# Electrorheological Effect of Anisotropic Solution of Poly(γ-benzyl-L-glutamate) Induced by Stepwise Electric Fields

KATSUFUMI TANAKA, RYUICHI AKIYAMA, KEIGO TAKADA

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

**ABSTRACT:** The electrorheological (ER) effect of an anisotropic solution of poly(γ-benzyl-L-glutamate)(PBLG) in 1,4-dioxane with a concentration of 15 wt % was measured at a shear rate of 2.6 s$^{-1}$ by our parallel-plate sliding rheometer. The solution under shear flow was stimulated by stepwise electric fields up to 3.0 kV/mm. Remarkable changes in the beginning of the transient ER response were observed according to the strength of the stepwise electric fields. The lower electric field gave a smaller increase in shear stress depending on the electric-field strength, while the larger electric fields above a critical strength tended to give a larger stress response. The maximum shear stress enhanced by the electric fields in the present experiment was in excess of 10 times the steady shear stress under no electric field. The ER effect was discussed in terms of the Miesowicz viscosities, the interaction among anisotropic domains, as well as the electrohydrodynamic instability. © 1997 John Wiley & Sons, Inc. J Appl Polym Sci **66:** 1079–1084, 1997

**Key words:** electrorheology; polymer solutions; liquid crystals; poly(γ-benzyl-L-glutamate)

## INTRODUCTION

Electrorheological (ER) fluids are known as fluids which show the ER effect, i.e., a large enhancement in apparent viscosity and recovery to the original viscosity by application and removal of an external electric field, respectively. Suspensions composed of polarizable particles and insulating solvents[1–3] and homogeneous fluids such as liquid crystals of small molecules[4–6] and solutions of flexible polymers with a polar side group[7] show the ER effect. Although the homogeneous fluids are free from the sedimentation of particles in the ER suspensions, which seems to be a favorable feature for a practical purpose, the enhancement

of the apparent viscosity by the electric fields for these homogeneous fluids is much smaller, typically by several times, than that of the ER suspensions. However, the ER fluids based on liquid crystalline polymers have attracted intense interest since an outstanding breakthrough showing remarkable enhancement in shear stress induced by the electric fields as reported by Inoue and Maniwa[8] using a thermotropic liquid crystalline polymer of the side-chain type. The fluids based on the side-chain-type liquid crystalline polymers showed stress enhancement of more than 3000 Pa in absolute value[9] and more than 10 times in the ratio to the steady shear stress under no electric field over a wide range of the shear rate.[9,10] Inoue and Maniwa[10] also reported the ER behaviors under the steady and oscillatory shear flows for a lyotropic liquid crystalline polymer showing a helical (or rodlike) structure in a solvent. The liquid crystalline polymers composed of rodlike mole-
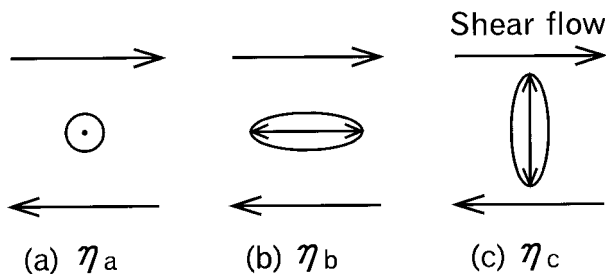
**Figure 1** Miesowicz viscosities[13]: (a) director perpendicular to flow direction and to velocity gradient; (b) director parallel to flow direction; (c) director parallel to velocity gradient. ($\eta_a$, $\eta_b < \eta_c$).

cules with a large aspect ratio are also expected[11,12] to show much larger stress enhancement compared with liquid crystals of small molecules on the basis of the Miesowicz viscosities[13] as shown in Figure 1. They pointed out that different mechanisms were involved in the ER effect of thermotropic liquid crystalline polymers, and lyotropic liquid crystalline polymers.[10] However, the mechanisms of the ER effect of these fluids based on liquid crystalline polymers are still unclear.

In the present article, the ER effect induced by stepwise electric fields is reported for an anisotropic solution of poly($\gamma$-benzyl-L-glutamate) (PBLG) in 1,4-dioxane and the ER effect is discussed in terms of the orientation of the rodlike molecules of PBLG induced by the external electric fields, the interaction among anisotropic domains, as well as the electrohydrodynamic instability.[13]

## EXPERIMENTAL

### Samples

Poly($\gamma$-benzyl-L-glutamate) (PBLG) with an average molecular weight based on a viscosity of $1.18 \times 10^5$ was purchased from Sigma Chemical Co. The molecular weight distribution of the PBLG dissolved in chloroform at room temperature was characterized by GPC. The GPC was performed with a microprocessor-controlled HPLC pump (Jasco Corp., 880-PU) and an RI detector (Jasco Corp., 830-RI). A combination of four polystyrene gel columns of TSK H8, TSK GMH6, Hitachi GL-A120, and Hitachi GL-A130 was used. The molecular weight was determined by calibrating with polystyrene standards. The polydispersity index $M_w/M_n$ was 67 with a broad distribution of the molecular weight. The weight-average mo-

lecular weight was deduced to be $3.5 \times 10^5$ using the polystyrene standards. The PBLG as received was dissolved in 1,4-dioxane. The concentration of the solution was 15 wt %, and the solution was found to be anisotropic at that concentration and at room temperature from the optical observation as mentioned in the next section.

### Optical Microscopic Observation

Texture of the solution in a quiescent state was observed by an optical microscope (Olympus, BH-2) equipped with a camera and crossed polarizers. All micrographs were taken at room temperature through a $\times 10$ magnification objective lens. External electric fields up to 1.6 kV/mm were applied to the solution using a dc power supply. The details of the experiments were reported elsewhere.[12]

### Electrorheological Measurements

Rheological response was measured by a rheometer with parallel plates of a sliding type.[3,12] In the rheometer, a mechanical sensor (a strain gauge of a bending type) is perpendicularly connected to an aluminum rod supported horizontally by two thin and rigid plates of phosphor bronze. The rod is also connected to one of the parallel plates of glass (upper one). Another plate (bottom one) is mounted on a translation stage to allow the application of constant shear deformations by sliding to one direction driven by a motor. The copper electrodes are attached to the glass plates. The bottom plate is slid and the small displacement of the upper plate is detected by the sensor. The maximum shear rate is limited mainly by the rotational speed of the motor which drives the translational stage. The stress response was measured by the rheometer at a shear rate of 2.6 s$^{-1}$ and at room temperature. The solution sandwiched between the two parallel plates with a gap of 0.4 mm was deformed at the shear rate to be a steady flow. The sheared solution was stimulated by stepwise electric fields with strength up to 3.0 kV/mm. The stepwise electric fields were applied to the solution in the direction perpendicular to the parallel plates using a piezo-drive amplifier (MESS-TEK Co., M-2628) driven by a signal generator.

## RESULTS AND DISCUSSION

Figure 2 shows polarized optical micrographs of the PBLG solution in a quiescent state under no
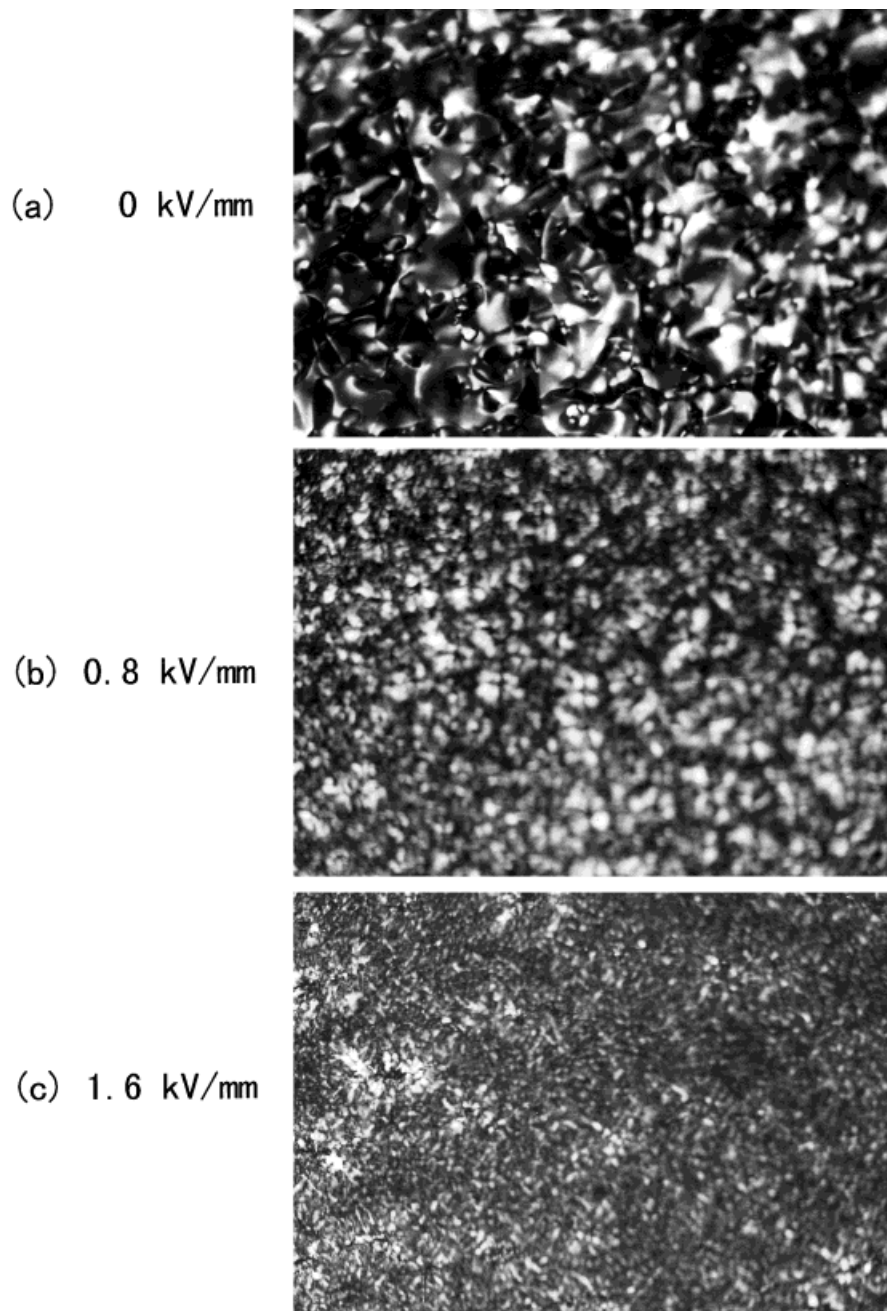
**Figure 2**  Polarized optical micrographs of a 15 wt % solution of PBLG in a quiescent state (a) under no electric field and under electric fields of (b) 0.8 kV/mm and (c) 1.6 kV/mm. The gap between electrodes was 25 $\mu$m.

electric field (a) and external electric fields (b, c). In Figure 2(a), a colorful polydomain texture of an anisotropic solution of the PBLG was clearly seen. Each domain in the polydomain texture becomes smaller and the texture becomes darker when the strength of the applied electric fields increases as shown in Figure 2(b,c). No electrohydrodynamic instability, which is accompanied by the secondary flow[4,5] such as macroscopic or local vortices and is caused by the electrical conduction of charge carriers from electrodes,[13] was observed when the strength of the external electric field increased to 1.6 kV/mm. PBLG molecules in a solvent show the $\alpha$-helix form with a permanent dipole moment along the helix axis per monomer unit.[14] Then, it is considered that each domain
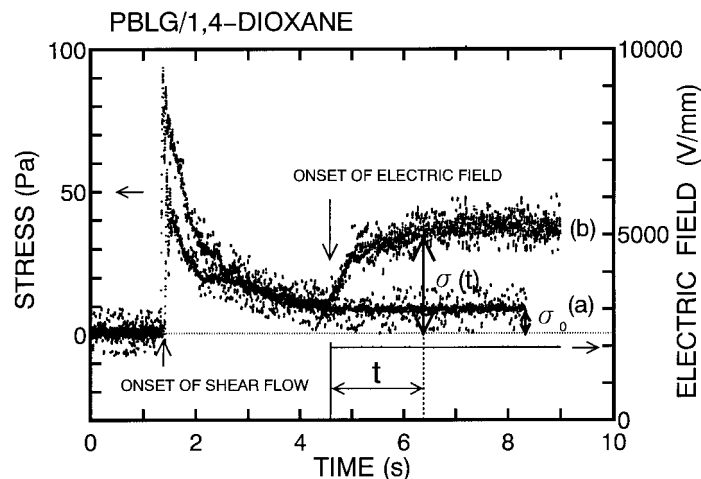
**Figure 3** Typical transient stress responses (a) under no electric field and (b) under an electric field of 2.0 kV/mm of a 15 wt % solution of PBLG plotted against time. The applied stepwise electric field is also plotted against time. The data of stress were smoothed by the simple moving average method among the nearest three data.

in our concentrated solution of PBLG with each permanent dipole moment tended to orient parallel to the external electric field. The homeotropic orientation of the PBLG molecules is expected to be obtained if an external electric field with sufficiently large strength is applied to the solution. When the external electric field of 1.6 kV/mm [as shown in Figure 2(c)] was removed, the polydomain texture such as the texture shown in Figure 2(a) was also seen in the optical microscopic observation.

Figure 3 shows transient stress responses of the PBLG solution plotted against time. In Figure 3, an applied stepwise electric field of 2.0 kV/mm is also plotted against time. The solution was suddenly sheared at a constant shear rate of 2.6 s$^{-1}$ (around the time of 1.5 s pointed by an arrow). The stepwise electric field was applied to the sheared solution (around the time of 4.5 s pointed by an arrow). In the present experiment, the solutions as sandwiched between the electrodes were used for the rheological measurements. Therefore, the orientation (or the size of anisotropic domains) of the PBLG molecules was not controlled in advance of the onset of the shear deformation. In Figure 3, the stresses at the onset of the shear flow are relatively large. However, the stresses gradually decrease to reach a steady stress $\sigma_0$ of 8.7 Pa, which was obtained under no electric field as shown in Figure 3(a). It is supposed that the anisotropic domains, with distributed orientation immediately after onset of the shear flow, were tilted toward a stable tilt angle or aligned parallel

to the electrode surfaces by the shear deformation under no electric field. The stepwise electric field was applied when the solution showed almost a steady stress. After application of the stepwise electric field, the stress increases from the steady stress of $\sigma_0$ in Figure 3(b). In the present article, the stress response to the stepwise electric fields is normalized by $\sigma_0$. The normalized ER response is defined here as $[\sigma(t) - \sigma_0]/\sigma_0$, where $\sigma(t)$ is the stress at the time after onset of the stepwise electric fields.
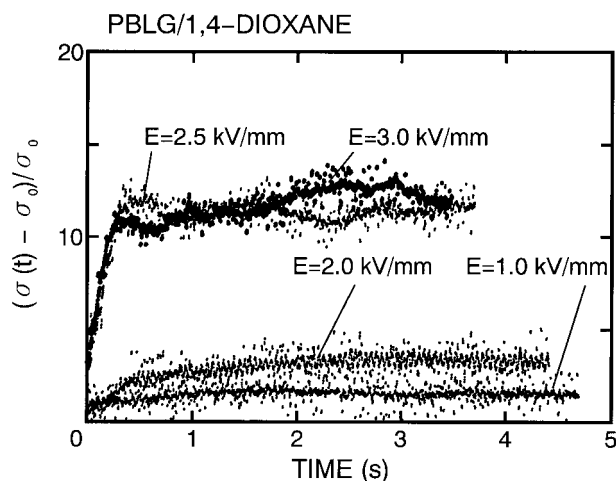


**Figure 4** Normalized ER responses of a 15 wt % solution of PBLG to stepwise electric fields after application of the electric fields. The data of the normalized ER responses were also smoothed by the same method as in Figure 3.

Figure 4 shows the normalized ER responses to stepwise electric fields. In Figure 4, remarkable changes in the beginning of the normalized ER response are seen according to the strength of the stepwise electric fields. The lower electric field caused the smaller increase in shear stress depending on the electric-field strength, while the larger electric fields above a critical strength tended to cause a larger increase in stress although the steady shear stress could not be necessarily measured by the sliding rheometer which limited the maximum shear strain. (In the present experiment, the rheological measurements were performed at a shear rate of 2.6 s$^{-1}$ but the shear rate can be changed up to about 5 s$^{-1}$ in the rheometer used.) The maximum shear stress enhanced by the electric fields in the present experiment was in excess of 10 times the steady shear stress under no electric field. (In addition, the ER response of the order of 10 times was measured by a rotational rheometer at a shear rate [the one at the edge of the parallel plates] of 2.6 s$^{-1}$ for the PBLG solution (prepared similarly to the present experiment) to a sinusoidal electric field with a sufficiently low frequency of 0.01 Hz and an amplitude of 2.5 kV/mm.)

The ER effect of liquid crystals composed of small and rodlike molecules is caused mainly by the electrohydrodynamic instability[4,5] and the changes in contribution of the Miesowicz viscosities induced by external electric fields. The shear stress enhancement of 10 or more times by the electric field as shown in Figure 4 is larger than that of several times in the typical ER response of liquid crystals of small molecules. It is also reported that the stress enhancement of an anisotropic solution of large and rodlike molecules of poly($n$-hexyl isocyanate) (PHIC) by an external electric field was in excess of 20 times the steady-shear stress under no electric field and that the anisotropic domains were relatively stable against the electrohydrodynamic instability.[11,12] Therefore, the larger enhancement of the PBLG solution than the enhancement of liquid crystals of small molecules is closely related to the larger aspect ratio of helical molecules of PBLG. On the other hand, it is well known that anisotropic solutions of large and rodlike molecules, especially for the case of concentrated solutions of PBLG, exhibit the polydomain texture composed of anisotropic domains during shear flow under no electric field.[15] Inoue and Maniwa[9,10] pointed out that the weakness of the ER effect for the liquid crystals of small molecules

can be caused by the weakness of the interaction among anisotropic domains when the domains themselves are aligned in an electric field, thus making the domains vulnerable to mutual movement under shear. (They introduced a flexible molecular chain which could effectively form a link between adjacent domains.[8,9]) The electrostatic interaction among the domains composed of large and helical molecules with a permanent dipole moment along the helix axis per monomer unit is much larger than that of small molecules, and the anisotropic domains of our PBLG would show much larger Miesowicz viscosity $\eta_c$, which can be proportional to the length of molecular axis. In an ideal case, the changes in the orientation of the rodlike molecules induced by an external electric field cause the changes in the Miesowicz viscosities from $\eta_a$ or $\eta_b$ to $\eta_c$ as shown in Figure 1. Therefore, the maximum ER response of the rodlike molecules is expected to be proportional to the aspect ratio of the molecules.

Further, remarkable changes in the beginning of the normalized ER response observed above a critical strength of the electric field as shown in Figure 4 would correspond to the critical changes in the orientation or the effect of inertia of the anisotropic domains of PBLG above the electric-field strength. From our preliminary results[16] of the ER response for the PBLG solution to sinusoidal electric fields with a frequency of 1 Hz and different amplitudes, the stress response at an amplitude of 1.0 kV/mm was much smaller than that of 2.5 kV/mm. The waveform of the stress was sinusoidal at 1.0 kV/mm and it was nonsinusoidal, containing higher-order harmonics at 2.5 kV/mm. We consider at the present stage that the PBLG molecules (domains) were fully rotated by the sinusoidal electric field at 2.5 kV/mm and that the full rotation of the PBLG molecules can be closely related to the effect of inertia which cannot be neglected for the ER response to the stepwise electric field as well. The electrohydrodynamic instability could also affect the critical changes in the ER response because the electric-field strength which gave the maximum ER response was larger than the maximum electric field strength in the optical observation as shown in Figure 2. If the secondary flow such as macroscopic or local vortices are induced by the electrohydrodynamic instability, rodlike molecules of PBLG can 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.

Inoue and Maniwa[10] also reported that the enhancement of the complex dynamic viscosity $\eta^*$ of a 25 wt % solution of PBLG in 1,4-dioxane at a frequency of an oscillating strain of 5 Hz, which corresponds to a lower shear rate, was 10 times as large by the application of an electric field of 2.0 kV/mm, while the enhancement of the steady shear stress at sufficiently higher shear rates was several times as large, at best, by the electric field. The electrostatic interaction among the anisotropic domains of PBLG is not thought to be strong enough under the higher shear flow so that the alignment of the domains toward the external electric field could not be stable. For the enhancement of the interaction among the domains under high shear flow, it can be effective to introduce flexible molecular chains linking the anisotropic domains topologically.[10] However, the excessive enhancement of the interaction may cause excessive viscosity even under no electric field, and it may also cause no remarkable or faster changes in the orientation of the domains induced by the electric field. Therefore, the appropriate control of the interaction among the anisotropic domains is one of the most essential factors to design the ER fluids based on liquid crystalline polymers composed of rodlike molecules.

## CONCLUSIONS

The electrorheological (ER) effect induced by stepwise electric fields was reported for an anisotropic solution of poly($\gamma$-benzyl-L-glutamate) (PBLG) in 1,4-dioxane measured at a constant shear rate. Remarkable changes in the beginning of the transient ER response were observed according to the strength of the stepwise electric fields. The maximum shear stress enhanced by the electric fields in the present experiment was in excess of 10 times the steady shear stress under no electric field. The ER effect was discussed in terms of the orientation of the rodlike molecules of PBLG induced by the external electric fields, the interaction among anisotropic domains, as well as the electrohydrodynamic instability. It was pointed out that the appropriate control of the interaction among the anisotropic domains is one of the most essential factors to design the ER fluids based on liquid crystalline polymers composed of rodlike molecules.

## REFERENCES

1. W. M. Winslow, *J. Appl. Phys.,* **20,** 1137 (1949).
2. H. Block and J. P. Kelly, *J. Phys. D,* **21,** 1661 (1988), and references therein.
3. K. Tanaka, A. Sahashi, R. Akiyama, and K. Koyama, *Phys. Rev. E,* **52**(4), R3325 (1995).
4. T. Honda, T. Sasada, and K. Kurosawa, *Jpn. J. Appl. Phys.,* **17,** 1525 (1978).
5. T. Honda, K. Kurosawa, and T. Sasada, *Jpn. J. Appl. Phys.,* **18,** 1015 (1979).
6. M. Fukumasa, K. Yoshida, S. Ohkubo, and A. Yoshizawa, *Ferroelectrics,* **147,** 395 (1993).
7. K. Tanaka, A. Fujii, and K. Koyama, *Polym. J.,* **24,** 995 (1992).
8. A. Inoue and S. Maniwa, Eur. Pat. EP 478,034A (1992).
9. A. Inoue and S. Maniwa, *J. Appl. Polym. Sci.,* **55,** 113 (1995).
10. A. Inoue and S. Maniwa, *J. Appl. Polym. Sci.,* **59,** 797 (1996).
11. I.-K. Yang and A. D. Shine, *J. Rheol.,* **36,** 1079 (1992).
12. K. Tanaka, R. Akiyama, and K. Takada, *Polym. J.,* **28**(5), 419 (1996).
13. P. G. de Gennes and J. Prost, *The Physics of Liquid Crystals,* 2nd ed., Oxford University Press, New York, 1993, Chap. 5.
14. A. Wada, *J. Chem. Phys.,* **31,** 495 (1959).
15. R. G. Larson and D. W. Mead, *Liq. Cryst.,* **12**(5), 751 (1992).
16. A. Takahashi, K. Tanaka, A. Kubono, and R. Akiyama, *Rep. Prog. Polym. Phys. Jpn.,* **39,** 265 (1996).