

Necessary conditions for shear thickening in associating polymer networks

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Abstract

We study shear-thickening phenomena observed in thermoreversible gels of telechelic associating polymers on the basis of the transient network theory. We introduce nonlinear models for the elongational properties of the middle chain; the tension along middle chains contains a nonlinear term with an amplitude A that diverges if the chain is fully stretched. Models for the dissociation rate of end chains from network junctions are also introduced; the dissociation rate is coupled to the middle-chain tension by a coupling constant g . The balance between the nonlinearity strength and coupling intensity determines the necessary condition for thickening. A strong nonlinearity in the tension caused by a large A leads to thickening if the dissociation rate of the end chains is weakly coupled to the middle-chain tension. In contrast, if it is strongly coupled, the end chains easily dissociate upon a small nonlinear elongation of the middle chains, thus leading to thinning. We present theoretical phase diagrams showing the boundary of the thickening/thinning transition in the A – g plane, and we show the existence of a critical point for thickening in these diagrams. © 2006 Elsevier B.V. All rights reserved.

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1. Introduction

Water-soluble associating polymers have attracted widespread interest in recent years due to their industrial application as rheology modifiers in paints, ink, cosmetics, and for enhanced oil recovery [1]. A well-known class of associating polymers is HEUR (hydrophobically modified ethoxylated urethane) that carries short alkyl chains at both ends of poly(ethylene oxide) (PEO) [2–10]. Owing to its well-defined structure, HEUR has been regarded as an ideal system of associating polymers, and its rheological properties in water has been well studied experimentally as well as theoretically with the intention of gaining a fundamental understanding of associating polymer systems.

One of the most outstanding rheological features of HEUR aqueous solutions is the shear-thickening behavior followed by shear thinning, i.e., under shear flow, the stationary viscosity of the solutions increases with the shear rate, attains a maximum, and decreases at higher shear rates. In contrast, these systems reveal relatively simple linear viscoelasticities described in terms of the Maxwell model with a single relaxation time [2,3,6,11]. From the viewpoint of scientific as well as industrial interests, the molecular origin of shear thickening has been debated over the past two decades on the basis of experimental [6,7,10,12,13] and theoretical [14–20] evidences and computer simulations [21–23]. So far, some possible explanations for thickening have been suggested. They are mainly classified into two categories. One of them ascribes thickening to the nature of middle chains and suggests that a nonlinear high tension along stretched chains beyond the Gaussian range can cause thickening [7,12,15,18,20,23]. The other attributes thickening to an association among the different chains: the shear-induced transformation of intramolecular association to intermolecular association [14,16] and the shear-induced incorporation of floating chains (or micelles) into the network backbone [6,17]. Both effects enhance bridge chains by increasing the shear rate, thereby leading to an increase in the viscosity. There is also another possible mechanism: imperfect relaxation of dangling chains detached from network junctions [10,18,19,21,22].

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The transient network theory developed by Tanaka and Edwards [24,25] (hereafter referred to as TE) successfully explained some typical rheological properties observed in telechelic associating polymers, such as temperature–frequency superposition onto Maxwellian fluid with a single relaxation time, breakdown of the Cox–Mertz rule, and stress overshoot. However, shear thickening was not predicted within the TE model under the assumption of a Gaussian chain. In this paper, we will systematically study the nonlinear effect of the tension along middle chains on the basis of the transient network theory, taking into account the tension-dependent breakage rate of end chains. A brief report of a part of this work has already appeared [20].

According to recent experiments, the thickening observed in an aqueous solution of telechelic PEO disappears as the number of carbon units in the end chains decreases [7]. Thus, the occurrence of thickening is determined by the number of carbon units for a given species of a middle chain. Quite recently, telechelic poly(*N*-isopropylacrylamide) (PNIPAM) end-capped with octadecyl end groups were synthesized, and their rheological properties in water were studied [27,28]. It was revealed that they exhibit only thinning, though telechelic PEO carrying the same number of carbon units in the end chain exhibits thickening [7]. Thus, the molecular nature of the middle chains controls the condition that thickening occurs if they bear the same number of carbon units in the end chains. The main aim of the present work is to determine the necessary condition for thickening in terms of the molecular parameters of the middle and end chains.

This paper is organized as follows. In Section 2, we introduce nonlinear models for the elongational properties of the middle chain together with models for the dissociation rate of end chains as a function of the middle-chain tension. We then derive the basic equations describing the time development of the distribution function for such model chains. In Section 3, we solve the equations defined in Section 2 for small oscillatory shear deformations and study the linear viscoelasticity of our transient network. In Section 4, we derive a formula for the nonlinear stationary viscosity from the equations introduced in Section 2 and find the condition for thickening according to this formula. Finally, in Section 5, we discuss the molecular parameters describing the model telechelic polymer.

2. Transient network theory

2.1. Assumptions for the treatment of transient networks formed by telechelic polymers

We treat monodisperse linear polymers comprising N statistical segments and having short chains that are capable of attaching themselves to other end chains. The polymer concentration is assumed to be above the critical value of gelation so that the polymers construct a network spanning the entire system by connecting their end chains to other end chains (see Fig. 1). The molecular weight of a chain is assumed to be smaller than the entanglement molecular weight and therefore the reptation dynamics of polymers is not dominant. We deal with a homogenous network, i.e., polymers in the network are uniformly distributed. Hydrodynamic flow caused in the system due to added macroscopic deformations is assumed to be so slow that the specific time of deformation is much longer than the single-chain Rouse relaxation time τ_R .

The nodes of the network are micellar junctions formed by the end chains of polymers. According to the manner in which end chains are incorporated into micellar junctions, polymers are classified into three types; these comprise the active chain with both ends associated with two distinct junctions, the dangling chain with only one end sticking to a junction, and the loop chain with both ends incorporated into the same junction (see Fig. 1). Free chains floating in the solvent are ignored because they contribute only indirectly to the viscoelasticity [17]. Active chains are assumed to be ingredients of the backbone of a network; when a macroscopic deformation is applied to the network, they change their conformations accordingly. We assume that an active chain deforms affinely to the applied deformation; when the velocity gradient tensor $\hat{\kappa}(t)$ is added to the system, the end-to-end vector \mathbf{r} of the active chain obeys the equation of motion $\dot{\mathbf{r}} = \hat{\kappa}(t)\mathbf{r}$. On the other hand, dangling chains and loop chains are practically always in equilibrium states; this is because their frictional resistance against the flow is negligible under the current assumption that τ_R can be regarded as 0 when compared with the characteristic time of the flow. Accordingly, both these types of chains do not significantly contribute to the viscoelastic properties of the system; only active chains contribute. Letting $f(r)$ be the tension along the middle chain, the

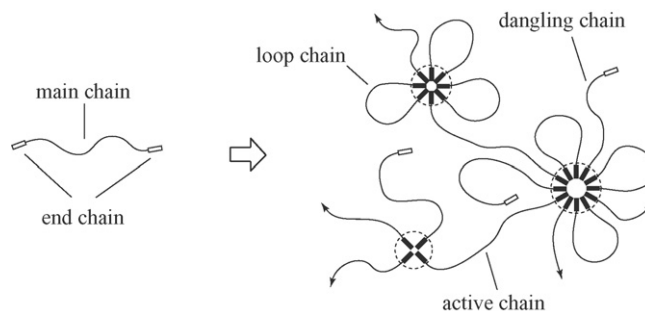


Fig. 1. Schematic representation of a telechelic polymer that has sticky short chains at both ends of a middle chain (left) and a model transient network formed by these telechelic polymers (right).

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