

Influence of Polymer Viscosity on the Morphological and Opto-Electronic Behavior of Polysiloxane Dispersed Ferroelectric Liquid Crystal Composite Thin Films

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ABSTRACT: Poly(dimethyl)siloxanes of different viscosity have been synthesized by hydrolytic condensation of dimethyldichloro silane. Polysiloxane dispersed ferroelectric liquid crystal (PDFLC) composite films were prepared simultaneously by solvent induced and polymer induced phase separation techniques (SIPS and PIPS, respectively). These composite films were prepared by mixing polymer and ferroelectric liquid crystal mixture in diethyl ether and then adding 0.2% of room temperature vulcanizer for crosslinking. Film morphology, droplet size, and electro-optic parameters of PDFLC systems have been studied by using polysiloxanes of different viscosity. We show that the

polymer viscosity affects the droplet size, morphological uniformity, electro-optic properties, and also the extent to which the phase separation is complete. These composite systems show the switching time of few microseconds. Structure-property correlation in these materials have been studied and explained on the basis of polysiloxane viscosity. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 94: 159–166, 2004

Key words: polysiloxanes; ferroelectric liquid crystal mixture; polymer dispersed ferroelectric liquid crystal composites; droplet morphology; electro-optic properties; spontaneous polarization; response time; flexible display devices

INTRODUCTION

Polymer/liquid crystal composite films are potentially useful for a variety of electro-optic applications including switchable windows and projection displays. In these films liquid crystals are imbedded in polymer matrix, either as dispersed droplets called PDLC or as continuous phase called polymer network LC (PNLC). In both cases, the films are self supported and this makes them useful for the application in flexible and large area displays.^{1–6} In the composite films, matrix polymer is plasticized by the dissolved LC molecules, which significantly reduces the glass transition temperature of polymer and provides the film with high flexibility. In addition, the absence of polarizers substantially reduces light loss and increases the brightness of both direct view and projection displays. These displays have a number of advantages: simple and minimal fabrication cost; flexible, high brightness; and small switching time.^{7–10}

Polymer dispersed ferroelectric liquid crystal composite systems for display applications is a relatively recent area because of their faster response compared

to that of nematic based displays. It has been reported that the contrast ratio and viewing angle of ferroelectric LC devices are superior to all other LC displays. For PDLC/PDFLC applications, polysiloxanes offer several advantages over the more rigid polyacrylate and polymethacrylate counterparts, particularly because of the greater flexibility of the backbone, which results in relatively low glass transition temperature.^{11–14} These materials have been used to make cells durable, flexible, and optically suitable for display applications.

The molecular orientation structure inside the droplets and consequently the electro-optic properties of the films are strongly dependent on parameters such as curing parameters, viscosity of the polymer, structure of the polymer, electric field, and temperature.^{15,16}

By changing any or all of these parameters, the electro-optic properties and the droplet morphology can be controlled to obtain the desired properties of the PDLC displays. Nevertheless, to date there has been little effort to find out the parameters that determine sample morphology and to relate them to the electro-optic behavior in PDFLC composites in polysiloxane matrix.

In this article, we report the systematic studies of synthesis of polysiloxanes, the dispersion of ferroelectric liquid crystal in them, and then seek to understand the influence of polymer viscosity on liquid crystal droplet morphology and electro-optic parameters.

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TABLE I
The Intrinsic Viscosity of the Polysiloxanes
Corresponding to the Reaction Time of Hydrolytic
Condensation of Dichloro Silanes

Reaction time (h)	Intrinsic viscosity (dl/g)
2	0.06
6	0.08
10	0.11
14	0.13
18	0.15
24	0.19

EXPERIMENTAL

Chemicals—dimethyldichloro silane, tetraethoxy silane, and dibutyl tin dilaurate ($\geq 98\%$ purity)—were procured from M/s Fluka (India). Diethyl ether (AR) and toluene (AR) were procured from M/S Ranbaxy (India). Ferroelectric liquid crystal mixture ZLI-3654 was procured from M/s E-Merck (Darmstadt, Germany). All the chemicals were used as received.

Synthesis of polysiloxanes

Linear poly(dimethyl)siloxanes were prepared by controlled hydrolytic condensation polymerization 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 30°C for different time intervals (2, 6, 10, 14, and 24 h, respectively) to get polymers of different viscosity grades. They were extracted with diethyl ether and then dried over anhydrous sodium sulfate. Vacuum treatments were carried out to remove the traces of the solvent impurities. The polysiloxanes as synthesized above were characterized by intrinsic viscosity in toluene at 30°C and analyzed by infrared (IR) spectroscopy using Perkin–Elmer model 1720X FTIR spectrometer (Wellesley, MA). The complete synthetic route for the synthesis of polysiloxanes and their oligomers is reported elsewhere.^{17,18}

Swelling measurements

The crosslinking density of poly(dimethyl)siloxanes of different viscosity was determined from swelling measurements in toluene by using Flory's equation. Each polysiloxane matrix of 2×2 cm² was taken and immersed in 20 ml of toluene. Swelling measurements were carried out in toluene at 30°C. The weight of the sample before and after attaining the equilibrium swelling was measured. % volume swell was determined using the following equation.

$$\% \text{ Volume swell} = \frac{\text{Volume of swollen sample}}{\text{Volume of dried sample}} \times 100$$

The crosslinking densities of polysiloxane in toluene were calculated using Flory's equation.

The equilibrium volume fraction of polysiloxane within the swollen network v_2 shows a constant value after an initial decrease of time.

The equilibrium volume fraction can be calculated using the equation

$$\phi = \frac{1}{v_2} \quad (1)$$

where

$$v_2 = \frac{1}{1 + \frac{\rho_p(\omega_b - \omega_a)}{\rho_s(\omega_a)}} \quad (2)$$

ρ_p and ρ_s are densities of polymer and solvent, respectively. 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

$$Z = \frac{v_2^{1/3} - v_2/2}{\ln(1 - v_2) + v_2 + \mu v_2^2} \quad (3)$$

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

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

Or

$$M_c = \frac{\rho_p V_s (v_2^{1/3} - v_2/2)}{\ln(1 - v_2) + v_2 + \mu v_2^2} \quad (5)$$

where

V_s = Molar volume of toluene (solvent).
 M_c = Molecular weight between the crosslinks.

TABLE II
The Influence of Polymer Viscosity on M_c at Constant
Curing Mixture Concentration

Intrinsic viscosity of polysiloxane	Molecular weight between crosslinks (M_c)
0.06	0271
0.08	0489
0.11	0927
0.13	1423
0.15	1654

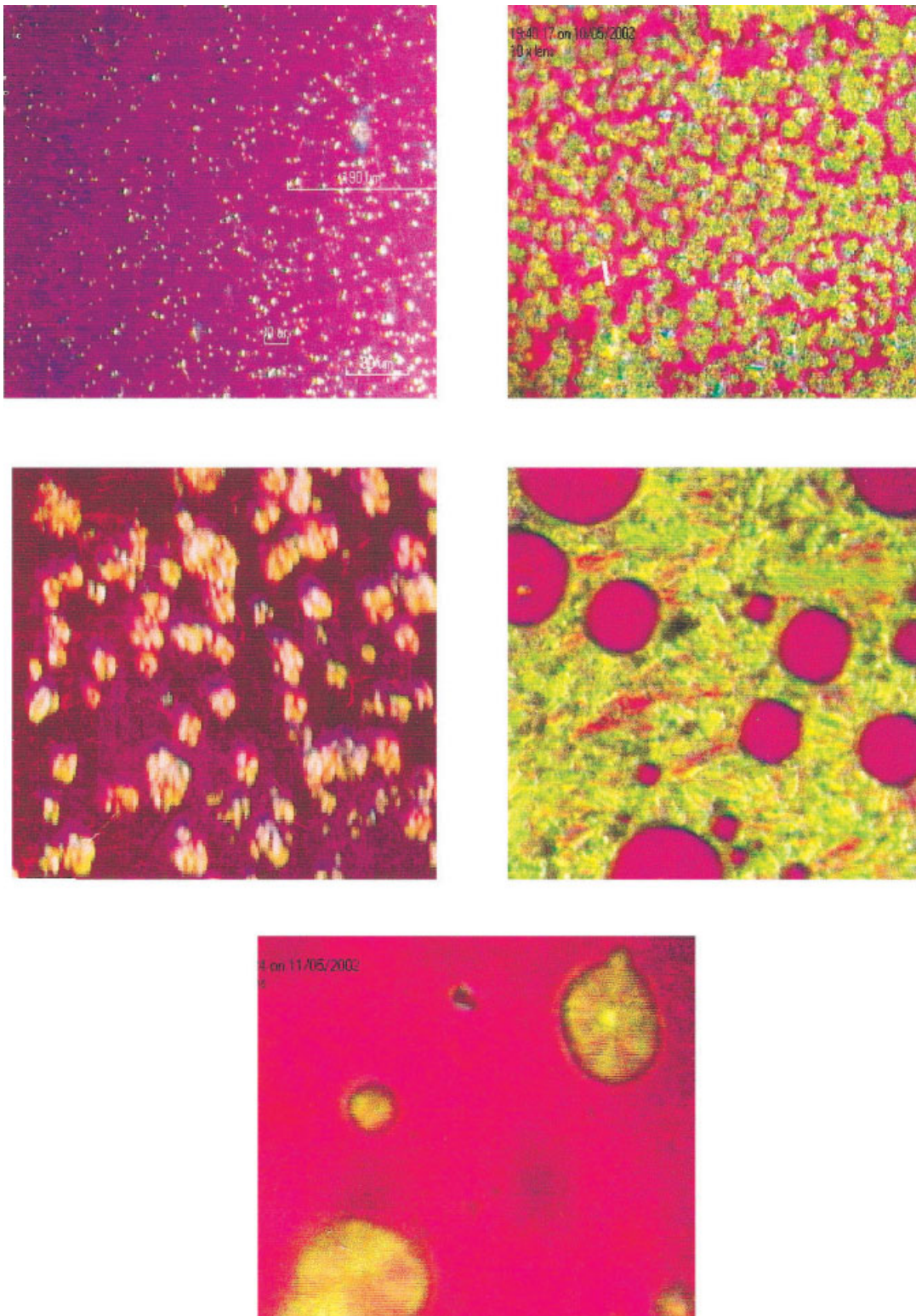


Figure 1 The droplet morphology of PDFLC composite systems at poly(dimethyl)siloxane intrinsic viscosity of: (a) 0.06 dl/g, (b) 0.08 dl/g, (c) 0.11 dl/g, (d) 0.15 dl/g, and (e) 0.18 dl/g, respectively.

Preparation of polysiloxane dispersed ferroelectric liquid crystals

Ferroelectricity in liquid crystals is a specific property of smectic C* liquid crystal phase. They exhibit

spontaneous polarization in the absence of the electric field due to molecular asymmetry, which makes them ideal for use in fast electro-optic switching display devices.

TABLE III
The Effect of the Polymer Viscosity on Droplet Size of PDFLC Composite Films

Intrinsic viscosity (dl/g)	Average droplet size in μm
0.06	3–5
0.08	15–20
0.11	25
0.13	40
0.15	50
0.19	80–100

The polysiloxane dispersed ferroelectric liquid crystal (PDFLC) composite films were prepared using ferroelectric liquid crystal mixture ZLI-3654 exhibiting SmC* phase between 30°C and 62°C and poly(dimethyl)siloxanes of different viscosity grades by solvent induced phase separation followed by the polymer induced phase separation techniques.^{1–3} The poly(dimethyl)siloxane and FLC mixture (ZLI-3654) in 1:1 ratio were properly mixed in diethyl ether solvent, and 0.2% room temperature vulcanizer (mixture of tetraethoxy silane and dibutyl tin dilaurate in 3:1 ratio) was used to prepare PDFLC composite systems. The PDFLC composite was sandwiched between two indium tin oxide (ITO) coated glass substrates separated by 10 μm Mylar spacer to control the film thickness.

RESULTS AND DISCUSSION

Characterization of polysiloxanes

Viscosity

The viscosity of polysiloxanes was measured using Ubbelohde viscometer at 30°C in toluene. The values of intrinsic viscosity $[\eta]$ were calculated by plotting a

graph between η_{sp}/C (specific viscosity/concentration) and concentration (C). The values of intrinsic viscosities corresponding to the reaction time are given in Table I. It was observed that by increasing the reaction time of hydrolysis, the viscosity of the polymers was also increased.

Infrared spectroscopy

Polysiloxanes synthesized in the present study have been analyzed using Perkin-Elmer Infrared spectrometer (Model FTIR 1720X). 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 IR spectrum of poly(dimethyl)siloxane are in conformity with the reported literature.²¹

Crosslinking density

The crosslinking densities of polysiloxanes of different viscosity grades at 0.2% curing mixture concentration were measured and the values of M_c with respect to the polymer viscosity are given in Table II.

It is found from our results that the M_c increases with the increase in the viscosity and the molecular weight of the polymer at constant concentration of room temperature vulcanizer. The M_c is inversely proportional to number of crosslinks (crosslinking density) of the system.

Droplet morphology of PDFLC systems

The optical textures of PDFLC (ZLI-3654) composite films using polysiloxanes of different viscosity grades were observed under cross polarizers using Olympus

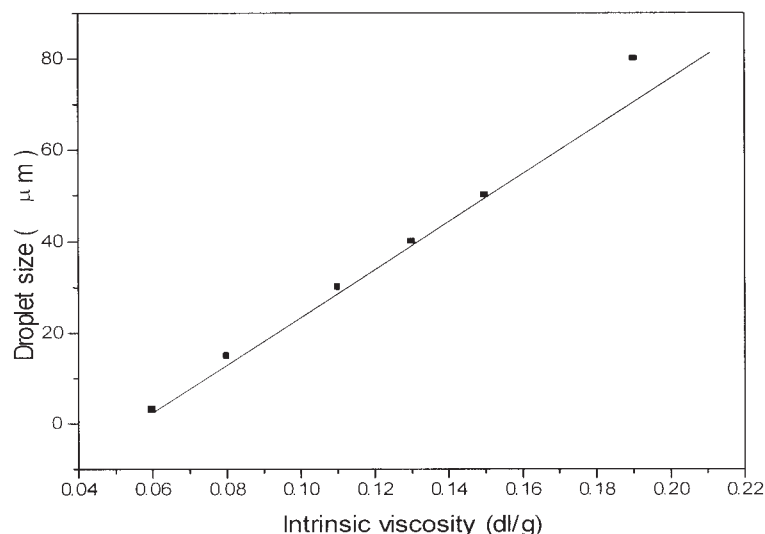


Figure 2 The liquid crystal droplet size as a function of intrinsic viscosity of the poly(dimethyl)siloxane.

polarizing microscope (model BX51P; Japan). The temperature of the samples was controlled at an accuracy of $\pm 0.1^\circ\text{C}$ in Linkam temperature programmer cum hot-stage (model TP 94 and THMS 600; United Kingdom). Figure 1 (a–e) shows the micro-textures of the liquid crystals dispersed in polymer matrix at 40°C . Linksys software was used to measure the droplet size. The variation of polysiloxane viscosity on the droplet size is shown in Table III.

The liquid crystal droplet size in polymer dispersed liquid crystals is determined by the rate of droplet formation. As observed in Table III, the liquid crystal droplet size is smaller in PDFLC systems of lower viscosity and increases as the viscosity increases. This increase may be due to the difficulty in the droplet formation in high viscous polymer matrix because of the strong surface forces exerted by it. Liquid crystal droplet size increases by increasing the polymer viscosity. The droplets appear uniformly dispersed in polymer matrix only in the low viscous polymers. This may be due to the partial solubility and better mutual interaction of polymer-LC systems for low molecular weight polymers.

The liquid crystal/polymer mutual solubility and rate of diffusion also play an important role in determining the LC droplet size. Diffusion of the droplets due to the concentration gradient might cause droplet collision. This effect, however, is negligible in a homogeneously mixed LC-polymer compound.

Lower viscosity of the polymer might induce greater liquid crystal solubility in the matrix. This, in principle, would decrease the droplet size. It was also found from our results that the smaller the droplet size in PDFLC composite systems, the better is the electro-optic response.

It was also observed that the LC droplets of uniform size and distribution were obtained when the densities of the LC and polymer were approximately the same. Droplet size was also controlled by the polymer curing rate. Faster rates would decrease the time for the polymer to cure to a threshold viscosity that freezes in the size of the droplets. Thus, the smaller and more uniform size and spacing distribution of the LC droplets would be produced.

The variation in the droplet size distribution and its uniformity can be explained using Stoke's equation^{15,20} and the crosslinking density measurements of the composite systems.

$$V_t = \frac{2g(\rho_p - \rho_{LC}) \cdot R^2}{9\mu} \quad (6)$$

where V_t is the terminal velocity of a dispersed droplet driven by sedimentation force; g is the gravitational acceleration; ρ_p and ρ_{LC} are density of polymer and liquid crystal, respectively; R is radius of droplet in PDLC system; and μ is viscosity of polysiloxane.

TABLE IV
Effect of Polymer Viscosity on Transition Temperatures of PDFLC Composite Films

Viscosity of polysiloxane (dl/g)	SmC* to SmA transition T_{C^*A} °C	SmA to isotropic transition T_{AI} °C
0.06	62	88
0.08	64	88
0.11	65	90
0.13	68	94
0.15	71	99

From equation (6), it is clear that the droplet size and its uniformity are dependent on the sedimentation force and the polymer viscosity. As the polymer viscosity increases, the size of the droplets increases and is in good agreement with our results (Table III).

The sedimentation-induced motion can lead to collisions between the droplets. As a result, the size uniformity of the droplets is expected to be more uniform as ρ_p/ρ_{LC} approaches unity. It was observed that LC droplets of uniform size and distribution were obtained at the polymer viscosity of 0.06 dl/g and at the polymer density of 1.24 g/ml. As the polymer viscosity increases, the density of the polymer also increases and the size of the droplets becomes non-uniform in high viscous polymers. Qualitatively, our results agree very well with the theory.

The increase in polymer viscosity in PDFLC increases the droplet size. A typical behavior of the intrinsic viscosity of polysiloxanes and the size of the droplets formed in polymer dispersed ferroelectric liquid crystal composite systems is shown in Figure 2. It clearly indicates that the size of the phase-separated droplets formed in PDFLC systems is linearly proportional to the intrinsic viscosity of the polymer.

The variation in the droplet size with increase in the viscosity of the polymer can also be explained based on their crosslinking density measurements.

Figure 1 shows the polarizing microscopic textures taken at crossed polarizers using polysiloxanes of different viscosities. It is observed from the textures that the droplet size is dependent on the free volume in the PDFLC systems, and on the crosslinking density.

With increase in the intrinsic viscosity of the polymer, the molecular weight and the chain length of the polymer increase. At constant curing mixture concentration, the molecular weight between the crosslinks increases and the number of crosslinks per unit volume (crosslinking density) decreases with the increase in the viscosity of the polymer. Therefore, from our results given in Table III, we can clearly indicate that the free volume in the polymer matrix of high viscosity is more compared to that of the low viscous polymer.

With the increase of M_c in the vulcanized polymer, the number of crosslinks in the polymer decreases and

TABLE V
Effect of Polymer Viscosity on Electro-Optic Parameters at Room Temperature and Bias Voltage 30 V (Peak to Peak)

Viscosity of the polysiloxane (dl/g)	Spontaneous polarization (nC/cm ²)	Response time (μ s)	Torsional viscosity (kg/ms)
0.06	21.28	544	0.34
0.08	15.21	693	0.31
0.11	08.31	802	0.20
0.13	04.62	933	0.13

enhances the free volume for diffusion. Therefore, at lower M_c value, the free volume for diffusion is low and the PDLC system attains smaller droplet morphology having more uniformly compared to higher M_c values in the polymer matrix.

Phase transition temperature shift

The phase sequence of the pure ZLI-3654²² is



The phase transition temperatures measured for PD-FLC systems showed an increase in both SmC* to SmA and SmA to isotropic phase over ZLI-3654 as given in Table IV.

We believe that the confined geometry of the LC droplets in the polymer matrix and their incomplete phase separation might have caused a shift in the phase transition temperatures of the liquid crystal mixture imbedded in the polymer material. It could have resulted in the broadening of the transitions as well as induction of new bi-phases into the initial

phase sequence. The observations were made using thermal polarization microscopy measurements with 0.1% accuracy. The observed phase shift may be due to the incomplete phase separation due to which a small amount of polymer material might have remained undissolved in the liquid crystal droplets.

These variations indicate that at lower viscosity, the transition temperature does not show significant changes compared to higher viscosities.

Influence of polymer viscosity on electro-optic parameters

Polarization switching response and other electro-optic parameters were measured using field reversal technique.¹⁹ The spontaneous polarization (P_s), response time (τ), and torsional viscosity (η) have been measured with respect to the polymer viscosity and the temperature at constant bias voltage of 30 V. We observed that the polysiloxanes produce significant effect on electro-optic properties of ferroelectric liquid crystal mixture. Table V shows the variation in these parameters as a function of viscosity at 35°C. The values of P_s and τ in ZLI-3654 at 35°C and 30 V are also measured and found to be 25 nC/cm² and 500 μ s, respectively.

The spontaneous polarization with respect to the polymer viscosity at room temperature and at constant bias voltage ($30 v_{pk-pk}$) is plotted and shown in Figure 3. It is seen that with the increase in polymer viscosity, the spontaneous polarization decreases and was negligibly small at higher viscosity. This may be due to the fact that at high viscosity, the surface forces resist the unwinding of helix even at higher applied electric fields. At lower viscosities, we believe that the winding and unwinding of the PDFLC composite sys-

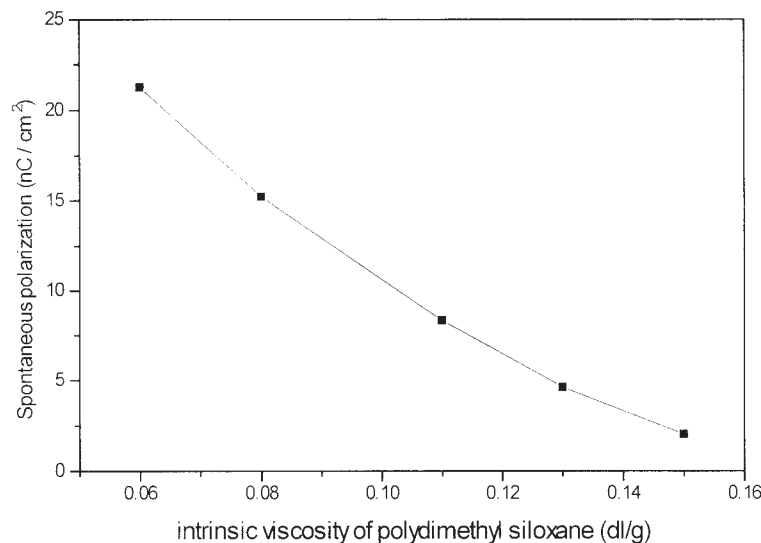


Figure 3 The influence of polymer intrinsic viscosity on spontaneous polarization of PDFLC composite systems.

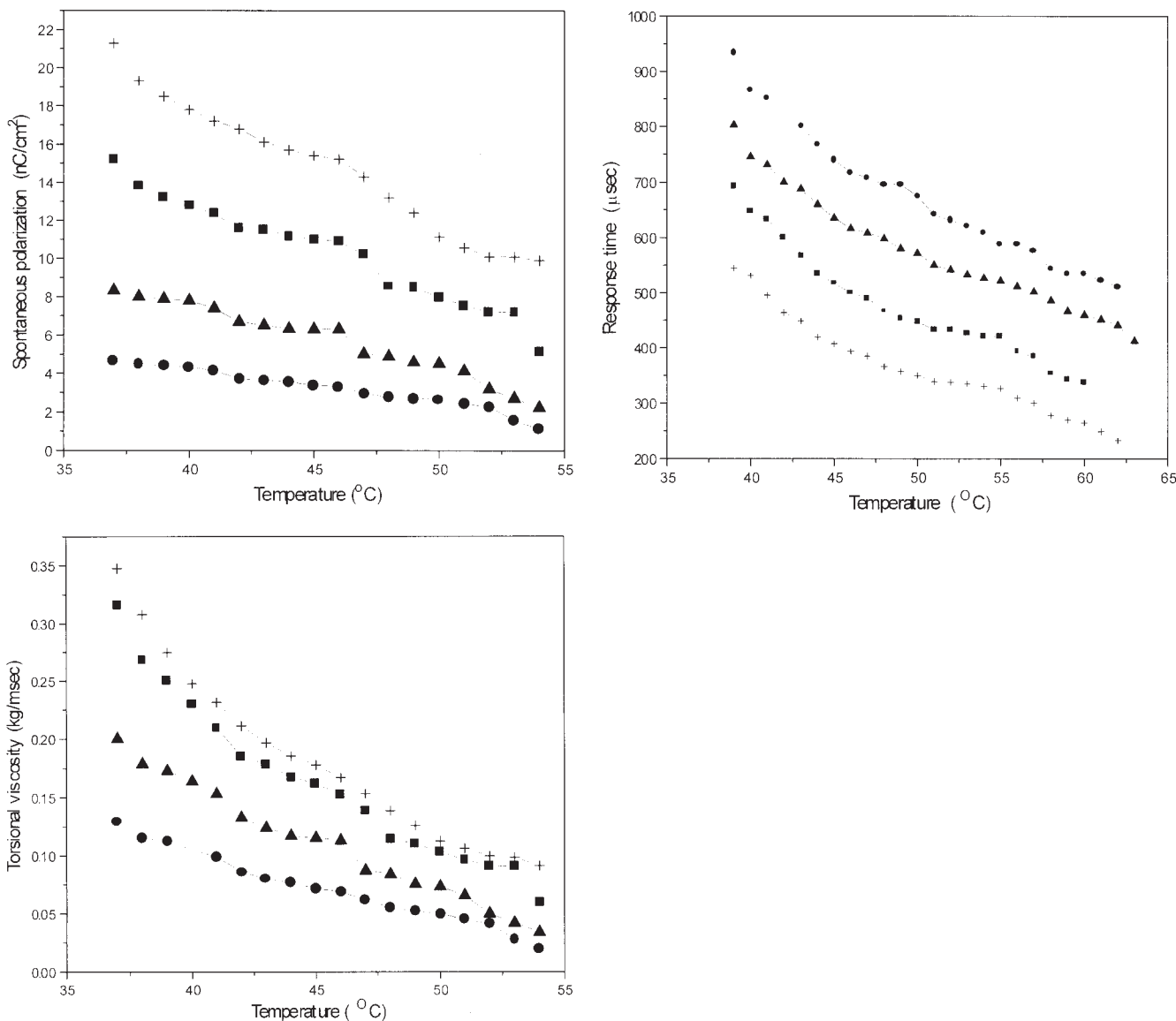


Figure 4 The effect of temperature as a function of: (a) spontaneous polarization, (b) response time, and (c) torsional viscosity of PDFLC films at different polymer intrinsic viscosities $[\eta]$ (+ 0.06, ■ 0.08, ▲ 0.11, and ● 0.13).

tems may not be restricted and therefore it shows higher polarization.

We observed that the response time slows down with the increase of polymer viscosity. The response time, which is the delay in switching between two stable states of polarization, increases from 544 μ s at $[\eta]$ 0.06 dl/g to 933 μ s at $[\eta]$ of 0.13 dl/g. However, the pure ZLI shows the response time of 500 μ s. This may also be due to the difficulty in helical unwinding in the polymer dispersed ferroelectric liquid crystal composites at higher viscosities.

Effect of temperature

Polarization switching. The polarization switching with respect to temperature at different polymer viscosity

was measured and given in Figure 4(a). From the results obtained for the dependence of spontaneous polarization (P_s) on temperature, it is observed that the value of P_s decreases with increase in the temperature. This trend of PDFLC can be explained on the basis of intra-molecular rotations and inter-molecular interactions in the system. The decrease in the P_s value with increase in the temperature may be due to the weak P-E (polarization-electric field) coupling and P- θ (polarization and tilt angle) coupling in ferroelectric liquid crystals at high temperatures.

Response time. Figure 4(b) shows that the response time decays almost exponentially with the increase of temperature for all PDFLC composite systems studied. The response time in microsecond range makes the system useful for flexible and fast response de-

vices. The influence of temperature and viscosity on torsional viscosity of the composite systems has also been studied and is given in Figure 4(c). The torsional viscosity also decays exponentially with increase in the temperature and decreases with the increase in the polymer viscosity.

CONCLUSION

1. The liquid crystal droplet size, and consequently the electro-optic properties, depends on various factors such as density ratio of polymer-FLC, the curing rate, free volume in the polymer network system, and polymer viscosity.
2. Liquid crystal droplet size increases with increase in the polymer viscosity. The droplets appear uniformly dispersed in polymer matrix only in the low viscous polymers. This may be due to the partial solubility and better mutual interaction of polymer-LC systems for low molecular weight polymers.
3. The spontaneous polarization decreases with increase in the polymer viscosity. The response time slows down with increase in the viscosity of the polymer. All PDFLC systems show microsecond-switching time.
4. As polysiloxane dispersed ferroelectric liquid crystals have many possible applications in displays due to low glass transition temperature (T_g), greater flexibility, and mechanical properties compared to the conventional polymers, they may find suitable and promising applications in flexible displays.

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