

Effect of Polymer Concentration on Polarization Switching in Polysiloxane-Dispersed Ferroelectric Liquid Crystals

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ABSTRACT: Ferroelectric liquid crystal–polysiloxane composite films were prepared after dissolving them in diethyl ether as a solvent. The crosslinking was done by adding room temperature vulcanizer (mixture of tetra ethoxy silane and dibutyl tin dilaurate) as curing agent. These composite films show good electro-optic properties with switching times on the order of few milliseconds. The preliminary

results show that these systems can be useful as functional materials in electronic displays. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 87: 1209–1215, 2003

Key words: polysiloxanes; ferroelectric liquid crystals; polarization switching

INTRODUCTION

Polymer-dispersed liquid crystals (PDLCs) are composite materials in which liquid crystals are dispersed generally in the form of micron-sized droplets in a polymer matrix. Nowadays, much attention is being given to the development of new materials for electro-optic liquid crystal displays. Electro-optic devices using PDLC films have some advantages over other conventional displays—they are flexible, use no polarizers, are simple to make, and have millisecond switching times.

Polymer dispersed liquid crystalline materials are currently under development for high intensity projection television, certain types of direct view displays, and Switchable windows. Some of the potential applications of PDLCs are switchable windows, infrared shutters, angular discriminating filters, thermoelectro-optic switches, memories, gas flow sensors, optical sensors, and optical gratings etc.^{1–5}

The currently available PDLC devices are not comparable with the switching time of electro-optic cells based on the ferroelectric liquid crystals (FLCs). So, the idea of creating new electro-optic materials on the basis of PDLCs using both the advantages of traditional PDLC film with very fast switching time of FLCs is of great interest.

Much work has gone into the study of PDLCs using polyacrylates, methacrylates, polystyrene, etc., for the

applications in switchable windows.^{6,7} To date no significant work has been reported on the dispersion of liquid crystals in polysiloxanes.

For PDLC applications, usually used in display applications, polysiloxanes offer several advantages over the more rigid polyacrylate and polymethacrylate counterparts,^{8,9} particularly because of the greater flexibility of the backbone, which results in relatively low glass transition temperature.

In this paper, an attempt has been made to study the effects of the dispersion of a FLC material in a polysiloxane matrix. The morphology and the electro-optic properties of thin polysiloxane-dispersed ferroelectric liquid crystal composite films with respect to the polymer concentration have been studied.

EXPERIMENTAL

Chemicals required for the present study—dimethyl dichloro silane, hydrogen methyl dichloro silane, tetraethoxy silane, and dibutyl tin dilaurate (of $\geq 98\%$ purity)—were procured from M/s Fluka and used as received. Diethyl ether (AR) was procured from M/S Ranbaxy and ferroelectric liquid crystal mixture ZLI 3654 was procured from M/s E- Merck, Darmstadt.

Synthesis of polysiloxanes

Linear polydimethylsiloxane diols were prepared by controlled hydrolysis of dichlorodimethyl silanes using aqueous saturated sodium chloride solution in 1:2 ratio (V/V) at 0–5°C over a period of 2 h. The reaction mixture was kept at room temperature for about 4 h, extracted with ether, and then dried over anhydrous sodium sulfate. Vacuum treatments were carried out

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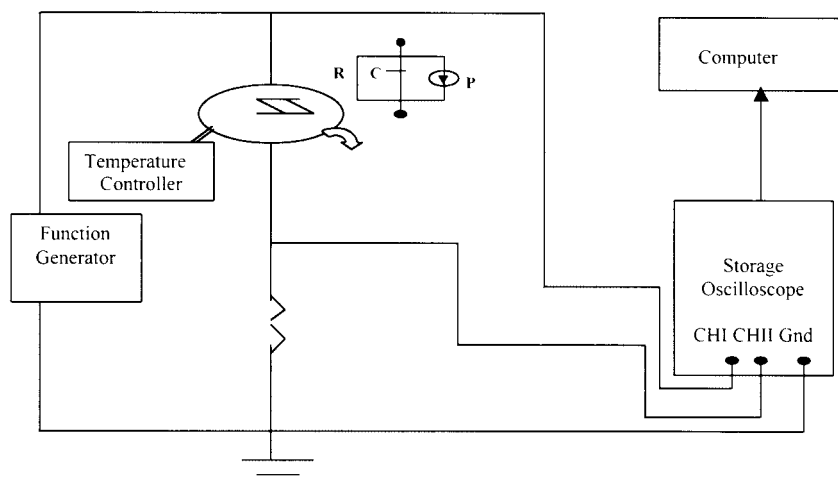


Figure 1 Experimental setup for the determination of polarization switching and response time of polymer-dispersed liquid crystals.

to remove traces of solvent. The polydimethylsiloxanes (PDMS) as synthesized above were characterized by intrinsic viscosity in toluene at 30°C and analyzed by infrared (IR) spectroscopy. The complete synthetic route for the synthesis of polysiloxanes and their oligomers is given elsewhere.^{10,11}

Preparation of polysiloxane-dispersed ferroelectric liquid crystals

Ferroelectricity in liquid crystals is a specific property of smectic-C liquid crystal phase. These molecules are asymmetric and exhibit spontaneous polarization in absence of the field.¹² This property has made them ideal for fast electro-optic switching devices.¹³ Within this area a great deal of attention has also been given to FLCs dispersed within a polymer network. Adding the polymer may act to enhance certain electro-optic properties and will substantially increase the mechanical strength of the ferroelectric liquid crystal system.^{14–16} The polymer dispersed ferroelectric liquid crystals (PDFLC) material was prepared by dispersing the polysiloxane–ferroelectric liquid crystal (ZLI-3654) mixture in the diethyl ether. The crosslinking was done with 0.2% of curing agent (tetra ethoxy silane and dibutyl tin dilaurate in 3:1 ratio). The curing time of the mixture was about 70 min. These liquid crystal materials were dispersed in the polysiloxane matrix. Proper dispersion was ensured after heating the mixtures to isotropic temperature, shaking them mechanically, and then degassed. The empty sample cells (20–25 μm thickness) consisting of conducting indium tin oxide (ITO) coated glass substrates, were filled with polysiloxane–liquid crystal–curing mixture by capillary action at 80°C (the isotropic transition temperature of the FLC sample). The cells were sealed by NOA-65 (Norland UV-cured transparent polymer) optical adhesive. The electrical connections were applied

to these cells using indium solder in order to study their other electrical properties.

Characterization of polymer dispersed ferroelectric liquid crystals

Determination of spontaneous polarization

Experimental setup for the measurement of spontaneous polarization is shown in Figure 1. The setup separates the resistive and capacitive terms from the polarization term by drawing a baseline. Illustration of current induced by application of triangular and square waves is given in Figure 2.

A symmetric triangular wave ($-10\text{V}-0\text{V}-+10\text{V}$) applied to ferroelectric liquid crystal mixture–polysiloxane composite material reorients the dipoles between two stable polarization states (i.e., UP and DOWN). As the field was switched on, the molecular realignments in the form of voltage drop were detected on the storage oscilloscope across a standard resistance R ($\sim 1\text{M}\Omega$).¹⁷

For a certain applied voltage V , the current response I consist of three components—the capacitive term I_C and the ionic conduction term I_R . The third term is polarization current I_p due to the charge induced by the dipole realignment in the form of a polarization hump.

$$I(t) = I_R + I_c + I_p$$

The area under the hump is a measure of the spontaneous polarization (P_s), which is given by

$$P_s = \frac{A(I \times t)}{\text{Area of Sample}}$$

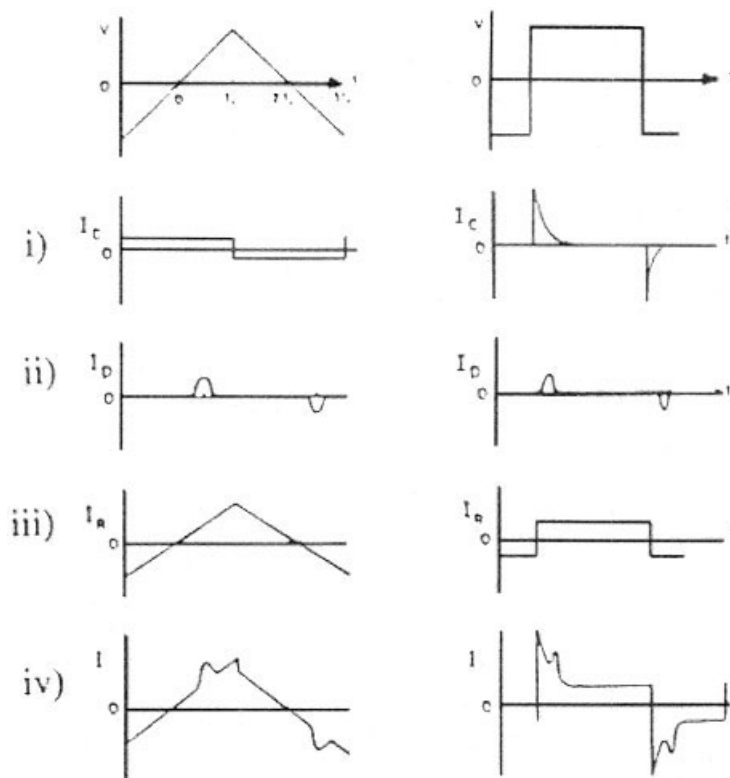


Figure 2 Illustration of current induced by application of triangular and square waves. (i) Capacitive contribution I_c ; (ii) polarization contribution I_p ; (iii) resistive term contribution I_R ; (iv) overall current profile.

where $A(I \times t)$ is the area under the curve measured by integrating the polarization hump in terms of voltage and time.

Determination of response time and torsional viscosity

The above technique can also be used to simultaneously measure response times and the effective torsional viscosities of these materials.

The delayed switching between the two stable sates is a measure of the response time written in the form

$$\tau_R = \frac{\eta}{P \cdot E}$$

where η is the torsional viscosity of the material, P is the polarization, and E is the applied electric field.

TABLE I
The Influence of Percent Curing Mixture on M_c

Percent of curing mixture	Molecular weight between crosslinks
0.2	1780
0.4	1192
0.6	0927
0.8	0717
1.0	0479

RESULTS AND DISCUSSION

Characterization of polysiloxanes

Viscosity

The intrinsic viscosities of the synthesized polydimethylsiloxanes were calculated and found to be very low (0.06–0.1 dL/g) and are in oligomeric range.

IR Spectroscopy

Polysiloxanes synthesized in the present study have also been characterized by IR using the Perkin-Elmer

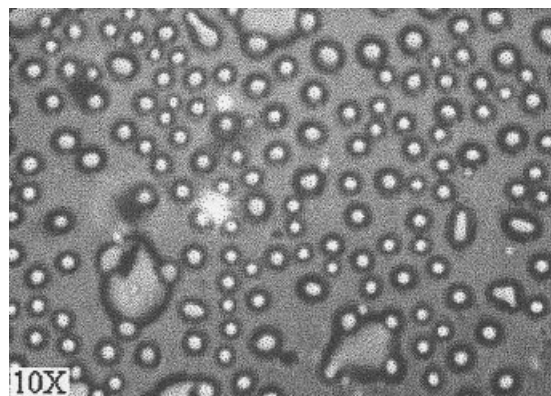


Figure 3 Microtexture of cured polysiloxane under crossed polarizers (magnification 10x) at 32°C.

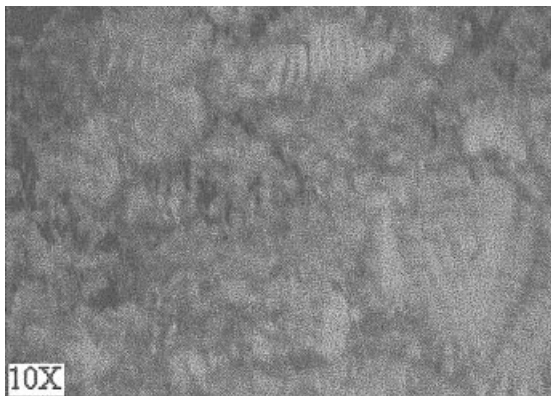


Figure 4 Microtexture of ZLI-3654 under crossed polarizers (magnification 10 \times) at 32 $^{\circ}$ C.

infrared spectrometer (model 1720X). This spectrum shows a strong peak at 1079 cm^{-1} due to the Si—O—Si bond, indicating the formation of siloxane polymers. Strong bands at 1210–1260 and 745 cm^{-1} may be due to the dimethyl groups attached to silicon atom [—Si(CH₃)₂]. Strong peaks at 2900 and 1400 cm^{-1} due to $\gamma_{\text{C—H}}$ and $\delta_{\text{C—H}}$ have also been observed in IR spectra of PDMS.

In this spectrum there was no peak at 666 cm^{-1} due to Si—Cl, confirming the formation of Si—O—Si bond during hydrolysis. Further presence of Si—O—Si, Si—C, and C—H peaks in the IR spectrum of poly-

dimethyl siloxane is in conformity with the reported literature.¹⁸

Crosslinking density measurements

The crosslinking densities of polysiloxane in toluene were calculated using Flory's equation. The equilibrium volume fraction of polysiloxane within the swollen network ϕ shows a constant value after an initial decrease of time.

This fraction can be calculated by using the equation

$$\phi = \frac{1}{\nu_2} \quad (1)$$

where

$$\nu_2 = \frac{1}{1 + \{[\rho_p(\omega_b - \omega_a)]/[\rho_s(\omega_a)]\}} \quad (2)$$

The ρ_p and ρ_s are densities of the polymer and solvent, respectively. The ω_a and ω_b are the weights of dried and swollen samples, respectively.

When the swollen gel is in equilibrium with the pure solvent, Flory's equation is applicable for calculating the molecular weight between crosslinks M_c .¹⁹

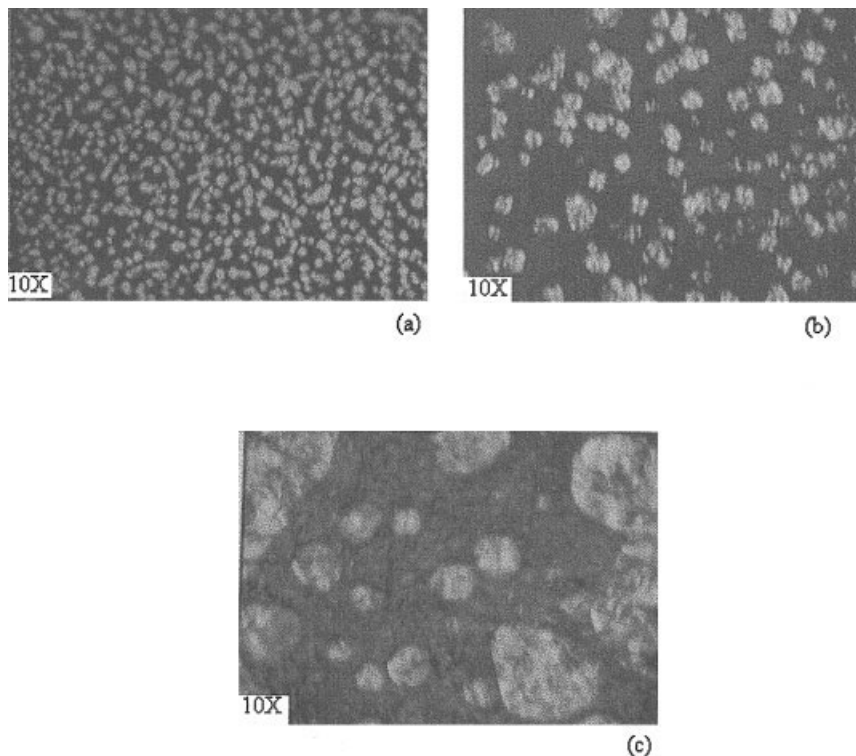


Figure 5 Microtexture of polymer-dispersed ferroelectric liquid crystal in the polymer:ZLI3654 ratio—(a) 2:1, (b) 1:1, and (c) 1:2—under crossed polarizers (magnification 10 \times) at 32 $^{\circ}$ C.

TABLE II
Influence of Polymer Concentration on Polarization Switching Response

Sample no.	Percent polymer in PDFLC system	Percent liquid crystal in PDFLC system	Percent of curing agent added	Molecular weight between crosslinks	Polarization (nC/cm ²)	τ (ms)	η (kg/ms)
1	0.00	100.00	—	—	25.71	1.00	0.25
2	33.33	66.66	0.2	1470	14.84	1.00	0.32
3	50.00	50.00	0.2	1192	10.60	1.13	0.50
4	66.66	33.33	0.2	927	8.67	1.33	0.66

$$Z = \frac{\nu_2^{1/3} - \nu_2/2}{\ln(1 - \nu_2) + \nu_2 + \mu\nu_2^2} \quad (3)$$

Z is the ratio of the volume of chain to solvent molecule and μ is the polymer–solvent interaction parameter.

$$Z = \frac{M_c}{\rho_p V_s} \quad (4)$$

or

$$M_c = \frac{\rho_p V_s (\nu_2^{1/3} - \nu_2/2)}{\ln(1 - \nu_2) + \nu_2 + \mu\nu_2^2} \quad (5)$$

where V_s is the molar volume of toluene (solvent) and M_c is the molecular weight between the crosslinks.

The value of M_c with respect to the curing mixture is given in Table I.

The M_c is shown to be inversely proportional to the concentration of curing mixture in polysiloxanes and number of crosslinks (crosslinking density) in the system.

The measurements of crosslinking densities are important to understand the droplet size in PDLC systems. It is observed that the size of the droplets formed in PDLC systems depend on the rate of droplet formation and crosslinking density of the systems.

Electro-optic effects

The optical textures of crosslinked polysiloxanes and polymer-dispersed ferroelectric liquid crystals under crossed polarizers using an Olympus polarizing microscope (model BX 51) are shown in Figures 3–5. The microstructure of cured polysiloxane without liquid crystal is shown in Figure 3. As can be seen from Figure 3, the liquid crystal can get diffused into the available free volume of the polysiloxane and the size of the droplets are proportional to the free volume of polysiloxane matrix. The microtexture of the pure ferroelectric liquid crystal ZLI-3654 in 25 μ thickness is shown in Figure 4.

The microtextures of polymer-dispersed ferroelectric liquid crystals at different concentrations (poly-

mer–liquid crystal ratio of 2:1, 1:1, and 1:2) at a curing concentration of 0.2% are given in Figure 5(a–c), respectively. It was observed that with the decrease of concentration of ferroelectric liquid crystal in PDFLC, the droplet size becomes small, the liquid crystal–polymer interaction becomes more significant, and a greater field-induced torque is required to unwind the helix of FLC in a PDFLC sample. It was also seen that with the increase in polymer content and decrease in the value of molecular weight between crosslinks (more number of crosslinks), the droplet morphology had changed from nonuniform droplet distribution to more uniform droplet distribution.

It is well known that liquid crystal droplet size in PDLC is determined by the rate of droplets formation, i.e., by the curing rate in polymer matrix.¹⁹ We observed that the value of molecular weight between crosslinks influences the morphology of the droplets in the polymer-dispersed liquid crystal systems.

Liquid crystal droplet formation is a result of phase separation process to the polymerization of the polysiloxane matrix. In this respect, the whole process can be regarded as linked to the liquid–solid phase transition of the matrix, and droplet formation can be treated as the nucleation of a solid from the liquid phase.

The two main steps of phase transformation are nucleation and growth. The rate of formation of the new phase measured in nuclei per second can be expressed as

$$\frac{dn}{dt} \propto \exp\left[\frac{\Delta g^* + \Delta g_D}{kT}\right]$$

where N is the number of formed liquid crystal droplets; Δg_D the activation energy for diffusion, which decreases with increase in temperature; and Δg^* the activation energy for nucleation, which increases with increase in temperature.

This model can explain the lowering of morphological uniformity of PDFLC films connected to the crosslinking density. Our data can be qualitatively explained assuming that at low curing mixture concentration, the correspondent temperature makes Δg^* lower than Δg_D so that nucleation rate is higher than

growth rate (exothermic reaction). In this situation, diffusion is quenched and the system keeps the degree of uniformity present before the curing process. On the contrary, if curing concentration increases, temperature increases as well and Δg^* becomes higher than Δg_D the growth rate is higher than nucleation rate and diffusion prevails on nucleation. Under these conditions, liquid crystal droplets become nonuniformly dispersed in the polymer matrix. The viscosity of PDFLC increases as the curing process goes on, so that morphological disuniformity remains frozen. If the curing process stopped before the end of phase separation, diffusion could occur because of the low viscosity and the droplets distribution tends to become uniform. Also, it is understood that the droplet morphology depends on the polymer concentration and free volume in the polymer matrix. Further experimental studies are in progress to understand the influence of crosslinking density on the morphology of polymer-dispersed ferroelectric liquid crystalline systems.

Polarization switching response—influence of polymer concentration

Polarization switching response (P_s) was measured using the field reversal technique.²⁰ The polarization, response time (τ), and torsional viscosity (η) have been measured with respect to the polymer concentration at 50 V and is given in Table II.

The spontaneous polarization (P_s) of the pure liquid crystal material ZLI-3654 was measured to be 25.71 nC/cm² at room temperature. Proceeding from this value, we have calculated the expected values and compared with the experimental values. The calculated values along with the experimental values are given in Table III.

In the PDFLC sample containing 33.33% polymer and 50% polymer, the deviation between the calculated and experimental values may be due to the incomplete phase separation. At the polymer concentration of 66.66%, we would expect the value of P_s to be 8.57 nC/cm² for the PDFLC sample, providing that the phase separation is complete. The value of 8.63 nC/cm² was measured at room temperature for the

TABLE III
Calculated and Experimental Values of Polarization of PDFLCs

Sample no.	Percent polymer in PDFLC system	Polarization (calculated) (nC/cm ²)	Polarization (experimental) (NC/cm ²)
1	0.00	25.71	25.71
2	33.33	17.13	14.84
3	50.00	12.85	10.60
4	66.66	8.57	8.63

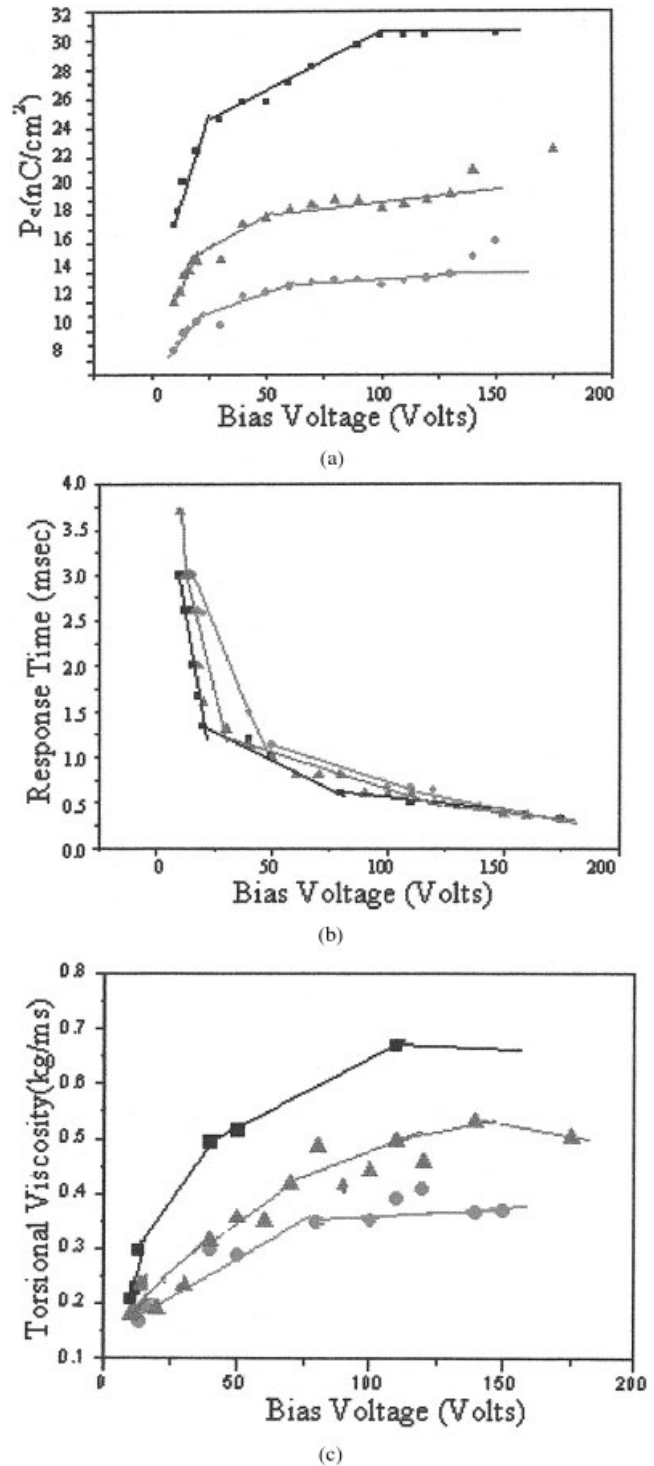


Figure 6 The effect of bias voltage as a function of (a) polarization, (b) response time, and (c) torsional viscosity of pure and polymer-dispersed ferroelectric liquid crystal systems at different concentrations [■: ZLI-3654; ▲: PDLC with polysiloxane: ZLI-3654 ratio (1:2); and ●: PDLC with polysiloxane: ZLI-3654 ratio (1:1)].

PDFLC device. This compares reasonably well with the calculated value and implies the complete phase separation occurred in the polymer matrix.

Influence of bias voltage on polarization

The effects of bias voltage on polarization switching, response time, and torsional viscosities is given in Figure 6(a–c), respectively.

In Figure 6(a), it can be seen that with the increase of bias voltage the spontaneous polarization increases and at a bias voltage greater than 50 V (~ 2 V/ μ m), the saturation polarization is achieved due to the complete unwinding of helix. In contrast, the undoped FLC mixture shows higher polarization. Our results indicate that with the increase of polymer content in the polymer-dispersed ferroelectric liquid crystal mixture, the spontaneous polarization values shows a sharp decrease.

Influence of bias voltage on response time

It is observed from Figure 6(b) that the response time shows an exponential decay with the increase of bias voltage. The response time, which is the delay in switching between two stable states of polarization, decreases from 3 ms at a bias voltage of 20 Voltage Peak-Peak (Vpp) to 500 μ s at a bias of 140 Vpp. Pure ZLI and PDFLCs at higher values of bias (≥ 50 Vpp) shows a same value of response time. The microsecond switching time makes them useful for the optical switches and flexible displays. A typical behavior of bias voltage on the torsional viscosity is shown in Figure 6(c). Saturation in torsional viscosity is observed at higher applied voltage.

CONCLUSIONS

1. Polysiloxanes were synthesized and characterized for the preparation of polymer-dispersed ferroelectric liquid crystal films.
2. The spontaneous polarization decreases with the increase in the polymer concentration.
3. There is no significant change in response time with the polymer concentration, and the switching time of polymer-dispersed ferroelectric liquid crystals is low compared to the traditional polymer-dispersed liquid crystals.
4. As polysiloxane-dispersed liquid crystals have many possible applications in displays due to low T_g , greater flexibility, and mechanical prop-

erties compared to conventional polymers, they may find suitable and promising functional electronic materials for applications in flexible displays.

5. Further studies are in progress to understand the influence of crosslinking densities on the morphology of the PDFLC systems and on the polarization switching of PDFLC materials.

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