

Molecular weight distribution and the electrorheological response for anisotropic solutions of poly(γ -benzyl-L-glutamate) induced by the convection of the electrohydrodynamic instability

Katsufumi Tanaka,* Akio Takahashi, and Ryuichi Akiyama

Department of Polymer Science and Engineering, Kyoto Institute of Technology, Matsugasaki, Kyoto 606-8585, Japan

Noriyuki Kuramoto

Graduate Program of Human Sensing and Functional Sensor Engineering, Graduate School of Engineering, Yamagata University, Yonezawa 992-8510, Japan

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Transient responses of stress to a sinusoidal electric field were reported for anisotropic solutions of poly(γ -benzyl-L-glutamate)s (PBLG's) with different distributions of the molecular weight. The transient stress, which was induced by the convection of the electrohydrodynamic instability, showed a steep and large increase when it was plotted against the instantaneous amplitude of the electric field. The maximum stress of a PBLG solution tended to increase with an increase in the maximum molecular weight of the PBLG in the molecular weight distribution. [S1063-651X(99)05505-1]

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The electrorheological (ER) effect is a rheological response of fluids under an external modulation of the electric field; that is, a large enhancement in the apparent viscosity and recovery to the original viscosity by application and removal of the electric field, respectively [1–4]. Recently, it has been found that the fluids based on liquid crystalline polymers, the side chain type [5] as well as the main chain type [6–8], show the ER effect. The ER effect for liquid crystalline polymers has attracted intense interest because of practical applications as well as the scientific aspect of the dynamics of rodlike molecules. The ER effect for liquid crystalline polymers composed of rodlike molecules can be basically explained by the changes in the contribution of the Miesowicz viscosities [9] induced by external electric fields and the electrohydrodynamic instability [2] that is accompanied by the secondary flow or convection, such as macroscopic vortices. In the previous paper, a new class of the ER response unexplained by the electrohydrodynamic instability was reported for an anisotropic solution of poly(γ -benzyl-L-glutamate) (PBLG) [8]. Further, it is proposed that the anisotropic domains composed of the larger molecules in the molecular weight distribution would only be oscillated around a tilt angle by the sinusoidal electric field with the lowest frequency at a given insufficient amplitude under shear flow, while they would be fully rotated by the sinusoidal electric fields with higher frequencies because of the inertia effect of the anisotropic domains [8]. The full rotation of the anisotropic domains can also be induced much more remarkably by the different mechanism of the convection of the electrohydrodynamic instability. It is expected that the maximum stress response of a PBLG solution, which is induced by the convection of the electrohydrodynamic instability, to a sinusoidal electric field with sufficiently low frequency increases with an increase in the maximum molecular weight of the PBLG because the Miesowicz viscosity η_c ($> \eta_a, \eta_b$)

would be proportional to the maximum molecular weight (the maximum length) of the rodlike molecules. The remarkable difference of the mechanism between the full rotation of the PBLG molecules caused by the inertia effect [8] and that by the convection of the electrohydrodynamic instability is the range of the frequency of the applied sinusoidal electric field. The full rotation by the former case is not caused by the sinusoidal electric field with lower frequencies approaching zero, much less by the dc electric field. On the other hand, the full rotation by the latter case is easily caused by the electric field with lower frequencies because the threshold voltage of the electrohydrodynamic instability decreases as the frequency of the electric field decreases [10]. In the present paper, transient responses of stress to an external sinusoidal electric field are reported for anisotropic solutions of PBLG's with different distributions of the molecular weight, and the transient stresses plotted against the instantaneous amplitude of the sinusoidal electric field are investigated for the solutions with or without the electrohydrodynamic instability.

Samples of PBLG's with the average molecular weight based on viscosity of 4.2×10^4 (PBLG A), 1.5×10^5 (B), and 2.8×10^5 (C) were purchased from Sigma Chemical Co. Further, a sample of PBLG (D), which contains the larger molecular weight components as discussed later, was synthesized after the NCA polymerization, the ring-opening polymerization of α -aminoacid-N-carboxyanhydride (NCA) monomers, at the laboratory of Yamagata University to show the effect of the larger molecular weight components. The NCA of γ -benzyl-L-glutamate was prepared in the previous paper [11]. The polymerization was carried out in dioxane at 25 °C with triethylamine as an initiator. The distributions of molecular weight for the PBLG's dissolved in chloroform at room temperature were also characterized by gel permeation chromatography (GPC) [7]. The results are shown in Fig. 1. The polydispersity indexes of M_w/M_n were 2.4, 230, 140, and 590, respectively for PBLG A, B, C, and D. The weight average molecular weights were deduced to be 2.4×10^3 , 5.9×10^5 , 8.9×10^5 , and 3.5×10^6 , respectively, for PBLG A,

*Author to whom correspondence should be addressed. Electronic address: ktanaka@ipc.kit.ac.jp

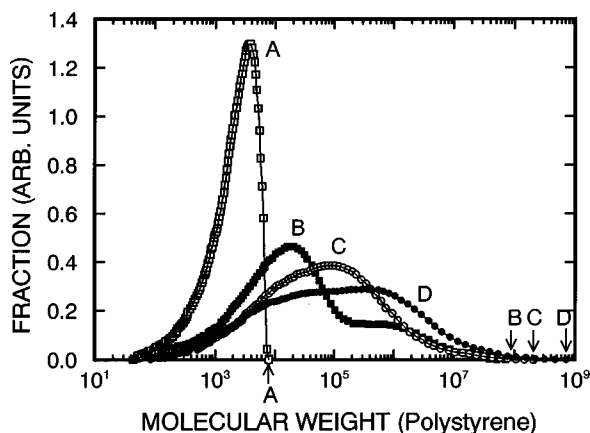


FIG. 1. Distributions of the molecular weight based on polystyrene standards for PBLG's characterized by gel permeation chromatography. The maximum components of the molecular weight for the PBLG's are also shown by the arrows in the figure.

B, *C*, and *D*, using the polystyrene standards [7]. It should be noted that the maximum molecular weight of PBLG *A* is less than 10^4 , which is obviously lower than the maximum molecular weights of the other PBLG's. The PBLG's as received were dissolved in 1,4-dioxane. More than two grades of purity of 1,4-dioxane such as an infinitely pure grade and a reagent grade, etc., were used for the purpose of inhibition and promotion of the electrohydrodynamic instability. The concentration of the PBLG's was 15 wt. %, and the solutions were found to be anisotropic at the concentration and room temperature from the optical observation [7]. External electric fields up to 3.2 kV/mm were applied to the solutions using a dc power supply or a high voltage power amplifier driven by a signal generator as mentioned below. Therefore, we can ascertain whether a solution of PBLG shows the electrohydrodynamic instability or not in advance of the ER measurements.

The stress responses were measured with a rotational rheometer (Rheology Engineering, MR-300V2E) at a shear rate (the one at the edge of the parallel plates) of 2.6 s^{-1} [8]. The sheared PBLG solutions were stimulated by sinusoidal electric fields with an amplitude (E_m) of 2.5 kV/mm and frequencies (f) from 0.01 Hz to 1 kHz. The sinusoidal electric fields were applied to the PBLG solutions using a high voltage power amplifier (Trek, Model 609-D), which has a current monitor, driven by a signal generator. At the same time, the current passing through the solutions was measured by the current monitor as mentioned above or another current monitor (Trek, Model P0529). The detected signals of stress response, electric field, and current were digitized at the same time by a 12-bit analog-to-digital converter which has four channels of the analog-to-digital converting units. These data were stored in a personal computer. In the present paper, attention is focused on the results of stress response induced by the electric field with a frequency of 0.01 Hz because the electrohydrodynamic instability, if it exists, can be induced easily at the frequency. The threshold of the electrohydrodynamic instability can also be determined conveniently with the sinusoidal electric field, which is well assumed at the quasistatic electric field with different strengths. In addition, most researchers apply the dc electric field to the ER fluids. Therefore, the ER effect under the electric field with a fre-

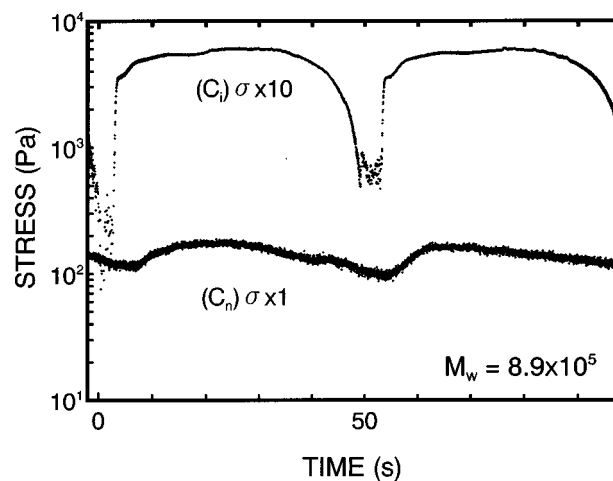


FIG. 2. Typical transient responses of stress to a sinusoidal electric field plotted as a function of time for the solutions of PBLG *C* with, (C_i), or without, (C_n), the electrohydrodynamic instability. The stress response (C_i) is vertically shifted to a higher order as shown in the figure.

quency of 0.01 Hz is closely related to the ER effect under the dc electric field.

Figure 2 shows typical transient responses of stress (σ) for the solutions of PBLG *C* with, (C_i), or without, (C_n), the electrohydrodynamic instability to a sinusoidal electric field [E as defined in Eq. (1)] plotted as a function of time (t),

$$E = E_m \sin[2\pi f(t - t_0)], \quad (1)$$

where t_0 is a delay time of 50 s in the case of the results shown in Fig. 2. (In the present paper, the subscript “*n*” refers to the solution without the electrohydrodynamic instability, and the subscript “*i*” refers to the solution with the electrohydrodynamic instability.) The stress response (C_i) is vertically shifted to a higher order as shown in the figure. (Similar shifts are performed in Figs. 3 and 4.) The sinusoidal electric field was applied when the PBLG solutions showed a saturated stress under no electric field. The fundamental frequency of both of the stress responses (C_n) and (C_i) is about twice the frequency of the applied electric field. However, the wave form of (C_i) is much different from that of (C_n). The instantaneous amplitude of the stress response (C_i) increases and decreases discontinuously at relatively lower critical instantaneous amplitude of the electric field, and the stress response is almost constant over a half-period of the electric field. On the other hand, the instantaneous amplitude of the stress response (C_n) increases and decreases continuously and it synchronizes with the applied electric field. It is noted that the maximum of the stress response (C_i) is much larger than that of the stress response (C_n). The observation of a polarized optical microscope showed that the convection of the electrohydrodynamic instability of solution (C_i) was remarkably induced by a dc electric field with a strength lower than 1 kV/mm. The optical observation also showed that the homeotropic orientation of solution (C_n), in which the PBLG molecules aligned perpendicular to the electrode surface, was induced by the dc electric field with a strength of 3.2 kV/mm. Therefore, PBLG molecules (or anisotropic domains) of solution (C_n) would

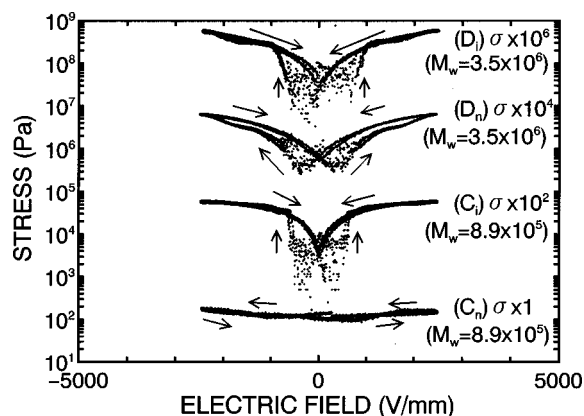


FIG. 3. Transient responses of stress shown in Fig. 2 plotted against the instantaneous amplitude of the applied sinusoidal electric field. The results of the solutions of PBLG D with, (D_i), or without, (D_n), the electrohydrodynamic instability are also shown, and the responses of stress are vertically shifted as shown in Fig. 3.

be oscillated around a tilt angle by the sinusoidal electric field with an insufficient amplitude of 2.5 kV/mm under shear flow. On the other hand, PBLG molecules in solution (C_i) would be fully rotated by the convection of the electrohydrodynamic instability, and the contribution of the Miesowicz viscosity η_c to the apparent viscosity would be increased.

Figure 3 shows the transient responses of stress (σ) shown in Fig. 2 plotted against the instantaneous amplitude of the applied sinusoidal electric field (E). Further, in Fig. 3 (the σ - E curve), the results of the solutions of PBLG D with or without the electrohydrodynamic instability are shown. The feature of the σ - E curves as shown in Fig. 3 is symmetric with respect to the vertical axis of $E=0$ kV/mm, but it changes remarkably depending on whether the solution showed the electrohydrodynamic instability or not. [Further, the feature of the j - E curves was symmetric with respect to the point of the origin of the coordinates. Therefore, we will discuss the σ - E (and j - E) curves at $E \geq 0$ kV/mm.] In Fig. 3, solution (C_n) shows a synchronous response with no hysteresis, which is characteristic of the σ - E curve induced by the lowest frequency of the electric field for a PBLG solution without the electrohydrodynamic instability [8]. On the other hand, solution (C_i) shows the σ - E curve with a much steeper and larger increase in stress at a critical instantaneous amplitude of the electric field, which is characteristic of the σ - E curve for a PBLG solution with the electrohydrodynamic instability. [In the j - E curve measured at the same time, the current density of solution (C_i) was slightly non-Ohmic above the critical instantaneous amplitude of the electric field as discussed in Fig. 3, and the maximum of the current density of solution (C_i) of $40 \mu\text{A}/\text{cm}^2$ was much larger than that of solution (C_n) of $10 \mu\text{A}/\text{cm}^2$.] It is thought that the solvent of 1,4-dioxane used for solution (C_i) contained many more impurities than the solvent used for solution (C_n). The conduction current, which comes from the impurities, would induce the electrohydrodynamic instability of solution (C_i). In Fig. 3, solutions (D_n) and (D_i) show similar tendencies as discussed for solutions (C_n) and (C_i), respectively. However, solution (D_n) shows hysteresis in Fig. 3. Further, the maximum of the stress response for so-

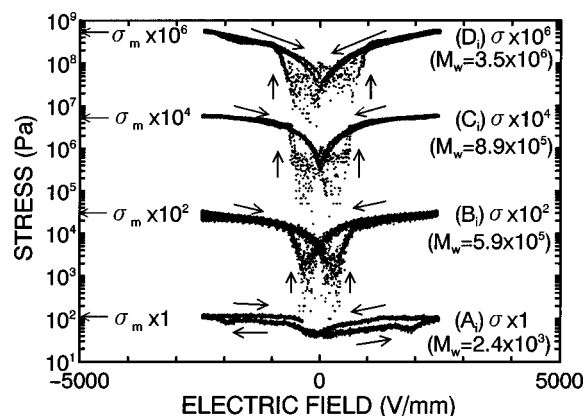


FIG. 4. Transient responses of stress plotted against the instantaneous amplitude of the applied sinusoidal electric field for the solutions of PBLG A (A_i), B (B_i), C (C_i), and D (D_i) with the electrohydrodynamic instability. The responses of stress are vertically shifted as shown in the figure.

lution (D_n) is almost identical to that for solution (D_i). The observation of a polarized optical microscope showed no convection and no homeotropic orientation (but only polydomain texture) of solution (D_n) under the dc electric field with a strength of 3.2 kV/mm. The optical observation also showed the convection, which was not so remarkable, of the electrohydrodynamic instability of solution (D_i). Because PBLG D contains a much higher fraction of the larger molecular weight components than the other PBLG's as shown in Fig. 1, solution (D_n) showed hysteresis and no synchronous response of stress to the sinusoidal electric field with an amplitude of 2.5 kV/mm and an insufficiently low frequency of 0.01 Hz. [A sinusoidal electric field with the same amplitude and a frequency much lower than 0.01 Hz would induce a synchronous response of stress with no hysteresis for solution (D_n).] The hysteresis of stress response (D_n) as shown in Fig. 3 is quite similar to the hysteresis induced by sinusoidal electric fields with frequencies slightly higher than the lowest one, as shown in Fig. 4 in Ref. [8]. Therefore, the maximum of the stress response (D_n), which is identical to that of the stress response (D_i) as shown in Fig. 3, would be induced by the effect of inertia of the anisotropic domains [8].

Figure 4 shows the σ - E curves for the solutions of PBLG A (A_i), B (B_i), C (C_i), and D (D_i) with the electrohydrodynamic instability. The solution (B_i) also shows the σ - E curve with a steep and large increase in stress at a critical instantaneous amplitude of the electric field, which is characteristic of the σ - E curve for a PBLG solution with the electrohydrodynamic instability. However, the σ - E curve for solution (A_i) is much different from the σ - E curves of the other solutions in the figure. The stress response of solution (A_i) is almost constant against the instantaneous amplitude of the electric field, and no critical instantaneous amplitude of the electric field or the threshold electric field can be seen in the σ - E curve. The observation of a polarized optical microscope for solution (A_i) showed remarkable convection of the electrohydrodynamic instability induced by a dc electric field with a strength of 0.4 kV/mm or lower. [The maximum of the current density passing through solution (A_i) was approximately one order higher than the maxima of the

other solutions.] Further, it can be found in Fig. 4 that the threshold electric field for a solution tends to decrease as the weight average molecular weight decreases. Therefore, an undetectably low threshold electric field for solution (A_i) in the σ - E curve is consistent with the tendency of the threshold electric field as mentioned above. On the other hand, the maximum of the stress response for a solution, σ_m , tends to increase with an increase in the weight average molecular weight or the maximum component of the molecular weight as shown by the arrows in Fig. 1. Especially, σ_m for solution (A_i) is much smaller than σ_m 's for the other solutions in Fig. 4. As discussed in Fig. 1, the maximum molecular weight of PBLG A is obviously lower than the maximum molecular weights of the other PBLG's. Therefore, the Miesowicz viscosity η_c for solution (A_i) would be much lower than η_c 's for solutions of the other PBLG's, so that σ_m for solution (A_i), which was measured at a constant shear rate and was

induced by the convection of the electrohydrodynamic instability, is much smaller than σ_m 's for the other solutions shown in Fig. 4. It is thought that σ_m tends to increase with an increase in the maximum molecular weight of PBLG. Accordingly, these results show the convection of rodlike molecules with the maximum length contributing clearly to the ER response induced by the electrohydrodynamic instability.

Finally, it is noted that enormous increases in stress for solutions (C_i) and (D_i) were effectively induced by the convection of the electrohydrodynamic instability at relatively lower instantaneous amplitudes of the electric field. Generally, the instantaneous amplitudes of the electric field to induce the convection of the electrohydrodynamic instability will be lower than the threshold electric field of the electrical breakdown, which is favorable for practical applications of the ER effect.

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