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Polymer network liquid crystals from u.v. curable polyurethane acrylate

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Polymer network liquid crystals (PNLC) were prepared from u.v. curable polyurethane acrylate and a nematic liquid crystal mixture (BL001) at a fixed film composition of 2/8 (polymer/LC) by weight. The polymer networks were obtained upon curing the reactive mixture of hydroxyethyl acrylate terminated polyurethane prepolymer, monoacrylate and triacrylate (4/3/3 or 4/4/2).

The effects of photoinitiator (PI) concentration, prepolymer molecular weight and cure temperature were studied in terms of morphology, off-state transmittance–temperature relationship, thermal and electro-optic performance of the films. It was found that an optimum PI concentration exists. Below and above the optimum concentration, phase separation is too slow and too fast, respectively, and proper morphology is not obtained regarding the electro-optic performance. The increase in prepolymer molecular weight gave larger phase separation and decreased threshold (V_{10}) as well as driving (V_{90}) voltages, together with reduced heating–cooling hysteresis and depression of nematic–isotropic transition temperature. Cure at and slightly below the isotropic temperature gave ideal morphology for PNLC giving rise to the lowest V_{10} and V_{90}. © 1998 Elsevier Science Ltd. All rights reserved.

(Keywords: polymer network liquid crystals; polyurethane acrylate)

INTRODUCTION

Thin composite films composed of micron-sized droplets of low molecular weight liquid crystal (LC) of positive dielectric anisotropy dispersed in an optically isotropic polymer matrix have potential for a variety of electro-optic applications ranging from switchable window to information display[1–4]. In one form, they consist of LC droplets dispersed in a polymer matrix known as polymer dispersed liquid crystal (PDLC)[2–4]. In the other form, LC becomes continuous phase, and three-dimensional polymer networks are dispersed in liquid crystals to form polymer network liquid crystal (PNLC)[5,6]. Practically, PDLC saves expensive liquid crystals, whereas PNLC reduces driving voltage and response time.

These composite films offer a number of advantages over the conventional nematic devices such as twisted nematic (TN) and supertwisted nematic (STN) as well as ferroelectric or emissive ones[7]: (i) they require no polarizers, thus increasing the brightness of both direct view and projection displays, minimizing heat control problems and reducing power and weight; (ii) they require no alignment layers or stringent thickness control, thus greatly simplifying the manufacturing process, and enabling large area displays; (iii) they have a large viewing angle in all directions and a high contrast ratio. Especially for the projection system, not using a polarizer is highly appreciated because of the considerable decrease of light losses as compared with more commonly used TN and STN materials.

We consider the preparations and properties of PNLC from the u.v. curable polyurethane acrylates (PUA). The effect of photoinitiator (PI) concentration, oligomer (polymer precursor) molecular weight and cure temperature on the morphology, off-state transmittance–temperature relationship, thermal and electro-optic properties of the composite films have been studied.

OPERATING PRINCIPLES

The composite film operates based on a fairly simple principle. The nematic LC molecule is optically uniaxial, and thus it has an ordinary refractive index (n_o) and extraordinary refractive index (n_e). In the absence of an external field (unpowered), the orientation of the optic axis and, hence, the nematic director vary randomly from droplet to droplet and, consequently, light propagating normal to the film surface will probe a range of refractive index between n_o and n_e. Since the optical anisotropy ($\Delta n = n_e - n_o$) of LC molecules used in PDLC is sufficiently large for many reasons, such as to reduce the driving voltage and rise time and to augment the contrast ratio[8], the effective refractive index given below is not generally matched with the refractive index of the polymer (n_p), and light will be scattered by the droplets. The effective refractive index (n_θ) encountered by the incoming light is given by[9,10]

$$n_\theta = \frac{n_e n_o}{(n_e^2 \cos^2\theta + n_o^2 \sin^2\theta)^{1/2}} \qquad (1)$$

where θ is the angle between the Poynting vector of the incoming light and the nematic director. For the typical droplets (0.1–10 μm), droplet concentration (~60 vol.%) and film thickness (~50 μm), light scatters many times while passing through the film, and these multiple scatterings cause the translucence of the unpowered film.

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In the presence of an electric field (powered), liquid crystals tend to align themselves with the directors either parallel or perpendicular to the field direction, with the extent of director orientation depending on the electric field. With positive dielectric anisotropy, molecules align with their long axis parallel to the applied field to minimize their energy. In this state, the refractive index for incident light is equal to n_o, and if n_o is matched with n_p, the film will transparent. Upon removal of the external field, the nematic directors are returned to their random alignment by the interface energy, and the film becomes opaque.

MATERIALS REQUIREMENTS

A number of factors contribute to the electro-optic performance of the films. These include the method of cell preparation, type of polymer matrix, polymer–LC interactions and miscibility, in addition to the film composition[11,12].

Regarding the type of materials, more requirements are imposed for use at a high multiplexing level which can be realized in an active matrix substrate, usually a thin film transistor (TFT). Coates *et al.*[8] reviewed that the most fundamental of these films must have a high charge holding ratio so that an addressed pixel must retain its charge, and thereby the induced orientation of LC, until it is readdressed by the refreshing cycle. A holding ratio of at least 95% of the original charge must remain on the pixel after 200 ms[13]. A second requirement is the low operating voltage. Normal PDLC films operate at *ca.* $25V_{\mathrm{rms}}$. However, the operating voltage can be further lowered by using more LCs. In the extreme case, only a network of polymer exists (PNLC)[14,15]. Finally, a hysteresis of less than $0.1V_{\mathrm{rms}}$ is required so that the same grey levels can be achieved irrespective of whether the final voltage is arrived at from a previously higher or lower voltage state.

A high charge holding ratio is obtained with terminal chloro compounds rather than the terminal cyano compounds, together with polymer of high resistivity. On the other hand, the driving voltage depends on the droplet size, shape and interaction between the polymer and LC. Hysteresis presumably occurs due to the slow and fast responses of LC molecules adjacent to the polymer walls and those away from the interfaces[16]. That is, hysteresis occurs when the director orientation is not only determined by the electric force (on switching) or elastic force (off switching), but also by the anchoring force at the interface. So, the energy losses in overcoming the anchoring force can cause the hysteresis, and it is inherently coupled with the material properties of polymer as well as LC.

U.V. CURABLE SYSTEMS

Polymers which can satisfy the various above-mentioned properties can be developed with u.v. curable acrylate systems[8]. Consequently u.v. curable materials, notably Norland 65, have most often been encountered as the polymer matrix. Nolan *et al.*[17] reported that rapid cure (high u.v. power) gives less LC remaining in the polymer. The LC which remains in the polymer matrix lowers the glass transition temperature (T_g) of the polymer (plasticizing effect) and increases the refractive index of the polymer. They showed that T_g of the polymer decreased more with slow cure. The increased n_p often causes great index mismatch with n_o, and lowers the on-state clarity of the film.

Fujisawa *et al.*[18] reported that multifunctional acrylates are essential components for phase separation with LC upon curing, and give excellent properties for multiplexing. The cure temperature, slightly higher than the nematic–isotropic transition temperature (T_{NI}) is also critical for forming the desired PNLC morphology. De Baets *et al.*[16] realized that a certain type of monoacrylate drastically reduces the hysteresis width, presumably by lowering the anchoring energy of LC molecules to the surface of the cured polymer. Ono and Kawatsuki[19] found that the driving voltage and response time were significantly decreased by adding a small amount of photocurable acrylates to the polyvinyl alcohol (PVA)/LC system. The improvement was interpreted in terms of interface modification, i.e. the cured acrylates form an interface layer between the PVA and LC.

In the u.v. curable system, liquid crystal and prepolymer (often called polymer precursor) are initially mixed to form a single phase[20,21]. Prepolymer is an oligomer of a certain type of acrylate or polyurethane which is encapped with acrylate to allow u.v. cure in the subsequent step. To this mixture, reactive diluent and photoinitiator are added before the mixture is irradiated. Reactive diluents are typically mono- and multifunctional acrylates and are added for two reasons, i.e. to reduce the viscosity of the prepolymer and to build up the molecular weight of the polymer by chain extension (monoacrylate) and/or crosslinkings (multifunctional acrylates). The extent of crosslinking depends on the average functionality of the reactive diluent as well as the extent of cure.

In the u.v. curable system, phase separation occurs with the progress of cure reaction because of the unfavourable increase in Gibbs free energy of mixing (ΔG_{mix}) owing to the decrease in the entropy of mixing (ΔS_{mix}) since a progressively smaller number of molecules become involved:

$$\Delta G_{\mathrm{mix}} = \Delta H_{\mathrm{mix}} - T\Delta S_{\mathrm{mix}} \tag{2}$$

where T is the absolute temperature. It should be kept in mind that the phase separation phenomenon in a polymerization-induced phase separation system is a rate process where the transport parameters can take an important role in determining the domain size and amount of LC separated from the polymer matrix. That is, the diffusion of LC molecules through the highly viscous medium is extremely slow[22], and this slow rate process may not follow the rapid cure rate, depending on the cure conditions.

EXPERIMENTAL

Materials and oligomer syntheses

Polypropylene glycols with three different molecular weights ($M_n = 400$, 1000 and 2000 g mol^{-1}) (Korea Polyol) were dried at 80°C and 0.1 mmHg for several hours until no bubbling was observed. A nematic type LC (BL001 (BDH), $n_o = 1.5216$, $n_e = 1.7462$, $T_{\mathrm{NI}} = 61$°C) with positive anisotropy was employed to prepare the cell. Chemical reagents of isophorone diisocyanate (IPDI, Huls) and hydroxyethyl acrylate (HEA) were used without further purification. Molar excess of IPDI was reacted with PPG for 3 h at 80°C to obtain isocyanate terminated prepolymers. The reaction mixtures were then cooled to 45°C before HEA was added and reacted for 3 h at 60°C with agitation to obtain HEA capped urethane acrylate oligomers. The reactions are outlined in *Figure 1*, and the detailed

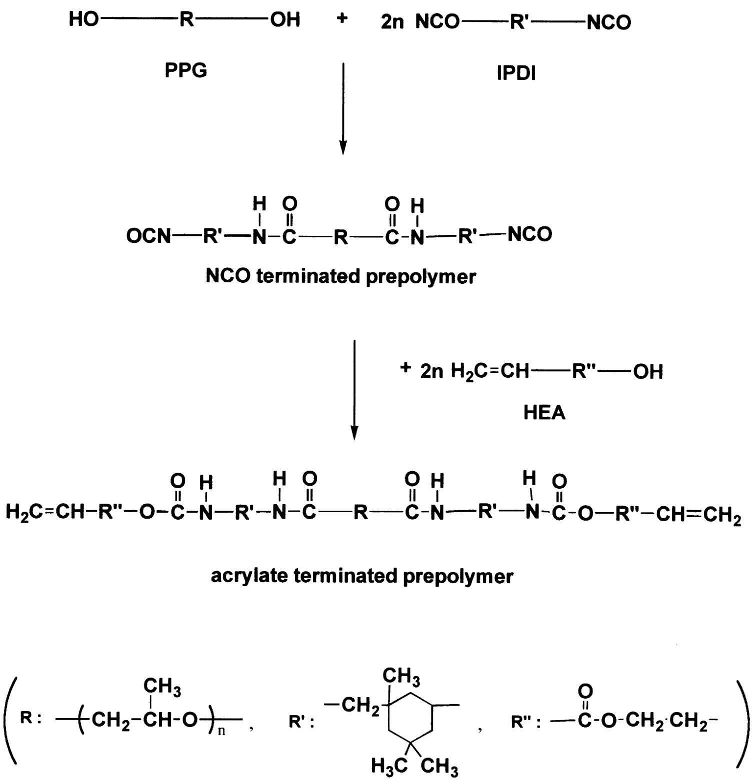


Figure 1 Oligomer synthesis procedure

procedures for preparing the prepolymers are described elsewhere[23–25].

Cell preparations

The oligomers are highly viscous and immiscible with LC, which necessitates the use of reactive diluents[26,27]. The reactive diluents used in these experiments include both 2-ethyl hexyl acrylate (EHA) and trimethylol propane triacrylate (TMPTA), and composition of oligomer/monofunctional/trifunctional diluents was 4/3/3 or 4/4/2 by weight. Liquid crystals were then added to the prepolymer mixture at a fixed composition of prepolymer/LC = 2/8 by weight, together with a photoinitiator, i.e. 1-hydroxy cyclohexyl phenyl ketone (HCPK)[28]. The reactive mixtures were mechanically mixed thoroughly before they were filled into the ITO coated cell by capillary action. Cell thickness was adjusted to 15 μm using glass bead spacers. The mixtures were then cured using a u.v. lamp (100 mW cm^{-2}, 365 nm) for 3 min. Basic stoichiometry for preparing PUA is shown in *Figure 1*. The effect of PI concentration was studied with PPG1000 (number designates molecular weight) based PUA, whereas the effect of oligomer molecular weight was studied with 3 wt% PI, and both were cured at 28°C. The effect of cure temperature was examined with PPG1000 based PUA and 3% PI.

Morphology and thermal property

The morphology of the films was studied using a scanning electron microscopy (SEM, Jeol JSM820). The u.v. cured cells were first fractured in liquid nitrogen, followed by extraction of LC in methanol for 24 h, and were cleaned in an ultrasonic cleaner. Samples were sputtered with gold before viewing under the SEM. The thermal property of the films was determined using a d.s.c. (Du Pont 1090) at a heating rate of 10°C min^{-1}.

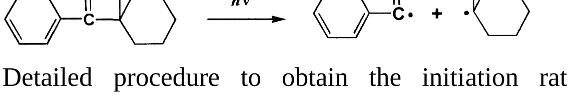
Electro-optic measurements[29,30]

The u.v. cured PNLC films sandwiched between two ITO coated cells were placed normal to the direction of collimated beam of an He/Ne laser (wavelength 632.8 nm). When the effects of temperature were measured, the cells were placed in a heating stage. the transmitted light intensity without any polarizer was measured with a photodiode. The output from a function generator was amplified and used to drive the shutter. The drive signal and the response of the photodiode were monitored with a digital storage oscilloscope (Hitachi VC-6023). The distance between the cell and photodiode was about 300 mm. The lined-up facilities, controlled by a laboratory computer, were turned up for about 1 h before the data were taken.

RESULTS AND DISCUSSION

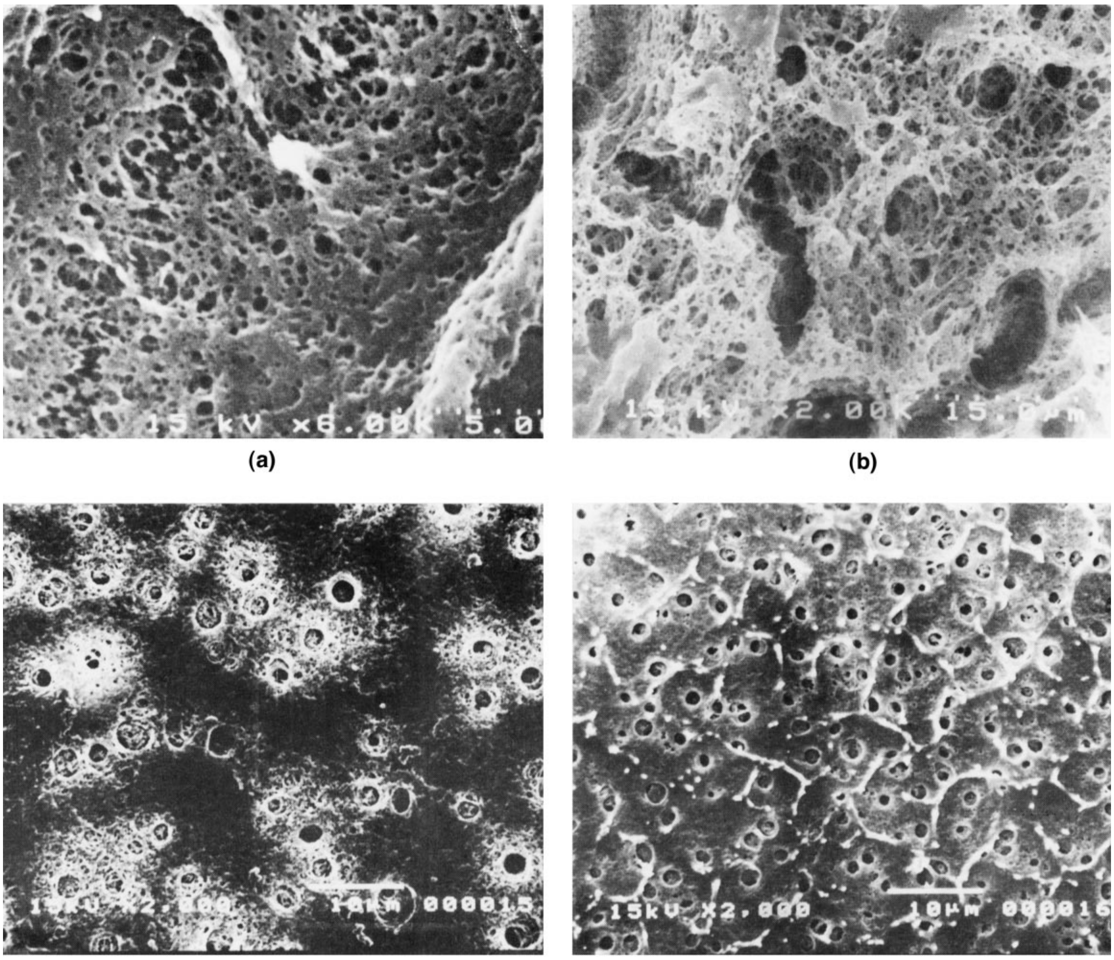
Effect of photoinitiator concentration

The series of experiments are based on PUA3 (to be defined) with a prepolymer molecular weight of about 2700, calculated from the formulation, and the resin composition of PUA3/EHA/TMPTA = 4/4/2 by weight. *Figure 2* shows SEM micrographs (top view) of the films as a function of photoinitiator concentration. In photoinitiated polymerization, the photoinitiator undergoes excitation by u.v. absorption and subsequent decomposition into radicals. HCPK (shown below), as well as benzophenone and acetophenone, is a most commonly encountered photoinitiator[31].



(3)

Detailed procedure to obtain the initiation rate (R_i) and polymerization rate (R_p) given below are available elsewhere[31,32].



(a) (b) (c) (d)

Figure 2 Effect of PI concentration on SEM morphology of the PNLC (LC has been extracted in methanol): (a) 1; (b) 3; (c) 6; and (d) 10 wt%

$$R_i = 2\varphi\varepsilon I_o[A]b \tag{4}$$

$$R_p = k_p[M]\left(\frac{\varphi\varepsilon I_o[A]b}{k_t}\right)^{\frac{1}{2}} \tag{5}$$

In these equations, φ, ε, I_o, and b are the initiation efficiency, molar absorptivity, incident light intensity and sample thickness, respectively. $[M]$ and $[A]$ are the concentrations of monomer and species which undergo photoexcitation, k_p and k_t are rate constants for propagation and termination reactions, respectively. It is seen that R_i is directly proportional to the concentration of PI, whereas R_p is directly proportional to the square root of PI concentration.

At a low enough initiator concentration, polymerization as well as the initiation rate is too slow[32], and owing to the insufficient molecular weight build-up, demixing of LC molecules from the polymer is insignificant. This leads to a poor phase separation (*Figure 2a*). As the initiator concentration increases, cure rate, extent and, hence, demixing increase (*Figure 2b*). Further increase in initiator concentration leads to a hardened thermoset polymer from which part of the LCs are phase separated to form well-defined spherical droplets (*Figure 2c,d*). It is seen that droplet size decreases with increasing initiator concentration (*Figure 2d* as compared with *Figure 2c*). This may in part be due to the difficult droplet coalescence through the hardened polymer resins (binodal decomposition)[12,27], but it seems more likely that the phase separation cannot follow the rapid curing when the cure rate is too fast.

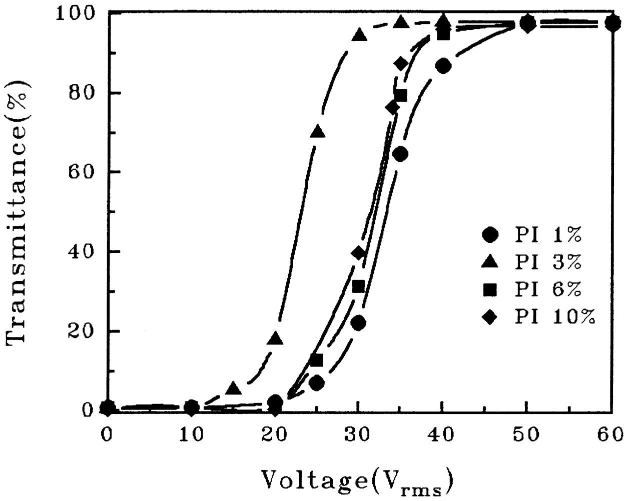


Figure 3 Effect of PI concentration on transmittance *versus* applied voltage of the PNLC at 1 kHz

Figure 3 shows the effects of PI concentration on the transmittance–voltage relationship. The initial increase in PI concentration from 1 to 3 wt% lowers the threshold (V_{10})

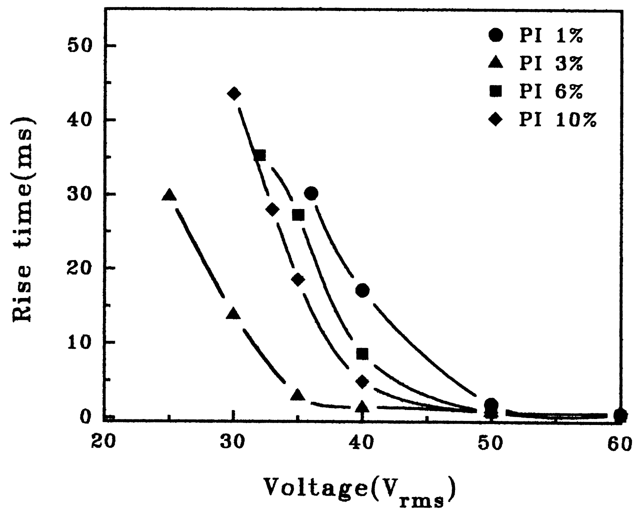


Figure 4 Effect of PI concentration on rise time *versus* applied voltage of the PNLC at 1 kHz

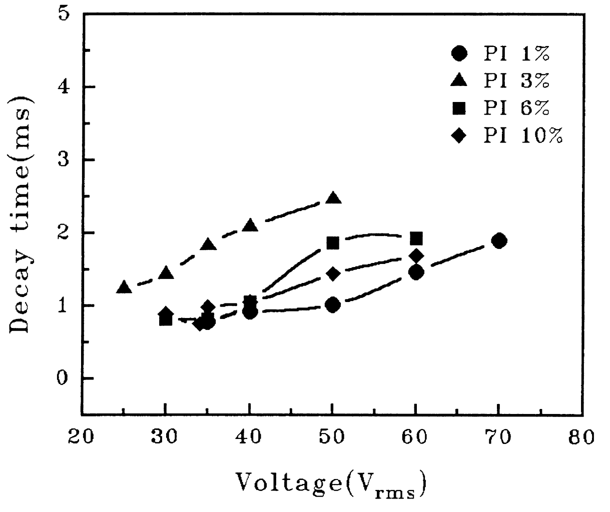


Figure 5 Effect of PI concentration on decay time *versus* applied voltage of the PNLC at 1 kHz

and driving (V_{90}) voltage. However, V_{10} and V_{90} increase with further increase in PI concentration and give results similar to 1% PI. The PI-dependent transmittance–voltage relationships are in line with the PI-dependent domain size. It seems that no matter what the state of cure is, the size and shape of LC domains are the key parameters for controlling the voltage characteristics of the film.

Figures 4 and *5* show the rise time (τ_R) and decay time (τ_D) of these films as functions of applied voltage. Rise time decreases rapidly with applied voltage owing to the rapid alignment of nematic directors along the field direction. Regarding the effect of PI, 3 wt% PI gives the quickest response to the electric field probably due to the morphological effect of this film. In general, smaller domains give larger τ_R, since they have to overcome more surface anchoring energy, and lower τ_D due to the higher elastic energy of the deformed state. Decay time is a response after switching off and is expected to be independent of the voltage. However, our results show a small increase in τ_D with voltage. In this regard, Jain and Rout[33] proposed two-stage relaxation depending on the type of film and field strength. At high applied voltage, alignment of the LC molecules and bipolar axes along the field would

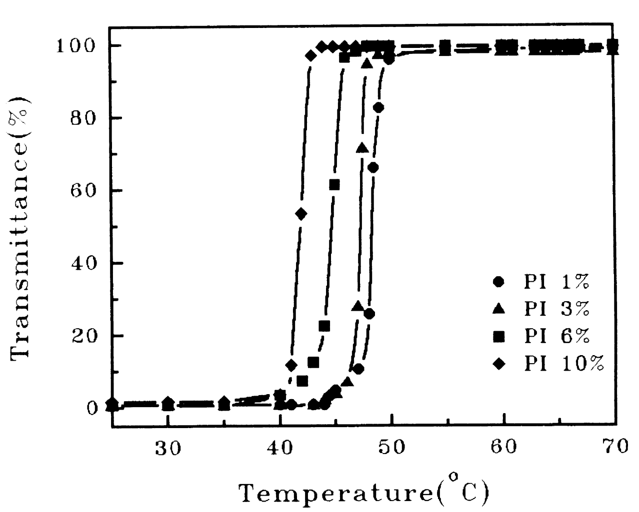


Figure 6 Effect of PI concentration on transmittance *versus* temperature in the absence of external field

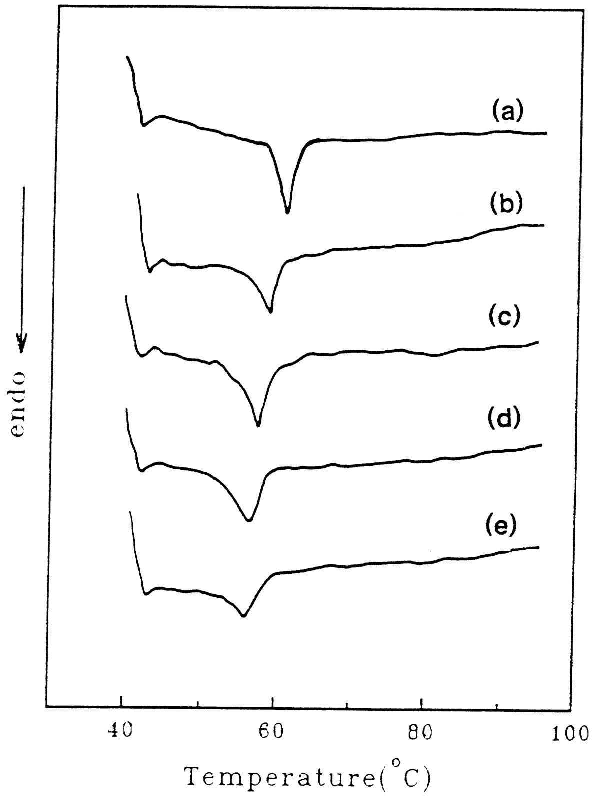


Figure 7 Effect of PI concentration on d.s.c. thermograms for PNLC: (a) pure LC; (b) 1; (c) 3; (d) 6; and (e) 10 wt%

complete. This involves much greater distortion of the director and, in turn, a greater restoring energy. So upon field removal, this state would first quickly return to an intermediate state where the molecular alignment in the LC droplet in the off state is essentially bipolar with the axis still remaining oriented along the field direction. Eventually, the orientations of the bipolar axis become random. This relaxation proceeds slowly, especially for spherical droplets since there is little difference in the elastic deformation energy between the intermediate state and this final relaxed state[34,35]. Though the 3 wt% PI gives relatively large τ_D, it is of the order of 1 ms, which is about 1/10 of the rise time.

Figure 6 shows the off-state transmittance as a function of temperature during heating. The off-state transmittance shows an abrupt increase from the opaque to the transparent state at a certain temperature, which decreases monotonically with increasing PI concentration. The transition is caused by several factors such as the decrease in birefringence, decrease in index mismatch, and increase in mutual solubility. The transition temperature is closely related to the T_{NI}[36]. T_{NI} may be either depressed owing to the impurity effects of polymer compounds, or raised owing to the preferential dissolution of the light component of the LC mixture[20]. Since the LC being used in our experiment is a mixture of four compounds of different molecular weights, it is reasonable to assume that lower molecular weight compounds are preferentially dissolved in polymer, contributing to an increase in T_{NI}[37]. However, the results, together with the d.s.c. results to follow, indicate that factor contributing to depress the T_{NI} is dominant, with the effect more pronounced at higher PI concentration. The increase in polymer solubility in LC with increasing PI concentration can be put as follows. R_p as well as R_i increases with the increase in PI. However, the dependence of R_i on PI ($\propto$ PI) is greater than that of R_p on PI($\propto (\mathrm{PI})^{1/2}$), so the molecular weight build-up or gelation is less plausible with a high PI concentration. Consequently, more oligomeric species which have relatively lower molecular weight or are less crosslinked and, hence, soluble in LC are produced with high PI, giving rise to greater depression of T_{NI}, as our results indicate. It should also be noted that the transition is very sharp, occurring only within a few degrees.

Figure 7 shows the d.s.c. thermograms of the films. The T_{NI} of pure LC is approximately 61°C, and it decreases monotonically with increasing PI concentration, and reaches 55°C with 10 wt% PI. This is due to the fact that the molecular weight of polymer decreases with increasing initiator concentration as mentioned above, which allows greater solubility of polymer in LC, as well as LC in polymer. It is also possible that unreacted PI, especially when used at high concentration, can remain in LC and acts as a placticizer to decrease the T_{NI}.

Effect of oligomer molecular weight

This series of experiments is based on the resin composition of PUA/EHA/TMPTA = 4/3/3. *Figure 8* shows the SEM micrographs of the films, prepared with different prepolymer molecular weight. The prepolymer molecular weights, calculated from the formulations, are respectively 1076, 1676 and 2676 for PUA1, PUA2 and PUA3. It is clearly seen that the LC domain significantly increases in size with increasing prepolymer molecular weight. Since the prepolymers were encapped with HEA, which were subsequently cured, the prepolymer molecular weight corresponds to the molecular weight between crosslinks (M_c). Since the LCs are entrapped between crosslinks, larger M_c should give larger LC domains. M_c essentially controls the LC domain size, whereas the chemical composition of the PUA modifies the interfaces between polymer and LC. This is an advantage of using prepolymer to control the scale of phase separation in u.v. curing. It is also expected that PUA1 exerts stronger

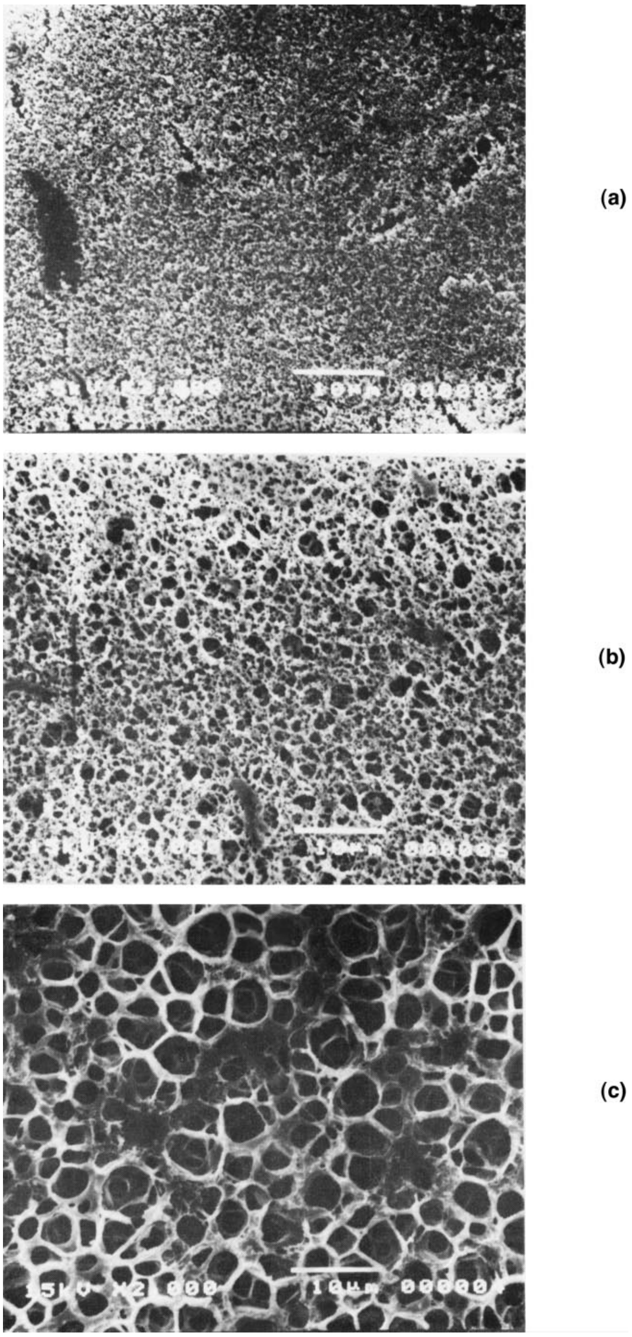


Figure 8 SEM photographs of the PNLC with various oligomer molecular weight (LC has been extracted in methanol): (a) PUA1; (b) PUA2; and (c) PUA3

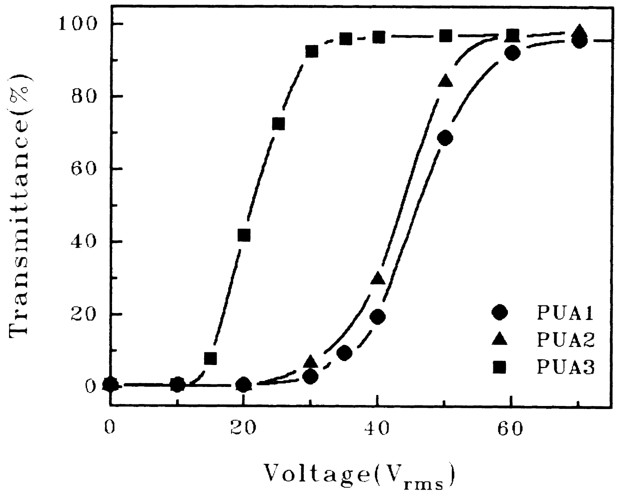


Figure 9 Effect of oligomer molecular weight on transmittance *versus* applied voltage of the PNLC at 1 kHz

interfacial interactions with LC, since it has more urethane groups than the other two.

Figure 9 shows the transmittance *versus* applied voltage for the three types of films. It is seen that the curves move toward lower voltage with the increase in prepolymer molecular weight. Generally in bipolar orientation the threshold voltage for a single drop is obtained as follows

$$V_{\text{th}} = \frac{d}{3a}\left(\frac{\rho_{\text{P}}}{\rho_{\text{LC}}}+2\right)\left(\frac{K(l^2-1)}{\varepsilon_0\Delta\varepsilon}\right)^{1/2} \tag{6}$$

In this equation, d, a, ρ, K and l represent film thickness, major dimension, resistivity, elastic constant (single con-

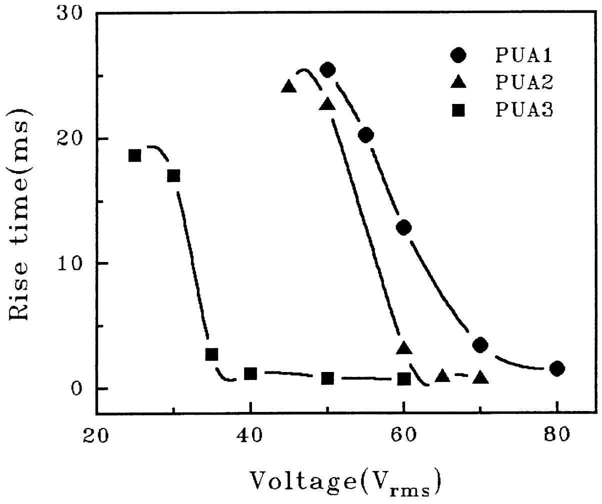


Figure 10 Effect of oligomer molecular weight on rise time *versus* applied voltage of the PNLC at 1 kHz

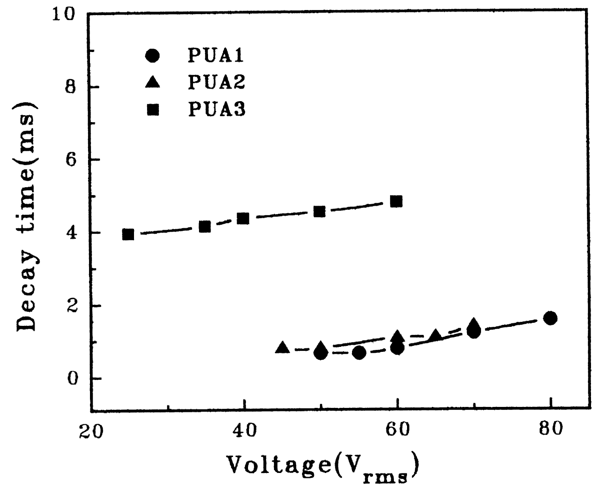


Figure 11 Effect of oligomer molecular weight on decay time *versus* applied voltage of the PNLC at 1 kHz

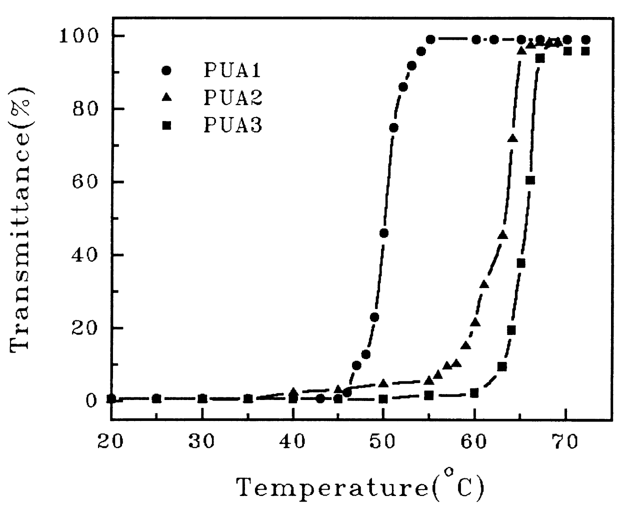


Figure 12 Effect of oligomer molecular weight on transmittance *versus* temperature during heating in the absence of external field

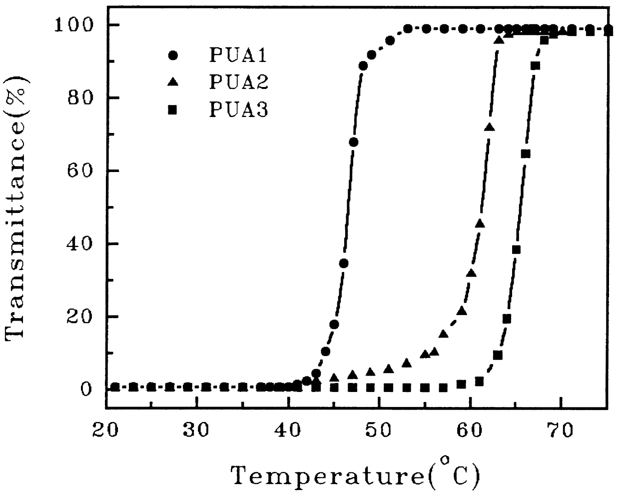


Figure 13 Effect of oligomer molecular weight on transmittance *versus* temperature during cooling in the absence of external field

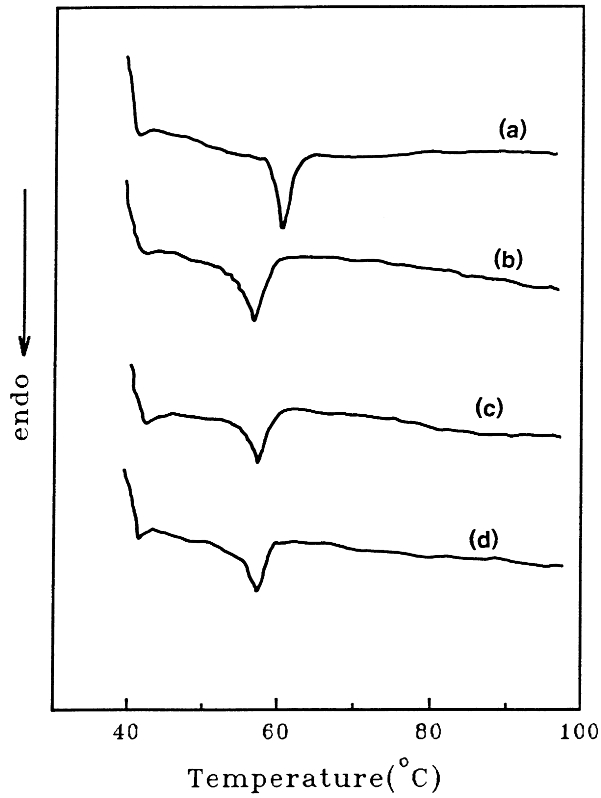
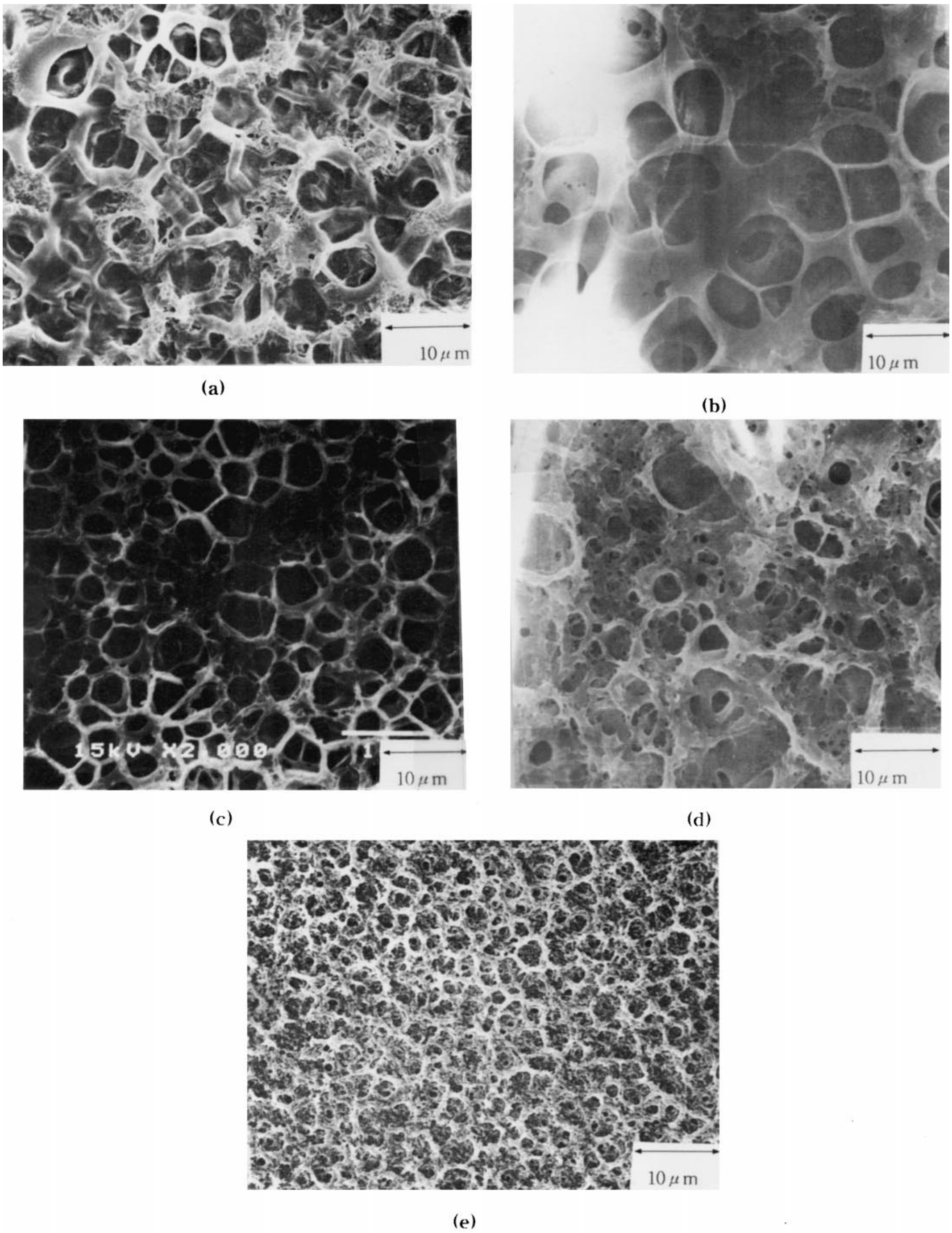


Figure 14 Effect of oligomer molecular weight on d.s.c. thermograms for PNLC: (a) pure LC; (b) PUA1/LC; (c) PUA2/LC; and (d) PUA3/LC

stant approximation) and aspect ratio of LC domain, respectively, and subscripts P and LC denote polymer and liquid crystal. The decrease in threshold voltage with increasing prepolymer molecular weight is directly related to the increased domain size which is qualitively predicted from equation 6.

Figures 10 and *11* show τ_R and τ_D of our films. It is seen that the prepolymer molecular weight exerts a significant effect on τ_R. That is, τ_R decreases significantly with the increase in prepolymer molecular weight. Decay times of PUA1 and PUA2 are significantly smaller than that for PUA3. It seems that the response times are governed by the domain size and interactions between polymer and LC. Relatively long τ_D of PUA3 is due to the relatively low crosslinking density, providing fewer interfaces and little interaction with LC.

Figures 12 and *13* show off-state transmittance change during heating and cooling. It is seen that PUA1 shows the lowest transition temperature owing to the greatest chemical affinity via polar interactions and solubility of this polymer in LC. High solubility of PUA1 is expected, since the lowest molecular weight prepolymers were involved in the cure. Notably, PUA3 shows almost no temperature hysteresis, i.e. the transmittance–temperature curves of heating and cooling shows little temperature lag. The decrease in temperature hysteresis with PUA3 is perhaps related to the larger M_c which gives lower crosslinkings and, hence, smaller viscosity, leading to the smaller anchoring energy of LC



(a) (b) (c) (d) (e)

Figure 15 Effect of cure temperature on SEM morphology of the PNLCs (LC has been extracted in methanol): (a) 26°C; (b) 28°C; (c) 30°C; (d) 34°C; and (e) 38°C

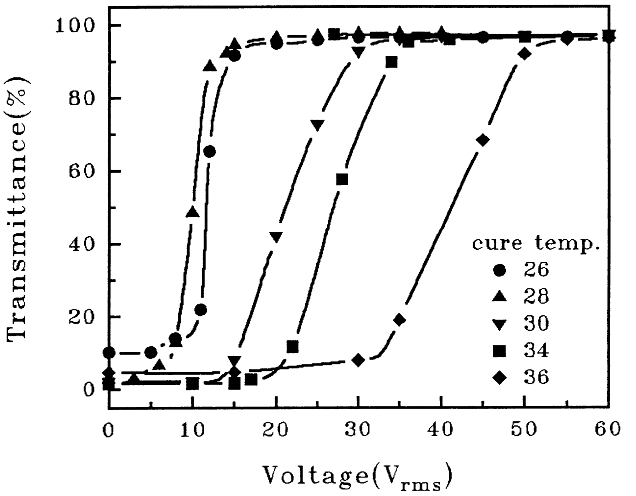


Figure 16 Effect of cure temperature on transmittance *versus* applied voltage of the PNLC at 1 kHz

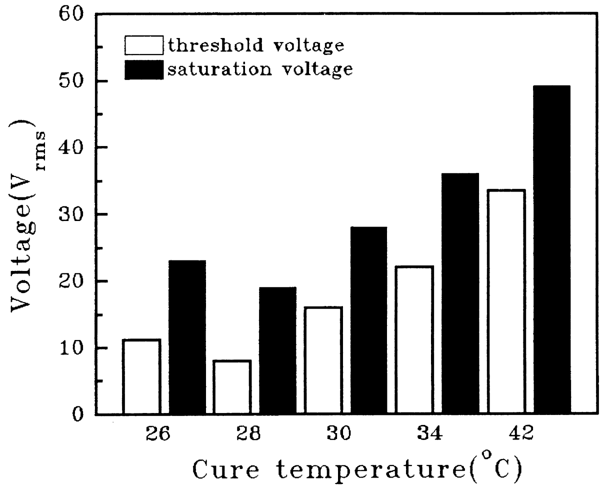


Figure 18 Effect of cure temperature on threshold and saturation voltages of the PNLC at 1 kHz

on the polymer wall. In this regard our results agree with those of Baets *et al.*, who reported that hysteresis width decreased with increasing monoacrylate content in the monoacrylate/diisocyanate system, presumably owing to the decreased opposing anchoring forces[16]. The low solubility of PUA3 in LC should also contribute to the low hysteresis of this material. In the other two cases, transmittance during cooling is higher than that of heating at the same temperature, owing mainly to the dissolved LC in the polymer during heating.

The d.s.c. thermogram of the films (*Figure 14*) shows that T_{NI} of LC decreases with PUA, and the effect is more pronounced with the decrease in prepolymer molecular weight.

Effect of cure temperature

The series of experiments is based on the resin composition of PUA/EHA/TMPTA = 4/3/3. *Figure 15* shows the SEM morphologies of the films cured at different temperatures. The isotropic temperature of these films is 28°C. Below and above the isotropic temperature, the mixture is hazy and transparent, respectively. When the film is cured below the isotropic temperature, undesirable phase separation prior to cure leads to the formation of large and irregularly shaped LC regions, resulting in non-uniform optical properties of the films. Domain size is the largest when cured at isotropic temperature. Further increase in cure temperature results in reduction in domain size due to the increased rate of cure. When the sample is cured at 36°C (the highest cure temperature) phase separation is too small and typical PNLC morphology is not obtained. At such high cure temperature, phase separations do not seem to follow the cure rate. The optimum morphology should be determined from the electro-optic performance of the films.

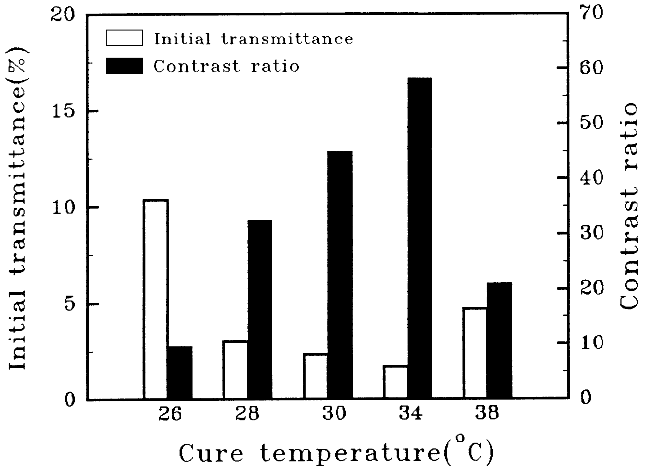


Figure 17 Effect of cure temperature on initial transmittance and contrast ratio of the PNLC at 1 kHz

Figure 16 shows transmittance–voltage relationships of the films cured at various temperatures. It is seen that cure temperature affects electro-optic performance of the films significantly. The lowest driving voltage with very sharp transition is obtained when the films are cured at and slightly below the isotropic temperature of the reaction mixture. This is apparently due to the relatively large LC domains of these films. Film cured below the isotropic temperature shows the lowest contrast ratio due to the high transmittance (*Figure 17*). Generally, initial transmittance decreases and, hence, contrast increases with increasing cure temperature, except the one cured at the highest temperature (38°C). The increase in initial transmittance for this particular film seems to be related to the dramatic reduction in domain size.

Threshold and saturation voltages are minimum when cured at isotropic temperature (*Figure 18*), and increase as the cure temperature deviates from the isotropic temperature. The isotropic temperature is the lowest temperature at which the reaction mixtures exist homogeneously, and is most vulnerable to phase separation by polymerization. This leads to the most appropriate phase separation upon polymerization and, hence, the greatest extent of phase separation. On the other hand, cure at higher or lower temperature retards phase separation from a thermodynamic point of view.

Rise and decay times of the films are shown in *Figures 19* and *20*. At low voltages, rise time is minimum and decay time is maximum when cured at and below isotropic temperatures, results consistent with the domain size of LC.

CONCLUSIONS

Effects of PI concentration, prepolymer molecular weight and cure temperature on the morphology and electro-optic

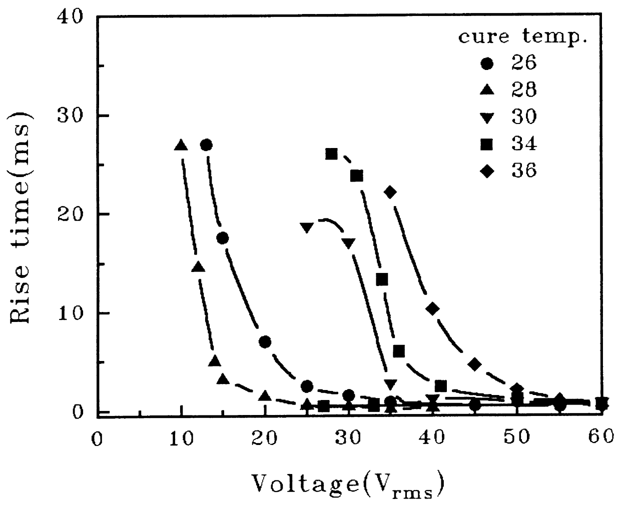


Figure 19 Effect of cure temperature on rise time *versus* applied voltage of the PNLC at 1 kHz

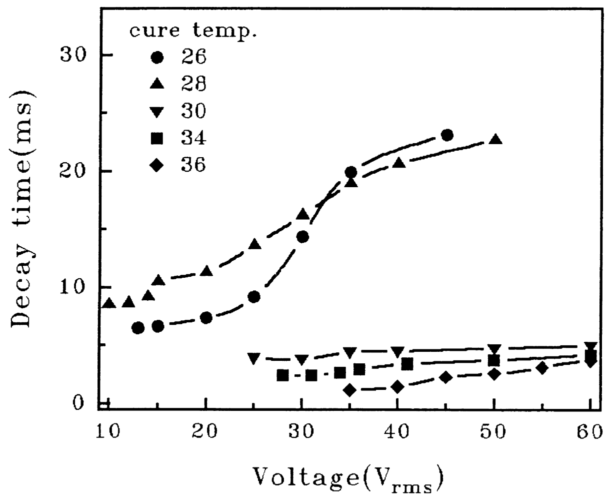


Figure 20 Effect of cure temperature on decay time *versus* applied voltage of the PNLC at 1 kHz

performance of PNLC have been studied and the following conclusions have been obtained.

There exists an optimum PI concentration for controlling the extent of phase separation which depends on the structure of the cured polymer as well as the cure rate. With low enough PI concentration (1%), initiation and propagation rates are too slow to induce significant demixing of LC molecules upon polymerization. However, the cured polymers have high molecular weight, preventing dissolution of polymer in LC, and resulting in less depression of T_{NI}.

As the PI concentration increases, initiation and propagation rates of cure increase to induce a proper phase separation (3%). But with still high PI concentration (6, 10%), cure rate is so fast that the polymers are cured before the LCs are demixed and form large domains. Consequently, spherical (uncoalesced) LC droplets are formed and the size of droplet decreases with increasing PI concentration. With high enough PI concentration, the average molecular weight of cured polymer becomes smaller owing to the significant difference between initiation and propagation rates. Lower molecuar weight polymers are easily dissolved in LC, leading to more depression of T_{NI}.

The size of phase separation was effectively controlled by the prepolymer molecular weight. Since the prepolymer molecular weight corresponds to the molecular weight between crosslinks, higher prepolymer molecular weight gives larger domain size and consequently lower V_{10} and V_{90}, and less depression of T_{NI}. Cure at and slightly below the isotropic mixture temperature seems necessary to create appropriate film morphology for electro-optic devices giving rise to the lowest V_{10} and V_{90}. Cure above the isotropic temperature increases cure rate to an extent that phase separations do not follow the cure process and, consequently, the phase separation is insufficient.

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