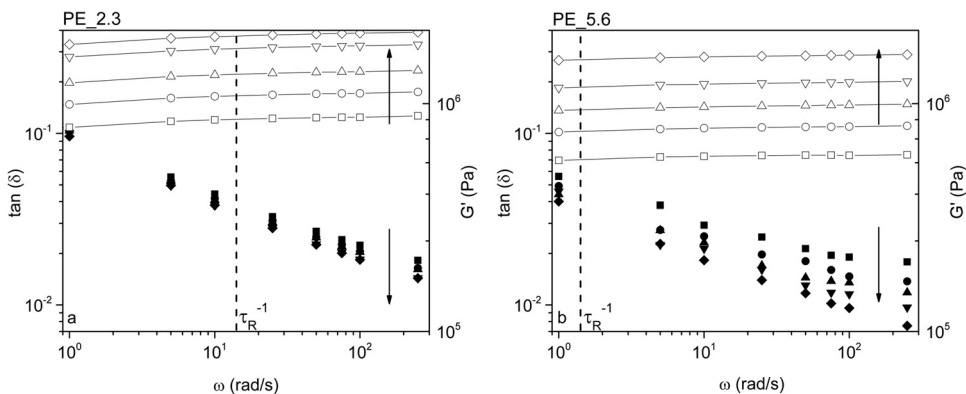


FIG. 2. Damping factor $\tan(\delta)$ (filled symbols) and elastic modulus G' (unfilled symbols) over a frequency range of 1–250 rad/s for UHMWPE polymers PE_2.3 and PE_5.6. Direction of the arrows refer to increasing time in the melt state and the dotted line indicates the Rouse frequency at equilibrium.

process will occur not only via Rouse dynamics but also via reptation-like movement. In order to study the relaxation process at longer times and have access to the relaxation process related to chain constraint renewal (close to the G'/G'' cross over), step-strain experiments are performed. In these experiments, a shear deformation is suddenly applied while keeping the small strain γ_0 constant during measurement of the stress σ . In order to discard problems due to slip or nonlinear response of the melt, step-strain experiments are performed using different strains in a range between 0.5% and 2.0%. As anticipated in the linear viscoelastic region, the relaxation modulus $G(t) = \sigma/\gamma_0$ shows no dependence on the applied strain. For both PE_2.3 and PE_5.6, the step-strain experiments are performed at different values of G' during the modulus build-up. In Fig. 3, the relaxation modulus $G(t)$ for both polymers shows a plateau at short times corresponding to the rubber plateau observed over frequency in G' , Fig. 2. In Fig. 3, the initial values of $G(t)$, e.g., 1.2 and 1.6 MPa in the case of PE_2.3, are related to the entanglement density at the beginning of the deformation. $G(t)$ decreases monotonically with time as the initial stress relaxes. The modulus is followed in time until its value has decreased by 90% of the initial value. Since entanglements in the nonequilibrium melt are able to constrain chains, stress relaxation requires chains to escape constraints, thereby renewing configurations by losing memory of the deformation imposed by the step-strain. In agreement to the results shown in Fig. 2, the renewal process might take place by chain reptation in a similar way as it would occur in the equilibrium melt, with the difference that, as chains in the nonequilibrium melt reptate, they might find themselves in a new environment with a larger number of entanglements.

In Fig. 3, beside the changes in the plateau modulus, the relaxation process is also affected. The higher the elastic modulus at the start of the experiment, the slower is the stress relaxation. This is more evident when the relaxation modulus is fitted using a discrete multimode version of the Maxwell model given in Eq. (3) [Ferry (1980)]

$$G(t) = \sum_{i=1}^N G_i \exp(-t/\tau_i). \quad (3)$$

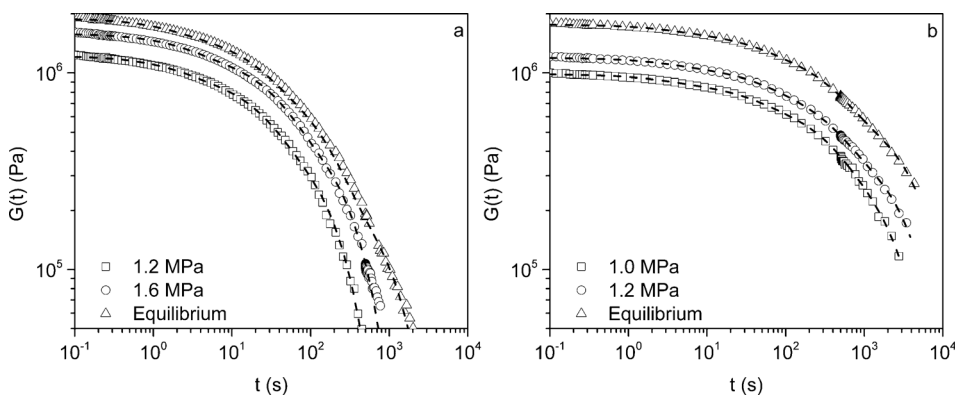


FIG. 3. (a) and (b) show the relaxation modulus $G(t)$ of PE_2.3 and PE_5.6, respectively, from step-strain experiments. The strain is applied at different values of the modulus build-up as well as at equilibrium. The dotted lines show the fit of the relaxation modulus using a discrete multimode version of the Maxwell model [Eq. (3)].

Here, G_i stands for the modulus corresponding to the relaxation mode with characteristic time τ_i and N is the total number of modes. The best fits for the modulus relaxation curves of polymers PE_2.3 and PE_5.6 are obtained using three and four modes, respectively. It was found that using a higher number of modes does not change significantly the value of the relaxation times close to the terminal region. The longest time modes are presented in Fig. 4(a) for the two polymers as a function of plateau modulus at the start of the step-strain experiment.

The time is normalized using the value of the largest relaxation time in the equilibrium state (400 and 5100 s for, respectively, PE_2.3 and PE_5.6). The normalization allows to overlap the values in an almost straight line with a slope of one. The lower modulus values are related to the confinement of the chain in a tube having a lesser number of entanglements, compared to the average tube in the equilibrium melt [Doi and Edwards (1986); Teng *et al.* (2012)]. This suggests that, in the nonequilibrium polymer melt, the relaxation process at large times takes place by a reptation process to renew a tube with a shorter primitive path compared to the one at equilibrium. Since in the nonequilibrium melt a heterogeneous distribution of molar mass between entanglements is expected, this approximation is valid only if the fluctuation in the distance between entanglements is much smaller than the tube path, which is plausible in the case of a highly entangled polymer such as UHMWPE.

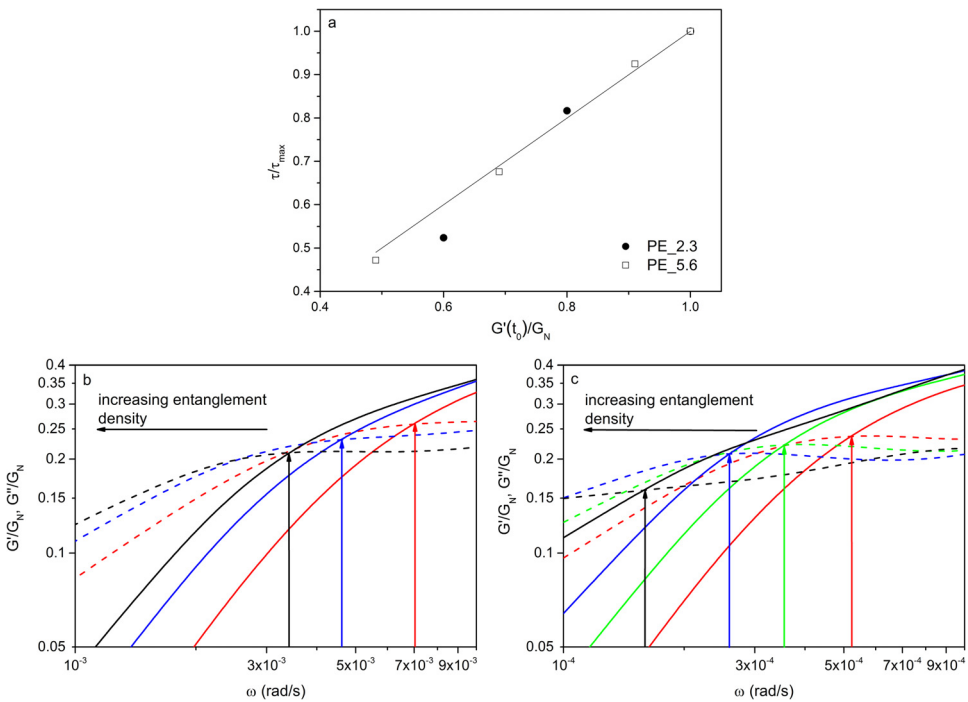


FIG. 4. (a) The largest relaxation time obtained from fitting Eq. (3) to each curve in Fig. 3 is shown as a function of the normalized linear elasticity $G'(t_0)/G_N$. Time axis is normalized by the longest relaxation time at equilibrium: 400 and 5100 s for, respectively, PE_2.3 and PE_5.6. The solid line shows a slope of one. (b) and (c) depict the shift of the cross over point to lower frequencies during the equilibration process, visualized by converting the total stress relaxation to the frequency space for PE_2.3 and PE_5.6, respectively. Arrows denote the cross over point when the step-strain experiment is started at the specific values of modulus build-up $G'(t_0)/G_N$ (0.6, 0.8, and 1.0 for PE_2.3; 0.5, 0.7, 0.9, and 1.0 for PE_5.6) from high to low frequency. The conversion is performed using the Maxwell model parameters [Eq. (3)].

To visualize the increase in the relaxation time as the polymer equilibrates, the total stress relaxation fit (including all modes) is converted to the frequency space for both PE_2.3 and PE_5.6, and Figs. 4(b) and 4(c) show the resulting normalized G' and G'' in the frequency region close to the modulus cross over. There is a clear shift in the cross over to lower frequency as the material approaches the equilibrium state. The value of the cross over frequency is largely determined by the longest relaxation time, with minor influences from the shorter timescale relaxation modes. We recognize that the polydispersity of the polymers used has an influence on the overall stress relaxation process and might aid the modulus build-up. McLeish (2007) pointed out that studies performed in monodisperse samples might ease data interpretation, since they would be free of heterogeneities caused by differences in dynamics among different molar mass components. However, with current synthetic techniques, it is not possible to obtain disentangled polyethylene having M_n larger than 1×10^6 g/mol with polydispersities smaller than 2.0. Moreover, in our work, the difference in the stress relaxation experiments observed during the equilibration process is mainly related to the heterogeneous distribution of entanglements in nonequilibrium states. This is clear since the comparisons are performed between nonequilibrium and equilibrium states of polymers having the same molar mass and molar mass distribution.

Since for a specific high molar mass polymer the Rouse time depends on the molar mass only, the changes in chain dynamics can be attributed to the increasing number of entanglements. Bearing this in mind, the following rescaling is proposed for the relaxation modulus $G(t)$ curves:

$$\overline{G}(\bar{t}) = G(t)/G'(t_0), \quad \bar{t} = t/\overline{G'}(t)^\mu, \quad \overline{G'}(t) = G'(t)/G_N. \quad (4)$$

Here, $G'(t_0)$ is the value of the elastic modulus just before starting the step-strain experiment and μ is a fitting parameter. Time normalization is chosen to compensate for the changes in chain dynamics due to the monotonic increase of entanglements, as quantified by the instantaneous value of the normalized elastic modulus, $\overline{G'}(t)$. When normalization in Eq. (4) is used, curves obtained for the specific polymer at different points of the build-up collapse onto a single master curve, Fig. 5. The linear dependence of the largest relaxation time with $\overline{G'}(t)$, as shown in Fig. 4(a), suggests a tentative value for $\mu = 1$. However, the complete stress relaxation curves shown in Fig. 3 also include a contribution from relaxation of shorter modes that might change at a slightly larger rate as the melt traverses from nonequilibrium to equilibrium. Changing μ to 0.9 corrects for these modes and provides a satisfactory collapse of the relaxation curves also at short times. In spite of this correction, a small discrepancy at the lowest starting modulus is observed in the two polymers. This discrepancy can be attributed to the fast build-up in modulus at the initial stages of entanglement formation. It is important to notice that to obtain the master curve, besides using the value of G' at the start of the step-strain test, the modulus build-up kinetic is used, establishing a relation between chain dynamics in the relaxation of stress and the relaxation of the melt toward equilibrium. In the nonequilibrium melt state, entanglement formation requires constraint renewal. At the same time, the increase in entanglements increases the constraint renewal time, decreasing the rate of further entanglement formation. It is important to notice that the step-strain experiments are performed in both build-up regimes, characterized by times τ_{m1} and τ_{m2} , respectively. In both regimes, the collapse of the modulus relaxation curves is possible, Eq. (4), suggesting that no kinetic barriers are responsible for the slow build-up as stated for other systems [Barbero and Steiner (2009)].

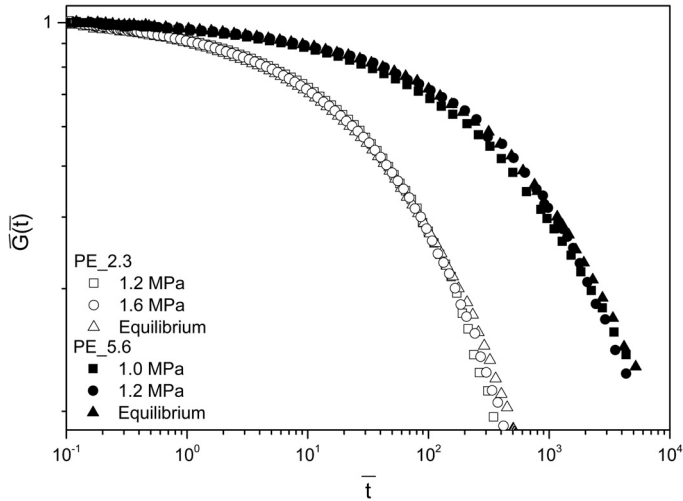


FIG. 5. Relaxation moduli from PE_2.3 (unfilled symbols) and PE_5.6 (filled symbols) when normalized by both the equilibrium plateau modulus (y -axis) and the instantaneous value of the elastic modulus (x -axis). The curves collapse onto a single master curve for each polymer, independent of the modulus value at which the step-strain was applied.

IV. CONCLUSIONS

In this study, with the help of controlled synthesis, it has been feasible to obtain a non-equilibrium melt state on melting of UHMWPE having a reduced number of entanglements in its nascent state. The equilibration process is well characterized by the monotonic increase of rubber elasticity in time and reaches a stable value at equilibrium. Using linear rheological techniques, it is demonstrated that with the transformation of the nonequilibrium melt, there are changes in the chain dynamics. Linear oscillatory rheology showed that Rouse dynamics is increasingly hindered as the melt transforms to the equilibrium state. The existence of a plateau region in G' showed that, even in nonequilibrium conditions, the presence of entanglements confines the chains, forcing them to renew their configurations by renewing their constraints. Presumably, the renewal process proceeds by chain reptation in a similar way as it occurs in the equilibrium melt state. Step-strain experiments allow studying the relaxation process related to the average constraint renewal. The relaxation modulus, $G(t)$, showed that as the melt elasticity increases, stress relaxation becomes slower, and therefore, the average constraint renewal time increases. Surprisingly, $G(t)$ obtained at different stages of the modulus build-up (including at equilibrium) collapses onto one single curve when using the build-up kinetics. This shows a clear relation between constraint renewal processes in the nonequilibrium melt state and its relaxation toward thermodynamic equilibrium. The viscoelastic response of the nonequilibrium melt and its correlation with the entanglement formation kinetics provides new opportunities in addressing chain dynamics of linear polymers in general.

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- See supplementary material at <http://dx.doi.org/10.1122/1.4898160> for build-up curves, and corresponding fitting parameters from Eq. (2) for polymers having a wide range of Mw, and molar mass determination of polymers PE_2.3 and PE_5.6 assuming pure reptation.