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Formation process of shear-induced onion structure made of quaternary system SDS/octanol/water/NaCl

Zenji Yatabe [a*], Yasufumi Miyake [a], Masatoshi Tachibana [a],

Chihiro Hashimoto [b], Robert Pansu [c], Hideharu Ushiki [d]

[a] Laboratory of Molecular Dynamics and Complex Chemical Physics, Department of Biochemistry and Biotechnology, United Graduate School of Agricultural Science, Tokyo University of Agriculture and Technology, 3-5-8 Saiwai-cho, Fuchu-shi, Tokyo 183-8509, Japan

[b] Department of Applied Chemistry and Biotechnology Niihama National College of Technology 7-1 Yakumo-Cho, Niihama, Ehime, 792-8580, Japan

[c] Laboratoire de Photophysique et Photochimie Supramoléculaires et Macromoléculaires UMR 8531 CNRS, D’Alembert Institute, ENS Cachan, 61 av. President Wilson, 94230 Cachan, France

[d] Laboratory of Molecular Dynamics and Complex Chemical Physics, Institute of Symbiotic Science and Technology, Division of Ecosciences, Tokyo University of Agriculture and Technology, 3-5-8 Saiwai-cho, Fuchu-shi, Tokyo 183-8509, Japan

[*]Author to whom correspondence should be addressed.

E-mail: zenji@cc.tuat.ac.jp

Abstract

The formation process of onion structure in a quaternary mixture made of water, NaCl, octanol and sodium dodecyl sulphate, have been investigated by two dimensional light scattering under various shear rates. In this paper, we investigated the size evolution of onion structure estimated by light scattering data with a nonlinear least-squares curve fitting method. The time evolution of onion size showed a good agreement with a stretched exponential function. The formation process of onion structure is briefly discussed from the viewpoint of the physical meaning of fitting parameters based on the integral transformation method.

1. Introduction

The shear-induced structural transition from lamellar structure to onion structure under shear flow has been studied by many researchers [1-12]. After onion structure is formed under shear flow, this structure is comparative stable and decayed to stationary state slowly, that is, their size slowly decreases with time course reaching to its final stationary state [2-4]. These researches for onion structure can apply to cosmetics and pharmacology such as drug delivery system in the near future [5].

In previous works, both nucleation process [6] and buckling mechanism [7] proposed for the formation of shear induced onion structure. More recently, the theoretical works [8,9] and experimental works [3,4] supported buckling mechanism based on the coupling between thermal undulations of the membranes and the flow.

It is now well known that the stationary onion size *R* of formed from a lamellar phase is given by $R \sim \dot{\gamma}^{-1/2}$, where $\dot{\gamma}$ is applied shear rate, namely, the onion size results from balance between the elastic energy of the membrane and the applied shear stress [10,11]. Furthermore, Courbin *et. al*. [12] showed that the size *R* varies as the inverse of shear rate $\dot{\gamma}^{-1}$ in case of onion formed from a lamellar-sponge mixture. This behaviour is similar to emulsion system [13]. However, detail of the formation process of onion structure toward the stationary state is still under debate.

In this report, we investigate the formation process of the onion structure toward the stationary state under shear flow. Once onion structure is formed in lamellar structure under shear flow, onion structures are of micrometric size. Therefore the two dimensional light scattering measurement can detect their time evolution of the size. It is found that the best fitting function, that is, phenomenological function $I(t)$, in order to describe a position of the Bragg peak q_{max} as function of time.

In complex physics, the curve fitting method for time evolution phenomena is very important and excellent technique, for example, polymer chain dynamics [14,15], volume phase transition processes of gels [16,17] and sedimentation behaviours of aggregates [18]. Many researchers found the fact that relaxation processes can be described by some power law functions, for examples, Debye type, Cole-Cole type [19], Davidson-Cole type [20], Williams-Watts type [21], in natural phenomenological facts. However, it is difficult to understand the physical meaning of power law, namely, their relaxation functions were empirical formula even after the concept of fractal dimension was proposed by B. B. Mandelbrot [22], P. G de Genne [23] and U. Evesque [24].

In our previous paper [15-18], it was shown that the concept of integral transformation method in order to clarify the mechanisms of complex fluid. The definition of the method is shown as:

$$I(t)=\int_0^\infty F(t,\tau)D(\tau)d\tau \qquad (1)$$

where $I(t)$, $F(t,\tau)$, $D(\tau)$, were phenomenological, elementary and distribution functions, respectively. This formula exhibits that the obtained phenomenological functions $I(t)$ are represented by the convolution integrals with the distribution functions $D(\tau)$ of parameters, that is, the phenomenological function $I(t)$ describes the gathered elementary function $F(t,\tau)$ having various τ values such as distribution function $D(\tau)$.

For example, fluorescence intensity decay curves, $I(t)$ show a good agreement with stretched exponential function ($0 < \beta < 1$) [14]. In this case, elementary function $F(t,\tau)$ is monoexponential function with a fluorescence life time, τ. Therefore, Eq.(1) means Laplace transform, that is, it is possible to calculate distribution function $D(\tau)$ directly from the phenomenological function $I(t)$ based on well known CONTIN program [15,25]. Furthermore, in cases of volume phase transition processes of gels [15,16] and sedimentation behaviours of aggregates [18], phenomenological function $I(t)$ show a good agreement with stretched exponential function ($\beta > 1$) and elementary function $F(t,\tau)$ is heaviside function. In these cases, distribution function $D(\tau)$ was given by the just derivative of $I(t)$. Therefore, integral transformation method is very effective to estimate parameters of power law and distribution function.

We are making suggestion by integral transformation method to be available for research fields of complex fluid. The aim of this study is to find a best phenomenological function $I(t)$ by using curve fitting method for the formation dynamics of onion structure under shear flow. Furthermore we will briefly discuss about physical meaning of fitting parameters.

2. Experimental

2.1. Materials

The system is studied a quaternary lyotropic lamellar phase, which is composed of sodium dodecyl sulfate (SDS), octanol, NaCl and water [26]. SDS was purchase form Wako Co, (98% purity) and used without further purification. The lamellar phase was prepared by dissolving 9% SDS and 11% octanol in brine (20g/L NaCl in distilled water). Experiments were performed after approximately two week, until the samples had reached homogeneous.

2.2. Measurements

We measured the time evolution of onion size under various shear rate $\dot{\gamma}$. The onion structures are micrometrical size, therefore, light scattering measurement were performed under shear flow with 1 mm gap homemade plate-plate type cell, one of which is turned at an angular rotation speed ω. The incident light (10mW He-Ne laser) was scattered in sample cell, and the scattering light could be visualized by use of projection on a screen (Fig. 1). All the experiments were performed at controlled room temperature (20 ℃). When onion structures were formed, the light scattered from the sample gave a characteristic ring in the forward direction whose radius was related to the onion size. The light scattering patterns were filed by CCD video camera. Softwares for graphical analysis and curve fitting were coded by Delphi (Borland Software Co.). The fitting function could be always estimated for all data curves using the nonlinear-least squares method based on the quasi-Marquardt algorithm as a software part of PLASMA [14-17].

3. Results and discussion

Once onion structure is formed in lamellar solution under shear flow, a characteristic scattering ring suddenly appears on the screen. Then, their scattering vectors slowly and continuously increases with time until the stationary state is reached. This formation behavior is good agreement with previous works of Nettesheim *et al*. [2] and Courbin *et al*. [3,4]. The evolution of the scattering vector that is calculated from the scattering ring is shown in Fig. 2. We assumed that the following stretched exponential function could fit the time evolution of the Bragg peak $q_{max}(t)$ from phenomenological viewpoint based on integral transformation method [15-18].

$$q_{max}(t) = q_1 + q_2\left[1 - \exp\left\{-\left(\frac{t - t_0}{\tau}\right)^{\beta}\right\}\right] \qquad (2)$$

q_1 is initial scattering vector when the onion structure are formed in lamellar solution and t_0 is their time delay, q_2 is prefactor, τ is the relaxation time and β is the power component. Very good fits were obtained between experimental data and stretched exponential function (Fig. 2). The monoexponential function was also applied to the curve fitting of time evolution of the Bragg peak $q_{max}(t)$. Obtained all fitting parameters and the value of χ^2 for the stretched exponential function and the monoexponential function are listed in Table 1 and Table 2, respectively. In general, the goodness of fitting to a measure data with a trial function is evaluated quantitatively by a value of χ^2 in the least square calculation. The monoexponential function is not in agreement measured data, because and the value of χ^2 is larger than stretched exponential function and also the fitting parameter t_0 in the monoexponential function is not positive value. Thus the stretched exponential function is appropriate to express the time evolution of the Bragg peak $q_{max}(t)$. Let us explain a physical meaning of each parameters on the stretched exponential function (Eq.(2)) as follows.When t approaches t_0, then $q_{max}(t)$ approaches q_1. Therefore, q_1 indicate that initial scattering vector q_1 when onion structure are formed in lamellar solution and t_0 is its time delay. Fig. 3 shows the double log plots of the q_1 (open symbol: left axis) and t_0 (closed symbol: right axis) as a function of applied shear rate $\dot{\gamma}$, and their slopes are obtained 1/3, -1, respectively. These results of slopes are in good agreement with the prediction theory by Zilman *et al.* [7] and experimental result by Courbin *et al.* [3,4]. Therefore, our results from fitting parameters support that the shear-induced formation of onions occur through a buckling instability [3,4,7] not through a nucleation [6].

In case of t approaches infinity, $q_{max}(t)$ approaches q_1+q_2. Therefore q_1+q_2 represents the scattering vector at stationary state of onion structure. Fig. 4 shows the double log plots of the q_1+q_2 as a function of applied shear rate $\dot{\gamma}$. The straight line indicates power low behavior and slope are obtained as 1/2. Roux *et al.* showed that the final position of scattering vector scales like $\dot{\gamma}^{1/2}$ at stationary state, because of the stationary size of the onion structure results from the balance between the elastic energy of the membrane and the applied shear stress [10]. Our results showed that the stretched exponential function (Eq.(2)) can estimate the scattering vector at transition of onion structure in lamellar solution and their equilibrium state.

Fig. 5(a) shows the graph for relaxation time τ as a function of shear rate $\dot{\gamma}$. The relaxation time decreases with increasing of shear rate. As mentioned above, once the onions are formed under shear flow, their size slowly decreases with time course reaching to its final stationary state, that is, their elastic energy of the membrane of onion structure is balanced by the applied shear stress at equilibrium state (Fig. 2) [10]. This result suggest that balance between the elastic energy and the applied shear stress to reach at equilibrium state are reflected in relaxation time.

We have plotted in Fig. 5(b) the power component β versus the shear rate $\dot{\gamma}$. β is close to 0.5 all over the shear rate range. To interpret the meaning of β, let us assume the following two points. First, the mechanism of the size decreasing of an onion is described by the collective diffusion equation, that is, the temporal evolution of a single onion radius R is expressed by a monoexponential function [17, 27,28].

$$R \sim \exp\left(-\frac{t}{\tau_R}\right) \qquad (3)$$

The characteristic relaxation time of the size decreasing τ_P is given by $\tau_R \sim R_0^2/D$, where R_0 and D are the initial single onion radius and the diffusion coefficient , respectively [17,27,28]. Second, the number of the initial onion radius R_0 is represented as n_{R0} by the following Boltzmann distribution

$$n_R \sim \exp\left(-\frac{\Delta F}{k_B T}\right) \quad (4)$$

where ΔF, k_B and T are the free energy change by the onion formation, the Boltzmann constant and temperature, respectively. The free energy change ΔF is given by $\Delta F \sim 4\pi\sigma R_0^2$, where σ is the surface free energy. Based on the integral transformation method [15-18], the temporal evolution of the average onion size, $R(t)$ is expressed by Eq.(3) and Eq.(4) as follows :

$$R(t) = \int_0^\infty \exp\left(-\frac{\Delta F}{k_B T}\right)\exp\left(-\frac{t}{\tau}\right) dR_0 \quad (5)$$

Solving Eq.(5) by using saddle point theory [29], the temporal evolution of onion size $R(t)$ is given by a stretched exponential function as: $R(t) \sim \exp\left(-ct^{1/2}\right)$, where c is a constant. The power component is 1/2 and a good agreement with the obtained fitting parameter value of β (Fig. 5(b)). Thus we can give a suggestion that the mechanism of the size decreasing of onion structure is described by the collective diffusion and the initial size distribution of onions is Boltzmann distribution of the surface free energy..

4. Conclusion

In this report, we observed the formation process of onion structures under shear flow. We have shown for the first time that the time evolution of onion size showed a stretched exponential function

(Eq.(2)) with good agreement. The values of fitting parameters of eq. (2), q_1, t_0 and q_1+q_2, are in good agreement with previous works [3,7,10]. The relaxation time of onion structure strongly depends on the shear rate $\dot{\gamma}$. The power component, β was close to 0.5 all over the shear rate range. Assuming that the size decreasing of onion structure undergoes by the collective diffusion and that the initial size of onions obeys the Boltzmann distribution of the surface free energy, the value 0.5 of β was deduced based on the integral transformation method. We can conclude that a stretched exponential function is useful for analyzing formation process of onion structure.

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Figure Caption

Fig.1. Apparatus of two dimensional light scattering system for observation of time evolution of size of onion structure.

Fig.2. Graph for the time vs Bragg peak $q_{max}(t)$, observed two dimensional light scattering after a shear rate of $\dot{\gamma}$ = 141 s^{-1} is applied. The solid line is the best fit stretched exponential curve (Eq.(2)). The upper graph indicates residuals of the fitting result.

Fig.3. Log-log plot of shear rate vs fitting parameter q_1 (Eq. (2)) (○) (right-hand side axis). The solids lines correspond to the best power law fit. And Log-log plot of shear rate vs fitting parameter t_0 (Eq.(2)) (▲) (right-hand side axis). The solids lines correspond to the best power law fit.

Fig.4. Log-log plot of shear rate vs fitting parameter q_1+q_2 (Eq.(2)). The solid line correspond to the best power law fit.

Fig.5(a). Graph for the shear rate vs the relaxation time τ (Eq.(2)).

Fig.5(b). Graph for the shear rate vs the power component β (Eq.(2)). The solid line is a guide for the eye (corresponding to β = 0.5).

Table. 1 Fitting parameters and χ^2 values of the streched exponential function (Eq.(2)) function at various shear rate.

Table. 2 Fitting parameters and χ^2 values of the monoexponential function at various shear rate.

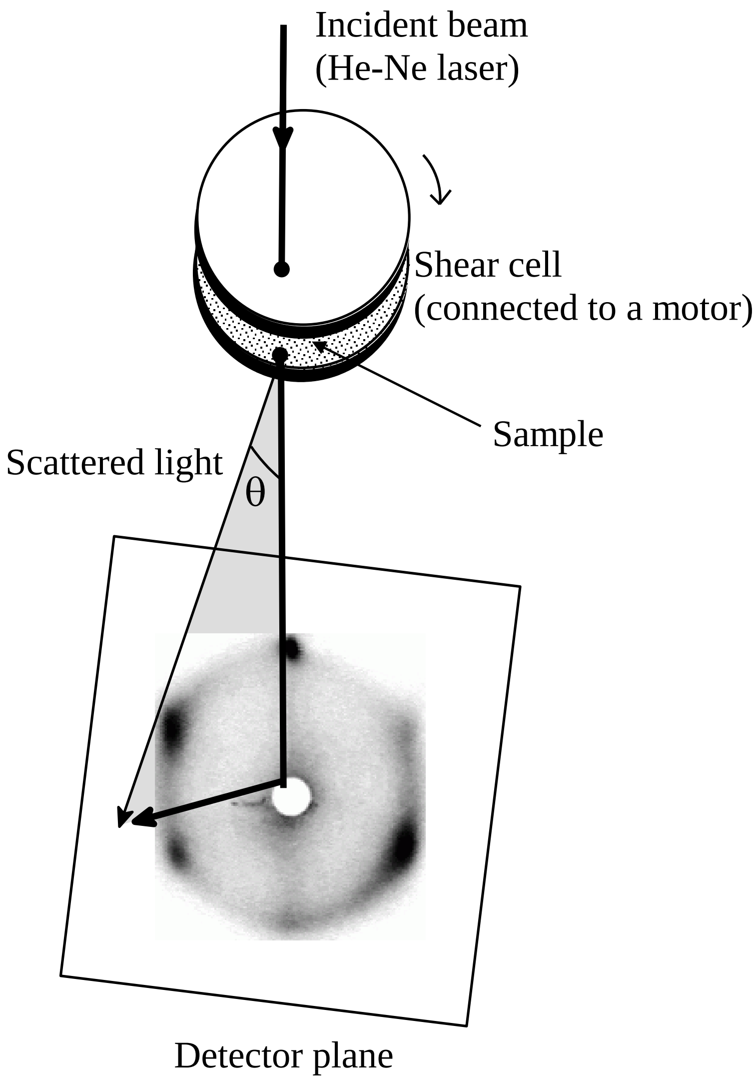
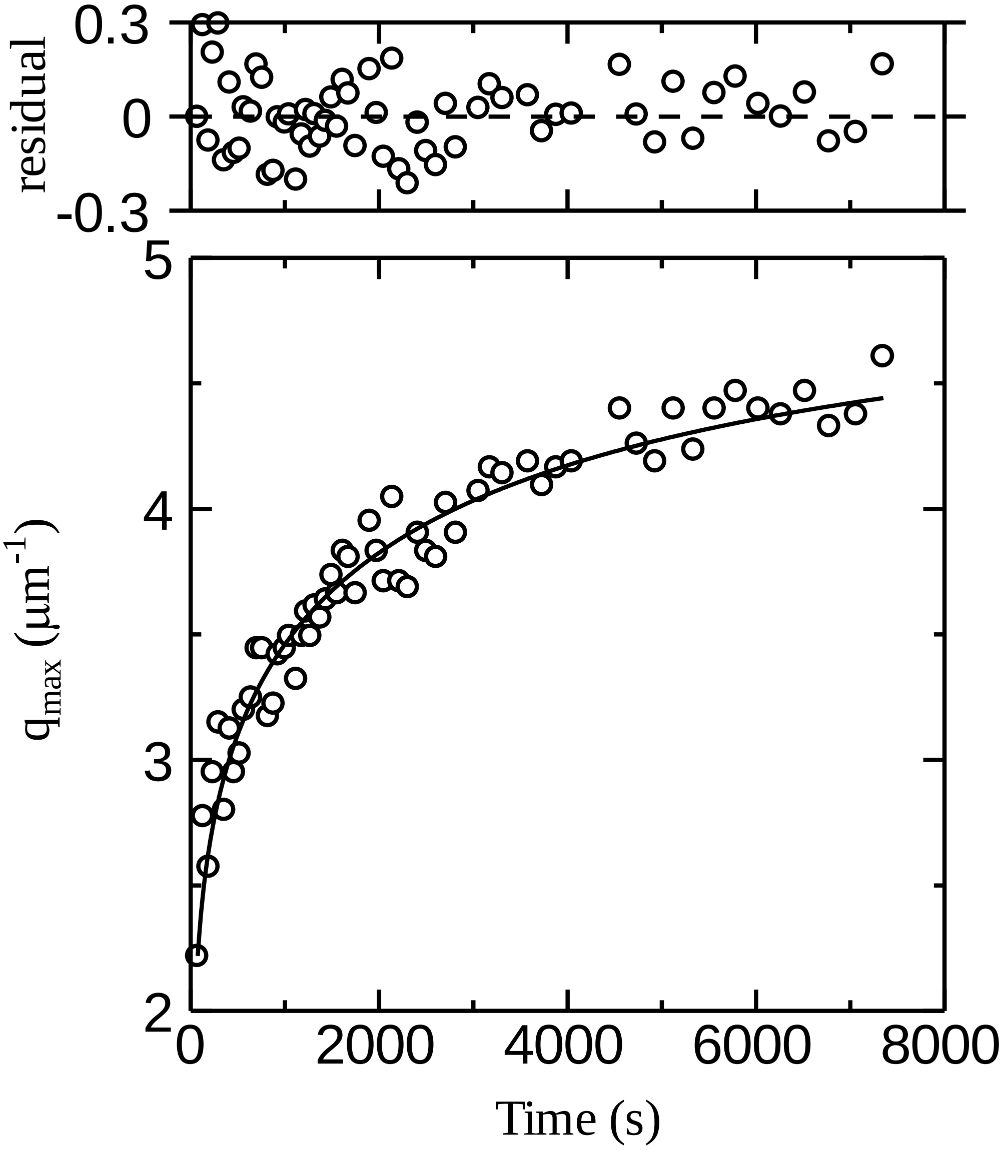

Incident beam
(He-Ne laser)
Shear cell
(connected to a motor)
Sample
Scattered light
θ
Detector plane

Figure 1



1

2 Figure 2

3

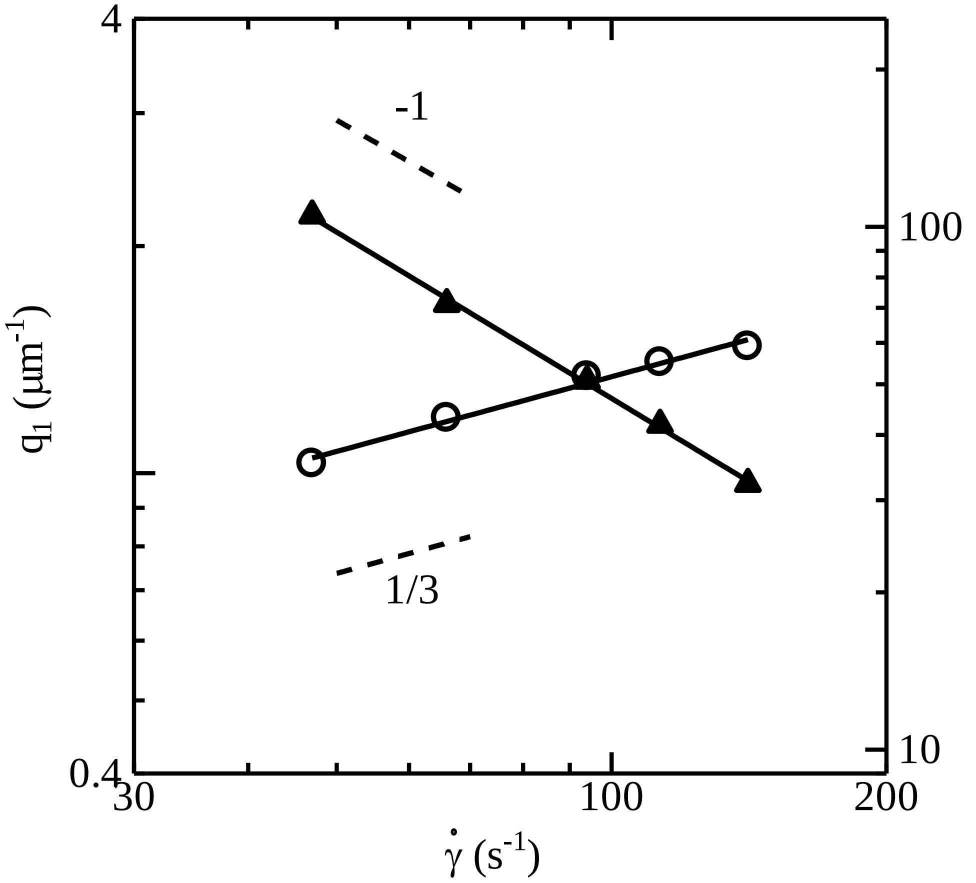
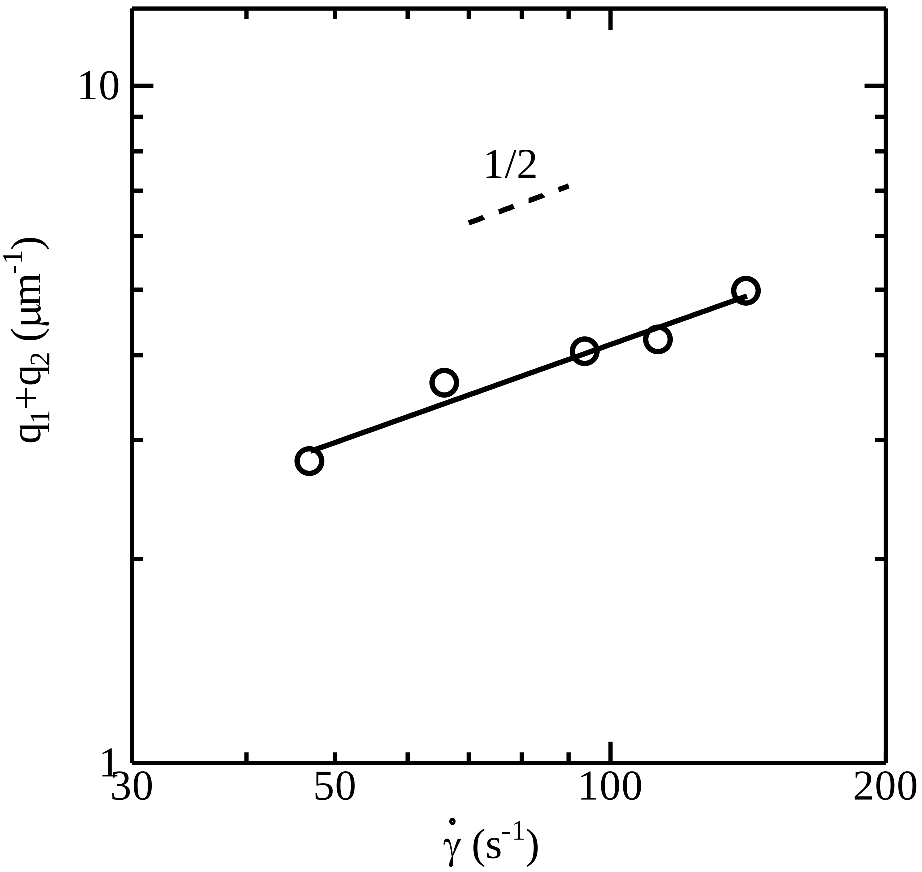


Figure 3



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2 Figure 4

3

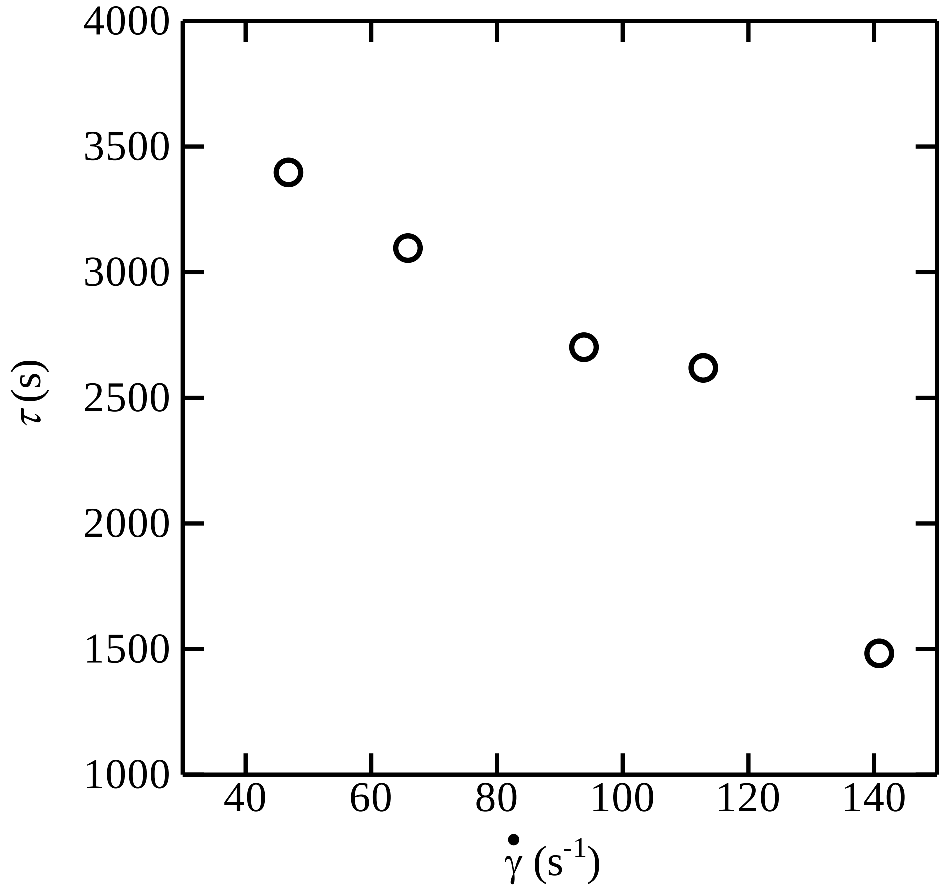
4000
3500
3000
2500
2000
1500
1000
τ (s)
40
60
80
100
120
140
$\dot{\gamma}$ (s^{-1})

Figure 5a

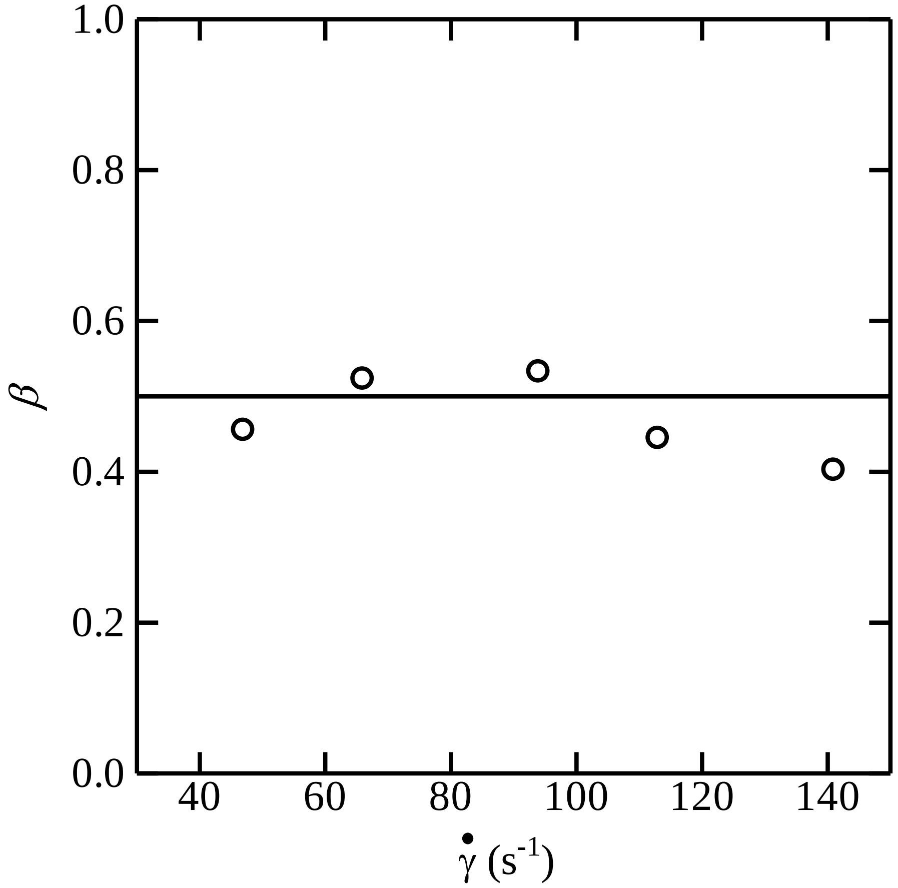

Figure 5b

Table 1

Shear rate (s^{-1})	q_1	q_2	t_0	τ	β	χ^2
47	1.03	1.75	1.05×10^{2}	3.39×10^{3}	4.55×10^{-1}	2.561×10^{-3}
66	1.18	2.45	7.12×10^{1}	3.09×10^{3}	5.23×10^{-1}	4.517×10^{-3}
94	1.34	2.70	5.08×10^{1}	2.70×10^{3}	5.32×10^{-1}	6.664×10^{-3}
113	1.40	2.80	4.19×10^{1}	2.61×10^{3}	4.44×10^{-1}	9.368×10^{-3}
141	1.47	3.49	3.23×10^{1}	1.48×10^{3}	4.02×10^{-1}	1.442×10^{-2}

Table 2

Shear rate (s^{-1})	q_1	q_2	t_0	τ	χ^2
47	9.60×10^{-1}	1.48	-1.23×10^{2}	3.00×10^{3}	3.615×10^{-3}
66	1.20	1.99	-4.13×10^{3}	2.56×10^{3}	4.618×10^{-3}
94	1.32	2.17	-6.75×10^{2}	2.16×10^{3}	8.289×10^{-3}
113	1.37	2.23	-8.08×10^{2}	2.06×10^{3}	1.237×10^{-2}
141	1.67	2.73	-7.06×10^{2}	1.72×10^{3}	1.770×10^{-2}