

Time-Resolved Experimental Study of Shear Viscosity in the Course of Spinodal Demixing

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A large transient surge of shear viscosity is observed in the course of spinodal demixing caused by off-critical quenching of a polymer solution. A characteristic length is derived from light scattering measurements along with a related relaxation time τ_M whose value agrees with previous independent experiments. Viscosity peak values plotted versus $S\tau_M$ (where S is the shear rate) lie on a master curve of the type $(S\tau_M)^{-p}$, where $p \approx 2$. This scaling procedure helps bring into focus the mechanism responsible for the novel observation.

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Spinodal demixing under shear in low-molecular-weight binary systems and in polymer solutions has attracted considerable attention in recent years [1–8]. Its interest spans from fundamental questions such as critical fluctuations, scaling, and critical and hydrodynamic interactions to technological applications. Time-resolved experiments are highly desirable, and are possible in polymer solutions or melts, where the time scale becomes macroscopic, due to slow diffusional modes [9]. Effects of shear on the time evolution and equilibrium properties of the structure function and of the morphology of solute-rich and solvent-rich domains have been widely studied [2–7], and provide solid bases for understanding the underlying physical mechanisms.

A complementary aspect is that of the rheological effects occurring in binary systems undergoing spinodal demixing under shear [1,2,6–8]. The crucial parameter is the ratio of the rate of shear S to a relaxation rate τ^{-1} , characteristic of the system [1,4,6,7]. This is a measure of the ratio of the shear forces to the relaxation forces, or else of the relative deformation caused by the shear during the relaxation time τ . Interesting effects are expected for $S\tau(\xi) > 1$. Two contributions to rheological effects have been considered. One is due to concentration fluctuations and related to the relaxation time $\tau(\xi) = (k_B T)^{-1} 6\pi\eta\xi^3$, where ξ is the correlation length [7]. Another is due to demixed domains, and is related to their interface relaxation time, $\tau(r) = (k_B T)^{-1} 6\pi\eta r^3$, where r is the average size of domains [1,2]. For this case a transient increase of viscosity is predicted, caused by domain deformation “burst.”

Our present time-resolved experiments concern aqueous solutions of agarose at 0.05%–0.5% weight/volume (w/v) polymer concentrations, well below the coil overlap threshold and critical concentration [10,11]. Agarose is a widely found, unbranched, and essentially electrically uncharged biostructural polysaccharide. In previous extensive studies [10–15] of this system the following have been shown: (i) Its phase diagram in the T - c plane with a critical temperature $T_c = 54 \pm 0.6^\circ\text{C}$, a critical concentration c_c in the neighborhood of 1.5% w/v [10,11], and

the unambiguous occurrence of a spinodal demixing in the conditions chosen for the present work. The spinodal mechanism of demixing, as distinct from the nucleated mechanism, is evidenced by a variety of experiments [10–13] and in particular by the linearity of Cahn plots of elastic light scattering data [10] which is the typical signature of the spinodal mechanism. (ii) The neat separation in time (within the range of conditions of the present experiments) [10] between demixing and the *subsequent and distinct* occurrence of the known polymer conformational transition and gelation [14–17]. (iii) The occurrence, at sufficiently low concentrations and for sufficiently low quenching temperatures (conditions also covered in the present work), of disconnected, freely diffusible polymer-rich domains, as the result of spinodal demixing [12]. At the lowest concentration used in the present work, the sizes of such domains were in the range of 0.2–0.3 μm [11]. It was also shown that at concentration values used in the present work, entanglement effects are negligible in the homogeneous solution [13]. They are expected to become relevant in the polymer-rich domains generated by spinodal demixing.

A computer-interfaced Contraves Low-Shear 30 Viscometer was used. This is a Couette-type viscometer, having a rotating cylindrical cup and a measuring inner coaxial bob, with a 0.5-mm gap between. The solution fills this gap. Nonuniformity of the shear rate in the sample, due to the cylindrical geometry, amounts to $\pm 5\%$ maximum. Average values are calculated exactly for Newtonian fluids. For non-Newtonian samples (as in the present case) evaluation of the average value of the rate of shear requires an appropriate correction [18] which was performed in all cases and amounted to 10% maximum. The correction did not affect the $\pm 5\%$ shear-rate nonuniformity or the precision of our average values. Samples were protected against evaporation and related artifacts by an upper oil film. For shear-viscosity measurements a constant shear rate (in the range 1.6×10^{-2} – $1.2 \times 10^2 \text{ sec}^{-1}$) was applied and maintained throughout the experiment. For static and dynamic light scattering experiments, a He-Ne laser (632.8 nm) was

used. Data were automatically collected at different angles with Brookhaven BI2030AT and BI200SM instruments. All light scattering experiments were performed in the absence of shear. Sample temperature was controlled within $\pm 0.2^\circ\text{C}$ by a thermostated circulating bath. Agarose was from Seakem Ltd. [type HGT(P), lot No. 62933, $M=120000$, sulphate content less than 0.15%]. The powder was dissolved in freshly prepared Millipore Super Q water, at 100°C . After 20 min of boiling, the solution was filtered at $80\text{--}90^\circ\text{C}$ through $0.22\ \mu\text{m}$ hydrophilic filters, and put quickly in the prethermostated measuring cells. In this way, samples underwent off-critical quenches in the instability region, at quenching depths $\varepsilon_{\text{sp}}=(T_{\text{sp}}-T)/T_{\text{sp}}$ in the range $10^{-3} < \varepsilon_{\text{sp}} < 10^{-2}$. Here T_{sp} is the temperature on the spinodal curve, at a given polymer concentration, determined as described below.

Experiments on different aliquots of the same solution quenched at the same temperature were simultaneously performed for various concentrations and quench temperatures. Viscosity η was recorded at constant rate of shear. Using a companion identical sample, the growth of scattered light intensity at different angles, $I(q)$, was independently recorded, in the absence of shear. A typical result is shown in Fig. 1, left. The observed angular dependence of the growth rates of scattered light is shown in Fig. 1, right, in the form of a Cahn plot [19]. The closely linear dependence confirms the spinodal process

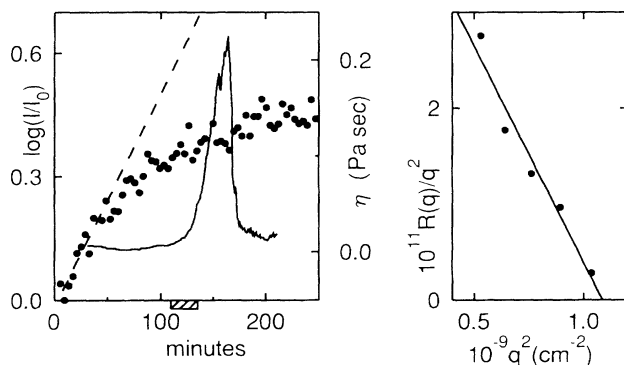


FIG. 1. Left: typical time-resolved behavior of shear viscosity (continuous line) and scattered light (dots), after quenching in the instability region. The best-fitting straight line of the initial growth of scattered light is also shown (dashed line). The box on the time axis marks the occurrence of a stable ring in low-angle scattered light and of a low-frequency component in the noise of scattered light intensity. In this specific case, the scattering vector was $q=2.3 \times 10^{-4}\ \text{cm}^{-1}$ ($\vartheta=10^\circ$), the shear rate was $1.9 \times 10^{-2}\ \text{sec}^{-1}$, concentration was 0.5% w/v, and quench temperature was 48.6°C . Right: Cahn plot of the rates of growth of scattered light (i.e., slope of the best-fitting straight line shown to the left) showing the behavior typical of spinodal demixing. The scattering vector is q . The characteristic length is obtained from the maximum of $R(q)$, as $L_M=2\pi/q_M$. The concentration and quench temperature are the same as in the left panel.

[10]. Best fittings of such plots provided evaluations of the scattering vector corresponding to maximum rate of growth. In this way and for each experimental condition it was possible to evaluate the characteristic length $L_M=2\pi/q_M$ (a few microns in the conditions of the present experiments) of the developing pattern of polymer-rich and solvent-rich regions. At decreasing quenching depth, L_M increased and the rate of growth at a given scattering angle decreased, as a power law of ε_{sp} [10,11]: Best-fitting procedures allowed the determination of T_{sp} (within $\pm 0.3^\circ\text{C}$, at each sample concentration) with no need for experiments in the metastable region.

During the initial (linear) stage of demixing when the scattered light intensity increases exponentially, we measured poorly reproducible and barely detectable viscosity changes. After a delay time, which depends on the quenching depth, a large and well reproducible surge of viscosity was observed (with viscosity increasing by up to 2 or 3 orders of magnitude) followed by a return towards values slightly larger than those at the start. The surge is observed at a stage of demixing when the growth of $I(q)$, at all different q 's, is no longer exponential. In experiments performed at different shear rates, the viscosity peak decreases remarkably at increasing shear rate, and in our conditions it falls below detectability at $S > 0.2\ \text{sec}^{-1}$. In Fig. 2 the peak value of $\Delta\eta/\eta$ is plotted versus S^{-1} , for three concentrations and different quench temperatures. Inverse power laws with exponents in the range $p=-1.86 \pm 0.06$ satisfactorily fit all data in the whole range $0.016 < S < 0.2\ \text{sec}^{-1}$. After the transient surge, the final value of viscosity also decreases at increasing shear rate, but this time approximately as $S^{-0.85}$.

Parallel identical experiments were performed at the lowest agarose concentration, with small amounts of polystyrene microspheres of radius $R=40\ \text{nm}$ added to the sample. The microspheres diffusional motion was studied by photon correlation in the absence of external shear. Concurrently with the appearance of the macroscopic viscosity peak, more than 50% of the probes experience an increase of viscosity by a factor 5 to 10, monotonically increasing with time, without any peak. This 50% fraction appears too large to be assigned to probes trapped in the few polymer-rich domains. Further, the angular dependence of the correlation function showed the appearance of motional hindrances, on a motional range above $0.4\ \mu\text{m}$.

We remark that (i) the large size and the $\approx S^{-2}$ shear-rate dependence of the viscosity surge suggest the existence of a relevant relaxation time τ such that the relation $S\tau > 1$ holds in all our experimental conditions; and (ii) the similarity of the viscosity peak and its shear-rate dependence in all cases studied shows that the observed phenomenon is the same at all concentrations used.

As to the mechanism responsible for our observations,

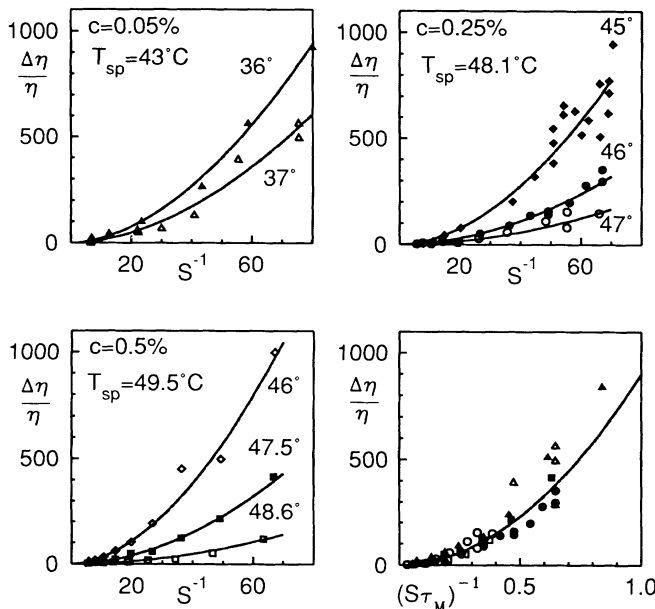


FIG. 2. Shear-rate dependence of the viscosity peak, given as $\Delta\eta/\eta = [\eta(\text{peak}) - \eta(t=0)]/\eta(t=0)$ at different concentrations and quenching depths. Concentration c (in w/v), spinodal temperature T_{sp} , and quenching temperatures are given. Shear-rate values are corrected for non-Newtonian behavior. Continuous lines are power-law best-fitting curves. $\Delta\eta/\eta = \text{const} \times S^{-p}$. Best-fitting p values are as follows: Upper left (top to bottom): $p=1.81, 1.83$. Upper right (top to bottom): $p=1.85, 1.90, 1.91$. Lower left (top to bottom): $p=1.80, 1.89, 1.92$. Lower right: same data plotted vs $S\tau_M$. Here τ_M is the relaxation time related to the interdomain distance L_M obtained from light scattering (see Fig. 1, left). One single master curve, $\Delta\eta/\eta = \text{const} \times [S\tau_M]^{-1.97}$ (continuous line), is seen to fit all data.

we consider lengths and related relaxation times associated with relevant quantities and processes in the system. The correlation length $\xi = \xi_0 \varepsilon^{-\nu}$ can be evaluated by taking the polymer coil size, $R=15$ nm [13], as an extreme value for ξ_0 . This gives a ξ value in the range 0.1–0.2 μm , and a related relaxation time in the range 0.01–0.2 sec, so that $S\tau \ll 1$. Therefore, the interaction of shear flow with concentration fluctuations does not appear to qualify as the mechanism responsible for the observed viscosity surge [20].

Next, we consider the size r of demixed domains. At the lowest concentration studied and at our quenching temperatures, photon correlation spectroscopy shows that this is in the range 0.2–0.3 μm [11]. Accordingly, the longest relaxation time of domain deformation, $\tau = (kT)^{-1} 6\pi\eta r^3$, is of the order of 0.03–0.1 sec, again giving $S\tau \ll 1$. Taking into account hydrodynamic interactions would result in an even shorter relaxation time [1,21]. We can conclude that the mechanism of deformation and breaking of domains cannot be responsible for our observations. However, we may expect that domains will be considerably deformed by shear, as predicted by

hydrodynamic calculations [21] and experimentally observed under conditions comparable with ours [5].

The next relevant length is L_M , associated with the maximum of the structure function $S(q)$ as measured by light scattering. This is about 2–3 μm and it corresponds to the average distance between centers of neighboring domains. A mechanism associated with L_M is conceivably related to the distortion and disruption by shear of the three-dimensional correlations among domains developing in the course of the spinodal process of demixing. The relaxation time related to L_M can be written as $\tau_M = (kT)^{-1} 6\pi\eta L_M^3$. This is of the order of 100 sec, so that the relation $S\tau_M > 1$ holds now in the whole range of our experimental conditions. We can test the relevance of τ_M by a scaling procedure, that is by representing the peak values of $\Delta\eta/\eta$ vs $S\tau_M$. This is done in Fig. 2, lower right, which contains all our data points. The corresponding best-fitting “master curve” represents an inverse power-law curve, with exponent $p=1.97 \pm 0.08$. We note that in this plot we have used L_M values measured at the initial stage of spinodal demixing, corresponding to fluctuations having a maximum rate of growth. Since the increase of this length with time is known to follow a universal law [22], this merely amounts to a proportional underestimate of all τ_M values. We also note that, in conditions unperturbed by shear, the onset of a longer relaxation time (of just about 100 sec and initially not present) was indeed observed in earlier, independent measurements of noise in scattered light intensity [13]. The onset occurred at the same stage of demixing in the same systems and conditions as in the present experiments, so that mutually consistent values of L_M and τ_M are independently measured. We note that the relaxation time $\tau = \eta L/\sigma$ (where σ is the surface tension) classically used in hydrodynamics is more than 2 orders of magnitude smaller than the τ_M used in Fig. 2, lower right. Use of this τ value give $S\tau \ll 1$ and does not yield a master curve. These considerations, and specifically the master curve in Fig. 2, lower right, appear to evidence a mechanism of viscous dissipation due to distortion and breaking of some *interdomain* links or correlations in the direction perpendicular to the flow.

The viscous dissipation evidenced here strongly suggests the presence of hitherto unsuspected linkings or forces of some sort among polymer-rich domains generated by spinodal demixing. This agrees with the above-mentioned results concerning the motion of polystyrene microspheres even in the lowest concentration samples. We recall that (i) our observed viscous dissipation refers in all cases to liquid, free-running samples; (ii) gelation only occurs at much longer times in the sample at the highest and intermediate values of concentration, and it does not occur at all at the lowest concentration; (iii) in the latter, a fraction of polymer-rich domains was shown by photon correlation data [12] to diffuse freely. Accordingly, interdomain linkings, while required, are not induced by shear, are much weaker than those of the gel,

and are probably not extended throughout the sample. As to their origin, we note that the optical rotation signal, which is the unambiguous signature of double helices (necessary for gelation), is not concurrently observed, indicating that gelation has not started, even within the polymer-rich regions. Nevertheless, since the presence of a small fraction of helices would not be detected by optical rotation, we may not exclude the presence of a few single or double polymer helices or stretched chains, providing some linkings. The presence of shear is expected to cause some anisotropy in the shape of domains. But the most relevant and new effect revealed by the present experiments is that the shear causes distortion and rupture of interdomain links, whichever their detailed origin, giving rise to the large observed energy dissipation peak.

In conclusion, our results illustrate the interest of time-resolved experiments and bring into focus the appearance of a new rheological contribution in the course of off-critical spinodal demixing, hitherto not taken into consideration. The features of this transient contribution are regulated by the characteristic length and time scales generated by spinodal demixing.

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