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# Enormous stress response of anisotropic solution of poly($\gamma$-benzyl-L-glutamate) to sinusoidal electric fields with low frequencies unexplained by the electrohydrodynamic instability

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Transient stress responses to sinusoidal electric fields with frequencies lower than 1 Hz were reported for an anisotropic solution of poly($\gamma$-benzyl-L-glutamate). An enormous increase in stress with hysteresis was found at higher frequencies of the electric fields, while the smaller increase in stress with no hysteresis was found at the lowest frequency. These results are unexplained by the electrohydrodynamic instability.
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The electrorheological (ER) fluids are known as the fluids which show the ER effect, that is, large enhancement in apparent viscosity and recovery to the original viscosity by application and removal of an external electric field, respectively. It is known that suspensions composed of polarizable particles and insulating solvents [1–3], and homogeneous fluids such as liquid crystals of small molecules [4] and solutions of flexible polymers with polar side group [5] show the ER effect. Recently, liquid crystalline polymers, the side chain type [6,7] as well as the main chain type [8,9], have attracted intense interest because of the comparable enhancement of apparent viscosity to the ER suspensions. In the case of the ER effect for liquid crystalline polymers, the interaction among anisotropic domains should be taken into account because liquid crystalline polymers usually do not show the monodomain texture [10] which liquid crystals of small molecules easily show under weak shear flow. However, the ER effect for liquid crystalline polymers composed of rodlike molecules can be basically explained by the following factors similar as the ER effect for liquid crystals composed of small molecules; that is, the changes in contribution of the Miesowicz viscosities [11] induced by external electric fields and the electrohydrodynamic instability [4] that is accompanied by the secondary flow such as macroscopic vortices. The electrohydrodynamic instability is caused by an anisotropy of the conductivity or of the dielectric constant in a liquid crystal itself [12] and it is sometimes caused by the electrical conduction of charge carriers injected from electrodes even in the case of isotropic liquids [12–15]. It should be noted that the threshold voltage of the electrohydrodynamic instability for a liquid crystal decreases as the frequency of applied alternating electric fields decreases [14,15].

In the present paper, unexpected results of transient stress responses of an anisotropic solution of poly($\gamma$-benzyl-L-glutamate) (PBLG) to sinusoidal electric fields with frequencies lower than 1 Hz are reported. The reported results are discussed in terms of the changes in contribution of the Miesowicz viscosities induced by external electric fields and the electrohydrodynamic instability. However, the reported results are unexplained by the secondary flow induced by the electrohydrodynamic instability, which suggests the effects of inertia of anisotropic domains in our PBLG solution induced by the external electric fields.

Poly($\gamma$-benzyl-L-glutamate) with an average molecular weight based on viscosity of $1.18\times10^5$ was purchased from Sigma Chemical Co. The molecular weight distribution of the PBLG dissolved in chloroform at room temperature was also characterized by gel permeation chromatography. The polydispersity index $M_w/M_n$ was 67 with a broad distribution of the molecular weight. The weight average molecular weight was deduced to be $3.5\times10^5$ using the polystyrene standards [9]. The PBLG as received was dissolved in 1,4-dioxane. The concentration of the PBLG was 15 wt. %, and the solution was found to be anisotropic at the concentration and room temperature from the optical observation [9]. Texture of the solution in a quiescent state was observed by an optical microscope (Olympus, BH-2) equipped with a camera and crossed polarizers. External electric fields up 1.6 kV/mm were applied to the solution using a dc power supply. The stress responses were measured with a rotational rheometer (Rheology Engineering, MR-300V2E) in the presence and absence of external electric field. A fixture of parallel plates with a constant gap of 0.4 mm was used as electrodes when an electric field was applied to the PBLG solution. The PBLG solution was deformed at a shear rate (the one at the edge of the parallel plates) of 2.6 $s^{-1}$ to be a steady flow. The sheared PBLG solution was stimulated by sinusoidal electric fields with amplitudes up to 2.5 kV/mm and frequencies lower than 1 Hz. The sinusoidal electric fields were applied to the PBLG solution in the direction perpendicular to the parallel plates using a piezo-drive amplifier (MESS-TEK Co., M-2603B) driven by a signal generator. The detected signals of stress response were digitized by a 12-bit analog-to-digital converter, and the data were stored in a personal computer. The details of the experiments were reported elsewhere [7,9].

Figure 1 shows the stress responses to sinusoidal electric fields [$E$ as defined in Eq. (1)] with a frequency ($f$) of 1 Hz and different amplitudes ($E_m$) plotted semilogarithmically as a function of time ($t$),

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

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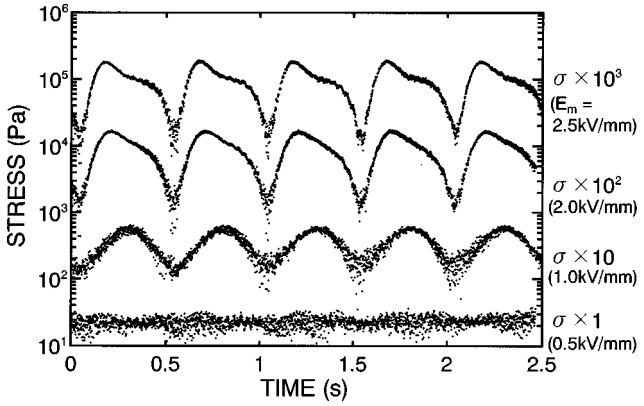


FIG. 1. Stress responses to sinusoidal electric fields with a frequency of 1 Hz and different amplitudes plotted semilogarithmically as a function of time.

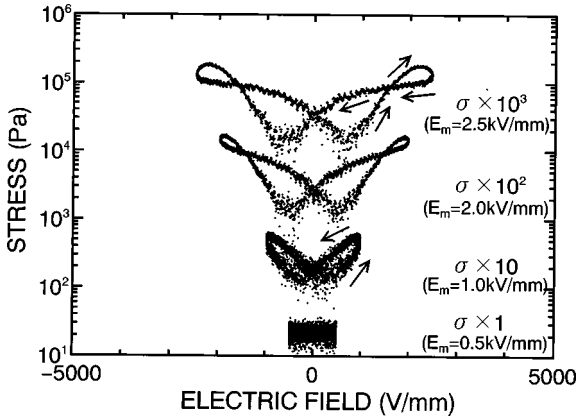


FIG. 2. Transient stress as shown in Fig. 1 plotted against the instantaneous amplitude of external sinusoidal electric fields with different amplitudes.

where $t_0$ is a delay time of 0 s in the case of the results shown in Fig. 1. The stress responses are vertically shifted to higher orders, as shown in Fig. 1. The sinusoidal electric fields were applied when the PBLG solution showed a saturated stress under no electric field. The waveform of the stress response at $E_m=1.0$ kV/mm is much different from the waveforms at $E_m=2.0$ and 2.5 kV/mm in the figure. The waveform, which was plotted on a linear scale [16], was sinusoidal at $E_m=1.0$ kV/mm and it was nonsinusoidal containing higher order harmonics at $E_m=2.0$ and 2.5 kV/mm. [The waveform of the stress response at $E_m=0.5$ kV/mm can be also sinusoidal. The stress at $E_m=0.5$ kV/mm was obviously larger than the saturated stress ($\sigma_0$) of 8.7 Pa measured by the rotational rheometer under no electric field.] The fundamental frequency of the stress responses is about twice the frequency of applied electric fields. The amplitude of the stress responses increases with an increase in the amplitude of applied electric fields. Further, the normalized maximum ER response, which is defined here as $(\sigma_m-\sigma_0)/\sigma_0$, where $\sigma_m$ is the maximum stress over a period of each sinusoidal electric field, is 20 for $E_m=2.5$ kV/mm and $f=1$ Hz. The resulting normalized maximum ER response is much larger than the normalized ER response [9] of 11, which was induced by the stepwise electric field with a strength of 2.5 kV/mm.

Figure 2 shows the transient stress as shown in Fig. 1 plotted against the instantaneous amplitude of external sinusoidal electric fields ($\sigma$-$E$ curve) with different amplitudes. The hysteresis of the $\sigma$-$E$ curves as shown in Fig. 2 is symmetric with respect to the vertical axis of $E=0$ kV/mm and it changes depending on $E_m$. (We will discuss the hysteresis at $E\geqslant 0$.) At $E_m=1.0$ kV/mm (and probably at $E_m=0.5$ kV/mm), $\sigma$ shows the maximum at $E_m$. Above $E_m=2.0$ kV/mm, $\sigma$ shows the maximum at a smaller instantaneous amplitude than $E_m$ and an additional hysteresis loop can be seen. The area of additional hysteresis loop (or total hysteresis loop) at $E_m=2.5$ kV/mm is much larger than that at $E_m=2.0$ kV/mm. It is considered that the PBLG molecules (or domains in the polydomain texture, such as those shown in Ref. [9]) with a large permanent dipole moment along helix axis were tilted toward a stable tilt angle or aligned parallel to the electrodes surfaces by the shear deformation under no electric field. The PBLG molecules (domains) would be oscillated around a tilt angle by the sinusoidal electric fields with $E_m=0.5$ and 1.0 kV/mm under shear flow. On the other hand, the PBLG molecules (domains) were thought to be fully rotated by the sinusoidal electric fields with $E_m=2.0$ and 2.5 kV/mm, and the reverse orientation of the dipole moment would be induced by the electric fields. The full rotation of the PBLG molecules can be closely related to the effect of inertia induced by the external sinusoidal electric fields. Similar critical changes in the stress response as mentioned above were also found when the stepwise electric fields were applied to the PBLG solution. However, the critical strength of the stepwise electric field of 2.5 kV/mm [9] was slightly larger than the critical amplitude of the sinusoidal electric field with $f=1$ Hz, which suggests that the critical response of the PBLG domains to the external electric fields depends on the frequency of the external electric fields as discussed later. Further, the electrohydrodynamic instability could also affect the critical changes in the ER response because the amplitude of the electric field of 2.0 kV/mm, which gave the critical changes in the waveform of stress response was larger than the maximum strength of dc electric field in the optical observation ($E=1.6$ kV/mm) at which no electrohydrodynamic instability was observed [9]. If the secondary flow such as macroscopic or local vortices are induced by the electrohydrodynamic instability, rodlike molecules of PBLG can also rotate on a large scale in the solution between parallel plates and the contribution of the Miesowicz viscosity $\eta_c$ ($>\eta_b, \eta_a$) to the apparent viscosity can be increased.

Figure 3 shows the stress responses to sinusoidal electric fields [$E$ as defined in Eq. (1)] with an amplitude of $E_m=2.5$ kV/mm and different frequencies plotted semilogarithmically as a function of $f(t-t_0)$, where $t_0$ is a delay time of $0.575f^{-1}$ s in the case of the results shown in the figure. In Fig. 3, the smaller increase in stress response is found at $f=0.01$ Hz. Further, $f(t-t_0)$ at the minimum of the stress response gradually approaches zero as $f$ decreases. The latter dependence of $f(t-t_0)$ suggests the stress response at $f=0.01$ Hz was synchronized with the external sinusoidal electric field.

Figure 4 shows the transient stress as shown in Fig. 3 plotted against the instantaneous amplitude of external sinusoidal electric fields with different frequencies. The hyster-

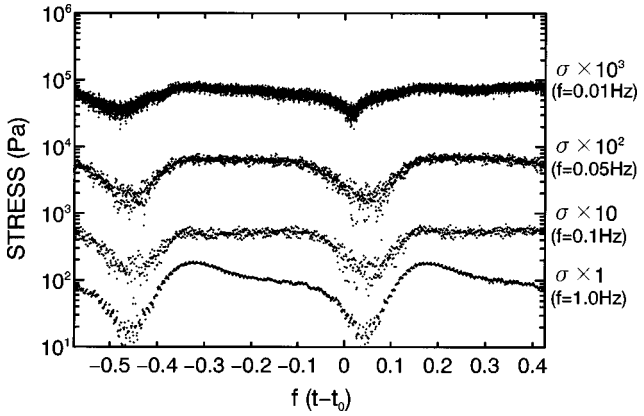


FIG. 3. Stress responses to sinusoidal electric fields with an amplitude of $E_m = 2.5$ kV/mm and different frequencies plotted semilogarithmically as a function of $f(t-t_0)$.

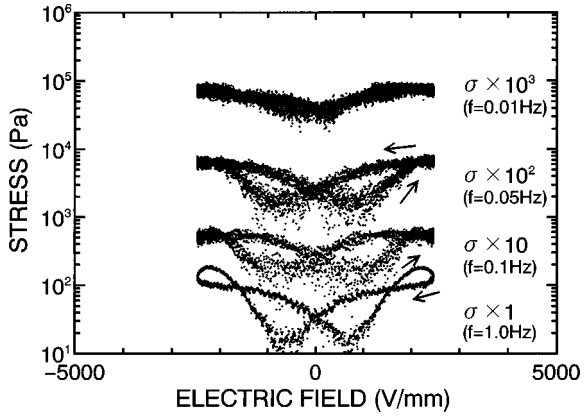


FIG. 4. Transient stress as shown in Fig. 3 plotted against the instantaneous amplitude of external sinusoidal electric fields with different frequencies.

esis of the $\sigma$-$E$ curves as shown in Fig. 4 is also symmetric with respect to the vertical axis of $E = 0$ kV/mm and it changes remarkably depending on $f$. In Fig. 4, the area of the $\sigma$-$E$ curves (or hysteresis loops) decreases remarkably as $f$ decreases. The additional hysteresis loop at $f = 1$ Hz disappears in the $\sigma$-$E$ curves at the lower frequencies. Below $f = 0.1$ Hz, $\sigma$ tends to show a constant maximum above an instantaneous amplitude smaller than $E_m$. A synchronous response with no hysteresis is found in the $\sigma$-$E$ curve at the lowest frequency of 0.01 Hz in the present experiment. Further, the normalized maximum ER response of 9 is induced by the sinusoidal electric field with $f = 0.01$ Hz and $E_m = 2.5$ kV/mm which is in good agreement with the normalized ER response of 11 induced by the stepwise electric field with a strength of 2.5 kV/mm for the PBLG samples prepared similarly as the present study [9].

It should be noted that the maximum shear stress enhanced by the sinusoidal electric field with $f = 1$ Hz as shown in Fig. 4 is much larger than that with $f = 0.01$ Hz and the stress response is synchronized with the sinusoidal electric field with $f = 0.01$ Hz. The above results are unexplained by the secondary flow induced by the electrohydrodynamic instability: The threshold voltage of the electrohydrodynamic instability for a liquid crystal decreases as the frequency of applied alternating electric fields decreases [14,15]. Accordingly, the threshold voltage (or electric field in the present experiment) at $f = 0.01$ Hz should be lower than that at $f = 1$ Hz. The secondary flow induced by the electrohydrodynamic instability at $f = 0.01$ Hz should be more remarkable than that at $f = 1$ Hz and the contribution of the Miesowicz viscosity $\eta_c$ $(> \eta_b, \eta_a)$ to the apparent viscosity can be increased more remarkably in the former case. However, the tendency of our results is opposite to the expectation as mentioned above. Further, the synchronous response with no hysteresis that was found in Fig. 4 is also unexplained by the electrohydrodynamic instability. The stress response should not be synchronized with the sinusoidal electric field in the case of the electrohydrodynamic instability. These results suggest the effect of inertia of anisotropic domains in our PBLG solution induced by the external sinusoidal electric fields. Finally, the molecular weight distribution of the PBLG is broad and it contains larger molecular weight components. It is considered that the larger molecular weight components would be oscillated around a tilt angle by the sinusoidal electric fields with $f = 0.01$ Hz at a given insufficient amplitude of 2.5 kV/mm under shear flow, while they would be fully rotated by the sinusoidal electric fields with $f = 1$ Hz even at $E_m = 2.0$ and 2.5 kV/mm because of the inertia effect of the anisotropic domains.

[1] H. Block, J. P. Kelly, A. Qin, and T. Watson, Langmuir **6**, 6 (1990).
[2] K. Tanaka, A. Sahashi, R. Akiyama, and K. Koyama, Phys. Rev. E **52**, R3325 (1995).
[3] W. Y. Tam, G. H. Yi, W. Wen, H. Ma, M. M. T. Loy, and P. Sheng, Phys. Rev. Lett. **78**, 2987 (1997).
[4] T. Honda, K. Kurosawa, and T. Sasada, Jpn. J. Appl. Phys. **18**, 1015 (1979).
[5] K. Tanaka, A. Fujii, and K. Koyama, Polym. J. (Tokyo) **24**, 995 (1992) (in English).
[6] A. Inoue and S. Maniwa, J. Appl. Polym. Sci. **55**, 113 (1995).
[7] K. Tanaka, Y. Oiwa, R. Akiyama, and A. Kubono, Polym. J. (Tokyo) **30**, 171 (1998) (in English).
[8] I-Kuan Yang and A. D. Shine, J. Rheol. **36**, 1079 (1992).
[9] K. Tanaka, R. Akiyama, and K. Takada, J. Appl. Polym. Sci. **66**, 1079 (1997).
[10] R. G. Larson and D. W. Mead, Liq. Cryst. **12**, 751 (1992).
[11] P. G. de Gennes and J. Prost, *The Physics of Liquid Crystals*, 2nd ed. (Oxford University Press, New York, 1993), Chaps. 3 and 5.
[12] W. Helfrich, J. Chem. Phys. **51**, 4092 (1969).
[13] H. Gruler and G. Meier, Mol. Cryst. Liq. Cryst. **16**, 299 (1972).
[14] Orsay Liquid Crystal Group, Phys. Rev. Lett. **25**, 1642 (1970).
[15] Orsay Liquid Crystal Group, Mol. Cryst. Liq. Cryst. **12**, 251 (1971).
[16] A. Takahashi, K. Tanaka, A. Kubono, and R. Akiyama, Rep. Prog. Polym. Phys. Jpn. **39**, 265 (1996).