

Electrorheological Effect of Liquid Crystalline Polymers

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SYNOPSIS

Large increases in shear stress upon application of a 2.0 kV/mm electric field were observed in homogeneous fluids composed of polysiloxane-based liquid crystalline polymers (LCPs) in dimethyl silicone at a shear rate of 200 s^{-1} . The increase was largest (about 3,000 Pa at 50°C) with LCP consisting of a polysiloxane bearing mesogenic groups as side chains. With LCP having the mesogenic groups within the main chain, the maximum increase was about 1,300 Pa at 90°C. It was about 400 Pa at 30°C with LCP having the mesogenic groups at both ends only (biterminal), and several Pa at 30°C with LCP having the mesogenic group at one end only (monoterminal). The increases were smaller with mesogenic groups of lower positive dielectric anisotropy in the side chain LCP. The side chain, biterminal, and monoterminal LCPs exhibited Newtonian flow in the electric field and shear stress yield at low shear rates in its absence. The complex dynamic modulus and viscosity of the side chain LCP in the electric field showed no dependence on strain at deformation displacements approaching 5°, but in its absence were generally strain-dependent, and suggest the strong electrorheological effect of these homogeneous LCP fluids is related to a flexible-chain linkage between their crystalline domains. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

Electrorheological (ER) fluids have long held promise for use in vibration control and torque transmission devices, based on the characteristic dependence of their viscosity on applied electric field strength. Since their initial discovery by Winslow many particle-dispersion ER fluids, consisting of dielectric particles dispersed in insulating oil, have been reported, but their practical utilization has been limited by their tendencies for particle sedimentation, aggregation, or solidification; particle or electrode abrasion; and poor durability or temperature dependence.

Polar liquids,¹ liquid crystals,²⁻⁵ ferroelectric polymer solutions,⁶ and other homogeneous ER fluids have been proposed as a means of avoiding these problems, but in all cases their ER effect has been found too weak for practical use.

We have been particularly interested in liquid crystals, because of their response to weak electric fields. On the assumption that the weakness of their ER effect was attributable to the weakness of interaction between the crystalline domains of fluids composed of low molecular weight liquid crystal molecules in an electric field, and that a stronger interaction could be obtained if the domains were linked by flexible molecular chains, (illustrated in Fig. 1), we prepared liquid crystalline polymers (LCPs) composed of a relatively flexible main chain and numerous mesogenic groups, and investigated their ER behavior.

As previously reported, we found that homogeneous systems containing LCPs composed of substituted benzoic acid phenylester LC groups bound to a silicone molecule chain exhibit ER effects superior to those of the conventional dispersed-particle ER fluids.^{7,8}

In the present study, we investigated the relationship between the molecular structure of these LC silicones and their ER effects, and the characteristics and mechanism of these effects.

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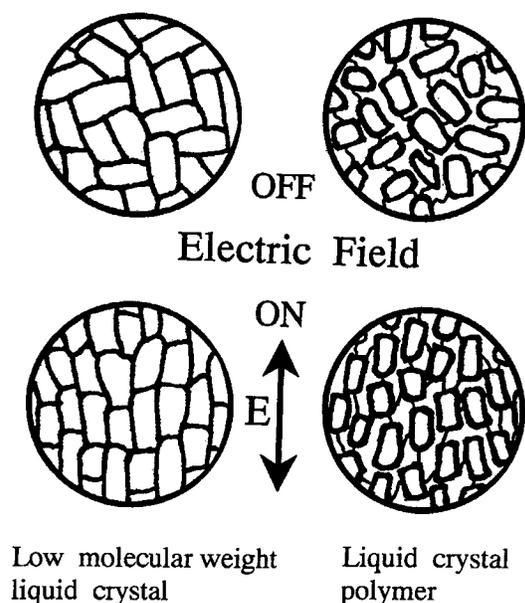


Figure 1 Presumed mechanism of ER effect.

EXPERIMENTAL

Mesomorphic Groups

Substituted benzoic acid phenylester LC groups bearing the allyl $\text{CH}_2=\text{CH}-\text{CH}_2-$ were prepared

in the manner previously described.⁷ The structures were as indicated in Figure 2 and, for the investigation related to mesogenic group dielectric anisotropy, as indicated in Figure 3.

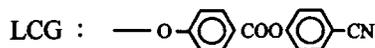
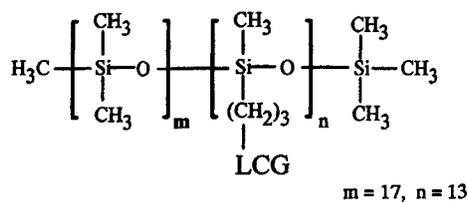
LC Silicones

LC silicones were prepared by hydrosilylation of the allyl-bearing substituted benzoic acid phenylester LC groups with silicone having Si—H groups, at 60°C in tetrahydrofuran with a platinum chloride catalyst as described previously.⁷ The resulting LC silicone structures were determined by IR and NMR spectral analysis to be of four types, as shown in Figure 2: (A) side chain, having mesogenic groups as pendants to the main chain; (B) main chain, having mesogenic groups within the main chain; (C) biterminal, having mesogenic groups only at the two ends of the main chain; and (D) monoterminal, having mesogenic groups only at one end of the main chain.

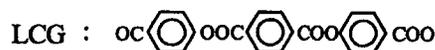
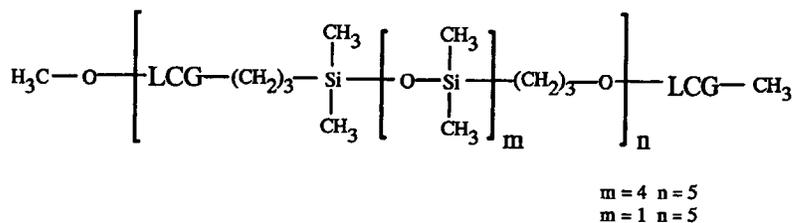
The isotropic transition temperature (measured by an optical polarization microscope) of each type was: (A) 55°C; (B) 140°C for both $m = 1$ and $m = 4$ forms; (C) 30°C; and (D) no observable isotropic transition temperature.

Because of their high inherent viscosity, types A, B, and C were each mixed with dimethylsilicone

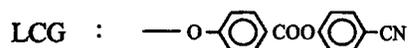
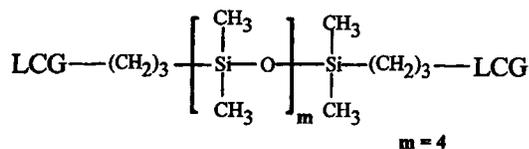
Side chain type LC silicone [A]



Main chain type LC silicone [B]



Biterminal LC silicone [C]



Monoterminal LC silicone [D]

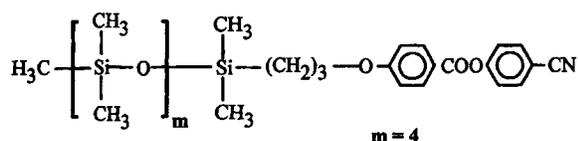


Figure 2 Structure of LC silicones.

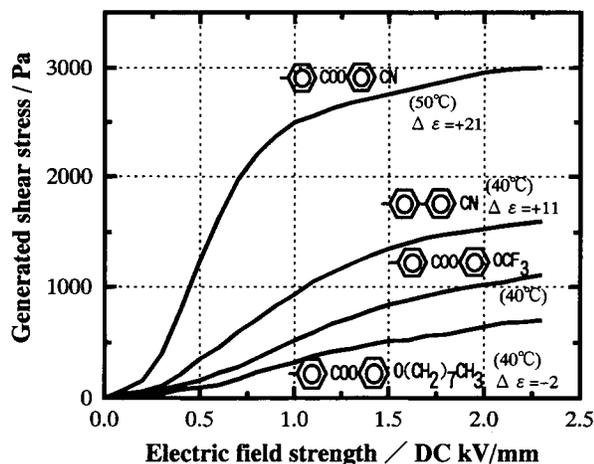


Figure 3 Influence of mesogenic group's dielectric anisotropy on generated shear stress of side chain LC silicones at various electric field strengths, at 200 s^{-1} .

(DMS; 20 cst) in a weight ratio of 100:50, prior to determination of their shear stress characteristics.

Also for comparison, a hydrous silica particle dispersion was prepared by adding 30 wt % of DMS to silica particles (Mizusawa K.K.; AMT 300, approx. $3 \mu\text{m}$ diameter, 8 wt % water content).

Measurements

Shear stress was measured with a parallel-plate rotating viscometer (Model MR300, Rheology Co., Ltd.) modified to permit the application of 0.0, 0.2,

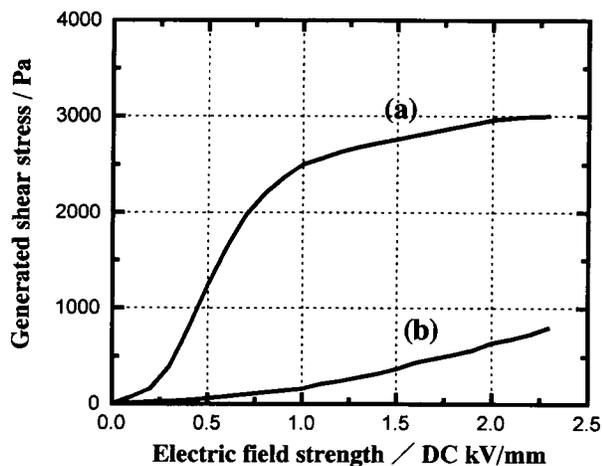


Figure 4 Generated shear stress of side chain LC silicone and hydrous silica dispersion, at 200 s^{-1} . (a) type A LCP/DMS = 2/1 by wt at 50°C ; (b) hydrous silica particles/DMS = 3/7 by wt at 25°C .

0.5, 1.0, 2.0, or 3.0 kV DC/mm across the 0.5 mm between its upper and lower plates by a voltage generator (Model PT-3503, Toa Denpa Co., Ltd.), at a constant (200 s^{-1}) or increasing ($0\text{--}100$ or $0\text{--}250 \text{ s}^{-1}$) shear rate. Generated shear stress was defined as the difference between the measured shear stress with and without application of the electric field. The measurement temperatures shown throughout this report were those resulting in the maximum generated shear stress for the described systems and conditions.

RESULTS AND DISCUSSION

Side Chain LC Silicones

Applied Voltage and Generated Shear Stress

The side chain LC silicone (type A, Figure 2) exhibited a generated shear stress of 3,000 Pa in an electric field of 2.0 kV/mm (200 s^{-1} shear rate, 50°C), as shown in Figure 4. Under similar conditions the generated shear stress of the substituted benzoic acid phenylester LC (low molecular weight) was 10 Pa (70°C). That of other low molecular weight LCS is reportedly at most about 20 Pa.⁹

The generated shear stress of the side chain LC silicone was also higher than that of the hydrous silica/DMS dispersion (3/7 by weight) at all electric field strengths. It increased rapidly, in nearly direct proportion to the field strength up to an apparent region of saturation above approximately 1 kV/mm, rather than with the square of the field strength as found in particle-dispersion systems.

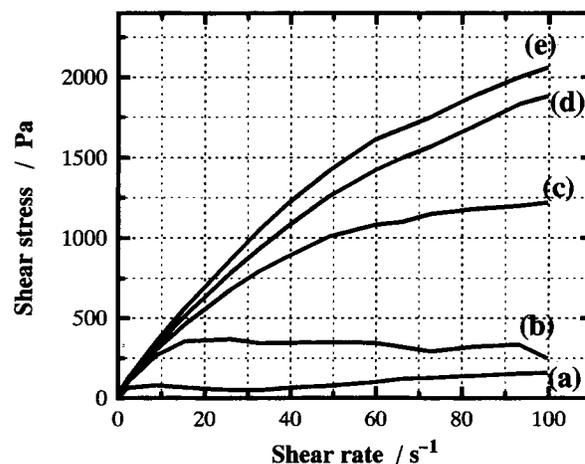


Figure 5 Shear stress of side chain LC silicone (type A) vs. shear rate, at 50°C in electric fields of (a) 0.0, (b) 0.2, (c) 0.5, (d) 1.0, and (e) 2.0 kV/mm.

The shear stress curves of the same side chain LC silicone at various electric field strengths are shown in Figure 5. In all cases, the increase in shear stress was approximately proportional to the increase in shear rate, up to an apparent saturation point that tended to increase with increasing field strength. At low shear rates (less than 10 s^{-1}), the shear stress varied in a nearly linear relation with the shear rate regardless of the strength of the electric field or its absence.

Influence of LC Group Structure

Side chain LCPs bearing different LC groups were prepared and the generated shear stress of each was measured, in essentially the same manner as described above. Figure 6 shows the results at the temperature of maximum ER effect for each of these LCPs. The LCPs having greater dielectric anisotropy¹⁰ tended to exhibit larger ER effects, presumably because of a stronger orientation of the LC domains formed by them upon application of an electric field.

Main Chain LC Silicones

The generated shear stress of the LCPs having the substituted benzoic acid phenylester LC groups located within the main chain, at an electric field of 2.0 kV/mm and a shear rate of 200 s^{-1} , was about $1,100 \text{ Pa}$ at 100°C with one siloxane per monomeric unit ($m = 1$, Fig. 2) and about 500 Pa at 90°C with four siloxanes per monomeric unit ($m = 4$, Fig. 2). The higher generated shear stress of the former may

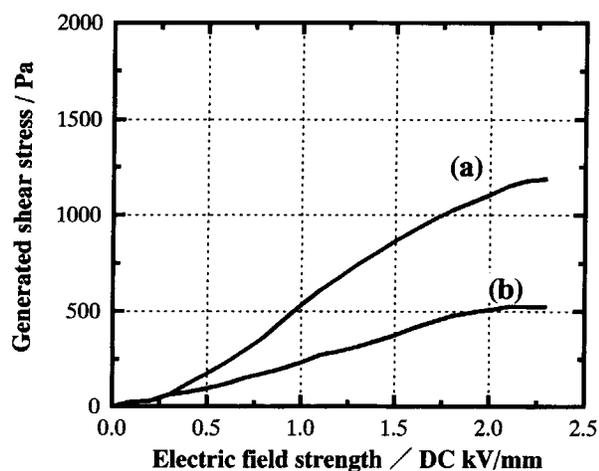


Figure 6 Generated shear stress of two main chain LC silicones (type B, LCP/DMS = 2/1 by wt) at 200 s^{-1} ; (a) $m = 1$ at 100°C , (b) $m = 4$ at 90°C .

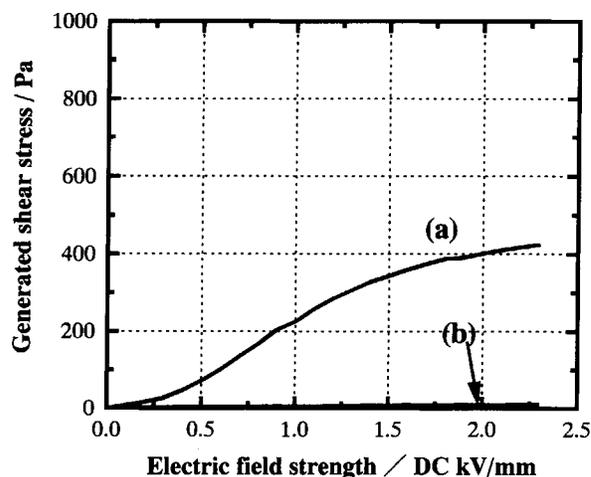


Figure 7 Generated shear stress of (a) biterminal and (b) monoterminal LC silicones; type C (LC silicone/DMS = 2/1 by wt) and type B; at 200 s^{-1} and 30°C .

be attributable to its better compatibility with the DMS used as diluent. Although both values are lower than that obtained with the side chain LCP (type A), they are nevertheless much higher than those generally obtained with nonpolymeric LCs.

Biterminal and Monoterminal LC Silicones

As shown in Figure 7, the generated shear stress of the biterminal LC silicone (type C in Fig. 2) was

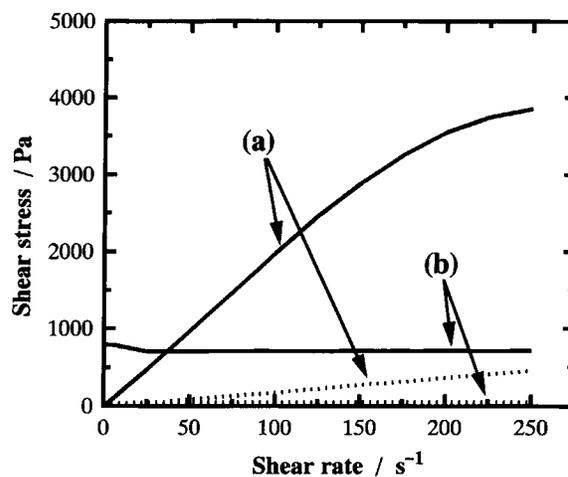


Figure 8 Generated shear stress of side chain LC silicone and hydrous silica dispersion, in 2 kV/mm electric field: (a) type A LCP/DMS = 2/1 by wt at 50°C ; (b) hydrous silica particles/DMS = 3/7 by wt at 25°C . Solid curves represent the results under the electric field. Dotted curves represent the results under no electric field.

about 400 Pa at a shear rate of 200 s^{-1} and temperature of 30°C ; that of the monoterminal LC silicone (type D in Fig. 2) was only a few pascals under the same conditions.

These results suggest that the high generated shear stress of LC silicones is an effect of a linkage between the LC domains of the ER fluid, consisting of a flexible polysiloxane chain spanning neighboring domains and anchored in each by one or more of its LC groups, and a related suppression of domain disorientation in the presence of an electric field. With the side chain and main chain LC silicones, several of their LC groups may be anchored in or otherwise interact with each domain. With the biterminal LC silicone, the anchor can form only at each end of the flexible chain. With the monoterminal LC silicone, the flexible chain can be anchored in only one domain, and no linkage between domains is therefore possible.

Shear Rate Characteristics

Figure 8 shows the shear rate characteristics of the side chain LC silicone (type A in Fig. 2), in comparison with those of a conventional particle-dispersion ER fluid consisting of hydrous silica particles suspended in a silicone oil. The particle-dispersion system shows Newtonian flow in the absence of an electric field, and Bingham flow in an applied electric field. The LC silicone shows Newtonian flow in both cases. Although not shown here, the main chain and the biterminal LC silicones also exhibited Newtonian

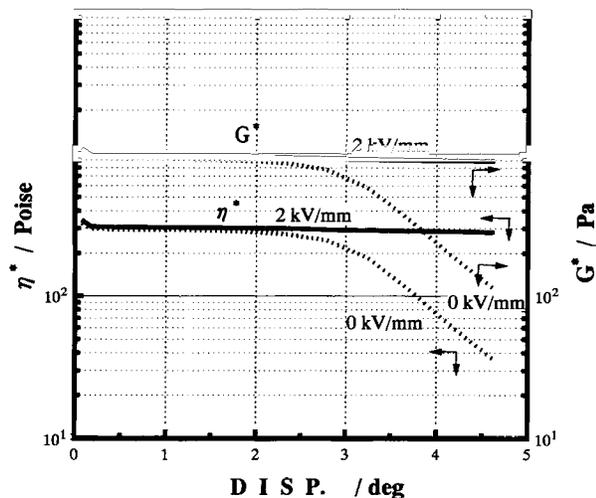


Figure 9 Strain dependence of G^* and η^* of side chain LC polymer (type A); 0.0 and 2.0 kV/mm electric fields, 5 Hz vibration frequency, 50°C .

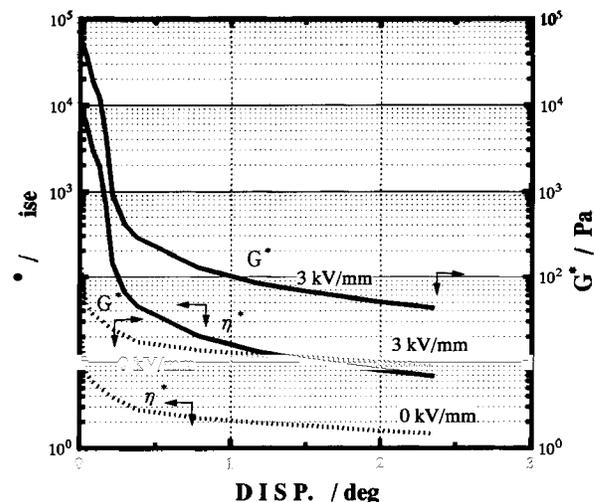


Figure 10 Strain dependence of G^* and η^* of hydrous silica dispersion (hydrous silica particles/DMS = 3/7 by wt); 0.0 and 3.0 kV/mm electric fields, 5 Hz vibration frequency, 20°C .

ian flow both with and without the applied electric field.

The dynamic viscoelastic (deforming dispersion) characteristics of the side chain LC silicone (type A) and the hydrous silica particle-dispersion system are shown in Figure 9 and 10, respectively. In the particle-dispersion system, with 5 Hz vibration at 20°C , both the complex viscosity (η^*) and the complex modulus (G^*) were increased by a factor of $10^{1\sim 3}$ by application of an electric field (3.0 kV/mm) in the measured displacement range. In the LC silicone system, at the same vibration frequency and a temperature of 50°C , the complex viscosity and the complex modulus did not undergo a rapid decrease in the absence of an electric field until the displacement was increased to about 1.5° or more. And in the presence of the 2.0 kV/mm electric field showed no decrease throughout the measured displacement range.

In short, the side chain LC silicone exhibited no increase in viscosity or modulus under small displacements even in the absence of an electric field, and the effect of the electric field on these characteristics was exhibited only under relatively large displacement. This is also in accord with the relation shown in Figure 5 between shear stress and shear rate for the same LC silicone in the region of low shear rates, in which all of the curves are of nearly

the same slope regardless of the strength of the applied electric field.

CONCLUSIONS

Both side chain and main chain LC silicones were found to exhibit Newtonian flow under applied electric fields, and ER effects much stronger than those of the conventional particle-dispersion ER fluids even under applied electric fields of low strength. The difference between the moderate ER effect of the biterminal LC silicone and the comparatively weak ER effect of the monoterminal LC silicone suggests that the existence of flexible molecular chains between crystalline domains in the LC silicone fluids is related to their strong ER effect. The dynamic viscoelasticity characteristics of the LC silicones also suggest that their ER effect is caused by a suppression of domain disorientation in the presence of an electric field.

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