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Effects of shear flow on a semidilute polymer solution under phase-separating condition

Maya K. Endoh [a,1], Mikihito Takenaka [a], Takeji Hashimoto [a,b,*]

[a] *Department of Polymer Chemistry, Graduate School of Engineering, Kyoto University, Katsura, Kyoto 615-8510, Japan*
[b] *Advanced Science Research Center, Japan Atomic Energy Agency, Tokai-mura, Ibaraki 819-1195, Japan*

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Abstract

We studied the effects of a step-up shear flow from zero shear rate to the given shear rate, $\dot{\gamma}$, on formation of shear-induced structures for a semidilute polystyrene (PS)/diethyl malonate (DEM) solution below its cloud point temperature where the solution undergoes phase separation via spinodal decomposition (SD) in quiescent state. We elucidated that the effects of step-up shear can be divided into two regions: below and above a critical shear rate, $\dot{\gamma}_{c,SD}$. At $\dot{\gamma} < \dot{\gamma}_{c,SD}$, growing phase-separated domains via SD are found to be deformed under the flow, so that FFT spectra of the shear-microscopy images become elliptical with the wave number q_{mx} at the maximum intensity parallel to the flow being smaller than the corresponding wave number q_{mz} parallel to the neutral axis. However, strikingly enough, the aspect ratio q_{mz}/q_{mx} of the elliptic spinodal ring observed for this system was much smaller than that observed for binary fluids. The unique feature was proposed to be the elastic effect inherent in this system. When $\dot{\gamma}$ is larger than $\dot{\gamma}_{c,SD}$, however, initially phase-separating structures via SD are strongly deformed and distorted. Interestingly enough, the light scattering pattern was transformed from the isotropic ring pattern into the butterfly pattern. This is interpreted as follows: when $\dot{\gamma} > \dot{\gamma}_{c,SD}$, there may not be enough time for the domains composed of elastically deformed swollen-network chains to relax, and consequently the domains are cooperatively disrupted. The disrupted domains tend to squeeze solvent in order to release the elastic free energy stored in the deformed swollen-network chains, resulting in anisotropic domain more extended to neutral axis than flow direction and hence giving rise to the butterfly pattern.

Keywords: Phase-separation; Semidilute solution; Butterfly pattern

1. Introduction

In the last three decades, the shear-induced concentration fluctuations and/or phase separation have been extensively investigated for thermodynamically stable, single-phase, and semidilute polymer solutions in quiescent state [1–7]. However, there are no experimental studies on the effects of a shear flow on the phase-separation processes of semidilute polymer solutions in two-phase region at quiescent state, although there are some reports concerning two-dimensional (2D) computer simulations [8]. Therefore, in this paper, we shall present our works that challenged to study how the shear flow affects the phase-separating structure in semidilute polymer solutions. This may further enrich our knowledge concerning the formation of dissipative structure (ordered structures developed in open nonequilibrium systems) in the thermodynamically unstable state as well as the stable state. For this purpose, we first quenched our system into the thermodynamically unstable state to develop the isotropic phase-separating structure via spinodal decomposition (SD) in a quiescent solution, and then imposed the step-up shear flow to the same system which has the as-developed SD structure. We investigated the time changes in the phase-separating structure after the onset of the step-up shear flow as a function of shear rate.

* Corresponding author at: Advanced Science Research Center, Japan Atomic Energy Agency, Tokai-mura, Ibaraki 819-1195, Japan.
E-mail addresses: hashimoto.takeji@jaea.go.jp, hashi2@pearl.ocn.ne.jp (T. Hashimoto).
[1] Present address: 31 Perigee Dr., Stony Brook, NY 11790, USA.

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Before going into detailed discussion, we shall first describe the background of present work.

If the dynamical properties of each component in binary mixtures, such as viscosity and self-diffusion coefficient, are symmetric, the shear-induced mixing and/or homogenization occurs for the systems in thermodynamically unstable state or two-phase region, provided that the segregation power or interfacial tension is sufficiently small compared to the mechanical energy imposed to the systems [9–17]. The shear-induced homogenization or single-phase formation is clearly demonstrated by a distinct difference in the scaled structure factors before and after the homogenization [9,14]. Theoretically, the dynamics of concentration fluctuations of dynamically symmetric binary fluids, such as simple liquid mixtures and polymer blends, is expressed by so-called model H [18] which includes the effects of the hydrodynamic interactions. The model H predicts that the hydrodynamic interactions shift downward the critical temperature as also suggested by Onuki [17].

On the other hand, if the systems are dynamically asymmetric, such as semidilute solutions of high molecular weight polymers and polymer mixtures having a large difference in molecular weights [3–7,9,17,19–21] or glass transition temperature, T_g [22], the shear-induced concentration fluctuations and/or phase separation occur even in the case of thermodynamically stable state or one-phase region. We have explained this phenomenon by the solvent squeeze mediated by the elastic effects [6,7,20,21]. In quiescent semidilute polymer solutions, there are thermal concentration fluctuations, giving rise to regions of higher and lower polymer concentrations which have higher and lower number densities of entanglement couplings, respectively. The stress built-up in the systems is borne only by the slow component, which is a polymer, because solvent (the fast component) relaxes much faster than polymer. As a result, stress imbalance arises [23–26]. When the shear flow is imposed on such systems, the stress borne by polymers tends to become higher in the more entangled regions due to the concentration dependence of the viscosity and the normal stress coefficients. The stress or the elastic free energy stored in the solutions by deformation of the swollen entangled polymer chains is relaxed by disentanglements, when the shear rate, $\dot{\gamma}$, is smaller than the terminal relaxation rate, τ_w^{-1}, of the solution. However, when $\dot{\gamma}$ is higher than τ_w^{-1}, the elastic free energy is released only by squeezing of solvent: squeezing of solvent can relax conformation of the deformed swollen entangled chains and hence stored elastic energy. The higher the concentration is, the larger the stored elastic free energy is, and therefore the more the solvent is squeezed. As a result, concentration fluctuations are built up under the shear flow against the osmotic pressure.

The theoretical framework for the dynamically asymmetric systems is proposed by Helfand and Fredrickson [23], Milner [24], and Onuki [25,26] (HFMO). The HFMO theory takes into account the dynamical coupling between stress and diffusion. This coupling becomes dramatically remarkable when the constituents of a mixture have a very large dynamical asymmetry. According to the theory, the dynamics of concentration fluctuations is described by the following generalized time-dependent Ginzburg–Landau (TDGL) type equation where the coupling between stress and diffusion is incorporated in the second term of the bracket in right hand side (rhs) of the equation below,

$$\left(\frac{\partial}{\partial t}+\mathbf{v}\times\nabla\right)\phi=\nabla\times L\left[\nabla\frac{\delta F}{\delta\phi}-\alpha\nabla\times\sigma^{(n)}\right] + \left(\text{H.D. term}\right)+\theta_\phi \quad (1)$$

where $\mathbf{v}$ is the volume average velocity, ϕ the volume fraction of polymer, L the Onsager kinetic coefficient, F the free energy functional, $\sigma^{(n)}$ the stress tensor of the polymer under a flow, H.D. term the hydrodynamic interaction term [27], and θ_ϕ is the thermal noise term. Here α is the dynamical asymmetry parameter.

In the case of dynamically symmetric systems, α becomes zero, so that Eq. (1) reduces to model H [18]. However, α is not zero for dynamically asymmetric systems and becomes $\alpha \cong 1/\phi$ for polymer solutions. When such systems in a thermodynamically single-phase state are brought under the shear flow, the stress term produces the instability of concentration fluctuations [28]. Therefore the shear-induced concentration fluctuations and/or phase separation occurs, even though the systems are in one-phase region at quiescent state.

When the solutions are subjected to a shear flow in the thermodynamically unstable region at quiescent state, the term associated with the thermodynamic force ("*the first term*" in the square bracket of rhs of Eq. (1)), the hydrodynamic interaction term, and the noise term, θ_ϕ, as well as the stress term ("*the second term*" in the square bracket of rhs of Eq. (1)) enhance the concentration fluctuations. On the other hand, the stress term is the only trigger to enhance the concentration fluctuations when the solutions are in a thermodynamically stable state at quiescent state.

We expect that the second term becomes significantly important relative to the first term for the formation of shear-induced structures with increasing $\dot{\gamma}$. Thus we anticipate that there may be a critical shear rate, defined hereafter as $\dot{\gamma}_{c,SD}$, above which the second term dominates the first term; $\dot{\gamma}_{c,SD}$ is defined as the critical shear rate, when the system is in the spinodal region in the phase diagram. We aim to investigate whether there are some dramatic differences in the shear-induced structures below and above $\dot{\gamma}_{c,SD}$. $\dot{\gamma}_{c,SD}$ should formally correspond to the critical shear rate, $\dot{\gamma}_c$, in the thermodynamically stable solutions where the second term for enhancing concentration fluctuations outweighs the first term for decaying concentration fluctuations.

2. Experimental methods

2.1. Materials

The system studied is polystyrene (PS) dissolved in diethyl malonate (DEM). The weight-average molecular weight, M_w, of PS is 5.48×10^6, and the heterogeneity index for the