Non-Newtonian Rheology of Entangled Polymer Solutions and Melts

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ABSTRACT: Molecular theory based scaling arguments relating the extent of entanglement depletion to the prevailing flow intensity are utilized for the quantitative description of the shear thinning rheology of entangled linear polymer solutions and melts. A power law decay with respect to shear rate ($\dot{\gamma}$) is assumed for the viscosity, $\eta \sim K\dot{\gamma}^{n-1}$, and the first normal stress coefficient, $\Psi_1 \sim L\dot{\gamma}^{m-2}$. Following experience and the Doi−Edwards molecular theory, the lower rate limit of the non-Newtonian regime is taken equal to the inverse of the relaxation time of the whole chain. By analogy, and consistent with Menezes and Graessley's model for polymer relaxation under fast flow, it is assumed that shear thinning ceases at a characteristic higher rate equal to the frequency of the swiftest entanglement renewal process. Within these two $\dot{\gamma}$ limits which define the non-Newtonian regime, estimates for the n and m exponents are made connecting them to molecular relaxation characteristics. Expressions for the K and L coefficients are also derived, relating them to the molecular weight, chain rigidity, polymer concentration, and temperature.

1. Introduction

The non-Newtonian flow properties constitute the most essential piece of rheological information as far as designing and optimizing polymer processing operations which they invariably occur in the shear thinning range of flow intensities.[1] In these engineering applications, a constitutive relationship representing the material response to the kinematic stimulus is coupled with the pertinent flow geometry. By thus solving the fluid mechanics of the process, estimates may be obtained for its energetic requirements, processing capacities, possible exposure to prohibitive shear or thermal fields.[2]

Although not capturing the initial Newtonian plateau, "power law" constitutive expressions for the viscosity, η, the first normal stress coefficient, Ψ_1, and the recoverable compliance, J, as functions of shear rate, $\dot{\gamma}$, are the most commonly used:[1,3]

$$\eta(\dot{\gamma}) \approx K\dot{\gamma}^{n-1} \tag{1}$$

$$\Psi_1(\dot{\gamma}) \approx L\dot{\gamma}^{m-2} = 2\eta^2(\dot{\gamma})J(\dot{\gamma}) \tag{2}$$

For entangled polymers of linear architecture, the present work attempts to evaluate the coefficients K and L, and the exponents n and m ($0 \leq n \leq 1$, $0 \leq m \leq 2$) by relating them to basic material variables like the polymer molecular weight, M, molecular rigidity, and polymer concentration, c. Associated with these variables is the square end-to-end distance of the polymer[4]

$$\langle R^2 \rangle = (M/m)^{2\nu}b^2 \tag{3}$$

where m is the molecular weight of an effective monomer, b is the effective bond length, a measure of the molecular thickness and rigidity, and ν is the characteristic exponent. For polymers diluted in good solvents ν approaches 0.6, while in Θ solvents it is equal to 0.5. For melt states as well as entangled solutions, $\nu = 0.5$, irrespective of the solvent goodness;[5] since the focus here is on dense polymer systems, this last value is used throughout this work.

The nonlinear viscoelastic behavior originates from the ability of the moving matter for microstructural rearrangements for the purpose of decreasing its energetic requirements for flow; this is usually accomplished by a reversible reduction of the material connectivity. It has long been understood that in the case of entangled polymer solutions and melts this connectivity reduction is achieved by an effective decrease of the entanglement density.[6] The Doi−Edwards (DE) molecular theory quantifies the implications of this physical phenomenon to the steady shear and first normal stress difference (σ and N_1) as follows[7,8]

$$\eta(\dot{\gamma}) \equiv \frac{\sigma(\dot{\gamma})}{\dot{\gamma}} = \int_0^\infty G\left(\frac{\xi}{\lambda}\right)\frac{\partial[h(\dot{\gamma}\xi)\xi]}{\partial\xi}d\xi \tag{4}$$

$$\Psi_1(\dot{\gamma}) \equiv \frac{N_1(\dot{\gamma})}{\dot{\gamma}^2} = \int_0^\infty G\left(\frac{\xi}{\lambda}\right)\frac{\partial[h(\dot{\gamma}\xi)\xi^2]}{\partial\xi}d\xi \tag{5}$$

where $G(t/\lambda)$ is the time dependent relaxation modulus,[3] ξ is the elapsed time, and λ is the relaxation time. The damping function, $h(\gamma)$, represents the weakening of the temporary polymer network due to the imposition of a shear strain of magnitude γ.

For linear chains, DE theory predicts a universal $h(\gamma)$ which for relatively small γ is subject to the following quadratic approximation:

$$h(\gamma) \approx 1 - (\gamma/\gamma_0)^2 \tag{6}$$

If the above $h(\gamma)$ is introduced in eqs 4 and 5 and combined with a single-exponential relaxation modulus (as it is in essence the reptation one for monodisperse polymers), $G(t) \approx G(0)\exp(-t/\lambda)$, the shear thinning behavior is estimated analytically as follows[9]

$$\eta(\dot{\gamma}) = \eta(0)[2e^{-1/\Gamma}(1 + 3\Gamma + 3\Gamma^2) + 1 - 6\Gamma^2] \tag{7}$$

$$\Psi_1(\dot{\gamma}) = \Psi_1(0)[e^{-1/\Gamma}(1/\Gamma + 5 + 12\Gamma + 12\Gamma^2) + 1 - 12\Gamma^2] \tag{8}$$
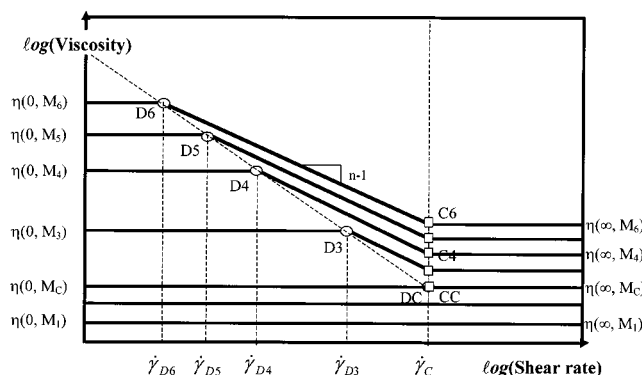
Figure 1. Viscosity vs shear rate corresponding to various linear polymer molecular weights, M_i, above and below the entanglement threshold, M_C: $M_1 \leq ... \leq M_C \leq M_3 \leq ... \leq M_6$. Horizontal lines signify Newtonian behavior while thicker, inclined lines correspond to the non-Newtonian regime, which spans $\dot{\gamma}_{Di} \leq \dot{\gamma} \leq \dot{\gamma}_C$. First normal stress difference coefficient depiction (Ψ_1) would have followed similar lines, but with a non-Newtonian decay slope of $m - 2$, instead of $n - 1$.

where $\Gamma \equiv \dot{\gamma}\lambda/\gamma_0$. The DE value for γ_0 is roughly equal to $\sqrt{5}$. On the other hand, the fact that at low shear rates

$$\eta(\dot{\gamma} \rightarrow 0^+) \approx \eta(0)[1 - 6\,\Gamma^2] \qquad (9)$$

$$\Psi_1(\dot{\gamma} \rightarrow 0^+) \approx \Psi_1(0)[1 - 12\,\Gamma^2] \qquad (10)$$

and the observation that the viscosity decays to 80% of its Newtonian value[6] at a characteristic rate equal to $\dot{\gamma} \approx 1/(3\lambda)$ indicates a somewhat lower value: $\gamma_0 \approx (10/3)^{1/2} = 1.826$.

The Doi–Edwards theory is successful in providing a complete picture of polymer dynamics, in discovering the physical origin of viscoelastic nonlinearities in the form of the fast chain retraction process of "equilibration", and in properly describing the onset of shear thinning and its early development. Nevertheless, the DE model also predicts constitutive instabilities occurring exceedingly early in the rate spectrum, followed by a catastrophic shear thinning decay. In our case, for example, eq 7 suggests that a flow instability should be expected at $\dot{\gamma} = \gamma_0/(2.4\lambda)$, i.e., when $d[\ln(\eta)]/d[\ln \dot{\gamma}] \leq -1$, but then the viscosity has only been reduced to half of its Newtonian value.

As lucidly reviewed by Pearson,[10] the realism of the molecular picture was further improved with the addition of parallel relaxation processes like constraint release and contour-length fluctuations (chain breathing) which with their action assist reptation in the total renewal of chain conformation. Progress has also been made in understanding the polymer behavior under very fast flows,[11–15] as with the "convective constraint release" hypothesis[16–19] which stipulates that sweeping of constraining entanglements under high $\dot{\gamma}$ conditions is much more dramatic than anticipated.

Despite of all this effort, a workable model has yet to appear that utilizes the advances in molecular comprehension in scientifically estimating the most applied of all viscoelastic properties: the ones that govern steady polymer flow under reasonably high shear intensities. This work is an attempt to rectify that. It is first recognized that the unnaturally narrow breadth of the predicted non-Newtonian region is due to the corresponding sharpness of the spectrum of relaxation times of the original DE model, which recognizes reptation as
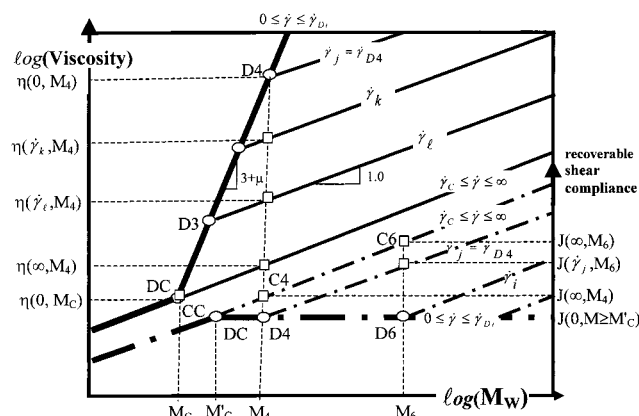

Figure 2. Viscosity (continuous lines in upper part of figure) and recoverable compliance (dashed lines in lower part) vs molecular weight, M_i, at various shear rates, in the shear thinning range and beyond ($0 \leq \dot{\gamma}_{Di} \leq \dot{\gamma}_i \leq ... \leq \dot{\gamma}_l \leq \dot{\gamma}_C \leq \infty$). $\dot{\gamma}_{Di}$ signifies the onset of non-Newtonian behavior and here, $\dot{\gamma}_i = \dot{\gamma}_{D6}$, $\dot{\gamma}_j = \dot{\gamma}_{D4}$, and $\dot{\gamma}_l = \dot{\gamma}_{D3}$. Thicker lines and circular points signify Newtonian behavior while thinner lines and square points correspond to non-Newtonian values. The rest of the symbols stand as in Figure 1, whose information is equivalent to that of Figure 2 but presented in an alternative fashion.

the only means of molecular relaxation, after equilibration. When the impact of the co-current relaxation mechanisms is properly taken into account, the spectrum of relaxation times of the theoretical $G(t)$ broadens and, consequently, the prediction of constitutive instabilities (from eq 4) is properly transposed to realistically higher shear rates. By exploitation of this concept in the present work, a semiempirical quantitative model for the description of the non-Newtonian behavior in entangled solutions and melts of monodisperse linear polymers is constructed. The conventional constitutive approach (like the one followed in eqs 4–8) is thus circumvented, in view of its present limitations and in anticipation of the practical usefulness of the expected results. In doing so, it is assumed that all viscoelastic nonlinearities are only due to the reversible dissolution of entanglements under high shear; any shear thinning attributed to finite chain extensibility, flow-induced changes in excluded volume, or intramolecular hydrodynamic interactions is neglected.

Figure 1 presents a complete yet considerably abstract diagram of the viscosity as a function of shear rate, with the molecular weight kept as a parameter. It is based not only on gathered pieces of phenomenology but also on basic assumptions made herein concerning the behavior in the high $\dot{\gamma}$ region for which little experience exists. A plot of the first normal stress coefficient would have followed similar lines. Figure 1 illustrates the two characteristic regions of flow behavior: The upper part, $M \geq M_C$, pertains to polymers that are sufficiently long and mutually interacting and, therefore, are able to manifest shear thinning for a certain range of shear rates. The bottom part ($M < M_C$) corresponds to molecules that are short or diluted to the point that are unable to form entanglements with neighboring chains; there, since no opportunity of network connectivity reduction exists, the rheology is unconditionally Newtonian.[6,20] Newtonian behavior is manifested even in entangled chains at sufficiently low shear rates, $\dot{\gamma} < \dot{\gamma}_D$, and seems to reappear at very high shear rates,[21,22] $\dot{\gamma} > \dot{\gamma}_C$; in Figure 1, this is depicted in the flat regions that flank the non-Newtonian regime.

The η and J variation with respect to polymer molecular weight implied in Figure 1 and explained in the ensuing analysis is shown in Figure 2. The general picture is consistent with the observations by Schreiber et al. on linear polyethylene[20] and with their interpretation of similar data on polystyrene by Spencer and Dillon.[23,24] In both Figures 1 and 2, abrupt point transitions between any two regimes (e.g., points D and C) are, of course, idealizations of regions where a smoother transition actually takes place. Nevertheless, C and D represent matching points where dissimilar molecular relaxation processes generate rheological response of identical value; as such, they constitute useful idealizations for supporting the scaling arguments presented here. Elements from the molecular theory of the Newtonian behavior are reviewed next, as an essential prelude to the non-Newtonian model development.

2. The Newtonian Regime

2.1. Short Chain Rheology. The rheology of polymer melts or dense solutions of unentangled polymers is described by the Rouse model[7] according to which, the shear invariant viscosity, η_R, and the molecular relaxation time, λ_R, are given by the following expressions:[25]

$$\eta(\dot{\gamma}, M < M_C) = \eta_R(M) = \frac{2cR_GT}{M}\lambda_R = \frac{cN_A\zeta\langle R^2 \rangle}{12m} = \frac{cN_A\zeta b^2}{12m}\left(\frac{M}{m}\right) \quad (11)$$

Here, the subscript R signifies the Rouse regime, c is the polymer concentration, N_A the Avogadro number, R_G the gas constant ($R_G = 8.3$ J/mol·K) and M/m is the number of monomers per chain.

The monomeric friction coefficient, ζ, is a sensitive function of both temperature, T, and polymer volume fraction, φ ($\equiv c/\rho$, where ρ is the polymer density). Its temperature dependence is governed by the variation of the fractional free volume, f, and for $T - T_g \leq 100$ K may be described by the WLF equation[3]

$$\log\left(\frac{\zeta(\varphi, T)}{\zeta(1, T_g)}\right) \equiv \log(a_T) = \frac{-C_{1g}(T - T_g)}{C_{2g} + T - T_g} \quad (12)$$

where a_T is the temperature shift factor, referenced at T_g, the glass transition temperature of the polymer. The WLF constants are equal to $C_{1g} \approx B/(2.303f_g)$ and $C_{2g} \approx f_g/\alpha_f$, where B is a constant of order unity, f_g is the fractional free volume at T_g, and α_f is the thermal expansion coefficient of f; for a large class of polymers and for $B \approx 1$, $f_g \approx 0.025$ and $\alpha_f \approx 4.8 \times 10^{-4}$ are the most probable values. Equation 12 also presents a proper way for accommodating dilution effects since all molecular parameters involved (i.e., T_g, f_g, and α_f) are profoundly affected by φ.

The zero shear recoverable compliance, a measure of the elasticity of the fluid, is

$$J(\dot{\gamma}, M < M_C) = J_R(M) = 2M/(5cR_GT) \quad (13)$$

and the first normal stress difference coefficient is

$$\Psi_1(\dot{\gamma}, M < M_C) = \Psi_{1R}(M) = 2J_R\eta_R^2 \quad (14)$$

It is later assumed (eqs 23 and 24) that Rouse model applicability extends, approximately, even for $M > M_C$, provided it refers to fast moving chains who have shed all their entanglements in order to minimize their energetic requirements for flow.

2.2. Newtonian Behavior in the Entangled State. There is an accelerated zero-shear viscosity increase above a critical molecular weight, M_C (Figure 2). The molecular explanation is that above M_C, polymers entangle with their immediate neighbors to form a temporary network of interacting chains that slows the flow.[6] Evidently, since two entanglements per chain are needed for the establishment of a through-out network connectivity, $M_C = 2M_e$; M_e is the average molecular weight between two successive entanglements along a single chain. Both M_C and M_e are microstructural parameters whose values increase with the chain rigidity and, in the case of solutions, with the solvent concentration. Both are also affected by shear rate since, under fast flow conditions, a chain releases a number of its associations with its neighbors in order to facilitate its motion:

$$M_C(\dot{\gamma}, \varphi) \approx M_C(0, 1)\, \dot{\gamma}^g(\varphi)^{-(1+\epsilon)} \quad (15)$$

The mean field approach demands that the chain contacts be proportional to the square of the polymer concentration[10] and, therefore, $\epsilon = 0$; nevertheless, semidilute solution theory[26,27] and experimental evidence[28,29] indicate a somewhat higher value, $\epsilon = 0.25$. The positive exponent, g, is evaluated in the course of this paper (eq 33).

As shown in both Figures 1 and 2, for $\dot{\gamma} < \dot{\gamma}_{Di}$, even in well-entangled chains for which $M_i \gg M_C$, there is a region of sufficiently slow motion where Newtonian behavior persists. The physics of that region of quiescent polymer dynamics and linear viscoelasticity has been adequately explained by the de Gennes−Doi−Edwards (DGDE) theory[7] and its extensions. According to this theory, an inverse measure of the speed of molecular motions is the disengagement relaxation time, λ_D which signifies the time required for the disassociation of a polymer chain from all of its former neighbors and the formation of an equal number ($2M/M_C$) of fresh entanglements with new neighbors.

$$\lambda(0, M \geq M_C) = \lambda_D(M) = \frac{\langle R^2 \rangle}{36D} = \frac{\zeta b^2}{24kT}\left(\frac{M_C}{m}\right)^2\left(\frac{M}{M_C}\right)^{3+\mu} \quad (16)$$

D is the diffusion coefficient while the subscript D signifies the DGDE regime and k is the Boltzmann constant ($R_G = N_A k$). μ (~ 0.5) describes the deviations from the DGDE reptation exponent of 3 due to co-current path fluctuations.[30] The quasi-equilibrium plateau modulus is a measure of the rigidity of the fluid and increases with the number density of entanglements:[4]

$$G(0, M \geq M_C) = G_D(M) = 2cR_GT/M_C \quad (17)$$

The low shear Newtonian viscosity in the presence of

entanglements is therefore equal to

$$\eta(0, M \geq M_C) = \eta_D(M) = G_D \lambda_D =$$
$$\frac{c N_A \zeta b^2}{12m} \left(\frac{M_C}{m}\right) \left(\frac{M}{M_C}\right)^{3+\mu} \quad (18)$$

The zero shear compliance is

$$J(0, M \geq M_C) = J_D(M) = M_C/cR_G T \quad (19)$$

and the first normal stress difference coefficient is

$$\Psi_1(0, M \geq M_C) = \Psi_{1D}(M) = 2\eta_D \lambda_{DW} = 2\eta_D^2 J_D \quad (20)$$

where $\lambda_{DW} = \eta_D J_D$ is the first moment (or weight-average) of the relaxation time, an alternative measure of the time needed for complete chain disengagement. For monodisperse samples, $\lambda_{DW} = 2\lambda_D$.

Evidently, both the Rouse and DGDE models should be equally appropriate in describing the rheological behavior in the threshold of an entangled network formation; i.e., at $M = M_C$, $\eta_D = \eta_R$ and, similarly, at $M = M'_C$, $J_D = J_R$. When this last equality is combined with eqs 13 and 19, it suggests that $M'_C = 2.5M_C$.

3. The Non−Newtonian Model

3.1. Non-Newtonian Behavior of Entangled Linear Chains. Shear thinning is initiated with the loss of the first entanglement and the resulting incremental growth of the mesh size of the temporary polymer network. Phenomenology[6] complements molecular theory (eq 9) in indicating that this occurs at a characteristic rate, $\dot{\gamma}_D$, roughly equal to the inverse of the first moment of the relaxation time

$$\dot{\gamma}_D \approx 1/\lambda_{DW} = (\eta_D J_D)^{-1} \quad (21)$$

There is an increasing difficulty for each additional physical junction dissolution until non-Newtonian behavior ceases with the stripping of the last remaining entanglement from the moving chain. This happens at a rate, $\dot{\gamma}_C$, roughly equal to the inverse of the time required for the swiftest entanglement depletion process. Evidently, this characteristic time is associated with the dissolution of an entanglement lying on and/or formed by a chain end. This is because the lifetime of an *entanglement*, λ_{ij}, formed by the association of two chains or chain segments, i and j, which relax at significantly dissimilar rates (e.g., $\lambda_j \gg \lambda_i$) is controlled by the relaxation time of the faster relaxing partner:[31] $\lambda_{ij} \approx 2\lambda_i \lambda_j/(\lambda_i + \lambda_j) \approx 2\lambda_i$. Retraction of the *chain end* of an entangled neighbor due to reptation takes $\sim\lambda_D (M_C/M)^2$. This is equal to the time required for that very chain to release the first entanglement at its fringes, and it would have suggested that $\dot{\gamma}_C \sim (M/M_C)^2/\lambda_D \sim 2D^*/a^2$, where $a = (M_C/2m)^{0.5} b$ is the size of a single inter-entanglement segment and D^* the curvilinear diffusion coefficient. Faster yet is a disentanglement caused by the release if an end-chain segment of a neighbor, when motivated by belated equilibration of that neighbor; such a release may take as little as $\sim 2\lambda_R(M_C)$ seconds to occur. Implicit here is the assumption that not only the geometric center but also any point along a chain path, including points close to the tip, can occasionally act as a pivot to the chain equili-

bration process. Therefore

$$\dot{\gamma}_C(M) = [2\lambda_R(M_C)]^{-1} \approx \lambda_{DW}^{-1}(M_C) = (\eta_C J_C)^{-1} =$$
$$(12kT/\zeta b^2)(M_C/m)^2 \quad (22)$$

The subscript C refers to a property at M_C. Beyond $\dot{\gamma}_C$, the rheology of the fully disengaged polymer resumes being Newtonian, and the Rouse model (eqs 11−14) may again be used for its approximate description; this is inferred by Menezes and Graessley's[11] incisive and well tested[32] conjecture which extends the DE theory into very high shear:

$$\eta(\dot{\gamma} \geq \dot{\gamma}_C, M \geq M_C) \approx \eta_R(M) \quad (23)$$

$$\Psi_1(\dot{\gamma} \geq \dot{\gamma}_C, M \geq M_C) \approx 2\eta_R^2(M) J_R(M) \quad (24)$$

Smaller molecular weights or further dilution causes a narrowing of the range of shear rates where non-Newtonian behavior is manifested (Figure 1). Ultimately, at $M = M_C$, shear thinning merely occurs at a "single" shear rate: $\dot{\gamma}_C = \dot{\gamma}_D(M_C)$, and the upper and lower Newtonian property plateaux coincide (DC ≡ CC in Figure 1). This characteristic rate represents the flow intensity necessary for the M_C polymer to release its one and only network forming entanglement.

Knowing the two shear rate limits that define the non-Newtonian regime, $\dot{\gamma}_D$ and $\dot{\gamma}_C$, as well as the property values on both Newtonian plateaus that flank this regime, one may complete the quantitative description of the rheological behavior under steady shear by calculating the associated constants of eqs 1 and 2, namely, n, m, K, and L. The viscosity in the shear thinning region, for example, is evaluated by first matching the stipulated power law decay at the low shear rate limit with the DGDE result:

$$\frac{\eta(\dot{\gamma}, M)}{\eta(0, M)} = \frac{\eta(\dot{\gamma}, M)}{\eta_D(M)} \approx \left(\frac{\dot{\gamma}}{\dot{\gamma}_D}\right)^{n-1} \approx (\dot{\gamma}\lambda_{DW})^{n-1} \quad (25)$$

The above expression is then forced to comply with the fact that: $\eta(\infty, M) \approx \eta(\dot{\gamma}_C, M) \approx \eta_R(M)$. As a result

$$\frac{\eta_R}{\eta_D} = \left(\frac{M_C}{M}\right)^{2+\mu} \approx \left(\frac{\dot{\gamma}_D}{\dot{\gamma}_C}\right)^{1-n} = \left(\frac{J_C \eta_C}{J_D \eta_D}\right)^{1-n} \quad (26)$$

By substituting for the Newtonian viscosity and compliance from the previous section

$$K \approx \frac{\eta_D^n}{J_D^{1-n}} = \left(\frac{cRT}{m}\right) \left(\frac{\zeta b^2}{12kT}\right)^n \left(\frac{M}{m}\right) \left(\frac{m}{M_C}\right)^{2(1-n)} \quad (27)$$

and by equating the M exponents from both sides of the new expression

$$n = \frac{1}{3 + \mu} \quad (28)$$

Similarly, for the elasticity coefficient in the power law region

$$\frac{\Psi_1(\dot{\gamma}, M)}{\Psi_1(0, M)} = \frac{\Psi_1(\dot{\gamma}, M)}{Y_{1D}(M)} \approx \left(\frac{\dot{\gamma}}{\dot{\gamma}_D}\right)^{m-2} \approx (\dot{\gamma}\lambda_{DW})^{m-2} \quad (29)$$

This has to accommodate the fact that under high shear, $\Psi_1(\infty, M) \approx \Psi_1(\dot{\gamma}_C, M) \approx \Psi_{1R}(M)$. Consequently, Ψ_{1D}/Ψ_{1R}

$= 2.5(M/M_C)^{3+4\mu} \approx (\dot\gamma_C \lambda_{DW})^{2-m} = (\eta_D J_D/\eta_C J_C)^{2-m}$ and, therefore, from eqs 11–21

$$m = \frac{3}{3+\mu} \tag{30}$$

$$L \approx \frac{2\eta_D{}^m}{J_D{}^{1-m}} = \frac{2cRT}{m}\left(\frac{\zeta b^2}{12kT}\right)^m\left(\frac{M}{m}\right)^3\left(\frac{m}{M_C}\right)^{2(2-m)} \tag{31}$$

A direct consequence of these results is the following relationship between shear and normal stresses

$$\frac{N_1(\dot\gamma)}{N_1(0)} = \left(\frac{\sigma(\dot\gamma)}{\sigma(0)}\right)^{(2-m)/(1-n)} = \left(\frac{\sigma(\dot\gamma)}{\sigma(0)}\right)^{(3+2\mu)/(2+\mu)} \tag{32}$$

and the deciphering of the rate dependence of the recoverable shear compliance, the plateau modulus and the inter-entanglement molecular weight:

$$\frac{J(\dot\gamma)}{J(0)} = \frac{G(0)}{G(\dot\gamma)} = \frac{M_C(\dot\gamma)}{M_C(0)} \approx (\lambda_{DW}\dot\gamma)^{m-2n} = (\eta_D J_D \dot\gamma)^{1/(3+\mu)} \tag{33}$$

Phenomenology[3] along with recent theoretical findings[33] concerning the implications of the "chain breathing" mechanism indicate that $\mu \approx 0.5$. As a result, in well-entangled systems, $n = m/3 = {}^2/_7$ and, consequently, not inconsistent with experience, $\eta \sim \dot\gamma^{-0.714}$, $\Psi_1 \sim \dot\gamma^{-1.143}$, and $J \sim M_C \sim \dot\gamma^{0.286}$.

The predicted terminal viscosity exponent, $n - 1 \approx -0.71$, is identical to the "universal" value empirically produced by Vinogradov and Malkin[34] upon extensively surveying the evidence. It is also in agreement with Graessley's observation (Figure 8.9 of ref 6) that, eventually, in well-entangled solutions of narrowly distributed polystyrenes or poly(α-methylstyrenes), $1 - n$ tends to a constant value, despite the fact that is initially a function of the coil overlap parameter, $c[\eta] \approx \varphi(M/m)^{1/2}$, where $[\eta]$ is the intrinsic viscosity. His observation, which may be quantified as follows

$$1 - n \approx 0.72 - 0.62 \exp(-2c[\eta]/25) \tag{34}$$

essentially means that while shear thinning at infinite dilution is negligible (consistent with the observations by Schreiber et al.),[20] the appearance of sufficient entanglements causes $(1 - n) \rightarrow 0.72$.

Yet, the above results (eqs 28–31) are not valid in some fringes of the $M - \dot\gamma$ phase diagram; these exceptions are examined next.

3.2. Non-Newtonian Behavior at the Entanglement Threshold. As illustrated in Figure 2 and described by eq 19, the effects of interchain associations on fluidity become apparent earlier than in the elastic properties: In the range $M_C \leq M \leq M'_C$, the presence of entanglements has already instigated a sharp increase in viscosity while not yet tempering the linear growth of compliance with the molecular weight. Evidently, in this lightly entangled region the results of the previous section have to be modified. Following methods similar to the ones employed in the preceding section it may be shown that now, the viscosity constants are

$$n' = \frac{2}{4+\mu} \tag{35}$$

and

$$K' \approx \frac{\eta_D{}^{n'}}{J_R{}^{1-n'}} = \frac{5cRT}{2m}\left(\frac{\zeta b^2}{30kT}\right)^{n'}\left(\frac{M}{m}\right)\left(\frac{m}{M_C}\right)^{n'(2+\mu)} \tag{36}$$

while the elasticity parameters are

$$m' = \frac{4}{4+\mu} \tag{37}$$

$$L' \approx \frac{2\eta_D{}^{m'}}{J_R{}^{1-m'}} = \frac{5cRT}{m}\left(\frac{\zeta b^2}{30kT}\right)^{m'}\left(\frac{M}{m}\right)^3\left(\frac{m}{M_C}\right)^{m'(2+\mu)} \tag{38}$$

For $\mu \approx 0.5$, one finds $n' = m'/2 = {}^4/_9$. As a result, $N_1(\dot\gamma) \sim \sigma^2(\dot\gamma) \sim \dot\gamma^{0.889}$ and $J(\dot\gamma) \sim \dot\gamma^0$, thus correctly predicting that, in the entanglement threshold, nonlinearities in the elastic properties set in later than in viscosity. This smoother non-Newtonian behavior should also hold for any M, at the other neighborhood of rarefied entanglement presence, i.e., for $\dot\gamma$ values which are slightly lower than $\dot\gamma_C$.

4. Parametric Dependence on *T, c,* and Chain Rigidity

It is of importance in both polymer processing and characterization to be able to quantify the dependence of rheology on basic material parameters like the degree of polymerization, $N \equiv M/m$, the chain rigidity, a measure of which is $N_{C1} \equiv M_C(\varphi = 1)/m$, the polymer volume fraction, $\varphi = c/\rho$, and the prevailing temperature, T. On a first level, this may be accomplished by introducing eqs 12 and 15 to the stress coefficient expressions derived in section 3.1. It can thus be shown that for concentrated solutions or melts, in both Newtonian and fully developed non-Newtonian regime, these results may be compactly stated as follows

$$\sigma, {}^1/_2 N_1 \approx \left(\frac{\rho RT}{m}\right)\left(a_T\dot\gamma\frac{\zeta(1,T_g)b^2}{12kT}\right)^p \frac{N^{(3+\mu)p}}{N_{C1}{}^{1+(1+\mu)p}}\varphi^{(2+\epsilon)+(1+\epsilon)(1+\mu)p} \tag{39}$$

where p stands for the shear or normal stress exponent of n or m, not excluding the corresponding zero-shear values of 1 and 2.

In polymer science and rheology, there is currently a renewal in the old quest of relating chain chemistry and microstructure with macroscopic behavior. It is propelled by the need to be able to foresee the properties of new species, synthesized by novel catalytic methods, that seem to be able to produce an infinite variety of chain microstructures.[35] It has long been stipulated[36–46] that several of the molecular parameters involved in polymers are interdependent, and that the basic variable on which they ultimately depend is the *characteristic ratio*, C_∞, representing the polymer rigidity. The Graessley−Edwards scaling law,[39] for example, relates the inter-entanglement molecular weight in quiescent conditions with microstructural characteristics and the polymer volume fraction, φ ($=c/\rho$); this law is analytically expressed here as

$$\frac{M_C}{m} \approx \left(\frac{27}{2+\epsilon}\right)^{2+\epsilon}\left(\frac{m}{N_A\rho l^3}\right)^{1+\epsilon}\frac{1}{\varphi^{1+\epsilon}C_\infty{}^{1+2\epsilon}} \tag{40}$$

where l ($\sim$1.5 Å) is the actual bond length, $(b/l)^2 = C_\infty$,

while ϵ represents the deviations from the mean field entanglement dilution law which states that $M_C(\varphi) = M_C(1)/\varphi$. There is still considerable phenomenological and theoretical research done on verifying and improving eq 40, understanding its physical origin, and evaluating ϵ ($0 \leq \epsilon \leq 1$).

A subtle relationship may also be obtained between m and C_∞ by assuming that any change in the monomer mass affects equally the lateral and longitudinal dimensions of the statistical unit; therefore, m is related to its volume as follows: $m \sim b^3 \sim C_\infty^{3/2}\beta^3$. This assumption tests successfully against a list of 13 polymers (Table 1 of ref 41) from which the proportionality constant is found to be equal to 0.73:

$$d/\rho \equiv m/(N_A \rho \beta^3) \approx 0.73 \, C_\infty^{3/2} \quad (41)$$

Introducing eq 41 into eq 40 produces

$$\frac{M_C}{m} \approx \frac{4}{3}\left(\frac{20}{2+\epsilon}\right)^{2+\epsilon} \frac{C_\infty^{0.5(1-\epsilon)}}{\varphi^{1+\epsilon}} \quad (42)$$

This bridges the apparent discrepancy between eq 40 and several well documented correlations[40] or theories[45] indicating that M_C/m increases with C_∞. It should, however, be understood that the validity of eq 41 is very approximate. As surmised by Privalko's early observations,[38] it most likely represents an average trend between the cases of "slim" macromolecules for which the m dependence on C_∞ is less sensitive than the one expressed in eq 41, and the case of polymers with bulky pendant groups for which the dependence is somewhat stronger.

As already mentioned, the molecular property the most sensitive on the free volume fraction variations is the elusive molecular friction coefficient

$$\zeta(\varphi, T) = \zeta(1, T_g) \exp[1/f(\varphi, T) - 1/f(1, T_g)] \equiv$$
$$\zeta(1, T_g) a_T \quad (43)$$

where a_T is the temperature/dilution shift factor, of which the WLF expression (eq 12) with φ-dependent parameters is a valid representation.

Although expectable on physical grounds, establishing a relationship between molecular friction and chain rigidity is a difficult task, given the uncertainties in extracting ζ from viscoelastic data. Against all convention, $\zeta_g \equiv \zeta(1, T_g)$, the value of the friction coefficient at the glass transition temperature and zero dilution is far from universal (e.g., see Table 12-III of ref 3). The same is true for $f_g \equiv f(1, T_g)$, the fractional free volume at T_g, on which ζ_g depends. Since d, in eq 41, represents the most efficient molecular packing theoretically possible, $d/\rho \sim C_\infty^{3/2}$ may be considered as a measure of the "free volume" present in the system at a given thermal state (e.g, at $T = T_g$). This should come as no surprise, since free volume availability should be positively affected by packing inefficiencies caused by increased polymer rigidity.

A rational attempt to quantify $\zeta(1, T_g)$ may therefore outlined as follows. It starts with Stokes' law applied
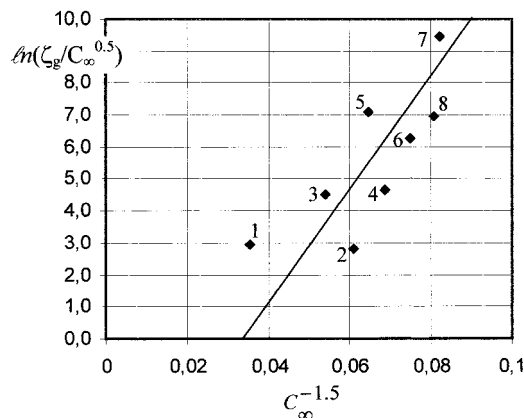

Figure 3. Correlation of molecular friction coefficient at T_g vs chain rigidity for (1) polystyrene, (2) polyethylene, (3) 1,2-polybutadiene, (4) ethylene−propylene (E/P) copolymer (56/44), (5) polyisobutylene, (6) ethylene−propylene copolymer (16/84), (7) *cis*-polyisoprene, and (8) atactic polypropylene. $\zeta(1, T_g)$ values, in g/s, are from ref 3 except for (2) and (8) which are extrapolated estimates from the copolymer data. C_∞ values are from refs 39 and 43, except for the E/P copolymers which are interpolations from the pure polymer data. Straight line stands for: $\zeta(1, T_g) = (250)^{-1}(C_\infty)^{0.5} \exp(174/C_\infty^{1.5})$

to a monomer:

$$\zeta_g \equiv \zeta(1, T_g) \sim 3\pi\eta_S(1, T_g)b \sim 3\pi\eta_S(1, T_g)\, l C_\infty^{1/2} \quad (44)$$

The "solvent" viscosity, η_S, retains its physical meaning even in the undiluted state by representing the resistance to motion on a single monomer exerted by the surrounding medium of neighboring monomers.[47] As such, $\eta_S(1, T_g)$ is a decreasing function of the free volume available at T_g and, therefore, of C_∞. Preliminary correlation presented in Figure 3 of some of the aforementioned experimental evidence indicates that for several hydrocarbon polymers the following law is roughly followed:

$$\eta_{Sg} \equiv \eta_S(1, T_g) \sim \zeta_g/b \sim \exp(1/f_g) \sim \exp(174/C_\infty^{3/2}) \quad (45)$$

Introducing all this information to the stress coefficient expressions derived earlier (eq 39), and for $\mu = 2\epsilon = 0.5$, the following parametric dependence is predicted for the viscosity and first normal stress coefficient in the entanglement regime, for any n and m, including the Newtonian limit values of 1 and 2:

$$\eta(\dot{\gamma}) \sim (\eta_{Sg} a_T)^n \frac{T^{1-n}\varphi^{2.25+1.875n}N^{3.5n}}{C_\infty^{1.875-0.9375n}\dot{\gamma}^{1-n}} \quad (46)$$

$$\Psi_1(\dot{\gamma}) \sim (\eta_{Sg} a_T)^m \frac{T^{1-m}\varphi^{2.25+1.875m}N^{3.5m}}{C_\infty^{1.875-0.9375m}\dot{\gamma}^{2-m}} \quad (47)$$

For $n = m/3 \approx 2/7$, the shear thinning exponents evaluated in section 3.1, one finds

$$\eta(\dot{\gamma}) \sim (\eta_{Sg} a_T)^{0.286} \frac{T^{0.714}\varphi^{2.79}N}{C_\infty^{1.61}\dot{\gamma}^{0.714}} \quad (48)$$

$$\Psi_1(\dot{\gamma}) \sim (\eta_{sg} a_T)^{0.857} \frac{T^{0.143}\varphi^{3.86}N^3}{C_\infty^{1.07}\dot{\gamma}^{1.143}} \quad (49)$$

On the basis of the above results, the following rule, useful for interpolating estimates between dissimilar polymer fluids, may be stated: At any given shear rate, the stress coefficient of a polymer with a higher C_∞ is lower in value than that of a more flexible species, provided that all other material parameters (φ, $N = M/m$), including the temperature distance from the corresponding T_g are kept equal. The opposite should hold for the self-diffusion coefficient, since by eq 16, and for the quiescent case

$$D \sim \frac{C_\infty^{0.0625}}{\eta_{sg}a_T N^{2.5}\varphi^{1.875}} \qquad (50)$$

This stronger molecular weight dependence than the believed $D \sim N^{-2}$, is not out of line with recent experimental findings.[48]

5. Discussion and Conclusions

The shear-thinning rheology of linear polymers was modeled semiempirically, by circumventing the orthodox constitutive approach which predicts inappropriately strong and early flow instabilities. The model is based on the current knowledge on quiescent polymer dynamics, on phenomenology, and on heuristic arguments backed by physical reasoning.

The magnitude of the derived shear thinning exponents ($1 - n \approx 5/7$, $2 - m \approx 8/7$) is consistent with experience[3,6,34] and not far from the Graessley's classic theory predictions[49] ($1 - n \approx 9/11$, $2 - m \approx 16/11$). As implied by eqs 28 and 30 (or eqs 35 and 37) small n and m variations may be indicative of the relative importance of alternative chain relaxation mechanisms, assisting reptation. Nevertheless, the scaling approach pertains to fully developed shear thinning and does not capture the smooth transition from Newtonian to non-Newtonian behavior, expressed as a curvature around the D points in Figures 1 and 2; the corresponding smooth transition upon Newtonian flow resumption under high shear (i.e, around the C points) is analytically described by eqs 35–38.

The model complies with the observed *rate–temperature superposition* principle,[3] i.e., the fact that, for a given material, nonisothermal stress data may merge into a single curve when plotted against the $\dot{\gamma}a_T$ product.[6] It is also in accord with the long established *rate–concentration superposition*, applicable to well-entangled polymer solutions of any φ, which suggests the universality of the $\eta(\dot{\gamma},\varphi)/\eta(0,\varphi)$ vs $\dot{\gamma}/\dot{\gamma}_D(\varphi)$ behavior (e.g., Figure 8.10 in ref 6 or Figure 2.59 in ref 34). It correctly predicts that η and Ψ_1 demonstrate a much weaker molecular weight dependence under shear thinning than in the zero shear limit. In the Newtonian limit ($n = m/2 \approx 1$), it reproduces within a numerical constant of order 1 both Ferry's (eq 10.50 of ref 3) and Berry and Fox's[36] zero-shear viscosity empirical relations; the fluidity-rigidity rule stated at the end of the previous section is implied by the relative piling sequence of the various material curves in the famous Figure 1 of this last reference. Lack of systematically collected K and L data on well-characterized monodisperse linear polymers prevents any further assessment of the model's success in predicting the details of the molecular parameter dependence of the associated non-Newtonian prefactors.

Extending the model applicability to materials with molecular size polydispersity and to branched polymers,

where there are more opportunities to test its predictive capacity, is the next pursuit. In either case, there is a marked increase in the elasticity of the fluid, which translates to a higher J value.[31] This causes an earlier appearance of non-Newtonian behavior (appropriately accommodated by eq 21) while practically leaving the characteristic rate of shear thinning cessation intact (eq 22). Consequently, and in accord with the evidence, the predicted shear thinning decay is now smoother, the n and m exponents are higher (yet, still $(2 - m)/(1 - n) \approx 1.6$) while the K and L stress coefficients are lower in value. Turning these descriptive arguments into a detailed quantitative analysis is relatively straightforward but lengthy and, therefore, deserves to be presented separately.

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