# Influence of Dilution by Polydimethylsiloxane on Electrorheological Effect of Side-Chain Liquid Crystalline Polysiloxane

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ABSTRACT: A liquid crystalline polysiloxane (LCP), having an ether bond in the spacer between its siloxane main chain and its mesogenic-group side chains, exhibited a very small electrorheological (ER) effect or increase in shear stress upon application of an electric field, but mixtures of the LCP and polydimethylsiloxane (PDMS) exhibited a sharply increasing ER effect with increasing PDMS content throughout the tested range of up to 0.5 of PDMS weight fraction. When phenyl-substituted PDMS (Ph-PDMS) at a weight fraction of 0.3 was used instead of PDMS, however, the ER effect decreased with increasing phenyl content and became nearly undetectable with Ph-PDMS having a phenyl content (ratio of substituted phenyl groups to initial methyl groups) of approximately 15%. DSC analyses showed that the ER effect of the LCP/ PDMS mixtures occurred undiminished throughout a temperature range in which LCP itself is an isotropic liquid in the absence of an applied electric field and suggested that the LC structure of the LCP was maintained even when it was diluted with PDMS in weight fractions of 0.5 or higher, but disrupted when diluted by a 0.3 weight fraction of Ph-PDMS having a 15% phenyl content. Optical microscopic observation of the mixtures of the LCP with a 0.3 weight fraction of PDMS or Ph-PDMS (15% phenyl content) showed that both consisted of uniformly dispersed micron-sized droplets which became elongated in the direction of the applied electric field when it was applied alone but became smaller when both the electric field and shear were applied. These results suggest that the phase separation between the LCP and the dilution oil, as well as the existence and orientation of LC domains, is essential for the generation of a large ER effect. © 1997 John Wiley & Sons, Inc. J Appl Polym Sci 64: 1319-1328, 1997

**Key words:** liquid crystal; electrorheology; polysiloxane; dilution; morphology

# **INTRODUCTION**

Electrorheological (ER) fluids that respond to an applied electric field with an instantaneous increase in apparent viscosity have been widely investigated since Winslow reported his first observation of ER effects with respect to suspensions of water-containing particles in insulating oils about a half-century ago.<sup>1</sup> Efforts have been made to develop practical utilizations of such suspensions in active control devices such as dampers, shock absorbers, clutches, and brakes, but have remained unsuccessful due to such problems as particle sedimentation, aggregation, or solidification, particle or electrode abrasion, and poor durability or temperature dependence.<sup>2–7</sup>

The ER effect of homogeneous fluids<sup>8,9</sup> which contain no dispersed particles has also been long investigated; early observations of such an effect were already reported for glycerin and paraffin

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oil in the 1890s<sup>10</sup> and for polar liquids and nonpolar liquids in the 1930s.<sup>11,12</sup> Furthermore, investigations were again carried out for the ER effect of polar liquids and nonpolar liquids containing ionic compounds in the late 1970s.<sup>13,14</sup> In all these cases, however, the increases in viscosity on application of an electric field were two or at most three times the original viscosity without an electric field and were too small for any practical application.

Liquid crystals are a unique class of materials in that they are composed of rod-shaped molecules and display self-organizing phases called mesophases. Although they are homogeneous liquids, they exhibit anisotropy in most of their physical properties, and as a result, they have an inherent tendency for instantaneous orientation of their molecular structures, or domains, even in weak electric fields.<sup>15</sup> Attempts have been made since the 1960s to obtain viscosity changes in low molar mass liquid crystalline (LC) materials by taking advantage of their ability to align in an electric field, but it has been found that their maximum viscosity change is only 50 Pa in shear stress at  $300 \text{ s}^{-1}$  of shear rate, or five times the zero-field viscosity, which is not sufficient for practical applications.<sup>16–20</sup> Recently, such liquid crystals have also been employed as the continuous phase in particle-dispersed ER fluids to improve their ER performance.<sup>21,22</sup>

Our own attempts to obtain a larger ER effect, defined as the increase in shear stress upon application of an electric field, in LC materials began with a consideration of the physical structure and, particularly, their low molecular weight and the conjecture that their small ER effect might be attributable to the weak interaction between their LC domains and consequent mutual movement of these domains under applied shear even when they were aligned in an electric field. For the purpose of reinforcing the domain interaction and preventing the mutual slippage between the domains, we considered the introduction of a flexible molecular chain into the LC molecules, thus forming a network structure through the linkage between adjacent domains. On this assumption, we prepared thermotropic LC polymers containing numerous mesogenic groups attached to a flexible main chain and found large ER effects in side chain and main chain LC polysiloxanes (LCPs).<sup>23-25</sup> Determination of the ER effect in these investigations was carried out for mixtures of the LCPs with a plain polydimethylsiloxane (PDMS) oil of 20 cSt viscosity. The dilution by PDMS was initially intended to compensate for the high intrinsic viscosity of the LCPs and thereby achieve the low zero-field viscosity which is suitable for practical applications of an ER fluid. During the course of the investigation, however, we found that PDMS appears to play some role in the generation of a large ER effect, in addition serving as a dilution medium. Here, we describe an investigation of this role, in terms of the influence of the structure of the dilution oil and the ratio of its mixture with the LCP.

# **EXPERIMENTAL**

#### Materials

The structure of the side-chain LCP used in this study is shown in Scheme 1, as **6**, together with the scheme of its synthesis. Poly(hydrogen-



**Scheme 1** Synthesis of LC polysiloxane (LCP).

methyl-co-dimethylsiloxane) 5 was purchased from Shin-Etsu Chemical. Polydimethylsiloxane (PDMS, viscosity 20 cSt) and phenyl-substituted PDMS (Ph-PDMS), used as dilution oils having the structures shown in Figure 1, were purchased from Toray Dow Corning Silicone and Petrarch Systems. The water content of both of these materials was less thann 30 ppm as determined by the Karl Fisher method. The structure and composition of the polysiloxanes synthesized from these materials were determined by <sup>1</sup>H- and <sup>29</sup>Si-NMR measurements. The synthesized polysiloxanes were used neat, unless otherwise noted. Mixtures of 6 with PDMS or Ph-PDMS were prepared by dissolving them in tetrahydrofuran (THF, water content 20 ppm max by specification) followed by complete evaporation of the solvent under vacuum at 60°C. The ratio between 6 and PDMS or Ph-PDMS was 2 : 1 by weight unless otherwise noted.

#### Measurements

<sup>1</sup>H-NMR (400 MHz) and <sup>29</sup>Si-NMR (79.4 MHz) spectra were recorded on a JEOL JNM-LA400 spectrometer and FTIR spectra were recorded on a Perkin-Elmer 1640 spectrometer. Shear stress was measured with a parallel-plate rotational viscometer (Model MR 300, Rheology Co.) modified to permit the application of an electric field over the range of 0.0–2.0 dc kV/mm by a high-voltage power supply (Model PT-3503, Toa Electronics Ltd.). The upper plate (32 mm diameter) was connected to the torque meter, and the lower plate (40 mm diameter), to the motor. The distance between electrodes was 0.5 mm throughout this study and measurements were performed at a constant (100 or 200 s<sup>-1</sup>) or stepwise increasing  $(0-200 \text{ s}^{-1})$  shear rate. Preliminary trials showed good correlation between the values obtained with this viscometer and those obtained with a standard cylindrical viscometer for silicone oil (100 poise) at shear rates of up to  $300 \text{ s}^{-1}$ . A Perkin-

PDMS 
$$CH_3 - Si - O - (Si - O)_{23} Si - CH_3$$
  
 $CH_3 - Si - O - (Si - O)_{23} Si - CH_3$   
 $CH_3 - CH_3 - CH_3$   
 $CH_3 - CH_3$   
Ph-PDMS  $- (Si - O)_p (Si - O)_q$   
Ph Content (%) =  $-\frac{p}{2(p+q)} \times 100$ 

Figure 1 Structures of PDMS and Ph-PDMS.

Elmer DSC-7 differential scanning calorimeter (DSC) equipped with an Intracooler II was used to determine the thermal transition temperature and enthalpy changes. Heating and cooling rates were 10°C/mm. An Olympus BH-2 optical microscope equipped with a Linkam TH600 hot stage and TH600RH control unit was used to observe morphological changes. An electric field was applied across the sample on the hot stage using a Matsusada Precision Devices HEK-10P-AK high-voltage power supply. Details of the sample preparation and microscopic observation are given in the Discussion section.

# **Synthetic Procedures**

# 2-(Allyloxy)ethyl Tosylate (2)

A solution of p-toluenesulfonyl chloride (93.3 g, 0.489 mol) in CH<sub>3</sub>CN (400 mL) was added dropwise to a stirred, cooled  $(0^{\circ}C)$  mixture of ethylene glycol monoallyl ether 1 (60.0 g, 0.587 mol), triethylamine (69.3 g, 0.685 mol), and CH<sub>3</sub>CN (300 mL) over 1 h. The mixture was allowed to warm to room temperature and stirred overnight. CH<sub>3</sub>CN was evaporated off, and the residual mixture was diluted with ethyl acetate and washed with water twice. The aqueous layer was extracted with ethyl acetate, and the combined organic layers were dried over anhydrous  $MgSO_4$ . The solvent was evaporated off, and the remaining crude product was purified by column chromatography (silica gel;  $CH_2Cl_2$ ) to give a colorless liquid (123.1 g, 98.2%). <sup>1</sup>H-NMR (CDCl<sub>3</sub>, TMS):  $\delta$  7.80 (d, J = 8.4 Hz, 2ArH, ortho to  $-SO_2$ -), 7.34 (d, J = 8.4 Hz, 2ArH, ortho to  $-CH_3$ ), 5.82 (m, 1H,  $CH_2 = CH - 0$ , 5.22 (*m*, 1H,  $CH_2 = CH - trans$ ), 5.16 (m, 1H,  $CH_2 = CH - cis$ ), 4.17 (m, 2H,  $-CH_2OSO_2-$ ), 3.94 (*m*, 2H, CH<sub>2</sub>=CHCH<sub>2</sub>O-), 3.63 (m, 2H,  $-OCH_2CH_2OSO_2-$ ), 2.45 (s, 3H,  $-PhCH_3$ ).

#### 4-[2-(Allyloxy)ethoxy]benzoic Acid (3)

A solution of KOH (84.2 g, 1.50 mol) in water (100 mL) was added to a mixture of *p*-hydroxybenzoic acid (82.9 g, 0.600 mol), ethanol (400 mL), and water (100 mL). Then, a solution of **2** (146.5 g, 0.571 mol) in ethanol (50 mL) was added dropwise to the stirred, heated (80°C) mixture over 30 min, and stirring was continued at 80°C for 2.5 h. The mixture was cooled to room temperature, diluted with water (800 mL), and acidified with 36% HCl (ca. 75 mL). The resulting white precipi-

tate was filtered, washed with water, and dried. The crude product was recrystallized from ethanol to give colorless crystals (68.5 g, 53.9%). <sup>1</sup>H-NMR (DMSO-d<sub>6</sub>, TMS):  $\delta$  12.61 (bs, 1H, -COOH), 7.90 (d, J = 8.4 Hz, 2ArH, ortho to -COOH), 7.03 (d, J = 8.4 Hz, 2ArH, ortho to -OCH<sub>2</sub> CH<sub>2</sub>O-), 5.91 (m, 1H, CH<sub>2</sub>=CH-), 5.28 (m, 1H, CH<sub>2</sub>=CH- trans), 5.16 (m, 1H, CH<sub>2</sub>=CH- cis), 4.19 (m, 2H, -CH<sub>2</sub>OPh-), 4.03 (m, 2H, CH<sub>2</sub>=CHCH<sub>2</sub>O-), 3.74 (m, 2H, -OCH<sub>2</sub>CH<sub>2</sub>OPh-).

#### 4-Cyanophenyl 4-[2-(Allyloxy)ethoxy]benzoate (4)

A mixture of 3 (68.3 g, 0.307 mol), thionyl chloride (109.9 g. 0.924 mol), and five drops of N,Ndimethylformamide was stirred at 40°C for 2.5 h. Excessive thionyl chloride was removed under a vacuum. The remaining crude acid chloride was diluted with dry THF (100 mL) and was added dropwise to a stirred, cooled  $(0^{\circ}C)$  mixture of phydroxybenzonitrile (36.6 g, 0.307 mol), triethylamine (40.5 g, 0.400 mol), and dry THF (300 mL)under a nitrogen atmosphere. The mixture was allowed to warm to room temperature and stirred overnight. THF was evaporated off, and the residual mixture was diluted with CH<sub>2</sub>Cl<sub>2</sub> and washed with water twice. The aqueous layer was extracted with  $CH_2Cl_2$ , and the combined organic layers were dried over anhydrous MgSO<sub>4</sub>. The solvent was evaporated off, and the remaining crude product was recrystallized from ethanol to give colorless crystals (93.0 g, 93.7%). <sup>1</sup>H-NMR  $(CDCl_3, TMS): \delta 8.13 (d, J = 8.5 Hz, 2ArH, meta$ to  $-OCH_2CH_2O-$ , 7.72 (*d*, J = 8.3 Hz, 2ArH, ortho to -CN), 7.35 (d, J = 8.3 Hz, 2ArH, meta to -CN), 7.02 (*d*, J = 8.5 Hz, 2ArH, ortho to  $-OCH_2CH_2O-)$ , 5.95 (*m*, 1H, CH<sub>2</sub>=CH-), 5.33 (m, 1H, CH<sub>2</sub>=CH- trans), 5.23 (m, 1H,  $CH_2 = CH - cis)$ , 4.23 (*m*, 2H,  $-CH_2OPh - )$ , 4.11 (*m*, 2H,  $CH_2 = CHCH_2O = (m, 2H, 2H)$  $-OCH_2CH_2OPh-).$ 

# Synthesis of Side-chain LC Polysiloxane (LCP) (6)

In a typical experiment, a solution of H<sub>2</sub>PtCl<sub>6</sub>· 6H<sub>2</sub>O in dry THF (7.1 × 10<sup>-3</sup> mmol) was added to a stirred, heated (40°C) mixture of **4** (8.0 g, 24.8 mmol), poly(hydrogenmethyl-*co*-dimethylsiloxane) **5** ( $M_w$  approximately 2400, m + n = 30~ 50,  $n/(m + n) = 0.2 \sim 0.4$  as shown in Scheme 1, 3.0 g, 17.7 mmol SiH) and dry THF (45 mL) under a nitrogen atmosphere. Then, the mixture was heated to 60°C, and stirring was continued for 6 h. The reaction was followed by monitoring the decrease of the SiH band at 2155 cm<sup>-1</sup> using FTIR. The reaction mixture was added to methanol (500 mL), and the recovered polymer was isolated by centrifugation and dried at 60°C under a vacuum. The <sup>1</sup>H-NMR spectrum of the polymer (LCP **6**,  $M_w$  approximately 5200) is shown in Figure 2.

# **RESULTS AND DISCUSSION**

#### Effect of the Dilution by PDMS

The relation between shear stress and shear rate for LCP 6 and for the mixture LCP/PDMS (2:1 by weight) measured under electric fields of 0.0 and 2.0 dc kV/mm at 60°C is shown in Figure 3. With LCP alone, the increase in shear stress on the application of the electric field was very small. As described previously,<sup>23-25</sup> we originally conjectured that this small increase in shear stress in LCPs might be attributable to a tendency for their high inherent viscosity to restrict the motion of the side-chain mesogenic groups and thereby impede their orientation under the electric field. When LCP was diluted with PDMS, a large increase in shear stress was observed along with a decrease in the zero-field shear stress, as shown for the mixture LCP/PDMS in Figure 3. In Figure 4, the shear stresses under the electric fields of 0.0 and 2.0 dc kV/mm and the shear rate of 200  $s^{-1}$  are plotted as a function of temperature for LCP and for the mixture LCP/PDMS. It is obvious



Figure 2 <sup>1</sup>H-NMR spectrum of LCP 6.



**Figure 3** ER effect of LCP **6** and LCP **6**/PDMS mixture (2 : 1 by weight) measured at 60°C.

from the figure that dilution with PDMS results in large shear stress changes over a wide temperature range (50°C to over 150°C) and that the dilution makes the shear stress of LCP less dependent on the temperature.

# Effect of the Concentration of PDMS in the Mixture LCP/PDMS

Figure 5 shows the shear stress of the LCP/PDMS mixture measured under 0.0 and 2.0 dc kV/mm at 60°C, 100 s<sup>-1</sup>, as a function of the weight frac-



**Figure 4** Temperature dependence of the ER effect of LCP **6** and LCP **6**/PDMS mixture (2:1 by weight) measured at 200 s<sup>-1</sup>.



Figure 5 Dependence of shear stress on the composition of LCP 6/PDMS mixture measured at  $60^{\circ}$ C,  $100 \text{ s}^{-1}$ .

tion of PDMS in the mixture. There was only a slight difference between the two shear stresses in the presence and in the absence of an electric field when the weight fraction of PDMS was less than 0.1, but with higher weight fractions, the shear stress without an electric field falls rapidly with increasing weight fraction due to the dilution effect, while the shear stress under an electric field remains almost unchanged or decreases more gradually. Consequently, the changes in shear stress are increased from twice the zerofield shear stress at the weight fraction of 0.17 to as much as 17 times that at the weight fraction of 0.5. This clearly shows that high dilution is preferable to obtain large shear stress changes on application of an electric field. However, the phase separation of PDMS from the mixture becomes evident in the region where the PDMS weight fraction is over 0.5.

# DSC Analyses of LCP and LCP/PDMS

When PDMS was added to LCP at more than 50 wt %, the mixture took the appearance of a cloudy fluid even above the isotropization temperature of LCP, suggesting insolubility of the LCP in PDMS. To investigate their miscibility, DSC analysis was performed for LCP and its mixture with PDMS in various ratios. Figure 6(a) shows the DSC thermogram of LCP taken during the first cooling scan. When the isotropic liquid was cooled down, it formed a smectic A phase followed by an unidentified higher-order smectic phase. The transition temperatures and enthalpy changes as-



Figure 6 (a) DSC thermogram  $(10^{\circ}C/min, cooling)$  of LCP 6 and (b) dependence of the transition temperatures and associated enthalpy changes of peaks 1 and 2 on the composition of LCP 6/PDMS mixture.

sociated with the two transitions, i.e., peaks 1 and 2 in Figure 6(a), were measured for the mixtures with various PDMS weight fractions and were plotted in Figure 6(b). As can be seen from this figure, the two transition temperatures remain constant over the full composition range, and both enthalpy changes show linear dependence on the weight fraction of PDMS. This clearly demonstrates that PDMS, when mixed with LCP, does not disturb the formation of the LC structure (the domains) of LCP, but rather forms a phase-separated structure with LCP. Another important message drawn from this figure is that the temperature range over which the mixture exhibits the ER effect (see Fig. 4) corresponds to the isotropic phase of LCP; LCP displays smectic phases below 15.8°C, whereas the mixture LCP/PDMS exhibits the ER effect over the range from 50 to 150°C. On this basis, it would be difficult to explain the mechanism of the ER effect for this system only in relation to the existence of LC domains. It must be noted, however, that the DSC measurements were made without the applied electric field and shear and that the phase transitions would occur at higher temperatures in its presence.

#### Effect of Dilution by Ph-PDMS

Consideration of the results shown in Figure 6 led to the question of whether or not the phase separation of PDMS from LCP is necessary for the generation of a large ER effect. To clarify the role of PDMS, phenyl-substituted polydimethylsiloxane (Ph-PDMS) with various phenyl group



Figure 7 DSC thermograms (10°C/min, cooling) of LCP 6, LCP 6/PDMS mixture, and LCP 6/Ph-PDMS mixtures with various Ph contents (2 : 1 by weight).

contents was therefore used instead of PDMS. Figure 7 summarizes the normalized DSC thermograms of the base LCP and those of the mixtures between LCP and PDMS or Ph-PDMS with different phenyl contents, measured during the first cooling scans. The ratio of LCP to PDMS or Ph-PDMS was 2 : 1 by weight in all cases. The ER effects of these mixtures were also measured at 60°C and their generated shear stress, the difference between the shear stress under 0.0 and 2.0 dc kV/mm, was plotted as a function of shear rate in Figure 8. Figures 7 and 8 indicate that if the dilution oil is partially soluble in LCP the ER effect of the mixture is markedly decreased. The mixture of LCP with Ph-PDMS (Ph = 4.1%) showed a DSC trace identical to that of the base LCP except that the two enthalpy changes are lower. This DSC behavior is the same as that observed for PDMS (Ph = 0%), and as may therefore be expected, the two mixtures obtained from PDMS and Ph-PDMS (Ph = 4.1%) exhibit the same level of ER effect, as shown in Figure 8.

For the mixtures of LCP and Ph-PDMS with 15 and 32% phenyl contents, on the other hand, the two transition peaks were shifted to a lower temperature and the associated enthalpy changes were reduced, indicating that the liquid crystallinity of LCP was disrupted because Ph-PDMS was partially soluble in this base polymer. It may also be noted that the mixtures of either of these Ph-PDMSs with LCP were noticeably more transparent in appearance than was the mixture of PDMS and LCP. Both the mixtures with Ph-



**Figure 8** Influence of the Ph content of Ph-PDMS on the generated shear stress of LCP **6**/Ph-PDMS mixture (2 : 1 by weight) measured at 60°C, 2.0 dc kV/mm.

PDMS (Ph = 15 and 32%) exhibited very little generated shear stress, as shown in Figure 8.

#### **Morphological Observations**

The changes in the morphology of several of the mixtures were observed by an optical microscope with the shear and/or electrical field applied by two different procedures. In the first procedure, the observations were made after subjecting the mixture to shear only or to both shear and the electric field. The results for the mixture LCP/ PDMS (2:1 by weight) are shown in Figure 9. The mixture was first subjected to  $334 \text{ s}^{-1}$  shear for 3 min at 60°C by parallel plates of the rotational viscometer, and a sample was then immediately placed between microscope glass slides, with a sample thickness of approximately 10  $\mu$ m, and placed on the microscope stage and observed at room temperature (ca. 25°C), resulting in the observation of the uniformly dispersed droplet structure shown in Figure 9(a). The same procedure was repeated for the mixture immediately after it had been subjected to simultaneous shear (334  $s^{-1}$ ) and the electric field (2.0 dc kV/mm) (3 min, 60°C) in the rotational viscometer, with the resulting sample structure shown in Figure 9(b). As had been expected from the DSC studies, PDMS is not soluble in LCP and the mixture following subjection to shear alone showed a structure composed of uniformly dispersed, micronsized droplets [Fig. 9(a)]. The size of the droplets was reduced by the simultaneous subjection to shear and the electric field [Fig. 9(b)]. When the mixture which had been subjected to both shear and the electric field [represented by Fig. 9(b)] was next subjected once more to shear alone and a sample was observed, its structure was again the same as that shown in Figure 9(a). Identical results were obtained in 10 further repetitions of the complete cycle of shear alone and simultaneous shear and the electric field.

The second procedure was designed to permit microscopic observation while the mixture was in the electric field. When the mixture of LCP with PDMS (2:1 by weight) was placed between ITO-coated electrically conducting glass slides and observed along the direction of the electric field, no appreciable changes in morphology were detected upon its application. To permit the observation of morphological changes perpendicular to the electric field, the mixture was placed between two aluminum strip electrodes (thick-



**Figure 9** Optical micrograph of (a) LCP **6**/PDMS mixture (2 : 1 by weight,  $60^{\circ}$ C) and (b) its morphological change under the influence of shear (334 s<sup>-1</sup>) and electric field (2.0 dc kV/mm).

ness 15  $\mu$ m) formed on a glass slide with a gap of 1 mm and was spread uniformly to a thickness of 15  $\mu$ m with a spatula tip. The glass slide was then fixed in the hot stage which was maintained at 60°C with the electrodes connected to a highvoltage power supply. No glass cover was used. Representative optical micrographs taken in the absence and in the presence of the electric field (1.0 dc kV/mm) are shown in Figure 10(a) and (b), respectively. Figure 10(a) shows uniformly dispersed, micron-sized droplets which upon application of the electric field were deformed along the direction of the electric field so as to exhibit the elongated, columnlike structure shown in Figure 10(b). The same result was already observed in a mixture of an LCS (having no ether bond in the spacer) with PDMS.<sup>26</sup>

Figure 11 shows representative optical micrographs of the mixture of LCP and Ph-PDMS with 32% phenyl content (2 : 1 by weight) obtained under the same conditions as in Figure 10. The droplet structures are not so clearly seen as in Figure 10 and apparently larger than in Figure 10, most probably because Ph-PDMS is partially soluble in LCP, but the applied electric field nevertheless clearly causes an elongation of the droplets again, as shown in Figure 11(b).

Since shear is generally applied to the fluid in the direction perpendicular to the applied electric field, it may be surmised that an elongated, columnlike structure formed in response to an electric field may, upon subjection to the shear, be broken into droplets of reduced sizes as seen in Figure 9(b). It should be noted, however, that the morphological changes shown in Figures 10 and 11 cannot be directly related to the ER effect, because the mixture of LCP and Ph-PDMS with the 32% of phenyl content shows the elongation of the droplets under the applied electric field, and yet it exhibits only a very small ER effect (Fig. 8).

As microscopic observations such as these are essentially observations of light transmitted through the sample cell, the complex texture of the observed image is actually a superimposition



Figure 10 Optical micrograph of (a) LCP 6/PDMS mixture  $(2:1 \text{ by weight, } 60^{\circ}\text{C})$  and (b) its morphological change under the influence of electric field (1.0 dc kV/mm).



**Figure 11** Optical micrograph of (a) LCP **6**/Ph-PDMS (Ph = 32%) mixture (2 : 1 by weight,  $60^{\circ}$ C) and (b) its morphological change under the influence of electric field (1.0 dc kV/mm).

of phase-separated structures on the order of microns. Consequently, it has yet to be confirmed which of LCP, (Ph-)PDMS, or the mixture of LCP and (Ph-)PDMS can be assigned to the droplets observed in Figures 10 and 11. If it is assumed that LCP which has a higher dielectric constant than that of (Ph-)PDMS forms droplets in the mixture, the applied electric field causes dielectric polarization inside the droplets, with their surface-induced positive and negative charges attracted toward electrodes, resulting in the elongation of the droplets in the direction of the electric field.

# **CONCLUSIONS**

The results of the investigation may be summarized as follows:

1. LC polysiloxane (LCP) of the structure used in this study alone exhibits only a

very small ER effect, but mixtures of the LCP with polydimethylsiloxane (PDMS) exhibit a far larger ER effect.

- 2. The change in shear stress by the application of an electric field increases with increasing PDMS content in the mixture. This is apparently a direct result of the very gradual decrease in shear stress under an applied electric field, but a sharp decrease with no electric field, that occurs with increasing weight fractions of PDMS.
- 3. The ER effect of the mixture of the LCP and pheny-substituted PDMS (Ph-PDMS) decreases with increasing phenyl content in the Ph-PDMS and becomes nearly undetectable when the phenyl content is 15% or higher.
- 4. DSC analysis showed that the ER effect of the mixture LCP/PDMS occurred throughout a broad temperature range in which the LCP is an isotropic liquid. Further study is necessary, however, to determine the effect of applied shear and electric field on the phase-transition temperatures.
- 5. DSC analysis also suggested that the LC structure of the LCP was maintained even when it was diluted with PDMS in weight fractions of 0.5 or higher. On the other hand, in the mixture of the LCP and Ph-PDMS having a 15% phenyl content, which exhibited no substantial ER effect, the original liquid crystalline structure of the LCP was apparently disrupted.
- 6. When the mixtures of the LCP with a 0.3 weight fraction of PDMS or Ph-PDMS are observed with an optical microscope, they display a structure composed of uniformly dispersed, micron-sized droplets which undergo elongation in the direction of the applied electric field and which are reduced in size by the simultaneous application of shear and electric field.

These observations suggest that the existence of LC domains and their orientation<sup>23,24</sup> or the network formation of mesogenic groups<sup>27,28</sup> under an electric field are not sufficient for generation of the ER effect in the LCP. Phase separation of the dilution oil from the LCP is apparently also necessary for the generation of a large ER effect, and the increase in shear stress in the electric field is thus apparently controlled in large part by the morphological changes of the mixture. Further investigation of the phase changes, the influence of the electric field on the phase transition temperatures, and relation between the ER effect and the elongation of the droplets under an applied electric field will be necessary for a more definitive elucidation of the mechanism of the ER effect.

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