ALIGNMENT OF WORMLIKE MICELLES UNDER SHEAR FLOW: COMPARISON WITH POLYMERS

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ABSTRACT

We investigate the effect of scission on the alignment of wormlike micelles under shear flow. For this purpose, we conduct dissipative particle dynamics simulations of nonionic surfactant and polymer solutions. To compare the alignment of wormlike micelles and polymers, we introduce the Weissenberg number defined as the product of the shear rate and the longest relaxation time. Comparing their mean orientation angles demonstrates that wormlike micelles align less in the flow direction than polymers when the Weissenberg number is larger than a threshold value. By evaluating the average lifetime of wormlike micelles, we show that flow-induced scission causes the suppression of micellar alignments.

INTRODUCTION

It is well known that polymers under shear flow align more in the flow direction as the shear rate increases. Similarly to polymers, rodlike and wormlike micelles also align in the flow direction. However, unlike polymers, micelles constantly exhibit scission and recombination. Moreover, as the shear rate increases, scission occurs more frequently due to flow-induced scission[1]. Recent experimental results suggest that scission kinetics affects micellar alignment for high shear rates[2]. However, little is known about the effect of scission on micellar alignment because it is difficult to experimentally measure the scission frequency and observe the structures and dynamics of individual micelles in flowing solutions. In the present study, we investigate both the alignment and scission kinetics of wormlike micelles under shear flow using the dissipative particle dynamics (DPD) simulations. Specifically, to reveal the scission effect on micellar alignment, we compare the alignment of wormlike micelles and polymers (i.e., chains without scission kinetics) and evaluate the average lifetime of micelles under shear flow.

SIMULATION METHOD

The model of a nonionic surfactant molecule contains a hydrophilic head particle and two hydrophobic tail particles, which are connected by harmonic springs. The interaction parameters between particles are the same as in our previous study[1]. For DPD simulations of polymer solutions, we use
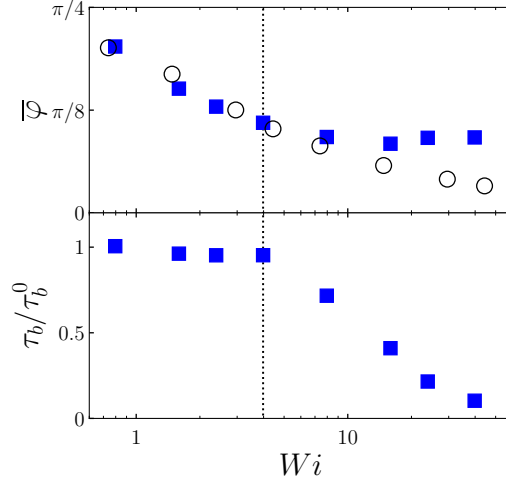
Figure 1: Weissenberg-number Wi dependence of mean orientation angle $\overline{\varphi}$ (top panel) for polymer chains (○) and micelles with $N_{\mathrm{ag}} = 400$ (■) and average lifetime τ_b (bottom panel) normalized by the value τ_b^0 at equilibrium. The black dotted line indicates the threshold Weissenberg number Wi_c for flow-induced scission.

the fully flexible polymer model used in the previous study[3]. To generate a uniform shear flow, we use the Lees-Edwards boundary condition and the SLLOD equations.

RESULTS

To investigate the effect of scission kinetics on micellar alignment, we compare the alignment of wormlike micelles and polymers (i.e., chains without scission kinetics). Since wormlike micelles and polymers have different timescales, we introduce the Weissenberg number $Wi = \tau\dot{\gamma}$ defined as the product of the longest relaxation time τ and the shear rate $\dot{\gamma}$. We estimate τ of polymers by fitting the autocorrelation function $C(t)$ of the end-to-end vector with an exponential function $C_0 \exp(-t/\tau)$[3]. For wormlike micelles, we employ the method proposed in our previous study[1]. This method considers the scission effect on micellar relaxation. We define the direction of micelles and polymers as the eigenvector $e^{(1)}$ of the gyration tensor with the largest eigenvalue. To evaluate the alignment in the flow direction, we focus on the angle φ defined by $\tan\varphi = e_y^{(1)}/e_x^{(1)}$. Here, x and y indicate the flow and gradient directions, respectively. In the following, we characterize Wi dependence of alignment with a mean orientation angle defined as $\overline{\varphi} = \langle e^{2i\varphi}\rangle/2$[4]. The top panel of Fig. 1 shows $\overline{\varphi}$ of micelles with the aggregation number $N_{\mathrm{ag}} = 400$ and polymers as a function of Wi. When Wi is smaller than the threshold Weissenberg number $Wi_c(\simeq 4)$, $\overline{\varphi}$ of micelles and polymers collapse on a single function of Wi, indicating the similar alignment behavior of wormlike micelles and polymers. In contrast, wormlike micelles have larger values of $\overline{\varphi}$ than polymers for $Wi \gtrsim Wi_c$. This deviation demonstrates the suppression of micellar alignments in stronger shear flow.

To explore the origin of the alignment suppression, we evaluate the average lifetime τ_b of wormlike micelles under shear flow. The definition of micellar scission and the method to evaluate τ_b are the same as in our previous study[1]. The bottom panel of Fig. 1 shows τ_b normalized by the value τ_b^0
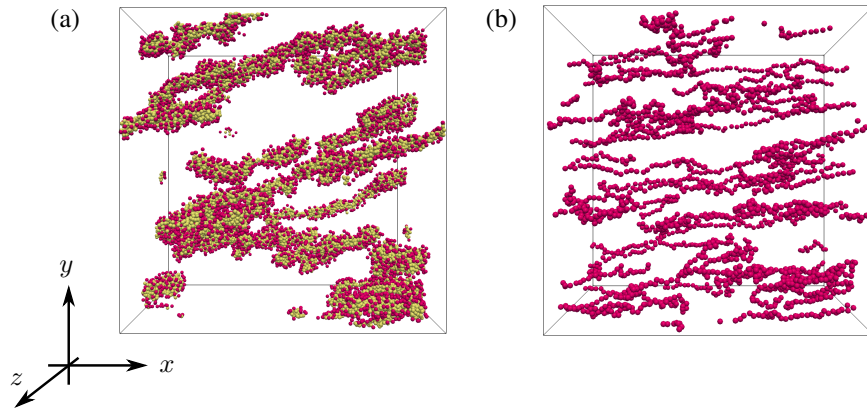
Figure 2: Visualization of (a) micelles with $200 \leq N_{\mathrm{ag}} \leq 600$ for $Wi = 48$ and (b) polymers for $Wi = 44$. In panel (a), hydrophilic and hydrophobic particles are indicated in red and yellow, respectively. In panel (b), some of the polymers in the system are shown for clarity.

at equilibrium as a function of Wi. Interestingly, $\tau_b/\tau_b{}^0 \simeq 1$ for $Wi \lesssim Wi_c$, whereas $\tau_b/\tau_b{}^0 \lesssim 1$ for $Wi \gtrsim Wi_c$. Therefore, we conclude that flow-induced scission occurs for $Wi \gtrsim Wi_c$ and it suppresses micellar alignments. Although one may think that the suppression is intuitively obvious considering the increase in the number of smaller micelles, we emphasize that we have evaluated the micellar alignment for fixed N_{ag}.

We also confirm the suppression of micellar alignments through visualization of wormlike micelles and polymers for a given Wi. Figure 2 (a) shows micelles with $200 \leq N_{\mathrm{ag}} \leq 600$ for $Wi = 48$, and Fig. 2 (b) shows some polymers which are randomly chosen for $Wi = 44$. In Fig. 2 (b), polymers significantly align in the flow direction, whereas wormlike micelles slightly tilt from the flow direction in Fig. 2 (a). This observation is consistent with the quantitative results shown in Fig. 1. In the conference, we will also demonstrate the mechanism of the alignment suppression due to flow-induced scission through the effective longest relaxation time under shear flow.

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