Electrorheological Behavior of Two Thermotropic and Lyotropic Liquid Crystalline Polymers

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SYNOPSIS

A thermotropic liquid crystalline (LC) polymer, consisting of an LC silicone having benzoic acid phenylester LC groups as side chains of the siloxane polymer main chain diluted with dimethylsilicone, and a lyotropic LC polymer solution, consisting of poly(γ-benzyl-L-glutamate) in 1,4-dioxane, both showed a large electrorheological (ER) effect, i.e., an instantaneous increase in shear stress upon the application of an electric field. In the electric field, the thermotropic polymer exhibited Newtonian-like flow and a dynamic viscoelasticity similar to that of low molecular weight liquid crystals, while the lyotropic polymer solution exhibited elastic flow and a dynamic viscoelasticity similar to that of particle-dispersion ER fluids. These differences in ER behavior suggest large differences in their ER mechanisms, with that of the thermotropic polymer dominated by interaction between its LC domains and that of the lyotropic polymer solution by the orientation of the dipoles of its LC groups. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

Electrorheological (ER) fluids showing large increases in apparent viscosity immediately upon application of an electric field were first reported about half a century ago, as suspensions of water-bearing dielectric particles in a nonconductive liquid.[1] The practical utilization of such suspensions has nevertheless proved difficult, primarily because of the poor physical durability of their particles and an excessive temperature dependence related to the water contained in these particles. In recent years, ER fluids employing semiconductor or other anhydrous particles and modified conductor components have been developed to overcome these problems,[2,3] but they have all involved inherent problems in particle sedimentation, solidification, or particle abrasion.

Certain homogeneous fluids, which contain no suspended particles and therefore are inherently free from these problems, have also long been known to exhibit an ER effect, at least in the broad sense of the term. Small increases in viscosity on application

of an electric field were found to occur in glycerine and paraffin oil in the 1890's[4] and in several polar and nonpolar liquids in the 1930's,[5,6] but the increase was at most a doubling of the zero-field viscosity and was therefore too small for any practical application. In the 1970s, polar liquids and nonpolar liquids containing ionic compounds were also shown to exhibit such an ER effect,[7,8] but the viscosity in electric fields was again limited to two or at most three times the zero-field viscosity.

Liquid crystalline (LC) materials represent a third class of substances which may be expected to show some form of ER effect. Though they are homogeneous liquids, they generally exhibit anisotropy in many of their characteristics and an inherent tendency for instantaneous orientation of their molecular structures, or domains, even in weak electric fields. Since their development and widespread availability in the 1960s, however, various studies have shown that they characteristically exhibit only a small increase in viscosity on application of an electric field, again only about three times their zero-potential viscosity.[9-11]

Consideration of the physical structure of liquid crystals and the interactions of their LC domains led us to investigate two different means of increas-

Electric Field

Low molecular weight   Liquid crystalline
liquid crystal   polymer

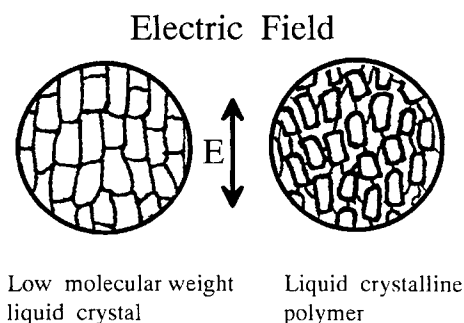**Figure 1** Presumed orientation of conventional liquid crystals and LC polymers under applied electric field.

Figure 2 Viscous anisotropy of liquid crystal.

ing the viscosity change in such materials in an applied electric field.

Our first approach involved a physical reinforcement of the electrical interaction between adjacent LC domains. We attributed the weakness of the ER effect in LC materials to the weakness of this interaction, even when the domains themselves are aligned in an electric field, thus making the domains vulnerable to mutual movement under shear. This led us to consider the introduction of a flexible molecular chain, which could effectively form a link between adjacent domains, in the belief that the natural extension and tautening of such chains when the domains were aligned by an electric field would create a resistance to mutual slippage between the domains and thus increase the viscosity of the fluid, as shown schematically in Figure 1. We investigated this possibility by using a thermotropic LC polymer consisting of many mesogenic groups attached to a flexible main chain and found large ER effects in thermotropic LC polysiloxanes (silicones) having either side-chain or main-chain mesogenic groups.[12-14]

The second approach involved a search for liquid crystals exhibiting high viscous anisotropy. LC molecules, or "domains," are generally rod-shaped. When these molecules are oriented, the LC material exhibits viscous anisotropy, which is generally referred to as Miesowicz's viscous anisotropy[15] ($\eta_a > \eta_b$ > η_c as shown schematically in Fig. 2). The viscous anisotropy may be expected to increase with increasing aspect ratio, i.e., the ratio of the LC molecule's length to its diameter. The aspect ratio in LC materials is generally 10 or less, but a few lyotropic LC polymers have far higher aspect ratios. We therefore investigated this type of polymer for evidence of large viscosity changes upon alignment of the LC molecules by an application of an electric field and found that solutions of poly (γ-benzoyl-L-
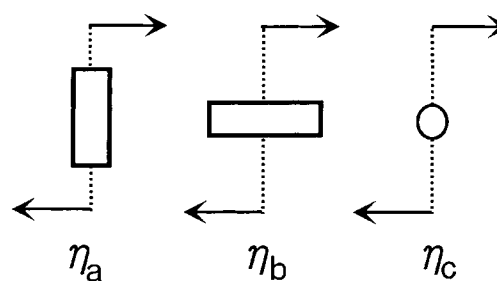
glutamate) (PBLG) in dioxane and dichloroethane did, in fact, exhibit such an ER effect.[16] Similar results have also been reported for a solution of poly(hexyl isocyanate) in xylene.[17]

Here, we investigate and compare the ER behavior of these two types of LC polymers, with a thermotropic polymer consisting of main chains bearing mesogenic groups and a lyotropic polymer consisting of high-aspect-ratio molecular chains.

EXPERIMENTAL

Test Samples

Side-chain LC Silicone (SLCS)

SLCS was synthesized by hydrosilylation of allyl-bearing benzoic acid cyanophenylester LC groups by polysiloxane having Si—H groups at 60°C in tetrahydrofuran with a platinum chloride catalyst as described previously.[12] Its structure, as determined by IR and NMR analyses, is shown in Figure 3. All SLCS test samples, which exhibited isotropic phase transition at 55°C under a polarizing microscopy, were in diluted form, containing 50 parts by weight of dimethylsilicone (DMS 20 cst), because of the high viscosity of the undiluted form (about 450 poise at 50°C).
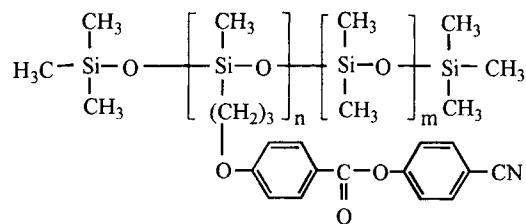
Randam co-polymer   m=17, n=13

Figure 3 Polymeric structure of side-chain liquid crystal silicone (SLCS).
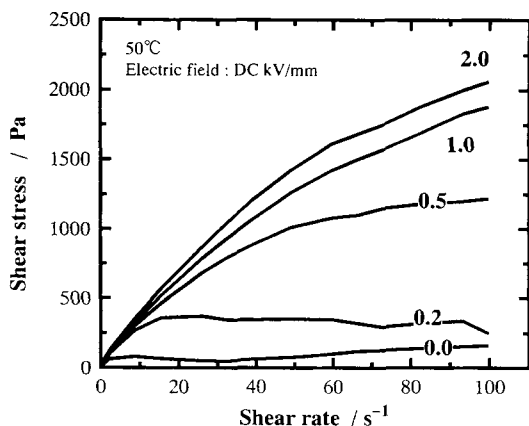
Figure 4   Shear stress of SLCS vs. shear rate, at 50°C under various electric field strengths.

Poly(γ-benzoyl-L-glutamate) Solution (PBLG)

A solution of 25 wt % PBLG (M_w, approximately 180,000; Polyscience Co.) in 1,4-dioxane, showing a cholesteric LC phase at room temperature, was prepared and used as the PBLG test sample.

Low Molecular Weight LC Compound

The low molecular weight LC compound E-7 (BHD Co.), containing the cyanophenyl group as its mesogenic group and like SLCS having a large positive dielectric anisotropy, was used as a sample for comparison.

Hydrous Particle Dispersion

Also, for comparison, a hydrous silica particle dispersion was prepared by adding 30 wt % of silica particles (Mizusawa K. K.; AMT 300, approximately 3 μm diameter, 8 wt % water content) to DMS (20 cst).

Measurements

Shear stress and dynamic viscoelasticity were measured with a parallel-plate rheometer (Model MR300, Rheology Co.) modified to permit the application of dc and ac (50 Hz) electric fields by a voltage generator (Model PT-3503, Toa Denpa Co.) at a constant (200 s^{-1}) or increasing ($0–200 \text{ s}^{-1}$) shear rate and having an electrode gap between the upper and lower plates of 0.5 mm. Measurements were made at 25°C for PBLG, E-7, and the particle dispersion, but at 50°C for SCLS because of its high viscosity at lower temperatures.

RESULTS AND DISCUSSION

Shear Rate Characteristics

The relations between shear stress and shear rate for SLCS and for PBLG as measured under electric fields of 0.0–2.0 DC kV/mm is shown in Figures 4 and 5, respectively.

With SLCS, as shown in Figure 4, the shear stress increased approximately in proportion to the increase in shear rate throughout the region of low shear rates (up to about 15 s^{-1}), and the slope of the curve gradually decreased thereafter with increasing shear rate up to an apparent saturation point. The saturation point, in terms of both shear rate and shear stress, increased with increasing electric field strength. Throughout the region of low shear rates, the slope of the curve was nearly the same for all applied electric field strengths. Successive increments in the applied electric field strength resulted in progressively smaller increases in shear stress, and increases beyond electric fields of 1.0 DC kV/mm or more resulted in little or no further increase in the shear stress.

These tendencies were all similar to those found with E-7, the low molecular weight LC compound containing no silicone chain, though the shear stress with SLCS was far larger than that with E-7 in all cases.

With PBLG, as shown in Figure 5, the shear stress exhibited saturation in the region of relatively low shear rates (less than 10 s^{-1}), and the slope of the shear stress/shear rate curve in that region was far higher than with SLCS. PBLG also exhibited large increases in shear stress with increasing electric field strengths above 1 kV/mm, a characteristic similar to that of particle-dispersion systems. With
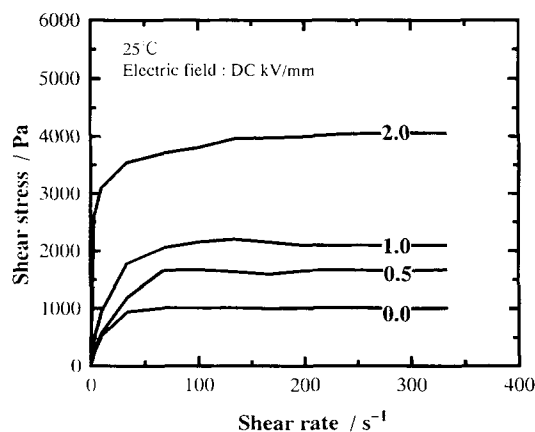

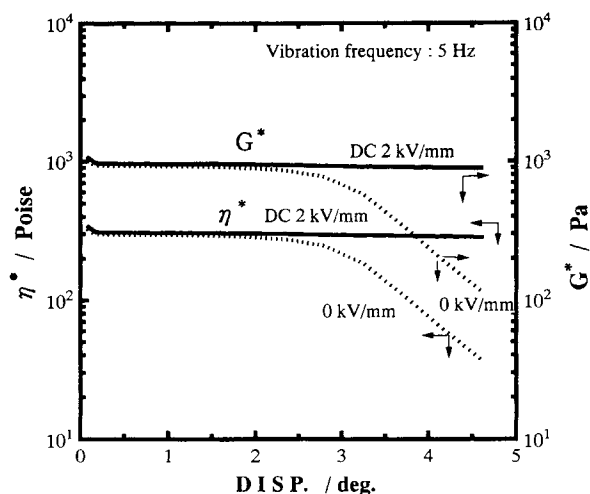**Figure 5**   Shear stress of PBLG vs. shear rate, at 25°C under various electric field strengths.

Figure 6 Strain dependence of complex dynamic modulus G^* and viscosity η^* of SLCS; 0.0 and 2.0 dc kV/mm electric fields, 5 Hz vibration frequency, 50°C.

both SLCS and PBLG, the shear rate characteristics in ac fields were essentially the same as those described above for dc fields.

Viscoelasticity

The dynamic viscoelasticities of SLCS and PBLG in the deforming dispersion mode, with 5 Hz vibration, are shown in Figures 6 and 7, respectively. With SLCS, both the complex viscosity (η^*) and the complex modulus (G^*) were nearly constant (about 2×10^2 poise and 1×10^3 Pa, respectively) throughout the measured displacement range under the applied electric field of 2.0 kV/mm. In the absence of the electric field, both remained at the same level as observed in its presence under displacements of up to about 2°, but then decreased rapidly with further increases in the displacement to 4° or more.

Under the same conditions (except for the temperature of 30°C rather than 50°C), as shown in Figure 8, the low molecular weight LC compound E-7 also exhibited a nearly constant complex viscosity and complex modulus (about 1.7×10^0 and 3.1×10^1, respectively) in the electric field throughout all the displacements tested except for a small increase at very small displacements (up to about 0.3°). With no electric field, it exhibited a rapid decline in both values (to about 1.1×10^0 and 0.2 $\times 10^{-1}$, respectively) at displacements of up to about 0.4° and little or no further change with further increases in the displacement. The underlying tendencies were thus similar to those of SLCS, except that in the electric field E-7 exhibited slight increases in complex viscosity and complex modulus
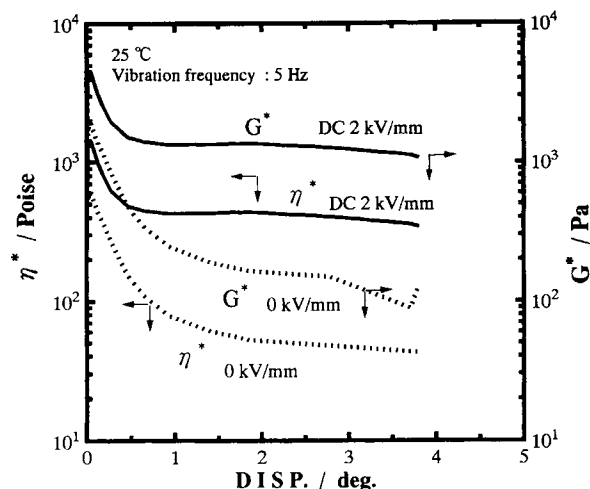
at very low displacements, and with no electric field, the displacements at which both parameters began to decrease rapidly were far smaller than those with SLCS. These results suggest that the flexible silicone chains which link adjacent LC domains in the SLCS fluid extend or tauten when the LC domains are aligned by an electric field and create a resistance to mutual slippage between the domains even under large applied displacements and thus support the putative mechanism illustrated in Figure 1.

With PBLG, on the other hand, both the complex viscosity and the complex modulus were increased by a factor of 10 by application of the electric field, but they decreased rapidly at first and slowly later
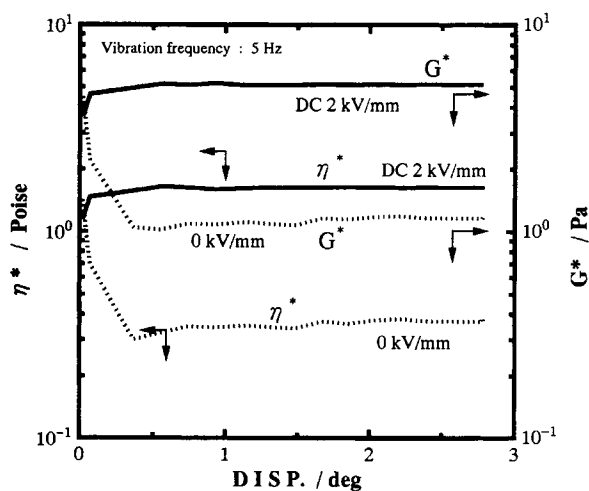

Figure 7 Strain dependence of G^* and η^* of PBLG; 0.0 and 2.0 dc kV/mm electric fields, 5 Hz vibration frequency, 25°C.

Figure 8 Strain dependence of G^* and η^* of low molecular weight liquid crystal (E-7); 0.0 and 2.0 dc kV/mm electric fields, 5 Hz vibration frequency, 30°C.
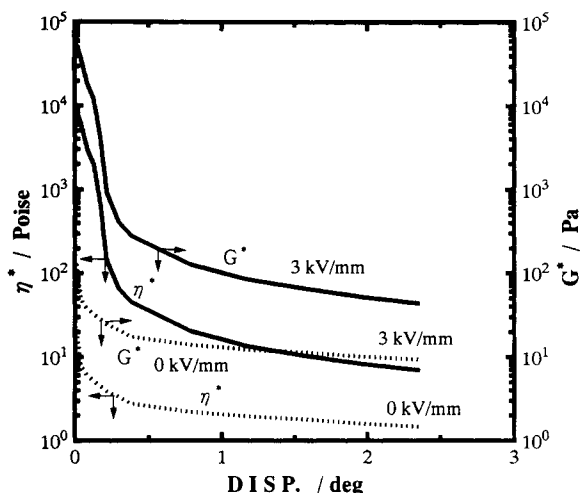
Figure 9 Strain dependence of G^* and η^* of hydrous silica dispersion (hydrous silica particles/DMS = 3.7 by wt); 0.0 and 3.0 dc kV/mm, 5 Hz vibration frequency, 20°C.

Figure 11 Strain dependence of tan δ of SLCS; 0.0 and 2.0 dc kV/mm, 5 Hz vibration frequency, 50°C.

with increasing displacement even under the electric field. The tendencies observed in PBLG were thus very similar to those of the hydrous silica dispersion shown in Figure 9 and quite different from those of SLCS, suggesting that the ER effects of PBLG and SLCS are the result of two quite different mechanisms.

The dynamic viscoelasticity of SLCS in the vibration dispersion mode, under 3° deformation vibration, is shown in Figure 10. As suggested by this figure, application of an electric field increased the complex viscosity and the complex modulus moderately at vibration frequencies of up to about 5 Hz (i.e., under low shear rates) with little dependence
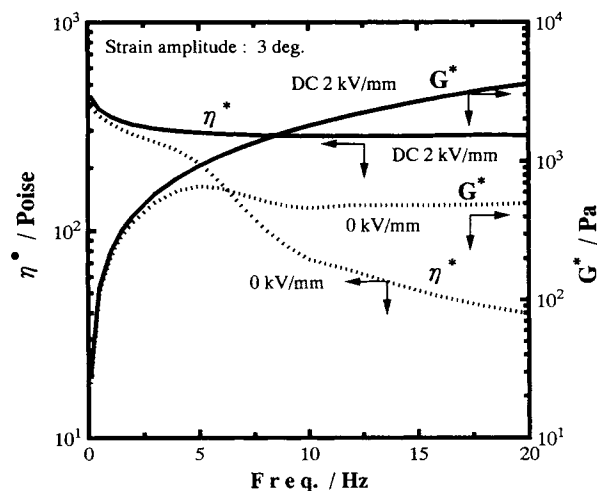
on the electric field strength and to a much greater degree and with a clear dependence on the field strength at higher vibration frequencies (i.e., under high shear rates), in agreement with the shear rate characteristics shown in Figure 5. Determination of the dynamic viscosity η' and the dynamic modulus G' showed results similar to those described above for η^* and G^*, respectively, in all cases.

Figures 11 and 12 show the dynamic loss (tan δ) of SLCS and PBLG, respectively, as measured in the deforming dispersion mode. The tan δ curves of SLCS with and without the applied electric field of 2.0 kV/mm both increased with increasing displacement, as shown in Figure 11, with the value of tan δ in the electric field only slightly lower than that without the electric field at all displacements throughout the test range of up to about 3.5°. This
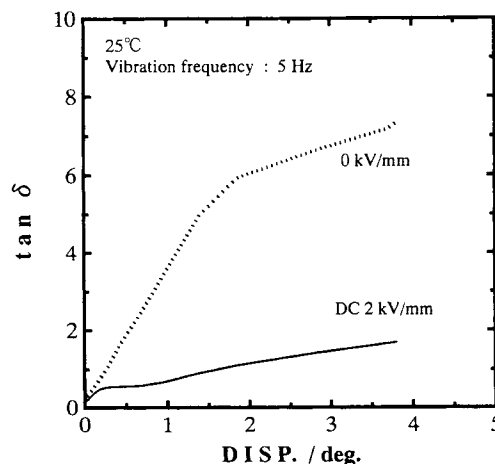

Figure 10 Vibration frequency dependence of G^* and η^* of SLCS; 0.0 and 2.0 dc kV/mm, 3° strain amplitude, 50°C.

Figure 12 Strain dependence of tan δ of PBLG; 0.0 and 2.0 dc kV/mm, 5 Hz vibration frequency, 25°C.

suggests that the size of its LC domains is changed only slightly by the application of an electric field and that the LC domains are not readily fractured by applied shear or vibration.

With PBLG, on the other hand, tan δ increased rapidly with increasing displacement in the absence of the 2 kV/mm electric field but only very moderately in its presence, as shown in Figure 12, indicating that the size of its LC domains or the strength of their orientation, or both, are changed substantially by the application of an electric field. The results the tan δ measurements, like those of the shear viscosity and the dynamic viscoelasticity measurements, thus indicate that different mechanisms are responsible for the ER effects of SLCS and those of PBLG.

CONCLUSION

This investigation of the ER effects of thermotropic LC polymers and lyotropic LC polymers, as represented by a side-chain LC silicone diluted with dimethyl silicone (SLCS) and a poly(benzyl-L-glutamate) solution (PBLG), respectively, showed the following:

- The dynamic viscoelasticities of SLCS and PBLG were quite different, with the former resembling that of low molecular weight LC compounds and the latter that of particle-dispersion systems.
- In the region of low shear rates, PBLG exhibited a much smaller rise in shear stress with increasing shear rate than did SLCS, under various electric fields. At higher electric field strengths (above 0.5 DC kV/mm), the shear rate increased substantially with further increases in the electric field strength for PBLG, but only slightly for SLCS.
- The results thus suggest that different mechanisms are involved in the ER effects of thermotropic LC polymers and lyotropic LC polymers.

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