SIMULATION STUDY OF UNENTANGLED POLYMERS UNDER FAST FLOW

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ABSTRACT

Viscosity η, 1st normal stress coefficient Ψ_1 and the chain dimension R under fast shear flow are calculated by using the Rouse model with excluded volume interaction among monomers of different chains. Simple application of the friction reduction (FR) model can describe the decrease of η and Ψ_1 at high shear rate, but it fails to describe the increase of R. On the other hand, the shear blob model can correctly predict η and R, but it is hard to describe Ψ_1. We are also studying unentangled polymer solutions by using Kremer-Grest model. Behavior of the steady elongational viscosity is qualitatively consistent with FR model, but the shear thinning in solution is rather close to that in melt, suggesting that FR alone can not describe this thinning.

SOFT CORE MODELS

The friction reduction[1,2] (FR) under fast flow is now considered as one of the key concepts for understanding the polymer dynamics. Since FR is believed to be independent of the entanglement, it is preferable to study unentangled polymers since we can avoid complications due to the entanglement. For this purpose, we can use the standard Kremer-Grest (KG) model with small number of monomers N per chain. But with short chains the effect of finite extensibility would start at relatively low strain rates. In order to extend the range of strain rate, we use models that allow long but unentangled chains.

First we tried soft core models such as DPD. In these models monomers can overlap and chains can cross with each other. We have found that these models show only very weak shear thinning. Experimentally[3], however, the steady shear viscosity $\eta(\dot{\gamma})$ of unentangled polymers shows shear thinning described by the following empirical formula:

$$\eta(\dot{\gamma}) = \frac{\eta(0)}{[1 + (\tau\dot{\gamma})^2]^{1/4}} \tag{1}$$

where $\dot{\gamma}$ is the shear rate and τ is the stress relaxation time. We will see that the excluded volume interaction is necessary to reproduce this shear thinning.

ROUSE MODEL WITH HARD CORE REPULSION

Next we use the Rouse model with excluded volume interaction. In this model, each chain is described by the Rouse model, but there is a hard core repulsion among monomers in different chains. This model is equivalent to the KG model in which the bond potential is replaced by a simple spring $U(r) = 3k_BT/\sigma^2$ (σ is the monomer diameter). Although monomers (of different chains) can not overlap, bonds can extend and the chain crossing can take place. We have confirmed that this model does not show entanglement up to $N = 800$. Under steady shear flow, this model shows the shear thinning as Eq.1. Moreover, we have found that the 1st normal stress coefficient $\Psi_1(\dot{\gamma})$ and $\eta(\dot{\gamma})$ satisfy

$$\frac{\Psi_1(\dot{\gamma})}{\Psi_1(0))} = \left(\frac{\eta(\dot{\gamma})}{\eta(0)}\right)^2 \tag{2}$$

According to the generalized Rouse model[4] by Watanabe et al., this relation indicates that the fluctuation-dissipation theorem holds even under shear flow in which the friction coefficient ζ is reduced. We've found, however, that the chain dimension under shear flow $R(\dot{\gamma})$ behaves at high shear rate as

$$\frac{R(\dot{\gamma})^2}{R(0)^2} \propto (\dot{\gamma}\tau)^{1/2} \tag{3}$$

This relation can't be explained by a simple application of the generalized Rouse model. On the other hand, the "shear blob" model by Colby et al.[3] can correctly predict the exponents in both Eq.1 and Eq.3. But we haven't yet succeeded to derive Eq.2 by this model. A kind of unification of the FR and blob models may be required.

POLYMER SOLUTION STUDIED BY KG MODEL

It is widely believed that in polymer solution the reduction of friction between the polymer segment and the surrounding solvent molecules is much weaker than in polymer melts. To see whether this can be reproduced by using coarse-grained model, we are studying polymer solutions by KG model (short chain). Here the solvent molecules is the same as the monomer of the polymer chain (athermal solvent).

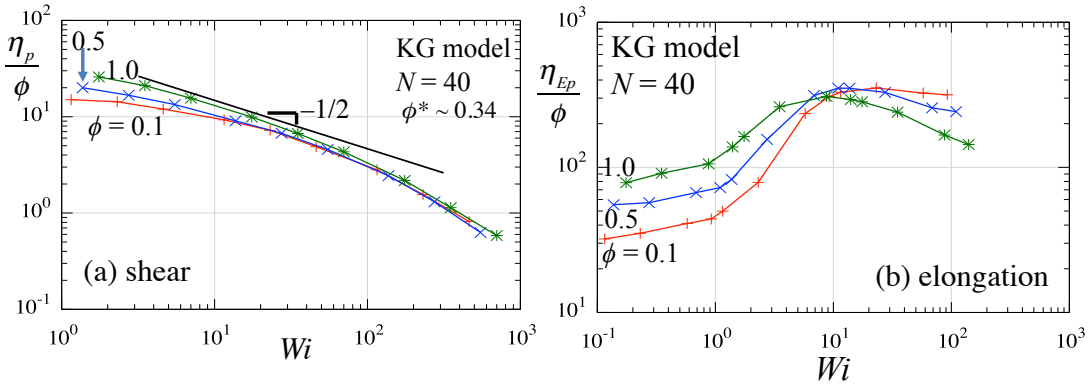

Figure 1: Steady shear (a) and elongational (b) viscosities of polymer solutions (KG model)

Fig. 1 shows the steady shear and elongational viscosities of polymer solutions as functions of the Weissenberg number Wi (elongational viscosity is calculated by the UEF package of LAMMPS). Here, ϕ is the volume fraction of the polymer, and $\eta_p = \eta - \eta_s$ (η and η_s is the viscosities of the solution and solvent). In the case of elongational flow, the hardening ($Wi \sim 1 \sim 10$) is stronger in solution, and the following thinning is weaker. This is at least qualitatively consistent with the FR model. In the case of shear flow, on the other hand, thinning in solution is only slightly weaker than in the melt. This indicates that the solution ($\phi = 0.1$) has similar FR as the melt, or there may be other cause(s) of the *shear* thinning. We also need to consider that KG model, with no angle/torsion potentials and no side chains, may have weaker friction than the real polymers even under no flow.

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