Effect of Overstretched Polymer Chains on Shear-Thickening Observed in Associating Polymer Gels

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1 Introduction

Shear-thickening phenomenon, or a growth of nonlinear viscosity with shear rate, is one of the characteristic rheological behavior observed in aqueous solutions of associating polymers. Despite many studies from both experimental and theoretical sides, molecular origin of shear-thickening behavior remains unclarified. We theoretically analyze shear-thickening on the basis of transient network theory[1] from the viewpoint of the overstretching effect of polymer chains beyond the Gaussian regime along the shear flow.[2]

2 Model

In order to examine the effect of overstretched polymer chains beyond the linear regime on the nonlinear viscosity, we adopt the chain tension given by the form

$$\tau(r/l) = f(r)a/k_BT = \frac{3r}{l} \left(1 + \frac{2A}{3} \frac{(r/l)^2}{1 - (r/l)^2}\right),$$

where $f(r)$ is the tension along the chain having end-to-end length $r$, $a$ is the monomer length, $l$ is the contour length of the chain ($k_B$ is the Boltzmann constant and $T$ is the temperature). Overstretching effect of the chain appears when its end-to-end length elongates longer than $\sim l/(1 + A)^{1/2}$. As the chain stretches longer along the flow, the possibility that the associative groups at chain ends dissociate from network junctions becomes higher due to higher tension of the chain. We assume that such dissociation rate is given by

$$\beta = \beta_0(1 + g\tau^2),$$

where the coupling constant $g$ gives the measure of how sensitively the dissociation rate is influenced by the tension.

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3 Thickening/Thinning Transition

In Figure 1 (i), we can see the transition from thinning to thickening with increasing $A$. To see the detail of thickening/thinning transition, we introduce the **nonlinear intrinsic viscosity coefficient** defined by

$$
\{\eta\} \equiv \lim_{\gamma \to 0} \frac{\eta(\gamma) - \eta(0)}{\eta(0) \gamma^2}.
$$

Shear-thickening should occur when $\{\eta\} > 0$. When $\{\eta\} < 0$, on the contrary, it is highly expected that only shear-thinning should appear. As shown in Figure 1 (ii), thickening/thinning transition occurs for $g$ below a certain critical value $g_c(N)$. ($g_c(N=100) \approx 0.4$ as seen in the figure.) When $g > g_c(N)$, we do not observe the transition from thinning to thickening because the chain does not overstretch before it dissociates from a junction due to large coupling $g$ between the chain tension the breakage rate. Thickening/thinning transition is summarized in Figure 1 (iii) which shows the boundary curves defined by $\{\eta\}(g, A) = 0$ separating the thickening region from the thinning region on the $A$-$g$ plane. Thus the balance between $A$ and $g$ determines the condition for shear-thickening.

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**References**
