Nonlinear viscoelasticity of entangled DNA molecules

D. Jary[1,2], J.-L. Sikorav[2] and D. Lairez[1]

[1] *Laboratoire Léon Brillouin, CEA-CNRS, CEA/Saclay*
91191 Gif sur Yvette Cedex, France
[2] *Service de Biochimie et Génétique Moléculaire, Département de Biologie Cellulaire et*
Moléculaire, CEA/Saclay - 91191 Gif sur Yvette Cedex, France

Abstract. – T4 DNA semi-dilute entangled solutions submitted to high shear rates show a region of weak dependence of the steady-state shear stress on the shear rate. For the highest concentration studied, this region extends over two decades of shear rate, and a plateau of shear stress is observed over one decade. The concentration dependence of the lower boundary of this region scales as the reciprocal of the disengagement time. The concentration dependence of the upper boundary is compatible with the scaling of the reciprocal of the Rouse relaxation time of the entire chain in its tube.

Solutions or melts of entangled polymers possess unusual rheological properties [1]. In particular, the dependence of the steady-state shear stress on shear rate varies with the magnitude of the shear rate. At very low shear rate, the system behaves as a Newtonian fluid, with the shear stress σ increasing linearly with the shear rate $\dot\gamma$. When the shear rate is further increased however, the viscoelastic behaviour becomes nonlinear.

The rheology of entangled polymers under high shear rates has been discussed theoretically by several authors [2-7]. According to the classical theory of Doi and Edwards [2], each polymer chain is confined within a virtual tube made up of the neighbouring chains. The longest relaxation time of the system is the disengagement (or reptation) time $\tau_{\rm d}$, which characterises the escape of the chain from its confining tube. At sufficiently low shear rates ($\dot\gamma\tau_{\rm d} < 1$), the entanglement network is nearly undisturbed. The system is expected to behave as a Newtonian fluid in agreement with experimental observations. At flow rates greater than $\tau_{\rm d}^{-1}$, the flow stretches the tube. The chain follows at first but then shrinks back by a retraction process. At these high shear rates, Doi and Edwards predict that the steady-state viscosity $\eta(\dot\gamma)$ is a decreasing function of $\dot\gamma$: $\eta(\dot\gamma) \propto \dot\gamma^{-3/2}$. Since $\sigma(\dot\gamma) = \eta(\dot\gamma) \times \dot\gamma$, the shear stress should increase at low shear rate, have maximum at $\dot\gamma_1 = \tau_{\rm d}^{-1}$, and then decrease at higher shear rate. Physically, the shear stress cannot decrease indefinitely as the shear rate is increased. It has been proposed that the shear stress would start to increase again at a higher rate $\dot\gamma_2$
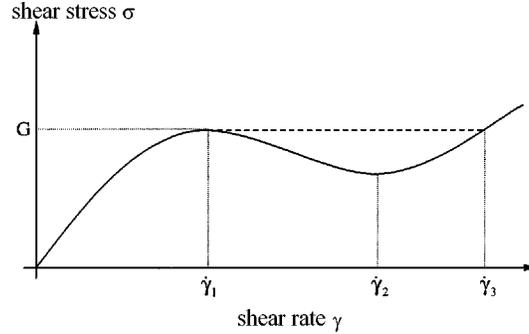
Fig. 1. – Theoretical steady-state shear stress σ plotted as a function of the shear rate $\dot{\gamma}$ (solid line). The unstable region corresponds to $\dot{\gamma}_1 \leq \dot{\gamma} \leq \dot{\gamma}_2$. Dashed line: expected plateau of stress resulting from flow splitting.

corresponding to the reciprocal of the equilibration (Rouse) time τ_R of the polymer within its tube (see fig. 1). In the interval between $\dot{\gamma}_1$ and $\dot{\gamma}_2$, the decrease of $\sigma(\dot{\gamma})$ with increasing shear rate implies that the flow is unstable. One expects the flow to split into two domains of low and high shear rates, in such proportion that the measured shear stress $\sigma(\dot{\gamma})$ will remain constant (broken line in fig. 1). The value of the upper boundary $\dot{\gamma}_3$ is still debated: $\dot{\gamma}_3$ could be of order $1/\tau_R$. Alternatively, Cates *et al.* [6] have suggested that $\dot{\gamma}_3$ corresponds to a much higher frequency $1/\tau_e$ equal to the Rouse relaxation rate of portion of the chain with a size equal to the diameter of the tube. Recently, Marrucci and Ianniruberto have proposed a new mechanism of constraint release by convection [7]. This new approach predicts a quasi-plateau of shear stress (rather than a true one) which becomes flatter and flatter as the number of entanglements per chain increases.

Experimentally, a true plateau of stress is usually not observed with melts of synthetic polymers. A nonlinear behaviour at $\dot{\gamma} > 1/\tau_d$ has been reported, but with a gently rising shear stress ($\sigma(\dot{\gamma}) \propto \dot{\gamma}^{0.2}$) [1]. The lack of experimental confirmations of the theory may result from several factors. First, the observation of the plateau requires that the separation of τ_d and τ_R be large enough (with a ratio τ_d/τ_R greater than 30 according to ref. [3]). Second, it should be noted that experiments performed at high shear rates often show a serious difficulty (for instance, in cone-and-plate experiments, the sample can be expelled from the apparatus). One way to overcome these difficulties is to work with semi-dilute solutions of extremely long chains. This has been done by Bercea *et al.* [8] with very high molecular mass poly(methyl metacrylate) ($M = 24 \times 10^6$ g/mol) having a polydispersity of about 1.2-1.3 (M. Bercea, personal communication). These authors have observed a behaviour similar to the one shown in fig. 1. However, the shear stress is not strictly constant but increases slightly with the shear rate in the plateau region. This may be due to the polydispersity of the chains, as theoretically expected [2].

In this letter, we report a study of semi-dilute solutions of bacteriophage T4 DNA chains submitted to high shear rates. T4 DNA has a molecular weight $M = 1.1 \times 10^8$ g/mol corresponding to 166000 base pairs. These chains are rigorously monodisperse. Due to the very large size, semi-dilute T4 DNA solutions have very long relaxation times τ_d (up to 1000 s), which facilitates their study in the nonlinear regime. From a biological point of view, the study of entangled DNA submitted to high shear rates can also lead to a better understanding of some physical aspects of cell division [9].

We have purified unmodified T4 DNA (cyt-DNA) using a standard protocol [10,11]. Semi-
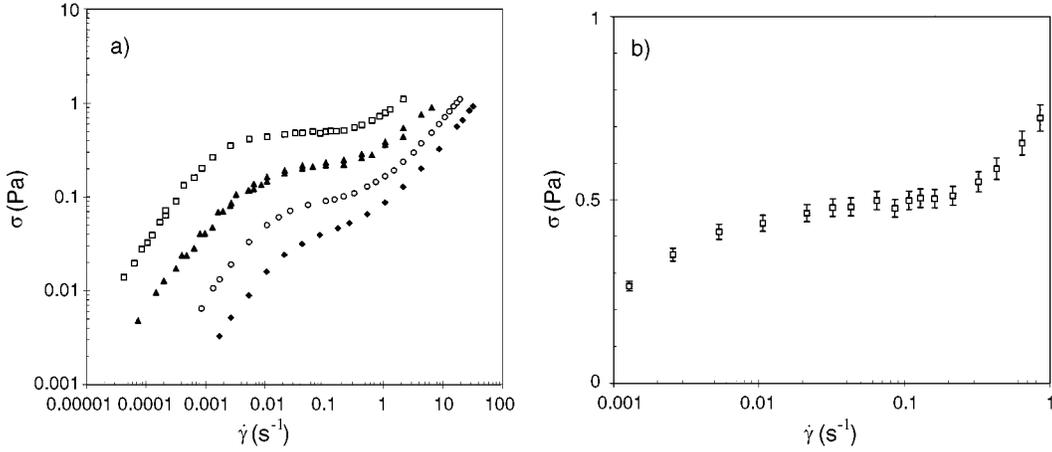
Fig. 2. – a) Shear stress σ measured in the steady-state regime as a function of the shear rate $\dot{\gamma}$ for different concentrations (open squares $C = 1.05$, full triangles $C = 0.70$, open circles $C = 0.49$, full diamonds $C = 0.35$ mg/ml). b) Linear-log plot of the shear stress σ as a function of the shear rate $\dot{\gamma}$ for the highest concentration. The error bars ($\pm 5\%$) indicate the accuracy of the measurements.

dilute DNA solutions with four different concentrations (0.35, 0.49, 0.7 and 1.05 mg/ml) were prepared in an aqueous buffer containing 50 mM Tris HCl pH 7.5, 100 mM KCl and 1 mM EDTA. The rheological experiments were performed at 30 °C in a magnetorheometer as described previously [12] (data not shown). The monodispersity of the solution was checked by pulse-field gel electrophoresis using a field inversion apparatus (Biorad). We observe no degradation of the DNA molecules, even after one month of rheological experiments.

The steady shear stress σ as a function of the shear rate $\dot{\gamma}$ has been measured for the four different concentrations (fig. 2a). For a given concentration, three regimes are observed when the shear rate is increased: a linear regime where σ is proportional to $\dot{\gamma}$, a second regime where this dependence is weakened, and a third regime where the shear stress increases back. In the second regime, the shear stress dependence on the shear rate decreases with increasing concentrations. This dependence is shown in greater detail for the highest concentration (1.05 mg/ml) in fig. 2b. The stress increases by only 30% over two decades of shear rate ($0.004 < \dot{\gamma}(\mathrm{s}^{-1}) < 0.4$), and a plateau of stress is observed over one decade ($0.02 < \dot{\gamma}(\mathrm{s}^{-1}) < 0.2$). This is our key observation.

According to the Doi and Edwards theory, the shear rate $\dot{\gamma}_1$ corresponding to the crossover between the first and the second regime should scale as the reciprocal of the disengagement time τ_{d}, while the corresponding steady-state shear stress should scale as the plateau elastic modulus G of the solution. To test this prediction we have determined the zero shear viscosity $\eta_{\dot{\gamma} \to 0}$ and τ_{d} for the four different concentrations. Our results are in excellent agreement with those obtained previously with T2 (164000 base pair long) chains [12] (data not shown). We have then deduced the plateau elastic modulus $G = (12/\pi^2) \times \eta_{\dot{\gamma} \to 0}/\tau_{\mathrm{d}}$ [2] from these measurements. We find that $G(\mathrm{Pa}) = 0.5 \pm 0.1 \times C^{2.3}$, where C is the DNA concentration expressed in mg/ml. This dependency on concentration is that expected for entangled chains [13, 14]. From the values of the plateau elastic modulus, it is possible to deduce the number of entanglements per chain $n = G/G_{\mathrm{Rouse}}$ with $G_{\mathrm{Rouse}} = kTC/M$, k being the Boltzmann constant ($G_{\mathrm{Rouse}}(\mathrm{Pa}) = 0.025 \times C$ for T4 DNA). We find $n = 22$ for the highest concentration.

In fig. 3, the reduced stress σ/G has been plotted as a function of the reduced shear rate
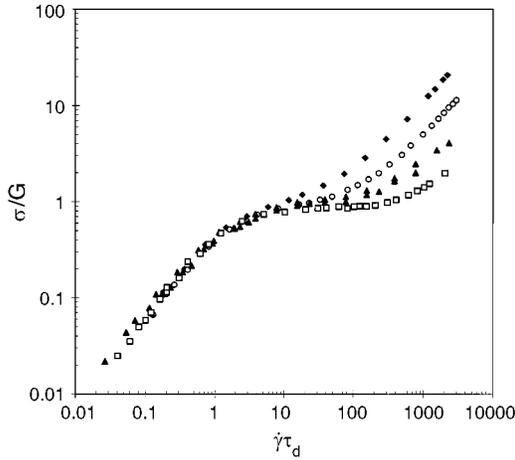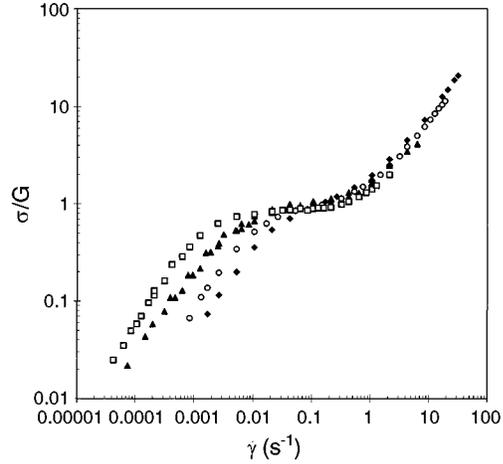
Fig. 3

Fig. 4

Fig. 3. – Reduced shear stress σ/G as a function of the reduced shear rate $\dot\gamma\tau_d$. The symbols meaning is the same as in fig. 2a. The measured longest relaxation time τ_d varies as $\tau_d = 850 \times C^{2.4}$ with C in mg/ml.

Fig. 4. – Reduced shear stress σ/G as a function of the shear rate $\dot\gamma$. The symbols meaning is the same as in fig. 2a.

$\dot\gamma\tau_d$. A good superposition of the curves obtained at the different concentrations is observed up to the onset of the nonlinear behaviour. The height of the plateau is found equal to $\sigma/G = 0.85 \pm 0.1$. Doi and Edwards have initially predicted $\sigma/G = 0.45$ [15], while taking into account Rouse relaxation, McLeish and Ball [3] have computed a higher value $\sigma/G = 0.66$. Our measurement is much closer to this latter prediction, but still higher.

In fig. 4, the reduced stress σ/G has been plotted as a function of the shear rate $\dot\gamma$. We observe a good superposition of the four curves for the highest shear rates. This indicates that the shear rate $\dot\gamma_3$ corresponding to the upper boundary of the plateau of stress depends very little on the concentration. This finding is compatible with the expectation that $\dot\gamma_3$ scales as the reciprocal of the Rouse time τ_R of the whole T4 chain in its tube, since this time has a weak concentration dependence, $\tau_R \propto C^{0.31}$ [14] (in contrast to the much smaller time τ_e proposed in ref. [6]: $\tau_e \propto C^{-2.31}$). The absolute value of the time $1/\dot\gamma_3$ that we observe, about 1 s, is also more compatible with the time τ_R rather than with τ_e.

Concluding remarks. – We have studied the dependence of the steady-state shear stress on shear rate in semi-dilute T4 DNA solutions. There exists an intermediate region where this dependence is weakened. Within this region, a plateau of stress is observed in the most concentrated solution. The value of the lower and upper boundaries of this region as well as its height are in good agreement with theoretical expectations. These DNA solutions also display an interesting transient behaviour which will be reported elsewhere. After the submission of this manuscript several important theoretical articles discussing the nonlinear viscoelastic behaviour of entangled polymers have appeared [16-18]. We plan to analyse our results in the light of these very recent works.

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