Relation Between Molecular Structure and Electrorheological Effects in Liquid Crystalline Polymers

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ABSTRACT: The influence of the molecular structure of homogeneous fluids comprised of liquid crystalline polysiloxanes (LCSs) diluted in polydimethylsiloxane (DMS), on the increase in their viscosity upon application of an electric field (electrorheological effect, or the ER effect) was investigated, particularly in relation to the degree of polysiloxane polymerization, the composition of their mesogenic side chains, and the composition of alkyl spacers inserted between these two components. A large ER effect was observed in LCSs having spacer length of 3 carbons (C3) and diluted with DMS, even though little such effect was observed with no DMS dilution. The ER effect generally increased with increasing DMS dilution and with increasing mesogenic group content, main chain length, and spacer length. At the same time, however, the miscibility of the DMS solvent with the LC polymer decreased, resulting in instability and difficulty in measuring the shear stress at temperatures up to 40°C or higher. When spacers containing an ether bond were employed, on the other hand, little or no polymer-solvent phase separation occurred, and the ER effect was strong and stable down to temperatures of 30°C or lower. With all of the LCSs, the ER effect was observed at temperatures above their isotropic phase transition temperature as measured by DSC. © 1997 John Wiley & Sons, Inc. J Appl Polym Sci **64:** 303–310, 1997

Key words: liquid crystal; electrorheology; polysiloxane; polydimethylsiloxane; mesogenic group

INTRODUCTION

The electrorheological (ER) effect is generally characterized as a large, immediate increase in the viscosity of a fluid when it is place in an electric field. Since the 1940s, it has most commonly been observed and studied in suspensions of water-bearing dielectric particles in a nonconductive liquid.[1]

Liquid crystalline (LC) materials may also be expected to exhibit an ER effect. They have been widely known since the 1960s for the anisotropy of their viscosity, magnetic properties, index of refraction, and other characteristics when their molecular domains are oriented under the influence of an electric field.[2–4] In recent years, the possibility of finding and adopting LCs with an ER effect sufficiently large for use as actuators in mechanical–electrical ("mechatronic") devices has become a subject of particular interest.[5–7] These efforts were generally frustrated, however, because their viscosity increase upon application of the electric field was at most about 50 Pa (under shear stress of 200 s^{-1}), or five times their zero-potential viscosity, and, thus far, smaller than the increase observed with dielectric particle dispersions.[9–11]

The rise in LC viscosity, though small, was found to be extremely rapid and to be induced by electric fields of comparatively low strength. Both of these characteristics are desirable for practical utilization of the ER effect, and we therefore

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$$CH_2 = CH(CH_2)_{S-2}\ Br$$

1) $HO-\langle\bigcirc\rangle-\overset{O}{\underset{\|}{C}}-OH$, KOH

2) H^+

$$CH_2 = CH(CH_2)_{S-2} - O-\langle\bigcirc\rangle-\overset{O}{\underset{\|}{C}}-OH$$

1) $SOCl_2$

2) $HO-\langle\bigcirc\rangle-CN$, $(CH_3CH_2)_3N$

$$CH_2 = CH(CH_2)_{S-2} - O-\langle\bigcirc\rangle-\overset{O}{\underset{\|}{C}}-O-\langle\bigcirc\rangle-CN$$
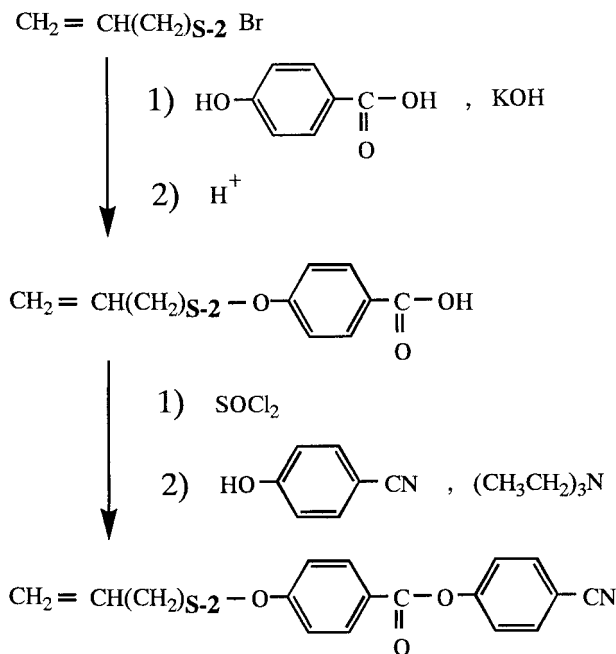
Figure 1 Synthesis of allyl-bearing mesogenic groups.

searched for new ways to increase its size. On the assumption that the ER effect in LCs was limited by the weakness of interaction between their molecular domains even when aligned under an electric field, thus permitting adjacent domains to slide past each other much like bricks laid without mortar, we attempted to reduce this tendency by attaching flexible side chains bearing mesogenic groups to the main polymer chains to obtain thermotropic LC polymers in which the side chains might, in the analogy with bricklaying, act as a "mortar" between adjacent domains. These investigations led to the discovery of a series of thermotropic LC polysiloxanes (LCSs) bearing such side chains, which exhibit an ER effect even larger than that of dielectric particle dispersions.[8–10]

Here, we describe several variations of the LCS molecular structure, involving the length of the main chain, the number of mesogenic groups in the side chains, and the number and composition of spacer groups between the two, and their influence on the ER effect of the LCS.

EXPERIMENTAL

Test Samples

LC Polysiloxane

LC polysiloxane (LCS) was synthesized as shown in Figures 1 and 2. Benzoic acid cyanophenylester

LC groups bearing allyl groups (length $S = 3$, 5, or 11 carbons) were hydrosilated by polysiloxane having Si–H groups at 60°C in tetrahydrofuran with a platinum chloride catalyst, as described previously.[8] The resulting LCS structure, as determined by infrared (IR) and nuclear magnetic resonance (NMR) analyses, is shown in Figure 2. Figure 3 shows the IR spectrum of one of these LCSs, referred to as LCS(C_3) based on the number of carbons in its spacer, having a main chain length of 30 silicons (Si = 30), a mesogenic group ratio (number of mesogenic groups per silicon) of $n/Si = 0.3$, and a spacer length of $S = 3$ (thus, $-CH_2CH_2CH_2-$).

Dilution

Commercially available polydimethylsilicone (DMS; 20 cst) was added in the prescribed quantities to LCS and dissolved uniformly by the addition of tetrahydrofuran (THF; approximately 3 times the LCS volume), and the THF was then removed completely by vacuum drying at 60°C. The quantity of DMS added is expressed throughout this paper as parts DMS per 100 parts LCS (phr; per hundred resin) by weight.

Measurements

ER Effect

Shear stress was measured with a parallel-plate rheometer (Model MR300, Rheology Co., Ltd.) modified to permit the application of a direct current (DC) electric field of 0.0 to 2.0 kV/mm across an electrode gap of 0.5 mm by a voltage generator (Model PT-3503, Toa Enpa Co., Ltd.) at shear rates of 0–300 s^{-1} and temperatures of 20 to 120°C. The ER effect was expressed as the generated shear stress, i.e., the difference between the measured shear stress prior to and following the application of the electric field.

LCS Phase Transition

The LCS phase transition was determined by measurement on a differential scanning calorimeter (DSC; Perkin-Elmer Model DSC7) with repeated cycles of heating at 10°C/s to 120°C and cooling to 20°C. All determinations were based on the values obtained during the heating phase of the second heating-cooling cycle.

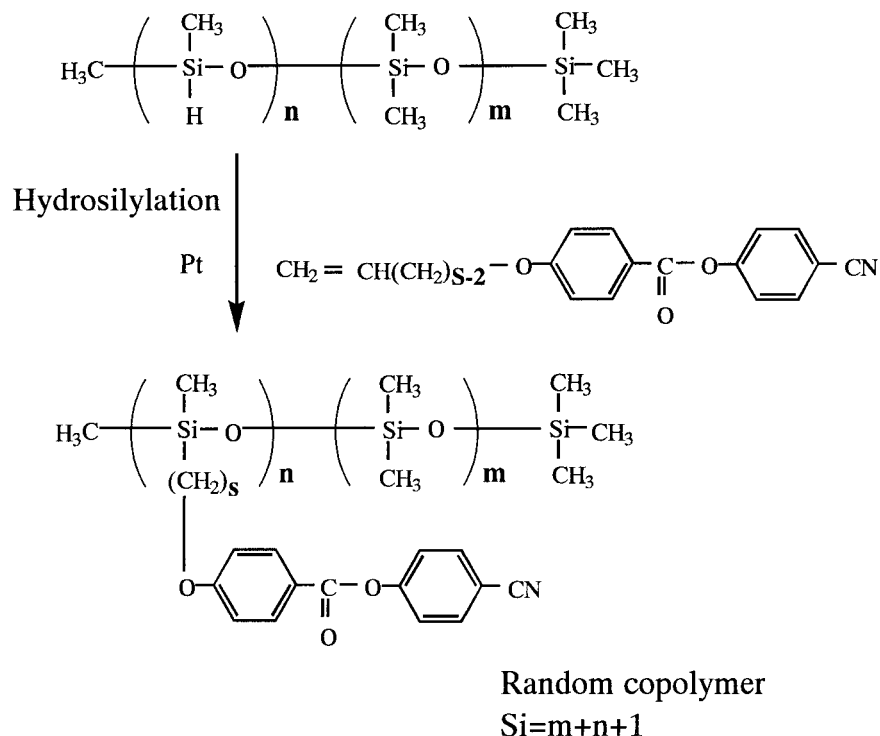**Figure 2**   Synthesis of liquid crystalline polysiloxane (LCS).

RESULTS AND DISCUSSION

Spacer length

Figure 4 shows the zero-field viscosities of three undiluted LCSs having the same main chain length (Si = 30) and mesogenic group ratio (n/Si = 0.3) but different spacer lengths (S = 3, 5, and 11; having 3, 5, and 11 carbons, respectively), as
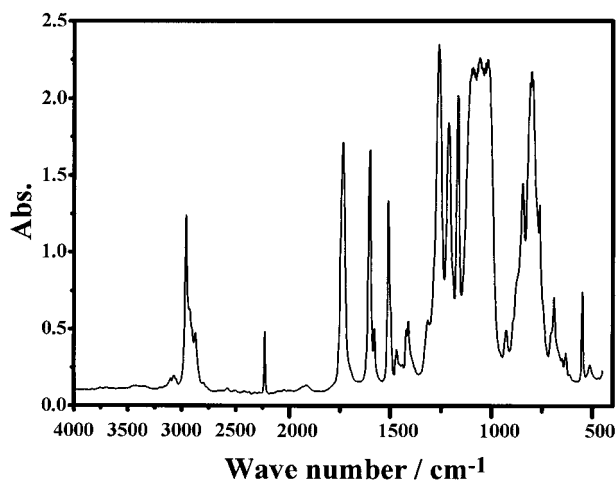

Figure 3   IR spectrum of LCS(C_3); Si = 30, n/Si = 0.3, spacer length S = 3; on Perkin-Elmer 1640.

measured in the temperature range of 40 to 120°C. The general tendency was for longer spacers to result in both higher zero-field viscosities and higher crystallization temperatures (minimum temperatures permitting viscosity measurement). At temperatures above 100°C, however, the LCS with spacers of length S = 11 [termed LCS(C_{11})] showed a lower viscosity than that with spacers of length S = 5 [LCS(C_5)], suggesting that the longest spacer tends to result in a greatly increased side-chain flexibility at high temperatures.

The shear stress of the three LCSs with and without the electric field of 2.0 kV/mm is shown in Figure 5. The generated shear stress, defined as the difference between the shear stress with and without the electric field, was largest in LCS(C_{11}) and appeared to become smaller with decreasing spacer length.

DMS Content

The high zero-field viscosity and apparent absence of an ER effect in the undiluted LCS(C_3) may be related to the inflexibility of the side chain, with the short spacers restricting movement of the long mesogenic groups and, thus,
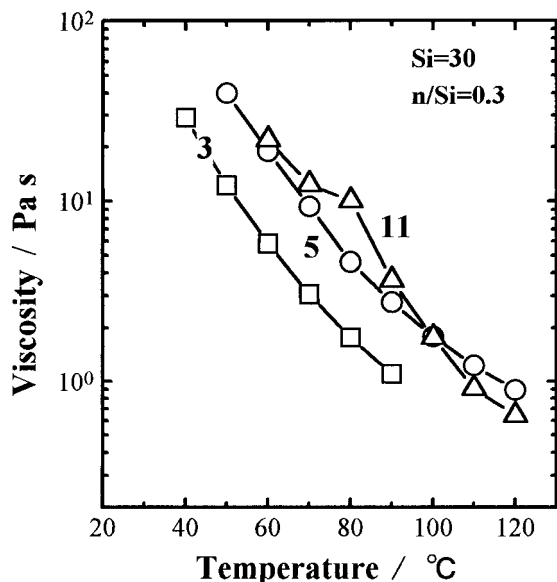
Figure 4 Viscosity of undiluted LCSs having different spacer lengths of $LCS(C_3)$, $LCS(C_5)$, and $LCS(C_{11})$, containing spacers with 3 ($S = 3$), 5, ($S = 5$), and 11 ($S = 11$) carbons, respectively; Si = 30, $n/Si = 0.3$; at 200 s^{-1} shear rate.

tending to impede the formation of crystalline molecular domains and the orientation of its domains and mesogenic groups even under an electric field.

We therefore investigated the effects of diluting $LCS(C_3)$, again having the same main-chain
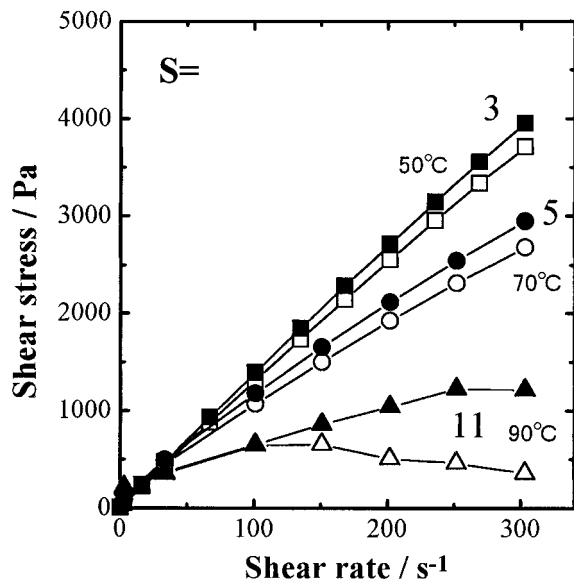

Figure 5 Shear stress of LCSs having different spacer lengths ($S = 3$, 5, and 11); Si = 30, $n/Si = 0.3$; filled marks in 2.0 kV/mm; unfilled marks in 0.0 kV/mm.
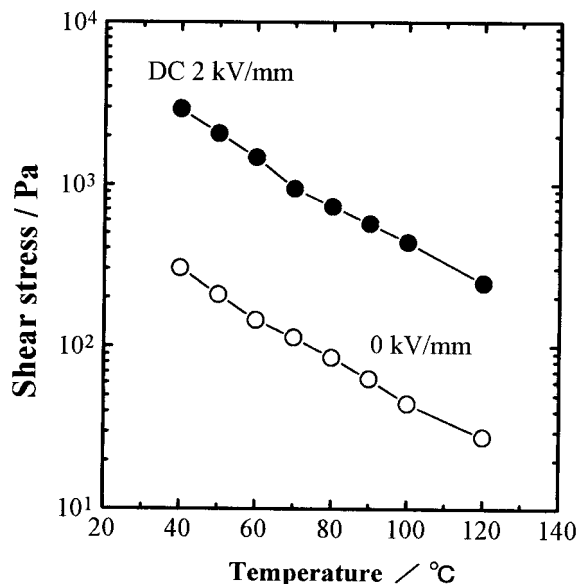

Figure 6 ER effect of $LCS(C_3)$ diluted with DMS; Si = 30, $n/Si = 0.3$, 50 phr DMS by weight; at 200 s^{-1} shear rate.

length Si = 30 and mesogenic group ratio $n/Si = 0.3$, with various ratios of polydimethylsiloxane (DMS, 20 cst). With DMS at 50 phr, as shown in Figure 6, a remarkably large ER effect was observed throughout the measured temperature range of 30 to 100°C. Addition of DMS at less than 20 phr tended to result in high shear stress both with and without the applied electric field, but little or no generated shear stress, or ER effect, as shown in Figure 7. With further increases in the DMS concentration, however, large decreases were observed in the zero-field shear stress, while little or no decrease occurred in the shear stress under the applied electric field. The net result was a rapid increase in generated shear stress with increasing DMS content, throughout the range of 20 to 80 phr DMS. At 80 phr DMS, the shear stress (and thus the viscosity) in the 2 kV/mm field was about 30 times as high as that with no electric field. Even at the test temperature of 50°C, however, evidence of separation between the LCS and DMS phases, presumably because of limited miscibility, was observed when the DMS content was increased much above 50 phr.

Mesogenic Group Ratio

We next investigated the behavior of $LCS(C_3)$, again having the main-chain length Si = 30, spacer length C = 3, and dilution by 50 phr DMS,
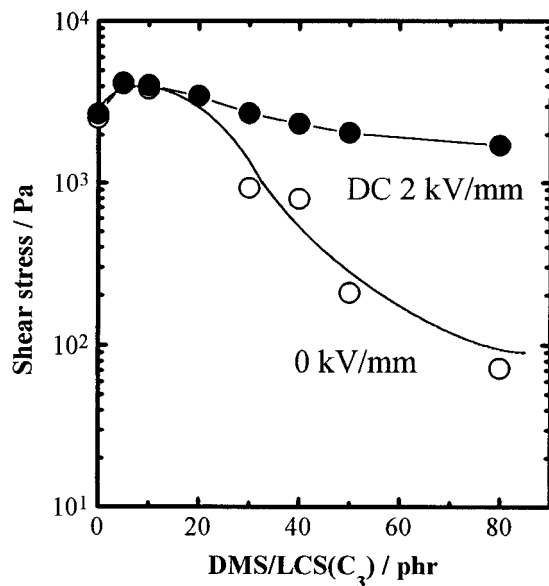
Figure 7 Influence of DMS dilution on ER effect of LCS(C_3); Si = 30, n/Si = 0.3; at 50°C, 200 s^{-1} shear rate.

but with mesogenic group ratios n/Si varying from 0.07 to 0.4. The results are shown in Figure 8, for temperatures ranging from 0 to 120°C. The ER effect was quite small when the n/Si ratio was 0.07, but increased in correspondence with increases in the ratio to 0.2, 0.3, and 0.4. The
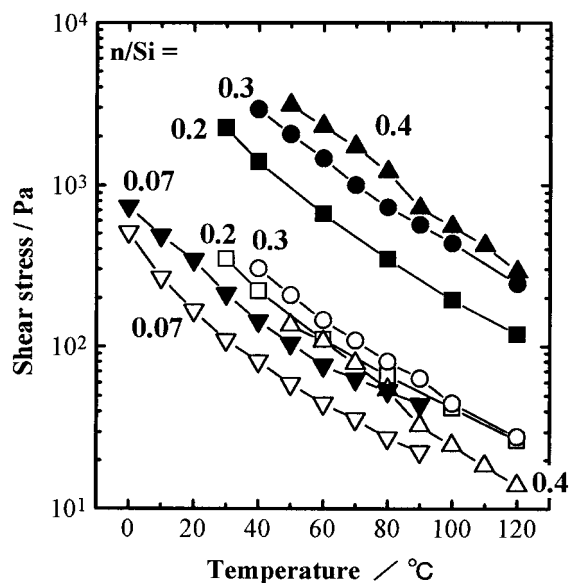

Figure 8 Influence of mesogenic group content on shear stress of LCS having Si = 30; S = 3, 50 phr DMS by weight; at 200 s^{-1} shear rate; filled marks in 2.0 kV/mm; unfilled marks in 0.0 kV/mm.
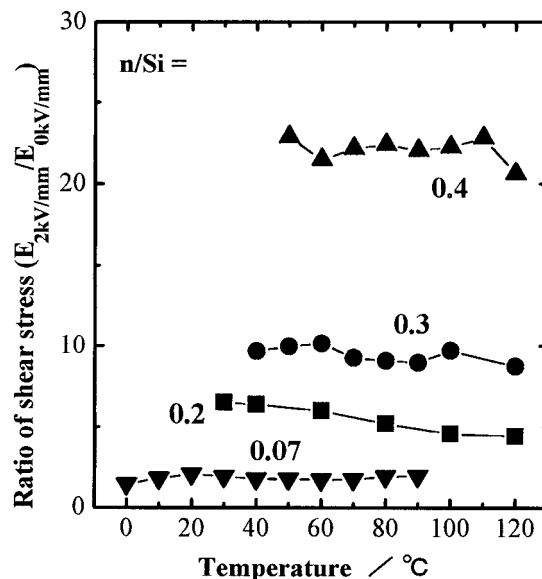

Figure 9 Mesogenic group content and shear stress ratio (ratio of shear stress in 2.0 kV/mm to that in 0.0 kV/mm); Si = 30, S = 3, 50 phr DMS by weight; at 200 s^{-1} shear rate.

higher mesogenic group ratios, however, also tended to result in lower miscibility between the LCS and the solvent, and it became difficult to obtain consistent shear stress values at temperatures of 40°C or less, particularly under no electric field. The lower limit for reliable measurement of the ER effect was about 50°C with a mesogenic group ratio of 0.4, and about 30°C when this ratio was 0.2.

Figure 9 shows the ratio between the shear stress (thus the viscosity) with and without the 2.0 kV/mm field for each of the four mesogenic group ratios. The very large increases in shear stress ratio observed with mesogenic group ratios of 0.3 and, particularly, 0.4, which was more than twice that with 0.3, are attributable in part to the tendency for the zero-field viscosity to decrease with increasing mesogenic group ratios at these higher ratios, in contrast to the reverse tendency between mesogenic group ratios of 0.07 and 0.2. We believe this is attributable to the reduced miscibility between the LCS and DMS, particularly at the mesogenic group ratio of 0.4, leading to phase separation and a resultant loss of viscosity in the solvent–LCS system with the 0.4 mesogenic group ratio. Figure 9 also clearly illustrates another remarkable characteristic of these LCS systems, which is the nearly constant shear stress ratio for each of them throughout most of the temperature range in which they were measured.
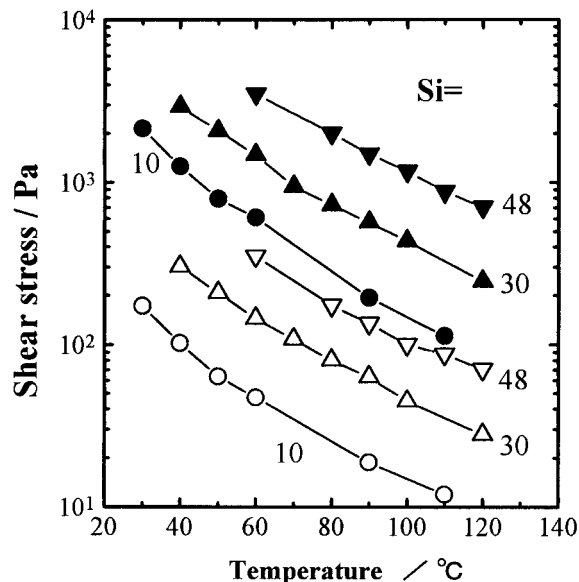
Figure 10 Degree of siloxane polymerization and shear stress; $n/Si = 0.3$, $S = 3$, 50 phr DMS by weight; at 200 s^{-1} shear rate; filled marks in 2.0 kV/mm; unfilled marks in 0.0 kV/mm.

Figure 11 Influence of mesogenic group content on shear stress of LCS having Si = 10; $S = 3$, 50 phr DMS by weight; at 200 s^{-1} shear stress; filled marks in 2.0 kV/mm; unfilled marks in 0.0 kV/mm.

Degree of Siloxane Polymerization

We next investigated the influence of the main chain length on the LCS behavior and characteristics, with polysiloxane chain lengths of Si = 10, 30, and 48, in all cases, having a mesogenic group ratio of $n/Si = 0.3$ and a spacer length of $S = 3$, thus being again in the category LCS(C_3), and a DMS content of 50 phr. The results are shown in Figure 10. Throughout most of the tested temperature range of 30 to 120°C, the shear stress generally increased with increasing values of Si, both with and without the application of the 2.0 kV/mm electric field, and the generated shear stress was quite large. It may be noted, however, that with the short-chain LCS (Si = 10), the ratio between the shear stress with and without the electric field was about 13 at relatively low temperatures but decreased to about 10 at high temperatures. The long-chain LCS (Si = 48), in contrast, exhibited a shear stress ratio of less than 10 at lower temperatures and about 13 or more at temperatures up to about 100°C. The trend with the intermediate-length LCS (Si = 30) was intermediate between those of the two other LCSs. These trends, and the temperatures at which changes in the shear stress ratios occurred, suggest that the changes were primarily the result of polymer-solvent phase changes, and largely unrelated to the phase transition temperatures of the LCSs.
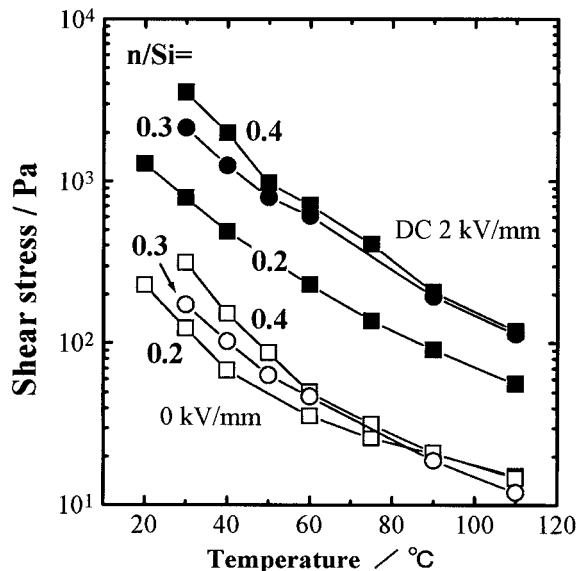
Figures 11 and 12 show the influence of the mesogenic group ratio on shear stress for LCS(C_3) with main-chain lengths of Si = 10 and Si = 48, respectively, in both cases, with 50 phr DMS. With the short main chain (Si = 10), the generated shear stress was generally larger than with
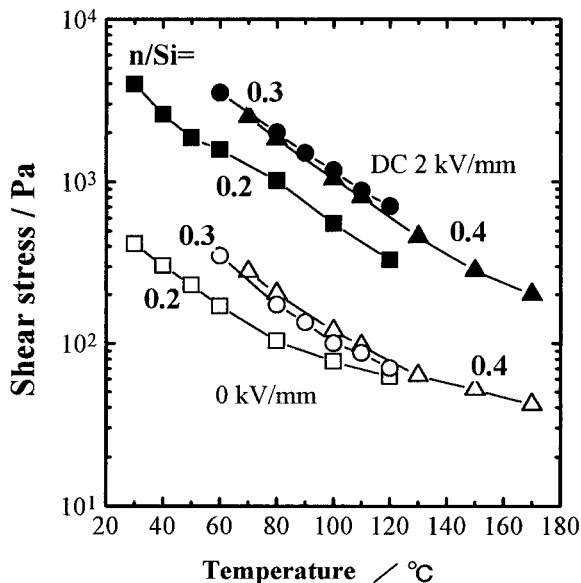

Figure 12 Influence of mesogenic group content on shear stress of LCS having Si = 48; $S = 3$, 50 phr DMS by weight; at 200 s^{-1} shear stress; filled marks in 2.0 kV/mm; unfilled marks in 0.0 kV/mm.

the long main chain (Si = 48), but was virtually uninfluenced by increasing the mesogenic group ratio from $n/Si = 0.3$ to $n/Si = 0.4$; and at the higher $n/Si = 0.4$ ratio, it was therefore nearly the same as that with the longer main chain. This indicates that the miscibility between the DMS solvent and the LCS(C$_3$) liquid crystal is more easily influenced by the mesogenic group ratio than by the degree of polysiloxane polymerization and that the tendency for solvent-polymer phase separation is small with low mesogenic group ratios, even at low temperatures. Taken together, these results strongly suggest that the optimum configuration for obtaining a large ER effect at relatively low temperatures is the combination of a low mesogenic group ratio and a high degree of polysiloxane polymerization.

Molecular Structure of the Spacer

We next investigated the influence of various spacers on the generated shear stress, in all cases with a main-chain length of Si = 30, a mesogenic group ratio of $n/Si = 0.3$, and a DMS content of 50 phr. The spacers used were C$_3$, C$_5$, C$_{11}$, and C$_{3E}$ consisting of —CH$_2$CH$_2$CH$_2$OCH$_2$CH$_2$—, and the LCSs therefore identified as LCS(C$_n$). The results for LCS(C$_3$), LCS(C$_5$), and LCS(C$_{11}$) are shown in Figure 13, and those for LCS(C$_3$) and
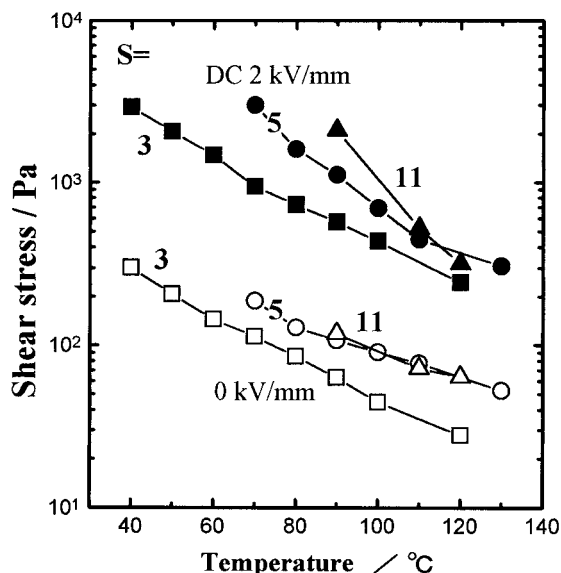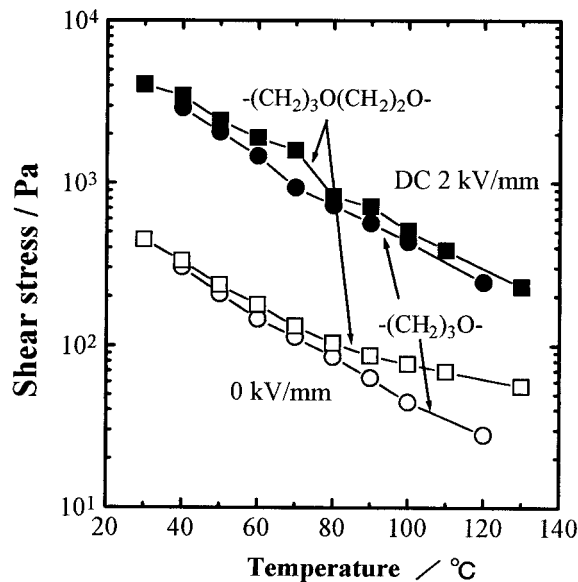
Figure 14 Influence of spacer structure on ER effect; Si = 30, $n/Si = 0.3$, 50 phr DMS by weight; at 200 s^{-1} shear rate.

LCS($_{3E}$) are compared in Figure 14. As shown by Figure 13, the generated shear stress increased with the length of the alkyl spacer, but the longer spacers also tended to result in solvent-polymer phase separation. Instability associated with phase separation occurred in LCS(C$_{11}$) at temperatures of up to 90°C and in LCS(C$_5$) at up to 70°C.

In LCS(C$_{3E}$), however, with the spacer containing the ether bond, no apparent phase separation occurred at temperatures as low as 30°C, even though the spacer was presumably about three carbons (corresponding to its —OCH$_2$H$_2$CH$_2$— component) longer than the C$_3$ spacer, and the generated shear stress was nearly as large as that of LCS(C$_3$).

LCS Phase Transition Temperature

The temperature of transition from the glassy to the isotropic phase was determined by DSC for the undiluted LCSs having main chain length Si = 30; spacer length $S = 3$; and mesogenic group ratios n/Si of 0.2, 0.3, and 0.4. The phase transition temperature rose from 12°C with $n/Si = 0.2$ to 28°C with $n/Si = 0.3$, and further to 38°C with $n/Si = 0.4$. The phase transition in LCSs diluted with 50 hpr DMS were similarly investigated, with essentially the same results.

The ER effect was clearly observed in these LCSs not only below but also well above their phase transition temperatures, at 50°C and sub-

Figure 13 Influence of spacer length (S) on ER effect; Si = 30, $n/Si = 0.3$, 50 phr DMS by weight; at 200 s^{-1} shear rate.

stantially higher, thus suggesting that the occurrence of the ER effect is not limited to the crystalline phase of these materials. Further study will be required to confirm this observation, however, since the test conditions of the DSC determinations did not include the application of shear stress or electric field and were therefore substantially different from the ER effect test conditions. In particular, it will be necessary to determine more clearly the influence of shear and electric field on their crystalline phase and phase transition temperature.

CONCLUSION

The results of the present study show the following relationships between the molecular structure and the ER effect of liquid crystalline polysiloxanes (LCSs).

- LCS(C_3), with a mean molecular composition of 30 silicons in its main chain, 9 mesogenic groups in its side chains, and alkyl spacers containing 3 carbons at the root of the side chains, exhibits a large ER effect when diluted with DMS but little or no such effect in undiluted form.

- Increasing the degree of siloxane polymerization (thus, the main-chain length), the mesogenic group ratio (the number of mesogenic groups per silicon), or the length of the alkyl spacers increases the strength of the ER effect but also decreases the miscibility of the LCS in DMS, resulting in polymer-solvent phase separation and ER effect instability at temperature up to 40°C or higher.

- This tendency for phase separation at low temperatures can be reduced or eliminated, and a large, stable ER effect maintained, by introducing a group containing an ether bond into the spacer.

- The ER effect occurs in LCS(C_3) at temperatures substantially above its isotropic phase transition temperature, as well as below.

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