Nonlinear Rheology of Polymer Melts under Shear Flow

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ABSTRACT: The nonlinear rheology of an unentangled polymer melt under shear flow is considered theoretically. The finite chain extensibility is taken into account explicitly. The tangential stress and the first and the second normal-stress differences are calculated as a function of shear rate $\dot\gamma$. It is shown that in the shear thinning regime, the viscosity η decreases as $\dot\gamma^{-2/3}$.

1. Introduction

In the last decades considerable progress has been made in the rheology of polymer solutions and polymer melts.[1–3] At the same time, the nanorheology of confined polymer systems, the rheology of liquid crystalline polymers, and the rheology of block-copolymer systems is still in its infancy. In the present paper, one of these problems, namely nonlinear rheology of polymer melts, will be considered. The essential ingredient of our analysis is the finite extensibility of polymer chains. All effects connected with topological entanglements are ignored; i.e. the polymer chains are assumed to be relatively short.

Experiments demonstrate that the bulk polymer melts consisting of short chains exhibit nonlinear behavior for extremely high shear rates.[4–8] However, when the melt is confined between two walls at a distance of the order of the size of the polymer coil, the nonlinear effects emerge at essentially small shear rates.[4–8] The principal reason for this behavior is connected with the strong suppressing of the relaxational processes in the confined state.[4–9]

Here we consider the nonlinear rheology at high shear rates in the unconfined bulk. The confined situation is considered in ref 12 for the case of strong adsorption and in ref 13 for the case of weak adsorption.

Our approach will be a scaling analysis based on the following model. Let us divide the chains in N statistical segments of length a, so that $Na^2 = \langle \mathbf{R}^2 \rangle$, where $\mathbf{R}$ is the end-to-end distance vector, and excluded volume $v = V/N$, where V is the excluded volume of whole chain. The melt is an incompressible system; therefore equilibrium chain statistics in the bulk is essentially Gaussian.[10] Throughout the paper, energy will be expressed in units $k_B T$.

2. Nonlinear Rheology in the Bulk

Let us introduce Cartesian coordinates (x, y, z) and assume that the velocity field, directed along the x-axis, is characterized by a shear rate $\dot\gamma$. The velocity gradient is along the z-axis (Figure 1).

The case where the chain is described as a Rouse chain with infinite extensibility will be considered first. The flow elongates the chain by the friction force
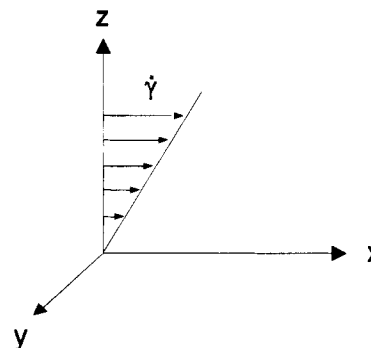
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Figure 1. Definition of the coordinate system.

$$F_x \sim N\zeta\dot\gamma R_z \tag{1}$$

where ζ is the friction coefficient of a segment and R_z is the size of the polymer coil in the z direction ($R_z \sim aN^{1/2}$). Due to this force the chain becomes elongated along the x-axis with end-to-end distance

$$R_x \sim a^2 N F_x \sim (\dot\gamma\tau)N^2 R_z \tag{2}$$

where $\tau \sim \zeta a^2$ is the characteristic relaxation time of a segment.

The tangential and normal stresses in the system can be calculated from the well-known equation for the stress tensor.[1,2,10] Let us assume that a statistical segment with index n along the chain is elongated by means of the friction force $\mathbf{f}^{(n)}$ and that the end-to-end distance vector for the segment is $\mathbf{r}^{(n)}$. In this case the stress tensor is given by

$$\sigma_{ij} = c \sum_{n=1}^{N} \langle f_i^{(n)} r_j^{(n)} \rangle \tag{3}$$

where c is the concentration of the chains in the bulk, i.e. $c \sim 1/(Nv)$. For our situation the friction force $f_x^{(n)} \sim F_x$, $f_y^{(n)} = f_z^{(n)} = 0$. Furthermore, $\sum_{n=1}^{N} \mathbf{r}^{(n)} = \mathbf{R}$. After substitution of eqs 1 and 2 and averaging with respect to the Gaussian distribution function ($\langle R_z \rangle = 0$, $\langle R_z^2 \rangle \sim a^2 N$) [note that the friction forces, $f_x^{(n)}$, acting in the x direction, do not affect the chain statistics in the y, z directions: the chain keeps unperturbed Gaussian dimensions along these axes], the well-known results of the Rouse model for the tangential stress σ_{xz} and the first N_1 and second N_2 normal-stress difference are recovered.[1,2]

$$\sigma_{xz} \sim (\dot\gamma\tau)N/v$$

$$N_1 = \sigma_{xx} - \sigma_{zz} \sim (\dot{\gamma}\tau)^2 N^3/v \qquad (4)$$

$$N_2 = \sigma_{zz} - \sigma_{yy} = 0$$

Of course, the effective viscosity $\eta = \sigma_{xz}/\dot{\gamma} \sim \tau N/v$ is proportional to the molecular weight of the chains.

For large enough shear rates eq 2 implies that the component R_x of the end-to-end vector will be very large. However, real macromolecules are characterized by a limited extensibility: the end-to-end distance cannot become larger than the contour length, R_{max}, which is proportional to N ($R_x \sim aN$). This fact leads to nonlinear chain elasticity and to nonlinear properties of the melt. The idea of coupling between nonlinear chain elasticity and the corresponding nonlinear dynamics beyond perturbation theory was first considered in ref 11 and later applied to the description of nonlinear rheology of confined polymer melts with strong adsorbing walls.[12]

In the general case the chains are characterized by the following relation between the elastic force **F** and the end-to-end distance **R**

$$\mathbf{F} = \frac{3\mathbf{R}}{a^2 N}\varphi\!\left(\frac{\mathbf{R}^2}{R_{max}^2}\right) \qquad (5)$$

with

$$\varphi(x) = 1 + \kappa_1 x + \kappa_2 x^2 + \dots \quad x < 1$$

$$\varphi(1) = \infty \qquad (6)$$

where $\kappa_1, \kappa_2, \dots > 0$ are numerical coefficients. This functional relation is well-known for random flight models.[14-16] When the chain is stretched, the tangential deformation R_x, due to the nonlinearity (i.e. finite extensibility), induces an additional normal elastic force $\Delta F_n = F_n(R_n,R_x) - F_n(R_n,R_x = 0)$, where $R_n = \sqrt{R_y^2 + R_z^2}$. If the elongation is small, $R_x \ll aN$, the relation between tangential and normal forces can be calculated by perturbation theory:

$$\Delta F_n \sim \frac{R_n}{N}F_x^2 \qquad F_x < \frac{1}{a} \qquad (7a)$$

If, on the other hand, $R_x \sim aN$ and $\varphi \gg 1$, then $\Delta F_n/F_x = R_n/aN$ or

$$\Delta F_n \sim \frac{R_n}{aN}F_x \qquad F_x > \frac{1}{a} \qquad (7b)$$

It is clear from eq 7b that, when the elongation force satisfies $F_x > 1/a$, the induced normal force for $R_z \sim aN^{1/2}$ satisfies $\Delta F_z > 1/(aN^{1/2})$ and, hence, exceeds the thermal force. As a consequence, the characteristic normal size R_z of the chain must decrease. This effect appears for shear rates $\dot{\gamma} > \dot{\gamma}^*$, where the critical shear rate $\dot{\gamma}^*$ follows from the condition $F_x \sim 1/a$

$$\dot{\gamma}^* \sim \frac{1}{\tau}N^{-3/2} \qquad (8)$$

The characteristic normal size, $R_z = \xi$, for higher shear rates can be derived from the following arguments. The flow causes elongation of the chain by the friction force (1). This force is large enough (for large N) to almost completely extend the chain in the x direction and to suppress its fluctuations in the normal direction. In fact, the force F_x tends to extend the chain
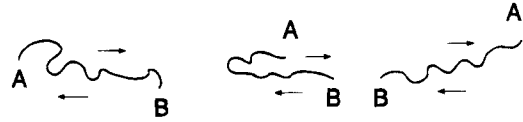
Figure 2. Schematic picture of chain motion for high shear rates.

as much as possible: its end-to-end projection onto the x-axis is $R_x \sim R_{max}$ (for simplicity we assume that a pair of forces is applied to the chain ends). Any deviation of the chain in the z direction (on a distance $\sim\xi$) will imply a decrease of R_x by at least $\Delta R_x \sim \xi^2/R_x$. The typical ξ is given by the condition

$$\Delta R_x F_x \sim 1 \qquad (9)$$

Equations 1 and 9 give the result

$$\xi \sim a(\dot{\gamma}\tau)^{-1/3} \qquad (10)$$

Obviously, fluctuations take place on smaller scales as well. Let us consider a blob consisting of g segments (i.e. any part of the chain containing g segments) with a typical normal size $r_{g,y} \sim r_{g,z} \sim \xi_n \sim ag^{1/2}$, and fixed end-to-end distance $r_{g,x} \sim ag$. The flow impacts on this blob by the friction force

$$f_{g,x} \sim g\zeta\dot{\gamma}r_{g,z} \qquad (11)$$

The fluctuations in the normal direction imply fluctuations along the x direction with characteristic amplitude $\Delta_x \sim \xi_n^2/(ag) \sim a$. The maximum blob for which the flow does not affect its size in the normal direction can be obtained from the condition $\Delta_x f_{g,x} \sim 1$. From this the previously derived result eq 10 is found again. The characteristic number of segments g in the maximum blob is

$$g \sim (\dot{\gamma}\tau)^{-2/3} \qquad (12)$$

For high shear rates ($\dot{\gamma} > \dot{\gamma}^*$), the motion of the chains is more complicated. If the projection of the end-to-end vector onto the z-axis is negative, $R_z < 0$, the chain will rotate (Figure 2). The characteristic rotation time is given by

$$T_{rot} \sim (aN)/(\dot{\gamma}\xi) \sim \tau N(\dot{\gamma}\tau)^{-2/3} \qquad (13)$$

This effect is not important for the present discussion but will be important for a discussion of oscillatory shear.[17]

Now let us consider the stresses in the bulk. We start with small shear rates, $\dot{\gamma} < \dot{\gamma}^*$. The shear stress and the first normal-stress difference, N_1, coincide in this regime with the corresponding results for the Rouse model, eq 4. Within the approximations used (the Rouse model + incompressibility) the flow parts of σ_{yy} and σ_{zz} stresses are zero. Compare 3 where $\mathbf{f}^{(n)}$ is the additional hydrodynamic force due to the macroscopic flow acting on the nth link. For the Rouse model this force is proportional to the flow velocity and therefore has only an x component unequal to zero. Hence,

$$N_2 = 0 \qquad (14)$$

In order to calculate the stresses for high shear rates ($\dot{\gamma} > \dot{\gamma}^*$), the essential parameter is the tension force along the x-axis of a statistical segment, which is (Figure 3)
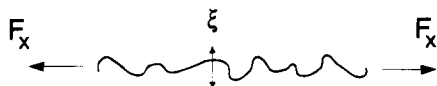
Figure 3. Characteristic conformation of the chains for high shear rate.
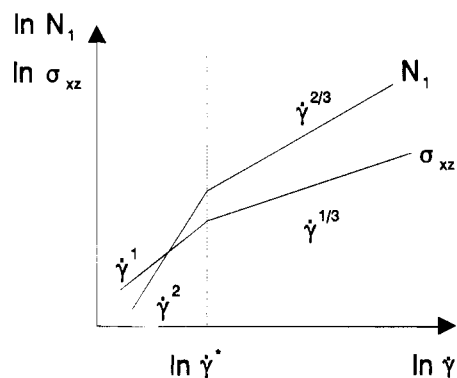
Figure 4. Tangential (σ_{xz}) and normal (N_1) stresses as a function of shear rate $\dot\gamma$.

$$f_x^{(n)} \sim F_x \sim \frac{N}{g}(1/a) \sim N(\dot\gamma\tau)^{2/3}/a \qquad (15)$$

Therefore, the tangential component of the stress is

$$\sigma_{xz} \sim \frac{1}{Nv}\sum_{n=1}^{N}\langle f_i^{(n)} r_j^{(n)}\rangle \sim \frac{1}{Nv}(F_x\xi) \sim (\dot\gamma\tau)^{1/3}/v \qquad (16)$$

the first normal-stress difference is given by

$$N_1 \sim \sigma_{xx} \sim \frac{1}{Nv}\langle F_x R_x\rangle \sim N(\dot\gamma\tau)^{2/3}/v \qquad (17)$$

The second normal-stress difference is still zero also for the nonlinear regime. The qualitative dependence of σ_{xz}, N_1 on $\dot\gamma$ is shown in Figure 4.

From eq 17 the following expression for the viscosity is obtained

$$\eta = \sigma_{xz}/\dot\gamma \sim \tau(\dot\gamma\tau)^{-2/3}/v \qquad (18)$$

Thus the viscosity for shear thinning satisfies the familiar $-2/3$ power law (Figure 5). This power law has been obtained analytically before[3] for the non-Hookean dumbbells model with a force law obeying eq 5 with
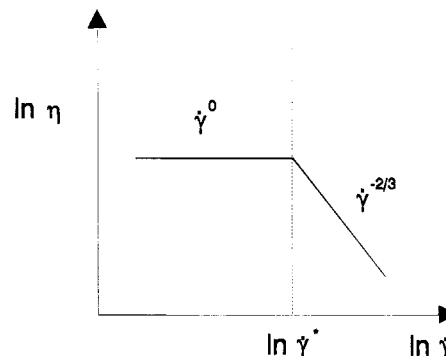
$$\varphi\left(\frac{\mathbf{R}^2}{R_{max}^2}\right) = 1/\left(1 - \left(\frac{\mathbf{R}^2}{R_{max}^2}\right)\right) \qquad (19)$$

In the present paper we show that the $-2/3$ power law of shear thinning is universal for systems with finite extensibility.

3. Concluding Remarks

In this paper a theory for nonentangled polymer melts in the bulk state has been developed. Taking into account finite extensibility of the chains, the tangential and the first and the second normal-stress differences were calculated and it was demonstrated that the viscosity in the shear thinning regime decreases by a $-2/3$ power law.

This law has been found experimentally and by computer simulations for strongly confined short chain systems.[6-9] The principal difference between bulk and confined melt consists in the scale of the relaxation

times. To date, no consistent description of the mechanisms that lead to a strong increase of the relaxational times in the confined melt exists. However, experiments show[4-8] that the relaxational processes are strongly suppressed in the confined state. As a result nonlinear rheological behavior for confined polymer melts is manifested for much smaller shear rates than for the bulk. This is connected with the fact that the characteristic shear rate for shear thinning is inversely proportional to the relaxation time of the polymer segments (eq 8).

Figure 5. Schematic behavior of effective viscosity η as a function of shear rate $\dot\gamma$.

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